DOE/MC/30097 --55
(DE9700219
Distribution Category UC-1

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

Semi-Annual Report
January 1- June 30, 1996

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

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ACKNOWLEDGMENT

This semiannual was prepared with the support of the U.S. Department of Energy (DOE) Morgantown 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 over-fire 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-pm 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) will focus 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 will be conducted to note particle-size formation and slagging deposition. Results will be used to support demonstration projects at the utility boiler scale. Results from this work should yield 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 will involve using a larger-scale combustion test facility to produce more realistic ash products and verify the previous work. The system that is being used 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. 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 of inside height with a 6-inch ID reducing down to 3 inches in the final heated section and finally reducing to 2 inches 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 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 exposed to molybdenum disilicide heating elements allowing operation to 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 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 oF (120°- 175 oC), 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 1500 °–1600°C (2732 °–2912°F) in the radiant section and can be maintained at 760 °–1200°C (1400 °–2200°F) in the convective pass section. Flue gas flow rates can be maintained at approximately 8 scfm as generated by the combustion of the fuel. The CEPS fabric filtration (baghouse) system shown in Figure 1 has three

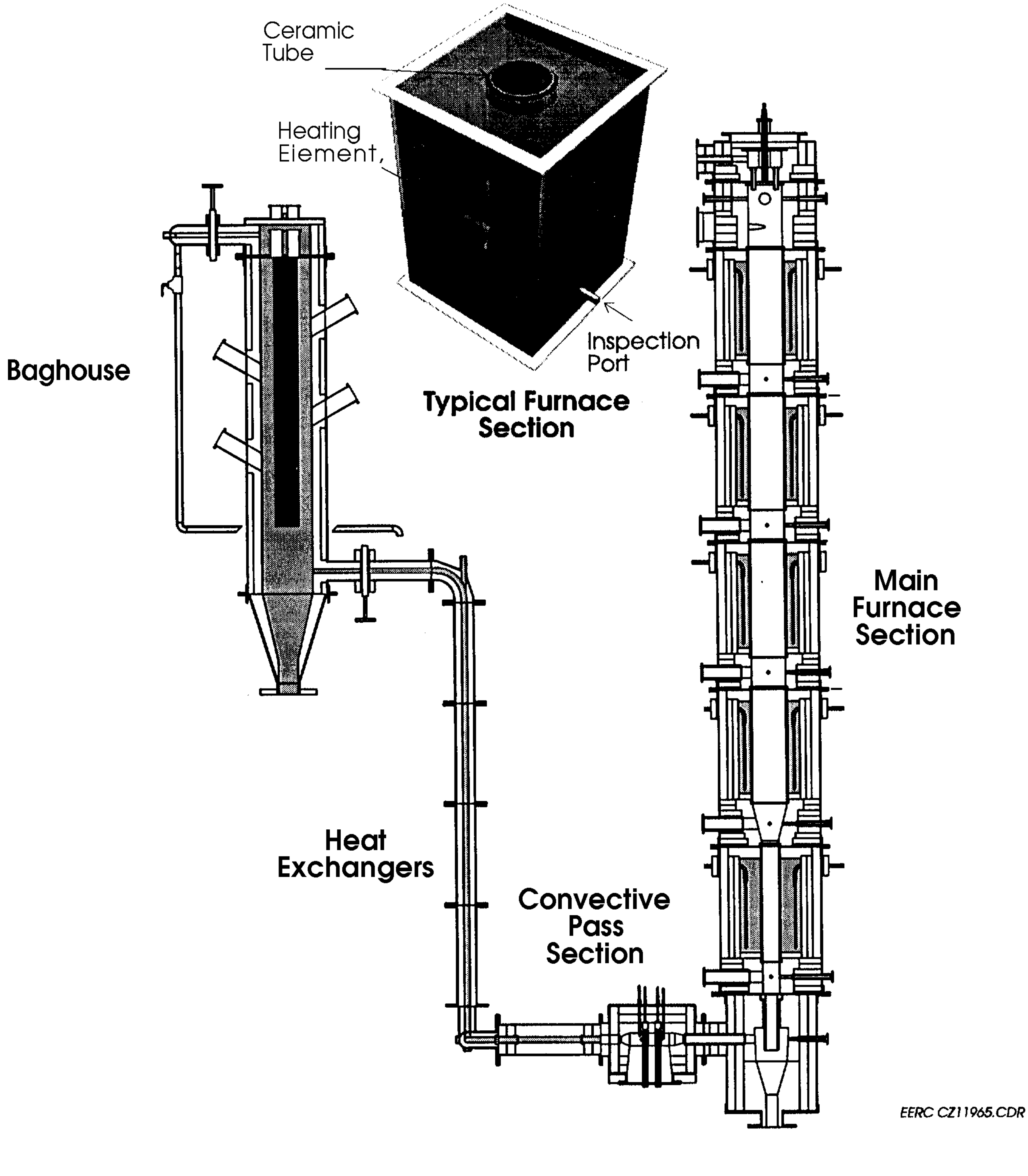

Figure 1. Design sketch of the CEPS showing the main and convective pass sections, heat exchangers, and baghouse.

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 wide by 9 inches deep by 6 feet high. Both bags are 16-ounce Huyglass material 4 inches in diameter by 4 feet 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 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, with normal operation at about 30 psig. 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 will be conducted using two different coals under conventional and low-NO_x combustion conditions. Pulverized coal sized at nominally 70%-80% -200 mesh will be used. Slight modifications to the CEPS to fire in a low-NO_x combustion mode are discussed in the results section.

4.0 RESULTS

4.1 Boiler Industry Review

A background perusal of utility engineers and operators was undertaken 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 carbon has actually decreased after a boiler has been converted to low-NO_x burners (3).

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 is beyond the scope of this project to perform in-depth testing of the effectiveness of additives; however, the understanding that will be 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, we can summarize that our 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 Modification of CEPS

The CEPS reactor is being slightly modified to burn the test coals in a low-NO_x combustion mode. Secondary air will be diverted to cause better mixing of the coal with the combustion air in substoichiometric fashion, and ternary air will be introduced into the coal stream further down in the primary combustion zone, thus creating a simulated low-NO_x combustion environment. Some additional plumbing will also be needed for the CEPS, and an ash deposition probe will be modified to collect slag at various residence times in the CEPS main furnace zone.

4.3 Experimental Test Approach

Based on the industry survey, a final test plan or approach was established for this project. Two coals were selected for testing, including a subbituminous Black Thunder and a bituminous Illinois No. 6. Typical properties of these coals are given in Table 1, with fresh analyses of the test coals forthcoming. The Black Thunder coal is fairly typical of coal from the Powder River Basin, with high magnesium and calcium bound organically in the coal, high aluminosilicate as kaolinite or illite clays, and low pyrite, iron, and sulfur. The Illinois No. 6 is typical of eastern U.S. coal, with high pyrite, iron, sulfur, and low quantities of alkali such as calcium. These coals will be ground to 80% -200 mesh and fired in the CEPS under conventional and low-NO_x combustion conditions.

Combustion testing will first involve shakedown testing of the CEPS reactor in order to determine the proper low-NO_x combustion arrangement and to test the particulate and slag deposit sampling probes. Black Thunder and Illinois No. 6 coals will then be fired in the CEPS under conventional and low-NO_x conditions. During combustion testing, on-line measurement of NO_x, SO_x, CO_2, and O_2 will be performed using gas analyzers, and on-line particle-size measurement will be accomplished using an aerodynamic particle sizer (APS). Isokinetic sampling of entrained ash will be performed at different combustion residence times and the ash samples analyzed for loss on ignition and chemical and mineral composition. Slag deposits will be collected primarily in the simulated near-burner region or "reducing" zone of the CEPS. For some of the test runs, the deposits and ash samples will be collected simultaneously. Analysis of the deposits will involve determining bulk chemistry, amorphous and crystalline phase composition, and morphology of the deposit mineral and amorphous components. It is possible that deposits may be analyzed using Mössbauer analysis for speciating the iron- and calcium-bearing components for detection of reduced mineral species. This work would be performed in collaboration with Dr. Calvin Bartholomew at Brigham Young University.

5.0 CONCLUSIONS

In conclusion, the project is just in its beginning stages, with the major accomplishments being the selection of the test coals, the completion of the design for modifying the intermediate-scale CEPS reactor to operate in a low-NO_x combustion mode, and the survey of the utility boiler

TABLE 1

Analysis of 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_2O_3	16.81	9.21
Fe_2O_3	5.69	12.33
$Ti0_2$	1.11	0,41
P_2O_5	1.17	0.04
CaO	22.09	1.45
MgO	4.79	0.67
Na_2O	0.93	0.41
K_20	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

industry to discern what the needs are in the area of fireside impacts on boiler performance resulting from 1ow-NO_x combustion. A good method for firing the CEPS in a representative low-NO_x mode has been developed whereby secondary air is diverted to cause better mixing of the coal with the combustion air in substoichiometric fashion and then adding ternary air into the coal stream farther down in the primary combustion zone, thus creating a simulated low-NO_x combustion environment.

An experimental approach and final plan has been established for this work. Combustion shakedown testing of the CEPS reactor will be performed in order to obtain the proper low-NO_x combustion arrangement and to test the particulate and slag deposit sampling probes. Black Thunder and Illinois No. 6 coals have been selected and acquired and will be fired in the CEPS under conventional and low-NO_x conditions. Work has begun on slightly modifying an existing isokinetic sampling probe for collecting entrained ash at different combustion residence times. The ash samples will be analyzed for particle size and morphology, loss on ignition, and chemical and mineral composition. A design has been established for modifying an existing deposition probe for sampling slag deposits in the simulated near-burner region or "reducing" zone of the CEPS. An evaluation will be made concerning the role of carbon carryover on ash deposition and the role of pyrite, iron, clays, and calcium in the formation of near-burner ash deposits or wall slag. Impacts of low-NO_x combustion on particle-size distribution of entrained ash will also be investigated.

6.0 FUTURE WORK

Upon completing combustion tests and summarizing some 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. Other methods for mitigation should also be tested, such as varying the firing arrangement or attempting to eliminate local reducing zones in the near-burner regions or waterwall areas where deposition frequently occurs, by blowing streams of air on experimental deposits being generated under reducing conditions to determine if corrosive slag development can be mitigated with the strategic positioning of air lances.

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