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INTEGRATED DRY NO_x/SO₂ EMISSIONS CONTROL SYSTEM
LOW-NO_x COMBUSTION SYSTEM SNCR TEST REPORT

(Test Period: January 11 to April 9, 1993)

DOE Contract Number DE-FC22-91PC90550

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November 1993

Final: June 1994

Patents Cleared by Chicago on JUN 30 1994

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DOE I.D. DE-FC22-91PC90550

Gentlemen:

We are sending herewith the final version of the *Low-NO_x Combustion System SNCR Test Report*. This final report has been modified to include your previous comments and has received the required patent clearance.

Please advise us if you have any questions.

Sincerely,

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ACKNOWLEDGEMENTS

The authors would like to thank Mr. George Brown (Plant Manager), Mr. Brad Govert (Results Engineer), and the Arapahoe Station maintenance and operating staff for the exceptional cooperation they have provided during this project. Special thanks are also deserved by Mr. Tom Arrigoni and Mr. David Hunter, at the PETC DOE office, whose advice and contributions are greatly appreciated. The advice and technical assistance provided by Mr. Jeff Stallings and Ms. Barbara Toole-O'Neil at EPRI have also been of great assistance throughout the project. The assistance provided by Mr. Jochen Steinberger of NOELL, Inc., during start-up and shake-down of the SNCR injection and conversion systems was also greatly appreciated. Last, but definitely not least, is our appreciation to the many PSCC Engineering and Construction personnel and other contractors who have made the integrated Dry NO_x/SO₂ Emissions Control System a success.

ABSTRACT

The DOE sponsored Integrated Dry NO_x/SO₂ Emissions Control System program, which is a Clean Coal Technology III demonstration, is being conducted by Public Service Company of Colorado. The test site is Arapahoe Generating Station Unit 4, which is a 100 MWe, down-fired utility boiler burning a low-sulfur western coal. The project goal is to demonstrate up to 70 percent reductions in NO_x and SO₂ emissions through the integration of: 1) down-fired low-NO_x burners with overfire air; 2) Selective Non-Catalytic Reduction (SNCR) for additional NO_x removal; and 3) dry sorbent injection and duct humidification for SO₂ removal. The effectiveness of the integrated system on a high-sulfur coal will also be tested.

This report documents the fourth phase of the test program, where the performance of the SNCR system, after the low-NO_x combustion system retrofit, was assessed. Previous to this phase of testing, a subsystem was added to the existing SNCR system which allowed on-line conversion of a urea solution to aqueous ammonium compounds. Both converted and unconverted urea were investigated as SNCR chemicals. Other parameters investigated included boiler load, the amount of chemical injected, as well as injection parameters (amount of mixing air, dilution water flow, and injector liquid orifice sizes).

Converted urea provided higher NO_x removals across the load range for a fixed level of NH₃ slip than urea. At full load with 10 ppm slip, NO_x removals of 44 and 47 percent could be obtained with urea and converted urea, respectively. However, the increased

removals with converted urea required higher chemical injection rates; thus, at loads of 80 MWe and higher, urea was the most efficient chemical. Byproduct N_2O emissions were lower for converted urea compared to urea.

Peak NO_x removals for urea injection with the retrofit low- NO_x combustion system were similar to those seen with the original burners, but the load at which the peak occurred increased from approximately 70 to 100 MWe. This shift was a result of a decrease in furnace exit gas temperature seen after the retrofit. On a normalized basis, both NH_3 and N_2O emissions with the retrofit combustion system were higher than those for the original burners, over the entire load range.

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LIST OF DEFINITIONS

AC	Alternating Current
B&W	Babcock & Wilcox
CEM	Continuous Emission Monitor
DCS	Distributed Control System
DOE	U. S. Department of Energy
DRB-XCL [®]	Dual Register Burner - Axially Controlled Low-NO _x
EDTA	Ethylenedinitro Tetracetic Acid
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
FEGT	Furnace Exit Gas Temperature
FERCO	Fossil Energy Research Corp.
FGR	Flue Gas Recirculation
gpm	Gallons Per Minute
HVT	High Velocity Thermocouple, suction pyrometry
LCP	Local Control Panel
LNB	Low-NO _x Burner
MWe	MegaWatts (electrical)
nm	Nanometers
N/NO	Molar Ratio of Nitrogen Injected (in the SNCR Chemical) to the NO Present in the Flue Gas
OFA	OverFire Air
OOS	Out Of Service
PLC	Programmable Logic Control
ppm	Parts Per Million
ppmc	Parts Per Million Corrected to 3 percent O ₂ level
PSCC	Public Service Company of Colorado
psig	Pounds per Square Inch Gauge
RATA	Relative Accuracy Test Audit
SCFM	Standard Cubic Feet per Minute, measured at 1 atmosphere and 60°F
SNCR	Selective Non-Catalytic NO _x Reduction

EXECUTIVE SUMMARY

This test report summarizes the technical activities and results for one phase of a Department of Energy sponsored Clean Coal Technology III demonstration of an Integrated Dry NO_x/SO₂ Emissions Control System for coal-fired boilers. The project is being conducted at Public Service Company of Colorado's Arapahoe Generating Station Unit 4 located in Denver, Colorado. The project goal is to demonstrate up to 70 percent reductions in NO_x and SO₂ emissions through the integration of existing and emerging technologies including: 1) down-fired low-NO_x burners with overfire air; 2) Selective Non-Catalytic Reduction (SNCR) for additional NO_x removal; and 3) dry sorbent injection and duct humidification for SO₂ removal.

Due to the number of technologies being integrated, the test program has been divided into the following test activities:

- Baseline tests with the original combustion system (completed)
- Baseline tests with the original combustion system and SNCR (completed)
- Low-NO_x Burner (LNB)/Overfire Air (OFA) tests (completed)
- LNB/OFA/SNCR tests (completed, subject of this report)
- LNB/OFA/Calcium Injection tests
- LNB/OFA/Sodium Injection tests
- LNB/OFA/SNCR Dry Sorbent Injection tests (integrated system)
- High-Sulfur Coal tests with the integrated system
- Air Toxics Characterization

This report presents the results of the Selective Non-Catalytic Reduction tests performed after the combustion system retrofit on the Arapahoe Unit 4 boiler. Previous to this phase of testing, a subsystem was added to the existing SNCR injection system which allows on-line conversion of a urea solution to ammonium compounds. Both converted and unconverted urea were investigated as SNCR chemicals. At the conclusion of this report, the NO_x reduction performance of SNCR with the retrofit low-NO_x combustion system is compared to that for the original combustion system as documented during the second phase of the program.

The LNB/OFA/SNCR test program was conducted over a thirteen (13) week period from January 11, 1993, to April 9, 1993. During this time period, a parametric investigation of the effects of boiler load, chemical injection rate, and injection system parameters (mixing air and dilution water flow rates) was conducted for both converted and unconverted urea. Liquid injection nozzle diameters were optimized with urea injection before the parametric performance tests were conducted. The affect of operating the SNCR system with various mill out of service patterns was also assessed with urea injection.

The parameters found to have the greatest effect on process performance were boiler load and chemical injection rate (N/NO molar ratio). The effects of mixing air and dilution water flow rates were found to be small over the range of flows tested. Variations in boiler load showed the largest effect on system performance, due to the impact on the local flue gas temperatures in the area of chemical injection. SNCR is a highly temperature-dependent process with only a narrow window available for maximum NO_x removal.

As expected, increased SNCR chemical flow rates yielded higher NO_x removals, with the tradeoff of higher NH₃ emissions accompanying the increased removals. The results showed that NO_x removals were higher with urea than with converted urea for a given chemical injection rate, over nearly the entire boiler load range. NH₃ emissions were also found to be higher with urea. Therefore, for a given NH₃ emission limit, converted urea

tended to provide higher NO_x removals than urea. As shown in Figure S-1, for a 10 ppm NH₃ emission limit NO_x removals of 19 to 47 percent were achievable with converted urea over the load range of 60 to 100 MWe, while urea injection resulted in removals of only 11 to 45 percent. However, over the load range of 80 to 100 MWe, urea was the most efficient chemical since the increased NO_x removals with converted urea required higher chemical feed rates.

Nitrous oxide (N₂O) emissions with converted urea were lower than with urea injection. With converted urea, the fraction of the NO_x reduced which was converted to N₂O ranged from 3 to 8 percent at a nominal N/NO molar ratio of 1.0, depending on load. With urea and a similar N/NO ratio, the conversion ranged from 29 to 35 percent.

Peak NO_x removals for urea injection with the retrofit low-NO_x combustion system were similar to those seen with the original burners, but the boiler load at which the peak occurred increased from approximately 70 to 100 MWe. This shift was a result of a decrease in furnace exit gas temperature seen after the retrofit. On a normalized basis, both NH₃ and N₂O emissions with the retrofit combustion system were higher than those for the original burners, over the entire load range. These increases are also attributed to reduced flue gas temperatures in the region of injection.

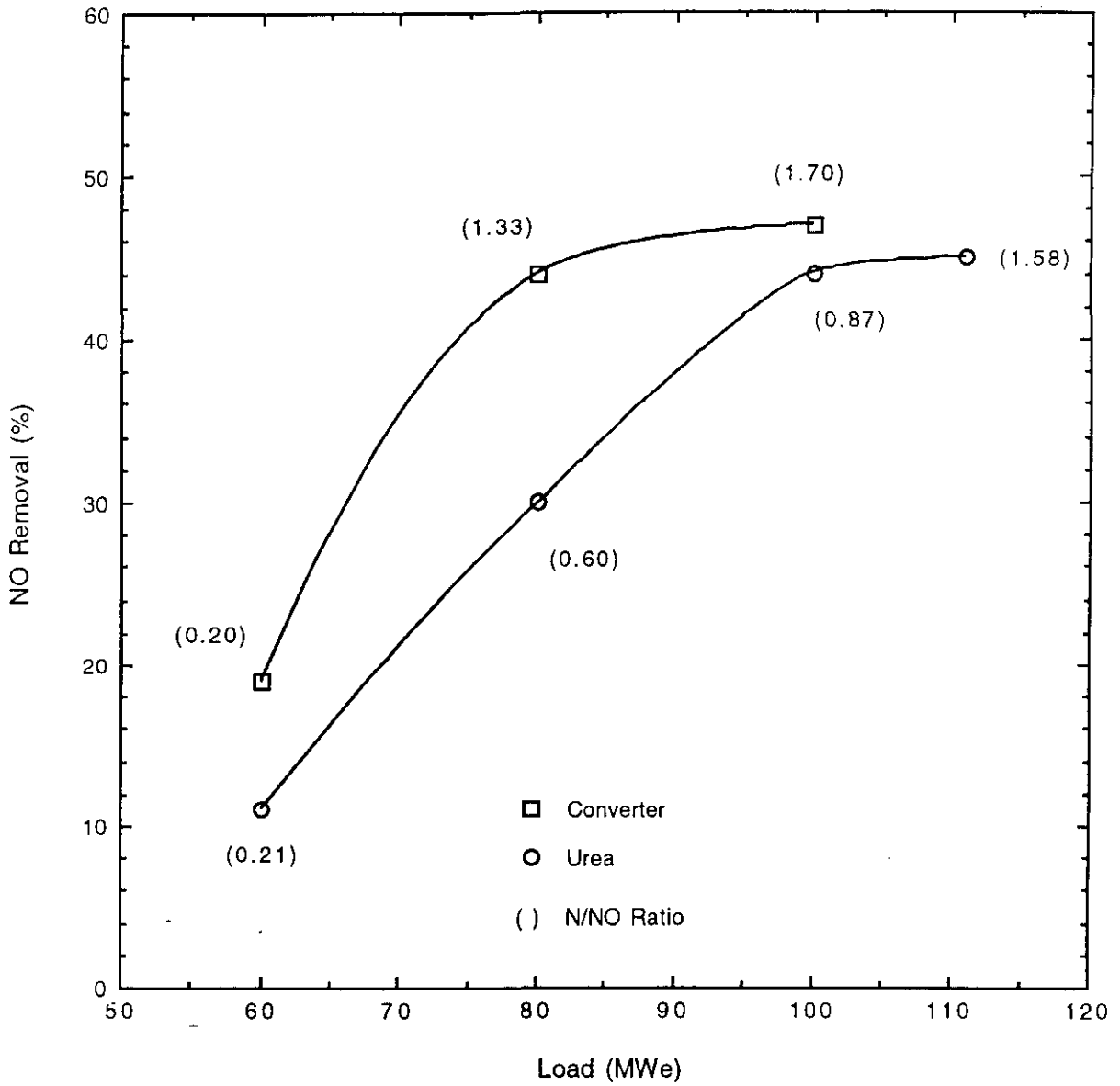


Figure S-1. Comparison of NO Removals for Urea and Converted Urea for a Fixed NH₃ Slip Level of 10 ppm

1

INTRODUCTION

This report presents the results from one phase of the Public Service Company of Colorado (PSCC) and the Department of Energy (DOE) sponsored Integrated Dry NO_x/SO₂ Emissions Control System program. The DOE Clean Coal Technology III demonstration program is being conducted by Public Service Company of Colorado at PSCC's Arapahoe Generating Station Unit 4, located in Denver, Colorado. The intent of the demonstration program at Arapahoe Unit 4 is to achieve up to 70 percent reductions in NO_x and SO₂ emissions through the integration of existing and emerging technologies, while minimizing capital expenditures and limiting waste production to dry solids that are handled with conventional ash removal equipment. The technologies to be integrated are: 1) a down-fired, low-NO_x burner system with overfire air; 2) Selective Non-Catalytic Reduction (SNCR) with urea and aqueous ammonia for additional NO_x removal; and 3) dry sorbent injection (calcium- and sodium-based compounds) and duct humidification for SO₂ removal. Figure 1-1 shows a simplified schematic of the integrated system as implemented at Arapahoe Unit 4.

During the demonstration program, these emissions control systems are being optimized and integrated with the goal of achieving up to 70 percent reductions in NO_x and SO₂. It is anticipated that the emissions control system will achieve these reductions at costs lower than other currently available technologies. It is also anticipated that these technologies will integrate synergistically. For example, an undesirable side effect of sodium-based sorbent injection for SO₂ control has been oxidation of NO to NO₂, resulting in plume colorization. Pilot-scale testing, sponsored by the Electric Power Research

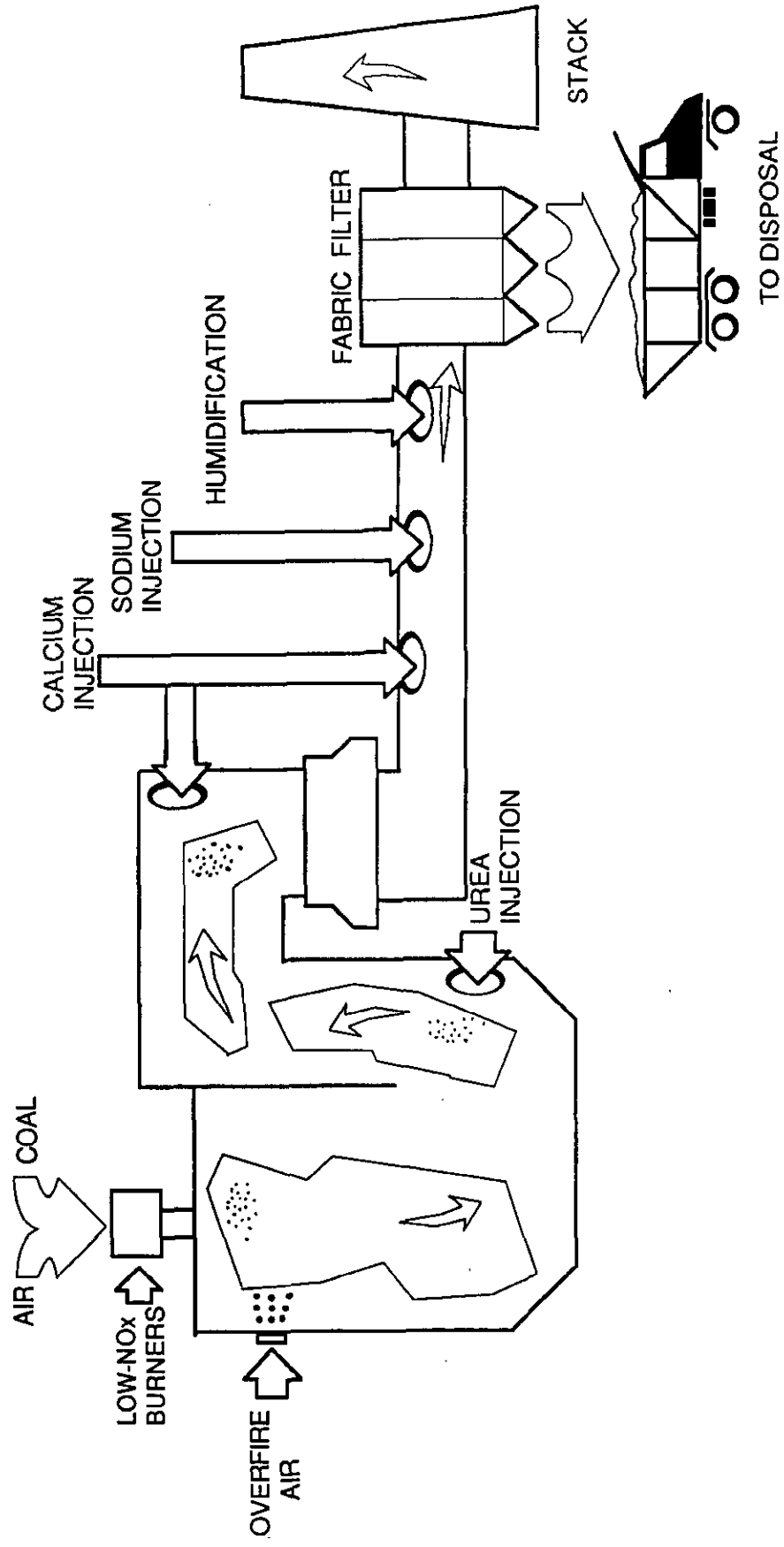


Figure 1-1. Arapahoe Unit 4 Integrated Dry NO_x/SO₂ Emissions Control System

Institute (EPRI), has shown that the presence of NH_3 can reduce the NO_2 emissions resulting from sodium-based dry sorbent injection. In the integrated system, the byproduct NH_3 emissions from the urea injection system will serve to minimize NO_2 formation. An additional objective of this program is to test the effectiveness of the integrated system on a high-sulfur coal.

Due to the number of technologies being integrated, the test program has been divided into the following test activities:

- Baseline tests of the original combustion system. These results provide the basis for comparing the performance of the individual technologies as well as that of the integrated system. (completed)
- Baseline combustion system/SNCR tests. Performance of urea and aqueous ammonia injection with the original combustion system. (completed)
- Low- NO_x burner (LNB)/overfire air (OFA) tests. (completed)
- LNB/OFA/SNCR tests. NO_x reduction potential of the combined low- NO_x combustion system and SNCR. (subject of this report)
- LNB/OFA/calcium-based sorbent injection. Economizer injection and duct injection with humidification.
- LNB/OFA/sodium injection. SO_2 removal performance of sodium-based sorbent.
- Integrated Systems test. NO_x and SO_2 reduction potential of the integrated system using LNB/OFA/SNCR/dry sorbent injection using calcium- or sodium-based reagents. Integrated system performance.
- High-sulfur coal tests. NO_x and SO_2 reduction potential of the integrated system while using an eastern bituminous coal. Dry sorbent injection will be calcium-based using the most efficient injection location determined from previous testing.

In addition to investigation of NO_x and SO_2 emissions, the test program will also investigate air toxic emissions. Air toxic emission levels were obtained during the testing of the low- NO_x combustion system, and with urea injection. Two additional tests will be

conducted during the calcium and sodium injection tests to determine the potential air toxics removal of these pollution control technologies. The air toxics test results will be documented in separate reports.

This report presents the results of the selective non-catalytic reduction tests performed after the combustion system retrofit on the Arapahoe Unit 4 boiler. Previous to this phase of testing, a subsystem was added to the existing SNCR injection system which allows on-line conversion of a urea solution to ammonium compounds. Both converted and unconverted urea were investigated as SNCR chemicals. At the conclusion of this report, the NO_x reduction performance of SNCR with the retrofit combustion system is compared to that for the original combustion system as documented during the second phase of the program.

2

PROJECT DESCRIPTION

The following subsections will describe the key aspects of the technologies being demonstrated, the project participants, and the boiler and the original combustion system. This will be followed by a description of the retrofit low-NO_x combustion system and a brief review of the results of the low-NO_x burner/overfire air tests. Finally, a review of the results of the Selective Non-Catalytic Reduction tests with the original combustion system will be presented.

2.1 Process Description

The Integrated Dry NO_x/SO₂ Emissions Control system consists of five major control technologies that are combined to form an integrated system to control both NO_x and SO₂ emissions. NO_x reduction is accomplished through the use of low-NO_x burners, overfire air, and SNCR, while dry sorbent injection (using either calcium- or sodium-based reagents) is used to control SO₂ emissions. Flue gas humidification will be used to enhance the SO₂ removal capabilities of the calcium-based reagents. Each of these technologies is discussed briefly below.

2.1.1 Low-NO_x Burners

NO_x formed during the combustion of fossil fuels consists primarily of NO_x formed from fuel-bound nitrogen, and thermal NO_x. NO_x formed from fuel-bound nitrogen results from the oxidation of nitrogen which is organically bonded to the fuel molecules. Thermal NO_x forms when nitrogen in the combustion air dissociates and oxidizes at flame

temperatures. Thermal NO_x is of primary importance at temperatures in excess of 2800°F.

To reduce the NO_x emissions formed during the combustion process, Babcock and Wilcox (B&W) Dual Register Burner-Axially Controlled Low- NO_x (DRB-XCL[®]) burners were retrofit to the Arapahoe Unit 4 boiler. Most low- NO_x burners reduce the formation of NO_x through the use of air staging, which is accomplished by limiting the availability of air during the early stages of combustion. This lowers the peak flame temperature and results in a reduction in the formation of thermal NO_x . In addition, by reducing the oxygen availability in the initial combustion zone, the fuel-bound nitrogen is less likely to be converted to NO_x , but rather to N_2 and other stable nitrogen compounds. The B&W DRB-XCL[®] burner achieves increased NO_x reduction effectiveness by incorporating fuel staging in addition to air staging. Fuel staging involves the introduction of fuel downstream of the flame under fuel-rich conditions. This results in the generation of hydrocarbon radicals which further reduce NO_x levels. The fuel staging is accomplished through the design of the coal nozzle/flame stabilization ring on the burner. Additionally, combustion air to each burner is accurately measured and regulated to provide a balanced fuel and air distribution for optimum NO_x reduction and combustion efficiency. Finally, the burner assembly is equipped with two sets of adjustable spin vanes which provide swirl for fuel/air mixing and flame stabilization.

2.1.2 Overfire Air

Low- NO_x burners and overfire air reduce the formation of NO_x by controlling the fuel/air mixing process. While low- NO_x burners control the mixing in the near burner region, overfire air controls the mixing over a larger part of the furnace volume. By diverting part of the combustion air to a zone downstream of the burner, initial combustion takes place in a near stoichiometric or slightly fuel-rich environment. The remaining air necessary to ensure complete combustion is introduced downstream of the primary combustion zone through a set of overfire air ports, sometimes referred to as NO_x ports. Conventional single-jet overfire air ports are not capable of providing adequate mixing across the entire

furnace. The B&W dual-zone NO_x ports, however, incorporate a central zone which produces an air jet that penetrates across the furnace and a separate outer zone that diverts and disperses the air in the area of the furnace near the NO_x port. The central zone is provided with a manual air control disk for flow control, and the outer zone incorporates manually adjustable spin vanes for swirl control.

The combined use of the low-NO_x burners and overfire air ports is expected to reduce NO_x emissions by up to 70 percent.

2.1.3 Selective Non-Catalytic Reduction

NO_x reduction in utility boilers can also be accomplished by Selective Non-Catalytic Reduction (SNCR). This process involves the injection of either urea or ammonia (anhydrous or aqueous) into the combustion products where the gas temperature is in the range of 1600 to 2100°F. In this range, NH₂ is released from the injected chemical which then selectively reacts with NO in the presence of oxygen, forming primarily N₂ and H₂O. A SNCR system is capable of removing 40 to 50 percent of the NO from the flue gas stream.

Urea and ammonia each have their own optimum temperature and range within which NO_x reduction can occur. An example of such a temperature "window" is shown conceptually in Figure 2-1. At temperatures above the optimum, the injected chemical will react with O₂ forming additional NO_x, thereby reducing the NO_x removal efficiency. At temperatures below the optimum, the injected chemical does not react with NO, resulting in excessive emissions of NH₃ (referred to as ammonia slip). Chemical additives can be injected with the urea to widen the optimum temperature range and minimize NH₃ emissions.

The SNCR chemical of primary interest for the present program is urea. The urea is generally injected into the boiler as a liquid solution through atomizers. The atomizing medium can be either air or steam, although air is used in the current installation. The

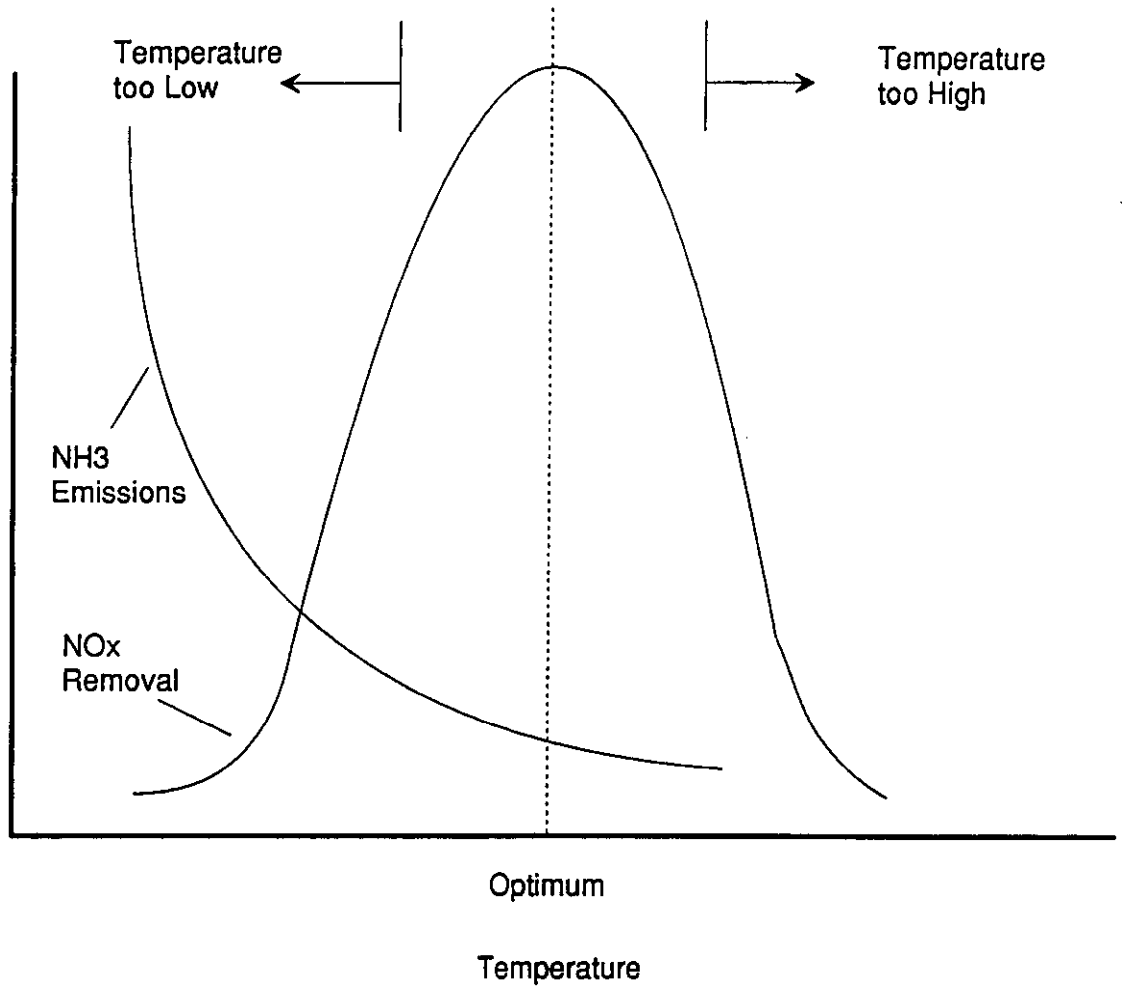


Figure 2-1. Conceptual Temperature Window for the SNCR Process

urea and any additives are stored as a liquid and pumped through the injection atomizers. At Arapahoe Unit 4, a system has also been installed to catalytically convert the urea solution to ammonium compounds.

2.1.4 Dry Reagent SO₂ Removal System

The dry reagent injection system consists of equipment for storing, conveying, pulverizing and injecting calcium- or sodium-based reagents into the flue gas between the air heater and the particulate removal equipment, or calcium-based reagents upstream of the economizer. The SO₂ formed during the combustion process reacts with the sodium- or calcium-based reagents to form sulfates and sulfites. These reaction products are then collected in the particulate removal equipment together with the flyash and any unreacted reagent and removed for disposal. The system is expected to remove up to 70 percent of the SO₂ when using sodium-based products while maintaining high sorbent utilization.

Although dry sodium-based reagent injection systems reduce SO₂ emissions, NO₂ formation has been observed in some applications. NO₂ is a red/brown gas; therefore, a visible plume may form as the NO₂ in flue gas exits the stack. Previous pilot-scale tests have shown that ammonia slip from urea injection reduces the formation of NO₂ while removing the ammonia which would otherwise exit the stack.

In certain areas of the country, it may be more economically advantageous to use calcium-based reagents, rather than sodium-based reagents, for SO₂ removal. SO₂ removal using calcium-based reagents involves dry injection of the reagent into the furnace at a point where the flue gas temperature is approximately 1000°F. Calcium-based materials can also be injected into the flue gas ductwork downstream of the air heater, but at reduced SO₂ removal effectiveness.

2.1.5 Humidification

The effectiveness of the calcium-based reagent in reducing SO₂ emissions when injected downstream of the air heater can be increased by flue gas humidification. Flue gas conditioning by humidification involves injecting water into the flue gas downstream of the air heater and upstream of any particulate removal equipment. The water is injected into the duct by dual-fluid atomizers which produce a fine spray that can be directed downstream and away from the duct walls. The subsequent evaporation causes the flue gas to cool, thereby decreasing its volumetric flowrate and increasing its relative and absolute humidity. It is important that the water be injected in such a way as to prevent it from wetting the duct walls and to ensure complete evaporation before the gas enters the particulate removal equipment or contacts the duct turning vanes. Since calcium-based reagents are not as reactive as sodium-based reagents, the presence of water in the flue gas, which contains unreacted reagent, provides for additional SO₂ removal. Up to 50 percent SO₂ removal is expected when calcium-based reagents are used in conjunction with flue gas humidification.

2.2 Project Participants

PSCC is the project manager for the project, and is responsible for all aspects of project performance. PSCC has engineered the dry sorbent injection system and the modifications to the flyash system, provided the host site, trained the operators, provided selected site construction services, start-up services and maintenance, and is assisting in the testing program.

B&W was responsible for engineering, procurement, fabrication, installation, and shop testing of the low-NO_x burners, overfire air ports, humidification equipment, and associated controls. They are also assisting in the testing program, and will provide for commercialization of the technology. NOELL, Inc. was responsible for the engineering, procurement and fabrication of the SNCR system. Fossil Energy Research Corp. is conducting the testing program. Western Research Institute is characterizing the waste materials and recommending disposal options. Colorado School of Mines is conducting

research in the areas of bench-scale chemical kinetics for the NO₂ formation reaction with dry sorbent injection. Stone & Webster Engineering is assisting PSCC with the engineering efforts. Cyprus Coal and Amax Coal are supplying the coal for the project, while Coastal Chemical, Inc. is providing the urea for the SNCR system.

2.3 Boiler and Original Combustion System Description

Arapahoe Unit 4 is the largest of four down-fired boilers located at the Arapahoe station and is rated at 100 MWe. The unit was built in the early 1950's and was designed to burn Colorado lignite or natural gas. Currently, the main fuel source for the station is a Colorado low-sulfur bituminous coal. Although the unit can be run at full load while firing natural gas, this fuel is only occasionally used to provide load when pulverizers or other equipment are out of service. An elevation view of the boiler is shown in Figure 2-2.

The original furnace configuration was a down-fired system employing 12 intertube burners located on the roof and arranged in a single row across the width of the furnace. A single division wall separates the furnace into east and west halves, each with six burners. Downstream of the burners, the flue gas flows down the furnace and then turns upward to flow through the convective sections on the boiler backpass. After reaching the burner level elevation, the gas passes through a horizontal duct and is then directed downward through a tubular air heater. After leaving the air heater, the flue gas passes through a reverse gas baghouse for particulate control. Induced draft fans are positioned downstream of the baghouse and deliver the flue gas into a common stack for Units 3 and 4.

The original intertube burners were not comparable to a more common wall-fired burner. Each burner consisted of a rectangular coal/primary air duct which was split into 20 separate nozzles arranged in a four by five rectangle that injected the coal/air mixture evenly across the furnace roof. A secondary air windbox surrounded each burner and allowed air flow around each of the individual coal nozzles, resulting in a checkerboard



pattern of coal/primary air and secondary air streams. The burners had no provisions to control the rate of fuel and secondary air mixing.

The burners were numbered one through twelve from west to east. Each of the four attrition mills supplied primary air and coal to three of the burners. The coal piping allowed each mill to supply two burners in one furnace half and one in the other half. Figure 2-3 shows the original burner firing configuration and coal distribution arrangement from the four mills. The secondary air ducts were positioned behind the burners and included a secondary air damper for each burner. When a single burner was removed from service, the secondary air flow was also stopped by closing the associated secondary air damper. The dampers were manually controlled at the burner deck and were intended for on/off duty only.

2.4 Low-NO_x Combustion System Description

The low-NO_x combustion system retrofit at Arapahoe Unit 4 was comprised of work in three areas: the installation of the low-NO_x burners, the addition of an overfire air system, and modifications to the existing boiler control system. Each of these areas is discussed separately in the sections that follow.

2.4.1 Low-NO_x Burners

To reduce the NO_x emissions formed during the combustion process, B&W DRB-XCL^R burners were retrofit to the Arapahoe Unit 4 boiler. Figure 2-4 shows a simplified schematic of the burner. The burner has two main design features which limit the formation of NO_x. First is the addition of a sliding air damper. In many older burner designs, a single register is used to control both total secondary air flow to the burner and also the swirl (i.e., the rate of fuel/air mixing). The use of the sliding damper separates the functions and allows the secondary air flow to be controlled independently of the swirl. The burner includes a circular pitot tube array which provides a relative indication of the secondary air flow to each burner. The second feature is the addition of dual spin vane registers. The most important variable in controlling the formation of NO_x is the rate at

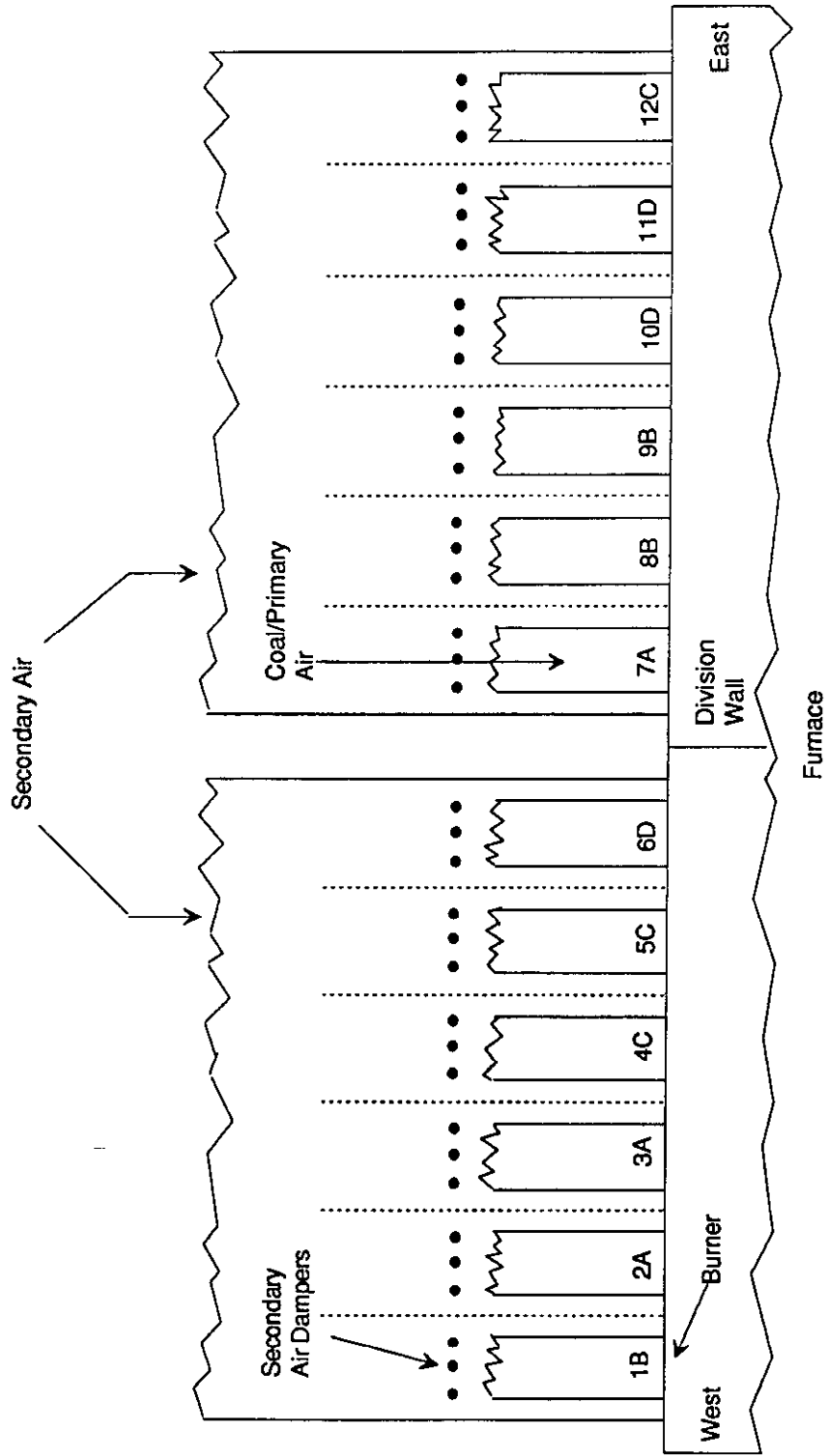


Figure 2-3. Original Burner-Mill Arrangement - Looking to the North
 (Note: the letter next to each burner designates one of the four pulverizers)

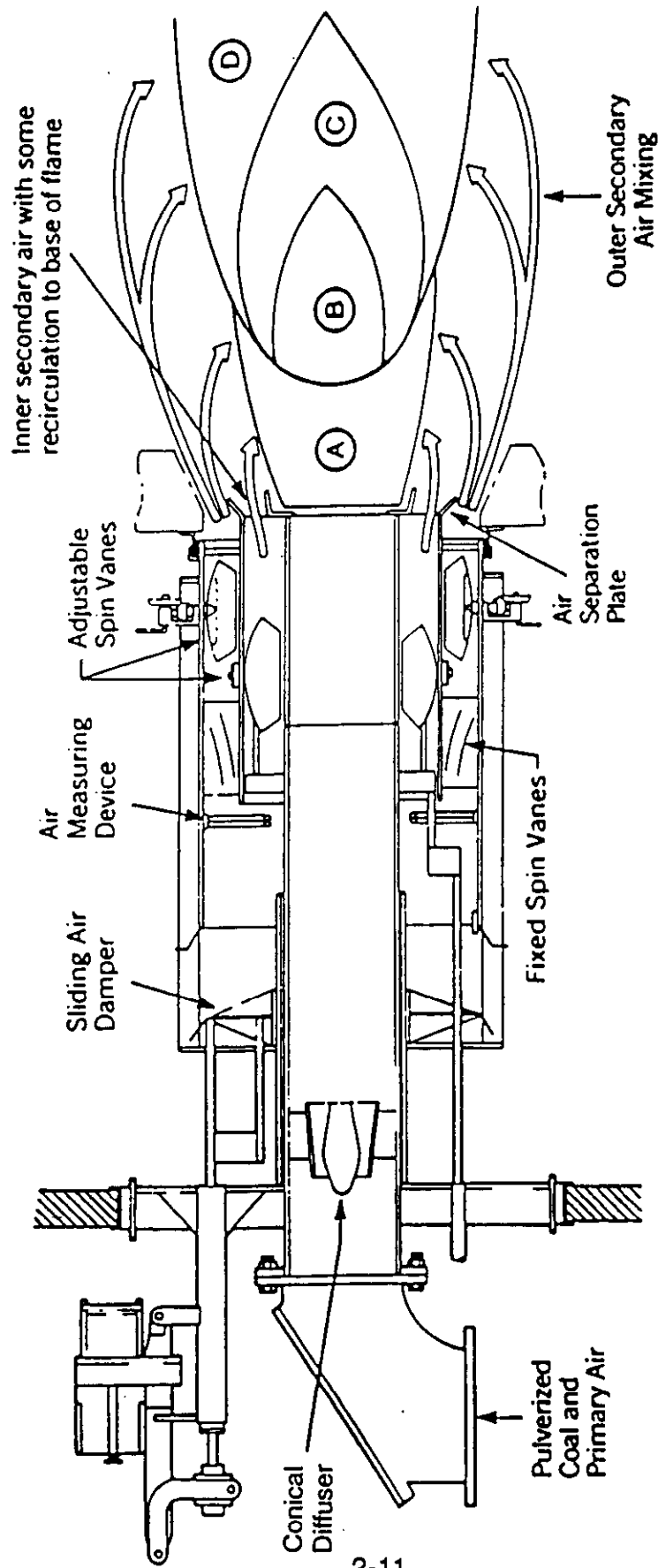


Figure 2-4. B&W DRB-XCL™ Low-NO_x Burner

which oxygen is mixed with the fuel. The dual spin vane registers provide a great amount of control over the amount of swirl imparted to the secondary air, and thus the rate of fuel/air mixing in the near-burner region.

An electric linear actuator is used to adjust the sliding damper which controls the total secondary air to each burner. The control system allows for three disc positions: cool, light and normal. The cool position is used while a burner is out of service and provides a minimum amount of cooling air so that the burner metal temperatures do not exceed the design limit of 1300°F. The light position is used to provide slightly more air while the gas ignitors are firing. The normal position is used while the burners are fired with either coal or natural gas. Limit switches in the actuator are used to adjust the three disk positions. The adjustment of these limit switches allows the secondary air to be individually adjusted at each burner, if burner-to-burner imbalances occur.

The low-NO_x combustion system retrofit at Arapahoe Unit 4 was much more involved than a similar modification to a normal wall- or tangential-fired unit. The original intertube burners were not comparable to "normal" burners, as they required only small openings in the roof tubes. The modifications began by removing everything from the boiler roof tubes to the roof of the boiler enclosure, including the windbox roof, coal and gas piping, and the secondary air supply duct. New roof tubes with twelve circular openings were welded in place to accommodate the new burners.

The burners were placed in 4 rows of 3 burners as shown in Figure 2-5. The boiler has a full division wall that separates the furnace into two approximately square sections. A major problem encountered during the retrofit was the limited space available for burner placement. The outer edge of the burners on each side of the division wall are located within a few inches of each other.

The secondary air duct originally entered the windbox at the rear (south side) of the furnace roof as shown in Figure 2-2. Since the new burners required significantly more

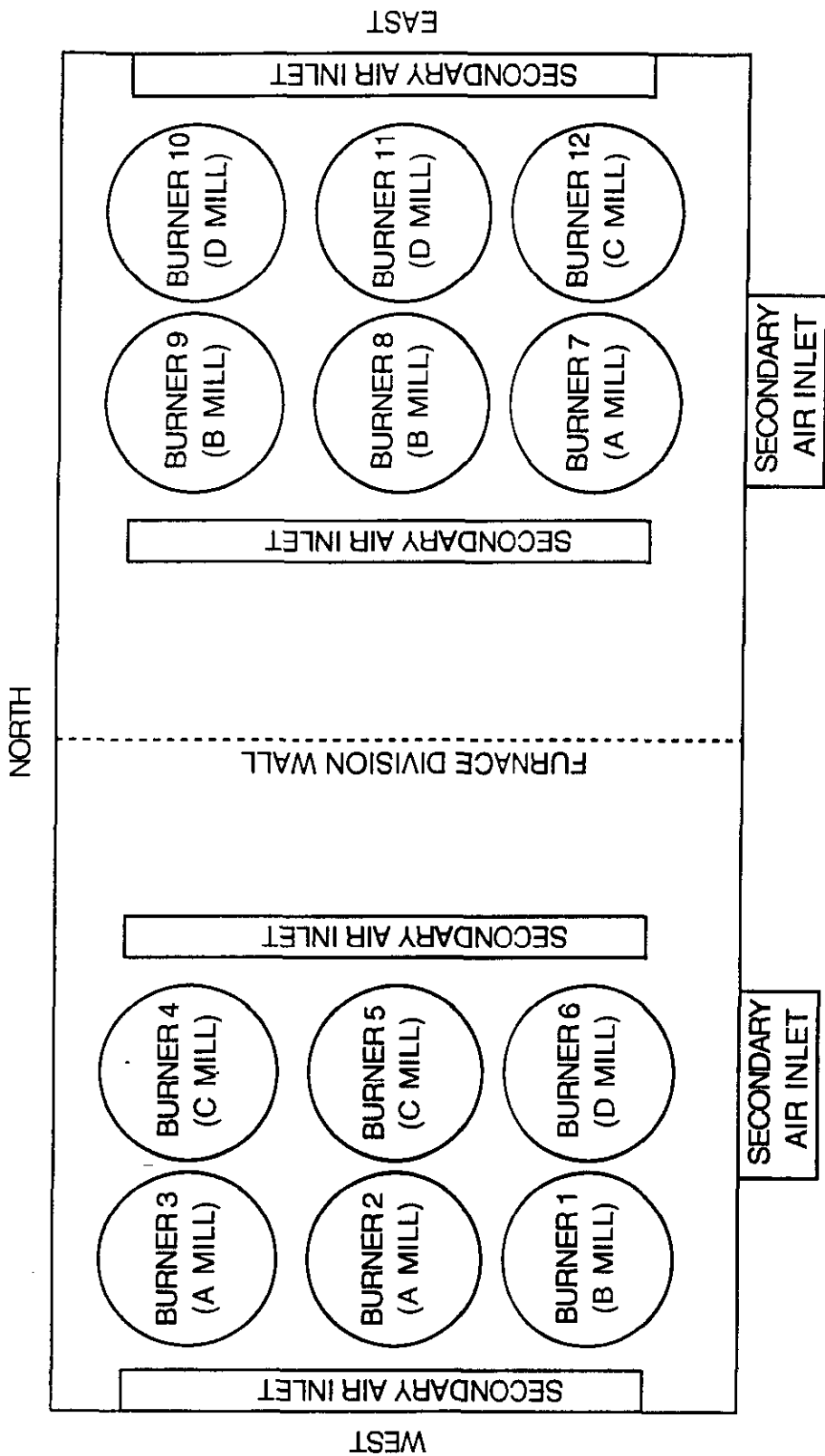


Figure 2-5. Plan View of Burner Arrangement after Retrofit

roof area than the intertube burners, and there were now four burners where the secondary air duct was originally located, providing sufficient secondary air to the windbox became a challenge. The majority of the air is introduced through four "pant-leg" ducts as shown in Figure 2-6. The Arapahoe 4 boiler was originally designed to use flue gas recirculation (FGR) for steam temperature control. However, the system was no longer in use, so two abandoned FGR ducts which entered the front (south) wall of the windbox were used to provide the balance of the secondary air.

The retrofit also included new gas burners, gas ignitors and flame scanners. Arapahoe Unit 4 was originally designed with the ability to fire 100 percent 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 capability to fire 100 percent natural gas was maintained by the use of a gas ring header located at the tip of each burner. No modifications were made to the original Riley pulverizers, although new variable speed feeder drives were added to provide more consistent coal feed.

2.4.2 Overfire Air System

An overfire air system (or in this case, an "underfire" air system due to the down-fired configuration) was also retrofit to the Arapahoe Unit 4 boiler. Three B&W Dual-Zone NO_x Ports were added to the east and west sides of the furnace approximately 20 feet below the boiler roof. A numerical modeling study was performed by B&W in order to determine the optimum size and location for the ports. These ports were designed to inject up to 25 percent of the total secondary air through the furnace sidewalls.

Conventional single-jet overfire air ports are not capable of providing adequate mixing across the entire furnace. The B&W Dual Zone NO_x Ports, however, incorporate a central zone which produces an air jet with sufficient axial momentum to reach across to the division wall and a separate outer zone that diverts and disperses air in the region near the wall. This two-stage injection provides faster mixing and more equal distribution of

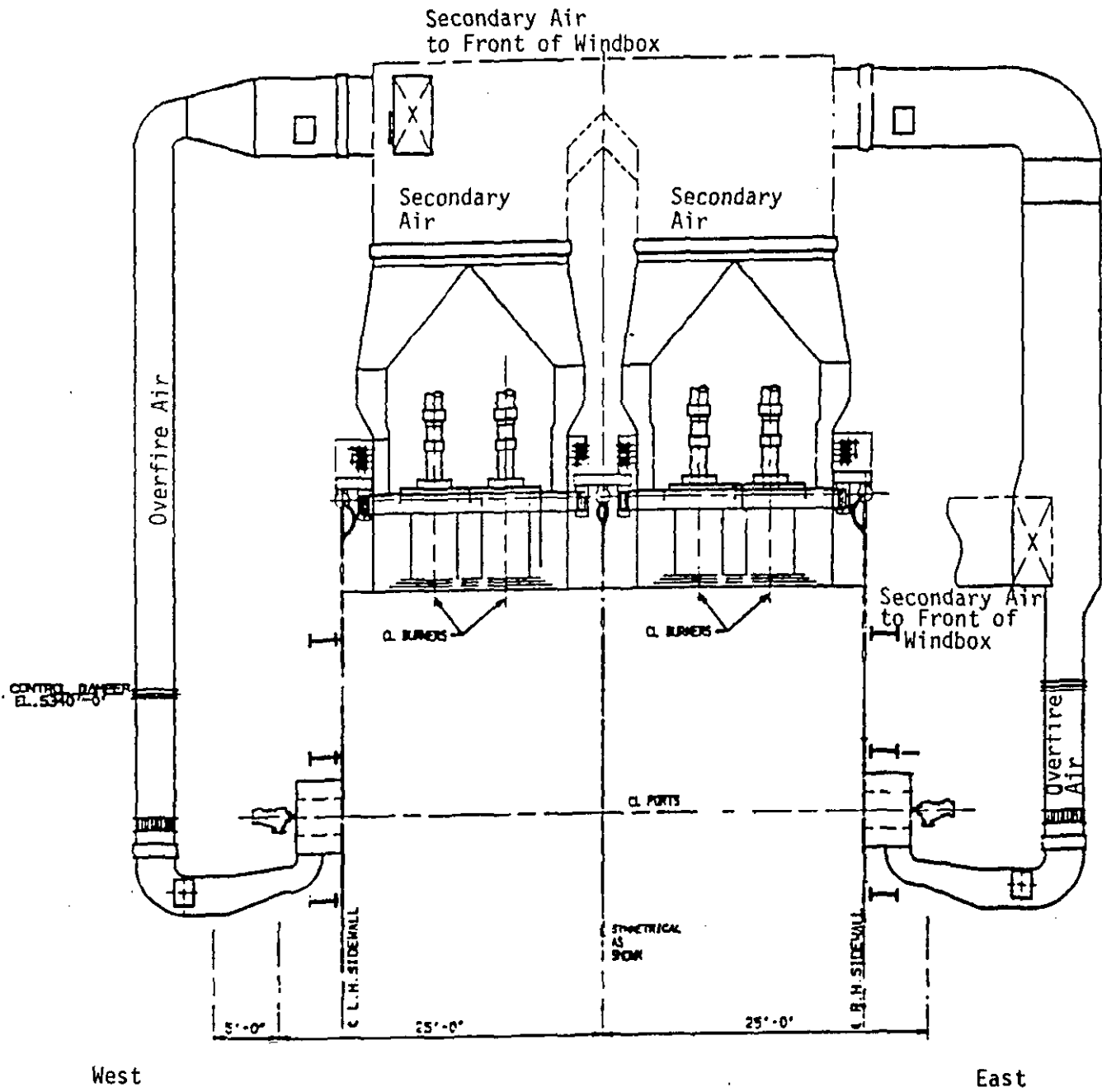


Figure 2-6. Front Sectional of View of Upper Furnace - Looking North

air into the furnace. A schematic of the NO_x port is shown in Figure 2-7. The central zone has a manual air control disk for flow control, and the outer zone incorporates manually adjustable spin vanes for swirl control. Two circular pitot tube arrays provide a relative air flow measurement between the inner and outer flow areas of each port.

The overfire air ports are located on each side of the furnace in a small windbox, as shown in Figure 2-8. New ductwork was added that directs secondary air from the boiler roof to the sidewalls as shown in Figure 2-6. Each of the ducts that supply the overfire air windboxes contains an opposed blade louver damper to control air flow, and a pitot tube grid with a flow straightener to measure total overfire air flow to each side of the furnace. As two sootblowers were originally located on each side of the furnace at the location chosen for the overfire air ports, the retrofit also entailed lengthening (in order to accommodate the depth of the new windboxes) and a slight relocation of these sootblowers.

2.4.3 Control System Modifications

Arapahoe Unit 4 was originally controlled with a Bailey pneumatic control system. The boiler had limited control for burner management and was operated manually. Due to the complexity of the retrofit, a new distributed control system (DCS) was necessary to control the boiler and other pollution control equipment added as part of the Integrated Dry NO_x/SO₂ Emissions Control system. The new burner management system includes both infrared and ultraviolet flame scanners as well as automated controls for most boiler functions. The ignitors and main gas systems were modified for automatic control of all vent and main fuel valves so that the boiler may now be safely started from the control room. The DCS also allows better control of the equipment so that a more efficient control of fuel and air may be maintained during the rapid load swings that occur during load following under automatic control.

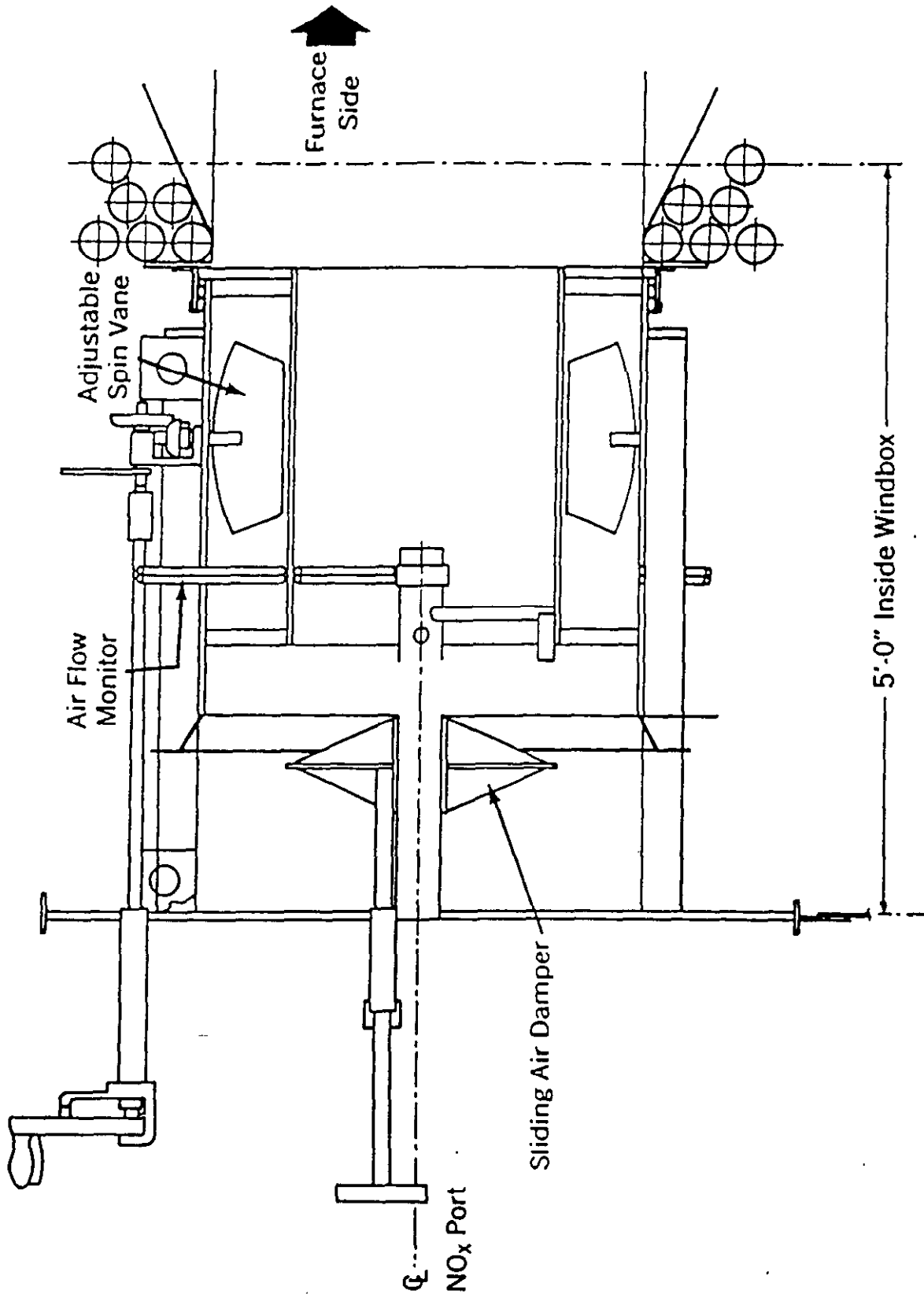


Figure 2-7. B&W Dual Zone NO_x Port

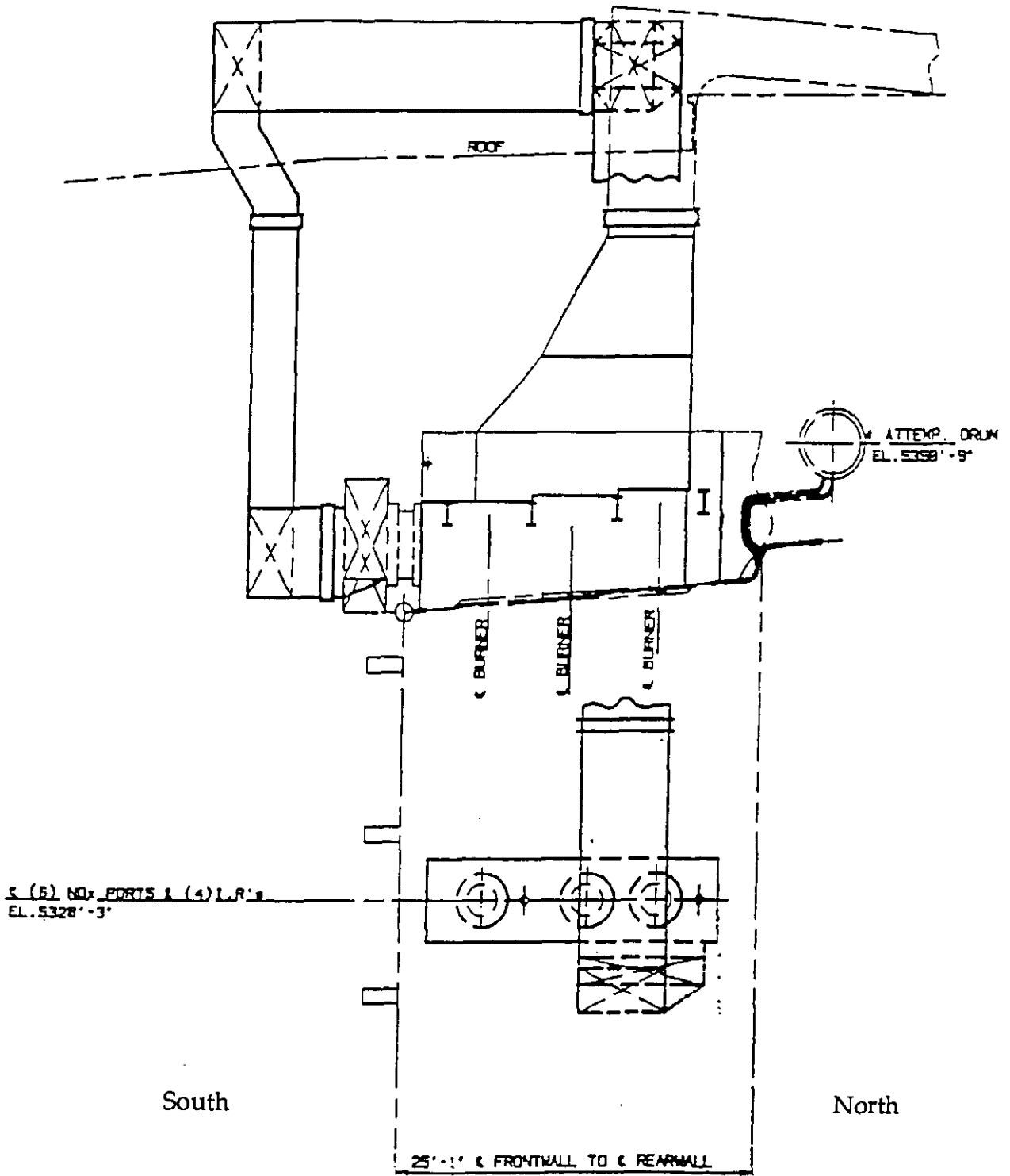


Figure 2-8. Side Sectional View of Upper Furnace - Looking West

2.5 Low-NO_x Burner/Overfire Air Test Results

This section presents a brief summary of the results of the low-NO_x burner/overfire air tests performed after the combustion system retrofit on the Arapahoe Unit 4 boiler. During these tests, the performance of the new combustion system was compared to that of the original system, as documented during the baseline test program. Complete documentation of the baseline and LNB/OFA tests is contained in separate reports^(1,2).

The low-NO_x burner/overfire air test program was conducted over a twelve week period from August 6 to October 29, 1992. The test program consisted of two separate phases. During the first, optimum operating conditions and settings for the burners and overfire air ports were identified. The second phase consisted of a detailed series of tests to assess the performance of the low-NO_x combustion system as a function of various operating parameters. These parameters included boiler load, excess air level, overfire air flow rate, and number of mills in service. These parameters represent the primary factors influencing NO_x and CO emissions and flyash carbon levels. Immediately following the completion of the baseloaded optimization and parametric tests, the boiler was operated for two months (November and December 1992) under normal load following conditions. During this time, emissions data were collected automatically with a Continuous Emissions Monitor (CEM).

NO_x emissions with the retrofit combustion system were 63 to 69 percent lower than those for the original combustion system, depending on boiler load (Figure 2-9). These results were obtained under baseloaded conditions with maximum overfire air (corresponding to 24 percent of the total secondary air flow at full load). OFA port cooling requirements precluded reducing the overfire air flow to zero at this particular installation, thereby limiting the minimum overfire air condition to 15 percent of the total secondary air. Increasing the overfire air flow from 15 to 25 percent resulted in only a 5 to 10 percent increase in NO_x removal. This suggests that the majority of the NO_x removal was due to the low-NO_x burners, and not the overfire air system. However, it must be realized

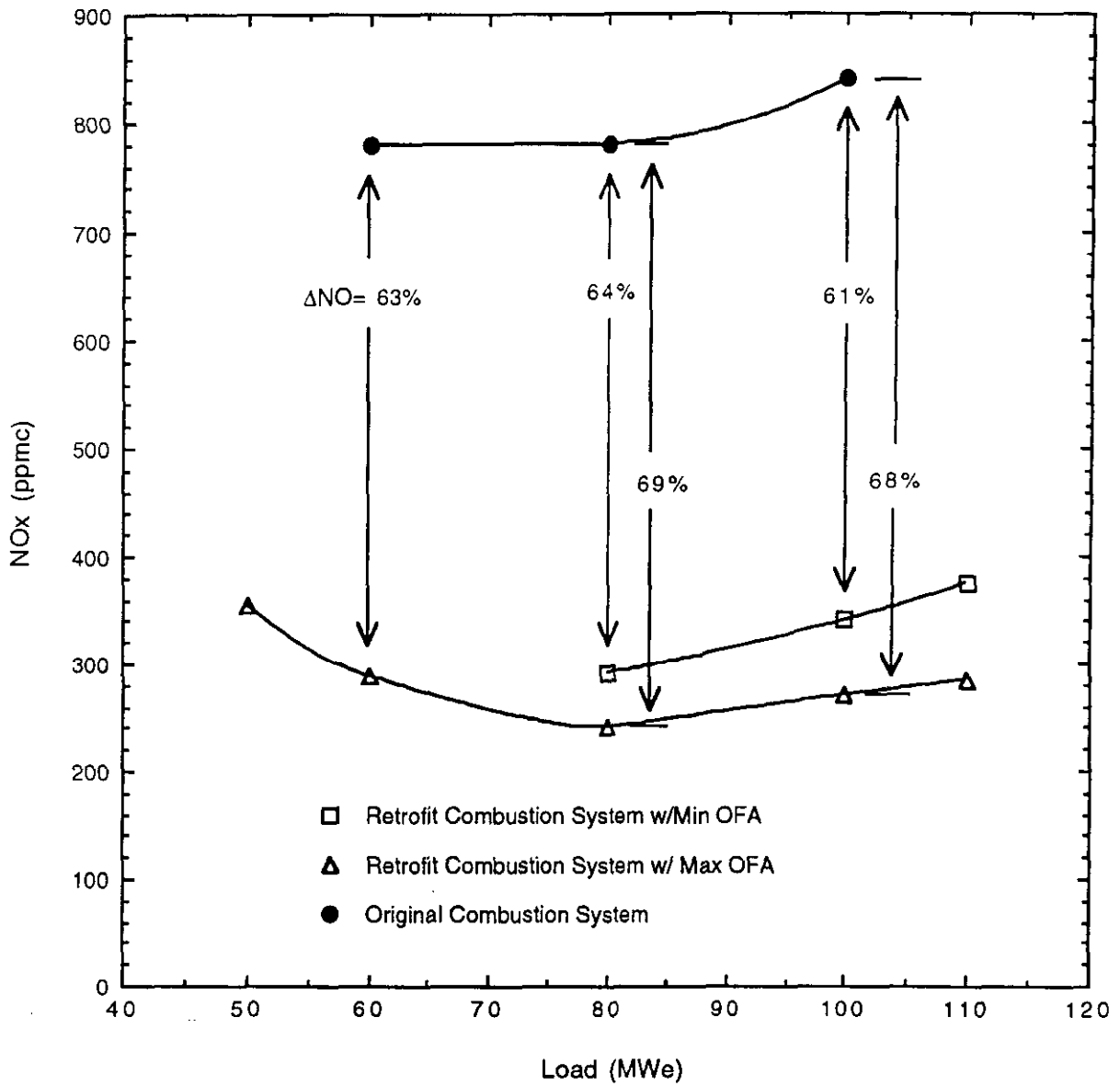


Figure 2-9. NO_x Emissions as a Function of Boiler Load for the Original and Retrofit Combustion Systems

that it was not possible to completely separate the relative roles of the burners and overfire air system at this particular installation due to the inability to reduce the overfire air flow to zero.

For this retrofit, significant reductions in CO emissions and flyash carbon levels were seen with increasing overfire air flow rates. This was contrary to what was expected, and is attributed to increased overfire air penetration to the center of the furnace and increased mixing at the higher flow rates. Overall CO emissions and flyash carbon levels did not increase during baseloaded operation as a result of the combustion system retrofit.

The long-term CEM data showed that NO_x emissions increased by up to 20 percent during normal load following operation when compared to baseloaded conditions. The increase was due to the higher excess air levels normally maintained during load following operation. The long term data also showed that CO emissions increased substantially. *Part of the increase was due to maldistribution of the overfire air, which will be corrected in the future.* The remainder of the increase was due to variations in boiler operating parameters which are inherent in load following operation.

Limited testing showed that while firing natural gas, increases in overfire air flow result in decreased NO_x emissions and higher CO emissions. This NO_x/CO relationship was different from that seen for coal firing, and was attributed to a separation of the mixing effects of the low-NO_x burners and overfire air ports due to the shorter combustion zone under gas-fired conditions.

No major operational problems have developed due to the boiler modifications, although the retrofit combustion system has resulted in a decrease in furnace exit gas temperature of approximately 200°F. This has resulted in an increase in the amount of excess air required to maintain adequate steam temperatures at reduced boiler loads.

2.6 Baseline SNCR Test Results

This section presents a brief summary of the results of the baseline SNCR tests with the original combustion system on the Arapahoe Unit 4 boiler. Complete documentation of the baseline SNCR tests is contained in a separate report⁽³⁾. The objectives of these tests were twofold. First, to start up and check out the functional performance of the SNCR hardware. Second, to provide a preliminary characterization of the SNCR process performance with the original combustion system. This characterization would then serve as a basis of comparison of the combined LNB/OFA/SNCR system to the use of SNCR alone.

The baseline SNCR test program was conducted over a five (5) week period from February 4, 1992, to March 6, 1992. The short time period did not allow a complete optimization of the injection system. In fact, a detailed optimization was not necessarily warranted, as the combustion modifications scheduled for April and May, 1992, were expected to impact operation of the boiler, and therefore change the optimal SNCR operating parameters. A limited parametric investigation of the effects of boiler load, chemical injection rate, and injection system parameters (i.e., injection location, mixing air and dilution water flow rates, and injection nozzle orifice sizes) was accomplished during the five-week period. The injection system parameters were optimized while utilizing urea as the SNCR chemical. The effects of boiler load and chemical injection rate were then assessed for both urea and aqueous ammonia (NH_4OH) injection.

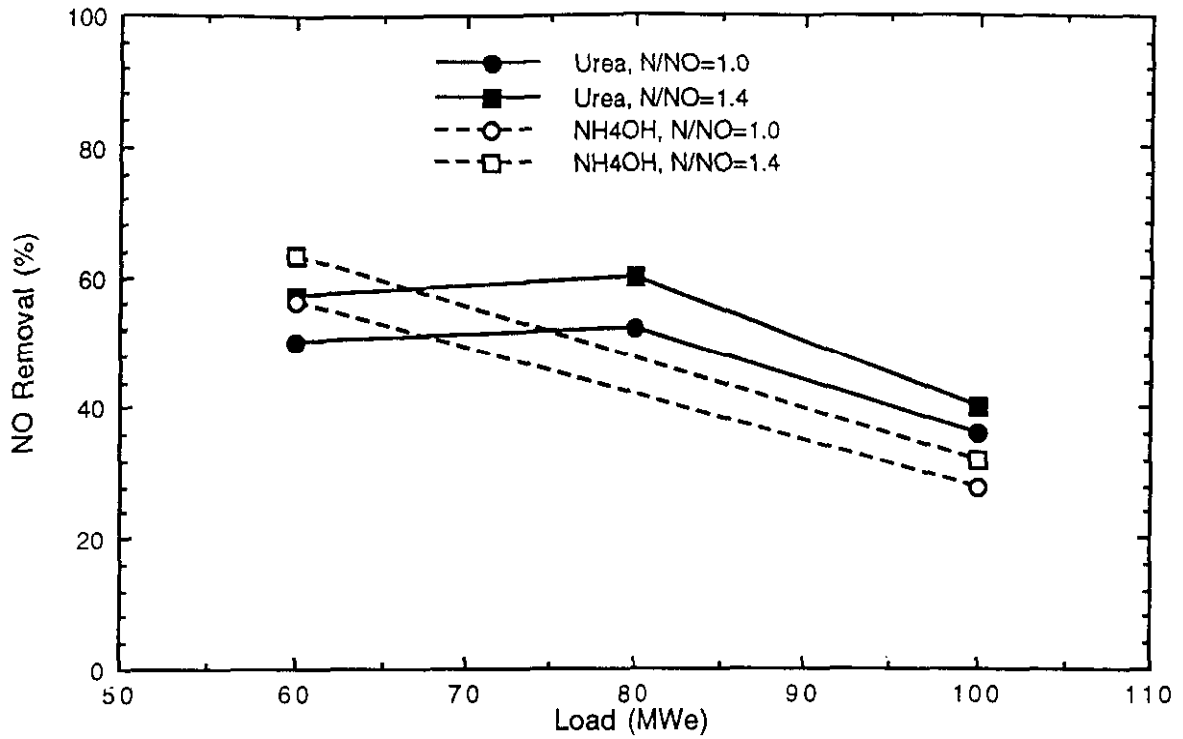
The parameters found to have the greatest effect on process performance were boiler load, chemical injection rate (N/NO molar ratio), and mixing air and dilution water flow rates. The effects of mixing air and liquid orifice sizes were found to be minimal. Although mixing air flow rate had only a slight effect on NO_x removal, large increases in NH_3 emissions resulted from decreased mixing air flow rates. Variations in boiler load and dilution water flow showed the largest effects on system performance, due to their impact on the local flue gas temperatures in the area of chemical injection. SNCR is a highly temperature dependent process with only a narrow window available for maximum NO_x removal.

As expected, increased SNCR chemical flow rates yielded higher NO_x removals, with the tradeoff of higher NH₃ emissions accompanying the increased removals. The results (Figure 2-10a) showed that NO_x removals were higher with urea than with NH₄OH for a given chemical injection rate, over nearly the entire boiler load range. NH₃ emissions were also found to be higher with urea (Figure 2-10b). Therefore, for a given NH₃ emission limit, NH₄OH injection tended to provide higher NO_x removals than urea. As shown in Figure 2-11, for a 10 ppm NH₃ emission limit NO_x removals of 26 to 36 percent were achievable with NH₄OH over the load range of 60 to 100 MWe, while urea injection resulted in removals of only 16 to 36 percent. However, over the load range of 65 to 100 MWe, urea was the most efficient chemical since the increased NO_x removals with NH₄OH required higher chemical feed rates.

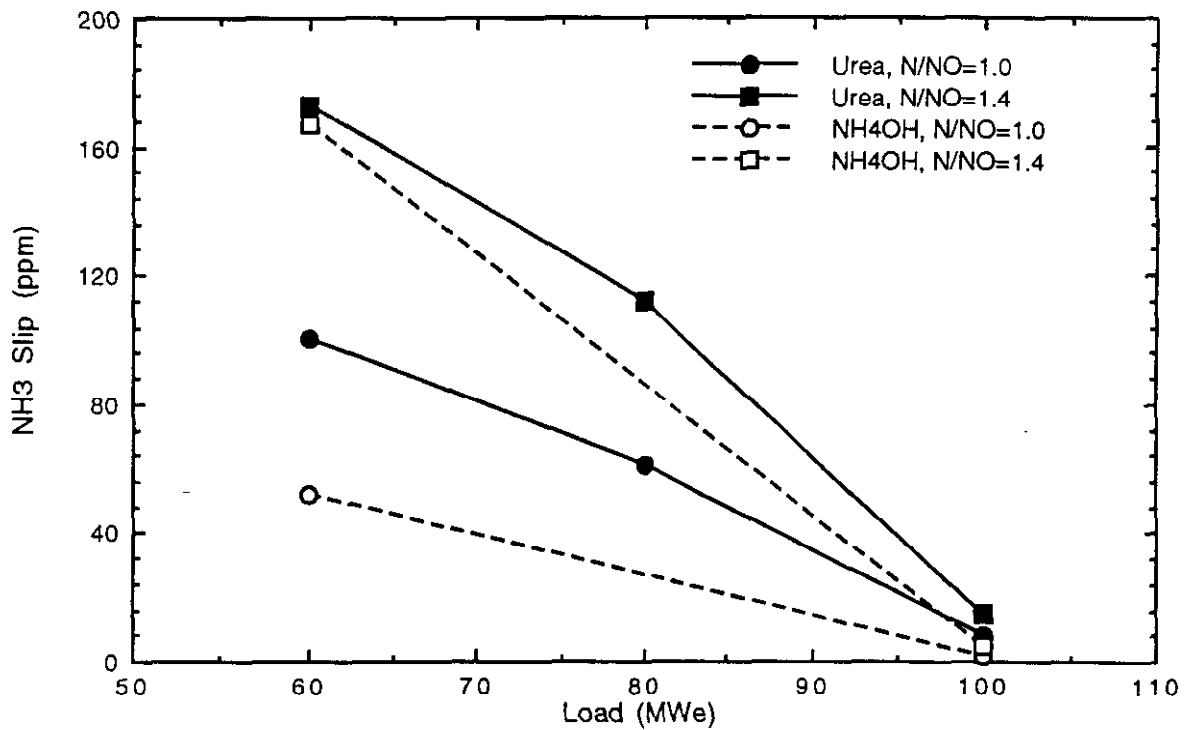
Consistent with previous studies, nitrous oxide (N₂O) emissions with NH₄OH injection were lower than with urea injection. With NH₄OH, the fraction of the NO_x reduced which was converted to N₂O was less than 2 percent at a nominal N/NO molar ratio of 1.0, irrespective of load. With urea and a similar N/NO ratio, the conversion ranged from 9 to 15 percent at 100 and 60 MWe, respectively.

In addition to byproduct emission of NH₃ and N₂O, it was also found that the SNCR process increased CO emissions. The increase in CO emissions with NH₄OH injection was found to be lower than that for urea injection. With NH₄OH, the increase in CO emissions was on the order of 8 ppm at a nominal N/NO molar ratio of 1.0, irrespective of load. With urea and a similar N/NO ratio, the increase in CO emissions ranged from 10 to 40 ppm at 100 and 60 MWe, respectively.

The above comparisons of the performance of urea and NH₄OH are for injection through the same set of injectors, and for the same set of injection conditions (mixing air and dilution water flow rates). The conclusions may not apply to a system that has been independently optimized for the two different SNCR chemicals.



a) NO Removal



b) NH₃ Emissions

Figure 2-10. SNCR Performance with Original Combustion System
(Initial NO_x Level Approximately 850 ppmc)

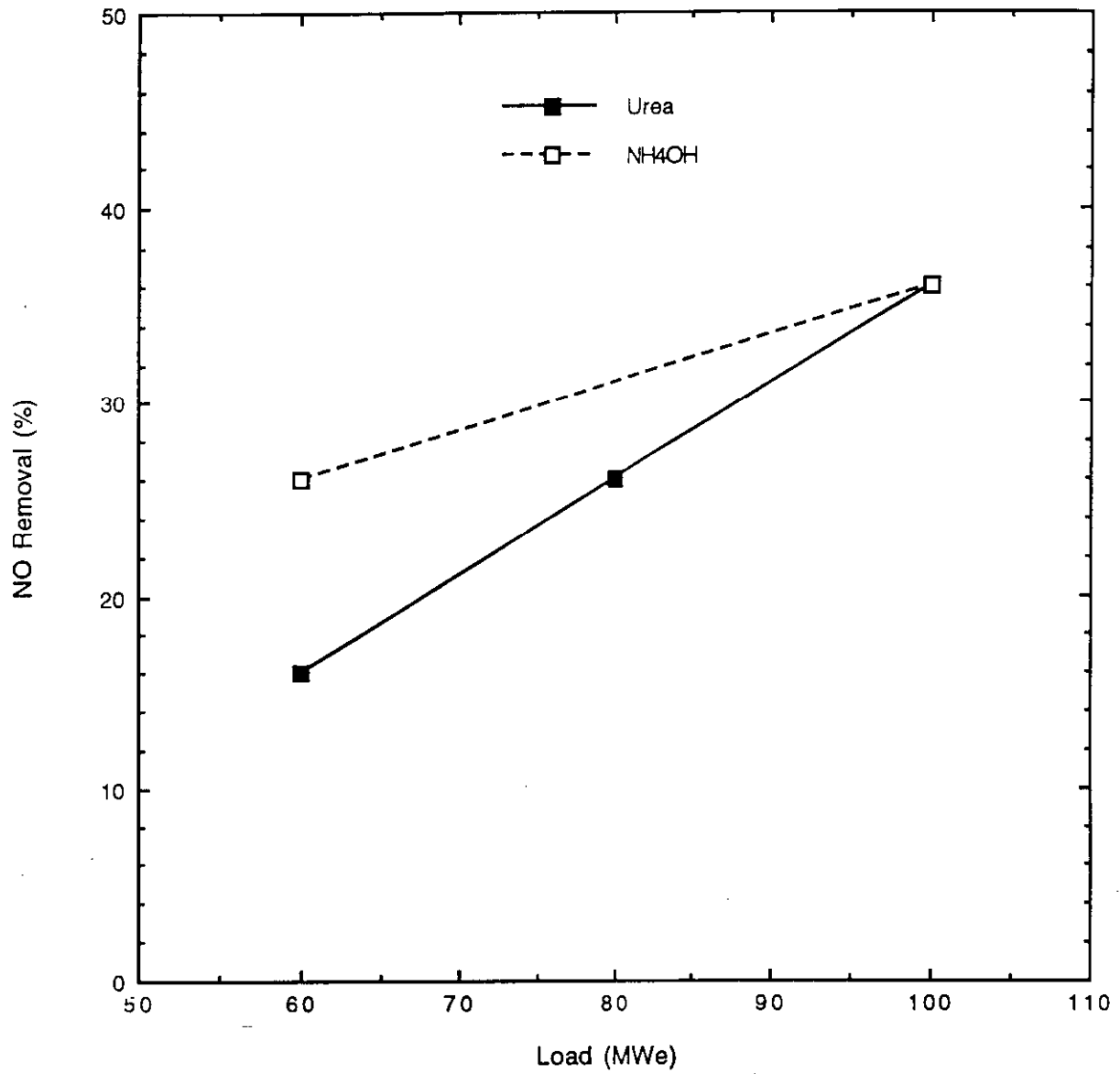


Figure 2-11. Comparison of NO Removals for Urea and NH₄OH for a Fixed NH₃ Slip Level of 10 ppm with the Original Combustion System

before the start of the baseline SNCR tests. The measurements were made in order to locate the temperature regions where urea injection was believed to be most effective (1650 to 1950°F). While it was expected that the combustion modifications would alter the temperature distribution within the boiler, it was believed that the change would be minimal (on the order of only 25°F). Acoustic and suction pyrometry (HVT) techniques were used simultaneously to obtain the gas temperature measurements. The results of these measurements are briefly summarized below, and complete documentation of the temperature measurement tests is contained in a separate report⁽⁶⁾. Figure 3-4 shows the parts used for the temperature measurements. Since the acoustic temperature measurement technique requires a clear line of sight across the furnace at the measurement location, the first available location with acceptable access for the instrument was through a pair of ports just downstream of the first set of screen tubes (Location G in Figure 3-4).

The results of the HVT and acoustic temperature tests made during April 1991 are summarized in Table 3-1. The table shows the average HVT value for each location which is computed from the mean values recorded at each traverse point. The high and low temperatures recorded during each HVT traverse are also indicated, and the averages of the acoustic measurements are shown for each of the three locations where measurements were possible.

Although the table shows that the temperature at each position is a function of load, it also shows an overall temperature distribution which is similar for each load condition. The average temperatures as a function of load are plotted in Figure 3-5 for selected port locations. From this distribution, a generalization regarding the flow field may be inferred. Namely, the upward turn from the furnace exit through the first set of screen tubes forces most of the gas along the back (north) wall of the unit as it enters the convective section. The relatively cool temperatures measured at Port D are likely the result of a recirculation zone which is set up as the gases flow around the wall separating the furnace and convective sides of the unit. In fact, one-tenth scale flow visualization studies (discussed later in this section) confirm the existence of a recirculation zone at this location.

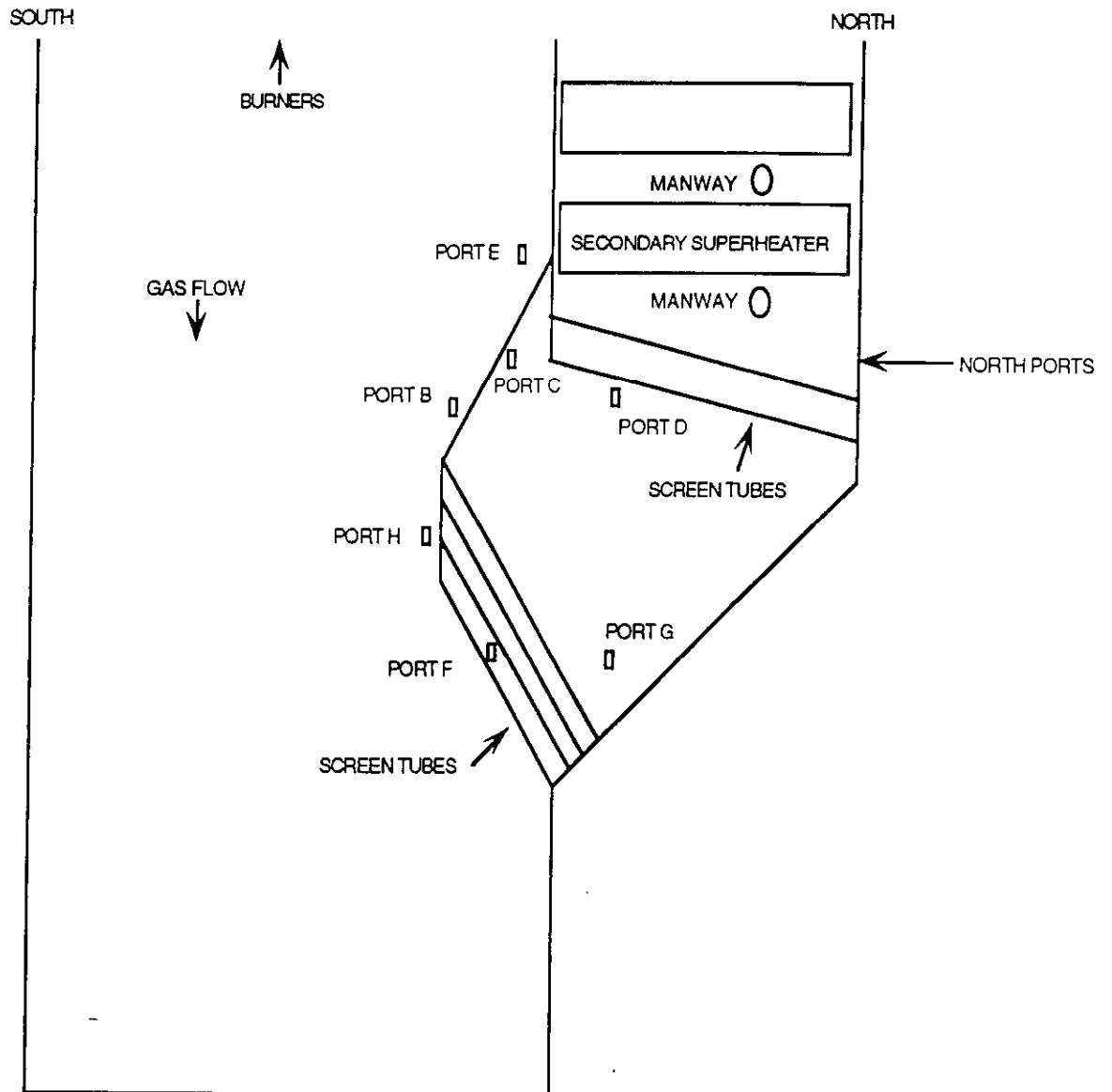


Figure 3-4. Port Locations for Temperature Measurements
(view looking from east)

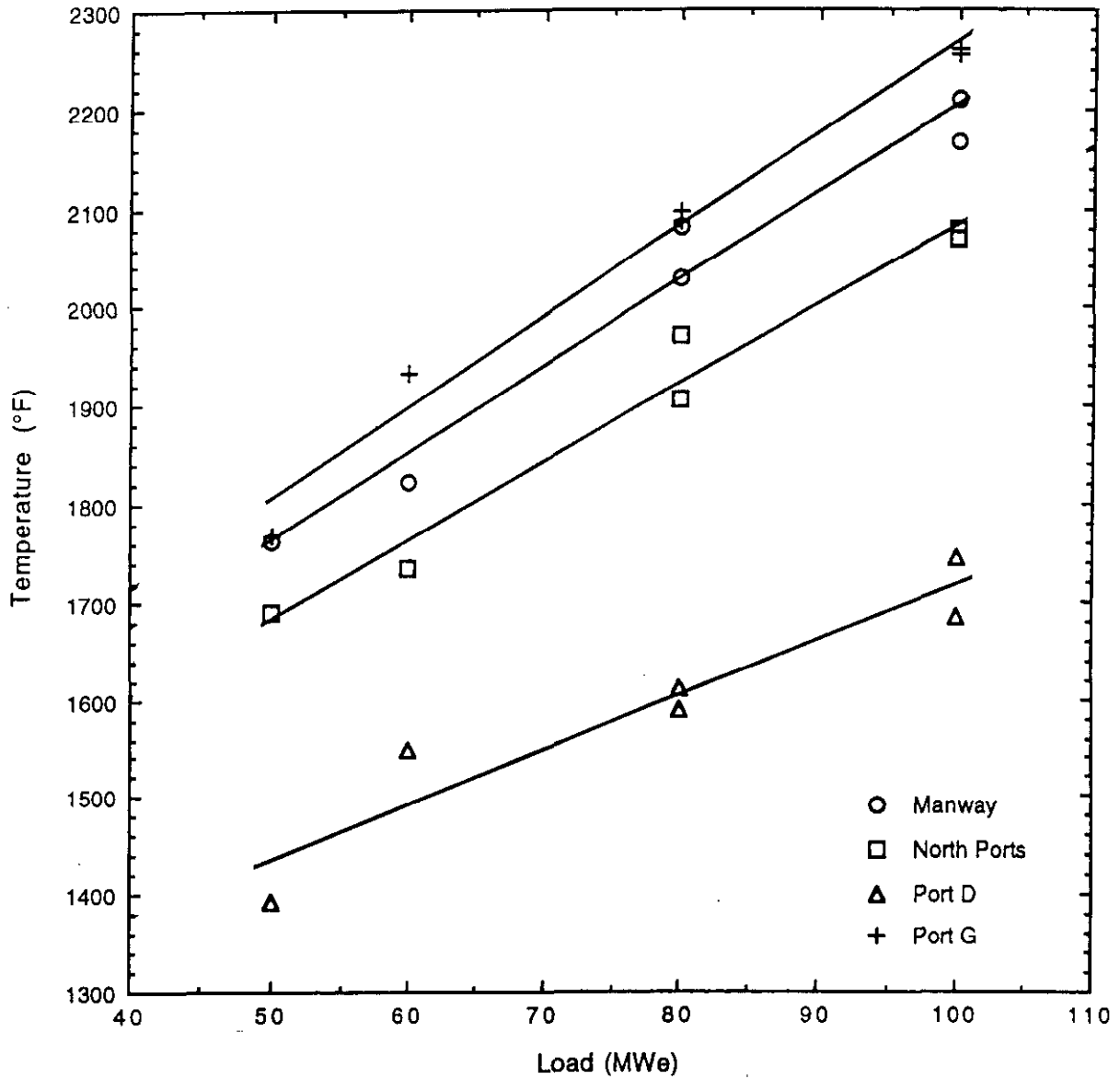


Figure 3-5. Effect of Load on Flue Gas Temperature at Selected Locations in the Furnace (Measurements Performed April 15 to 19, 1991)

Table 3-1

Flue Gas Temperature Measurement Results
(April 15 to 19, 1991)

Boiler Operating Condition	Measurement Type	Port H (West Side)	Port F (West Side)	Port G (West Side)	Port D (West Side)	North Ports (Manway)
100 MWe, All Mills	HVT Avg. (F) HVT Range (F) Acoustic (F)*	2451 2380-2535 None	2346 2290-2425 None	None None 2256	1750 1570-1871 1744	2079 1817-2231 2167
100 MWe, B Mill OOS	HVT Avg. (F) HVT Range (F) Acoustic (F)*	2568 2505-2630 None	2346 2220-2490 None	2260 2185-2320 2302	None None 1685	2069 1817-2245 2209
80 MWe, All Mills	HVT Avg. (F) HVT Range (F) Acoustic (F)*	2401 2350-2430 None	2239 2100-2300 None	None None 2087	1618 1462-1754 1588	1905 1655-2083 2028
80 MWe, B Mill OOS	HVT Avg. (F) HVT Range (F) Acoustic (F)*	2263 2250-2270 None	2000 1943-2040 None	None None 2097	None None 1612	1971 1756-2175 2081
60 MWe, B Mill OOS	HVT Avg. (F) HVT Range (F) Acoustic (F)*	2288 2190-2360 None	1982 1833-2095 None	1720 1669-1728 1934	1513 1416-1612 1549	1735 1551-1945 1822
50 MWe, B and C Mills OOS	HVG Avg. (F) HVT Range (F) Acoustic (F)*	1908 1900-1930 None	1630 1545-1705 None	1487 1430-1533 1767	1447 1326-1531 1393	1690 1513-1810 1762

*Acoustic measurements are a line-of-site average across the boiler.

The data discussed above are average data obtained at each of the port locations. The performance of the SNCR system can also be impacted by spatial temperature variations that might occur at each of the measuring planes. This can be the result of a number of factors, including the division wall in the furnace or the number of mills in service. The extent of this variation is shown in Figure 3-6, which shows the average west-to-east temperature profiles at the north port location for three and four mill operation at 100 MWe. As can be seen, the temperature variations along the east-west direction can be in excess of 300°F. Lower temperature regions were measured near the outer walls of the furnace and near the center of the furnace, downstream of the furnace division wall.

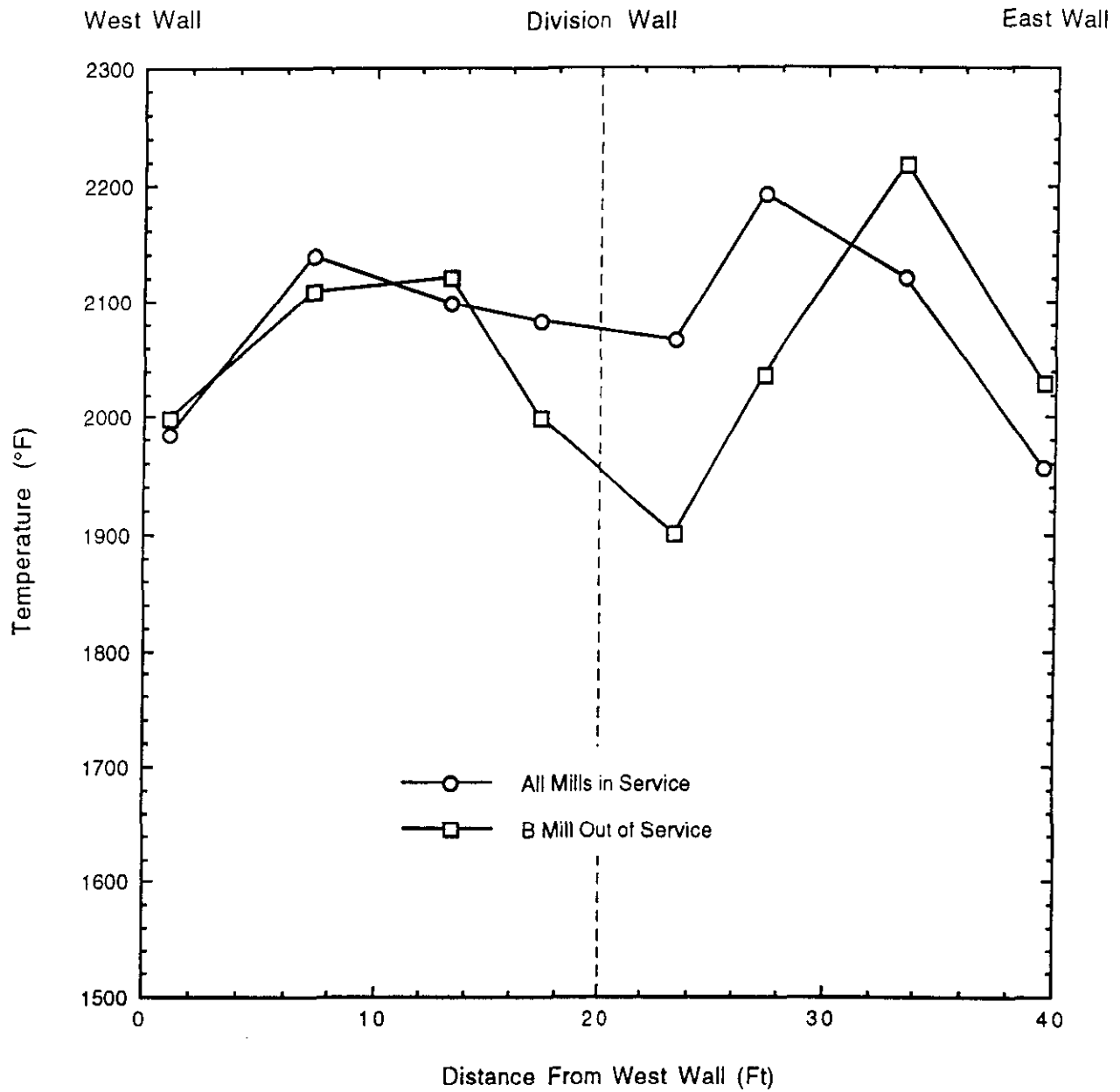


Figure 3-6. Average North Port Temperature Profiles at 100 MWe
 (Measurements Performed April 15 to 19, 1991)

Table 3-1 also indicates that, in the areas probed, the most promising location for urea injection is the area downstream of the second set of screen tubes (near the north ports), where the average HVT temperatures range from 1690 to 2080°F over the load range.

3.2.2 Cold Flow Modeling

In addition to temperature, the degree of chemical mixing with the bulk flue gas is critically important to the SNCR process. Maldistributed chemical injection results in lower overall NO_x reduction and higher ammonia slip. With the appropriate temperature regions identified by the temperature measurements, the next step in the design process by NOELL, Inc. was design of the injector system. This was accomplished with cold flow modeling techniques incorporating both flow visualization and tracer gas measurements to quantify and optimize a "mixing" parameter. A 1:10 scale cold flow model of the Arapahoe Unit 4 furnace and convective section was used for this part of the design procedure. Bulk flow characteristics were examined, as well as several injection scenarios, using flow visualization and tracer gas measurements. Injection configurations were optimized using a tracer gas technique to quantify the mixing between the injected chemical and the bulk flue gas. The results of these tests are briefly summarized below, and complete documentation of the cold flow modeling effort is contained in a separate report⁽⁷⁾.

Approach. The flue gas temperature measurements indicated that the general vicinity of the north ports provided access to the necessary urea injection temperatures over the load range. The north ports were easily accessible (46 inches above a walkway) and represented a good location for wall mounted injectors. On the basis of this information, a scenario using two rows of wall injectors was developed. The injectors would be installed, running across the north wall of the convective section at roughly the same elevation as the north ports. One row of injectors would be installed at the exact same elevation as the north ports, pointed slightly upward, essentially parallel to the screen tubes (see Figure 3-7). Another row would be placed lower, below the screen tubes, pointed slightly downward, essentially parallel to the connective section bottom. With this

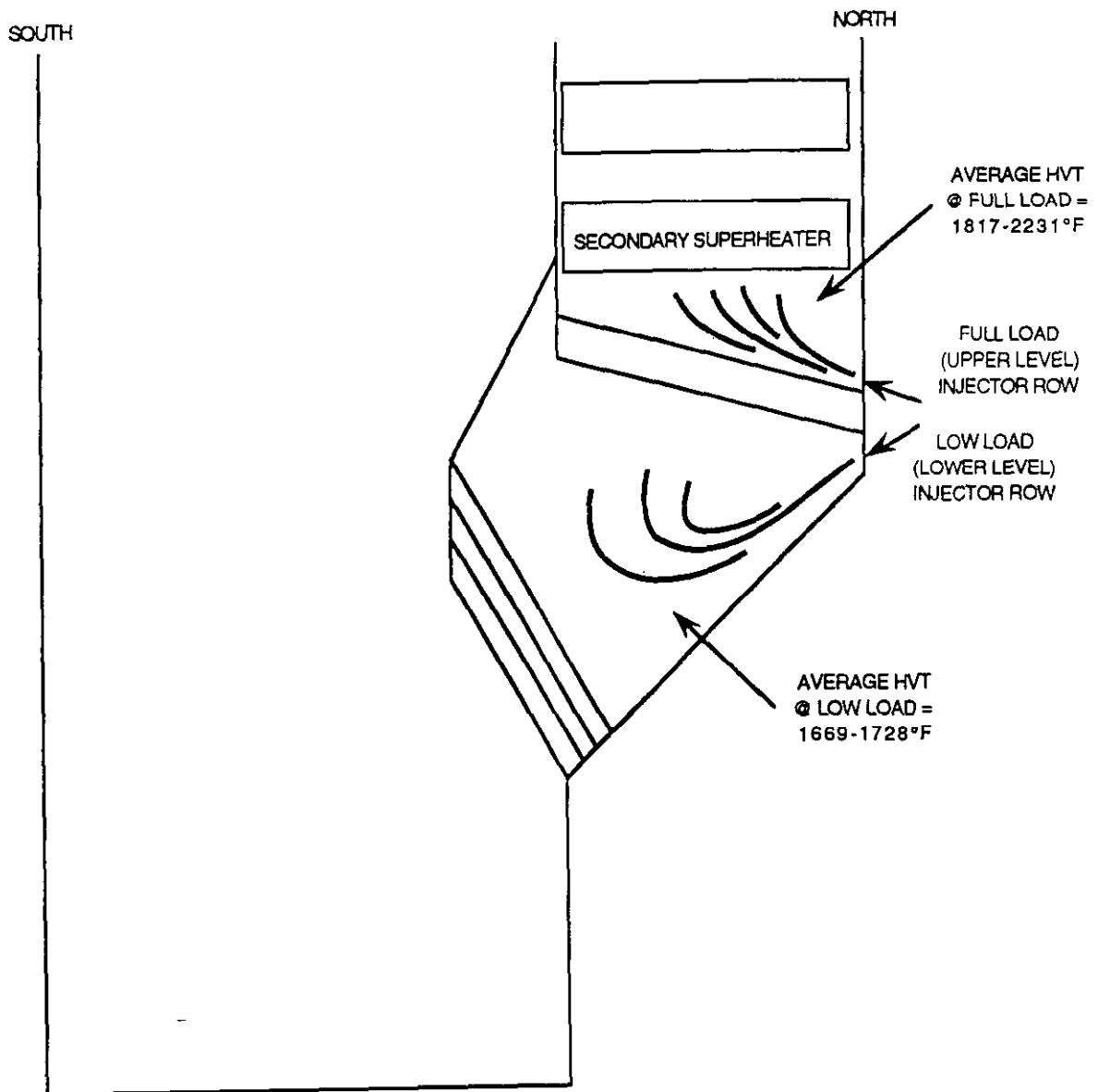


Figure 3-7. Injector Placement Scenario Based on Flue Gas Temperature Measurements

injector configuration, a load following procedure was developed. The upper injector level would be used at high loads where the cavity temperature was appropriate for efficient NO_x removal, and as load was reduced and temperature dropped below the optimum, the lower (i.e., hotter) level of injectors would be used. It was also anticipated that the downward oriented injectors would inject the chemical in a direction counter flow to the bulk gas flow, resulting in enhanced mixing and longer residence times. This scenario served as the basis for the cold flow modeling test procedure.

Methodology. Geometric and dynamic similarity between the full-scale boiler and the 1:10 scale model were maintained for the cold flow testing. Model Reynolds numbers were kept well above 15000 to simulate the gross turbulent mixing of the full-scale system. In examining the interaction of the injection flow with the bulk flow, equivalent full-scale and model momentum ratios were maintained.

With respect to flow visualization, two techniques were used. The bulk flow patterns were obtained by seeding the main burner flow with neutrally buoyant bubbles. For the higher velocity jets, smoke was used for flow visualization.

In order to provide a basis for quantifying and comparing the degree of mixing achieved with each injection system configuration, the injection air was seeded with a tracer gas. Sixty-point sample and velocity traverses were conducted over the entire cross-sectional area of the convective section. The location at which these traverses were conducted was dependent upon the injection level, and the locations of the planes of measurement are shown in Figure 3-8. The measured concentrations were converted into a contour map to visually assess the uniformity of mixing achieved with a given injector configuration. In effect, however, this was only marginally more quantitative than flow visualization. A method was developed to better quantify mixing between different injection configurations, as well as to directly compare the measurements by negating any differences in overall tracer gas concentration or velocity distribution. This method normalizes the tracer gas measurements and accounts for a non-uniform velocity field in

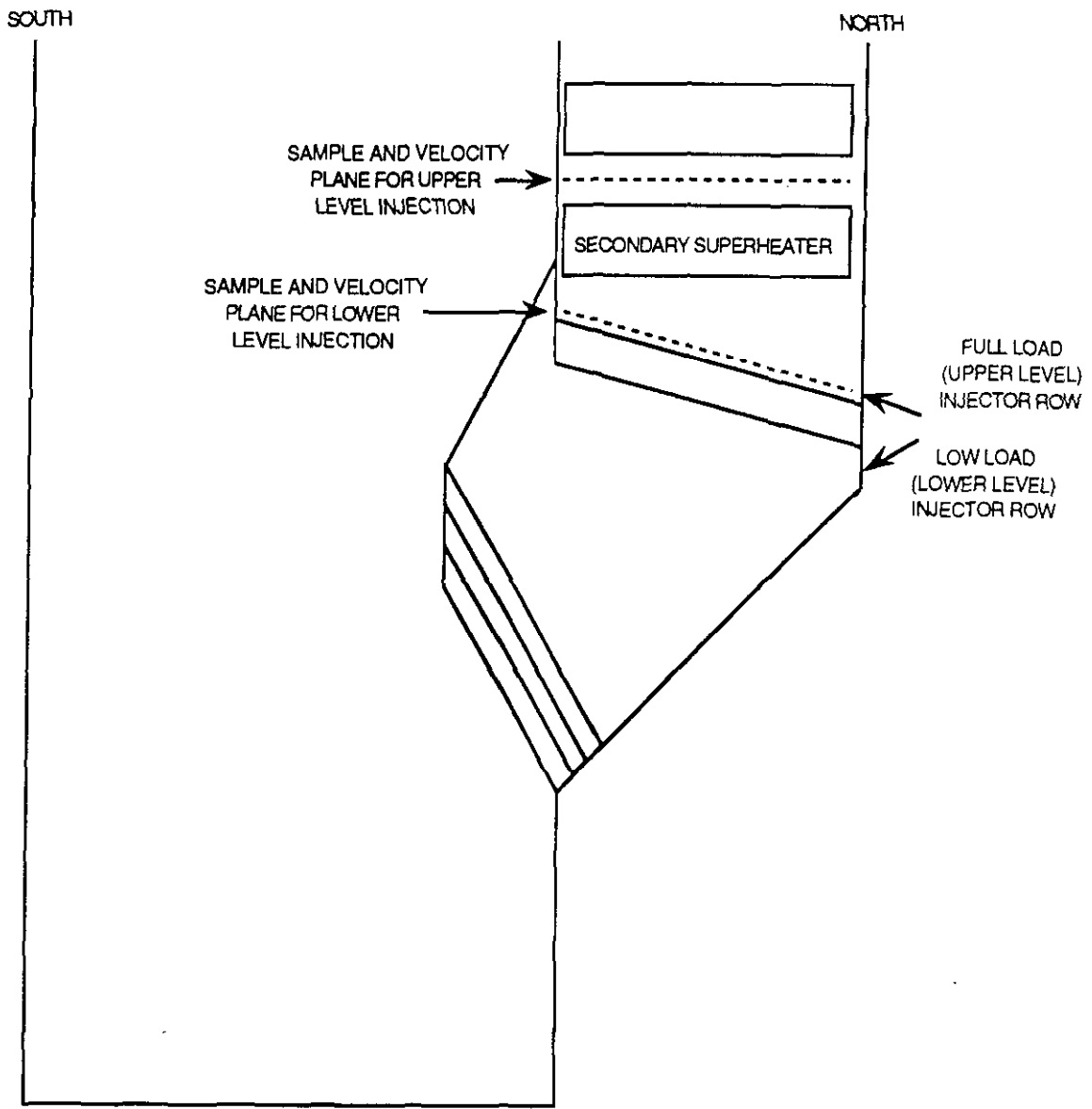


Figure 3-8. Sample and Velocity Traverse Planes for Tracer Gas Measurements

the overall mixing determination. The method is based on the assumption that if the flowfield was perfectly mixed, each sample point in the 60-point grid would exhibit a normalized value of one, and the standard deviation would be zero. At the other extreme, if the flowfield was totally unmixed and all of the tracer gas was measured within a single sample cell, a normalized value of 60 would be obtained in one cell, while all other sample cells exhibited a value of zero. The standard deviation of this latter case is a maximum. Intermediate levels of mixing will possess standard deviations of the normalized tracer gas concentration between these two extreme values. Each standard deviation value represents a certain mixing percentage, with zero standard deviation representing 100 percent mixed, and the maximum standard deviation representing zero percent mixed. This method for quantifying the degree of mixing was used to optimize the following parameters for the upper and lower injector rows (or "levels"):

- number of injectors
- injector angle
- injector diameter
- amount of mixing air.

Results. A synopsis of the overall model bulk flow patterns is shown in Figure 3-9. At the convective section entrance, the flow encountered a 50 percent reduction in cross-sectional area as well as an immediate 180° upward turn. This resulted in a high velocity region running up against the north wall, and a large recirculation zone extending nearly halfway across the convective section. The flowfield entering the first convective tube bank was clearly non-uniform.

The design injection air flow rate was nominally two percent of the total boiler flow at full load. Previous design experience had shown this flow rate to provide high levels of mixing while not being excessive from the standpoint of compressor power costs. At full scale, the velocity at the injection nozzle is kept sonic. Thus, the evaluation of different injection configurations began by keeping the injection air flow and the injector nozzle velocity constant (thereby setting the momentum ratio constant) and varying the number of injectors. As the number of injectors changed, the jet diameter was also changed to

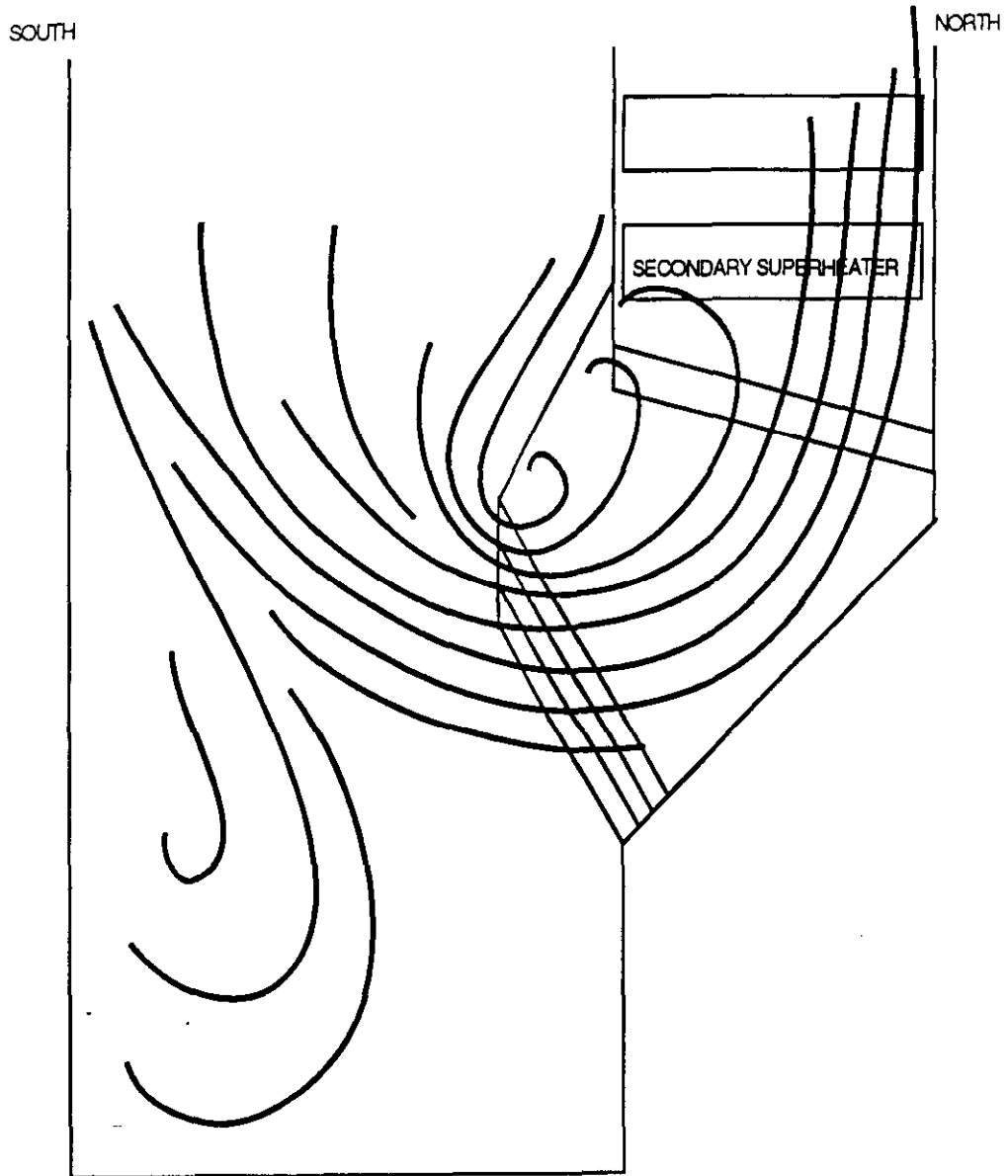


Figure 3-9. Overall Bulk Flow Patterns

maintain constant injection air flow. Optimizing the number of injectors involved the testing of four different scenarios: 8, 10, 12 and 20 jets. These tests were performed at the full load test condition with the upper level of injectors aimed $+15^\circ$ (upward) from horizontal. The results of the mixing tests are shown in Figure 3-10. As the number of jets varied, there were trade-offs between jet penetration and lateral dispersion in the east-west direction. Figure 3-10 shows that ten jets provided the highest mixing of the four cases at 71 percent. In this case, the ten jets penetrated to the middle of the plane and mixed very well laterally. Although the eight jet configuration resulted in increased penetration, the decrease in lateral mixing resulted in reduced mixing. At the other extreme, the lateral dispersion with twenty jets was good, but it was accompanied by a large decrease in penetration. These results are directly applicable to the lower injection level as well, since the variations in the lateral flowfield (east to west) was minimal as the bulk flows through the model were changed from the high load condition to the low load condition.

After it was determined that 10 injectors was the optimum number, the injector angles were optimized for both levels. At the upper level, the angle was varied from -15° to $+15^\circ$ from horizontal with essentially no change in the mixing. As the angle was increased above $+15^\circ$, the mixing degraded. Angles below -15° were not tested, since jet penetration into the upper screen tube bank was not desirable. At the lower injection level, tests were run pointing the jets directly horizontal (0°), and also directly counterflow to the bulk gas flow (-45°). Mixing was relatively poor at 59 percent with the jets aimed horizontally, but increased dramatically to 85 percent when the jets were aimed in the counterflow direction.

3.2.3 System Design Summary

The main conclusions reached as a result of the flue gas temperature measurement and cold flow modeling efforts are summarized below.

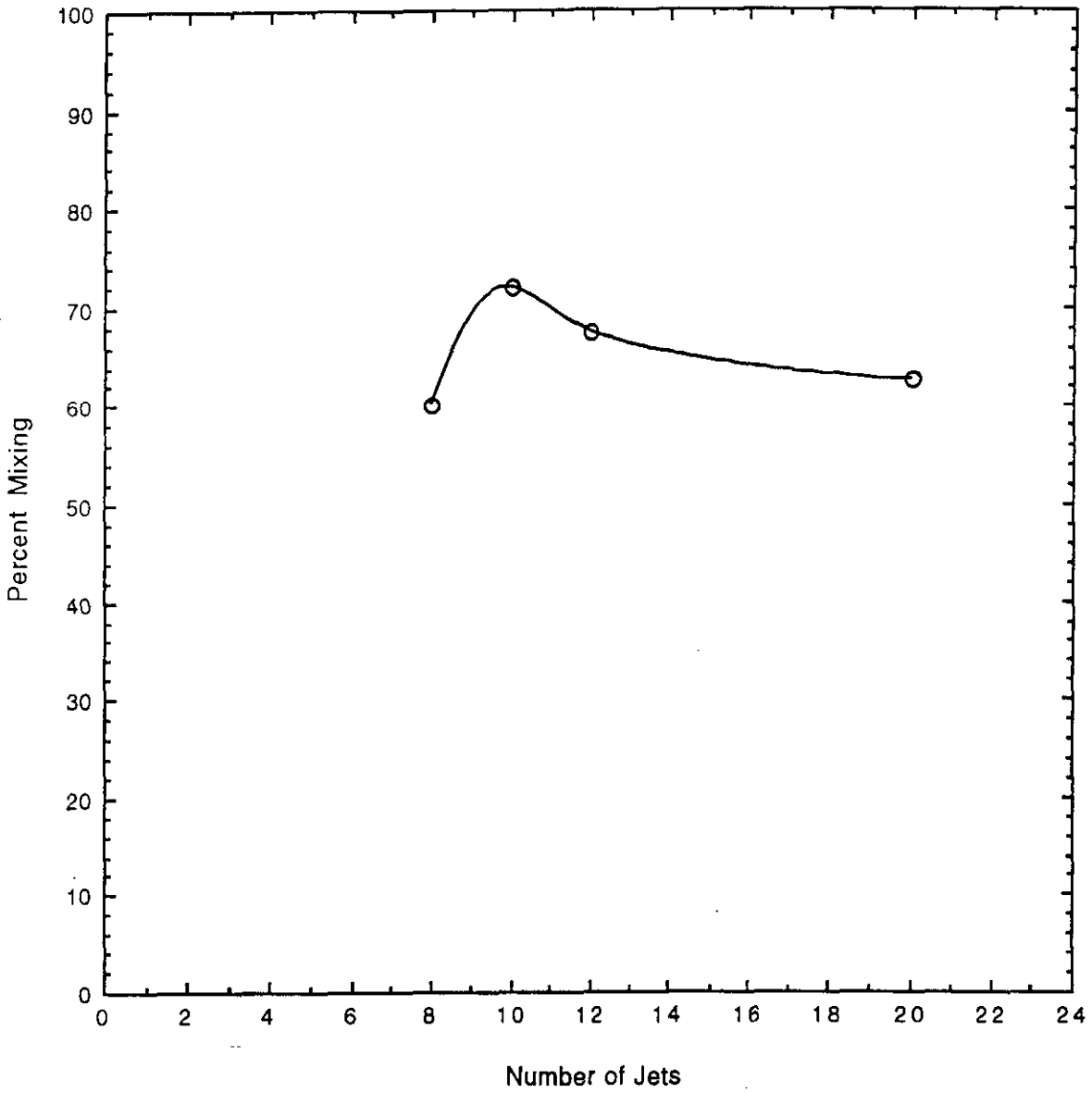


Figure 3-10. Effect of Number of Jets for Upper Level Injectors Angled +15° from Horizontal

- Flue gas temperature measurements showed that the general vicinity of the north ports provided the necessary chemical injection temperatures. The results also indicated that two different levels of injectors were required to optimize the SNCR process over the load range. At full load an upper level would be used, while at reduced loads a lower level would be necessary. This arrangement allows chemical injection into the proper temperature zone over the load range.
- Cold flow modeling showed that at full load with the upper level injectors at approximately elevation 5306 feet (relative to sea level), mixing was optimal using the following injection configuration:
 - number of evenly spaced injectors = 10;
 - injector diameter = 1.61 inches full scale;
 - injector angle = $15^\circ \pm 5^\circ$ from horizontal.
- Cold flow modeling showed that at reduced load, with the lower level injectors at approximately elevation 5302 feet, mixing was optimal using the following configuration:
 - number of evenly spaced injectors = 10;
 - injector diameter = 1.08 inches full scale;
 - injector angle = $-45^\circ \pm 5^\circ$ from horizontal (directly counterflow).

3.3 System Description

The NOELL, Inc., SNCR injection system is designed to achieve a high degree of mixing between the flue gases and the reducing reagent in short residence times. Figure 3-11 shows a simplified flow diagram of the system as implemented at Arapahoe Unit 4. The system may be separated into four simple subsystems; urea recirculation, injection, ammonia conversion, and atomization.

The urea recirculation loop handles the storage and heating of the base urea chemical. Urea is received in a 65 percent (by weight) liquid solution and is stored in one of two 20,000 gallon tanks. A 65 percent solution must be maintained above 115°F to prevent crystallization of the urea. At Arapahoe Unit 4, the solution temperature was maintained by circulating with one of two 200 gpm recirculation pumps through an electric heater.

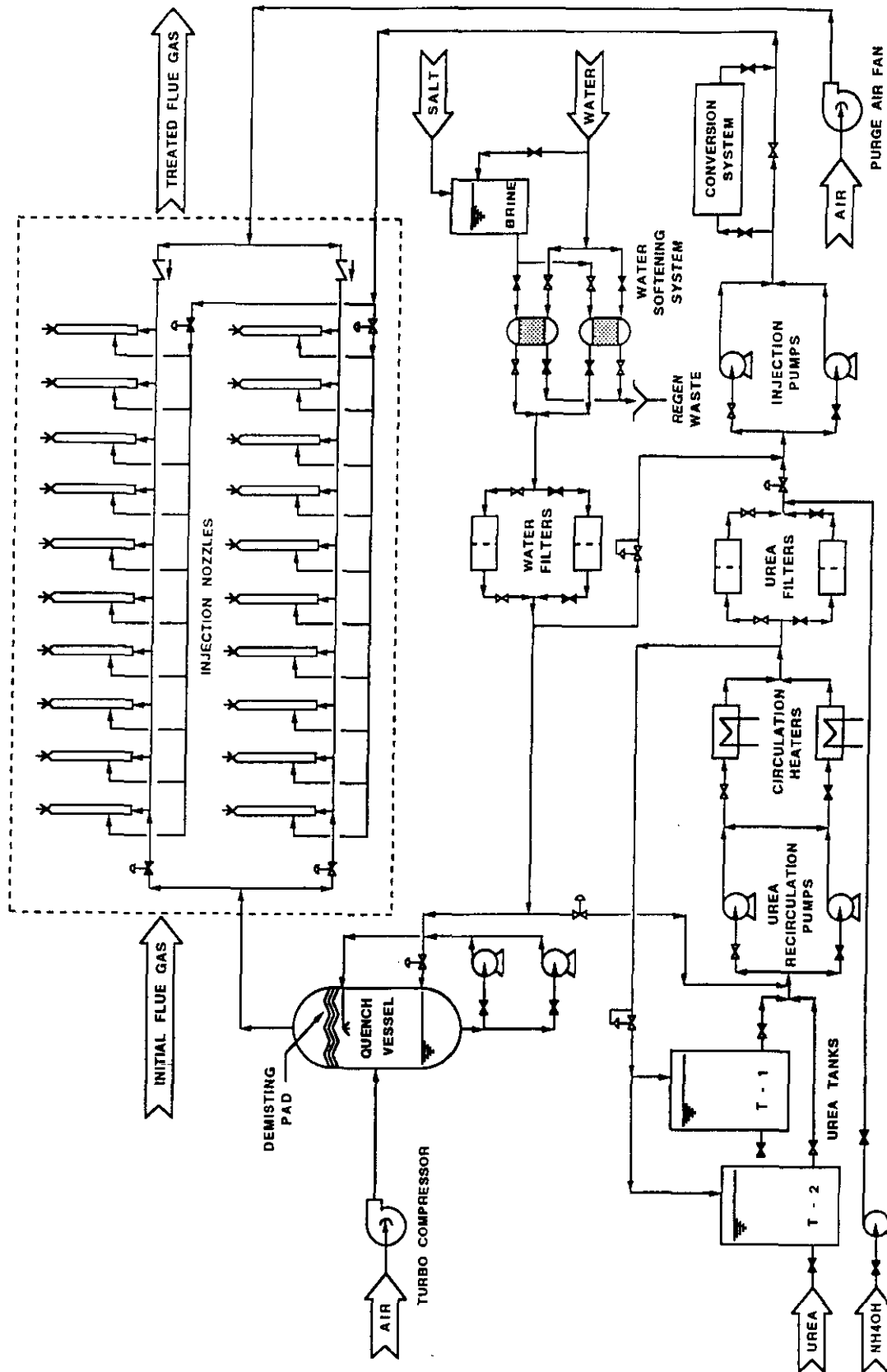


Figure 3-11. Arapahoe Unit 4 SNCR System Flow Diagram

During the baseline SNCR testing, it was found that maintaining this concentrated urea solution at the elevated temperature could cause some ammonia vaporization in the storage tank and a slight ammonia odor would be noticed on some days. This problem was solved by diluting the urea, after delivery to approximately a 37.5 percent concentration. Urea at this concentration reduces the crystallization point to below 14°F as shown in Figure 3-12. Storing the dilute solution has eliminated any ammonia vaporization and, in addition, saves the energy required to constantly recirculate and heat the solution.

In the injection system, a small slipstream of the urea from the recirculation loop is filtered, mixed with softened water to further dilute the urea, and is then pumped at high pressure (100 to 1000 psig) to the atomizers. The liquid transfer lines are insulated and heat traced to 50°F to prevent crystallization of the urea. The system at Arapahoe Unit 4 uses one of two positive displacement pumps driven by AC variable speed drives. The variable speed drives allow the total liquid flow to be varied from 2.0 to 10.5 gpm. The ability to vary the total flow allows some control over the effective flue gas injection temperature. When the flue gas in the injection area is at or below the optimum temperature for effective NO_x removal (recall Figure 2-1), low flows are desirable so that the flue gas temperature is not significantly reduced by the evaporation of excess water. When the flue gas temperatures are higher than the optimum, larger flows allow some gas temperature cooling by evaporating the water before the urea begins reacting with the NO_x.

The ammonia converter is a new system that was added after the original SNCR test program was conducted with the original burners. It was found that at low flue gas temperatures at low loads, urea was not very effective for NO_x removal. A short test showed that aqueous ammonia reacted both faster and at a lower temperature in the boiler, and was also more effectively utilized at lower temperatures than urea. Although ammonia was more effective, it remained desirable to store urea due to safety concerns. NOELL, Inc., suggested an on-line conversion system that would convert the urea into

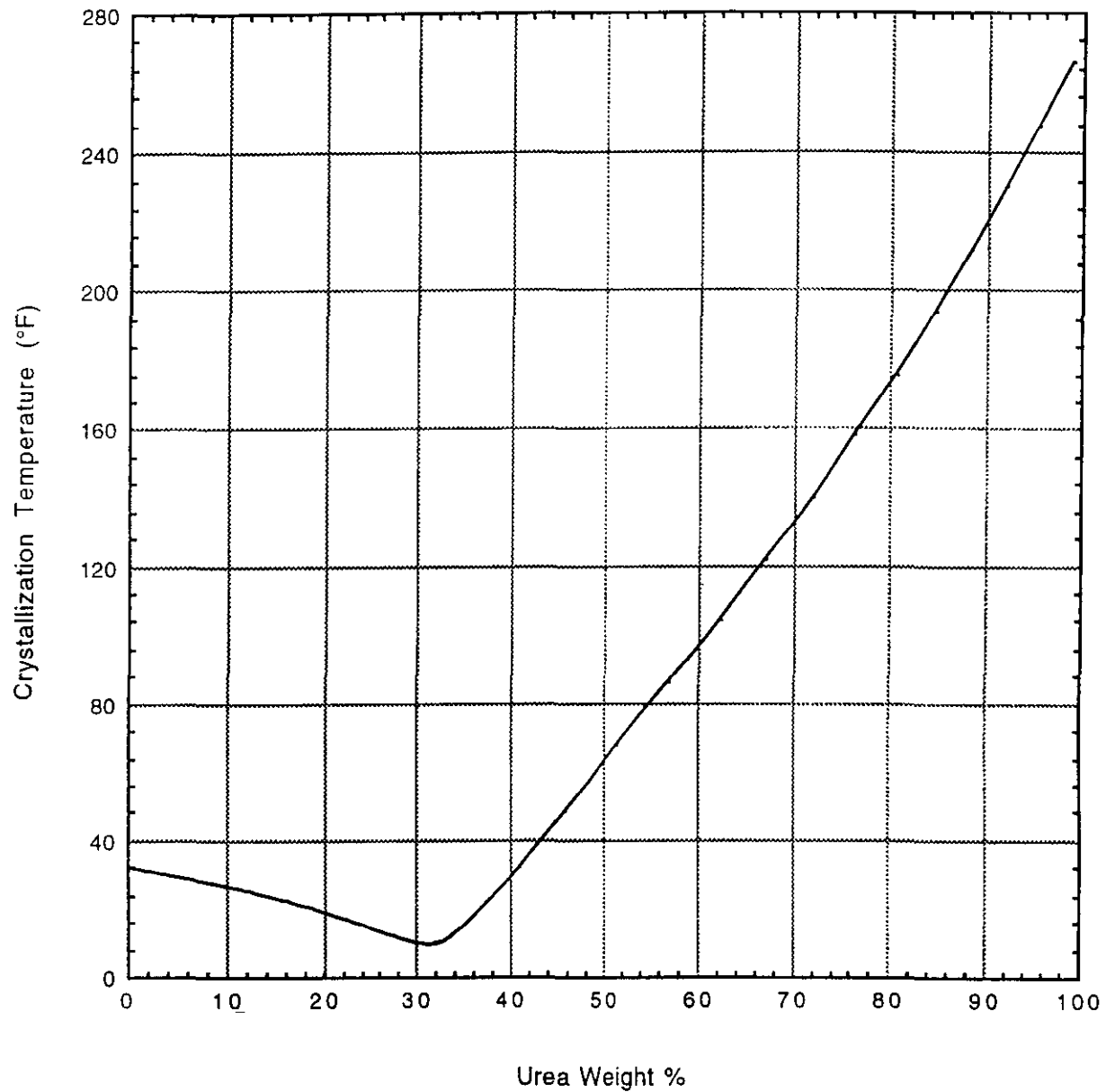


Figure 3-12. Crystallization Point of Aqueous Urea Solutions as a Function of Concentration

ammonia compounds. This system first heats the urea and then passes the urea over a proprietary catalyst that causes the urea to convert to ammonia based compounds. The system can be bypassed so that either urea or ammonia compounds may be injected as selected by the control operator.

The SNCR system at Arapahoe Unit 4 uses NOELL, Inc.'s proprietary dual-fluid injection nozzles to distribute the urea or ammonia compounds evenly into the boiler. A centrifugal compressor is used to supply a large volume (up to 9000 scfm) of medium pressure (4 to 12 psig) air to the injection nozzles to help atomize the solution and rapidly mix the chemical with the flue gas. The volume of air supplied is controlled by variable inlet guide vanes and a variable diffuser assembly, which automatically delivers a preset discharge pressure. Upon exiting the compressor, the air passes through a quench vessel which cools the hot compressed air by recirculating, spraying, and evaporating water. The quench skid has redundant pumps for water recirculation, and the water level within the quench vessel is maintained automatically by a switch operated solenoid valve.

Two rows of ten wall-mounted injection nozzles were installed on the Arapahoe Unit 4 boiler; one at elevation 5302'6" and one at elevation 5306'3", which placed the two levels immediately upstream and downstream of the second set of screen tubes, as shown in Figure 3-13. The injection angle for the lower level of nozzles (Level 1) is oriented 45° down from horizontal, and the angle of the upper level nozzles (Level 2) is 15° above horizontal.

The purpose of two levels of injectors was to have some means of temperature control for the urea injection system. The upper nozzles were expected to operate in the range of 80 to 100 MWe. As the load was further reduced and flue gas temperatures decrease, the lower level would be used. During the initial test program, it was found that either the flue gas was too cold or the residence times too low over the entire load range for effective NO_x reduction at the upper level. Therefore, all further testing was completed with the Level 1 injectors.

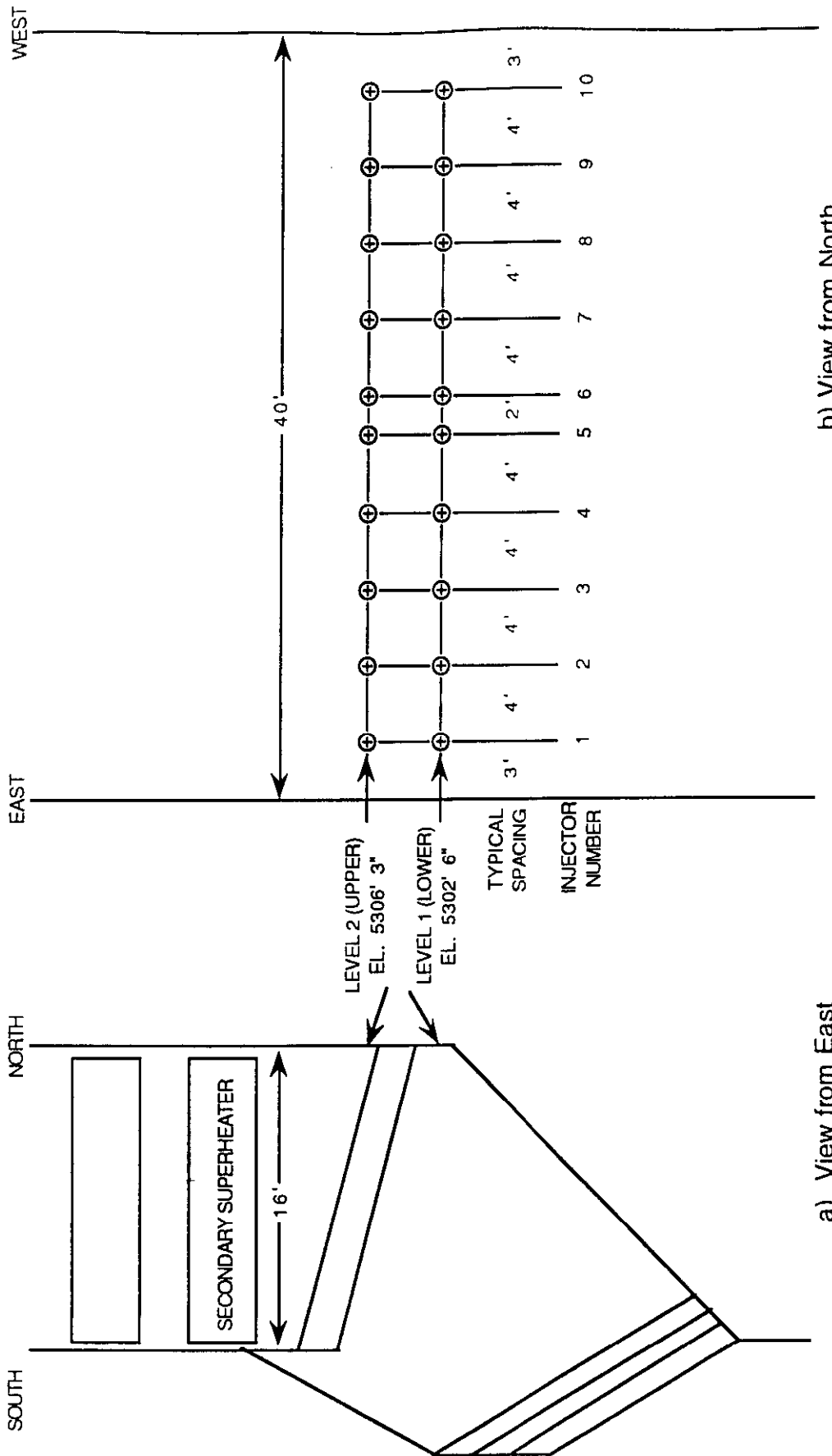


Figure 3-13. Arapahoe Unit 4 SNCR Injection Nozzle Location

Purge air is used to keep the level of injection lances not in service cool and free of ash build up. The air is supplied by a purge air fan which draws ambient air through a filter and silencer. The air is fed through the air lines not in use, up to the air header on the level not injecting urea, and then through the nozzles.

The urea injection system is controlled by a programmable logic controller (PLC). The PLC is operated using an IBM compatible computer and controls all the functions of the system (equipment on/off, valves open/close, etc.), except for three local control systems in local control panels (LCPs); the centrifugal compressor, the circulation heaters and the water softening skid. These LCPs control the equipment and receive the main commands and transmit the key information to and from the PLC. Some of the valves need manual pre-selection for redundant equipment, i.e., urea recirculation pump, quench pump, or filter inlet and outlet valves.

From the local computer, the SNCR system can be either manually set, or operated under automatic control. Under automatic control operation, the urea flow rate is set by a feed forward control function using a boiler load signal. The system also utilizes feedback control to trim the urea flow rate by ± 30 percent. The feedback control loop can use either a stack NO_x signal or a stack NH_3 signal.

4

MEASUREMENT METHODS

The evaluation of the performance of the selective non-catalytic reduction system required the documentation of gaseous emissions, NH₃ slip levels, and furnace exit gas temperatures, as well as boiler operational performance parameters. This section summarizes the measurement methods that were utilized during the LNB/OFA/SNCR test phase of the program.

4.1 Gas Analysis Instrumentation

The gas analysis instrumentation utilized during the current phase of testing was different from that used during the baseline SNCR tests performed during February and March of 1992. Complete documentation of the earlier system is contained in a separate report⁽³⁾. An Altech 180 continuous emission monitoring (CEM) system was purchased as part of the Integrated Dry NO_x/SO₂ Emissions Control System and installed during the low-NO_x combustion system retrofit. The CEM system utilizes a Perkin Elmer MCS 100 infrared gas analyzer which is capable of continuously analyzing eight gas species simultaneously, using either gas filter correlation or single beam dual wavelength techniques.

The analyzer cycles through and measures all eight gas species in approximately 22 seconds. In that time, two readings are made for each gas species to be measured. The first reading is a reference value at a known wavelength and gas concentration (either 0 or 100 percent), and the second is a measured reading to determine the quantity of the desired species in the sample stream. Table 4-1 provides a listing of the full scale range, measurement technique, and interfering species for each of the gases measured.

Table 4-1. Gas Species Measured by Perkin Elmer MCS 100 Analyzer

Measured Species	Range	Measurement Technique	Interfering Species
NO	0-500 ppm	Gas Filter Correlation	H ₂ O
CO	0-400 ppm	Gas Filter Correlation	H ₂ O
SO ₂	0-400 ppm	Single Beam Dual Wavelength	NH ₃ , H ₂ O
NO ₂	0-100 ppm	Single Beam Dual Wavelength	NH ₃ , SO ₂ , H ₂ O
CO ₂	0-20 volume %	Single Beam Dual Wavelength	H ₂ O
H ₂ O	0-15 volume %	Single Beam Dual Wavelength	None
N ₂ O	0-100 ppm	Single Beam Dual Wavelength	CO, CO ₂ , H ₂ O
NH ₃	0-50 ppm	Gas Filter Correlation	CO ₂ , H ₂ O

Using the gas filter correlation technique, the system takes a reference reading at a known wavelength and a known concentration of gas, usually 100 percent. The system then takes another reading at the same wavelength for the sample gas and records the energy absorbed by the sample. The relative difference in energy is then representative of the concentration in the sample gas.

Likewise in the single beam dual wavelength method, a reference reading is taken at a wavelength where the desired species does not absorb energy (zero percent reference). The system then takes a measured reading at a wavelength where the desired species is known to absorb energy. The relative difference in energy is again representative of the concentration of the species in the sample stream.

Once the ratio of reference to measure energy is calculated, the energy level is corrected to account for interferences via reference tables for each specific gas. After correction for interferences, the data is zero adjusted, converted to the appropriate units, calibration corrected, and output for display and recording.

Since O₂ is not infrared active, the CEM system also contains an Ametek O₂ analyzer. The sample cell is a zirconium oxide closed end tube with electrodes of porous platinum coated onto the inside and outside of the tube. The cell produces a millivolt signal

proportional to the relative difference of O₂ inside and outside of the cell. The millivolt signal is converted to percent O₂, scaled (0 to 25 percent), and then displayed and recorded.

All CEM analyzer and sampling system functions, including a daily automatic calibration sequence, are controlled by the MCS 100 Programmable Logic Controller (PLC). The measured gas concentration data is displayed on a dedicated 486-based computer, which also provides data logging, manipulation and reporting capabilities.

A Relative Accuracy Test Audit (RATA) was performed on March 5, 1993, in order to verify the accuracy of the CEM system. The audit was performed by TRC Environmental Corp. in accordance with the requirements established in 40 CFR, Part 60, Appendices A and F. Complete documentation of the audit is contained in a separate report⁽⁶⁾, and the results are summarized in Table 4-2.

Table 4-2

CEM RATA Results

Parameter	Relative Accuracy (%)
CO ₂ (% <i>, wet</i>)	2.64
Moisture (%)	7.86
O ₂ (% <i>, wet</i>)	17.81
NO (ppm, <i>wet</i>)	1.53
NO (lb/MMBtu, <i>wet</i>)	5.93
NO (ppm, <i>dry</i>)	1.02

Calculated on an O₂ basis

Acceptance criteria for RATA evaluation of component instruments of the CEM is 20 percent. Based upon the results, all individual parameters were found to be within the acceptance criteria.

4.2 Gas Sampling System

As shown in Table 4-1, the MCS 100 was configured to measure NH_3 . This capability imposes special requirements upon the design of the CEM sampling system. In order to maintain the integrity of the sample, the entire sampling system (probe, sample line, pump, flowmeter, and sample cell) must be maintained at 230°C (445°F). Due to these heat tracing requirements, the CEM system was configured to sample from only two different single-point locations. One at the exit of the air preheater in the duct leading to the fabric filter, and one downstream of the fabric filter and induced draft fans, in the duct leading to the common stack for Units 3 and 4.

In order to obtain a representative composite gas sample, as well as provide the ability to look at discrete areas of the flue gas flow, Fossil Energy Research Corp. provided a sample gas conditioning system which would allow sampling from additional unheated sample probes. Although the MCS 100 is utilized as the gas analysis instrumentation, the measurement of NH_3 at the additional sampling locations is not possible due to the lack of high temperature heat tracing. A schematic of the sample gas conditioning system is shown in Figure 4-1. The system can accommodate up to 24 individual sample lines. Up to 12 of these can be composited together and then analyzed. Each of the individual sample streams is dried in a refrigerated dryer where the gas is cooled and the moisture is dropped out in a trap. Each stream then passes through a metering valve and rotameter, after which all the streams are blended together in a manifold and directed to a pair of sample pumps. The rotameters are used to balance the individual flows in order to provide an accurate composite blend. Downstream of the pumps, a portion of the composited sample is diverted to a final pass through the condenser (where the increased pressure aids in the removal of any remaining moisture), through a final particulate filter, and then to the Altech CEM for analysis.

The location of the unheated sample probes during the current phase of testing was identical to that for the baseline SNCR tests, namely: 12 at the exit of the economizer,

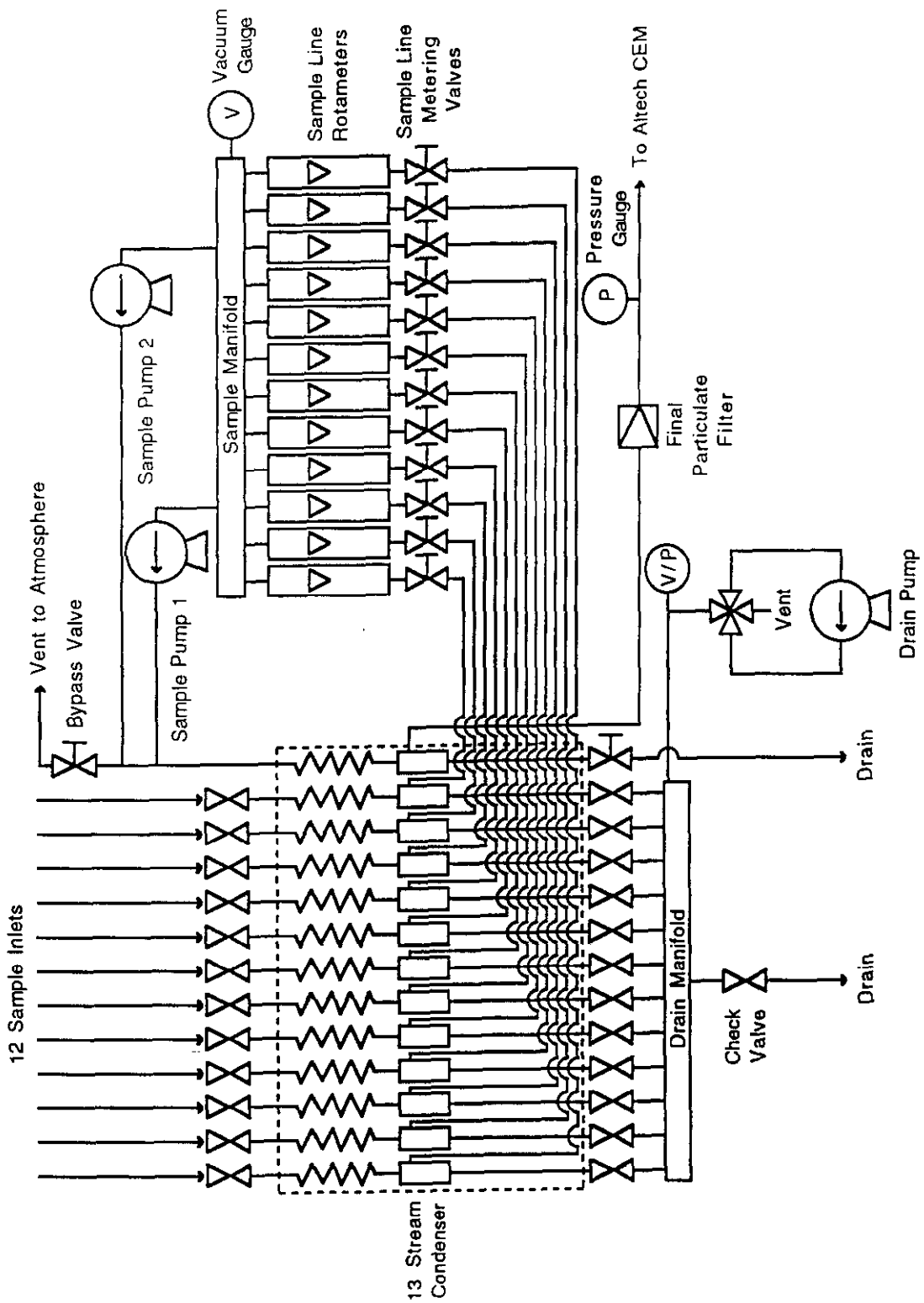


Figure 4-1. Sample Gas Conditioning System

6 at the exit of the air preheater, and one in the fabric filter outlet duct leading to the stack. The sample probe grid in the horizontal duct at the economizer exit is shown in Figure 4-2. Although this duct is 40 feet wide, it is only 7 feet deep, so an array of probes positioned two high by six wide was deemed adequate to obtain a representative gas sample. The short probes were located at one-fourth of the duct depth, and the longer probes at three-fourths of the duct depth. This spacing vertically divided the duct into equal areas. The use of two probe depths also provided the opportunity to ascertain any vertical stratification of gas species within the duct. Individual sample probes consisted of stainless steel tubing with sintered metal filters on the ends. The sample lines which transported the gas to the sample conditioning system, consisted of polyethylene tubing which was heat traced and insulated to prevent freezing during the winter months.

Figure 4-2 also shows the location of the four PSCC O₂ probes at the economizer exit which are used for boiler trim control. The PSCC equipment uses *in situ* probes that determine the O₂ concentration on a wet basis. These probes (numbered A, B, C and D) are located approximately three feet upstream of the Fossil Energy Research Corp. (FERCo) grid, and very near probe numbers 3, 5, 7 and 9. Two additional sampling ports were available at the economizer exit which were used for limited SO₃ measurements during the baseline burner and low-NO_x combustion system tests.

The importance of the position of the 12-point grid relative to the four PSCC probes was realized during the baseline burner tests when it was found that the average O₂ measured from the grid was nominally one percent higher than the average indicated in the control room. This difference was attributed to the inability of the four PSCC probes to detect the elevated O₂ levels along the east and west sides of the duct which result from both air in-leakage and overfire air that didn't penetrate to the center of the furnace. A comparison between the control room and average economizer exit O₂ levels was made during the low-NO_x combustion system tests in order to determine if the retrofit had any effect on the difference between the two. This comparison also permitted correlation of

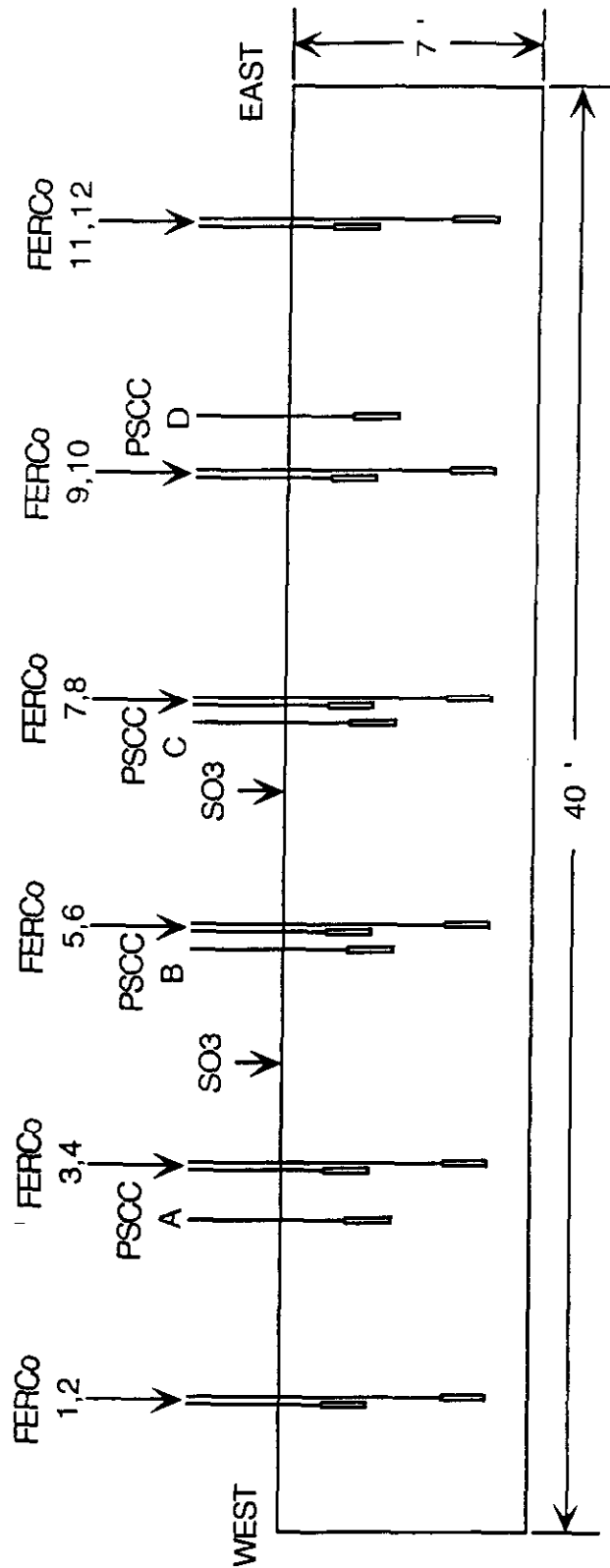


Figure 4-2. Economizer Exit Sampling Locations

the typical control room data with the results presented in this report. Figure 4-3 shows a comparison of the two average O₂ values for all the parametric tests performed during the retrofit burner characterization. The average economizer exit O₂ levels were nominally one percent higher than those indicated from the four PSCC probes. Approximately 0.3 to 0.4 percent O₂ of this difference can be attributed to the wet versus dry measurement basis between the two analyzers. The balance of the difference is due to the non-uniform O₂ distribution across the duct, and the placement of the PSCC probes relative to the east and west walls. A significant amount of data scatter is seen in Figure 4-3, although it must be noted that variations in boiler operating parameters such as the number of mills in service or overfire air flow can affect the O₂ distribution, and thereby affect the difference in the average O₂ measured by each method.

Additional gas sample probes were installed at the air heater exit and the stack (fabric filter outlet duct) locations. Whereas, the 12-point economizer exit sampling grid would be utilized for detailed point-by-point measurements, the air heater exit and stack sampling probes would be used only to obtain general duct averages at these locations, and will be necessary during the NO_x and SO₂ reduction tests. Therefore, only a limited number of probes were utilized at these test locations; six at the air heater exit and a single probe at the stack location. Figure 4-4 shows the location of the probes at the air heater exit. These sample probes and tubing were similar to the installation at the economizer exit. The staggered probes were installed at one-fourth and three-fourths duct depths, similar to the economizer exit. The figure also shows the location of the heated probe for the CEM system at the exit of the air heater. This probe is not in the same plane as the six-point grid, but approximately 3 feet upstream. At the stack sampling location, the heated probe for the CEM system is approximately 20 feet upstream of the unheated probe installed during the baseline burner tests. Only a single probe is used for both the CEM and the unheated probe locations since both are downstream of the fabric filter and induced draft fans where little stratification of the flue gas stream is expected. Figure 4-5 shows the installation of the unheated probe in the fabric filter outlet duct.

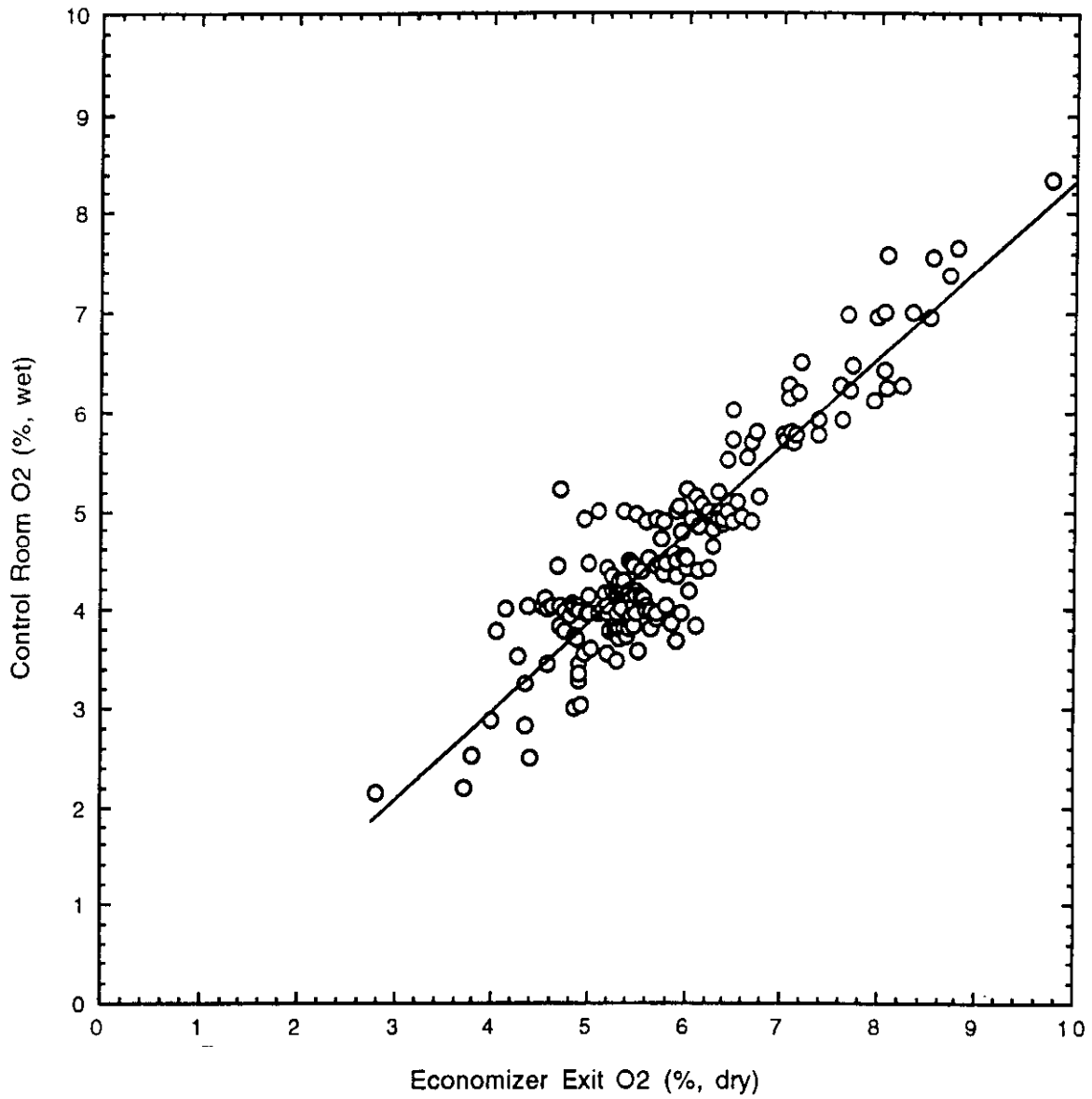


Figure 4-3. Comparison between Control Room O₂ and Economizer Exit Grid O₂ Measurements

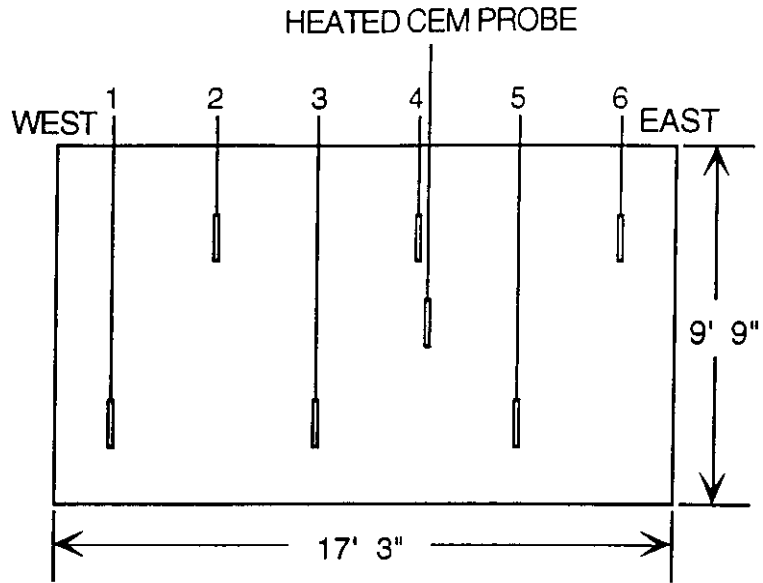


Figure 4-4. Air Heater Exit Sampling Locations

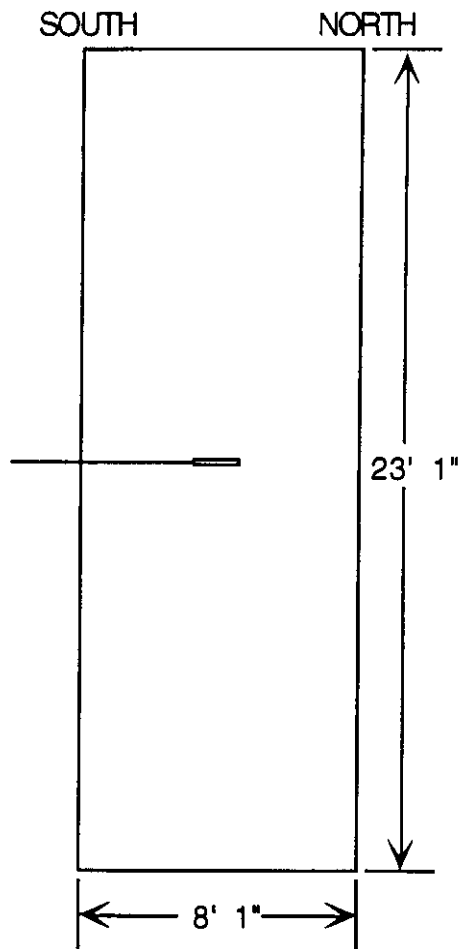


Figure 4-5. Fabric Filter Outlet Duct Sampling Location

4.3 NH₃ Measurements

The measurement of NH₃ emissions is an important aspect of quantifying the performance of a SNCR system. Traditionally, batch or wet chemical sampling techniques have been used for this purpose. However, the time delay between the collection of the sample and the delivery of the results, due to the required laboratory analysis, is less than optimal when trying to optimize process performance in a field test situation. Recently, a number of continuous ammonia analyzers have become available, which could provide the on-line performance desirable for a field test program. However, these analyzers are considered to be in a developmental and proving stage, due to difficulties in obtaining and preserving valid gas samples, especially in sulfur-laden environments.

Wet chemical NH₃ analysis was the primary measurement used during the current test program. Although an EPA method is not available for NH₃ measurement, the method described below has been utilized by Fossil Energy Research Corp. and others during numerous test programs and has been proven sufficiently accurate. Flue gas samples are withdrawn from the duct through a stainless steel probe, and are then passed through three impingers as shown in Figure 4-6. The first two impingers contain 0.02N sulfuric acid (H₂SO₄) and the final impinger is dry. Nominally two cubic feet of flue gas is passed through the impinger train during each test at a rate of approximately 0.2 ft³/min. Total sample times were nominally 10 to 12 minutes for each test. At the conclusion of each test, the sample probe, teflon line, and sampling train glassware are washed with dilute H₂SO₄ into the bottle containing the impinger solution. The sample solution is then analyzed for ammonia.

During the baseline SNCR tests, the sample solutions were analyzed with a specific ion electrode. Although this type of analysis is a standard technique and is considered quite accurate, it is very temperature-sensitive in that it is most important that the standard and sample solutions be at the same temperature when analyzed. The time required to assure thermal equilibrium can lead to a substantial time delay between the collection of the sample and the delivery of the results. In order to provide a more rapid turn around

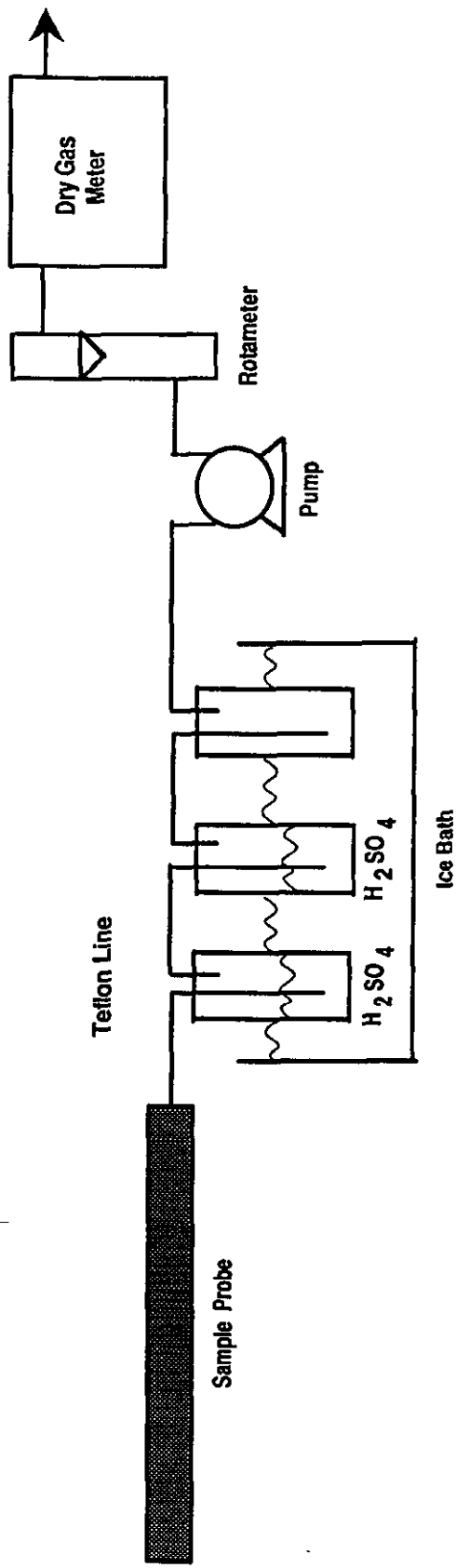


Figure 4-6. NH₃ Sample Train Schematic

of NH_3 data during the LNB/OFA/SNCR tests, the sample solutions were analyzed on-site using the Direct Nesslerization Method. In this method, the Nessler reagent and a stabilizing agent (EDTA) are added to the sample solution and mixed thoroughly. After the reaction is complete (a minimum of ten minutes is required), the light absorbance of the sample is determined photometrically at 425 nm. The reading is compared to the absorbance of standard solutions to determine the ammonia concentration in the sample. Using this method, an NH_3 emission value could be obtained in a manner of minutes after the completion of a test.

The rapid turnaround of NH_3 emission data was used to quickly diagnose and guide the test program during the optimization of the SNCR injection system. However, a portion of each sample solution was also later analyzed with a specific ion electrode since this analysis is considered the standard technique. Figure 4-7 shows a crossplot of the NH_3 data from the two different analyses. The results show a reasonable correlation between the two, but a significant amount of scatter is also apparent. All wet chemical NH_3 emission values discussed in the remainder of this report are from the specific ion analyses.

The majority of the wet chemical ammonia samples were obtained from a set of six ports located in the air heater exit duct (just upstream of the ports used for the continuous gas analysis samples shown in Figure 4-4). A more limited number of samples was obtained downstream of the fabric filter. Unless noted otherwise, the ammonia values represented in the results section are composite samples obtained along the centerline of the duct at the air heater exit.

With the availability of the on-site analysis equipment, it was not uncommon to have the results of the Nessler analysis before the boiler and injection system were stabilized at the next test condition. This was a great advantage in addressing an NH_3 sampling problem which was discovered at the low-load operating condition. Near the end of the initial day of testing at the 60 MWe, it was found that the NH_3 emission results were not

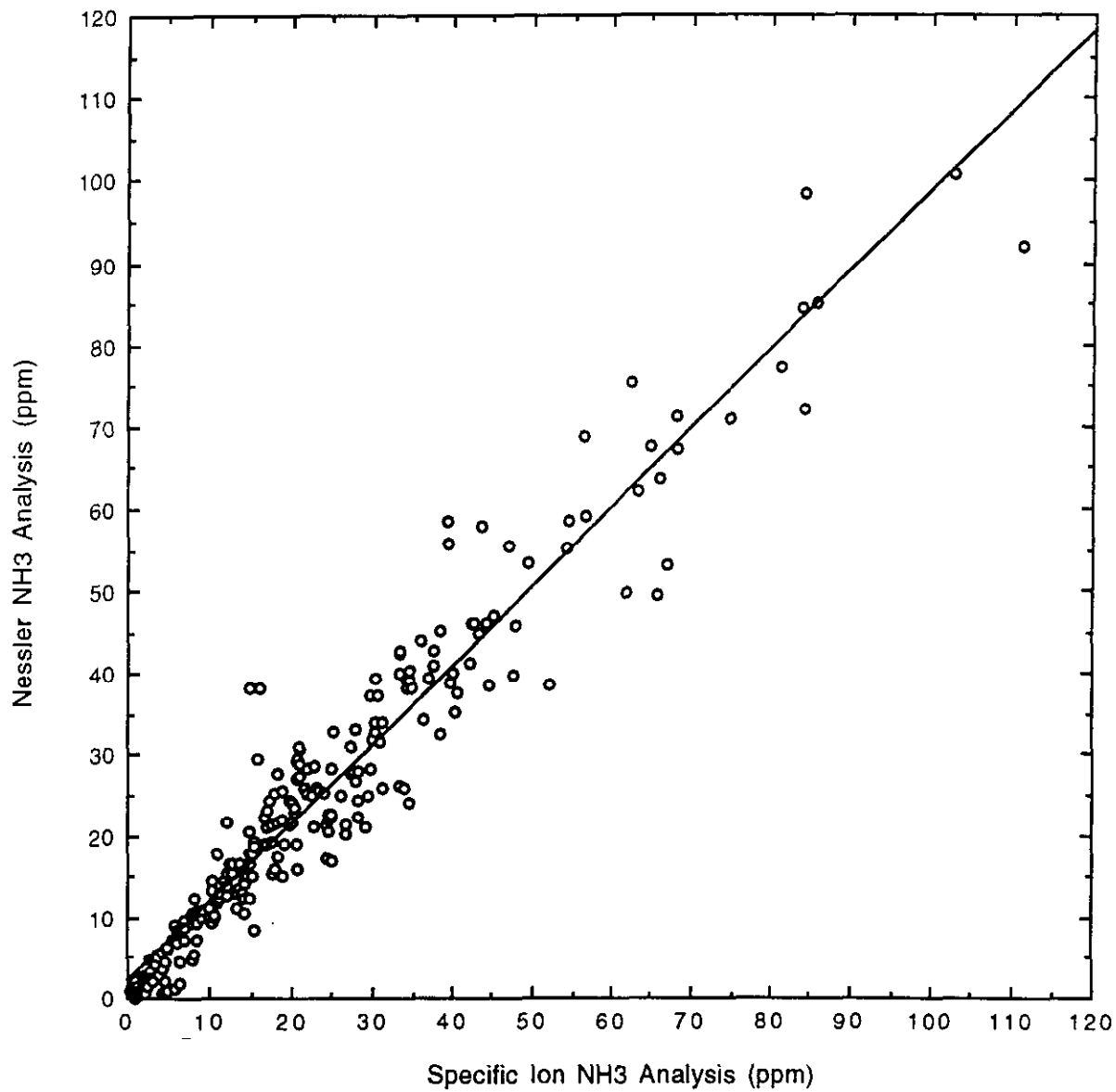


Figure 4-7. Crossplot of Nessler and Specific Ion NH₃ Analyses Results

responding as expected to changes in the N/NO ratio. A repeat of the first test condition of the day showed that although the NO removals at the beginning and end of the day were in agreement, the measured NH₃ emissions were over three times higher at the end of the day. A significant amount of testing had been previously completed at boiler loads of 80, 100 and 100 MWe, and a lack of repeatability of this magnitude had never occurred before. It was hypothesized that at 60 MWe, flue gas temperatures were low enough to allow adsorption and desorption of NH₃ by flyash deposits in the duct. This behavior was seen during the baseline SNCR tests⁽³⁾, where NH₃ measurements at the stack indicated that the ash in the baghouse provided a substantial capacity for the adsorption and desorption of NH₃. Tests performed during the earlier phase of testing showed that with the ash in the baghouse free of NH₃, it would take up to three hours for NH₃ emissions measured at the exit of the baghouse to equal that measured at the inlet.

During the current phase of testing, a test was conducted at the low-load condition, where a constant N/NO ratio was maintained for nearly three hours. This test was run after the SNCR system had been shut down for approximately 18 hours. The results (Figure 4-8) show that a substantial amount of time (on the order of one hour) was necessary for the NH₃ emissions measured at the air heater exit to stabilize, even though the NO removal measured at the same location was stable after only a few minutes. As stated above, this type of behavior was not seen at boiler loads greater than 60 MWe, and for all tests performed at these loads, waiting 15 to 20 minutes after starting a test (i.e., changing an injection parameter) before starting the NH₃ sampling procedure was more than sufficient to assure consistent and repeatable results. However, all subsequent tests at 60 MWe were run with a minimum waiting period of one hour, in order to allow the NH₃ emissions to stabilize. No further repeatability problems with the wet chemical technique were encountered after the adoption of this test protocol.

Although the wet chemical technique was the primary measurement method for NH₃ during the current test program, the CEM NH₃ measurements at the air heater exit and stack sampling points were also recorded on a test-by-test basis, thus providing an

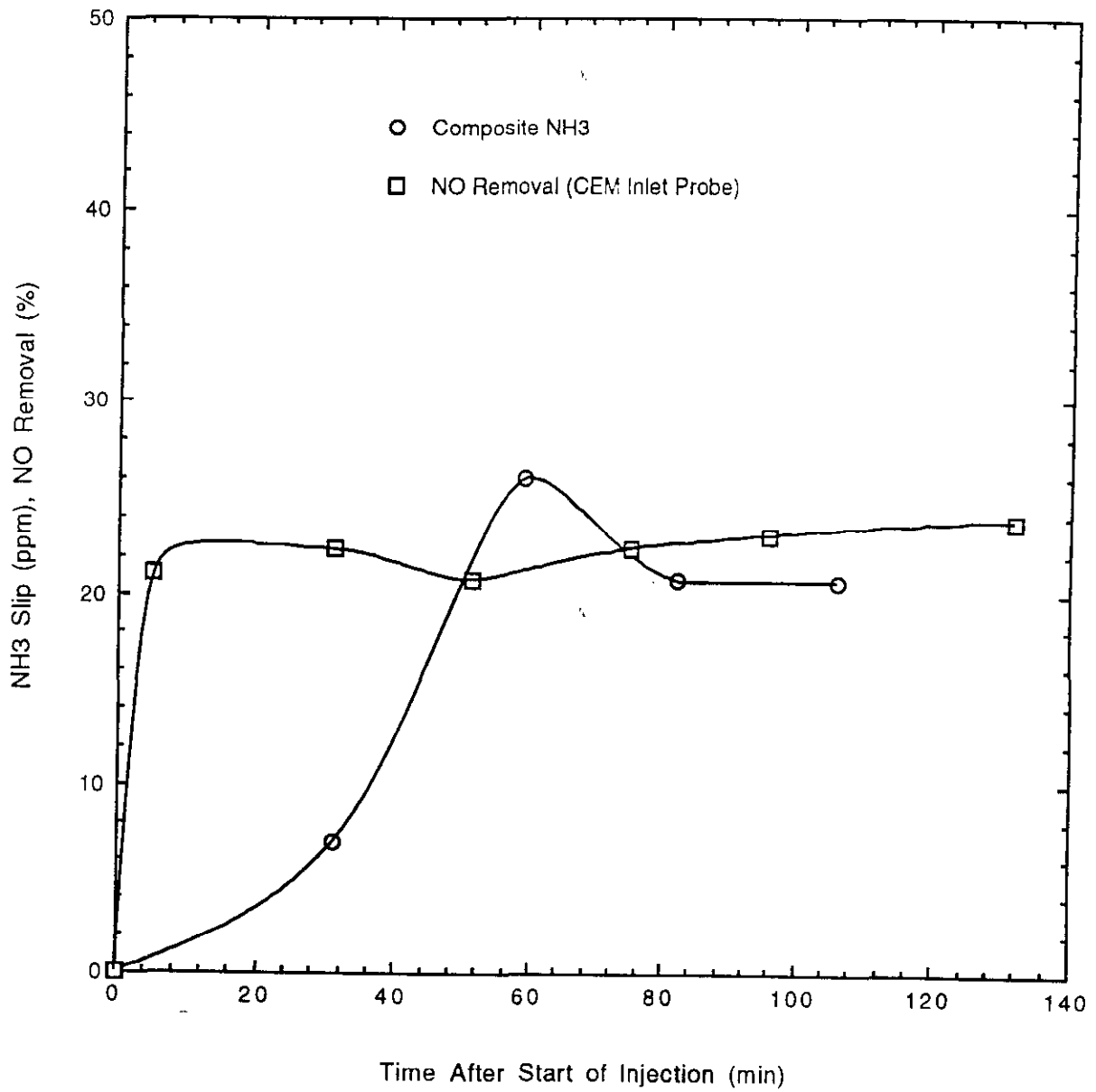


Figure 4-8. NH₃ Emissions and NO Removal at Air Heater Exit (Test Number 548)

opportunity to compare the performance of the continuous instrument to the standard technique. The vast majority of the wet chemical measurements made at the air heater exit were collected in the manner described above (i.e., composite samples across the width of the duct). However, individual samples were often collected through each of the six sampling ports (recall Figure 4-4), in order to assess the distribution of NH_3 across the duct. These measurements showed that the NH_3 profile was far from uniform, and therefore, the single CEM sampling point would not provide an accurate assessment of the average NH_3 concentration at this location. In order to provide the most reasonable comparison, the CEM data at this location was compared to the individual measurements made through the Number 4 port (again, see Figure 4-4). The results (Figure 4-9) show good agreement between the two methods, considering that there was a small difference in the sampling locations.

In order to check for accuracy of the CEM NH_3 measurements at the stack, a limited number of wet chemical NH_3 samples were also collected at this location. Although the wet chemical samples were made at a point in the duct approximately 20 feet downstream of the CEM stack probe, both were far enough downstream of the baghouse and induced draft fans that stratification of the flow was much less of a concern than at the air heater exit. The results (Figure 4-10) show good agreement between the two methods, although the CEM measurements are approximately 15 percent lower than the wet chemical results. This apparent bias is primarily due to the 5 ppm difference between the CEM and wet chemical results for the one high NH_3 slip data point in the figure, and the fact that there are only nine data points in the entire set. If the high slip point is removed from the data set, the correspondence between the two methods is nearly one-to-one. It is therefore reasonable to assume that if the number of data points was to increase, the effect of the one point would decrease, and the correlation between the two methods would be better.

Overall, the performance of the CEM in regard to the measurement of NH_3 emissions was found to be quite good. As the test program progressed, and more experience with

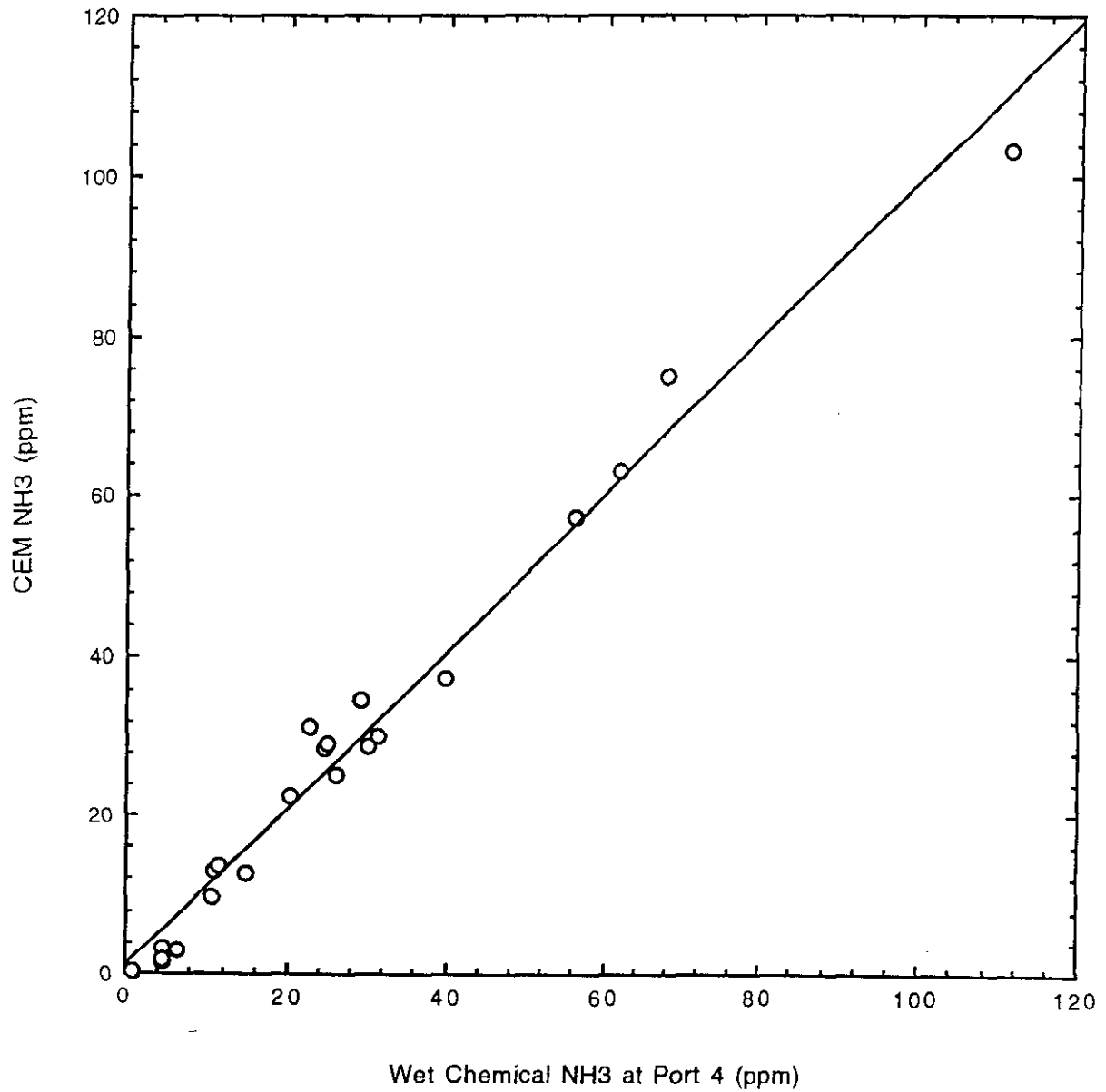


Figure 4-9. Comparison between CEM and Wet Chemical NH₃ Analyses at Air Heater Exit

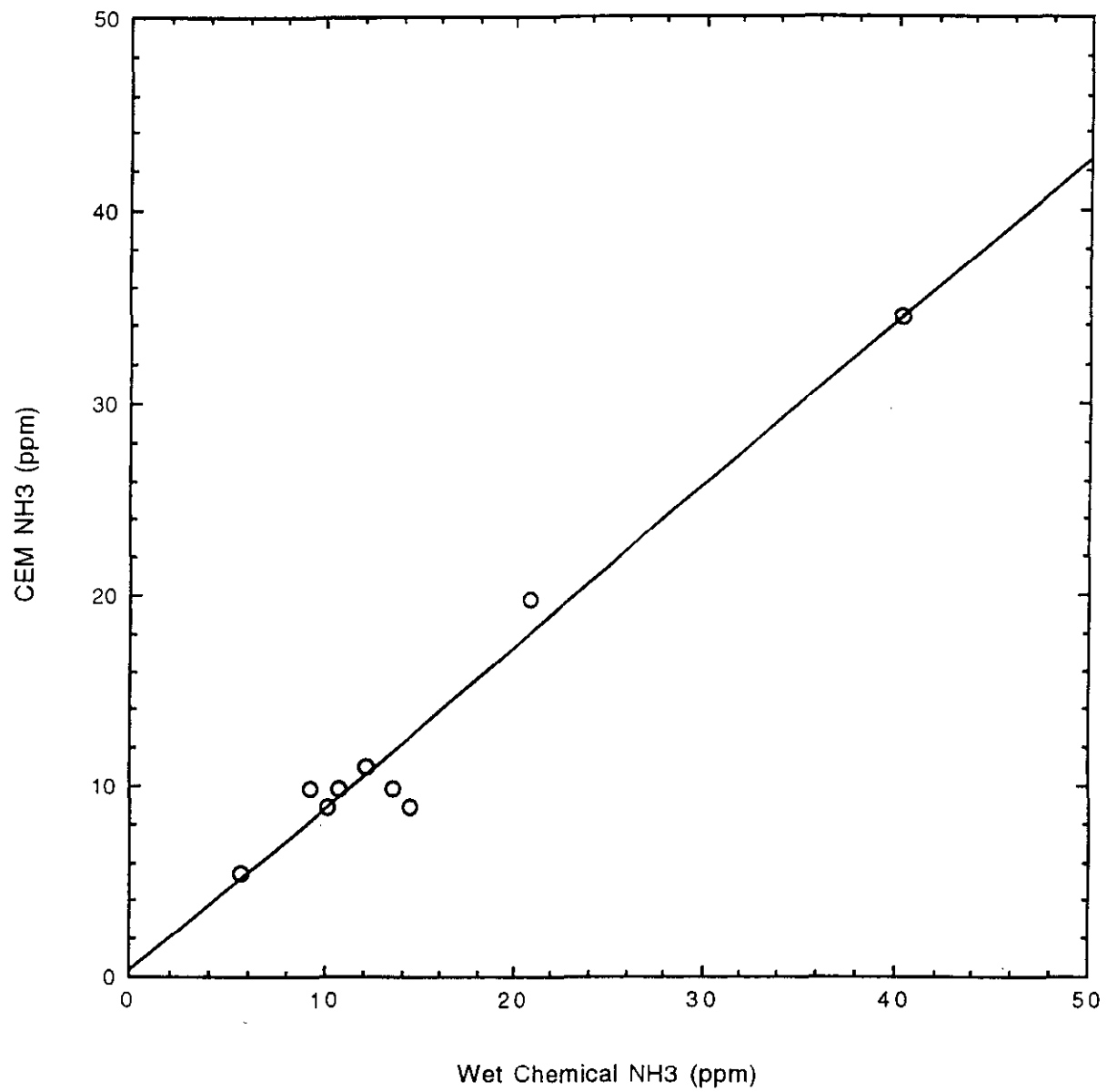


Figure 4-10. Comparison between CEM and Wet Chemical NH₃ Analyses at Stack

the instrument was gained, the monitor was used more frequently as a quick indication of trends in NH_3 slip at the air heater exit. However, it could never be used as an absolute measurement due to the stratification of the flue gas at this location. At the stack location, the CEM was believed to be accurate enough to provide a valid indication of NH_3 slip.

4.4 Furnace Exit Gas Temperature Measurements

During the course of the current test series, furnace exit gas temperature (FEGT) measurements were made in order to provide a comparison with those recorded after the combustion system retrofit during the LNB/OFA tests. The temperature measurements were made using an acoustic pyrometer.

An acoustic pyrometry system, manufactured by Combustion Developments Ltd. of England, was utilized to provide a continuous assessment of the furnace exit gas temperatures. The acoustic pyrometer sends a sound pulse across the furnace; the transit time for the pulse is measured and, thus, the mean speed of sound across the furnace is determined. The average temperature along the path can then be determined from the speed of the sound pulse. The acoustic temperature measurement technique requires a clear line of sight across the furnace at the measurement location. Since the boiler has a division wall running the length of the furnace, the first available location with acceptable access for the acoustic instrument was through a pair of ports just downstream of the first set of screen tubes (Location G in Figure 3-4).

5

RESULTS

The results section has been divided into the following subsections:

5.1 Flue Gas Temperature Measurements

As the performance of the SNCR system is highly dependent on the flue gas temperature at the injection location, this subsection will provide a review of the temperature measurements made in the vicinity of the injection location both before and after the low-NO_x combustion system retrofit.

5.2 System Optimization Tests

Before conducting the parametric performance tests with urea and converted urea, a short series of tests was conducted with the goal of providing an even flue gas composition across the furnace at the injection location, as well as minimizing the effect of any areas which exhibit uncharacteristically high NH₃ slip levels. The results of these activities, which included biasing the coal mills and varying the diameter of the liquid injection nozzles, are presented in this subsection.

5.3 Urea Injection Test Results

The results of the parametric performance tests with urea are presented.

5.4 Converted Urea Test Results

The results of the parametric performance tests with converted urea are presented.

Before presenting the test results, it is of value to discuss the impacts that the various SNCR injection parameters can have on the process. In some cases, these effects are coupled and may have offsetting impacts on the overall SNCR process. Changing an injection system parameter can 1) change the overall level of mixing of the chemical with

the combustion products, 2) change drop size and thus evaporation times, 3) change local temperatures, and 4) change the location in the furnace where the chemical mixes with the combustion products. The general effect of these various changes are summarized in Table 5-1.

As is apparent from Table 5-1, changing an injection parameter can impact the process in a number of ways. For instance, increasing the mixing air flow rate, while potentially increasing the mixing, will also provide localized cooling of the combustion products. Thus, depending upon the local temperatures, increasing the mixing air flow rate may or may not have an overall beneficial effect on the SNCR process performance.

Table 5-1
General Effects of Injection System Parameters

Increasing	Jet Penetration	Overall Mixing	Drop Size	Local Temperature
Mixing Air Pressure ⁽¹⁾	+	+	-	-
Dilution Water Flow	+	0	-	-
Air Orifice Size ⁽²⁾	-	-	+	0
Liquid Orifice Size ⁽³⁾	+	0	+	0

⁽¹⁾ Same air orifice size increases air flow rate

⁽²⁾ Same air flow rate decreases injection velocity

⁽³⁾ Same liquid flow decreases atomization

Localized cooling of the flue gas occurs when the air/liquid mixture is injected due to 1) the energy required to heat the mixing air, 2) the energy required to vaporize the liquid and 3) the energy required to heat the vaporized liquid to the local combustion product temperature. Table 5-2 summarizes the nominal cooling effects for the range of injection system parameters investigated during the current series of tests. The local cooling effect can range from 34 to 66°F at full load conditions depending on the injection system parameters. The cooling effect can be higher at lower boiler operating loads.

Table 5-2

Summary of Local Combustion Gas Cooling by the SNCR Injection Jets

Load (MWe)	Injection Parameters		Calculated Localized Cooling, ΔT (°F)
	P_{Air} (psig)	Q_{Liq} (gpm)	
100	12	6	66
100	12	4	60
100	12	2	54
100	8	6	50
100	4	6	34

Before the results are presented, it is also worthwhile to discuss how the tests were actually run and, in particular, how the chemical injection rate and NO removals were defined. The relative chemical feed rate for a particular test is indicated by the N/NO molar ratio (i.e., the molar ratio of the amount of nitrogen injected to the amount of NO in the untreated flue gas). Before each test, a target N/NO ratio was decided upon, and a baseline NO level measured at the economizer exit. From these two values, a chemical feed rate was calculated and the injection pump speed and urea control valve settings determined. At the conclusion of the test, the N/NO ratio was calculated from the average urea flow and baseline NO level. Since the urea flow may vary slightly over the duration of a test, and the baseline NO level may vary over the course of the day (baseline NO levels were not checked after each individual test, but periodically throughout each day), the calculated N/NO ratio was often slightly different than the target value. Throughout the text of this report, the target (or nominal) N/NO ratios will be utilized in the discussion of test conditions (i.e., a nominal N/NO ratio of 1.0 will indicate a calculated N/NO ratio in the region of 0.9 to 1.1).

From the preceding discussion, it is apparent that the N/NO ratio for each test was based on the boiler NO emission level existing after the low-NO_x combustion system retrofit. The amount of NO removal for each test was also calculated relative to this post-retrofit baseline. Although an individual test may result in a calculated NO removal of 40 percent, it must be realized that this is in addition to the 63 to 69 percent achieved with

the low-NO_x combustion system (recall Figure 2-9). For this example, the overall NO removal due to the cumulative effect of the low-NO_x combustion system and SNCR would be approximately 80 percent.

Finally, recall that during the early part of the baseline SNCR test program, it was found that the flue gas temperature at the upper (second) injection level was too cold for effective NO_x removal even at full load. All subsequent testing was conducted with the lower (first) level of injectors and, therefore, all of the results presented in this report are for Level 1 injection only unless otherwise noted.

5.1 Flue Gas Temperature Measurements

Flue gas temperatures have been measured during five separate test campaigns at Arapahoe Unit 4. The first temperature measurements were made in April of 1991 to support the design of the SNCR injection system⁽⁶⁾. Subsequent temperature measurements have been made during the baseline tests with the original combustion system⁽¹⁾, the baseline SNCR testing⁽³⁾, retrofit low-NO_x combustion system testing⁽²⁾, and during the current phase of testing with the SNCR system and low-NO_x combustion system.

Figure 5-1 summarizes the flue gas temperature measurements made at the furnace exit (Port G, see Figure 3-4) using the acoustic pyrometer. Acoustic temperature measurements made during the baseline burner and baseline SNCR tests showed that the furnace exit gas temperatures were significantly lower than those measured in April 1991 in support of the SNCR system design phase. The data collected during the baseline burner and baseline SNCR tests agree well with each other, but are on the order of 150 to 200°F lower than those measured in April 1991. Although no definitive explanation can be put forth, possible reasons for the difference in temperatures were discussed in References 1 and 3.

As seen in Figure 5-1, temperature measurements made following the low-NO_x burner retrofit, and more recently during the current SNCR testing, indicate a decrease in furnace

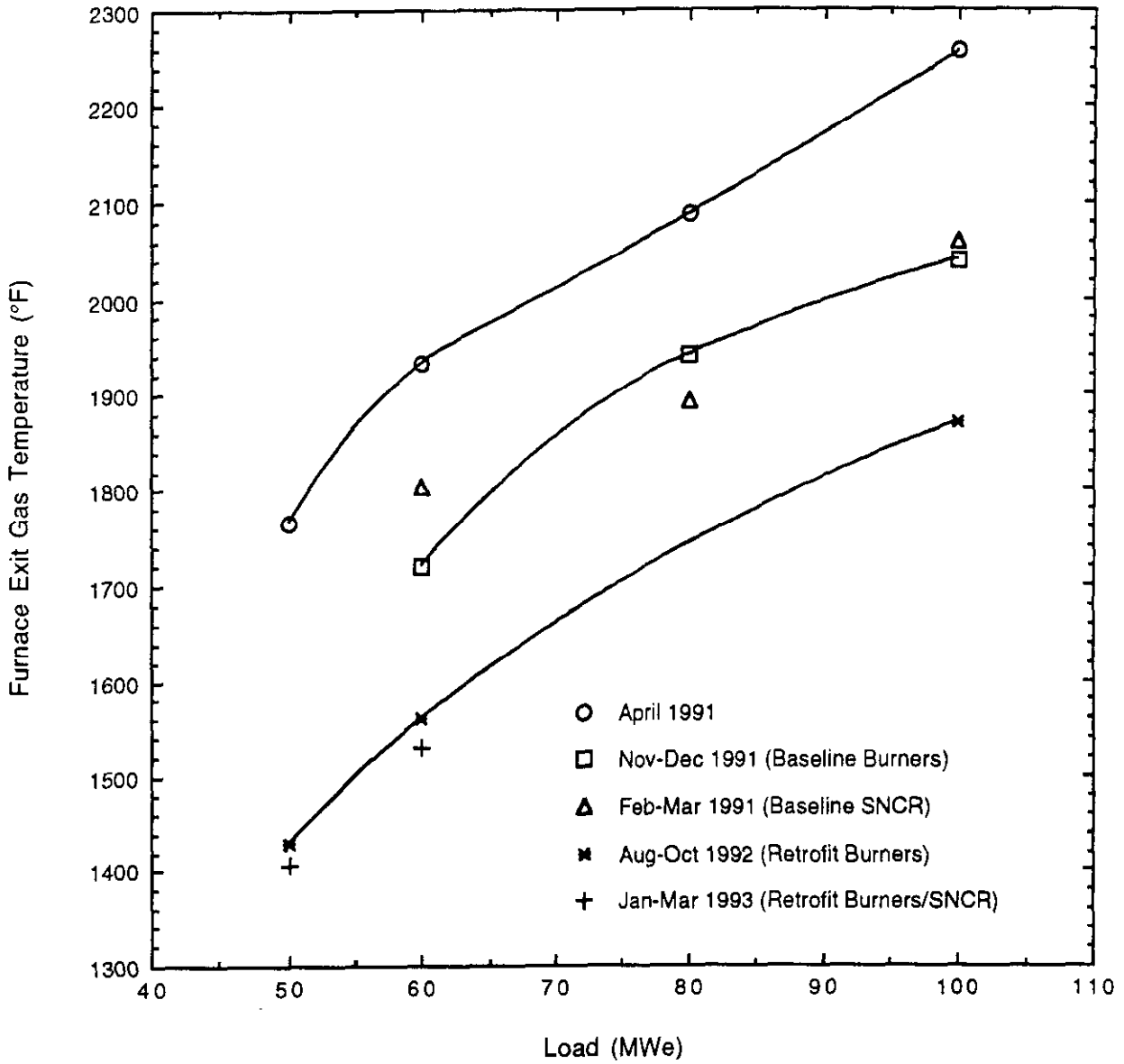


Figure 5-1. Historical Variation of Furnace Exit Gas Temperature as a Function of Boiler Load

exit gas temperatures of 180 to 240°F (relative to the measurements made during the baseline burner and baseline SNCR testing).

After the combustion system retrofit, suction pyrometry (HVT) temperature traverses were also made through the eight ports along the north side of the boiler downstream of the second set of screen tubes (recall Figure 3-4). These measurements were made to assess the effect of the retrofit on the flue gas temperatures in the immediate vicinity of the SNCR injection location. Measurements at 2, 4, 6, and 8-foot depths were made through each of the eight ports, resulting in a 32-point grid. Figure 5-2 shows the average of the 32 temperature measurements as a function of boiler load, and compares the results to those found measured prior to the retrofit. The data show a post-retrofit decrease in temperature on the order of 250°F across the load range. Figure 5-3 shows the average post-retrofit temperature profiles at the north port location for boiler loads of 60, 80, and 110 MWe. In this figure, each point represents the average of the four measurements made through a particular port. Excluding the points near the outside walls, all three curves show a temperature variation across the boiler on the order of 200°F. The variation at 60 MWe is the greatest, and is likely due to the three mills in service operating condition at this load.

The burner retrofit has resulted in a furnace exit gas temperature decrease on the order of 200°F. This has impacted the amount of excess air required to maintain steam temperature at reduced loads. As will be seen, this decrease in temperature has also impacted the performance of the SNCR system.

5.2 System Optimization Tests

Prior to parametrically characterizing the performance of the SNCR system with the low-NO_x combustion system, the optimum operating conditions and settings for the SNCR system were identified. This optimization involved two activities. In the first, the individual coal mills were biased to provide a more even gas composition across the furnace (west to east). In the second, the individual SNCR injection nozzle sizes were varied in order to minimize NH₃ slip. These two optimization exercises were done from the standpoint

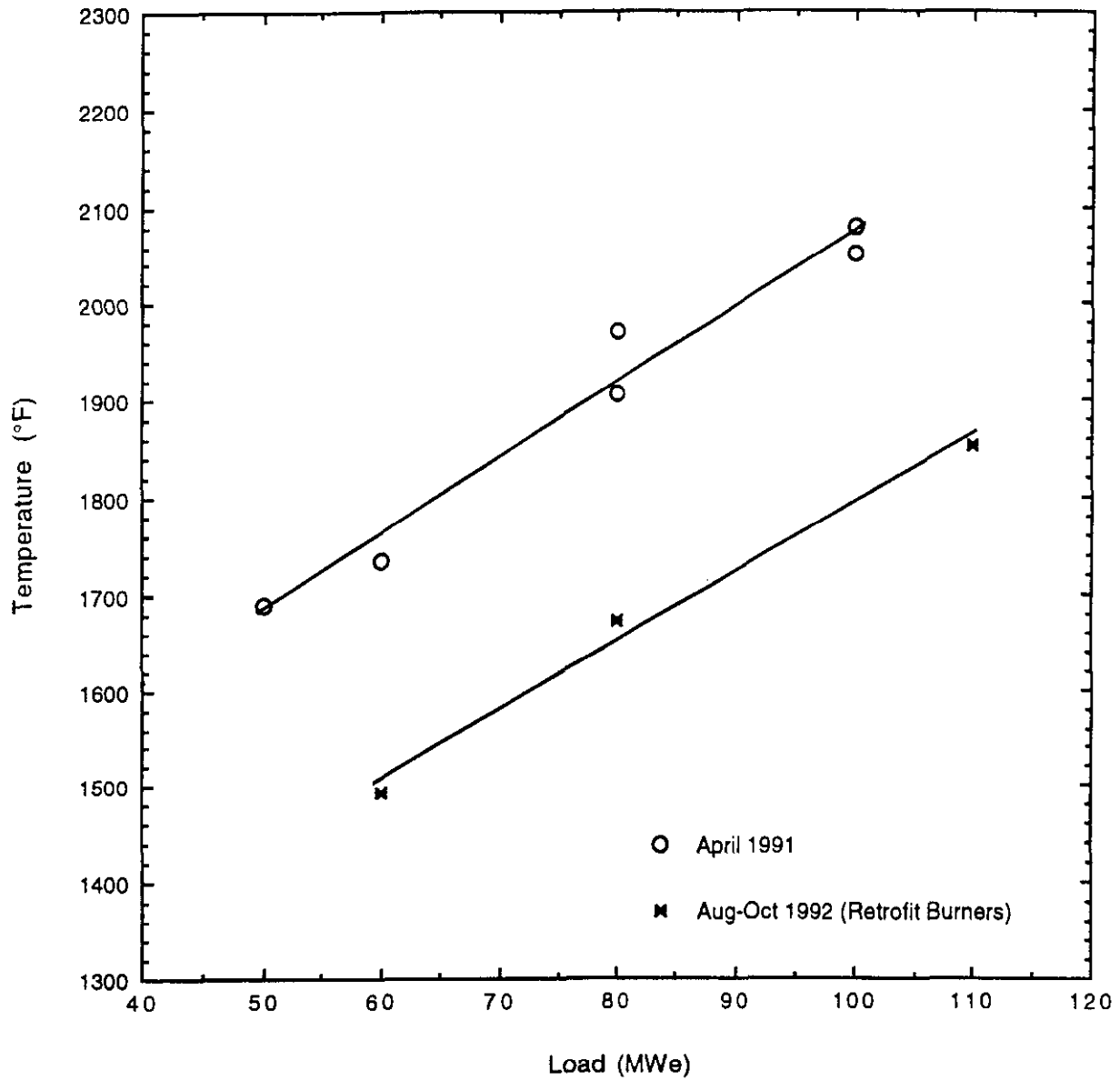


Figure 5-2. Pre- and Post-Retrofit North Port Average Temperatures as a Function of Boiler Load

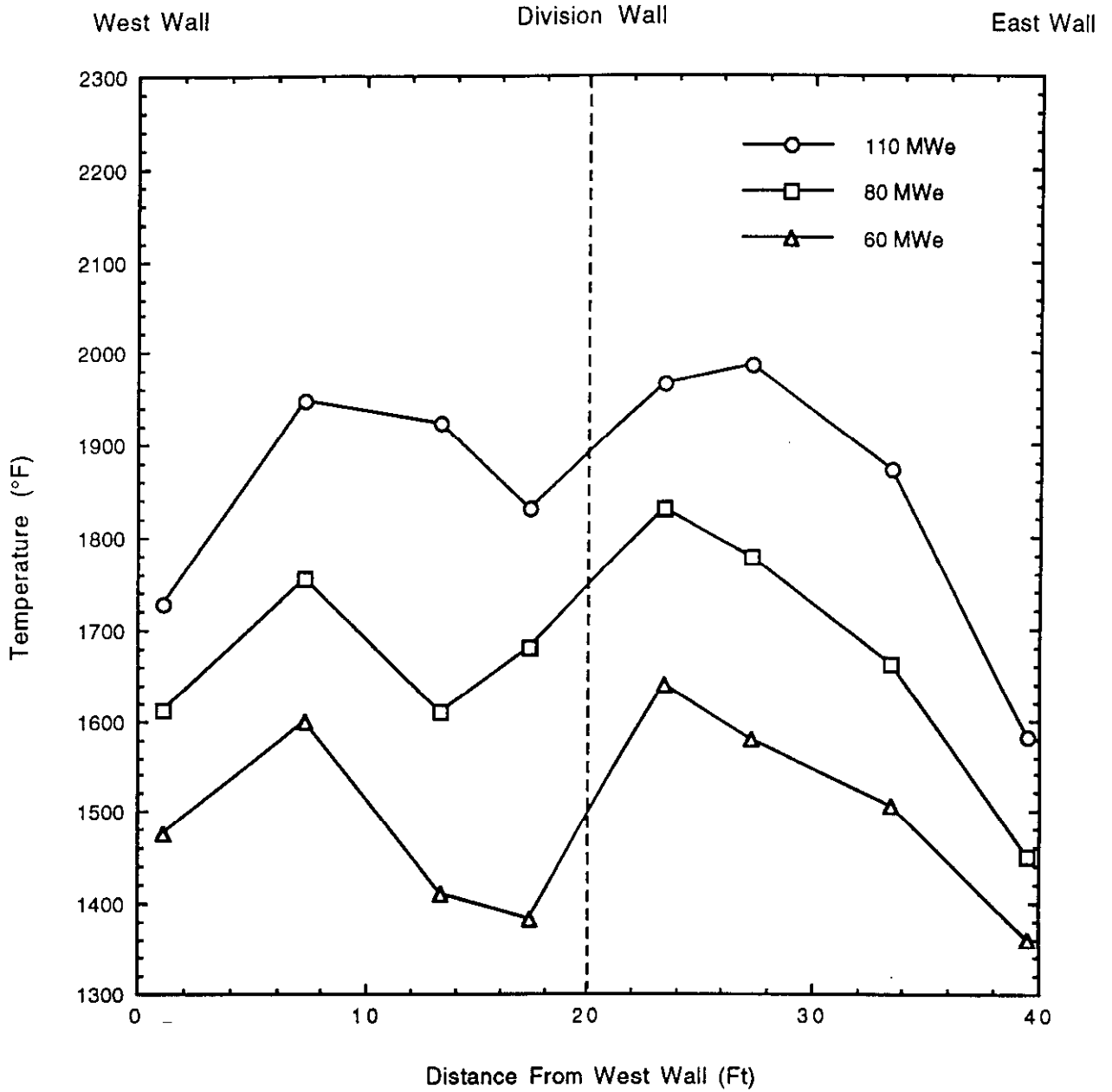


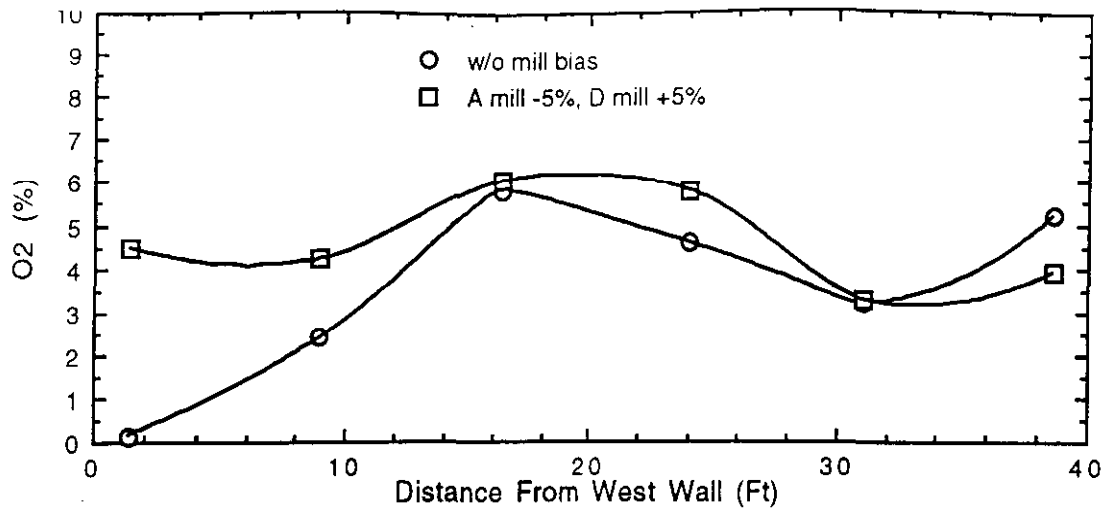
Figure 5-3. Post-Retrofit Average North Port Temperature Profiles at 60, 80 and 110 MWe

of hardware or operational changes that could be easily incorporated into the day-to-day operations of the unit. For instance, the injection nozzle sizes were optimized at the full load condition with all four coal mills in service because this is considered the most common operating condition. Additionally, it also would not be operationally feasible to specify different size nozzles for different loads or mill-in-service conditions, since this would require removing individual injectors and manually changing the nozzles.

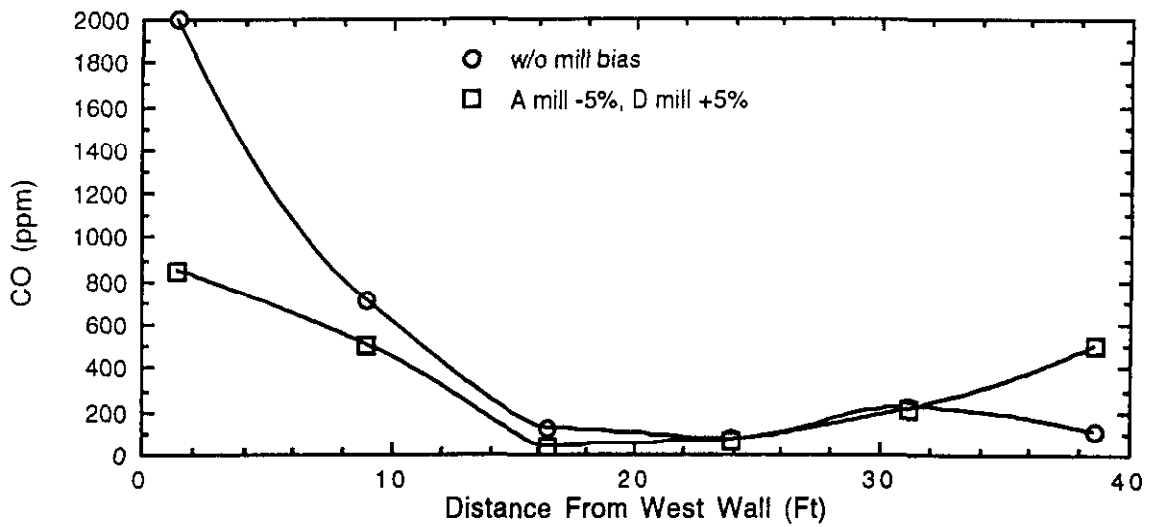
5.2.1 Mill Biasing

During the retrofit burner test program⁽²⁾, it was found that the west side of the furnace typically yielded high levels of CO. Balancing the secondary air flows to individual burners, while reducing the overall levels, did not completely eliminate this high CO region. Since this was shown to have little effect on NO emissions, this air balancing effort was not further pursued during the retrofit burner test program. In addition, the flue gas temperature measurements showed lower temperatures on the east wall of the furnace (recall Figure 5-3).

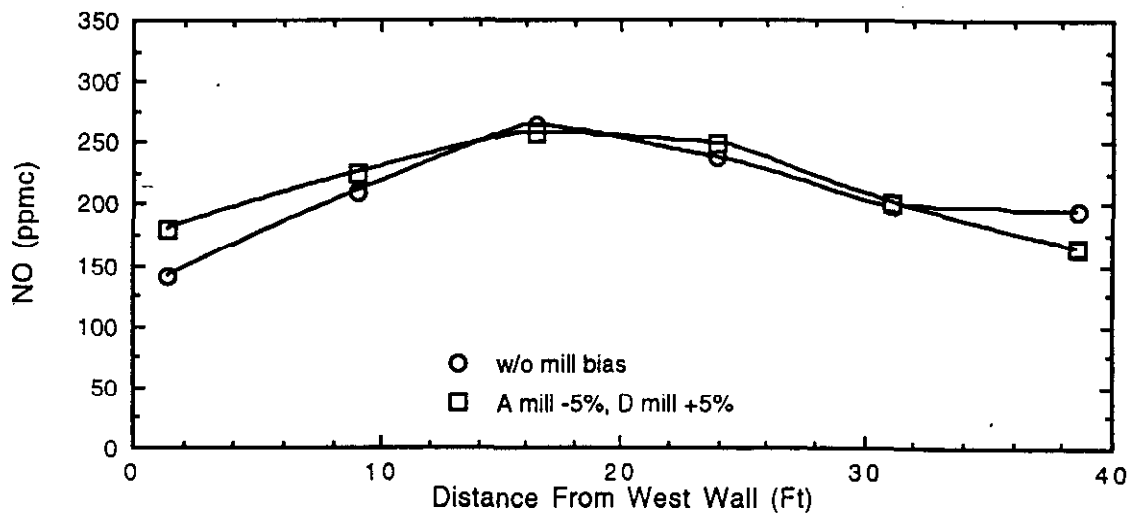
Prior to extensive SNCR testing with the retrofit burners, an effort was made to minimize the high CO region on the west side of the furnace while increasing the flue gas temperature near the east wall. This was accomplished by biasing the fuel feed to the individual coal mills. A number of mill bias patterns were tested. The best result was obtained by biasing A and D Mills. Recall that A Mill supplies coal to two burners on the far west side of the furnace, while D Mill supplies coal to two burners on the far east side (see Figure 2-5). In order to compensate for the high CO levels on the west side and low temperatures on the east side, the fuel feed to A Mill was increased and the feed to D Mill decreased. Biasing in this way would move coal primarily from the west side of the furnace to the east side. Biasing each mill 10 percent (A Mill -10 percent; and D Mill +10 percent) resulted in a large an impact on steam temperatures and a shift of the high CO region from the west wall to the east wall. The bias was reduced until the steam attemperation rates on the east and west sides of the furnace were not markedly different. This was accomplished by a -5 percent bias on the A Mill and a +5 percent bias on the D Mill. Figure 5-4 shows the effect of this level of mill bias on the west-to-



a) O₂ Profiles



b) CO Profiles



c) NO Profiles

Figure 5-4. Effect of Mill Bias at 100 MWe with 3.5 Percent Control O₂

east distribution of O₂, CO and NO. The data shown in Figure 5-4 was collected at 100 MWe with an O₂ control set point of 3.5 percent and no SNCR chemical injection. Biasing the A and D Mills at this condition increased the O₂ on the west side of the furnace as well as decreased the CO level at this location from over 2000 ppm to under 900 ppm. A change in the NO profiles across the furnace is also evident. Reducing the amount of coal fed to the west side of the furnace increased the local NO level near the west wall from nominally 140 ppmc (dry corrected to 3% O₂) to approximately 160 ppmc. Conversely, with the increased coal flow through the D Mill, the local NO level near the east wall decreased from nominally 200 ppmc to 165 ppmc on the east side.

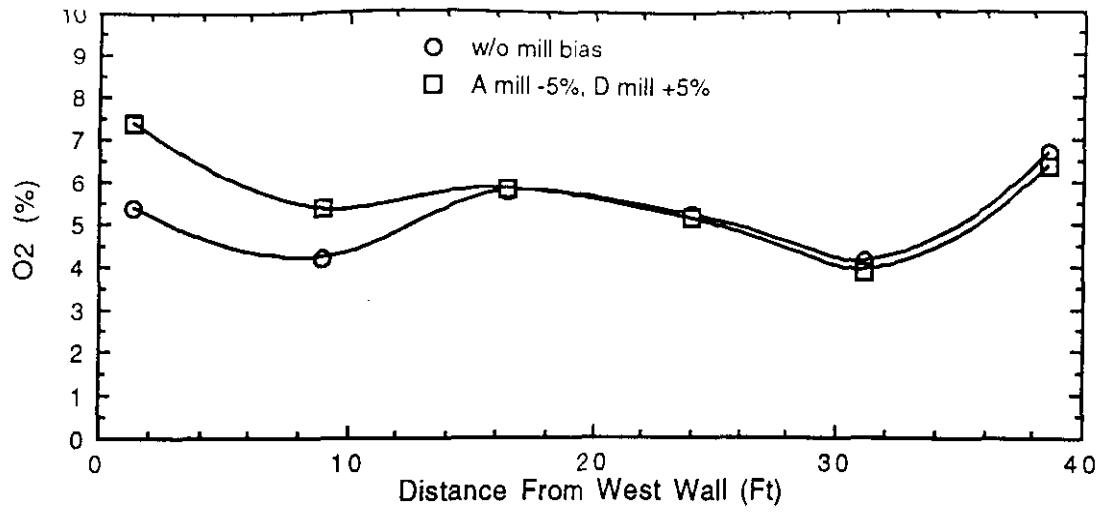
A second set of mill bias tests were performed at a higher O₂ control setpoint of 4.0 percent. The results of these tests are shown in Figure 5-5. At the higher O₂ setting, the same general trends are seen in the CO and NO profiles. However, for this test condition without any mill bias, the furnace did not exhibit the extremely low O₂ behavior near the west wall seen at the previous tests condition. But again, the CO levels in this region were high for the unbiased case, and were reduced by biasing the A and D Mills -5 percent and +5 percent, respectively.

Biasing the mills also had a visual impact on the flue gases at the furnace exit. When viewed from the west side through Port G (recall Figure 3-4), without the mill bias the gases were opaque, typically to the point where one could not see the furnace division wall. The east side, however, was always quite clear. Biasing A Mill down 5 percent, and D Mill up 5 percent, cleared up the west side such that there was no visual difference between the two sides.

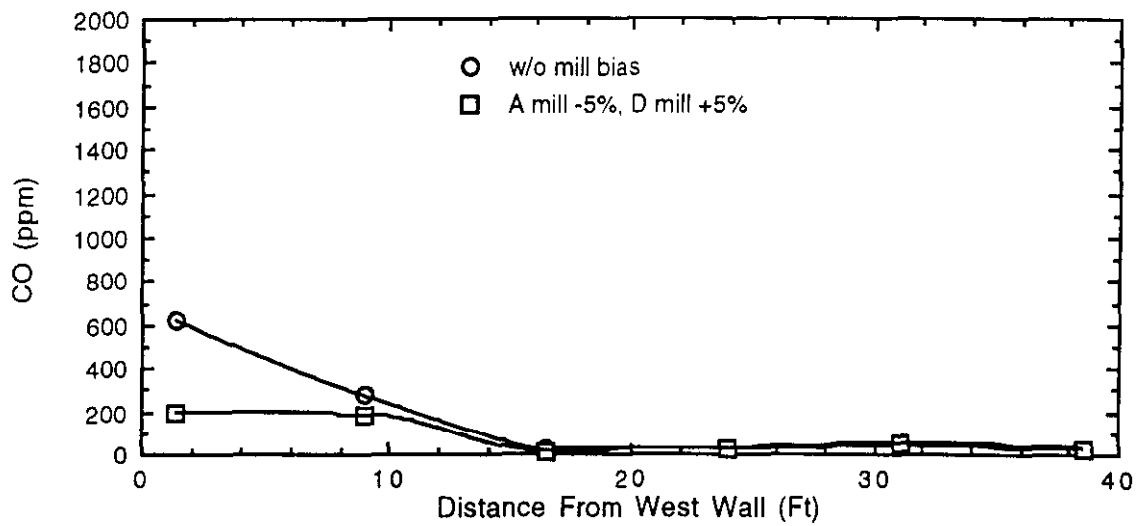
Unless otherwise noted, the SNCR results presented in this report were conducted with a -5 percent bias on A Mill and a + 5 percent bias on D Mill.

5.2.2 SNCR Injector Optimization

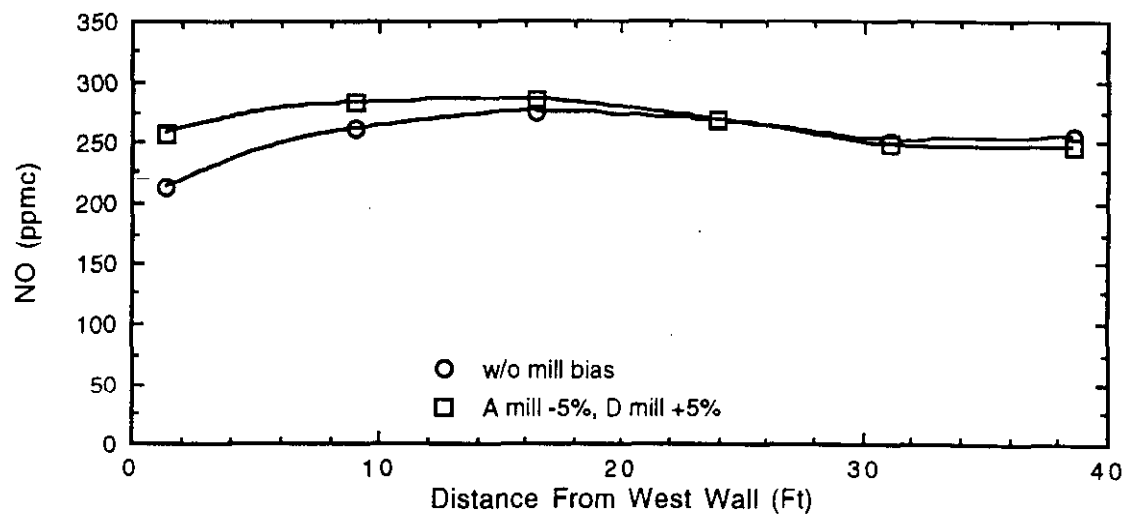
The SNCR system consists of two injection levels, each having 10 injectors running west to east across the furnace. As was shown in Figure 3-13, Injector Number 1 is on the



a) O₂ Profiles



b) CO Profiles



c) NO Profiles

Figure 5-5. Effect of Mill Bias at 100 MWe with 4.0 Percent Control O₂

west side of the furnace, with injector Number 10 on the east side. Even with the optimum mill bias settings discussed above, preliminary testing showed a tendency for higher NH₃ slips on the east side of the unit. In an attempt to reduce the local NH₃ slip on the east side, a test series was conducted at 100 MWe with urea injection, where the liquid orifice size for Injectors 9 and 10 were reduced. Reducing the liquid orifice size on these injectors would locally reduce the urea flow, increasing the flow to the balance of the injectors, and hopefully reduce the overall NH₃ slip levels while increasing the overall NO removals.

The results of these tests are shown in Figure 5-6. Figure 5-6a shows that reducing the liquid orifice size on the Number 10 injector resulted in a significant increase in NO removal (approximately 6 percentage points at a nominal N/NO ratio of 1.15). No further improvement was seen when the liquid orifice in injector Number 9 was also reduced. The NH₃ slip results in Figure 5-6b show similar improvements. A decrease in NH₃ emissions was seen when the Number 10 liquid orifice size was reduced, but no further reductions were realized when the Number 9 liquid orifice diameter was also reduced.

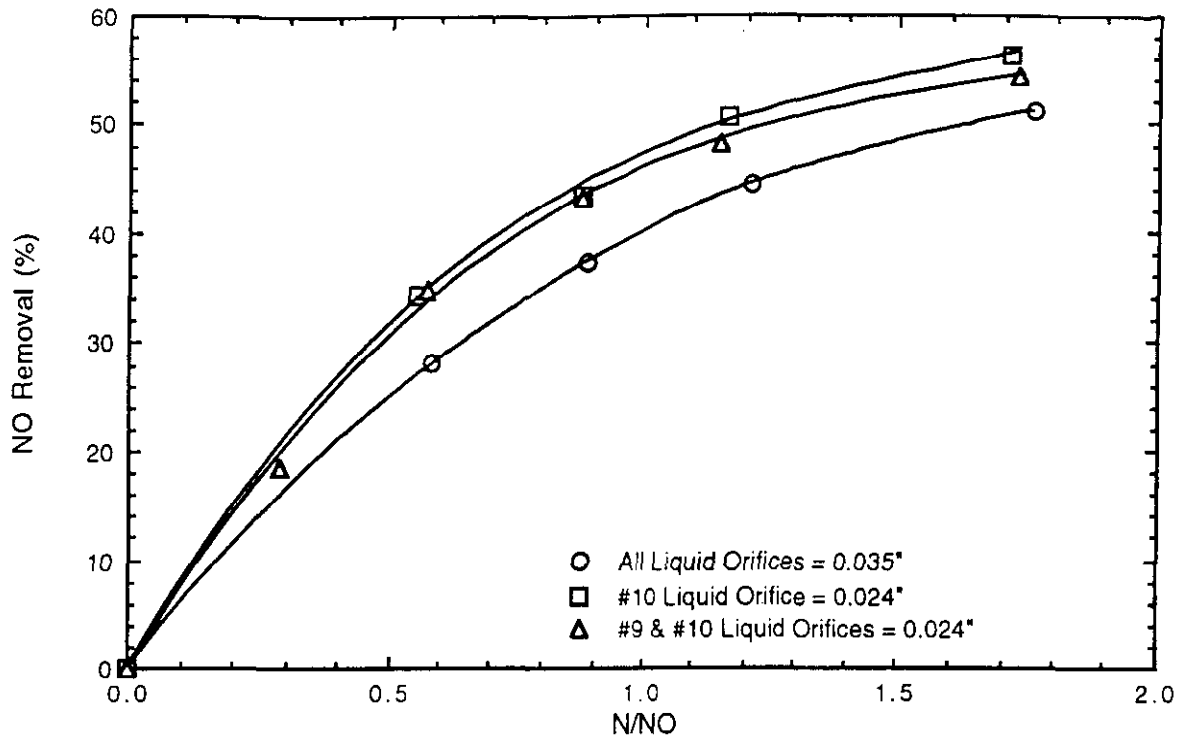
Based on the above tests, using a smaller liquid orifice in the Number 10 injector provided an increase in NO removal while reducing NH₃. The balance of the SNCR testing was conducted with the following liquid orifice configuration:

Injectors 1 through 9:	0.035-inch diameter
injector 10:	0.024-inch diameter

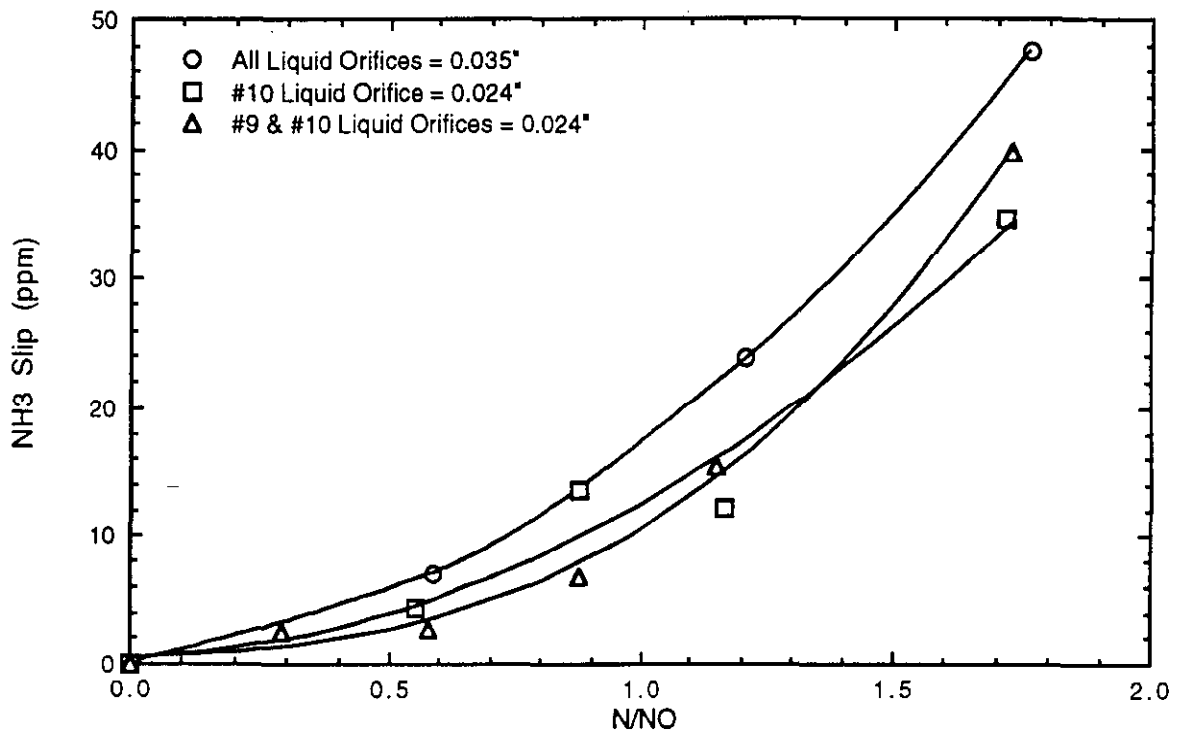
5.3 Urea Injection Test Results

Following completion of the system optimization tests, a series of parametric tests was conducted with urea injection. The results of these tests will be presented in the following subsections:

- 5.3.1 Point-by-Point Gaseous Traverses
- 5.3.2 Effect of Boiler Load and Chemical Injection Rate
- 5.3.3 Effect of Mills Out of Service
- 5.3.4 Effect of Total Liquid Flow Rate



a) NO Removal



b) NH₃ Emissions

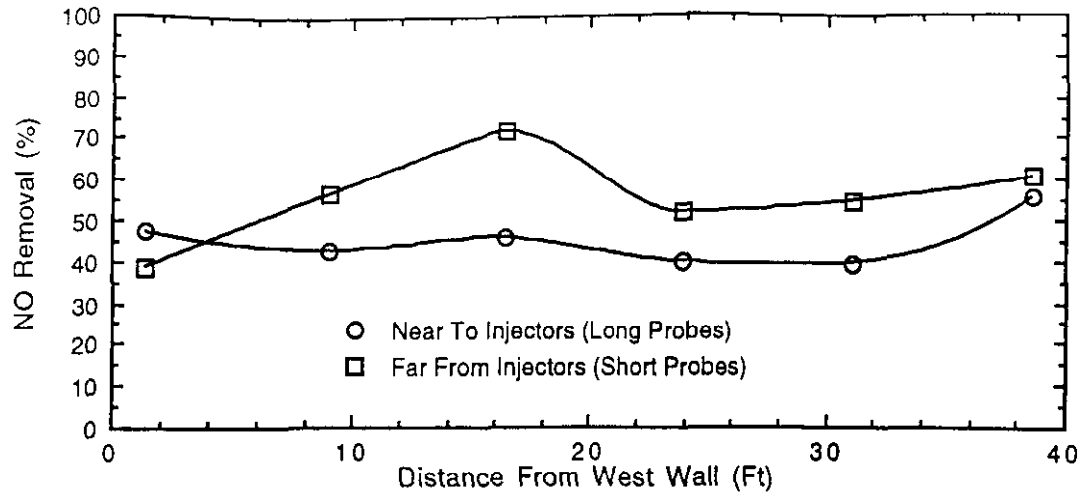
Figure 5-6. Effect of Liquid Orifice Size on Urea Injection at 100 MWe
(6.0 gpm total liquid flow, 8 psig air)

- 5.3.5 Effect of Mixing Air Pressure
- 5.3.6 Effect of Bi-Level Injection
- 5.3.7 Nitrous Oxide (N₂O) Emissions
- 5.3.8 CO Emissions

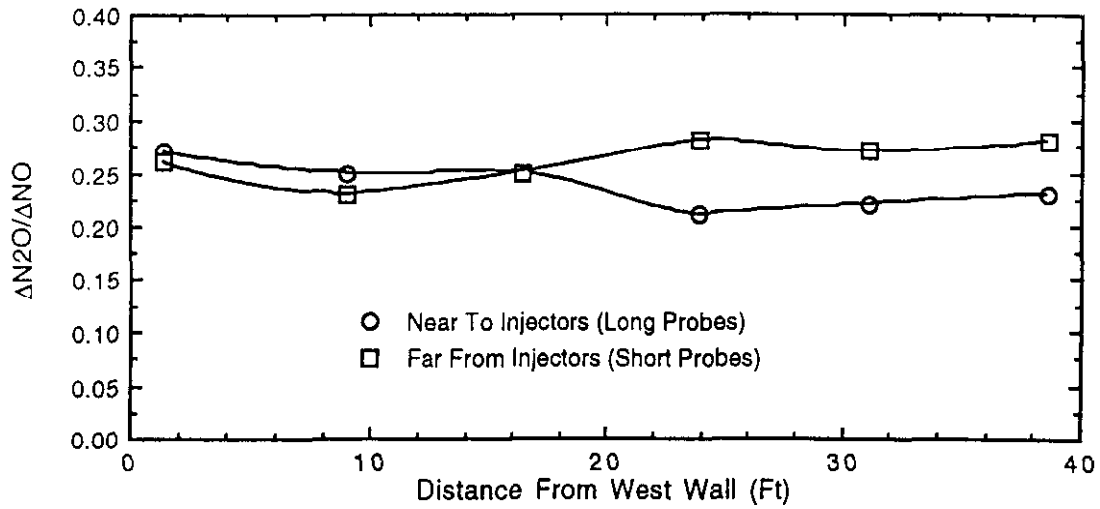
5.3.1 Point-by-Point Gaseous Traverses

In order to provide more insight into how effectively the injection system distributed the urea in the furnace, a test was conducted at a boiler load of 100 MWe with a urea injection rate corresponding to a N/NO ratio of 1.15. Point-by-point measurements were made at the 12-point grid at the economizer exit (recall Figure 4-3) to characterize the local NO removal and N₂O production. In addition, point-by-point measurements of NH₃ slip were made at the six ports located at the air heater exit (recall Figure 4-4). At each air heater exit port the NH₃ measurement was made at a single vertical location at the center of the duct.

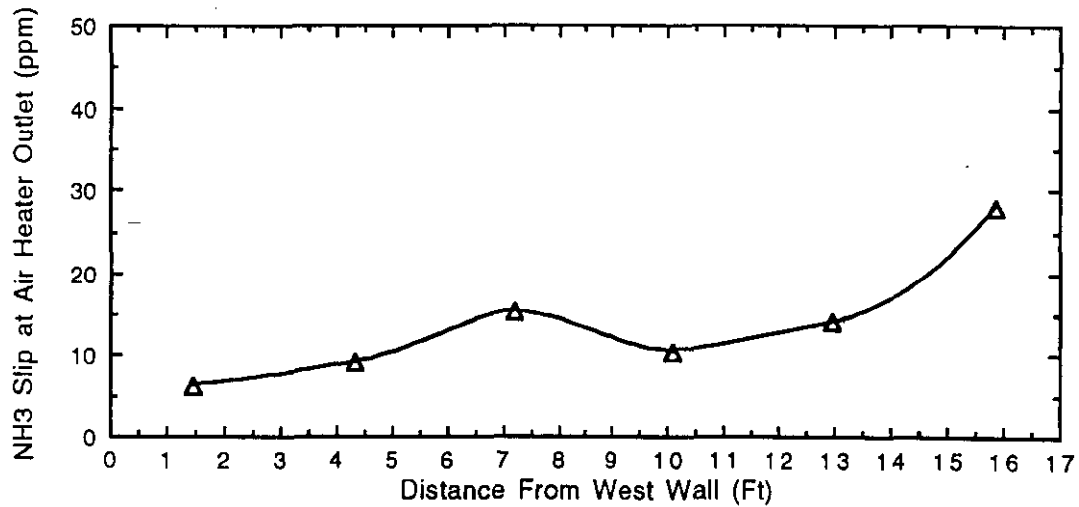
Figure 5-7 shows the results of this test. The NO removals and N₂O production are shown in Figures 5-7a and 5-7b, respectively. Recall that if stream lines were drawn from the point of injection vertically up and over to the tubular air preheater, the "short probes" at the economizer exit location would tend to sample flue gas toward the south wall of the convective section away from the urea injectors. From Figure 5-7a, the local NO removals are highest from the short probes (i.e., the flue gas farthest from the injectors). It is difficult to say whether the higher removals far from the injectors are due to 1) the distribution of more urea out and away from the injectors, or 2) a flue gas temperature stratification in the north-south direction. The HVT temperature measurements made through the north ports during the retrofit burner tests showed the temperature increasing as the probe insertion depth increased. However, due to physical constraints, the suction pyrometer could only probe 8 feet away from the wall, which is only half-way across the 16-foot depth at this location. Acoustic pyrometry measurements⁽⁶⁾, on the other hand, have shown a lower temperature region at Port D (recall Figure 3-4), which is in a region beyond the reach of the suction pyrometer through the north ports. As will be discussed in the next subsection, the temperature on average



a) NO Removal



b) N₂O Production



c) NH₃ Emissions

Figure 5-7. Point-by-Point Profiles for Urea Injection at 100 MWe
(N/NO = 1.15, 6.0 gpm total liquid flow, 8 psig air)

appears to be on the high side of the SNCR temperature window at 100 MWe. This would suggest that the higher NO removals far from the injectors is due to the urea reaching the cooler, more optimum, temperature region in the vicinity of Port D. But again, the effect of differences in chemical distribution cannot be discounted.

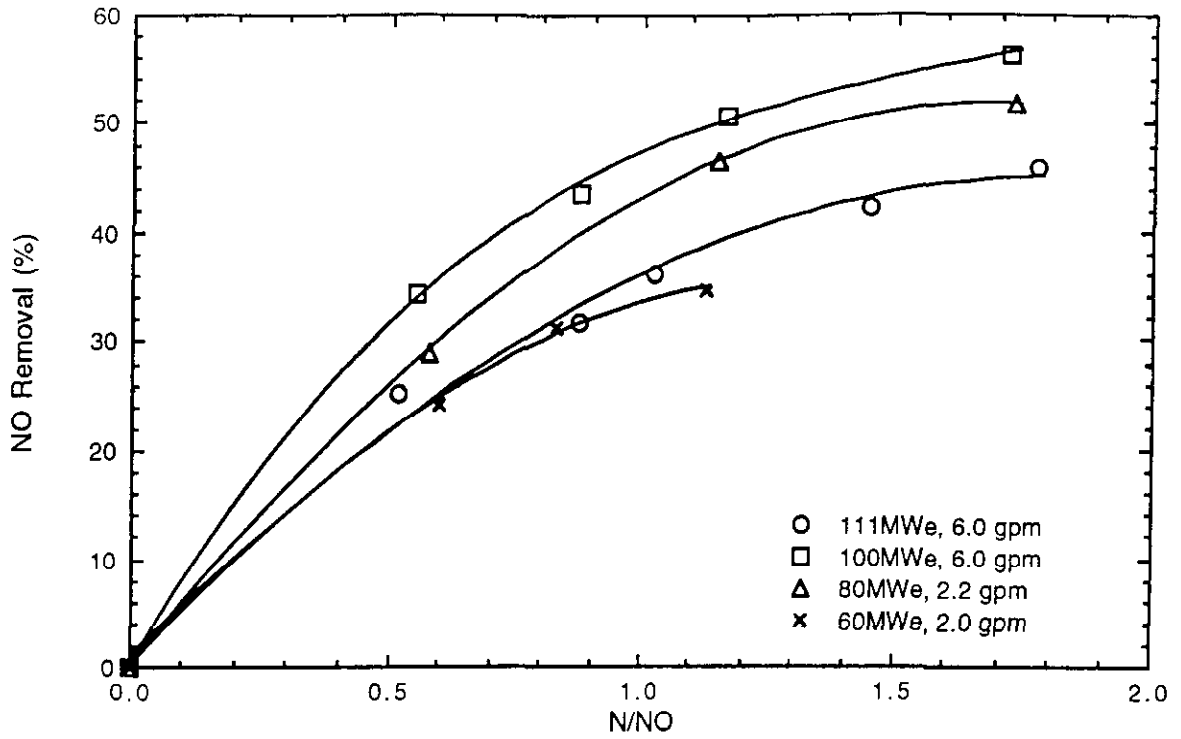
The N₂O production is shown in Figure 5-7b. In this figure, the N₂O is shown as the ratio of the amount of N₂O produced by urea injection divided by the amount of NO reduced (i.e., the fraction of the NO reduction converted to N₂O). The local N₂O production is fairly uniform with somewhat higher N₂O levels for the gas "far" from the injectors on the east side.

The NH₃ slip, profile measured at the air heater exit is shown in Figure 5-7c. The distribution is fairly uniform with a slightly increasing trend west to east with levels less than 15 ppm, except for the far east port where the local NH₃ slip level approaches 30 ppm. This is consistent with the prior discussion indicating lower temperatures on the east side (even though mill biasing helped smooth out the gas species and temperature profiles).

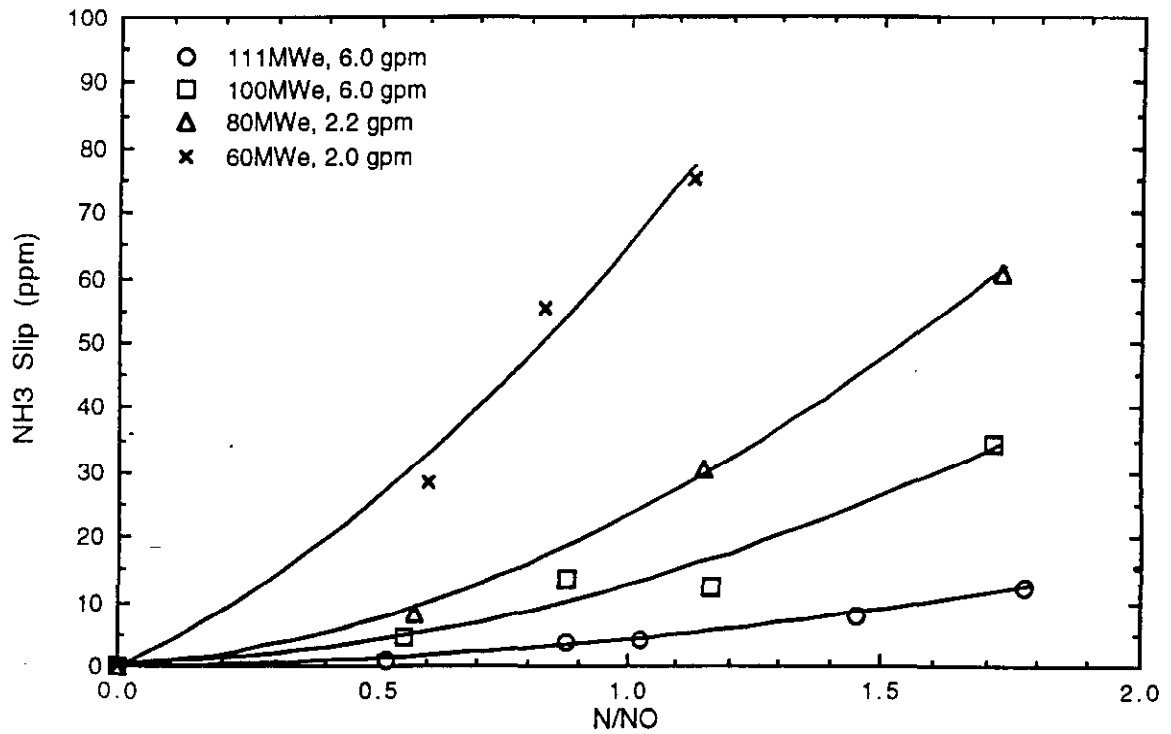
While there appear to be some variations in local SNCR performance that may be attributed to either, or both, chemical distribution and temperature stratification, overall the results indicate that the injection system is performing well in terms of injection and mixing. There don't appear to be any regions in the furnace that are largely devoid of chemical, or any where there is too much chemical.

5.3.2 Effect of Boiler Load and Chemical Injection Rate

The two most important parameters that will affect the SNCR performance are the boiler load and the chemical injection rate (N/NO molar ratio). Boiler load primarily affects the temperature in the region of chemical injection, although changing load will also change the available residence times. The effect of load and N/NO ratio is shown in Figure 5-8. Figure 5-8a shows NO reduction as a function of N/NO ratio for loads of 111, 100, 80 and 60 MWe. Figure 5-8b shows the corresponding levels of NH₃ slip. (The NH₃ slip values



a) NO Removal



b) NH₃ Emissions

Figure 5-8. Effect of Boiler Load and N/NO Ratio for Urea Injection (8 psig air)

are a composite wet chemical measurement made through the six ports at the air preheater exit.) For these tests, total liquid flow rates of 6.0 gpm were used for the 100 and 111 MWe tests, while a flow rate of 2.0 to 2.2 gpm was used for the reduced load tests. As discussed in a later subsection, this range total liquid flow rate has a minimal effect on SNCR performance. Also, boiler operation at 80 MWe and above was with all four coal mills in service. The tests at 60 MWe were with three coal mills in service.

The trends in NO reduction and NH₃ slip with increasing N/NO ratio are as expected, as both are shown to increase with increasing N/NO ratio. At 100 MWe, 57 percent NO removal was achieved at a N/NO ratio of 1.7, with a corresponding NH₃ slip of 35 ppm. At a N/NO ratio of 1.15, 51 percent NO removal was achieved with less than 15 ppm NH₃ slip.

The performance at the various boiler loads provides insight into the region of the "SNCR temperature window" at which the injection system is operating. NO removals were maximum at 100 MWe. A slight decrease was seen at 80 MWe, and a larger decrease occurred as the load was further dropped to 60 MWe. Likewise, increasing the load from 100 to 110 MWe resulted in a decrease in NO reduction performance equivalent to the load change from 100 to 60 MWe. This suggests that peak temperatures for SNCR performance with urea occur near the injection level at a load of 90 to 100 MWe.

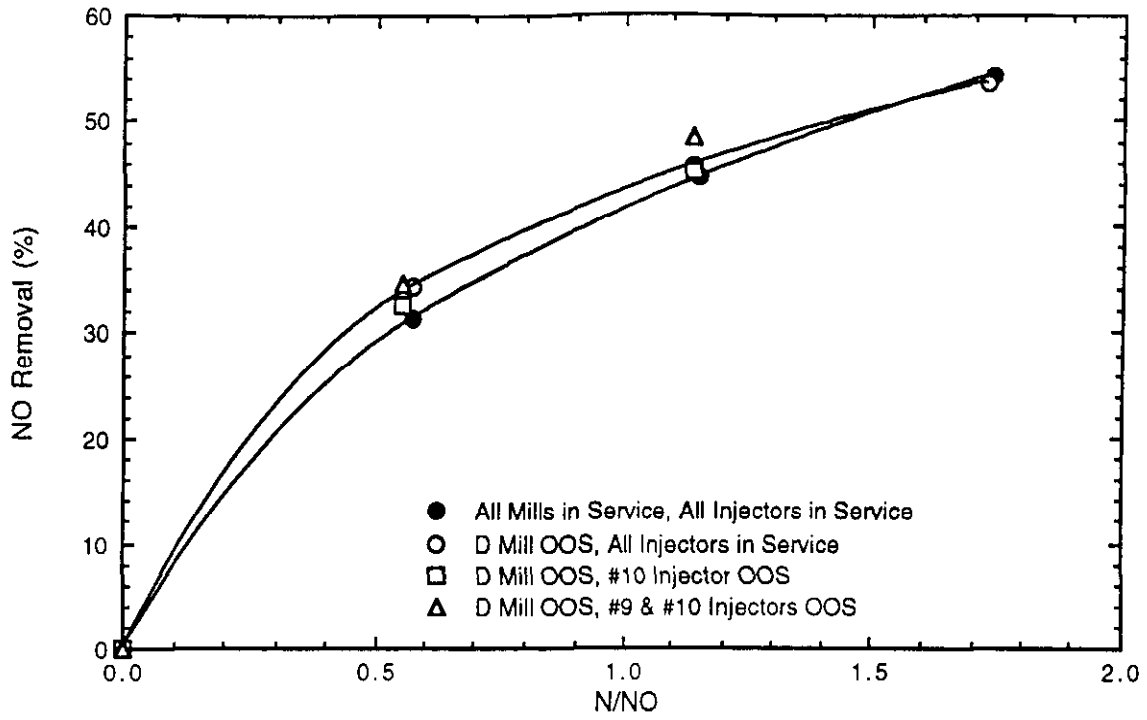
Figure 5-8b shows that the levels of NH₃ slip increase monotonically with decreasing load, consistent with decreasing flue gas temperatures at the point of chemical injection. The large increase in NH₃ slip levels seen between the 60 and 80 MWe cases could be due to two factors, with the primary factor being decreasing flue gas temperatures with decreasing load. A secondary factor could be the 3 mills in service operating condition at the lower load creating greater temperature and gas species non-uniformity at the point of urea injection. The effect of the number of mills in service is discussed in more detail in the section below.

5.3.3 Effect of Mills Out of Service

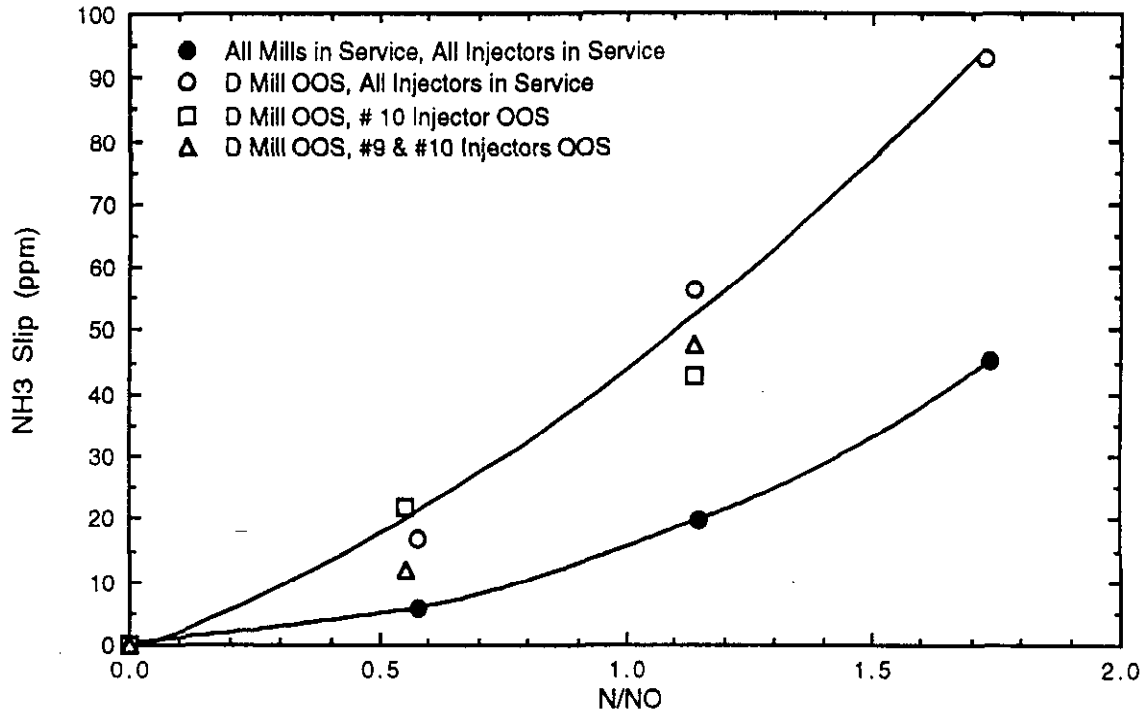
Arapahoe Unit 4 typically operates under normal dispatch conditions over the load range from 80 to 115 MWe with all four mills in service. If extended operation is anticipated at 80 MWe or below, one mill will be removed from service. Long-term operation at 60 MWe or less will typically be with two mills out of service (OOS). Since operation with various mills out of service is typical, it was important to determine the impact on SNCR performance. It was anticipated that various mill out of service operations would primarily affect NH₃ slip. To this end, tests were also conducted to see if it was possible to vary the number of chemical injectors in service to compensate for a particular coal mill being out of service.

Figure 5-9 compares the performance of the SNCR system at 80 MWe with all four mills in operation, to that with only three mills in service (D Mill OOS). Although operating with the three mill condition had essentially no effect on the NO removals, the NH₃ emissions more than doubled. This was not unexpected, as the maldistribution of coal feed to the furnace was expected to increase local temperature variations, thereby negatively impacting the NH₃ slip.

While operating with D Mill out of service, tests were conducted where the urea injectors on the east side of the furnace (Numbers 9 and 10) were taken out of service in an attempt to reduce the NH₃ emissions. Recall that D Mill feeds coal to two burners located on the far east side of the furnace, and likewise, Injectors 9 and 10 are also on the far east side. During these tests, the injection system was operated: 1) with all 10 injectors in service; 2) with injector Number 10 out of service; and 3) with both injectors 9 and 10 out of service. The results in Figure 5-9 indicate that there was no effect on NO removals, and only a marginal affect on NH₃ slip. The valves utilized to remove injectors from service are manually operated and located at the injection levels. The slight reduction in NH₃ slip does not warrant manually changing the number of injectors in service whenever a mill is removed from service. For automatic operation, a more likely approach will be to reduce the N/NO ratio if a constant level of NH₃ slip is to be maintained. However, it must be noted that this will also compromise the NO removals.



a) NO Removal



b) NH₃ Emissions

Figure 5-9. Effect of Mill in Service Pattern and Removal of Select Injectors from Service on Urea Injection at 80 MWe (6 gpm total liquid flow, 8 psig air)

Figure 5-10 shows the results of two tests conducted at a load of 60 MWe. The first test was performed with D Mill out of service and the second test with both A and D Mills out of service. For both tests, the urea was injected at a nominal N/NO ratio of 0.6.

With just D Mill out of service, 30 percent NO removal was achieved with 31 ppm NH₃ slip. With both A and D Mills out of service, the NO removal dropped to 21 percent and the NH₃ slip to 23 ppm. The drop in NO removal might be expected due to greater temperature variations in the furnace. However, the drop in NH₃ slip was not expected. Larger temperature variations at the injection region with two coal mills out-of-service would have expected to create colder regions with higher NH₃ slip. Further testing is warranted during the integrated phase of the test program to confirm this observation.

5.3.4 Effect of Total Liquid Flow Rate

For the current phase of testing, the urea was stored as a nominal 37.5 weight percent solution which was diluted at the pump skid prior to injection. At 100 MWe and an injection rate corresponding to N/NO = 1, the flow rate of the 37.5 percent solution is nominally 1.3 gpm. (This will vary somewhat depending on the initial NO level.) The pump skid can provide dilution water such that the total liquid flow rate can be varied from nominally 2 gpm up to 9 gpm. During the baseline SNCR tests, the injection system was set up to operate from nominally 6 to 28 gpm. From an operational point of view, it is desirable to operate with as little dilution water as possible since this water has a direct impact on heat rate. High dilution water flow will also result in local flue gas cooling which can affect steam temperature control.

Figure 5-11 shows the effect of changing the total liquid flow rate from 2.1 gpm to 6 gpm while maintaining a N/NO ratio of 1.15 at 100 MWe. The NO removal increased from 46 percent to a little over 50 percent with a slight decrease in NH₃ slip. However, the change in NH₃ slip (14 ppm versus 12 ppm) is within the range of experimental repeatability and probably not significant. The data shown in Figure 5-8 suggested that peak NO removals would be expected at a boiler load of 90 to 100 MWe; for the 100 MWe tests reported in Figure 5-8 with a total solution flow of 6 gpm was utilized. As seen

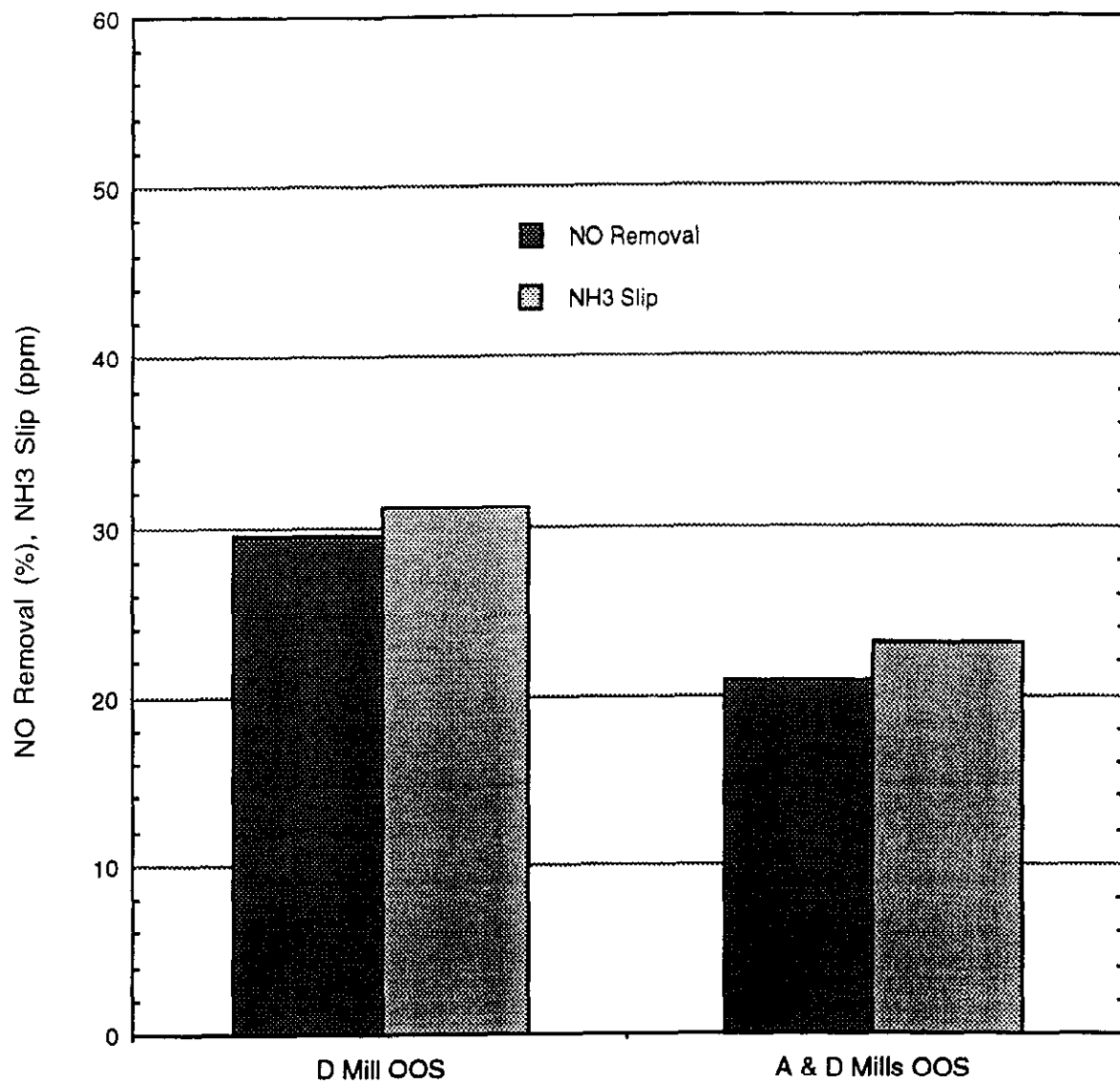


Figure 5-10. Effect of Mill in Service Pattern on Urea Injection at 60 MWe
 (N/NO = 0.6, 2.1 gpm total liquid flow, 8 psig air)

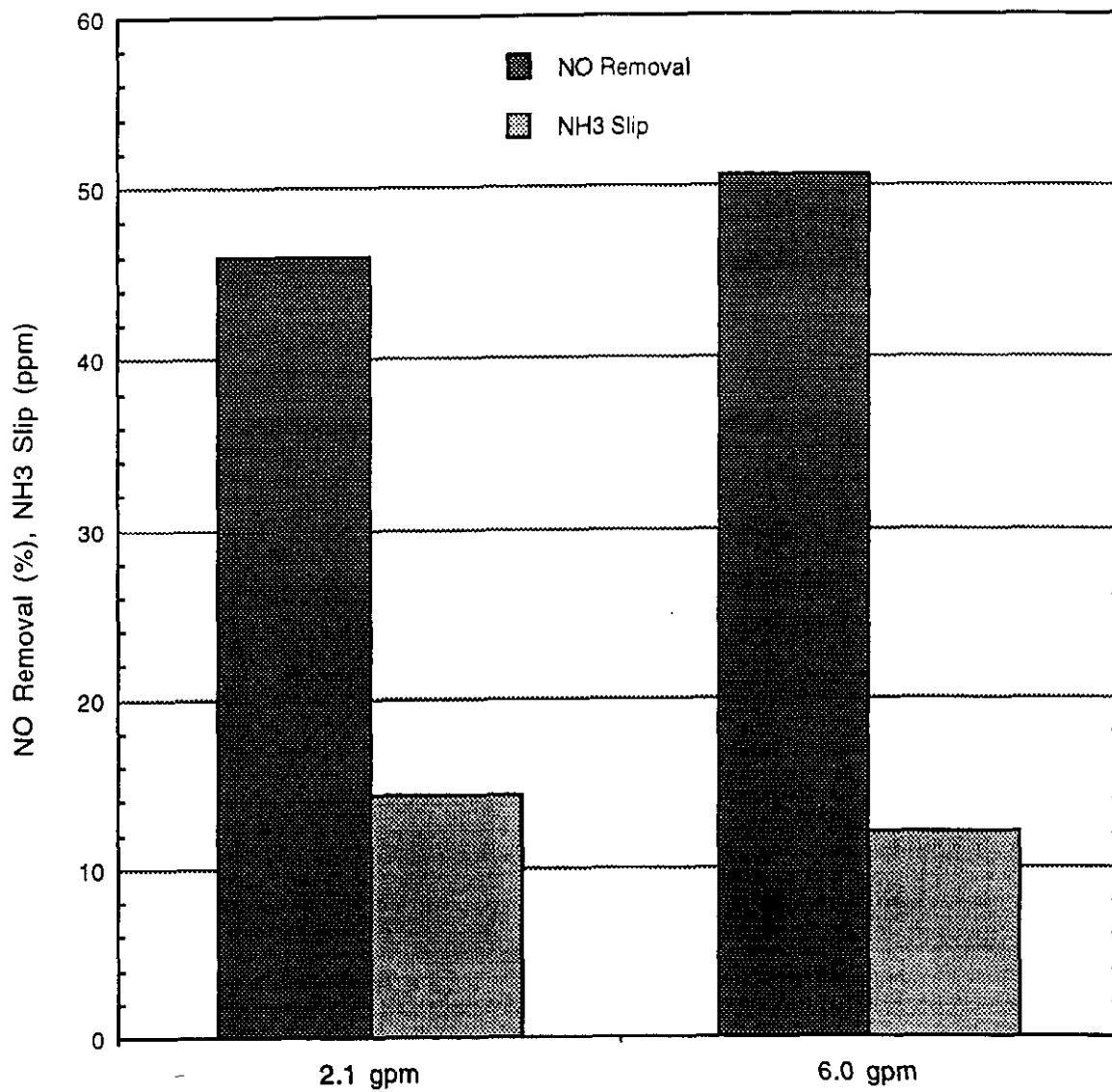


Figure 5-11. Effect of Total Liquid Flow Rate on Urea Injection at 100 MWe
(N/NO = 1.15, 8 psig air)

in Figure 5-11, decreasing the solution flow from 6 to 2.1 gpm decreased the NO removal which would be consistent with a decrease in local cooling due to vaporization and heating of the injected solution. For reference, injecting 6 gpm of water at 100 MWe will locally cool the combustion products nominally 18°F during vaporization. The cooling will actually be somewhat less due to the exothermic nature of the urea/NO reactions.

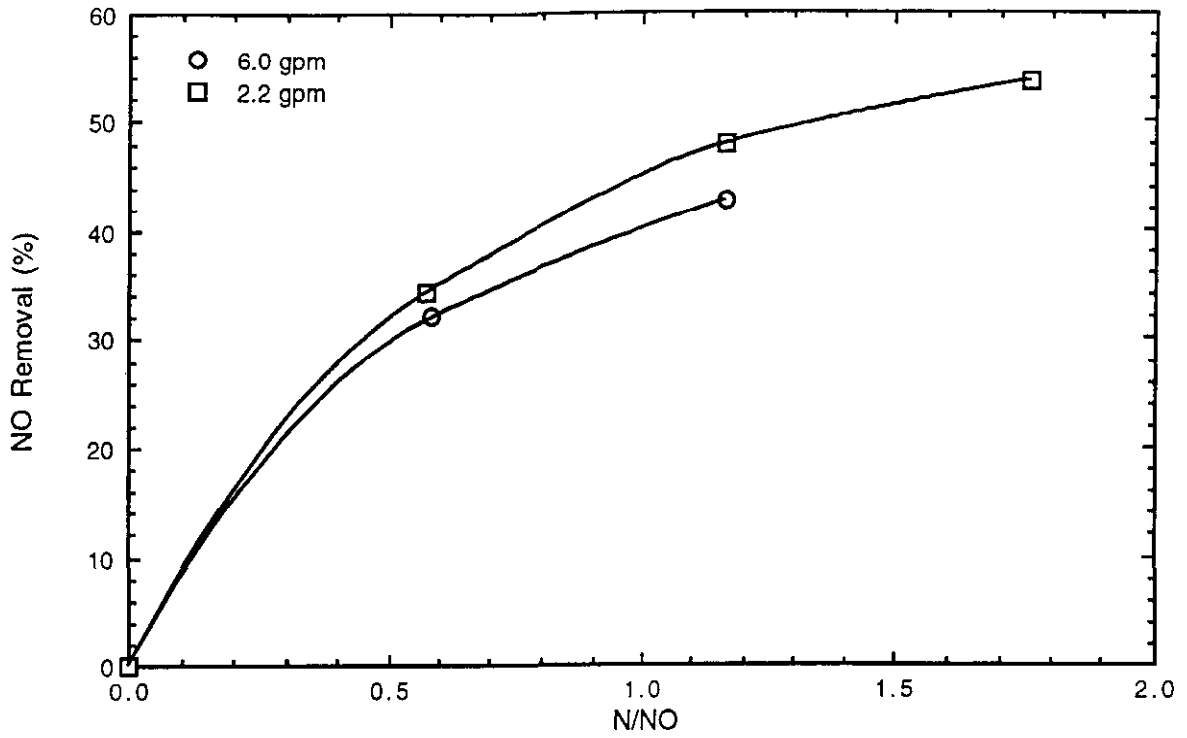
At a reduced load of 80 MWe, decreasing the total liquid flow rate from 6.0 to 2.2 gpm increased NO removal as shown in Figure 5-12. At this load, no impact on NH₃ slip was observed. Consistent with the previous results, this would suggest that 80 MWe is just on the low temperature side of the window. Increasing the total liquid flow rate increased the local cooling effect, thereby decreasing the NO removals.

While the effect of total liquid flow rate can largely be explained by local cooling effects, varying the flow rate can impact other factors. With the NOELL, Inc., SNCR system, mixing is dominated by the transport air used with the injectors. However, varying the solution flow rate could alter the drop size of the spray slightly, or change the evaporation history of the drops. These factors may also be influencing the results shown in Figures 5-11 and 5-12, although there is no definitive way to separate these effects from the local cooling effect.

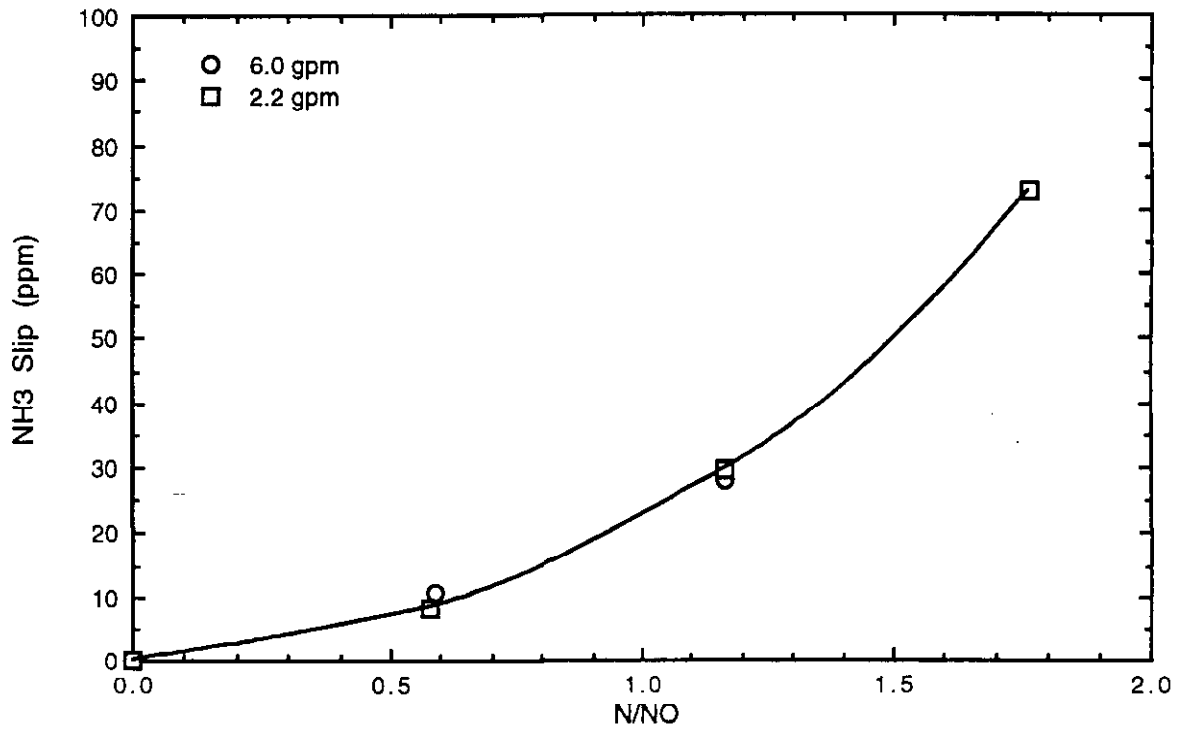
The results shown above indicate that up to a load of 80 MWe, the total liquid flow rate should be kept at the minimum value of nominally 2 gpm. No specific tests varying solution flow rate were conducted at 60 MWe. However, the data shown in Figure 5-8 indicate that the SNCR injectors are clearly on the low side of the temperature window at this boiler load, and the local cooling effect should be minimized.

5.3.5 Effect of Mixing Air Pressure

The NOELL, Inc., SNCR system uses a flow of medium pressure air to provide the primary source of energy to mix the injected chemical with the flue gas. During the current test program, the mixing air pressure was varied from 4 to 12 psig, and the injector air orifice sizes were held constant. Injector air orifice size was shown to have



a) NO Removal



b) NH₃ Emissions

Figure 5-12. Effect of Total Liquid Flow Rate on Urea Injection at 80 MWe (8 psig air)

little effect on system performance during the baseline SNCR tests.⁽³⁾ With fixed air orifice sizes, changing the air supply pressure from 4 to 12 psig increases the mixing air flow rate by approximately 73 percent. The effect of increasing the mixing air pressure at boiler loads of 60, 80 and 100 MWe are shown in Figures 5-13 to 5-15, respectively. At 60 MWe, increasing the air pressure from 5 to 12 psig increased NO removal from nominally 24 to 29 percent. The NH₃ slip also appears to increase with increasing air pressure, although the increase is small.

At 80 MWe (Figure 5-14), increasing air pressure again resulted in increased NO removals. The majority of the increase occurred with a pressure change from 4 to 8 psig, and there was essentially no benefit of a further increase to 12 psig. NH₃ emissions were reduced with an air pressure increase from 4 to 8 psig, and a further increase to 12 psig resulted in a slight increase in the NH₃ slip. Similar trends are seen in Figure 5-15 for a load of 100 MWe, where increasing the air pressure from 8 to 12 psig increased both NO removal and NH₃ slip slightly.

While the impact of mixing air variation on SNCR performance was generally small for pressure variations of 4 to 12 psig, a number of factors could be at play. First, increasing the mixing air flow rate (i.e., pressure) will increase the overall level of mixing. This would be expected to enhance overall SNCR performance. However, the increased mixing air flow can increase local cooling which would tend to degrade SNCR performance at loads under 100 MWe. Finally, it appears that there may be a cool region of the gas, caused by a recirculation zone at the wall opposite the injectors. Increased air flow will increase penetration into this region, which could contribute to the observation of both increasing NO removal and increasing NH₃ slip for some of the tests.

The overall effect of the mixing air flow rate is generally small for the range of air pressures and corresponding flow rates tested. The actual flow rate used for long-term operation will be a trade-off between the modest increases in SNCR performance and the operating costs of providing the air flow. Based on the parametric tests to date, a constant air flow rate corresponding to an air pressure of 8 psig is optimal.

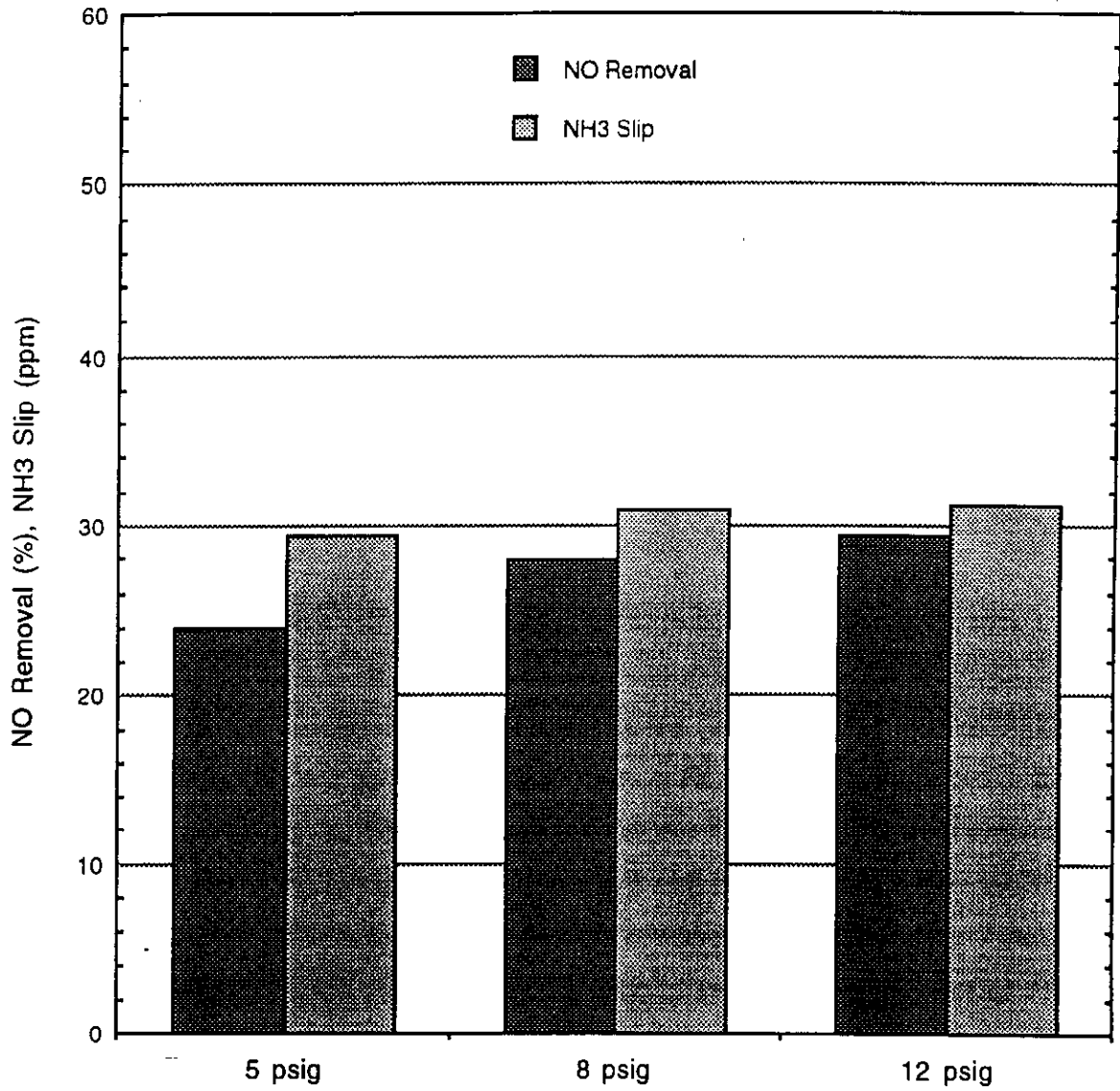


Figure 5-13. Effect of Mixing Air Pressure on Urea Injection at 60 MWe
 (N/NO = 0.6, 2.1 gpm total liquid flow)

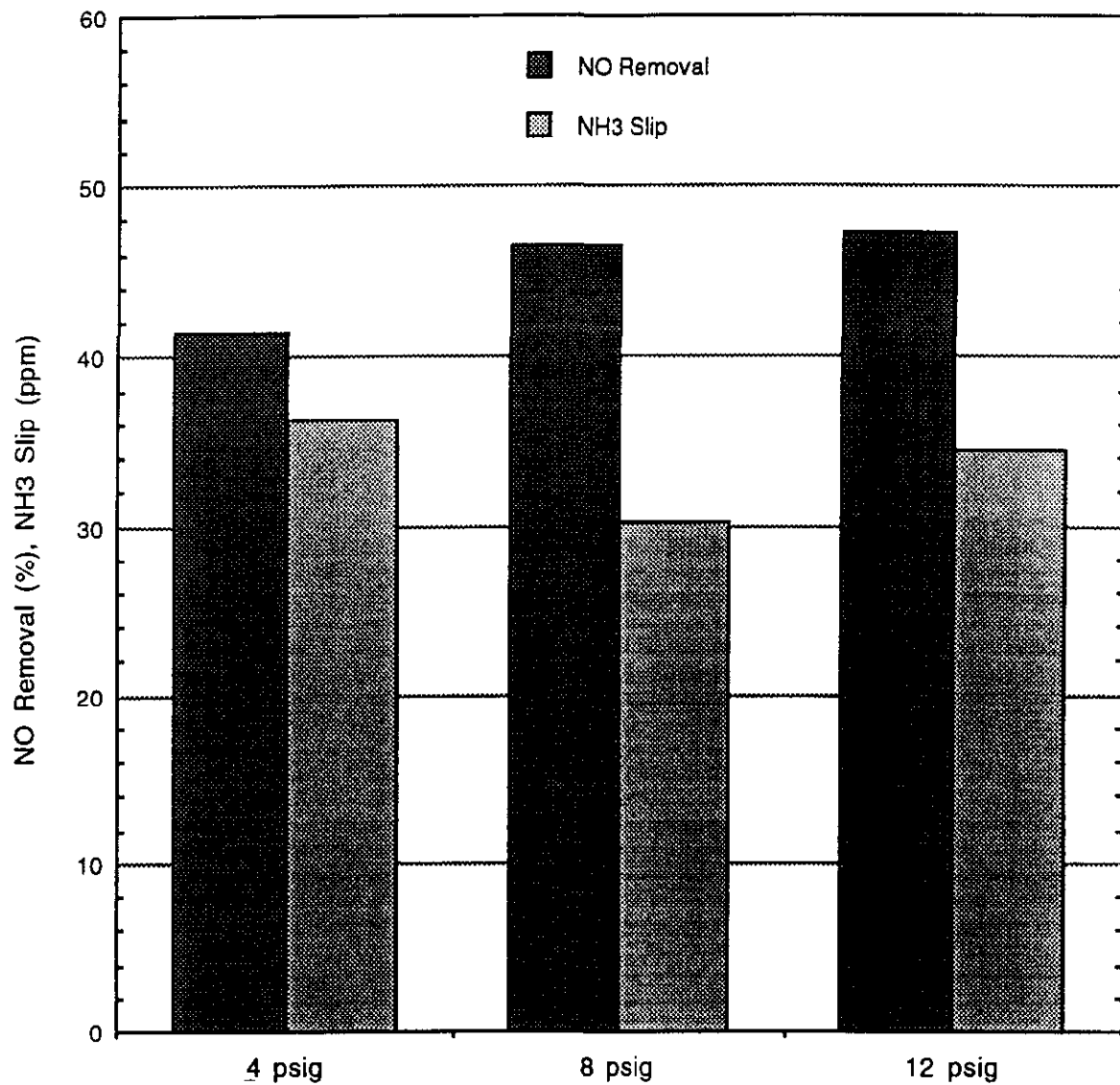


Figure 5-14. Effect of Mixing Air Pressure on Urea Injection at 80 MWe
(N/NO = 1.15, 2.2 gpm total liquid flow)

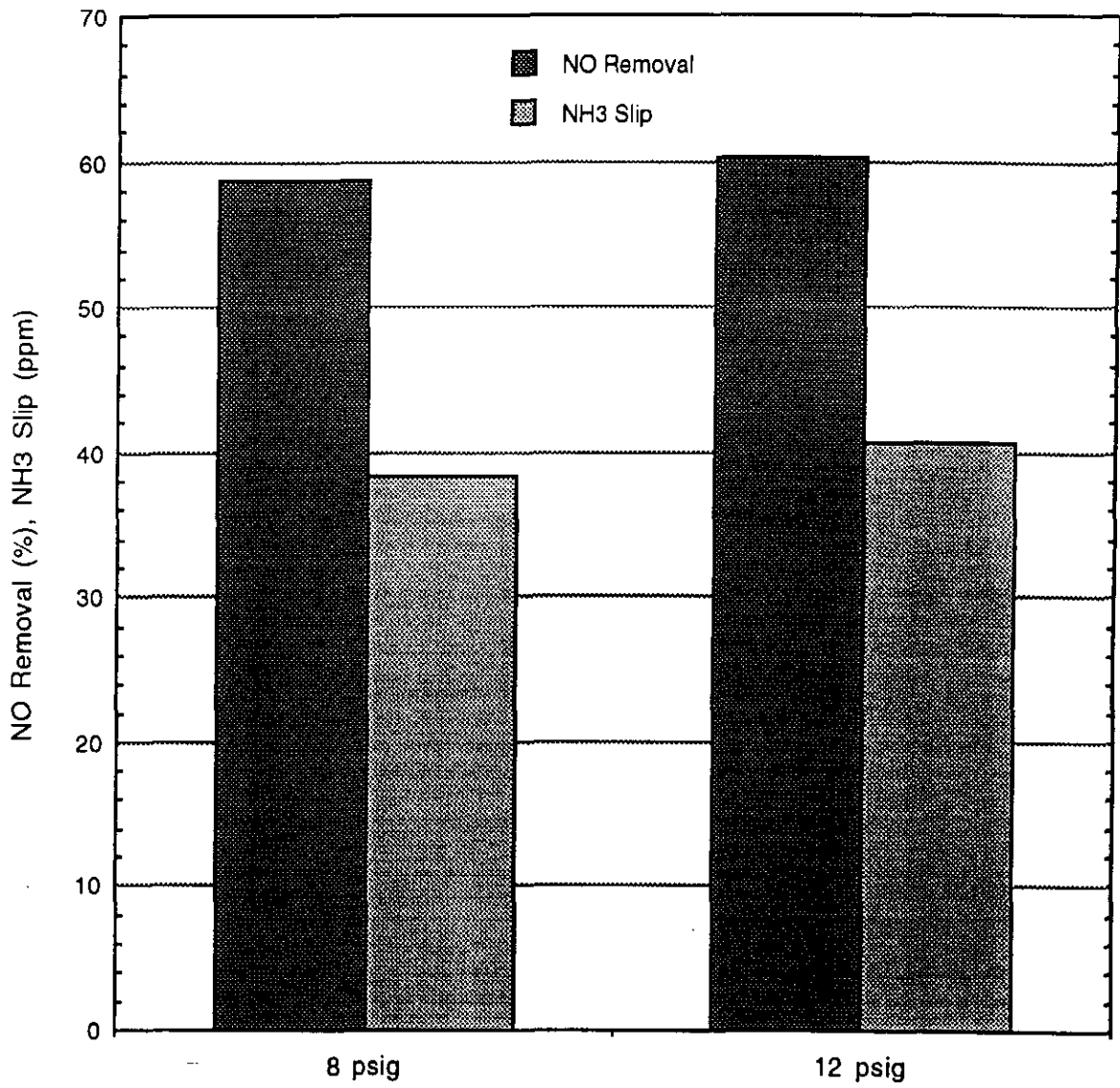


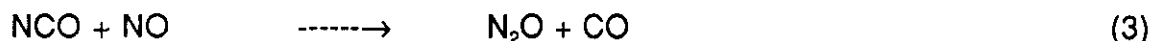
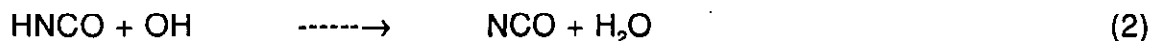
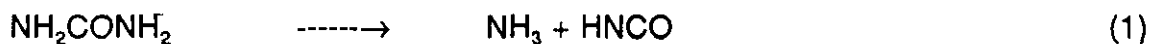
Figure 5-15. Effect of Mixing Air Pressure on Urea Injection at 100 MWe
 (N/NO = 1.7, 6 gpm total liquid flow)

5.3.6 Effect of Bi-Level Injection

During the baseline SNCR test program⁽³⁾, the upper level of injectors (Level 2) was found to be in too cold a region with limited residence time for effective SNCR performance. Since the combustion product temperatures further decreased with the low-NO_x burner retrofit, there was little expectation that the upper level of injectors would be of much benefit. However, a limited number of tests were conducted to investigate if there was any performance benefit to distributing the urea between both levels of injectors. These tests were conducted at a load of 113 MWe with 6 gpm total liquid flow, and a N/NO ratio of 1.15. These tests were run without biasing the coal mills, and with all Level 1 injectors with 0.035-inch diameter liquid orifices and Level 2 injectors with 0.024-inch orifices. With this arrangement, 67 percent of the solution was injected through the bottom level of injectors and 33 percent through the top level. The tests were conducted at mixing air pressures of 4 and 8 psig (the pressure for both levels being the same). The results (Figure 5-16) showed no benefit to bi-level injection in terms of NO removal. Since no benefit was seen at this high load condition where temperatures are highest, no further bi-level testing was pursued with urea injection.

5.3.7 N₂O Emissions

N₂O emissions were also monitored during the urea injection tests. While not a regulated species, there is interest in N₂O emissions due to potential impacts on stratospheric ozone chemistry and potential contributions to the greenhouse effect. Prior pilot-scale and full-scale studies have shown N₂O to be a product of the urea injection process^(9,10). As discussed in Section 3.1, N₂O is currently thought to form through a mechanism of the form:



Whether the N₂O remains and is emitted from the stack, or is reduced in the flue gas stream depends primarily on the following destruction reaction mechanism:

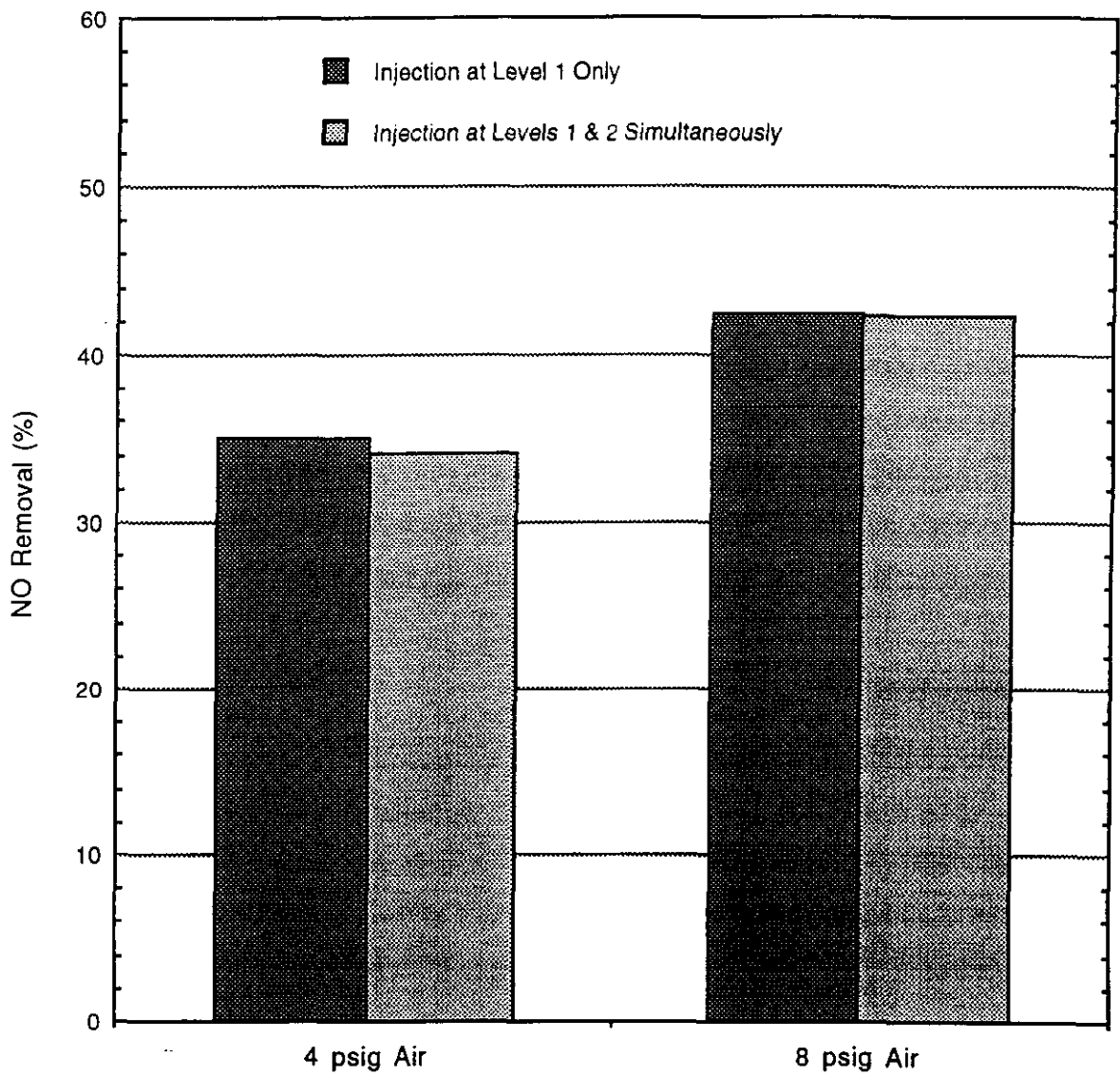


Figure 5-16. Effect of Bi-Level Injection of Urea at 113 MWe
(N/NO = 1.15, 6 gpm total liquid flow)



In reaction (6), "M" represents one of any number of "general molecules" which can react with N_2O and reduce it to N_2 . Reaction (3) shows that N_2O is formed as a direct consequence of a reaction with NO ; thus, it is appropriate to quantify the N_2O formation in terms of the amount of N_2O formed divided by the amount of NO reduced. This is essentially the fraction of NO reduced that was converted to N_2O .

The baseline SNCR tests showed that with the original combustion system and initial NO levels of about 850 ppmc, the amount of N_2O produced was 7 to 17 percent of the NO reduced⁽³⁾. The data also indicated that the highest levels of N_2O were produced at reduced loads.

The N_2O production from urea injection measured during the current phase of testing is shown in Figure 5-17. With the retrofit combustion system, the N_2O conversion ranged from 20 to 35 percent, with the lowest levels occurring at reduced loads. This is markedly different from the results seen with the original combustion system. First, the overall levels of N_2O production are higher in terms of the percent conversion of NO to N_2O . Secondly, with the original combustion system, N_2O production was seen to increase with decreasing boiler load. With the retrofit low- NO_x combustion system, the N_2O production was seen to decrease with decreasing load. While no definitive explanation for this effect can be offered, it can be speculated that it is related to the reduction of the flue gas temperatures in the injection region seen after the retrofit.

N_2O exhibits a temperature window for formation which is similar to the SNCR temperature window for NO reduction^(10,11). In the case of the original combustion system, urea injection was likely on the high temperature side of the N_2O formation window so that decreases in boiler load (i.e., flue gas temperature) resulted in increased N_2O production. Recall that the furnace exit gas temperatures were shown to be 180 to 240°F lower after the retrofit than before (Figure 5-1). Therefore, with the retrofit combustion

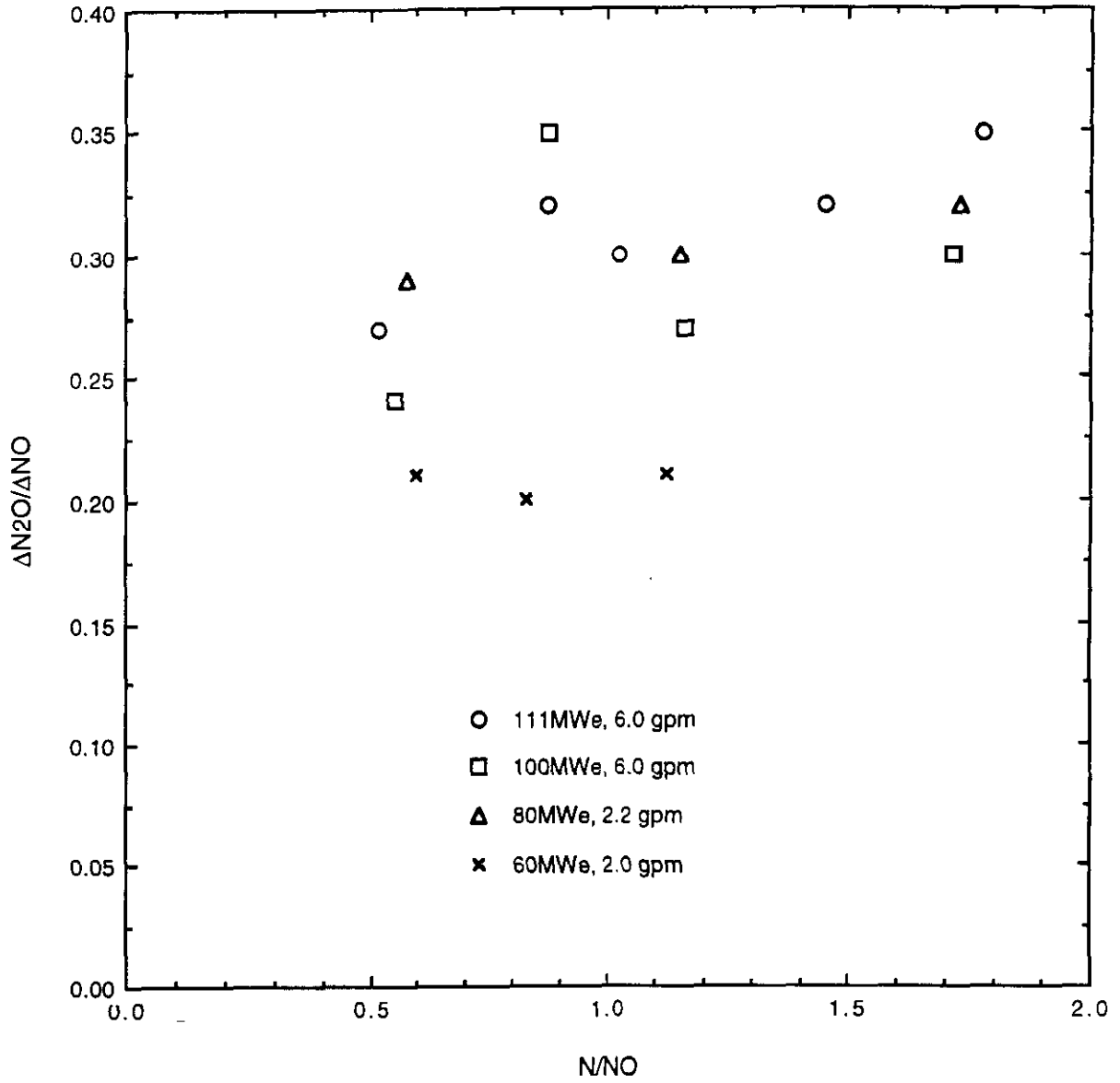


Figure 5-17. N₂O Emissions with Urea Injection (8 psig air)

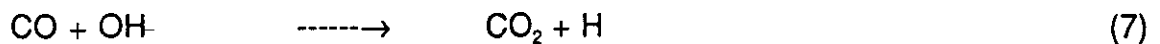
system, urea injection is now likely on the lower temperature side of the window, resulting in decreasing N₂O production with decreasing load.

Furthermore, it is expected that residence time may also play a role. It has been shown that residence time is important since the N₂O decomposition reactions occur relatively slowly⁽¹⁰⁾. Therefore, changes in available residence times at a given temperature may also be contributing to the higher N₂O production.

A final point to be made is the change in the initial NO level. With the original combustion system, the initial NO level was nominally 850 ppmc and with the retrofit burners it was 250 to 300 ppmc. The role that the initial NO level plays in the fraction of the NO reduced which is converted to N₂O is unclear. However, even with the higher overall conversions, the absolute level of N₂O emissions with the retrofit burners is lower than that measured with the original combustion system. At 100 MWe and a nominal N/NO ratio of 1.0, N₂O emissions with the original combustion system were nominally 54 ppmc, compared to 37 ppmc with the retrofit burner system.

5.3.8 CO Emissions

There is the potential for increases in CO emissions with application of SNCR to a utility boiler. This increase can be due to two mechanisms. First, if urea is used as the SNCR chemical, the carbon present in the urea can contribute to the CO levels. This occurs when the CO released from the urea decomposition reaction is not oxidized to CO₂. Second, CO generated from the combustion process is oxidized to CO₂ primarily through the reaction



With either urea or ammonia injection, OH is utilized in the SNCR reaction process (recall Figure 3-3). If CO is still being oxidized in the vicinity where the SNCR chemistry is taking place, the SNCR reactions can compete for the OH radicals. This can result in an inhibition in the oxidation of the CO from the combustion process.

The baseline SNCR tests showed that with the original combustion system, CO production for urea injection decreased with increasing boiler load, and increased with increasing N/NO ratio. At a nominal N/NO ratio of 1.0, maximum CO emissions were approximately 35 ppm. With the retrofit low-NO_x combustion system, CO emissions at a N/NO ratio of 1.0 were at most 20 ppm, and there was no obvious trend with either boiler load or N/NO ratio.

5.4 Converted Urea Test Results

In addition to assessing the SNCR system performance with urea, the test program also investigated the SNCR performance when the urea was processed through a catalytic converter before injection. As discussed in Section 3.3, the converter catalytically converts the liquid urea solution to a solution of ammonium compounds. This subsection will present the results of this portion of the test program, and the results will be presented in a manner which generally parallels the previous subsection on the urea injection results:

5.4.1 Converter Performance

5.4.2 Effect of Boiler Load and Chemical Injection Rate

5.4.3 Effect of Total Liquid Flow Rate

5.4.4 Effect of Mixing Air Pressure

5.4.5 Effect of Bi-Level Injection

5.4.6 Effect of Coal Properties

5.4.7 Nitrous Oxide (N₂O) Production

5.4.8 CO Emissions

Before the results of the converted urea tests are presented, it is of value to discuss how the tests were actually run, since it was necessary to modify the test procedure slightly when using the conversion system. During the urea injection tests reported in the previous subsection, the conversion system was bypassed and the urea was pumped

directly from the metering skid, where the final dilution occurred, to the injection level on the boiler. An optimum total liquid flow rate was determined for each boiler load based upon where the system was operating on the SNCR temperature curve for urea. Variations in N/NO ratio for a fixed load were achieved by changing the concentration of the injected urea solution (i.e., changing the flow rate of the 37.5 weight percent urea solution while holding the total liquid flow rate constant). Since the internal volume of the liquid transfer lines between the metering skid and the injectors was very small, the time required for the system to react to changes in N/NO ratio was short. However, when the tests with the converted urea solution began, it was found that this approach was not practical because the internal volume of the converter was so much larger than the volume of the liquid transfer lines. The time required for the conversion system to stabilize after a change in solution concentration could be as long as two to three hours depending on the total liquid flow rate. It was decided that the best approach was to hold the concentration of the injected solution constant, and vary the N/NO ratio by changing the total liquid flow rate. Unfortunately, this approach also had its limitations, in that if the total flow rate was changed too quickly, converter temperatures and pressures would become unstable and start to oscillate. Unless otherwise noted, the results presented in this report for injection of the converted urea solution are for operation with total liquid flow rates of nominally 2, 4 and 6 gpm for nominal N/NO ratios of 0.5, 1.0 and 1.5, respectively.

5.4.1 Converter Performance

In an effort to quantify the performance of the conversion system, samples of the converted urea solution were obtained on a regular basis during the current phase of testing. The samples were diluted 1,000:1, and analyzed for ammonia content using a specific ion electrode. A total of twenty seven samples were analyzed, but many of them were collected before consistent and reliable operation of the conversion system was achieved. Calculated conversion efficiencies (urea to ammonium compounds) for the samples collected during the later, more well controlled, tests ranged from 75 to 100 percent (Figure 5-18).

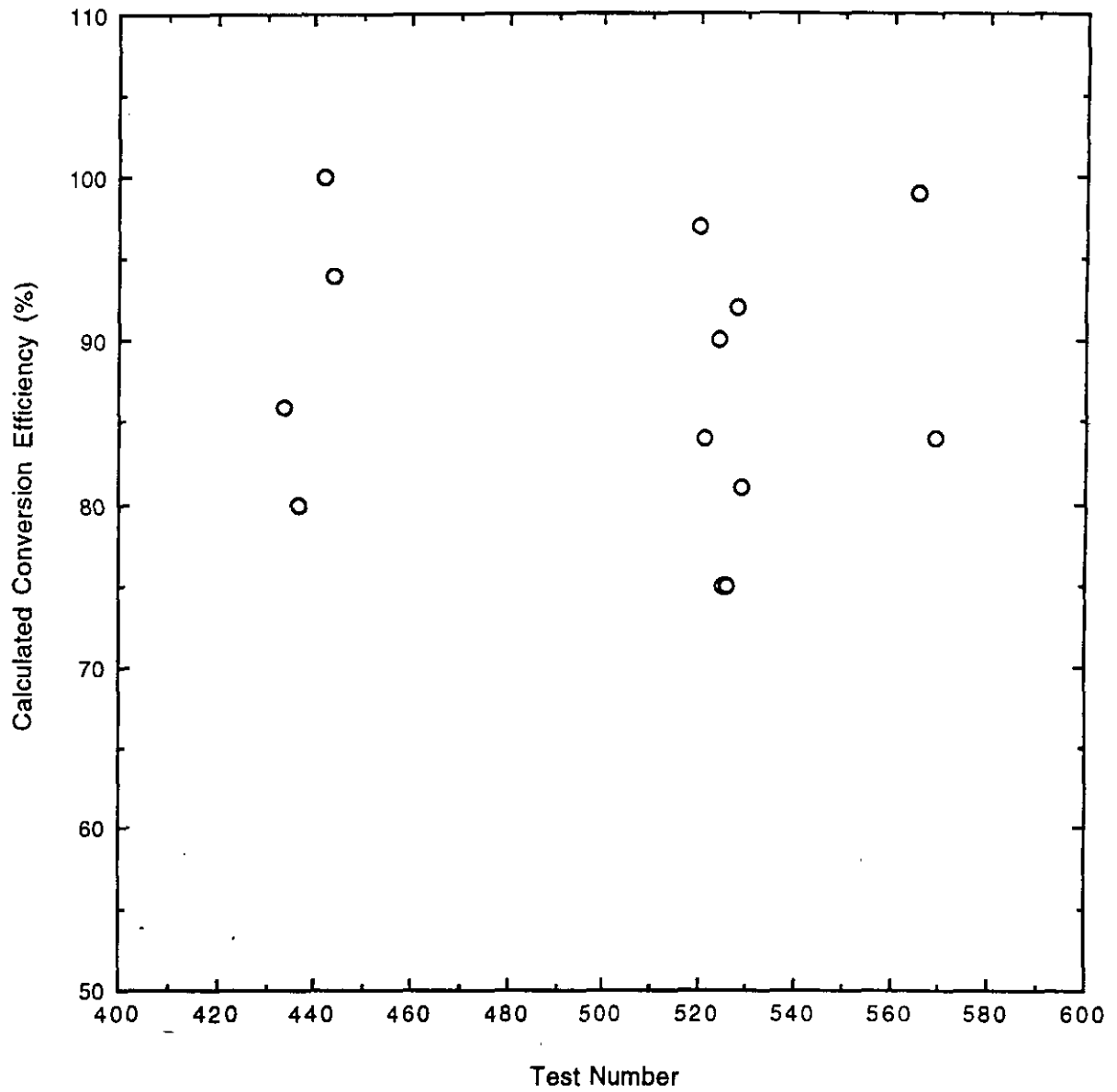


Figure 5-18. Calculated Conversion Efficiencies (Urea to Ammonium Compounds) for Tests 434 to 569

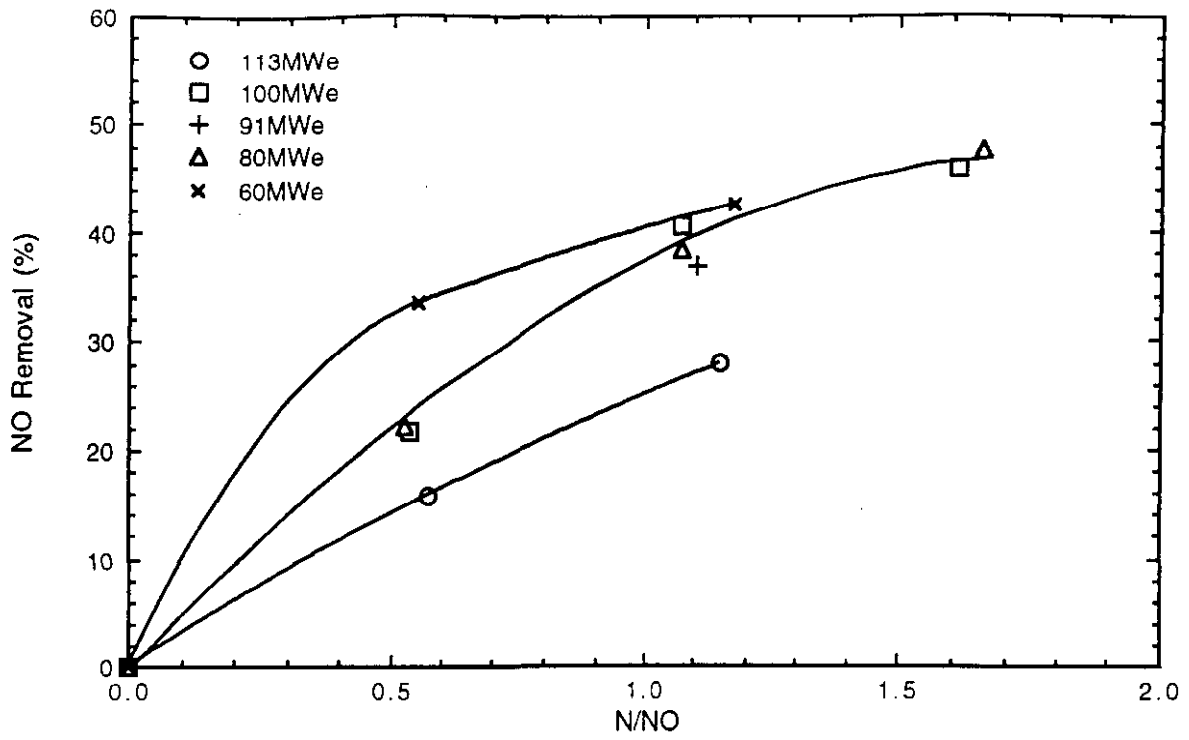
5.4.2 Effect of Boiler Load and Chemical Injection Rate

The effect of boiler load and chemical injection rate (N/NO ratio) is shown in Figure 5-19 for operation with the converted urea solution. As with the urea injection tests, operation at boiler loads of 80 MWe and above was with all four mills in service. The 60 MWe tests were conducted with three mills in service (D Mill OOS). The results shown in Figure 5-19a indicate that maximum NO removals occur at 60 MWe. Although, with the exception of the 60 MWe data point at N/NO = 0.6, there is little difference in the NO reduction performance of the converted urea over the load range from 60 to 100 MWe. At 113 MWe, NO removals decreased due to the higher temperatures at the injection location. Some of the differences in the performance of the converted urea at 60 MWe may be attributed to changes in the performance of the converter. During this phase of testing, operating procedures for the converter were being fine-tuned in terms of controlling converter temperatures and pressures.

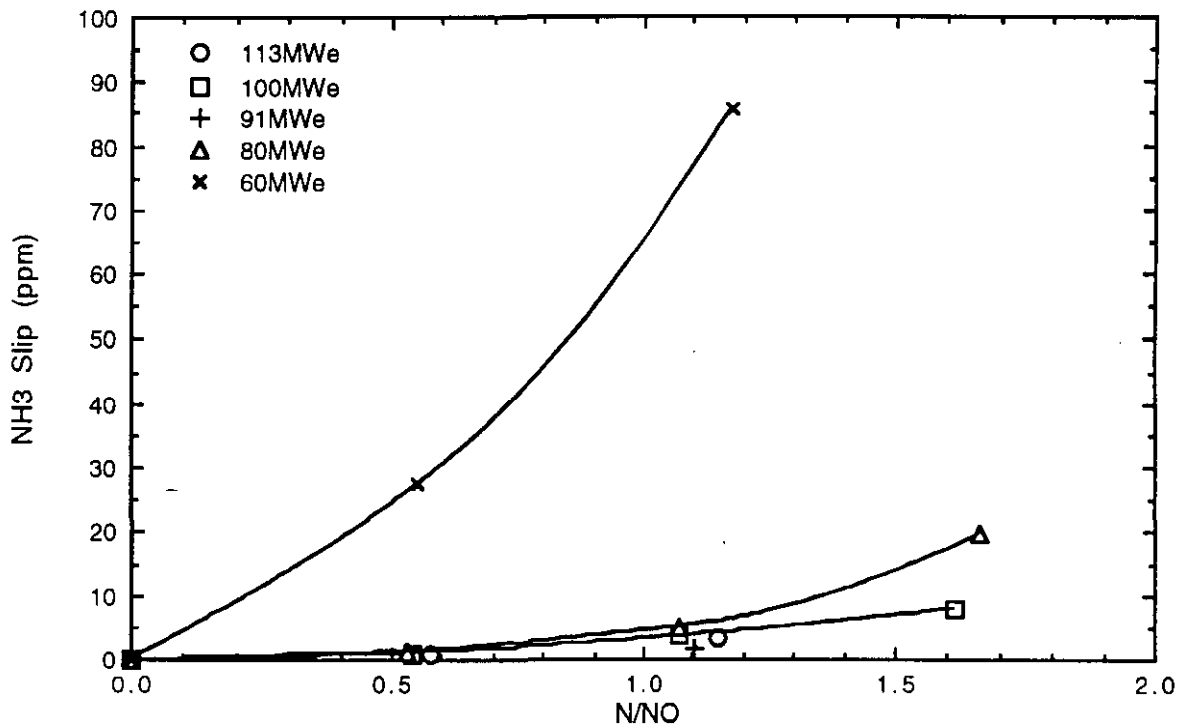
The NH₃ emissions in Figure 5-19b indicate generally low levels of NH₃ with the converted urea solution. Except for the 60 MWe tests, NH₃ emissions were less than 20 ppm even at N/NO ratios approaching 1.7. As with the urea injection results, the higher NH₃ slip levels at 60 MWe can be due to both lower flue gas temperatures at the injection location, and boiler operation with only three mills in service.

5.4.3 Effect of Total Liquid Flow Rate

The effect of total liquid flow rate on SNCR performance with the converted urea solution is shown in Figure 5-20 for boiler loads of 60, 80 and 91 MWe. For all of these tests, the N/NO ratio was nominally 1.15. The data indicate that changing the total liquid flow rate with the N/NO ratio fixed, had little effect on both NO removal and NH₃ emissions. At 60 and 91 MWe, increasing the total liquid flow rate from nominally 2 to 4 gpm resulted in slight increases in NO removal. At 80 MWe, increasing the solution flow rate slightly increased the NH₃ slip levels. Since there has not been a great amount of operating experience with the converter system, it is difficult to conclude whether the differences in Figure 5-20 are 1) significant, 2) due to the impact of total liquid flow rate on furnace



a) NO Removal



b) NH₃ Emissions

Figure 5-19. Effect of Boiler Load and N/NO Ratio on Converted Urea Injection (8 psig air)

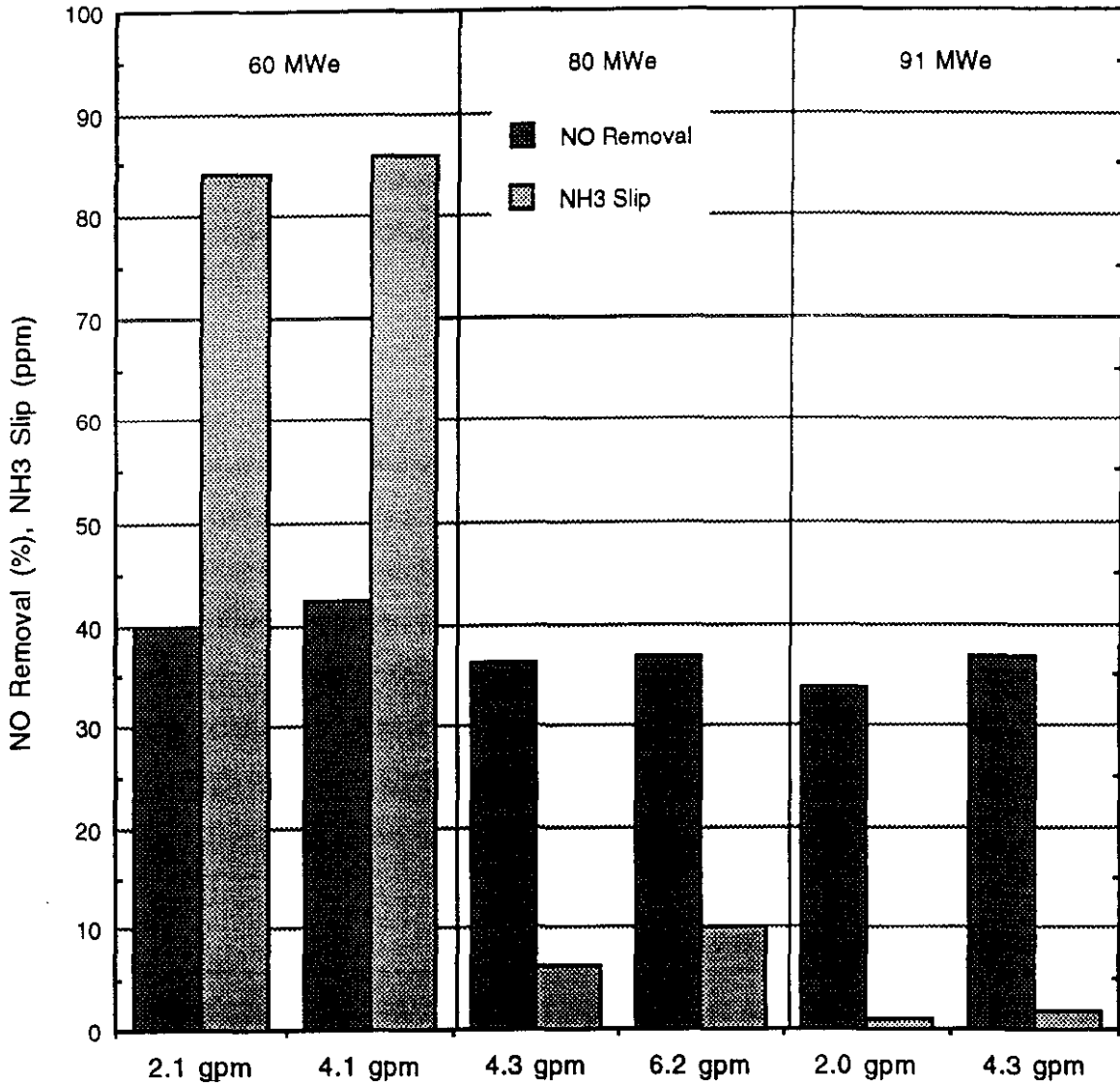


Figure 5-20. Effect of Total Liquid Flow Rate on Converted Urea Injection
(N/NO = 1.15, 8 psig air)

parameters, or 3) due to differences in converter performance with different solution concentrations.

5.4.4 Effect of Mixing Air Pressure

The effect of mixing air pressure on SNCR performance with the converted urea solution was assessed at 80 MWe with a nominal N/NO ratio of 1.15. During these tests, the mixing air pressure was varied from 4 to 12 psig. Recall that this increases the mixing air flow rate by nominally 73 percent when the air orifice size remains constant. The results of these tests are shown in Figure 5-21, and indicate no significant impact on either NO reduction performance or NH₃ emissions.

5.4.5 Effect of Bi-Level Injection

Since the converted urea solution appears to operate at a lower temperature window than the baseline urea solution, a test using bi-level injection was conducted at a boiler load of 113 MWe. The injector configuration was identical to that for the bi-level injection tests with urea discussed in Subsection 5.3.6. The results at a nominal N/NO ratio of 1.15 are shown in Figure 5-22, and indicate no beneficial effect on NO reduction performance. Since there was no benefit at the high temperature condition of 113 MWe, one would not expect enhanced performance at lower loads. Thus, additional bi-level injection tests with the converted urea solution at reduced boiler loads were not conducted.

5.4.6 Effect of Coal Properties

Arapahoe Unit 4 burns coal from two different sources. While the properties of the two coals are similar, one has a higher sulfur content and slightly different combustion characteristics. When the higher sulfur coal is burned, SO₂ emissions will typically increase from nominally 440 to 600 ppmc. Also, the higher sulfur coal has a tendency to produce higher CO emissions at an equivalent excess air level.

During the tests with the converted urea, the coal source changed a few times and there appeared to be some impact on the performance of the SNCR system. These

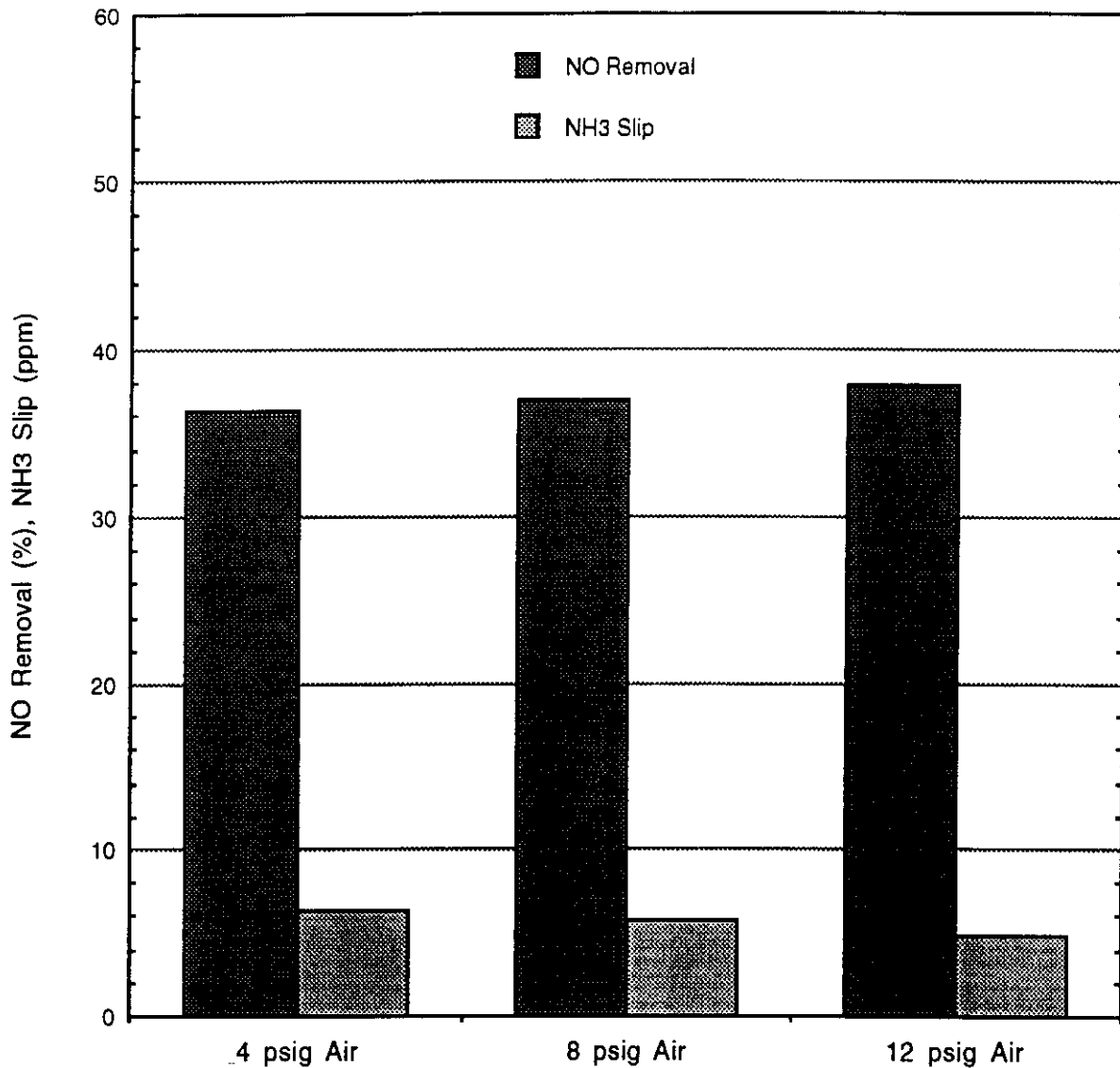


Figure 5-21. Effect of Mixing Air Pressure on Converted Urea Injection at 80 MWe
(N/NO = 1.15, 4.3 gpm total liquid flow)

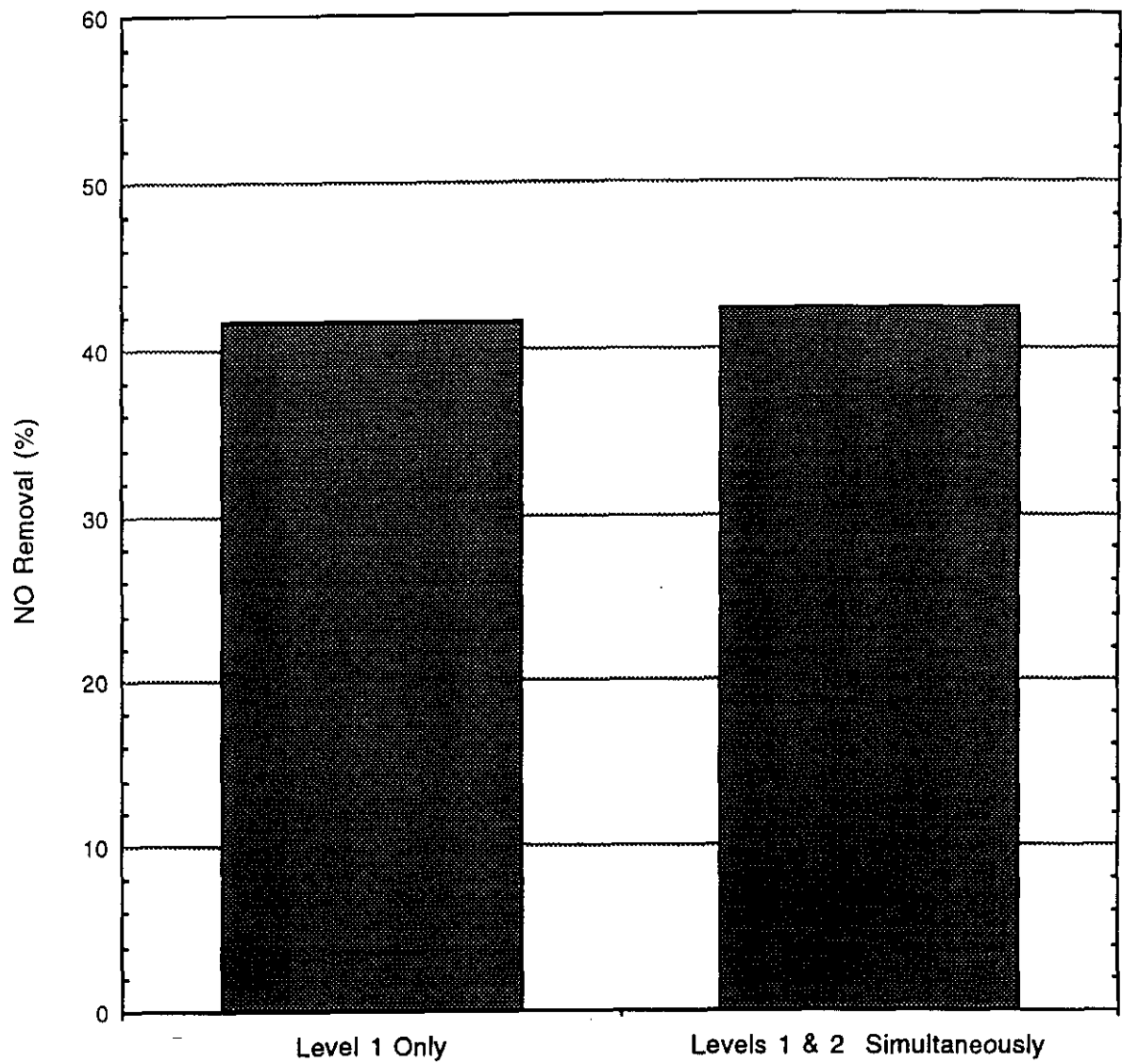


Figure 5-22. Effect of Bi-Level Injection with Converted Urea at 113 MWe
(N/NO = 1.15, 6 gpm total liquid flow, 8 psig air)

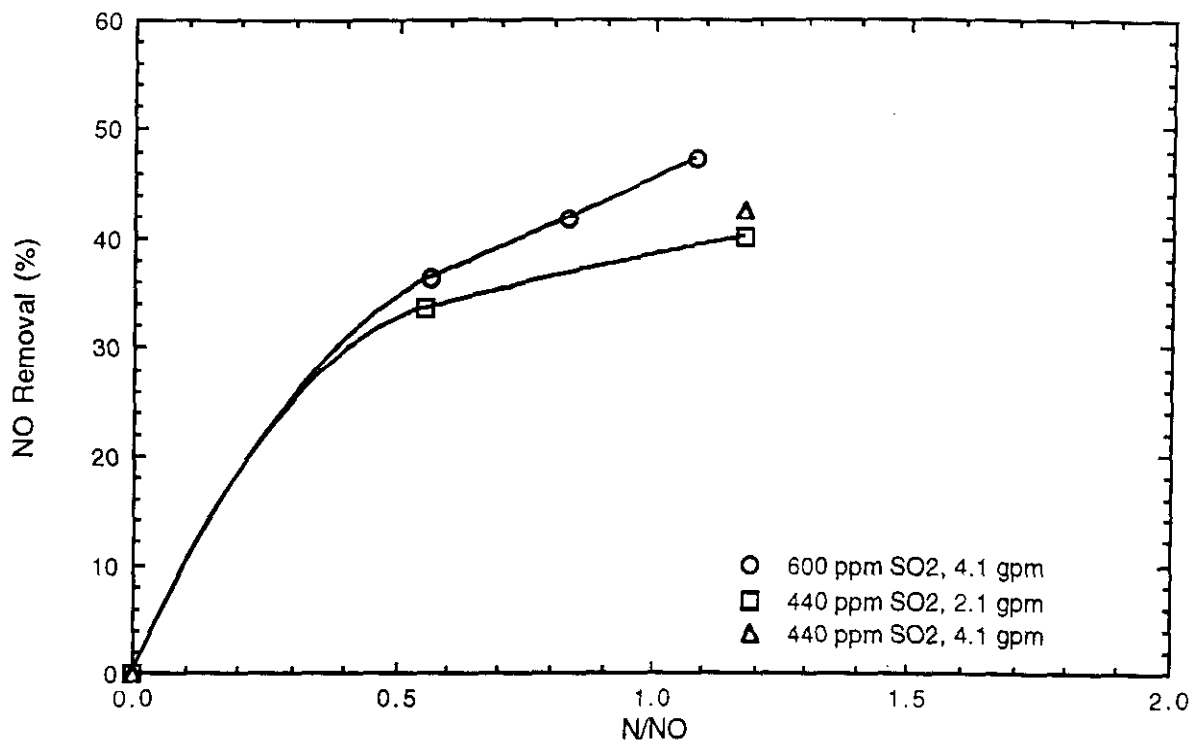
observations are summarized in Figure 5-23 for a boiler load of 60 MWe. In this figure, the two coals are denoted by the differences in SO₂ concentration. This is not to suggest that the SO₂ level is itself responsible for the difference in performance. At 60 MWe, the tests with the higher sulfur coal appear to yield increased NO removals as well as slightly lower levels of NH₃ slip. The factors contributing to this observation are not known and can only be speculated upon. This higher sulfur coal may burn somewhat differently, thereby changing the temperatures at the chemical injection location. Or, since the higher sulfur coal tends to produce higher CO emissions (as measured at the economizer exit), there will likely also be higher levels of CO at the injection level. Pilot-scale tests have shown that elevated levels of CO have the effect of lowering the temperature window for the SNCR process⁽⁵⁾.

5.4.7 Nitrous Oxide (N₂O) Emissions

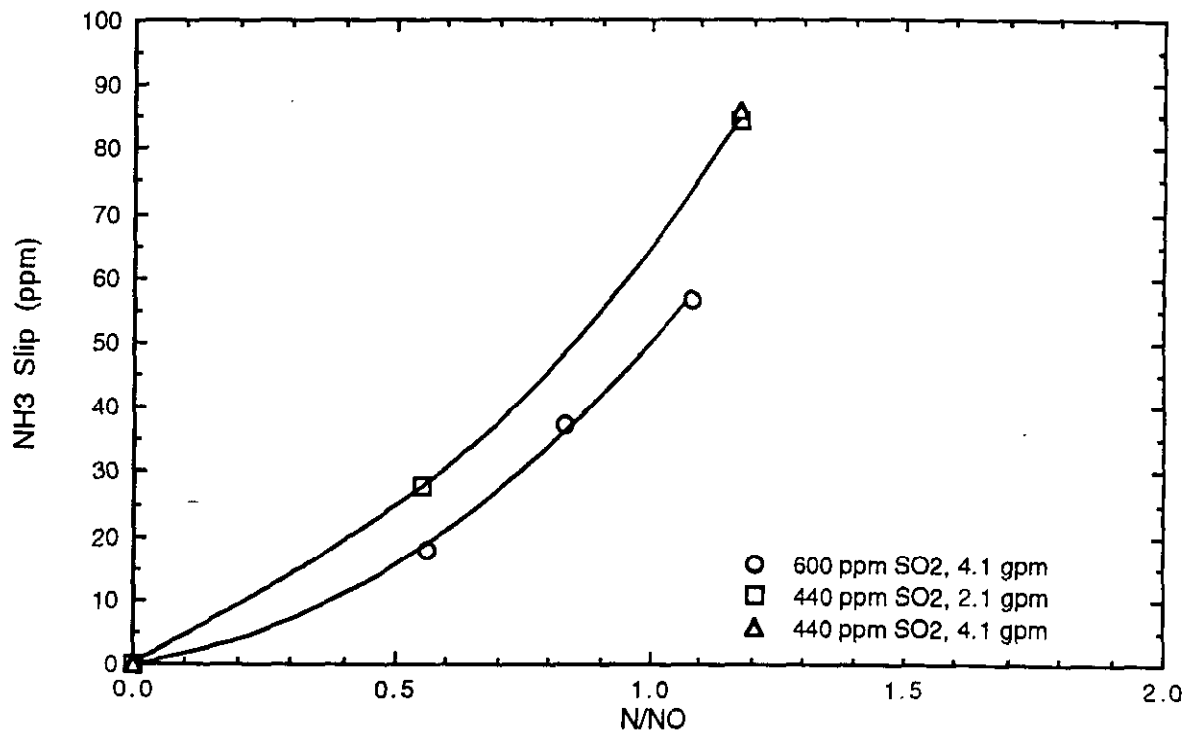
The N₂O production with the converted urea solution over the boiler load range from 60 to 113 MWe is shown in Figure 5-24. The N₂O production is significantly lower than seen with urea injection. With converted urea, 2 to 10 percent of the NO reduced appears as N₂O in the products. There is a slight trend of increasing N₂O with increasing N/NO ratio, although there is no clear trend in N₂O with boiler load. It is not known whether the changes in N₂O shown in Figure 5-24 are primarily related to performance of the urea converter or to processes occurring in the furnace. In any event, injection of the converted urea solution has markedly reduced N₂O production compared to that for the direct injection of urea.

5.4.8 CO Emissions

Increases in CO emissions with the converted urea were found to be small (less than 20 ppm). There was no discernable trend with either N/NO ratio or boiler load. As with the direct injection of urea, it is difficult to ascertain what mechanism contributes to this small increase in CO (see Section 5.3.8). Depending on the ammonium compounds formed in the converter, either or both of the two mechanisms discussed previously could be operative.



a) NO Removals



b) NH₃ Emissions

Figure 5-23. Effect of Coal Properties with Converted Urea at 60 MWe (8 psig air)

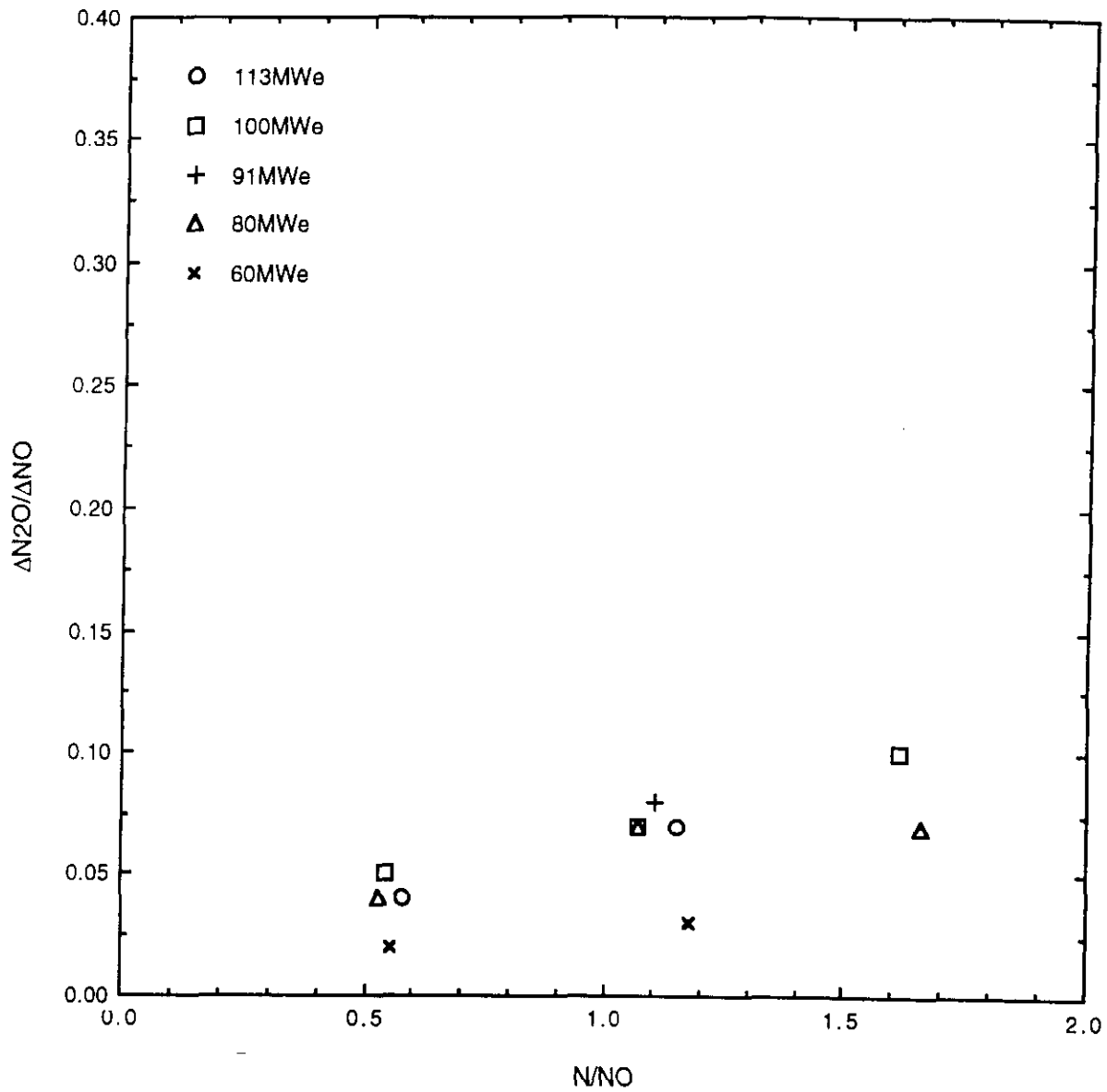


Figure 5-24. N₂O Emissions with Converted Urea Injection (8 psig air)

6

LONG-TERM LOAD FOLLOWING TEST RESULTS

The results of the parametric tests presented in the previous section were obtained at baseloaded operating conditions with testing personnel closely monitoring all boiler variables. However, Arapahoe Unit 4 is generally operated in a load following mode under automatic control. Under these conditions, oxygen levels can vary significantly and rapidly. This mode of operation tends to increase CO emissions and can also lead to higher NO emissions. Following completion of the baseloaded parametric tests, the boiler was operated for a period of five days (April 5 to 9, 1993) under normal load following conditions. A urea injection schedule was established based on the parametric tests, that would limit NH₃ slip to 10 ppm over the load range. This injection schedule is shown in Table 6-1.

Table 6-1

Long-Term Urea Injection Parameters

Injection Level:	Level 1		
Liquid Orifices:	Injectors 1 thru 9, 0.035" dia. Injector 10, 0.024" dia.		
Injection Air Pressure:	8 psig		
Load (MWe)	Total Liquid Flow Rate (gpm)	Target N/NO	
60	2.0	0.2	
80	2.2	0.54	
100	6.0	0.75	
110	6.0	1.39	

During this period, the control operators were instructed to operate the boiler as they would normally. There were no specific instructions given as to control room O₂ settings, coal mill biases, overfire air settings, etc. This test period was intended to assess the potential long-term SNCR performance possible without imposing operational constraints on the boiler.

Gaseous emission data were collected automatically with the CEM alternating between the two heated sampling locations at the air heater exit and stack. The CEM was programmed to calculate and record 10-minute averages for all the measured gas species, as well as boiler load. The NO_x data presented in this section are from the stack location only, and have been corrected to dry conditions for comparison to the results from the parametric tests.

The results of these tests are shown in Figure 6-1. In this figure, the data from the four day SNCR load following tests are compared to the long-term data collected over the November-December 1992 time period with the retrofit low-NO_x combustion system⁽²⁾. For the retrofit burners data, each point represents an hourly average of the 10-minute CEM averages. For the retrofit burner/urea injection tests, each point represents a 10-minute average. The data show that, with or without urea injection, there is a significant amount of scatter in the outlet NO_x levels across the load range. Although there does not appear to be as much scatter with urea injection as without, this is likely due to the much shorter test period with urea. In any event, the scatter is due to transient effects due to load changes during normal dispatch operation, as well as different operator preferences for various boiler control settings. The trends with urea injection do show lower outlet NO_x levels at higher loads, consistent with the higher target N/NO ratios shown in Table 6-1. Note that the control system did not maintain a constant N/NO ratio. Rather, based on the parametric data and an average inlet NO level at a given load, a urea injection rate was specified. The specified urea injection rate should yield, on average, the N/NO ratio shown in Table 6-1. If the actual inlet NO level changed due to varying boiler operations, then there would be a corresponding change in the N/NO ratio.

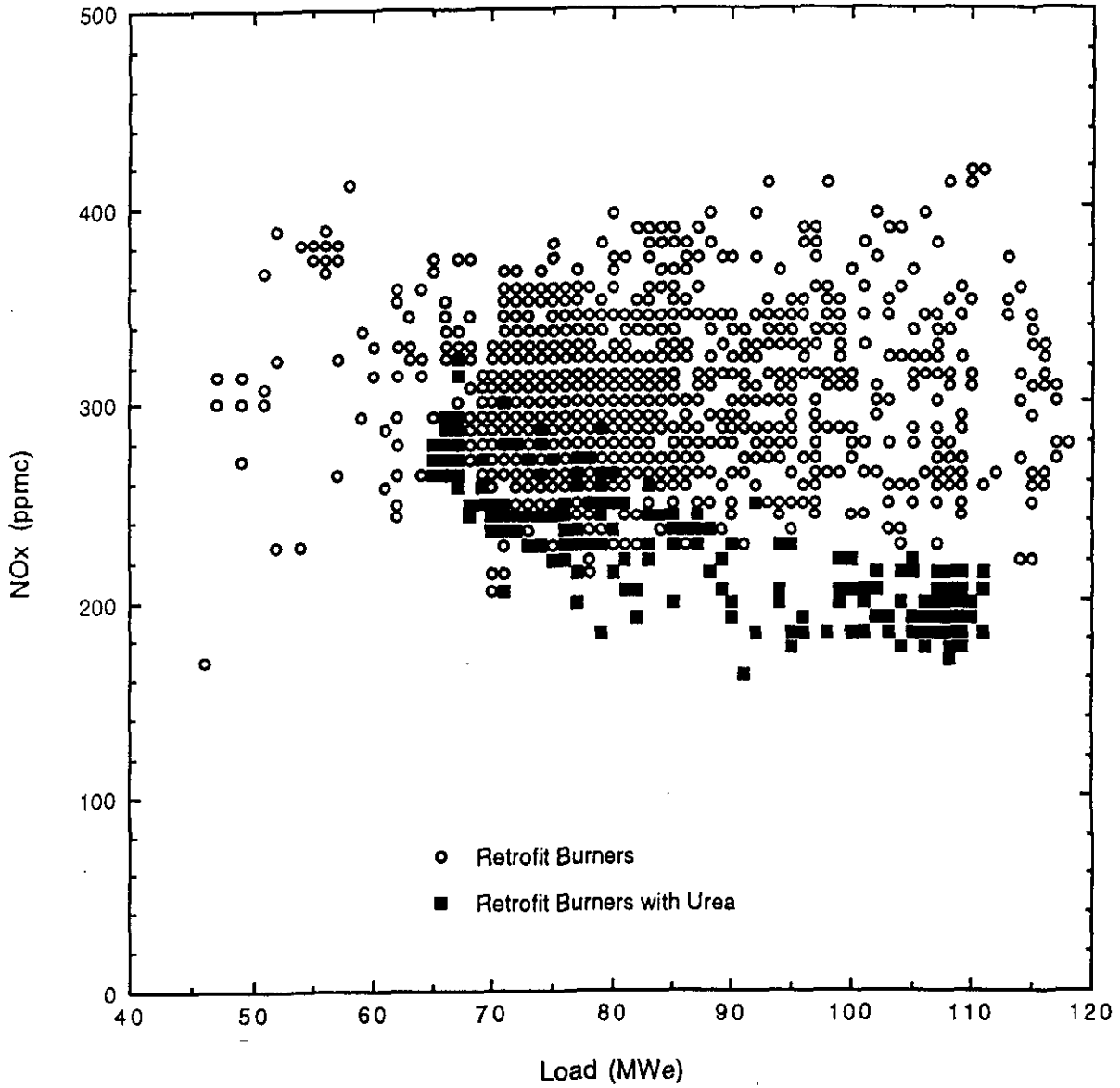


Figure 6-1. Comparison of Long-Term Load Following NO_x Emissions with and without Urea Injection

The individual data points in Figure 6-1 have been averaged and replotted in Figure 6-2. In this figure, each point represents the average of all of the data points shown in Figure 6-1 which are within a 10 MWe range (i.e., the 100 MWe data point is the average of all of the CEM points between 95 and 105 MWe). Based on these averages, the nominal NO reduction is also noted at each load. It should be noted that with the SNCR system continuously operating, it is impossible to obtain a "true" baseline NO value. Therefore, the baseline NO values utilized in calculating the NO removals in Figure 6-2 are estimated and based upon the long-term load following data collected during the Low-NO_x Burner/Overfire Air tests⁽²⁾. For comparison, the NO removals achieved during the parametric tests (Section 5.3), where boiler operating conditions were closely controlled, are noted in parentheses in Figure 6-2. The results show that the NO removals achieved with long-term unattended operation are lower than those achievable under carefully controlled conditions. It is expected, however, that the difference between the unattended results and controlled results can be made smaller by specifying certain boiler operating conditions at each boiler load. In particular, control room O₂ set point, coal mill biases, overfire air setting. These steps will be pursued during the integrated systems test portion of the test program.

The urea injection schedule shown in Table 6-1 was based upon limiting the NH₃ slip at the air heater exit to 10 ppm. However, as the "baseline" NO levels during the long-term tests were likely different from those during the parametric tests (due to differences in boiler operating practices), it also is likely that the SNCR system was either under- or over-injecting at any one particular time. Figure 6-3 shows the average CEM NH₃ measurements at the air heater exit and stack locations. The data has been averaged in a manner similar to that for Figure 6-2 (i.e., over 10 MWe increments). As discussed in Section 4.3, the single-point CEM NH₃ measurement at the air heater exit is not a valid representation of the average NH₃ slip, due to the non-uniformity of the NH₃ emission profile at that location. However, the CEM data does provide an indication of the general trends of NH₃ emissions in that region. The results show that the emissions at the air heater exit range from 6 to 18 ppm, with an average over the entire boiler load

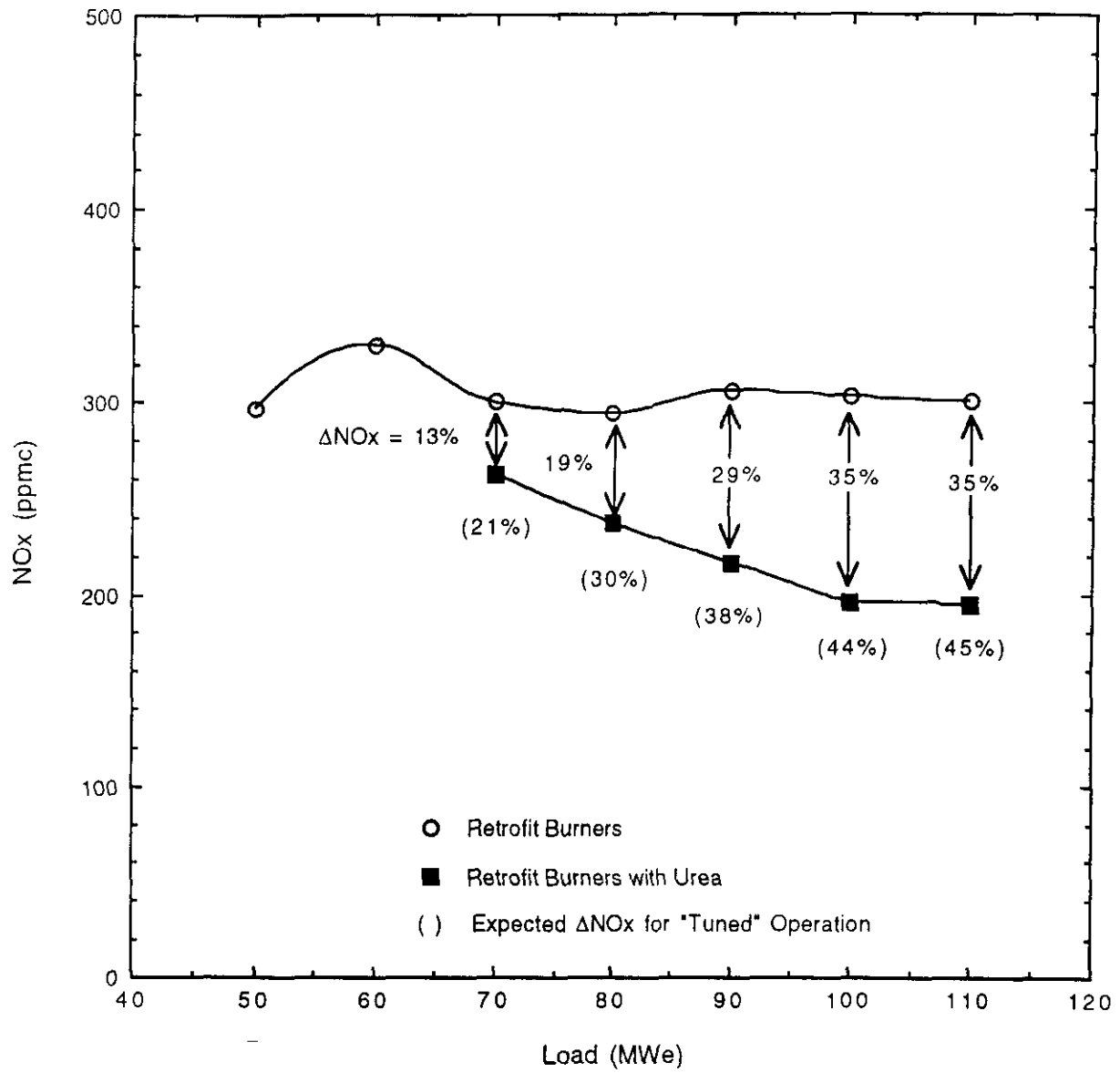


Figure 6-2. Average Long-Term Load Following NO_x Emissions With and Without Urea Injection

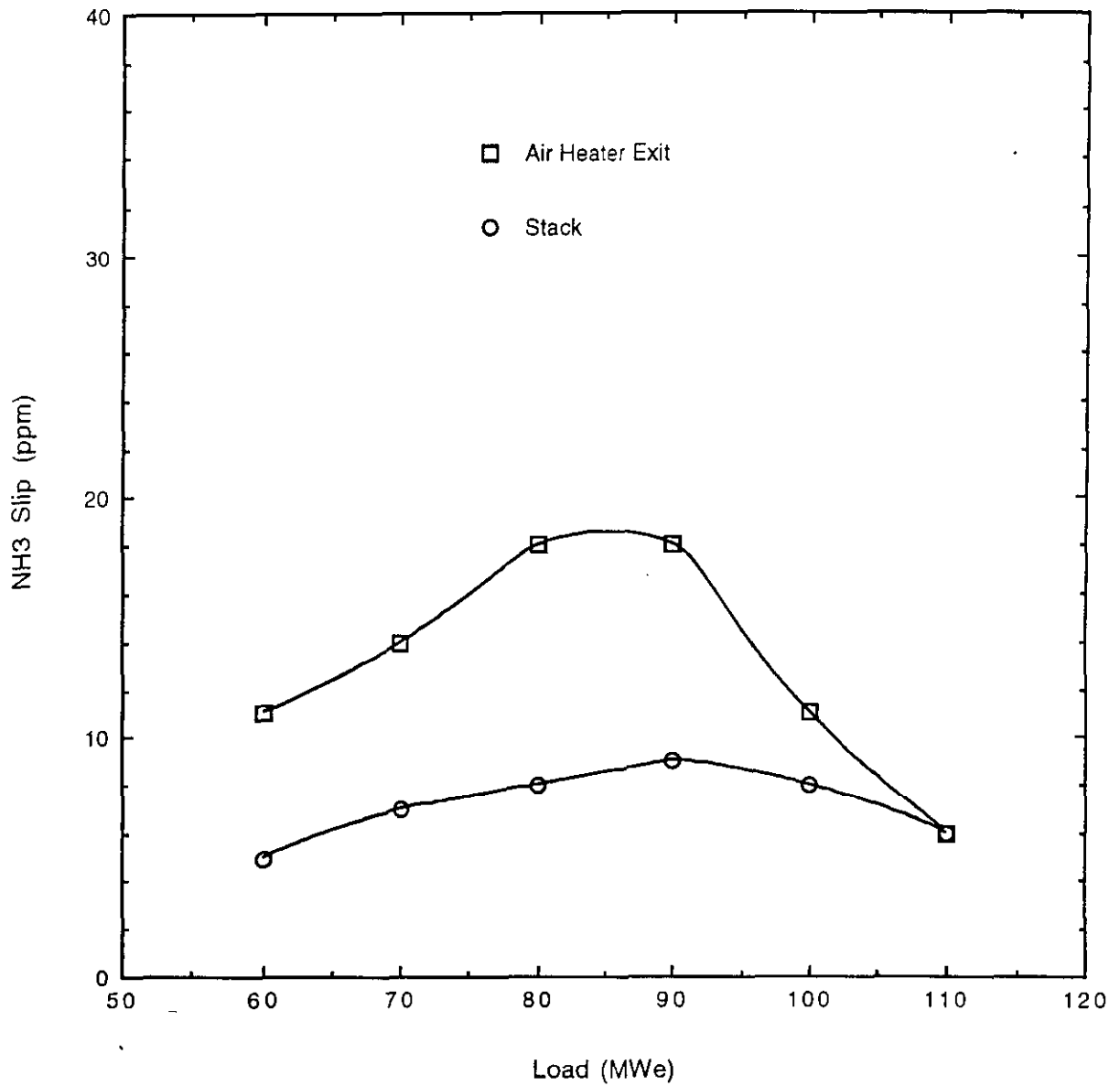


Figure 6-3. Average NH₃ Emissions During the Long-Term Load Following Tests

range of 13 ppm. The NH₃ emissions at the stack are a better indicator of the overall performance, as they are not susceptible to biases due to flue gas stratification in the duct. Figure 6-3 shows that the stack emissions ranged from 5 to 9 ppm, with an average over the entire boiler load range of 7 ppm.

DISCUSSION

The primary purpose of this section is to present 1) a comparison of the performance of urea to converted urea, and 2) to compare the performance of the SNCR system when operating with the pre- and post-retrofit combustion systems. Before proceeding with the comparison, some discussion is warranted to put the comparisons in context, in particular, when comparing SNCR performance with the pre- and post-retrofit combustion systems. There has been a large change in the initial NO levels, as well as approximately a 200°F reduction in the flue gas temperatures at the chemical injection location. In terms of NO emissions, a 50 percent reduction with SNCR corresponds to an outlet NO emission level of nominally 425 ppmc with the original combustion system. Whereas, with the retrofit low-NO_x combustion system, a 50 percent NO reduction with SNCR corresponds to a NO emission level of nominally 140 ppmc. Thus, it was necessary to inject much more chemical in order to obtain an equivalent percentage NO reduction with the original combustion system. However, to gain further insight into the SNCR processes, it is of interest to compare the relative pre- and post-retrofit performance.

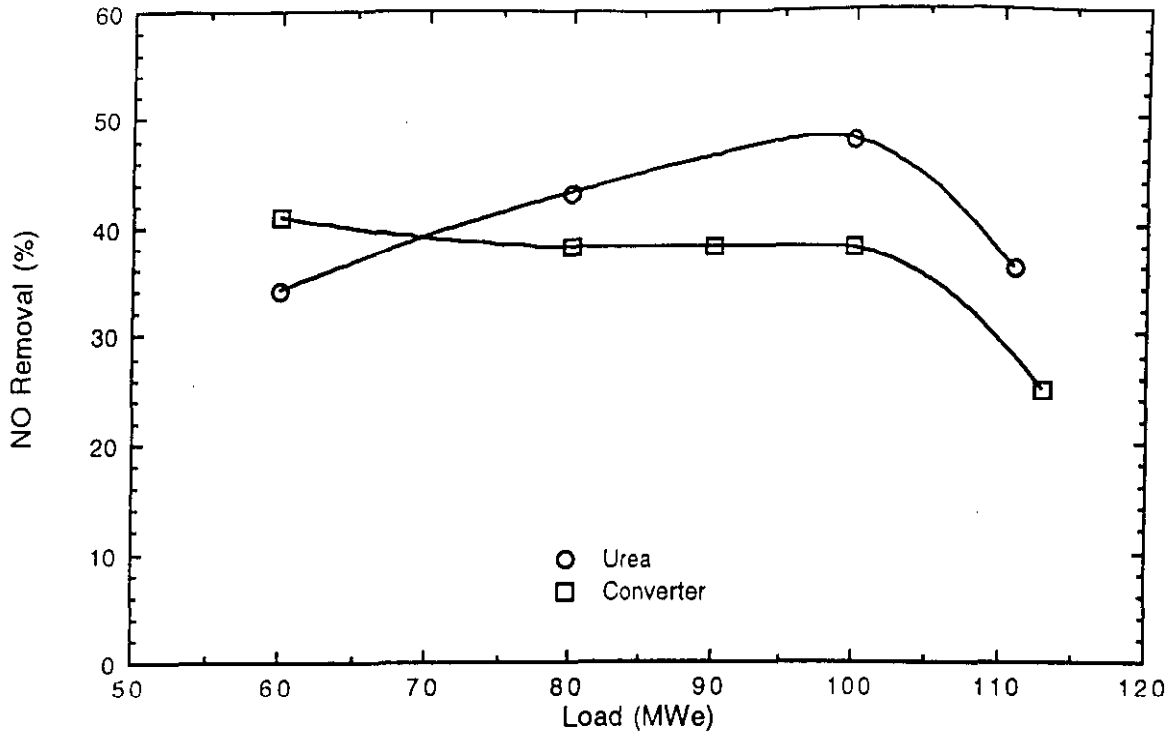
This section will also compare system performance when using ammonia hydroxide (NH₄OH) with the original combustion system, to the performance of the converted urea solution with the retrofit low-NO_x combustion system. It should be kept in mind that for this comparison not only are the combustion systems different (i.e., initial NO_x levels, gas temperatures, etc.) but also the SNCR chemicals. The NH₄OH used during the baseline SNCR tests was a pure 29.4 percent (by weight) aqueous ammonia solution. The converted urea, which to date has not been characterized in terms of the specific types of compounds, is likely a mixture of a variety of ammonium compounds (i.e., ammonium

carbonate, ammonium bicarbonate, etc.). This chemical difference may also contribute to differences in performance relative to aqueous ammonia (NH_4OH).

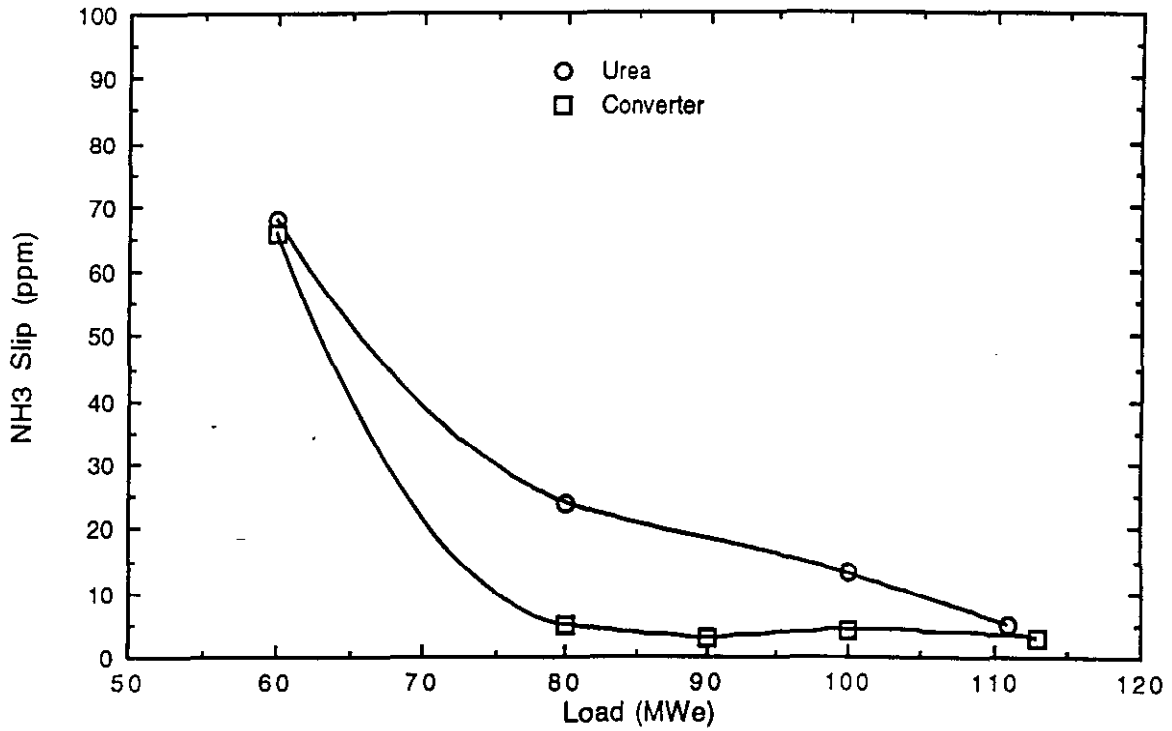
7.1 Comparison of SNCR Performance with Urea and Converted Urea

The first comparison to be addressed is the relative performance of urea and converted urea. Figure 7-1 compares the NO removals and NH_3 emissions for the two compounds over the load range from 60 to 110 MWe at a N/NO ratio of 1.0. In order to provide a more accurate comparison of the performance of the two compounds, the data points in both figures were interpolated from the curves in Figures 5-8 and 5-18 for the "exact" (not "nominal") N/NO ratio of 1.0. With the exception of the 60 MWe point, urea injection yielded consistently higher NO removals over the load range than the converted urea. However, over the load range from 80 to 100 MWe, the NH_3 emissions with the converted urea solution were markedly lower than those for urea. At 60 and 100 MWe, the NH_3 emissions were comparable.

A better comparison of urea and converted urea is shown in Figure 7-2. In this figure, the NO removal attainable with 10 ppm NH_3 slip is plotted versus boiler load. As was done in Figure 7-1, the data points which define these curves were interpolated from the curves in Figures 5-8 and 5-18. The numbers in parentheses denote the corresponding N/NO ratio at each load. Over the load range, the converted urea consistently provided higher NO removals while limiting NH_3 emissions to 10 ppm. However, this increase in NO reduction with the converted urea is at the expense of higher N/NO ratios (i.e., lower urea utilization). For instance, at 100 MWe twice as much chemical is needed to achieve a 47 percent NO removal with the converted urea compared to a 43 percent NO removal with urea alone. This translates to an economic decision as to the tradeoffs between this higher chemical usage rate and the four percentage point increase in NO removal. Another point which may need to be considered is that the production of N_2O with the converted urea solution is much lower than with urea alone.



a) NO Removal



b) NH₃ Emissions

Figure 7-1. Comparison of SNCR Performance with Urea and Converted Urea at N/NO = 1.0

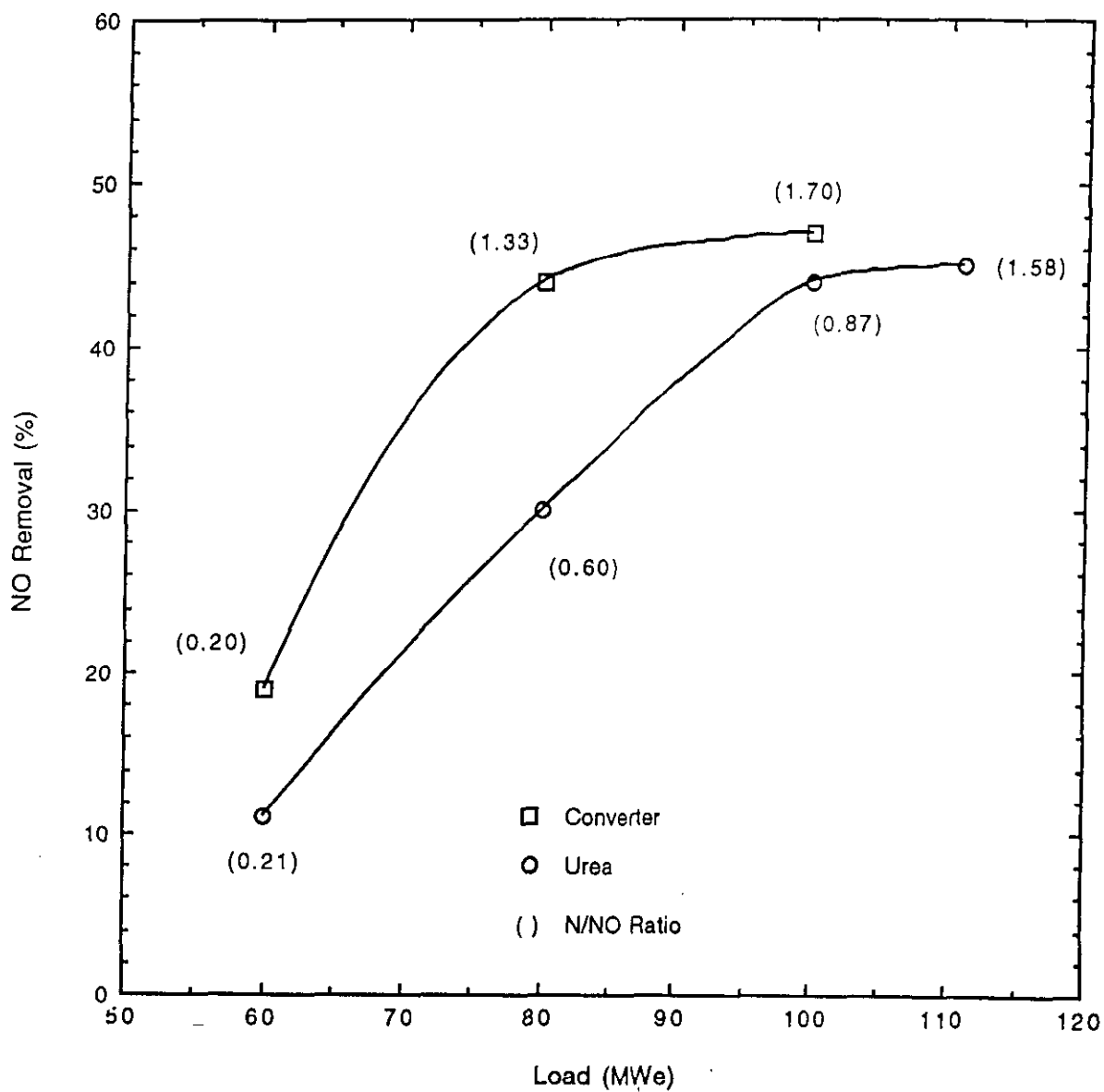


Figure 7-2. Comparison of NO Removals with Urea and Converted Urea for a Fixed NH₃ Slip Level of 10 ppm

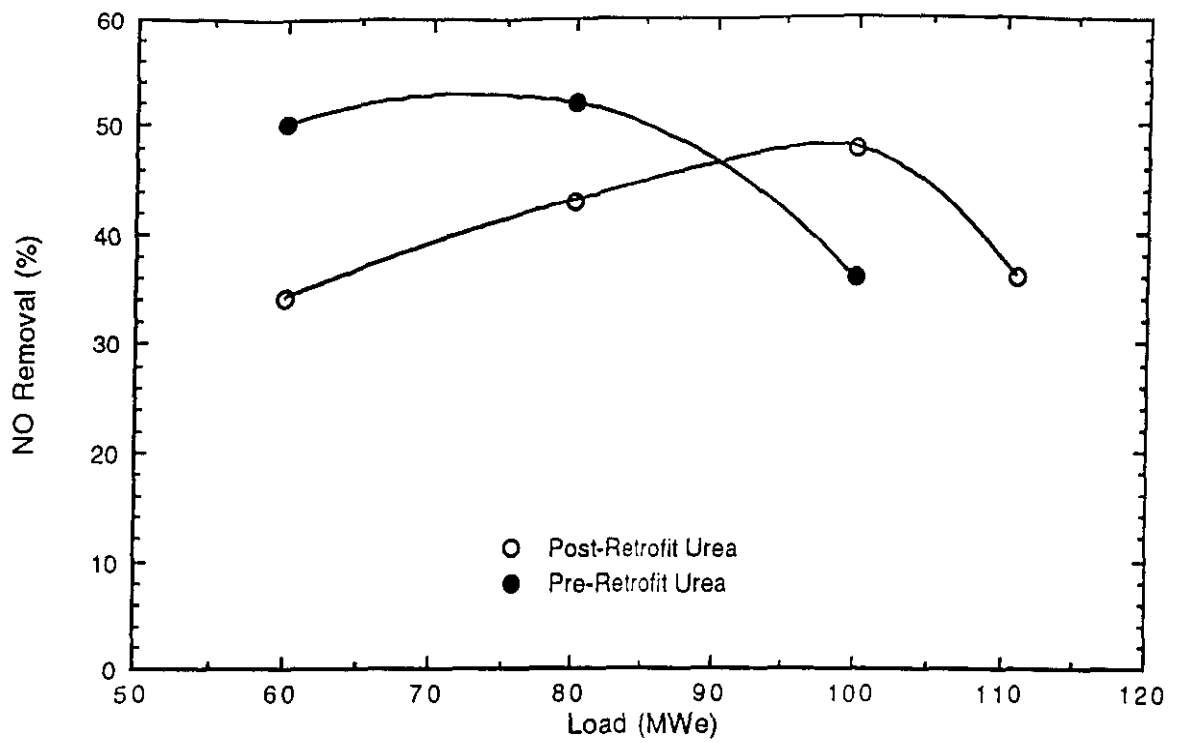
7.2 Pre- and Post-Retrofit SNCR Comparison

7.2.1 Urea Injection

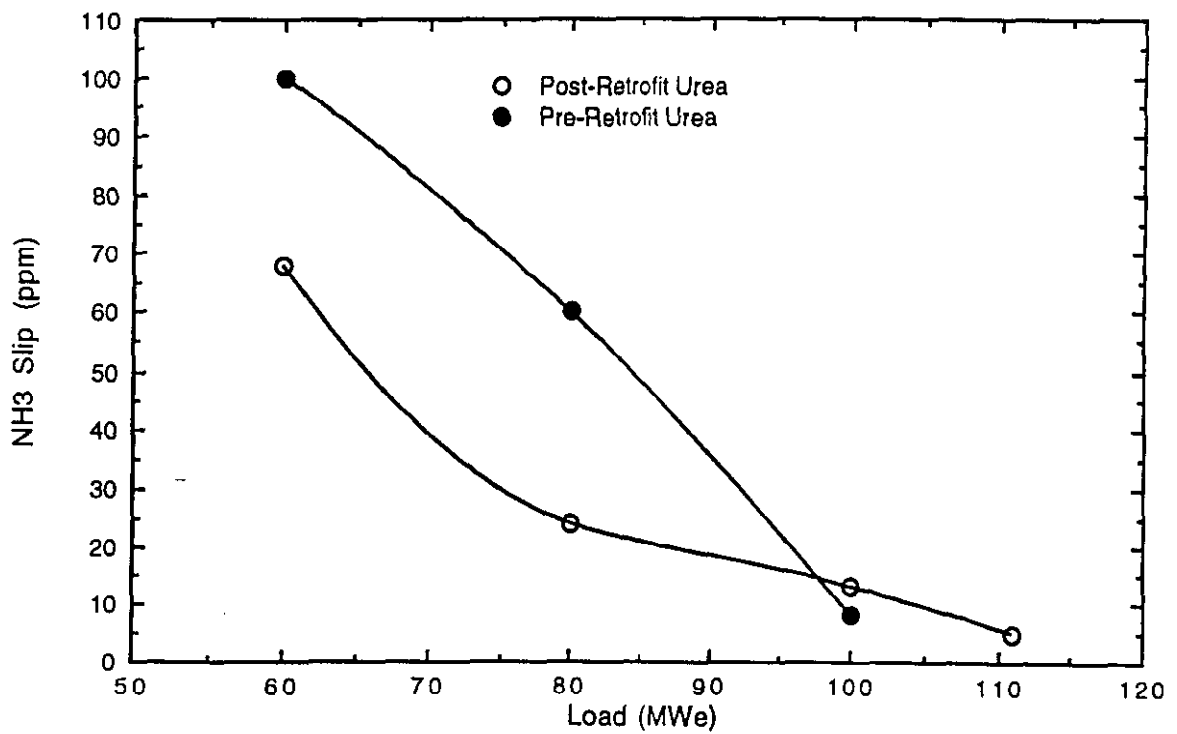
The SNCR performance of urea injection with the pre- and post-retrofit combustion system is shown in Figure 7-3. The data show similar behavior in terms of maximum NO removals achievable, but the boiler load for peak removal is higher with the retrofit low-NO_x combustion system. This effect has been discussed previously and is consistent with the lower furnace exit gas temperatures with the new combustion system.

The comparison of NH₃ emissions on an absolute part per million basis is shown in Figure 7-3b. Two factors affect the NH₃ slip. First, with the pre-retrofit combustion system, over three times as much urea is being injected due to the higher initial NO level. Second, the gas temperatures at a given load have shifted with the retrofit. At a load of 100 MWe, the lower NH₃ slip with the original burners is due to the higher gas temperatures. At lower loads, the NH₃ slip is higher with the original combustion system. This effect is dominated by the higher initial NO level and higher urea injection rate. To afford a better comparison of the NH₃ slip behavior, the data in Figure 7-3b has been normalized by the initial NO level (NO_i) and replotted in Figure 7-4. On this normalized basis, the NH₃ slip is higher with the retrofit low-NO_x combustion system, over the entire load range. Again, this is likely due to the shift in flue gas temperatures discussed previously.

Figure 7-5 shows another comparison of the performance of urea between the pre- and post-retrofit combustion systems. In this figure, the NO reduction performance is compared over the load range at a constant 10 ppm level of NH₃ slip. On this basis, the retrofit combustion system provides higher NO removal over the load range from 65 to 110 MWe. At 60 MWe, urea injection with the original combustion system yielded higher NO removals with a 10 ppm NH₃ slip level. This can be attributed to flue gas temperatures which are closer to the optimal temperature at this load with the original combustion system. The most likely reason for the better overall SNCR performance seen after the retrofit, when compared on a 10 ppm NH₃ slip basis, is the lower initial NO level as discussed in the introduction to this section.



a) NO Removal



b) NH₃ Emissions

Figure 7-3. Comparison of Urea Injection with Pre- and Post Retrofit Combustion Systems at N/NO = 1.0

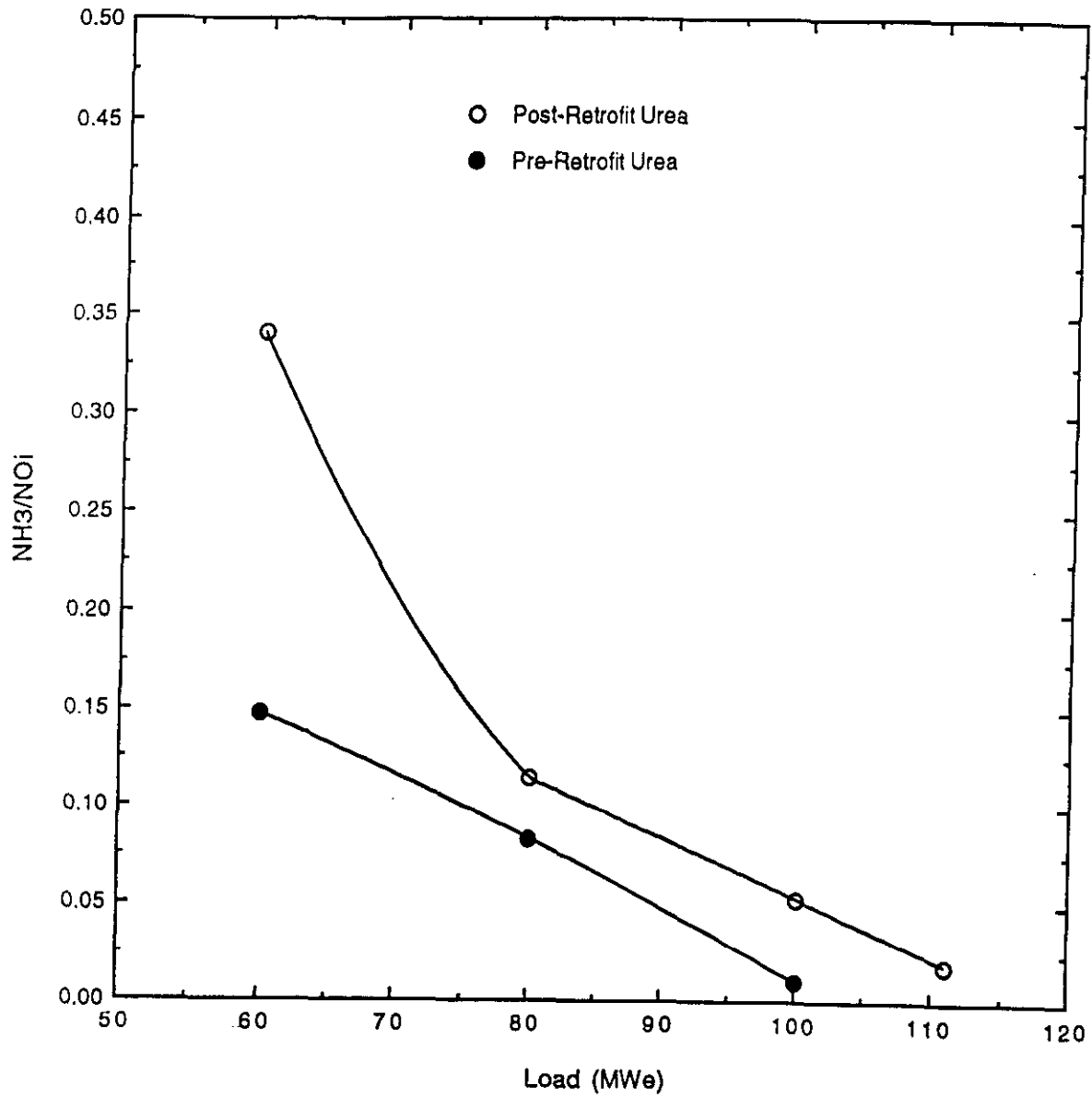


Figure 7-4. Comparison of Normalized NH_3 Emissions for Urea Injection with the Pre- and Post-Retrofit Combustion Systems at $\text{N}/\text{NO} = 1.0$

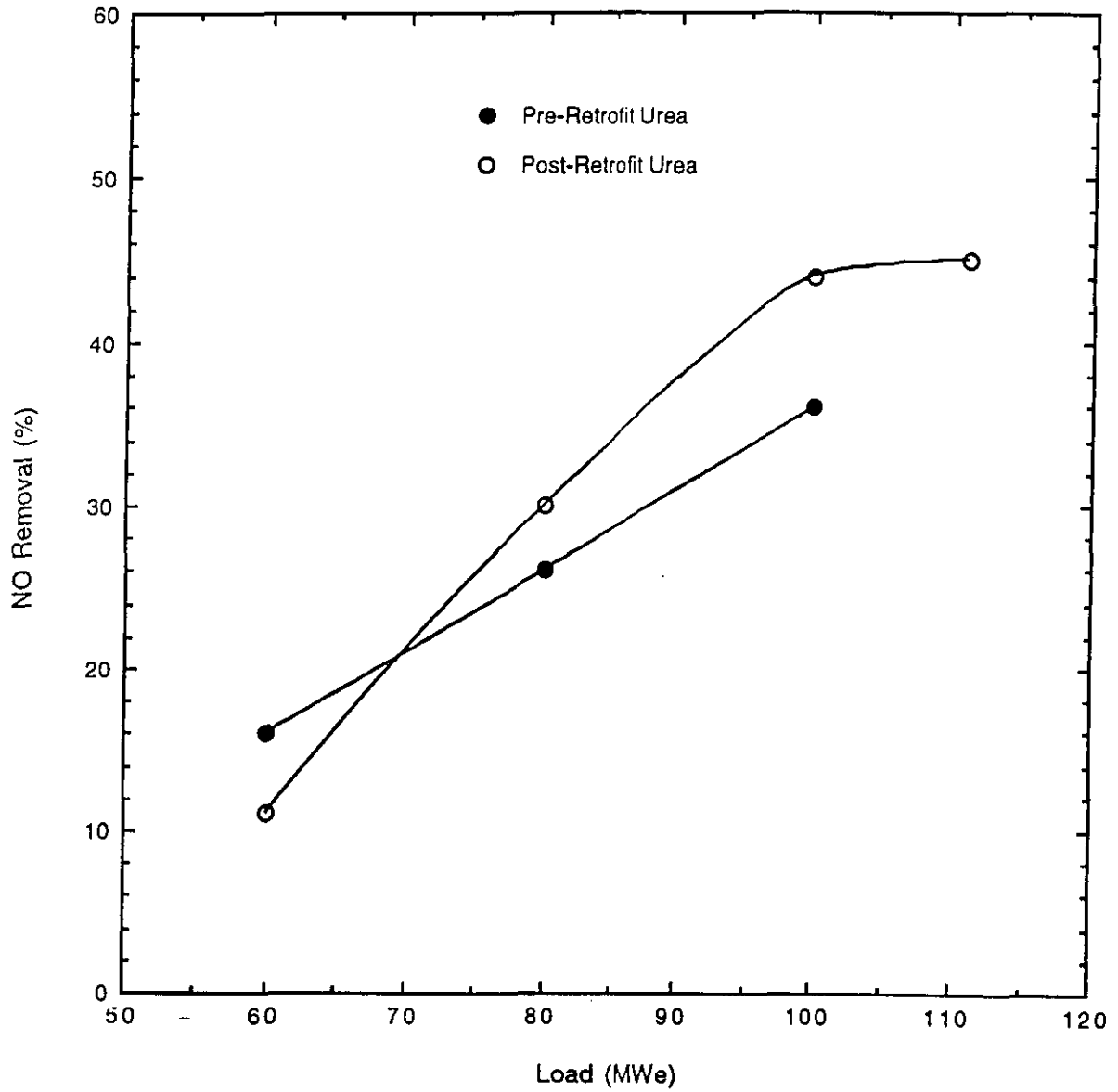


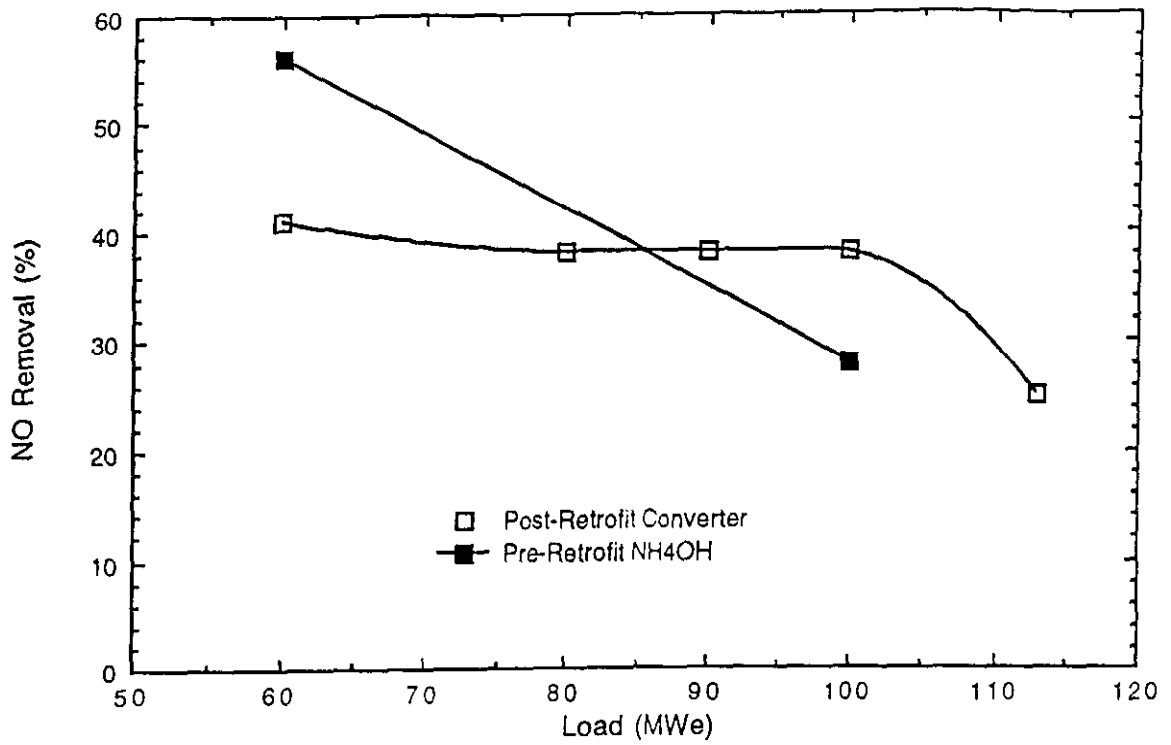
Figure 7-5. Comparison of Pre- and Post-Retrofit SNCR Performance with Urea at a Fixed NH_3 Slip of 10 ppm

7.2.2 *Converted Urea and Aqueous Ammonia*

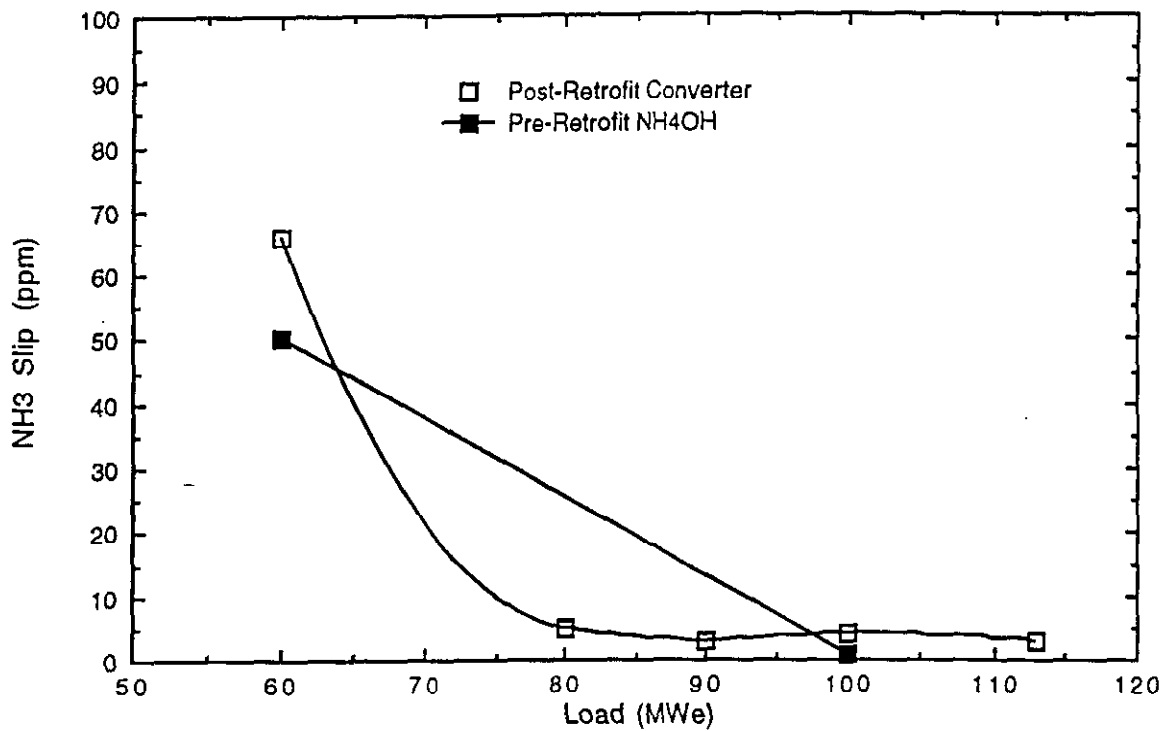
A pre- and post-retrofit comparison can also be made between the tests with aqueous ammonia (original burners) and converted urea (retrofit low-NO_x burners). Figure 7-6 shows this comparison over the load range at a N/NO ratio of 1.0. In addition to the initial NO level and the temperature effects discussed in Section 7.2.1, the converted urea differs chemically from the aqueous ammonia used during the baseline SNCR tests with the original burners. With the converted urea, the NO reduction performance was fairly flat from 60 to 100 MWe, decreasing at boiler loads above 100 MWe because of the higher flue gas temperatures. The performance of aqueous ammonia with the original combustion system was quite different. As seen in Figure 7-6a, NO removals increased as the load decreased from 100 to 60 MWe. It does not appear that these differences can be explained solely by a change in gas temperatures with the burner retrofit, as could be done with the comparison of urea performance (Section 7.2.1). With urea, peak removals were comparable but shifted to a higher boiler load with the burner retrofit. With converted urea, the NO removals were never as high as achieved with aqueous ammonia at 60 MWe. Thus, it might be speculated that the different mix of ammonium compounds exiting the converter may be contributing to this difference in performance.

The comparison of NH₃ emissions is shown in Figure 7-6b on an absolute parts per million basis, and in Figure 7-7 where the NH₃ emission values have been normalized by the initial NO levels. While the amount of data is not extensive, the normalized NH₃ slip data (Figure 7-7) show comparable low slip levels down to a boiler load of 80 MWe. At 60 MWe, the NH₃ emissions with the converted urea and retrofit combustion system is higher than for aqueous ammonia and the original combustion system. Even on an absolute basis, the NH₃ slip is higher at 60 MWe with the converted urea and retrofit combustion system. It is not possible to assess whether this is primarily a temperature affect or chemical difference between aqueous ammonia and the covered urea.

Finally, Figure 7-8 compares the NO removals achievable with aqueous ammonia to those for converted urea at a constant 10 ppm level of NH₃ slip. Except at the low load condition, converted urea with the retrofit burners yields higher NO removals with a



a) NO Removal



b) NH₃ Emissions

Figure 7-6. Comparison of SNCR Performance with NH₄OH (Pre-Retrofit) and Converted Urea (Post-Retrofit) at N/NO = 1.0

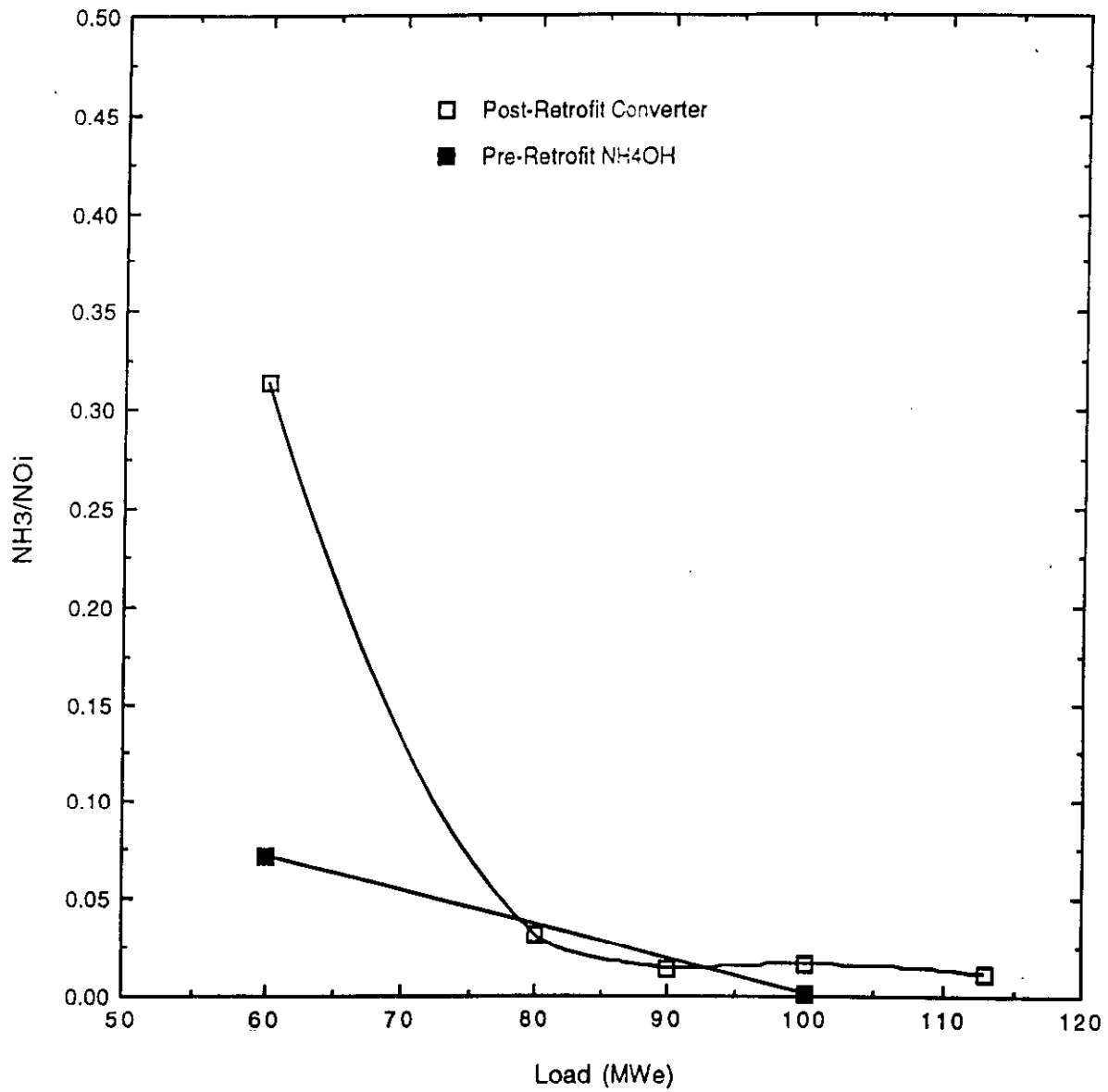


Figure 7-7. Comparison of Normalized NH_3 Emissions for NH_4OH (Pre-Retrofit) and Converted Urea (Post-Retrofit) at $\text{N}/\text{NO} = 1.0$

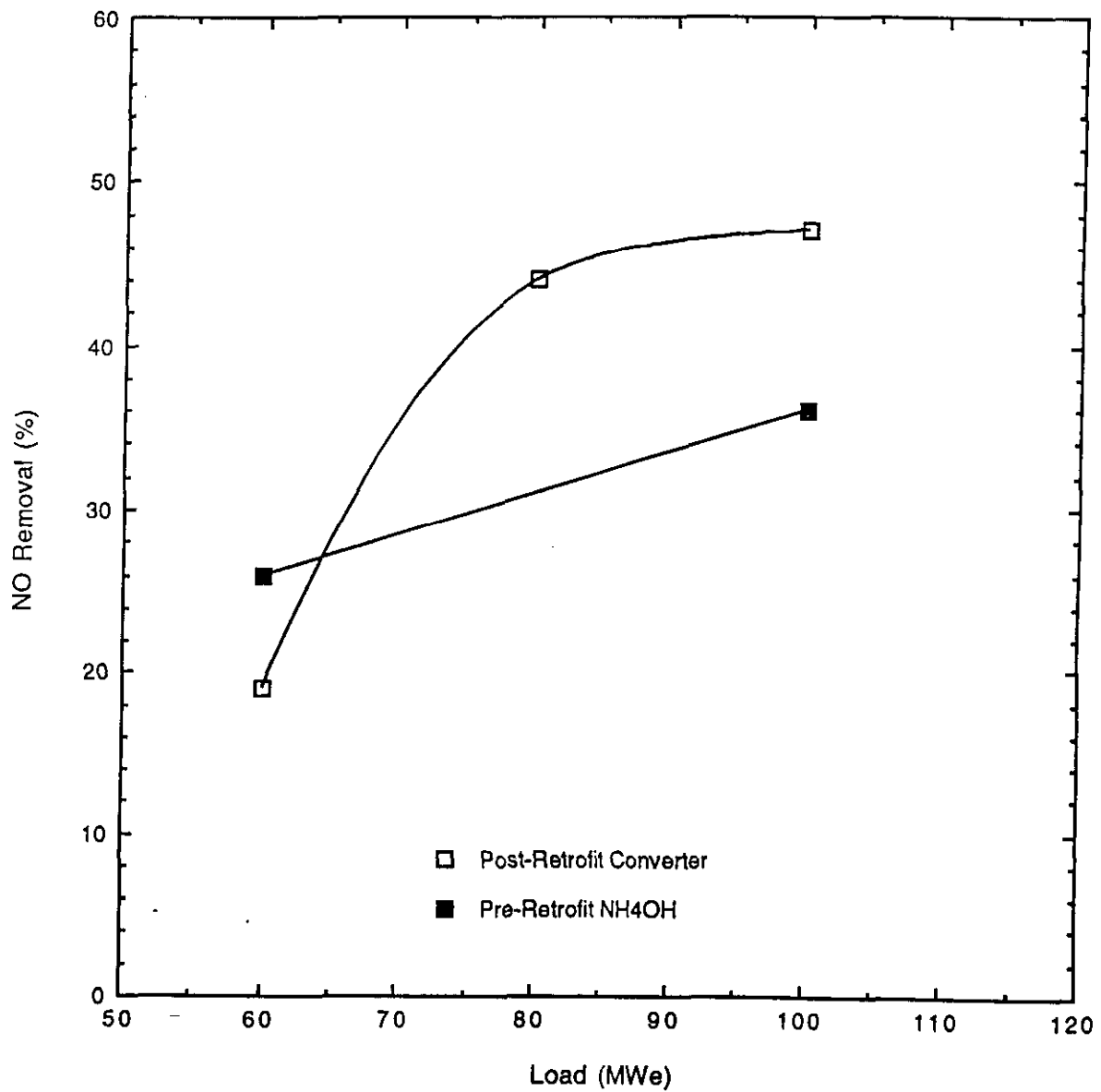


Figure 7-8. Comparison of NO Removals for NH_4OH (Pre-Retrofit) and Converted Urea (Post-Retrofit) at a Fixed NH_3 Slip of 10 ppm

10 ppm NH₃ slip limit than aqueous ammonia and the original burners. Again, this is likely due to the much higher initial NO levels with the original burners, and the associated higher chemical injection rate.

SYSTEM IMPACTS

Integrating an SNCR system into a utility boiler operation can result in a number of impacts to the balance of plant. While the SNCR testing to date at Arapahoe Unit 4 has not involved extensive long-term testing, there is sufficient data to at least address a number of the potential impacts that have occurred, or might occur, with long-term operation. In particular, this section of the report will discuss the following impacts and system integration issues:

- plume visibility
- NH_3 absorption in fly ash
- SO_3/NH_3 reactions and air preheater deposition
- boiler efficiency impacts, including steam temperature control.

8.1 Plume Visibility

As reported in the report documenting the baseline SNCR tests⁽³⁾, a detached visible plume was frequently encountered when NH_3 slip levels were relatively high. During the initial baseline SNCR tests, it was speculated that the detached plume was due to NH_3 reactions with either HCl or SO_2 resulting in the formation of an ammonium salt aerosol. Reactions between NH_3 and SO_3 are not a likely source of plume visibility since the measured levels of SO_3 in the Arapahoe Unit 4 flue gas is low (less than 1 ppm)^(1,3). Even if reactions between NH_3 and SO_3 were to occur, these reactions will take place upstream of the air heater where the flue gas temperatures are in the range of 400 to 600°F, and the products of these reactions (ammonium sulfate or ammonium bisulfate) would be removed in the baghouse.

Reaction between HCl and NH₃ would occur via the following reaction



Thermochemical calculations indicate that the solid ammonium chloride (NH₄Cl) will form in the post-stack region when the plume has entrained sufficient air to reduce the temperature to 200 to 230°F.

A number of chemical reactions can occur between NH₃ and SO₂:



Thermochemical calculations using the data in Reference 12 indicate that reactions (10) and (11) will lead to solid aerosol formation at the highest temperatures and concentrations of NH₃ and SO₂. Although for typical flue gas conditions at Arapahoe Unit 4 (275°F, 10 percent moisture, and 400 ppm SO₂), the plume would only form a solid aerosol if the entrained ambient air were less than about 30°F.

During the SNCR testing with the retrofit burners, there were still instances of a detached visible plume. Measurements of HCl concentrations in the stack gas showed concentrations of less than 2 ppm. Four HCl measurements were less than 0.5 ppm, with one at 1.9 ppm. These levels of HCl when reacted with NH₃ would not be expected to result in plume visibility. This seemed to suggest that the primary source of the plume visibility was an aerosol formed in the detached plume due to reactions between SO₂ and NH₃. This was further substantiated by the following observation. On test days late in winter, ambient temperatures in the morning would frequently vary between 15 and 30°F. During the cold mornings, a detached visible plume would occur when the SNCR system was operating with NH₃ slip levels of 10 ppm or above. During the course of the day, as the ambient temperature increased into the 30 to 50°F range, the detached visible plume would disappear, even though the SNCR system was still operating with comparable NH₃ slip levels. If the plume were due to HCl/NH₃ reactions, this change in ambient

temperature would have little effect on the post stack aerosol formation. Thus, the available data and observations suggest detached visible plume formation is due to SO_2/NH_3 reactions and the entrainment of low temperature (i.e., less than 30°F) ambient air.

8.2 NH_3 Absorption by Fly Ash

At Arapahoe Unit 4, the fly ash collected in the fabric filter is not sold for secondary use, so the absorption of NH_3 on the fly ash poses primarily a personnel problem during ash handling and disposal. During the baseline SNCR testing, the NH_3 content of fly ash samples taken from the fabric filter hoppers ranged from 11 to 40 ppm (by weight) when the SNCR system was operated with an NH_3 slip of 8 to 10 ppm⁽³⁾. During the current phase of testing, fly ash samples were collected by Western Research Institute during the four day period of "long-term" urea tests (see Section 6). NH_3 concentrations for these samples ranged from 72 to 108 ppm (by weight). While the urea injection system was set up to operate with 10 ppm NH_3 slip, the continuous NH_3 measurement at the outlet of the fabric filter indicated time periods when the NH_3 slip levels were over 20 ppm. Additional fly ash samples were collected under more well controlled and documented conditions during the air toxics test conducted with urea injection. The report documenting these results is forthcoming.

8.3 SO_3/NH_3 Reactions with Air Heater Deposition

Air preheater deposition and plugging can occur due to reactions between SO_3 and NH_3 . These reactions occur in the temperature region of 330 to 375°F , where the formation of ammonium bisulfate occurs. The actual reaction temperature depends on the concentrations of SO_3 and NH_3 . Deposition and plugging will be more severe with regenerative air preheaters because the flow passages are small when compared to those for tubular air preheaters. Arapahoe Unit 4 has a tubular air preheater and the flue gas SO_3 concentrations are low (less than 1 ppm)^(1,2). As a consequence, with the SNCR operation to date, no change in air preheater performance has been observed. However, if the SNCR system is operated on a long-term basis, (i.e., months), air preheater

performance (heat transfer, and pressure drop) should be documented to insure that no long-term effects occur.

8.4 Boiler Efficiency Impacts

Boiler efficiency will be impacted by the SNCR system due to 1) power to run the mixing air compressor, liquid pumps, and heaters, 2) additional dry gas losses in the boiler due to the mixing air, and 3) additional water vapor losses due to the injection of the aqueous chemical. (Note: depending on the actual solution concentration, the exothermic energy released by the NO reduction reactions will partially offset the vaporization losses.)

Mixing Air

Based on the parametric tests, the recommended operating pressure for the mixing air is 8 psig, which corresponds to a mixing air flow rate of 3900 scfm. The energy needed to operate the compressor is nominally 260 kW (i.e., 350 hp) or 0.26 to 0.43 percent of the unit output over the load range from 100 to 60 MWe, respectively. In terms of additional dry gas stack losses, 3900 scfm corresponds to 2.4 to 1.8 percent of the total flow over the boiler load range from 60 to 100 MWe. This additional air flow through the unit will produce an efficiency loss of 0.09 to 0.05 percent.

Vaporization Losses

Efficiency penalties due to the net effect of vaporization of the aqueous solutions and exothermic energy release of the SNCR reactions will depend on the total liquid flow rate and operating N/NO ratio. Based on the parametric test results with urea injection, the total liquid flow rates will be 2 gpm at boiler loads of 60 to 80 MWe and 6 gpm at loads above 80 MWe. Operating N/NO ratios, based upon an NH₃ slip limit of 10 ppm (Figure 7-2) will be 0.20 and 1.70 for boiler loads of 60 and 100 MWe, respectively. The net effect will be boiler efficiency penalties of nominally 0.15 percent at 60 MWe and 0.10 percent at 100 MWe.

Total Efficiency Penalties

Including the electrical power to run the liquid pumps (injection and recirculation), the boiler efficiency penalties due to use of the SNCR system will vary with load and be on the order of 0.71 percent at 60 MWe and 0.44 percent at 100 MWe. At both loads, the dominant factor is the mixing air. Although, as the load is increased from 60 to 100 MWe, the vaporization losses associated with the increasing total liquid flow rate become more important.

8.5 Steam Temperature Control

With the retrofit burner system, slagging in the radiant furnace was reduced⁽²⁾. This resulted in some difficulties maintaining design steam temperatures, particularly during low load operation. To compensate for the reduced furnace exit gas temperatures, the operating excess air level has been increased at low loads. The use of the SNCR system can potentially further aggravate this problem. With the SNCR system, both the mixing air and the vaporization of the aqueous solutions will result in local cooling of the flue gas at the entrance to the convective section. If the unit is already operating with the steam attemperators closed, then steam temperature control may be compromised. Recall that for urea injection at boiler loads of 80 MWe and below the recommended total solution flow rate was 2 gpm (compared to 6 gpm at higher loads). This flow rate was chosen for two reasons. First, at reduced loads, the SNCR system is operating on the low side of the temperature window and additional cooling of the flue gas is undesirable. Second, operating with the minimum total solution flow rate had the minimum effect on steam temperatures. For reference, order of magnitude estimates of the local cooling effect of the mixing air and vaporization are summarized in Table 8-1.

Table 8-1

Approximate Local Gas Cooling Effects Due to SNCR Injection

Load (MWe)	Mixing Air Flow Rate (scfm)	Solution Flow Rate (gpm)	Local Gas Cooling		
			Mixing Air (°F)	Vaporization (°F)	Total Cooling (°F)
60	3900	2	40-45	8	48-53
100	3900	6	30-35	18	48-53

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and observations can be made regarding the performance of the SNCR system on the Arapahoe Unit 4 boiler with the retrofit low-NO_x combustion system.

Urea

- Optimum NO reduction performance occurred at a boiler load of 100 MWe. For a nominal N/NO ratio of 1.0, the NO removal was 48 percent with a NH₃ slip of 14 ppm.
- Boiler load was the parameter which was shown to have the largest effect on system performance, as it was the predominant factor in determining the local flue gas temperature at the injection location.
- Variations in total liquid flow and mixing air flow had small effects on both NO removal and NH₃ emissions over the range of flows tested (nominally 2.0 to 6.0 gpm and 2800 to 4800 scfm, respectively).

Converted Urea

- At a nominal N/NO ratio of 1.0, peak NO removals of 38 to 42 percent occurred over the boiler load range of 60 to 100 MWe. NH₃ emissions were at or below 5 ppm for loads of 80 to 100 MWe. At 60 MWe, NH₃ emissions increased to nominally 65 ppm.

Comparison of Urea and Converted Urea

- Although NO removals were found to be higher with urea than with converted urea for a fixed N/NO ratio over nearly the entire load range (70 to 113 MWe). NH₃ emissions were also found to be higher.

- On an equal ammonia slip basis, converted urea provides higher NO removals than urea. For a 10 ppm NH₃ emission limit, NO removals of 19 to 47 percent were achievable with converted urea over the load range of 60 to 100 MWe, while urea injection resulted in removals of 11 to 45 percent. However, the increased NO removals with converted urea required higher chemical injection rates (i.e., higher N/NO rates), and therefore, at boiler loads of 80 MWe and greater, urea was the most efficient chemical.
- N₂O emissions with converted urea were lower than those for urea. For converted urea, the fraction of NO converted to N₂O at a nominal N/NO ratio of 1.0 ranged from 3 to 8 percent, depending on boiler load. With urea, the conversion ranged from 29 to 35 percent.

Comparison of Pre- and Post-Retrofit SNCR Performance

- Peak NO removals for urea injection with the retrofit combustion system were similar to those seen with the original burners, but the boiler load at which the peak occurred increased from approximately 70 to 100 MWe. This shift was a result of the decrease in furnace exit gas temperature seen after the retrofit.
- On a normalized basis, the NH₃ emissions for urea injection with the retrofit combustion system were higher than those for the original burners, over the entire load range. This is also attributable to lower furnace exit temperatures.
- With urea injection, N₂O emissions, in terms of percent of the NO reduction converted to N₂O, were higher with the retrofit combustion system.

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APPENDIX

DATA SUMMARY

