

JUN 8 0 1992

DEVELOPMENT OF ADVANCED NO_x CONTROL CONCEPTS
FOR COAL-FIRED UTILITY BOILERS

DOE Contract No. DE-AC22-90PC90363

Period of Performance: September 26, 1990 to October 26, 1992

DOE/PC/90363--T5

DE92 019856

Quarterly Technical Progress Report No. 4

Period Covered by Report: July 1, 1991 to September 30, 1991

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

prepared by:

A. Evans
J. Newhall
G. England
W.R. Seeker

Energy and Environmental Research Corporation
18 Mason
Irvine, California 92718

Date Submitted: June 23, 1992

prepared for:

Mr. Charles E. Schmidt
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

MASTER

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.0	INTRODUCTION	1-1
2.0	PILOT-SCALE ADVANCED REBURNING TESTS	2-1
2.1	Advanced Gas Reburning	2-4
2.1.1	Effect of Local Stoichiometry on Agent Injection	2-4
2.1.2	Effect of Agent Atomization	2-5
2.1.3	Effect of Agent Injection Temperature	2-8
2.1.4	Effect of Burnout Air Injection Temperature	2-8
2.1.5	Optimum Advanced Gas Reburning Configuration at BSF	2-11
2.2	Advanced Coal Reburning	2-11
2.2.1	Effect of Agent Atomization	2-11
2.2.2	Effect of Agent Injection Temperature	2-15
2.2.3	Effect of Burnout Air Injection Temperature	2-15
2.2.4	Optimum Advanced Coal Reburning Configuration at BSF	2-15
2.3	By-Product Emissions for Advanced Reburning	2-20
2.3.1	CO and N ₂ O Emissions	2-20
2.3.2	Ammonia Emissions	2-20
2.3.3	Carbon Burnout	2-23
3.0	LAB-SCALE METHANOL INJECTION TESTS	3-1
3.1	Experimental Set-up	3-1
3.2	Test Results	3-3
3.2.1	Effect of Methanol Injection Temperature	3-3
3.2.2	Effect of Stoichiometry	3-3
3.2.3	Effect of Methanol Concentration	3-6
3.2.4	Effect of Residence Time	3-6
3.2.5	Effect of Initial NO Concentration on NO Conversion	3-11
3.2.6	Effect of Ammonia Presence on NO Conversion	3-11
3.2.7	Formaldehyde Formation	3-14

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2-1 Boiler Simulation Facility (BSF)	2-2
2-2 Advanced reburning nomenclature	2-3
2-3 Effect of local stoichiometry	2-3
2-4 Effect of agent atomization for gas reburning	2-7
2-5 Effect of urea injection temperature	2-9
2-6 Effect of burnout air on CO and NO	2-10
2-7 Optimum advanced gas reburn configuration at BSF	2-12
2-8 Breakdown of NO reduction to individual processes	2-13
2-9 Effect of agent atomization for coal reburning	2-14
2-10 Effect of urea injection temperature for coal reburning	2-16
2-11 Effect of burnout air injection temperature for coal reburning	2-17
2-12 Optimum advanced coal reburn configuration at BSF	2-18
2-13 Breakdown of NO reduction to individual processes for coal reburning	2-19
2-14 CO and N ₂ O emissions for gas and coal advanced reburning	2-21
2-15 Ammonia emissions for both natural gas and coal reburning	2-22
2-16 Percent carbon remaining in ash for both natural gas and coal reburning	2-24
3-1 Methanol injection lab-scale experimental set-up	3-2
3-2 Effect of methanol injection temperature on NO and CO	3-4
3-3 Effect of O ₂ on NO conversion	3-5
3-4 Effect of O ₂ on CO production	3-7
3-5 Effect of methanol concentration on NO to NO ₂ conversion	3-8
3-6 Effect of methanol concentration on CO production	3-9
3-7 Effect of residence time on NO conversion	3-10
3-8 Effect of initial NO concentration	3-12
3-9 Effect of ammonia on NO conversion	3-13
3-10 Effect of ammonia on NO conversion at 1470°F	3-15
3-11 Effect of ammonia on NO conversion at 1740°F	3-16
3-12 Formaldehyde formation during methanol injection	3-17

I. INTRODUCTION

CombiNO_x is a NO_x reduction process which incorporates three different NO_x control technologies: reburning, selective non-catalytic reduction (SNCR), and methanol injection. Gas reburning is a widely used technology that has been proven to reduce NO_x up to 60% on full-scale applications. Selective non-catalytic reduction (SNCR) is simply the injection of a XN carrier (ammonia, ammonia sulfate, urea, etc.) at appropriate temperature and stoichiometric conditions. Reburning and SNCR maintain a synergistic relationship. SNCR has been proven to be more effective in CO rich environments; this environment can be supplied as a consequence of reburning. The combination of reburning and SNCR has been dubbed Advanced Reburning. The third step in the CombiNO_x process, methanol injection, is intended to convert NO to NO₂. Methanol may also aid in the conversion of SO₃ to SO₂. NO₂ and SO₂ can then be removed in a conventional SO₂ scrubber.

The specific goals of the CombiNO_x project are:

- 70% NO_x reduction at 20% of the cost of selective catalytic reduction;
- NO_x levels at the stack of 60 ppm for ozone non-attainment areas;
- Demonstrate coal reburning;
- Identify all undesirable by-products of the process and their controlling parameters;
- Demonstrate 95% NO₂ removal in a wet scrubber.

Before integrating all three of CombiNO_x's technologies into a combined process, it is imperative that the chemistry of each individual process is well understood. Pilot-scale SNCR tests and the corresponding computer modeling were studied in detail and discussed in the previous quarterly report. This quarterly report will present the results obtained during the pilot-scale advanced reburning tests performed on EER's Boiler Simulation Facility (BSF).

Since methanol injection is a relatively new NO_x control technology, laboratory-scale tests were performed to better understand the conditions at which methanol is most effective. The experimental set-up and results from these tests will be discussed.

2.0 PILOT-SCALE ADVANCED REBURNING TESTS

All of the pilot-scale tests were performed on the Boiler Simulation Facility (BSF) located at EER's Santa Ana test site. The BSF, as displayed in Figure 2-1, is a 1 million Btu/hr, down fired furnace capable of burning both coal and natural gas. Illinois coal was used as the primary fuel for all tests in this reporting period; both coal and natural gas were used as reburn fuels. Quench rate variation within the furnace is made possible through the insertion of cooling rods and cooling panels. The quench rate was maintained at approximately 350°/sec for the advanced reburning tests.

The specific goals of the advanced reburning tests were to:

1. Determine the optimum stoichiometric conditions for agent injection;
2. Identify a temperature window in which SNCR is most effective while simultaneously performing 10% reburning.
3. Optimize burnout air injection location/temperature.

The ability to use coal rather than natural gas as the reburn fuel is economically attractive. Coal reburning was evaluated in detail along with the more common natural gas reburning. In both cases, only 10% reburning fuel was used, as compared to the 20% used in most reburning applications. Reducing the reburning fuel keeps costs down, and reduces slagging and corrosion problems that accompany the highly fuel-rich environment of 20% reburning.

A spraying systems 180° twin fluid nozzle with good atomization properties was used to inject the SNCR agent. A 15% aqueous solution of urea was used, and the transport medium was varied between N₂, O₂, and air. Urea and transport gas flow rates were kept constant for all tests so that atomization would not be a variable.

The nomenclature presented in Figure 2-2 will be used to differentiate between the processes being performed. The region before reburning occurs is the first major section of interest; it will be referred to with a subscript of 1 (SR₁, NO_i). Subscript #2 pertains to the region after the reburn fuel is added (SR₂, NO_{ii}). Agent injection signifies the change to subscript 3, and burnout air addition marks the final change, indicated as NO_f and SR_f.

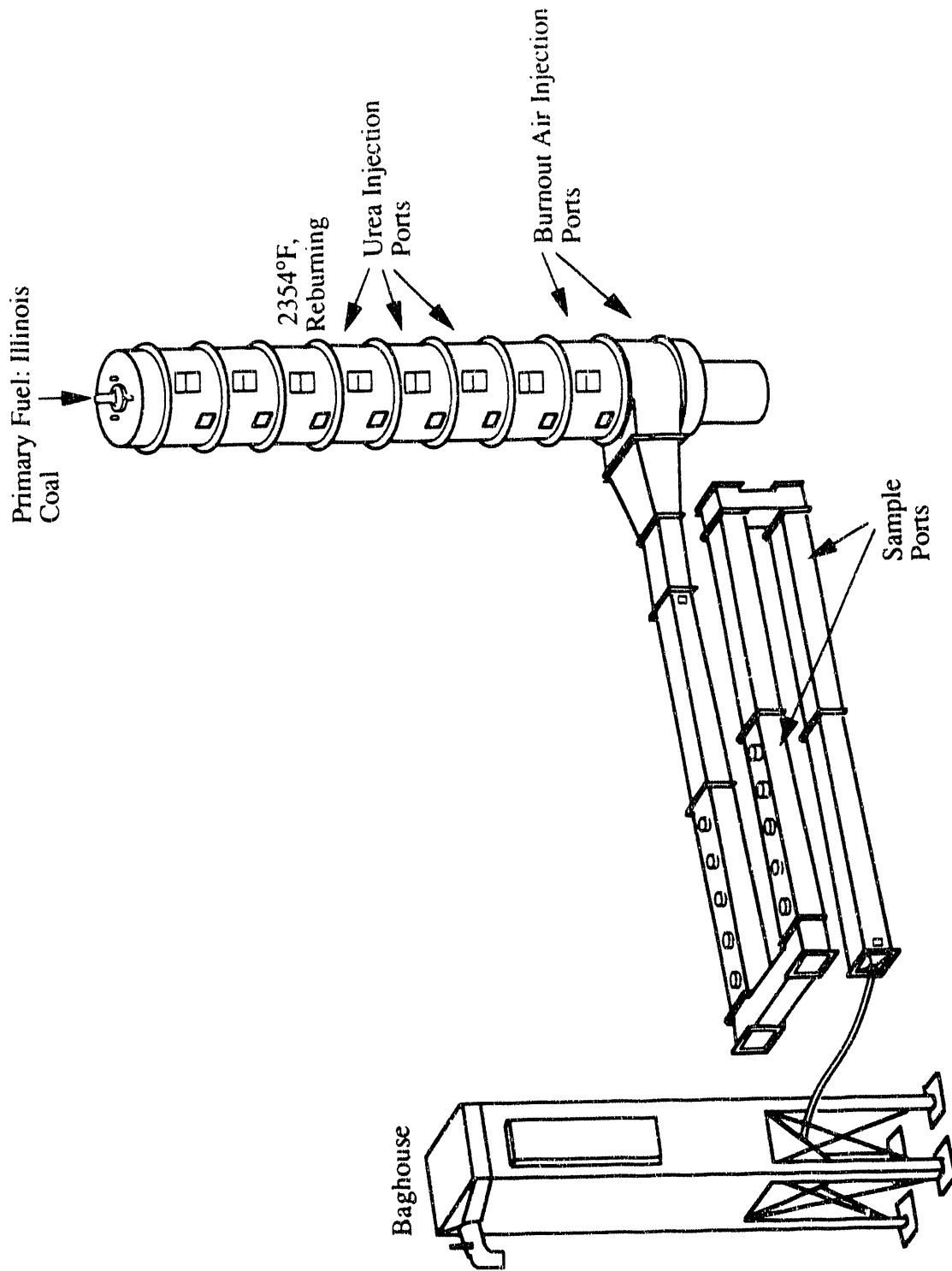


Figure 2-1. Boiler Simulation Facility (BSF).

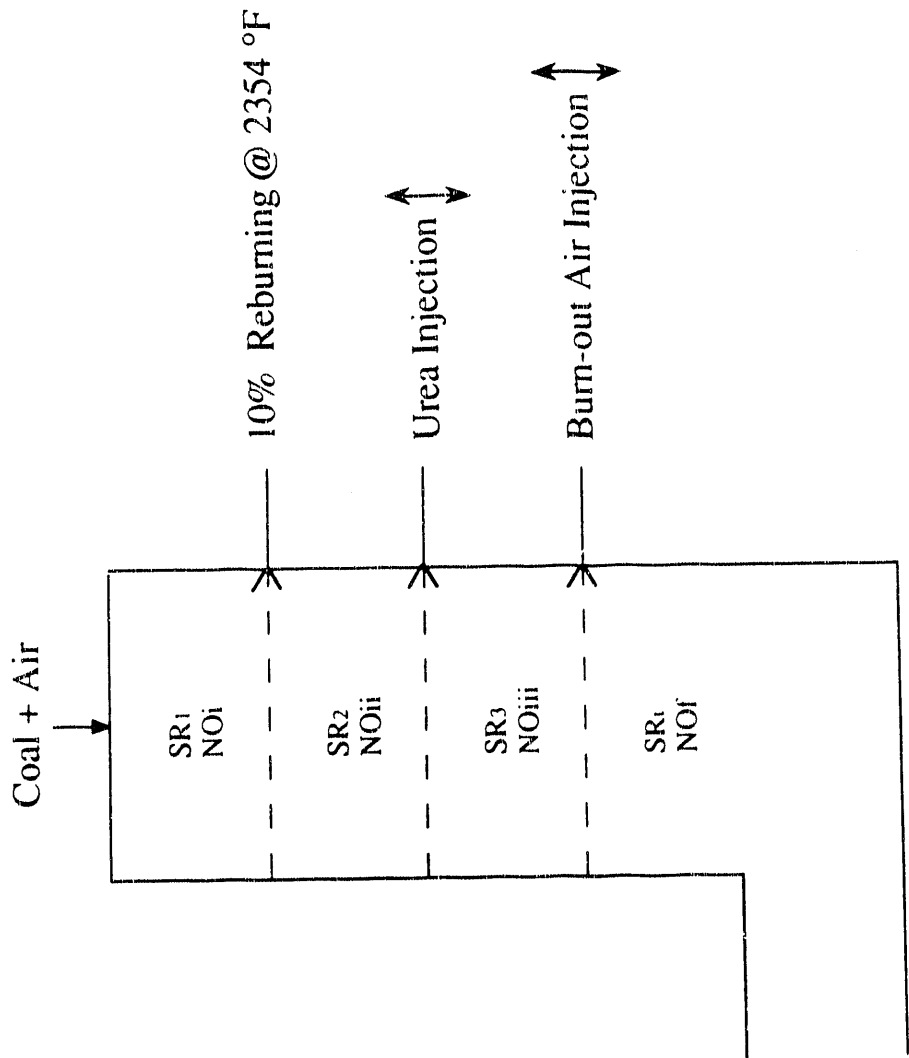


Figure 2-2. Advanced Reburning Nomenclature.

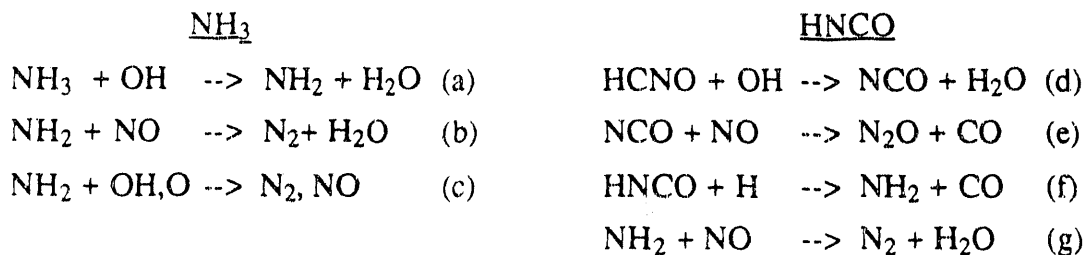
2.1 Advanced Gas Reburning

Advanced gas reburning (AGR) combines the technologies of gas reburning and thermal deNO_x. It was proposed that the combination of the two would reduce NO up to 70%. Tests were performed to evaluate the effects of agent injection temperature and reburn zone stoichiometry.

2.1.1 Effect of Local Stoichiometry for Agent Injection

NO reduction due to SNCR agent injection has been proven to be more effective in a reducing environment. More specifically, the presence of oxidizing CO promotes the deNO_x reactions. This concept prompted the studies involving the side chamber approach that was discussed in Quarterly #3. The idea behind the side chamber approach was to co-inject CO with the agent. It was concluded from these tests that there is an optimum CO level; too much CO in direct contact with the agent will reduce performance. The pilot scale tests have focussed on using reburning to generate CO. The question is, what is the effect of CO level on agent performance?

For the pilot scale advanced gas reburning tests, urea was used for the SNCR agent. The urea decomposition reactions that occur are as follows:



The urea decomposes into two different deNO_x agents, NH₃ and HNCO. Free oxygen and hydroxide radicals play an important role in the NO reduction process. Too many available radicals will produce adverse effects by causing reaction (c) to occur, thereby either creating NO or wasting the agent instead of using it to reduce NO. The goal is to provide enough radicals to motivate

reactions (b) and (g), but, at the same time, keep the conditions fuel rich enough to prevent reaction (c) from taking place.

Thermal deNO_x performance is good inside of a narrow temperature window. The high injection temperature side of the window is limited by an overabundance of radicals (at higher temperatures, more radicals are present). Radicals oxidize the SNCR agent instead of allowing it to reduce NO to molecular nitrogen. The low temperature side of the temperature window is limited by a lack of radicals (low temperature, fewer radicals). The presence of oxidizing CO in the vicinity of the SNCR agent can enhance and broaden the performance window on the low temperature side. For every CO molecule that oxidizes, two radicals are formed:

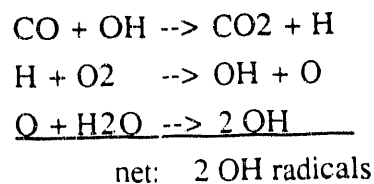


Figure 2-3 demonstrates the effect of CO concentration in the SNCR injection zone. The high temperature side of the curve is approximately the same for all CO levels except for the 5,000 ppm case. It appears as if the additional CO has little effect on the already existing pool of radicals that exists in this high temperature region. 5,000 ppm of CO, however, does have an impact, creating too many radicals for SNCR to be successful. This increase in radicals shifts the optimum temperature towards a cooler region, where fewer radicals are present.

The low temperature side of the curve in Figure 2-3 is limited by the lack of radicals available for oxidation of NH₃ to NH₂, a crucial step for NO reduction. The presence of oxidizing CO (increased radical concentration) in this region allows SNCR to be successful at the lower temperatures, therefore broadening and improving the temperature window.

2.1.2 Effect of Atomizing Fluid

Agent atomizing fluid was varied in order to obtain the desired local conditions for optimum NO reduction. N₂, O₂ and air were evaluated. Results for NO reduction and N₂O formation are displayed in Figure 2-4.

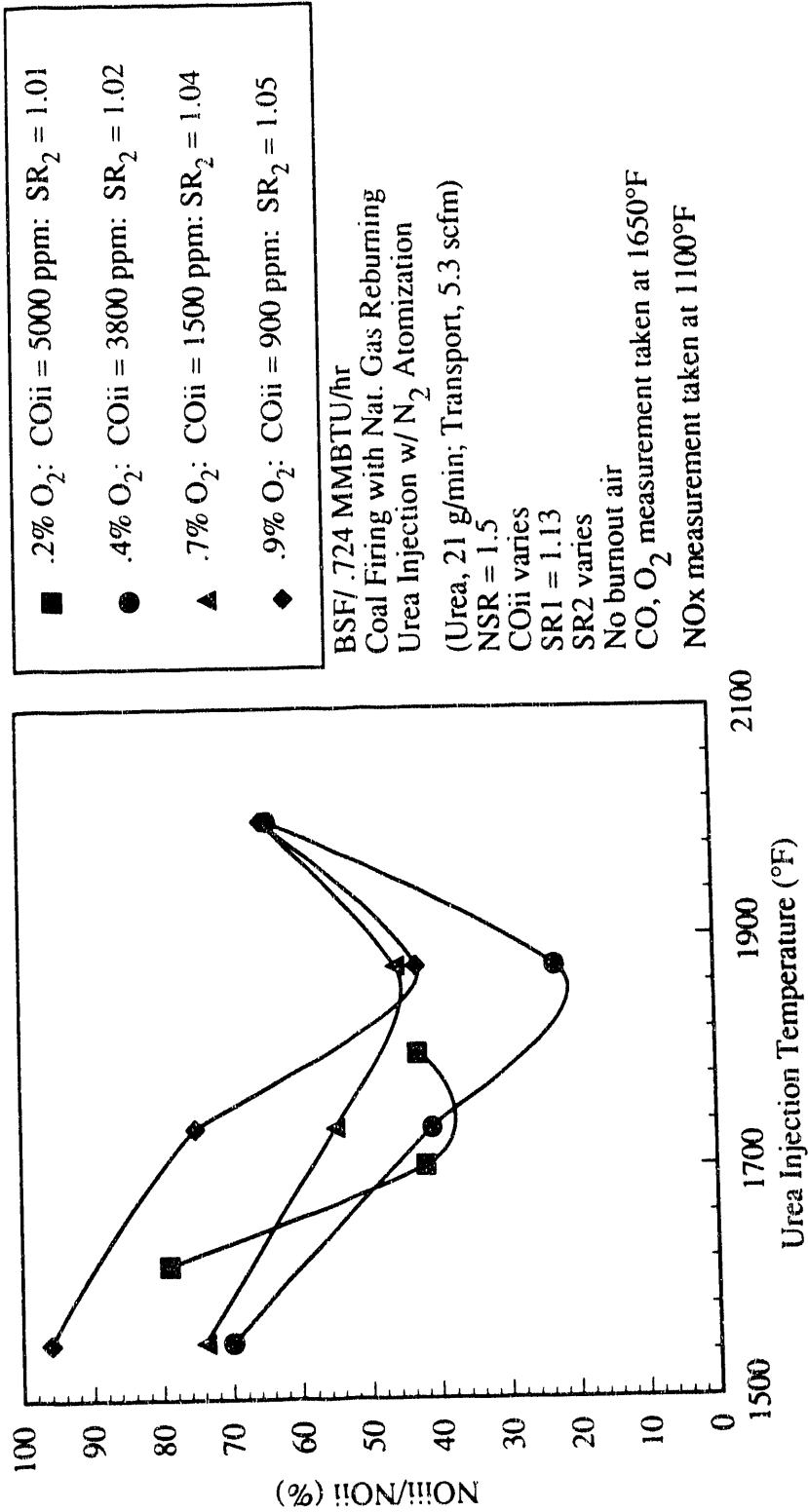


Figure 2-3. Effect of local stoichiometry.

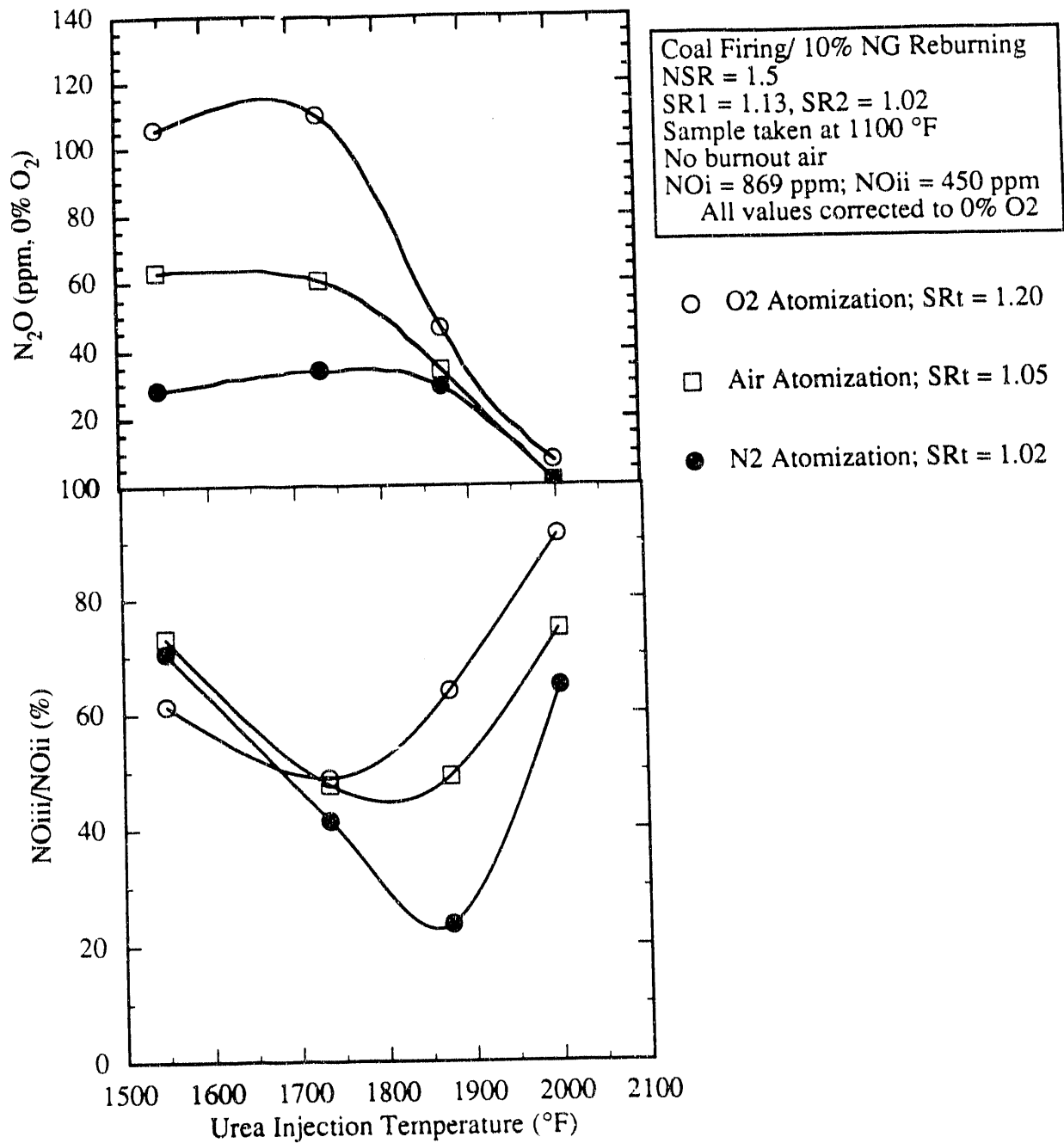


Figure 2-4. Effect of agent atomization.

Again, a SR of 1.02 resulted in optimum NO reductions. When atomizing with O₂ or air, too many free radicals are available to combine with NH₂. This combination will result in either NO formation (equation(c)), or just wasteful oxidation of NH₂. Ideally, the NH₂ will combine with NO to form N₂.

N₂O is a known product of the deNO_x chemistry mentioned earlier. A highly oxidizing environment tends to promote N₂O formation, therefore N₂ atomization resulted in the lowest N₂O emissions. When atomizing with N₂, the reducing environment promotes reactions (f) and (g) over reactions (d) and (e) in the urea chemistry. N₂O production is therefore reduced.

2.1.3 Effect of Agent Injection Temperature

Urea injection temperature was varied while burning coal and reburning with natural gas (Figure 2-5). SR₁ was kept at 1.13 and SR₂ at 1.02; these were determined as optimum conditions in the previous tests. 75% NO reduction occurred when urea was injected at the optimum temperature of 1850°F. N₂O and CO were both at their peak values when NO reduction was best. This insinuates that reaction (c) of the urea chemistry is taking place. Note that burnout air was not added for these tests, therefore CO values are artificially high. The effect of burnout air on CO emissions will be discussed in Sections 2.1.4 and 2.3.2.

2.1.4 Effect of Burnout Air Injection Temperature

As discussed earlier, urea performance suffers when too many O₂ and OH radicals are present. This makes it beneficial to inject the reburning burnout air downstream of the urea. Burnout air injection was varied between 1450° and 1650°F, and the corresponding NO reduction due to advanced gas reburning was observed (Figure 2-6). When burnout air is co-injected with the SNCR agent, NO reduction due to AGR was 72%. NO reduction improved to 76% when the burnout air was moved downstream to 1700°F, with increasingly better reduction as the burnout air was moved even further downstream. There is a tradeoff, however, between the NO reduction and CO emissions. As shown in Figure 2-6, CO fails to burnout when the burnout air is injected below

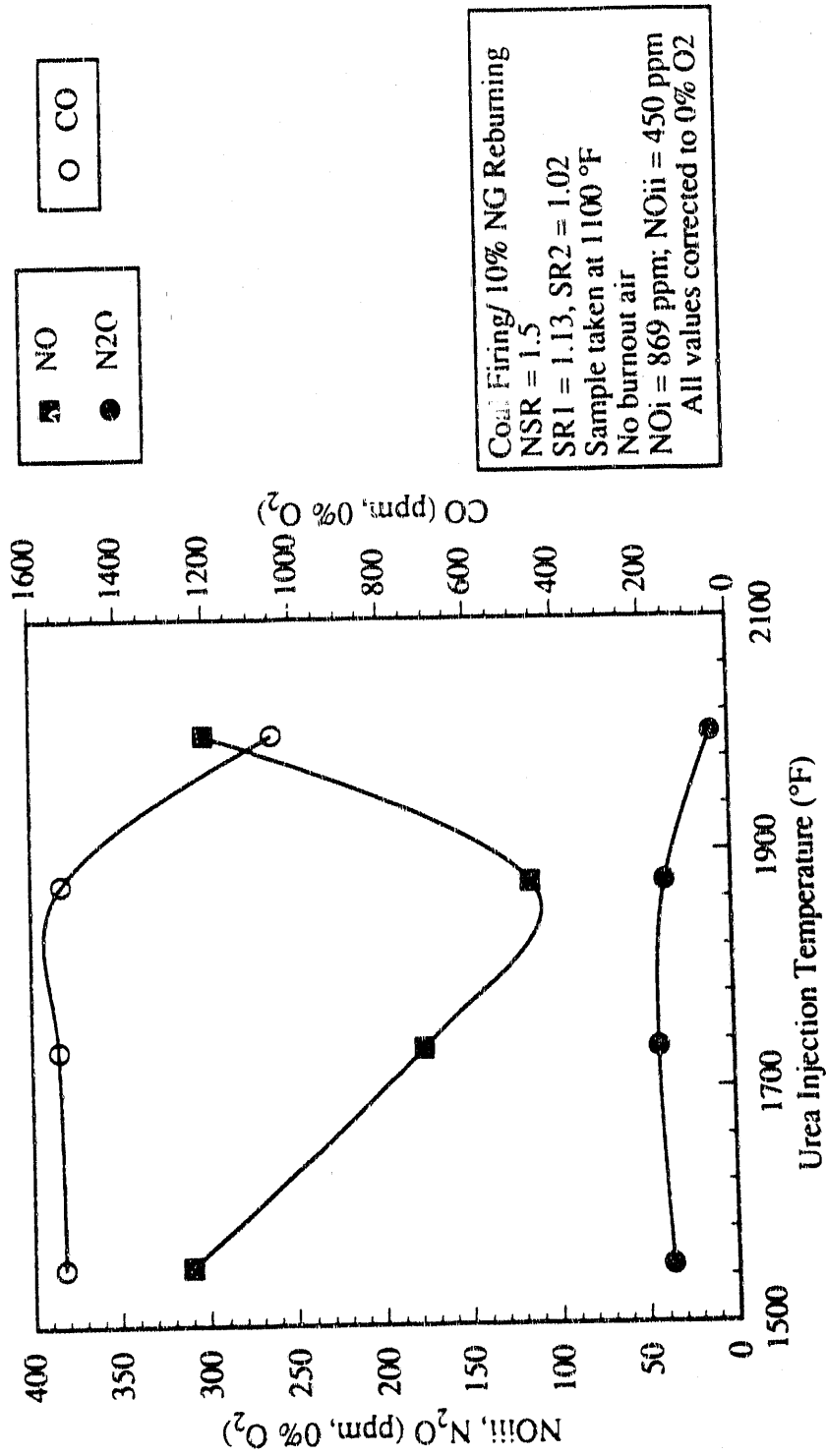


Figure 2-5. Effect of urea injection temperature.

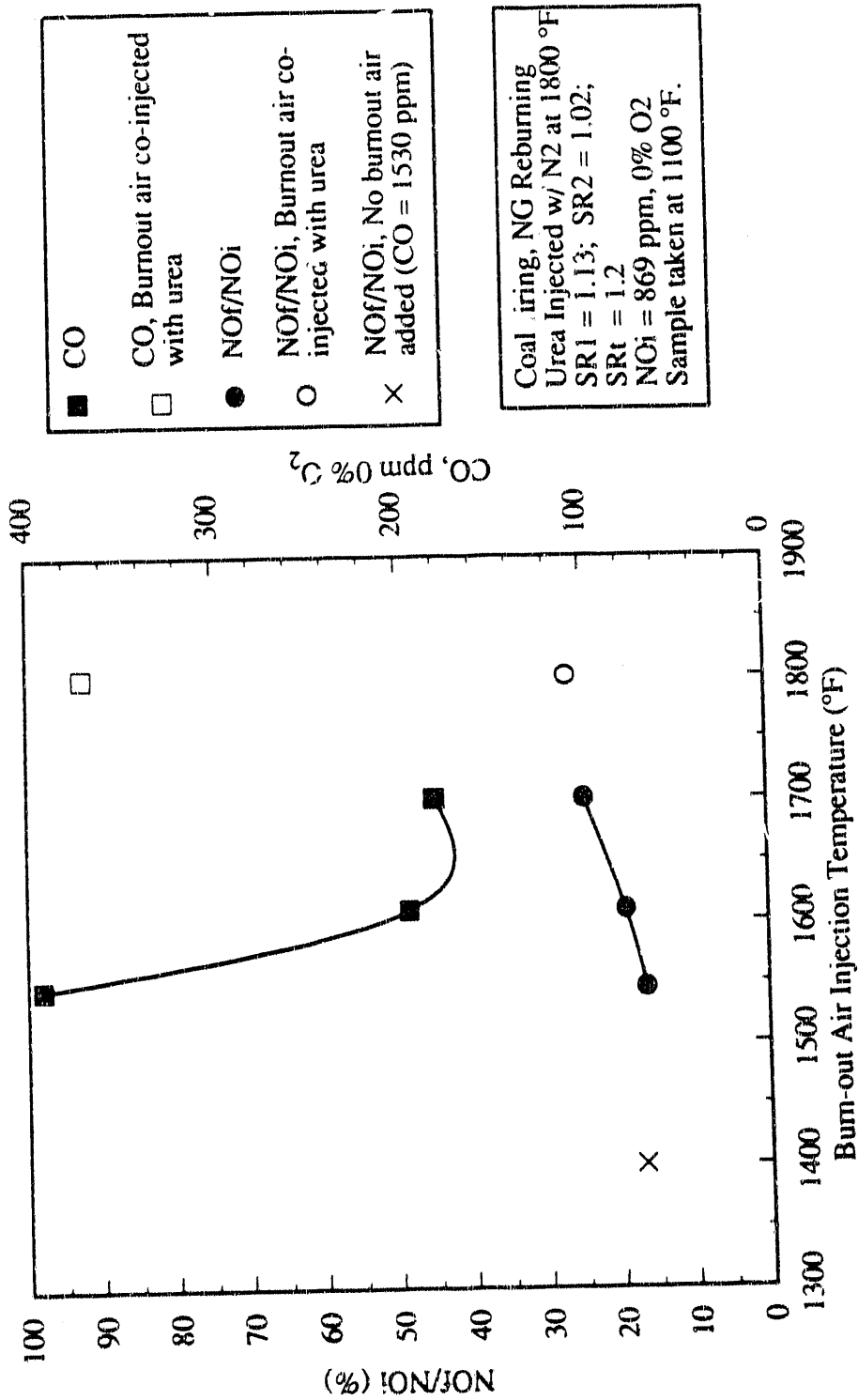


Figure 2-6. Effect of burnout air on CO and NO.

1600°F, therefore burnout air should be introduced at or above 1600°F for optimum performance on the BSF.

2.1.5 Optimized Advanced Gas Reburning Configuration at BSF

Results of the advanced gas reburning experiments suggest that the injection configuration displayed in Figure 2-7 was the most effective at the BSF. 10% gas reburning was performed at 2350°F and resulted in a stoichiometric ratio of 1.02. This SR corresponded to an ideal CO level of 3800 ppm. This CO level may not be ideal in a full-scale application, but the future tower tests will address this. Urea works best when transported with nitrogen (nitrogen simulates steam which would be used in a full-scale application), and should be injected around 1850°F. Burnout air addition at cooler temperatures is better for NO_x control, but only at the expense of high CO levels. A compromise between the two would have to be made. The final stoichiometric ratio was 1.20.

The individual contributions of gas reburning and urea injection to the overall NO_x reduction achieved by advanced gas reburning is shown in Figure 2-8. 10% gas reburning alone reduces NO by 50%. Urea injection by itself is capable of 63% NO reduction when injected in a non-CO promoted atmosphere (SR = 1.2). Together, reburning and urea injection can reduce 83% of total NO, resulting in a final NO concentration of 127 ppm at 3% O₂.

2.2 Advanced Coal Reburning

Advanced coal reburning (ACR) tests were performed in the same fashion as AGR. SNCR, reburning zone stoichiometry, and agent and burnout air injection temperatures were optimized.

2.2.1 Effect of Agent Atomization

N₂ and air were compared as agent atomizations. Results are displayed in Figure 2-9. As in the natural gas reburning tests, N₂ resulted in better NO reductions and lower N₂O production

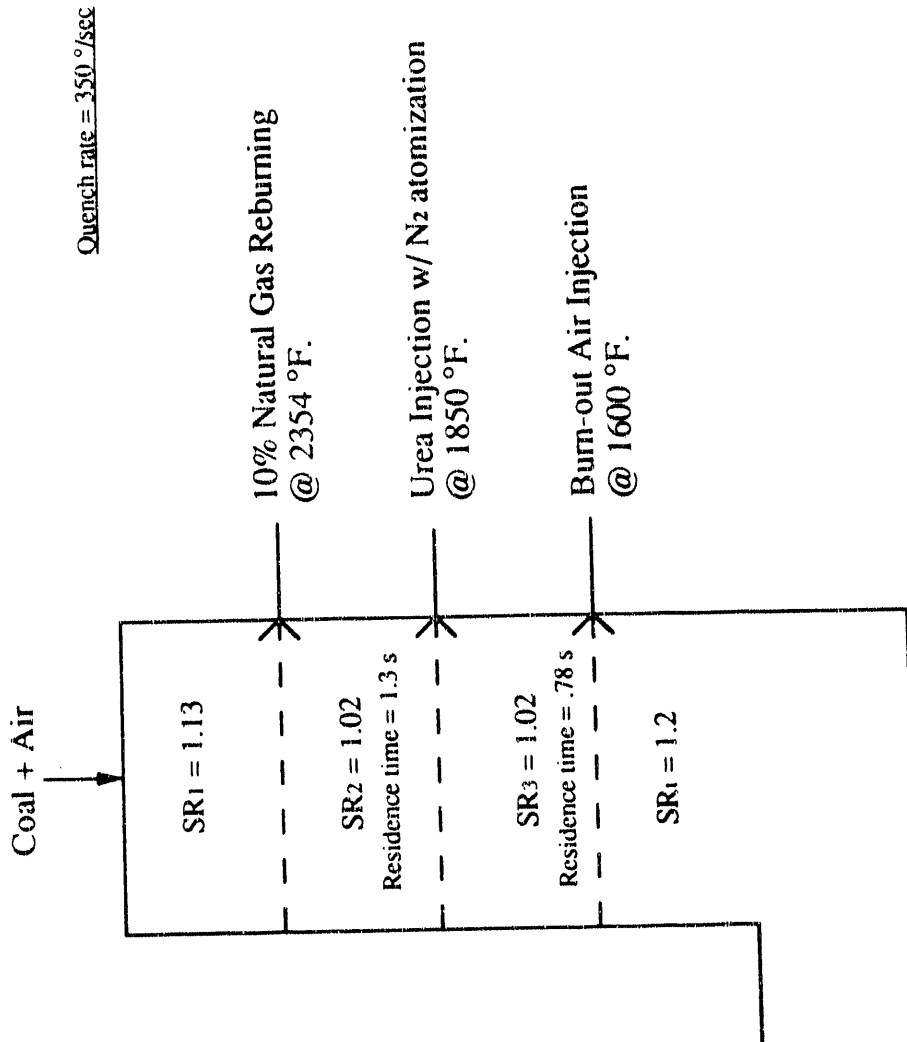


Figure 2-7. Optimum Advanced Gas Reburn Configuration.

Coal Firing, NG Reburning
 SR1 = 1.13; SR2 = 1.02; SRt = 1.2
 Samples taken at 1100 °F
 When applicable:
 Urea injected w/ N₂ at 1800 °F
 Burn-out air injected at 1545 °F
 NOi = 869 ppm 0% O₂

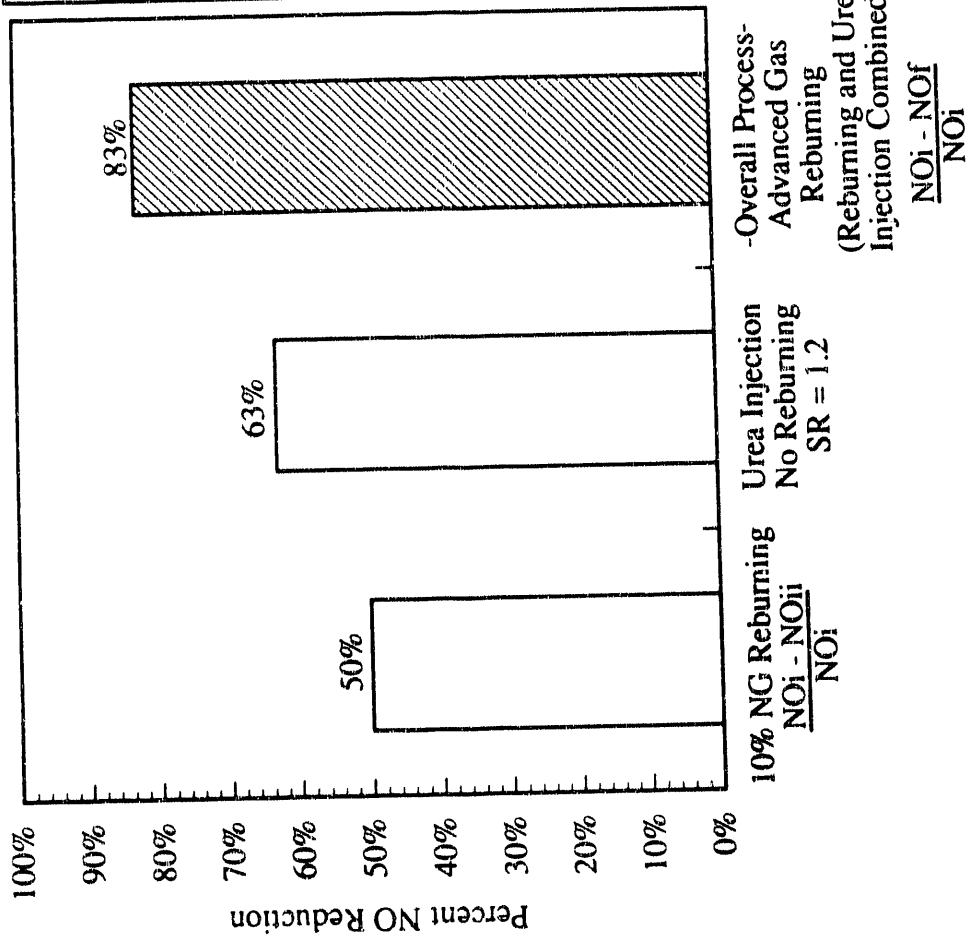


Figure 2-8. Breakdown of NO reduction to individual processes.

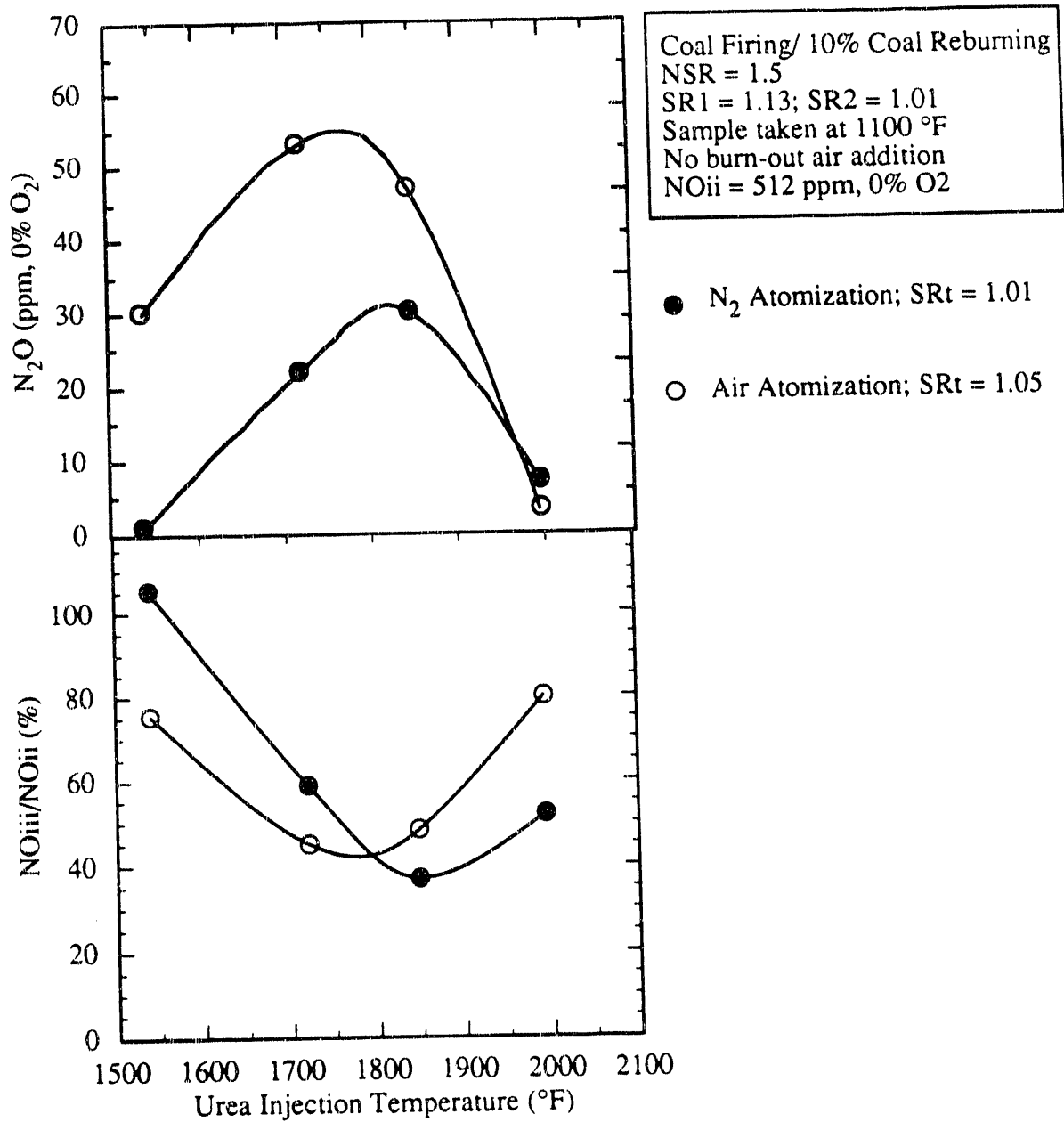


Figure 2-9. Effect of agent atomization.

than the air atomization. This can be contributed to the radical availability as explained in Section 2.1.2.

2.2.2 Effect of Agent Injection Temperature

Figure 2-10 shows that, when injected at 1850°F, urea can reduce NO up to 64% in a coal fired, coal reburning furnace. CO remained constant throughout the urea injection and N₂O increased slightly, reaching a maximum of 40 ppm.

2.2.3 Effect of Burnout Air Injection Temperature

Burnout air injection was varied between 1450° and 1650°F, and the corresponding NO reduction due to advanced coal reburning was observed (Figure 2-11). When burnout air is co-injected with the SNCR agent, NO reduction due to ACR was 73%. NO reduction improved to 84% when the burnout air was moved downstream to 1650°F, however, it did not improve much more as burnout air was moved even further downstream. CO fails to burnout when the burnout air is injected below 1575°F, therefore burnout air should be introduced at approximately 1600°F.

2.2.4 Optimum Advanced Coal Reburning Configuration at BSF

The results of the advanced coal reburning tests indicate that the injection configuration displayed in Figure 2-12 will produce the best NO reduction at the BSF. 10% coal reburning occurred at 2350°F producing a stoichiometric ratio of 1.01. Urea was injected with the use of a twin fluid 180° nozzle and nitrogen carrier at 1850°F. Burnout air was injected at approximately 1600°F producing a final stoichiometry of 1.20.

Figure 2-13 displays the NO reduction performed by the individual processes of coal reburning and urea injection. 10% coal reburning reduced NO by 54%, and urea contributed a 73% NO reduction when injected in the reburning zone (SR = 1.01). The overall advanced coal reburning process reduced NO by 87%, resulting in a final NO of 97 ppm at 3% O₂.

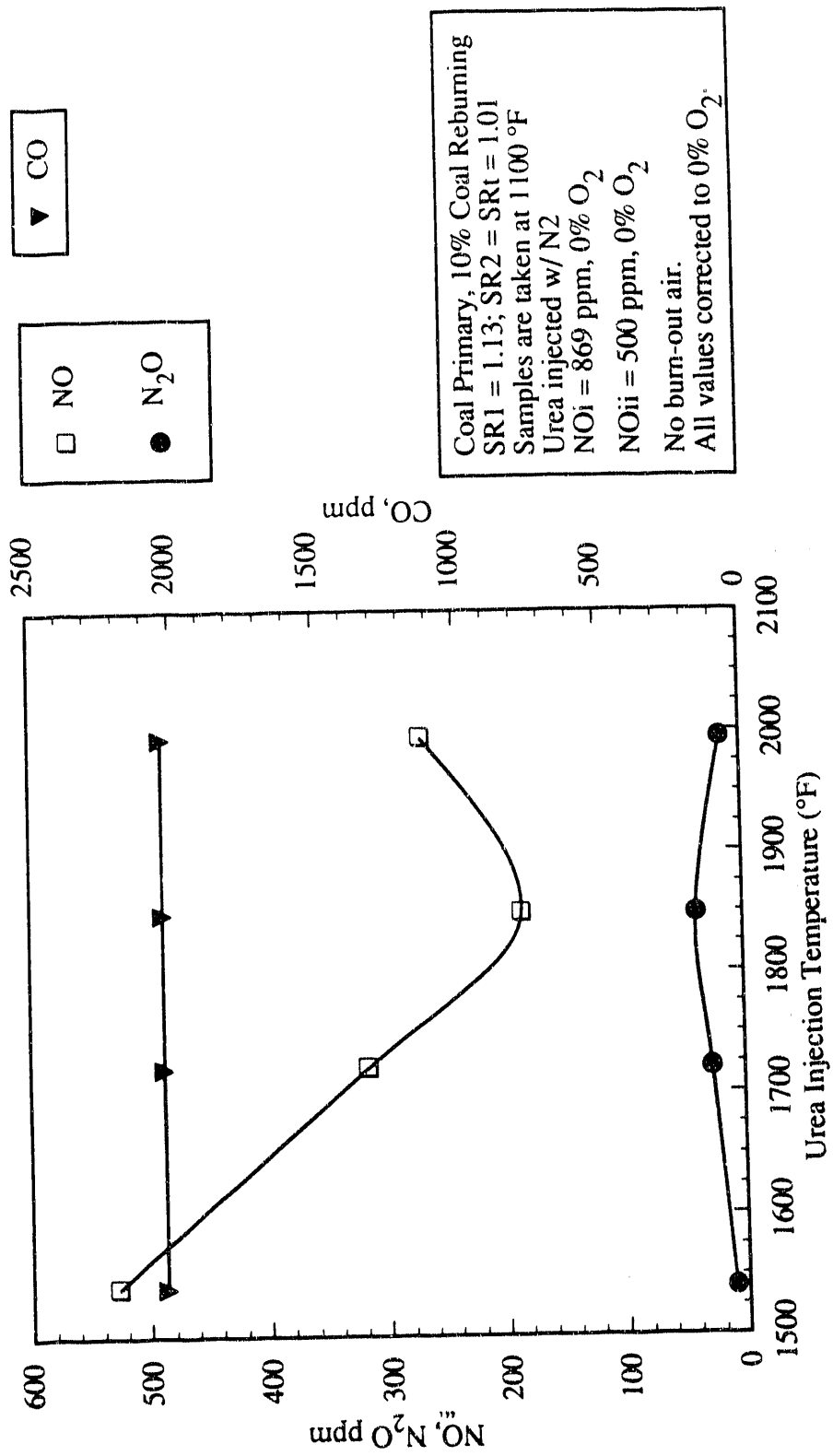


Figure 2-10. Effect of urea injection temperature.

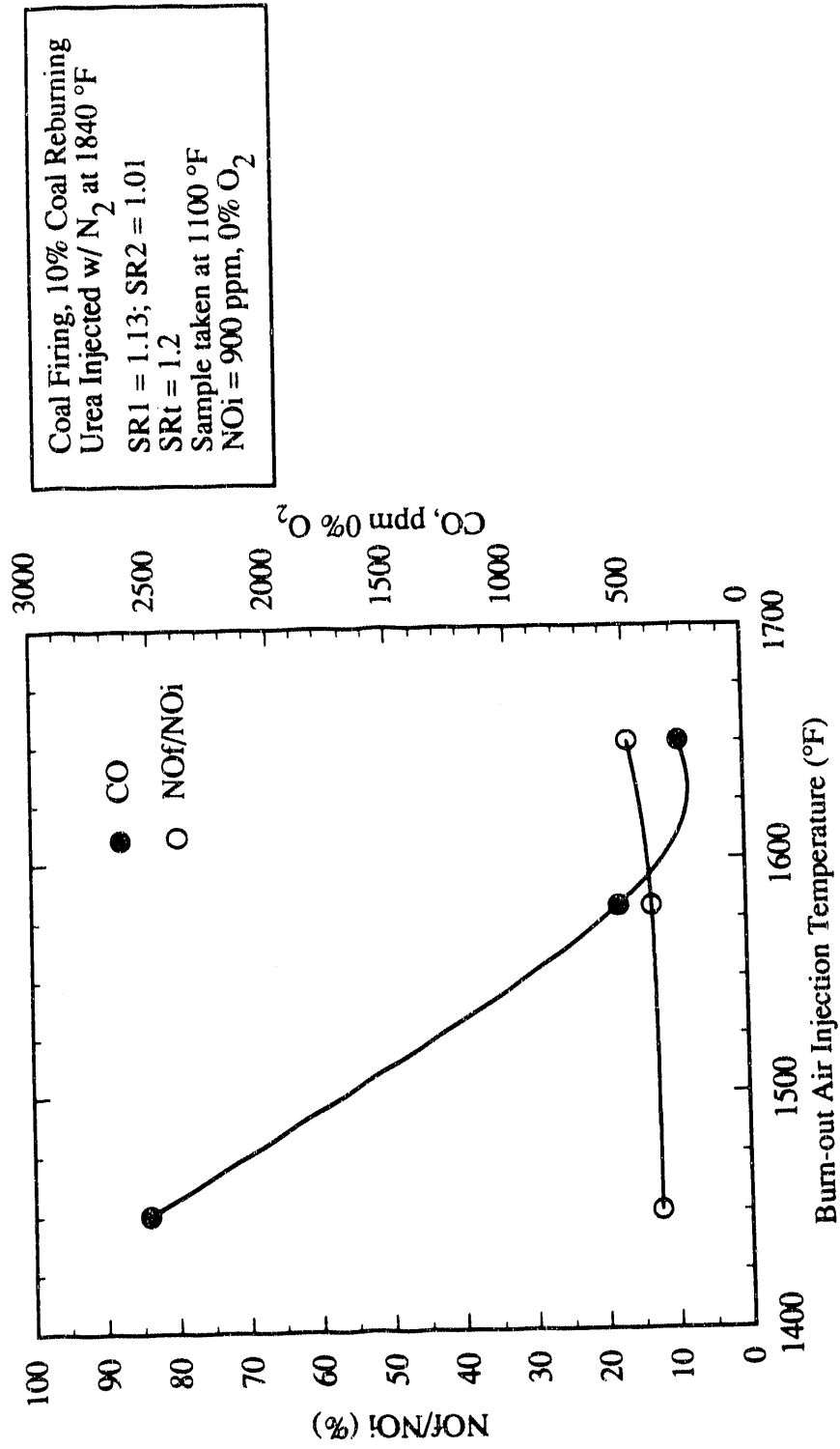


Figure 2-11. Effect of burnout air injection temperature.

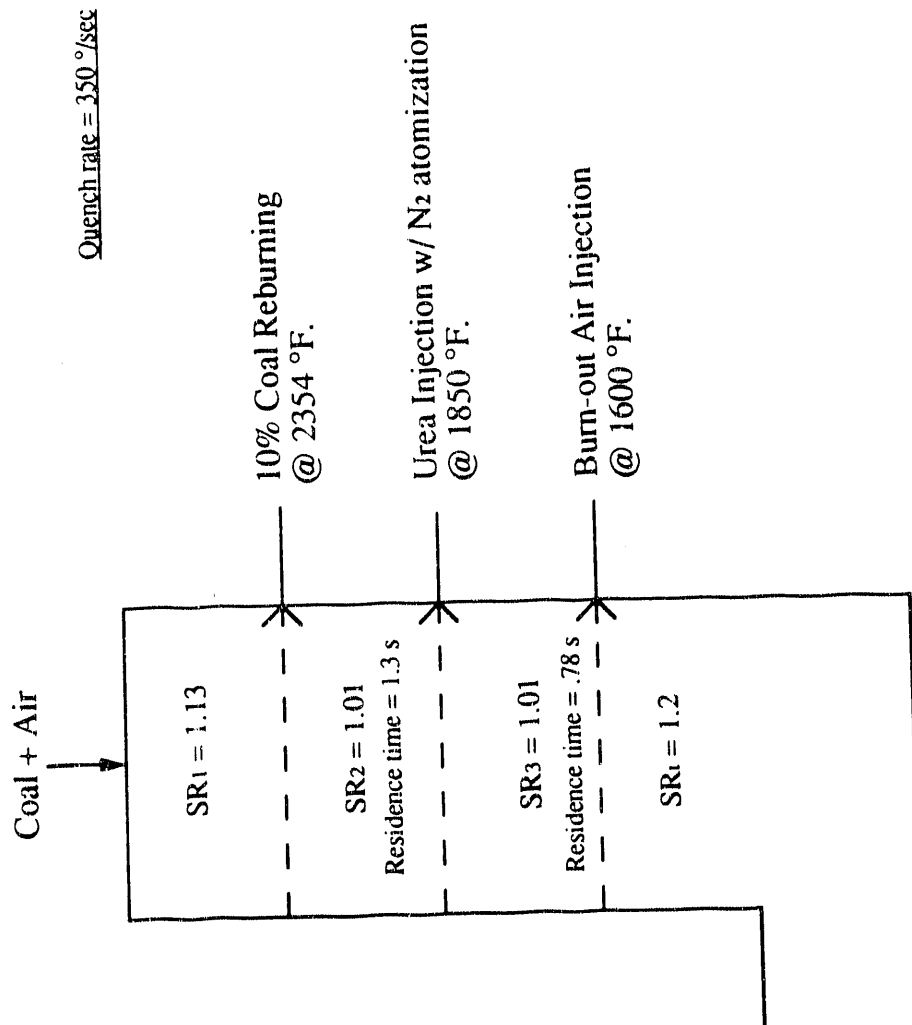


Figure 2-12. Optimum Advanced coal rebum configuration.

Coal Firing, Coal Reburning
 SR1 = 1.13; SR2 = 1.01; SRt = 1.2
 Samples taken at 1100 °F
 When applicable:
 Urea injected w/ N₂ at 1840 °F
 Burn-out air injected at 1450 °F
 NOi = 869 ppm, 0% O₂

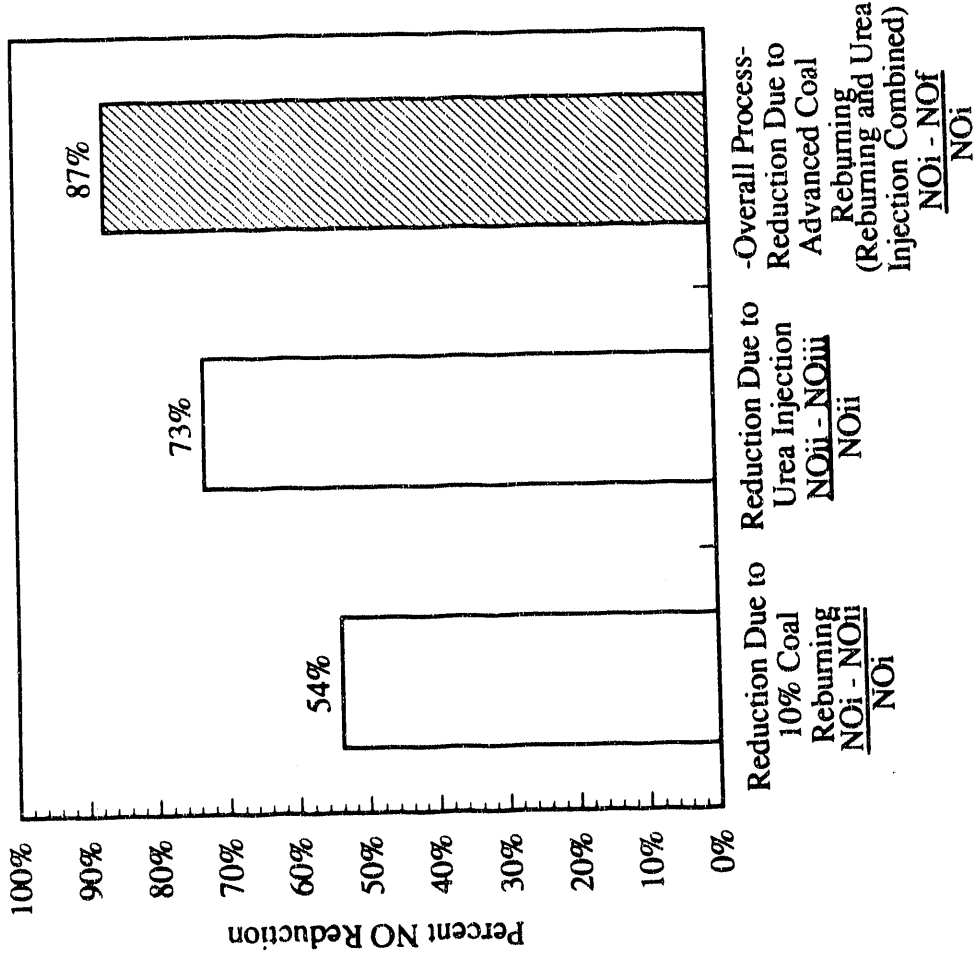


Figure 2-13. Breakdown of NO reduction to individual processes.

2.3 By-Product Emissions for Advanced Reburning

Whenever the concentration of a species in a flue gas has been reduced, the threat of other species increasing persists. NO_x reduction performed by urea injection introduces the possibility of forming ammonia slip. N_2O production has also been associated with urea injection. Reburning may increase CO levels or prevent complete burnout of the ash carbon. This section will describe the by-products created while performing advanced reburning on the BSF.

2.3.1 CO and N_2O Emissions

Figure 2-14 displays the CO and N_2O formation that occurs for both advanced natural gas reburning and advanced coal reburning. Advanced coal reburning resulted in approximately 450 ppm more CO than advanced gas reburning. This difference was noted prior to the injection of urea, therefore the elevated CO level is a result of the coal reburning and not the urea injection. Notice that burnout air was not injected, therefore incomplete burnout of the CO is understandable.

N_2O emissions were as high as 43 ppm while reburning with natural gas, and 39 ppm with coal. Again, N_2O is a known product of the deNO_x reactions, and maintaining a reducing environment helps minimize N_2O emissions. Equation (e) in Section 2.1.1 indicates that the presence of O and OH radicals will initiate the N_2O forming reactions over the other reactions.

2.3.2 Ammonia Emissions

Ammonia slip is always a concern that is associated with urea injection. If the urea is injected at too cool of a temperature, complete burnout of the ammonia will fail to occur. Figure 2-15 displays the ammonia levels for both advanced gas and coal reburning. Average ammonia levels for coal reburning were 2.4 ppm, and for natural gas reburning 1.7 ppm. Even though these levels are small, ammonia slip needs to be closely monitored, especially for advanced reburning systems that may not be optimized.

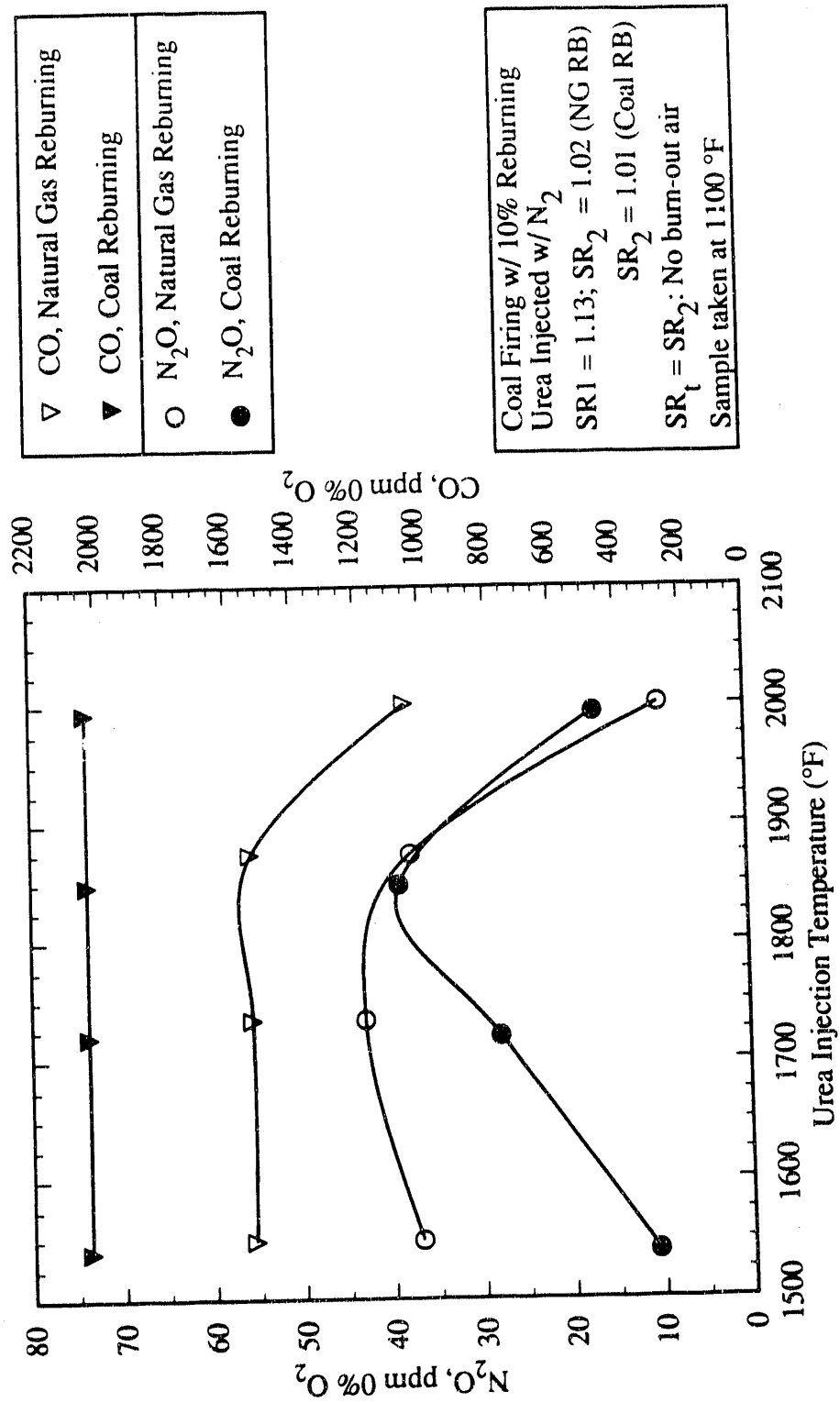


Figure 2-14. CO and N₂O emissions for gas and coal advanced reburning.

Coal Firing, 10% Reburning
 Urea Injected w/N₂ at 1780 °F
 SR1 = 1.13, SR2 = 1.02 (NG)
 SR2 = 1.01 (Coal)
 SRT = 1.2
 Sample taken at 1100 °F

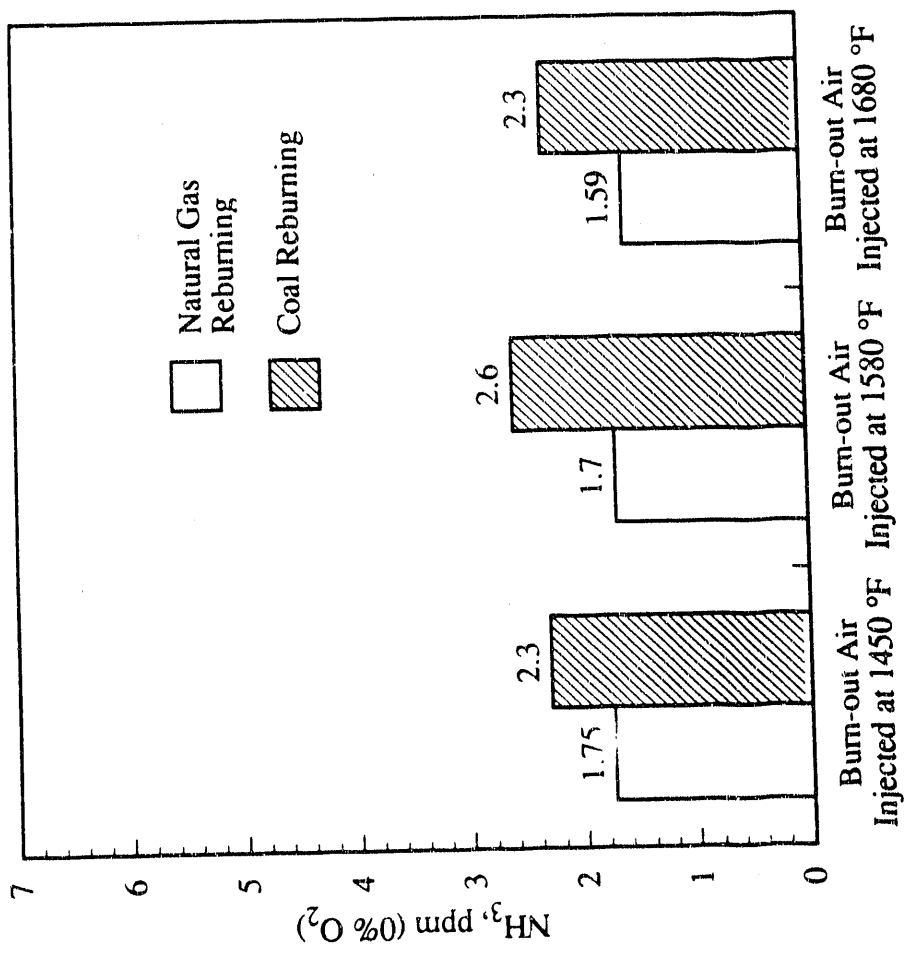


Figure 2-15. Ammonia emissions for natural gas and coal reburning.

2.3.3 Carbon Burnout

Ash samples collected from the furnace while performing the advanced reburning tests were dark black in color, suggesting a high carbon content. An outside lab analysis was performed to determine how much carbon still existed in the captured ashes. Results are displayed in Figure 2-16. Two uncontrolled cases (straight coal firing with no reburning) with different oxygen environments were examined. Samples were also taken while performing both gas and coal reburning and varying burnout air injection temperature. As would be expected, coal reburning resulted in a greater carbon in ash content than natural gas reburning. Even with the slow quench rate and excellent mixing properties of the BSF, 3.45% carbon in ash was still detected for one coal reburning case. This indicates that further examination of coal reburning must be conducted to assure carbon burnout is not an associated problem.

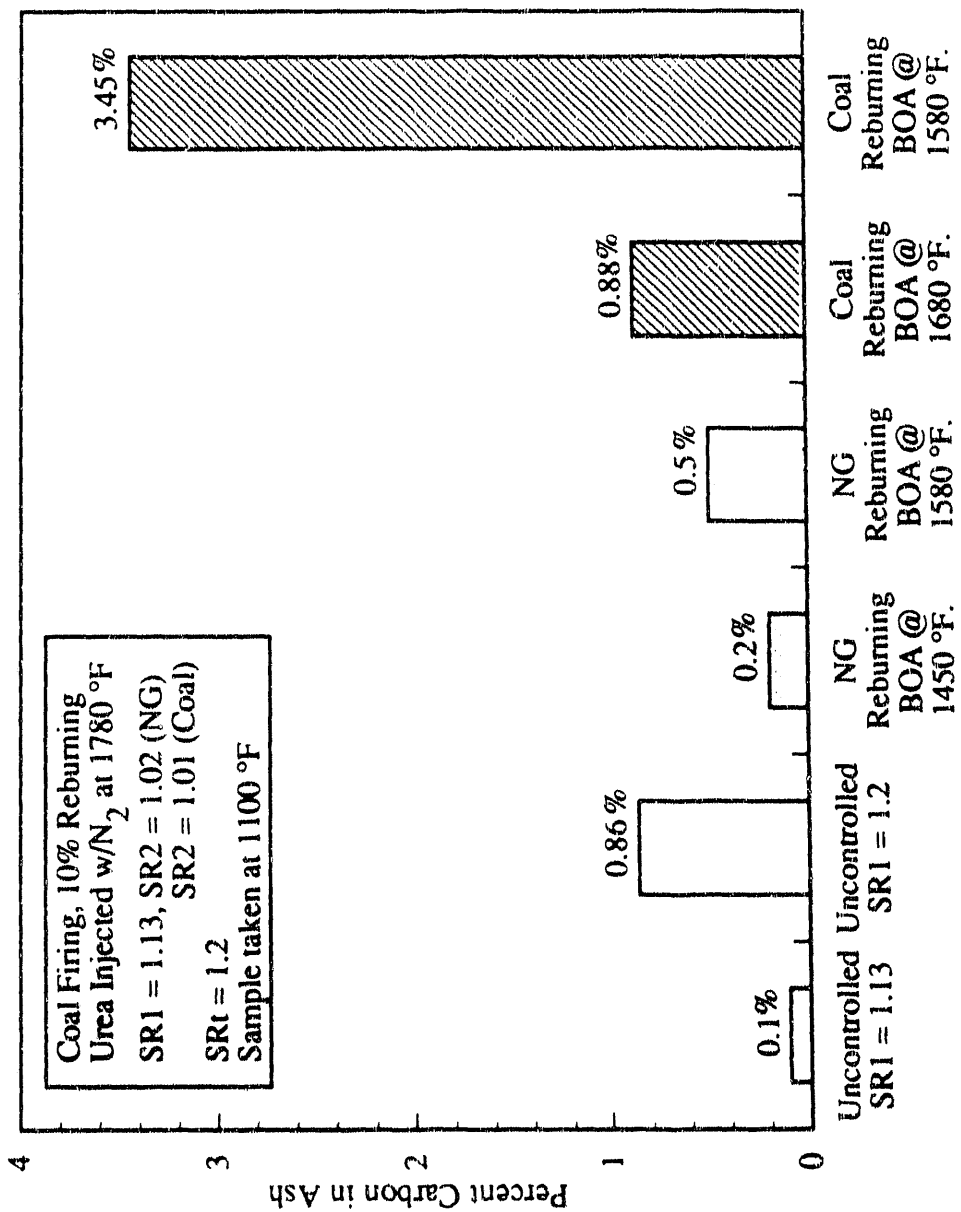


Figure 2-16. Percent carbon remaining in ash for both natural gas and coal reburning.

3.0 LAB-SCALE METHANOL INJECTION TESTS

The methanol injection step of the CombiNO_x process serves to convert NO to NO₂. The lab-scale tests were designed to generate a data base to define the following:

- effect of methanol injection temperature for a given flue gas composition;
- impact of amount of methanol injected on the NO conversion efficiency;
- impact of local stoichiometry on NO conversion efficiency;
- impact of initial NO concentration on NO conversion efficiency;
- impact of the above on the formation of byproducts such as CO and formaldehyde;
- impact of residence time on methanol effectiveness;
- effect of ammonia presence on NO conversion efficiency.

3.1 Experimental Set-Up

The experimental set-up, displayed in Figure 3-1, consists of a gas blending system which generates a simulated flue gas. Methanol is added to the dry flue gas via a saturator using N₂ as the carrier gas. The amount of methanol is adjusted by varying the bath temperature. Knowledge of the vapor pressure of methanol allows the methanol concentration to be calculated. A known amount of water is added to the simulated flue gas via a precision metering pump.

The mixture is rapidly heated to a set temperature in a quartz tube reactor where it remains for a finite, variable length of time. It is assumed that the temperature rise is an ideal step function. Finally, the flue gas passes through a water trap on its way to the NO_x, SO₂, O₂, and CO analyzers. The NO_x analyzer will be operated in NO mode only. The final NO level will be compared to the initial NO level to determine the conversion efficiency.

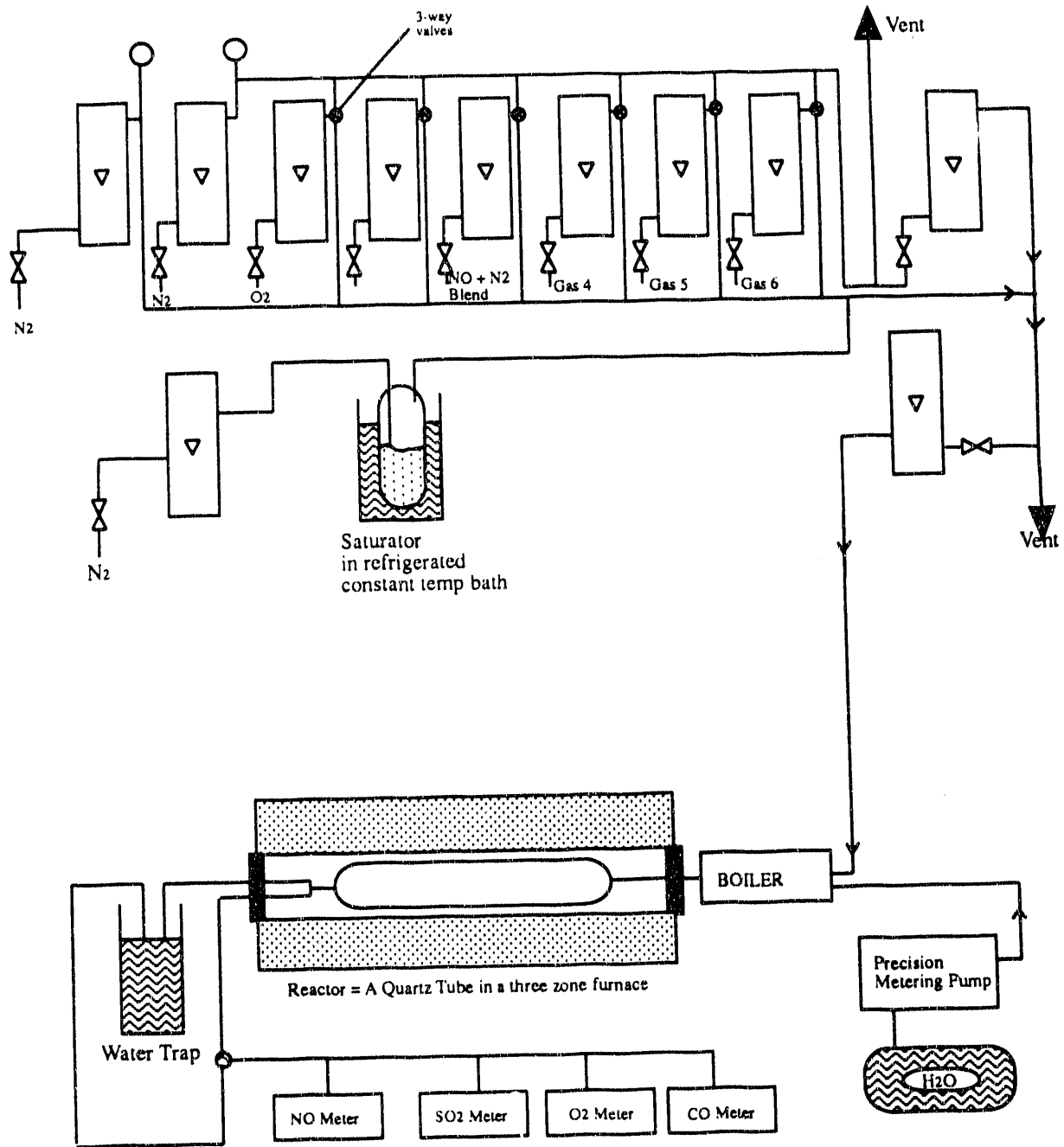
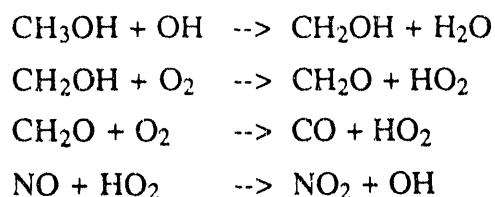


Figure 3-1. Methanol Injection Lab-Scale Experimental Set-Up.

3.2 Test Results

When methanol is injected into the flue gas at ideal conditions, a conversion of NO to NO₂ occurs by means of the following chemical process:



It was of interest to determine at which conditions these reactions are most likely to occur. The variables taken into consideration were injection temperature, stoichiometry, methanol concentration, initial NO concentration, and residence time.

3.2.1 Effect of Methanol Injection Temperature

For an initial NO of 100 ppm and a methanol-to-NO ratio of 1.16, NO reductions were observed as the methanol injection temperature was varied (Figure 3-2). The optimum methanol injection temperature for these conditions was concluded to be approximately 1470°F.

Figure 3-2 also displays the resulting CO production that occurs as methanol injection is optimized. According to the methanol chemistry mentioned previously, a 1 to 1 ratio of methanol injected to CO produced should occur (assuming perfect mixing). Results show this to be the case, with slight room for imperfect mixing affects. Approximately 100 ppm of CO was formed when 116 ppm of methanol was injected.

3.2.2 Effect of Stoichiometry

As noted above, oxygen is necessary for the NO to NO₂ conversions to occur. The more oxygen available, the better the chance for the methanol process to be completed. Figure 3-3 shows that experimental results confirm this to be true. As oxygen levels are increased, the methanol

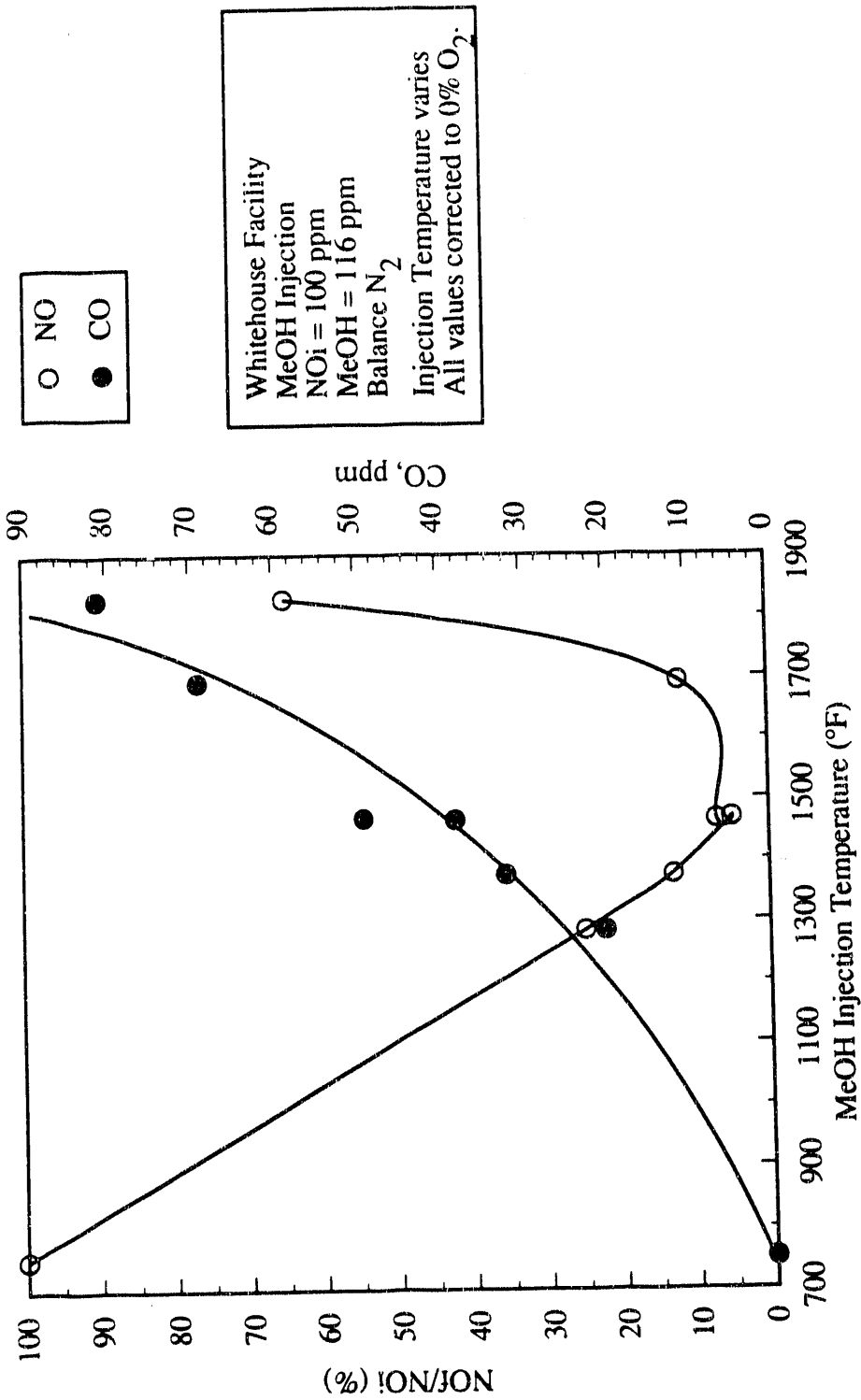


Figure 3-2. Effect of methanol injection temperature on NO and CO.

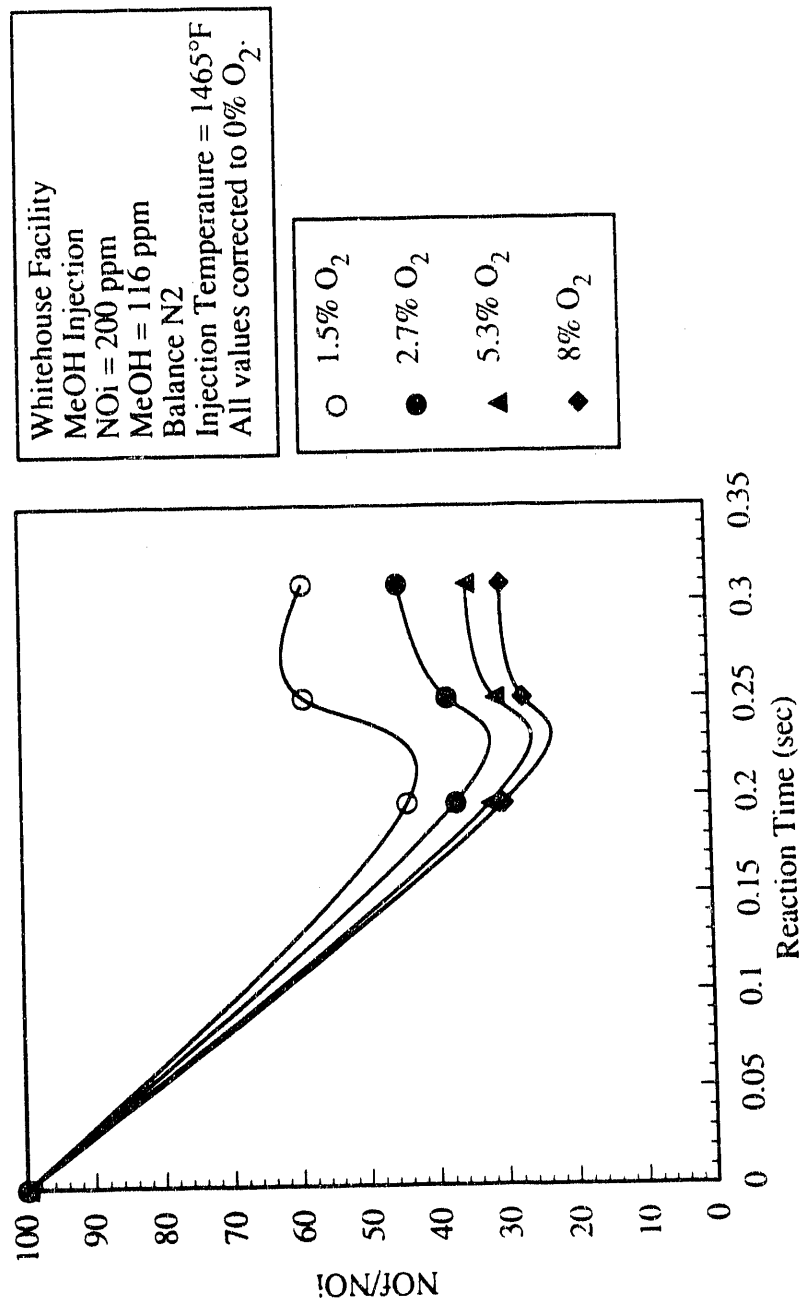


Figure 3-3. The effect of O₂ on NO conversion.

becomes more effective in its NO-to-NO₂ conversion. This improvement, however, tapers off at 5% O₂.

Figure 3-4 displays the CO trends that occur as O₂ is varied. All cases remain within 15 ppm of each other with no particular oxygen level performing consistently better or worse than the others. 116 ppm of methanol is injected, therefore 116 ppm of CO formation is expected if perfect conditions were to exist. Experimental results showed that approximately 88 ppm of CO was formed for the optimum condition.

3.2.3 Effect of Methanol Concentration

NO conversion was found to improve as methanol concentration was increased (refer to Figure 3-5). However, the improvement tapered off for methanol concentrations above 510 ppm (MeOH/NO_i = 5.1), a diminishing returns effect.

Again, as demonstrated by the methanol chemistry, CO is expected to increase in a 1-to-1 ratio with NO as it is converted to NO₂. Figure 3-6 displays the CO emissions as methanol concentration is increased. It should be noted that, even though methanol concentrations above 510 ppm do not improve the NO to NO₂ conversion, CO production continues to increase. Appropriate amounts of methanol should be carefully considered to avoid unnecessary formation of CO.

3.2.4 Evaluate Residence Time

It was of interest to see how residence time effected the methanol NO to NO₂ conversion. Allowing more time for the conversion to occur should be beneficial to the process. The results are displayed in Figure 3-7.

This figure shows NO conversion as a function of reaction time for various methanol injection temperatures. When methanol was injected at 752°F, temperatures were too cold for any NO-to-NO₂ conversions to occur, no matter how long the gases remained in contact with each other. As temperatures were increased to 1092° and 1283°F, an extended residence time of 1 full

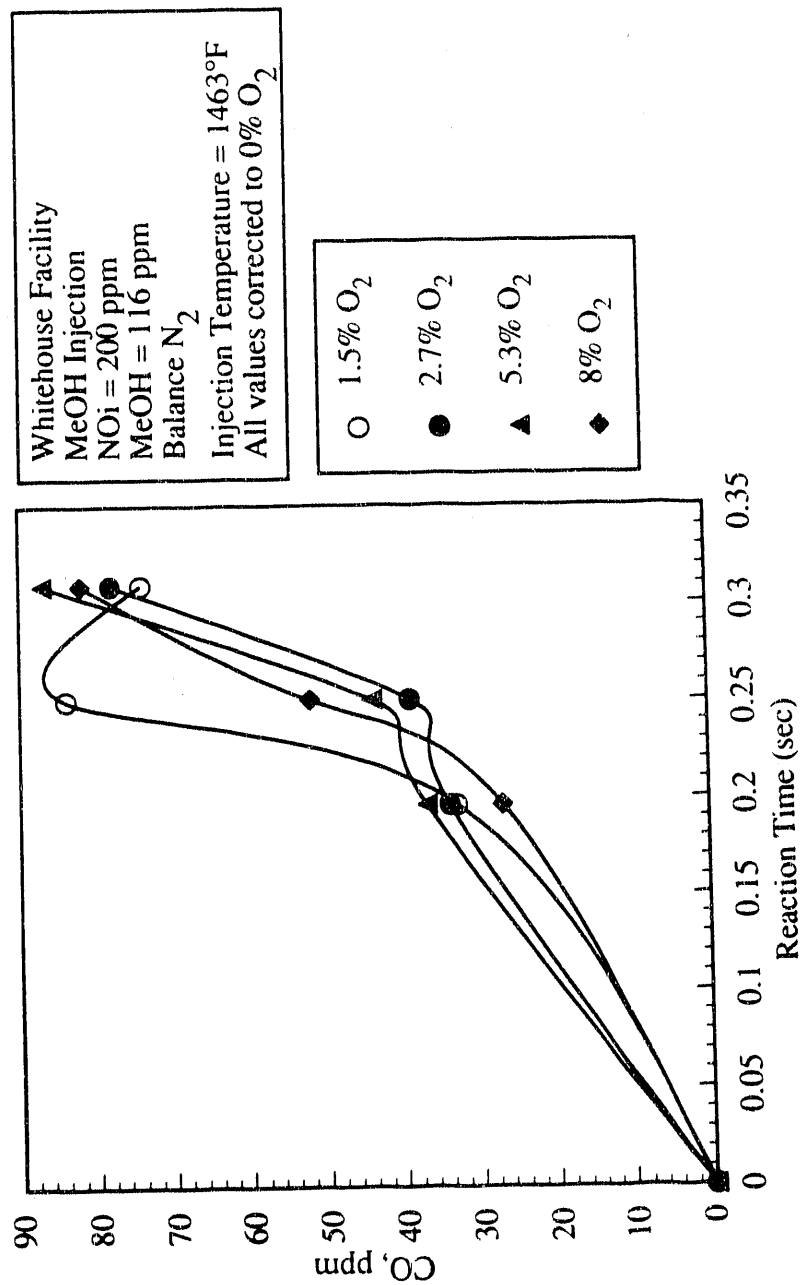


Figure 3-4. The effect of O₂ on CO production.

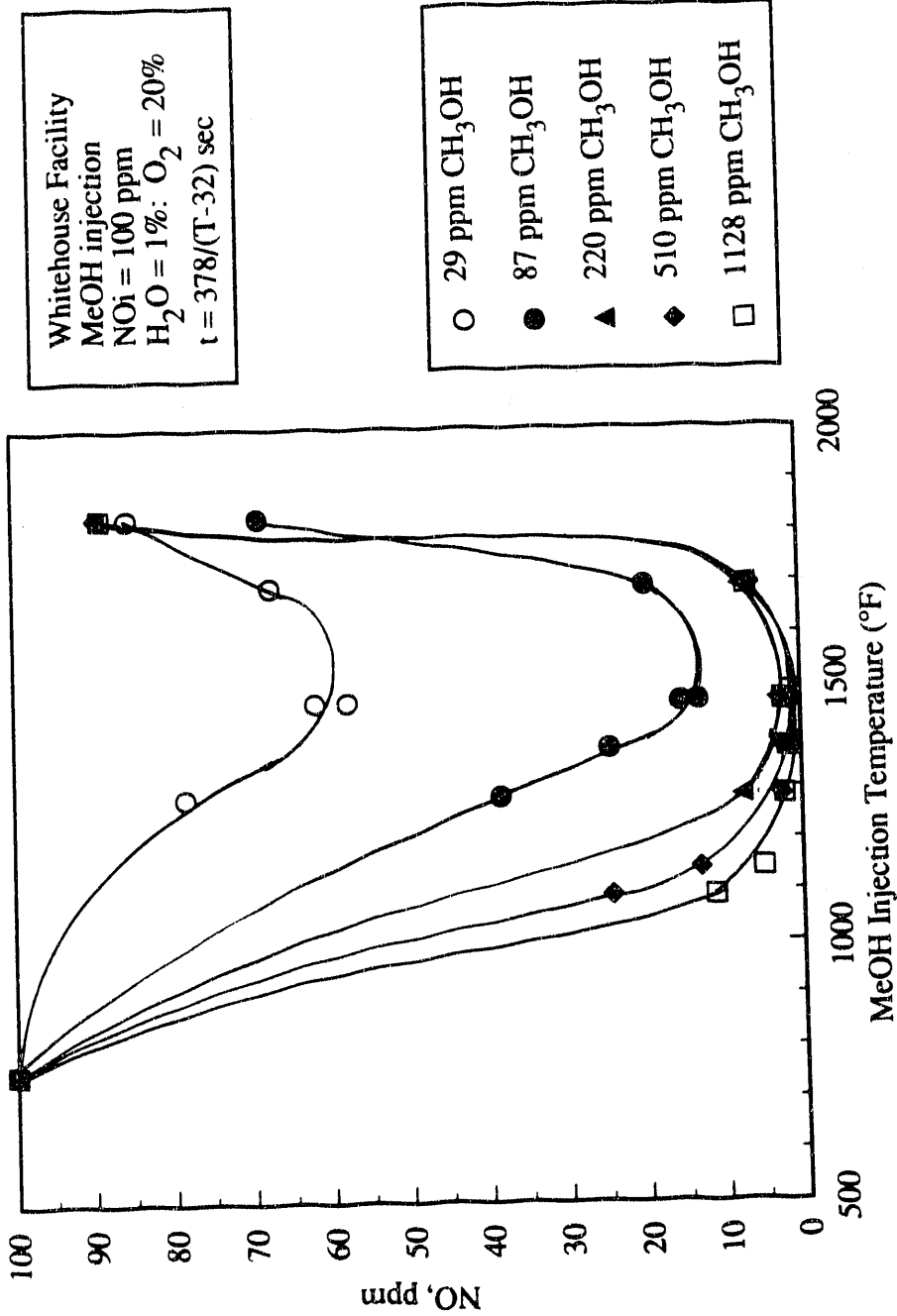


Figure 3-5. Effect of methanol concentration on NO to NO₂ conversion.

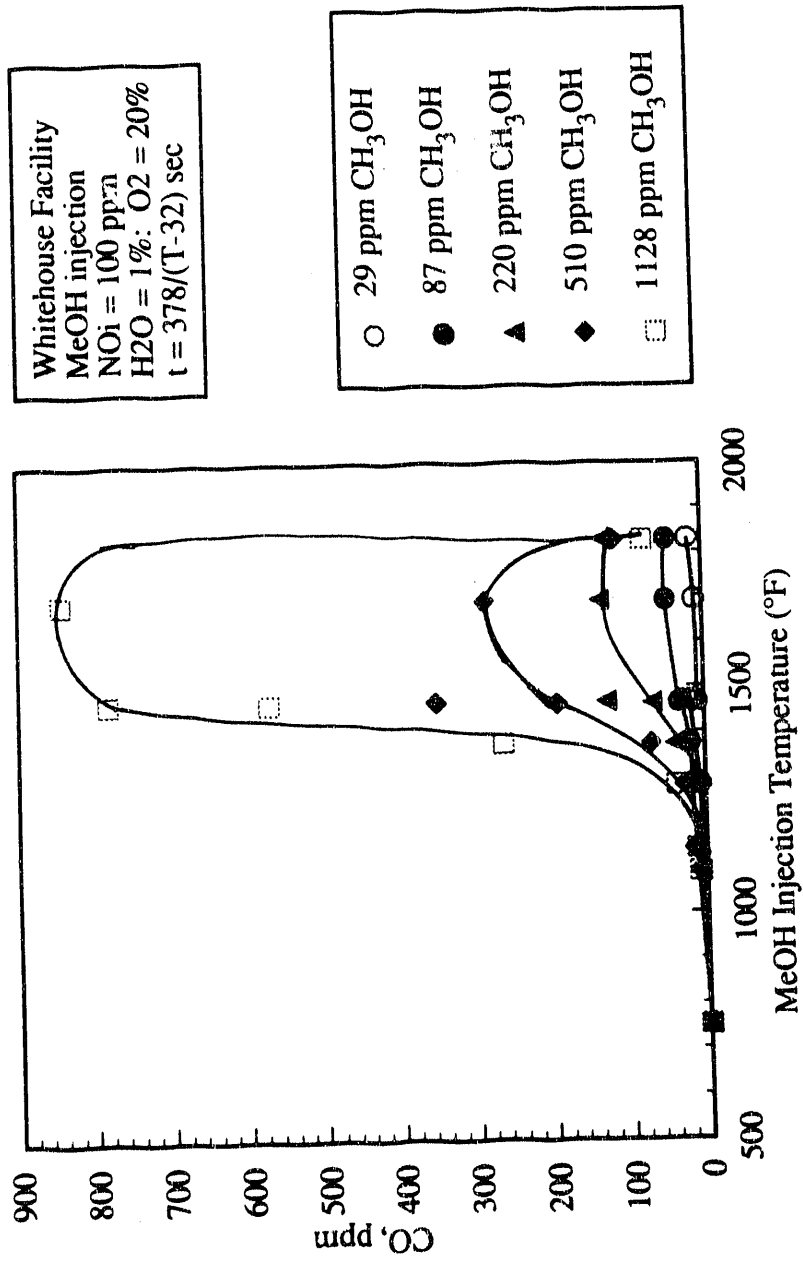


Figure 3-6. Effect of methanol concentration on CO production.

Whitehouse Facility
 MeOH Injection
 NO_i = 50 ppm
 CH₃OH = 114 ppm
 H₂O = 1%: O₂ = 20%
 Balance N₂

○ MeOH injected at 752°F
 ● MeOH injected at 1092°F
 ▲ MeOH injected at 1283°F
 ◇ MeOH injected at 1463°F
 □ MeOH injected at 1654°F
 ■ MeOH injected at 1740°F

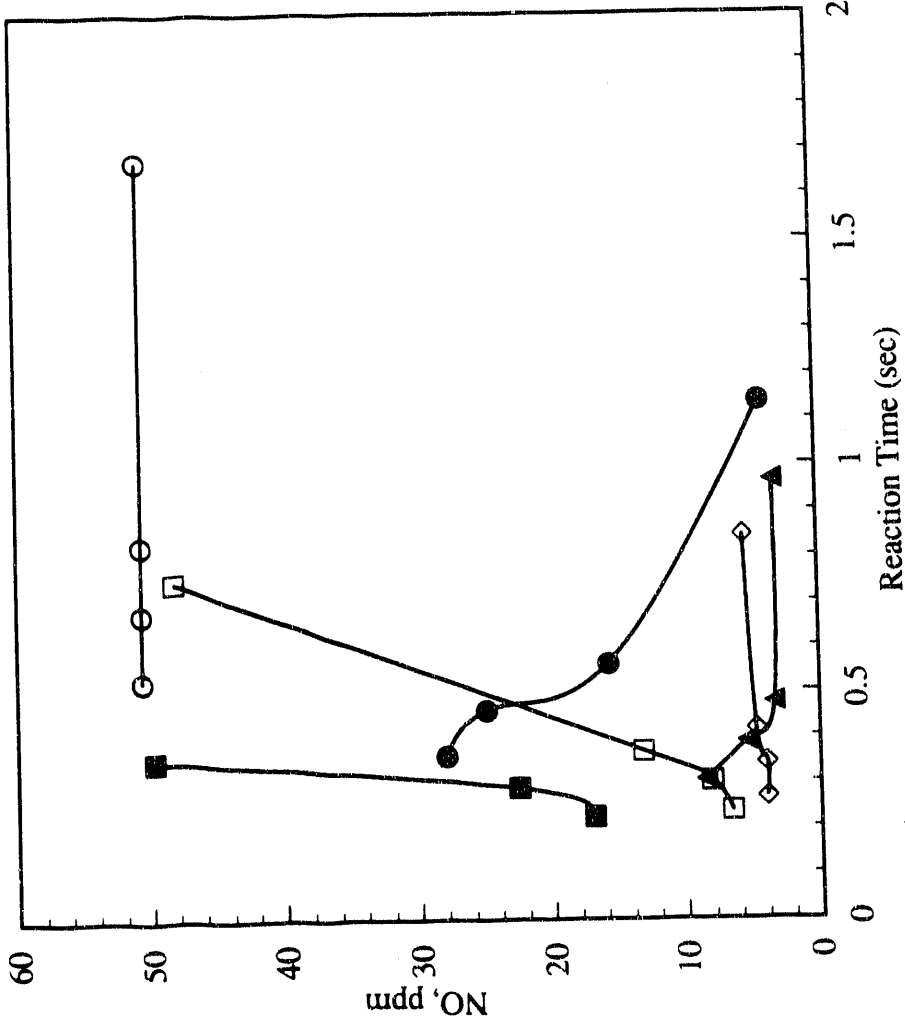


Figure 3-7. The effect of residence time on NO conversion.

second was needed for the methanol NO conversion to reach completion. At the highest temperatures of 1654° and 1740°F, the methanol appeared to react instantaneously with the NO to begin the NO-to-NO₂ conversion. Increasing the residence time in this situation was detrimental to the NO conversion; the NO₂ began converting back to NO when the gases were kept at high temperatures for too long.

3.2.5 Effect of Initial NO Concentration on NO Conversion

Past experiments performed for SNCR de-NO_x have demonstrated that NO reduction improves as initial NO concentration is increased. Figure 3-8 displays that the same may be true for methanol injection. NO concentration is varied from 50 to 200 ppm as the ratio of methanol-to-NO stays at approximately 1.1. NO conversion improves with increasing NO concentration due to the higher availability of NO species with which the methanol can react. Since the methanol-to-NO ratio remains constant, methanol concentration increases as NO concentration increases. This can also contribute to the better performance for the larger NO concentration cases.

CO emissions from methanol injection also increased with increasing NO_i concentration. Looking back to the methanol chemistry, this is a logical occurrence. For the larger NO_i concentrations, a greater NO conversion occurred due to methanol injection, therefore a larger change in CO is expected with an approximate 1-to-1 ratio of NO conversion to CO production.

3.2.6 Effect of Ammonia Presence on NO Conversion

It was of interest to see if the presence of ammonia had an effect on the methanol NO conversion. Methanol injection was performed for cases with and without ammonia present in the simulated flue gas. Figure 3-9 compares NO conversion for a case with 128 ppm of ammonia present to one with no ammonia present. A difference in performance is detected, however this difference is small and probably not of great concern considering that most CombiNO_x applications will consist of much lower ammonia concentrations.

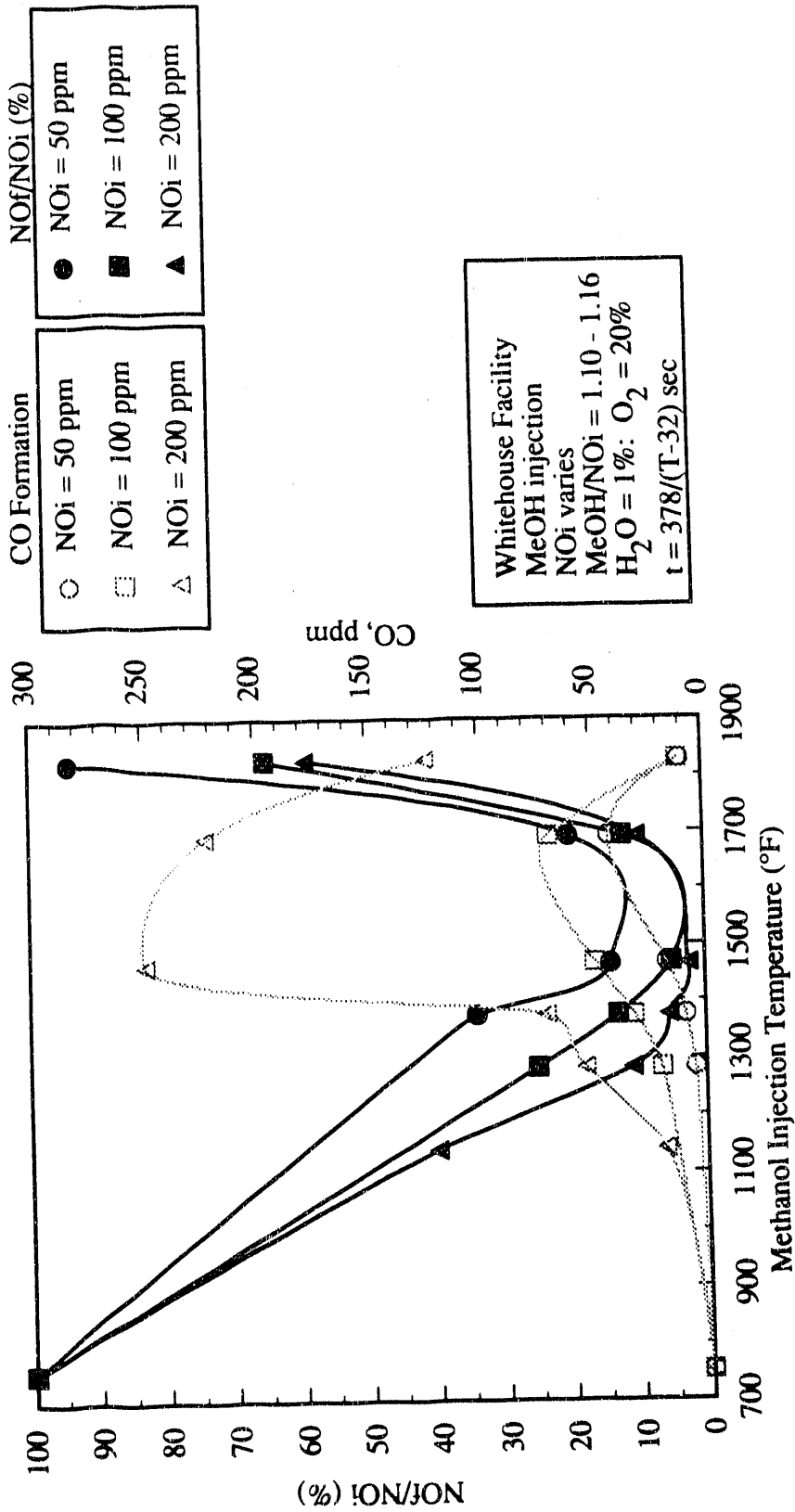


Figure 3-8. Effect of initial NO concentration.

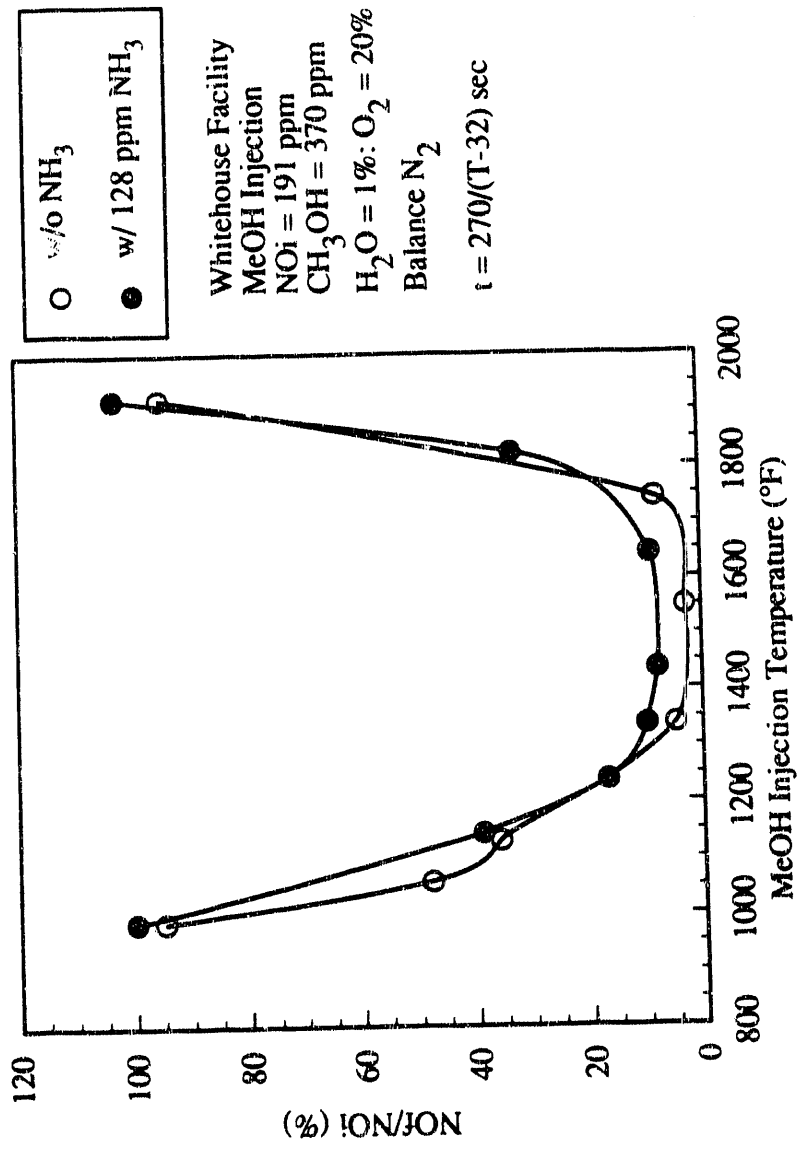


Figure 3-9. Effect of ammonia on NO conversion.

Figures 3-10 and 3-11 display NO conversion in the presence of 400 ppm of ammonia as reaction time is varied. Reaction temperature between the two figures differs. Figure 3-10 shows that when methanol is injected at 1470°F, 400 ppm of ammonia critically hampers the NO conversion. When the reaction time is increased to .25 seconds, the additional ammonia tends to convert to NO. When no ammonia is present in the simulated flue gas, methanol NO conversion appears to be independent of residence time.

Figure 3-11 shows the same conditions except reaction temperature is increased to 1740°F. At this temperature, the ammonia present in the simulated flue gas begins to perform thermal de-NO_x, decreasing NO even more than when no ammonia is present. This temperature is actually too high for the methanol to be effective in NO-to-NO₂ conversion, as can be seen in the case with no ammonia present. The reaction time window in which methanol is effective in NO-to-NO₂ conversion at this temperature is so small, that trying to obtain such a condition would be impractical.

3.2.7 Formaldehyde Formation

Formaldehyde is an intermediate product of the methanol injection chemistry, therefore the possibility of increasing its emission through methanol injection is a concern. Figure 3-12 addresses this concern. Displayed are the formaldehyde emissions as a function of injected methanol concentration. A reference to the corresponding NO conversion is also made. Until 600 ppm of methanol is injected (MeOH/NO_i = 6), formaldehyde formation never increases above 2 ppm. When greater than 700 ppm of methanol is injected, formaldehyde increases to 12 ppm. This increase can be explained through the availability of oxygen. When large amounts of methanol are injected, more oxygen is needed to complete the methanol reactions. If this oxygen is not supplied, intermediate products of the methanol combustion will fail to burnout. Hence, the production of formaldehyde. This is another reason appropriate amounts of methanol should be carefully determined to avoid unwanted, unnecessary emissions.

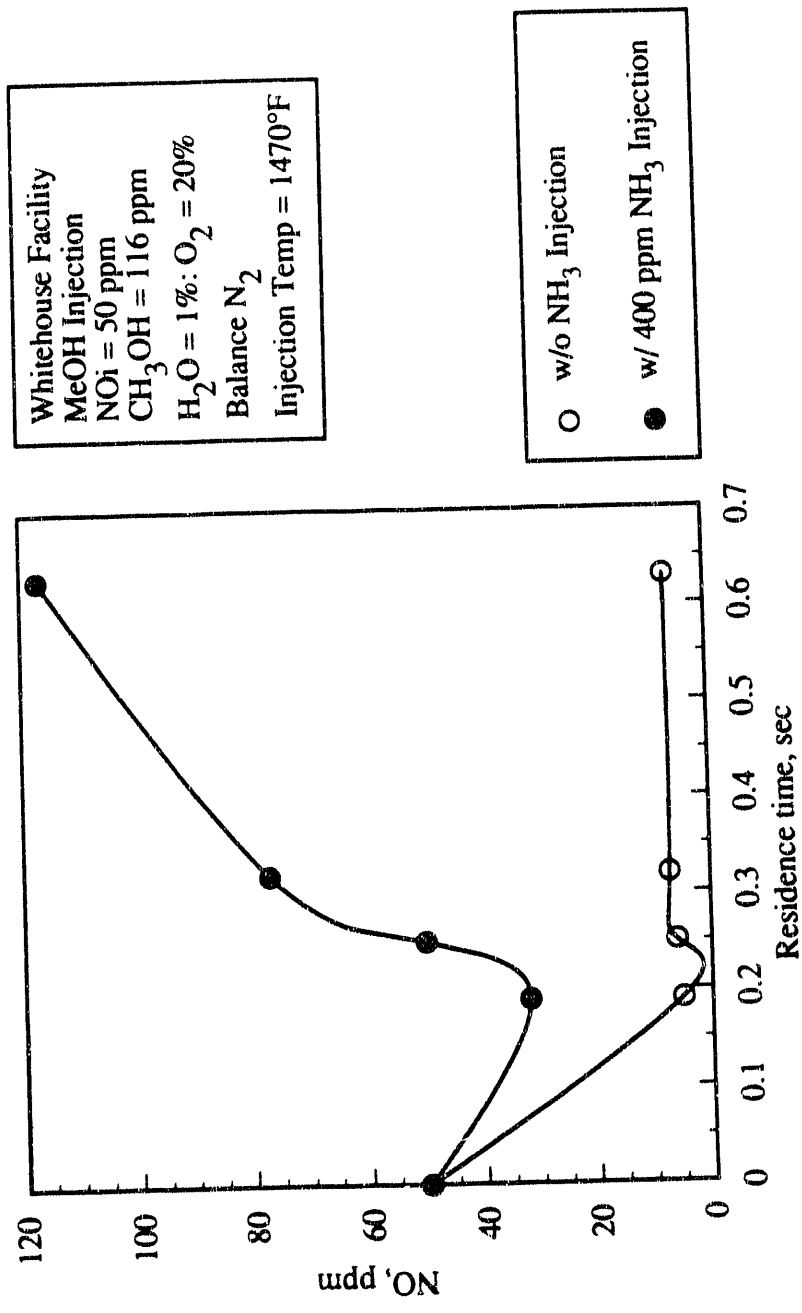


Figure 3-10. Effect of ammonia on NO conversion at 1470° F.

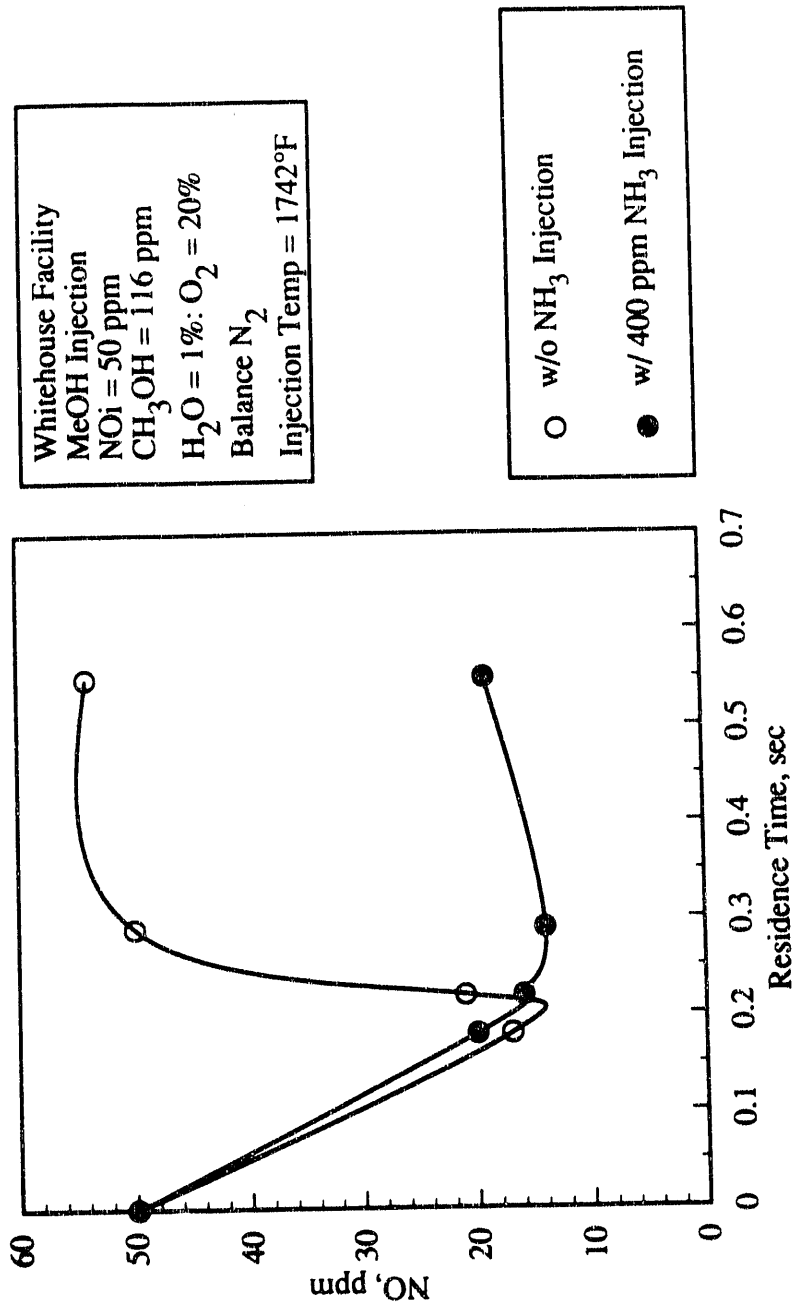


Figure 3-11. The effect of NH₃ on NO reduction at 1740 °F.

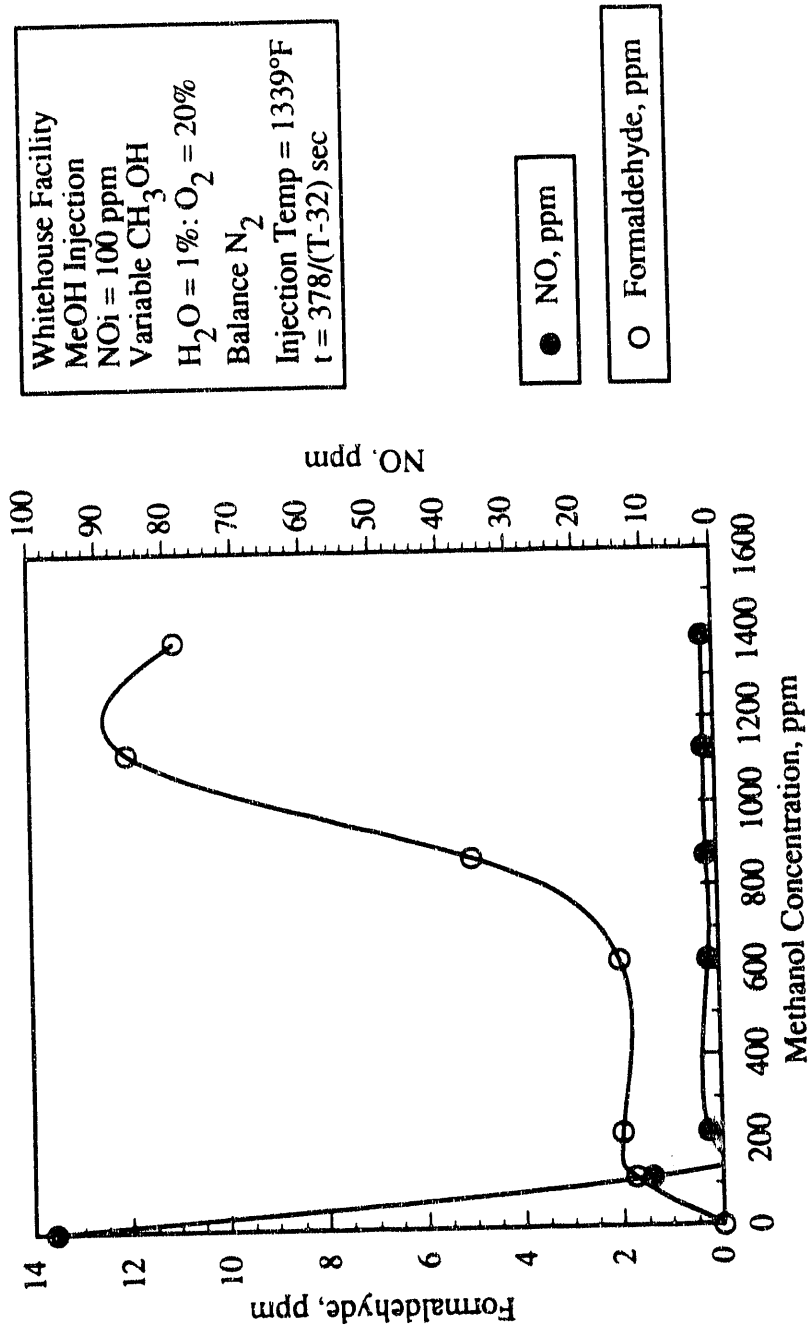


Figure 3-12. Formaldehyde formation during methanol injection.

END

**DATE
FILMED**

10 / 26 / 92

