SECOND GENERATION ADVANCED REBURNING
FOR HIGH EFFICIENCY NO_x CONTROL

Quarterly Report No. 6 for Period
January 1 – March 31, 1999

Prepared by:
Vladimir M. Zamansky, Peter M. Maly and Vitali V. Lissianski

April 29, 1999

DOE Contract No. DE-AC22-95PC95251--14

Submitted by:
Energy and Environmental Research Corporation
18 Mason, Irvine, CA 92618

Disclaimer

Abstract

This project is designed to develop a family of novel NO_x control technologies, called Second Generation Advanced Reburning which has the potential to achieve 90+ NO_x control in coal fired boilers at a significantly lower cost than Selective Catalytic Reduction. The sixth reporting period in Phase II (January 1 – March 31, 1999) included experimental activities and combined chemistry-mixing modeling on advanced gas reburning. The goal of combustion tests was to continue the work on identifying prospective promoters for the advanced reburning process. Tests were conducted in Controlled Temperature Tower (CTT) and Boiler Simulator Facility (BSF). Tests showed that some promoters significantly affect the reburning process when co-injected with NH_3. The promoters injected into reburning zone without NH_3 in the amount 30 ppm do not significantly affect the reburning process. The modeling effort was focussed on the description of Na effect on CO emissions in advanced reburning. Increase in CO concentration in flue gas upon Na injection results from inhibition of CO oxidation by Na species in the burnout zone.

Table of Contents

Section Page

Abstract 3
Executive Summary 5
1.0 Evaluation of Alternative Promoters for Advanced Reburning 6
2.0 Kinetic Modeling 9
3.0 Future Work 13
4.0 Bibliography 14

List of Figures

Figure Page

Figure 1.1 Effect of $FeSO_4$ on the reburning process 6
Figure 1.2. Effect of fly ash injection on NO reduction 7
Figure 1.3 Reburning performance of activated char 8
Figure 1.4 Promoter screening tests... 8
Figure 2.1. Rate coefficient of the reaction $NaOH + H \rightarrow Na + H_2O$ 12
Figure 2.2. Comparison of modeling predictions with experimental data on CO emissions 12
Figure 2.3. CO emissions in advanced reburning process as a function of flue gas temperature.. 13

Executive Summary

This project is designed to develop a family of novel NO_x control technologies, called Second Generation Advanced Reburning which has the potential to achieve 90+ NO_x control in coal fired boilers at a significantly lower cost than SCR. The sixth reporting period in Phase II (January 1 – March 31, 1999) included experimental activities and combined chemistry-mixing modeling on advanced gas reburning.

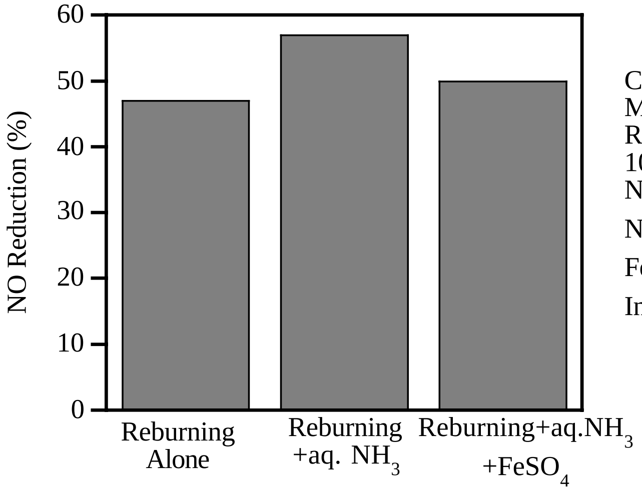
The goal of combustion tests was to continue the work on identifying prospective promoters for the advanced reburning (AR) process. Tests were conducted in 20 kW Controlled Temperature Tower (CTT) and 300 kW Boiler Simulator Facility (BSF). Tests in CTT showed that $FeSO_4$ co-injected with NH_3 has a minor effect on the AR process. Several compounds were selected for tests in which promoters were injected into reburning zone without NH_3. These tests showed that 30 ppm of promoters promoters do not significantly affect the reburning process. The largest promotion effect (about 4% NO reduction in comparison with unpromoted process) was observed for injection of Na compounds and was much smaller than the effect produced by the same compounds co-injected with NH_3 (about 50% NO reduction in comparison with unpromoted process). Tests in BSF demonstrated that injections of fly ash and char into the reburning zone do not significantly affect NO_x reduction.

The modeling efforts during the reporting period concentrated on further model development to describe the effect of promoter addition on CO emissions. In contradiction with experimental data, previous modeling efforts showed that co-injection of Na promoter with NH_3 decreases CO concentration in comparison with unpromoted process. Sensitivity and flux flow analyses identified reactions in Na sub-mechanism that have significant effect on CO concentration in flue gas. Adjustment of the rate coefficient expressions of two reactions resulted in dramatic improvement of the agreement between modeling predictions and experimental data. An increase in CO concentration in flue gas upon Na injection results from inhibition of CO oxidation by Na species in burnout zone.

1.0 Evaluation of Alternative Promoters of Advanced Reburning

The goal of these tests is to identify prospective promoters of the advanced reburning (AR) process other than Na_2CO_3. The previous report [1] described tests in the 20 kW Controlled Temperature Tower (CTT) in which several alternative promoters were identified. Activities in search of alternative promoters were continued during the reporting period and included testing other compounds in the CTT and Boiler Simulator Facility (BSF). The EER's 300 kW BSF was described in Quarterly Report No. 2 [2]. The promoters were co-injected into the reburning zone with NH_3. In some tests, additives were injected in the reburning zone without ammonia.

Figure 1.1 shows effect of $FeSO_4$ on the AR process. These tests were conducted in CTT. The promoter was co-injected with NH_3 in the reburning zone. In all tests the reburning fuel (natural gas) was injected at 1670 K and overfire air (OFA) was injected at 1300 K as shown in Figure 1. The use of $FeSO_4$ provided 50% NO reduction, which less than the effect of NH_3 alone. Thus, injection of $FeSO_4$ resulted in inhibition of the NO reaction with ammonia.



CTT: 20 kW
Main Fuel : Natural gas
Reburning Fuel: Natural gas
10% Reburn @ 1670 K, OFA @ 1300 K
NO_i = 600 ppm
NH_3/NO_i = 1.5
$FeSO_4$ = 30 ppm
Injection temperature = 1460 K.

Figure 1.1 Effect of $FeSO_4$ on the reburning process.

Figure 1.2 shows the effect of fly ash injection in the reburning zone with no NH_3 injection. These tests were conducted in BSF at 18 % heat input from reburning fuel. The ash was co-injected with the reburning fuel. Three types of ash were used: as received, calcined, and calcined/hydrated. The ash was calcined by heating it in an oven overnight. As seen in Figure 1.2, fly ash has little if any effect on the reburning process. Fly ash calcination and hydration improved performance marginally.

Additional BSF tests were conducted in which char comprised part of the reburning fuel. For these tests the char was activated by heating it to 600 K for one hour. The total reburning heat input was held constant at 18% and the reburning heat input of the char was varied from 0 to 8%. Figure 1.3 shows that impact of char on reburning performance was minimal.

Previous tests [1] showed that some additives affect the AR process when co-injected with NH_3 in the reburning zone. It is worthwhile to determine if the same additives can affect the reburning process when injected alone. Figure 1.4 shows the effect of several additives on the reburning process. The tests were conducted in the BSF. Injection of sodium compounds without NH_3 provides up to 4% additional reduction in comparison with the unpromoted process. This effect is much smaller than the effect of combined injection of NH_3 and Na compounds [1].

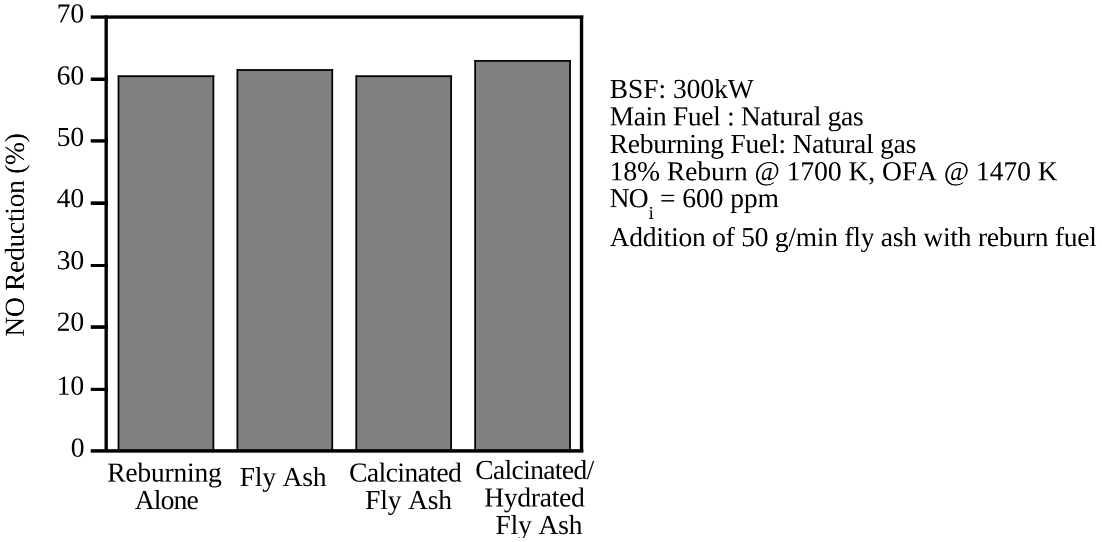


Figure 1.2. Effect of fly ash injection in the reburning zone.

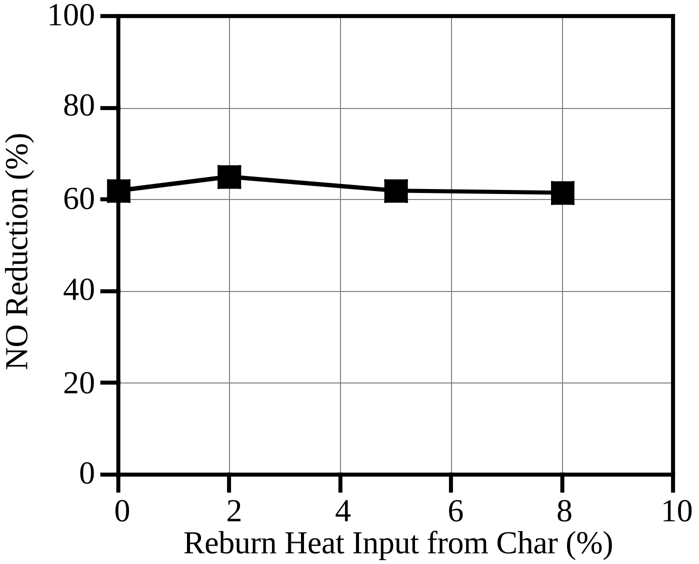
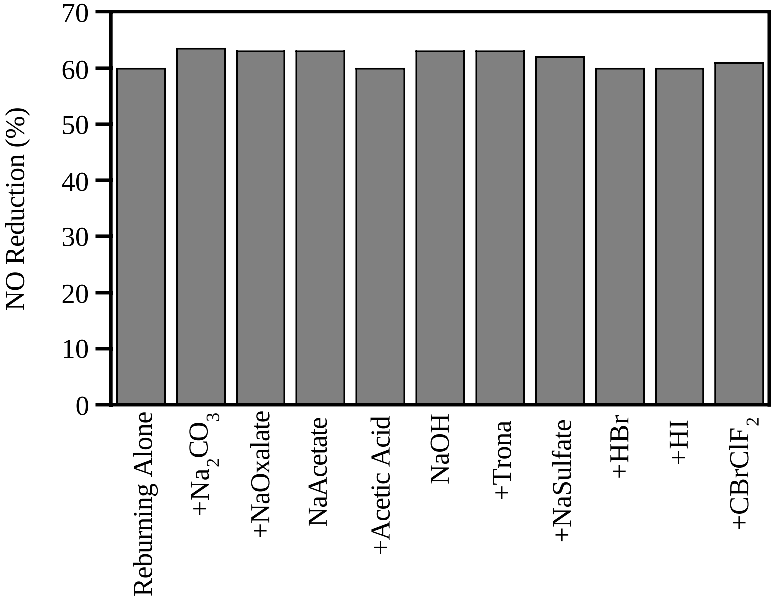


Figure 1.3 Reburning performance of activated char as a function of char reburning heat input (same conditions as in Figure 1.2).



BSF: 300 kW
Main Fuel : Natural gas
Reburning Fuel: Natural gas
20% Reburn @ 1700 K,
OFA @ 1470 K
NO_i = 600 ppm
30 ppm of promoter
Promoter co-injection
with reburning fuel

Figure 1.4 Promoter screening tests.

2.0 Kinetic Modeling

This section describes ongoing efforts to model the AR process. Previous work [1] demonstrated that main features of AR can be described by using a detailed chemical mechanism [3] supplemented with reactions of Na-containing species [4] and with a one-dimensional representation of mixing. It was shown that injection of NH_3 and a sodium promoter in the reburning zone results in an increase of NO reduction. However, in contradiction with experiments, modeling predicted that co-injection of Na promoter with NH_3 slightly decreases CO concentration in flue gas. Experimental data (obtained at low overfire injection temperatures) show that injection of Na promoter results in a significant increase in CO concentration. The modeling efforts during the reporting period concentrated on further model development to improve the agreement with experimental data on CO emissions.

The kinetic model included 447 reactions of 65 C-H-O-N chemical species and was supplemented with 20 reactions of four Na-containing species. The mixing times for injections of all steams (reburning fuel, NH_3 and Na promoter, and OFA) were 150 ms and were estimated using 2D spray and 2D jet-in-cross-flow models. The EER chemical kinetic code ODF, for “One Dimensional Flame” [5] was employed to model the experimental data.

Modeling shows that fuel oxidation in the reburning zone generates a significant amount of CO. For 10% reburning heat input, the concentration of CO at the end of the reburning zone is about 3800 ppm. The CO formed in the reburning zone is oxidized to CO_2 when OFA is injected to complete combustion. The temperature of OFA injection should be high enough to provide complete CO oxidation. Modeling predicts that concentration of CO in the flue gas decreases to 56 ppm after addition of OFA at 1300 K. This concentration is higher than that found in experiments (around 10 ppm) which can be attributed to the significant (–1240 K/s) temperature gradient in the experimental facility (CTT). Small uncertainties in the measured temperature profile can appreciably affect modeling predictions.

In agreement with experiments, modeling predicts that injection of NH_3 in the reburning zone results in a decrease of CO concentration in flue gas. Modeling shows that only a small fraction of the NH_3 reacts in the reburning zone. The remaining NH_3 reacts with oxygen in the OFA zone. This process generates active species (OH radicals, H atoms and others) which contribute to CO oxidation and account for the smaller CO concentration in flue gas.

However, modeling predictions were in contradiction with experiments when a Na promoter was co-injected with NH_3. Species flux calculations showed that a decrease in CO concentration predicted in modeling is a result of faster rate of CO oxidation in the presence of Na. To improve the model, routes for CO oxidation in the presence of Na-containing species were studies and identified to be the following:

$$CO + NaO \rightarrow CO_2 + Na \qquad (1)$$

$$CO + NaO_2 \rightarrow CO_2 + NaO \qquad (2)$$

The rate of CO oxidation in reaction (2) is much faster than that in reaction (1). Reaction (2) accounts for almost 100% of the total increase in CO oxidation observed in modeling. Reactions (1) and (2) have not been studied experimentally. Perry and Miller [6] estimated rate coefficients of these reactions to be 1.0×10^{14} $cm^3mol^{-1}s^{-1}$. Our modeling shows that to avoid decreasing the CO concentration in flue gas in the presence of Na promoter, rate coefficient of the reaction (2) must be $\leq 1.0\times10^{10}$ $cm^3mol^{-1}s^{-1}$.

Adjustment of the rate coefficient for reaction (2) improved the agreement with experimental data. However, modeling still predicted much lower CO concentrations in flue gas than found in experiments. Sensitivity calculations showed that among reactions of Na-containing species the reaction

$$NaOH + H \rightarrow Na + H_2O \qquad (3)$$

has the largest effect on the rate of CO oxidation. This reaction inhibits oxidation process by removing H atoms which otherwise react with O_2 via

$$H + O_2 \rightarrow OH + O. \tag{4}$$

Since CO oxidation mainly occurs in the reaction with OH radicals

$$CO + OH \rightarrow CO_2 + H \tag{5}$$

which are mostly produced in reaction (4), the rate of reaction (3) actually controls the rate of CO oxidation in the burnout zone when Na-containing species are present.

Review of the literature data shows that reaction (3) has not been studied extensively. Available information on the rate coefficient of reaction (3) at high temperatures is limited to flame measurements by Jensen and Jones [7] (Figure 2.1). Perry and Miller [6] gave an estimate of the rate coefficient of reaction (3) 5.0×10^{13} $cm^3mol^{-1}s^{-1}$ which is larger than experimentally reported value [7]. Our modeling shows that reasonable agreement with experimental data on CO emissions can be achieved if the rate coefficient of reaction (3) is equal to 1.0×10^{14} $cm^3mol^{-1}s^{-1}$.

Figure 2.2 shows comparison of modeling predictions with experimental data on CO emissions. Adjustment of the rate coefficients of reactions (2) and (3) resulted in dramatic improvement of the agreement between modeling predictions and experimental data. Although modeling results and experiments still do not agree quantitatively, modeling qualitatively describes the main features of the process.

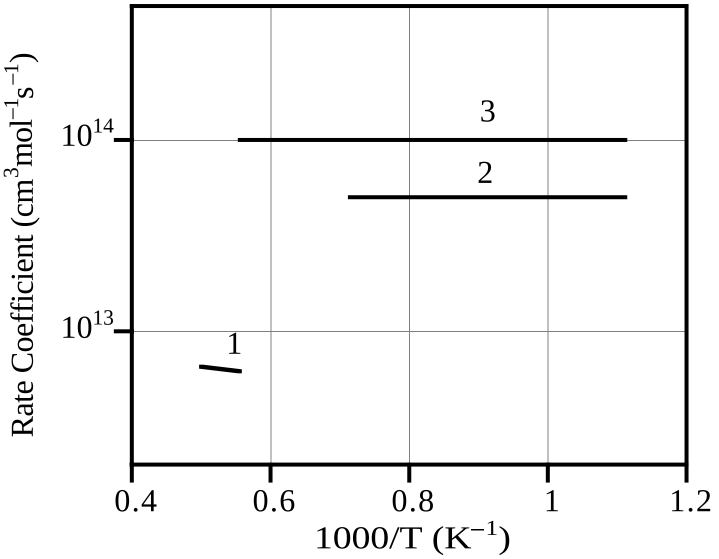


Figure 2.1. Rate coefficient of the reaction NaOH + H $\rightarrow$ Na + H_2O. 1 – Jensen and Jones [7] measurements, 2 – Perry and Miller [6] estimate, 3 – this work.

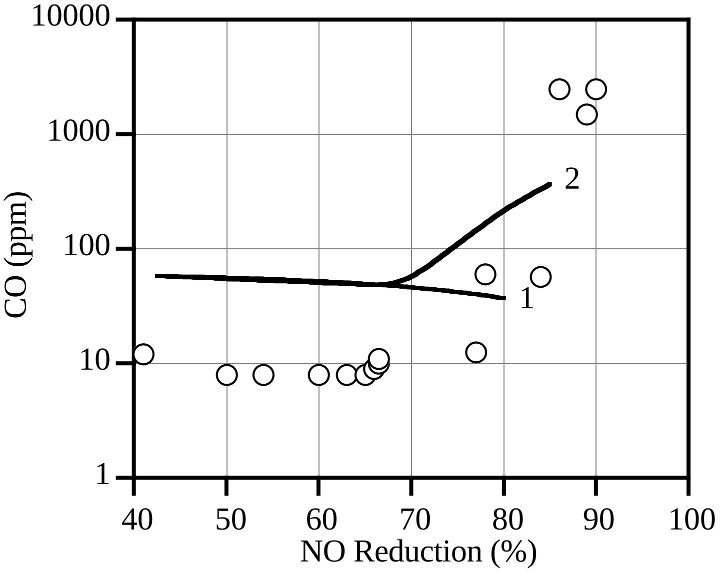


Figure 2.2. Comparison of modeling predictions (lines) with experimental data (symbols) on CO emissions. OFA is injected at 1300 K. 1- modeling with default k_2 and k_3, 2 – modeling with k_2 and k_3 adjusted.

Modeling predicts that CO emissions in the presence of NH_3 and Na additives depend on flue gas temperature at the point of OFA injection. Figure 2.3 shows that a decrease in this temperature results in an increase in CO emissions. Since OFA and the flue gas have different temperatures before mixing, the mixing area in the OFA zone is characterized by non-uniform temperature distribution and significant temperature fluctuations. This is the most likely reason why modeling predictions and experimental data do not agree quantitatively.

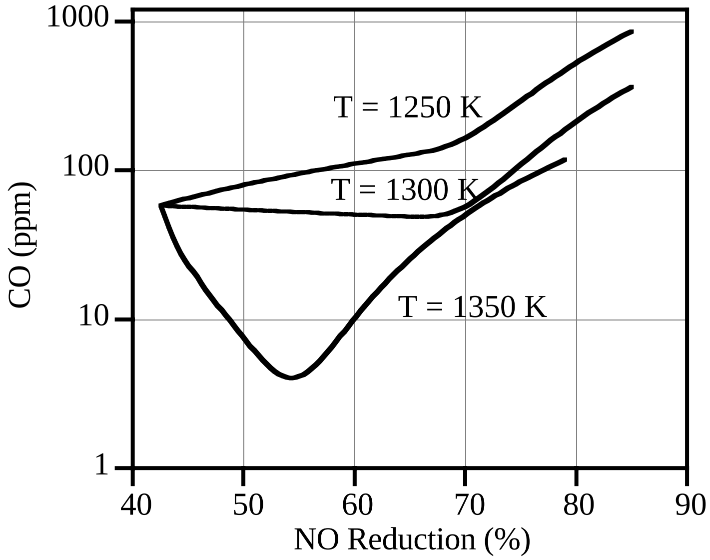


Figure 2.3. CO emissions in advanced reburning process as a function of flue gas temperature at the point of OFA injection.

To avoid high CO concentration in flue gas, OFA has to be added at higher than 1300 K temperatures. Figure 2.3 shows that an increase in OFA injection temperature results in a decrease in CO emissions in the AR process.

3.0 Future Work

This report describes ongoing efforts to evaluate the effect of alternative promoters on the AR process. Future activities will include an assessment of the effect of the promotive additives on AR. Kinetic modeling will support these activities. The effect of additives will be predicted using the model and compared with experimental data. Future activities will also include evaluation of coal as the reburning fuel in AR.

4.0 Bibliography

1. Zamansky, V.M., Lissianski, V.V., and Maly, P.M. (1998) Second Generation Advanced Reburning for High Efficiency NO_x Control. *Quarterly Report No. 5, DOE Contract No. DE-AC22-95PC95251*.
2. Zamansky, V.M., and Maly, P.M. (1998) Second Generation Advanced Reburning for High Efficiency NO_x Control. *Quarterly Report No. 2, DOE Contract No. DE-AC22-95PC95251.*
3. Glarborg, P., Alzueta, M.U., Dam-Johansen, K., and Miller, J.A. (1998) *Combust. Flame* 115, 1.
4. Zamansky, V.M., Lissianski, V.V., Maly, P.M., Ho, L., Rusli, D., and Gardiner, W.C., Jr. (1999) *Combust. Flame*, 117:821.
5. Kau, C.J., and Tyson, T.J. (1987) A Computer Program for General Flame Analysis. *U.S. Environmental Protection Agency Report No. EPA-6000/7-87-027*.
6. Perry, R.A., and Miller, J.A. (1996) *Int. J. Chem. Kinetics*, 28:217.
7. Jensen, D.E., and Jones, G.A. (1982) *J. Chem. Soc. Faraday Trans.* 1, 78:2843.