Second Generation Advanced Reburning for High Efficiency NO_x Control

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Abstract

Energy and Environmental Research Corporation is developing a family of high efficiency and low cost NO_x control technologies for coal fired utility boilers based on Advanced Reburning (AR), a synergistic integration of basic reburning with injection of an N-agent. In conventional AR, injection of the reburn fuel is followed by simultaneous N-agent and overfire air injection. The second generation AR systems incorporate several components which can be used in different combinations. These components include:

- Reburning Injection of the reburn fuel and overfire air.
- N-agent Injection The N-agent (ammonia or urea) can be injected at different locations: into the reburning zone, along with the overfire air, and downstream of the overfire air injection.
- N-agent Promotion Several sodium compounds can considerably enhance the NO_x control from N-agent injection. These "promoters" can be added to aqueous N- agents.
- Two Stages of N-agent Injection and Promotion Two N-agents with or without promoters can be injected at different locations for deeper NO_x control.

AR systems are intended for post-RACT applications in ozone non-attainment areas where NO_x control in excess of 80% is required. AR will provide flexible installations that allow NO_x levels to be lowered when regulations become more stringent. The total cost of NO_x control for AR systems is approximately half of that for SCR. Experimental and kinetic modeling results for development of these novel AR systems are presented. Tests have been conducted in a 1.0 MMBtu/hr Boiler Simulator Facility with coal as the main fuel and natural gas as the reburning fuel. The results show that high efficiency NO_x control, in the range 84-95%, can be achieved with various elements of AR. A comparative byproduct emission study was performed to compare the emissions from different variants of AR with commercial technologies (reburning and SNCR). For each technology sampling included: CO, SO_2, N_2O, total hydrocarbons, NH_3, HCN, SO_3, fly ash mass loading and size distribution, PM10, and carbon in ash. AR technologies do not generate significant byproduct emissions in comparison with basic reburning and SNCR processes under similar conditions. In most cases, byproduct emissions were found to be lower for the AR technologies. Kinetic modeling predictions qualitatively explain the experimental trends observed in the combustion tests. The detailed reaction mechanism can describe the interaction of NO and ammonia in the reburning and overfire air zones, the effect of mixing times, and the sodium promotion effect.

1.0 INTRODUCTION

Reburning controls NO_x via injection of reburn fuel above the main burners, to form a reburning zone in which NO_x is reduced under fuel rich conditions. Overfire air (OFA) is injected downstream to complete combustion. Reburning is a commercial technology capable of providing about 60% NO_x reduction in flue gas from coal-fired utility boilers. Energy and Environmental Research Corporation (EER) recently developed the Advanced Reburning (AR or AR-Lean) process (*Seeker et al., 1992*), an integration of basic reburning and N-agent injection. In AR-Lean, the reburning zone is deliberately de-tuned by injecting a small amount of the reburning fuel, thus establishing a reburn zone stoichiometry of 0.98 - 1.0. Then, an N-agent (ammonia or urea) is injected along with the overfire air at a relatively low temperature (1250-1400 K) in comparison with basic reburning, in which OFA is injected at about 1450-1550 K. By creating near stoichiometric conditions in the reburning zone, the system is adjusted to optimize the NO_x reduction due to the N-agent. With AR-Lean, the NO_x control from the N-agent injection is enhanced to about 80% because the temperature window of the NO-NH_3 interaction is considerably broadened and deepened.

Several other AR variants have been recently reported (*Zamansky et al., 1996a; Zamansky et al., 1996b*). They incorporate injection of an N-agent into the reburning zone and enhancement of the effect of N-agents through the use of promoters. In AR-Lean, the N-agent is injected along with OFA in flue gas providing fuel-lean conditions. However, the N-agent can also be injected into the reburning zone (AR-Rich). This allows two stages of N-agent injection for deeper NO_x control (Multiple Injection AR - MIAR). Both N-agents can be injected with promoters which considerably enhance the NO_x control from N-agent injection. The promoters are water soluble sodium salts (*Zamansky et al., 1996a; Ho et al., 1993*) which can be added to aqueous N-agents. Experimental data on different AR systems (AR-Lean, AR-Rich, and MIAR) were recently obtained (Zamansky et al., 1996b) in 30 and 300 kW combustors firing natural gas as the main and reburning fuels. The results of the combustion experiments demonstrated that NO reduction is enhanced if N-agents are injected into the reburning zone with a delay time after injection of the reburning fuel. Furthermore, the presence of sodium compounds, such as sodium carbonate, promote the effect of both “lean” and “rich” N-agents. Over 90% NO_x control was achieved by injections of 10% reburning fuel (stoichiometric ratio SR~0.99), N-agents (ammonia or urea) and only 15 ppm Na_2CO_3 in comparison with about 50% NO_x reduction by 10% reburning alone. Kinetic modeling qualitatively described the chemical processes responsible for NO_x reduction.

Figure 1 presents a general schematic of the AR processes. The N-agent can be injected with or without promoters at one or two locations into the reburning zone, along with OFA or downstream in the burnout (SNCR) zone. Accordingly, there are six AR variants, as shown in Table 1.

The objective of this study was to examine different variants of AR in a pilot scale combustor firing coal, explain the test results by kinetic modeling, and evaluate the economics of AR technologies. The sections below present a description of the test facility, measurement techniques, experimental conditions, test variables, results of NO_x and byproducts measurements, and brief results of kinetic modeling and economic evaluation.

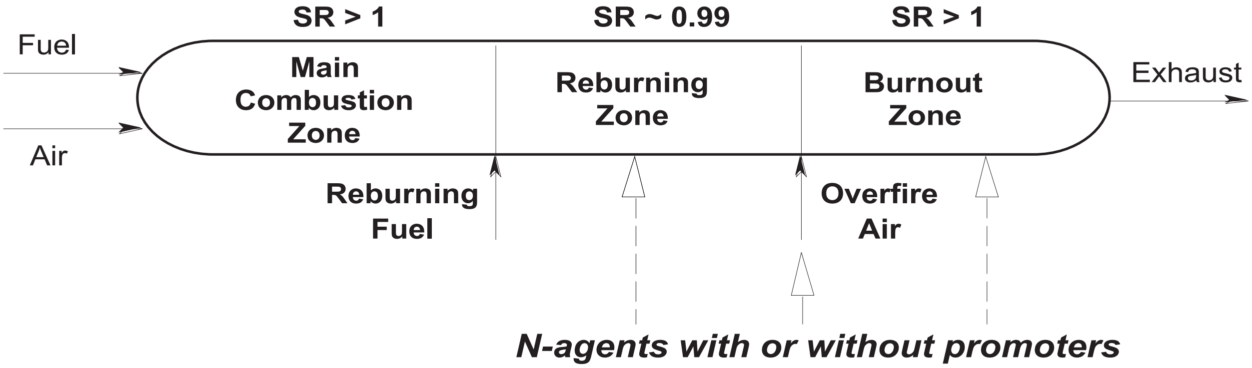


Figure 1. Schematic of different AR variants.

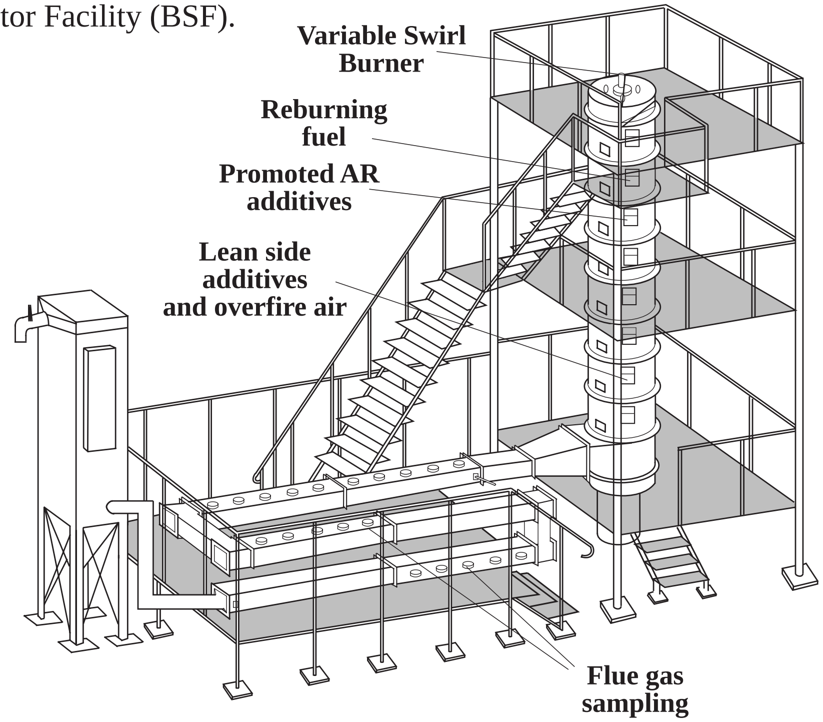
Table 1. AR variants (each N-agent can be injected with or without promoters).

AR Technology	Description
Advanced Reburning Lean - AR-Lean	Injection of the N-agent along with overfire air.
Advanced Reburning Rich - AR-Rich	Injection of N-agent and promoter into the reburning zone.
Multiple Injection AR - MIAR	Injection of N-agents and promoters both into the reburning zone and with overfire air.
AR-Lean + SNCR	Injection of N-agents and promoters with overfire air and into the SNCR zone.
AR-Rich + SNCR	Injection of N-agents and promoters into the reburning zone and into the SNCR zone.
Reburning + SNCR process.	Basic reburning followed by the promoted SNCR

2.0 EXPERIMENTAL

The pilot scale tests were 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. A schematic of the BSF is shown in Figure 2.

Figure 2. Boiler Simulator Facility (BSF).



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. 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 56 cm. 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 is controlled such that the residence time-temperature profile matched that of a typical full scale boiler. A suction pyrometer is used to measure furnace temperatures. The temperature gradient in the range 1200-1700 K is about -250 K/s.

Puléerized bituminous low sulfur Utah coal and high sulfur Illinois coal were used as main fuels. In all tests, stoichiometries in the main, reburning, and burnout zones were SR_1=1.1, SR_2=0.99, and SR_3=1.15, respectively. The initial uncontrolled NO concentration was 800-1000 ppm. Municipal natural gas was used as the reburning 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 (bottled nitrogen) was added along with the reburn natural gas to provide sufficient momentum for good mixing with the furnace gas. The reburning fuel (10%) was injected at 1644 K. OFA was injected through an elbow-shaped injector to burn out combustibles in the reburn zone.

Urea and sodium carbonate promoter were injected as aqueous solutions. In all tests, the Nitrogen Stoichiometric Ratio (N/NO) was 1.5. Twin fluid atomizers made by Delavan Corp. were used, employing nitrogen as transport media. The additives were injected into the reburn zone, burnout zone, and/or with the OFA. In the latter case, the OFA itself was used as the atomization medium.

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:

- O_2: paramagnetism, 0.1%
- NO_x: chemiluminescence, 1 ppm
- CO: nondispersive infrared spectroscopy, 1 ppm
- CO_2: nondispersive infrared spectroscopy, 0.1%
- SO_2: nondispersive ultraviolet spectroscopy, 1 ppm
- N_2O: nondispersive infrared spectroscopy, 1 ppm
- Total hydrocarbons: flame ionization detection, 0.1 ppm

In addition to the CEMS, the following manual method sampling was performed:

- NH_3: ion chromatography, 0.1 ppm
- HCN: ion chromatography, 0.1 ppm
- SO_3: controlled condensation method, 1 ppm
- Fly ash mass loading, size distribution, and PM10: EPA Method 5 and cascade impactor
- Carbon in ash: sampling with induction furnace analysis

3.0 TEST RESULTS

3.1 Advanced Reburning - Lean

In the AR-Lean tests the OFA was injected along with aqueous urea and sodium carbonate at different temperatures. Figure 3 demonstrates that 55-60% NO reduction was achieved by 10% reburning alone during Utah coal firing.

Performance strongly depends on the urea/OFA injection temperature. Injection of urea with the OFA has virtually no effect at high injection temperatures, 1480-1580 K. Under these conditions, the concentration of CO was about 40 ppm without Na and 60 ppm in the presence of Na. At urea/OFA injection temperatures lower than 1480 K, NO is substantially reduced by 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, corresponding to 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 natural gas firing tests (*Zamansky et al., 1996b*).

3.2 Advanced Reburning - Rich

The performance of AR-Rich depends on the OFA injection temperature. Figures 4 and 5 demonstrate experimental results for Utah coal with injection of OFA at 1166 and 1300 K, respectively. Urea (NSR=1.5) and different amounts of sodium (0-200 ppm) were injected at different temperatures. A 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 1166 K (Figure 4) and 70-77% NO control with OFA at 1300 K (Figure 5). The effect of sodium was less than for natural gas firing (*Zamansky et al., 1996b*). A possible reason for this is interaction of sodium compounds with SO_2 or HCl present in coal flue gas to form sodium salts with lower promotion efficiency.

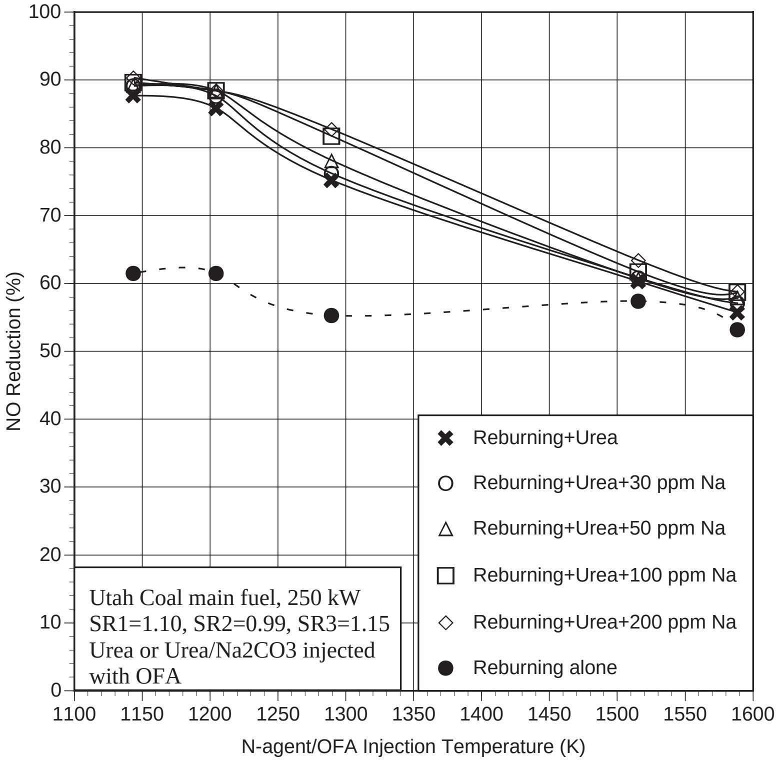


Figure 3. NO reduction by AR-Lean.

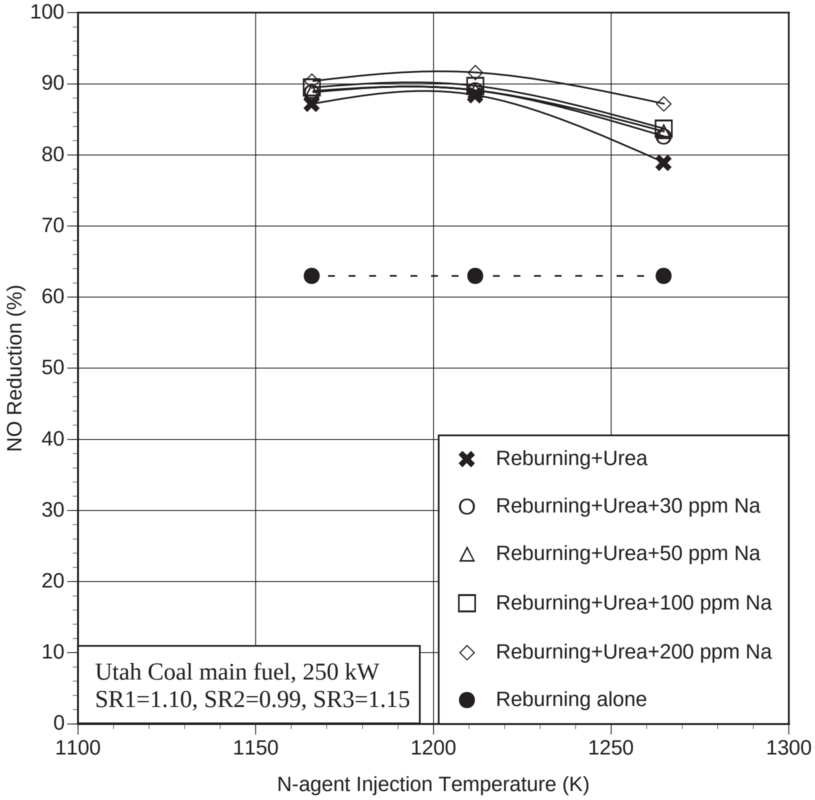


Figure 4. NO reduction by AR-Rich with OFA at 1166 K.

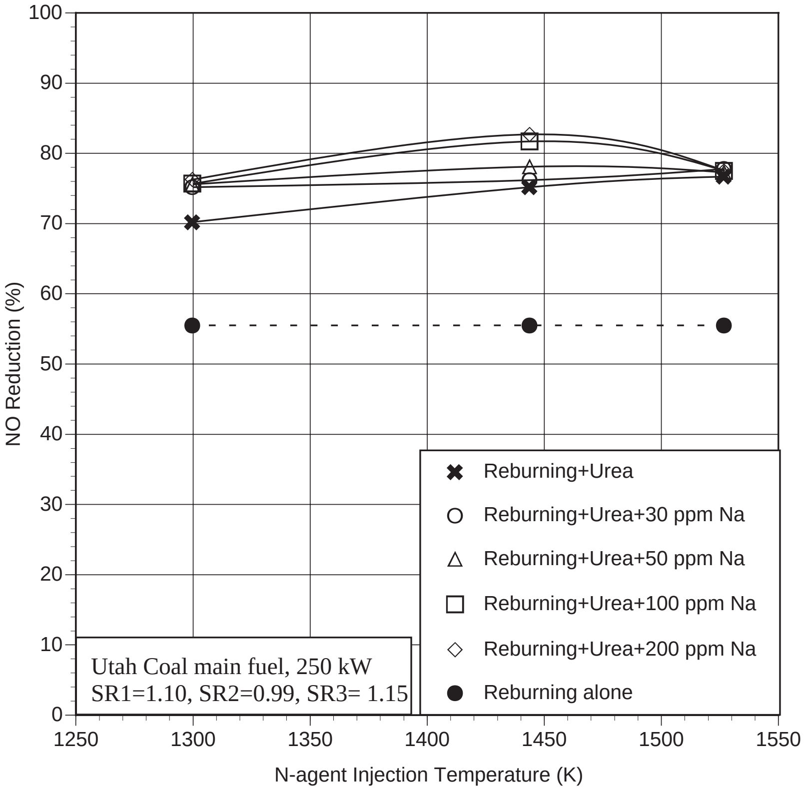


Figure 5. NO reduction by AR-Rich with OFA @ 1300 K.

For injection of OFA at 1166 K, 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 1300 K, CO emissions were about 40 and 60 ppm in the absence and in the presence of sodium, respectively. Variation of the OFA injection mode, which could help to control CO emissions was not conducted in the test program.

AR-Rich tests were also conducted with Illinois coal with OFA injected at 1310 K. Figure 6 shows NO reduction as a function of the N-agent injection temperature. Performance increased with decreasing injection temperature, with greatest NO reduction obtained at 1366 K. Maximum NO control was 86% with no promoter and 93% with 150 ppm sodium. The incremental benefit provided by the sodium promoter in Illinois coal firing appeared to increase with decreasing temperature.

Previous test work showed that with natural gas as the main fuel, small amounts of sodium promoter (less than 30 ppm) can dramatically improve AR performance (*Zamansky et al., 1996a*). However, with coal as the main fuel, probably SO_2 and HCl present in flue gas can partially deactivate the sodium, requiring that more Na be added to obtain promotion.

Illinois coal AR-Rich tests were also conducted in which the sodium promoter concentration was varied from 0 to 2000 ppm. Additives were injected at 1450 K, and OFA was injected at 1366 K. NO reduction increased from 63% at 0 ppm sodium to 86% at 2000 ppm sodium. The main drawback of high sodium level is the potential for increased boiler fouling. A sodium concentration of 150 ppm was selected for most of the tests as a concentration providing significant promotion while being low enough to minimize fouling effects.

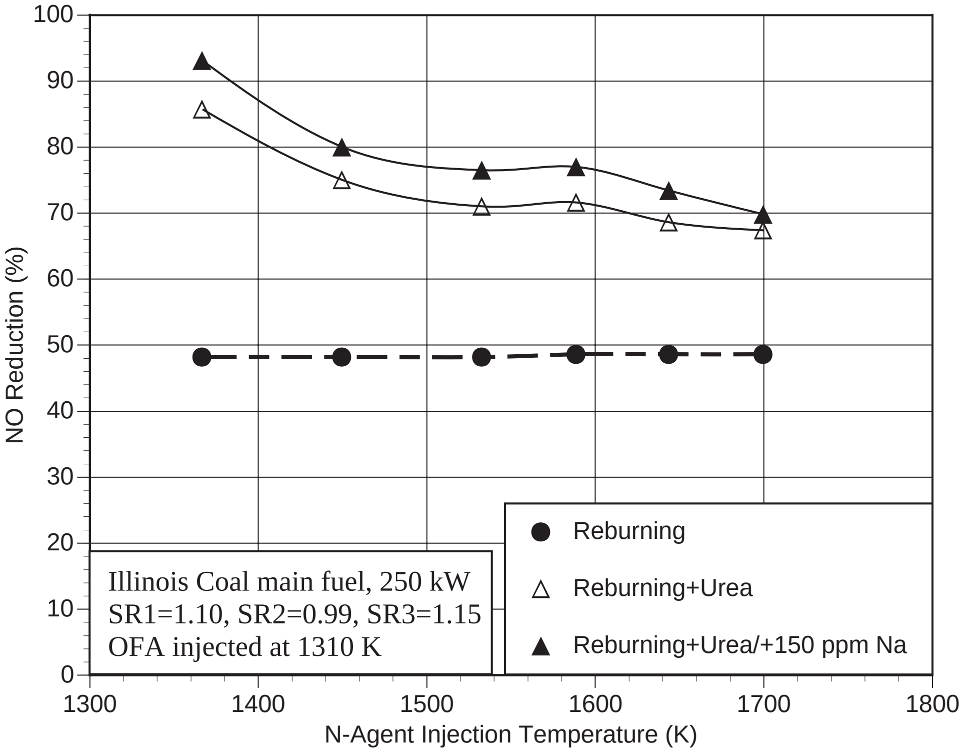


Figure 6. NO reduction by AR-Rich with OFA at 1310 K: Illinois coal firing.

3.3 Multiple Injection Advanced Reburning - MIAR

MIAR components include both AR-Rich and AR-Lean. Test variables included AR-Rich injection temperature, AR-Lean injection temperature, and sodium promoter concentration. Illinois coal was used as the main fuel. Figure 7 shows NO reduction as a function of the rich side urea injection temperature. OFA was injected at 1310 K.

Reburning alone gave 48% NO reduction. MIAR NO reduction increased with decreasing first additive injection temperature. Sodium promoter was added to each N-agent individually and to both agents. Adding promoter to both N-agents provided an incremental performance increase of about 5 percentage points at each temperature. Maximum NO reduction was about 94%, obtained with promoter added to both N-agents at rich-side N-agent injection temperature of 1366 K. It is also noteworthy that performance remained relatively good at high injection temperatures. NO reductions above 80% were obtained at injection temperatures below 1600 K. This insensitivity can provide greater flexibility for application to boilers with limited furnace access for injectors.

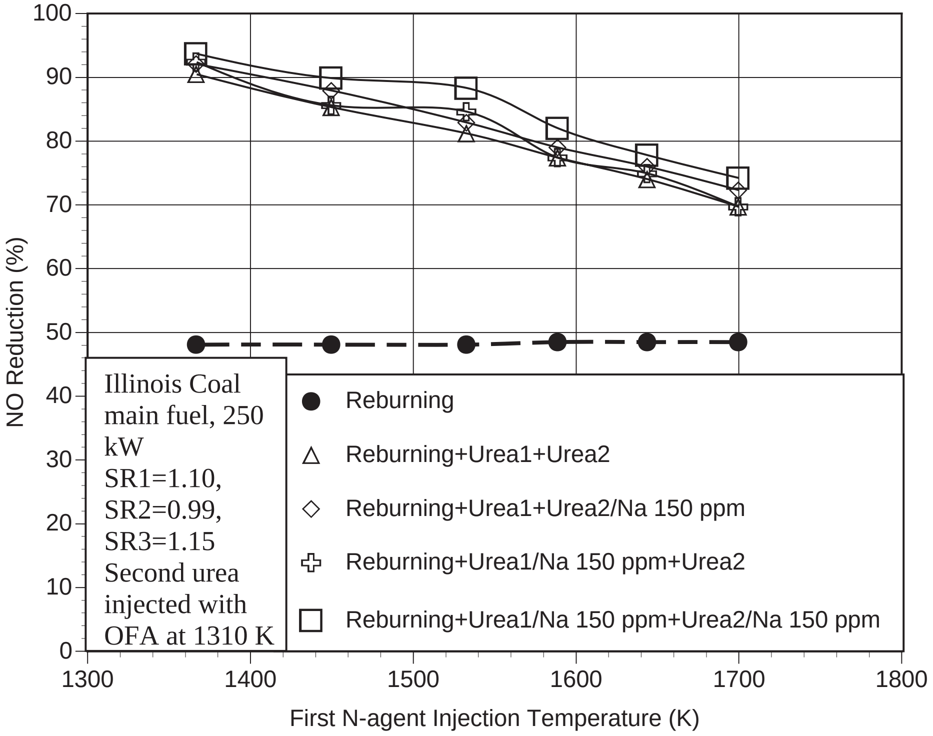


Figure 7. NO reduction by MIAR: effect of first N-agent injection temperature.

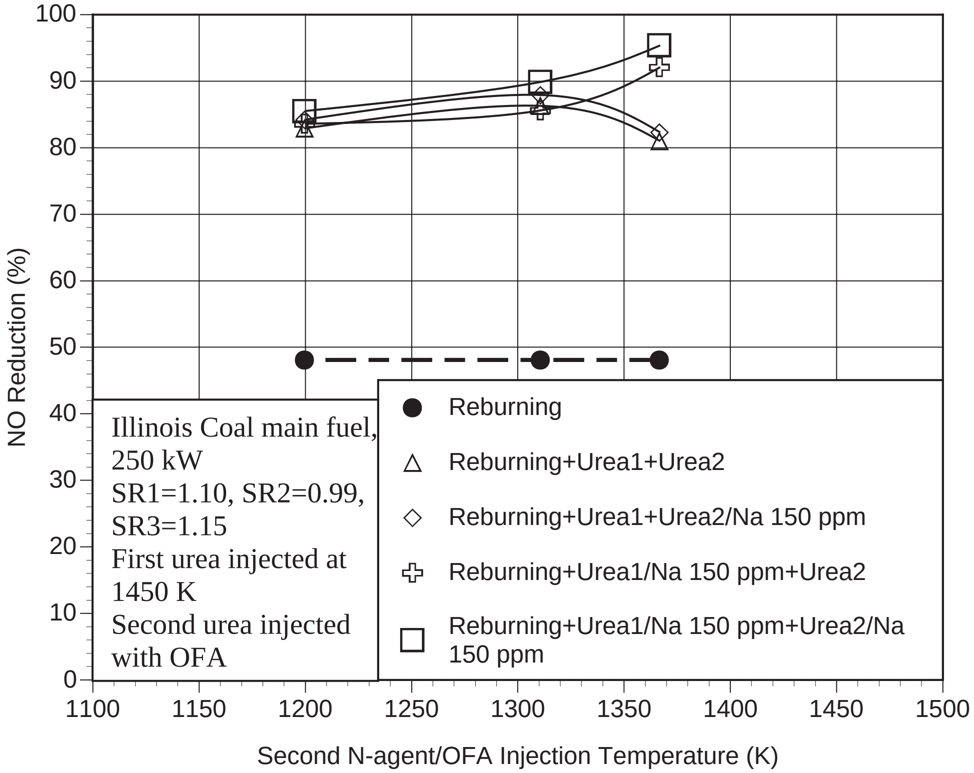


Figure 8. NO reduction by MIAR: effect of second N-agent injection temperature.

MIAR tests were then conducted in which the lean-side N-agent injection temperature was varied, with the temperature of the second N-agent fixed at 1450 K (Figure 8). The lean-side urea was co-injected along with the OFA. The second additive/OFA injection temperature was then varied. As shown in Figure 8, reburning alone gave 48% NO reduction. With two N-agents with no promoters, a maximum of 86% NO reduction was obtained. The optimum temperature was 1310 K, and performance decreased as additive injection temperature increased to 1366 K. However, with 150 ppm sodium promoter added to the first N-agent, performance increased with increasing temperature. Highest NO reduction was 95%, obtained when the lean-side urea was injected at 1366 K. Apparently, adding sodium with the first N-agent at higher temperatures makes it available to promote reduction of NO by the second N-agent.

3.4 Other AR Methods

Combustion experiments have been also conducted on AR-Rich+SNCR, AR-Lean+SNCR, and Reburning+SNCR. In AR-Rich+SNCR tests, the first N-agent was injected at 1590 K and the second in the range 1230-1400 K. NO_x reduction was 83-88% without sodium and 89-92% with 150 ppm Na.

Results on AR-Lean+SNCR have been reported elsewhere (*Zamansky et al., 1997*). This method is capable of achieving up to 94% NO_x reduction with coal firing and 98% with gas firing.

Finally, combination of reburning and SNCR resulted in 88 and 93% NO reduction in the absence and presence of sodium, respectively. However, the temperature window of NO control was narrow, which could result in significant ammonia slip.

In summary, the parametric tests showed that the AR technologies are able to provide effective NO_x control for a high-sulfur coal fired combustor. Sodium was found to significantly promote performance when added at 150 ppm. Maximum NO reductions achieved by the promoted AR technologies were 90% for AR-Lean, 93% for AR-Rich, 94% for reburning plus SNCR, and 95% for MIAR.

3.5 Byproduct Sampling Tests

While the AR technologies have shown the ability for effective NO_x control, another consideration is whether they generate any undesirable byproducts. Specifically, it was sought to determine whether the different variations of AR generate byproduct emissions greater than those of commercially accepted technologies such as SNCR and reburning. To answer this question, byproduct sampling tests were performed at the BSF. The following seven conditions were tested: baseline coal firing, SNCR, reburning, AR-Rich, AR-Lean, Reburning+SNCR, and MIAR.

Test conditions, including urea injection temperatures, promoter amounts and OFA temperatures, were selected as providing NO control performance in the 80-90% range. All test conditions and analytical data are summarized in Table 2. Even without significant byproduct optimization efforts, the AR technologies do not generate more byproducts than reburning or SNCR. Results for each of the byproduct compounds tested are described below.

SO_2 concentrations were in the range of 3010 to 3140 ppm (@ 0% O_2) for each condition, and were not affected by the AR technologies.

Table 2. Byproduct test conditions and results.

Baseline firing configuration:
Illinois coal @ 250 kW
NOi=1000 ppm as measured
SR1=1.10, SR3=1.15

Test conditions:
NSR=1.5
N-agent: Urea
Na promoter: Na2CO3

	Test Case						
Parameter	Baseline Coal	SNCR	Reburning	AR-Rich	MIAR	Reburning +SNCR	AR-Lean
Test Conditions							
Reburn heat input (%)	None	None	20%	10%	10%	10%	10%
Rich side additive T (K)	None	None	None	1420	1370	None	None
Rich side Na (ppm)	None	None	None	150	150	None	None
OFA T (K)	None	None	1530	1310	1310	1530	1310
Lean side additive T (K)	None	1900	None	None	1310	1310	1310
Lean side Na (ppm)	None	None	None	None	0	None	150
NOx reduction (%)	0	64.7	46.4	82.2	88.5	85.2	81.3
Sampling Results							
CO (ppm @0% O2)	58	120	57	75	95	129	95
SO2 (ppm @0% O2)	3140	3011	3011	3050	3012	3120	3045
N2O (ppm @0% O2)	1	73	1	1	38	98	69
THC (ppm @0% O2)	2	2	2	2	2	2	2
NH3 (ppm @0% O2)	0.0	47.3	0.0	0.0	4.4	50.1	0.0
HCN (ppm @0% O2)	0.0	0.0	0.5	1.1	1.2	1.6	1.0
SO3 (ppm @0% O2)	2.0	0.8	1.2	1.3	1.1	1.7	2.8
Particle loading (gr/dscf)	2.0	2.3	2.1	1.8	1.9	2.2	2.3
Fly ash MMD (microns)	8.1	8.7	8.5	10.8	10.1	8.2	8.6
PM10 (%)	54.4	52.1	53.5	49.2	49.8	55.4	53.0
(gr/dscf)	1.09	1.21	1.10	0.88	0.93	1.24	1.23
Carbon in ash (%)	0.08	0.03	0.08	0.17	0.26	0.07	0.10

Total hydrocarbon (THC) emissions were 2 ppm for each test condition, and were not affected by the AR technologies.

Emissions of CO and N_2O generally increased during application of the NO_x control technologies relative to baseline coal firing. The largest increases were associated with the low temperature N-agent injection technologies, i.e. SNCR and reburning + SNCR. For SNCR, CO increased from 58 to 120 ppm, and N_2O increased from 1 to 73 ppm. Thus AR-Lean, AR-Rich, and MIAR generate lower concentrations of CO and N_2O than does SNCR under similar conditions. It is believed that CO and N_2O concentrations could be further reduced by injecting OFA at a higher temperature.

NH_3 emissions were fairly high (>40 ppm) for the two SNCR conditions, but were below 5 ppm for all other conditions (including MIAR). Thus AR-Lean, AR-Rich, and MIAR generate significantly lower NH_3 emissions than does SNCR under similar conditions. For the SNCR cases, it is believed that a higher reagent injection temperature would also minimize NH_3 emissions.

HCN emissions were below 2 ppm for baseline coal and all AR test conditions. These results would appear to indicate that as long as the N-agent(s) are added with or upstream of the OFA, NH_3 and HCN emissions can be minimized.

SO_3 emissions can impact electrostatic precipitator performance and, if present in high concentrations, can cause boiler corrosion problems. SO_3 emissions were measured using the controlled condensation method (*"Process...", 1973*). The sample probe was operated at a temperature of 590 K. The SO_3 concentration for baseline coal firing was about 2 ppm. For each of the NO_x control technologies, SO_3 remained below 3 ppm. It is concluded that none of the technologies cause a significant change in SO_3 emissions.

Fly ash particle size can affect dust control equipment efficiency as well as raising respirability and health issues. Particle size distribution was measured using a cascade impactor. Fly ash mass mean diameter (MMD) was between 8 and 11 microns for each condition. The AR technologies did not appear to significantly alter overall size distribution.

PM10 is defined as the fraction of fly ash material of diameter less than 10 microns. EPA Method 5 and cascade impactors were used to determine total particle loading and PM10. Total particulate loading was 2.0 gr/dscf for baseline coal firing, and ranged from 1.8 to 2.3 gr/dscf for the different NO_x control technologies. PM10 was about 1.1 gr/dscf for baseline coal firing, and ranged from 0.9 to 1.2 gr/dscf for the different technologies. These results would appear to indicate that the AR NO_x control technologies do not significantly impact particulate loading or PM10.

Poor carbon burnout can adversely impact boiler thermal performance, along with the salability of collected fly ash. Ash samples were collected from the BSF convective pass using a volumetric sampler and were analyzed for carbon by a contract laboratory. For all conditions, carbon in ash was well below 1%. Thus it is concluded that the AR technologies do not significantly decrease carbon burnout.

In summary, byproduct emissions were generally found to be low for the AR technologies. The only emissions which showed potential for significant increase were CO, N_2O and NH_3, for SNCR conditions. However, these emissions can be minimized by adding the second N-agent at higher temperature.

4.0 KINETIC MODELING

This Section briefly presents kinetic modeling results. Detailed description is presented elsewhere (*Zamansky et al., 1996c and 1996d*). Three kinetic programs were used for modeling: Chemkin-II (*Kee et al., 1989*), Senkin (*Lutz et al., 1987*), and EER's One Dimensional Flame code (ODF). The reaction mechanism based on the GRI-Mech version 2.11 (*Bowman et al., 1995*) was used for modeling with additional reactions characterizing the Thermal DeNO_x process and the effect of sodium. The Thermal DeNOx reactions which are absent in the GRI-Mech were selected from the SNCR scheme suggested by *Bowman, 1996*. These reactions are described elsewhere (*Zamansky et al., 1996a*). The sodium reactions are presented in Table 3. Rate constants of the first three reactions were measured in the scope of this project by V.V. Lissianski and W.C. Gardiner at the University of Texas at Austin. Rate constants for other reactions were selected from the NIST database (*NIST, 1994*) or estimated. The total mechanism included 355 reactions of 65 species.

Table 3. Sodium reaction mechanism in Chemkin Interpreter format.
$k = A T^n \exp(-E/RT)$ (cm, mol, s, cal)

Reactions	A	n	E
NA2CO3=>NA2O+CO2	2.54E+06	0.0	26080.0
NA2O+CO2=>NA2CO3	1.11E+05	0.0	-15160.0
Na2O+H2O=2NAOH	9.18E+12	0.0	3120.0
NA+N2O=NAO+N2	1.69E+14	0.0	3159.0
NAO+H2O=NAOH+OH	1.32E+13	0.0	0.0
NAO+O=NA+O2	2.23E+14	0.0	0.0
NAO+NO=NA+NO2	9.04E+13	0.0	0.0
NAO+H2=NAOH+H	1.25E+13	0.0	0.0
NA+O2+M=NAO2+M	1.74E+21	-1.3	0.0
H2O	Enhanced by 5.000E+00		
CO2	Enhanced by 3.000E+00		
CO	Enhanced by 2.000E+00		
H2	Enhanced by 2.000E+00		
NAOH+H=NA+H2O	5.00E+13	0.0	0.0
NA+OH+M=NAOH+M	1.82E+21	-1.0	0.0
NAO+OH=NAOH+O	2.00E+13	0.0	0.0
NAO+HO2=NAOH+O2	5.00E+13	0.0	0.0
NAO+H2=NA+H2O	3.13E+12	0.0	0.0
NAO+CO=NA+CO2	1.00E+14	0.0	0.0
H+NAO2=HO2+NA	2.00E+14	0.0	0.0
NAO+H=NA+OH	2.00E+14	0.0	0.0
NAO+OH=NA+HO2	3.00E+13	0.0	0.0
NA+HO2=NAOH+O	1.00E+14	0.0	0.0
NAO2+H=NAO+OH	5.00E+13	0.0	0.0
NAO2+OH=NAOH+O2	2.00E+13	0.0	0.0
NAO+HO2=NAO2+OH	5.00E+13	0.0	0.0
NAO2+H=NAOH+O	1.00E+14	0.0	0.0
NAO2+CO=NAO+CO2	1.00E+14	0.0	0.0
NAO2+O=NAO+O2	1.00E+14	0.0	0.0
NAO+NH3=NAOH+NH2	1.00E+13	0.0	0.0

Modeling activities were focused on the following three issues:

1). Identification of the most important elementary reactions responsible for chemical processes in the reburning and burnout zones. This was accomplished by conducting sensitivity analysis under various conditions.

2). Evaluation of the mixing effects. Calculations assuming instantaneous mixing and mixing times of 0.03 and 0.3 s. were compared for several selected process conditions.

3). Identification of the chemical reactions responsible for sodium promotion. This was also done by sensitivity analysis.

Modeling was performed without variation of rate constants for SR_2=0.99 and a plug flow reactor with 300 K/s temperature decrease in the reaction zone and for the following initial mixture entering the reburning zone: 8% CO_2 - 15% H_2O - 1.74% O_2 - 600 ppm NO (balance N_2). Modeling does not quantitatively describe the experimental results, and therefore, the goal of the modeling effort was to provide insight into the controlling factors of the process and to qualitatively describe the observed reaction trends.

4.1 Identification of Important Elementary Reactions

Kinetic curves do not provide information about the importance of specific elementary reactions with respect to increasing or decreasing concentrations of certain components. This information is necessary for understanding chemistry of the processes under investigation: NO removal with low emissions of other nitrogen compounds, NH_3 and HCN. The sensitivity analysis was done to obtain this information. Sensitivity analysis is a procedure to quantitatively determine the dependence of the model solution on the elementary reaction rate constants. It provides insight about how important certain reactions are to the model's predictions. The sensitivity analysis was performed with the use of the Senkin code (*Lutz et al., 1987*). Senkin is a FORTRAN computer program for predicting the species and temperature histories and for calculating the first order sensitivity coefficients of each species with respect to the elementary reaction rate parameters.

Three types of graphs were obtained and compared:

- species mole fraction plots (kinetic curves),
- contribution factors for most important species (NO, NH_3, and HCN), and
- sensitivity factors for the same species.

If methane is injected as the reburning fuel an injection temperature of 1700 K and $SR_2 = 0.99$, CH_4 is rapidly converted to CO and H_2. The NO concentration decreases during the first 2-3 ms from the initial 600 ppm to about 540 ppm, and then slowly decreases to 502 ppm. Thus, there are two regions of NO reduction: the initial fast decrease which lasts for a very short period of time, followed by the slow decrease. Concentrations of NH_3 and HCN are lower than 1 ppm, but relatively significant amounts of O_2 are present.

The most important steps of NO reduction in the fast region are reactions:

$HCCO + NO = HCNO + CO$, and
$CH_2 + NO = H + HNCO$

The chain branching steps

$H + O_2 = O + OH$
$CH_3 + O_2 = O + CH_3O$

are responsible for the boost of radicals occurring after injection of the reburn fuel. In these reactions, each H atom and CH_3 radical forms several active species. The increased radical pool generates carbon-containing radicals (HCCO and CH_2) which reduce NO.

Two reactions

$N + NO = N_2 + O$ and
$NH + NO = N_2O + H$

primarily contribute to NO removal in the slow region.

If 800 ppm ammonia is injected with the reburning fuel at SR_2=0.99 and 1700 K, the NO concentration jumps from 600 to about 900 ppm and then slowly decreases to 800 ppm. Thus, part of the ammonia is converted to molecular nitrogen and another part to NO.

However, if 800 ppm NH_3 is injected into the reburning zone with a 0.1 s delay after the reburning fuel, this delay dramatically changed the NO concentration as well as concentrations of other species. NO was reduced to slightly above 100 ppm and about 150 ppm NH_3 is present in the mixture at t=0.5 s. The most important NO reducing reactions are:

$NH_2 + NO = N_2 + H_2O$ and
$NH_2 + NO = NNH + OH$

4.2 Distributed Injection: Mixing Studies

To evaluate the effect of mixing time, three mixing scenarios were applied to each conventional or advanced reburning condition modeled: instantaneous mixing, 30 ms mixing, and 300 ms mixing. ODF was used to model the mixing effects. The same mixing time was applied to all external streams (reburn fuel, N-agent, and overfire air), and mixing over 30 or 300 ms was applied at a uniform rate of mass addition. The instantaneous mixing case is the limiting case corresponding to Chemkin modeling. 30 ms mixing may be considered fast, corresponding to bench and small pilot scale combustion systems such as the BSF. 300 ms mixing is more typical of large pilot-scale systems and full-scale industrial combustors.

In general, better NO reductions were obtained with longer mixing times and with about 0.1 s delay in ammonia injection for both AR-Rich and AR-Lean systems. Very long delays in ammonia injection and low (1200 K) overfire air injection temperatures led to poor performance.

The mixing studies demonstrate that the rate of mixing of injected streams may have a significant impact on basic or advanced reburning performance. The predicted impacts of mixing time may provide guidance in selecting injection nozzles for a given installation.

4.3 Effect of Sodium

The work focused on the chemistry of the AR-Rich reburning zone, with or without a sodium promoter. When included, the sodium promoter is 50 ppm Na_2CO_3. N-agent and sodium promoter are co-injected at 0.1 s after the beginning of reburn fuel injection.

The net impact of promotion is illustrated in Figure 9, which shows the concentration of NO in the reburn zone at 1300 K (1.33 s after the start of reburn fuel injection), with and without sodium promotion. At instantaneous mixing, the promoter has a very slight negative effect on emissions. However, for mixing times as short as 30 ms, promotion begins to show a beneficial effect. For longer mixing times representative of industrial installations, the effect is quite pronounced.

Figure 10 shows the effect of the delay time of ammonia injection with and without sodium on the final NO concentration (after burnout). Mixing time for each injection was 30 ms in this calculation, and OFA was injected at 1300 K. Injection of 10% reburning fuel decreases NO from 600 ppm to about 360 ppm. Injection of the reburn fuel with sodium slightly increases the NO concentration.

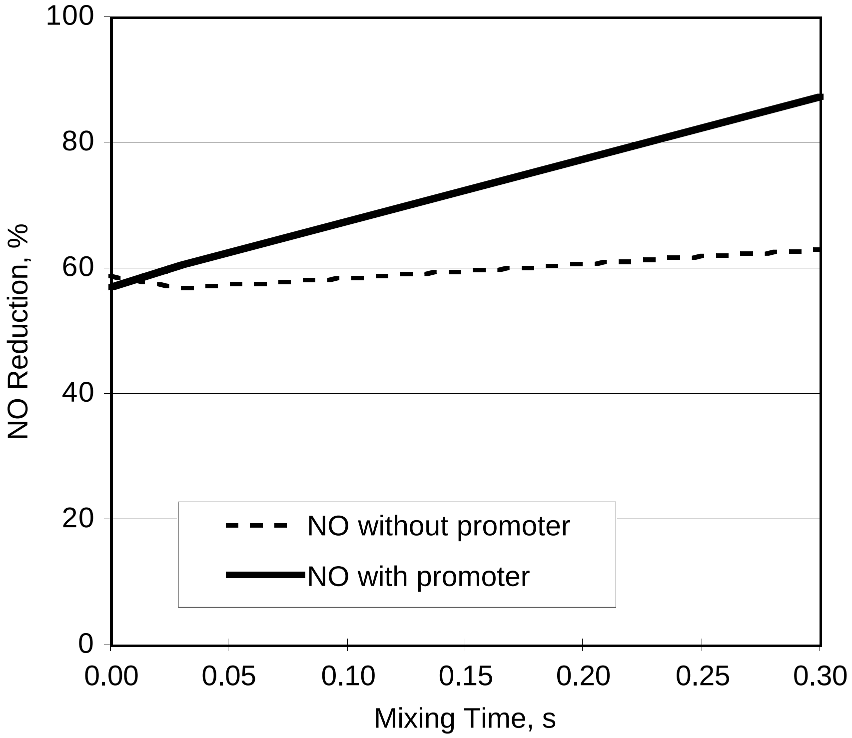


Figure 9. Effect of mixing times and Na promotion on AR-Rich.

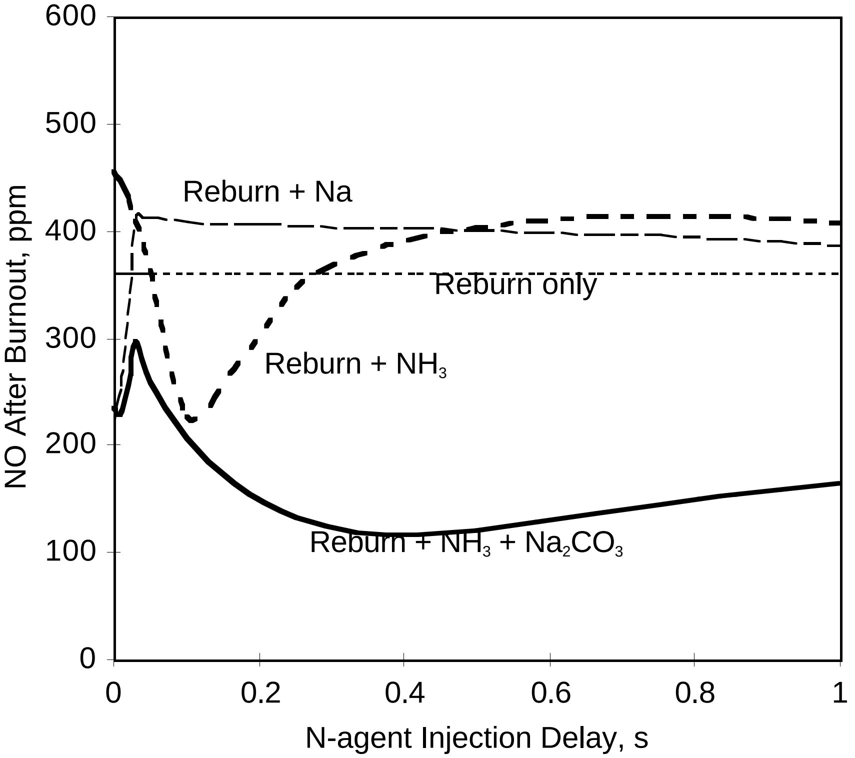


Figure 10. Effect of delayed NH_3/Na injection on AR-Rich.

Injection of ammonia without sodium decreases NO if injected with a delay time about 0.1 s. Finally, if ammonia is injected with sodium, the NO concentration is significantly reduced within a wide range of delay times.

The effect of sodium can be explained by 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:

$Na_2CO_3 = Na_2O + CO_2$
$Na_2O + H_2O = 2NaOH$

Then, NaOH reacts with H atoms to form Na atoms and H_2O molecules:

$NaOH + H <=> Na + H_2O$ (1)

The Na atoms can then recombine with OH radicals to return NaOH:

$Na + OH + M <=> NaOH + M$ (2)

The total reaction (1)+(2) is a Na-promoted H and OH recombination into water:

$H + OH + M <=> H_2O + M$

The equilibrium of reactions (1) and (2) under different process conditions may affect the promotion of NO removal. On the one hand, injection of sodium compounds (Na_2CO_3 or NaOH) increases the formation of Na atoms via reaction (1) and (-2), as well as the concentration of OH radicals (-2). On the other hand, if a high concentration of OH radicals is formed in the presence of Na compounds, it can be decreased via the chain (2) and (1). Thus, sodium compounds can either form or remove OH radicals under different process conditions.

Kinetic modeling of processes in the reburning zone (*Zamansky et al.*, *1996a*) demonstrated that there exists an optimum rate of radicals formation which results in maximum NO removal. If the rate of radicals formation is higher or lower than the optimum rate, NO removal is not so effective. Sodium compounds affect the concentrations of OH and H species through reactions 1 and 2, and, therefore, they can create near optimum conditions for NO reduction. In this case, sodium compounds act as promoters of the $deNO_x$ reaction between NO and NH_3.

Thus, in the AR-Rich process, the N-agent and sodium promoter are injected into the reburning zone with a delay after fast depletion of the oxygen concentration via interaction with the reburning fuel. At the moment of sodium injection, the concentration of radicals is relatively low. Under these conditions, sodium carbonate is converted to sodium hydroxide which participates in the chain process, and the amount of OH and H species can be increased due to reactions (-2) and (-1). The OH radicals rapidly react with NH_3, thus forming NH_2 and removing NO.

5.0 ECONOMIC AND MARKET EVALUATION

5.1 Methodology and Technology Specific Inputs

To evaluate the cost effectiveness of the AR technologies, an economic analysis has been conducted using the EPRI Technology Assessment Guide (TAG) methodology, which is widely used in the utility industry to evaluate advanced emission control technologies. The TAG methodology calculates the total levelized annual costs including capital and operating cost components. This can be expressed in terms of \$/ton of NO_x controlled. The total installed cost (capital cost) of the NO_x control technology is estimated and distributed over the operating life in a series of uniform annual costs by applying a Capital Recovery Factor (CRV). The CRV depends on the operating life, time value of money, depreciation, etc. In this analysis, a CRV of 0.131 was utilized. This is equivalent to simple amortization at an annual interest rate of 10% over a 15 year operating life. The annual operating costs for the technology are calculated for the first year and then levelized over the life of the technology by applying an annual levelization factor. In this TAG analysis, a constant dollar approach was utilized so that the levelization factor is 1.0.

AR technologies can be applied to all types of combustion systems including the three most common utility boilers (wall, tangential and cyclone fired). Two applications have been selected for the economic evaluation: A cyclone fired boiler and a dry bottom wall fired unit equipped with low NO_X burners. The assumptions utilized in the analysis and those specific to the two applications (cyclone and wall-fired) are summarized in Table 4.

Table 4. Economic data.

Parameter	Units		
Unit Specifications			
Unit Capacity	MW	200	
Capacity Factor	%	65	
Heat Rate	Btu/KWH	10,000	
Fuels data			
Coal Sulfur	lb/10^6 Btu	1.2	
Coal Heating Value	Btu/lb	12,000	
Coal cost	\$/10^6 Btu	1.50	
Gas cost	\$/10^6 Btu	2.5	
Coal ash content	%	10	
Unit costs			
Value of SO_2 Reduction	\$/ton	125	
Ash Disposal Cost	\$/ton	10	
Economic Factors			
Capital Recovery Factor		0.131	
Escalation		Constant dollar	
Boiler Data			
Firing Configuration		Cyclone	Wall-Fired
Baseline NO_X controls		None	Low NO_X Burners
Baseline NO_X	lb/10^6 Btu	1.2	0.46

The NO_X control technologies selected for evaluation are presented in Table 5.

Table 5. Evaluated NO_x control technologies.

Technology	NO_x Reduction (%)	Application	
		Cyclone	Wall
Conventional NO_x Controls			
Overfire Air	25		X
Selective Non-Catalytic Reduction (SNCR)	40	X	X
Selective Catalytic Reduction (SCR)	80	X	X
Selective Catalytic Reduction (SCR)	95	X	X
Reburning NO_x Controls			
Basic Reburning	60	X	X
Advanced Reburning — Rich (AR-Rich)	80	X	X
Advanced Reburning — Lean (AR-Lean)	80	X	X
Promoted Advanced Reburning — Lean (PAR-Lean)	90	X	X
Promoted Advanced Reburning — Rich (PAR-Rich)	90	X	X
Multiple Injection Advanced Reburning (MIAR)	95	X	X

The reburning technologies were evaluated using both gas and coal as reburning fuels. The key technology specific assumptions are presented in Table 6 and are discussed further below.

The performance of SNCR is highly site specific. A typical performance in full scale applications with modest ammonia slip is in the range of 40% NO_X reduction with injection of a nitrogen agent at a nitrogen stoichiometric ratio (NSR) of 1.5. The capital cost was based on discussions with SNCR vendors. The nitrogen agent was Nalco Fuel Tech NO_xOut A, a commercially available aqueous urea solution.

Costs and performance for SCR were obtained from an EPA report (*Phase II, 1996*) which presented DOE estimates for a high sulfur coal fired unit of 200 MW capacity with initial NO_x of 1.0 lb/10^6 Btu and 80% NO_x reduction. These conditions were scaled to those utilized here.

Reburning costs and performance were based on EER's extensive data base and the projected performance of AR systems. For the coal reburning systems, costs were included for the pulverizers to produce the fine-grind (micronized) coal necessary to minimize carbon loss. There is no incremental fuel cost (except for efficiency penalty) since the normal plant coal is used for reburning. For gas reburning systems, no pulverizers are required, but the gas cost is greater than coal. A differential of 1.00 \$/10^6 Btu was assumed. It is assumed that coal and gas reburning technologies can achieve comparable NO_x reduction.

Table 6. NO_x control technology data.

	Units	OFA	SNCR	Basic Reburn	AR rich/lean	PAR rich/lean	MIAR	SCR (80%)	SCR (95%)
NO_x									
NO_x Reduction	%		40	60	80	90	95	80	95
Cyclone Final NO_x	lb/10^6 Btu		0.72	0.48	0.24	0.12	0.06	0.24	0.06
Wall Fired Final NO_x		0.35	0.28	0.18	0.09	0.05	0.02	0.09	0.02
SO_2 Control (via gas)	%	0	0	15	10	10	10	0	0
Capital Cost									
Gas Reburning	$/kw			15	20/22	20/22	27		
Coal Reburning	$/kw			25	30/32	30/32	37		
Conventional	$/kw	10	5					80	109
Reburning fuel firing	%			15	10	10	10		
Catalyst Life	Years							4	4

5.2 Economic Results

Figures 11 and 12 show the results of the economic comparison as plots of the total annual cost of NO_X reduction versus percentage NO_X reduction. Lines of constant unit cost of NO_X control ($/ton of NO_X reduced) are also plotted as fans. As discussed above, the unit cost of NO_X control is the appropriate figure of merit since utilities will apply controls to a number of units, bubbling to achieve the lowest total cost.

Figure 11 shows the cyclone results. The conventional NO_X controls, SNCR and SCR have the highest unit cost of NO_X control in the range of 800-1100 $/ton. The reburning based technologies are considerably lower in cost. Based on the assumptions used for this study, the costs for coal as the reburning fuel are lower than for gas. However, it should be noted that site specific considerations may favor gas in some situations. Factors favoring gas include a low gas-coal cost differential, problems related to carbon loss which are more significant with coal as the reburning fuel, and space limitations which make pulverizer installation expensive, difficult or impossible.

Figure 12 shows the wall fired results. Since the baseline NO_X is lower than for the cyclone application (0.46 versus 1.2 lb/10^6 Btu), the unit cost of NO_X control is higher. As with the cyclone results, the reburn technologies have a considerable cost advantage. Overfire air (OFA) has been included for this application (it cannot be applied to cyclone fired units). While the total annual cost of OFA is low, the low NO_X reduction (25%) results in higher unit cost of NO_X control than all except the SCR technologies. The lower baseline NO_X for this application reduces the amount of nitrogen agent required improving the unit cost of NO_X control for SNCR. These results show the significant economic advantage of the AR technologies for the projected NO_X control market characterized by deep NO_X control. For example, in the cyclone application, the total annual cost of SNCR is comparable to MIAR, but MIAR provides more than twice the NO_X reduction.

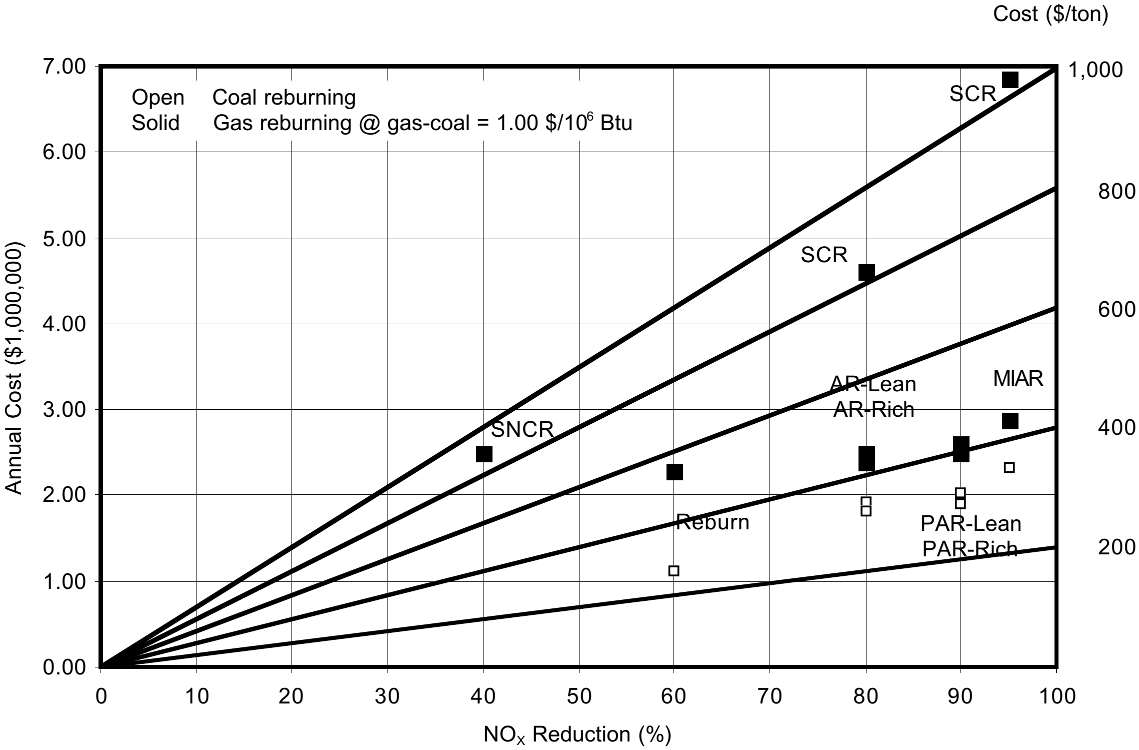


Figure 11. Cyclone fired boiler NOx economics.

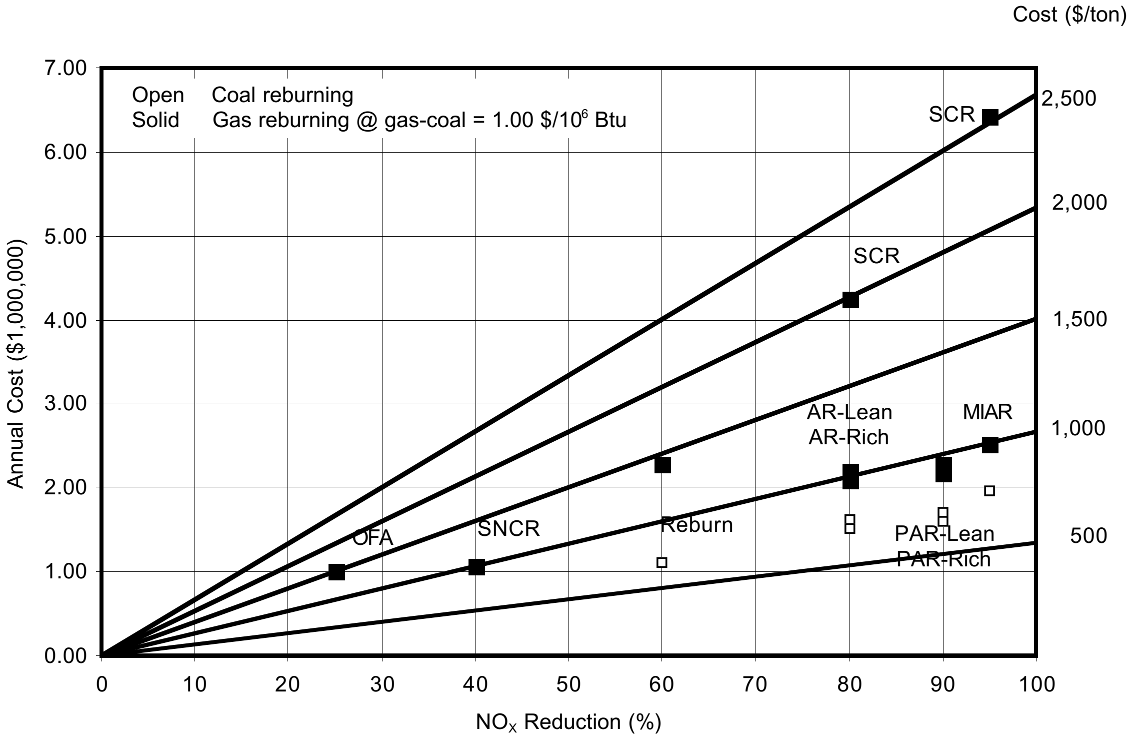


Figure 12. Wall fired boiler NO_X control economics.

5.3 Market Assessment

The size of the market for AR technologies has been estimated by considering the existing and projected Clean Air Act Amendment regulations, the power plants affected by the regulations, and industry projections for the mix of NO_x control technologies necessary for cost effective compliance with these regulations.

At present, NO_x control regulations requiring reductions of up to 75% have been established in the Northeast Ozone Transport Region (NEOTR). A recent study conducted by ICF Kaiser evaluated the alternatives for cost effective NO_x control compliance in this region. It was projected that 9,880 MW of coal fired units will be retrofitted for deep NO_x control, assumed to be SCR. This is the AR market potential and corresponds to $296 million at the mean installed cost for AR of 30 $/kw (range 22-37 $/kw). Although AR is projected to be considerably more cost effective than SCR, a number of factors will reduce AR's market penetration such as the lack of full scale operating experience at the time the retrofit decision is required. If the market is shared equally between SCR and AR, AR will be installed on 4,900 MW at a total cost of $148 million.

EPA is now considering expanding the NEOTR to the 37 state Ozone Transport Assessment Group (OTAG) region. NO_x reductions as high as 85% are being discussed for units in this region. A recent study of NO_x control alternatives in this area was conducted by *Hewson and Stamberg, 1995* using an approach similar to the ICF Kaiser study. Using similar assumptions, the total market for deep NO_x control in the expansion region is 102,000 MW corresponding to $3.07 billion. If the market is shared equally between SCR and AR, AR will be installed on 51,000 MW at a total cost of $1.54 billion. The total market is the sum of the NEOTR and expansion region.

6.0 CONCLUSIONS

The results of the pilot scale tests demonstrated that the AR technologies are able to provide up to 95% NO_x control for a high-sulfur coal-fired combustor. Sodium was found to significantly promote performance. Maximum NO reductions achieved by the promoted AR technologies were 90% for AR-Lean, 93% for AR-Rich, and 95% for MIAR. Up to 90% NO reduction was achieved without sodium injection. AR technologies do not generate significant byproduct emissions in comparison with basic reburning and SNCR processes under similar conditions. In most cases, byproduct emissions were found to be lower for the AR technologies.

The sensitivity analysis revealed the most significant elementary reactions affecting formation and destruction of fuel-N compounds in the reburning zone under various conditions. Modeling with different mixing times demonstrated the importance of delayed mixing modes for efficient NO reduction. Modeling predicts that sodium promotion can improve AR-Rich performance by sustaining the radical pool when it is needed. This effect is most pronounced in systems with long characteristic mixing times, as is typical in full-scale industrial applications. Therefore, promoted advanced reburning shows promise for commercial implementation.

Economic analysis demonstrates a considerable economic advantage for the AR technologies, particularly for deep NO_x control, with cost savings at least 50% in comparison with SCR. The resulting market for AR technologies is estimated to be above $1.5 billion.

7.0 FUTURE ACTIVITIES

The period of project performance is five years which include Phase I, 10/1995-09/1997, and Phase II, 10/97-09/2000. The main activities of the next year will include completing the Phase I studies and the transition to Phase II. Future activities within the Phase II project, if granted by DOE FETC, will include:

- development of alternative AR promoters based on understanding of the sodium promotion mechanisms studied in Phase I;
- development of a combined AR chemistry/mixing model to determine optimum NO_x control conditions;
- optimization of prospective AR variants and process synergism with alternative promoters at 1 MMBtu/hr scale;
- evaluation of different AR variants with the use of coal as the reburning fuel;
- scale-up of the AR technologies and 10 MMBtu/hr Proof-of-Concept tests; and
- validation of the design methodology for AR technologies, its application to a full scale boiler, final economic evaluation, and market analysis.

8.0 ACKNOWLEDGMENT

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