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Bed Material Agglomeration During Fluidized Bed Combustion

Final Report

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Abstract

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.

A survey of agglomeration and deposit formation in industrial fluidized bed combustors (FBCs) indicate that at least five boilers were experiencing some form of bed material agglomeration. Deposit formation was reported at nine sites with deposits most commonly at coal feed locations and in cyclones. Other deposit locations included side walls and return loops.

Three general types of mineralogic reactions were observed to occur in the agglomerates and deposits. Although alkalis may play a role with some "high alkali" lignites, we found agglomeration was initiated due to fluxing reactions between iron (II) from pyrites and aluminosilicates from clays. This is indicated by the high amounts of iron, silica, and alumina in the agglomerates and the mineralogy of the agglomerates. Agglomeration likely originated in the dense phase of the FBC bed within the volatile plume which forms when coal is introduced to the boiler.

Secondary mineral reactions appear to occur after the agglomerates have formed and tend to strengthen the agglomerates. When calcium is present in high amounts, most of the minerals in the resulting deposits are in the melilite group (gehlenite, melilite, and akermanite) and pyroxene group (diopside and augite). 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).

A third type of reaction that acts to strengthen agglomerates involves the filling of void space between agglomerate particles with recrystallized calcium sulfate. In some agglomerates, particles are rimmed by larger grains of calcium sulfate than found in the cores. It appears as though this material is the result of recrystallization of fine particles of calcium sulfate present in the combustor as an aerosol.

A laboratory-scale fluidized bed combustor was used to test the hypothesis that reducing conditions facilitate bed material agglomeration, even when bed temperatures remain below typical ash fusion temperatures. Combustion tests were conducted using sand or limestone as the bed material with varying amounts of combustion air. Bed material was observed to agglomerate as the equivalence approached 0.50, even when combustion temperatures remained below the ash fusion temperature. The experiments suggest that changes in the hydrostatic pressure gradient across the bed might be used to detect and monitor agglomerate growth.

Introduction

The objective of this research project was to determine the physical and chemical reactions which lead to the undesired agglomeration of bed material during fluidized bed combustion of coal. It was a further objective to relate these reactions to specific causes within the combustion environment.

The approach to this project consisted of two distinct parts. The first part involved formulation of hypotheses on the mechanisms of agglomerate formation based on chemical and mineralogic analyses of deposits collected from several industrial-scale fluidized bed boilers in the United States. The second part involved testing these hypothesized mechanisms in a laboratory-scale fluidized bed combustor by simulating conditions found in industrial-scale boilers. The methods employed and the results obtained for these two parts of the investigation are discussed separately in the following sections.

Part 1. Mechanisms of agglomerate formation

BACKGROUND

Fluidized bed combustion is an advanced coal combustion technology which offers an effective and environmentally cleaner method for the combustion of coal. Some of the advantages of fluidized bed combustion include lower NO_x emissions, better heat transfer, and greater fuel flexibility compared to pulverized coal boilers. The industrial application of fluidized bed combustion (FBC) reflects a growing trend towards co-generation in which FBC boilers produce both steam and electricity for industrial processes. During the combustion of high-sulfur coals, limestone may be added with coal to capture sulfur released during combustion. This process involves a series of physical and chemical reactions that result in particles of iron oxides and reacted calcium sulfate. To maintain the proper fluidization of these particles, it is very important that they do not cohere or "stick-together" when individual particles come into contact. This phenomena, which can lead to a loss of fluidization, has been observed for combustion of both bituminous and lower-rank coals [1,2,3].

Industrial fluidized bed boilers (in the United States) were surveyed to determine the extent of agglomeration and deposit formation. Agglomerates and deposits from several of these facilities were analyzed and the chemical and mineralogic reactions responsible for the agglomerates were inferred from the deposit composition.

ANALYTICAL METHODS

Bulk chemical compositions (major, minor, and trace elements) of agglomerates and deposits were determined by x-ray fluorescence (XRF) using a Siemens wavelength-dispersive XRF spectrometer and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The accuracy of all analytical techniques was monitored using standards, run as unknowns, and the analyzed values were compared to published values. Polished sections of the agglomerates were made for optical and scanning electron microscopy. Polarized-light microscopy was performed using a Zeiss research microscope. Photographic "maps" made using reflected and transmitted light, were also used for scanning electron microscopy (SEM). Elemental analyses of individual particles and layers within the deposits were obtained using a JEOL JSM-840A SEM equipped with a Kevex Delta V energy-dispersive microanalyzer. Other analyses were performed using an ARL electron microprobe at Iowa State University. X-ray diffraction analyses were performed using a Siemens X-ray diffractometer with K- α copper radiation.

RESULTS AND DISCUSSION

The survey of agglomeration and deposit formation in industrial fluidized bed boilers was conducted and a summary of the results is given in *Table 1*. Deposit formation was reported at nine sites with these deposits being found most commonly at coal feed locations and in cyclones. Other deposit locations included side walls and return loops. At least five boilers surveyed were experiencing some form of bed material agglomeration. It was observed that large particles were forming in the bed which were larger than the feed. Four operators could confirm that the larger bed particles had formed due to bed particles sticking together or agglomerating.

Deposits and agglomerates were received from three facilities. Samples were received from the Iowa State University Heating Plant where agglomerates and deposits were found on the walls in coal feed locations, in the loop seal, in the corners of the floor, and in the cyclone. A boiler deposit was also received from a Texas-New Mexico and a Montana-Dakota facility. A proximate and ultimate analyses of the fuel feed in each of the plants is given in *Table 2*.

Table 1 Results of agglomeration and deposition survey of thirteen industrial fluidized bed boilers.

	<u>No. of facilities</u>	
	<u>YES</u>	<u>NO</u>
<u>Bed agglomerates</u>		
Large particles in bed	6	7
<u>If large particles in bed</u>		
Bed particles larger than feed	5	1
Bed particles sticking together	4	2
<u>Deposit formation</u>		
Observed Deposits	9	4
<u>Deposit locations</u>		
Coal feed locations	6	3
Side walls	3	6
Cyclone	5	4
Return loop	3	6
<u>Suspect problems are due to:</u>		
Temperature	0	13
Alkali	0	13
Low-rank fuel	1	12

Table 2 Proximate and ultimate analyses of coal used at the time of deposit formation at the Iowa State University Heating Plant, a Texas-New Mexico utility and a Montana-Dakota utility. (As received, oxygen and hydrogen include water).

	<u>Texas-New Mexico</u>	<u>Montana Dakota</u>	<u>Iowa State</u>
Moisture (%)	14.6	30.6	6.1
Ash (%)	10.3	15.0	17.3
Volatile Matter (%)	42.5	30.4	33.7
Fixed Carbon (%)	32.6	24.0	43.0
Sulfur (%)	1.2	1.2	2.8
Carbon (%)	53.9	40.7	61.2
Hydrogen (%)	4.2	3.9	4.4
Nitrogen (%)	0.8	0.8	1.0
Oxygen (difference) (%)	29.7	38.4	14.0

Texas-New Mexico Deposit

The bulk composition of the boiler deposit is given in *Table 3*. The deposit has high concentrations of calcium and sulfur which are probably the result of limestone or dolomitic limestone used as a sulfur sorbent. The deposit also contains about 20 wt% silica, 12 wt% alumina, almost 7 wt% iron and 1.3 wt% titanium. *Figure 1* is a photomicrograph from a thin section of the deposit. The deposit was formed in layers which appear to be formed by flows of viscous material.

Table 3 Major and minor (wt.%) element abundance of deposit from a Texas-New Mexico Power Company.

	<u>Tex</u>	<u>STD</u> ^a	<u>Publ</u> ^b
SiO ₂	19.82	49.35	48.78
Al ₂ O ₃	12.20	27.08	27.02
Fe ₂ O ₃	6.70	13.92	13.44
MgO	4.55	0.70	0.75
CaO	44.87	15.4	15.9
Na ₂ O	0.00	3.04	3.05
K ₂ O	0.03	2.09	2.26
TiO ₂	1.33	1.43	1.33
P ₂ O ₅	0.05	0.39	0.38
SO ₃	14.41	0.11	0.18
SrO	0.22	0.13	0.08
BaO	0.04	0.20	0.15
LOI	<u>0.65</u>	<u>0.27</u>	0.00
Total	99.25	101.54	

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

^b Publ = published values of standards

The mineral phases present are given in *Table 4*. The mineral phases present in the deposit indicate that localized reducing conditions may have been present in portions of the boiler. The calcium sulfide (CaS) and calcium sulfite (CaSO₃) certainly indicate reduced sulfur species. With sufficient oxygen, calcium sulfite will oxidize to calcium sulfate (CaSO₄).

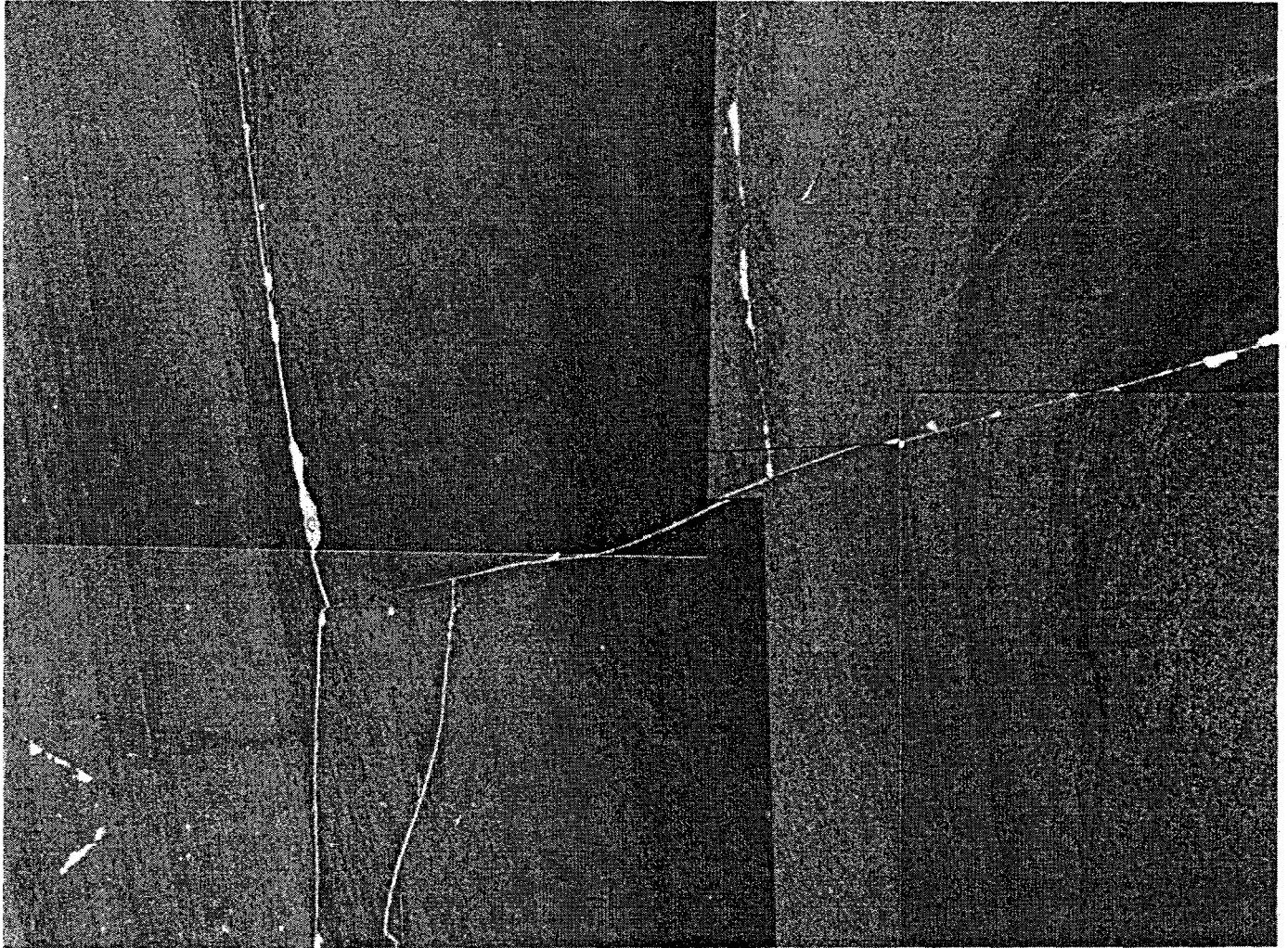


Figure 1. Optical photomicrograph showing layering in a boiler deposit found in a fluidized bed boiler from a Texas - New Mexico power company. The field of view is about one centimeter.

The mineral hercynite ($\text{Fe}^{+2}\text{Al}_2\text{O}_4$) is a spinel mineral which most likely formed from an interaction between iron in the +2 state and aluminosilicate materials. The iron most likely originated from pyrite in the coal. Alumina originated from clays also in the coal. The presence of this mineral also indicates that local reducing conditions were present during deposit formation. If sufficient oxygen were present, iron in the +2 state from pyrite in the coal would oxidize to form +3 iron oxides (hematite Fe_2O_3).

Table 4 Mineral phases present in a deposit formed in a boiler at a Texas-New Mexico Power Company.

<u>Minerals present</u>	<u>Approximate wt % of components</u>
Calcium aluminum Silicate (Gehlenite)	57
Calcium Sulfide (Oldhamite)	14
Calcium Silicate Ca_2SiO_4	11
Iron Aluminum Oxide (Hercynite)	9
Calcium Sulfite (CaSO_3)	9

The mineral gehlenite ($\text{Ca}_2[\text{Al}_2\text{SiO}_7]$) is a member of the melilite group. Replacement of the calcium with iron causes a marked lowering of the melting point of this mineral; however, the melting temperatures of these phases are still well above the operating temperatures of a fluidized bed boiler. This mineral is found in natural environments, as a result of thermal metamorphism of siliceous limestones or dolomites. The calcium silicate phase is indicative of interaction between calcium oxide and silicate phases during combustion. These may be solid-solid reactions and have been observed in agglomerates from laboratory tests.

Montana-Dakota Deposit

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 5* contains the bulk chemical analyses of the deposit core and rim. *Table 6* 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 7* shows electron microprobe analyses of minerals obtained from thin sections made from the agglomerate. *Figures 2 and 3* are optical photomicrographs which show examples of the mineral phases present.

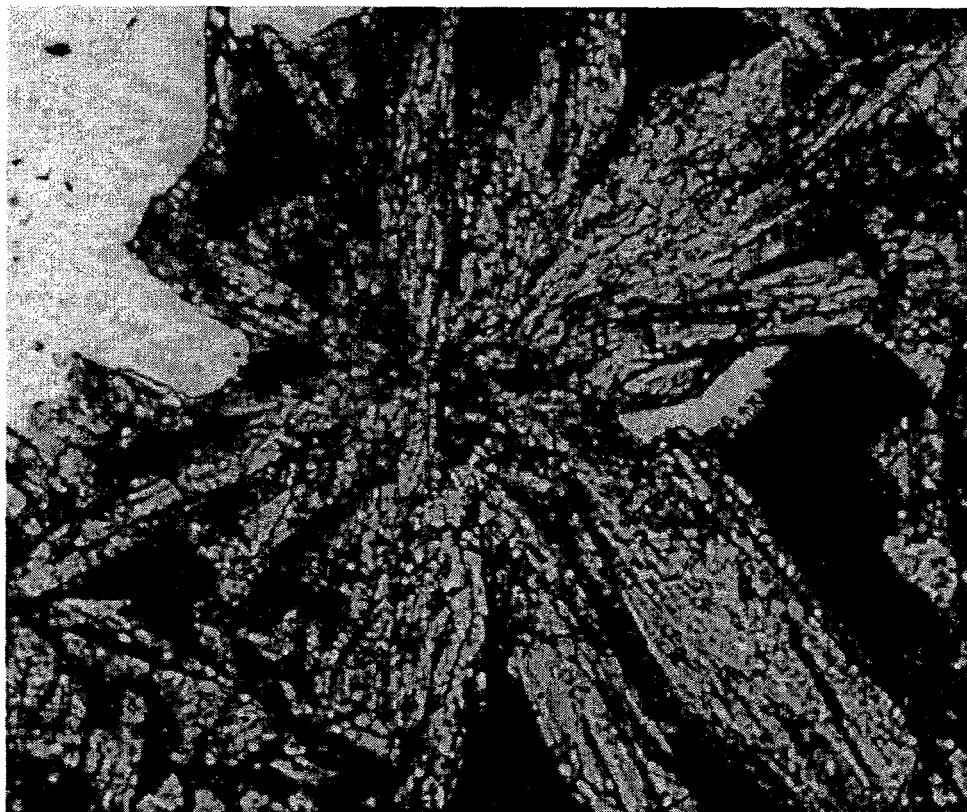


Figure 2. Radial crystal growth in deposit from a dust collector at the Heskett Station Unit 2, Montana Dakota Utilities. Field of view is 0.7 millimeters.

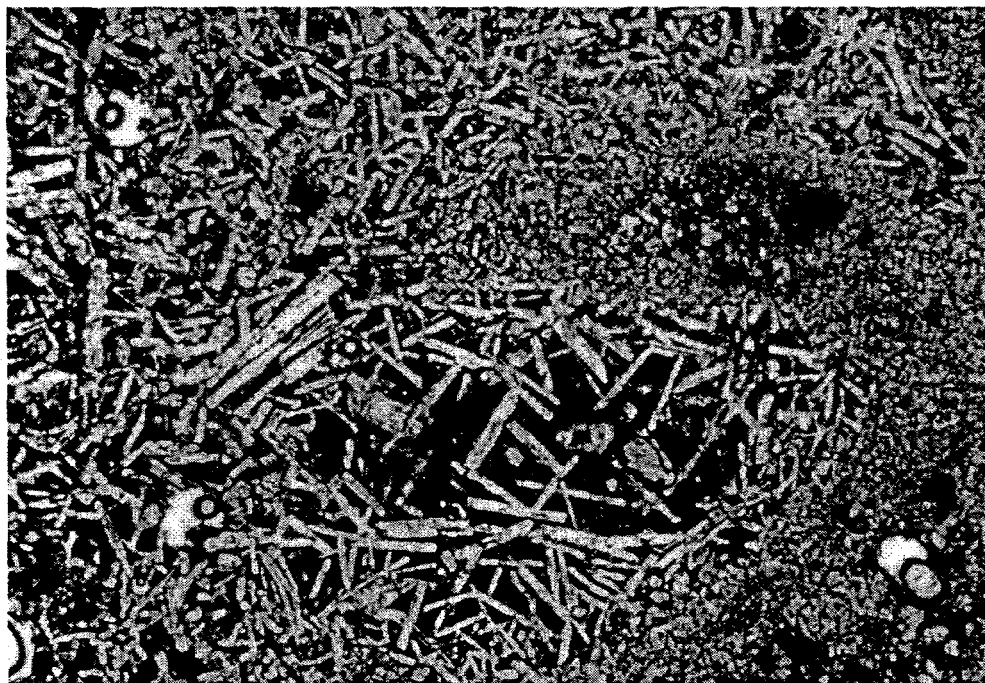


Figure 3. Calcium aluminosilicate minerals growing into voids. These minerals also contain high amounts of iron and magnesium. Field of view is 2.7 millimeters.

Table 5 Major and minor (wt.%) element abundance of deposit from Hassett Station, Montana - Dakota Power.

	Core	Rim	STD ^a	Publ ^b
SiO ₂	36.46	50.60	49.35	48.78
Al ₂ O ₃	13.25	13.54	27.08	27.02
Fe ₂ O ₃	8.88	8.14	13.92	13.44
MgO	8.27	5.46	0.70	0.75
CaO	24.70	17.12	1.33	1.55
Na ₂ O	3.46	2.88	0.00	0.23
K ₂ O	0.71	1.29	2.09	2.26
TiO ₂	0.61	0.54	1.43	1.33
P ₂ O ₅	0.25	0.18	0.39	0.38
SO ₃	1.42	1.50	0.11	0.18
SrO	0.38	0.23	0.13	0.08
BaO	0.84	0.50	0.20	0.15
LOI	<u>0.65</u>	<u>0.27</u>		
Total	99.89	102.23		

^aSTD = Analyses of standards used to monitor accuracy of analyses

^bPubl = published values of standards

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 2* and *3*, 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 2*) or, more commonly, randomly oriented with larger crystals growing in void spaces (*Figure 3*).

Most of the minerals which formed in the deposit are in the melilite group (gehlenite, melilite, and akermanite) 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 [5]. 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 CO_2 (Figure 3 from [6], reaction 27, Diopside + Calcite $\rightarrow$ Akermanite). The melilite group of minerals is also unstable below 500°C where minerals break down to form clinopyroxenes (diopside and augite, single chain silicate minerals).

Table 6 Minerals present in agglomerate from Heskett Station Unit 2, Montana Dakota Utilities.

<u>Minerals present</u>	<u>Approximate % of components</u>
<u>Rim</u>	
Diopside $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$	34
Akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$	19
Quartz SiO_2	13
Gehlenite $\text{Ca}_2\text{Al}(\text{Al},\text{Si})_2\text{O}_7$	5
possible: Calcium Strontium Aluminum Silicate $\text{CaSrAl}_2\text{SiO}_7$	21
possible: Nepheline $(\text{K},\text{Na})\text{AlSiO}_4$	6
possible: Sodium Aluminum Silicate Hydrate $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot x\text{H}_2\text{O}$	2
<u>Core</u>	
Akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$	73
Augite $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$	10
Quartz SiO_2	5
Possible: Iron Sulfide FeS	12

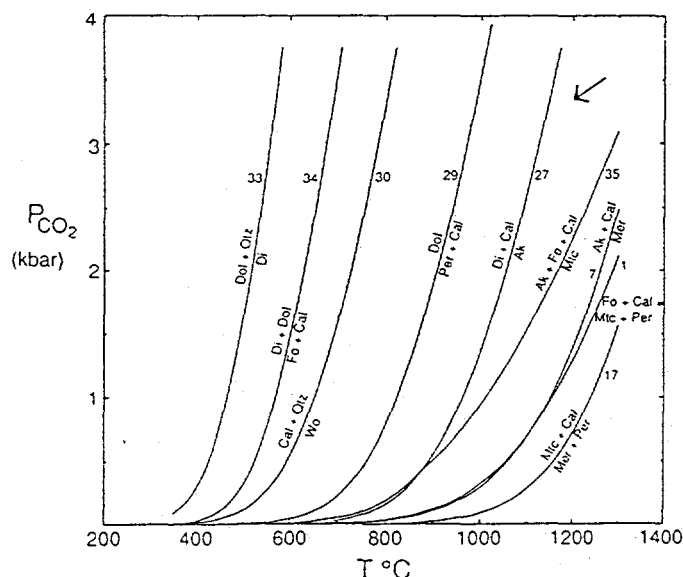


Figure 4 P_{CO_2} - T diagram illustrating the effect of CO_2 pressure on reaction 27 [7].

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 [7].

It is likely that this agglomerate originated in the dense phase of the FBC bed. Because fluidized bed combustors operate 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.

Iowa State University Deposits

Agglomerates from the loop seal area resembled stalactites and were up to twelve inches in length. Agglomerates found on the wall of the combustor were several inches in thickness and red and brown in color. *Table 7* contains the bulk chemical analyses of the deposits and unagglomerated bed material. *Table 8* lists the mineralogic composition of the samples and an estimate of the relative percentage of the mineral phases. *Figures 5, 6 and 7* are optical photomicrographs which show examples of the mineral phases and textures.

Compositionally, the agglomerates consist primarily of calcium, silica, and alumina with relatively high abundances of iron. Compared to unagglomerated bed material, the agglomerates found in the loop seal contained more iron (22 wt% compared to 3 wt% in the bed) and less

calcium (33 wt% compared to 47 wt% in the bed). The agglomerate found on the walls of the combustor contained more alumina (6-14 wt% compared to 3 wt% in the bed), silica (15-30 wt% compared to 14 wt% in the bed), and iron (9-17 wt% compared to 3 wt% in the bed) than unagglomerated bed material. Mineralogically, the agglomerates consist of what appear to be agglomerated bed particles and other material deposited by either very an accumulation of fine particles ($<1\text{ }\mu\text{m}$) or as a "flow" of viscous material. Compositional analyses of thin sections of the deposit indicate particles would stick together on surfaces which are enriched in silica and alumina. Aluminosilicates (clays) in the ash probably became "sticky" due to fluxing reactions with pyrite (FeS_2). This is indicated by the increased abundances of iron in both the loop seal agglomerate and the deposits on the wall. As can be seen from the photomicrographs, what were formally bed particles can be seen as "outlines" of particle rims which are high in alumina, silica, and iron. The areas which were probably voids between particles in the loop seal deposit are now filled with calcium sulfate (*Figure 5*). In areas of the agglomerate found on the combustor wall, rims of calcium sulfate can be seen (*Figure 6*). Based on our study of other agglomerates, the rims rich in alumina, silica, and iron were most likely formed as iron-rich particles "wetted" the surface of reacted calcium particles. It appears as though the outer rims of calcium sulfate and the calcium sulfate which now fills voids in parts of the agglomerates formed later, after the agglomeration of the bed particles. We suspect that this material was either calcium oxide or reacted calcium sulfate present in the combustor as an aerosol. These reactions are significant because they tend to add strength to the agglomerates as voids are filled with material.

Table 7 Major and minor (wt.%) bulk element abundances of agglomerates and bed material from a circulating fluidized bed combustor at Iowa State University Power Plant (170,000 lb/hr steam).

	Loop Seal	Loop Seal	Wall (Red)	Wall (Brown)	Bed	STD ^a	Publ ^b
SiO ₂	8.53	8.55	15.23	30.07	13.86	49.42	50.38
Al ₂ O ₃	2.51	2.50	6.28	14.74	3.34	27.21	27.91
Fe ₂ O ₃	21.67	21.93	9.10	16.87	3.25	13.86	13.88
MgO	0.38	0.30	0.76	0.97	0.54	0.70	0.75
CaO	33.13	33.39	32.97	27.41	47.08	1.33	1.55
Na ₂ O	0.00	0.00	0.00	0.00	0.00	2.72	-
K ₂ O	0.05	0.05	0.15	0.31	0.25	2.13	2.33
TiO ₂	0.23	0.23	0.58	1.31	0.26	0.40	1.43
P ₂ O ₅	0.12	0.11	0.21	0.36	0.10	0.13	0.39
SO ₃	37.79	37.78	38.49	9.22	36.00		
SrO	0.07	0.07	0.10	0.11	0.08	0.10	0.13
BaO	0.01	0.01	0.05	0.09	0.00	0.16	0.20
LOI	<u>0.14</u>	<u>0.14</u>	<u>0.23</u>	<u>0.00</u>	<u>1.30</u>	<u>1.11</u>	
Total	104.63	105.09	104.15	101.27	106.05	99.03	

^aSTD = Analyses of standards used to monitor accuracy of analyses (NIST 1633a).

^bPubl = Published values of standards.

LOI = Loss on ignition at 1000°C.

Table 8. Mineral composition of agglomerates and bed material from a circulating fluidized bed combustor at Iowa State University Power Plant (170,000 lb/hr steam).

<u>Minerals present</u>	<u>Approximate wt % of components</u>
<u>Bed Material</u>	
Calcium Sulfate, Anhydrite (CaSO_4)	60
Calcium Oxide, Lime (CaO)	26
Silicon Oxide, Quartz (SiO_2)	14
<u>Loop Seal</u>	
Calcium Sulfate, Anhydrite (CaSO_4)	91
Iron Oxide, Hematite (Fe_2O_3)	9
<u>Wall (Brown)</u>	
Calcium Aluminum Silicate, Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$)	49
Sodium Aluminum Silicate, ($\text{NaAlSi}_3\text{O}_8$) Albite	15
Calcium Silicate, (CaSiO_3) Wollastonite	11
Silicon Oxide, (SiO_2) Quartz	9
Iron Oxide, (Fe_2O_3) Hematite	9
Anorthite, ((Ca, Na)(Al, Si) $_2\text{Si}_2\text{O}_8$)	7
<u>Wall (Red)</u>	
Calcium Sulfate, Anhydrite (CaSO_4)	85
Silicon Oxide, Quartz (SiO_2)	8
Iron Oxide, Hematite (Fe_2O_3)	7
<u>Upper Cyclone Inlet</u>	
Calcium Sulfate, Anhydrite (CaSO_4)	60
Silicon Oxide, Quartz (SiO_2)	15
Calcium Carbonate, Calcite (CaCO_3)	15
Calcium Oxide, Lime (CaO)	10
<u>Bottom (Corner)</u>	
Calcium Sulfate, Anhydrite (CaSO_4)	61
Calcium Carbonate, Calcite (CaCO_3)	21
Calcium Oxide, Lime (CaO)	10
Silicon Oxide, Quartz (SiO_2)	5
Iron Oxide, Hematite (Fe_2O_3)	3

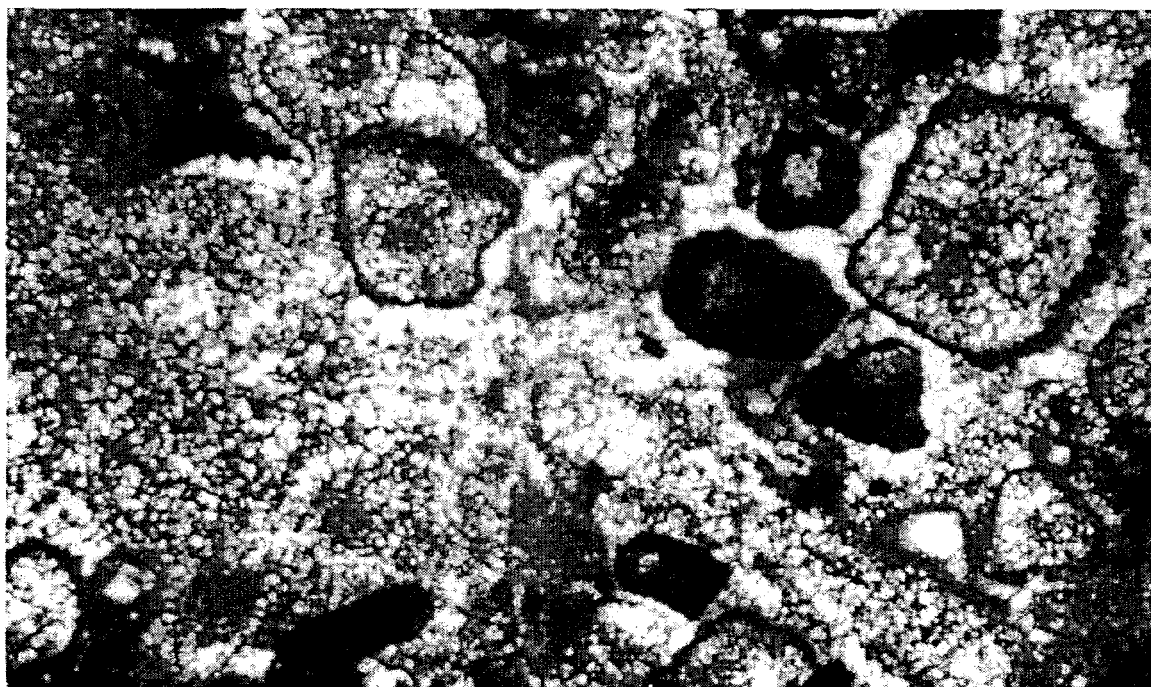


Figure 5. Photomicrograph of agglomerate in the loopseal area of a circulating fluidized bed combustor. Notice that the area between the particles has been filled with calcium sulfate. See text for discussion. (Field of view across the bottom of the photo is 0.7 mm).



Figure 6. Photomicrograph of a particle from an agglomerate found on the wall in a circulating fluidized bed combustor. Particles are developing rims of calcium sulfate. See text for discussion. (Field of view across the bottom of the photo is 0.7 mm).



Figure 7. Thin section of agglomerate found on combustor wall. Light colored areas are agglomerates of bed particles. Dark areas are very fine grained and may result from either deposition of very fine particles or flow of a viscous material. Length of the section is about one inch.

HYPOTHESES FROM PART 1

Three general types of mineralogic reactions were observed to occur in the agglomerates and deposits. Although alkalis may play a role with some "high alkali" lignites, we found agglomeration was initiated due to fluxing reactions between iron (II) from pyrites and aluminosilicates from clays. Agglomeration likely originated in the dense phase of the FBC bed within the volatile plume which forms when coal is introduced to the boiler. Secondary mineral reactions appear to occur after the agglomerates have formed and tend to strengthen the agglomerates. A third type of reaction that acts to strengthen agglomerates involves the filling of void space between agglomerate particles with recrystallized calcium sulfate. It appears as though this material is the result of recrystallization of fine particles of calcium sulfate present in the combustor as an aerosol.

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Part 2. Laboratory evaluation of agglomeration mechanisms hypothesized in Part 1

INTRODUCTION

Fluidized bed combustion is a widely accepted method to produce steam for process heat and electricity generation by burning coal and other low-grade fuels in an environmentally acceptable manner. The advantages of using a fluidized bed combustor (FBC) over other conventional methods of combustion include the capability of burning high-sulfur fuels, better heat transfer characteristics, and lower operating temperatures. Lower operating temperatures of fluidized bed combustors decrease NO_x emissions. The ability to burn high-sulfur fuels is achieved by adding sorbents to the bed during combustion, thus decreasing the need for flue gas scrubbers.

The bed material usually consists of an inert solid (e.g., sand) or a sorbent (e.g., limestone or dolomite) which is "fluidized" by an air stream at the bottom of the combustor. Problems can occur when bed material begins to cohere or "agglomerate", forming larger particles. As a result, a loss of fluidization may occur, leading to combustor shutdown. Dawson et al. [1,2] suggest that agglomeration of bed particles is the result of reactions involving aluminosilicate and iron particles, catalyzed by localized reducing (oxygen depleted) environments within the combustor.

A laboratory-scale FBC was used to simulate the physical and chemical conditions thought to initiate and contribute to the formation of agglomerates in industrial-scale boilers. This research tested the hypothesis that localized reducing conditions facilitate bed material agglomeration, even when bed temperatures remain below typical ash fusion temperatures [3]. Reducing conditions were induced by controlling the combustion air. Natural gas, in some tests, was injected into the already substoichiometric coal combustion zone, creating locally oxygen-depleted conditions. A method to detect agglomerates and monitor their growth was also employed during these tests. This method utilizes hydrostatic pressure gradient data to predict agglomeration.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic of the laboratory-scale FBC is shown in *Figure 1*. The combustor measures 20 cm in diameter and 2 m in height. A 2.5 cm thick layer of refractory lines the inner wall of the combustor. The combustion chamber is encompassed by a water jacket, which removes excess heat from the combustor. A 6.4 mm stainless steel tube is used to inject a plume of natural gas into the bed, which creates an extremely fuel-rich region in the bed. Bed pressure gradient, bed temperature, air flow rate, and gas composition are monitored and recorded every five seconds by a computer.

Exhaust gases exit the combustor near the top of the freeboard. Particles entrained in the exhaust are removed by a high-efficiency Stairmand cyclone designed to capture 90% of all particles 10 μm and larger. Exhaust gases are sampled by a 1 cm diameter probe located in the exhaust pipe. The gases pass through a tar trap to remove hydrocarbon tars present in the sample due to incomplete combustion. Particles remaining in the sample line are removed by a Balston type 30/12 particulate filter. An acid-mist filter and a Perma-Pure heatless dryer remove corrosive vapor and water vapor from the sample, respectively, before it is distributed to gas analyzers. Four gas analyzers are used to provide continuous measurement of exhaust gas composition, including O_2 , CO_2 , CO , and SO_2 . Two Beckmann model 820 non-dispersive infrared analyzers are used to measure CO and CO_2 . A Beckmann model 755 oxygen analyzer monitors O_2 concentration, while a Horiba model VIA-500 monitors SO_2 concentration.

Table 1 Proximate and ultimate analyses of Illinois #6 and Pittsburgh #8 coal (as received)

	Illinois #6	Pittsburgh #8
Moisture (%)	4.8	1.2
Ash (%)	26.5	27.5
Volatile (%)	32.1	34.8
Fixed Carbon (%)	36.6	36.5
Total	100.0	100.0
Carbon (%)	54.4	59.9
Hydrogen (%)	4.0	4.4
Nitrogen (%)	0.9	1.0
Total Sulfur (%)	4.9	4.9
Ash (%)	26.5	27.5
Oxygen (difference) (%)	9.3	2.3
Total	100.0	100.0

Each experiment used either sand or limestone as the bed material. Both sand and limestone were sieved to $850 \times 600 \mu\text{m}$. Either Illinois #6 or Pittsburgh #8 coal was used for these tests. The coal was sieved to $2.36 \times 9.5 \text{ mm}$. Table 1 shows the proximate and ultimate analysis for Illinois #6 and Pittsburgh #8 coal. The coal has a high ash content.

Two 9.5 mm stainless steel taps, located 2 and 4 inches above the distributor plate, are used to monitor pressure fluctuations in the bed. The hydrostatic pressure gradient across the two taps is measured by a 0 - 1250 Pa differential pressure transducer. The pressure gradient, Δp , in the

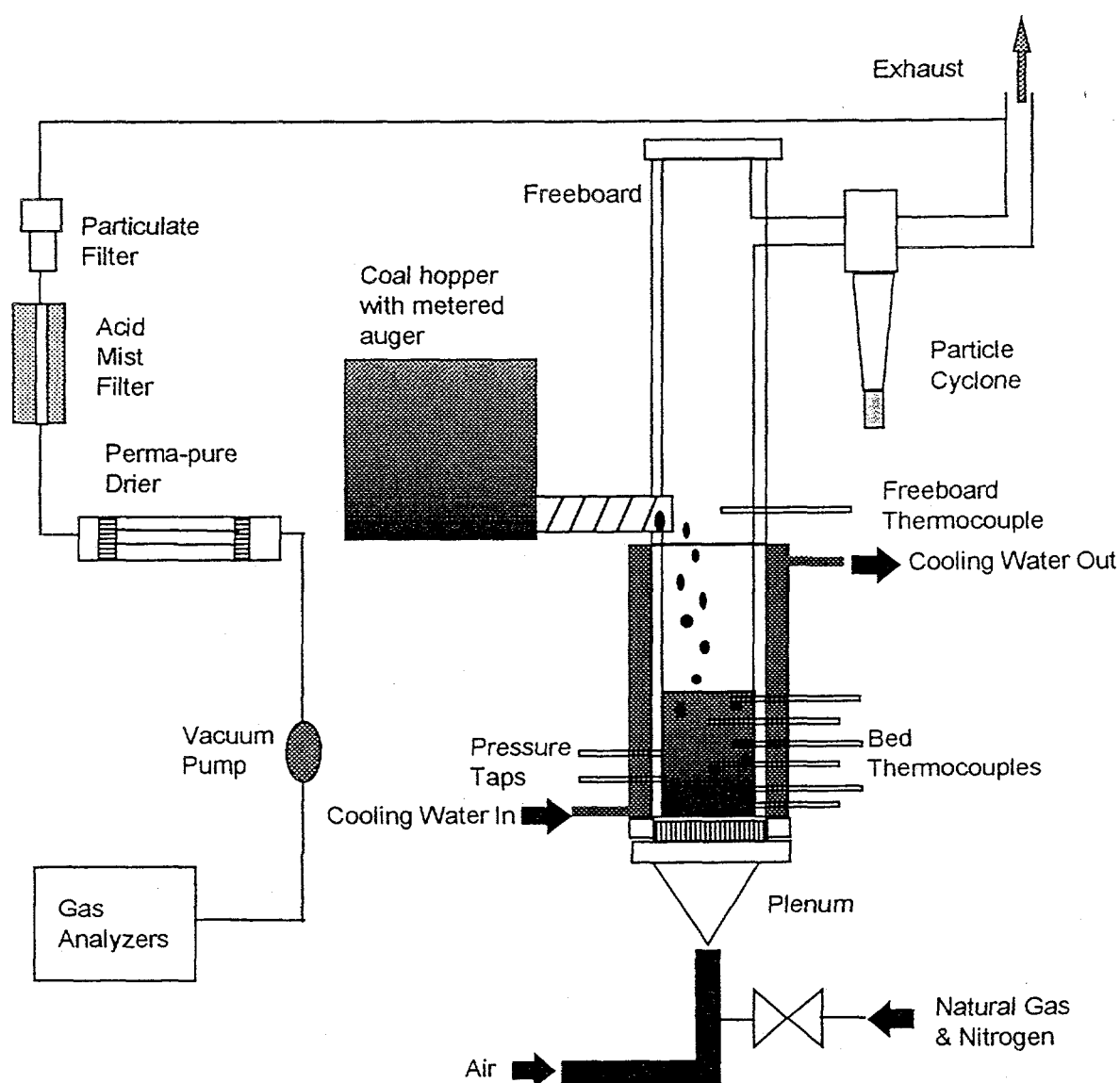


Figure 1 Schematic of laboratory-scale fluidized bed combustor

fluidized bed is directly related to the weight, W , of the material located between the pressure taps and inversely related to the cross-sectional area, A , of the combustor by the following equation [4]:

$$\Delta p = \frac{W}{A} \quad (1)$$

Also, the average magnitude of the bed pressure gradient is relatively independent of the fluidization gas flow rate. The bed pressure gradient will change, however, if the density of the material between the taps changes or if the bed material defluidizes between the taps. The bed pressure gradient will decrease as limestone calcines due to the decreased density of calcium oxide (CaO) compared to calcium carbonate (CaCO_3). In contrast, sulfation of calcium oxide to calcium sulfate (CaSO_4) will result in a bed pressure gradient increase due to the higher density of calcium sulfate compared to calcium oxide.

Bed material agglomeration is thought to cause abnormal fluctuations and/or a decrease in the bed pressure gradient. We used such irregularities in the bed pressure gradient to detect and monitor agglomerate formation. As agglomerates grow, they eventually become too large to remain fluidized. The agglomerated particles may then contribute to slugging, jetting, or defluidization of the bed material. A slugging or jetting bed may result in abnormal bed pressure gradient fluctuations. A decrease in the bed pressure gradient usually indicates defluidization, because bed material density generally remains constant.

A method employed to monitor changes in the bed pressure gradient and detect agglomerates is based on a modified moving average analysis of the pressure gradient data. The modified moving average of the bed pressure gradient, $\Delta \bar{p}[n]$, for a given data point, n , is determined by the following equation:

$$\Delta \bar{p}[n] = \frac{\sum_{j=0}^{100} \Delta p[n-j]}{100} - \frac{\sum_{k=0}^{10} \Delta p[n-k]}{10} \quad (2)$$

A moving average is calculated by determining the statistical mean of the current data point and a given number of previous data points. The calculated value is the difference between a 100 point moving average and an "instantaneous" 10 point moving average. During steady-state operation the difference between the ten and one-hundred moving point averages should be

small, on the order of ± 10 Pa. Instability within the combustor due to agglomeration, evidenced as increased pressure gradient fluctuations or change in magnitude of the bed pressure gradient, can be recognized as larger deviations from zero, on the magnitude of ± 35 Pa. A positive value of the modified moving average indicates the bed pressure gradient is decreasing in magnitude while a negative value indicates the bed pressure gradient is increasing in magnitude over time.

Type K thermocouples located throughout the bed material monitor the mixing condition of the bed. Uniform bed temperatures are characteristic of a well-mixed bed. A temperature gradient within the bed indicates partial defluidization of the bed may be occurring, generally near the distributor plate. Large diameter ash particles (high ash content in coal) may settle out of the actively fluidized bed and come to rest at the bottom of the bed. The combusting coal particles and hot bed material are unable to interact with the defluidized ash particles, which results in decreasing temperatures near the distributor plate.

Methane was used to preheat the bed to 700°C at which point coal was fed into the combustor. The coal feed rate was increased and the methane flow rate decreased simultaneously until the bed was burning only coal. The air flow and coal feed rates were adjusted to achieve the desired bed temperature, fluidization velocity, and equivalence ratio (air/fuel ratio). Baseline tests were conducted at 110% theoretical air while fuel rich tests were conducted at 50% theoretical air. The fluidization velocity was held at 0.75 m/s by using a combination of air and nitrogen to fluidize the bed. Bed temperature ranged from $825 - 925^{\circ}\text{C}$. For some experiments conducted under reducing conditions, methane was injected into the base of the bed to produce a highly fuel rich plume in the bed. We hypothesized that the fuel-rich plume might initiate reactions unique to conditions found near coal feed points in industrial-scale combustors.

The exhaust gas composition is representative of the conditions under which combustion is taking place. Exhaust gas composition does not indicate agglomerate formation and cannot be used to detect or monitor agglomeration. For baseline tests, excess oxygen will be present. For tests conducted under reducing conditions, air/fuel ratios less than unity, the oxygen level will be at or near zero. Carbon dioxide levels are dependent on fuel flow rate and oxygen availability does not give a direct indication of combustion conditions. Carbon monoxide will be emitted in high concentrations during experiments with an air/fuel ratio less than unity but will have a relatively low concentration during baseline experiments. Sulfur dioxide emissions are high for

experiments which utilize a sand bed. Sulfur dioxide is virtually non-existent in the exhaust gas stream, when limestone is used as the bed material. However, in laboratory batch tests, as the experiment proceeds and calcium oxide is consumed, sulfur dioxide emissions will increase.

RESULTS AND DISCUSSION

Experiments were performed to determine the effect theoretical air and bed material composition have on formation of agglomerates. The effect of a fuel-rich plume, created by injecting methane in the bed, was also tested. Results of these experiments are summarized in *Table 2*. The results show that agglomerates formed during experiments when reducing conditions and a methane plume were present, when either sand or limestone was used as the bed material. Agglomerates were also formed in a limestone bed operating with 50% theoretical air and no methane plume, but were not formed within a sand bed. No agglomerates were formed during baseline experiments. Several different test conditions are discussed below in detail.

Table 2 Summary of experiments using a laboratory scale fluidized bed combustor

Test	Equivalence Ratio	Bed Material	Fluidization Velocity (m/s)	Methane Plume	Agglomerates Formed	Temperature Excursion
1	1.20	Limestone	0.55	No	No	No
2	1.20	Limestone	0.75	No	No	No
3	0.50	Limestone	0.75	No	Yes	Yes
4	0.50	Limestone	0.75	No	Yes	Yes
5	0.60	Limestone	0.75	No	Yes	No
6	0.50	Limestone	0.75	No	Yes	No
7	0.70	Limestone	0.75	Yes	No	No
8	0.50	Limestone	0.75	Yes	Yes	Yes
9	0.50	Limestone	0.75	Yes	Yes	Yes
10	0.50	Limestone	0.75	Yes	Yes	No
11	1.10	Sand	0.60	No	No	No
12	1.10	Sand	0.75	No	No	No
13	0.70	Sand	0.75	No	No	No
14	0.60	Sand	0.55	No	No	No
15	0.60	Sand	0.55	No	No	No
16	0.50	Sand	0.75	No	No	No
17	0.50	Sand	0.75	No	No	No
18	0.50	Sand	0.75	Yes	Yes	No

Oxidizing conditions with limestone as the bed material

This experiment used approximately the same amount of excess air as industrial-scale combustors. The experiment is a baseline case to be compared with tests performed under reducing conditions. A minimum equivalence ratio of 1.20, or 120% theoretical air, was maintained throughout the experiment. No agglomerates formed during this experiment even though ash particles released from the coal eventually caused partial defluidization of the bed. Ash particles accumulate at the bottom of the bed since the combustor is not equipped to remove bottom ash.

Figure 2 and Figure 3 display temperature and bed pressure gradient data from Test 2. A bed temperature of 860°C was maintained during most of the experiment. The temperature increase 52 minutes into the experiment corresponds to the completion of the endothermic calcination reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). The temperature near the bottom of the combustor began to decrease due to ash-induced defluidization 225 minutes into the experiment. The initial decrease in the magnitude of the bed pressure gradient is also a result of the calcination reaction. The subsequent increase in the bed pressure gradient is a result of the sulfation reaction ($\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4$), which increases the average density of the bed material. The bed pressure gradient began to decrease in magnitude 230 minutes into the experiment. This decrease is small compared to instances when agglomerates occur, and its origin is unclear.

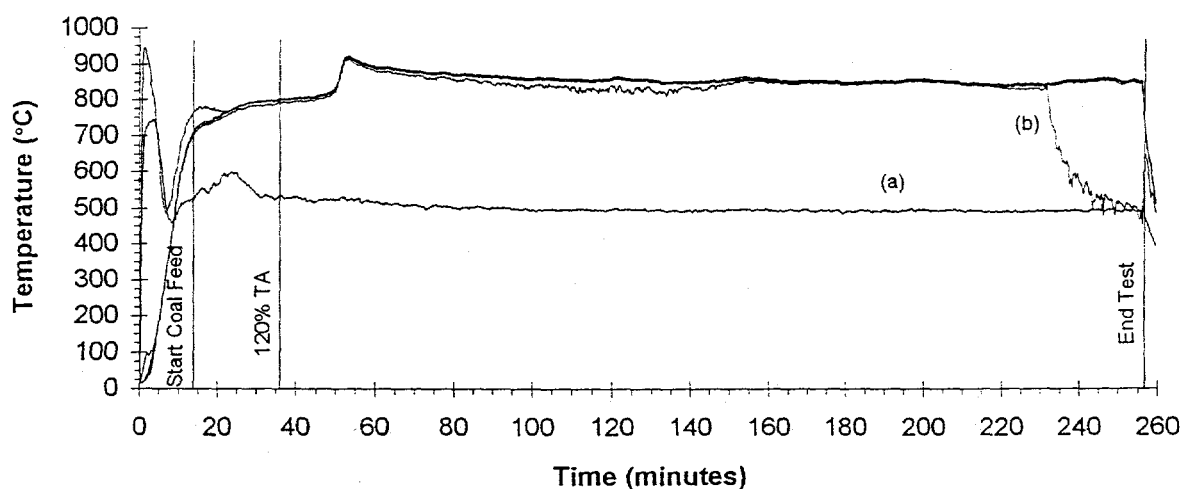


Figure 2 Combustor temperatures for equivalence ratio of 1.20 (120% theoretical air). (a) freeboard temperature, (b) temperature decrease near distributor plate due to defluidization of large ash particles

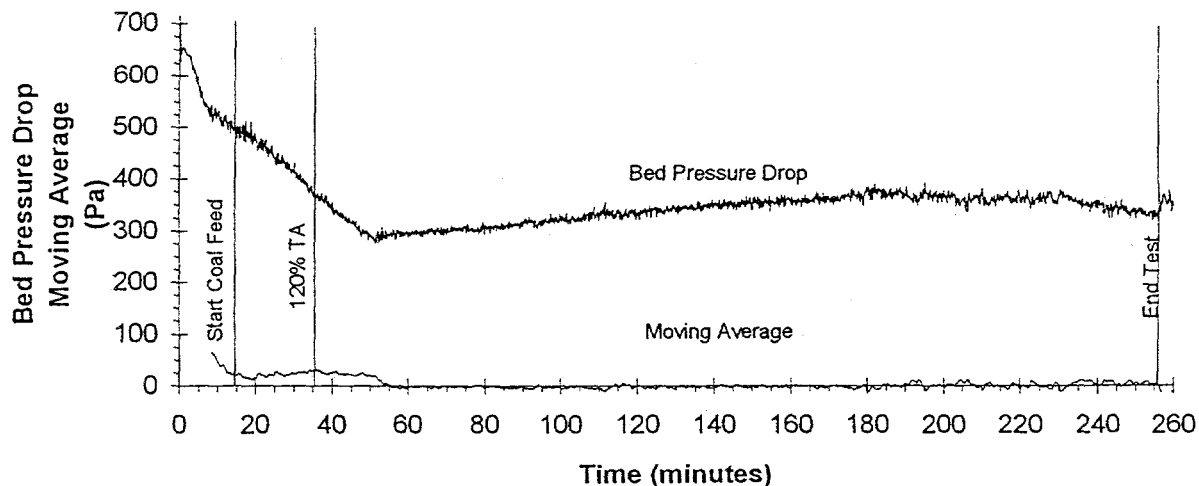


Figure 3 Bed pressure gradient and modified moving-average bed pressure gradient for equivalence ratio of 1.20 (120% theoretical air)

Reducing conditions with limestone as the bed material.

It was hypothesized that reducing conditions near coal feed locations in industrial size combustors may contribute to bed material agglomeration. To test this hypothesis, an equivalence ratio of 0.50, or 50% theoretical air, was investigated in a limestone bed. Upon completion of the test, agglomerates measuring 1 to 3 cm in diameter were retrieved from the bed. The agglomerates appear to be composed of coal char and coal ash with limestone particles covering the surface. The agglomerates were a blackish-gray color with a speckled white surface.

Figure 4 and Figure 5 display the temperature and bed pressure gradient data from Test 6. Bed temperatures ranged from 860 - 900 °C after the calcination reaction was complete. The temperature increase at time 50 minutes corresponds to completion of the calcination reaction. The temperature near the bottom of the combustor began to decrease due to ash-induced defluidization 58 minutes into the test. The progression of the defluidization is evident in decreasing temperatures at subsequent thermocouple locations. The initial decrease in the magnitude of the bed pressure gradient is also a result of the calcination reaction. The bed pressure gradient then stabilized at a value of 300 Pa until time 68 minutes when it began to decrease steadily until the experiment was terminated. The decrease in magnitude and increase in fluctuations of the bed pressure gradient is consistent with the formation of agglomerates in the fluidized bed.

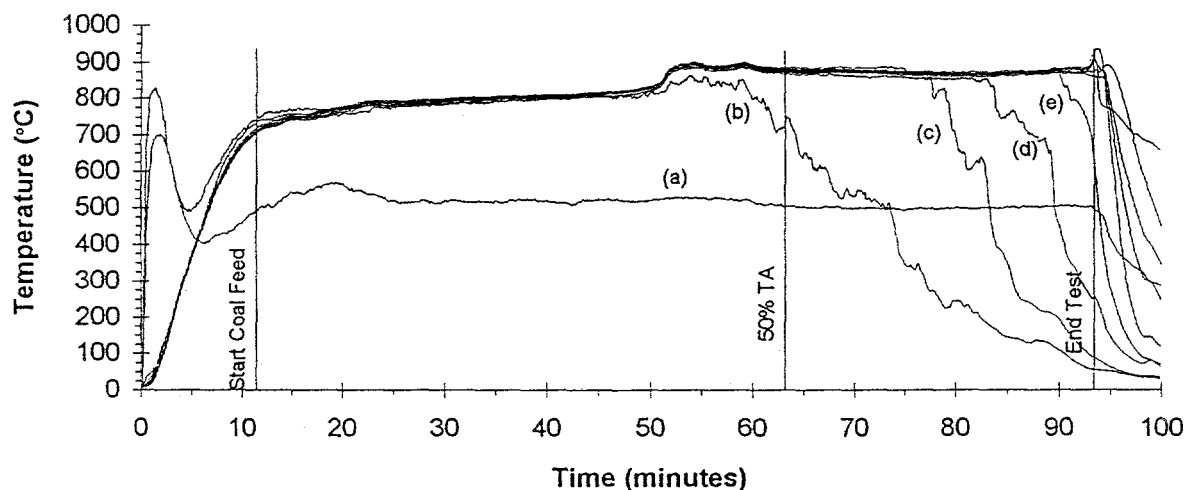


Figure 4 Combustor temperatures for equivalence ratio of 0.50 (50% theoretical air). (a) freeboard temperature, (b-e) temperature decrease near distributor plate due to defluidization of large ash particles

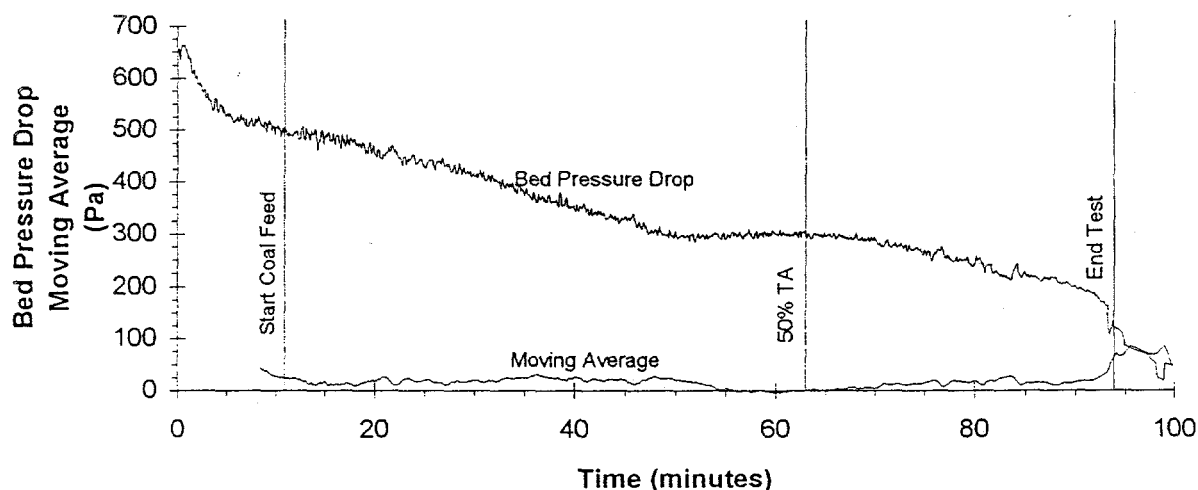


Figure 5 Bed pressure gradient and modified moving-average bed pressure gradient for equivalence ratio of 0.50 (50% theoretical air)

Reducing conditions and methane plume with limestone as the bed material.

These experiments are similar to previous tests except for the addition of a methane plume in the bed. For example, in Test 10, an equivalence ratio of 0.50, or 50% theoretical air, was achieved in a limestone bed. The temperature and bed pressure gradient data are very similar to that of the limestone test with reducing conditions and no methane plume. Ash-induced

defluidization occurred near the distributor plate. The bed experienced large pressure gradient fluctuations and bed pressure gradient decreased towards the end of the experiment, consistent with agglomerate formation in the bed. Agglomerates, similar in size and appearance to those formed in Test 2, were retrieved from the bed.

Oxidizing conditions with sand as the bed material.

These experiments are similar to the limestone-bed test with oxidizing conditions except that sand was used as bed material. Test 12 is a baseline case to be compared with tests performed under fuel-rich conditions. A minimum equivalence ratio of 1.10, or 110% theoretical air, was maintained throughout the experiment. In the absence of limestone, the characteristic changes in the bed pressure gradient and temperature due to calcination and sulfation are not observed for sand-bed tests. A monotonic bed pressure gradient is consistent with the fact that no agglomerates formed during this experiment. Ash-induced defluidization occurs in both limestone-bed and sand-bed tests.

Reducing conditions with sand as the bed material.

These experiments are similar to limestone-bed tests with reducing conditions except that sand was used as bed material. An equivalence ratio of 0.50, or 50% theoretical air, was investigated in Test 17. The temperature and bed pressure gradient data remained constant throughout the experiment (except for the ash-induced defluidization and subsequent cooling near the distributor plate). No agglomerates formed during this experiment even though particles within the bed defluidized within a reducing environment. Also, calcium, which may be a contributing factor for agglomeration, is introduced to the reactor via limestone and is not present in these experiments.

Reducing conditions and methane plume with sand as the bed material.

Experiments with a methane plume injected into the bed were an attempt to produce agglomerates in a sand bed. From the previous experiment it is clear that agglomeration does not

occur for equivalence ratios above 0.50. However, self-sustaining combustion below an equivalence ratio of 0.5 was not possible in the laboratory combustor. The injection of a methane plume allowed a strongly oxygen-depleted zone to be produced in the bed. It is hypothesized that such extreme reducing conditions may occur near coal feed points in industrial scale combustors. For Test 18, the combustor was operated with an equivalence ratio of 0.50 and a methane plume injected into the bottom of the sand bed. The temperature data remained constant throughout the experiment (except for the ash-induced defluidization and subsequent cooling near the distributor plate). The bed pressure gradient remained constant until the end of the experiment when fluctuations increased and the magnitude decreased, indicative of agglomeration. Upon completion of the test, a single agglomerate, approximately 3 cm in diameter, was retrieved from the combustor. The agglomerate appeared to be composed of coal char and coal ash with little sand present.

Mechanism of Agglomeration

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 6 is a scanning electron back-scatter image of an agglomerate formed in a sand bed at low 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 7* shows an example of new mineral phases formed within the melt and around bed particles. The results of the laboratory-scale combustor agglomerate analyses resemble analyses of agglomerates retrieved from industrial-scale FBCs [1,2].

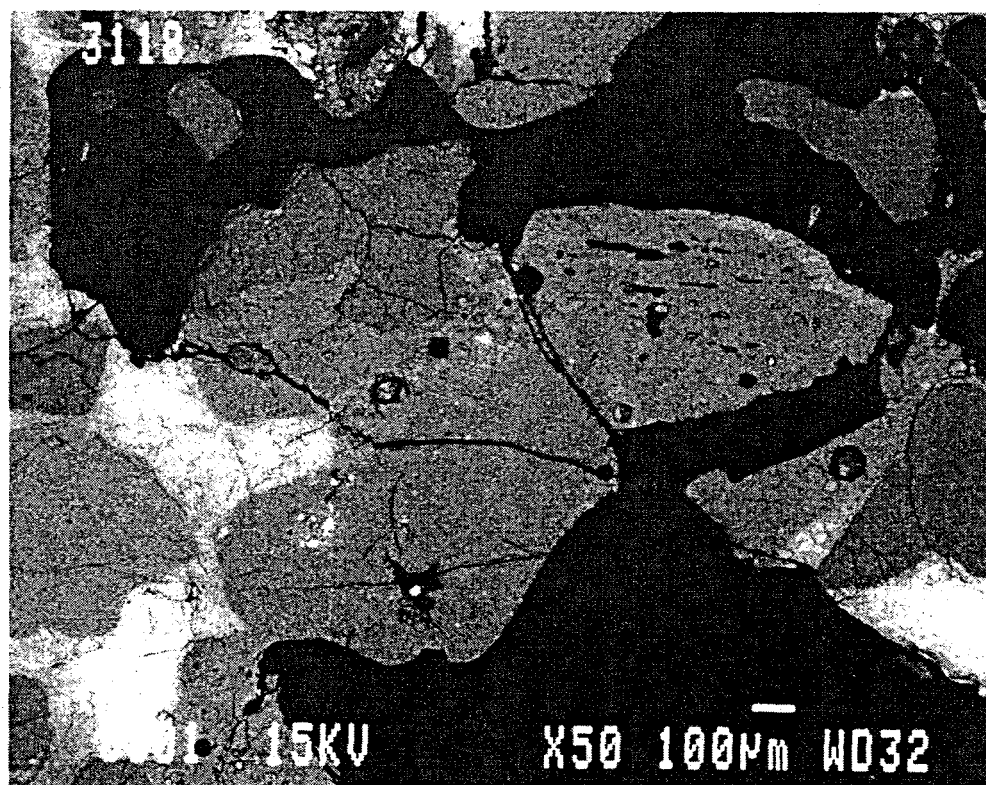


Figure 6 Scanning electron photograph (back-scattered electrons) of agglomerated bed particles. Darker areas contain materials with higher atomic numbers. The darker gray areas are bed particles which have been cemented together by the lighter gray material. Black areas are voids. See text for discussion.



Figure 7 Photomicrograph showing mineral reactions around quartz grains in the agglomerated bed material. Field-of-view is 0.7mm. See text for discussion.

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 feldspar 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. 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 2θ . The composition of the melted material was characterized by electron microprobe and was found to be somewhat variable.

Because of the high alkalis in the glass (Na, K, and Ca), 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.

The other dominant mineralogical reaction in the agglomerates may be the result of solid-solid reactions involving calcium and magnesium with aluminosilicate minerals or calcium and magnesium with the aluminosilicate melt. *Figure 7* 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 [5].

CONCLUSIONS

Results obtained using the laboratory-scale combustor may be applied to industrial-scale combustors. The method of feeding coal into industrial-scale combustors is of utmost importance. If coal feed is limited to one location localized reducing zones may occur. These localized reducing zones may lead to agglomeration as shown by this research. It is also important to maintain a well-mixed bed. Poor lateral bed mixing may lead to fuel rich zones or local hot spots and subsequent agglomeration.

Experiments performed in a laboratory-scale FBC support the hypothesis that a reducing atmosphere during fluidized bed coal combustion contributes to the formation of agglomerates. It is hypothesized the reducing conditions induced in the laboratory-scale FBC simulate conditions which may be found in industrial size combustors. These localized reducing conditions may arise from either poor lateral bed mixing or oxygen-starved conditions at coal feed locations. Reducing conditions are imposed by controlling the amount of combustion air supplied to the combustor, 50% of theoretical in these experiments.

Bed pressure gradient data may be used to detect and monitor agglomerate formation. Deviations from steady-state operating values in bed pressure drop may indicate the presence of agglomerates. These deviations are monitored by employing a modified moving average analysis.

Three general types of mineralogic reactions were observed to occur in the agglomerates and deposits. Although alkalies may play a role with some "high alkali" lignites, we found agglomeration was initiated due to fluxing reactions between iron (II) from pyrites and aluminosilicates from clays. Agglomeration likely originated in the dense phase of the FBC bed within the volatile plume which forms when coal is introduced to the boiler. Secondary mineral reactions appear to occur after the agglomerates have formed and tend to strengthen the agglomerates. A third type of reaction that acts to strengthen agglomerates involves the filling of void space between agglomerate particles with recrystallized calcium sulfate. It appears as though this material is the result of recrystallization of fine particles of calcium sulfate present in the combustor as an aerosol.

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