# ENHANCING THE USE OF COAL BY GAS REBURNING AND SORBENT INJECTION

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# ABSTRACT

The Gas Reburning-Sorbent Injection (GR-SI) Process was demonstrated on a 71 MWe net tangentially fired boiler at Hennepin, Illinois, and is being demonstrated on a 33 MWe net cyclone-fired boiler at Springfield, Illinois as a Clean Coal Technology Round I demonstration project. The Hennepin demonstration was completed after more than 2,000 hours of successful operation. In long-term demonstration testing at a Ca/S molar ratio of 1.75 and 18 percent gas heat input, 53 percent $SO_2$ reduction and 67 percent $NO_x$ reduction were achieved without any adverse impacts on boiler performance or electrostatic precipitator performance with flue gas humidification. These achievements exceeded the project goals of 50 and 60 percent, respectively. The $CO_2$ reduction due to the use of 18 percent natural gas was 8 percent.

# INTRODUCTION

The Energy and Environmental Research Corporation (EER) has conducted a project entitled "Enhancing the Use of Coals by Gas Reburning-Sorbent Injection." The goal of the project was to evaluate Gas Reburning-Sorbent Injection (GR-SI) for reduction of emissions of nitrogen oxides ($NO_x$) and sulfur dioxide ($SO_2$) from a coal-fired boiler. The specific goal was a reduction in $NO_x$ emissions by 60 percent and $SO_2$ emissions by 50 percent. The host site for the project is Illinois Power's Hennepin Station Unit 1, which is a 71 MWe (net) tangentially-fired unit designed by Combustion Engineering. The unit was retrofitted with a GR-SI system designed by EER, then underwent start-up activities, optimization testing, and long-term (one year) testing. The project is sponsored by the U.S. Department of Energy (DOE), the Gas Research Institute (GRI), Illinois Power Company, the State of Illinois Department of Energy and Natural Resources (ENR), and City Water, Light, and Power of Springfield, Illinois. This paper describes the performance of the Hennepin Unit 1 GR-SI system, the impacts of GR-SI operation on the unit, and the environmental impacts.

Coal-fired boilers have been known to be major contributors to acid rain precursors, $NO_x$ and $SO_2$, which are widely believed to have damaged lakes and forests in the northeastern United States and eastern Canada. In response to growing concern regarding pollutant emissions from

coal-fired power plants, DOE initiated the Clean Coal Technology (CCT) program. This EER project is one of several in Round I of the U.S. DOE CCT program. It is one of three carried out simultaneously by EER on a tangentially fired unit (Illinois Power's Hennepin Station Unit 1) and a cyclone-fired unit (Lakeside Station Unit 7 of City Water, Light, and Power in Springfield, Illinois) in CCT Round I, and a wall-fired unit (Cherokee Station Unit 3 of Public Service of Colorado) under a CCT Round III project. The wall-fired unit has a Gas Reburning-Low $NO_x$ Burner System only.

The project goal was a reduction in $NO_x$ emissions by 60 percent, from an as-found baseline (at Hennepin) of 0.75 lb/MMBtu (323 mg/MJ) to 0.30 lb/ MMBtu (129 mg/MJ), and $SO_2$ emissions by 50 percent, from a baseline of 5.30 lb/MMBtu (2,280 mg/MJ) to 2.65 lb/MMBtu (1,140 mg/MJ). The GR process consists of injection of natural gas, corresponding to 15 to 20 percent of the heat input, at a location above the coal burners to create a fuel-rich zone, resulting in the formation of hydrocarbon fragments and radicals which reduce $NO_x$, formed in the coal zone, to molecular nitrogen. Overfire air is injected at a higher elevation to burn out the fuel combustibles under fuel lean conditions. In the SI process, a calcium-based sorbent, such as calcium hydroxide [$Ca(OH)_2$], is injected into the upper furnace to react with flue gas $SO_2$, resulting in formation of calcium sulfate ($CaSO_4$) and calcium sulfite ($CaSO_3$). These solids are carried from the boiler and captured with the fly-ash in the particulate collection device.

The project began in June 1987 and was carried out in three phases:

| | |
|---|---|
| Phase I | Design and Permitting |
| Phase II | Construction and Start-Up |
| Phase III | Operation, Data Collection, and Reporting |

This paper describes the Phase III test program and its results.

## The Test Program

### The Boiler and Process Systems

Figure 1 shows an overview of the GR-SI and humidification systems installed on this unit. Details of the gas, overfire air, and sorbent injection locations are shown in Figure 2.

### The Test Program Objectives and Schedules

The test program was quite detailed in scope in order to evaluate the many parameters which affect the process performance and its impact on the boiler system (Figure 3). Figure 4 indicates the measurements which were carried out during this program. The parametric test results have been discussed in an earlier paper[1] and will be detailed in the final report now in preparation. Therefore, the emphasis here will be on the long-term demonstration testing results and on the work with promoted sorbents, which have performed better than the standard hydrated lime. Several references on Gas Reburning-Sorbent Injection [2-12] are available.

## Long-Term Emissions Performance

The parametric testing data were analyzed to establish the operating conditions under which the program target emissions would be achieved. Several parameters were established, including the primary zone stoichiometric ratio, reburning stoichiometric ratio (and corresponding percent gas heat input), and the Ca/S molar ratio. To achieve the target $NO_x$ and $SO_2$ emissions while maintaining low CO emissions, the nominal operating conditions for the long-term demonstration tests were established as:

| | |
|---|---|
| Coal Zone Stoichiometric Ratio | = 1.10 |
| Reburning Zone Stoichiometric Ratio | = 0.90 |
| Burnout Zone Stoichiometric Ratio | = 1.20 |
| Gas Heat Input | = 18% |
| Ca/S Molar Ratio | = 1.75 |

GR-SI long-term demonstration tests were carried out from January 10, 1992, to October 20, 1992, to verify the system performance over an extended period. The unit was operated at constant loads and with the system under dispatch operation where the load was varied to meet the plant power output requirement. With the system under dispatch, the load fluctuated over a wide range, in some cases, from a low of 40 MWe to the maximum load of 75 MWe, and in

other cases, over a more narrow range. Over the long-term demonstration test series, the following operating parameters were in close agreement with the desired settings above:

| | |
|---|---|
| Primary Zone Stoichiometric Ratio | = 1.09 |
| Reburning Zone Stoichiometric Ratio | = 0.90 |
| Exit Zone Stoichiometric Ratio | = 1.21 |
| Gas Heat Input | = 18.2% |
| Ca/S Molar Ratio | = 1.76 |

Over the long-term demonstration period, the average gross power output was 62 MWe. Linwood hydrated lime was used throughout these tests except for a few days when Marblehead lime was used.

For the long-term demonstration testing, the average $NO_x$ reduction of 67.3 percent and the average $SO_2$ reduction of 52.6 percent correspond to emissions of 0.246 lb $NO_x$/MMBtu (106 mg/MJ) and 2.51 lb $SO_2$/MMBtu (1,080 mg/MJ) as shown in Figure 5. The reductions are calculated from the baseline emissions of 0.75 lb $NO_x$/MMBtu (323 mg/MJ) and 5.30 lb $SO_2$/MMBtu .280 mg/MJ). Emissions of CO were below 50 ppm (at 3 percent $O_2$) in many cases but were higher during operation at low load. Emissions of CO averaged 57 ppm over all GR-SI tests. Hydrocarbon emissions were generally very low, averaging 1.9 ppm with a range of 0.1 to 18.2 ppm (at 3 percent $O_2$). A significant reduction in $CO_2$ emissions was also measured. This is due to partial replacement of coal with natural gas having a lower C/H ratio. This cofiring with 18% natural gas results in a theoretical $CO_2$ emissions reduction of 7.9 percent from the coal-fired baseline level.

Emissions of $N_2O$ were of concern due to its potential impact on the atmosphere. $N_2O$ is believed to contribute to the global-warming greenhouse effect and impact the ozone concentration in the stratosphere. Due to these concerns, emissions of $N_2O$ were measured during GR, GR-SI, and SI testing. The $N_2O$ emissions during GR-SI operation ranged from 0.5 to 3.2 ppm. The emissions during baseline testing averaged 0.8 ppm, and during SI testing, the

$N_2O$ emissions were in the 1.0 to 1.3 ppm range. These levels are very low, indicating that GR-SI may be operated without unacceptably high $N_2O$ emissions.

## Long-Term Thermal Performance

GR-SI was expected to have a minor impact on the thermal performance and operation of Hennepin Unit 1. This section summarizes the thermal performance data associated with GR-SI over the long-term demonstration test period. Extensive data were collected and evaluated to ensure that the Hennepin Unit operated at its rated capacity with proper steam temperatures and pressures. Furthermore, it was important to verify that no adverse impacts would result due to GR-SI operation.

During the design phase, two important goals were established. The first goal was that Hennepin Unit 1 would produce steam at its rated capacity during GR-SI operation, albeit with slightly lower thermal efficiency and some minor changes in heat absorption profiles. The second goal was that steam temperatures could be controlled to their design values using the existing steam temperature control systems. These conclusions were based on performance predictions for nominal GR-SI conditions. During the long-term test program, these predictions were validated over a wide range of boiler loads.

Various thermal performance parameters were collected or calculated on the EER's PC-based on-line Boiler Performance Monitoring System. The database that was established included the following thermal performance parameters:

- Steam production, temperature, and pressure,
- Steam attemperation,
- Gas side temperatures,
- Heat transfer to steam,
- Cleanliness factors,
- Boiler efficiencies, and
- Boiler heat rate.

Table 1 summarizes the thermal performance of the Hennepin unit during the long-term demonstration program for Gas Reburning-Sorbent Injection operation. Since the demonstration was conducted during dispatch control, the data are summarized for low, mid, and high load. In addition, results are compared to modeled predictions to evaluate the validity of the design methodology.

## Humidification

Sorbent injection systems often impact ESP performance due to an increase in particulate loading and increased fly-ash resistivity. Typically, sorbent injection may double or triple particulate loading. In addition, the presence of spent sorbent may increase fly-ash resistivity by as much as 2 orders of magnitude. The particulate size distribution may also decrease. The increase in fly-ash resistivity may result in degradation in the ESP electric field power and therefore result in a reduction in collection efficiency. The flue gas humidification system was designed to reduce the gas temperature to within 70°F (39°C) of adiabatic saturation by injection of atomized water in the duct between the air heater and the ESP. Dual fluid Delavan nozzles were used. Figure 6 shows the essential parts of the humidification duct design. The design residence time is approximately 2 seconds at full load. Five screw conveyors were provided to move the ash out of the duct into the plant sluicing system. Adjustable turning vanes and a perforated plate are used to smooth out the flow pattern of the flue gas entering the humidification zone. The humidification system typically operated at the much higher approach to saturation of 120°F (67°C). With flue gas humidification, ESP collection efficiencies greater than 99.8 percent and particulate emissions less than 0.025 lb/MMBtu (11 mg/MJ) were measured even with an increase

in inlet particulate loadings. These are comparable to the measured baseline emissions of less than 0.035 lb/MMBtu (15 mg/MJ) and collection efficiencies greater than 99.5 percent. This has permitted operation with sorbent injection and continued adherence to the regulatory limit of 0.10 lb particulate matter/MMBtu (43 mg/MJ).

## Fly-Ash Resistivity

In-situ measurements were conducted at the ESP inlet ports using a point-to-plane probe. The method entails creating an electric field between an electrode and a grounded collecting plate. As the flue gas passes between the electrode and the collecting plate, a V-I curve is obtained, first with a "clean" plate and then with a "dirty" plate. The resistivity is calculated from the difference of the two V-I curves and the measurement of the layer of the fly-ash on the "dirty" plate.

Baseline and gas reburning tests showed fly-ash resistivity results in the order of the mid $10^{10}$ ohm-cm at temperatures of about 330°F (165°C), which is typical of fly-ash from bituminous coal with a sulfur content of about 3 percent. For the GR-SI tests, the measurements indicated resistivities ranging from $6 \times 10^{10}$ ohm-cm at 180°F (82°C) to $6 \times 10^{11}$ ohm-cm at 300°F (149°C). The in-situ resistivities measured by the V-I method at 70 MWe are shown in Figure 7. The resistivities quoted in the mid $10^{11}$ ohm-cm at the higher temperatures are lower than expected. It could be possible that the unreacted hydrated lime helped to moderate the fly-ash resistivity.

Good to excellent precipitation of the ash-sorbent mixture can be expected at $6 \times 10^{10}$ ohm-cm. However, resistivities higher than $6 \times 10^{12}$ ohm-cm at the higher temperature will result in lower ESP operating voltages due to possible back corona and/or premature sparkover. The increased sparkover and resulting reduced operating voltage will also reduce current input into the ESP fields by a factor of 6 to 10 at the $6 \times 10^{11}$ ohm-cm resistivity.

## Extended Operation

The Hennepin Unit 1 is a cycling unit which typically operates about 12-14 hours per day. After optimizing the sootblowing scenario, several extended GR-SI runs were carried out. Prior to these runs, the system had operated for 8 hours per day or less. One of these extended runs was for 55 hours at variable loads (45-62 MWe dispatch controlled). No difficulties were encountered with the ESP performance. A more rigorous test was a 32-hour run at full load. This required sootblowing for about 84 percent of the operating time to control the furnace exit temperature such that the humidification system could properly regulate the gas temperature entering the ESP. Figure 8 shows the thermal performance of the boiler during this 32-hour run. These extended runs demonstrated that GR-SI is a technically feasible $NO_x/SO_2$ control process for a utility boiler of this type.

## Promoted Sorbent Tests

Following the completion of the long-term tests, three specially prepared sorbents were tested. Two were manufactured by EER at the California test site. They contained proprietary additives to increase their reactivity toward $SO_2$. In the section below, they are referred to as PromiSORB™ A and B. The other special sorbent was developed by the Illinois State Geological Survey. It is a high surface area hydrated lime (HSAHL) which uses alcohol to form a material which, upon its evacuation, gives rise to a much higher than normal surface area per unit weight than the atmospherically hydrated limes. The system was unmodified even though the densities of these materials were somewhat lower than the standard hydrated lime.

All test results discussed below are without gas reburning although a number of GR-SI tests were also carried out. Figure 9 shows that the $SO_2$ capture at the nominal 1.75 Ca/S molar ratio was 66 percent for PromiSORB™ B, 59 percent for HSAHL, 54 percent for PromiSORB™ A, and 42 percent for Linwood lime. The data on PromiSORB™ B are more scattered than the others, suggesting a nonuniform composition. At a 2.6 Ca/S, the PromiSORB™ B gave 80 percent $SO_2$ reduction. The calcium utilization plots shown in Figure 10 show a similar pattern at the nominal

1.75 Ca/S:   38 percent for PromiSORB™ B, 34 percent for HSAHL, 31 percent for PromiSORB™ A, and 24 percent for Linwood.

The optimum temperatures for the promoted materials are somewhat lower than that for the standard hydrated lime and utilization was found to increase at low loads and with higher furnace oxygen concentration.   PromiSORB™ A also improved $NO_x$ reduction by 15-35 percent, depending on test conditions, owing to a proprietary additive in the sorbent.

The very low density of the HSAHL prevented testing Ca/S ratios above 1.8.  The Fuller-Kinyon screw pump was designed for 30-35 lbs./cu.ft. (0.48-0.56 $g/cm^3$) material, compared to the HSAHL density of 20 lbs/cu. ft. (0.32 $g/cm^3$).

All of these sorbents showed encouraging results and the potential for further improved performance with optimized system design for their somewhat different physical properties.

## Lakeside GR-SI Project Status

This project uses the same basic process as the Hennepin unit. The equipment is installed on a 33 MWe cyclone-fired pressurized boiler.  Construction and start-up are complete, and the testing phase has just begun.  Initial GR and SI tests indicate that the 60 percent $NO_x$ and 50 percent $SO_2$ reduction goals can be achieved in the cyclone-fired boiler like in the tangentially-fired boiler.

## SUMMARY

1.    Gas Reburning, Sorbent Injection, and Gas Reburning-Sorbent Injection technologies have been successfully demonstrated on a 71 MWe (net) tangentially fired boiler at Hennepin, Illinois.  A similar project is being conducted on a 33 MWe (net) cyclone-fired boiler at Springfield, Illinois.

2. During the period of the long-term demonstration, Gas Reburning-Sorbent Injection at a nominal natural gas heat input of 18 percent and a nominal Ca/S molar ratio of 1.75 achieved an average $NO_x$ reduction of 67 percent and an average $SO_2$ reduction of 53 percent. These levels of emission reductions have exceeded their respective design goals of 60 percent and 50 percent. Illinois Power, the host company, has decided to retain the Gas Reburning system.

3. The Gas Reburning-Sorbent Injection technology also reduced $CO_2$ emissions by 8 percent.

4. Flue gas humidification is effective in enhancing the electrostatic precipitator performance during sorbent injection.

5. Three promoted sorbents including PromiSORB™ B, High Surface Area Hydrated Lime, and PromiSORB™ A have demonstrated improved performance over regular hydrated lime in $SO_2$ capture and calcium utilization.

6. Gas Reburning, Sorbent Injection, and Gas Reburning-Sorbent Injection are ready for commercial applications.

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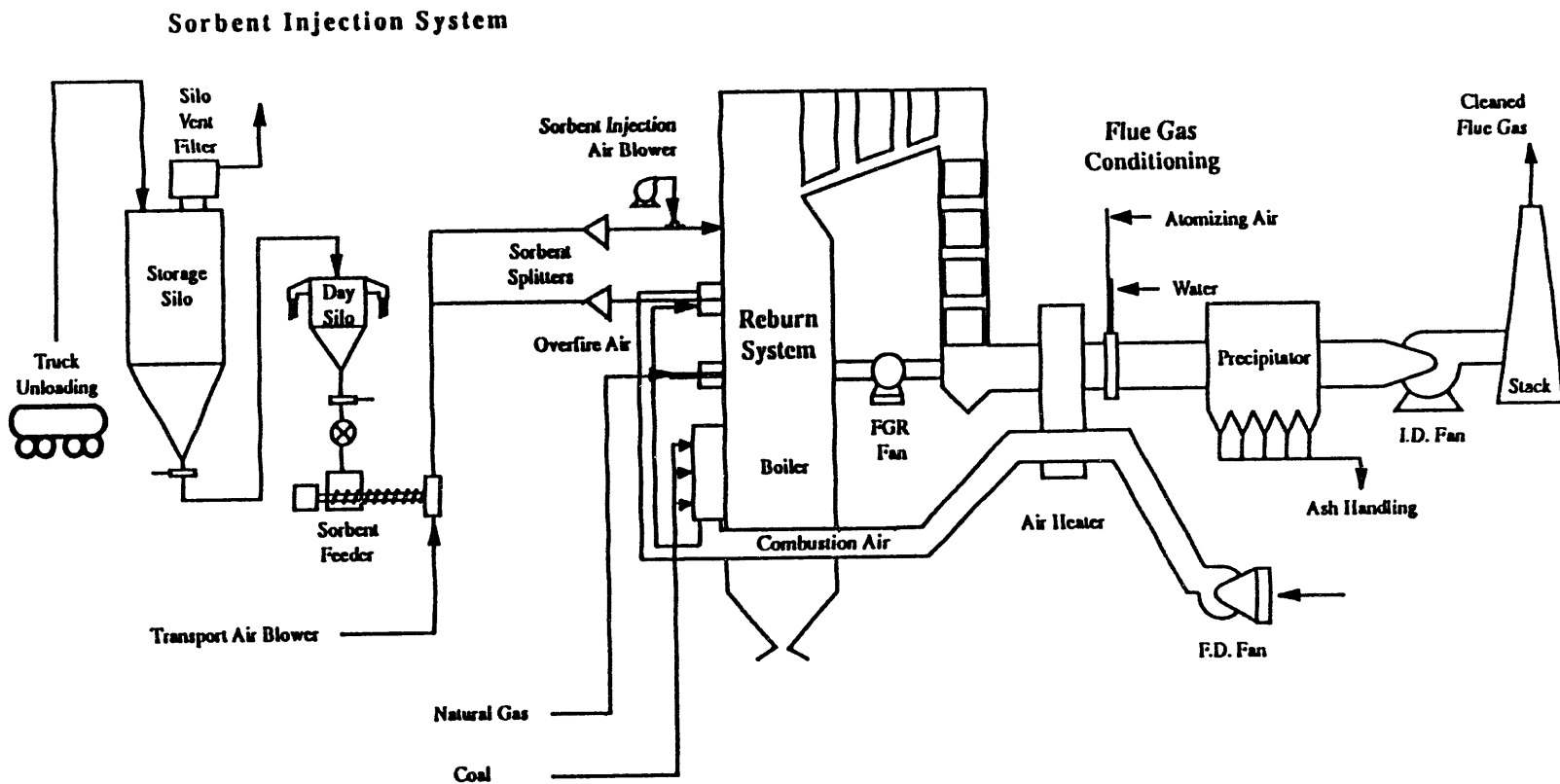
**Sorbent Injection System**



Figure 1. Overview of the GR-SI and humidification systems at Hennepin.

**SORBENT**

- EL 553' - 0"
- Six 3" Injectors
  - 4 on Front Wall
  - 2 on Side Walls
- Transport Air is 3% of Total Combustion Air

**OVERFIRE AIR**

- EL 530' - 9"
- Four 15" x 30" Ports
  - 575°F
  - Adjustable Vanes

**REBURNING FUEL**

- EL 520' - 6"
- Four Injector Assemblies
  - Tangential/Tilting
  - Each Has 4 Nozzles on 11" Centers
  - NG + FGR
- FGR is 3% of Total Flue Gas Flow

Existing Coal Burners
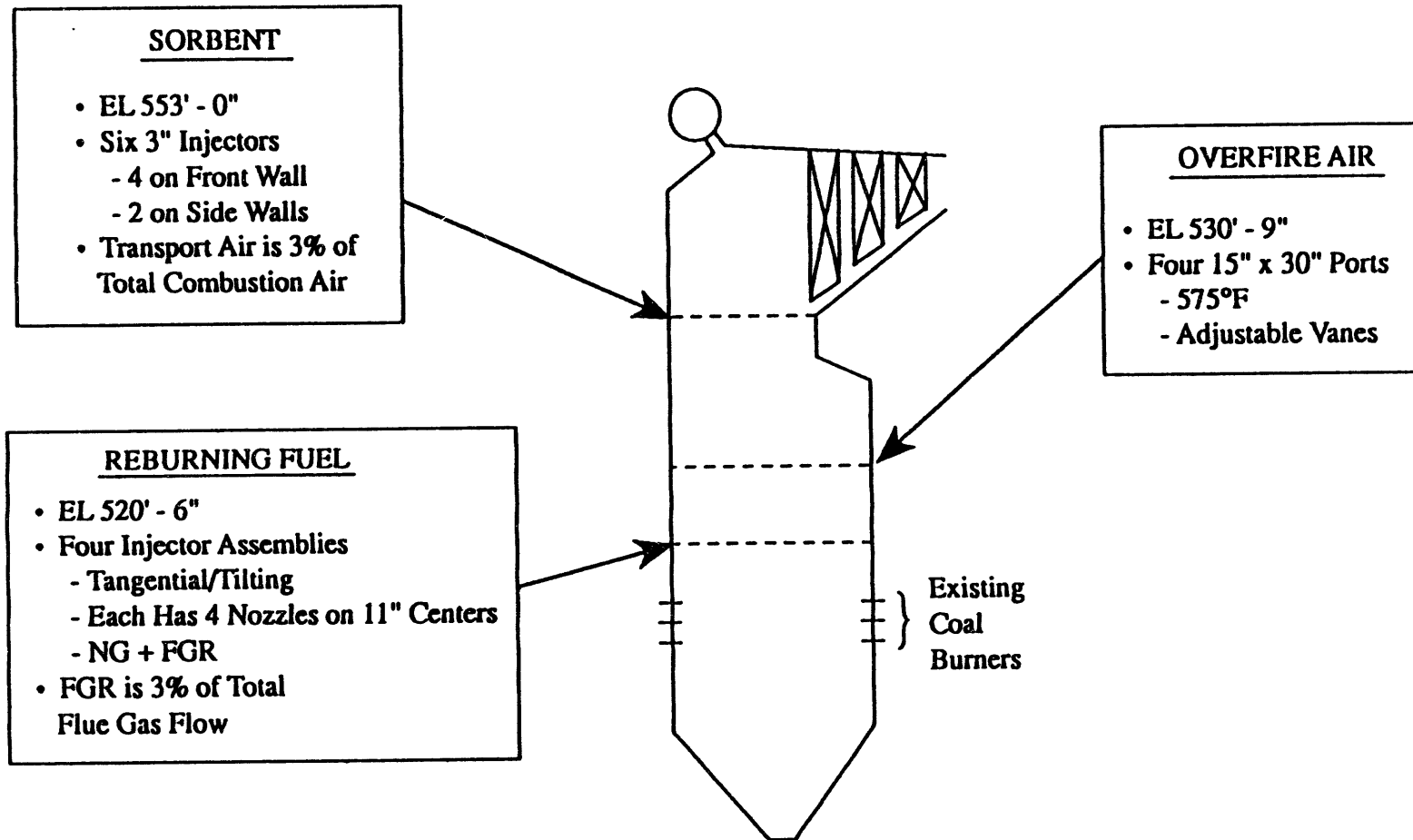
Figure 2. GR-SI injector specification for Hennepin Unit 1.

| | 1990 | | | 1991 | | | | | | | | | | | | 1992 | | | | | | | | | | | | 1993 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | O | N | D | J | F | M | A | M | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S | O |
| Start–Up and Performance Verification | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| QA/QC Tests | | | | | | | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Gas Reburning Parametric Tests | | | | | | | | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sorbent Injection Parametric Tests | | | | | | | | | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| GR–SI Optimization Tests | | | | | | | | | ■ | | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | |
| Gas Cofiring Tests | | | | | | | | | | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Boiler Outage | | | | | | | | | | | ■ | | | | | | | | | | | | | | | | ■ | | | | | | | | | | |
| Long Term GR–SI Demonstration Tests | | | | | | | | | ■ | | ■ | ■ | ■ | ■ | | | | | | ■ | ■ | ■ | | | | | | | | | | | | | | | |
| Alternate Sorbents | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | | | | | | | | | | |
| Test Report | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
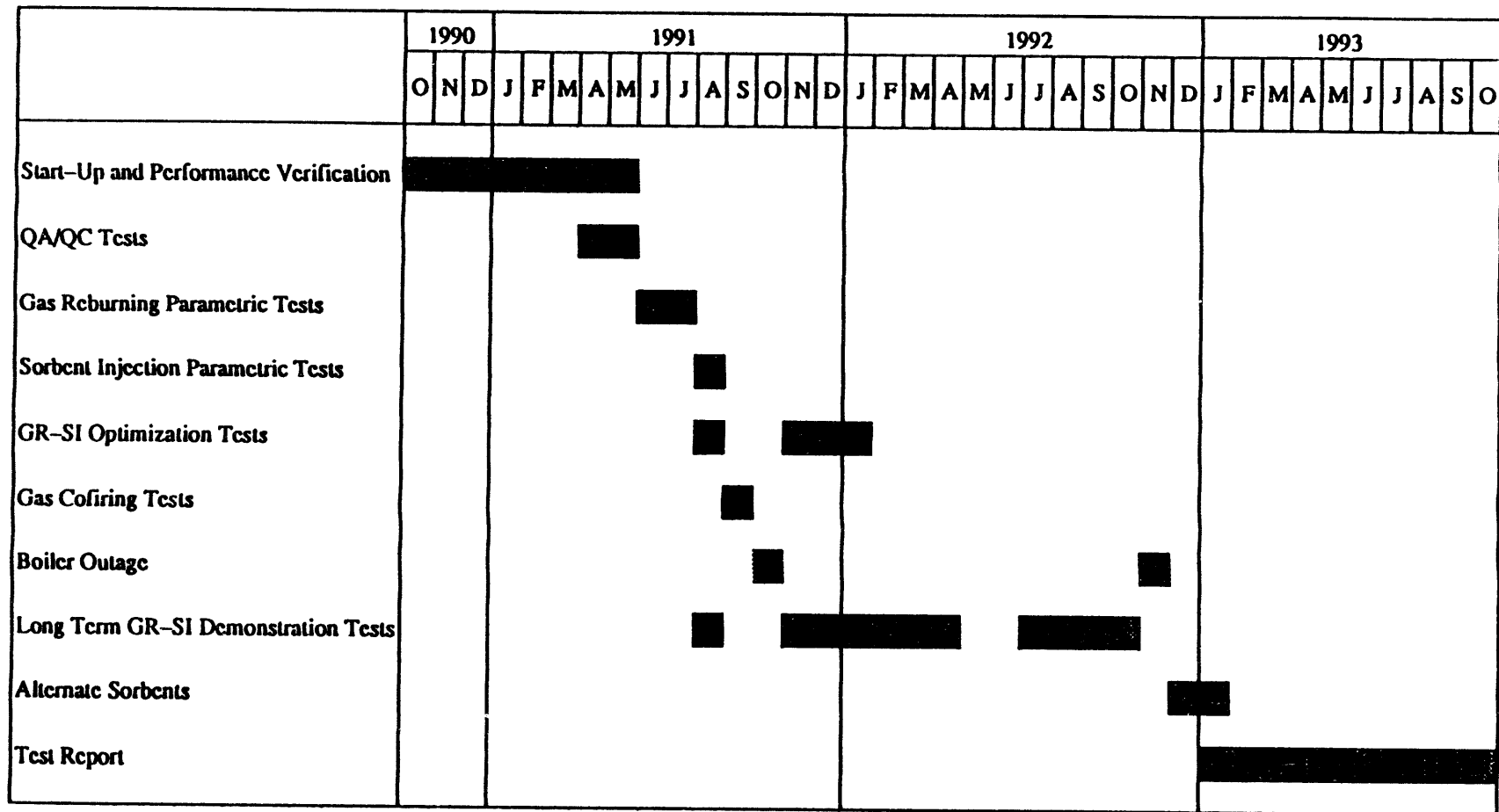
Figure 3. Test schedule for the GR–SI evaluation at Hennepin Unit 1.

**UPPER FURNACE**
- TEMPERATURE
- VELOCITY
- FOULING

**BOILER PERFORMANCE BPMS**

**BOILER EXIT**
- CEMS
- CARBON IN ASH
- Ca/S STRATIFICATION

**ESP OUTLET**
- (CEMS)
- $N_2O$
- OPACITY
- PARTICULATE SIZE DISTRIBUTION AND LOADING
- SO3
- FLY ASH RESISTIVITY

SORBENT + AIR

**REBURNING ZONE**
- CO & H2S
- HEAT FLUX
- TEMPERATURES & VELOCITY
- FOULING/SLAGGING
- FLAME OBSERVATION

OFA

NG + FGR

COAL + AIR

ESP

FLUE GAS

ASH

ASH

**BOILER & ESP OPERATING DATA**
- BURNER AIR REGISTER SETTINGS
- COAL ANALYSIS
- GR-SI OPERATING DATA
- ESP OPERATING VOLTAGE AND CURRENT

**ESP INLET**
- PARTICULATE SIZE DISTRIBUTION AND LOADING
- SO3
- FLY ASH RESISTIVITY

Figure 4  Measurement overview.

**Average NOx Reduction 67.3%; Average NOx 0.245 lb/MMBtu**
**Average SO2 Reduction 52.6%; Average SO2 2.51 lb/MMBtu**
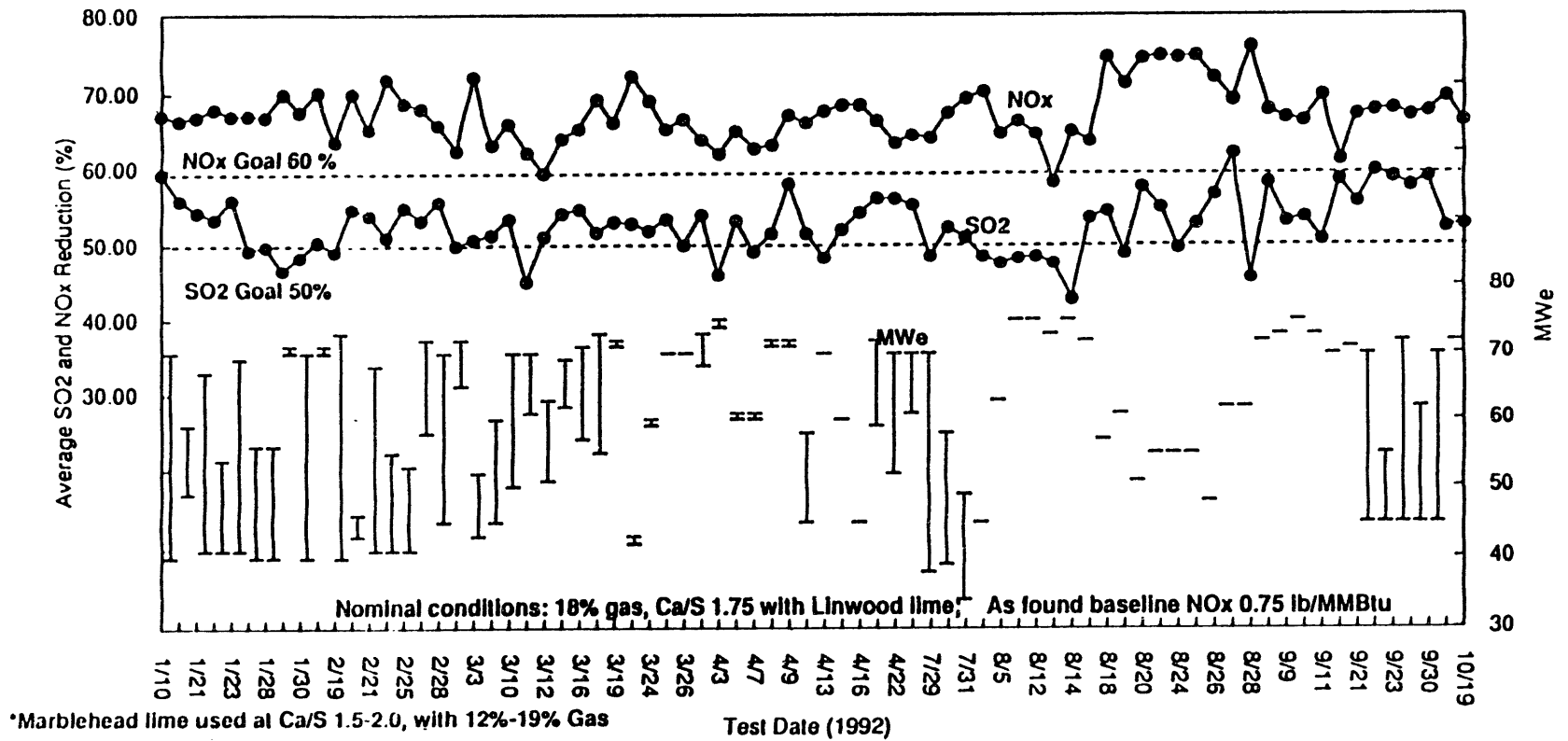


Figure 5. Emissions of $NO_x$ and $SO_2$ from long-term GR-SI testing.

Figure 6. Air heater outlet and humidification duct arrangement.
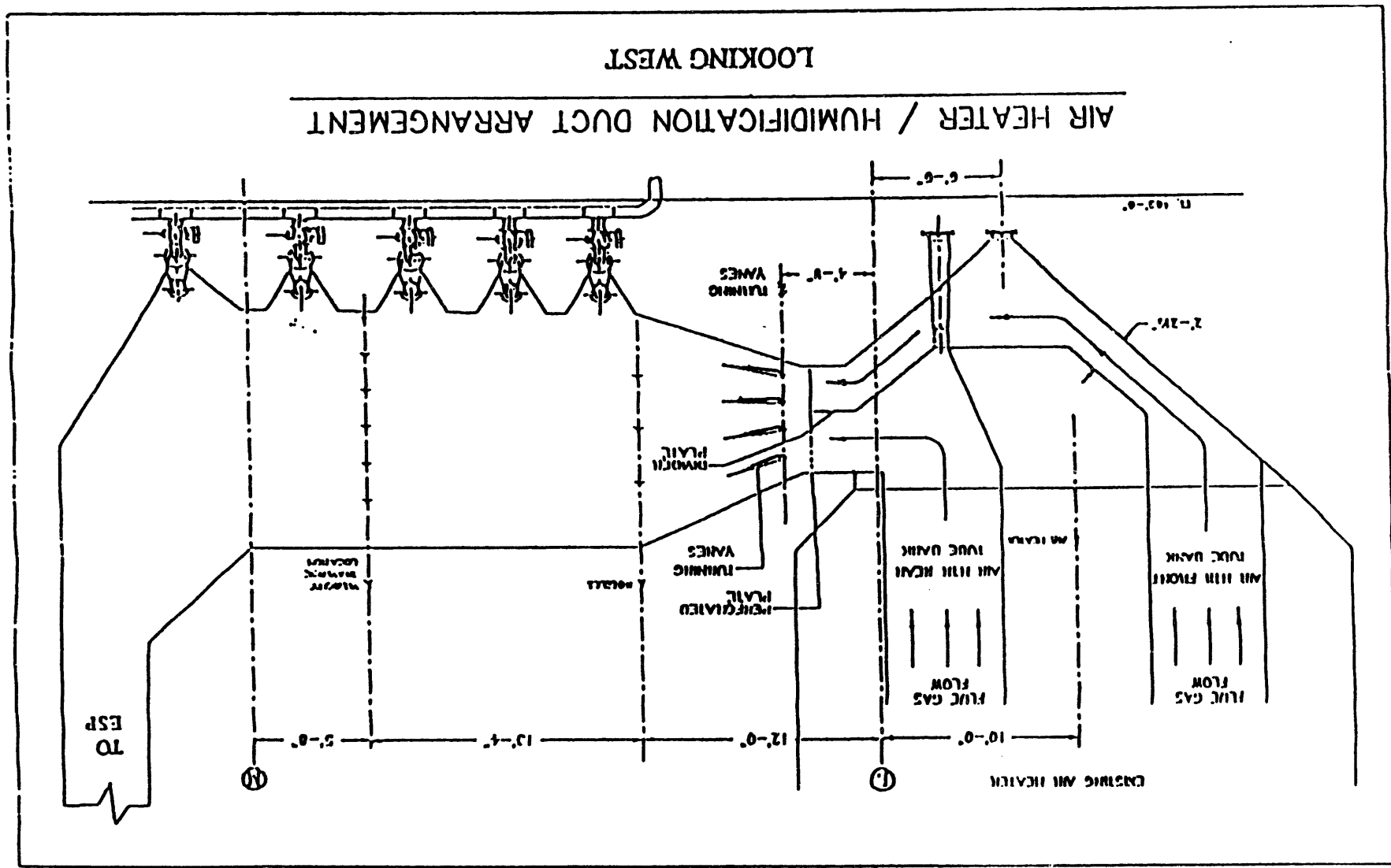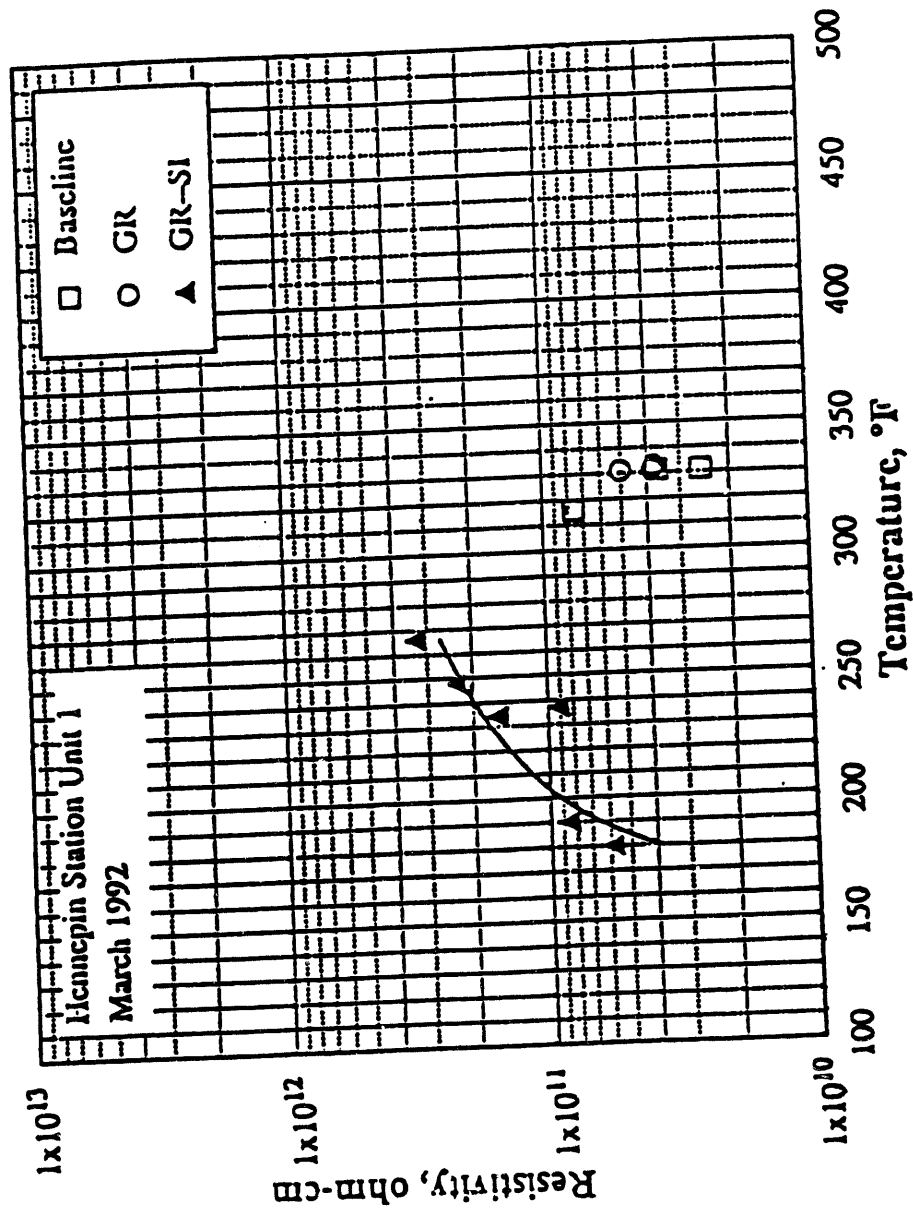
Figure 7. In-situ resistivity measurements by the V-I method at 70 MWe.

Economizer Inlet Gas
Temperature, °F

Econ In ———— ASME

Load : 70 MWe
GR on : 9:25 19 October 1992
SI on : 9:36 19 October 1992
SI off : 17:43 20 October 1992
GR off : 18:20 20 October 1992

ASME Heat Loss
Efficiency, %

Time
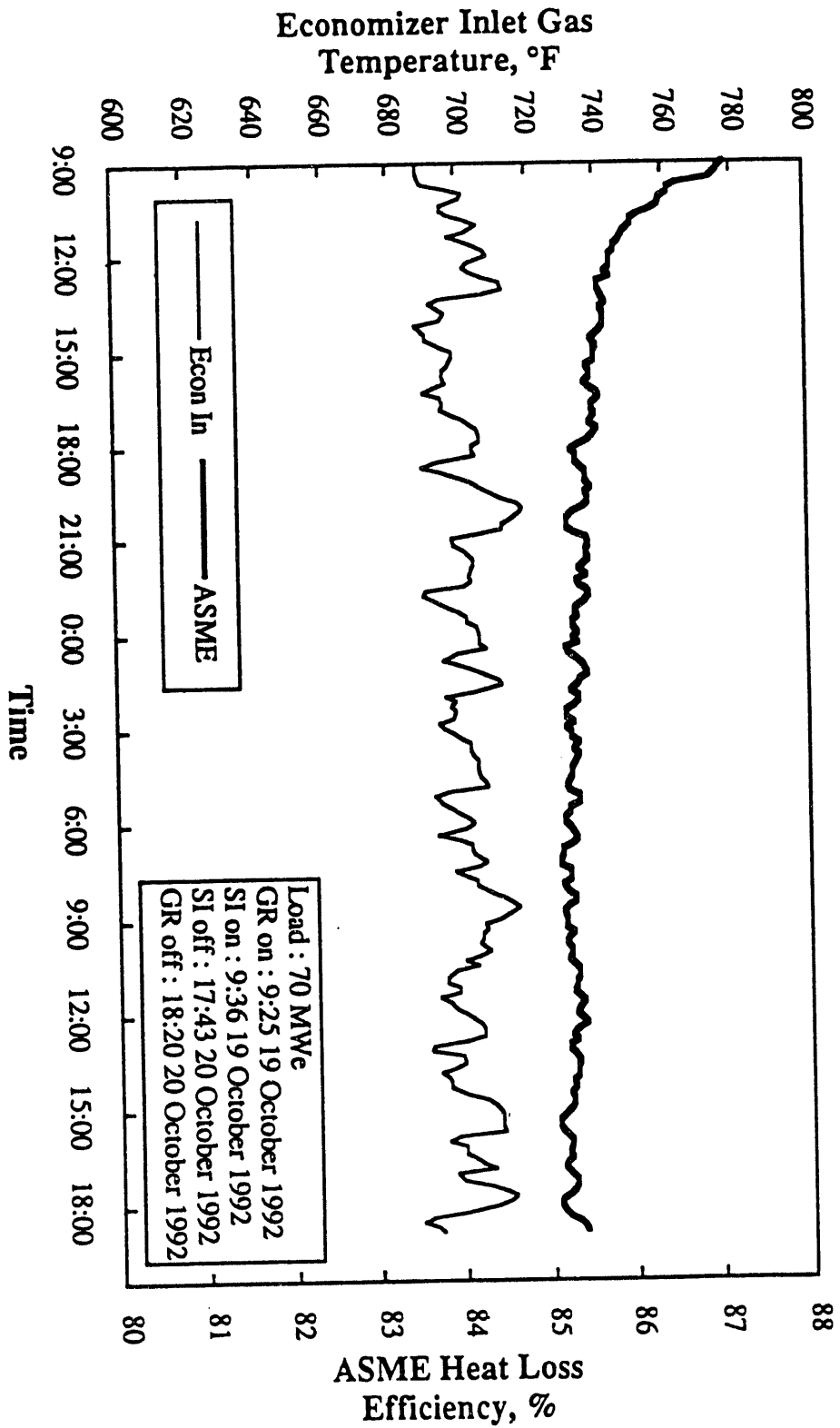
Figure 8.  Economizer inlet gas temperature and boiler efficiency during 32 hour GR–SI test run.
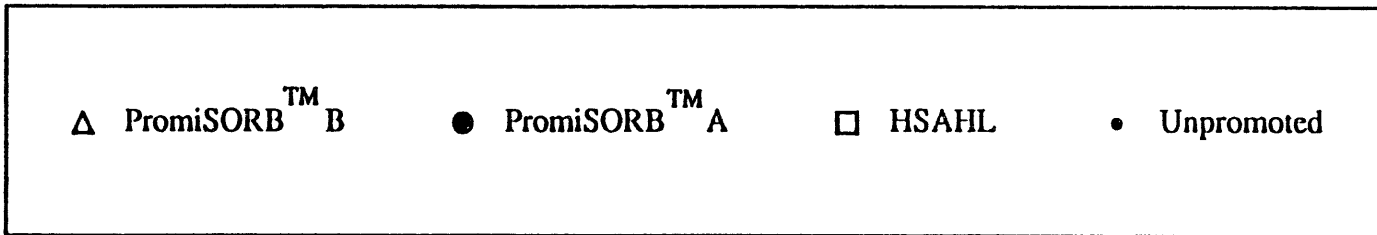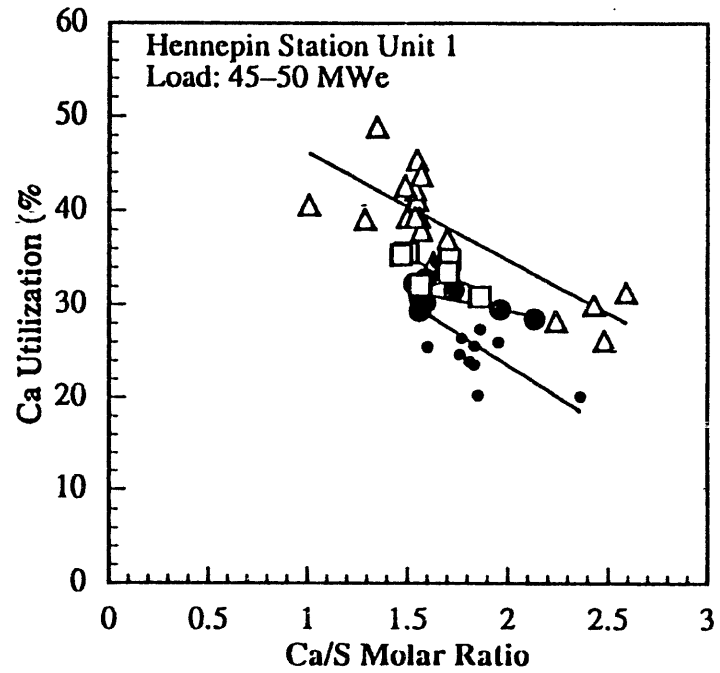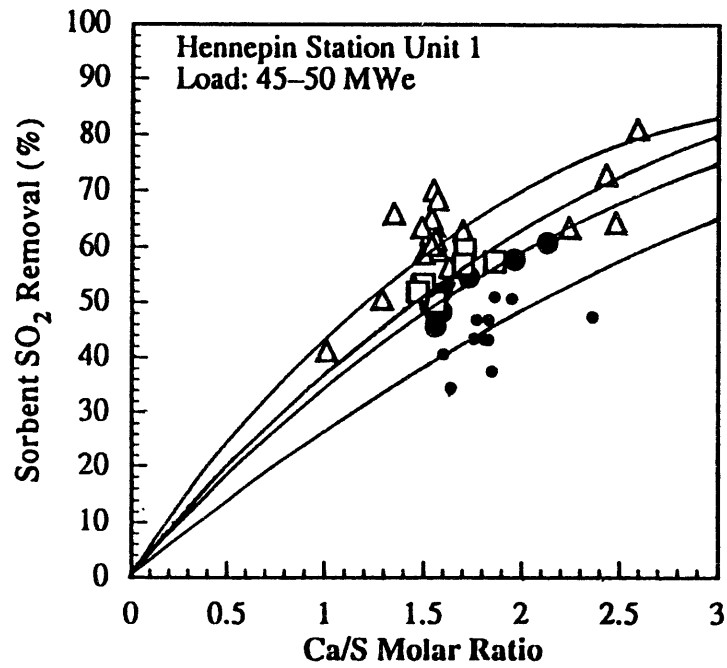
Figures 9 and 10. $SO_2$ removal and calcium utilization with promoted sorbents vs. standard hydrated lime.

## TABLE 1. SUMMARY OF GR–SI LONG–TERM THERMAL PERFORMANCE

| Thermal Parameters | 45 MWe | 60 MWe | 70 MWe | Predicted* |
|---|---|---|---|---|
| **Process Variables** | | | | |
| Percent Gas Heat Input | 19 | 18 | 17 | 18 |
| Ca/S Molar Ratio | 1.79 | 1.79 | 1.80 | 2.00 |
| Exit Plant O2 (%) | 3.40 | 3.06 | 2.84 | 2.80 |
| **Steam Side Temperatures (°F/°C)** | | | | |
| Exit Secondary Superheater | 980/527 | 989/532 | 994/534 | 1,005/541 |
| Exit Primary Superheater | 827/442 | 861/461 | 883/473 | 868/464 |
| Exit High Temp Reheater | 930/499 | 964/518 | 987/531 | 1,005/541 |
| SH Steam Attemperation (lb/hr) | 3,863 | 9,215 | 12,783 | 16,500 |
| (kg/hr) | 1,752 | 4,180 | 5,798 | 7,484 |
| **Heat Transfer (10⁶ Btu/hr) (GJ/hr)** | | | | |
| Furnace Waterwalls | 215/227 | 293/309 | 344/363 | 349/368 |
| Secondary Superheater | 37/39 | 47/50 | 54/57 | 61/64 |
| Reheater | 43/45 | 57/60 | 67/71 | 74/78 |
| Primary Superheater | 72/76 | 107/113 | 129/136 | 133/140 |
| Economizer | 16/17 | 20/21 | 23/24 | 29/31 |
| **Cleanliness Factors** | | | | |
| Furnace | 1.083 | 1.058 | 1.042 | N.D.# |
| Secondary Superheater | 0.903 | 0.911 | 0.916 | N.D. |
| Reheater | 0.921 | 0.954 | 0.977 | N.D. |
| Primary Superheater | 1.023 | 1.069 | 1.100 | N.D. |
| Economizer | 0.930 | 1.006 | 1.057 | N.D. |
| Sootblowers On (% of time) | 19% | 27% | 31% | N.D. |
| Econ. Inlet Gas Temp (°F/°C) | 668/353 | 697/369 | 716/380 | N.D. |
| **Heat Loss (percent)** | | | | |
| Dry Gas | 6.19 | 6.16 | 6.14 | 5.26 |
| Moisture from Fuel | 1.44 | 1.45 | 1.46 | 1.20 |
| Moisture from Combustion | 5.21 | 5.17 | 5.14 | 5.35 |
| Combustibles in Refuse | 0.30 | 0.37 | 0.42 | 0.54 |
| Radiation | 0.39 | 0.36 | 0.34 | 0.33 |
| Unmeasured | 1.50 | 1.50 | 1.50 | 1.50 |
| ASME Heat Loss Efficiency (%) | 84.98 | 84.99 | 85.00 | 85.82 |
| Net Heat Rate (Btu/kWh) | 10,658 | 10,571 | 10,512 | 10,338 |
| (kJ/kWh) | 11,244 | 11,152 | 11,090 | 10,907 |

# N.D. - Not determined
* 75 MWe

# SOx-NOx-Rox Box™ DEMONSTRATION PROJECT REVIEW

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## ABSTRACT

The SOx-NOx-Rox Box™ (SNRB™) process is a combined $SO_x$, $NO_x$ and particulate (Rox) emission control technology developed by Babcock & Wilcox in which high removal efficiencies for all three pollutants are achieved in a high-temperature baghouse. A 5-MWe equivalent demonstration of the technology cosponsored by the U.S. Department of Energy, the Ohio Department of Development/Ohio Coal Development Office and the Electric Power Research Institute has recently been completed at the Ohio Edison R.E. Burger Plant.

SNRB incorporates dry sorbent injection for $SO_x$ emission control, selective catalytic reduction (SCR) for reducing $NO_x$ emissions, and a pulse-jet baghouse operating at 450 to 850 °F for controlling particulate emissions. The unique, high-temperature baghouse/catalyst configuration provides for integrated particulate capture, $SO_2$ removal, and $NO_x$ reduction as well as the potential for reducing emissions of selected air toxics. The simultaneous, multiple emission control performance of SNRB is summarized using operating data generated in over 2,000 hours of operation at the demonstration site.

## INTRODUCTION

The SNRB™ emission control process is a combination of three technologies:

- Dry sorbent injection for $SO_2$ removal
- Selective Catalytic Reduction (SCR) for $NO_x$ reduction
- High-temperature fabric filtration for particulate control

These technologies are combined as illustrated in Figure 1. The process is a post-combustion emission control technology which would be integrated into a power plant or industrial process between the combustion zone and the downstream heat recovery equipment.

The SNRB™ process includes several innovative characteristics which provide for a unique, high efficiency combined emissions control process. Operation of a pulse-jet baghouse at high temperatures requires that the filter bags be made of a fabric which can withstand exposure to flue gas at 800 to 900 °F while maintaining high particulate collection efficiency and flexibility. Integration of the SCR catalyst to minimize unreacted ammonia emissions and permit bag cleaning using conventional pulse-jet technology required development of a circular monolith catalyst. The unique features of the process provide several distinct advantages in comparison with competing emissions control technologies. These general advantages include:

- Multiple emissions control in a single component
- Low plan area space requirements
- Operating simplicity
- Flexibility for optimal overall control economics
- Enhanced SCR operating conditions
- Improved $SO_2$ sorbent utilization
- Dry materials handling

In certain applications, the initial SNRB™ system capital costs are lower than a combination of conventional systems for comparable emissions control.

## Figure 1 - SNRB™ Process Schematic



Figure 1 - SNRB™ Process Schematic

Labels in figure:
- HIGH TEMPERATURE CERAMIC BAG
- CLEAN FLUE GAS
- ALKALI-RICH ASH
- CATALYST
- ALKALI INJECTION
- AMMONIA INJECTION
- INLET FLUE GAS
  - NO$_x$
  - SO$_x$
  - PARTICULATES
- ASH

Development of the SNRB™ process at Babcock & Wilcox began with pilot testing of high-temperature dry sorbent injection for SO$_2$ removal in the 1960's. Integration of NO$_x$ reduction was evaluated in the 1970's. Pilot work in the 1980's focused on evaluation of various NO$_x$ reduction catalysts, SO$_2$ sorbents and integration of the catalyst with the baghouse. This early development work led to the issuance of two US Process patents to Babcock & Wilcox - # 4,309,386 and # 4,793,981. An additional patent application for improvements to the process is pending. The Ohio Coal Development Office (OCDO) has been instrumental in working with B&W to develop the process to the point where a larger scale demonstration of the technology was feasible.

## Figure 1 - SNRB™ Process Schematic



Development of the SNRB™ process at Babcock & Wilcox began with pilot testing of high-temperature dry sorbent injection for $SO_2$ removal in the 1960's. Integration of $NO_x$ reduction was evaluated in the 1970's. Pilot work in the 1980's focused on evaluation of various $NO_x$ reduction catalysts, $SO_2$ sorbents and integration of the catalyst with the baghouse. This early development work led to the issuance of two US Process patents to Babcock & Wilcox - # 4,309,386 and # 4,793,981. An additional patent application for improvements to the process is pending. The Ohio Coal Development Office (OCDO) has been instrumental in working with B&W to develop the process to the point where a larger scale demonstration of the technology was feasible.

## SNRB™ FLUE GAS CLEAN-UP DEMONSTRATION PROJECT

The Clean Coal Technology Program demonstration is a key component in the SNRB™ technology commercialization effort. The demonstration provided for optimization of the catalyst integration arrangement, evaluation of operating conditions for maximizing simultaneous emissions control, investigation of alternative bag fabrics and evaluation of $SO_2$ sorbents for enhancing $SO_2$ removal. The project also permitted an assessment of the bag and catalyst suppliers ability to produce these key components to commercial specifications.

The SNRB™ Flue Gas Clean-Up Demonstration Project was selected for funding in the second round of the Clean Coal Technology Program. The $13.3 million project was co-sponsored by the US Department of Energy, the Ohio Coal Development Office, Babcock & Wilcox, the Electric Power Research Institute and Ohio Edison. In-kind contributions were provided by 3M, Norton Chemical Process Products and Owens-Corning Fiberglas. DOE provided 45.8% of the total project funding. The Cooperative Agreement with DOE was signed in December, 1989 and completion of the project is scheduled for December, 1993.

The project scope was comprised of four primary test programs:

- Base demonstration project
- Filter fabric assessment
- Alternative bag demonstration
- Air toxics emissions testing

The overall project objectives included demonstration of greater than 70% $SO_2$ removal and 90% or higher reduction of $NO_x$ emissions while maintaining particulate emissions below 0.03 lb/$10^6$ Btu. A 5-MWe slipstream demonstration of the technology was the focus of the project. The demonstration incorporated commercial scale bag/catalyst assemblies.

## Base demonstration project

The base SNRB™ project focused on the engineering, design and construction of a facility for evaluation of the emission control performance and operability of key components of the technology. The SNRB™ demonstration facility was constructed at the R.E. Burger Plant of Ohio Edison. The plant is located on the Ohio River south of Shadyside, Ohio.

Detailed design activity included pilot testing to finalize details of the filter bag and catalyst configurations and to screen operating conditions for the larger facility. Both pellet and honeycomb or monolith catalysts were evaluated in the design stage. The need for a cylindrical monolith catalyst to minimize the potential for emission

of unreacted ammonia was identified and provisions were made by Norton Chemical Process Products to extrude cylindrical catalyst sections for the demonstration.

Construction of the facility was completed in November, 1992. A five month start-up and shakedown period followed. The test program was initiated in May, 1992 and completed in April, 1993.


## Filter fabric assessment program

A pilot baghouse was installed at a coal-fired utility to provide extended exposure testing for high-temperature filter bag fabrics. Three alternative fabrics were evaluated in a 1,300 ACFM slipstream pilot installed on Boiler #7 of the City of Colorado Springs Utilities Martin Drake Plant [1]. The baghouse was operated at 600 to 720 °F for a total of 3,700 hours over a 12 month period. Each bag experienced approximately 11,200 cleaning pulses.

Filter bags made of Nextel ceramic fibers, S2-Glass fiberglass fibers and Silontex were evaluated. The Nextel and S2-Glass fabrics demonstrated acceptable cleaning and strength characteristics. The Nextel bags were selected as the base filter bag for the 5 MWe demonstration.


## Alternative bag demonstration

To continue evaluation of the S2-Glass filter bags, which are potentially a lower cost alternative to the Nextel bags, one module of the SNRB™ demonstration baghouse was equipped with these fiberglass bags. The bags were exposed to integrated SNRB™ operating conditions for a total of 1,490 hours. The S2-Glass filter bags held up well at operating temperatures of 800 to 900 °F through numerous start-ups and exposure to uncontrolled $SO_2$ and HCl emissions.


## Air toxics emissions testing

A comprehensive air toxics emissions characterization test program was performed in which emissions at the inlet and outlet of the SNRB™ baghouse were compared to emissions from the host boiler and the Burger plant ESP. A detailed discussion of the test program has been provided by Czuczwa [2]. Emissions of targeted air toxics were measured over a six day period in April and May, 1993. The emissions monitored included trace metals, VOCs, semi-volatile organics, aldehydes, halides and radionuclide species. The test results have not yet been released for publication by the sponsors.

# R.E. BURGER PLANT DEMONSTRATION

The components of the 5-MWe SNRB™ demonstration facility are summarized in Table 1. Key design characteristics of the major components are summarized in Table 2.

## Table 1 - SNRB™ Demonstration Facility

- Six compartment pulse-jet baghouse
- Commercial scale bag/catalyst assemblies
- Independent injection/baghouse operation temperature control
- Pneumatic materials handling
- Dry sorbent storage and injection
- Anhydrous ammonia storage and injection

## Table 2 - Design Specifications of Key Components

**Pulse-jet baghouse**

| | |
|---|---|
| Flue gas flow | 30,000 ACFM @ 800 °F |
| Air-to-cloth ratio | 4:1 |
| Operating temperature | 450-900 °F |
| Filter bags | 20'long x 6" diameter |
| Number of filter bags | 252 (6 x 42) |
| Bag material | |
| 3M | Nextel ceramic fibers |
| Owens Corning Fiberglas | S2-Glass fiberglass |
| Cleaning air pressure | 30-40 psig |
| Cleaning air pulse | 80-100 milliseconds |
| Catalyst | |
| Norton | NC-300 series zeolite |

**Sorbent handling**

| | |
|---|---|
| Storage | 2,350 ft³ |
| Hydrated lime | 300 to 700 lb/hr |
| Sodium bicarbonate | 300 to 1300 lb/hr |

**Ammonia injection**

| | |
|---|---|
| Storage | 1000 gallons |
| Dilution | 19:1 |
| Flow rate | 3 to 30 lb/hr |

The SNRB™ process treated a slip stream of flue gas from the Burger Plant boiler #8. The gas tie-in was between the economizer and the combustion air heater where the flue gas temperature was approximately 600 to 650 °F. This nominal 160-MWe, pulverized coal, wall fired B&W boiler has been in operation since 1955. Ohio Edison fired a blend of bituminous coals in the boiler with an average sulfur content of 3 to

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4%. At the SNRB™ process inlet, the flue gas contained 2000 to 3000 ppm $SO_2$, 350 to 500 ppm $NO_x$ and 3 to 4 grains/scf particulates.

The SNRB™ demonstration facility was operated for approximately 2,300 hours with sorbent and ammonia injection for emissions control. The facility experienced more than 25 cold start-up cycles. Despite these numerous start-ups, no degradation of the catalyst or filter bags was observed. The initial performance goals were exceeded. It is particularly worth noting that significantly higher $SO_2$ removal was obtained by optimizing the sorbent injection and baghouse operating temperatures and through the use of modified lime hydrates. In three periods of continuous operation for over 200 hours each, system availability averaged 99%.

## SNRB™ DEMONSTRATION PERFORMANCE HIGHLIGHTS

The emission control performance observed at the SNRB™ demonstration over a range of operating conditions has previously been reported in detail [1,3,4]. This discussion will focus on a brief review of key operating results.

Table 3 summarizes performance with commercial grade hydrated lime injection and operation of the baghouse at 855 °F. This data reflects the average of several tests conducted at similar operating conditions at various times throughout the demonstration program.

### Table 3 - SNRB™ Emission Control Performance

| | Emissions ($lb/10^6$ Btu) | |
| --- | --- | --- |
| | Boiler Outlet | SNRB™ Baghouse |
| $SO_2$ | 4.313 | 0.544 |
| $NO_x$ | 0.660 | 0.067 |
| Particulate | 5.660 | 0.018 |

| SNRB™ Operation | |
| --- | --- |
| Ca/S | 1.95:1 |
| $NH_3/NO_x$ | 0.84:1 |

## SO₂ Emission Control

$SO_2$ emission control at the demonstration was optimized through evaluation of the sorbent injection and baghouse operating temperatures, operation over a range of Ca/S stoichiometric ratios and investigation of alternative $SO_2$ sorbents. A. R. Holmes has discussed the effects of each of these primary factors on $SO_2$ removal in detail [3].

As shown in Figure 2, with the baghouse operating above 830 °F, outlet SO₂ emissions were reduced to less than 1.2 lb/10⁶ Btu using Ca/S ratios of 1.4 and above.

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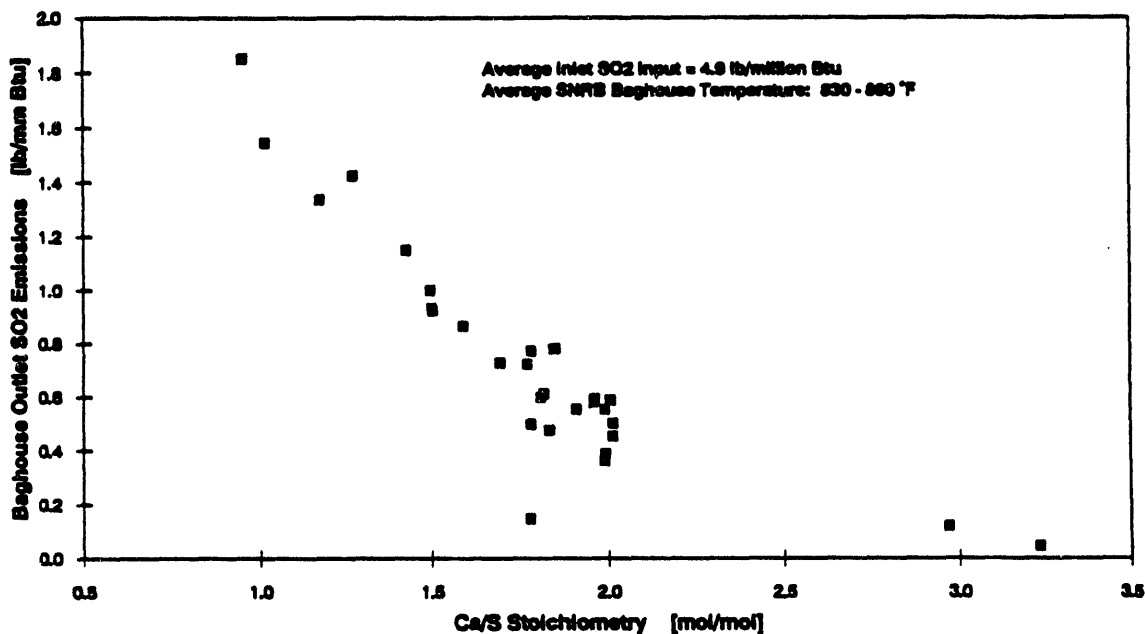Figure 2 - Effect of Ca/S Ratio on $SO_2$ Emissions



A commercial grade hydrated lime supplied by Dravo Lime Company was used for most of the operation of the SNRB™ demonstration. Approximately 225 tons of hydrated lime were used in the demonstration test program. Dravo also supplied approximately 90 tons of two alternative limes with the potential to improve $SO_2$ removal. Slight modifications were made to the operation of a commercial hydrator to produce finer mass mean diameter products through the addition of lignosulfonate or a sugar solution the hydrator [5]. At a Ca/S ratio of 2, both alternative hydrates yielded approximately an 8% improvement in performance over the base sorbent, pushing $SO_2$ removal over 90%.

The use of sodium bicarbonate, $NaHCO_3$, as the $SO_2$ sorbent provides for $SO_2$ emission control at a lower temperature. The observed performance with sodium bicarbonate injection for $SO_2$ control is summarized in Table 4. The system inlet $SO_2$ concentration ranged from 4 to 5 lb/$10^6$ Btu.

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### Table 4 - $SO_2$ Removal with Sodium Bicarbonate

|  |  | % $SO_2$ Removal | $SO_2$ Emissions lb/10⁶ Btu |
|---|---|---|---|
| Baghouse Operation @ 450 - 460 °F |  |  |  |
| $Na_2/S$ | 1.0 | 84 | 0.78 |
|  | 2.0 | 98 | 0.08 |
| Baghouse Operation @ 600 - 625 °F |  |  |  |
| $Na_2/S$ | 1.0 | 74 | 1.01 |
|  | 2.0 | 92 | 0.40 |

Sorbent grade-extra fine sodium bicarbonate was supplied by Church & Dwight for these tests. The bicarbonate was 98% less than 200 mesh with a surface area of 4.5 $m^2/gram$. A 95% $NaHCO_3$ purity was measured. In general, the use of $NaHCO_3$ results in a higher sorbent utilization than possible with hydrated lime.

The following key points characterize SNRB™ system $SO_2$ removal performance in the demonstration test program:

- Injection of the sorbent directly upstream of the baghouse at 825 to 900 °F resulted in higher overall $SO_2$ removal than injection further upstream at temperatures up to 1200 °F.

- With the baghouse operating above 830 °F, injection of a commercial hydrated lime sorbent injected at Ca/S ratios of 1.8 and above resulted in $SO_2$ removals over 80%.

- $SO_2$ removals of 85 to 90% were obtained with Ca utilizations of 40 to 45%. This is significantly higher than the 60% removal, 30% utilization typical of other dry $Ca(OH)_2$ injection processes.

- The use of $NaHCO_3$ as the $SO_2$ sorbent permitted high removal efficiencies at significantly reduced baghouse operating temperatures.

- $SO_2$ emissions were reduced to less than 1.2 lb/10⁶ Btu with a 3 to 4% sulfur coal with Ca/S ratios as low as 1.5 and $Na_2/S$ ratios less than 1.

## NO$_x$ Emission Reduction

The unpromoted, zeolite SCR catalyst installed at the demonstration was formulated for optimal performance at temperatures above 750 °F. In this temperature region, outlet $NO_x$ emissions were reduced to less than 0.05 lb/10⁶ Btu with $NH_3/NO_x$ ratios of 0.85 and above with the
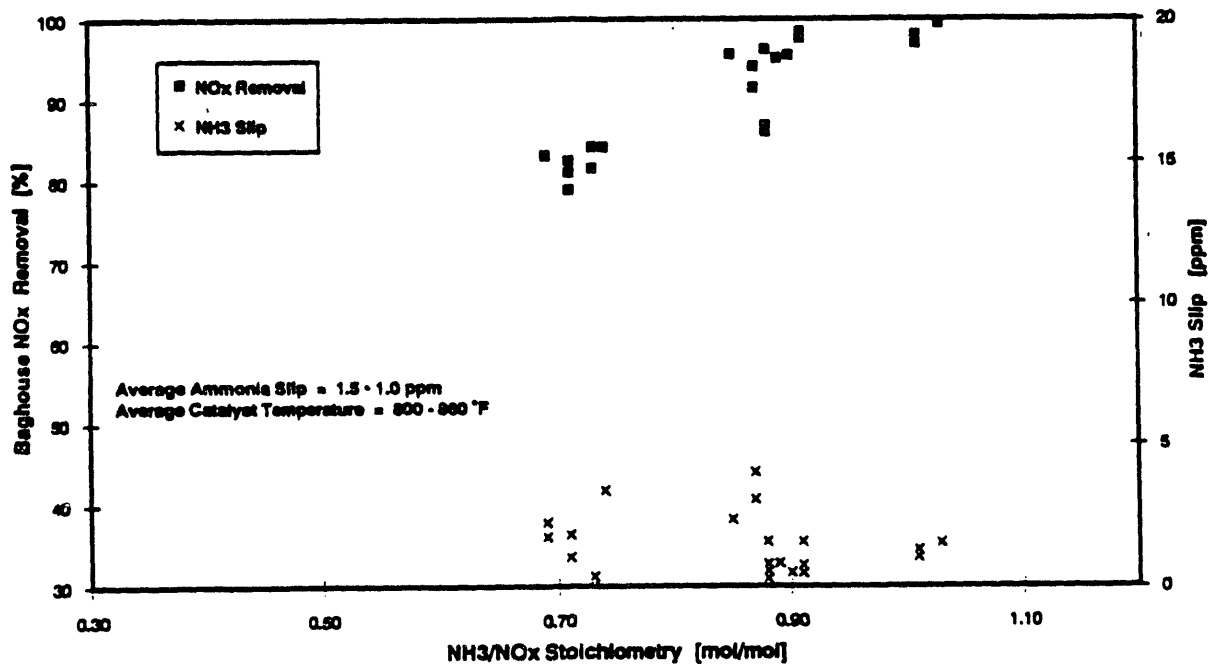
baghouse operating temperature above 800 °F. $NO_x$ emission reduction for baghouse operating temperatures of 790 to 865 °F is summarized in Table 5.

Table 5 - Average $NO_x$ Emissions at the Burger Plant Demonstration

| | $NO_x$ Emissions lb/$10^6$ Btu |
|---|---|
| SNRB™ Inlet | 0.54 to 0.72 |
| SNRB™ Outlet | |
| NH$_3$/NO$_x$ ratio | |
| 0.5 | 0.30 |
| 0.7 | 0.14 |
| 0.9 | 0.03 |

The emission of unreacted ammonia downstream of an SCR unit is a primary concern with SCR system operation. Periodic ammonia slip measurements were obtained using a modified EPA Method 5 sample train over a range of operating conditions. Figure 3 presents $NO_x$ removal and ammonia slip data obtained by a third party testing contractor.

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Figure 3 - NO$_x$ Removal and Ammonia Slip

Ammonia slip levels below 5 ppm are well within the limits typically found for commercial SCR installations. Short term operation of a continuous $NH_3$ analyzer confirmed the low ammonia slip measured with the flue gas sampling trains.

Key SNRB™ $NO_x$ reduction observations from the demonstration tests may be summarized as follows:

- 90% $NO_x$ emission reduction was readily achieved with ammonia slip limited to less than 5 ppm. This performance reduced $NO_x$ emissions to less than 0.10 lb/10⁶ Btu.

- $NO_x$ reduction was insensitive to temperature over the catalyst design temperature range of 700 to 900 °F.

- Catalyst space velocity (volumetric gas flow/catalyst volume) had a minimal effect on $NO_x$ removal over the range evaluated.

- Turndown capability for tailoring the degree of $NO_x$ reduction by varying the rate of ammonia injection was demonstrated for a range of 50 to 95% $NO_x$ reduction.

- No appreciable physical degradation or change in catalyst activity was observed over the duration of the test program.

- The degree of oxidation of $SO_2$ to $SO_3$ over the zeolite catalyst appeared to be less than 0.5%. $SO_2$ oxidation is a concern for SCR catalysts containing vanadia to promote the $NO_x$ reduction reaction.

- TCLP analysis of the catalyst after completion of the field tests confirmed that metal concentrations were well below regulatory limits and the catalyst remained non-hazardous for disposal.


Particulate Emissions

EPA Method 5 sampling downstream of the baghouse confirmed that particulate emissions were consistently below the NSPS standard of 0.03 lb/10⁶ Btu. Variations in particulate emissions could not be correlated with the hydrated lime injection rate, air-to-cloth ratio, baghouse pressure drop, bag cleaning frequency or combination of modules in service. The average of over 30 baghouse particulate emission measurements was 0.018 lb/10⁶ Btu. A detailed discussion of particulate emission control at the demonstration has been provided by Evans, et al [1].

The results of cascade impactor sampling of the baghouse inlet and outlet flue gas streams are shown in Figure 4. The comparison clearly

shows the increased fineness of the solids at the baghouse inlet when hydrated lime is injected at 270 to 420 lb/hour. The size distribution of the baghouse emissions was consistent with and without lime injection.

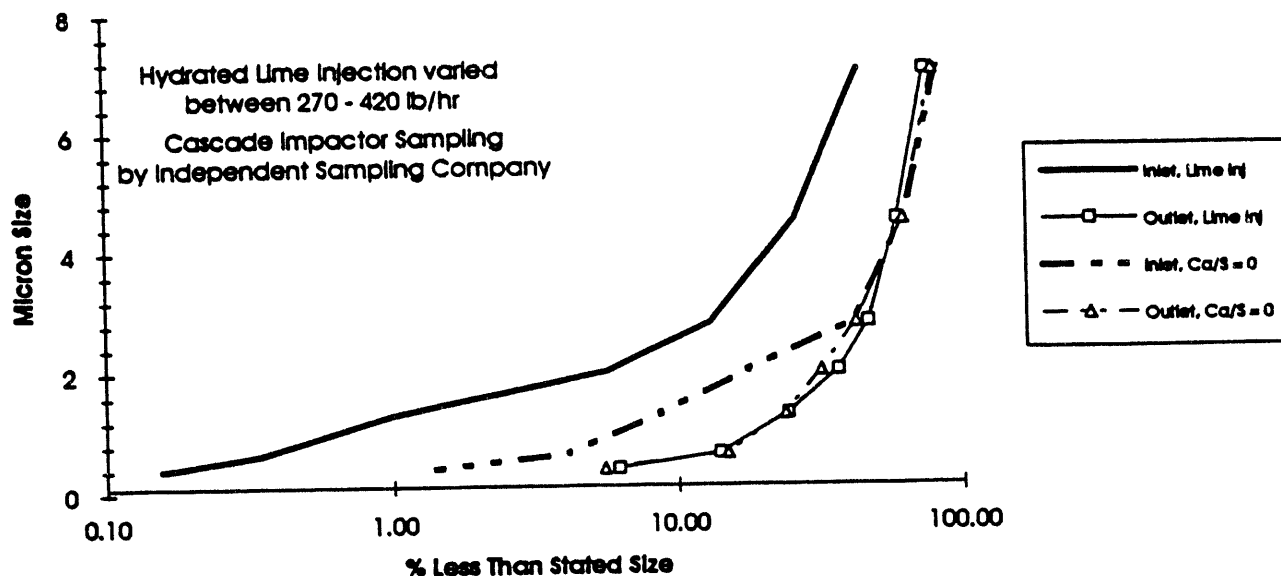Figure 4 - Average Particle Size Distributions



Additional particle size distribution measurements of the baghouse outlet emissions using cyclone collectors revealed that on average about 80% of the emissions were less than 10 microns and 40% were less than 1 micron.

A summary of key observations related to particulate collection at the SNRB™ follows.

- Hydrated lime injection increased the baghouse inlet particulate loading from an average of 5.6 to 16.5 lb/10⁶ Btu (3.2 to 9.3 grains/SCF).

- Emission testing with and without the SCR catalyst installed revealed no apparent difference in collection efficiency.

- On-line cleaning with a pulse air pressure of 30 to 40 psi was sufficient for cleaning the bag/catalyst assemblies.

- Typically, one of the five baghouse modules in service was cleaned every 30 to 150 minutes.

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## Byproduct Characterization

Operation of the demonstration generated a total of approximately 830 tons of fly ash and byproduct solids. Approximately 30 tons of this material was used for evaluation of potential applications. The remaining solids were disposed of in a solid waste landfill.

Table 6 provides a typical composition of the baghouse solids with injection of commercial hydrated lime at a Ca/S ratio of 2. The coal contained approximately 3.5% sulfur and 12% ash.

### Table 6 - SNRB™ Solids Composition

| Constituent | Weight % of Total |
|---|---|
| Fly ash | 32.8 |
| $CaCO_3$ | 23.9 |
| $CaSO_4$ | 20.5 |
| $CaSO_3$ | 15.4 |
| CaO | 7.4 |

The key characteristics of the solids collected in the SNRB™ baghouse are as follows:

- The moisture content of the baghouse product was typically below 0.5% and the product showed little affinity for picking up moisture even after outdoor storage for several months.

- Leach potential (TCLP) well below regulatory limits for solid waste disposal.

- No ammonia was detected in the baghouse solids.

- The pH of the solids ranged from 10.5 for sodium bicarbonate injection to 12.4 for hydrated lime injection.

A variety of potential uses for the solids have been investigated. Spreadability tests for soil amendment applications were performed with several types of agricultural lime spreaders. These tests indicated the low bulk density and moisture content of the material may require an intermediate pelletizing step for efficient application of the material for agricultural liming. The SNRB™ solids were found to have a pozzolanic activity index above the minimum required for fly ash to be used in concrete. The final compressive strength of the mortar using SNRB™ solids was comparable to that of the base mortar indicating the solids could be used as a partial cement replacement to lower the cost of the concrete. Further evaluations of potential applications for the byproduct solids are planned.

## Corrosion Study

A concern for application of SCR to coal fired boilers is the oxidation of $SO_2$ to $SO_3$. Subcontractor testing indicated the SNRB SCR configuration results in minimal, if any, net oxidation of $SO_2$ to $SO_3$. To some extent, the $SO_3$ content of the flue gas determines the minimum exit temperature at which the combustion air heater can be operated to minimize corrosion of the heat transfer surfaces. This minimum exit temperature influences the net thermal efficiency of the power plant.

An air-cooled deposition probe was installed downstream of the outlet flue gas cooler to expose coupons of carbon steel (A36) and Corten (A588) to a flue gas temperature range of 150 to 260 °F. The probe was exposed for approximately 300 hours of operation with $Ca(OH)_2$ injection upstream of the baghouse resulting in an average $SO_2$ emission rate of 1.13 lb/$10^6$ Btu. The concentration of $SO_3$ in the flue gas downstream of the baghouse was on the order of 5 to 10 ppm. Analysis of the corrosion rate as a function of probe temperature indicated that operation below approximately 250 °F resulted in an unacceptable level of corrosion. Additional, longer term testing is needed to further assess the impact of reduced operating temperature on heat recovery equipment performance downstream of a SNRB™ emission control system.

## PROJECTED COMMERCIAL SNRB™ ECONOMICS

A preliminary cost model has been used to evaluate the projected capital costs of a SNRB™ system for various utility boiler emission control applications. For a 250-MWe boiler fired with 3.5% sulfur coal and generating 1.2 lbs $NO_x$/$10^6$ Btu, the projected capital cost of a SNRB™ system is approximately $260/kW which includes various technology and project contingency factors. A combination of a fabric filter, SCR and a wet scrubber for achieving comparable emissions control has been estimated at $360 to $400/kw [3]. A comparison of the SNRB™ system with a combination of SCR, dry scrubbing for $SO_2$ control and a baghouse has indicated SNRB™ system capital costs are competitive with this combination for smaller units burning lower sulfur coal [6]. The capital cost of the SNRB™ system was projected to be 20% less than a SCR/dry scrubber/baghouse combination for a 100-MWe plant burning 1.5% sulfur coal. The levelized costs expressed as $/ton of $SO_2$ and $NO_x$ removed were also lower for SNRB™.

Variable operating costs are dominated by the cost of the $SO_2$ sorbent for a system designed for 85 to 90% $SO_2$ removal. Fixed operating costs primarily consist of system operating labor and projected labor and materials for the hot baghouse and ash handling systems.

## COMMERCIALIZATION

Relatively few long term Clean Air Act compliance decisions such as installing wet scrubbers have been made by utilities for Phase 1 compliance. Fuel switching provides utilities with time to evaluate the allowance trading market and consider emerging clean coal technologies such as SNRB™ as a future compliance option [7]. SNRB™ can compliment a near term fuel switching strategy for $SO_2$ emission compliance by adding the flexibility of variable sorbent injection rates to enhance existing emissions reduction and providing a greater degree of fuel supply flexibility while integrating $NO_x$ emission control and upgrading particulate emission control capability.

B&W is actively exploring potential power generation and industrial coal-fired boiler applications. Activity to date has been focused on smaller units where the cost advantages appear to be greatest. Potential applications to waste-to-energy plant emission control are also being investigated.

For smaller, low-capacity-factor units, the SNRB™ system provides quick on/off sorbent injection flexibility for short term operation with variable coal sulfur contents. The sorbent injection system represents a relatively minor component, projected to be less than 15%, of the total system capital cost. Integration of the SNRB™ system with fuel switching strategies or low $NO_x$ combustion modifications provides a high overall level of emissions reduction with reduced capital and operating costs.

Commercialization efforts will benefit from successful installations of pulse-jet fabric filters for controlling particulates and selective catalytic reduction for $NO_x$ emission control in a variety of industrial and utility applications. High-temperature filtration is gaining interest for integrated, combined cycle system designs.

In 1996, the first US pulverized coal fired utility equipped with SCR for controlling $NO_x$ emissions will begin operations [7]. The 440 MW Stanton Unit 2 is owned by the Orlando Utilities Commission. The $NO_x$ control portion of the SNRB™ system capital and operating costs should follow the costs of more conventional SCR systems which have shown a dramatic decline in recent years.

The retrofit market is influenced by several factors including local $NO_x$ emission regulations, performance of existing particulate control equipment, boiler age and planned service life and potential air toxics emission regulations.

## SUMMARY

The SNRB™ system provides for high efficiency control of the primary emissions from coal-fired boilers. The system is capable of exceeding the $SO_2$ emission control performance of existing dry sorbent injection technologies. $NO_x$ emission reduction comparable to commercial, conventional SCR systems has been demonstrated. In fact, emissions control at the SNRB™ demonstration exceeded the initial project goals. Additional work scope funded by the project cosponsors addressed several key questions for commercialization of the technology such as expected filter bag life and air toxics control potential. Commercial-scale components used in the demonstration performed well and the component manufacturers demonstrated the ability to produce the components to commercial specifications. In all of the extended periods of continuous operation, the process achieved a high level of reliability and the operability of the subsystems was clearly demonstrated.

B&W is pursuing commercial application of the technology, using the successful 5-MWe demonstration as proof of the technical feasibility of the process and evaluating the unique requirements of specific new and retrofit applications as opportunities are identified.

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# PERFORMANCE RESULTS FROM THE 35 MW SNOX DEMONSTRATION AT OHIO EDISON'S NILES STATION

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## ABSTRACT

The SNOX Process is a highly efficient catalytic process that removes $SO_2$ and $NO_x$ from flue gas and generates salable sulfuric acid. The integrated design of the process enables high removal efficiencies, no waste production, and increased thermal efficiency of the boiler. As part of the Clean Coal Technology Program, this process is being demonstrated under joint sponsorship from the U.S. Department of Energy, Ohio Coal Development Office, ABB Environmental Systems, Snamprogetti, and Ohio Edison.

The project objective is to demonstrate the $SO_2$ and $NO_x$ reduction efficiencies of the SNOX process on a U.S. electric power plant firing high-sulfur Ohio coal. This 35-MWe demonstration is being conducted by retrofitting a 108-MWe existing power plant -- Ohio Edison Niles Station boiler No. 2 -- in Trumbull County, Ohio.

Initial performance results indicate efficiencies in excess of the goals of 90% $NO_x$ removal and 95% $SO_2$ removal. Sulfuric acid concentration has also met the design goal of >93 wt. %, and color and clarity meet expectations. Information from approximately one year of the twenty-two month test program is presented in this paper.

# INTRODUCTION

The SNOX Demonstration Project is a flue gas treatment facility designed to treat one-third of the flue gas from the 108 MWe Ohio Edison Niles Power Station Unit No.2 boiler. The process utilizes selective catalytic reduction (SCR) for $NO_x$ control and a unique sulfuric acid recovery process for $SO_2$ removal. More than 95% of the sulfur dioxide and 90% of the nitrogen oxides are expected to be removed while producing high purity sulfuric acid as the only by product. The SNOX Process was developed in Denmark by Haldor Topsøe A/S and is offered under license in North America by ABB Environmental Systems.

The Department of Energy (DOE) is funding 50% of this $31.4 million demonstration project in Niles, Ohio under the Clean Coal Technology II program. Co-sponsors of the project include the Ohio Coal Development Office, Ohio Edison Company, Asea Brown Boveri Environmental Systems (ABBES) and Snamprogetti USA Inc.

The Cooperative agreement between DOE and ABB was signed on December 20, 1989, officially initiating the start of the demonstration project. Engineering and design began on January 2, 1990, and was part of a twenty-five month design/construction period. Site construction activities began in the fall of 1990. Initial operation started in March 1992 and testing is scheduled to continue until the end of 1993.

Although this is the first application in the United States to demonstrate this process, commercial scale plants are operating successfully in Denmark and Sicily. Denmark has the largest SNOX operation which was successfully retrofitted to a 300 MW coal fired boiler in Vodskov, Denmark. The power station is owned by NEFO, the North Jutland Electricity Supply Company, and burns a blend of 2.8% sulfur coal, part of which is imported from Ohio. The NEFO plant started operations in October 1991 and is currently operating at full load with impressive removal efficiencies of 95% for $SO_2$ and $NO_x$. The 30,000 tors of commercial grade acid produced per year from the NEFO SNOX plant are sold to the fertilizer industry.

A primary objective of the Niles demonstration project is to determine the competitiveness of

this process from both capital and operating cost bases as compared with other technologies employed in the United States.

## SNOX PROCESS DESCRIPTION

The SNOX technology consists of five (5) key process areas: particulate collection, nitrogen oxides ($NO_x$) reduction, sulfur dioxide ($SO_2$) oxidation, sulfuric acid ($H_2SO_4$) condensation and sulfuric acid management. Heat transfer and recovery also represent a significant part of the SNOX system. The integration of these individual steps is shown in Figure 1, which is the process flow diagram for the system installed on the Niles Unit 2 boiler.

Referring to Figure 1, a slip stream from the Unit 2 boiler is taken upstream of the existing electrostatic precipitator and heated to approximately 400°F by an in-line natural gas fired burner before entering a fabric filter for particulate collection. The flue gas is heated to simulate the inlet temperature to a SNOX system for a full size installation. After passing through a booster fan, the flue gas is heated to above 700°F through the primary side of a gas/gas heat exchanger (GGH).

An ammonia and air mixture is then added to the gas prior to the selective catalytic reactor (SCR) where nitrogen oxides are reduced to free nitrogen and water. The flue gas leaves the SCR, its temperature is raised slightly by an in-line burner, and enters the $SO_2$ Converter which oxidizes $SO_2$ to sulfur trioxide ($SO_3$). The $SO_3$ laden gas is passed through the secondary side of the GGH where it is cooled as the incoming flue gas is heated.

The processed flue gas is then passed through a falling film condenser (the WSA Condenser) where it is further cooled with ambient air to below the sulfuric acid dewpoint. Acid condenses out of the gas phase on the interior of borosilicate glass tubes and is subsequently collected, cooled and stored. The flue gas is discharged from the process at about 210°F and cooling air leaves the WSA Condenser at approximately 400°F. In a full size, integrated system the hot air is used for process support and as boiler combustion air after collecting more heat through the air preheater. For the SNOX demonstration at the Niles facility, the WSA Condenser
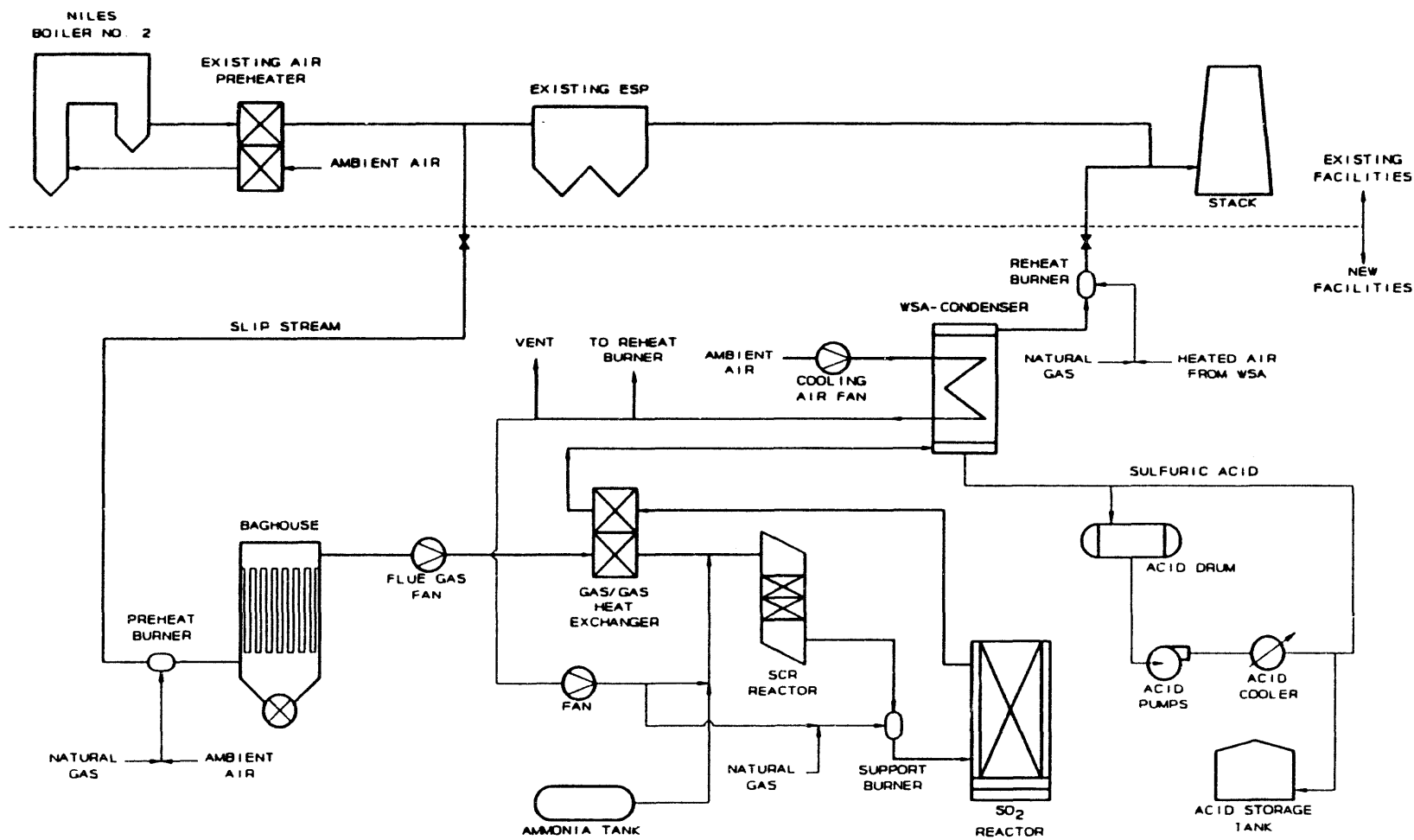
**Figure 1**
**Niles Station Process Flow Diagram**

cooling air is vented and not returned to the boiler air preheater because the entire boiler flue gas output is not being treated.

The hot, concentrated sulfuric acid product at about 400°F is collected and circulated through a thermoplastic lined system consisting of a holding tank, circulation pumps, and a water-cooled shell and tube heat exchanger. The purpose of this loop is to cool the acid to more conveniently manageable temperatures (70-100°F). Acid from the recirculation loop is then pumped to the main acid storage tank.

## TEST PROGRAM AND STATUS

In order to demonstrate and evaluate the performance of the SNOX process during the Clean Coal Technology Program, general operating data is being collected and parametric tests conducted to characterize the process and equipment. An outline of the plan is presented below along with a description of the status of the parametric testing program. The primary objectives for the SNOX Demonstration Project are as follows:

1. Demonstrate NOx and $SO_2$ removals of 90 and 95%, respectively.
2. Demonstrate the commercial quality of the product sulfuric acid.
3. Satisfy all Environmental Monitoring Plan requirements.
4. Perform a technical and economic characterization of the technology.

The following secondary objectives are identified in order to fully establish a basis for the technical and economic evaluation of a commercial application of this technology.

1. Execute parametric test batteries on all major pieces of equipment.

- Fabric Filter
- SCR System
- $SO_2$ Converter
- WSA Condenser
- Gas/Gas Heat Exchanger
- Catalyst Screening Unit

2. Quantify process consumptions.
- Power
- Natural Gas
- Catalysts
- Cooling Water

- Potable Water
- Ammonia

3. Quantify process productions.
   - Sulfuric Acid
   - Heat

4. Quantify personnel requirements.

5. Evaluate all materials of construction.

All information required to monitor the general health and environmental performance of the SNOX Plant is archived through the computerized Distributive Control System at six minute intervals into a magnetic media data base. The specific parameters include such items as temperatures, pressures, flows, gaseous concentrations, etc; and comprise 67 different data bits. Routine analyses of inputs and outputs of the process requiring manual sampling are also made and their results are fed into the Master Data Base. The following lists the parameters that are tested, the analytical methods used, and the frequency of each test.

| Stream | Parameter | Method | Frequency |
|---|---|---|---|
| Coal | $H_2O$,Ash,S,Btu/lb | Proximate | Daily |
| | C,H,N,O | Ultimate | Monthly |
| | Trace Elements (1) | (2) | Quarterly |
| | Cl,F | (2) | Quarterly |
| Product Acid | wt.% | Titration | Each Load |
| | Color | APHA Standards | Each Load |
| | Fe | (2) | Each Load |
| | Trace Elements (1) | (2) | Monthly |
| | Cl,F | (2) | Monthly |
| | $SO_2$,$NO_3$,$NH_4$ | (2) | Monthly |
| Acid Dilution Water | Trace Elements (1) | (2) | Quarterly |
| | Cl,F | ISE (3) or IC (4) | Quarterly |
| | Alkalinity | Titration | Quarterly |
| | $SO_2$,$NO_3$,$NH_4$ | (2) | Quarterly |
| Ammonia | wt.% | (2) | Quarterly |
| | Oil | (2) | Quarterly |

| | | | |
|---|---|---|---|
| Flyash | Trace Elements (1) | (2) | Quarterly |
| Catalyst Siftings | Heavy Metals | EP Toxicity | Each Occurrence |
| | Heavy Metals | TCLP | Each Occurrence |
| | Trace Elements (1) | (2) | Each Occurrence |

(1)     Trace Elements defined as As, B, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, V, Zn.
(2)     Best Available Method
(3)     Ion Specific Electrode Method
(4)     Ion Chromatography

To initiate the SNOX system parametric testing program, a group of tests were conducted on the Unit 2 boiler to characterize its gaseous and particulate emissions ahead of the existing electrostatic precipitator and also at the stack discharge. At both locations, tests have been conducted for:

- Flow, temperature, pressure;
- Particulate loading and size distribution;
- $SO_2$, $SO_3$, NO, $NO_2$, $N_2O$, $O_2$, $CO_2$, CO, $H_2O$, HCl, F, $NH_3$; and
- As, B, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, V, Zn.

Many tests for the SNOX system are designated to be conducted at three SNOX system loads - 75%, 100%, and 110% of design capacity. At this time, the following major tests have been conducted, most at all three load conditions:

- System venturi calibration;
- Fabric filter characterization (in and out) for same items as Unit 2 testing;
- Gas/gas heat exchanger pressure drop, temperature profiles, overall performance;
- SCR inlet flow and temperature distribution, $NO_x$ and $NH_3$ in and out;
- $SO_2$ converter catalyst beds temperature and flow distribution;
- WSA Condenser $SO_2$ and $SO_3$ outlet concentrations by compartment, as well as compartment flow, temperature, and $O_2$ concentration; and
- Simultaneous manual samples at the system inlet and outlet for $SO_2$ and $NO_x$.

Results from these tests as well as instrument data is currently being analyzed to assess system performance and make adjustments to system parameters and components. The cumulative SNOX plant operating time is shown in Figure 2, which in June 1992 totalled more than 5200 hours.

**Hours**
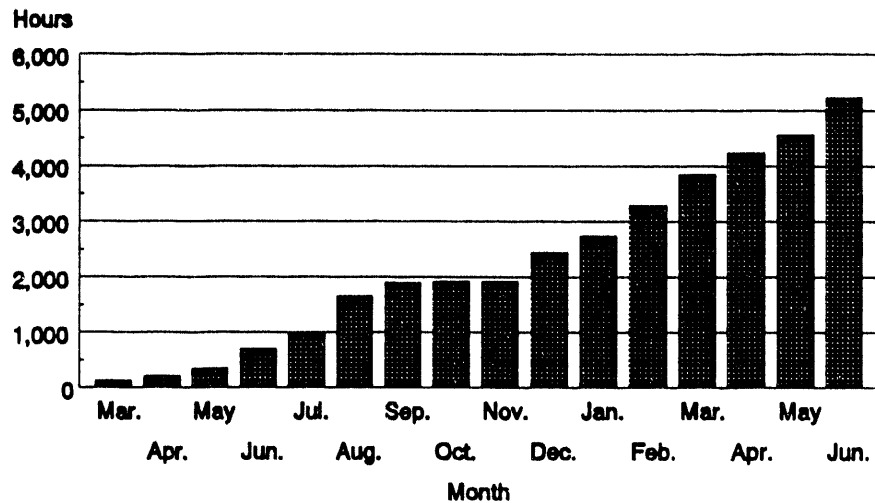


**Figure 2**
SNOX Plant Cumulative Operating Time

## SYSTEM PERFORMANCE

### Particulate Collection

The fabric filter employed at the SNOX Demonstration Plant is a six-module unit with pulsed air cleaning. Each module or compartment is approximately 13 feet x 10 feet and contains 266 bags, each 14 feet long by 6 inches in diameter. The filter bags are constructed of PTFE membrane on fiberglass backing and a total of 1596 bags are in the six compartments, resulting in a total area of 35,098 square feet. Net air to cloth ratio was designed for 4.55 acf/ft² but normally operates at about 4.4 acf/ft² at the "design" full load of the SNOX plant (78,000 scfm @ 60°F). Net air to cloth ratio is calculated based on five modules in service.

As will be described further in the $SO_2$ removal discussion, the $SO_2$ catalyst has a semi-molten surface at operating temperature and removes about 90% of the particulate which passes across it. For this reason, high efficiency particulate collection upstream of the SNOX process is an advantage in that it minimizes the frequency that this catalyst must be cleaned. Prior to operation it was estimated that the cleaning frequency with PTFE membrane bags would be

**Table 1**

| | Particulate Loadings at Baghouse Inlet and Outlet, and System Outlet | | | | | |
|---|---|---|---|---|---|---|
| Date | Baghouse Inlet | | Baghouse Outlet | | System Outlet | |
| | gr/ dscf | mg/ dNm³ | gr/ dscf | mg/ dNm³ | gr/ dscf | mg/ dNm³ |
| 7/11/92 | .7564 | 1858 | .0047 | 11.5 | | |
| 7/11/92 | .5887 | 1446 | .0133 | 32.7 | | |
| 7/13/92 | .6108 | 1500 | .0087 | 21.4 | | |
| 12/18/92 | .6885 | 1691 | .0056 | 13.7 | .0033 | 8.10 |
| 12/18/92 | .7886 | 1937 | | | | |
| 12/20/92 | .6915 | 1698 | .0034 | 8.35 | .0114 | 28.0 |
| 12/20/92 | .9824 | 2413 | | | | |
| 12/21/92 | .7166 | 1760 | .0230 | 56.5 | .0032 | 7.86 |
| 12/21/92 | .7534 | 1850 | | | | |

about one year. It was also planned to purposely increase the particulate loading to higher values in order to determine its impact on ash build-up rate in the SO₂ catalyst. While high efficiency particulate collection is an advantage, it is not a necessity with the SNOX process and higher loadings only increase the catalyst cleaning frequency.

Particulate loadings have been sampled twice at this stage of the test program. The first set of samples were taken in July of 1992 and the second set in December of 1992. Results from these tests are listed in Table 1. At inlet loadings of .59 - .98 gr/dscf the outlet loadings were very variable. While three outlet loadings were grouped between .003 and .006 gr/dscf, the other three were significantly higher and ranged from .0087 to .023 gr/dscf. These outlet loadings were much higher than anticipated for PTFE membrane bags - closer to .0004 gr/dscf was expected. At the system outlet, three samples were taken during the December 1992 test runs. Two of the values were very close, .0032 and .0033 gr/dscf, while the third appears to be an anomaly. In this sample, as well as some of the higher bag filter outlets, large particles were present on the filter causing the high values.

Prior to the unit being started in March of 1992 a "black light" test had been conducted to identify any leaks in compartments or bags. Corrections had been made at that time to eliminate any leaks before the particulate tests were conducted. The high inlet loadings indicated that the condition of the fabric filter bags needed to be examined again. In subsequent filter bag examinations it was determined that the ash layer was significantly acidic, and that the bag material had lost much of its original strength. As a result, small pinholes were forming in some of the bags. A problem also existed with high pressure drop across the bags due to an uncleanable portion of deposit. It appears that this "sticky" layer of ash was the more acidic portion and was contributing to both the high pressure drop and bag deterioration.

As to the cause of the acidic ash, it appears that start up problems related to the natural gas fired, in-line burner upstream of the fabric filter contributed to periods of acid condensation occurring on the flyash before the fabric filter or in the fabric filter. The purpose of this in-line burner is to both prevent the flue gas temperature from dropping below the acid dewpoint and to raise the flue gas to a temperature ($\approx$ 400°F) which is typical of what would occur in a full size, integrated SNOX plant when the WSA Condenser cooling air is used as combustion air to the boiler air preheater (raising the temperature of the flue gas exiting the air preheater). Given the condition of the bags, it was decided to replace all of the them during June of 1993. Although particulate loadings leaving the baghouse have been higher than anticipated for much of the first 13 months of operation, valuable data has been obtained concerning operation of the SNOX plant at loadings which are more typical of electrostatic precipitator outlets. The impact of these higher loadings will be presented in the section discussing the $SO_2$ Converter.

## NO$_x$ Reduction

Nitrogen oxides are converted to nitrogen and water vapor in the SNOX Process via selective catalytic reduction with ammonia ($NH_3$). The catalyst and SCR reactor design used for this project were supplied by Haldor Topsøe A/S, the developer of the SNOX Process. This design is a top down gas flow arrangement with three (3) catalyst bed levels, two (2) of which are initially filled and one (1) is spare. The reactor casing is constructed of A-204 high temperature steel and sized for an effective design space velocity of about 7500 h$^{-1}$.

The DNX-932 catalyst used in this design is a high activity, titanium oxide based monolithic type which operates in the temperature range of 650-800°F. This low particulate loading version of the DNX line has a hydraulic diameter of 0.122 in. and a specific area of 235 $ft^2/ft^3$.

This project incorporates a unique form of ammonia evaporation and dilution prior to its injection across the SCR inlet duct. Liquid ammonia is atomized into a slipstream of hot (≈ 400°F) discharge cooling air from the WSA Condenser. Thus, the ammonia is evaporated and diluted in one step involving a relatively low cost valve/atomizer unit. Conventional systems employ an evaporator which has higher associated capital and operating costs.

The strategic location of the SCR reactor in the SNOX Process as compared to conventional high dust SCR applications results in several benefits. First, the post fabric filter, low dust environment allows the use of high specific area catalyst and thus lower catalyst volumes. In addition, much lower catalyst erosion can be expected as well as less potential for poisoning from gaseous arsenic. Both of these aspects significantly increase catalyst lifetime. Also as a result of the low dust stream, sootblowers are not necessary.

Second, the location of the SCR reactor upstream of the $SO_2$ Converter allows operation at an ammonia surplus of 1.02 to 1.05 without the potential of downstream ammonium sulfate and ammonium bisulfate condensation which is a usual result of excess ammonia slip. All ammonia slip in the SNOX Process is oxidized in the downstream oxidation reactor. Operation with this ammonia surplus greatly reduces the catalyst volume necessary for a given $NO_x$ removal. The relative location of the two reactors has one other benefit. In conventional SCR applications, catalysts are required not to oxidize more than about one (1) percent of the inlet $SO_2$ to $SO_3$ in order not to increase the downstream sulfuric acid dewpoint significantly. This requirement often has a side effect of reduced catalyst $NO_x$ removal activity and thus higher catalyst volumes. The SNOX Process does not have this limitation since any $SO_2$ oxidation in the SCR reactor only benefits the oxidation reactor downstream. Therefore, very high activity SCR catalyst is utilized.

A series of initial tests have been run to characterize the baseline performance of the SCR

system at the Niles facility. Inlet and outlet transverses were run for $NO_x$ as well as outlet traverses for $NH_3$. The tests were executed at 100% load and at various stoichiometric ratios (SRs) of $NH_3$ to $NO_x$. A SR of 1.0 resulted in 99.7% $NO_x$ destruction across the SCR reactor. All SRs from 1.02 to 1.09 resulted in 99.9% removal. These performance results were obtained at inlet $NO_x$ concentrations of 500 - 700 ppmv. Ammonia slip through this test series ranged from zero (0) ppm for substoichiometric operation to about 70 ppm for 1.09 SR cases. The ammonia slip corresponding to the design SR of 1.02 ranged between 10 and 16 ppm. $NO_x$ removal across the entire system, based on manual samples, averaged about 94%. Data from the most recent month available, June, showing inlet and outlet $NO_x$ and removal efficiency is contained in Figures 3 and 4.

It should be noted that this test series was executed with SCR inlet temperatures below design by about 20°F. Additional test series around the SCR reactor are planned during the remainder of the project to fully characterize the effects of variations in load, inlet temperature, SR, and inlet $NO_x$ on $NO_x$ removal. Repetitious tests over the life of the project are also planned in order to document catalyst activity relative to operating time. Periodically small samples of the catalyst are removed and analyzed by the manufacturer, Haldor Topsøe, to further quantify variations in activity.
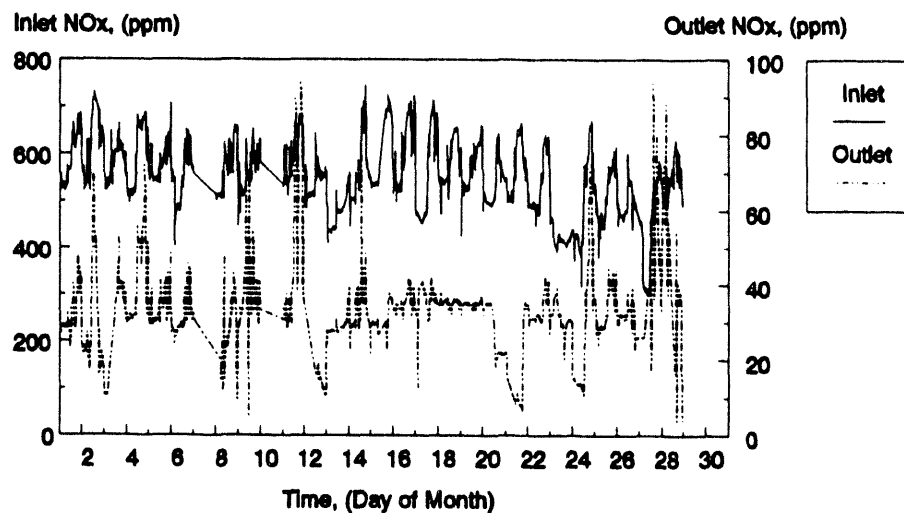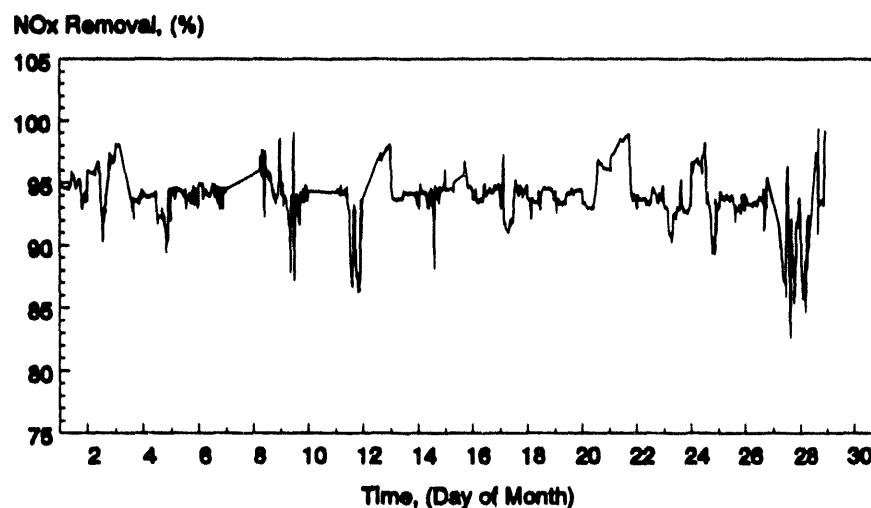


**Figure 3**
**Inlet and Outlet NOx Concentrations - June 1993**

NOx Removal, (%)



Figure 4
NOx Removal Efficiency - June 1993

The SCR system is very passive and has provided reliable, maintenance free operation. One equipment selection hurdle, however, was encountered during startup. The originally installed ammonia pump, which was of a diaphragm type, operated satisfactorilly only at low ammonia flow rates. As the pump stroke was increased to provide additional flow, flashing occurred in the pump suction. Some modifications were made to the pump suction piping and ammonia storage tank operating level, but only minimal performance improvement was obtained. This problem was corrected by a change to a spur gear pump for ammonia pressurization. This pump selection has performed very well and allows the full range of design ammonia flow rates.

During normal operation of the plant, SCR system performance has been as expected with the exception of two developments resulting from the operation of other, upstream equipment. First, the low temperature zone at the inlet to the SCR reactor, discussed earlier, has necessitated the restriction of $NH_3$ addition in the affected area. This small, outboard zone, however, is a low mass flow region and has not affected $NO_x$ removal significantly. The installation of a thermal mixing device during the next extended outage will allow the final optimization of the SCR system for $NO_x$ removal and $NH_3$ consumption.

Second, higher than expected particulate emissions from the fabric filter have resulted in the accumulation of dust on the upper surface of the first SCR catalyst bed. This accumulation has been identified during planned inspections. Even though no performance degradation has resulted from this accumulation, the dust has been evacuated during these inspections.

## SO₂ Removal

Sulfur dioxide removal in the SNOX Process is controlled by the efficiency of the $SO_2$ to $SO_3$ oxidation which occurs as the flue gas passes through the oxidation catalyst beds. The $SO_2$ Converter, which contains the catalyst, is a vessel constructed of high temperature, carbon steel containing four panels installed in parallel, each with two vertical beds. The beds are filled with Haldor Topsøe VK-WSA sulfuric acid catalyst. Excess amounts of catalyst exist in the top and bottom of the converter. The flue gas is distributed uniformly over the eight catalyst beds through five inlet nozzles. After passing through the catalyst beds, the flue gas is discharged through four outlet nozzles. Each outlet has a damper capable of stopping flow through the associated catalyst panel. The $SO_2$ Converter also has an associated Catalyst Screening System which is used to remove particulates from the catalyst periodically.

The catalyst is a vanadium-based oxidation catalyst in the shape of 0.4 inch O.D./0.16 inch I.D. x 0.35 inch rings. Due to the fact that the active compounds contained in the catalyst matrix are in a semi-molten state, most of the flyash entering the catalyst beds will be retained on the catalyst surface. For this reason, the catalyst must be removed from the vessel at periodic intervals to remove the flyash; the frequency of which will depend on the flyash loading.

To dedust the $SO_2$ oxidation catalyst when the $SO_2$ Converter differential pressure reaches a maximum level and restore the normal pressure drop, the Catalyst Screening System is operated. The major pieces of equipment involved in the cleaning system are two containers for catalyst transfer, one vibrating pan feeder to adjust the flow rate of catalyst to the screen, one vibrating screen to mechanically dedust the catalyst, one collection vessel for the catalyst sifting, and four capstan motors for catalyst container transfer throughout the system. The catalyst flow into the catalyst containers is controlled by pneumatic valves, one on the bottom of each catalyst bed.

**Table 2**

## Flue Gas Flowrates in SO₂ Converter Outlet Ducts

| Duct | Volumetric Flow | | Velocity | Deviation |
| | acfm | dscfm | fps | % |
|---|---|---|---|---|
| A | 47,216 | 18,896 | 42.2 | + 0.73 |
| B | 48,608 | 19,458 | 43.4 | + 3.7 |
| C | 46,796 | 18,902 | 41.8 | + 0.76 |
| D | 43,944 | 17,777 | 39.2 | - 5.2 |
| Total | 186,553 | 75,036 | | |
| Average | 46,638 | 18,759 | 41.6 | |

Oxidation efficiency through the catalyst beds is controlled primarily by two factors - space velocity and bed temperature. Space velocity governs the amount of catalyst which is necessary at design flue gas flow conditions and gas and bed temperature must be high enough to "ignite" or activate the $SO_2$ oxidation reaction.

In the tests conducted to date, temperature and flow measurements have been taken for the four catalyst panels. In order to have uniform space velocity for each panel, the flue gas flow to each must also be uniform. Because an in-line, trim burner is used at the Niles SNOX plant, temperature distribution entering the panels was measured since uniformity can be more variable with this type of heat source. A tubular heater can also be employed in this location and will minimize the possibility of temperature maldistribution.

Table 2 lists results from the flow measurements and Table 3 contains the results from the temperature measurements. The flow measurements were made at the four outlet nozzles or ducts and temperature measurements were done at the five inlet

**Table 3**

## Flue Gas Temperatures in SO₂ Converter Inlet Ducts

| Duct | Temperature Deg F | Deviation % |
|---|---|---|
| A | 806 | - 0.62 |
| B | 798 | - 1.6 |
| C | 844 | + 4.1 |
| D | 801 | - 1.2 |
| E | 804 | - 0.86 |
| Average | 811 | |

nozzles or ducts. Flow through the four catalyst panels is acceptably uniform and all quantities are within 6% of the average. With respect to temperature, it is also uniform and the temperatures in the five inlet ducts are within about 4% of the average.

**Table 4**

### Sulfur Dioxide Removal Efficiency

| Date | Inlet (ppm) | Outlet (ppm) | Efficiency (%) |
|---|---|---|---|
| 12/18/92 | 1719 | 57.6 | 96.6 |
| 12/18/92 | 1880 | 68.0 | 96.4 |
| 12/18/92 | 1927 | 81.2 | 95.8 |

$SO_2$ concentrations at 3% $O_2$

Oxidation efficiency in the $SO_2$ Converter is measured by sampling for sulfur dioxide at the outlet of the WSA Condenser. Sulfur dioxide removal efficiency of the SNOX system is controlled by the oxidation efficiency of the $SO_2$ Converter. During particulate testing which was conducted in December of 1992, manual samples were also taken for inlet and outlet $SO_2$. These values are shown in Table 4. Removal efficiency was about 96% in these tests. Also, as was shown for the $NO_x$ performance, $SO_2$ inlet and outlet values along with removal efficiency for the month of June are contained in Figures 5 and 6.

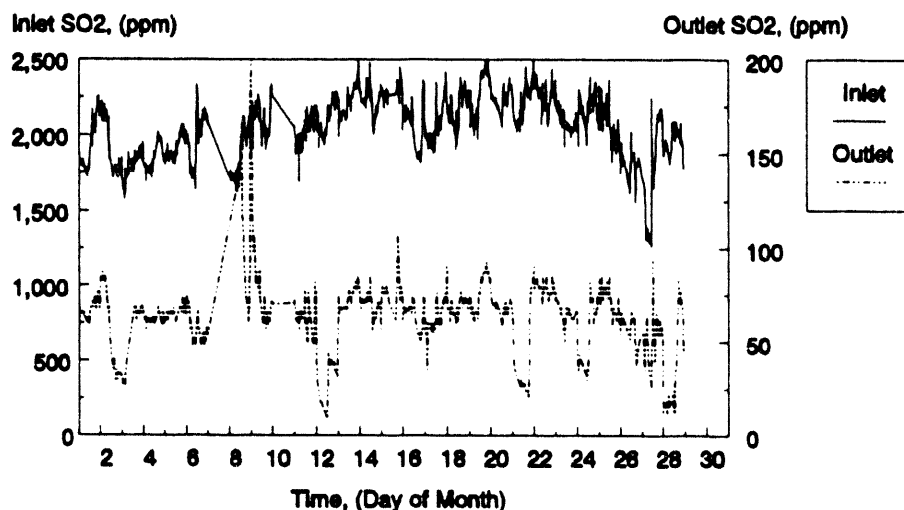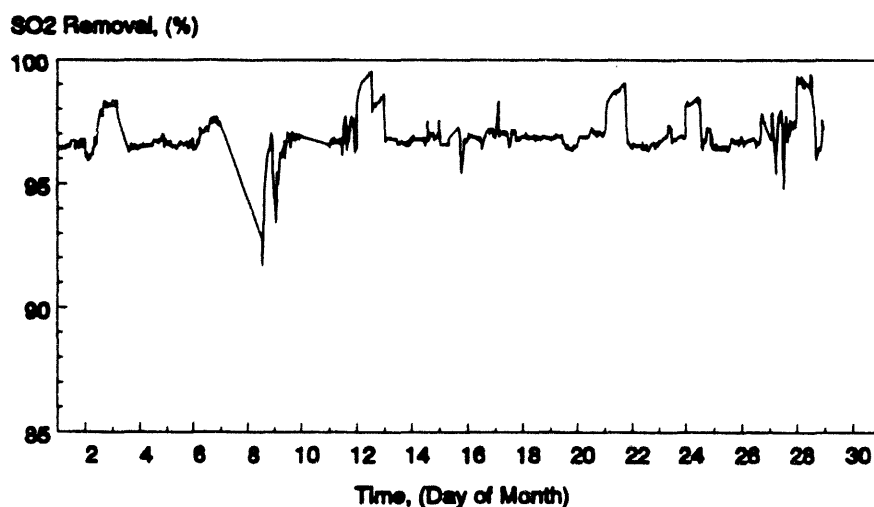As has been mentioned, the surface of the $SO_2$ catalyst is tacky at operating temperature and will



**Figure 5**
$SO_2$ Inlet and Outlet Concentrations - June 1993

**Figure 6**
SO$_2$ Removal Efficiency - June 1993

remove a portion of the particulate matter which enters the catalyst beds. Clean catalyst beds will have a pressure drop of about 2-3 inches w.g. and are operated until the pressure drop exceeds 5 inches before they are dedusted. At a particulate loading of 0.0004 gr/dscf it was estimated that the catalyst would require cleaning about once a year based on the European pilot plant experience.

At the time of preparation of this report, June 1993, the system has operated on flue gas for about 5200 hours and the SO$_2$ Converter pressure drop is at 3-4 inches w.g. This is less than was expected given the higher than anticipated particulate loadings which have been entering the SO$_2$ Converter. This result may be due to the catalyst capturing less particulate than predicted, the settling of catalyst in the beds since start up of the unit, or unrepresentative particulate loading samples. When settling occurs, the top of the catalyst beds are open and some of the flue gas is bypassed. The converter beds were checked in April of 1993 and filled with catalyst. The beds had settled about 1 foot of their original 15 foot height.

With respect to the measured particulate loadings, some samples have had large particles on the filter which can cause false high values. While it is possible that baghouse emissions may have

been in the 0.003 to 0.004 gr/dscf range, it is unlikely that the values higher than these are representative. If loadings were very high ( > .008 gr/dscf), the catalyst beds pressure drop would increase more rapidly than experienced.

Although catalyst bed pressure drop has not exceeded the limit of 5 inches w.g., one of the eight catalyst beds was emptied and put through the cleaning cycle in May of 1993 to verify equipment performance. All components performed correctly and the cleaning was successfully completed. This initial cleaning was performed with the unit cold and off line to check equipment, but subsequent dedusting will be performed with the unit on line; and the hot catalyst beds will be isolated, emptied, and cleaned.

During operation of the SNOX plant to date, one mechanical component of the $SO_2$ Converter has required replacement and redesign. At the four outlets of the converter, expansion joints are employed to connect to the main header. Given the high temperature (800°F), $SO_3$ content of the flue gas, and static pressure of 20 inches w.g.; these expansion joints must handle a severe environment. The initial joints employed a PTFE coated fiberglass material and were insulated on the outside to prevent condensation of sulfuric acid on the inner surface of the joints. However, temperatures were too high for the joint material and eventually caused failure.

The second design employed was a metal foil joint which was also insulated on the outside. These joints could not handle the degree of mating flange movement and the foil ripped soon after installation. At this time a more elaborate and expensive solution was considered based on the Danish SNOX plant experience. A joint purged with hot air and constructed with an internal permeable material is used in this plant. The seal is made with PTFE based materials on the outside which are not exposed to flue gas temperature.

Before this solution was attempted at Niles, it was decided to evaluate another conventional joint with insulation on the inside of the PTFE coated sealing membrane. In this way, the PTFE can operate below its degradation temperature and any flue gas leakage past the insulation will not damage the joint if any condensation occurs. These joints have been in service about 800 hours

at this time and have not had any early problems.

## Sulfuric Acid Condensation

After the flue gas has passed through the $SO_2$ Converter which has oxidized greater than 95% of the incoming $SO_2$ to $SO_3$, the gas must be cooled to induce the condensation of sulfuric acid. This cooling must be performed strategically as high $SO_3$ concentrations can represent a very aggressive atmosphere should condensation occur in the presence of unsuitable materials of construction. Depending on the actual concentrations of $SO_3$ and water, the acid dewpoint of this flue gas stream is in the range of 400°F.
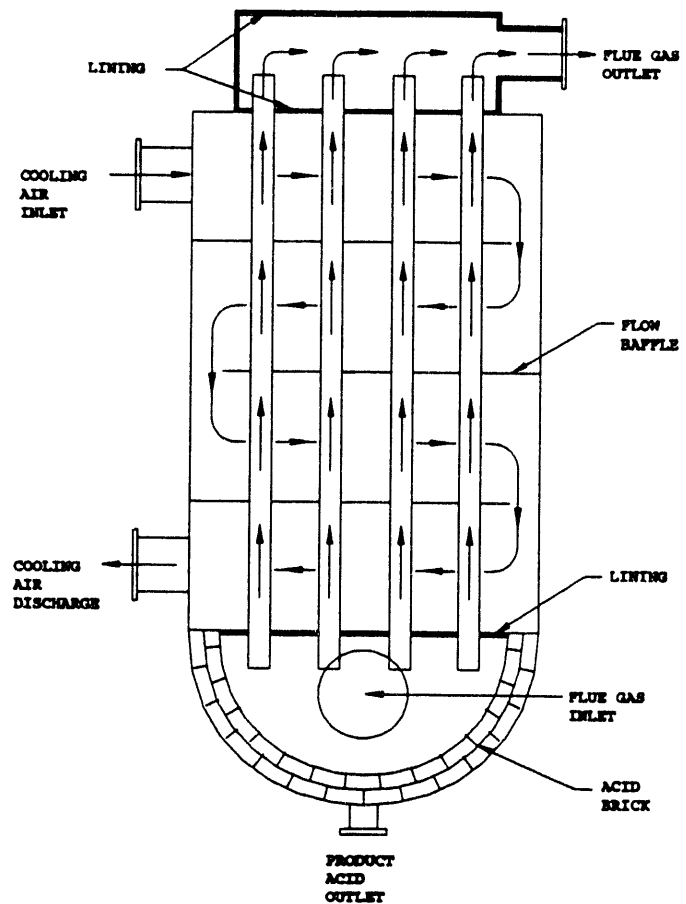
Figure 7
WSA Condenser

The cooling of the gas is performed through two pieces of equipment - first the hot side of the gas/gas heat exchanger and then the WSA Condenser. As heat is transferred to the SCR reactor inlet stream via the GGH, the gas cools to about 510°F. This temperature change drives most of the $SO_3$ to hydrate with available water to form $H_2SO_4$ vapor. The precooled gas enters the bottom of the condenser which is lined with an acid resistant brick. The gas then flows up through the interior of borosilicate glass tubes. Ambient air is passed across the exterior of the glass tubes countercurrently to the flue gas flow. In this manner the fluegas is cooled to about 210°F and the cooling air is heated to about 400°F. Figure 7 illustrates the gas flows through an individual WSA Condenser compartment.

During the flue gas cooling, sulfuric acid vapor condenses in a filmwise fashion on the inner

walls of the tubes and drains into the acid collection trough in the bottom of the condenser. The design of this piece of equipment allows for very high collection efficiency of $SO_3/H_2SO_4$ in the gas stream with outlet concentrations of between 2 and 5 ppm of aerosol mist. This concentration is below the $SO_3$ normally emitted in the flue gas of boilers burning medium to high sulfur coal (5 - 20 ppm). The collected acid is of very high quality and concentration, 94 to 98 wt.% depending on the process conditions of the particular installation.

The WSA Condenser at Niles consists of ten compartments in a 2 x 5 arrangement, each with 720 glass tubes. The lower portion of the lower tube sheet, the upper portion of the upper tube sheet, and the outlet hoods are lined with fluoropolymers. Thus, all materials of construction in contact with the flue gas are acid resistant. It should be noted that the WSA Condenser at Niles is of commercial, full scale size. Larger gas flowrates merely require multiple condenser modules. One exception is that these modules are now commonly offered in a 2 by 6 arrangement, i.e. 12 compartments per condenser module.

The process performance of a WSA Condenser is marked by three criteria:

- Complete condensation of $H_2SO_4$ with minimal aerosol mist carryover,
- High quality, high concentration (> 93 wt. %) acid product with water clarity,
- A minimum flowrate of discharge cooling air at a maximum temperature to facilitate efficient energy recovery in the furnace.

Baseline testing of the WSA Condenser of Niles was executed early in the Testing Phase of the demonstration. This testing focused on the fluegas effluent and acid product streams. Acid mist carryover was measured to be at 2 to 5 ppm depending on plant load and operating temperatures around the condenser. Mass balances around the system have yielded tight closure for sulfur compounds. The sulfuric acid product from the process has consistently been of 94 to 95 wt. % concentration with water clarity. The acid has been analyzed regularly for trace compounds to compare with commercial acid specifications. Results are given in the last report section. All acid product from this facility has been purchased by a local acid distributor and utilized by local industry.

Although the heat energy recovered in the condenser cooling air at Niles is not used for

preheated furnace combustion air as will be the case for fullscale applications, the cooling air flowrates and temperatures have been on design and as expected. As the testing phase progresses, a full parametric study of the WSA Condenser operation will be performed in order to fully verify all design criteria.

The airside, inlet flue gas, and outlet flue gas areas of the condenser module have been inspected regularly during scheduled plant outages. Of key concern is the identification of potential corrosion sites which might result in mechanical damage. Thus far, all coverings such as the acid brick and fluoropolymer linings of the upper and lower tube sheets and outlet hoods have shown no compromise in integrity. All PTFE components and the 7200 glass tubes, as would be expected, have been virtually unaffected by the aggressive atmosphere. A small fraction, about 0.17%, of the tubes have broken due to the combination of localized misalignment and thermal cycling. This small fraction of tube breakage is expected and designed for in the sizing of the condenser. Furthermore, this quantity is consistent with the breakage rate experienced at other SNOX installations and does not warrant replacement or correction.

## Acid Production

Sulfuric acid concentration and composition has also been excellent and has met or exceeded the requirements of the Federal Specification for Class 1 for species analyzed to date. Results from the analyses are shown in Table 5 along with the values from the federal specification. Three components, sulfurous acid ($H_2SO_3$), antimony and

**Table 5**

**Typical Niles SNOX Plant Acid Composition Versus U.S. Specification O-S-801E**

|                      | Spec. | Niles |
|----------------------|-------|-------|
| Concentration (%)    | 93.2  | 93.5  |
| $H_2SO_3$ (ppmw)     | 40    | NA    |
| Iron (ppmw)          | 50    | 10    |
| Copper (ppmw)        | 50    | < 1   |
| Zinc (ppmw)          | 40    | < 1   |
| Arsenic (ppmw)       | 1     | 0.4   |
| Antimony (ppmw)      | 1     | NA    |
| Selenium (ppmw)      | 20    | 1.4   |
| Nickel (ppmw)        | 1     | < 1   |
| Manganese (ppmw)     | 0.2   | < 1   |
| Nitrate (ppmw)       | 5     | *     |
| Ammonium (ppmw)      | 10    | 3     |
| Chloride (ppmw)      | 10    | 2.5   |

NA - Not Analyzed, * - Resolving analysis

nitrates, have not been documented at this time. Sulfurous acid and antimony were inadvertently omitted from the analytical laboratory's specification initially, and the nitrate values obtained to date are being evaluated as to correct analytical technique.

During design and construction of the SNOX Demonstration Project at Niles Station, arrangements were made with a sulfuric acid supplier to purchase and distribute the acid from the plant once operation began. The supplier, PVS Chemicals, is a large regional marketer and producer of sulfuric acid serving the industrial Midwest in New York, Ohio, Michigan and Illinois. This material has been sold primarily to the agriculture industry for the production of di-ammonium phosphate fertilizer, and to the steel industry for pickling. As of June 1993, approximately 3400 tons have been produced and distributed as shown in Figure 8.
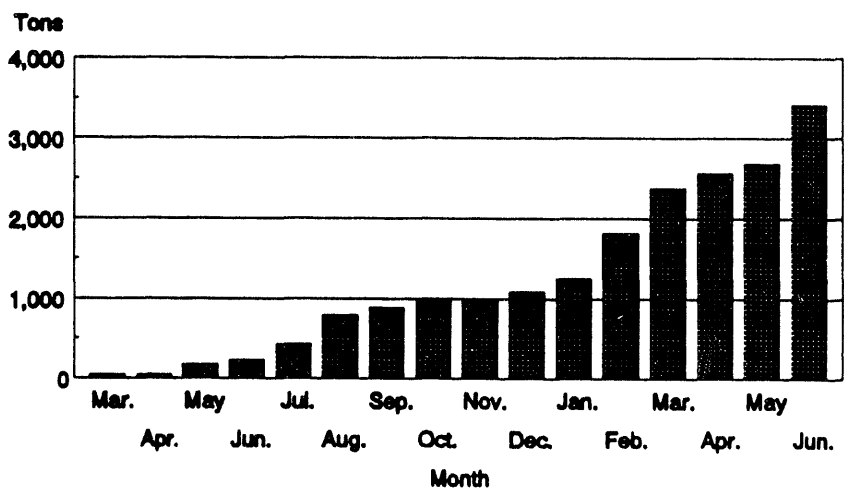


**Figure 8**
**Cumulative Acid Production**

# Preliminary Performance and Operating Results from the Integrated Dry NO$_x$/SO$_2$ Emissions Control System

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## ABSTRACT

The Integrated Dry NO$_x$/SO$_2$ Emissions Control System was installed at Public Service Company of Colorado's Arapahoe 4 generating station in 1992 in cooperation with the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI). This full scale 100 MWe demonstration combines low-NO$_x$ burners, overfire air, and selective non-catalytic reduction (SNCR) for NO$_x$ control and dry sorbent injection with humidification for SO$_2$ control. Operation and testing of the Integrated Dry NO$_x$/SO$_2$ Emissions Control System began in August 1992 and will continue through mid 1994. Preliminary results of the NO$_x$ control technologies show that the original system goal of 70% NO$_x$ removal has been easily met and that NO$_x$ removals of up to 80% are possible at full load with the combustion and SNCR systems. Testing of the dry sorbent injection system with low sulfur coal began in April 1993 using a calcium-based reagent. A maximum SO$_2$ removal of 40% has been achieved with duct injection of commercial calcium hydroxide and humidification to a 25°F approach to saturation. Sodium-based dry sorbent injection is expected to achieved up to a 70% SO$_2$ reduction.

## INTRODUCTION

There are many technologies for NO$_x$ reduction but the four that are currently receiving the most attention are low-NO$_x$ burners, staged combustion using overfire air, selective catalytic reduction (SCR), and selective non-catalytic reduction (SNCR).

Various government and industry sponsored demonstration programs have been conducted showing that low-$NO_x$ burners with or without overfire air can economically and efficiently reduce $NO_x$ emissions of wall- and tangentially-fired boilers. However, no research or demonstration projects have been completed on the less popular top-fired boiler. There are only a small number of top-fired boilers in the United States but PSCC operates seven of these boilers in the Denver Metro area. Characteristics of a top-fired boiler are a small furnace with a very turbulent flame. These conditions generally lead to much higher $NO_x$ emissions than on the more common wall- and tangentially-fired boiler.

SCR has been proven effective at reducing $NO_x$ emissions in Germany and Japan but has not been successfully demonstrated on U.S. coal-fired utility boilers. This technology is generally the most expensive technology for reducing $NO_x$ emissions although estimated costs are decreasing rapidly. The major advantage of SCR is that $NO_x$ reduction, with a proper design, is higher than other competing technologies. SCR has the disadvantages of requiring considerable space in a retrofit situation and the user must be aware of the possible waste disposal concerns of the spent catalyst.

SNCR is substantially less expensive to install than the competing SCR but it cannot attain as high $NO_x$ removals. SNCR has been successfully demonstrated on gas-fired boilers in the United States, industrial boilers, and has limited experience in Europe on other fuels. However, previous to this project, the technology had not been demonstrated on a U.S. coal-fired utility boiler. While less expensive than SCR, SNCR has the disadvantage of possible higher ammonia slips and $N_2O$ generation.

A demonstration of the most promising of these technologies was required to show that high efficiency $NO_x$ removal can be retrofit to top-fired units. The combination of the latest generation low-$NO_x$ burners, overfire air, and SNCR offers the potential to obtain very high $NO_x$ removals at potentially lower capital and operating costs than SCR alone. The demonstration is required as this is a first-use technology and cannot be commercially developed without a successful demonstration.

There are many technologies for reducing $SO_2$ emissions on utility boilers. The most popular and successful of these is the standard wet scrubber. Many variations and improvements have been made to wet scrubbers over the years and the units are economically achieving high efficiency $SO_2$ reduction on high sulfur coals. However, scrubbers have high initial cost and can be difficult to retrofit to older units which have limited available land area. In addition, older units often operate at reduced capacity factors and thus initial costs greatly affect the life cycle costs. On these units, other technologies have been proposed that generally have lower initial cost but higher operating cost. At reduced baseline $SO_2$ levels, the initial equipment cost can substantially increase the cost per ton of $SO_2$ removed.

One of these lower initial cost technologies is dry sorbent injection (DSI). In this process, either calcium hydroxide or sodium-based reagent is injected into the flue gas duct before the particulate control equipment. The solids react with gaseous sulfur oxides in the flue gas and convert them to a solid product. The solids are removed from the particulate

control device and landfilled. Humidification of the flue gas is required with calcium hydroxide in order to increase reagent utilization. DSI using calcium had been demonstrated on one full scale Eastern unit with high sulfur coal but has not been proven at very low initial $SO_2$ concentrations. Sodium-based reagent injection offers the advantage of not requiring humidification to obtain high $SO_2$ removal efficiencies. However, testing on large scale units has found that sodium injection converts some of the NO in the flue gas into $NO_2$. While the overall $NO_x$ is slightly reduced, the higher $NO_2$ can cause a visible brown/orange plume at the stack. Testing has shown that the visible plume can be reduced or eliminated if the $SO_2$ reduction reaction occurs in the presence of ammonia-based compounds. Another form of DSI injects calcium hydroxide upstream of the economizer section of the boiler. Pilot scale testing at temperatures below 1200°F has shown good $SO_2$ removal efficiencies but no full scale testing has been completed in the United States. While some types of DSI have been previously demonstrated, not all of the problems have been solved with the technology. A successful full scale demonstration is required to allow commercialization of these technologies.

Public Service Company of Colorado (PSCC) is an investor owned utility serving much of Colorado. PSCC has strived to be an environmentally responsible corporation and has tested and retrofit many pollution control technologies to its coal fired power plants. The Company decided that a demonstration of $NO_x$ and $SO_2$ removal technologies was important on a top-fired unit and began assembly of a competent team to prepare a proposal for Round 3 of the U.S. Department of Energy's (DOE) Clean Coal Technology Program. Table 1 shows the participants involved in the project and their major responsibilities. This project, called the Integrated Dry $NO_x/SO_2$ Emissions Control System, was the first demonstration of low-$NO_x$ burners, overfire air, and urea-based SNCR for a top-fired utility boiler. The project includes the use of dry sorbent injection using both sodium- and calcium-based reagents for $SO_2$ control.

### TABLE 1 - Project Participants

| Participant | Function |
|---|---|
| Public Service Company of Colorado | Project Manager, Design, Construction, Funding |
| Department of Energy | Funding |
| Electric Power Research Institute | Funding, Technical Assistance |
| Babcock & Wilcox | Combustion Modifications and Humidification System Design, Supply, and Erection |
| Noell, Inc | Urea Injection System Design, Supply |
| Fossil Energy Research Corporation | Testing |
| Stone & Webster Engineering Corporation | General Engineering and Design |
| Western Research Institute | Waste Analysis and Research |
| Colorado School of Mines | Sodium Injection Process Research |

## UNIT DESCRIPTION

PSCC selected Arapahoe Unit 4 as the demonstration site for this project. The station has four top-fired boilers supplied by Babcock and Wilcox in the early 1950s. Arapahoe 4 is a

nominal 100 MWe unit that began operation in September 1955. The boiler fires a low sulfur (0.4%) Colorado bituminous coal as its main fuel source but also has 100% natural gas capability. While Arapahoe 4 is an older unit with over 35 years of operation, PSCC plans to continue unit operation well into the next century.

This small turbulent boiler was an efficient coal combustor but was also effective at generating high $NO_x$ emissions. Baseline $NO_x$ levels for this boiler were approximately 1.10 lb/MMBtu. The pulverized coal was injected through twelve intertube burners located in the roof of the boiler as shown in Figure 1. The intertube burner is not comparable to a more common wall-fired burner. It consists of a splitter box that separates into 20 smaller nozzles that inject the coal and primary air mixture evenly across the furnace roof. Secondary air was injected beside the coal nozzles and the system contained no adjustments to control the rate of secondary air and fuel mixing.
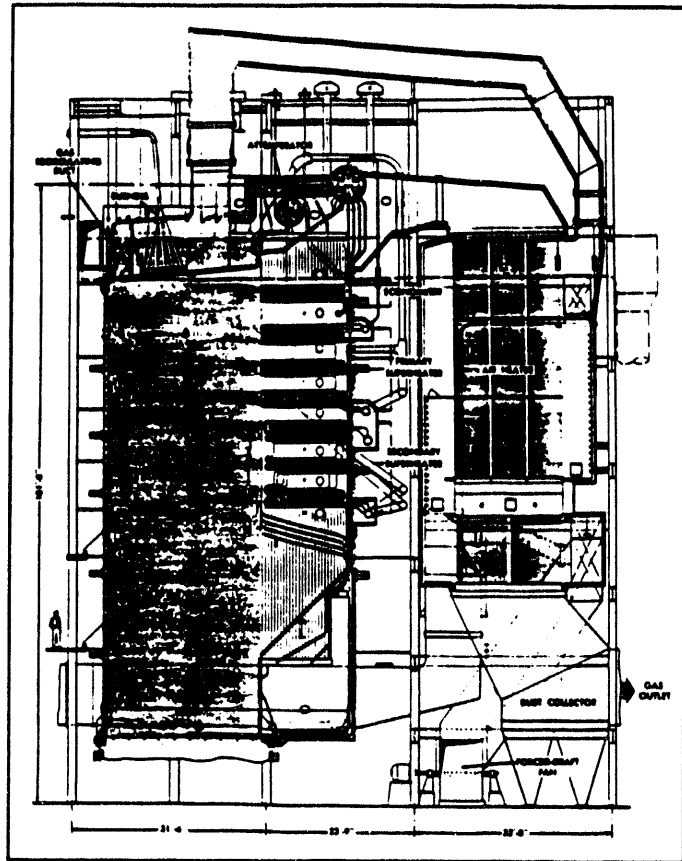


**Figure 1 - Boiler Elevation**

## PROJECT DESCRIPTION

The Integrated Dry $NO_x/SO_2$ Emissions Control System consists of five major control technologies that are combined to form an integrated system to control both $NO_x$ and $SO_2$ emissions. $NO_x$ reduction is obtained through the use of low-$NO_x$ burners, overfire air, and urea injection while dry sorbent injection using either sodium- or calcium-based reagents with humidification is used to control $SO_2$ emissions. The project goal is to provide up to a 70% reduction of both $NO_x$ and $SO_2$ emissions. The combustion modifications were expected to reduce $NO_x$ by 50%, with the expectation that the SNCR system would provide the remaining 20% reduction. Dry Sorbent Injection was expected to provide 50% removal of the $SO_2$ emissions while using calcium-based reagents. As sodium is much more reactive than calcium, it was expected to provide $SO_2$ removals of up to 70%. Figure 2 shows a simplified schematic of the Integrated Dry $NO_x/SO_2$ Emissions Control System as implemented at Arapahoe 4.
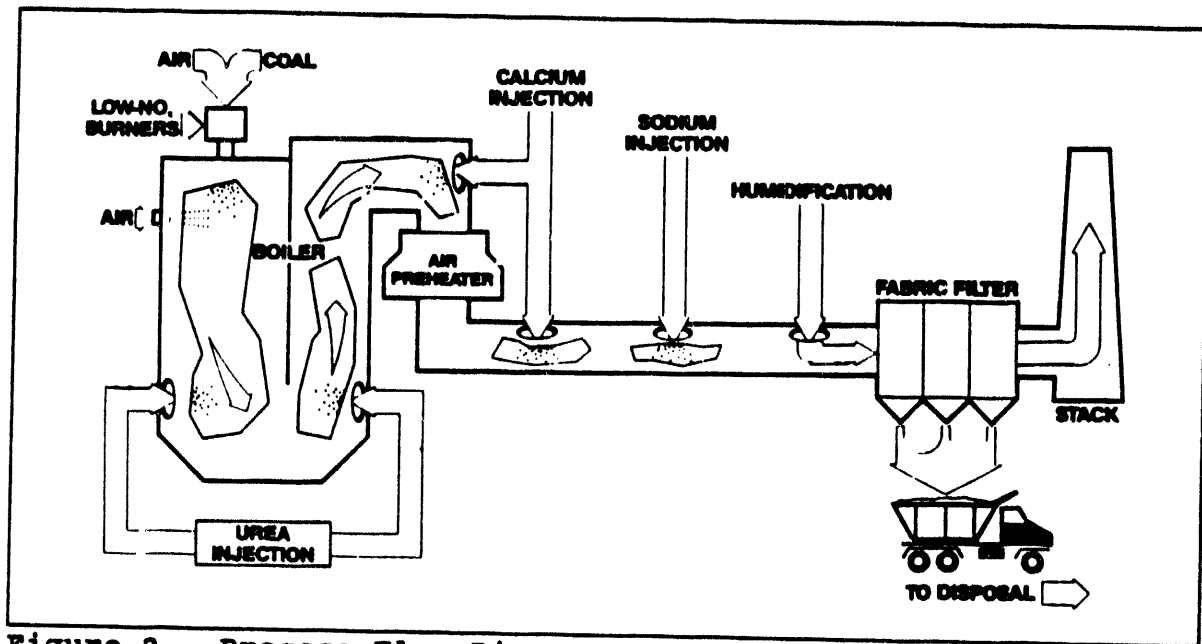
**Figure 2 - Process Flow Diagram**

The total estimated cost of this innovative demonstration project is estimated at $27,411,000. The project cost breakdown is shown in Table 2. Funding is being provided by the DOE (50.0%), PSCC (43.7%), and EPRI (6.3%). The DOE funding is being provided as a zero interest loan and is expected to be paid back from the proceeds obtained during commercialization of the technology over a 20 year period from the conclusion of the demonstration project.

**Table 2 - Project Cost**

| Task | Estimated Cost |
|---|---|
| Pre-Award | $358,000 |
| Design | $3,171,000 |
| Equipment Procurement | $8,445,000 |
| Construction | $8,292,000 |
| Operations & Maintenance | $6,600,000 |
| TOTAL | $27,411,000 |

## Low-NO$_x$ Burners

Babcock and Wilcox (B&W) was selected to provide the low-NO$_x$ burners for the Arapahoe 4 project. B&W's DRB-XCL® (Dual Register Burner-aXially Controlled Low-NO$_x$) burner had been successfully used to reduced NO$_x$ emissions on wall-fired boilers but had never

been used in a vertically-fired furnace. The burner has two main features which limit NO$_x$ formation as shown in Figure 3, a simplified schematic of the burner. The first feature is a sliding air damper. In many older burners a single register is used to control both total secondary air flow to the burner and also the rate of air/fuel mixing. The use of the sliding damper in the DRB-XCL® separates the functions and allows the secondary air flow to
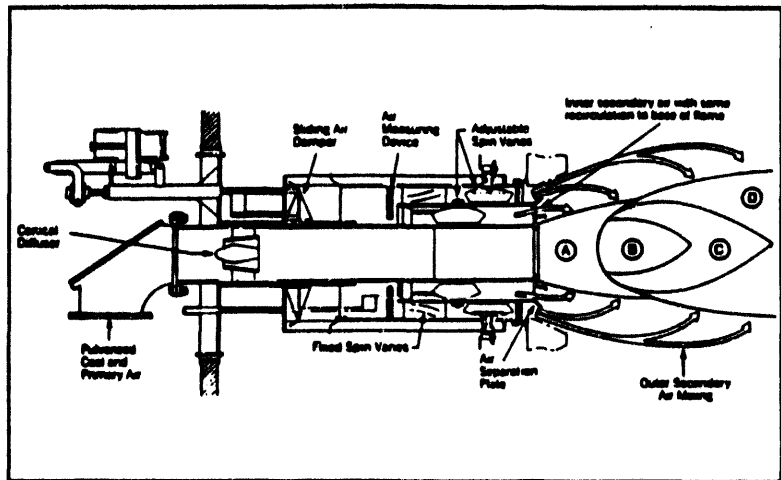


**Figure 3 - B&W DRB-XCL® Burner**

be controlled independently of the spin. The burner includes a 30 point pitot tube grid so that a relative indication of the secondary air flow at each burner is possible. The second feature of the burner is dual registers. The most important variable in the control of NO$_x$ is the rate at which oxygen is mixed with the fuel. The ability to adjust both inner and outer registers provides more control over the rate of combustion and thus the amount of NO$_x$ formed.

A low-NO$_x$ retrofit on a top-fired unit is much more involved than modifications to most wall- or tangential-fired units. At Arapahoe Unit 4, the modifications required the replacement of all boiler roof tubes to provide the circular openings required for a "normal" burner. The burners were placed in 4 rows of 3 burners. One major design problem of the retrofit was locating the secondary air ductwork. The secondary air duct originally entered the windbox at the rear of the furnace roof. The new burners required significantly more space than the intertube burners and there are now four burners where the secondary air duct was originally placed. Smaller ductwork was added to the furnace roof and the remaining combustion air was added through an abandoned gas recirculation duct that entered the front of the furnace.

The burner retrofit included new Class I gas ignitors. Arapahoe 4 originally included the ability to fire 100% natural gas. While coal is used as the main fuel, natural gas is used on occasion to provide load when pulverizers or other equipment are out of service. The natural gas firing was maintained with the DRB-XCL® burners by the use of a gas ring header located at the tip of the burner. No modifications were made to the original Riley pulverizers, although a new electronic variable speed feeder drive was added to provide more consistent coal feed.

Overfire Air

While low-NO$_x$ burners alone have proven to be effective for reducing NO$_x$, combustion staging can further reduce NO$_x$ emissions. Overfire air delays combustion by redirecting a portion of the secondary air downstream of the main combustion zone. As the initial

combustion occurs at lower stoichiometric ratios, less $NO_x$ is formed. At Arapahoe 4 three B&W dual zone $NO_x$ Ports were added to each side of the furnace approximately 20 feet below the boiler roof. These ports can inject up to 25% of the total combustion air through the furnace sidewalls. The $NO_x$ ports separate the overfire air into two streams as shown in Figure 4. The outer area of the port contains adjustable registers that can be used to spread the overfire air next to the wall. The center area of the port uses a sliding disk damper to control air



Figure 4 - B&W dual zone $NO_x$ port

flow. This core zone injects a high velocity jet across the furnace toward the division wall. This two stage air injection allows for faster mixing and more equal distribution of the air and combustion gases in the furnace.
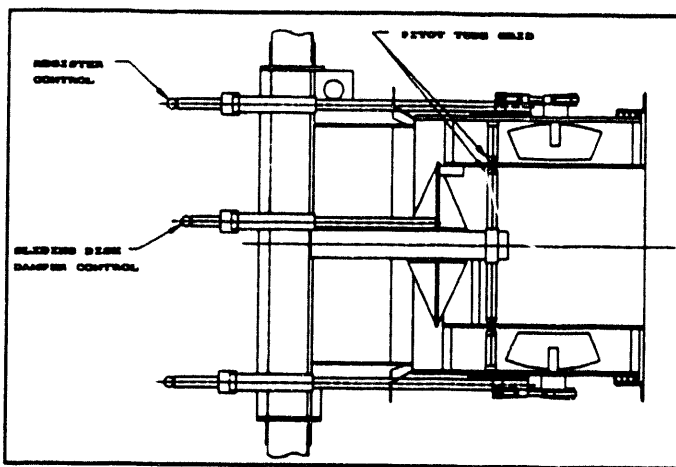
The $NO_x$ ports are located on each side of the furnace in a small windbox. New ductwork was added that directs secondary air from the boiler roof to the overfire air windbox. Each of the ducts that supply the overfire air windboxes contains an opposed blade louver damper to control air flow. The ducts also contain a pitot tube grid with a flow straightener to measure total overfire air flow.

## Selective Non-Catalytic Reduction

The purpose of the SNCR system at Arapahoe was to further reduce the final $NO_x$ emissions obtained with the combustion modification so that the goal of 70% $NO_x$ removal could be achieved. Urea was selected as the base chemical for the SNCR system, because urea, unlike either aqueous or anhydrous ammonia, is not a toxic chemical. Urea injection is a simple process. A liquid solution of urea is injected into the boiler. The urea decomposes at approximately 1700 to 1900°F and then reacts with $NO_x$ forming primarily nitrogen and water. The disadvantage of urea injection, as with any SNCR chemical, is that the process is very temperature sensitive. If the temperature is too high, some urea can be converted to $NO_x$. If the temperature is too low, more of the urea is converted to ammonia, which becomes an unacceptable new pollutant.

PSCC selected Noell, Inc. to design and supply the urea-based SNCR system. Figure 5 shows a simplified flow diagram of the system as implemented at Arapahoe Unit 4.

During original testing of the urea-based SNCR system, it was found that $NO_x$ reductions at low load were less than expected. A short term test using aqueous ammonia achieved greater $NO_x$ reduction than urea. Although ammonia was more effective than urea, it remained desirable to store urea due to safety concerns. A system was installed that allows on-line conversion of urea into ammonia compounds.
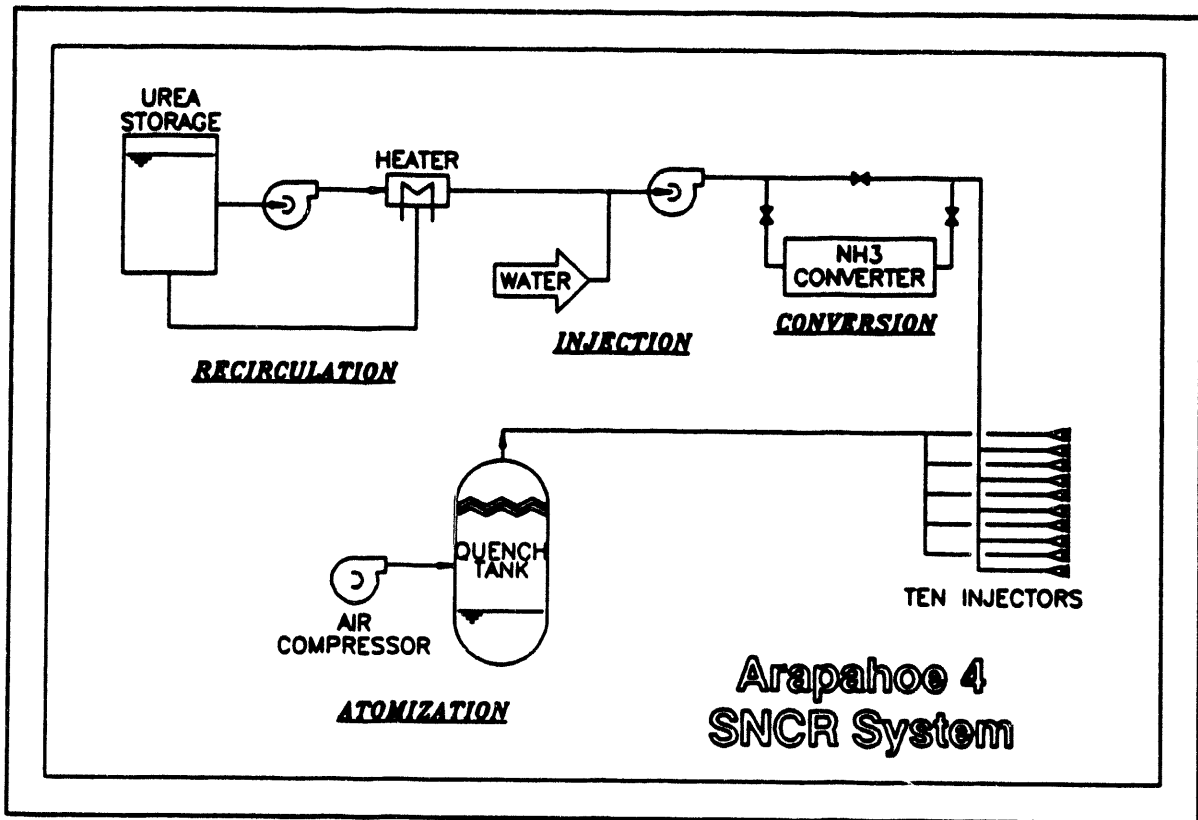
**Figure 5 - SNCR Flow Diagram**

The SNCR system at Arapahoe Unit 4 uses Noell's proprietary dual fluid injection nozzles to distribute the chemical uniformly into the boiler. A centrifugal compressor is used to supply a large volume of medium pressure air to the injection nozzles to help atomize the solution and rapidly mix the chemical with the flue gas.

Dry Sorbent Injection

A combination of dry technologies will be demonstrated at Arapahoe 4 to reduce $SO_2$ emissions. PSCC designed and installed a dry sorbent injection system that can inject either calcium- or sodium-based reagents into the flue gas upstream of the fabric filter. Figure 6 shows a simplified flow diagram of the equipment. The reagent is fed through a volumetric feeder into a pneumatic conveying system. The air and material then pass through a pulverizer where the material can be pulverized to approximately 90% - 400 U.S. Standard mesh. The material is then conveyed to the duct and evenly injected into the flue gas. A bypass can be installed to convey the material into the boiler upstream of the economizer in a region where the flue gas temperature is approximately 1000°F.

While significant $SO_2$ reductions can be achieved with sodium-based reagent, calcium hydroxide is less reactive. In order to improve $SO_2$ removal with calcium hydroxide, a humidification system has been installed. The system was designed by B&W and includes 84 I-Jet humidification nozzles to inject up to 80 gpm of water into the flue gas ductwork. The humidifier is located approximately 100 feet ahead of the fabric filter and there is no
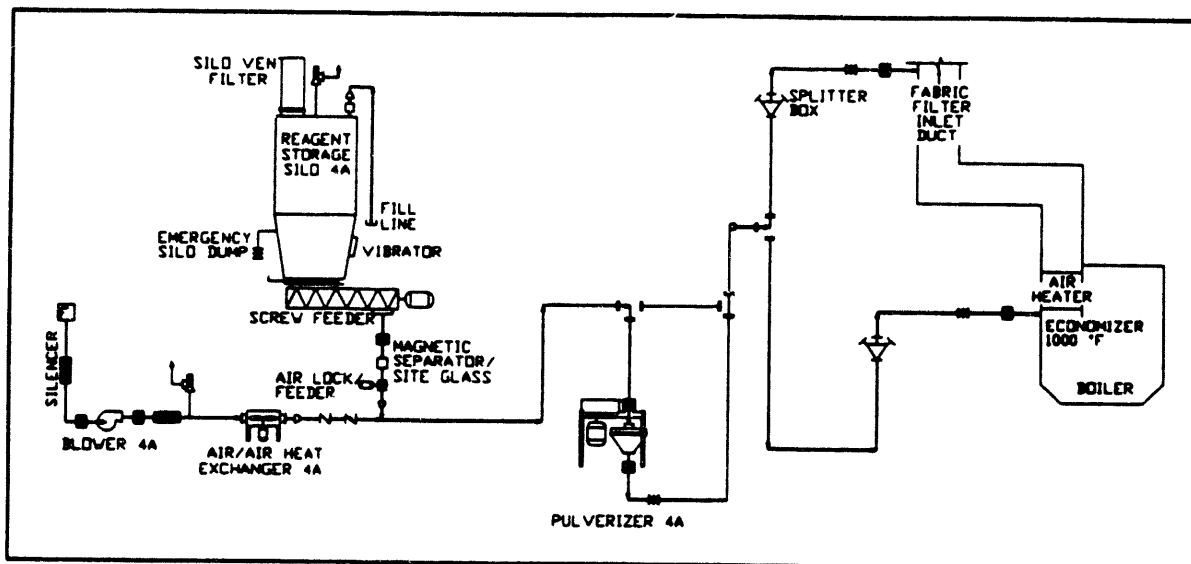
**Figure 6 - Dry Sorbent Injection Flow Diagram**

bypass duct. Although the system is designed to achieve a 20°F approach to saturation, it is not expected to operate the humidifier below a 40°F approach to saturation to protect the fabric filter.

## Balance of Plant

In addition to the major environmental equipment, the project also included required upgrades to the existing plant. Arapahoe 4 originally used a Bailey pneumatic control system with limited controls for burner management. Due to the complexity of the retrofit, a new distributed control system was required to control the boiler and other pollution control equipment added as part of the project. The flyash collection system was also converted from a wet to a dry collection system to allow dry collection of the injection waste products. A Continuous Emission Monitoring (CEM) system was installed at Arapahoe Unit 4 to collect data for the extensive test program. This monitor allows continuous measurements of $N_2O$, $NH_3$, $NO_2$, and $H_2O$ in addition to the more common pollutant measurements.

## PROJECT SCHEDULE

The Integrated Dry $NO_x/SO_2$ Emissions Control System began with selection by the DOE in December 1989. Negotiations for the project were finalized with approval of the Cooperative Agreement on March 11, 1991. Construction began in July 1991 and was completed in August 1992. Due to the many different technologies included in the Integrated Dry $NO_x/SO_2$ Emissions Control System, the test program includes individual parametric tests of each of the individual systems during the period August 1992 through October 1993. Longer term testing of the optimized integrated system will continue through mid 1994 and project completion is scheduled with the Final Report due in November 1994. Table 3 shows the project schedule.

## TABLE 3 - Project Schedule

| | 1991 | 1992 | 1993 | 1994 |
|---|---|---|---|---|
| Cooperative Agreement Approval | ■ | | | |
| Boiler Baseline Testing | ■ | | | |
| Urea Injection Installation | ■ | | | |
| Initial Urea Testing | | ■ | | |
| Combustion Modifications | | ■ | | |
| Combustion Testing | | ■ | | |
| Ammonia Conversion Installation | | ■ | | |
| Urea Testing | | | ■ | |
| Dry Reagent Testing | | | ■ | |
| Integrated Testing | | | ■ | |
| High Sulfur Coal Testing | | | | ▮ |
| Final Report | | | | ▬▬ |

## PRELIMINARY RESULTS

Fossil Energy Research Corporation (FERCo) of Laguna Hills, California was selected to perform all testing of the Integrated Dry $NO_x/SO_2$ Emissions Control System. Currently the individual testing of the low-$NO_x$ burners, overfire air, urea injection, calcium duct injection, and calcium economizer injection has been completed. Sodium duct injection testing will begin in July 1993 and continue through September 1993. Testing of the complete integrated system will continue through mid 1994 with up to four weeks of testing on a high sulfur (2.5%) coal. In addition to efficiency and emissions measurements, four tests will be conducted to determine baseline and removal capabilities of the system for many of the common air toxic emissions. Although all data have not been reviewed, some preliminary results of the individual technologies comprising the Integrated Dry $NO_x/SO_2$ Emissions Control System is available.

### Combustion Modifications

Figure 7 shows the original baseline $NO_x$ emissions compared to the tuned post-combustion retrofit emissions. Baseline $NO_x$ emissions for the unit before the retrofit were nearly uniform across the load range at approximately 800 ppmc (Corrected to 3% $O_2$, dry) or about 1.10 lb/MMBtu. The combination of low-$NO_x$ burners and overfire air have greatly reduced $NO_x$ emissions. The post-retrofit $NO_x$ emissions are shown for two staging configurations, maximum and minimum overfire air.
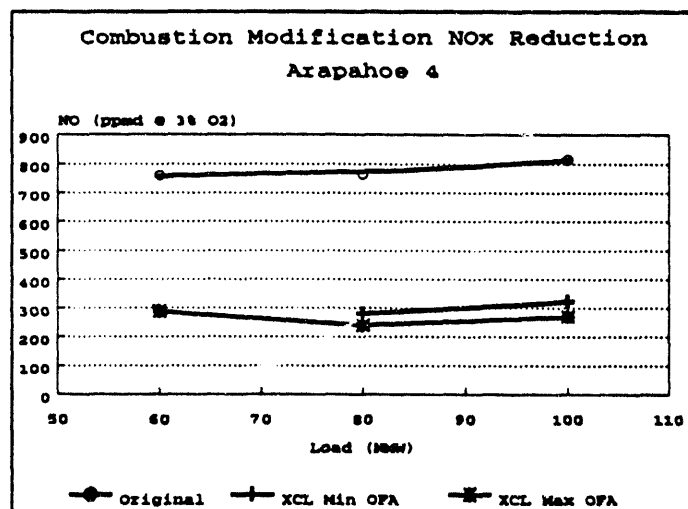
Figure 7 - $NO_x$ Comparison

With maximum overfire air, approximately 25% of the total combustion air is introduced through the overfire air ports at full load. With minimum overfire air, approximately 15% of the total combustion air is introduced as overfire air. It is impossible to eliminate the overfire air as the ports are located in a very hot section of the boiler and damage would result at lower air flows due to reduced cooling. With maximum overfire air, the $NO_x$ reduction varies from 62 to 69% across the load range. With minimum overfire air, $NO_x$ reduction is reduced slightly to 60 to 63%.

Low-$NO_x$ combustion modifications often increase flyash unburned carbon and increase carbon monoxide emissions. Figure 8 shows a comparison of unburned carbon in the flyash before and after the combustion modifications. Figure 9 shows a similar figure for CO emissions. Flyash unburned carbon is basically unchanged from the baseline levels and does not appear to be affected by the amount of overfire air. CO emissions are comparable to the baseline levels with maximum overfire air and increase slightly when the overfire air is reduced to the minimum value.

*Overfire Air*

Figure 10 shows data at a constant excess air level for two different loads. Overfire air flow is shown as a percentage of the total combustion air. The data indicate a slight decrease in $NO_x$ as the overfire air flow is increased but $NO_x$ reduction is less than generally expected. At 100 MWe, $NO_x$ is reduced approximately 10% as overfire air is increased from 15 to 25%. The $NO_x$ reduction is only approximately 8% at the 80 MWe load. It
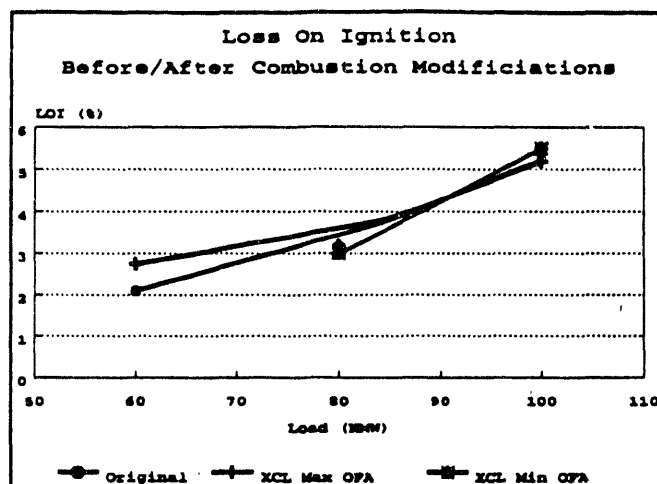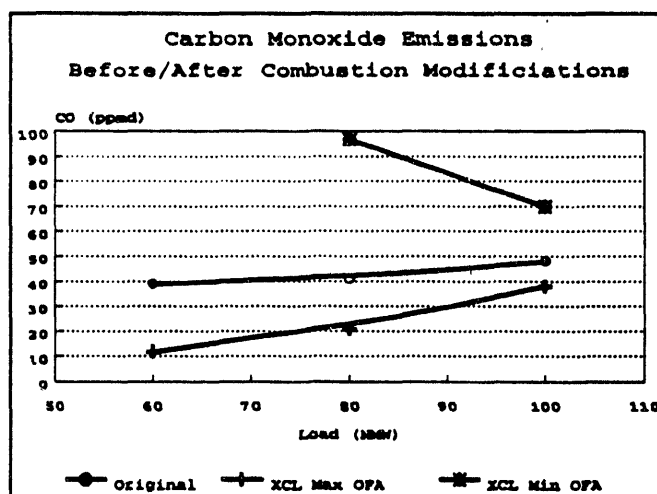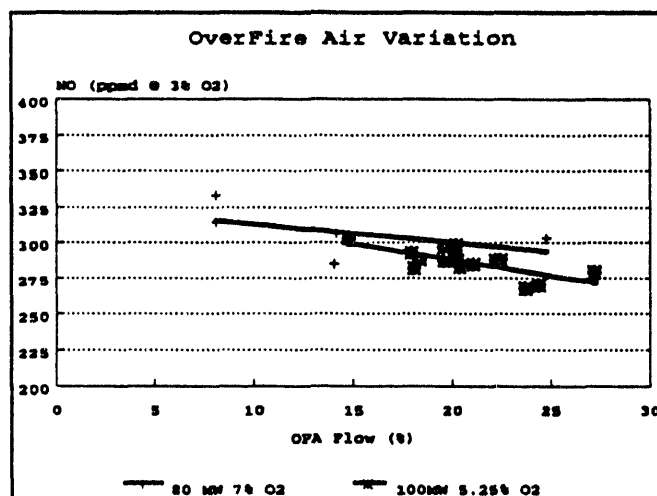
Figure 8 - Loss on Ignition

Figure 9 - Carbon Monoxide

Figure 10 - Overfire Air Variation

is impossible to operate at 0% overfire air to determine the total effect of overfire air, but it appears that the low-$NO_x$ burners are responsible for the majority of the $NO_x$ reduction.

It appears that increasing overfire may have a positive combustion affect on top-fired units at low excess air operating conditions. At Arapahoe 4, no significant correlation could be found for either unburned carbon or CO emissions at reduced loads. This is due to the increased excess air levels necessary to maintain steam temperatures at low loads. This additional excess air provides sufficient oxygen for carbon burnout regardless of overfire air flow rate. However, at full load it appeared that increases in overfire air actually reduced CO emissions as shown in Figure 9. It is theorized that on a top-fired unit there is less forced mixing of the combustion products downstream of the burners. On wall-fired boilers the flame must turn and travel upward. This forces mixing of the combustion gases and allows for carbon burnout. On a top-fired boiler, forced mixing does not occur until the gases turn at the bottom of the boiler. The injection of overfire air adds turbulence and may reduce CO emissions.

*Load Following $NO_x$ Emissions*

The $NO_x$ reduction data previously presented in this paper were obtained at baseload conditions with testing personnel closely monitoring all boiler variables and represents the lowest $NO_x$ emissions that can be obtained. Arapahoe 4 is generally operated as a load following unit under automatic control where oxygen levels can vary significantly and rapidly. This mode of operation tends to increase CO and $NO_x$ emissions. Immediately following the parametric combustion testing, the unit was operated for two months under normal load following conditions. Figure 11 shows a comparison of the $NO_x$ emissions of the DRB-XCL® burners with overfire air during baseload and load following operation. Depending on load, $NO_x$ emissions are from 10 to 20% higher during load following operation.
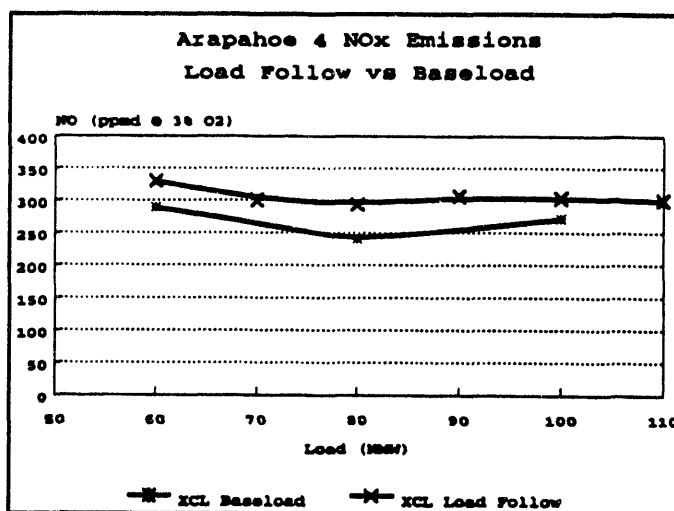


**Figure 11 - Load Follow Operation**

Selective Non-Catalytic Reduction Testing

Two phases of testing have been completed with the SNCR system. The system was originally tested with the high $NO_x$ baseline that existed with the original burners. After the combustion system was retrofit, additional testing was completed with the reduced $NO_x$ baseline.

## Combustion System Effects

Figure 12 compares the $NO_x$ removal and ammonia slip results at 100 MWe before and after the combustion modifications were completed. Note that with the original burners in-service and a $NO_x$ baseline of 800 ppmc, approximately 35% $NO_x$ reduction could be obtained with an ammonia slip of 10 ppm at the inlet of the fabric filter. After the combustion modification retrofit, the baseline $NO_x$ was reduced to approximately 260 ppmc, and it was found that urea injection worked substantially better. $NO_x$ reduction was increased to 42% while maintaining a 10 ppm ammonia slip. While this is not a large increase in $NO_x$ removal, the significance is that the increased removal was obtained with a nearly 40% reduction in the amount of urea injected.
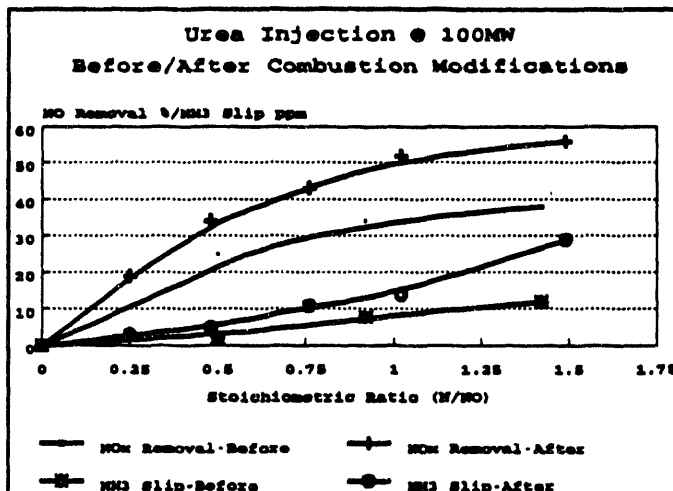


**Figure 12 - Urea Injection 100MW**

The data initially appear to show that SNCR is more effective at lower initial baseline $NO_x$ levels. However, the combustion modifications did more than just reduce $NO_x$ emissions. The modifications also reduced flue gas temperature in the area of urea injection by approximately 150°F across the load range. Urea injection is a very temperature sensitive process and minor temperature changes can significantly change both urea utilization and the maximum removal that can be achieved. It is currently believed that the primary reason for the increased urea utilization after the combustion retrofit is the decrease in flue gas temperature in the area of urea injection. With the original burners, the urea was being injected into a region that was too hot for efficient $NO_x$ removal. At the lower temperatures that exist with the new burners, better $NO_x$ reduction is obtained at equivalent urea flows but ammonia slip is increased. The net effect of the temperature change is higher $NO_x$ reduction with lower chemical injection rates while maintaining comparable ammonia slip levels.

## Load Variation

A series of parametric tests was completed over the normal load control range of Arapahoe Unit 4 of 60 to 110 MWe. The testing was conducted after the combustion modifications were complete with a $NO_x$ baseline of approximately 260 ppmc while injecting urea. Figure 13 shows the $NO_x$ removal and urea utilization with a constant 10 ppm ammonia slip at the fabric filter inlet. Utilization is used as a measure of the effectiveness of the urea and is defined as follows:

$$Utilization = NO_x\ Removal/Stoichiometry$$

For the current injection system, it appears that the most efficient $NO_x$ reduction occurs between boiler loads of 80 and 100 MWe. The flue gas temperature in the area of urea

injection at these loads is 1700 to 1800°F, which compares well with the expected optimum temperature for the process. As load is reduced to 60 MWe, the flue gas temperature cools and only 13% removal is possible at an acceptable ammonia slip. At the lower temperature, a significant amount of the urea converts to ammonia in a temperature range that is too cold to obtain $NO_x$ removal. This increases ammonia slip and thus urea flow must be limited.
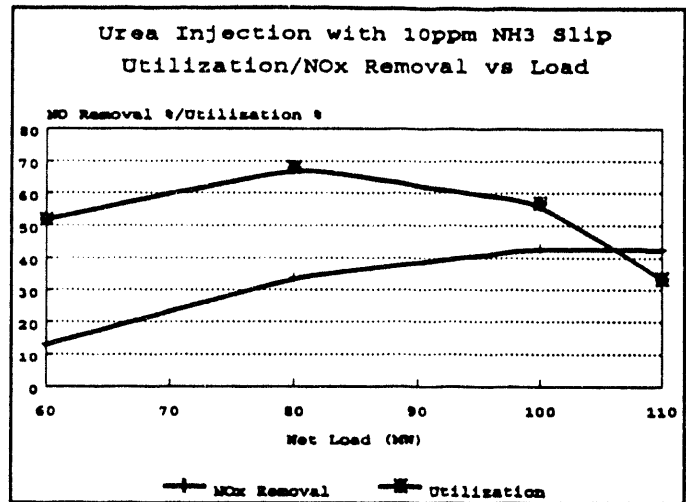
*Ammonia/Urea Comparison*



**Figure 13 - Urea Injection NOx Rem.**

While urea injection allows reasonable levels of $NO_x$ removal at higher loads, it was not very effective at low loads. In an effort to increase low load removal, the urea injection system was modified with an on-line ammonia conversion system. This system converts urea to liquid ammonia compounds immediately before injection into the boiler. As ammonia reacts faster than urea and in a lower temperature window, it was expected to provide higher $NO_x$ removal at low load. Although various ammonia compounds have been tested at other sites, this is believed to be the first site where both chemicals have been used on the same full scale coal-fired utility boiler. Figure 14 shows the $NO_x$ removal and utilization data obtained with ammonia verses urea injection. At all loads, ammonia injection provided slightly higher $NO_x$ reductions at an equivalent ammonia slip. However, ammonia was generally much less efficient than urea, as shown by the lower utilization at loads above 70 MWe. At 60 MWe ammonia utilization is nearly 75% while urea utilization is reduced to only 45%, at injection rates limiting $NH_3$ slip to 10 ppm.

As load is reduced below 60 MWe, the temperatures at Arapahoe Unit 4 are too cold for efficient $NO_x$ removal with either chemical. Although some $NO_x$ removal is possible at 10 ppm slip, the small quantities are not economically productive. The automatic control system has been programmed to stop chemical injection at loads below 60 MWe. As Arapahoe 4 is usually operated under dispatch control in the range of 60 to 110 MWe, this will not be a major issue. If a significant period of operation is expected below 60 MWe, the unit is removed from dispatch control. At that same time the urea
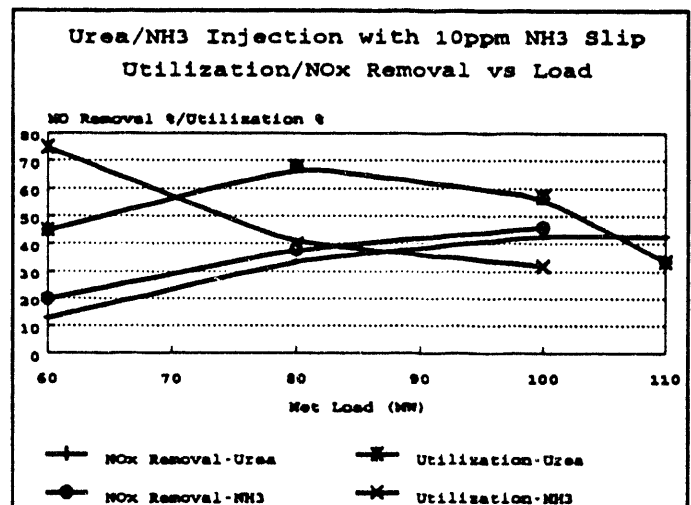


**Figure 14 - Urea/NH3 NOx Rem**

injection system will be shutdown and then restarted when load demand increases.

## N₂O Generation

In addition to creating unwanted ammonia emissions, SNCR can increase nitrous oxide (N₂O) emissions. Figure 15 shows the increase in N₂O emissions as a percentage of the NO$_x$ removed for three different loads. The N₂O generation at both 100 MWe and 80 MWe is very similar and is high at 25 to 30% of the total NO$_x$ reduction. At reduced loads, i.e. lower flue gas temperature, N₂O was substantially reduced to under 20%. It appears that N₂O generation is related to temperature as is NO$_x$ removal. At points where NO$_x$ removal is very efficient, N₂O generation is high. At lower temperatures where urea utilization is reduced, N₂O generation is also reduced.

Figure 16 shows the N₂O generation while injecting ammonia at three different loads. While the trends are similar to those for urea, the levels of N₂O generated are substantially less with ammonia injection; less than 8% conversion. It should also be noted that



**Figure 15 - Urea N₂O Generation**



**Figure 16 - NH₃ N₂O Generation**

the data shown in Figure 16 are for the converted urea. If conversion is not 100% to ammonia, then the N₂O levels would be expected to be somewhat higher compared to the injection of pure ammonia.

## Dry Sorbent Injection Testing

Testing of the dry sorbent injection (DSI) system at Arapahoe 4 using calcium hydroxide has just recently been completed. Unfortunately, only minimal data is available at this time. Testing consisted of three phases, duct injection with humidification, economizer injection without humidification, and economizer injection with humidification. All testing to date has been with low sulfur coal with baseline SO₂ emissions in the range of 400 ppmc.
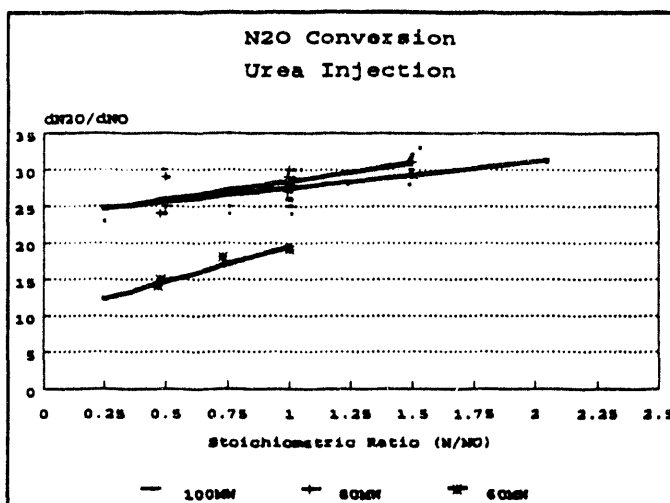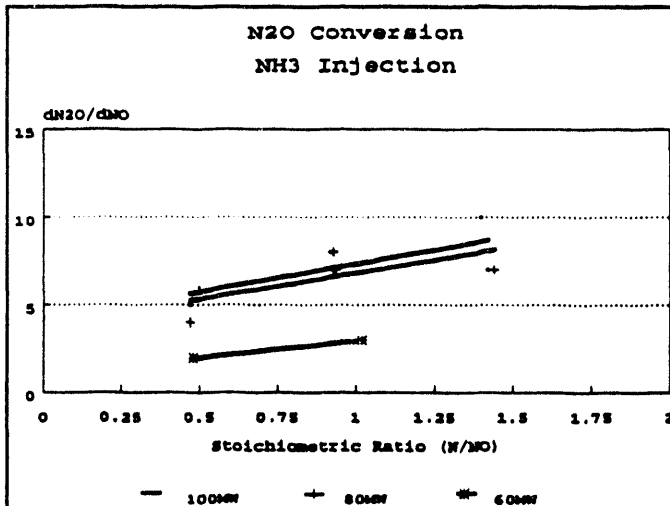
The most difficult testing task has been determining an accurate dry bulb temperature and the associated approach to saturation temperature ahead of the fabric filter . The original system consisted of a 12 point thermocouple grid 58 feet downstream of the humidification system. During initial operation it was found that the thermocouples within the grid were getting wet and thus the temperature obtained was not an accurate dry bulb temperature. A new 12 point thermocouple grid was installed at the entrance to the fabric filter 104 feet from the humidification system. The new temperature grid was more accurate than the original but at high loads generally under reported the dry bulb temperature. A portion of the thermocouples within the grid were then shielded to prevent direct water impact to the thermocouple. The inlet dry bulb temperatures now closely agree with the fabric filter outlet temperature and it is believed that an accurate approach to saturation temperature can be obtained.

The maximum $SO_2$ removal obtained has been in the range of 35 to 40%. This removal was obtained during a short term test with calcium hydroxide injected into the duct at a stoichiometric ratio of 2.0 and with the humidification system operating at a 20 to 25°F approach to saturation. Immediately after this test, problems developed with the flyash transport system and all bags in a small pulse jet filter were replaced. It is suspected that the low approach operation contributed to this problem although other possible causes for the replacement exist. It is currently believed that a 30°F approach temperature is more realistic and can be maintained for long periods without negative effects on the fabric filter. At this higher approach, $SO_2$ removal is reduced to a range of 25 to 30% at a stoichiometry of 2.0.

$SO_2$ removal has been substantially less than expected with calcium hydroxide injection at the economizer. Pilot scale testing in the range of 1000°F has shown the potential for $SO_2$ removals near 50%. At Arapahoe, initial testing at a stoichiometry of 2.0 without humidification resulted in $SO_2$ removals in the range of 5 to 8%. It was found that distribution of the sorbent with the original nozzles was very poor, and only approximately 1/3 of the flue gas was being treated. Although $SO_2$ removals of slightly above 30% were obtained in the area of treatment, the local stoichiometry in this area is estimated at 6.0. New nozzles that increase distribution to approximately 2/3 of the flue gas were installed on one-half of the boiler. With the improved distribution, $SO_2$ removal was increased to 10 to 12% at a stoichiometry of 2. Although distribution of the calcium reagent is not perfect, it appears that high levels of $SO_2$ removal are not possible at Arapahoe 4 using the current calcium hydroxide material; even in areas with high stoichiometries. Samples of the reagent have been analyzed for surface area and particle size; both parameters being important for economizer injection. The BET surface area of the $Ca(OH)_2$ is 14.8 m2/gm and the mass mean particle size diameter is 2.7 microns (determined by sedimentation). The relatively low surface area of the $Ca(OH)_2$ may be contributing to the low $SO_2$ removals obtained with economizer injection.

Operation of the humidification system during economizer injection increases $SO_2$ removal slightly. The economizer injection testing was completed before the addition of the thermocouple shields discussed above and the exact approach to saturation during this testing is unknown. At an estimated approach of 50°F, humidification increased the $SO_2$

removal of economizer calcium injection by approximately 4%. It is suspected that the calcium reagent has undergone chemical or available surface area changes that greatly decrease reactivity of the calcium hydroxide. Laboratory analysis of samples obtained upstream of the humidification grid are in progress to determine the reason for the low $SO_2$ removal efficiency during humidification.

## CONCLUSIONS

Public Service Company of Colorado, in cooperation with the U.S. Department of Energy and the Electric Power Research Institute, has installed the Integrated Dry $NO_x/SO_2$ Emissions Control System. The system has been in operation for over a year and preliminary conclusions are as follows:

- $NO_x$ reduction during baseload operation of the unit with the low-$NO_x$ burners and overfire air ranges from 62 to 69% with no increase in unburned flyash carbon or CO emissions.

- Low-$NO_x$ burners provided the majority of the $NO_x$ reduction, while the overfire air system supplied approximately 8 to 20% additional $NO_x$ reduction.

- $NO_x$ emissions increased by up to 20% at Arapahoe 4 during normal load following operation when compared to baseload operation.

- Urea injection allows an additional 13 to 43% $NO_x$ removal with an ammonia slip of 10 ppm at the fabric filter inlet. This increases total system $NO_x$ reduction to nearly 80%, significantly exceeding the project goal of 70%.

- Higher $NO_x$ reduction is possible using ammonia as the SNCR chemical, but significantly higher stoichiometric ratios are required at loads above 70 MWe.

- $N_2O$ generation is a potential concern with urea injection but was greatly reduced when ammonia compounds were injected.

- $SO_2$ removals with the calcium-based dry sorbent injection have been less than expected with a maximum short term removal rate approaching 40%.

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## ACKNOWLEDGEMENTS

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