

Task 3.7 - Fuel Utilization Properties

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TASK 3.7 - FUEL UTILIZATION PROPERTIES

1.0 INTRODUCTION

The goal of the Fuel Utilization Properties project was to determine the impacts of specific coal properties and additives on ash formation and deposition in advanced power systems. At the forefront of advanced power systems for coal utilization are pressurized fluidized bed (PFB) reactors and integrated gasifier-combined cycle (IGCC) reactors. Some of these systems are still in the infancy of their development and commercialization and very little is known about the types of ash deposition problems that could occur. Ash deposition in power generating systems is a significant problem that decreases efficiency and can lead to severe operational problems. During high temperature conversion of coal, the inorganic constituents in the coal are transformed into solid, liquid, and vapor species that differ in composition and size from the original inorganic constituents present in the coal. The chemical and physical properties of the intermediate ash stream are dependent in part upon the types, quantities and association of the minerals and other inorganics in the coal. There is a pressing need to obtain critical information on the aspects of inorganic transformations and deposit formation that will apply to advanced power systems so that mitigation measures can be prescribed such as predictive models, system design or operational changes, and the use of additives. The focus was on integrated gasification combined cycle (IGCC)-type systems, whereby small-scale furnaces were employed to simulate gasification or highly reducing conditions in order to produce entrained ash and deposits for analysis.

2.0 OBJECTIVES

The overall objectives of this project were to determine key fuel properties and mechanisms that impact ash formation and deposition in advanced power systems and to propose and test measures for mitigating ash deposition. Specific goals for this year's work in the area of ash formation and deposition in advanced power systems included the following:

- Determining the general chemical and physical properties of simulated entrained ash and deposits that may lead to operational problems.
- Identifying and testing methods to mitigate deposition in IGCC-type systems.

3.0 EXPERIMENTAL

Drop-tube furnaces were used for carrying out pressurized combustion and gasification tests (Figure 1). A pressurized drop-tube furnace (PDTF) and an atmospheric drop-tube furnace (ADTF) were used, both having the same dimensions; however the PDTF is encased in a water-cooled pressure vessel rated for up to ten atmospheres of pressure. Both systems act as laboratory-scale entrained flow reactors. The gas temperature, pressure, atmosphere, and particle residence time can be controlled closely in the drop-tube furnace. The ceramic reaction tube assembly is externally heated with two high-temperature tube furnaces capable of attaining a maximum of 1500°C. The top furnace, consisting of three separate zones, provides the desired temperature for

the reaction zone, while the bottom furnace controls the temperature in the sample deposition and collection zone. The temperature in each of the four heating zones is individually controlled by proportional-integral and derivative controllers. Feed rates are between 0.1–0.5 g/min with 1–5 actual liters of gas in the reaction during operation, corresponding to 4–20 standard liters of gas input.

Operation of the PDTF requires the initial pressurization of the entire vessel after the furnace has been brought up to the desired operating temperature, usually with an inert gas. During operation, the pressure of the reactor is controlled by metering the exit gas with an electronic pressure controller, balancing the outlet flow to the input of the feed gas plus any gas produced during operation.

Fluidized coal, typically 80% -200 mesh, is introduced into the reactor with a carrier (primary) gas through a water-cooled injector probe. This injector is mounted to a translating device, which moves the injector in the center of the reactor tube to various heights to allow variable residence times of the feed in the reactor zone. Optional secondary gas enters the reactor at the top of the reactor tube and flows down through the tube around the injector assembly and mixes with the primary gas and feed. The coal residue and process gases travel down the reactor tube in a laminar flow regime and pass through the accelerator, where they are collected by a water-cooled, nitrogen- quenched ash collection probe or a water-cooled deposition probe. Various collection devices can be attached to the outlet of the collection probe to collect the gases and solids. The process gases exiting the collection device are monitored by on-line O₂, CO, and CO₂ gas analyzers and by taking gas bag samples for off-line gas chromatography (GC). The remainder of the process gases are then routed out through a vent.

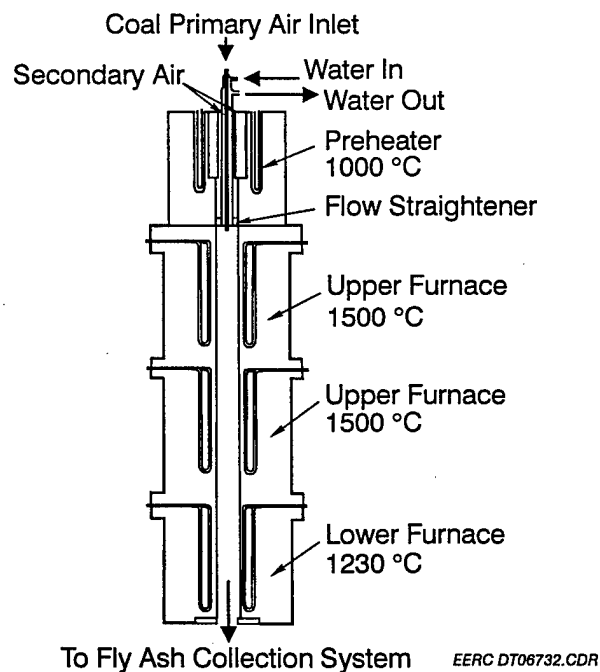


Figure 1. Schematic of the reaction tube and furnace assembly associated with the drop-tube furnace systems used for gasification tests.

4.0 ACCOMPLISHMENTS

Experiments were conducted on both the PDTF and the ADTF to determine ash transformations, fouling deposition mechanisms, and the effectiveness of additives for mitigating ash deposition in gasification applications. This project also has looked into the feasibility of modifying an existing ash formation model designed for conventional combustion to use for gasification applications. The two coals used were Black Thunder subbituminous and Illinois bituminous. Compositions of these coals are given in Table 1. Major initial coal inorganics in the Black Thunder consist of quartz, kaolinite, and an abundance of organically bound calcium aluminum, and magnesium. The organic association of the major elements was determined by chemical fractionation; approximately 80%–100% of oxide forms (Table 1) of calcium, magnesium, and sodium and 50% of the aluminum was organically bound. Illinois No. 6 consists mainly of quartz, illite, kaolinite, and pyrite. Quantities of organically bound ash are negligible in the Illinois coal.

TABLE 1

Analysis of Test Coals

	Black Thunder	Illinois No. 6
Proximate, wt%		
Moisture	24.30	11.70
Volatile Matter	35.88	34.97
Fixed Carbon	35.32	43.39
Ash	4.49	9.95
Ultimate, wt%		
Hydrogen	7.04	5.34
Carbon	52.84	61.99
Nitrogen	0.70	1.05
Sulfur	0.39	2.85
Oxygen	34.54	18.83
Ash	4.49	9.95
Elemental Oxides, wt%		
SiO ₂	32.57	23.54
Al ₂ O ₃	16.81	9.21
Fe ₂ O ₃	5.69	12.33
TiO ₂	1.11	0.41
P ₂ O ₅	1.17	0.04
CaO	22.09	1.45
MgO	4.79	0.67
Na ₂ O	0.93	0.41
K ₂ O	0.15	1.00
SO ₃	14.69	50.95
Minerals, wt%, mineral basis		
Quartz	24.1	23.30
Kaolinite	29.1	13.80
Illite	0.70	12.20
Pyrite	4.70	26.70
Calcite	0.0	6.0
Other	41.40	24.00

The reasons for selecting these coals are as follows:

- Black Thunder has levels of sodium, potassium, and calcium likely to cause deposition and fouling problems in an advanced gasification system and is already recognized as a problem coal in some conventional combustion systems. The level of calcium makes it likely that the lower-temperature calcium sulfide deposits will be formed. It also contains a small amount of kaolinite, which reduces the propensity for inherent interfering sorbing action of the ash in the flame. Kaolinite has been proven to be a good getterer of certain coal minor elements such as sodium in conventional combustion systems.
- Illinois No. 6 coal has only small amounts of calcium, minimizing the likelihood of low-temperature calcium sulfide deposits forming. Instead, the high levels of iron, primarily as pyrite, and aluminosilicates should form primarily high-temperature iron sulfide and iron aluminosilicate deposits.

4.1 Inorganic Transformations Under Gasification or Highly Reducing Conditions

Determination of mechanisms of coal inorganic transformations under reducing or gasification conditions was accomplished using the pressurized drop-tube furnace (PDTF). Several important upgrades and enhancements were made to the PDTF to improve operating performance and to allow effective operation under simulated IGCC system conditions. A new lower furnace was installed and furnace insulation replaced in the upper three furnace zones, as was the central ceramic reaction tube. The load cell that monitors the coal feed rate was upgraded to 0.01-gram accuracy, allowing more precise control of sample feeding. Of particular importance was the installation of additional gas-handling equipment and mass-flow controllers on the PDTF facility. The PDTF was upgraded to operate with gas mixtures of CO, CO₂, H₂, and water, which more closely simulate the reducing conditions encountered in advanced systems.

Entrained ash was produced for several coals using gas compositions, temperatures, and pressures similar to those used in current IGCC systems. A first-generation model of inorganic transformations under gasification conditions is in the process of being formulated by revising an existing Energy & Environmental Research Center (EERC) model called ATRAN, which predicts entrained ash particle-size and composition distribution for a conventional pulverized coal combustion system. Mechanisms of inorganic transformations which were deduced here were used in conjunction with another project to enhance the ATRAN code. Modifications were made to the existing ATRAN program by converting the original FORTRAN program to a more compact and faster C language program. Debugging and enhancements to some of the algorithms have also been completed. Enhancement of ATRAN to include mechanisms of coal inorganic transformations under reducing or gasification conditions appears to be feasible, however, this work was not intended to be fully performed under this program. The database for ATRAN was expanded to include data from Illinois No. 6, Pittsburgh No. 8, and Sufco coals. As a result of the gasification testing performed here, the formation of reduced ferrous oxidized iron species such as wüstite and iron sulfides, such as pyrrhotite, derived from the coal mineral pyrite, have replaced algorithms which were in place only for pyrite transformation to ferric oxide or hematite. Future work administered under other projects will need to focus more on the formation of sulfides of calcium and the interaction of calcium and iron with aluminosilicate material.

Mineral transformations during the combustion of Black Thunder and Illinois No. 6 coals were examined at atmospheric pressure under oxidizing conditions of 50% excess air and fuel-rich conditions of 0% and -50% excess air. These tests provided a basis of comparison with tests under strongly reducing pressurized conditions. The fly ashes produced were analyzed by computer-controlled scanning electron microscopy (CCSEM) to determine particle-by-particle composition and mineral phases.

Mineral phases as determined by CCSEM analysis for the bulk fly ashes are given in Table 2. Because of the large percentage of "unknown" material (16.6% to 45.4%), specific trends of mineral transformations should be treated with caution. For the Black Thunder ash, the effect of fuel-rich conditions appears to be an increase in quartz, calcite, dolomite, and calcium-rich phases, along with a decrease in gypsum-aluminosilicate phases. This may be the effect of the lower particle temperature and oxygen-lean atmosphere reducing the interaction and assimilation of pure quartz and organically bound calcium into mixed calcium aluminosilicate phases. The large (45%) unknown category for the Black Thunder under full air conditions is indeed dominated by particles composed predominantly of calcium, silicon, and aluminum. For the Illinois No. 6 ash, the fuel-rich conditions give a decrease in iron oxide, iron and sodium aluminosilicates, and iron silicate. There is a corresponding increase in pyrite and pyrrhotite, which were absent under full air conditions. The fuel-rich conditions appear to prevent the oxidation of pyrite and pyrrhotite to iron oxide, along with less assimilation of iron into mixed phases because of the lower temperatures.

An alternative method of examining mineral matter transformations is given in Figures 2 and 3 for calcium and iron. Here, the cumulative percentage of the total particles by volume is plotted versus the elemental concentration for specific elements. This allows visualization of the general behavior of the element without using specific mineral categories, thus avoiding the problem of the "unknown" category.

For the Illinois No. 6, calcium shows little change between oxidizing and fuel-rich conditions. Approximately 85% of the particle volume contains less than 15% calcium, and 15% of the volume contains greater than 80% calcium, with very few intermediate particles. By contrast, the Black Thunder shows 60% of the particle volume with calcium concentrations between 40% and 70% under oxidizing conditions. At 0% excess air, 60% of the particle volumes have little or no calcium, with the remainder having an evenly distributed increasing calcium concentration. At -50% excess air, the calcium concentration is separated, with 60% of the particle volumes having little or none, and 25% having very high calcium concentrations of 60% or greater. The interpretation is that under oxidizing conditions (full air) in the Black Thunder ash there is extensive interaction of calcium with the aluminosilicates to form calcium aluminosilicates of between 60% and 80% calcium. This is possibly a result of higher particle temperatures and the decomposition of calcium carbonates to calcium oxide. At more fuel-rich conditions of 0% excess air, some interaction still takes place, but to a lesser extent. Finally at -50% excess air, conditions are unfavorable for calcium-aluminosilicate interaction and favorable for the formation of calcium oxide and carbonates; hence the division into particles with very low and very high calcium levels.

Iron in the Black Thunder coal is a relatively minor component, and little change is seen between full air and fuel-rich conditions. For the Illinois No. 6 under full air, the iron concentration in the particle volumes is either quite low or quite high: less than 20% or greater than 80%. This is indicative of some interaction of iron with other species at low concentration,

TABLE 2

Mineralogy of the Bulk Filter Fly Ashes as Determined Using Computer-Controlled Scanning Electron Microscopy

	Black Thunder, full air	Black Thunder, 0% EA ¹	Black Thunder, -50% EA	Illinois No. 6, full air	Illinois No. 6, 0% EA	Illinois No. 6, -50% EA	Wyodak, full air
Quartz	9.8	16.8	17.0	19.4	18.2	18.8	13.0
Iron oxide	0.7	2.5	0.8	10.7	6.2	0.8	0.7
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.1	0.1	0.1	0.1	0.0	0.4	0.0
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcite	1.4	1.4	2.9	3.2	3.1	5.3	0.0
Dolomite	0.3	2.4	4.3	0.0	0.0	0.0	0.0
Ankerite	0.0	0.0	0.1	0.0	0.0	0.0	0.0
Kaolinite	4.5	11.5	7.0	4.4	7.1	4.8	1.9
Montmorillonite	1.1	2.8	0.7	6.6	7.6	4.9	2.5
K Al-Silicate	0.7	1.1	0.9	9.2	11.2	7.9	1.7
Fe Al-Silicate	0.2	0.1	0.1	7.9	6.0	3.0	0.3
Ca Al-Silicate	6.9	9.1	4.5	2.1	1.0	0.2	38.1
Na Al-Silicate	0.0	0.0	0.6	0.0	0.0	0.0	0.0
Aluminosilicate	0.7	2.6	0.8	3.1	3.0	0.8	1.5
Mixed Al-Silicate	0.7	0.4	1.2	4.4	2.8	6.8	2.7
Fe Silicate	0.0	0.0	0.0	1.9	1.0	0.3	0.1
Ca Silicate	4.7	6.0	5.7	0.1	0.4	0.5	1.2
Ca Aluminate	11.7	13.7	12.4	0.0	0.0	0.0	1.3
Pyrite	0.0	0.0	0.0	0.0	2.1	2.1	0.0
Pyrrhotite	0.0	0.1	0.0	0.0	3.1	7.6	0.0
Oxidized Pyrrhotite	0.0	0.0	0.4	0.1	0.8	2.0	0.0
Gypsum	0.0	0.0	0.0	0.4	0.0	0.3	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-Al-P	0.0	0.3	0.5	0.0	0.0	0.0	0.1
Gypsum-Al-Silicate	4.8	0.0	0.7	0.0	0.0	0.0	0.8
Si-Rich	0.9	3.6	2.8	9.2	8.8	8.7	5.4
Ca-Rich	4.2	7.4	9.2	0.2	0.1	0.3	0.4
Ca-Si-Rich	1.3	1.2	1.0	0.2	0.2	0.1	0.1
Unknown	45.4	16.8	26.2	16.8	17.1	24.3	28.1

¹Excess air.

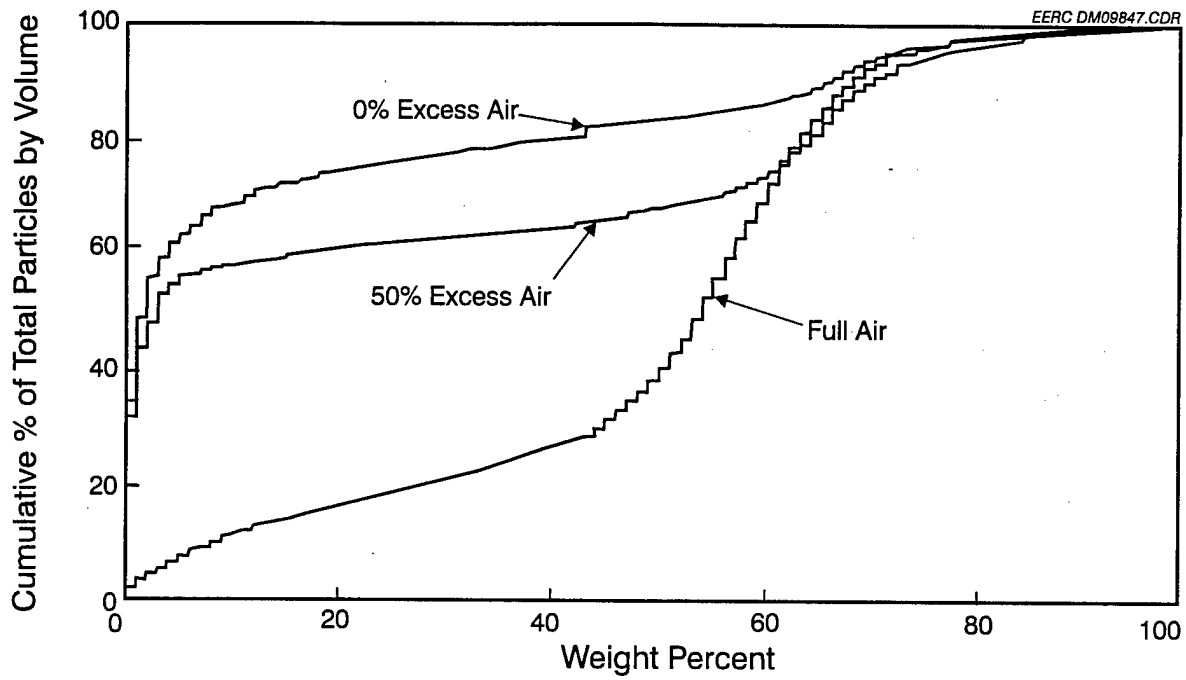


Figure 2a. Cumulative distribution of calcium in Black Thunder ash.

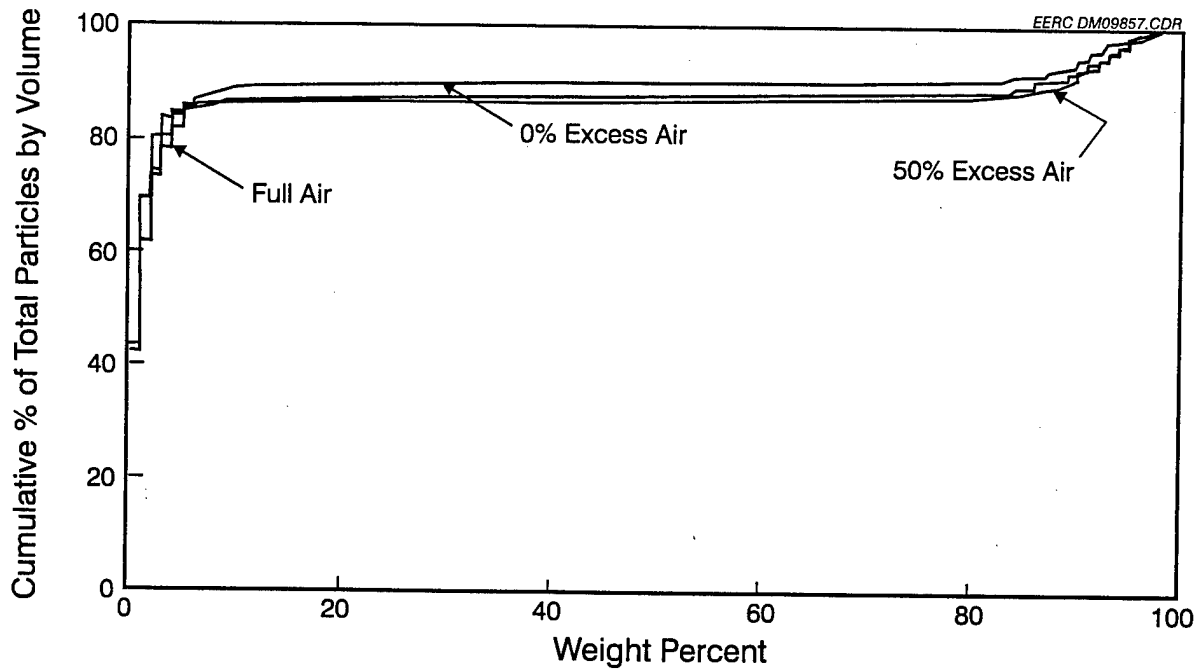


Figure 2b. Cumulative distribution of calcium in Illinois No. 6 ash.

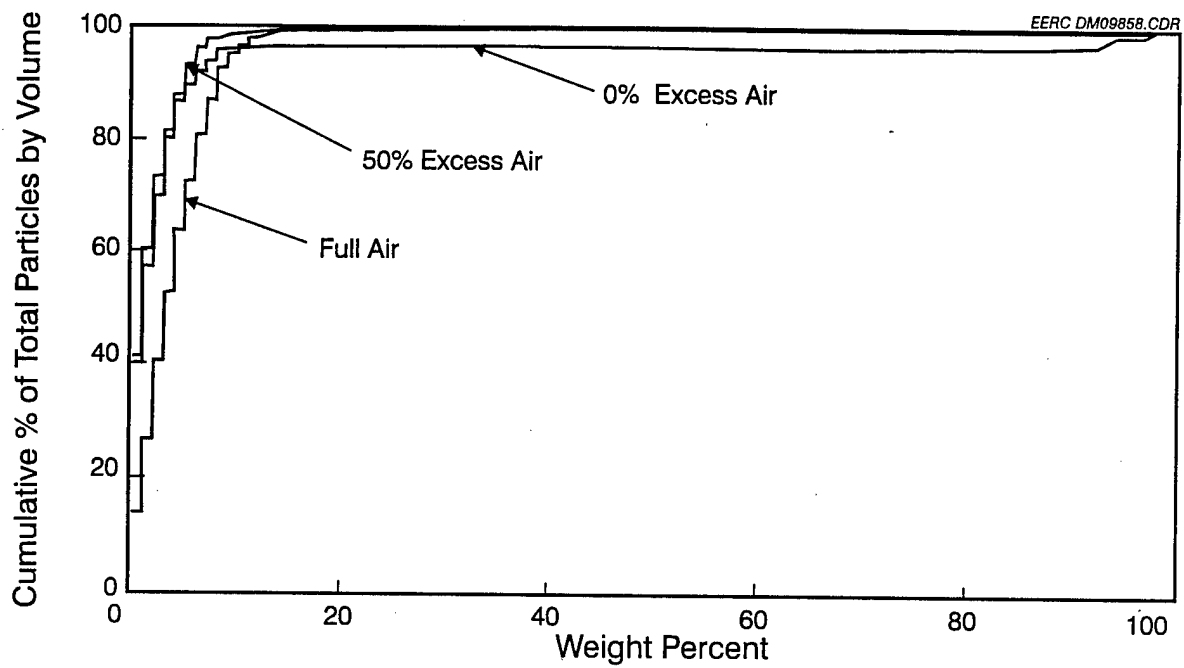


Figure 3a. Cumulative distribution of iron in Black Thunder ash.

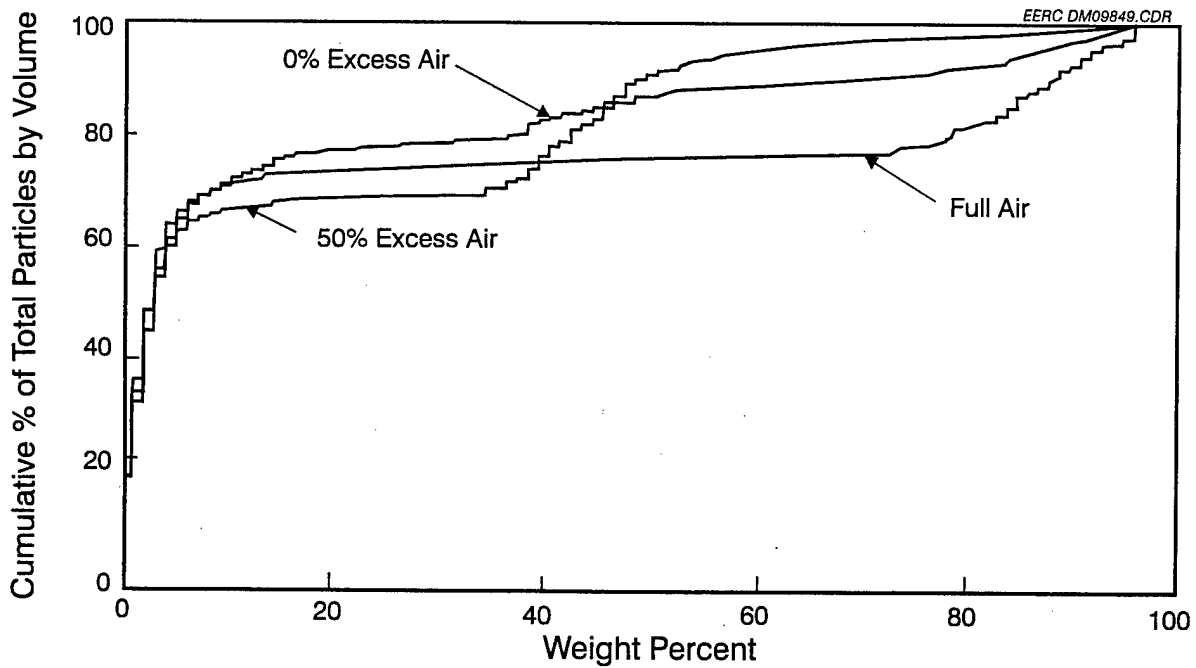


Figure 3b. Cumulative distribution of iron in Illinois No. 6 ash.

along with the formation of iron oxide particles under the highly oxidizing conditions. Under fuel-rich conditions, the percentage of iron oxide decreases, with a concurrent increase in particles with intermediate (40%–80%) iron concentration, corresponding to pyrite and pyrrhotite.

4.2 Mechanisms of Deposit Formation in IGCC-Type Systems

Deposits were generated in drop-tube furnaces to determine the effects of coal characteristics, system aerodynamics and transport mechanisms, pressure, temperature, and gas composition on the degree of deposit severity. Deposit severity was assessed based on the hardness, growth rate, and liquid-phase viscosity of the deposits that are formed. The deposits were analyzed using scanning electron microscopy, x-ray fluorescence, x-ray diffraction, and physical strength analysis.

Ash deposition tests were performed using pulverized Illinois No. 6 and Black Thunder coals, which were burned in the PDTF using gasification conditions. The goal was to produce gasification-type deposits at a temperature of 1500°C, a pressure of 120 psi, and an oxygen:carbon ratio of 1.25. Chemical properties of the coals are provided in Table 1. The actual maximum temperature attained during the initial test, designated as Run 235, was 1250°C at a pressure of 120 psi and an oxygen:carbon ratio of 1.25. Adjustments to gas flows were made in an additional test, designated as Run 237, to increase temperature. A temperature of 1375°C was attained at a pressure of 100 psi, and an oxygen:carbon ratio of 1.25 during the second test. The operating conditions for both tests are summarized in Table 3.

The deposit samples were analyzed using thermogravimetric analysis (TGA) and a scanning electron microscope (SEM). Both deposits were friable, consisting of char and ash particles. TGA was performed to determine the weight proportions of char in the deposits. The oxidation of iron during the analysis, however, prevented an accurate determination of char content. In fact, Deposit Sample 235 increased in weight during the TGA, which is consistent with the presence of ferrous iron (Fe^{2+}). Minerals that contain Fe^{2+} include wüstite (Fe_{1-x}O), troilite (FeS), and pyrrhotite (Fe_{1-x}S). SEM analysis of the deposits indicated that most of the inorganic constituents are finely dispersed within char particles. Chemical analysis of 150 individual ash particles in Deposit Sample 235 indicated the presence of iron oxide, iron sulfide, sodium and (Ca, Mg, Fe, Na, K)-aluminosilicates, and calcium carbonate as the major phases (Table 4). The iron sulfide phase had an average chemical formula of $\text{Fe}_{0.8}\text{S}$, which is consistent with the mineral pyrrhotite. The iron sulfide phase occurs predominantly as discrete spheres in the ash, whereas the aluminosilicate phases are commonly elongated and branching, as shown in Figure 4. Deposit Sample 237 contains significantly more SiO_2 than Sample 235. A preliminary investigation of the compositions of particles classified as (Ca, Mg, Fe, Na, K)-aluminosilicate indicates that Sample 237 contains significantly more Fe-aluminosilicate than Sample 235. Apparently, the higher-temperature conditions of Test 237 promoted the reaction of iron with aluminosilicates. In addition, the lack of sulfur-bearing phases in Sample 237 indicates that the higher-temperature conditions caused instability of sulfide species resulting in sulfur vaporization without recondensing. The morphology of ash particles in Sample 237 (Figure 5) was very similar to those in Sample 235.

Several more runs were made in the PDTF on the Illinois coal using high and low collection zone temperatures; the deposits were very similar to Tests 235 and 237 (Table 5). Additional tests made with the Black Thunder coal (Table 5) produced very little sintered deposit material because

TABLE 3

Pressurized Drop-Tube Furnace Experimental Parameters		
PDTF Test No.:	235	237
Maximum Gas Temperature, °C	1250	1375
Minimum Gas Temperature, °C	1010	1320
Deposit Collection Temperature, °C	610	800
Residence Time, sec	11	14
Oxygen:Carbon Ratio	1.25	1.25
Coal Feed Rate, g/min	0.24	0.21
Excess Air, %	50	50

TABLE 4

Inorganic Phase Composition of the PDTF Deposits, frequency %		
Deposit Sample No.:	235	237
Ca(O, OH, or CO ₃)	3	ND ¹
Fe ₇ O ₇	20	13
Fe _{1-x} S	3	ND
Ca(S or SO ₄)	2	ND
SiO ₂	5	18
(Ca, Mg, Fe, Na, K)-Aluminosilicates	60	63
Other	7	6

¹Not detected.

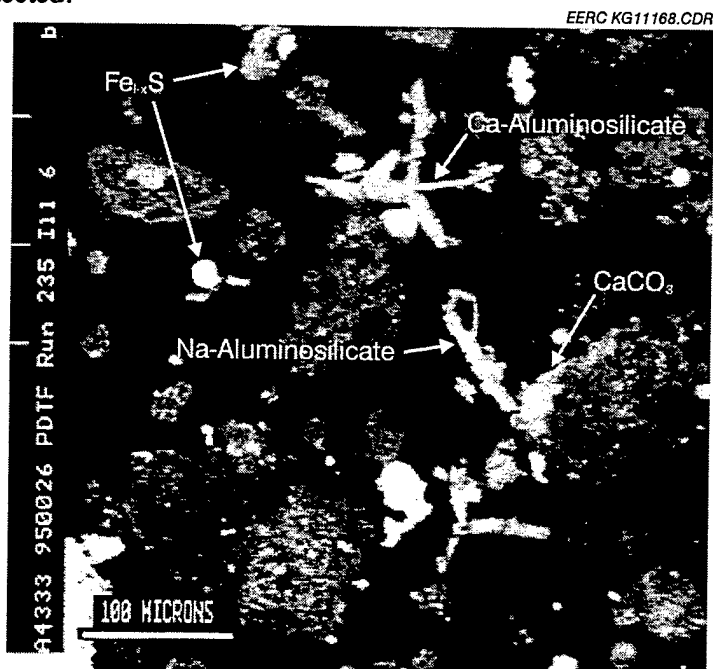


Figure 4. Backscattered electron image of Illinois No. 6 deposit produced during PDTF Test 235.

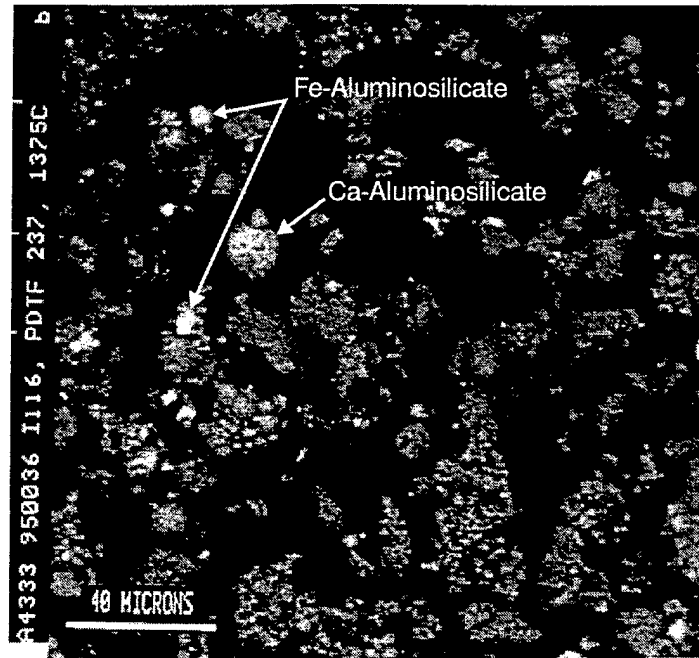


Figure 5. Backscattered electron image of Illinois No. 6 deposit produced during PDTF Test 237.

of the high carbon contents in the ash and problems with ash collection and maintaining gas temperature in the collection zone. No Black Thunder samples were analyzed for the pressurized conversion Tests 242–244.

4.3 Fouling Deposit Mitigation Measures

Inorganic additives can capture and immobilize, by a combination of adsorption and chemical reactions, the species that initiate ash deposition problems. Important characteristics of a potential additive include availability, cost, particle-size distribution, chemical composition, sorption rate, type of sorption (reversible or irreversible), and thermal stability. Additives were selected using the knowledge gained previously in the study of deposit formation mechanisms. Additives will most likely be alkali and sulfide getters acting to render these species ineffective for depressing melting points of entrained ash and deposit material. It is the lower-melting-point and lower-viscosity phases that can cause entrained ash to stick and deposits to form and acquire strength. Additives may also be selected that act to physically weaken deposits by diluting the bad-acting components or by creating a more porous and weakened deposit structure.

Previous work has shown that gasification-type deposits can consist of higher-temperature formations of alkali silicates or lower-temperature formations of iron and alkali sulfides. Selection of additives for precombustion injection was made primarily on the basis of the potential for the additive to provide the following:

- Adequate surface and structure for entrapment or physical contact between low-melting-point alkali species and the additive, within or shortly after the coal flame.

- Chemical compatibility for reactions that will promote the capture of alkali species within or shortly after the coal flame, primarily through chemical reaction between the components or nucleation of vapor-phase species. Capture of sulfur in a higher-melting-point phase may also be another mechanism of deposit mitigation.

Aluminosilicates are additive materials that work well for actual chemical reaction in the flame or shortly after the flame, especially those that can attain small particle sizes with some physical porosity or surface roughness. This characteristic allows for capture with subsequent chemical reaction. Potential candidate additives that meet this criterion are kaolinite, zeolite, vermiculite, emathlite, and bauxite. Unlike combustion, in the reducing environment of a gasification system, calcium-based materials such as limestone (CaCO_3) or lime (Ca(OH)_2) may actually aggravate rather than mitigate deposition.

Problems may arise in the area of operation and maintenance when coal with any of these additives is burned. Low-melting-point silicate-based eutectics may develop on the surface of entrained ash silicates when the aluminosilicate additives are used, causing fouling in the hotter sections of a gasifier heat-transfer zone. When calcium-based additives are used, calcium sulfide fouling may occur in the cooler regions of the heat-transfer area pass because of increased availability of calcium to form calcium sulfide deposits. Other operational concerns include the handling and feeding of the additive material. Most of the silicate materials are fairly conducive to handling and feeding; however, calcium-based materials can cause serious dust problems if the particle sizes are too small.

Additive candidates considered for this project were zeolite, kaolinite, and limestone. These materials are commercially available at reasonable costs. The zeolite material should provide maximum entrapment of alkali species in its layered and porous clay structure, while also providing an aluminosilicate matrix to react in the coal flame. Zeolite may also be tailored for desired chemical and physical properties if produced synthetically. Kaolinite is a good candidate for in-flame metal capture, primarily because of its fine size distribution and relatively pure inert composition, which adds only a minimum potential for detrimental boiler operation and maintenance side effects. Kaolinite has been shown to be effective in conventional combustion systems, but may perform differently under reducing conditions and may not have the physical entrapping effect of the zeolites. Lime may act as an additive to physically break up the deposits that form, or to combine with sulfur to circumvent formation of troublesome iron sulfides at intermediate temperature ranges of $800^\circ\text{--}1100^\circ\text{C}$.

A brief summary of important properties of three potential additives follows.

Kaolin

Kaolin consists of a very fine-grained mineral assemblage of kaolinite, halloysite, dickite, and nacrite. These minerals have essentially the same chemical composition ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) but different crystal structures. Kaolinite is the most common of the kaolin minerals. In 1987, the cost of kaolin ranged from about \$35 to as high as \$400 per ton, depending on the purity, physical properties, and intended application (1).

TABLE 5

Summary of PDTF Test Conditions and Deposit Analysis Information

PDTF Test	235	237	238	241	242	243	244
Coal	Ill. 6	Ill. 6	Ill. 6	Ill. 6	Blk. Thd.	Blk. Thd.	Blk. Thd.
Additive	None	None	None	None	None	None	None
Residence Time, sec.	11	14	13	13	13	1.5	1.8
O:C Ratio	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Pressure, psig	100	100	100	100	100	atm	atm
Deposit Formation Temp., °C	1200	1300	1500	1500	1500	1500	1500
Collection Zone Temp., °C	1150	1300	1400	1090	980	1060	1020
Deposit Substrate Temp., °C	610	745	660	465	430	545	585
Ash Collected, g	0.240	0.085	NR ¹	0.111	NR	0.045	0.036
Deposit Carbon, wt. %	NA ²	0.78	2.16	1.05	NA	NA	NA
SEMPC ³	Yes	Yes	Yes	Yes	NA	NA	NA
SEM Morphology	Yes	Yes	Yes	Yes	NA	NA	NA
XRD ⁴	NA	NA	NA	NA	NA	NA	NA

¹Not reported.²Not analyzed.³Scanning electron microscope point count.⁴X-ray diffraction.

During heating, kaolinite dehydrates at 550°C to form metakaolinite, which then transforms at 980°C to a binary mixture of amorphous aluminosilicate and spinel phases (2). At 1250°C, mullite crystallizes from the amorphous aluminosilicate phase, and the spinel phase transforms polymorphically to mullite. In conventional combustion systems, kaolinite decomposition products commonly react with sodium and calcium to form the sodium aluminosilicate polymorphs nepheline and carnegiete (3, 4) and the calcium aluminosilicate minerals anorthite and gehlenite (5), respectively.

Zeolite

Zeolite is a group of hydrous aluminosilicate minerals characterized by a (Al+Si):O ratio of 1:2 and by the reversible loss of H₂O at low temperatures. Ca and Na are the primary cations contained in zeolite minerals; less commonly they contain Ba, Mg, and Sr. Zeolite has a porous crystal structure; consequently, most of the surface area available to adsorb molecules occurs within the crystal structure and only about 1% occurs on the exterior of a zeolite particle (6). The relatively high cost of synthetic zeolites may be prohibitive for its use in sorbent injection. Natural zeolites, however, are more economically suited for such a large-scale application.

During heating, the zeolite structure collapses to an amorphous phase. Zeolite should be an effective additive if the temperature of zeolite structural collapse exceeds the temperature at which inorganic constituents are vaporized and released from the coal, and if the sorption rate is sufficient to capture significant quantities of inorganic species before the pores collapse.

Lime

Lime is commonly used in sorbent injection flue gas desulfurization systems of coal-fired boilers where it readily reacts with SO₂ in flue gases to form oldhamite (CaS) or anhydrite (CaSO₄), depending on the oxygen fugacity. The injection of lime, however, can cause fouling in the convective pass region of a boiler (7).

The final additives choices were kaolin and lime. Kaolin was expected to perform well in mitigating the high-temperature calcium-based deposition encountered with the Black Thunder ash, while lime was expected to perform a similar function with the iron-rich Illinois No. 6 deposits.

The additive tests were all conducted in the ADTF to improve control of the deposit collection zone temperatures and oxygen-to-carbon ratios, which previous tests proved to be critical. However in using the ADTF, the capabilities for testing under pressure in an atmosphere of CO-CO₂-H₂-air syngas were not available. The Illinois No. 6 and Black Thunder coals were tested with kaolin and lime additives at initial conversion temperatures of 1500°C and an oxygen-to-carbon ratio of 1.25. The additives were introduced at a level corresponding to 25% of the coal ash. Deposit collection zone temperatures were 750°C and 1000°C. Table 6 lists the summary of drop-tube furnace run conditions, parameters, and analysis performed.

The deposits formed at 750°C under all conditions were uniformly very weak, consisting of a pile of loose ash heavily mixed with unconverted char on the substrate. By contrast, the deposits formed at 1000°C exhibited strength development and deposit structure. Analysis focused on these latter 1000°C deposits.

Combining the results of SEM and XRD analysis allowed the mineralogy of the high-temperature deposits to be summarized in Table 7. Table 8 shows that the crushing strengths measured for the deposits with a pressure transducer connected to a penetrating rod indicated significant reductions in strength with both additives.

4.4 Composition of the Deposits and Formation Mechanisms

Both the baseline Illinois No. 6 deposit and the deposit with kaolin additive show CaO enrichment in the upper portion of what essentially is otherwise an Fe-Al-silicate melt (Table 9). This appears to be a result of favored inertial impaction of iron and aluminosilicate particles over that of smaller, more refractory calcium species in the lower deposit. As the deposit grows away from the relatively cool substrate, more calcium material is captured by the "sticky" deposit surface. The calcium is derived from the 6% calcite coal mineral content in the coal (Table 1). Although present in small amounts, magnesium shows the same trend.

The baseline deposit Fe-Al-silicate melt is encapsulating partially reacted quartz, iron sulfide, and clay ash material into the matrix. The melt phase typically showed Si:Al ratios of greater than two or three to one, with the aluminosilicate being derived from illite and kaolinite in the coal. When kaolin was added to the coal, with the formation of weaker deposits, similar Fe-Al-silicate material was found, with the Si:Al ratios usually less than two to one. It may be that the kaolin in reacting with available iron and dispersing it into the ash particles reduces the amount of molten low-viscosity material present. Some of the particles in the deposit grown with the kaolin additive show the characteristic near 1:1 ratio of Al-Si-rich particles with only 1%-10% iron present.

Illinois No. 6 deposits with the lime additive showed similar results to those with the kaolin, in that the presence of lime caused reactions with the iron present to form a more dispersed mixture at lower concentration. Particles rich in a mixture of Ca-Fe-Al-Si were evidence of these reactions. Some of the lime remained unreacted, which also may have acted to cause physical weakening of the deposits, by creating points of weakly sintered refractory material. Some of the iron may also have reacted with the calcium from the lime as sulfides early in the conversion process. Several particles were observed in the deposits, showing compositions comprised nearly completely of a mixture of Ca, Fe, and S. A potential problem with the use of lime as an additive, however, is that some fluxing was observed between calcium and Fe-Al-silicate particles. This could, given the right deposition temperatures and reaction time, cause stronger deposits than those with the kaolin additive. Kaolin is probably an overall better choice as an additive for mitigating ash deposit strength, as the crushing strength numbers indicate in Table 8.

The Black Thunder baseline deposits show primarily Ca-Al-silicate mixtures, with occasional unreacted quartz, kaolinite, and iron-rich particles. The Ca-Al-silicate matrix appears to be partly amorphous and acting as a glue. The addition of lime produces deposits greatly enriched in calcium, with concurrent dilution of the other elements. The analyses indicate interaction of the lime with these later species. For the base of the deposit formed with the lime additive, alumina, iron, and sodium are enriched relative to the baseline deposit along with calcium from the lime. This is indicative of reaction and formation of mixed sodium-iron-aluminum-calcium species. The upper portion of the deposit has alumina and sodium levels similar to the baseline deposit, but is still enriched in iron and calcium. The higher temperature seen by the upper portion of the deposit appears to inhibit interaction of the alumina and sodium with lime. However, the interaction of

iron with the lime stills occurs. As with the Illinois No. 6 deposits, addition of kaolinite as well as lime resulted in a significant decrease in deposit strength.

5.0 CONCLUSIONS

Gasification-type entrained ash and deposits were produced in a pressurized test furnace at high temperature. For the subbituminous Black Thunder coal, the effect of fuel-rich conditions was an increase in quartz, calcite, dolomite, and calcium-rich phases in the entrained ash. Lower particle temperatures, as compared to full air conventional combustion, and the oxygen-lean atmosphere may have caused a reduction in the interaction and assimilation of pure quartz and organically bound calcium into calcium aluminosilicate phases. For the Illinois #6 entrained fly ash fuel-rich conditions prevented the oxidation of pyrite and pyrrhotite to iron oxide. Lower temperatures within and surrounding char particles during reducing conditions combustion may have prevented the decomposition of pyrrhotite and enhanced the reaction of iron with aluminosilicate phases. The deposits show similar trends, with the Illinois #6 deposit grown under pressurized conditions at a lower temperature having Na and (Ca, Mg, Fe, Na, K) aluminosilicates, calcium carbonate, and an iron sulfide, probably pyrrhotite, present. At higher temperature, loss of sulfur occurs with the increased formation of iron aluminosilicate phases. The Illinois No. 6 and Black Thunder coals were tested with kaolin and lime additives under highly reducing conditions to simulate a gasification environment. The deposit collection zone temperature was varied from 750°C to 1000°C. Although no clear trends were evident for the interaction of kaolin or lime with the deposits, the deposits did become more porous, with greatly reduced strength shown for both additives.

6.0 REFERENCES

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TABLE 6

Summary of ADTF Test Conditions and Deposit Analysis Information

ADTF Test	484 & 485	486 & 496	494 & 495	481 & 499	490 & 498	492 & 497
Coal	Ill. 6	Ill. 6	Ill. 6	Blk. Thd.	Blk. Thd.	Blk. Thd.
Additive	None	Kaolin	Lime	None	Kaolin	Lime
Residence time, sec.	4	4	4	4	4	4
O:C Ratio	1.25	1.25	1.25	1.25	1.25	1.25
Deposit Formation Temp., °C	1500	1500	1500	1500	1500	1500
Collection Zone Temp., °C	1000	1000	1000	1000	1000	1000
Deposit Substrate Temp., °C	550	550	550	550	550	550
Ash Collected, g	0.3288	0.3328	0.2285	0.1094	0.1345	0.1005
Deposit Carbon, wt. %	NA ¹	NA	NA	NA	NA	NA
SEMP	Yes	Yes	Yes	Yes	Yes	Yes
SEM Morphology	Yes	Yes	Yes	No	No	Yes
XRD	Yes	Yes	Yes	Yes	Yes	Yes

¹Not analyzed.

TABLE 7

Qualitative Mineralogy of High-Temperature Deposits¹

Coal:	Ill. 6	Ill. 6	Ill. 6	Blk. Thd.	Blk. Thd.	Blk. Thd.
Additive:	None	Kaolin	Lime	None	Kaolin	Lime
Anhydrite	ND	?	X	?	ND	?
Brownmillerite	ND	ND	X	X	X	X
Clinopyroxene	ND	ND	X	ND	ND	ND
Hematite	X	X	X	X	X	X
Lime	ND	X	X	X	X	X
Melilite	ND	ND	X	X	X	X
Merwinite	X	X	ND	X	X	X
Mullite	X	X	ND	ND	ND	ND
Periclase	ND	ND	ND	X	X	X
Quartz	X	X	X	X	X	X
Spinel	X	X	ND	X	X	X

¹ND = not detected; ? = possibly present; X = present.

TABLE 8

Crushing Strengths for Illinois and Black Thunder Deposits with Additives, average psi

Coal:	Black Thunder			Illinois No. 6		
Additive:	None	Kaolin	Lime	None	Kaolin	Lime
Crushing Strength	43	19	17	76	11	16

TABLE 9

Composition of Top and Bottom Parts of Deposits

Averages	Black Thunder Baseline		Black Thunder + Lime		Illinois No. 6 Baseline		Illinois No. 6 + Kaolin		Illinois No. 6 + Lime	
	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top
Na ₂ O	1.22	0.72	2.06	0.53	2.81	1.45	1.39	1.18	1.61	0.94
MgO	5.02	5.40	2.12	1.84	0.45	0.77	0.31	0.37	0.44	0.44
Al ₂ O ₃	8.23	11.52	16.04	8.75	13.27	20.80	22.38	17.22	15.68	12.48
SiO ₂	51.54	36.16	27.20	35.86	47.33	45.78	48.28	53.94	36.47	43.67
P ₂ O ₅	0.26	0.43	0.15	0.42	0.12	0.05	0.09	0.08	0.28	0.06
SO ₃	0.86	1.51	0.45	0.75	1.47	0.06	0.46	0.05	4.95	0.36
ClO	0.04	0.14	0.07	0	0.02	0.04	0.07	0.05	0.04	0.05
K ₂ O	0.03	0.03	0.14	0.03	1.61	1.02	0.64	0.53	1.30	0.75
CaO	24.40	25.08	36.91	40.04	-0.79	6.02	0.92	7.94	26.78	14.53
TiO ₂	2.83	0.52	1.69	1.23	0.15	0.27	0.08	0.32	0	0.18
Cr ₂ O ₃	0.07	0.07	0	0.12	0	0	0.08	0.07	0.17	0
Fe ₂ O ₃	5.43	18.20	12.97	10.17	31.98	23.64	25.31	18.16	12.20	26.53
BaO	0.08	0.21	0.19	0.26	0	0.10	0	0	0.08	0

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