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**SECOND GENERATION ADVANCED REBURNING
FOR HIGH EFFICIENCY NO_x CONTROL**

DOE/PC/95251--T5

Progress Report No. 4 for Period
July 1 - September 30, 1996

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1.0 Introduction

This project is designed to develop a family of novel NO_x control technologies, called Second Generation Advanced Reburning (SGAR), which has the potential to achieve 90+% NO_x control in coal fired boilers at a significantly lower cost than SCR.

Phase I consists of six tasks:

- Task 1.1 Project Coordination and Reporting/Deliverables
- Task 1.2 Kinetics of Na₂CO₃ Reactions with Flue Gas Components
- Task 1.3 0.1 x 10⁶ Btu/hr Optimization Studies
- Task 1.4 1.0 x 10⁶ Btu/hr Process Development Tests
- Task 1.5 Mechanism Development and Modeling
- Task 1.6 Design Methodology and Application

During the period (October 1, 1995 - June 30, 1996), the bench-scale facility, 0.1 MMBtu/hr Controlled Temperature Tower (CTT), was prepared for the experimental program and bench scale CTT experiments were conducted on different variants of the AR technology (Task 1.3). A C-H-O-N chemical mechanism for description of the process chemistry was selected, and interaction of ammonia with NO in the reburning and overfire air (OFA) zones was modelled (Task 1.5). The effect of various additives to promote NO-NH₃ interaction in the reburning zone was also evaluated by modeling. A high-temperature flow system with GC analysis was prepared at the University of Texas at Austin for the experimental evaluation of sodium carbonate kinetics (Task 1.2).

The fourth reporting period (July 1 - September 30, 1996) included both experimental and modeling activities. The bench scale CTT experiments (Task 1.3) were completed. The 1 MMBtu/hr Boiler Simulator Facility (BSF) was prepared for the test program and experiments were conducted using natural gas (NG) as main and reburning fuels (Task 1.4). A few preliminary tests were also performed with coal firing. The results have been reduced and are reported below. Initial experimental data were obtained on reactions of sodium promoters (Task 1.2) at the University of

Texas in Austin (UT). The kinetic model was extended to include reactions of sulfur and sodium (Task 1.5).

As in previous quarterly reports, Figure 1.1 summarizes the nomenclature for the various regions of the Second Generation Advanced Reburning (SGAR) process.

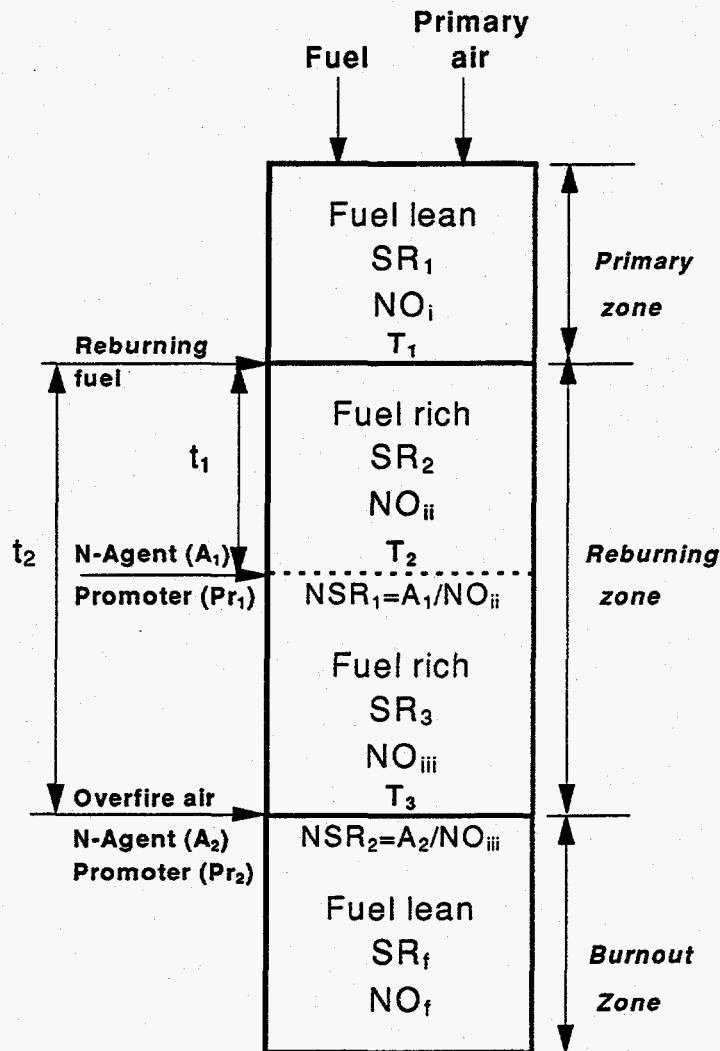


Figure 1.1 SGAR schematic - definitions.

The region upstream of the reburning fuel injection is referred to as the "primary zone". The primary zone Stoichiometric Ratio (SR_1) is maintained at $SR_1=1.1$ for all tests and the initial NO concentration in this zone is referred to by a single subscript "i". The region between the reburning fuel and overfire air (OFA) injection is referred to as the "reburning zone". The reburning fuel is injected at a temperature of T_1 . The first N-agent (A_1) is introduced into the reburn zone at T_2 with a Nitrogen Stoichiometric molar Ratio $NSR_1=A_1/NO_i$. This zone is divided into two fuel rich zones with stoichiometries SR_2 and SR_3 . NO concentration upstream of the first N-agent injection is referred to as "ii". NO reduction from NO_i to NO_{ii} is caused by reburning only. The first N-agent is injected with or without promoters (Pr_1) with a t_1 delay time after RF injection. NO concentration downstream of the A_1 injection is called NO_{iii} , and NO reduction from NO_{ii} to NO_{iii} is caused by the first N-agent. Overfire air is injected at T_3 with a t_2 delay time after RF injection. OFA is a carrier gas for injecting the second N-agent (A_2) which is injected with or without promoters (Pr_2). A_2 is injected with $NSR_2=A_2/NO_{iii}$. The downstream region is referred to as the "burnout zone". Stoichiometric ratio in this zone is SR_4 , and the final NO concentration is NO_f .

2.0 Bench Scale Combustion Tests

Most of the bench scale tests have been completed and reported previously (Zamansky and Maly, 1996). This section describes test results on injection of nitrogen agents in the reburning zone with small amounts of oxygen. The experiments were performed in the 0.1 MMBtu/hr Controlled Temperature Tower (CTT).

Kinetic modeling suggests (Zamansky and Maly, 1996; Zamansky, 1996) that small amounts of oxygen in the reburning zone can improve the NH_3 -NO interaction in the reburn zone and, consequently, the reburning efficiency. Modeling was conducted under ideal conditions with instantaneous and perfect mixing of the reagents. In combustion tests, however, mixing conditions play an important role and define local oxygen concentration. If oxygen is injected in the reburning zone, the local O_2 concentration will vary significantly from rather high level near the injection point to about zero in the remote regions. Therefore, it is necessary to optimize oxygen injection to approach the NO_x control predicted by modeling.

Several tests have been conducted on oxygen injection in the reburning zone under different conditions. In these tests, NG was fired in the main combustion zone and was also injected as the reburning fuel at 2500 F. Ammonia was added to the main portion of NG to provide an initial NO concentration of 600 ppm in all tests. The amount of reburning fuel was 10% of total heat input, which corresponds to a stoichiometry in the reburning zone of $SR_2=0.99$. Gaseous or aqueous ammonia was then injected into the reburning zone at $T = 1875$ F with $NSR_1 = 1.5$ followed by OFA injection at 1700 F. The ammonia was dispersed by nitrogen and different amounts of air were added to the atomization medium to provide oxygen concentrations in the reburning zone in the range of 0 - 5000 ppm. Reburning alone resulted in about 52% NO removal, injection of aqueous or gaseous ammonia caused about 66% NO reduction. Addition of sodium carbonate to the solution (30 ppm Na in flue gas) reduced NO by about 82%, which is consistent with previous measurements.

In the first test series, the oxygen concentration was varied. Injection of air along with aqueous or gaseous ammonia increased the remaining NO concentration at $[O_2]>200$ ppm, as shown in Figure 2.1. However, if gaseous ammonia and water were both injected at 1875 F and in the same amounts as in the tests with the solution, but through different nozzles, much higher NO reduction was observed, Figure 2.1. Moreover, an optimum O_2 concentration (about 200 ppm) exists which provides maximum NO reduction. This concentration is about the same as was found by modeling (see Figure 4.1.1 in the previous report, Zamansky and Maly, 1996). Mixing and thermal conditions are most likely responsible for the effect of water.

In the second test series, gaseous ammonia and water were injected through different nozzles at 1875 F, but the water flow rate was varied. It was found that the water flow rate has significant effect on reburning, Figure 2.2, curve 1. The water decreases temperature in the reburning zone while maintaining the same residence time between injections of the reburning fuel and OFA. This is consistent with modeling data. Modeling demonstrated (see Figure 2.1.7 in the previous report, Zamansky and Maly, 1996) that at $SR_2=0.99$ and constant residence time, lower reburn fuel injection temperature provides higher NO reduction. Injection of air along with ammonia caused almost no change in the reduction of NO, Figure 2.2, curve 2. However, downstream air injection at 1750 F through an injector aligned upwards (0.2 s after ammonia) caused a significant improvement of NO

Air added to atomization medium to provide oxygen in the reburn zone
 Main Fuel: Natural gas @ 70,000 Btu/hr
 10% Reburn @ 2500 F
 OFA @ 1700 F, Additive @ 1875 F
 SR1=1.10, SR3=1.15, N/NOi=1.5
 SR2 varies from 0.99 at 0 ppm oxygen to 1.02 at 5000 ppm oxygen

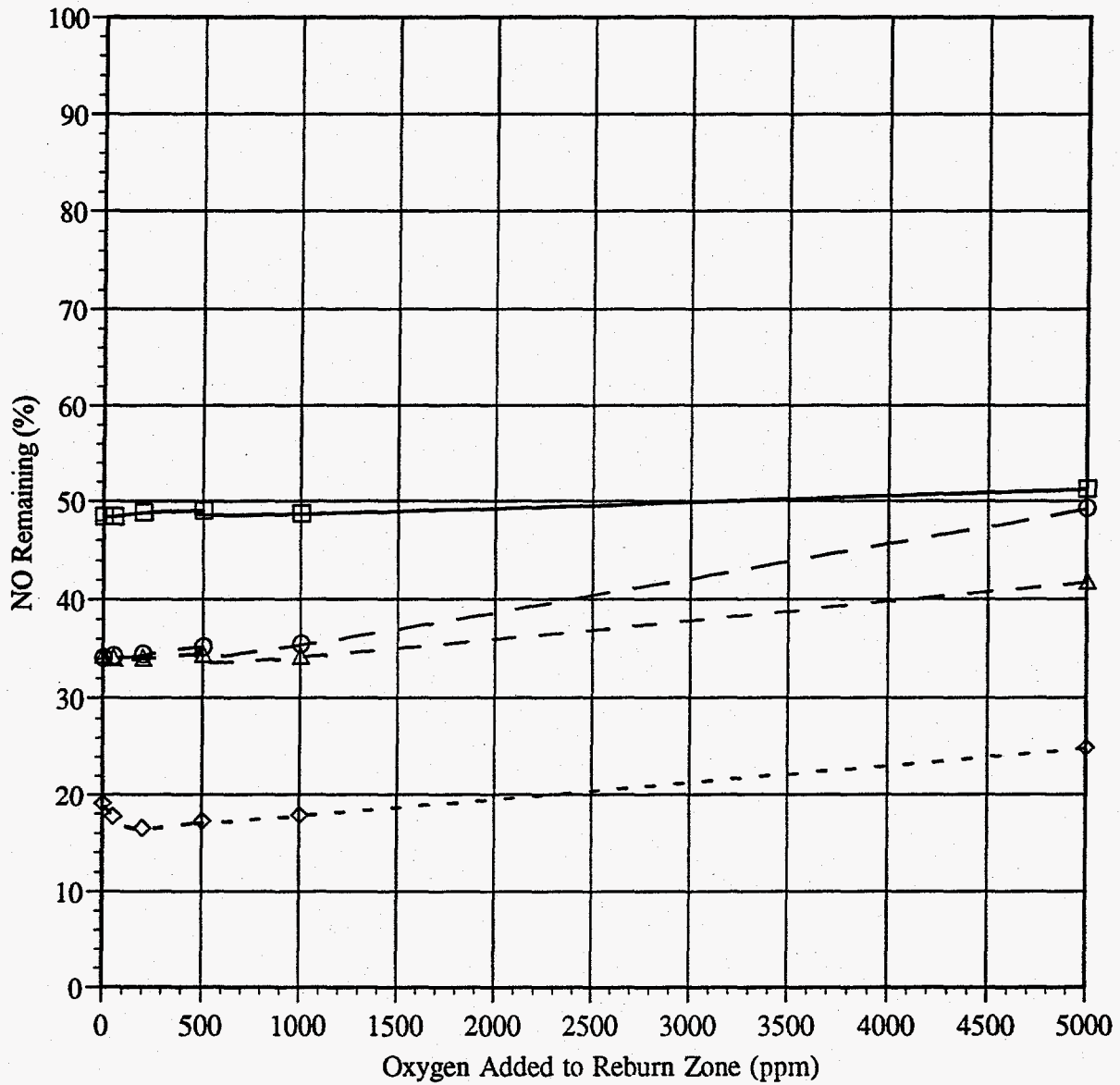
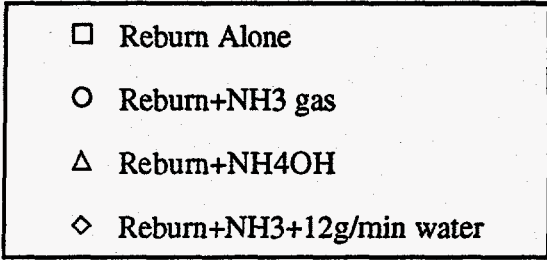


Figure 2.1. Effect of ammonia, Na_2CO_3 , and oxygen injection in the reburning zone on NO reduction.

No sodium promoter
 Main Fuel: Nat. gas @ 70,000 Btu/hr
 10% Reburn @ 2500 F, N₂ transport
 OFA @ 1700 F, Additive @ 1875 F
 SR₁=1.10, SR₂=0.99, SR₃=1.15
 NO_i=600 ppm as meas, N/NO_{ii}=1.5

Curve 2: Air added to atomization medium
 to provide oxygen in reburn zone
 Curve 3: Air added through injector aligned
 upwards @ 1750F. Res. time between
 NH₃ and O₂ injection=0.2 sec

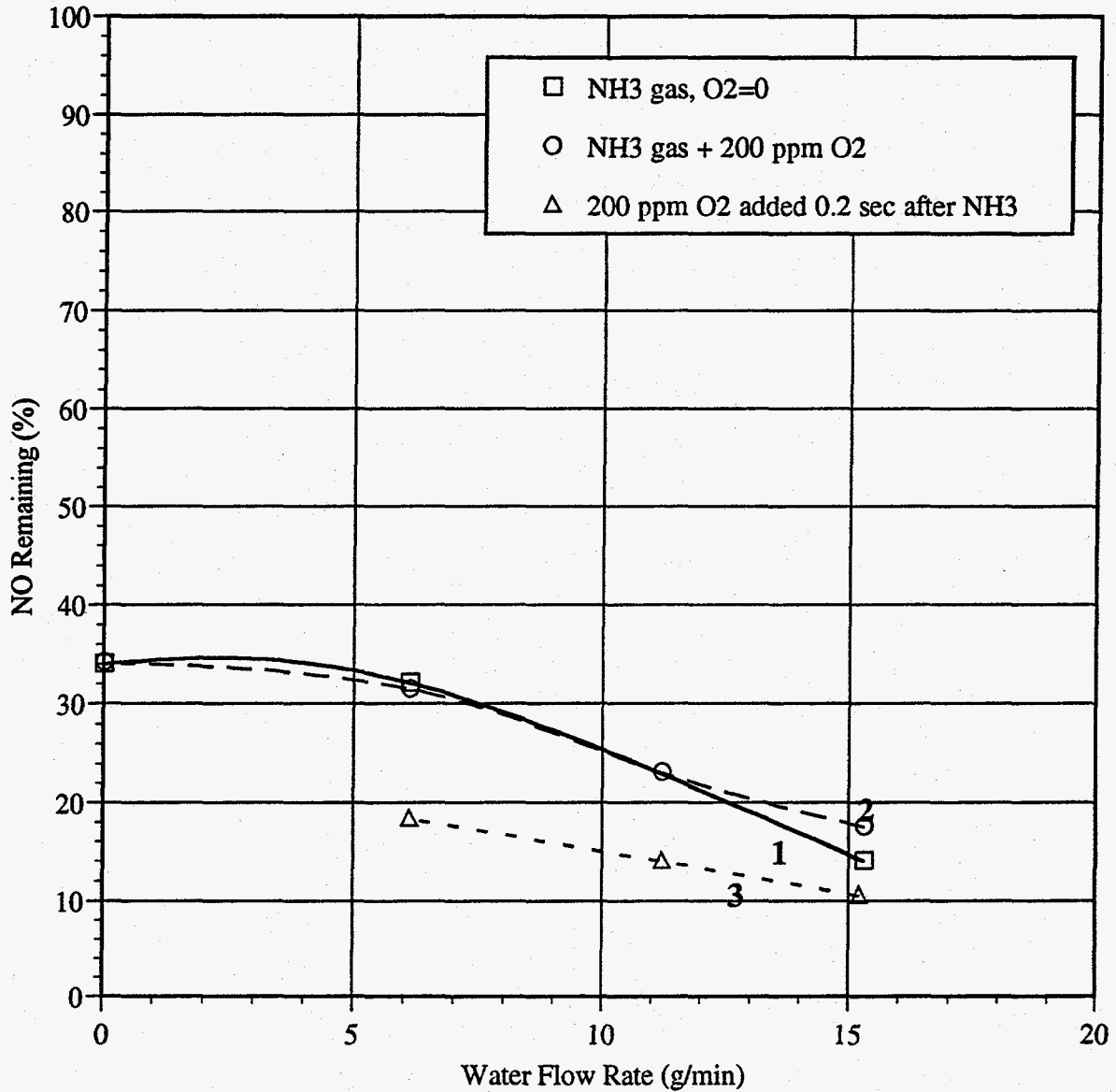


Figure 2.2. Effect of water flow rate in the reburning zone on NO reduction.

Air added to atomization medium to
provide oxygen in reburn zone
Solution flow rate=15 g/min
Main Fuel: Nat. gas @ 70,000 Btu/hr
10% Reburn @ 2500 F, N2 transport
OFA @ 1700 F, Additive @ 1875 F
SR1=1.10, SR2=0.99, SR3=1.15
NOi=600 ppm as meas, N/NOii=1.5
200 ppm O2 added to reburn zone

□ Reburn+Gaseous NH3+Na2CO3

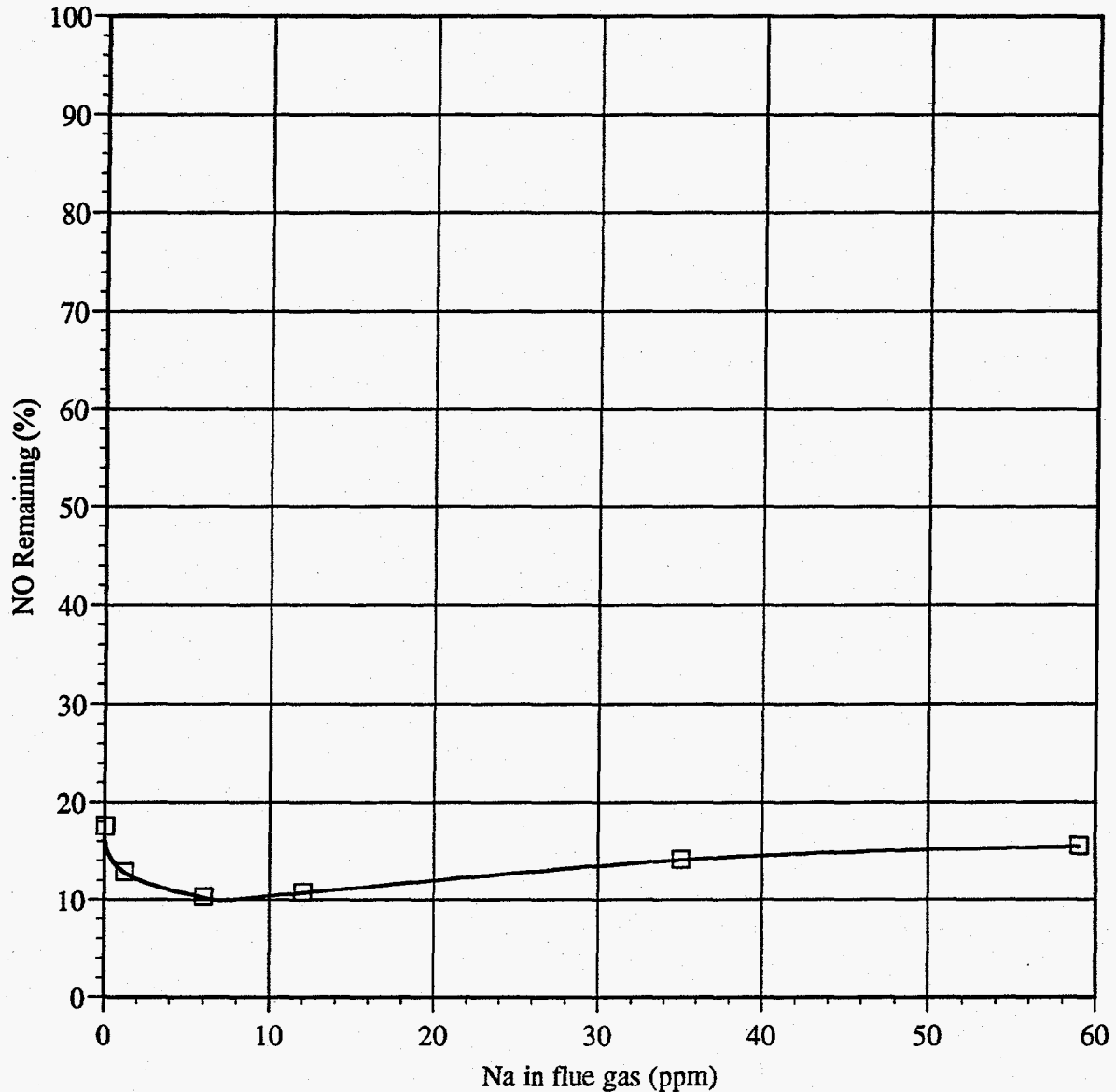


Figure 2.3. Effect of Na concentration in the presence of oxygen in the reburning zone on NO reduction.

reduction, Figure 2.2, curve 3. Thus, both water and oxygen, as well as the time of O₂ injection in the gas mixture, significantly affect reburning performance.

In the final test series, water and gaseous ammonia were again injected, but different amounts of sodium carbonate were dissolved in the water. The results are presented in Figure 2.3. An optimum was obtained with respect to sodium concentration. In all past tests performance always increased or was constant with increasing sodium level. In the presence of oxygen, NO reduction of 90% was achieved at only 6 ppm Na, corresponding to only 3 ppm Na₂CO₃.

In summary, the CTT results define the importance of promotion mechanisms on reburning performance. The following factors affect NO reduction in the reburning zone:

1. Water flow rate.
2. The amount and injection time of oxygen.
3. The presence of promoters. An optimum promoter concentration exists.
4. Mixing and thermal conditions.

These factors need to be investigated in future testing and modeling activities.

3.0 Preparation of the Pilot Scale Combustion Facility

The pilot scale test work was conducted in EER's 1.0 MMBtu/hr Boiler Simulation Facility (BSF). The BSF is designed to provide an accurate subscale simulation of the flue gas temperatures and composition found in a full scale boiler. Prior to the tests the BSF was configured to provide access for all required reburn, additive, and overfire air injectors.

3.1 Boiler Simulation Facility

A schematic of the BSF is shown in Figure 3.1. The furnace is designed with a high degree of flexibility to produce various combustion conditions typical of a full scale utility boiler. The BSF consists of a burner, vertically down-fired radiant furnace, and horizontal convective pass. A variable swirl diffusion burner with an axial fuel injector is used to simulate the approximate temperature and gas composition of a commercial burner in a full scale boiler. Primary air is injected axially, while the secondary air stream is injected radially through the swirl vanes to provide controlled fuel/air mixing. The swirl number can be controlled by adjusting the angle of the swirl vanes. Numerous ports located along the axis of the facility allow supplementary equipment such as reburn injectors, additive injectors, overfire air injectors, and sampling probes to be placed in the furnace.

The cylindrical furnace section is constructed of eight modular refractory-lined sections with an inside diameter of 22 inches. The convective pass is also refractory lined, and contains air cooled tube bundles to simulate the superheater and reheater sections of a full scale utility boiler. Heat extraction in the radiant furnace and convective pass was controlled such that the residence time-temperature profile matched that of a typical full scale boiler. A suction pyrometer was used to measure furnace temperatures. Figure 3.2 shows the BSF temperature profile during natural gas firing. Furnace temperatures are similar during coal firing.

Test fuels included natural gas and pulverized coal. Municipal natural gas was used, and was delivered by means of line pressure. The test coal employed was a low sulfur bituminous Utah coal. It was pulverized such that 70% passed through a 200 mesh screen. Coal was metered using a twin

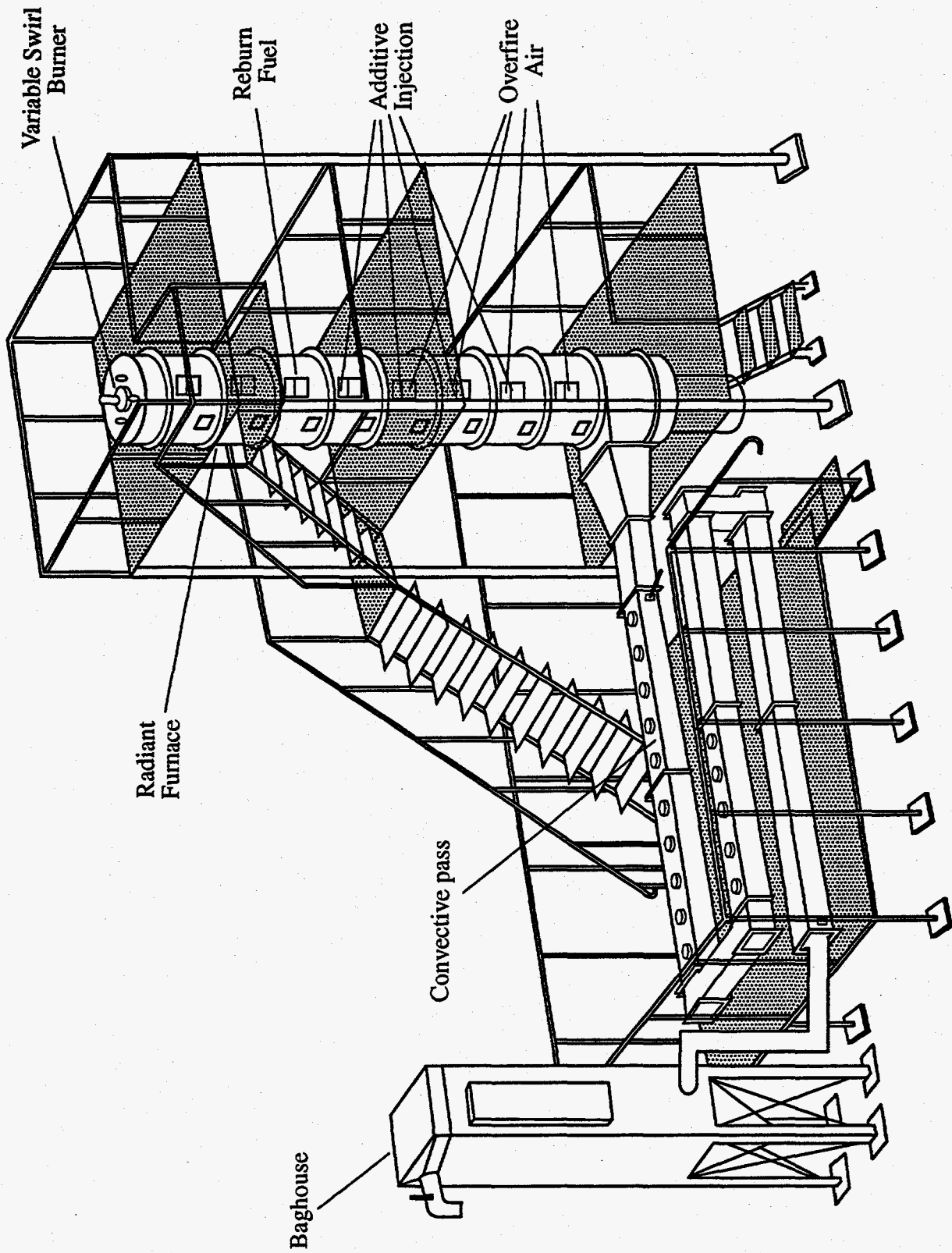


Figure 3.1. Boiler Simulator Facility (BSF)

Main Fuel: Natural gas
Firing rate: 0.71 MMBtu/hr
SR1=1.1
10% Reburning

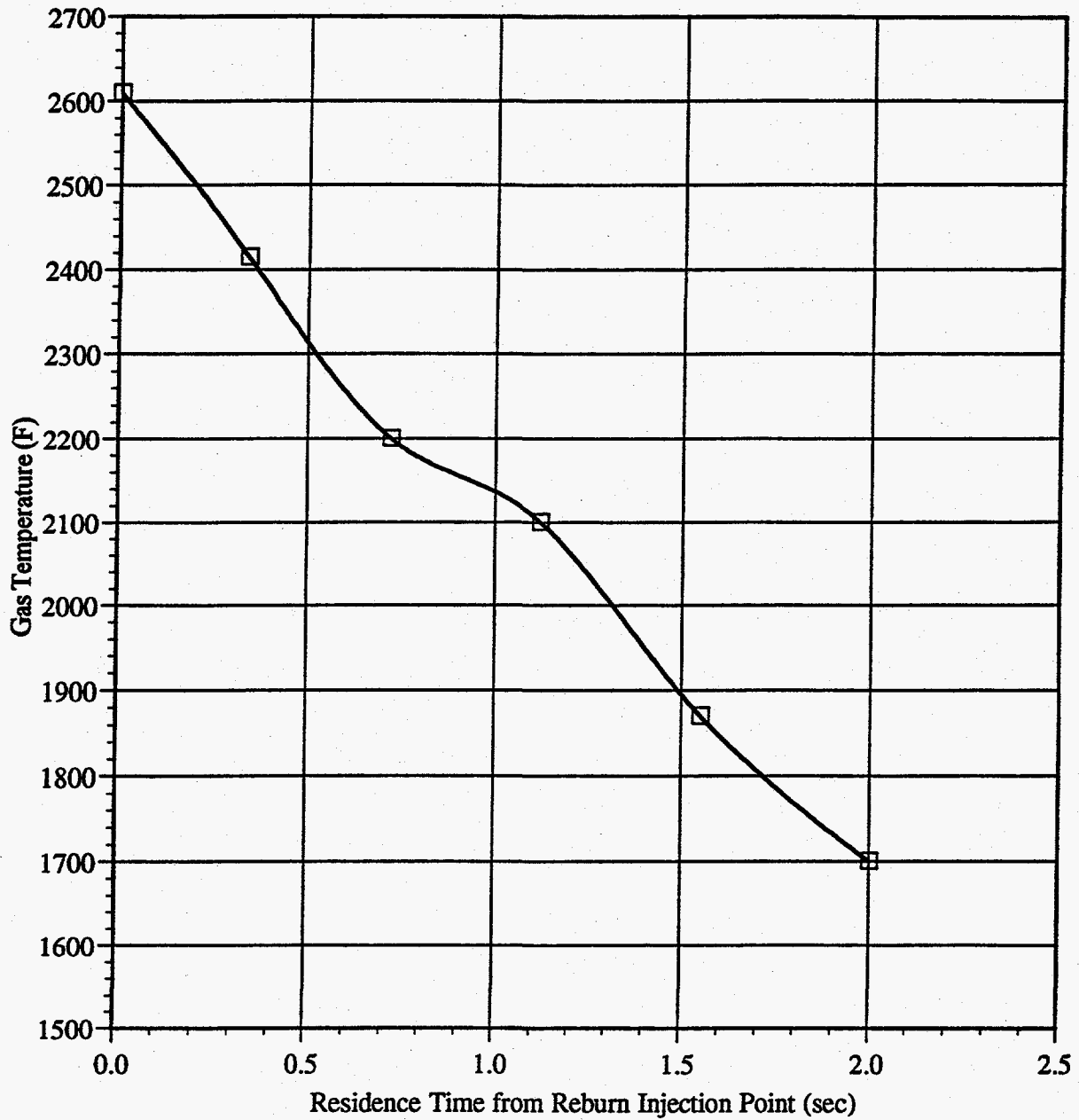


Figure 3.2. BSF Temperature Profile

screw feeder and was pneumatically transported to the burner.

3.2 Reburning and Additive Injection Systems

Natural gas was used as the reburn fuel. The reburn injector was elbow-shaped, and was installed along the centerline of the furnace, aligned in the direction of gas flow. A gaseous transport medium was added along with the reburn natural gas to provide sufficient momentum for good mixing with the furnace gas. Both air and bottled nitrogen were tested as transport media. Overfire air was injected through an elbow-shaped injector to burn out combustibles generated in the reburn zone. The overfire air injection temperature was varied as required by the test plan.

Nitrogen agents and sodium promoters were injected as aqueous solutions. Twin fluid atomizers made by Delavan Corp. were used, employing both air and nitrogen as transport media. The additives were injected into the reburn zone and/or with the overfire air. In the latter case, the overfire air itself was used as the atomization medium.

3.3 Sampling and Analysis Methods

A continuous emissions monitoring system (CEMS) was used for on-line flue gas analysis. CEMS components included a water cooled sample probe, sample conditioning system (to remove water and particulate), and gas analyzers. High purity dry nitrogen was used to zero each analyzer before and after each test. Certified span gases were used to calibrate and check linearity of the analyzers. Test data was recorded on both a chart recorder and a personal computer based data acquisition system. Species analyzed, detection technique, and precision were as follows:

- O₂: paramagnetism, 0.1% precision
- NO_x: chemiluminescence, 1 ppm precision
- CO: nondispersive infrared spectroscopy, 1 ppm precision
- CO₂: nondispersive infrared spectroscopy, 0.1% precision
- SO₂: nondispersive ultraviolet spectroscopy, 1 ppm precision
- N₂O: nondispersive infrared spectroscopy, 1 ppm precision

4.0 Pilot Scale Combustion Tests with Natural Gas Firing

In the initial pilot scale tests, NG was used as the main and reburning fuel. The initial NO concentration, 600 ppm, was established by addition of ammonia to primary natural gas. The reburning fuel (10%) provided slightly fuel-rich conditions in the reburn zone with $SR_2=0.99$.

4.1 Advanced Reburning - Lean

AR-Lean includes the injection of reburning fuel and then injection of OFA along with an N-agent. The N-agent can be injected with or without promoter which is dissolved in the aqueous N-agent solution. In all tests, the amount of N-agent corresponded to $NSR_2=1.5$.

Figures 4.1.1 and 4.1.2 demonstrate the performance of the AR-Lean process for injection of aqueous urea and ammonia, respectively. Reburning alone resulted in about 50% NO reduction. The process depends slightly on the OFA injection location. At OFA injection temperatures of about 1600 and 2300 F, NO was reduced by 52 and 47%, respectively, corresponding to 48 and 53% NO remaining. Results are shown in Figures 4.1.1 and 4.1.2. Injection of urea with OFA provided 53-82% NO reduction depending on the injection temperature. The performance of ammonia was lower, 45-81%. At an injection location of 1930 F, urea gave 78% NO reduction, while ammonia only 70%. The results with ammonia injection are qualitatively consistent with modeling (see Figure 4.2.1 in Zamansky and Maly, 1996) taking into account the fact that ammonia appears in the gas mixture with a short delay time that is necessary for evaporation of the solution. Addition of sodium carbonate to the N-agent greatly improved NO reduction. Performance was about equal for ammonia and urea, in the range of 54-94% with maximum of 89-94% for N-agent/sodium injection between 1700 and 2000 F. These data are in agreement with the previous CTT results, though a higher NO reduction (by about 2-5 percentage points) was observed in BSF. As in CTT tests, there is almost no difference in NO emissions between injection of 30 and 50 ppm Na.

Nat. Gas Main Fuel @ 705,000 Btu/hr
 10% Nat. Gas Reburning, N2 transport.
 Advanced Reburning, Urea injected w/ OFA,
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 Urea and Na2CO3 premixed, N2 atomization.

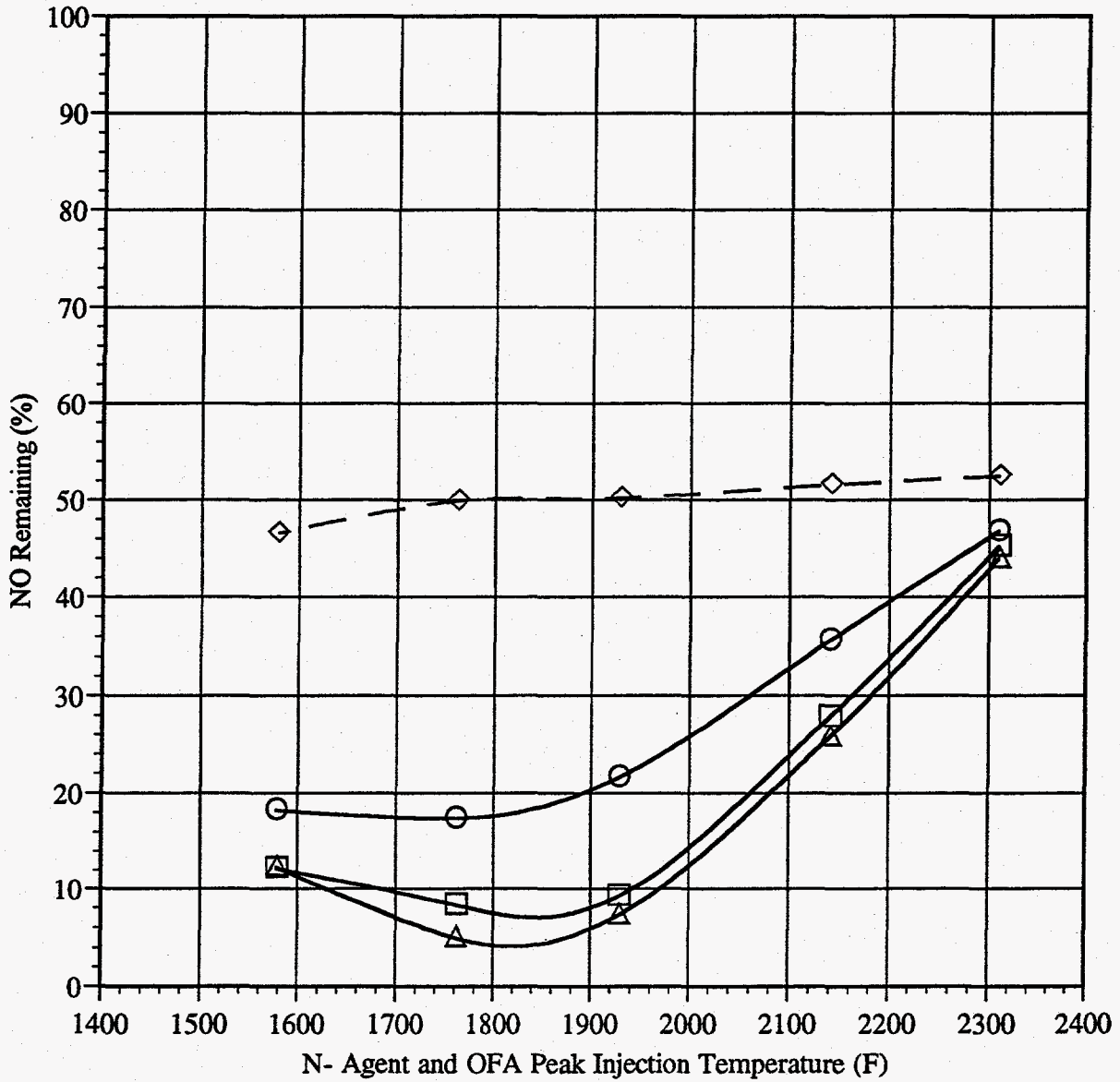
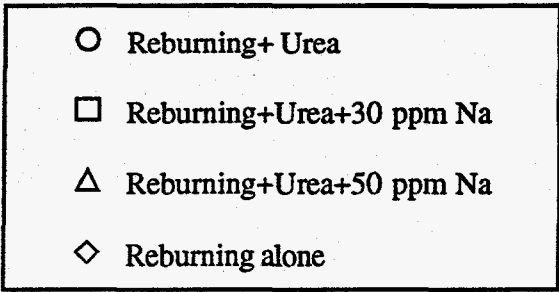


Figure 4.1.1. AR-Lean with aqueous urea/sodium injection.

Nat. Gas Main Fuel @ 705,000 Btu/hr
 10% Nat. Gas Reburning, N2 transport.
 Advanced Reburn, NH4OH injected w/ OFA,
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 NH4OH & Na2CO3 premixed, N2 atomization.

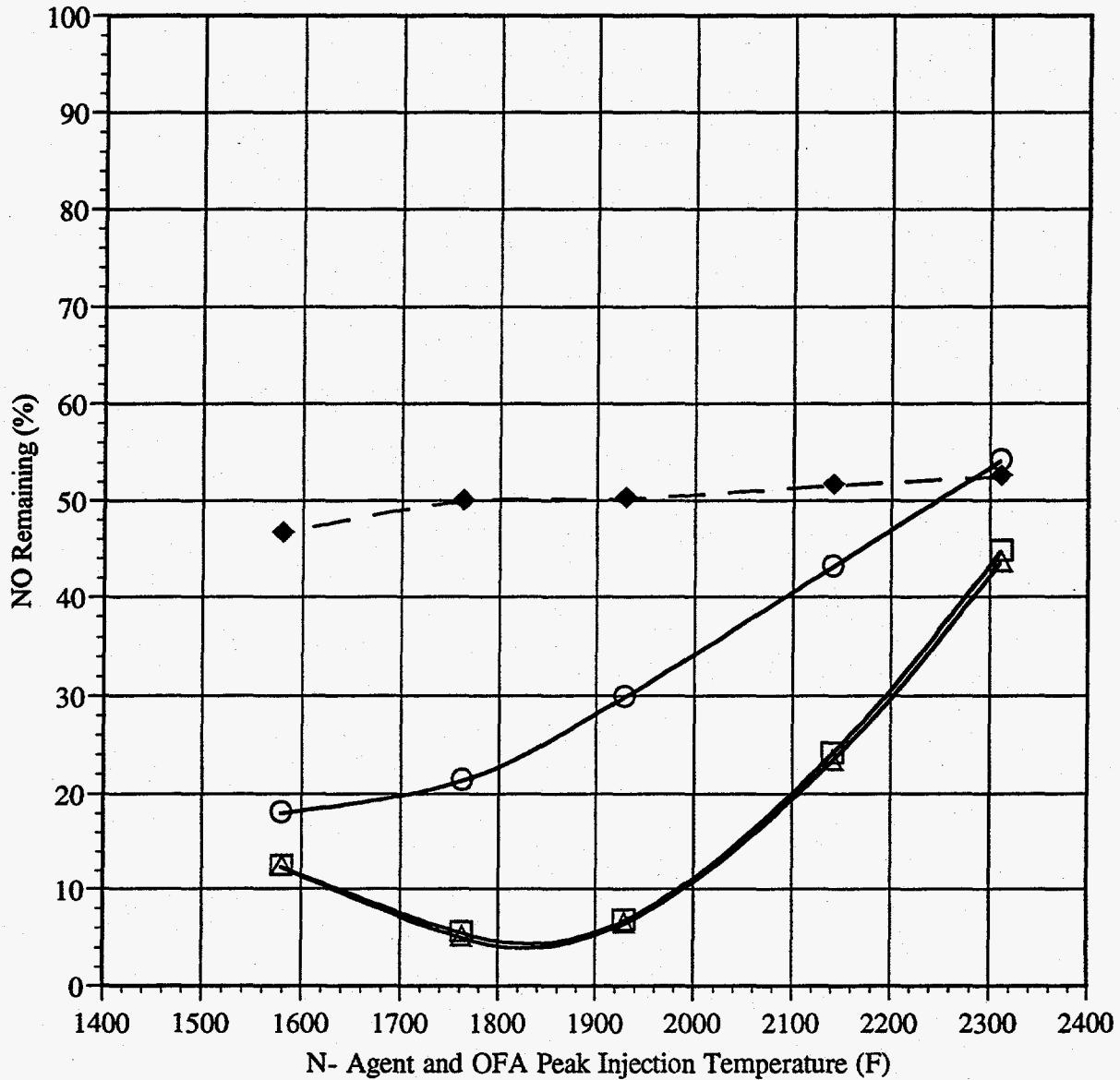
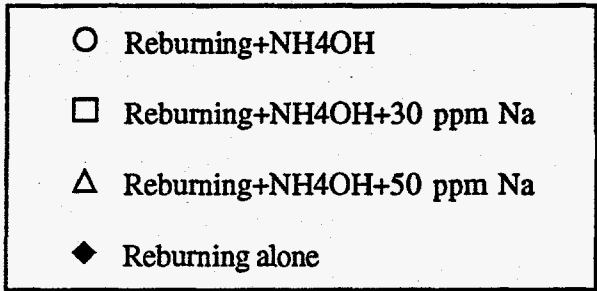


Figure 4.1.2. AR-Lean with aqueous ammonia/sodium injection.

Interestingly, the presence of small sodium amounts (30-50 ppm) affected CO emissions at low OFA injection temperatures. Without sodium, CO emissions were within 10-60 ppm if OFA/N-agent were injected at T=1760 F and 100-120 ppm at T=1580 F. In the presence of sodium, CO emissions were 60-100 ppm at 1760 F, and 120-320 ppm at T=1580 F. At OFA injection temperatures higher than 1760 F, the CO emissions were about 10-25 ppm even in the presence of sodium. Thus, the optimum OFA/N-agent injection temperature is about 1800-2000 F. At these temperatures, NO can be reduced by about 89-94% without increasing CO emissions.

4.2 Advanced Reburning - Rich

The AR-Rich process includes injection of a reburning fuel, injection of an N-agent in the reburning zone, and injection of OFA. The N-agent can be injected with or without promoter which is, as in AR-Lean, dissolved in an aqueous solution of the N-agent. In all tests, the amount of N-agent corresponded to $NSR_1=1.5$.

The performance of AR-Rich greatly depends on OFA injection temperature. Figures 4.2.1 and 4.2.2 show experimental results with injection of urea and ammonia, respectively, for OFA injection at 1660 F. Similar NO reduction was obtained for these two reagents. Each reagent provided about 70-77% NO reduction depending on temperature. However, addition of sodium carbonate at 30-50 ppm Na significantly improved NO reduction, up to 94-95%, or 5-6% NO remaining, as shown in Figures 4.2.1 and 4.2.2. Again, the reduction of NO in BSF was a few percentage points better than that in CTT.

Surprisingly, injection of 30-50 ppm sodium resulted in much higher CO emissions (at low OFA injection temperatures) than in the AR-Lean process. Without sodium, CO emissions were within 10-25 ppm, but injection of sodium caused greater than 2500 ppm CO emissions. This effect (higher CO emissions after injection of sodium under fuel rich conditions) was noticed earlier in the CTT tests, but measurement accuracy was considered to be questionable. In the BSF tests, CO measurements were carefully checked and repeated. High CO emissions show that in the presence of sodium the process of CO oxidation is inhibited. The inhibition effect is stronger under fuel rich

Nat. Gas Main Fuel @ 705,000 Btu/hr
 10% Nat. Gas Reburning, N2 transport.
 Advanced Reburn, Urea injected in reburn zone
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 Urea & Na2CO3 premixed, N2 atomization.

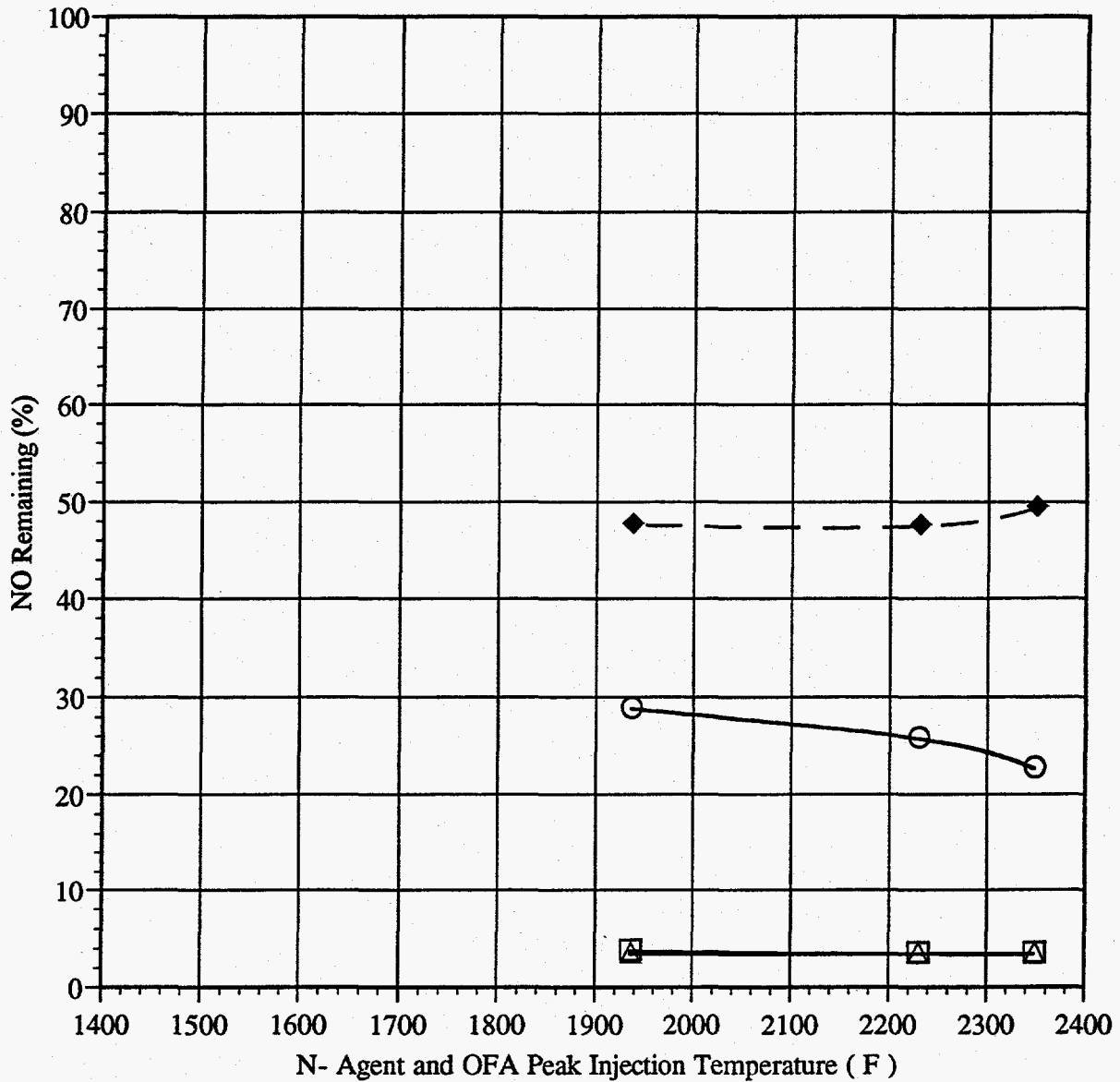
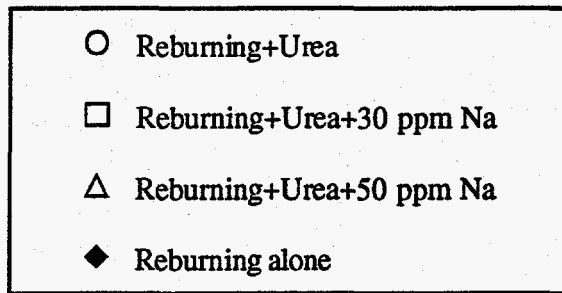


Figure 4.2.1 AR-Rich with urea/sodium injection. OFA is injected at 1660 F.

Nat. Gas Main Fuel @ 705,000 Btu/hr
 10% Nat. Gas Reburning, N₂ transport.
 Advanced Reburn, NH₄OH injected in reburn zone
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 NH₄OH & Na₂CO₃ premixed, N₂ atomization.

- Reburning+ NH₄OH
- Reburning+NH₄OH+30 ppm Na
- △ Reburning+NH₄OH+50 ppm Na
- Reburning alone

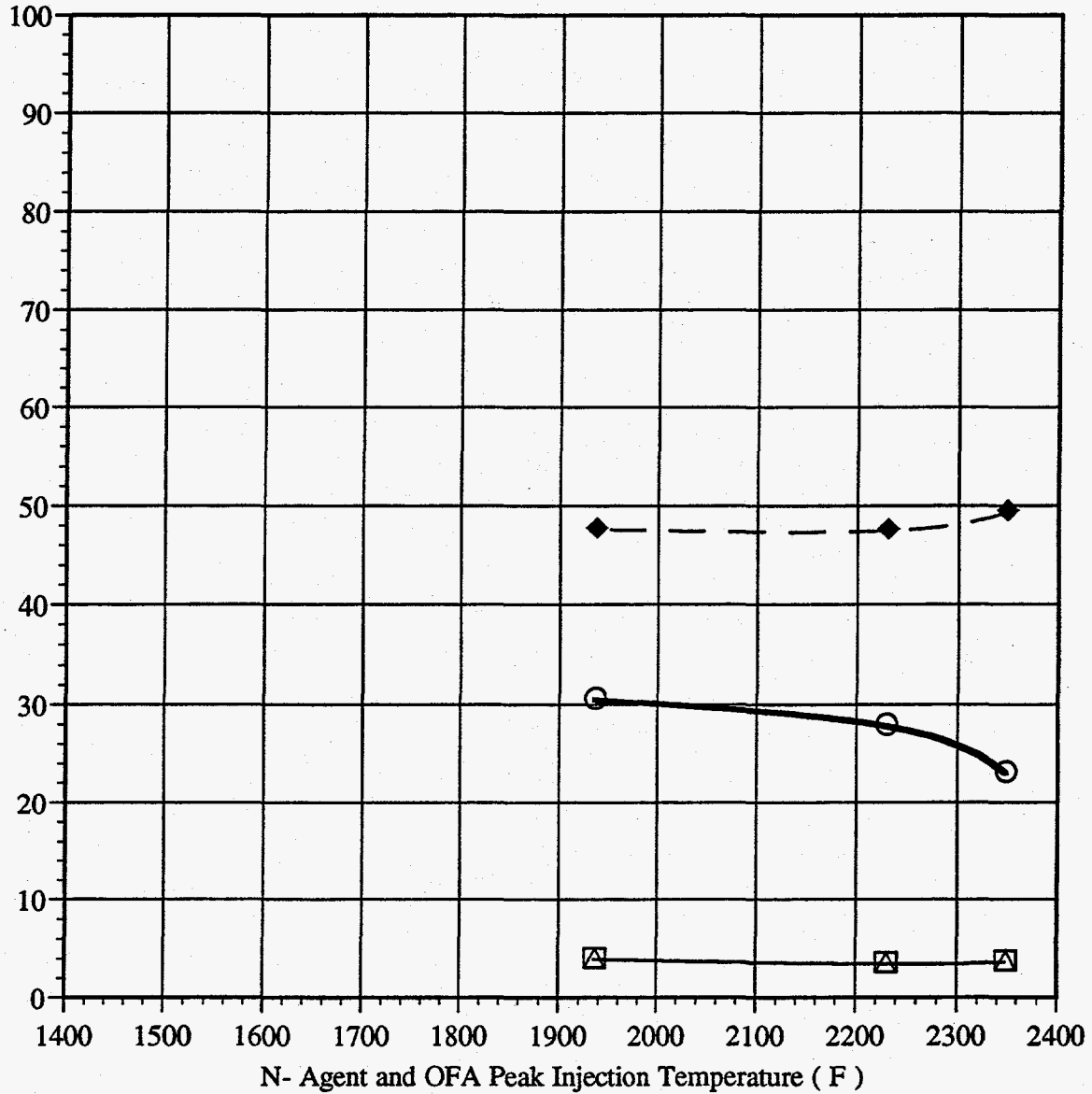
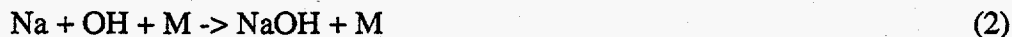
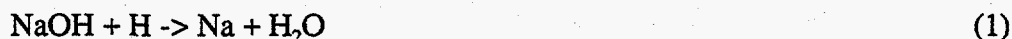


Figure 4.2.2 AR-Rich with ammonia/sodium injection. OFA is injected at 1660 F.

conditions. A possible explanation of this effect is the existence of the chain reaction involving sodium compounds, H atoms and OH radicals:



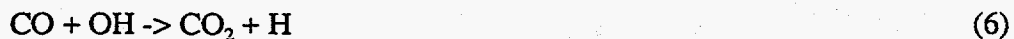
Sodium hydroxide, NaOH, can be formed via thermal decomposition of sodium carbonate followed by the reaction of sodium oxide with water vapor that is available in flue gas:



Then, NaOH reacts with H atoms via reaction (1) to form Na atoms and H₂O molecules. The Na atoms can then recombine with OH radicals to return NaOH (2). The total reaction (1)+(2) is just H and OH recombination into water:



Thus, under certain conditions, the total amount of H and OH radicals can be reduced, due to the presence of sodium compounds. As a result, CO can escape oxidation, since the main reaction of CO oxidation is the interaction with hydroxyl radicals:



Under fuel rich conditions, the total amount of radicals is typically lower than under fuel lean conditions. Therefore, this mechanism of radicals suppression can be more important under fuel rich conditions. The experimental effort at the University of Texas is being conducted to model and better understand the reactions of Na in flue gas. A preliminary reaction mechanism with Na reactions was selected and is presented in Section 6.0.

Similar to AR-Lean, a temperature increase of OFA injection can decrease the CO emissions in the presence of sodium. AR-Rich tests were conducted with two higher temperatures of OFA injection, 2030 and 2250 F. Figures 4.2.3 and 4.2.4 present the results. Injection of 20 g/min water in the reburning zone did not change NO reduction. When urea was added, about 60-70% NO reduction was achieved. Sodium promoted the reaction up to 80-90% NO reduction, 10-20% NO remaining.

It is also of interest to evaluate CO and N₂O emissions. Figure 4.2.5 shows emissions of CO and N₂O versus urea/sodium injection temperature at different OFA injection temperatures. Injection of urea or urea/sodium at 2230-2520 F followed by OFA at 2250 F did not cause any increase in CO and N₂O concentrations. If OFA is injected at 2030 F, urea again did not increase the CO and N₂O level, but, in the presence of sodium, the CO and N₂O concentrations were increased from 25 to 160 ppm and from 5 to 21 ppm, respectively.

Finally, Figure 4.2.6 demonstrates the effectiveness of sodium on NO reduction for AR-Rich. In these tests, urea/sodium were injected at 2280 F and OFA at 1920 F. An increase in Na concentration from 0 to 55 ppm resulted in improvement of NO reduction from 76 to 90%. However, the CO emissions increased from 20 ppm at Na=0 to 65 ppm at Na=22 ppm and to 500 ppm at Na=55 ppm. Thus, injection of sodium with a N-agent in the reburn zone requires a temperature of OFA injection higher than 2030 F to prevent CO formation. This result demonstrates the importance of sodium chemistry in NO control via reburning.

Main Fuel: Nat. gas @ 705,000 Btu/hr
 10% Reburn @ 2620 F, N2 transport
 SR1 = 1.10, SR2 = 0.99, SR3 = 1.15
 NOi = 600 ppm as measured
 OFA Temperature = 2030 F
 Na2CO3 Concentration = 15 ppm
 N/NOii = 1.5

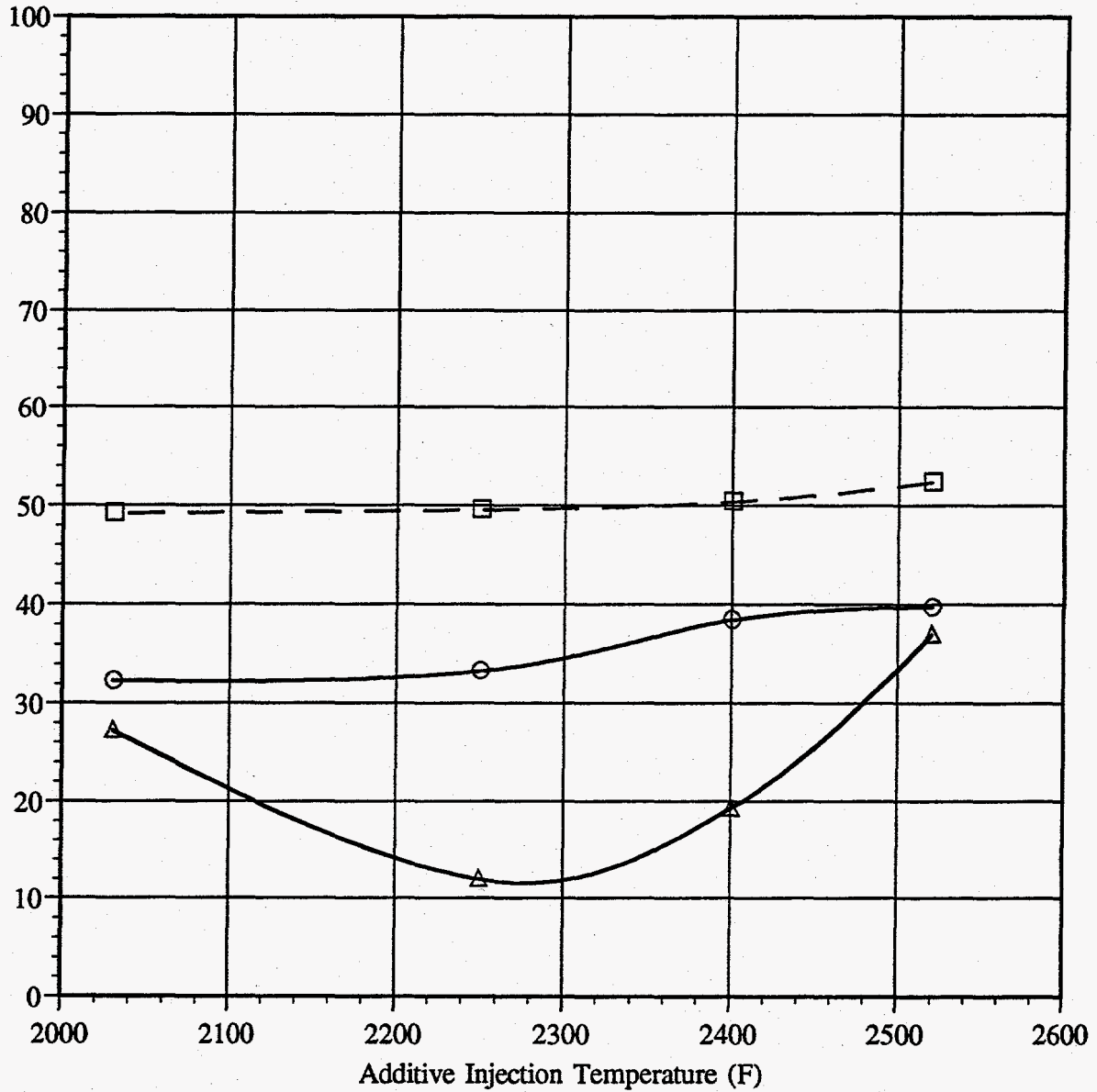
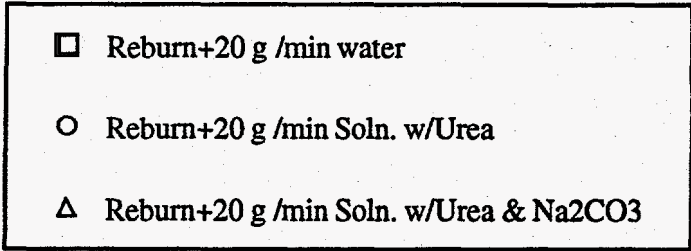


Figure 4.2.3. AR-Rich with urea/sodium injection. OFA is injected at 2030 F

Main Fuel: Nat. gas @ 705,000 Btu/hr
 10% Reburn @ 2620 F, N₂ transport
 SR1 = 1.10, SR2 = 0.99, SR3 = 1.15
 NO_i = 600 ppm as measured
 OFA Temperature = 2030 F
 Na₂CO₃ Concentration = 15 ppm
 N/NO_{ii} = 1.5
 CO below 20 ppm for all tests

- Reburn+20 g /min water
- Reburn+20 g /min Soln. w/Urea
- △ Reburn+20 g /min Soln. w/Urea & Na₂CO₃

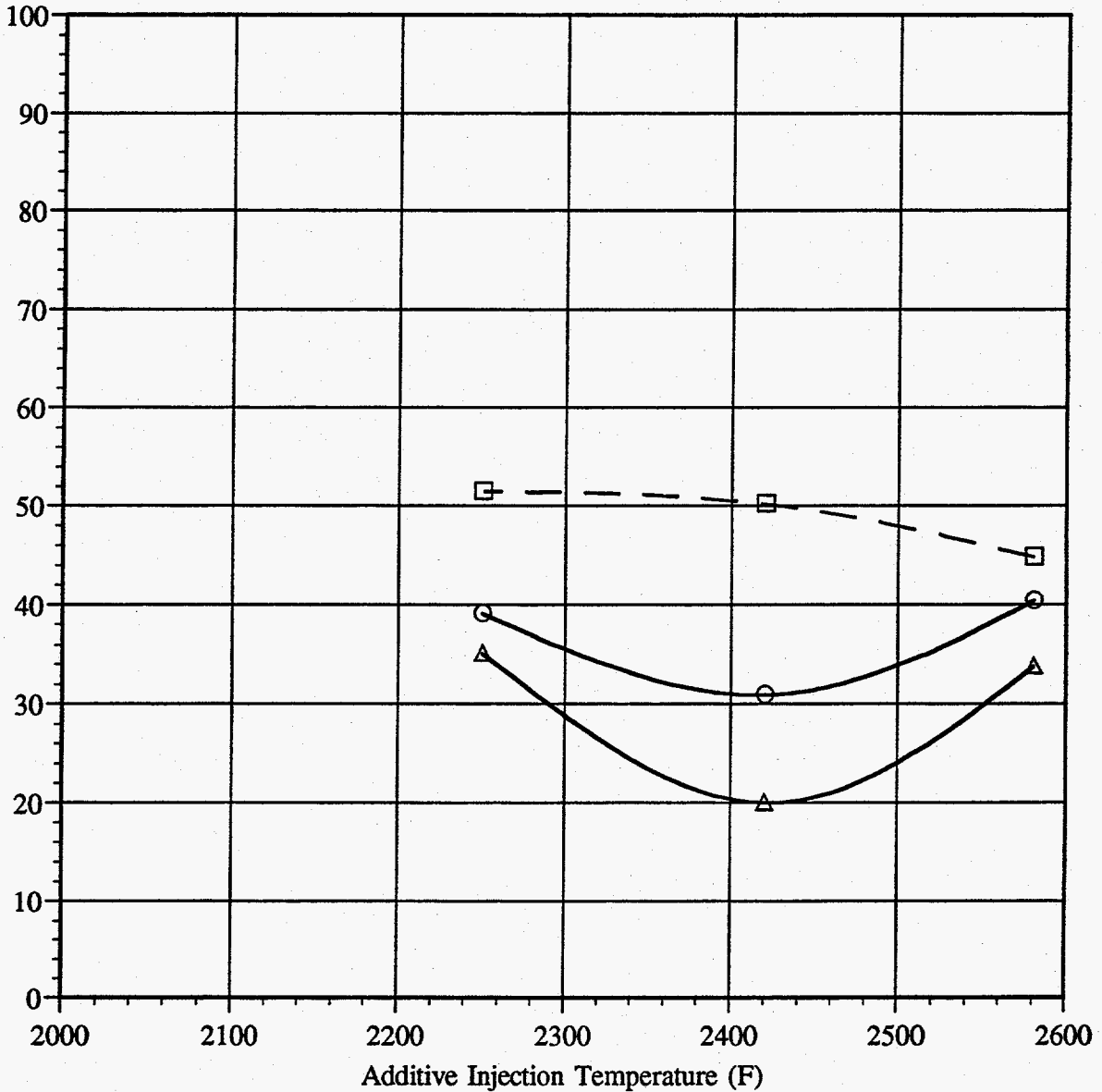


Figure 4.2.4. AR-Rich with urea/sodium injection. OFA is injected at 2250 F.

Main Fuel: Nat. gas @ 705,000 Btu/hr
 10% Reburn @ 2620 F, N2 transport
 SR1 = 1.10, SR2 = 0.99, SR3 = 1.15
 NOi = 600 ppm as measured
 Na2CO3 Concentration = 15 ppm
 N/NOii = 1.5

- Reburn+Urea: OFA = 2050F
- Reburn+Urea/Na2CO3: OFA = 2050F
- Reburn+Urea: OFA = 2250F
- Reburn+Urea/Na2CO3: OFA = 2250F

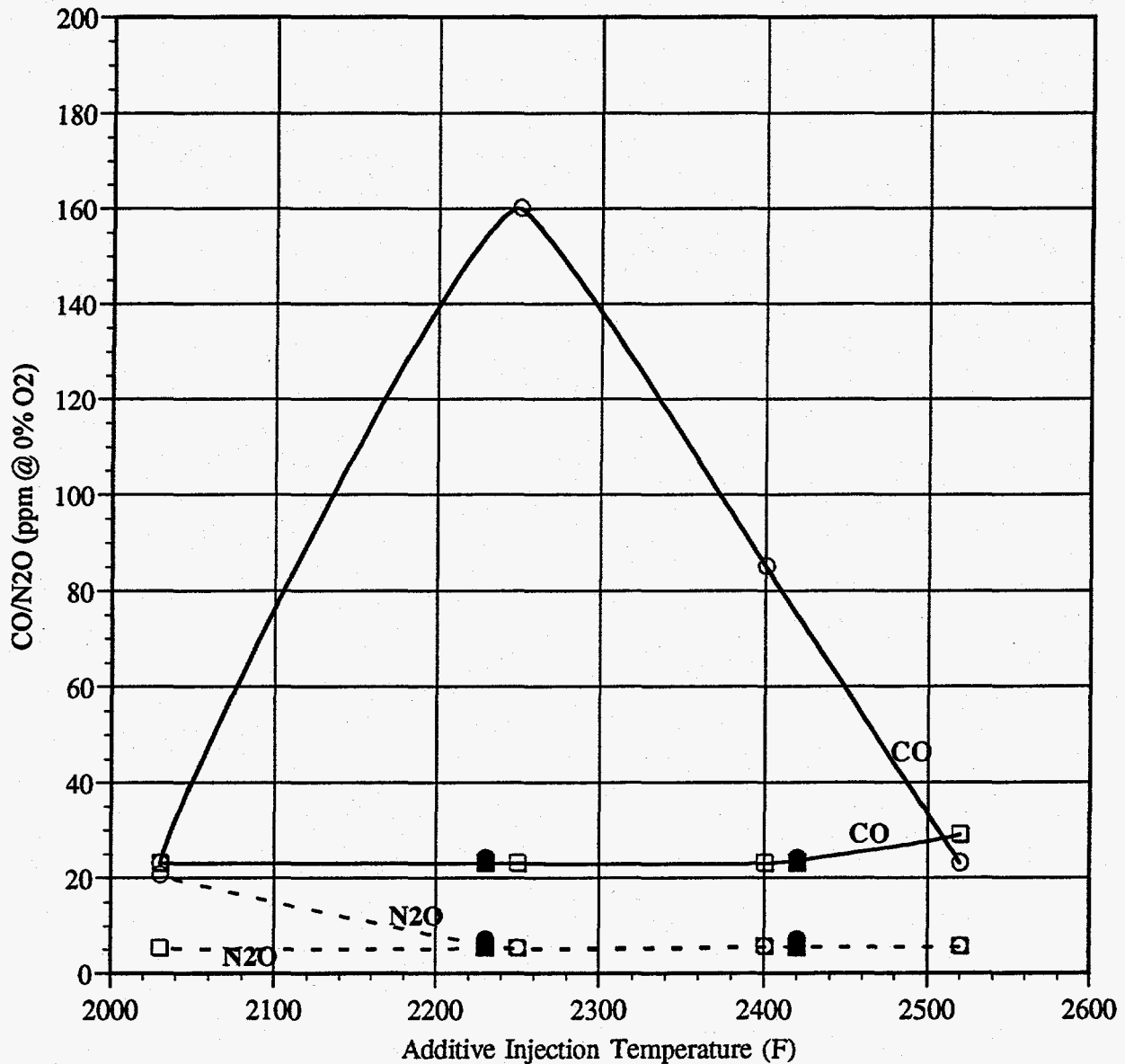


Figure 4.2.5. CO and N2O emissions for injection of urea/sodium and OFA at different temperatures.

Main Fuel: Natural gas @ 705,000 Btu/hr
10% Reburn with N₂ Transport
OFA at 1920 F
Urea and Na₂CO₃ injection at 2280 F
SR1 = 1.10, SR2 = 0.99, SR3 = 1.15
NO_i = 600 ppm as measured
N/NO_i = 1.5

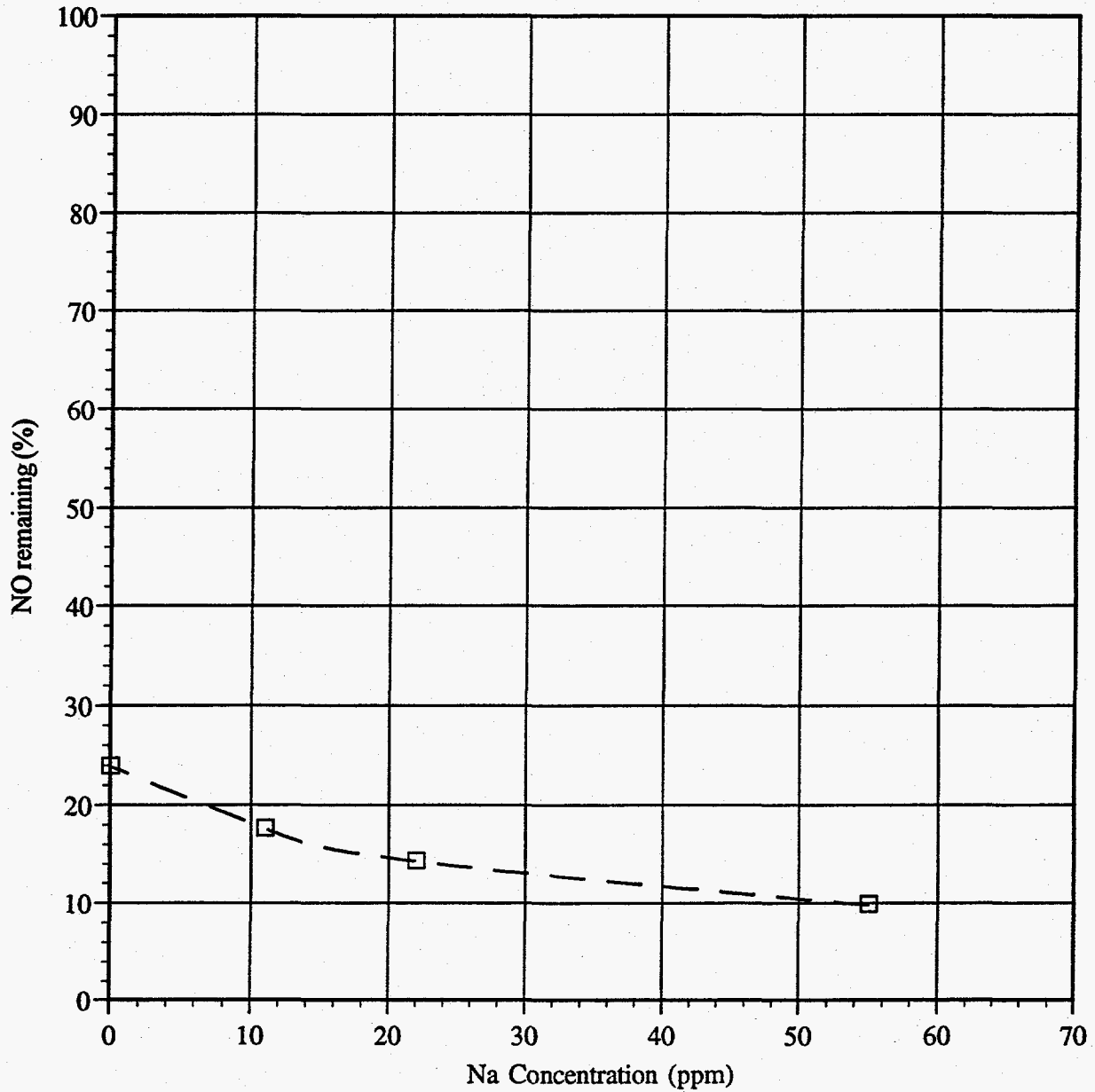


Figure 4.2.6. Effect of sodium on NO reduction in AR-Rich

4.3 Hybrid Advanced Reburning-Lean/SNCR

Combined AR-Lean/SNCR tests were also conducted. In these tests, the reburning fuel was injected at 2500 F and a N-agent (aqueous ammonia or urea) was added at 2000 F. Then, a second N-agent was injected under fuel lean conditions at 1625 F. Concentration of each N-agent corresponded to NSR=1.5. NO reduction was measured with and without addition of sodium carbonate to each N-agent. The amount of sodium was 100 ppm for each sodium carbonate addition. Figures 4.3.1 and 4.3.2 present the results for urea and ammonia, respectively. It is of interest to note that the performance with urea was somewhat greater than that with ammonia, although SNCR with ammonia usually performs better than with urea.

Reburning alone (bar A) gave about 53% NO reduction. Injection of urea with OFA, i.e. AR-Lean (Figure 4.3.1) resulted in 76% NO removal, bar B. The second N-agent increased the NO_x control to 85%, bar C. The best result was achieved when sodium was injected with the first N-agent, bar D. NO removal jumped from 85 to above 98%. Addition of sodium to the second N-agent was not effective, (see bars E and F): there is almost no difference in NO reduction for bars C and E, as well as for bars D and F.

Primary Fuel: Nat. gas @ 705,000 Btu/hr
 10.2% Natural Gas reburning
 SR1=1.10, SR2= 0.99, SR3= 1.15
 Location #1 is at 2000 F w/OFA, NH/NOii=1.5
 Location #2 is at 1625 F, NH/NOiii=1.5
 Na2CO3 Promoter, 100 ppm Na

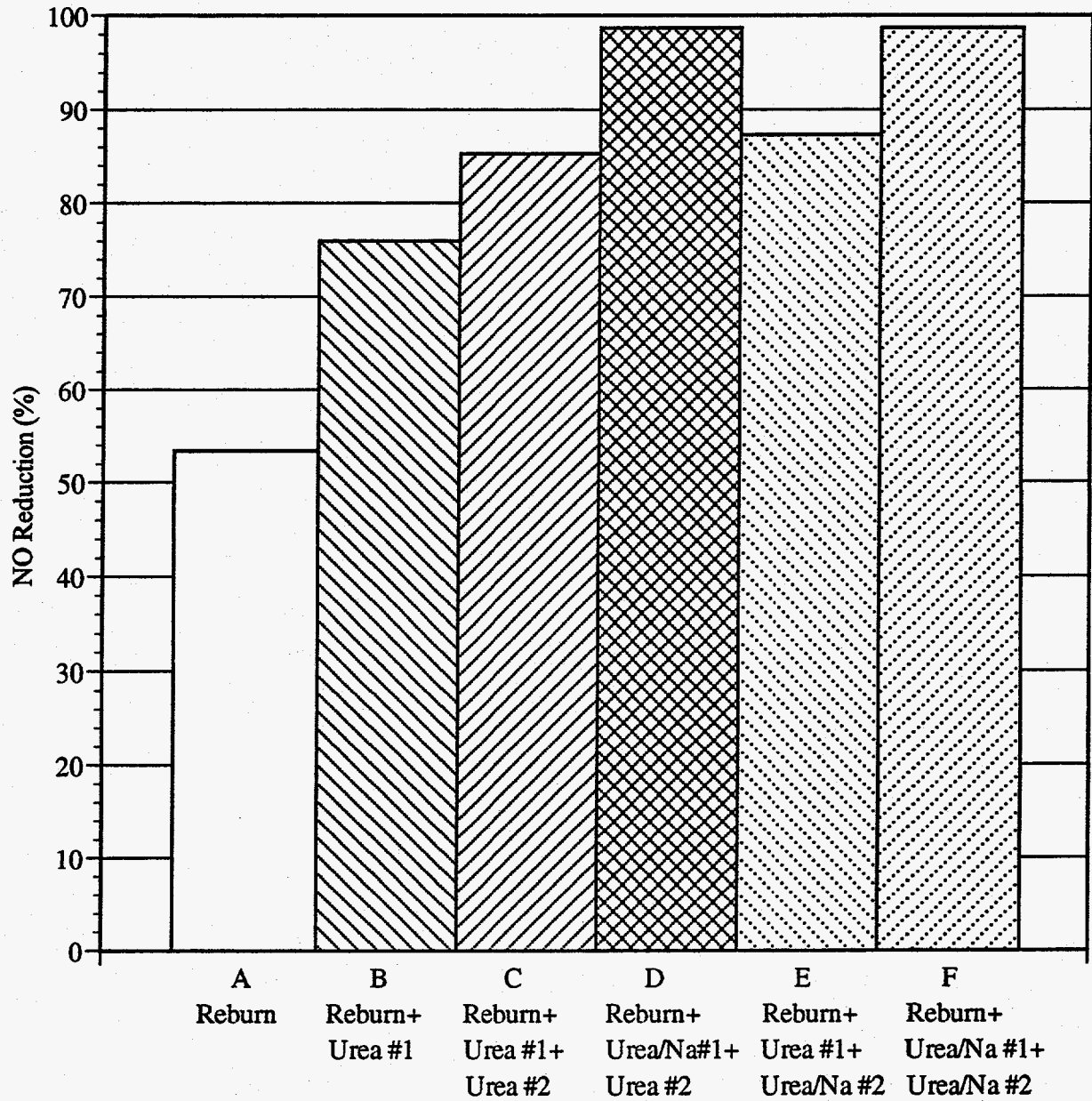


Figure 4.3.1. NO reduction during natural gas firing by combined AR-Lean/SNCR with urea injection at two locations

Primary Fuel: Nat. gas @ 705,000 Btu/hr
 10.2% Natural Gas reburning
 SR1=1.10, SR2= 0.99, SR3= 1.15
 Location #1 is at 2000 F w/OFA, NH/NOii=1.5
 Location #2 is at 1625 F, NH/NOiii=1.5
 Na2CO3 Promoter, 100 ppm Na

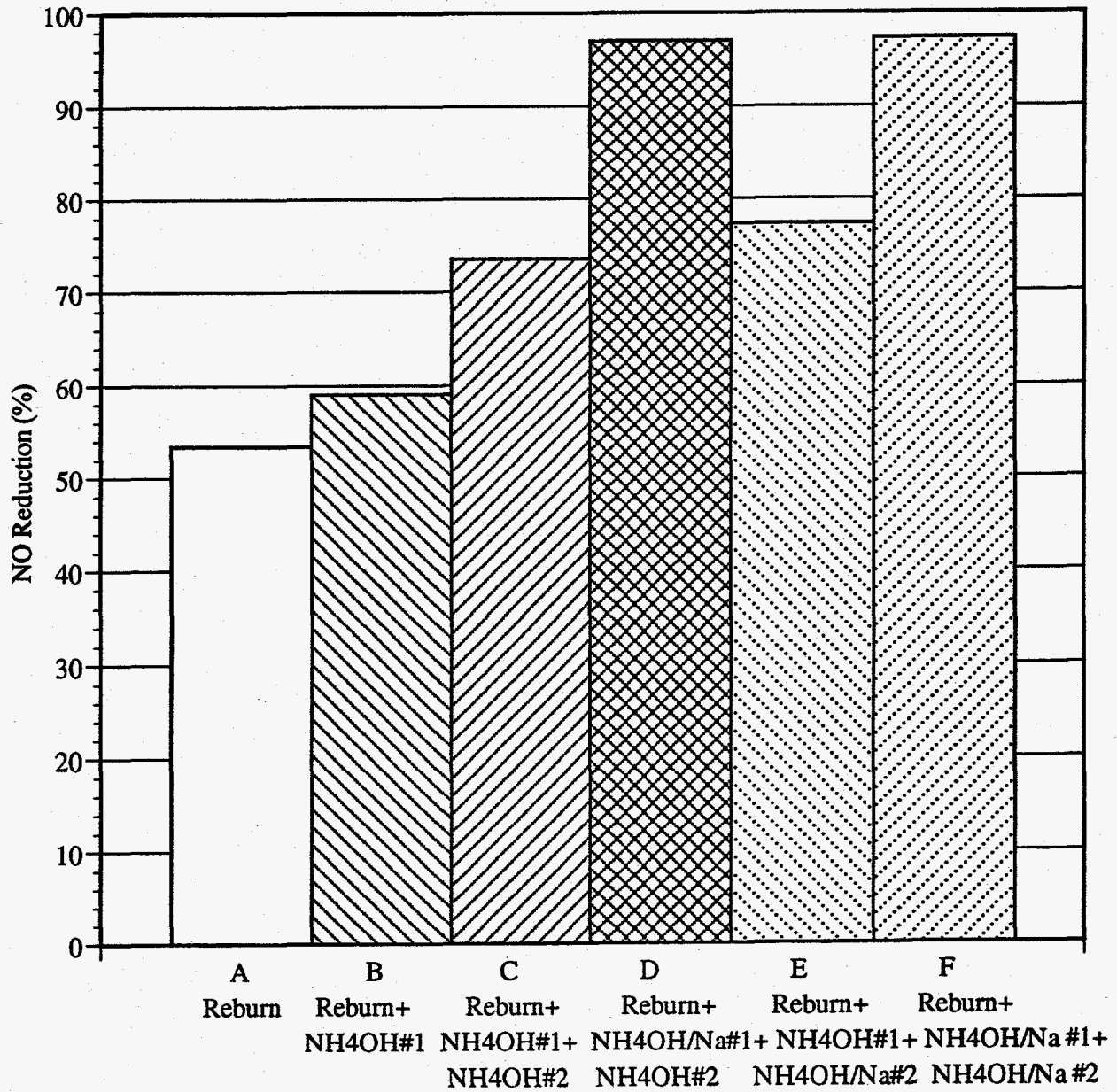


Figure 4.3.2. NO reduction during natural gas firing by combined AR-Lean/SNCR with NH4OH injection at two locations

5.0 Pilot Scale Combustion Tests with Coal Firing

5.1 Advanced Reburning - Lean

In these tests, Utah coal was used as the main fuel and NG as the reburning fuel. The initial uncontrolled NO concentration was about 900 ppm. The reburning fuel (10%) was injected at 2500 F and provided a stoichiometry in the reburn zone of $SR_2=0.99$.

The OFA was injected along with aqueous urea and sodium carbonate at different temperatures. Figure 5.1.1 demonstrates that 55-60% NO reduction was achieved by 10% reburning alone. Performance strongly depends on the urea/OFA injection temperature. Injection of urea with the OFA is almost ineffective at high injection temperatures, 2200-2400 F. Under these conditions, the emission of CO was about 40 ppm without Na and 60 ppm in the presence of Na. At urea/OFA injection temperatures lower than 2200 F, NO is substantially reduced, up to 90%. However, higher CO emissions were measured, 40-60 and 80-100 ppm CO in the absence and presence of sodium, respectively. The concentration of Na was varied from 0 to 200 ppm, or 100 ppm Na_2CO_3 in flue gas. The effect of sodium on NO reduction was noticeable, 2-8 percentage points, but not so great as in the NG firing tests.

5.2 Advanced Reburning - Rich

Similar to NG firing, the performance of AR-Rich during coal firing depends on OFA injection temperature. Figures 5.2.1 and 5.2.2 demonstrate experimental results for injection of OFA at 1640 and 1880 F, respectively. Urea ($NSR_1=1.5$) and different amounts of sodium (0-200 ppm) were injected at different temperatures. Lower OFA injection temperature provides better NO reduction. Reburning followed by urea injection in the reburn zone at different temperatures resulted in 78-88% NO control with OFA at 1640 F (Figure 5.2.1) and 70-77% NO control with OFA at 1880 F (Figure 5.2.2). The effect of sodium was less than for NG firing. A possible reason for this is interaction of sodium compounds with SO_2 to form sodium sulfite or sodium sulfate.

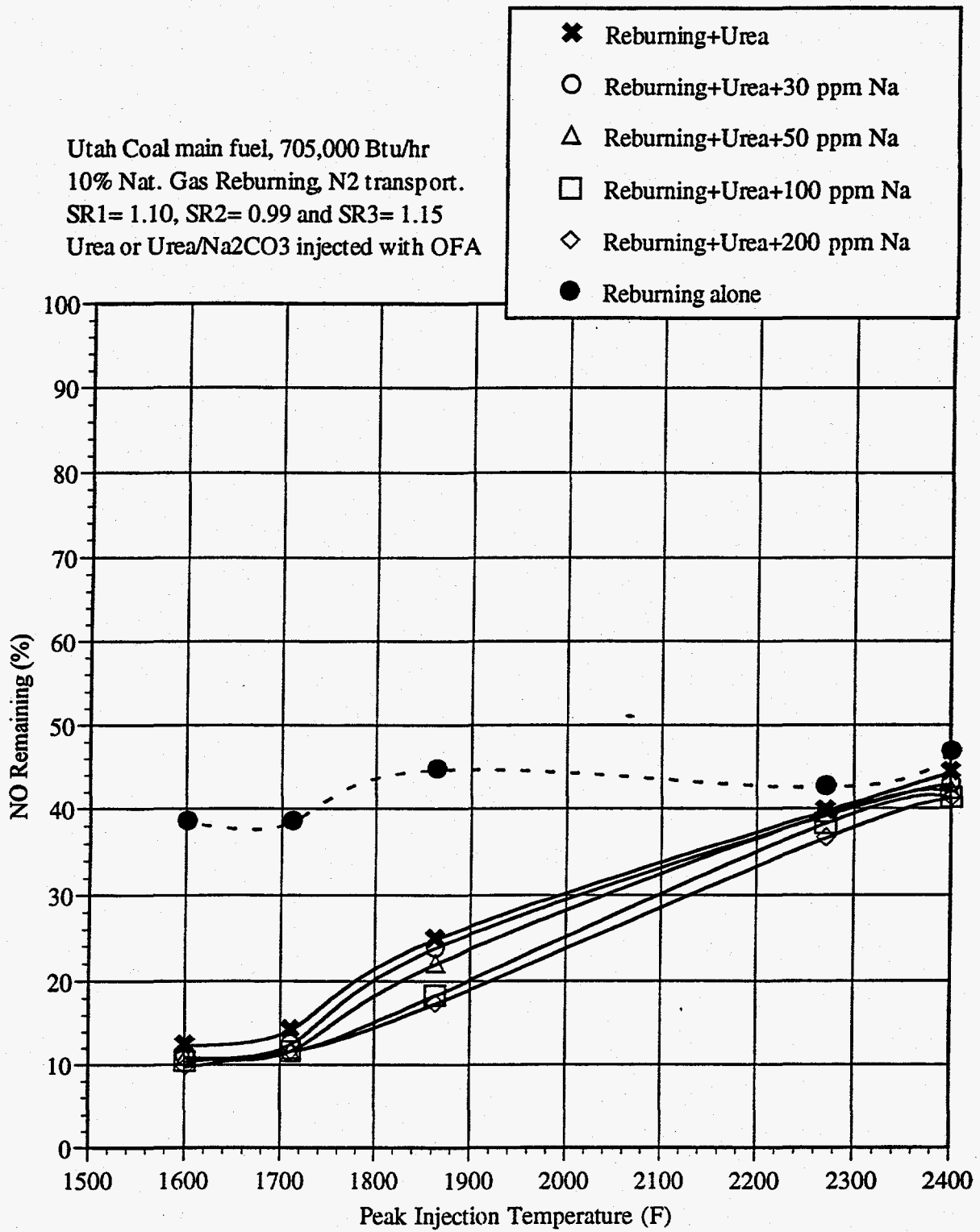


Figure 5.1.1. NO reduction by AR-lean during coal firing.

Utah Coal main fuel, 705,000 Btu/hr
 10% Nat. Gas Reburning, N2 transport.
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 NOi=800 ppm as meas.

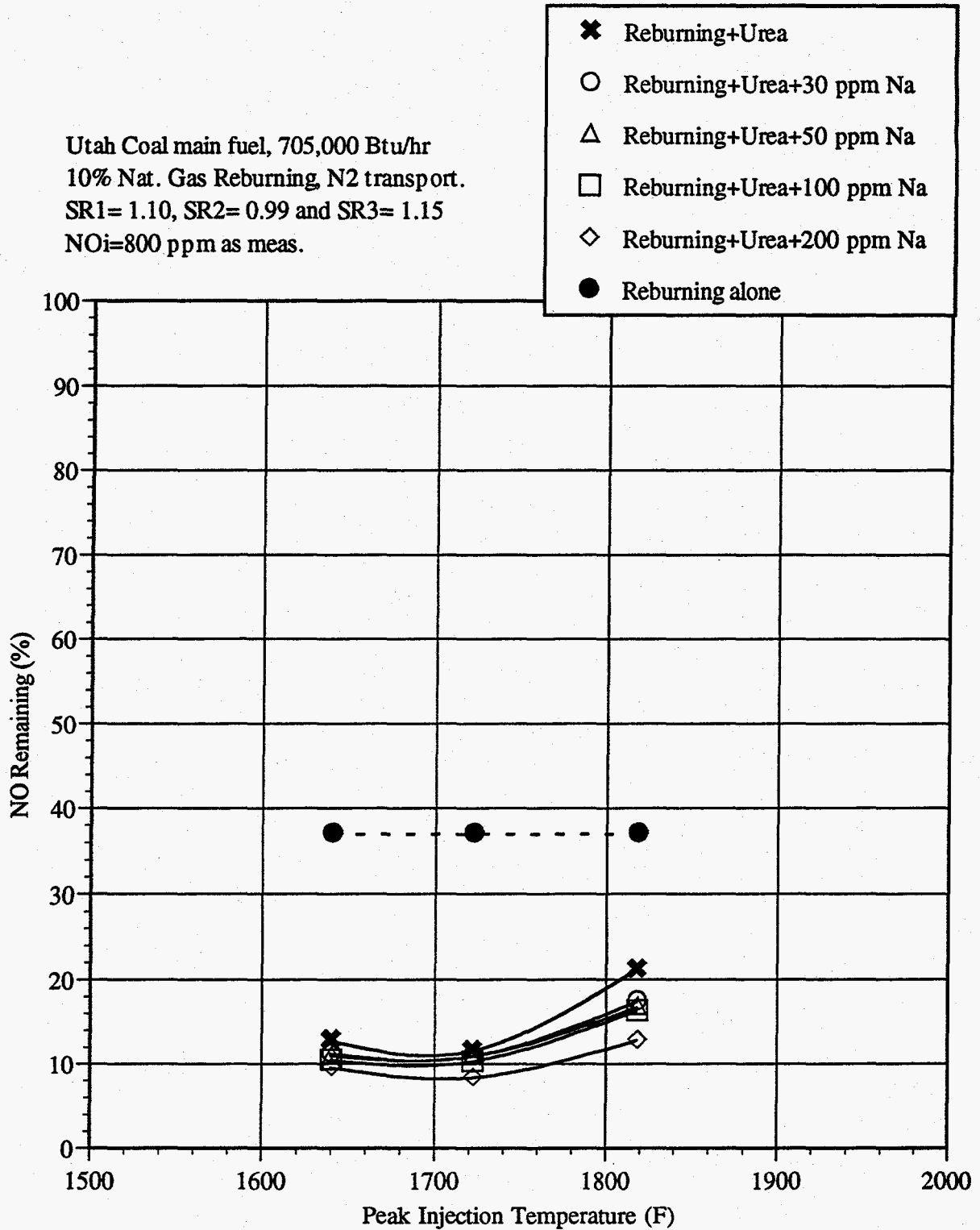


Figure 5.2.1. Effect of urea injection temperature and concentration of sodium on NO reduction in AR-Rich with coal firing. OFA injection temperature is 1640 F.

Utah Coal main fuel, 705,000 Btu/hr
 10% Nat. Gas Reburning, N2 transport.
 SR1= 1.10, SR2= 0.99 and SR3= 1.15
 NOi=800 ppm as meas.

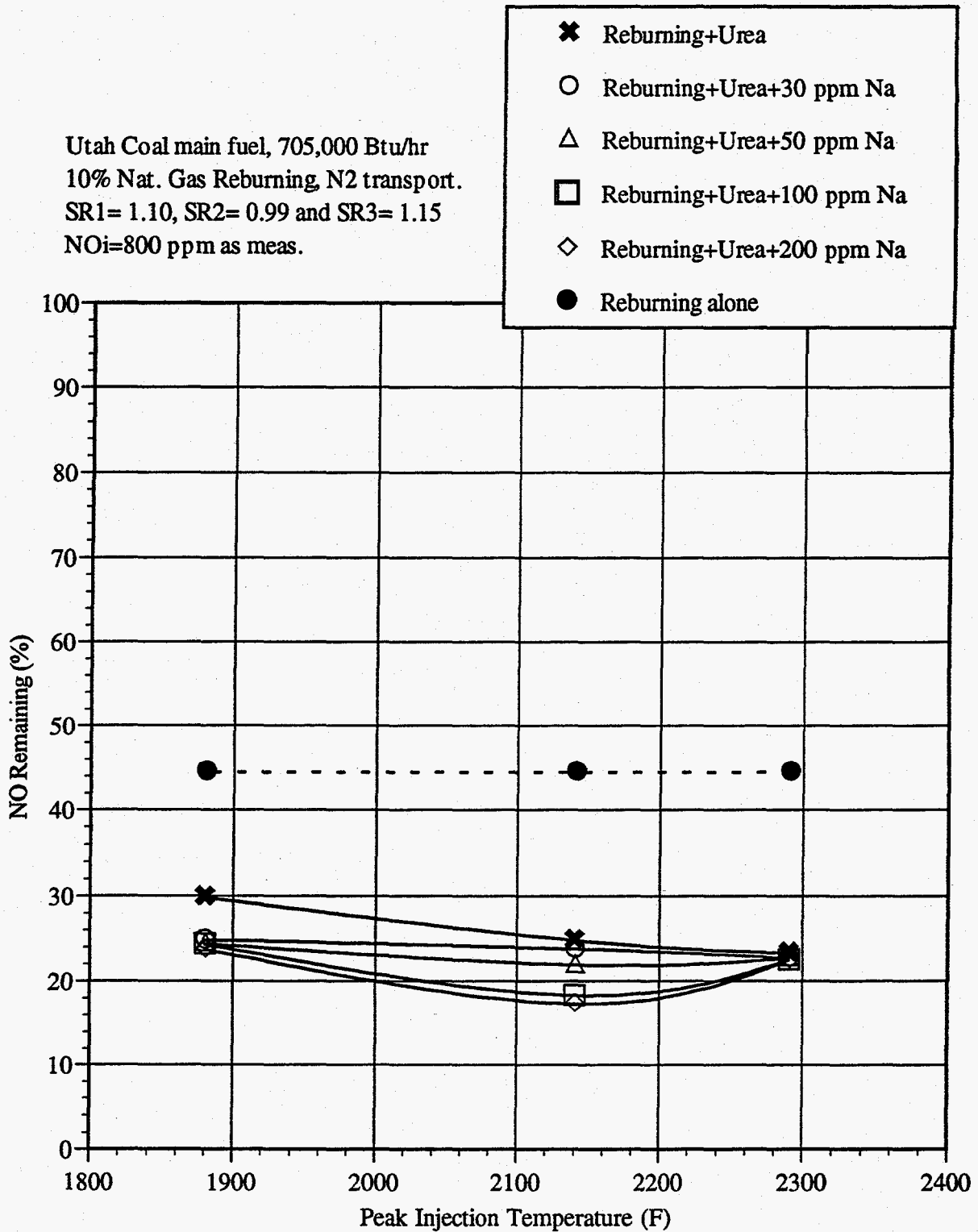


Figure 5.2.2. Effect of urea injection temperature and concentration of sodium on NO reduction in AR-Rich with coal firing. OFA injection temperature is 1880 F.

For injection of OFA at 1640 F, CO emissions were about 60 ppm without sodium and 100 ppm in the presence of sodium. Variation of the sodium concentration did not affect the CO level. At an OFA injection temperature of 1880 F, CO emissions were about 40 and 60 ppm in the absence and in the presence of sodium, respectively.

5.3 Hybrid Advanced Reburning-Lean/SNCR

As with NG firing, coal firing tests were also conducted on combined AR-Lean/SNCR. The conditions were about the same: the reburning fuel was injected at 2500 F, ammonia or urea was added at 2000 F, and 100 ppm Na was injected with each N-agent. NO reduction was measured with and without sodium. The second N-agent was injected under fuel lean conditions at 1700 F, a slightly higher temperature than in the NG firing tests. Figures 5.3.1 and 5.3.2 represent the results for urea and ammonia, respectively. In the case of coal firing, the performance with urea and ammonia was about the same.

It is of interest to compare the performance of the combined AR-Lean/SNCR process for NG and coal firing, Figures 4.3.1-4.3.2 and 5.3.1-5.3.2. These data are compared in Table 1.

Table 1. Comparison of NO reduction (%) for hybrid AR/SNCR with gas and coal firing (see Figures 4.3.1-4.3.2 and 5.3.1-5.3.2). Corresponding CO emissions in ppm are shown in parentheses.

Bar	Test Conditions	Natural Gas Firing		Coal Firing	
		Urea	Ammonia	Urea	Ammonia
A	10% Reburn@2500 F, OFA@2000 F	53(20)	53(20)	49(60)	49(60)
B	AR-Lean, OFA @ 2000 F	76(30)	58(30)	66(60)	62(60)
C	AR-Lean + SNCR	85(30)	73(30)	85(60)	84(60)
D	AR-Lean/Na + SNCR	98(190)	96(180)	91(60)	90(60)
E	AR-Lean + SNCR/Na	87(30)	78(30)	94(60)	93(60)
F	AR-Lean/Na + SNCR/Na	98(190)	96(180)	95(60)	94(60)

Primary Fuel: Utah coal @ 705,000 Btu/hr
 10.2% Natural Gas reburning
 SR1=1.10, SR2= 0.99, SR3= 1.15
 Location #1 is at 2000 F w/OFA, NH/NOii=1.5
 Location #2 is at 1700 F, NH/NOiii=1.5
 Na₂CO₃ Promoter, 100 ppm Na

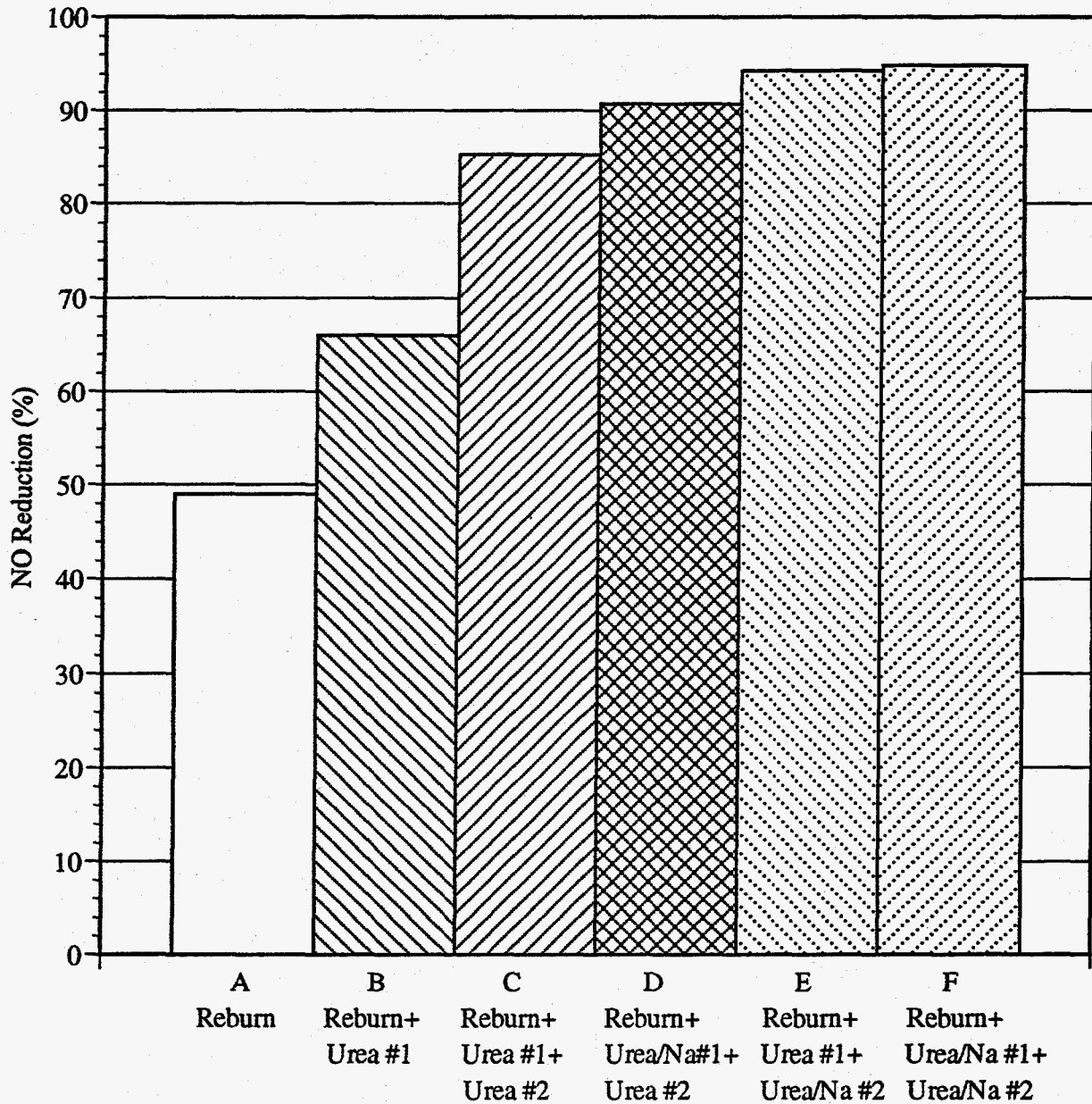


Figure 5.3.1. NO reduction during coal firing by combined AR-Lean/SNCR with urea injection at two locations

Primary Fuel: Utah coal @ 705,000 Btu/hr
 9.8% Natural Gas reburning
 SR1=1.10, SR2= 0.99, SR3= 1.15
 Location #1 is at 2000 F w/OFA, NH/NOii=1.5
 Location #2 is at 1700 F, NH/NOiii=1.5
 Na₂CO₃ Promoter, 100 ppm Na

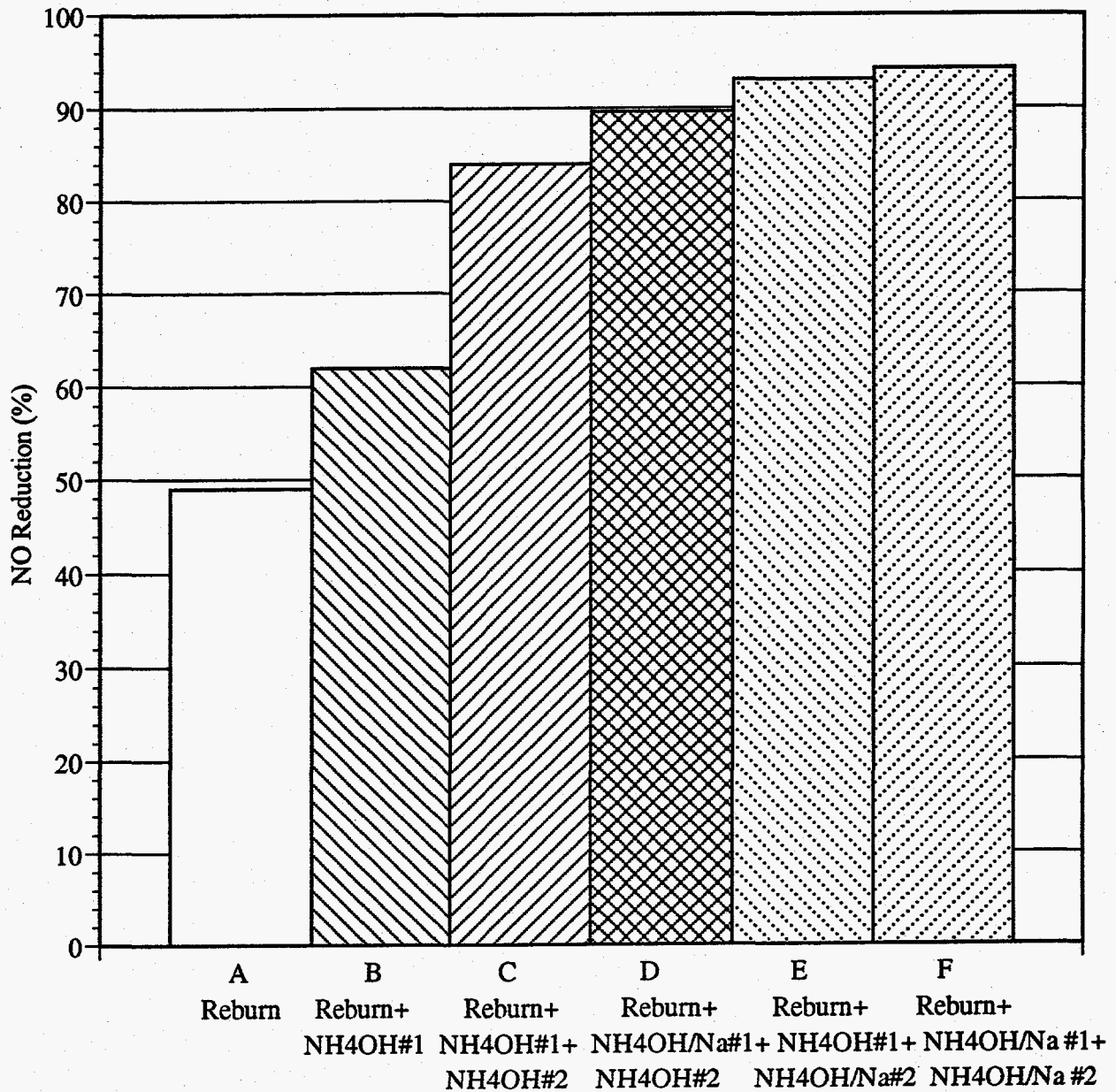


Figure 5.3.2. NO reduction during coal firing by combined AR-Lean/SNCR with NH₄OH injection at two locations

Reburning alone (bar A in Figures 5.3.1 and 5.3.2) provided about 53 and 49% NO reduction, the performance was better with NG firing. Mixed results were obtained for AR-Lean (bar B): 58-76% for NG and 62-66% for coal. AR-Lean + SNCR (bar C) provided up to 85% NO reduction for both NG and coal firing. The best results for NG firing were achieved by addition of sodium to the first N-agent (bar D), 96-98% NO control. Under the same conditions, 90-91% NO was reduced in coal firing. Sodium can likely react with SO₂, and therefore the performance is not as great in the coal firing tests. Addition of sodium to the second N-agent (bar E) can be considered as the best result for coal firing: 93-94% NO reduction. Surprisingly, the same arrangements with NG firing resulted in only 78-87% NO reduction. Coal flue gas includes vapors of some mineral compounds which can promote the reburning process, and therefore, the presence of the mineral matter in the reburn zone of coal combustion can improve NO reduction. Finally, addition of sodium to both N-agents (bar F) shows that the second Na additive is not effective for NG firing (bars D and F), and the first Na additive is almost ineffective for coal firing (bars E and F).

Data on CO emissions are also presented in Table 1. The CO emissions increased in some tests with NG firing, but not with coal tests. Two important conclusions can be made based on these hybrid AR/SNCR tests:

1. The hybrid AR-Lean/SNCR process is very effective for NO_x control and can achieve up to 95 and 98% NO reduction for coal and NG firing, respectively.
2. Addition of sodium to the second N-agent is more effective for coal rather than for NG firing. The first Na additive is more effective for NG than for coal firing.

6.0 Kinetics of Sodium Reactions

This Section of the report was prepared by W.C. Gardiner and V. Lissianski of the University of Texas at Austin.

General Objective of the work for the period 7/96 – 9/96:

Development of Na_2CO_3 solution injection system, calibration of injection system. Flow system study of decomposition of Na_2CO_3 . Reactions of Na_2CO_3 with components of flue gas.

Method: GC detection of CO_2 and components of flue gas.

During last three months experimental work concentrated on development of the injection system for Na_2CO_3 solution and on enhancing the gas-chromatographic sensitivity to CO_2 . The experimental work was significantly speeded up with the addition of a new team member, Dr. Vladimir Mastroikov, to the project. The newly developed injection system combined with an ultrasonic atomizing nozzle provided a reliable way to spray aqueous solution of Na_2CO_3 with salt concentrations up to 15% by weight. Figure 6.1 shows diagram of flow system. It was observed that when solution with a high concentration of salt was used, deposits of Na_2CO_3 were formed on the walls of the reactor. This problem was partially solved by preheating the carrier gas before and after mixing with solution and by rearranging the furnace in a vertical position, but a complete solution was not achieved until after the concentration of Na_2CO_3 in the solution was reduced to 1–3% by weight. This required solving another problem: with such a small concentration of salt, the amount of CO_2 produced during its decomposition was below the detection limit of the GC (200 ppm). The sensitivity of the GC was increased by replacing the GC column responsible for CO_2 separation and by using an additional amplification stage for the GC output signal. These modifications resulted in a sensitivity level of 10 ppm of CO_2 and permitted us to work with the flow system with levels of Na_2CO_3 close to those used by EER in field experiments.

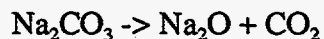
Preliminary experiments showed that temperature measurements taken inside of the reactor were significantly different from measurements taken in the furnace area originally used for temperature

determinations. To enable correct temperature measurements, the construction of the flow reactor was changed to enable thermocouples to be inserted directly into the flow of gas. Measurements showed that by adjusting current flows through each of three segments of the furnace, a uniform temperature distribution inside of the reactor can be maintained with temperature variations limited to ± 10 degrees.

Two drying systems were installed to dry gas after passing through the reactor. The first system was used to separate large quantities of water, before sending the outlet gas to the vent system, to prevent water condensation in communication lines. The second system used an acetone-dry ice trap to dry the gas before taking samples for GC analysis, this system being to protect the sensitive GC columns from being destroyed by basic solutions formed by the reaction between water and the Na_2O product of Na_2CO_3 decomposition.

Preliminary experiments on Na_2CO_3 decomposition at high temperatures were started. These experiments showed that at temperatures around 900 K at residence times from 0.5 to 1.0 s about 30 to 60 % of Na_2CO_3 decomposes. Detailed experimental measurements at different temperatures are under way.

Figure 6.2 shows dependence of ratio of initial concentration of Na_2CO_3 to its concentration in the mixture after passing through the reactor at temperature 644°C . These data show that decomposition of Na_2CO_3 closely follows first order. Rate coefficient of the reaction



determined from data presented in Figure 6. 2 is equal to 0.08 s^{-1} .

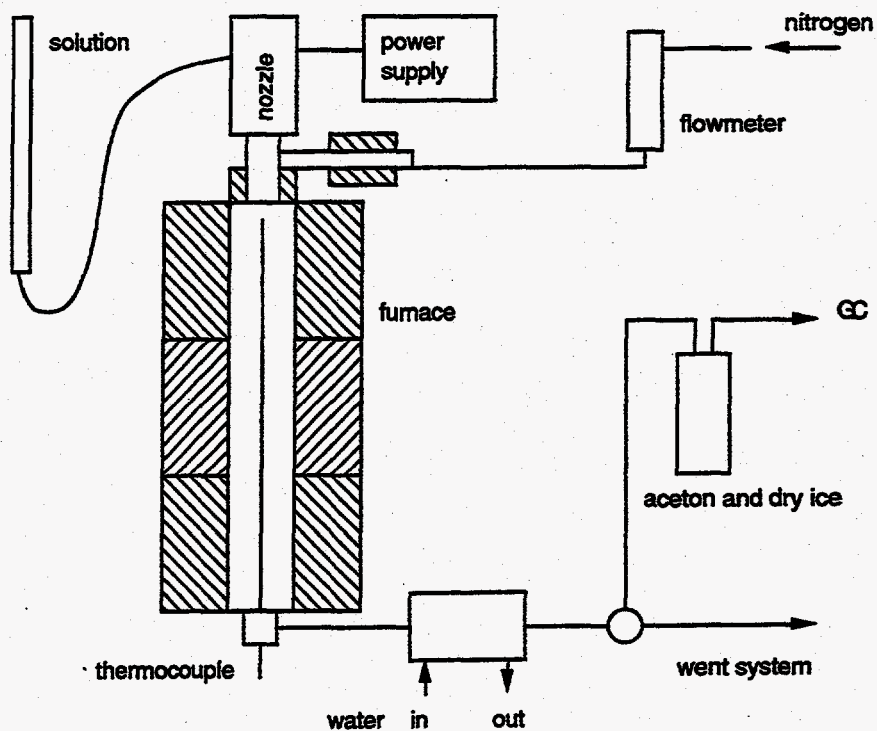


Figure 6.1. Diagram of the flow system.

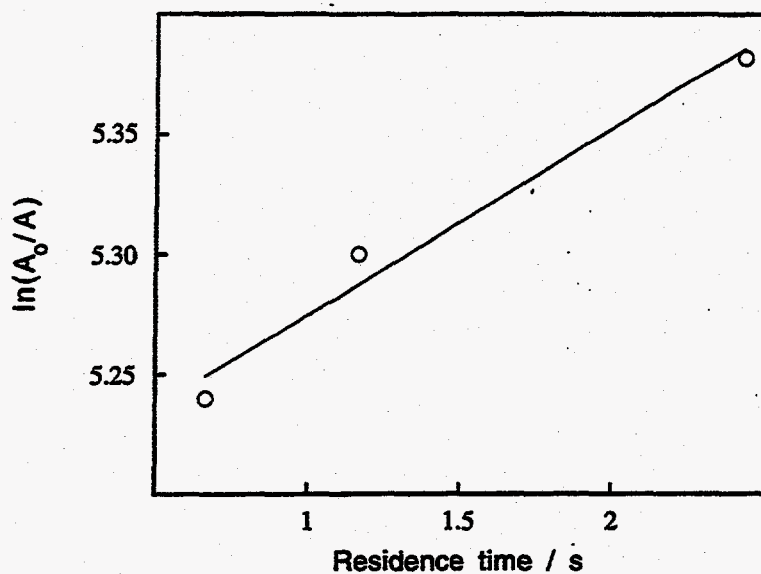


Figure 6.2. Dependence of Na_2CO_3 concentration on residence time. Aqueous solution of Na_2CO_3 with concentration of 3% by mass was used, temperature is 644°C .

7.0 Modeling Studies

In the 2nd and 3d quarterly reports (Zamansky, 1996; Zamansky and Maly, 1996), modeling studies of chemical interactions in the reburning and burnout zones were described. It was shown that delayed ammonia injection into the reburning zone is capable of reducing NO concentration and that certain additives, such as oxygen and active radicals, can promote the NO-NH₃ interaction in both reburning and burnout zones.

During the current reporting period, modeling activities were continued and focused on selecting chemical mechanisms for reactions of sodium, sulfur, and chlorine compounds. Experimental data demonstrate that sodium compounds, such as sodium carbonate and sodium hydroxide, can increase reburning efficiency. It was also found that sodium promoters are less effective in coal combustion flue gas than in NG flue gas. Coal includes sulfur and chlorine compounds which can react with sodium, decreasing its efficiency. The Na-, S-, and Cl-submechanisms will be added to the existing C-H-O-N mechanism to model the effect of sulfur and chlorine compounds on reburning efficiency and to understand the chemistry of sodium promotion under different conditions. All selected reactions are presented in Table 2. The reverse reactions will be automatically taken into account in modeling. This mechanism can be considered as a preliminary one since it will be updated at the end of the Phase I program to include the results of the study at the University of Texas.

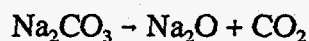
Table 2. Selected reactions of Na, S, and Cl. The rate constants are in Arrhenius format: $k = AT^n \exp(-E/RT)$ (cm, mol, s, cal, K).

No.	Reaction	A	n	E	Reference
<u>Reactions of sodium</u>					
1	NA+N2O=NAO+N2	1.69E+14	0.00	3159.	Plane, 1992
2	NAO+H2O=NAOH+OH	1.32E+13	0.00	0.	Ager and Howard, 1987
3	NAO+O=NA+O2	2.23E+14	0.00	0.	Plane and Husain, 1986
4	NAO+NO=NA+NO2	9.04E+13	0.00	0.	Ager et al., 1989
5	NAO+H2=NAOH+H	1.25E+13	0.00	0.	Ager and Howard, 1987
6	NA+O2+M=NAO2+M	1.74E+21	-1.30	0.	Plane and Rajasekhar, 1989
Third-body efficiencies: H2O=5, CO2=3, CO=H2=2					
7	NAOH+H=NA+H2O	5.00E+13	0.00	0.	Jensen and Jones, 1982
8	NA+OH+M=NAOH+M	1.82E+21	-1.00	0.	Jensen and Jones, 1982
9	NAO+OH=NAOH+O	2.00E+13	0.00	0.	Perry and Miller, 1996
10	NAO+HO2=NAOH+O2	5.00E+13	0.00	0.	Perry and Miller, 1996
11	NAO+H2=NA+H2O	3.13E+12	0.00	0.	Perry and Miller, 1996
12	NAO+CO=NA+CO2	1.00E+14	0.00	0.	Perry and Miller, 1996
13	H+NAO2=HO2+NA	2.00E+14	0.00	0.	Perry and Miller, 1996
14	NAO+H=NA+OH	2.00E+14	0.00	0.	Perry and Miller, 1996
15	NAO+OH=NA+HO2	3.00E+13	0.00	0.	Perry and Miller, 1996
16	NA+HO2=NAOH+O	1.00E+14	0.00	0.	Perry and Miller, 1996
17	NAO2+H=NAO+OH	5.00E+13	0.00	0.	Perry and Miller, 1996
18	NAO2+OH=NAOH+O2	2.00E+13	0.00	0.	Perry and Miller, 1996
19	NAO+HO2=NAO2+OH	5.00E+13	0.00	0.	Perry and Miller, 1996
20	NAO2+H=NAOH+O	1.00E+14	0.00	0.	Perry and Miller, 1996
21	NAO2+CO=NAO+CO2	1.00E+14	0.00	0.	Perry and Miller, 1996
22	NAO2+O=NAO+O2	1.00E+14	0.00	0.	Perry and Miller, 1996
23	NAO+NH3=NAOH+NH2	1.00E+13	0.00	0.	Est.
<u>Reactions of sulfur</u>					
24	SO2+O+M=SO3+M	1.45E+16	0.00	2000.	Atkinson et al., 1992
25	SO2+OH+M=HSO3+M	2.12E+25	-3.30	0.	Atkinson et al., 1992
26	HSO3+O2=HO2+SO3	7.83E+11	0.00	656.	Atkinson et al., 1992
27	NO2+SO2=NO+SO3	6.31E+12	0.00	27000.	Armitage and Cullis, 1971
28	O+SO3=SO2+O2	1.32E+12	0.00	6100.	Smith et al., 1982
29	NA+SO2=NASO2	1.21E+14	0.00	0.	Shi and Marshall, 1991
30	NASO2+NAO2=NA2SO4	1.00E+14	0.00	0.	Est.
31	NASO2+NAO=NA2SO3	1.00E+14	0.00	0.	Est.
<u>Reactions of chlorine</u>					
32	NAO+HCL=NACL+OH	1.69E+14	0.00	0.	Silver et al., 1984
33	NA+HCL=NACL+H	2.41E+14	0.00	130.	Husain and Marshall, 1986
34	NAOH+HCL=NACL+H2O	1.69E+14	0.00	0.	DeMore et al., 1987
35	NAO2+HCL=NACL+HO2	1.39E+14	0.00	0.	Silver and Kolb, 1986
36	CL+H2=HCL+H	1.45E+13	0.00	4370.	Baulch et al., 1981
37	H+CL2=CL+HCL	8.59E+13	0.00	1170.	Baulch et al., 1981
38	CL+CL+M	2.23E+14	0.00	-1800.	Baulch et al., 1981
39	O+HCL=CL+OH	6.87E+12	0.00	6697.	Baulch et al., 1981
40	CL+H2O=OH+HCL	1.68E+13	0.00	17230.	Baulch et al., 1981

7.1 Reactions of Sodium

High temperature chemistry of sodium compounds is not well understood. Only a few rate constants have been measured directly, and kinetic information on many reactions is absent. However, there are estimated numbers on several other rate constants.

Sodium carbonate was used as a promoter in most CTT and BSF experiments. It was also shown that sodium hydroxide has about the same efficiency as sodium carbonate. When sodium carbonate is injected into flue gas, it decomposes into oxides. The mechanism of Na_2CO_3 thermal decomposition and the corresponding rate constants are unknown and currently being studied at the University of Texas. Most likely, sodium carbonate dissociates at high temperatures to different oxides:



The oxides react with water molecules which are available in flue gas to form sodium hydroxide. This is a possible reason for the equal promotion efficiency of Na_2CO_3 and NaOH . In this preliminary Na-submechanism, the reactions of sodium carbonate were not included since their rate constants are unknown. Reactions of sodium hydroxide were included, and NaOH will be considered as an initial sodium compound for modeling the promotion effect.

The Na-submechanism in Table 2 includes 23 reactions. Reaction 1 is the most important for removing N_2O from flue gas. Several measurements of the rate constant agree rather well with each other (NIST Chemical Kinetic Database, 1994). Reactions 2-5 are important steps of NaO interaction with H_2O , O , NO and H_2 . Rate constant of these reactions have been measured, see references in Table 2. Reaction 6 represents oxidation of Na atoms by molecular oxygen. The rate constant of this reaction was measured several times and the most reliable value was selected. Reaction 7 can be important for N_2O removal under fuel rich conditions. If the reaction proceeds as written to form Na atoms, they will react with N_2O via reaction 1. If reaction 1 is faster in reverse

direction, reaction 1 will be not effective. Reaction 8 is probably important for defining the processes of radicals formation and removal. Indeed, if the recombination reaction 8 of sodium atoms and hydroxyl radicals is fast enough, the efficiency of the promoter will be low. Measurements by Jensen and Jones, 1982 were accepted as rate constants for reactions 7 and 8. Other reactions of sodium, 9-22, were recently estimated by Perry and Miller, 1996. The last sodium reaction, 23, represents a process of sodium-ammonia interaction. It was observed in experiments that sodium promoters are effective mainly in the presence of N-agents. However, no kinetic data on sodium-ammonia interaction was found in the literature. The rate constant was estimated to be close to the collision frequency and will be varied in modeling.

7.2 Reactions of Sulfur

Rate constants for SO_2/SO_3 reactions, 24-28, were taken from the literature review by Atkinson et al., 1992 and direct measurements by Armitage and Cullis, 1971 and Smith et al., 1982. Though many kinetic measurements of these reactions were reported in the literature, most of them were performed at relatively low temperatures, mainly below 260 F. Therefore, there is a significant uncertainty in high temperature kinetic data for SO_2/SO_3 interaction. Reactions 29-31 represent interaction of sodium and sulfur compounds. A single rate constant measurement for reaction 29 was reported by Shi and Marshall, 1991. Rate constants for reactions 30 and 31 were assumed to be close to that measurement.

7.3 Reactions of Chlorine

Chlorine is a constituent of coal. During the combustion process, most chlorinated compounds are converted into HCl. Therefore, to model the effect of chlorine on reburning efficiency and Na promotion, it is logical to perform modeling using the initial concentration of HCl in flue gas corresponding the amount of chlorine in coal.

Nine reactions of chlorine were included in the mechanism. The first four, 32-35, represent the reactions of sodium compounds (Na, NaO, NaO_2 , and NaOH) with HCl. All these reactions are fast,

and available experimental measurements of the rate constants were selected. Five other chlorine reactions, 36-40, include the well known steps of $\text{Cl}_2\text{-H}_2$ interaction. Their rate constants were taken from kinetic tables by Baulch et al., 1981.

8.0 Conclusions

1. The CTT experimental study demonstrates the importance of promotion mechanisms on reburning performance. The following factors affect NO reduction in the reburning zone: water flow rate; the presence of oxygen, its amount, and injection time; the presence of promoters; and mixing and thermal conditions. These factors need to be investigated in future testing and modeling activities.

2. Investigation of the AR-Lean and AR-Rich processes with natural gas firing shows that each of them can substantially increase the efficiency of basic reburning. The basic reburning process with 10% reburning fuel provides about 50% NO_x control. Injection of N-agents (urea or ammonia) increases NO reduction to 60-82% depending on conditions. Temperature of OFA injection is the most important factor affecting reburning efficiency. At lower OFA injection temperatures, NO reduction is higher, however, CO and N_2O emissions may increase. The optimum OFA injection temperature is in the range of 1800-2300 F. Addition of sodium carbonate to N-agents greatly increases NO reduction. Only 30 ppm Na (15 ppm Na_2CO_3) is capable of increasing NO removal up to 95% NO.

3. BSF experiments with Utah coal firing and NG reburning demonstrate that both AR-Lean and AR-Rich processes are effective for NO reduction. From 60 to 88% NO reduction was achieved in these tests under different conditions. As in NG firing tests, the temperature of OFA injection is an important factor affecting reburning efficiency. At lower OFA injection temperatures, NO reduction is higher, but CO emissions increase. Sodium additives are not as effective in coal firing which can be explained by interaction of sodium compounds with SO_2 and/or HCl in flue gas. Addition of 30-50 ppm Na improves NO reduction by 2-5 percentage points, and 200 ppm Na can increase NO control up to 8-10 percentage points. Up to 90-92% NO reduction was obtained in the presence of sodium at low OFA injection temperatures. However, high concentrations of sodium are

probably impractical because of the adverse effects of sodium on heat transfer surfaces.

4. The hybrid AR-Lean/SNCR process is very effective for NO_x control and can achieve up to 95 and 98% NO reduction for coal and NG firing, respectively. Addition of sodium to the second N-agent is more effective for coal rather than for NG firing. The first Na additive is more effective for NG than for coal firing.

9.0 Future Plans

The main activities of the next quarter will include continuation of the parametric experiments with the use of the pilot scale 1.0 MMBtu/hr boiler simulator facility. Modeling will focus on sensitivity analysis to define the most important elementary reactions under different conditions. Experimental program at the University of Texas will also be continued. Some experiments and modeling results will be presented at the 1996 Fall Meeting of the Western States Section of the Combustion Institute, University of Southern California, Los Angeles, October 29, 1996.

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