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Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report for the Period
April 1, 1995 - June 30, 1995

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Abstract

During this quarter, agglomeration tests were conducted in a laboratory-scale fluidized bed combustor using coal and "model" components which allowed controlled amounts of clays and pyrites to be added during the test. These tests permitted a more direct evaluation of the interaction between iron compounds and aluminosilicates. With additional clay and pyrite (under simulated local reducing conditions found at coal feed locations) large agglomerates formed. The agglomerates were many times larger than those formed with a standard coal feed. When only clay was added to the fuel (no additional pyrite), agglomerates formed but they were much smaller and very friable. These tests support the hypothesis that local reducing conditions promote the interaction of iron in a +2 state and aluminosilicate material in the coal which leads to agglomeration during fluidized bed combustion.

Also during this quarter, a deposit which formed in a fluidized bed boiler of a Texas-New Mexico Power Company was analyzed to determine the chemical and mineralogic mechanisms responsible for deposit formation. Mineral phases were determined by x-ray diffraction (XRD). Bulk chemical composition was determined by x-ray fluorescence spectroscopy (XRF). Polished sections of the deposit were made for optical and scanning electron microscopy.

The deposit was found to have high concentrations of calcium and sulfur, 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.

The mineral phases present in the deposit indicate that localized reducing conditions may have been present in portions of the boiler. Calcium sulfide (CaS) and calcium sulfite (CaSO₃) in the deposit certainly indicate reduced sulfur species. The mineral hercynite (Fe⁺²Al₂O₄) is a spinel mineral which most likely formed from interaction between iron in the +2 state and aluminosilicate materials. Iron in this mineral most likely originated from pyrite in the coal and alumina from clays also in the coal. 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 will oxidize to form +3 iron oxides (hematite Fe₂O₃).

The chemical composition of this deposit is consistent with other deposits and results of experimental studies which indicate that under local reducing conditions in a fluidized bed boiler, iron can react with aluminosilicate material from the coal and form a cohesive layer around sorbent particles causing them to become sticky and agglomerate.

Also during this quarter, a poster was presented at the contractors review meeting in Nashville, Tennessee. At that time, this project was also reviewed by the Department's Office of Energy Research (OER) Support Office from Oak Ridge National Laboratory (ORNL).

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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

Combustion Tests

During this quarter, tests were conducted using "model" components which introduced controlled amounts of clays and pyrites. These tests permitted a more direct evaluation of the interaction of iron compounds with aluminosilicates.

For these tests, coal derived pyrite was used. The pyrite was obtained by grinding coal to -40 mesh. Pyrite was separated from the coal and other minerals by wet processing using a Deister concentrating table. Clay minerals were obtained from a commercial product used primarily as a sorbent. This material was analysed by x-ray diffraction (XRD) to determine the mineral composition and by x-ray fluorescence spectroscopy (XRF) to determine the bulk chemical composition. The material was primarily clay from a group of minerals known as swelling clays, specifically from the montmorillonite group. Other minerals present include the clay mineral illite and the mineral quartz. The bulk chemical composition is shown in Table 1.

Clay and pyrite were added in the same proportion as found in the coal (about 2:1 clay to pyrite). In one test, clay and pyrite were added to simulate three times the amount of these materials normally found in the coal. The pyrite and clay were combined prior to combustion then added in batch amounts throughout the test. The fuel used for these tests was Pittsburgh 8 coal. Localized reducing conditions within a boiler were simulated using 60% theoretical air for combustion.

Table 1. Bulk chemical composition of clays added to combustion experiments.

SiO ₂	66.39
Al ₂ O ₃	10.65
Fe ₂ O ₃	4.43
MgO	2.14
CaO	1.40
Na ₂ O	0.00
K ₂ O	1.09
TiO ₂	0.48
P ₂ O ₅	0.10
SO ₃	0.28
SrO	0.05
BaO	0.06
LOI	<u>11.90</u>
Total	98.97

In the tests with both clay and pyrite added, large agglomerates were formed. The agglomerates were many times larger than those formed when coal was combusted with typical amounts of clay and pyrite. In tests in which additional clay was added to the fuel, agglomerates were formed but they were much smaller in size and very friable. These tests support the hypothesis that local reducing conditions promote the interaction of iron in a +2 state and aluminosilicate material in the coal which leads to agglomeration during fluidized bed combustion.

Analyses of Deposits from Commercial Facilities

During this quarter, a deposit which formed in a fluidized bed boiler of a Texas-New Mexico Power Company was analyzed to determine the chemical and mineralogic mechanisms responsible for deposit formation. The results from x-ray diffraction are shown in Table 2. The bulk composition of the boiler deposit is given in Table 3.

Table 2. Mineral phases present in a deposit formed in a boiler at a Texas-New Mexico Power Company.

<u>Mineral Phase Present</u>	<u>Approximate Amount Present</u>
Calcium aluminum Silicate (Gehlenite)	57
Calcium Sulfide (Oldhamite)	14
Calcium Silicate Ca ₂ SiO ₄	11
Iron Aluminum Oxide (Hercynite)	9
Calcium Sulfite (CaSO ₃)	9

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

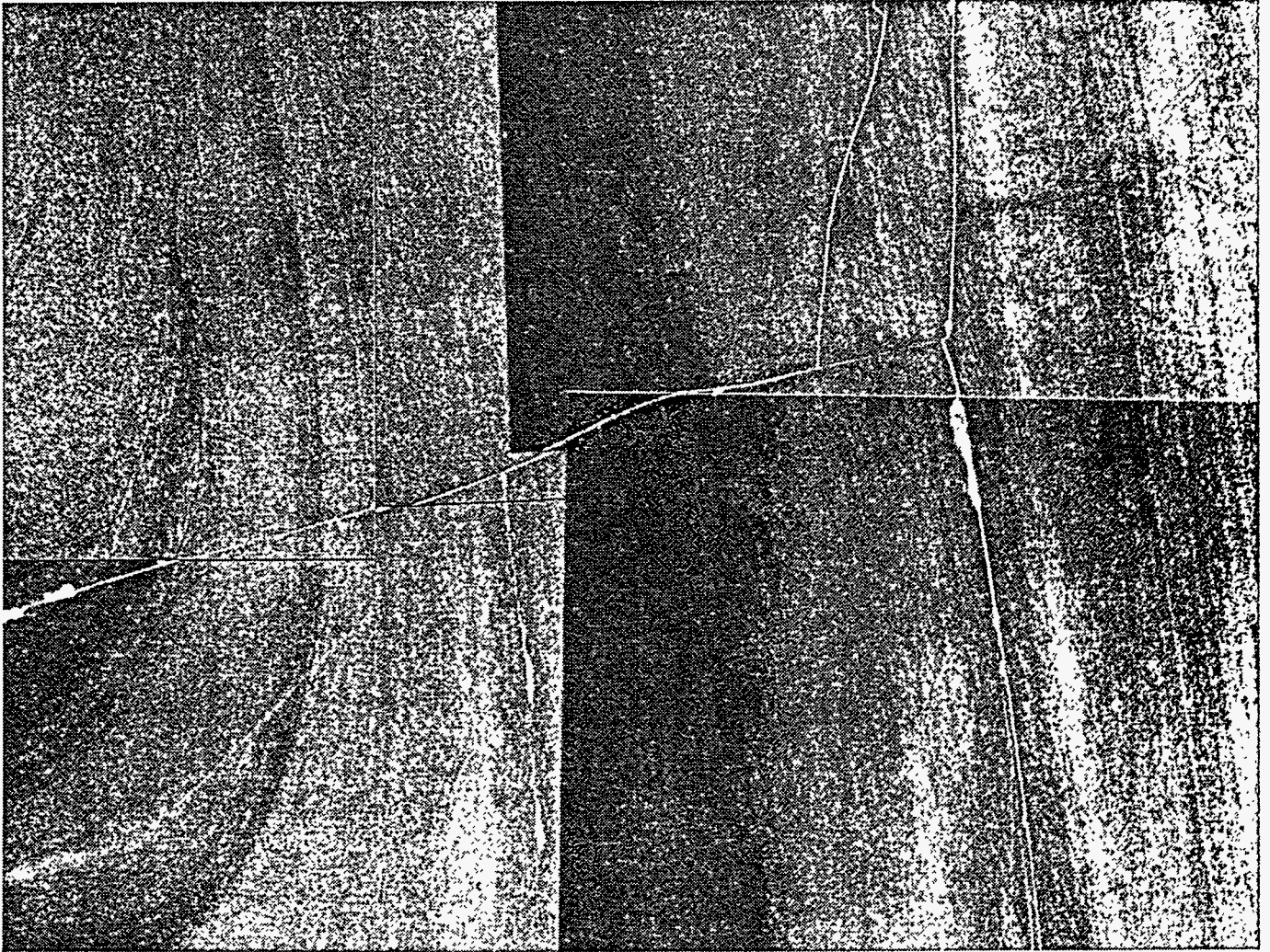
	<u>Tex</u>	<u>STD</u> ^a	<u>Publ</u> ^b
SiO ₂	19.82	49.35	48.78
Al ₂ O ₃	12.20	27.08	27.02
Fe ₂ O ₃	6.70	13.92	13.44
MgO	4.55	0.70	0.75
CaO	44.87	15.4	15.9
Na ₂ O	0.00	3.04	3.05
K ₂ O	0.03	2.09	2.26
TiO ₂	1.33	1.43	1.33
P ₂ O ₅	0.05	0.39	0.38
SO ₃	14.41	0.11	0.18
SrO	0.22	0.13	0.08
BaO	0.04	0.20	0.15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

Figure 1 is a photomicrograph from a thin section of the deposit. The deposit was formed in layers, perhaps from the viscous flow of material.

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.



Discussion

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.

The mineral phases present in the deposit (Table 2) 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). The mineral hercynite (Fe⁺²Al₂O₄) 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. 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 Fe₂O₃).

The mineral gehlenite (Ca₂[Al₂SiO₇]) 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 the 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.

The chemical composition of the Texas-New Mexico deposit is consistent with other deposits we have analysed. The implied mechanism of formation is also consistent with results of experimental studies which indicate that under local reducing conditions in a fluidized bed boiler, iron can react with aluminosilicate material from the coal and form a cohesive layer around sorbent particles causing them to become sticky and agglomerate. Secondary reactions between silicates and calcium may also act to strengthen the deposit.

Future Work

Work planned for the next quarter includes further testing of fuels with differing amounts of silica and iron. We will also be preparing a final report which will summarize our results.