

SECOND GENERATION ADVANCED REBURNING

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INTRODUCTION

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 hybrid reburning/SNCR schemes. These systems incorporate two improvements over basic reburning and EER's advanced reburning (AR) processes (Seeker *et al.*, 1992):

- N-agent Promotion There are additives which considerably enhance the NO_x control from N-agent injection. These "promoters" are water soluble inorganic salts which can be added to aqueous nitrogen agents (Ho *et al.*, 1993).
- N-agent Injection into the Reburning Zone In AR, the N-agent is injected along with the overfire air (OFA) in the fuel-lean gas (AR-Lean). 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).

The AR process is an integration of basic reburning and SNCR. With AR, by adjusting the reburning fuel injection rate to achieve near stoichiometric conditions (instead of the fuel rich conditions normally used for reburning), the CO level is controlled and the temperature window for selective NO_x reduction is considerably broadened and deepened.

Second Generation Advanced Reburning (SGAR) develops improved versions of AR. These systems have the potential to achieve 95% NO_x control on all types of coal fired boilers without massive hardware changes, without increasing air toxic and toxic waste problems, and at a cost for NO_x control on the order of half that of SCR. SGAR will provide flexible installations that allow NO_x levels to be lowered as new elements of the technology become available. The SGAR systems are intended for post-RACT applications in ozone non-attainment areas where NO_x control in excess of 80% is required.

Figure 1 presents general schematic of the SGAR process. It includes injection of a N-agent into the reburning zone, and then, injection of OFA with the second N-agent. Each N-agent can be injected with or without promoter. This work-in-progress paper presents initial experimental and modeling results on SGAR development: injection of N-agents and Na-promoters in the reburning zone and with OFA.

EXPERIMENTAL RESULTS

A 0.1 MBtu/hr bench scale Controlled Temperature Tower (CTT) was used in this study. The CTT is a vertically downfired combustor (Figure 2) with a 20 cm inside diameter and 3.5 m height. The facility is equipped with several ports to allow introduction of sampling and injection probes. For most tests the temperature gradient in the reaction zone was about 300 K/s.

Natural gas was used as the main and reburn fuels in these tests. Flue gas was sampled at the furnace exit. Performance was characterized by continuous emissions monitors (CEMs) for O₂, CO,

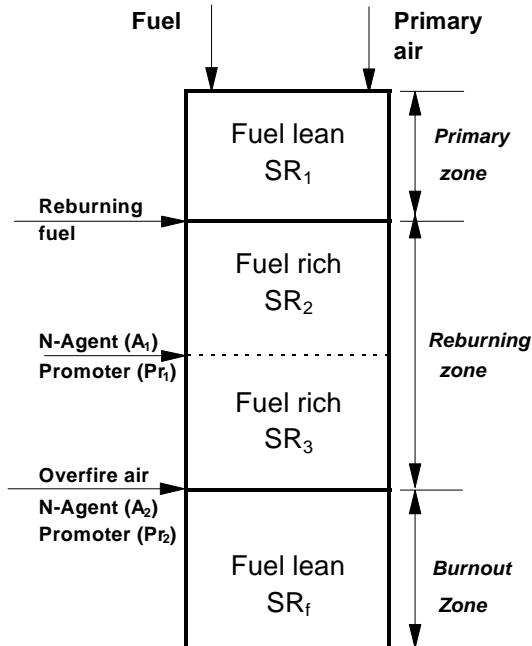


Figure 1. Second Generation Advanced Reburning schematic.

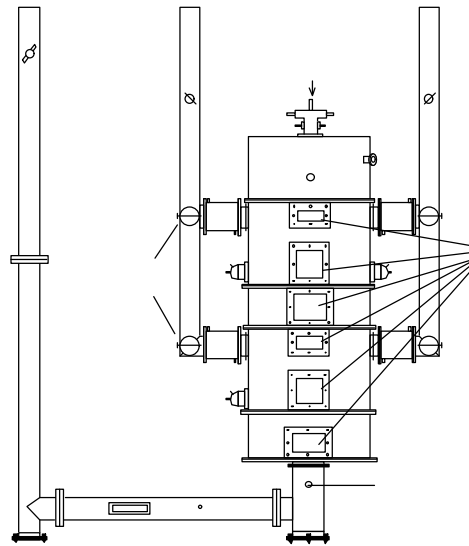


Figure 2. Controlled Temperature Tower schematic.

CO₂, NO/NO_x, and N₂O throughout the tests, and by sampling and analysis of NH₃ and HCN.

In all experiments the initial Stoichiometric Ratio in the main combustion zone was SR₁=1.1. Ammonia was added to the main fuel to provide an initial NO concentration of 600 ppm. The reburning fuel was injected at about 1600-1700K at two injection rates, 10 and 20% of heat input, providing stoichiometries in the reburning zone SR₂=0.99 and 0.88. Ammonia and urea were injected in the form of aqueous solutions with different Nitrogen Stoichiometric Ratios (NSR); ammonia was also injected in gas form. NSR is a molar ratio of N-agent to the NO concentration at the time of injection. N-agents were injected with a delay time, 0-0.7 s, after injection of the reburning fuel. Sodium carbonate was diluted in N-agent solutions. Concentration of Na₂CO₃ was varied from 0 to 120 ppm Na in flue gas. OFA was injected at different locations to provide a final stoichiometry SR_f=1.15.

Figures 4a and 4b compare two different hybrid reburn/SNCR processes: reburn + SNCR (i.e. injection of the reburning fuel, OFA, and then, N-agent) and AR-Lean (i.e. injection of the reburning fuel and OFA with N-agent). Reburn+SNCR with 20% reburning fuel achieves 73-84% NO control. AR-Lean requires only 10% reburning fuel and demonstrates 75-82% NO control. Temperature resolution in these experiments is relatively low, and performance can be perhaps higher at the optimum N-agent injection temperature. Previous EER data (*Seeker, 1992*) shows that AR-Lean can achieve up to 85% NO control.

Figures 4c and 4d demonstrate efficiency of the AR-Rich process, i.e. injection of the reburning fuel, delayed injection of a N-agent, with or without sodium carbonate, in the reburning zone, and then OFA. Only 15 ppm Na₂CO₃ (30 ppm Na) substantially improve performance of the process

to 88% NO control.

Figure 4e illustrates that injection of ammonia at two locations results in above 90% NO_x

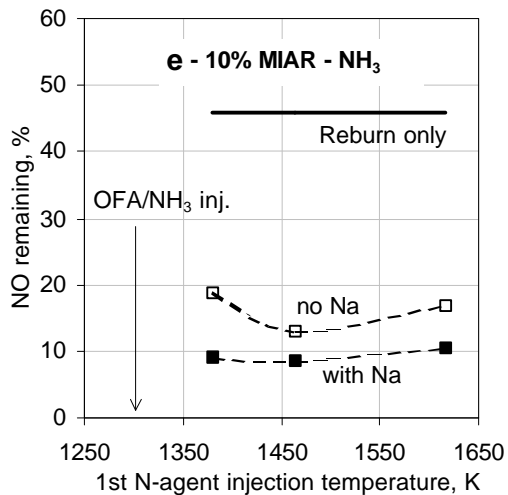
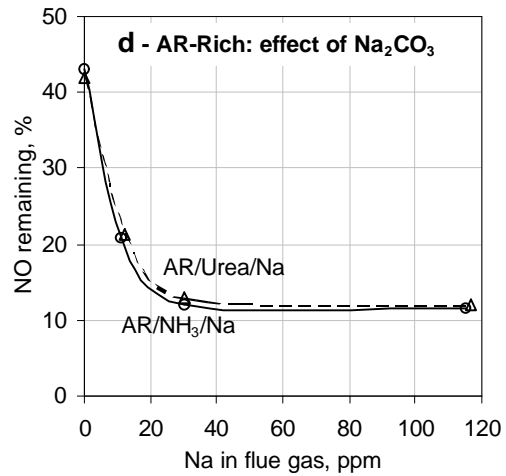
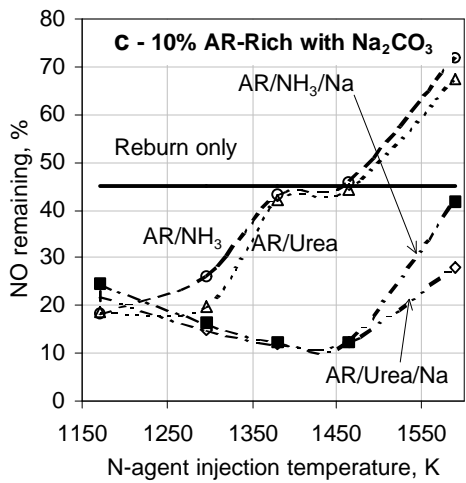
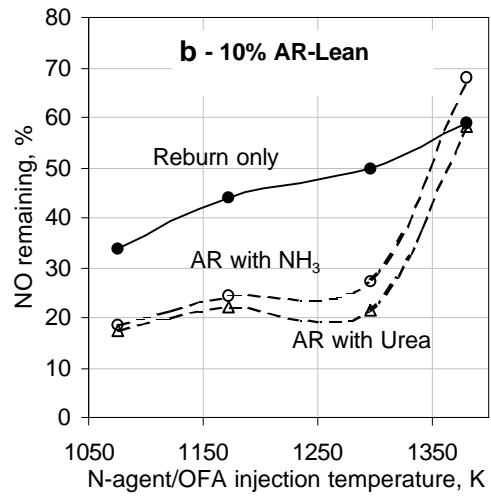
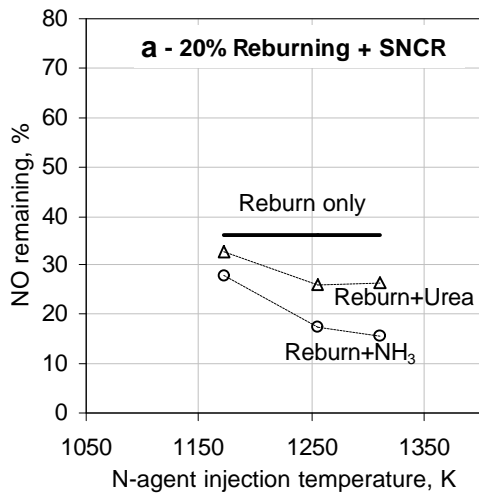


Figure 3. Experimental results. **a** - $SR_2=0.88$, OFA injected at 1530K, $NSR=1.5$; **b** - $SR_2=0.99$, N-agent injected with OFA, $NSR=1.5$; **c** - $SR_2=0.99$, OFA injected at 1155K, $NSR=1.5$; 15 ppm Na_2CO_3 added with N-agent; **d** - $SR_2=0.99$, OFA added at 1155 K, $NSR=1.5$, N-agent and Na_2CO_3 injected at 1380K; **e** - $SR_2=0.99$, 1st NH_3 injected at three different locations with or without 15 ppm Na_2CO_3 , 2nd NH_3 injected at 1297K with OFA.

control. In these experiments, 10% reburning fuel was injected at about 1620 K. The first NH_3 was injected in the reburning zone, with or without 15 ppm sodium carbonate, at three different locations: 1620 K (with the reburning fuel), 1450 K, and 1380 K. Figure 4e shows the performance of the process depending on the first NH_3 injection temperature. In all cases, OFA was injected at 1297 K with the second NH_3 without sodium. For both NH_3 injections, NSR was 1.5. Maximum performance achieved was about 92% NO_x removal. There is also a potential to increase this level of control in future experiments by optimizing injection temperatures for the N-agents, promoter composition, and using promoters in the second N-agent injection point.

KINETIC MODELING

The experimental work is paralleled by kinetic modeling which provides a scientific understanding of the process. The Chemkin-2 code (*Kee et al., 1989*) and the reaction mechanism based on the GRI-Mech version 2.11 (*Bowman et al., 1995*) were used for modeling. Thermal De NO_x reactions which are absent in the GRI-Mech, were selected from the scheme by *Bowman, 1996* and added to the mechanism. The total mechanism included 49 components and 312 reactions. Modeling was performed without variation of rate constants for a plug flow reactor with 300 K/s temperature decrease in the reaction zone and for the following mixture entering the reburning zone: 8% CO_2 - 15% H_2O - 1.74% O_2 - 600 ppm NO . Concentrations of reburning fuel and ammonia and delay times of ammonia injection were varied. Modeling does not quantitatively describe the experimental results. Observed discrepancies are explained by poor understanding of the chemical reactions between NO and carbon-containing radicals and differences in mixing conditions: instantaneous in modeling and within about 50 ms in experiments. Therefore, the goal of modeling was to provide insight into the controlling chemical factors of the process and qualitatively describe the observed main reaction trends, such as the effects of delayed N-agent injection and Na-promotion.

Experiments demonstrated (Figure 3) that addition of N-agents into the reburning zone improves NO_x reduction if the N-agent is injected in the form of solution shortly after introduction of the reburning fuel. Modeling shows that addition of the fuel to the reburning zone results in very fast oxygen consumption to form CO and H_2 . If N-agents are injected into the reburning zone, they form NH_i radicals (NH_2 , NH , N) which are active in NO removal reactions. The NH_i radicals can react either with O_2 into NO or with NO into N_2 . The NO reduction process is effective if the NH_i precursors (N-agents) appear in the gas mixture when concentration of oxygen has been significantly depleted by the reburning fuel, thus preventing oxidation of N-

agents into NO.

Results of calculations which demonstrate the effect of NO reduction by CH₄ reburning in the presence of NH₃ are presented in Figure 4 (curves 1-4). Curve 1 is the initial uncontrolled NO level of 600 ppm. Curve 2 models 10% reburning when CH₄ is added to the reburning zone at 1700K. The NO concentration decreases to 412 ppm in 1.5 s (the time of OFA addition at 1255K), or about 31% NO reduction. Curve 3 shows that if 800 ppm NH₃ is added simultaneously with the reburning fuel, the NO concentration is rapidly increased to 900 ppm and then reduced to 500 ppm in 1.5 s. Oxygen prevents NO reduction because the added NH₃ burns rapidly in the presence of O₂ to form additional NO. Therefore, it is logical to add ammonia not with the reburning fuel, but after the O₂ concentration has decreased through reaction with the reburning fuel: NSR=1.5 with 0.1 s delay in curve 4. In 1.5 s of the reaction time, the NO concentration drops to 113 ppm, but 144 ppm NH₃ is left in the reaction media, and thus, TFN=257 ppm as shown in Figure 4. Concentration of HCN was below 1 ppm at SR₂=0.99. Injection of OFA at 1255K resulted in 230 ppm final NO concentration, 62% NO reduction.

At higher reburning fuel concentration (20% reburning, SR₂=0.90), modeling shows formation of 229 ppm TFN in 1.5 s (70 ppm HCN, 115 ppm NH₃, and 44 ppm NO). Injection of OFA at 1255K results in a 200 ppm final NO level, corresponding to 67% NO reduction. Injection of ammonia (NSR=1.5) into the fuel-rich zone at SR₂=0.90 with a 0.1 s delay followed by OFA injection, does not significantly change the final NO level in modeling, and the same was shown experimentally. However, Na-promoters are effective even at SR₂=0.90.

It was assumed for modeling that sodium reacts with water at high temperature and forms active species (H and OH) at a faster rate than they are formed without sodium additives. The following empirical reaction was added to the mechanism: [(Na)HOH]+M=>(Na)+OH+H+M. This equation simulates fast interaction of sodium compounds with water molecules with formation of a complex, [(Na)HOH], which dissociates into OH and H. The initial concentration of [(Na)HOH] was assumed to be 100 ppm in modeling. The rate constant for [(Na)HOH] decomposition was selected in the form $A \exp(-20,000/T) \text{ cm}^3/\text{mol s}$ where the preexponential factor A was varied in the range from 10⁹ to 10¹². These values of the rate constant provided decomposition of the complex with characteristic times between approximately 0.1 and 100 s.

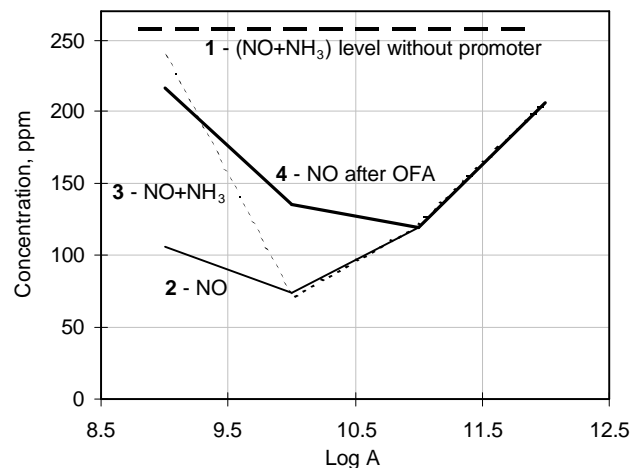
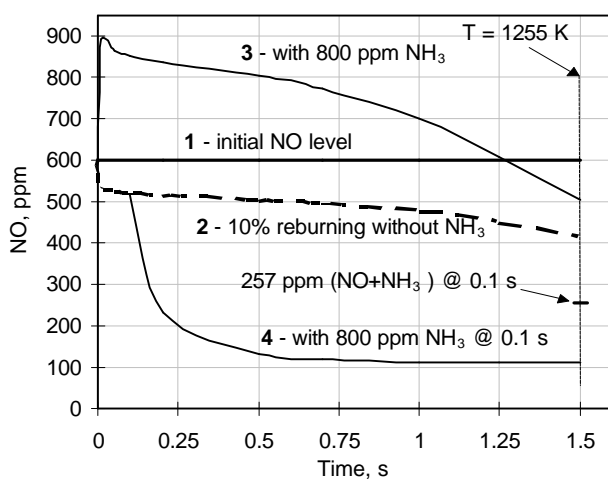


Figure 4. Modeling the effect of ammonia in the reburning zone (without OFA).

Figure 5. Modeling of the promotion effect at different preexponential factors A.

Figure 5 compares the results of modeling NO and NH₃ concentrations at t = 1.5 s (the same conditions shown by curve 4 in Figure 4 at T=1255K) at different values of the preexponential factor A. The promoter [(Na)HOH] was added into the reburning zone along with ammonia at a 0.1 s delay time. The level of TFN without promoter (257 ppm) is shown in Figure 5 (line 1) for comparison. In a wide range of the promoter decomposition rate, NO and TFN concentrations are substantially lower than their values without promoter. In the presence of the promoter there is a minimum of the final NO concentration at logA=10.5. Thus, there exists an optimum rate constant for formation of additional radicals which cause minimum NO emissions. Figure 5 compares NO (curve 2) and NO+NH₃ (curve 3) concentrations at T = 1255K before OFA injection and the final NO concentration after OFA injection (curve 4). In the OFA zone, some NO reacts with NH₃ due to the Thermal DeNO_x reactions, and the minimum level of NO at logA=10.5 after OFA injection is about 120 ppm. Hence, additional formation of radicals in the reburning zone can explain deeper NO reduction in the presence of Na-promoters.

CONCLUSIONS

The results of this study demonstrate a significant influence of N-agents and sodium promoters on NO removal via reburning. Delayed appearance of N-agents in the gas mixture provide the time which is necessary for depletion of the oxygen from the main combustion zone by the reburning fuel, thus preventing oxidation of the N-agents into NO. Sodium compounds, such as sodium carbonate, promote the effect of N-agents. The promotion effect can be explained by reactions of additional active radicals formed in the reburning zone via interaction of sodium compounds with water molecules. Further research on promotion mechanism is needed to better understand and optimize this effect. The following factors primarily control process efficiency: stoichiometric ratio in the reburning zone, delay time between injection of the reburning fuel and formation of NH_i radicals in the reburning zone, oxygen concentration at the time of N-agent injection, concentration of N-agent, and OFA injection location. About 88% NO reduction was achieved by injection of only 10% natural gas as reburning fuel (SR₂=0.99) at 1600K followed by 0.5 s delayed injection of aqueous ammonia or urea (NSR=1.5) with sodium carbonate (15 ppm in gas mixture) and injection of OFA at 1150-1300 K. Under similar conditions, injection of 20% reburning fuel results in about 90% NO_x control. Multiple injection AR is capable of achieving above 90% NO_x control with only 10% reburning fuel. Modeling predictions are in qualitative agreement with experiments and explain interaction of NO and ammonia in the reburning zone.

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