



Project Summary

Evaluation of Tubewall Corrosion Rates on a Coal-Fired Utility Boiler Using Staged Combustion for NO_x Reduction

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Nitrogen oxide (NO_x) emissions at a coal-fired utility boiler have been decreased by combustion modifications (CMs) using the boiler's existing hardware for combustion control. The CMs studied included decreased excess air and a variety of fuel/air ratios at selected burner elevations (i.e., biased combustion). Side effects of these operating conditions were also studied, including: changes in boiler efficiency (but not heat rate), other emissions, and (for the first time) detailed studies of boiler wall corrosion rate. Wall thickness measurements revealed that, averaged over the total measured area, the boiler walls lost 2.2 mils (5.2 mils/yr) during a 5-month baseline period: 2.6 mils (6.2 mils/yr) in the nonburner zones compared to 1.7 mils (4.0 mils/yr) in the burner zone. During a 12-month low-NO_x period, the non-burner elevations lost only 2.11 mils/yr, while the burner area lost 5.05 mils/yr; a slightly higher loss rate in the burner zone than for the same zone during the baseline period. Typically, near full load, CMs were used to achieve NO_x reductions of about 20% without significant side effects. The CMs included biased burner firing and decreased boiler excess air. The corrosion rates during extended low-NO_x operation would not appear to appreciably reduce the average expected life of the furnace tubes.

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, nitrogen oxide (NO_x) emission regulations can often be met by using combustion modification (CM) techniques such as decreased total excess air. However, this could result in a chemically reducing atmosphere within the furnace and increased corrosion potential. Consequently under EPA Contract 68-02-1415, Exxon Research and Engineering Company (ER&E) studied CMs for decreased NO_x emissions at several boilers and gas turbines. At the last boiler tested (Crist No. 7), special attention was given to corrosion. Thus, in addition to evaluating CM effects on NO_x emissions, the study was expanded to include the effects of CMs on boiler wall wastage rates. This report addresses the study of Boiler No. 7 at Gulf Power Company's Crist Generating Station in Pensacola, Florida.

Background

NO_x is not only injurious to human health, but also reacts chemically (with organic gases and other pollutants in the presence of sunlight) to produce a brown "smoggy" haze commonly observed in densely populated areas. NO_x also reacts in the atmosphere to form nitric acid (HNO₃), and is thus partially responsible for "acid rain." Hence, NO_x has been classified as a major pollutant, and a

great deal of effort has been aimed at its abatement. Typically, NO_x is a product of combustion. It is formed either from nitrogen in the fuel (fuel-NO_x) or from the high temperature reaction of nitrogen in the combustion air (thermal-NO_x).

Since 1971, EPA regulations have limited NO_x emissions from coal-fired steam generators. The National Ambient Air Quality Standards (NAAQS) set maximum limits on the concentration of NO_x in air, requiring NO_x emission reductions. Further NO_x reduction was required by the New Source Performance Standards (NSPS) of 1971. In 1978, more stringent NSPS for NO_x emissions from electric-utility coal-fired steam generators became effective. CMs (e.g., low excess air and staged firing) are ways of meeting regulations requiring decreased NO_x emissions. However, low-NO_x operation by CM brings with it the possibility of increased slagging and furnace tubewall corrosion, especially with high-sulfur coals.

Work Plan

The study at Crist No. 7 was designed to develop boiler operating guidelines for low-NO_x emissions and then to evaluate the possibly corrosive effects of such operation. To this end, the program was divided into several parts.

In the first part, "Boiler Characterization," about 100 short (1-hour) tests were performed to evaluate effects of CMs on stack emissions and other immediate side effects. These tests helped develop boiler operating guidelines for long-term low-NO_x operation. They also helped to define baseline conditions and establish an improved low-NO_x operating mode. Baseline operation was defined as the boiler's normal operating procedure before these tests began. The characterization tests led to an optimized operating procedure (low excess air, staged combustion, etc.) for decreased NO_x emissions. This became known as the low-NO_x operating mode. For the operating modes showing the greatest NO_x reduction, samples of combustion gas were withdrawn from along the furnace walls (by furnace gas taps) and analyzed for potentially corrosive local environments.

In the next part of the study, small pieces of boiler tube material (called corrosion probes) were inserted into the furnace through inspection doors to study local, short-term (30-1000 hours) corrosion effects. Also, longer term effects (a few months to 2 years) were studied by entering the boiler during scheduled outages and ultrasonically measuring

tubewall thicknesses at thousands of points inside the furnace. Additionally, selected sections of boiler wall were removed during the outages and replaced with specially characterized new sections of wall tubes (called corrosion panels) which were later removed and analyzed for corrosion.

Finally, detailed measurements were made of stack emissions at both baseline and low-NO_x operating modes. The measurements included trace metals, organics, and dust loading in the flue duct.

Boiler Description

Crist No. 7, a pulverized-coal-fired utility boiler designed by Foster Wheeler Energy Corporation, uses horizontally opposed firing in a natural circulation, radiant, reheat steam generator to produce steam for generating electric power. The furnace has 24 burners (12 on each of the front and rear walls), arranged in three rows of four on each wall. Its rated capacity is 1.64×10^6 kg of superheated steam per hour (3.6×10^6 lb/hr) at 17.2 MPa (2500 psi) and 810K (1000°F with an electric generating capacity of 500 MW.

Crist No. 7 is of pre-NSPS design and, under normal operation, was not designed to meet the NSPS for NO_x emissions. However, by use of appropriate combustion modifications, NO_x emissions were decreased significantly during the test period.

Results

Boiler Characterization

In the first part of this program (boiler characterization) several boiler CMs were investigated for NO_x reduction, including:

- Secondary air registers. (These were used to change the air distribution within the combustion zone.)
- Firing pattern. (Fuel distribution was changed by varying the coal feed rates to the six burner rows.)
- Load. (NO_x emission rates can be reduced by operating the boiler at less than full capacity.)
- Total air flow. (Firing with decreased excess air decreases NO_x emissions.)

Secondary air register setting (air distribution) and firing pattern (fuel distribution) were combined for maximum combustion staging. Staged firing was found to be an effective method of NO_x control. In this CM technique, fuel and air distribution were adjusted so that the bottom of the combustion zone was operated fuel-rich, while the upper

burners were supplied with excess air (fuel-lean). Or, in the extreme case, when load demand permitted, fuel to the upper burners was shut off completely, and they were operated on air only. Figure 1 shows that decreased fuel in the upper burner rows results in decreased NO_x emissions. However, in Figure 1, the effect is somewhat exaggerated because staging was accompanied by a slight drop in load and total excess air. (Reductions in load and excess air are known to decrease NO_x emissions somewhat, and the effect seen in Figure 1 may not be entirely due to staging.)

Load reductions had a beneficial effect on NO_x emissions. However, decreased load was not considered practical for NO_x control because load, usually determined by demand, is not conveniently under the operator's control.

Control of the total air flow was perhaps the most appropriate method found for controlling NO_x emissions. In this method, NO_x emission rates were reduced by using the fan-speed and damper controls to limit the amount of excess air available in the furnace's combustion zone. (Excess air is measured as percent oxygen in the flue gas.)

Trace Metals and Other Emissions

Evaluating the side effects of low-NO_x operation included measurements of particulate mass and size distribution in the flue duct, as well as volatile organics, trace elements, sulfur oxides, boiler performance, and furnace tube corrosion. Details of each may be found in the full report. However, as an example, some of the metal data are presented on Table 1, which shows metal data on stack emissions measured upstream of the precipitator under both baseline and low-NO_x conditions. At the levels of NO_x control practiced in this program, the analysis indicates that differences between baseline and low-NO_x firing conditions are minimal and that (from this point of view) no appreciable effect on boiler operation would be expected.

Corrosion Studies

Since the influence of NO_x controls on corrosion rates in the boiler was of special interest in this test program, several methods were used to assess corrosion under both baseline and low-NO_x operation, including:

- Furnace gas taps - Analysis of furnace gases (O₂ and CO) to identify chemically reducing atmospheres

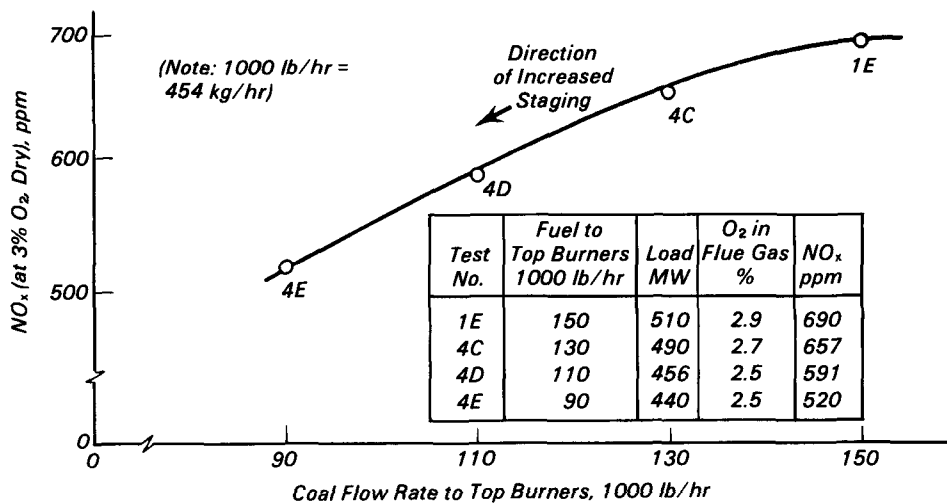


Figure 1. Staged combustion: NO_x vs. degree of staging.

(i.e., increased corrosion potential) near furnace walls.

- Corrosion probes - Exposure of small samples of boiler tubewall material inserted into the furnace through inspection doors.
- Corrosion panels - Installation of specially characterized sections of boiler wall which were later removed for corrosion analysis.
- Ultrasonic mapping - Non-destructive (echo sounding) measurements of tubewall thickness during periodic outages.

As expected, the furnace gas analysis showed that CO concentrations were high, where O₂ concentrations were low. Generally, one would expect decreasing CO concentrations (depletion through burnout) with increasing elevation (further downstream) in the boiler. However, in many of the tests, staged combustion was used to elongate the flame to achieve lower flame temperatures. This caused CO concentrations to remain high (> 1,000 ppm) further downstream in the flue. Nevertheless, even with the most extreme staging tested, CO depletion was always completed upstream of the boiler's economizer outlet. No other strong relationship between CO and height in the boiler was apparent.

The CO/O₂ ratio within the furnace was generally higher for low-NO_x firing patterns than for baseline conditions, indicating a greater potential for corrosion at low-NO_x conditions than at baseline. For "as-measured" furnace gas composition, the difference between baseline and low-NO_x conditions was most noticeable at the top burner elevation. At this elevation,

the CO readings (along the wall) were higher during low-NO_x operation than during baseline tests. Therefore, it was not surprising that, for this region of the furnace, corrosion rates were higher under low-NO_x conditions than under baseline.

Table 1. Summary of Metal Data on Stack Emissions^a (µg/m³)

	Baseline Test		Low NO _x Test
	First Analysis	Second Analysis	
Silver	NR ^b	NR	NR
Arsenic	151.5	151.2	215
Beryllium	28.1	28.1	45.7
Cadmium	2.01	2.01	22.8
Chromium	4363	4349	1153
Copper	249	249	369
Mercury	7.3	7.3	<19.9 ^c
Nickel	2702	2696	699
Lead	257	255	505
Antimony	39.9	38.2	49.6
Selenium	52.4	52.2	67
Titanium	10,174	10,507	17,938
Zinc	1596	1542	3012
Barium	3727	3860	8152
Bismuth	<8.3	<8.3	<12.7
Cobalt	223	226	264.5
Iron	50,471	41,830	106,216
Manganese	2011	1931	3465
Molybdenum	386	386	292
Tellurium	6.2	6.2	<6
Thallium	<791	791	<1477
Tin	11.7	11.7	18.2
Uranium	<402,549	<402,549	<321,648
Vanadium	743	730	1063
Zirconium	<40,255	40,255	32,163

^a Sample is from flue duct just downstream of air heater and just upstream of precipitator.

^b Not reported.

^c Below detection limit.

Wall thickness measurements (Table 2) showed that under low-NO_x operation, the burner area experienced more metal loss than the non-burner zone. Furthermore, the burner zone loss was greater under low-NO_x than under baseline. However, in the non-burner zone no explanation was found for the corrosion rate under baseline being almost triple the low-NO_x rate.

In the test panels, two types of metals were used so that the corrosion resistance of each could be evaluated. These included the normal boiler tube material as well as a material thought to be more resistant to corrosion. However, in this application, the analysis showed an insignificant difference in their corrosion rates.

During low-NO_x operation, burner-zone panels corroded faster than non-burner-zone panels. Also, for the panels in the burner zone, more corrosion occurred during low-NO_x than during baseline operation. The opposite was true for panels in non-burner zones.

Corrosion probe data (Figure 2) show that the rate of metal loss is fastest when the probe is first exposed in the furnace, but slows down as exposure time

Table 2. Wall Metal Loss Summary^a
 Gulf Power Company's Crist No. 7 Boiler
 mils (mils/yr)

	Non-burner zone (All walls)	Burner zone (All walls)	Furnace average
Baseline (5 months)	2.6 (6.2)	1.7 (4.0)	2.2 (5.2)
Low-NO _x (12 months)	2.1 (2.1)	5.0 (5.0)	3.4 (3.4)

^aData is from ultrasonic thickness measurements of boiler tubes performed inside the boiler during annual and regularly scheduled outages.

increases. During very short exposures (30 hours), burner-zone probes corroded faster than non-burner-zone probes under both baseline and low-NO_x condition. But longer term exposures (240-1000 hours) did not show significant corrosion rate differences between burner and non-burner zones, or between baseline and low-NO_x operation.

Conclusion

At Gulf Power Company's Crist No. 7 boiler, in one of the first studies of its kind, corrosion rates were related to CM techniques for controlling NO_x emissions. The CMs tested made use of existing boiler controls (no retrofits) to achieve a 20% decrease in NO_x emissions at full load, and up to about 50% decrease at lower loads during short-term tests. Operation for decreased NO_x was accomplished by staged combustion (with low excess air), by biasing the secondary air

flow and dedicating the pulverizers serving the lower burners to full load operation. Although there were no significant side effects from decreased NO_x operation, the tube wastage rate in the burner zone was increased enough that the boiler manufacturer feels that staged firing by itself with high-sulfur coal may be a questionable means of controlling NO_x from pre-NSPS boilers.

Other than NO_x, CO was the only gaseous emission that was seen to be significantly affected by CMs for NO_x control. However, adverse effects of NO_x controls on CO emissions were overcome by proper choice of air feed rate. This was especially easy when a continuous CO monitor was installed on the boiler.

As just mentioned, staged firing is an effective method of NO_x control, and is accomplished by adjusting fuel and air flows so that the bottom burners are operated fuel-rich, and the top ones fuel-lean. However, the effect of secondary air

register settings on NO_x was weak, and adjustment of fuel feed was the more effective method for staging.

Under this program, the CMs tested did not significantly affect the operation or performance of the boiler. However, the NO_x reduction methods used (fuel/air biasing and reduced excess air firing) require tight control of air feed rates, fuel distribution, etc., and will thus limit boiler flexibility. Furthermore, the NO_x control methods applied may not be as applicable with other coals.

Finally, the boiler's manufacturer feels that wastage rates on the boiler's side walls indicate that long-term operation under the reduced-NO_x biased-firing conditions could potentially result in a corrosion problem.

Recommendations

For existing boilers, decreased excess air is one of the most effective methods of controlling NO_x emissions. A CO monitor would help to establish the lowest safe level of excess air under most conditions. Where practical, it is recommended that such a monitor be installed. For Crist No. 7, the staging effect of the secondary air register settings was only marginally effective over the range tested. However, that range might be extended if the registers were controlled automatically. Additional staging could be accomplished by use of specially installed overfire air nozzles. However, this is not often viable as a retrofit. While effective on the boiler tested, the results obtained in this program may have limited applicability to other types of boiler designs. Therefore, before any general conclusions can be made, additional data should be gathered on NSPS boilers from several manufacturers.

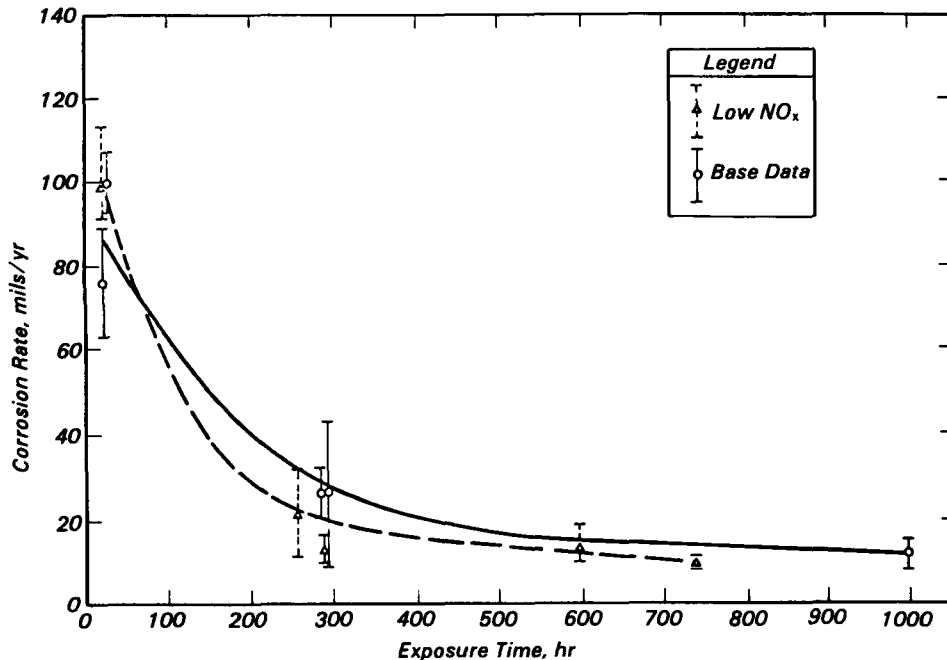


Figure 2. Corrosion probe data (comparison of corrosion rates using probes at Gulf Power Co., Crist Station, Boiler No. 7 pulverized-coal firing).

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The complete report, entitled "Evaluation of Tubewall Corrosion Rates on a Coal-Fired Utility Boiler Using Staged Combustion for NO_x Reduction," (Order No. PB 84-118 231; Cost: \$26.50, subject to change) will be available only from:

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