Task 3.15 - Impacts of Low- NO_x Combustion on Fly Ash and Slagging

**Topical Report
November 1997**

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Work Performed Under Contract No.: DE-FC21-93MC30097

For
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ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) Federal Energy Technology Center Cooperative Agreement No. DE-FC21-93MC30097. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of the DOE.

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SUBTASK 3.15 - IMPACTS OF LOW-NO_x COMBUSTION ON FLY ASH AND SLAGGING

1.0 INTRODUCTION

With the advent of the Clean Air Act Amendments of 1990, the coal-fired power industry began a more accelerated move toward using low-NO_x burner (LNB) technologies to reduce NO_x emissions. Most LNBs incorporate less oxygen with the coal initially, creating a cooler and somewhat substoichiometric initial combustion zone, with additional oxygen added further on in the combustion process to complete char combustion. Another method used to achieve lower NO_x emissions is to fire the coal substoichiometrically and add additional air through overfire air ports. Both of these methods create certain impacts on fireside performance that are different from conventional high excess air firing arrangements (1). Some of the impacts that have been noticed by the utility industry are higher levels of unburned carbon in the fly ash and bottom ash, increased boiler tube corrosion, higher particulate loadings on control devices, and changes in slagging in the main furnace (2, 3). Work on the fundamental mechanisms of entrained ash and ash deposit formation during low-NO_x combustion has been sparse. Preliminary work has shown that fly ash particle sizes may actually show an increase in size in the 1-10- μ m range for low-NO_x combustion (1, 3, 4). Also, it was often speculated by the boiler ash research community that the more reducing environment created by this new firing technology would create reduced inorganic phases in the radiant zone of the boiler (5). Reduced mineral species generally have lower melting points and tend to promulgate more wall slagging or even fouling. However, experience has shown that most utility boilers that have been converted to low-NO_x burners show very little if any fouling problems and usually upper main furnace slagging actually improves. Lower main furnace slagging, however, has increased for boilers that are burning higher-iron coals. It is now believed that improved upper furnace slagging is due to slightly lower gas temperatures which essentially suppress the formation of lower melting point phases. Increased lower main furnace slagging and eyebrow deposit formation around burners is probably the result of the very high gas temperatures and reducing environment zones that are created in the early combustion stages of low-NO_x combustion.

This project by the Energy & Environmental Research Center (EERC) focuses on the issues of entrained-ash formation and slagging for low-NO_x combustion systems in general. Time-resolved combustion tests under conventional and low-NO_x conditions have been conducted to note particle-size formation and slagging deposition. Results will be used to support demonstration projects at the utility boiler scale. The results from this work are yielding an increased understanding of the mechanisms of ash formation during low-NO_x combustion along with methods for enhancing heat transfer and fly ash collectability.

2.0 OBJECTIVES

Specific objectives of this research project include 1) determining whether initial char and ash generated under low-NO_x conditions have greater tendencies for slagging than conventionally generated ash and 2) determining the differences, if any, between particle size and composition for entrained ash generated under low-NO_x and conventional combustion conditions.

Implications behind this research for the industry are obvious. If low-NO_x burners actually decrease slagging and increase collectability of fly ash, then industry will want to take advantage of the benefit, and it will want to know what specific actions need to be taken to trigger the ash formation mechanisms that the EERC identified. By demonstrating expertise in low-NO_x combustion ash behavior through these seed efforts, a strong industrial consortium project will be attempted to further advance the efficient use of low-NO_x combustion technologies.

3.0 METHODS

Extensive combustion tests have already been conducted using a drop-tube furnace to produce conventional and low-NO_x combustion ash and deposits (1). Work under this project involves using a larger-scale combustion test facility to produce more realistic ash products and verify the previous work. The system used for the combustion testing is the conversion and environmental process simulator (CEPS). The CEPS is an extremely versatile intermediate-scale combustor designed to generate realistic combustion test results for a variety of fuels and combustion conditions. It has a downfired design for nominally top-firing 4.4 lb/hr (2 kg/hr) of pulverized coal with a heat output of 40,000 Btu/hr (42.2 MJ/hr). It is a modular system capable of simulating conditions of both the radiant and convective sections of a full-scale utility boiler. The vertical radiant furnace portion has 13 feet (3.96 m) of inside height with a 6-inch (15.24-cm) ID reducing down to 3 inches (7.62 cm) in the final heated section and finally reducing to 2 inches (5.08 cm) in the furnace exit section prior to the convective section. The combustion air is split and fed as primary and secondary air. The secondary combustion air is preheated to a maximum of 1740°F (950°C) and can be introduced into the CEPS vertically or tangentially. Five furnace sections make up the radiant furnace section and are constructed using a combination of ceramic tubes set into cast abrasion-resistant refractory containing sight and sampling ports. The ceramic tubes are surrounded by molybdenum disilicide heating elements allowing operation to 2730°F (1500°C). High-temperature fibrous insulating boards surround the high-temperature components housed inside the stainless steel shells. A portion of the particulate is removed prior to the combustion gas stream entering the horizontally oriented convective pass. The convective pass is about 4 feet (1.22 m) in length and constructed of a combination of ceramic tubing, refractory, and high-temperature fibrous insulating boards. There is the capability for studying deposition in the convective pass with two in-series highly instrumented air-cooled probes.

After the convective section, flue gas flows through a heat exchange section and then on to the particulate control device, which is either a baghouse or a cyclone. Flue gas temperatures are well controlled going into the control device section for typical operation between 250°–350°F (120°–175°C), and flexibility has been built into the system to allow experimentation at even higher flue gas temperatures. Beyond the control device, the flue gas proceeds through an air eductor and up to a stack. There is ample access to the inside of the CEPS for sampling, observation, and optical diagnostics through several access ports that penetrate through the ceramic tube reaction zones.

The heating elements are surrounded with state-of-the-art high-temperature fibrous insulating board. Temperatures of the flue gas can attain a maximum of 2730°–2910°F (1500°–1600°C) in the radiant section and can be maintained at 1400°–2200°F (760°–1200°C) in the convective pass

section. Flue gas flow rates can be maintained at approximately 8 scfm (226.5 slpm) as generated by the combustion of the fuel. The CEPS fabric filtration (baghouse) system shown in Figure 1 has three flanged sections. The main section is an internally insulated and refractory-lined stainless steel shell containing two fabric bags with inside dimensions of 14 inches (35.6 cm) wide by 9 inches (22.9 cm) deep by 6 feet (1.83 m) high. Both bags are 16-ounce (453.8 g) Huyglass material 4 inches (10.2 cm) in diameter by 4 feet (1.22 m) long with stainless steel cages used to support them. Refractory was selected as an inert lining to prevent contamination of the ash generated in the CEPS by having any contact with metal surfaces prior to its collection. Twelve tubular heaters, slightly less than ½ inch (1.27 cm) in diameter, are inserted horizontally through the refractory walls allowing the refractory to become radiant heaters to maintain a specified temperature within the baghouse from 300° to 800°F (150° to 425°C). There are two isolation ball valves at the inlet and exit to the baghouse to allow the flue gas flow to be bypassed through a stainless steel cyclone when the baghouse is not in operation. The attached collection hopper and exit plenum are also refractory-lined. Nominal operation will result in a gas-to-cloth ratio of one. The ratio can be reduced by altering gas flow, by removal of one of the bags, or by physically reducing the length of the installed bag/cage combination. There are a total of six sight ports located throughout the baghouse to permit observation of the buildup of the filter cake on the bag surface. There are two observation ports on the top and four on the sides at various elevations. The bags are cleaned periodically on demand or at timed intervals by a pulse-jet system. The air pressure is regulated to a maximum of 100 psig (690 kpa), with normal operation at about 30 psig (207 kpa). Thermocouples are used to monitor and record temperatures into, inside, and out of the baghouse. Pressure drops across the baghouse and cyclone are monitored.

The combustion tests for this project were conducted using two different pulverized coal sized at nominally 70%-80% -200 mesh (70%-80% < 75 μ m) fired under conventional and low- NO_x combustion conditions. Changes made to the primary and secondary gas distributions and furnace temperature profile allowed the CEPS to fire in a low- NO_x combustion mode without structural modifications to the combustor. Furnace operating and test parameters for both conventional and low- NO_x conditions are discussed in the results section.

4.0 RESULTS

4.1 Boiler Industry Review

A background perusal of utility engineers and operators was undertaken early in the project to determine the nature of slagging and corrosion problems that can be attributed to low- NO_x combustion technology. The primary concern for many utility boiler operators with low- NO_x combustion is the potential increase of carbon carryover in the fly ash. Carbon affects both the salability and disposal of fly ash, and many units that have switched to low- NO_x combustion have seen increases of carbon in the ash. Although the focus of this research is on ash formation and deposition, the impact of carbon carryover may be important if it correlates with ash deposition in the boiler. For example, carbon may be playing a role in creating reducing environments in the near-burner region, which would generally pose more of a problem for bituminous coals which have lower reactivity because reducing environments are usually associated with greater potential for slag or deposit development.

A survey of the boiler industry seems to show that bituminous coals have more problems with ash deposition; however, it is not clear whether this is due to the usual higher pyrite and iron, or if it is due to poorer burnout of carbon. Units that have been switched to low- NO_x burners and are burning subbituminous Powder River Basin coal or low pyrite (and, consequently, lower iron) coal, in general, seem to have less lower furnace wall slagging, burner eyebrow formation, and corrosion. It is also clear from examining various boilers that have been retrofitted with low- NO_x combustion capabilities that the distribution and diffusion of primary, secondary, and overfire air with the coal feed stream are critical for proper low- NO_x operation, as some examples in the utility industry are now surfacing where the amount of carbon has actually decreased after a boiler has been converted to low- NO_x burners (3).

EERC CZ11965.CDR

Figure 1. Design sketch of the CEPS.

Cyclone-fired systems have been given an exemption, at least for the time being, from NO_x regulations that are being imposed on conventional pulverized coal-fired systems. Therefore, the driving forces are not as great for developing viable technologies for reducing NO_x. Some designs for overfire air or reburn strategies have been tested or implemented, but it may be important to direct future research toward developing more novel options for NO_x reduction in cyclone boilers. For example, there have been some investigations in using additives mixed with the coal and firing into a cyclone under reducing conditions to try to establish a lower-NO_x combustion gas. The purpose of the additives would be to keep slag flowing out of the barrel at the lower temperatures under fuel-rich reducing conditions. Other additives may be identified and tested which directly react with combustion gases to lower NO_x.

Finally, it was noted in this limited survey that some utilities are using additives designed to mitigate slag deposition and corrosion by decreasing the production of reduced mineral phases. Additives such as magnesium or manganese oxides and, possibly, lime may act to mitigate the potential for the formation of reduced mineral species that initiate slagging and the formation of corrosive materials, such as pyrrhotite, alkali-iron-trisulfates, or even metallic iron. Other highly oxygenated silicates or oxides may be used as additives also to mitigate by reaction or dilution the formation of reduced mineral phases. The additives may also act to increase carbon combustion efficiency by acting as combustion catalysts.

It was beyond the scope of this project to perform in-depth testing of the effectiveness of additives; however, the understanding being gained with respect to the formation of slag and potentially corrosive ash deposits will provide a sound basis for recommending mitigating measures.

From the brief perusal of industry use of low-NO_x technologies, it was concluded that research in this project should focus on the following:

- Establishing a protocol for firing the CEPS in a representative low-NO_x mode.
- Evaluating the role of carbon carryover on ash deposition.
- Evaluating the role of pyrite and iron for combustion of bituminous coal and clays and calcium for combustion of subbituminous coal, in the formation of near-burner ash deposits or wall slag.
- Evaluating the fundamental mechanisms of entrained ash and deposit formation in order to make recommendations on the effectiveness of additives such as magnesium oxides on mitigating slagging and corrosion.
- Verifying the previous results of fine ash agglomeration in the larger test scale of the CEPS.

4.2 CEPS Conventional and Low-NO_x Operating Conditions

The operation of the CEPS combustor was slightly modified to burn the test coals in a low-NO_x combustion mode. Under conventional conditions, 20% of the total combustor oxygen is

injected through the primary air inlet with the balance through the secondary air inlets. To simulate low-NO_x conditions, all of the combustor oxygen is injected through the secondary air inlets, with none through the primary air inlet. A small amount of nitrogen (10% of the total inlet gas flow) is used to maintain gas velocities and to keep a constant overall gas flow rate. The temperature of the primary and secondary air/nitrogen mixture entering the furnace zone is also lowered by approximately 212° and 302°F (100° and 150°C), respectively, under low-NO_x conditions as compared to conventional conditions, along with a somewhat lower furnace temperature profile. Shakedown tests and the combustion tests result in NO_x reduction of approximately 50% that of conventional combustion conditions.

4.3 Combustion Testing

Two coals were selected for testing under the project, including a subbituminous Black Thunder and a bituminous Illinois No. 6. Properties of these coals are given in Table 1. The Black Thunder coal is fairly typical of coal from the Powder River Basin, with high levels of magnesium

TABLE 1

Analysis of the Test Coals

	Black Thunder	Illinois No. 6
Proximate		
Moisture	24.30	11.70
Volatile Matter	35.88	34.97
Fixed Carbon	35.32	43.39
Ash	4.49	9.95
Ultimate		
Hydrogen	7.04	5.34
Carbon	52.84	61.99
Nitrogen	0.70	1.05
Sulfur	0.39	2.85
Oxygen	34.54	18.8
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
Other	41.40	24.00

and calcium bound organically in the coal, high levels of aluminosilicate as kaolinite or illite clays, and low amounts of pyrite, iron, and sulfur. The Illinois No. 6 is typical of eastern U.S. coal, with high amounts of pyrite, iron, and sulfur and low quantities of alkali such as calcium. These coals were ground to 80% -200 mesh (80% < 75 μ m) and fired in the CEPS under conventional and low-NO_x combustion conditions.

After initial shakedown testing of the CEPS combustor in order to determine the proper low-NO_x combustion arrangement, the Black Thunder and Illinois No. 6 coals were then be fired in the CEPS under conventional and low-NO_x conditions. During combustion testing, on-line measurement of NO_x, SO_x, CO₂, and O₂ were performed using gas analyzers, and on-line particle-size measurements made using an aerodynamic particle sizer (APS) and a differential mobility particle sizer (DMPS). Entrained ash was sampled from the high-temperature zone (2320°-2370°F) (1270°-1300°C) in the near-burner region and from the low-temperature zone (300°-480°F) (150°-250°C) at the entrance to the baghouse collector. The on-line particle-size measurements were also performed at the baghouse entrance. Slag deposits were collected on uncooled ceramic probes at the same point in the high-temperature zone as the entrained ash samples were obtained. Table 2 gives the furnace parameters and other conditions for the combustion tests.

The entrained-ash samples were analyzed using computer-controlled scanning electron microscopy (CCSEM) to determine the ash chemical composition and size on a particle-by-particle basis. The analogous scanning electron microscopy point count (SEMPC) analysis method was used to examine the slag deposits obtained from the near-burner region. The morphology of both deposits and entrained-ash samples were also examined using the SEM. Table 3 gives the CCSEM results for the coals under conventional and low-NO_x test conditions. As found previously in the smaller drop-tube furnace tests, there is no major change in mineral composition due to the low-NO_x conditions. The Black Thunder ash has a high percentage of "unknown" material, apparently resulting from agglomeration of the entrained ash as it was drawn into the particulate collection probe. The bulk ash chemistry calculated from the CCSEM analyses is given in Table 4. There appear to be differences in the amounts Al, Si, and Ca present between the Black Thunder high- and low-temperature ashes, although the high-temperature ash has a similar bulk composition under conventional and low-NO_x conditions as does the low-temperature ash. The high percentage of S for the Black Thunder high-temperature low-NO_x ash is probably an anomaly. Little difference is seen between the high and low-temperature Illinois No. 6 ash under conventional and under low-NO_x conditions.

The SEMPC analysis of the slag deposits is provided in Table 5. The Black Thunder slag shows an increase in mixed silicon-rich phases and a decrease in what has been characterized by the mineral classification program as montmorillonite under low-NO_x conditions, while the opposite is seen for the Illinois No. 6 slag. As the slags were seen both visually and under the SEM to be quite homogeneous and having passed through a molten state, the "montmorillonite" identified appears to be a silica-alumina melt with that approximate composition. The bulk chemical compositions of both slags show an increase in silica, with a concurrent decrease in alumina and iron under low-NO_x conditions as opposed to conventional combustion conditions. The decrease in iron content is particularly striking for the Illinois No. 6 slag. The higher temperatures associated with the

TABLE 2

Furnace Parameters and Combustion Test Conditions

Parameter	Black Thunder Conventional	Black Thunder Low NO _x	Illinois No. 6 Conventional	Illinois No. 6 Low NO _x
Furnace Set Points, °C				
Preheater	1000	800	1000	800
Furnace 3	1500	1300	1500	1300
Furnace 4	1500	1350	1500	1350
Furnace 5	1450	1400	1450	1400
Furnace 6	1450	1400	1450	1400
Furnace 7	1200	1200	1200	1200
Furnace Temperatures, °C				
Preheater Air	777	624	776	624
Secondary Air	615	504	618	506
Section 2	1108	962	1139	998
Section 3	1360	1313	1369	1315
Section 4*	1308	1268	1315	1281
Section 5	1368	1313	1362	1311
Section 6	1342	1300	1339	1297
Section 7	1065	1033	1072	1022
Section 8	998	923	997	856
Baghouse Inlet**	248	151	237	163
NO _x Level, ppm	995	370	815	378
Gas Flows, std. L/min				
Primary Air	31	0	31	0
Primary Nitrogen	0	16	0	16
Secondary Air	120	151	120	151
Secondary Nitrogen	16	0	16	0
Purge Air	3	3	3	3
Total Air	154	154	154	154
Total Gas	170	170	170	170
Coal Feed Rate, kg/hr	1.395	1.318	1.055	0.999

* Slag and near-burner entrained-ash sample point.

** Baghouse entrained-ash and on-line size analysis sample point.

conventional combustion conditions appear to allow more high alumina and iron ash particles to become incorporated into the slag melt. The morphology of the Black Thunder slag produced under low-NO_x conditions also revealed more discrete particles on the slag surface which had not yet been incorporated into the molten phase.

The SEMPC data sets themselves were examined on a point-by point basis for evidence of low-oxidation-state iron (Fe⁺² or Fe⁰) by comparing the iron-oxygen ratios and the iron-oxygen region-of-interest ratios. No definite indication of such species could be found. The examination is complicated by the differences in iron content between conventional and low-NO_x combustion conditions for the Illinois No. 6 slags and the low iron content of the Black Thunder slags.

Assimilation of bulk aluminosilicate ash into the low-viscosity slags also tends to mask any change in the Fe-O ratios.

The CCSEM data sets were also examined on a particle-by-particle basis for compositional differences under conventional and low-NO_x combustion conditions. The data sets were binned at 2% intervals in particle composition on a particle volume basis with Al-Si-Ca and Al-Si-Fe ternary plots produced for the high- and low-temperature fly ash under conventional and low-NO_x combustion conditions. Examples of the high-temperature fly ash Al-Si-Fe and Al-Si-Ca ternary plots are shown in Figures 2-5. As seen in the figures, shifts in the peaks indicate that some changes in the interaction of these three elements occur under low-NO_x combustion as opposed to conventional combustion conditions.

Table 6 gives the particle size distributions obtained from the CCSEM analysis of the entrained ash from the near-burner region and from the baghouse inlet. The low-temperature Black Thunder entrained ash shows a decrease in the smallest particle sizes under low-NO_x conditions as compared to conventional conditions, while the Illinois No. 6 shows a modest increase in the finer size fractions. These results are consistent with previous results from small-scale drop-tube furnace tests. The high-temperature near-burner entrained ashes show the opposite trend, with the finer Black Thunder particle-size fractions increasing and the Illinois No. 6 fractions decreasing under low-NO_x conditions. The high-temperature entrained-ash results are apparently skewed by the formation of very large agglomerates formed during the collection of the entrained ash. The morphological examination of the entrained ash samples revealed many such agglomerates of 100 μ m or greater made up of agglomerations of much smaller ash particles.

On-line particle-size measurements were made using an APS and a DMPS at in the low-temperature collection zone (300°-480°F [150°-250°C]) at the entrance to the baghouse. The purpose of the on-line analysis experiments was to determine if an increase in particle size of submicron ash occurred under low-NO_x combustion conditions analogous to that observed for supermicron particles from the CCSEM results. Cumulative distributions for the two fly ashes under conventional and low-NO_x conditions are shown in Figures 6-9. The Black Thunder fly ash is seen to have the size distribution shifted to smaller submicron sizes under low-NO_x combustion from that of conventional combustion conditions. Further, the Black Thunder submicron fly ash is also finer than the Illinois No. 6 ash under conventional conditions. Because of experimental variability under low-NO_x conditions, no conclusions can be drawn for the Illinois No. 6 submicron fly ash between conventional and low-NO_x conditions.

5.0 CONCLUSIONS

A standard test protocol has been developed for firing the CEPS in conventional and in a low-NO_x mode by changing oxygen concentrations in the primary and secondary inlet air streams and changing the furnace temperature profile. The NO_x levels under simulated low-NO_x combustion conditions are reduced to approximately half those under conventional combustion conditions.

Based on the experimental approach and test plan established for this work, combustion tests with Black Thunder and Illinois No. 6 coals have been performed in the CEPS under conventional and low-NO_x conditions. Slag deposits were collected in the high-temperature zone corresponding

TABLE 3

CCSEM Analysis of Entrained Fly Ashes

Mineral	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
	Conventional	Low NO _x	Conventional	Low NO _x	Conventional	Low NO _x	Conventional	Low NO _x
	High-Temperature	High-Temperature	Low-Temperature	Low-Temperature	High-Temperature	High-Temperature	Low-Temperature	Low-Temperature
	Near Burner	Near Burner	Baghouse	Baghouse	Near Burner	Near Burner	Baghouse	Baghouse
Quartz	3.3	3.4	10.3	8.7	7.3	12.3	12.1	12.9
Iron Oxide	0.0	0.3	0.0	0.1	0.9	2.9	5.5	6.5
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.0	0.0	0.0	0.5	0.2	0.2	0.0	0.1
Alumina	0.0	0.0	0.1	0.2	0.0	0.0	0.0	0.0
Calcite	0.0	0.1	0.9	0.9	0.3	1.1	2.1	4.7
Dolomite	0.4	0.0	1.9	1.8	0.0	0.0	0.1	0.0
Ankerite	0.1	0.2	0.1	0.3	0.0	0.2	0.0	0.2
Kaolinite	0.4	0.9	3.3	3.8	7.4	19.4	11.3	13.6
Montmorillonite	0.0	0.3	0.2	0.8	7.5	8.3	10.5	10.4
K Al-Silicate	0.0	0.3	2.2	1.7	5.6	11.4	12.4	11.4
Fe Al-Silicate	0.0	0.0	0.1	0.4	24.4	10.0	13.6	8.4
Ca Al-Silicate	9.5	9.9	15.1	10.2	1.5	2.6	1.7	2.8
Na Al-Silicate	0.0	0.9	0.0	1.2	0.0	0.0	0.0	0.0
Aluminosilicate	0.0	0.0	0.2	0.4	2.5	2.5	3.8	1.9
Mixed Al-Silica	0.0	1.1	0.8	1.8	5.7	3.9	3.3	2.8
Fe Silicate	0.0	0.0	0.0	0.0	0.2	0.3	0.8	0.9
Ca Silicate	1.7	0.8	4.1	3.5	0.1	0.0	0.2	0.2
Ca Aluminate	6.2	8.4	11.4	13.8	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0
Oxidized Pyrrhotite	0.0	0.0	0.0	0.0	0.0	0.6	0.4	0.8
Gypsum	1.9	2.8	0.1	0.0	5.5	1.3	0.3	1.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.2	0.0	0.1	0.0	0.0
Ca Al-P	0.1	0.3	0.2	1.1	0.0	0.0	0.0	0.0
KCl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum/Al-Silicate	10.8	7.4	5.1	2.1	3.3	1.4	1.0	0.2
Si-Rich	0.1	1.2	0.4	1.4	6.3	4.9	5.3	6.3
Ca-Rich	1.2	0.7	1.5	2.5	0.1	0.6	1.5	0.9
Ca-Si-Rich	0.4	0.8	0.9	1.8	0.1	0.1	0.0	0.0
Unknown	64.2	60.1	41.2	40.3	21.0	15.9	14.0	14.0

TABLE 4

CCSEM Bulk Fly Ash Composition

Coal	Sample	Condition	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ba	Ti
Black Thunder	Conventional	High Temp.	0.48	4.68	14.62	21.70	1.93	4.93	1.87	1.20	41.99	3.26	1.61	1.73
Black Thunder	Conventional	Low Temp.	0.70	2.82	18.78	44.19	0.72	1.58	0.85	1.73	22.80	2.31	1.73	1.79
Black Thunder	Low-NO _x	High Temp.	0.81	3.64	13.23	18.80	1.61	13.13	1.80	1.27	40.01	2.74	1.44	1.52
Black Thunder	Low-NO _x	Low Temp.	0.68	3.61	17.73	35.91	1.11	1.26	0.64	1.15	31.96	2.82	1.50	1.64
Illinois No. 6	Conventional	High Temp.	0.56	0.64	17.86	50.19	0.47	7.29	1.42	3.48	6.14	8.72	1.92	1.33
Illinois No. 6	Conventional	Low Temp.	0.48	0.58	20.43	53.63	0.36	1.43	0.83	3.80	7.34	8.96	1.04	1.12
Illinois No. 6	Low-NO _x	High Temp.	0.55	0.57	19.73	52.49	0.29	2.26	0.97	3.27	8.61	9.12	0.93	1.20
Illinois No. 6	Low-NO _x	Low Temp.	0.46	0.55	17.69	50.40	0.34	1.36	0.73	3.19	10.98	12.08	1.13	1.10

TABLE 5

SEMPC Analysis of the Slag Deposits				
Coal:	Black Thunder	Black Thunder	Illinois No. 6	Illinois No. 6
Condition:	Conventional	Low NO _x	Conventional	Low NO _x
Mineral Name				
Oxide-Rich				
Aluminum Oxide	0.0	0.0	2.0	0.0
Mixed-Oxide-Rich	0.0	0.0	0.8	0.0
Total	0.0	0.0	2.8	0.0
Silicon-Rich				
Quartz	0.0	0.0	0.4	4.8
Kaolinite	0.0	0.4	0.0	0.8
Altered Kaolinite	2.4	0.8	5.2	0.4
Montmorillonite	94.8	80.0	4.8	77.2
Wollastonite	0.0	0.0	0.4	0.0
Mullite	0.0	0.0	0.4	0.0
Mixed-Silicon-Rich	2.4	8.8	86.0	15.2
Total	99.6	99.6	97.2	98.4
Other	0.4	0.4	0.0	1.6
Bulk Sample Composition				
SiO ₂	52.9	61.6	35.9	59.9
Al ₂ O ₃	26.5	17.6	27.6	18.4
Fe ₂ O ₃	9.0	7.1	26.2	8.1
TiO ₂	0.9	1.0	0.4	1.0
P ₂ O ₅	0.1	0.4	0.1	0.3
CaO	7.3	8.9	6.7	8.8
MgO	1.4	1.7	0.9	1.8
Na ₂ O	1.3	1.0	0.5	1.1
K ₂ O	0.5	0.5	1.5	0.5
SO ₃	0.0	0.1	0.1	0.1

Figure 2. Al-Si-Ca ternary plot of Black Thunder high-temperature fly ash under conventional conditions.

Figure 3. Al-Si-Ca ternary plot of Black Thunder high-temperature fly ash under low- NO_x conditions.

Figure 4. Al-Si-Fe ternary plot of Illinois No. 6 high-temperature fly ash under conventional conditions.

Figure 5. Al-Si-Fe ternary plot of Illinois No. 6 high-temperature fly ash under low- NO_x conditions.

TABLE 6

CCSEM Size Distribution of Fly Ashes, Cumulative %

Size, μm	Black Thunder	Black Thunder	Black Thunder	Black Thunder	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
	Conventional	Low NO_x	Conventional	Low NO_x	Conventional	Low NO_x	Conventional	Low NO_x
	High-Temperature Near Burner	High-Temperature Near Burner	Low-Temperature Baghouse	Low-Temperature Baghouse	High-Temperature Near Burner	High-Temperature Near Burner	Low-Temperature Baghouse	Low-Temperature Baghouse
1.0-2.2	8.3	14.5	27.3	18.7	9.2	32.2	14.7	27.5
2.2-4.6	33.6	52.2	61.2	47.4	70.6	83.5	49.2	57
4.6-10.0	59	74	76.8	82.2	88.4	92.7	78.8	86.9
10.0-22.0	78.9	91.8	94.2	97.4	96.7	98.2	97.3	98.3
22.0-46.0	89.6	96.6	99.7	100	98.6	99.8	99.7	99.8
46.0-100.0	99.9	100.1	100	100.1	100	100.1	100	100

Figure 6. Submicron size distribution of Black Thunder low-temperature fly ash under conventional conditions.

Figure 7. Submicron size distribution of Black Thunder low-temperature fly ash under low-NO_x conditions.

Figure 8. Submicron size distribution of Illinois No. 6 low-temperature fly ash under conventional conditions.

Figure 9. Submicron size distribution of Illinois No. 6 low-temperature fly ash under low-NO_x conditions.

to a utility boiler near-burner region and entrained-ash deposits obtained from this high-temperature zone and from the low-temperature entrance to the CEPS baghouse. In conjunction with these samples, on-line particle-size measurements were made at the baghouse entrance.

The ash and slag samples obtained were examined and analyzed for particle-size and chemical and mineral composition. No great changes in the compositions of the entrained ash samples were observed between conventional and low- NO_x combustion conditions. The slags produced show an increase in bulk silica and a decrease in bulk alumina and iron under low- NO_x conditions. The CCSEM particle-size distributions of supermicron ash for the low-temperature entrained ash collected at the baghouse inlet show a decrease in the finest particles sizes for the Black Thunder coal but not for the Illinois No. 6 coal, consistent with earlier small-scale drop-tube furnace studies. The high-temperature near-burner entrained-ash size distributions are biased to larger particle sizes by the presence of large ash agglomerates formed during the collection process.

The on-line particle-size analysis measurements indicated that the Black Thunder fly ash is seen to have the size distribution shifted to smaller submicron sizes under low- NO_x combustion from that of conventional combustion conditions. Further, the Black Thunder submicron fly ash is also finer than the Illinois No. 6 ash under conventional conditions. Because of experimental variability under low- NO_x conditions, no conclusions can be drawn for the Illinois No. 6 submicron fly ash between conventional and low- NO_x conditions. The evidence, although limited, for smaller submicron particle sizes for the subbituminous Black Thunder coal combusted under low- NO_x conditions may be of significance in light of the pending EPA PM_{2.5} regulations governing fine particulate emissions.

The SEMPC data sets were examined for reduced iron species, with no evidence of these found. Examination of interactions in the fly ash was made using Al-Si-Fe and Al-Si-Ca ternary plots. The plots indicate that there are differences in the interactions of these elements under low- NO_x conditions as compared to conventional conditions.

A survey of the boiler industry indicated that units that have been switched to low- NO_x burners and are burning subbituminous Powder River Basin coal or low pyrite (and, consequently, lower iron) coal, in general, seem to have less lower furnace wall slagging, burner eyebrow formation, and corrosion. Reduced mineral species generally have lower melting points and would be expected to promulgate more wall slagging or even fouling. However, experience has shown that most utility boilers that have been converted to low- NO_x burners show very little if any fouling problems and usually upper main furnace slagging actually improves. It appears that the lower melting points of ash under more reducing conditions is more than offset by the lower gas temperatures encountered firing under low- NO_x conditions which essentially suppress the formation of lower melting point phases.

6.0 FUTURE WORK

As a result of the combustion tests and a careful examination of the key fundamental aspects of ash formation and deposition under low- NO_x combustion conditions, we will propose follow-on work to conduct more rigorous studies at full-scale utility boilers to verify the results and to identify practical solutions to slagging and corrosion problems. Testing additives for effectiveness in mitigating slag formation or corrosivity of deposits is a subject of future research. A second area

for future work is the determination of submicron particle-size distributions under conventional and low-NO_x combustion conditions.

7.0 REFERENCES

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