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Project Summary

Long Term Optimum Performance/Corrosion Tests of Combustion Modifications for Utility Boilers—Host Site: Columbus and Southern Ohio Electric Company Conesville No. 5

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The report gives results of part of a study of corrosion in large utility boilers burning high-sulfur coal, as possibly affected by combustion modifications for decreased nitrogen oxide (NO_x) emissions. During the first part of this study, each boiler was characterized to learn the short term effects of various combustion modifications on boiler operation and emissions. Later, a Level 1 environmental assessment (EA) of boiler operation was performed, followed by tests to measure corrosion rates in the furnace. Also, two 30-day continuous emission monitoring (CEM) tests were performed. This report discusses work on Boiler No. 5 at Columbus and Southern Ohio Electric Co.'s Conesville (OH) generating station. During the *short-term characterization tests*, full load NO_x emissions (as equivalent NO_2) were reduced from 263 to 152 ng/J without adverse side effects. NO_x emissions during the 30-day CEM tests were log-normally distributed with a mean of 180-224 ng/J and a geometric dispersion of 1.13 - 1.19. The Level 1 EA revealed no unusual environmental hazards resulting from low-NO_x operation. For the nearly 2-year study, waterwall corrosion rates (measured ultrasonically) were similar to rates under normal operation at about 1 - 2 mils/yr.*

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

For coal-fired utility boilers, NO_x emission regulations can often be met by using such combustion modification (CM) techniques as decreased total excess air flow. However, this could lead to a chemically reducing atmosphere in the furnace and an increased corrosion potential. Under this program, methods of decreasing NO_x emissions were studied (characterization testing) from environmental and corrosion points of view. To this end, the program included four parts: boiler characterization, Level 1 environmental assessment (EA), corro-

**Readers more familiar with metric units may use the conversion factors at the end of this Summary.*

sion testing, and 30-day continuous emission monitoring (CEM). Several large utility boilers were studied during this long-term performance/corrosion study. This report deals with the No. 5 boiler at Columbus and Southern Ohio Electric Co.'s Conesville (OH) generating station.

Background

NO_x has long been considered an undesirable component of the earth's atmosphere. In parts-per-million concentrations, NO_x is considered to be a precursor to acid precipitation, photochemical smog, and irritation in human respiratory systems. Since the early 1970s, after coal-fired utility boilers were identified as a major NO_x source, EPA has supported research for NO_x control at these large boilers.

Under the sponsorship of the U.S. Environmental Protection Agency (EPA), Exxon Research and Engineering Co. studied the effects of boiler operating conditions on NO_x emissions. These and similar studies led to improved operating procedures for NO_x reduction. The new procedures (known as combustion modifications (CMs) included decreased excess air flow and staged combustion. However, these CMs could increase the chemically reducing nature of the gases in certain regions of the furnace, increasing the corrosion rate on the fireside of the boiler's waterwall tubes, especially in boilers burning high sulfur coal.

The program reported here was a follow-on to the earlier work. During this program, furnace wall corrosion was studied at several coal-fired utility boilers designed to use CM for reducing NO_x emissions. Some of the CMs included the use of overfire air and low-NO_x burners to meet the applicable new source performance standards (NSPS) for NO_x emissions (301 ng/J as NO_2).

Work Plan

The test program contained four phases: boiler characterization; corrosion testing by probes, panels, and wall measurements; Level 1 environmental assessment; and 30-day continuous NO_x monitoring.

During boiler characterization, effects of various boiler CMs were assessed and their ability to reduce NO_x emissions without causing short-term, adverse side effects (such as increased slagging) was evaluated. This resulted in optimized operating procedures for NO_x control and system flexibility. During this time, flue gas emissions and fuel and ash compositions were monitored. Also, furnace gas composition was monitored at various locations along the furnace wall (furnace gas tap sampling) to identify locally corrosive environments for further study.

Corrosion testing was initiated after boiler characterization. Three methods (corrosion probes, corrosion panels, and wall thickness mapping) were used to evaluate corrosion.

Corrosion probes were used to evaluate short term (30 to 1000 hour) corrosion effects. In this method, pieces of wall tube material (called corrosion coupons or test rings) were inserted at five different locations in the furnace for various times and then weighed to determine the rate of metal loss. This qualitative indirect method did not give a true reading of actual wall losses, but it was an economically attractive alternative to methods which require entering the furnace during an outage to measure the tubes directly, as discussed below.

The corrosion panel method was probably the most reliable method used for measuring corrosion. In this method, eight sections of the boiler wall were removed, and replaced by new sections (called corrosion panels) on which the tube wall thickness had been carefully measured. About 2 years later, the furnace was re-entered (during an outage) and the panels were remeasured. The wall thickness measurements were made ultrasonically, a nondestructive test in which high frequency sound waves are bounced off the inner wall of the tube and the thickness is determined from the echo time delay.

Wall thickness mapping involved ultrasonic thickness (UT) measurements of walls throughout the furnace. The first set of such wall measurements occurred during the outage in which the corrosion panels were installed, and the second set was about 2 years later (coincident with the final panel measurements).

During these long term corrosion tests, an EPA Level 1 environmental assessment (EA) test was performed. It included physical, chemical, and biological (toxicity) analysis of the major streams entering and leaving the boiler. The Source Assessment Sampling System (SASS) train was used to sample the flue gas stream, while EPA Method 17 was used to measure particulate removal efficiencies (i.e., electrostatic precipitator [ESP] collection efficiency). Other streams sampled included sluice water, coal, and ESP hopper ash.

Twice, during the 2-year corrosion exposure period, NO_x and other flue gases were monitored continuously for 30 days using a continuous emission monitoring (CEM) system. The 30-day CEM tests quantified flue gas emissions over normal boiler load cycles and for a longer period than was possible during the characterization tests. These tests also indicated how CEMs may be expected to perform (reliability, accuracy, maintenance needs, etc.) in similar situations.

Boiler Description

Conesville No. 5 is the fifth boiler constructed at Columbus and Southern Ohio Electric Company's (C&SOE) Conesville (OH) generating station. Burning nearly 200 tons/hr of high-sulfur coal (high corrosion potential) to generate more than 400 MW of electric power, its 20 burners use tangential firing in a single-compartment, balanced-draft, waterwall boiler to produce about 3,000, 000 lb/hr of super heated steam (1000°F, 2800 psi). Designed by Combustion Engineering (CE) Inc., it uses CMs (e.g., overfire air) to guarantee compliance with the applicable NSPS for NO_x emissions (301 ng/J NO_x as NO_2), and is one of the first utility boilers to be governed by this NSPS.

Results

Boiler Characterization

During the first part of this study, Exxon evaluated several CMs which could be used to reduce NO_x emissions. Three were selected for detailed study: decreased total excess air flow, increased overfire air flow, and upward overfire air nozzle tilt.

By optimizing these parameters (Figure 1), full load NO_x emissions (as equivalent NO_2) were decreased from 263 to 152 ng/J without adverse, short-term side effects. (The applicable NSPS emission rate is 301 ng/J as NO_2.)

In addition, by using the data from the boiler characterization tests, an improved operating procedure was adopted for medium and full load operation.

As expected, flue gas and fuel analysis for sulfur confirmed that most fuel sulfur is converted to SO_2 and then delivered to the scrubber for subsequent cleanup.

Furnace gas sampled in the combustion zone (near the furnace waterwalls) showed that the lowest CO concentrations were in the hopper zone, and that the region where corrosion was most likely (low O_2, high CO) was in the chemically reducing environment around the burner zone. After the characterization work, corrosion in this and other regions was studied in greater detail using corrosion

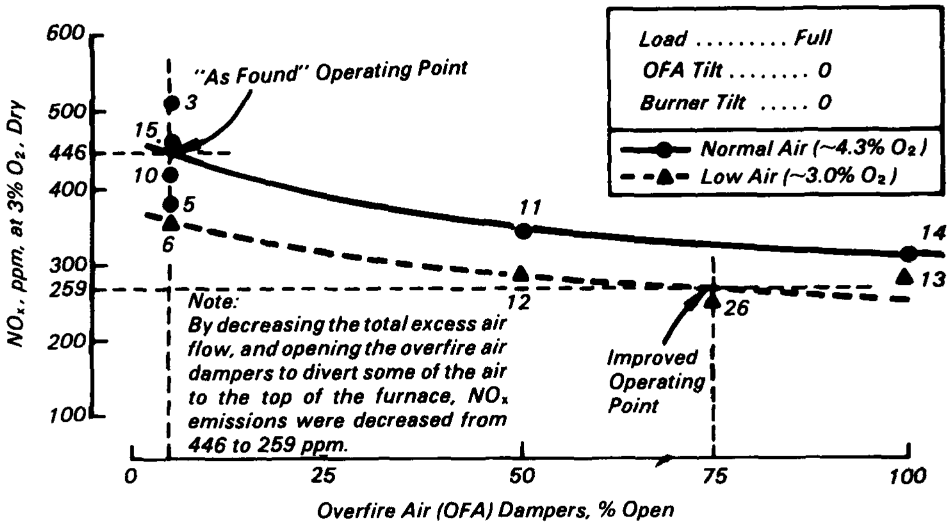

Figure 1. *NO_x versus overfire air, Columbus and Southern Ohio Electric Co., Conesville No. 5.*

probes and ultrasonic tubewall thickness measurement methods.

In the "as-found" condition, NO_x emissions from the Conesville No. 5 boiler were well within the applicable NSPS limit (301 ng/J). As a result of this program, the full load NO_x emissions, as NO_2, were reduced 42% (from 263 to 152 ng/J). These data were used to set up and "fine tune" the boiler, resulting in improved operating procedures with no adverse, short-term side effects. Long-term effects (such as corrosion) were studied in detail as the program continued.

Level 1 Environmental Assessment (EA) Testing

The Level 1 EA test at Conesville No. 5 involved the major inlet and effluent streams crossing the plant's process boundaries. The streams sampled included the inlet and outlet of the electrostatic precipitator (ESP), the ESP hopper catch, the fuel feed, and the sluice water flushing the furnace hopper.

The Level 1 test was performed as a screening study to determine potential pollutants in the various streams and included three types of analysis: (1) chemical analysis was used to determine the chemical composition of the various streams; (2) physical analysis of particles entrained in various streams provided information on shape and size; and (3) biological analysis provided information on the toxic or mutagenic effects of the various streams on living matter.

The test showed that, as expected, most of the flue gases leaving the combustor and going to cleanup devices are fixed gases (O_2, CO_2, N_2, etc.). Other components of this stream include sulfur compounds, hydrocarbons, and entrained particulate matter.

Measurements taken at the ESP showed that the particulate matter (fly ash) in the flue gas stream represents more than 60% of the total ash leaving the system (the rest, slag or bottom ash, exits by another stream; e.g., the sluice water stream to the settling pond). Also, more than 98% of the fly ash (mostly the larger particles) is removed by cleanup devices, never reaching the stack.

The particulate matter and entraining flue gases contained low levels of organics (mostly alkyl esters): concentrations of most metals were near or below detectable levels. (Table 1 lists the metals data for solid and liquid samples; EPA priority metals for wastewater are shown first.) Organic matter on particulate favored the smaller particles. At the precipitator inlet, the particles were generally spherical, and composed mostly of silicate material.

The fly ash particles sampled from the ESP hopper were less spherical than the particles at the ESP inlet, ranged from 1 to 40 μm, and, like the ash entering the ESP, contained mostly silicates.

While these tests were underway, supplemental tests were performed by Acurex Corporation under separate EPA contract. The Acurex data shows that, as the sluice water passes through the system, there is an increase in acidity, total suspended solids, chemical and biological oxygen demand, and total organic carbon. The effluent sluice water samples contained very low levels of metal anions.

The coal extract was separated into seven fractions, but the spectra of each fraction were generally too complex to be analyzed by EPA Level 1 procedures. Instead, the major peaks are listed in the full report, and show that the extract was highly aromatic, highly oxygenated material containing phenolic material, carboxylic acids, amides, and aliphatics. Most aromatic rings had two or more substituents. Mono-substituted aromatics were rare.

Biological tests (using living matter) were used to assess the environmental effect of process effluents on life forms. These tests indicated (Table 2) that the coal, ESP hopper ash, and sluice water are not mutagenic. The Rat Alveolar Macrophage (RAM) assays were also negative. The Chinese Hamster Ovary (CHO) cell assay yielded toxic responses with coal leachates and sluice water. Moderate to high toxicity was also recorded for some of the aquatic assays. Sluice water caused no toxicity in any of the aquatic species studied, but stimulated the growth of algae.

Corrosion Tests

To more fully evaluate the longer term side effects of low-NO_x operation, corrosion testing began after the characterization period, and included corrosion probes, corrosion panels, and wall thickness mapping.

With corrosion probes, as exposure time increased, the rate of metal loss seemed to decrease from more than 70 to less than 20 mils/yr; thus, the loss rate for the probes approached the loss rate for the furnace walls (which the probes were designed to simulate). The corrosion panels had an average loss rate of 1.04 mils/yr, which compares well with the average wall loss rate (Table 3) of 1.39 mils/yr.

Table 3 seems to indicate that tubes in the burner zone corrode faster than non-burner-zone tubes. However, the difference is small, and no strong correlation was found between corrosion rate and location in the furnace. Also, no eccentric tube wear or loss of roundness was noticed, and the tubes close to the burners did not corrode measurably faster than those farther from the flame. On the average, the rate of corrosion in this boiler was such that it would require more than 30 years for the tubes to lose half their thickness. Therefore, corrosion rates, while operating in compliance with NSPS NO_x regulations, appear to be acceptable.

Table 1. *Metal Concentrations and Emissions in Various Conesville No. 5 Process Streams*

(Results in µg of metal/g of each stream.)

Element	Flue Gas Stream: 10 and 3 µm Fly Ash Particles[a]	Flue Gas Stream: 1 µm Fly Ash Particles[a]	Fly Ash from Precipitator Hopper	Coal	Sluice Water
Ag	<1.8	<4.3	(5.6)[b]	<4.3	<0.0025
As	83.[b]	960.	220.[c]	(23.)[c]	<0.0103
Be	<0.43	4.1[b]	<1.1	12.[b]	<0.0006
Cd	11.[b]	26.[c]	33.[b]	<7.9	<1.0047
Cr	62.	290.	92.	<1.3	<0.0007
Cu	69.	200.	120.	20.	<0.0002
Hg	0.0018	0.0088	0.014	0.081	<0.0001
Ni	1.4	360.	240.	<11.	(0.0098)
Pb	<7.5	180.[c]	110.[b]	<13.	(0.0084)
Sb	<11.	(67.)[b]	(84.)[b]	<26.	(0.023)[c]
Se	66.[b]	130.[b]	(120.)[b]	<26.	(0.021)[c]
Tl	23.[b]	110.[b]	55.[b]	<8.2	<0.0048
Zn	180.	1000.	330.	50.	0.109
Al	64000.	110000.	15000.	15000.	0.20
Ba	590.	1600.	40.	41.	0.051
Ca	6800.	1600.	15000.	930.	260.
Co	(2.3)[b]	38.[c]	<3.8	15.	<0.002
Fe	130000.	160000.	210000.	44000.	0.27
K	9300.	19000.	17000.	1800.	13.
Li	100.	220.	180.	31.	0.13
Mg	2900.	6300.	4500.	440.	67.
Mn	200.	490.	330.	26.	0.13
Mo	66.[b]	260.[b]	130.[b]	(18.)[b]	(0.006)
Na	1600.	3400.	3200.	750.	47.
P	360.	3000.	850.	(85.)[c]	0.093[c]
Si	100000.	160000.	180000.	18000.	0.21
Sn	<5.7	60.[b]	<15.	<13.	<0.0078
Sr	240.	500.	400.	24.	0.57
Ti	3300.	5900.	5100.	440.	0.029
V	110.[c]	380.	170.[c]	(13.)[c]	<0.0045

[a]For metals on particulate matter (fly ash or dust), the data shows µg of metals/g of particles in the flue gas stream.
[b]Data unreliable due to strong interferences or weak signals.
[c]Data less reliable due to significant spectral or background interferences.
( )Less than 3 times the ICPES detection limit or the blank value. These results may not be significant since they are more easily affected by background fluctuations.
<The lower limit of detection for the element in that particular sample.

Table 2. *Conesville No. 5 Boiler Bioassay Results (Summary)*

	Bottom Ash/Water Slurry		Precipitator (ESP) Hopper Ash		Coal		ESP Outlet To Stack (XAD-2)	
	Exxon Data	Acurex Data	Exxon Data	Acurex Data	Exxon Data	Acurex Data	Exxon Data	Acurex Data
Ames Mutagenicity (Salmonella/Microsomal Mutagenesis Assay)	U	U	U	U	U[a]	-	-	L
Rat Alveolar (Lung) Macrophage Cytotoxicity Assay (RAM)	-	U	U	Ub	U	-	-	-
Rodent Cell Clonal Toxicity Assay (Chinese Hamster Ovary - CHO)	L	L	-	-	M	-	-	L
In Vivo Oral Rodent (Whole Animal Acute Toxicity - Rat)	U	-	U	U	U	-	-	-
Fresh-Water Fish (Fathead Minnow)	U	U[b]	U	U[b]	M	-	-	-
Fresh-Water Daphnia	U	U[b]	M	U[b]	H	-	-	-

Table 2. *Conesville No. 5 Boiler Bioassay Results (Summary) (cont.)*

	Bottom Ash/Water Slurry		Precipitator (ESP) Hopper Ash		Coal		ESP Outlet To Stack (XAD-2)	
	Exxon Data	Acurex Data	Exxon Data	Acurex Data	Exxon Data	Acurex Data	Exxon Data	Acurex Data
Magna (Water Flea)								
Fresh Water Algae	U		H		H	-	-	-
EC_{50}[c] (Dose that kills 50%)		2.5 to 6.7 mg/L		328 to 367 mg/L				
EC_{95}[c] (Dose that kills 95%)		4.4 to 16.2 mg/L		830 to 963 mg/L				

[a]Not mutagenic, but toxic to cells. (Up to the time of cell death, no mutations had been observed.)
[b]Dose = 1000 mg of sample/liter of culture.
[c]Bottom ash affected acidity in Acurex's algae test:
O ash, pH = 7.1; and
25 mg/L, pH = 3.6.

Key
H = High toxicity
M = Moderate toxicity
L = Low toxicity
U = Undetected
\- = Not tested (usually due to insufficient sample)

Table 3. *Conesville No. 5 Boiler Long Term Corrosion Results (On-line Time = 12,000 hr)*

Location	Wall Loss mils	Wall Loss mils/yr
Nose	0.8	0.6
	2.0	1.5
Burner Zone	2.1	1.6
	1.8	1.4
	2.9	2.2
Hopper	1.5	1.1
Averages:		
Burner Zone	2.3	1.7
Non-Burner Zone	1.4	1.1
Grand Average	1.9	1.4

Thirty-day Continuous Emission Monitor (CEM) Tests

Twice during the long-term operating period, flue gas emissions were measured for 30 days using continuous emissions monitors (CEMs). The data proved useful for evaluating boiler emissions over normal load cycles for longer periods than during the earlier characterization tests. The CEM data also helped to evaluate the abilities, potential problems, and performance limitations that might be associated with CEMs in similar situations. Table 4 summarizes the data.

Although the boiler steam load varied widely (e.g., from about 80 to 40% of maximum capacity during the first CEM test), the NO emission rate was fairly steady with mean values (Table 4) of 226 and 182 ng/J for the first and second tests. The standard deviation was about 10 percent of the mean value. The statistical parameters in Table 4 are in good agreement with the probability plots shown in the full report.

Similarly, for the second test, the NO_x emissions rate and excess oxygen levels were fairly steady: both showed standard deviations of about 9% of the mean value.

The CEM system (utilizing an extractive sampling system) passed the EPA performance specifications for accuracy, drift, response time, etc. and provided accurate gaseous emissions data for the test. However, both calibration of the instru-

Table 4. *Statistical Parameters for Conesville Unit No. 5 30-Day Continuous Emission Monitoring (CEM) Tests*

First 30-Day Test

	Load MW_{th}	O_2 %	CO_2 %	CO ppm[a]	CO ng/J	NO ppm[a]	NO ng/J	NO $lb/10^6 Btu$[b]
Mean	490.7	6.9	11.5	320	114	387	226	0.526
Minimum	646.0	5.7	10.2	0	0	303	177	0.412
Maximum	311.4	8.6	12.5	914	329	447	261	0.607
Range	334.6	2.9	2.3	914	329	144	84	0.195
Standard Deviation	101.1	0.9	0.7	280	100	40	23	0.053
Percent Deviation	20.6	13.0	6.1	87.5	87.5	10.3	10.3	10.3
Variance	10,214	0.81	0.49	78400	10000	1600	52.9	1.230
Count	29	29	29	29	29	29	29	29

Second 30-Day Test

	Load MW_{th}	O_2 %	CO_2 %	CO ppm[a]	CO ng/J	NO ppm[a]	NO ng/J	NO $lb/10^6 Btu$[b]
Mean	647.2	5.63	11.94	49.2	17.2	310.1	182.1	0.42
Minimum	445.1	4.5	10.5	14	5.0	233	137.0	0.32
Maximum	801.9	7.0	13.2	135	48.0	381	223.0	0.52
Range	356.8	2.5	2.7	121	43.0	148	86.0	0.20
Standard Deviation	87.7	0.524	0.558	25.07	8.86	28.46	16.32	0.04
Percent Deviation	13.6	9.3	4.7	52.0	52.0	9.0	9.0	9.0
Variance	7693.0	0.275	0.312	628.6	78.56	96172	266.3	0.0016
Count	35	35	35	35	35	34	34	34

[a]Corrected to 3% O_2, dry.
[b]As NO_2.

ments on a daily basis and maintenance of the sampling system were necessary.

Conclusions

Combustion modification effectively reduces NO_x emissions from coal-fired utility boilers, without adverse side effects. On the average, for the Conesville boiler, tube wall corrosion rates from low-NO_x operation will not decrease or limit the useful life of the boiler. The Level 1 test confirms that no unusual environmental hazards result from low-NO_x operation.

The 30-day CEM tests show that, through a good maintenance and calibration program, CEMs can be made to meet the EPA performance specifications.

Recommendations

When possible, combustion modifications (CMs) should be considered as an effective approach to NO_x control on coal-fired utility boilers. However, slagging and other possible side effects should be monitored to ensure that satisfactory operation continues.

Because CM for NO_x control requires close observation and tight control on boiler operations, a well maintained continuous emission monitor (CEM) for CO should be used to help decrease excess air to optimum levels.

Conversion Factors

Readers more familiar with the metric system may use the following factors to convert units to that system:

Non-metric	Times	Yields metric
°F	5/9(°F-32)	°C
lb	0.454	kg
mil	24.5	μm
psi	0.070	kg/cm^2

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The complete report, entitled "Long Term Optimum Performance/Corrosion Tests of Combustion Modifications for Utility Boilers; Host Site: Columbus and Southern Ohio Electric Company, Conesville No. 5," (Order No. PB 84-102 698; Cost: $26.50, subject to change) will be available only from:

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