

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

Quarterly Report No. 4 for Period
July 1 – September 30, 1998

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October 30, 1998

DOE Contract No. DE-AC22-95PC95251 -12
Phase II

Submitted by:
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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 SCR. The fourth reporting period in Phase II (July 1 – September 30, 1998) included experimental activities at pilot scale and combined chemistry-mixing modeling on gas reburning. The pilot scale tests reported in previous Quarterly Reports QR-2 and QR-3 were continued. The objective was to simulate furnace conditions at the Greenidge boiler No. 6 owned and operated by NYSEG and to improve the process performance. The tests were conducted in EER's Boiler Simulator Facility (BSF). During the reporting period, measurements of CO and ammonia emissions were conducted for reburn + SNCR conditions, as well as tests on the effect of sodium on NO_x control efficiency. Exhaust levels of CO remained below 100 ppm in all tests. Prospective process conditions for the full-scale facility have been identified that can provide over 80% NO_x reduction while maintaining ammonia slip below 4 ppm. Addition of sodium resulted in NO_x control improvement of about 7-10 percentage points. The objective of modeling work was to further understand the influence of the mixing process on gas reburning and to identify factors that can increase the effectiveness of NO reduction. Modeling results demonstrated that the main features of gas reburning could be described using a detailed chemical mechanism with one-dimensional representation of mixing.

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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 fourth reporting period in Phase II (July 1 – September 30, 1998) included experimental activities at pilot scale and combined chemistry-mixing modeling on gas reburning.

The pilot scale tests reported in previous Quarterly Reports QR-2 and QR-3 were continued. The objective was to simulate furnace conditions at the Greenidge boiler No. 6 owned and operated by NYSEG and to improve the process performance. The tests were conducted in EER's Boiler Simulator Facility (BSF). During the reporting period, measurements of CO and ammonia emissions were conducted for reburn + SNCR conditions, as well as tests on the effect of sodium on NO_x control efficiency. Exhaust levels of CO remained below 100 ppm in all tests. Prospective process conditions for the full-scale facility have been identified that can provide over 80% NO_x reduction while maintaining ammonia slip below 4 ppm. Addition of sodium resulted in NO_x control improvement of about 7-10 percentage points.

The objective of modeling work was to further understand the influence of the mixing process on gas reburning and to identify factors that can increase the effectiveness of NO reduction. Modeling results demonstrated that the main features of gas reburning could be described using a detailed chemical mechanism with one-dimensional representation of mixing. Inverse addition of reactants in the mixing area gives much better approximation of fuel rich environment in the reburning zone compared to mixing of reburning fuel into the main stream. Stratification in the mixing zone improves reburning efficiency for small heat inputs of the reburning fuel and degrades reburning efficiency for large heat inputs. Based on modeling observations, it is suggested that design of the injector should be different depending on the amount of the injected reburning fuel. Injection of large amounts of the reburning fuel provides better NO_x reduction if mixing of reactants is fast. Injection of small amounts of the reburning fuel, on the other hand, should result in significant mixture stratification for better NO_x control (as long as complete burnout is ultimately achieved).

1.0 INTRODUCTION

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

Task 2.1 Project Coordination and Reporting/Deliverables

Task 2.2 Studies of Other Prospective Additives

Task 2.3 Development of Combined Chemistry/Mixing Model

Task 2.4 Optimization of Process Synergism in 1×10^6 Btu/hr Tests

Task 2.5 10.0×10^6 Btu/hr Proof-of-Concept Tests

Task 2.6 Design Methodology Validation

Previous Quarterly Report, QR-3, described pilot scale testing of reburn+SNCR and comparison of the results on AR-Lean and reburn+SNCR with full-scale data. The pilot scale tests were performed with the objective of predicting furnace conditions of scheduled for fall 1998 full-scale reburn+SNCR tests at the Greenidge boiler and defining major factors controlling process performance. This work was continued during the current fourth quarter of the project (July 1 – September 30, 1998). The tests were conducted in EER's Boiler Simulator Facility (BSF) on measurements of CO and ammonia emissions for reburn + SNCR conditions, as well as on NO_x emissions in the presence of sodium.

Modeling effort was also continued. The objective of modeling was to further understand the influence of the mixing process on gas reburning and to identify factors that can increase the effectiveness of NO_x reduction. Previous work demonstrated that NO_x control efficiency of reburning and advanced reburning is affected by mixing. Modeling of mixing requires a combination of kinetic and gas dynamic equations. Current effort is directed towards utilization of state-of-the-art chemical mechanism with simplified fluid dynamics formulations based on One Dimensional Flame (ODF) model developed at EER. Results reported below were recently presented at the Western States Meeting of the Combustion Institute.

2.0 EFFECT OF SODIUM ON REBURN + SNCR PERFORMANCE

Tests were conducted in which the effects of sodium on reburn + SNCR performance were characterized under furnace conditions simulating a full-scale boiler. The EER's 300 kW Boiler Simulator Facility (BSF) was described in Quarterly Report No. 2 (Zamansky et al., 1998a). Cooling arrays were installed in the BSF furnace to simulate the boiler secondary superheater and reheater. Natural gas was used as the main fuel. To simulate the temporal fluctuations in furnace gas composition found in the boiler, a pulsing system was installed to cyclically vary the main natural gas flow rate. This system (also described in QR2) allowed the BSF to operate at high CO levels while still having a normal amount of excess air, as is found in the boiler convective pass. However, the pulsing system was not applied for these tests with sodium addition.

Reburn fuel was injected at 1700 K, just below the flame. Overfire air was injected at various locations depending on target injection temperature. N-agent was injected downstream of the OFA, also at varying locations. When sodium promoter was used, it was co-injected with the N-agent. To quantify emissions as a function of axial position in the furnace, continuous emissions monitor sampling was performed at three locations: just below the reburn fuel injector, between the secondary superheater and reheater cooling arrays, and at the furnace exhaust.

For the reburn + SNCR sodium injection studies, test variables included additive injection temperature, sodium concentration, and reburn heat input. In the first test series, additive injection temperature was varied from 1240 to 1340 K. Reburn heat input was set at 10% and OFA was injected at 1530 K. The additives consisted of either urea alone or urea plus Na_2CO_3 , at 30 ppm Na in the flue gas. Nitrogen Stoichiometric Ratio (NSR) was 1.0. Figure 2-1 shows NO reduction as a function of additive injection temperature. Reburning alone gave about 32% NO reduction. Sodium had a significant promotional effect at 1240 and 1300 K, but not at 1340 K. Maximum NO reduction achieved was 84%, obtained with urea plus sodium at an injection temperature of 1300 K.

Figure 2-2 shows NO reduction as a function of Na concentration at 10% reburning. The injection temperature was 1300 K, and NSR ranged from 1.0 to 2.0. NO reduction increased by 6 to 8 percentage points as Na was increased from zero to 10 ppm, and then increased minimally as Na was

further increased to 60 ppm. Maximum NO reductions were 97% at NSR=2.0 and 94% at NSR=1.5.

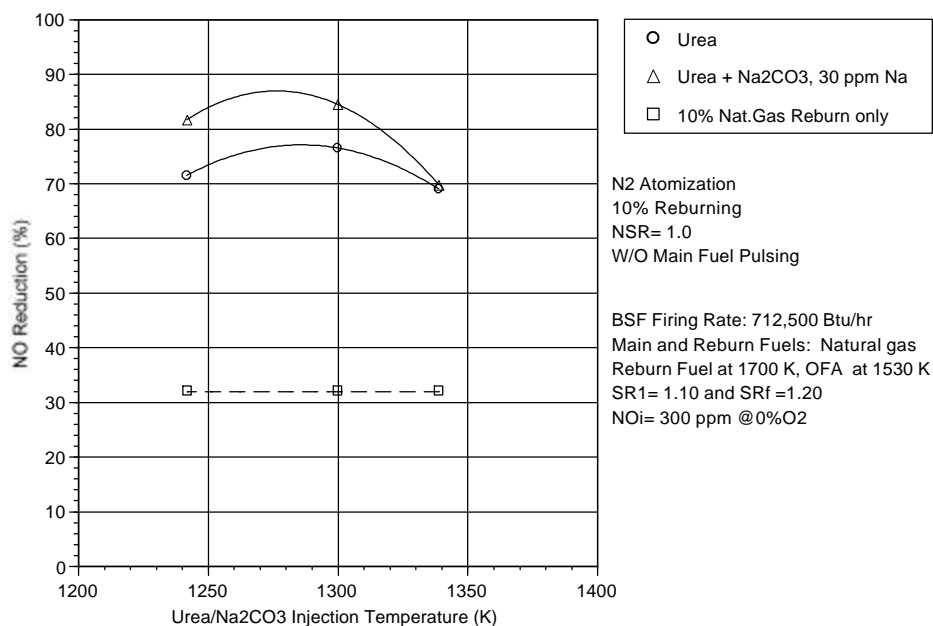


Figure 2-1. Promoted Reburn + SNCR performance as a function of additive injection temperature.

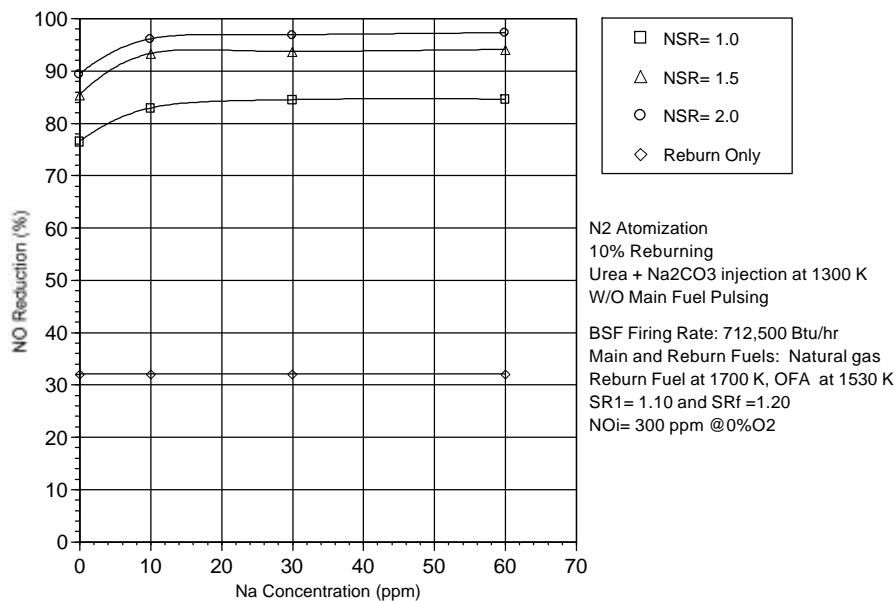


Figure 2-2. Promoted Reburn + SNCR performance as a function of sodium concentration.

Figure 2-3 shows the impact of sodium addition for different reburn heat inputs. The incremental performance benefit provided by urea is greatest at 10% and 15% reburning. The promotional effect of sodium is also largest at the lower reburn heat inputs.

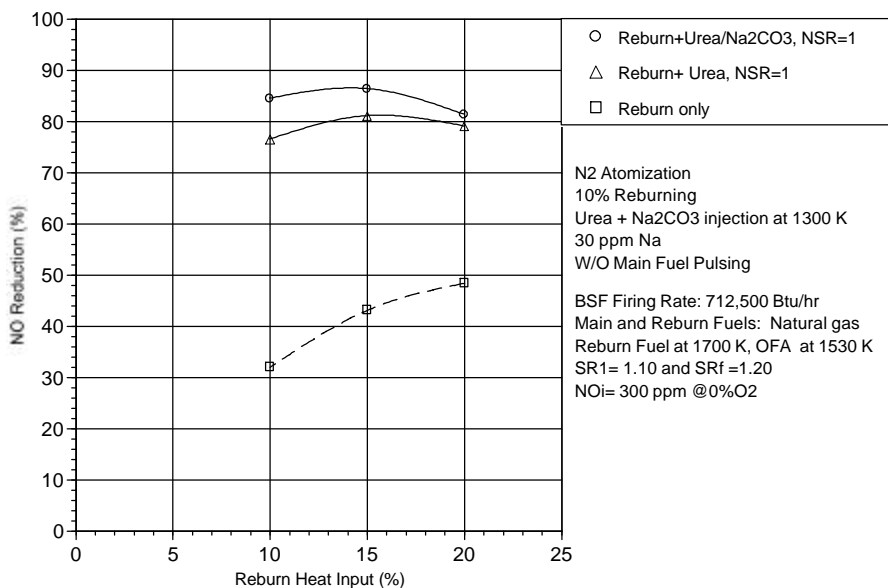


Figure 2-3. Promoted Reburn + SNCR performance as a function of reburn heat input.

3.0 EMISSIONS OF CO AND AMMONIA DURING REBURN + SNCR

A series of tests was conducted with the objective of using the results of the parametric tests to define process conditions providing high NO reduction with low byproduct emissions. Sampling was performed for CO by continuous monitoring and for NH₃ by manual methods at various reburn + SNCR test conditions. CO emissions were measured in the reburn zone, in the convective pass, and in the furnace exhaust. During implementation of main fuel pulsing, reburn zone CO concentrations were found to be as high as 38,000 ppm. However, exhaust CO levels remained below 100 ppm for all conditions.

For the ammonia slip tests, reburn heat input was 10%. N-agents tested included aqueous urea and gaseous NH₃. NSR was 1.0 for all tests. Injection temperatures ranged from 1270 to 1340 K. Tests were conducted both with and without the natural gas pulsing system. Sodium concentrations of zero

and 30 ppm were tested.

Figure 3-1 shows ammonia slip results, along with process conditions and corresponding NO reductions. NH_3 emissions were generally higher during pulsing, likely because mixing between the air and furnace gases was poorer during pulsing. Sodium evidently reduced ammonia slip. With urea injection at 1300 K with no sodium, ammonia slip results were 11.4 ppm with pulsing off and 16.9 ppm with pulsing on. At the same conditions with 30 ppm sodium added, ammonia slip results were 2.8 ppm with pulsing off and 2.7 ppm with pulsing on. NO reductions for these conditions were greater than 80%, and were also slightly better with sodium addition.

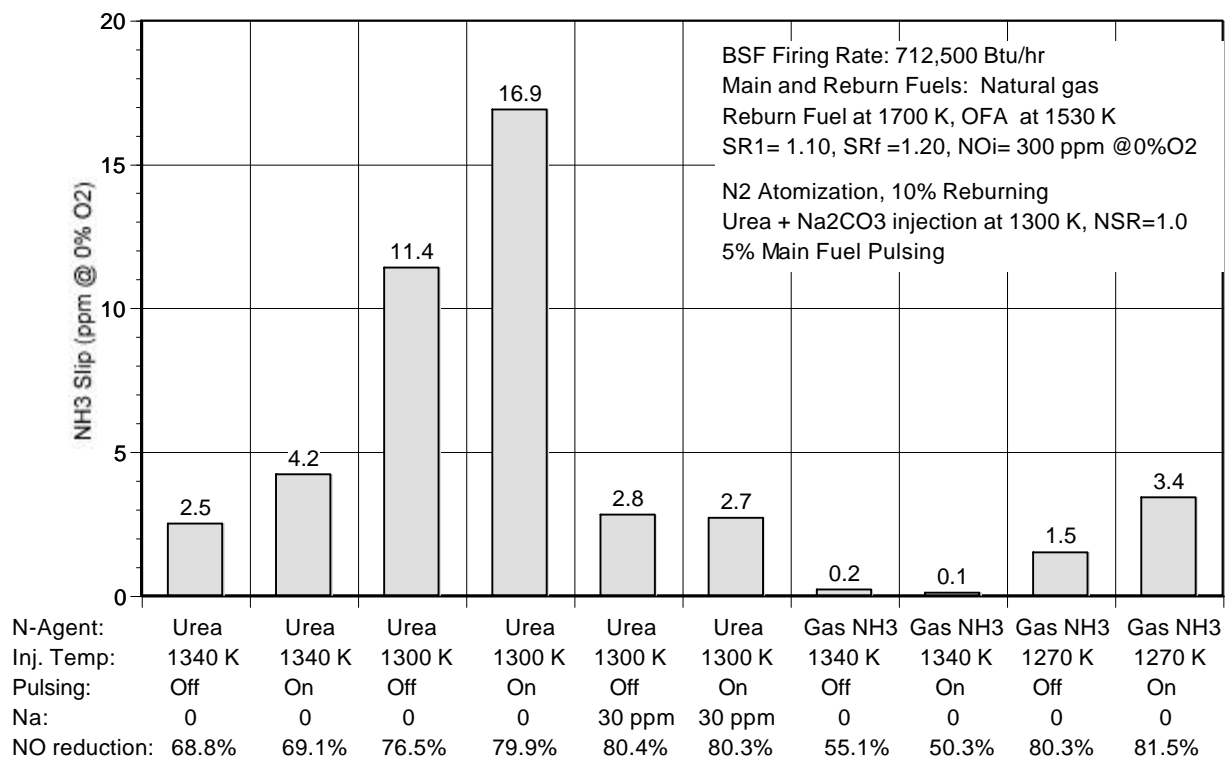


Figure 3-1. Ammonia slip results at different promoted Reburn + SNCR process conditions.

With gaseous NH_3 , ammonia slip measurements were made at injection temperatures of 1270 and 1340 K. At 1340 K, ammonia slip was extremely low (well below 1 ppm). However, only moderate NO control was achieved (i.e. 50%-55%). Decreasing the gaseous NH_3 injection temperature to 1270 K increased NO reduction to over 80%, while maintaining NH_3 slip below 4 ppm, both with and without

pulsing. Therefore, process conditions at the BSF have been identified that can provide over 80% NO reduction while maintaining ammonia slip below 4 ppm.

4.0 CHEMISTRY – MIXING MODELING OF GAS REBURNING

In previous Quarterly Report – QR-3 (Zamansky et al., 1998b), a Two-Stage Lagrangian (TSL) model was used to predict NO_x reduction in basic and advanced reburning processes. The TSL model is a powerful tool that allows greater insight into processes within the one-dimensional flame zone and interaction between fluid dynamics of mixing and chemistry. The model was developed in GRI sponsored studies (Broadwell and Lutz, 1998) and was applied to reburning problems in a joint effort by Stanford University and EER (Mungal et al., 1998).

In the current report, another possibility of combined chemistry-mixing modeling is explored. The effort is based on a modified EER's ODF model and is applied to basic gas reburning. The purpose of this work is to further understand the influence of the mixing process on reburning and to identify factors that can increase the effectiveness of NO reduction. Results are presented below. ODF-based chemistry-mixing modeling of advanced reburning is planned for the near future and will be based on current results.

Proper modeling of mixing requires a combination of kinetic and gas dynamic equations. Restrictions on computer time and storage requirements, however, allow one to use detailed chemistry modeling only with simplified fluid dynamics formulations; detailed three-dimensional modeling can be done only with simplified chemical reaction mechanisms. For a long time, modeling of the reburning process was subject to a choice between computational codes which focus on either multidimensional fluid mechanics with simplified chemical kinetics (for example, FLUENT) or one dimensional flow codes with instantaneous or simplified mixing and with detailed chemical kinetics (e.g. SENKIN and ODF). There were successful attempts (Luan et al., 1996; Alzueta et al., 1998 to modify the SENKIN code (Lutz et al., 1987) which assumes instantaneous mixing of reagents to describe one dimensional mixing by combining several plug flow reactors. This approach correctly represents fuel rich environment of the mixing zone. It fails, however, to take properly into account mixture stratification in the reburning zone which

requires more sophisticated representation of mixing. Since the kinetic mechanism of the reburning process is still not fully established, computational codes that simplify mixing processes and allow study of the detailed mechanism continue to be important modeling tools. Importance of the detailed chemistry in modeling of reburning became even more significant for advanced reburning applications. Interaction of N-agents and promoters with C-H-O-N chemistry can not be understood without utilization of detailed chemical mechanisms.

4.1 Model Setup

4.1.1 Model Formulation

The EER chemical kinetic code ODF, for “One Dimensional Flame” (Kau and Tyson, 1987) was employed in modeling. ODF treats a system as a series of one-dimensional reactors. Each reactor may be perfectly mixed (well-stirred - WSR) or unmixed (plug flow - PFR). Each ODF reactor may be assigned a variety of thermodynamic characteristics, including adiabatic, isothermal, or specified profiles of temperature or heat flux, and/or pressure. Process streams may be added over any interval of the plug flow reactor, with arbitrary mixing profiles along the reactor length. The flexibility in model setup allows many different chemical processes to be simulated in a variety of mixing regimes.

The reburning process was treated as series of five reactors (Figure 4-1). Each reactor described one of the physical and chemical processes occurring in a boiler: combustion of the main portion of fuel, addition of the reburning fuel (two parallel reactors as explained below), NO_x reduction as a result of the reaction with the reburning fuel, addition of overfire air, and oxidation of partially oxidized products in the burnout zone.

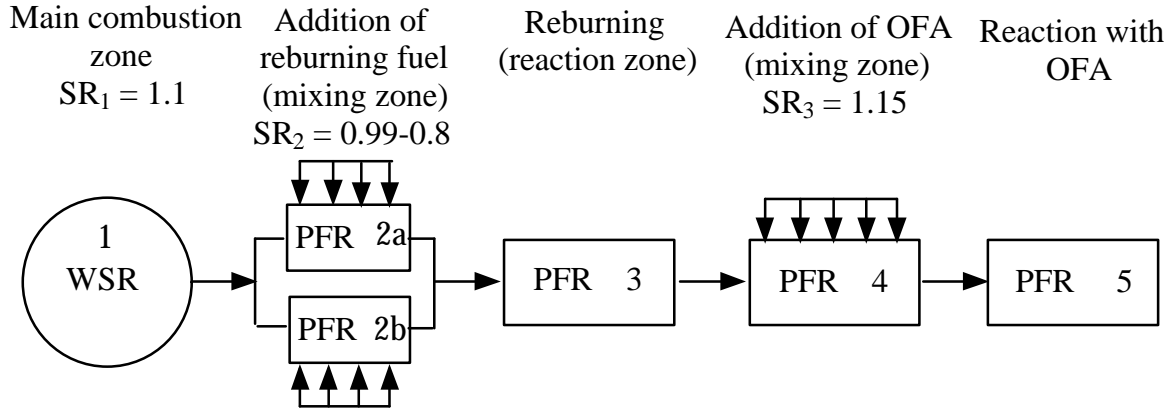
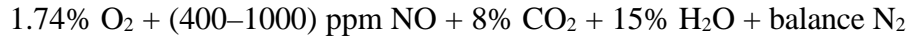


Figure 4-1. Reactor diagram of model setup.

The mixture entering the second reactor corresponds to products of natural gas combustion in air at $SR_1 = 1.1$ (first reactor). Assuming that the combustion process in the primary zone is complete, the mixture with $SR_1 = 1.1$ generates about 8% CO_2 and 15% H_2O . At the same time, 1.74% O_2 is left which is available for oxidation of the reburning fuel. The initial amount of NO was varied in calculations from 400 to 1000 ppm. Therefore, the premixed reactants entering the second reactor can be described as:



The reburning fuel was added to the main stream of reactants in the second reactor. The composition of natural gas was assumed to be the same as in experiments: 90.7% CH_4 + 7.5% C_2H_6 + 1.5% N_2 + 0.25% CO_2 + 0.05% O_2 . The amount of the reburning fuel varied to provide a stoichiometric ratio at the beginning of the second reactor SR_2 from 0.80 to 0.99. Values of SR_2 were calculated taking into account the total amount of fuel and oxygen added in the first and second reactors.

The third reactor described the process of NO removal in the reburning zone after the reburning fuel and flue gas are mixed. The forth reactor described the process of OFA mixing with flue gas. The amount of OFA added was varied such that the total mixture composition (including previously added fuel) at the beginning of the forth reactor corresponded to $SR_3 = 1.15$. The fifth reactor described oxidation of products of incomplete combustion.

Physically, the process in the second reactor can be described as mixing of the reburning fuel with the main stream of gases. The ODF code describes mixing in a simplified form. However, the main features of the mixing process were addressed in modeling. They are discussed below.

4.1.2 Mixing Time

Injected gases are available for the reaction over a certain period of time (mixing time) rather than instantaneously. Staged addition of fuel in the mixing zone was successfully used in the past (Kilpinen et al., 1992; Luan et al., 1996) to describe mixing processes. It was done by modification of the SENKIN code to represent the mixing zone as a number of plug flow reactors. In each reactor, only part of the reburning fuel is injected. The reaction products from one reactor enter the next reactor and mix with new portion of the reburning fuel. Thus in this approach the mixing zone has to be broken into many sub-zones. In ODF code, addition of reactants is described within a single plug flow reactor (divided by two parallel reactors as explained below), by mixing them into the main stream with a continuous (in this study, constant) rate over a specified mixing interval. Calculations were done at 100 ms mixing time for reburning fuel and OFA injection, in agreement with estimates made using a model of a single jet for typical BSF conditions.

4.1.3 Mixing Mode

Three different mixing modes were utilized in calculations. In the first one, natural gas was added at a constant rate to the stream of flue gas over the period of mixing time. The second mode was similar to the first one, except that the rate of natural gas addition linearly increased in time from zero to its final value. The third mode assumed that a mixture of NO, O₂, CO₂, H₂O and N₂ was slowly added to the stream of natural gas (so-called “inverse” mixing). This arrangement is opposite to apparent physical processes occurring in the combustor where reburning fuel is injected into the main stream, but from the kinetic point of view it provided description of the mixing process close to the real one: a high concentration of natural gas and low concentration of NO in the area of mixing. It was found that the mode of inverse mixing gives better description of

the experimental data, and it was employed in calculations. This finding is in agreement with Luan et al., 1996 and Alzueta et al., 1998 studies who found that fuel-rich environment of the mixing zone is better represented by addition of flue gases to the reburning fuel. The mixing process in the OFA zone was described as OFA being added to the main stream of gases with a constant rate.

4.1.4 Mixture Stratification

Injection of the reburning fuel results in mixture stratification, such that the composition in the mixing area is not uniform. Inverse addition of reagents partially addresses the issue of mixture stratification in the mixing area: at the first moments of mixing, the reaction occurs in a fuel-rich environment and then progresses gradually to the final composition determined by the amount of the injected fuel. Since mixture stratification is an important factor that significantly affects NO reduction, additional efforts were undertaken to take it into account. Ideally, the mixing zone can be divided into infinite (or as many as possible) subzones each representing the local mixture composition. As a first approximation, the mixing zone was divided into two reactors (2a and 2b in Figure 4-1) that represented two extreme cases of mixture stratification: one reactor was assigned with a more fuel-rich mixture than average, another one with a less fuel-rich mixture. Averaging fuel contents distributed between the two reactors gave SR_2 corresponding to the total amount of added reburning fuel. For each reactor, 2a and 2b, the inverse mixing model was used to describe the addition of the reburning fuel. Distribution of the reburning fuel between the two reactors was an adjustable parameter in modeling.

4.1.5 Estimation of Mixing Parameters

A single jet model JICFIS was used to estimate mixing time and mixture stratification in the reburning zone. JICFIS is a model developed at EER which numerically evaluates an integral solution to the trajectory and mixing of a single jet in cross flow. The mixing is determined by evaluating the entrainment rate of fluid from the crossflow into the jet. The model is based on a simplified two-dimensional representation of the fluid dynamic equations for the jet. These four equations (mass, two components of momentum, and energy) are integrated numerically,

marching along the jet centerline, using the Runge-Kutta technique. Major inputs for the model are shown in Table 1 and include the velocity and density ratios of the crossflow to jet, their relative orientation in two dimensional rectangular coordinates, and the initial conditions (diameter, velocity, and temperature) of the jet. The model has been validated against experimental data and successfully employed in a number of jet injection studies.

Table 1. Characteristics of mixing in BSF and jet parameters.

Zone	Total flow rate kg/s, $\times 10^2$	Injector description	Injector characteristics
Primary zone	6.88		
Reburning zone	7.12	8 jets oriented 27° upstream	Injection rate 42.8 m/s Jet diameter 0.31 cm
After OFA	7.85	12 swirl jets oriented perpendicular to the stream	Injection rate 5.5 m/s Jet diameter 0.94 cm

Figure 4-2 shows trajectory of the jet as predicted by JICFIS model for the injection of the reburning fuel.

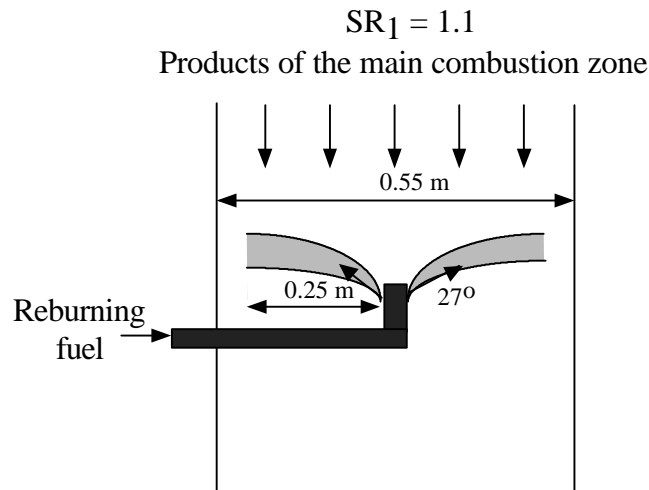


Figure 4-2. A diagram of jet injection and model setup in the reburning zone.

The JICFIS model was used up to the point where the amount of entrainment equals the main flux; after this, complete mixing is assumed (in Figure 4-2, this distance for the single jet corresponds to 0.25 m from the point of injection). For the reburning jet, the mixing time was calculated to be 100 ms. OFA air injection is handled in the same manner as the reburning fuel. For the overfire air jet, the mixing time was calculated to be 95 ms. These times are approximate since the actual geometry (8 radial jets for reburning fuel, a radial slot jet for overfire air) does not precisely match the single jet treated by the JICFIS algorithm. However, the results are considered to reflect the magnitude of the mixing rate based on the general scale of the problem. Based on the approximations in the model, a single mixing time of 100 ms was used for all injections.

Results of JICFIS modeling can be used to estimate the degree of mixture stratification in the mixing zone. Since the BSF arrangement is symmetrical, the interaction of single jet with flue gas was described as a mixing zone divided into two reactors (2a and 2b in Figure 4-1) with equal mass of combustion gas. It was assumed that the injected fuel was distributed between reactors unevenly. Fuel distribution between the two reactors was described by stratification coefficient K that can be determined as a ratio of the amount of reburning fuel in the first reactor to that in the second reactor. Value $K = 1$ corresponds to the case when the reburning fuel is distributed uniformly between two reactors.

Estimation of K is based on the following simple consideration. The area of complete mixing (within 0.25 m radial distance in Figure 4-2) corresponds to the final mixture composition with the amount of fuel determined by SR_2 . In the area of incomplete mixing, unmixedness changes from 100% (100% unmixedness means that no oxygen is present in the mixture; this condition exists at the base of the jet) to 0% (mixture composition is determined by SR_2 ; exists in the jet at the point of complete mixing). Assuming that unmixedness within the jet is, on average, 50% (amount of fuel is 50% higher than that in the area of complete mixing), a geometrical consideration with distances shown in Figure 4-2 results in $K = 1.5$. It actually means that the mixture in the reactor 2a has 40% more fuel than that in the reactor 2b. This estimation is a simple approximation representing non-uniformity of mixture composition along the jet. However, it

provides a starting value of K for model development. Final results were obtained using K as a variable and are reported for $K = 1.8$.

4.2 Model Validation

4.2.1 Influence of the Initial NO Concentration

Modeling was done with the kinetic mechanism described by Glarborg et al., 1998. The mechanism included 447 reactions of 65 chemical species. Injection of the reburning fuel and OFA occurred at 1700 K and 1422 K, respectively. Temperature measurements in the BSF showed that the temperature along the reactor decreases with approximately linear rate. All calculations reported here were done with a constant quench rate of -300 K/s. Calculations with -250 K/s rate showed similar results.

Performance of the current model was verified against experimental data on NO reduction at different initial NO concentrations, $[\text{NO}]_i$. Figures 4-3 a-c show comparison of modeling predictions with experimental data for $[\text{NO}]_i = 416, 600, \text{ and } 970$ ppm, respectively. Uncertainty of the experimental data was estimated to be $\pm 10\%$ from the measured amount of NO. For all initial amounts of NO the model at least qualitatively agrees with experiments within the data scatter. Modeling slightly underpredicts NO reduction efficiency at low reburning fuel heat inputs for all initial NO amounts. Modeling overpredicts NO reduction at the highest initial NO concentration for all but the lowest reburning fuel heat inputs.

It was observed that efficiency of NO reduction increases as the amount of the reburning fuel increases. However, at large heat inputs, the efficiency decreases so that there is an optimum amount of the reburning fuel that results in the largest efficiency of NO reduction. As $[\text{NO}]_i$ increases, the optimum slightly shifts toward larger heat inputs.

4.2.2 Concentrations of Intermediate Species in the Reburning Zone

Figures 4-4a,b compare modeling and experimental data on concentrations of NO, NH₃, HCN, and TFN (Total Fixed Nitrogen) at the end of the reburning zone (before OFA injection). NH₃ and HCN are formed in the reburning zone as a result of reactions between CH_i radicals and NO.

The concentration of NO at the end of the reburning zone depends on the heat input of the reburning fuel and decreases with an increase of fuel heat input. For all heat inputs (except for very low) concentrations of NH₃ and HCN at the end of the reburning zone are significant. The model qualitatively describes these trends. In an agreement with experiments, the model predicts that the TFN concentration at the end of the reburning zone is minimal for 18% reburning fuel input.

The chemical mechanism (Glarborg et al., 1998) used in modeling is the current state of the art, but it is far from completion. The mechanism overpredicts NH₃ and underpredicts NO concentrations in the reburning zone, especially at large heat inputs of the reburning fuel.

4.2.3 Influence of the OFA Injection Location

Due to the temperature gradient in a boiler, injection of OFA at different locations results in different flue gas temperatures at the point of injection. The position of the injector also determines the residence time in the reburning zone. For example, when OFA is injected at 1500 K, the reaction time available for NO reduction in the BSF reburning zone is 0.7 s. For OFA injection at 1300 K, the residence time doubles.

Figure 4-5 shows influence of flue gas temperature at the point of OFA injection on NO removal. For 10% heat input modeling predicts slightly lower efficiencies of NO reduction than that observed in experiments. This deviation is due to the fact that at low heat inputs of the reburning fuel the model slightly underpredicts efficiency of the reburning for all [NO]_i (Figure 4-3 a-c).

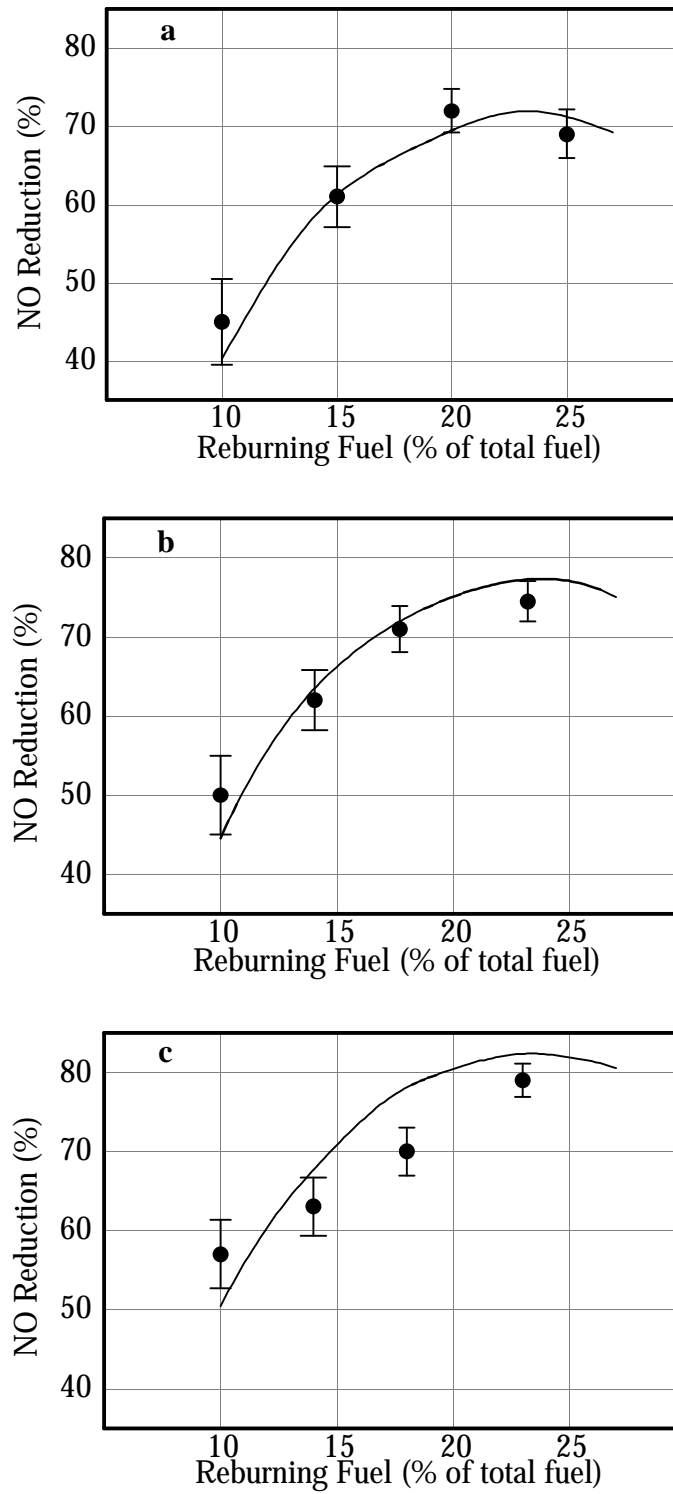


Figure 4-3. Comparison of test results on reburning (symbols) with modeling predictions. Reburn fuel added at 1700 K, OFA at 1422 K. a: $[\text{NO}]_i = 416$ ppm, b: $[\text{NO}]_i = 600$ ppm, c: $[\text{NO}]_i = 970$ ppm.

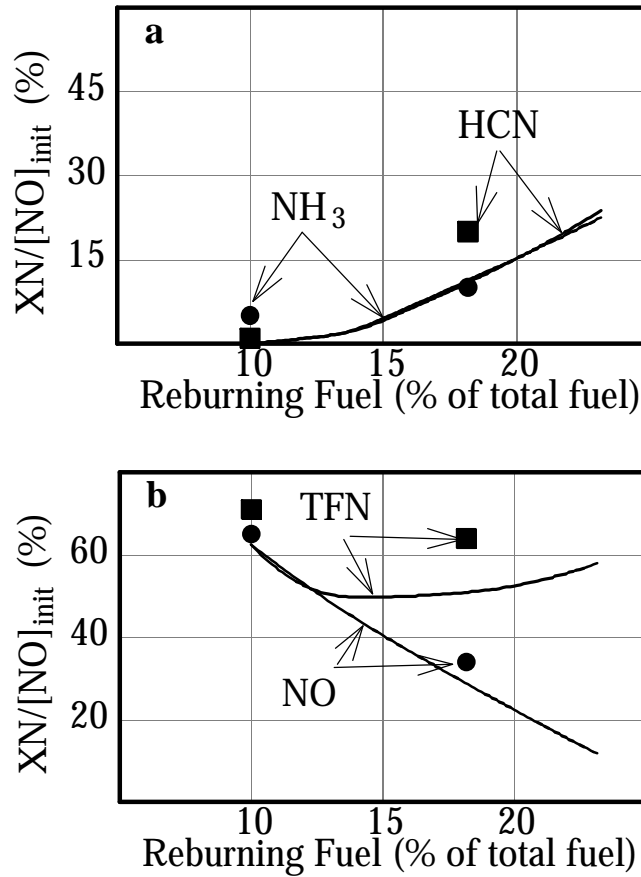


Figure 4-4. Modeling and experimental data (symbols) on concentrations of N-containing species at the end of the reburning zone. $[NO]_i = 600$ ppm. a: NH_3 and HCN , b: NO and TFN . Residence time in the reburning zone is 0.93 s.

However, modeling represents main features of the process correctly. Modeling shows that temperature of flue gas at the point of OFA injection has a weak effect on the efficiency of the reburning process. Small dependence of NO reduction efficiency on location of OFA injector at low heat inputs of the reburning fuel indicates that NO reduction in the reburning zone occurs in early reactions and is not affected by residence time in the reburning zone above some minimum value.

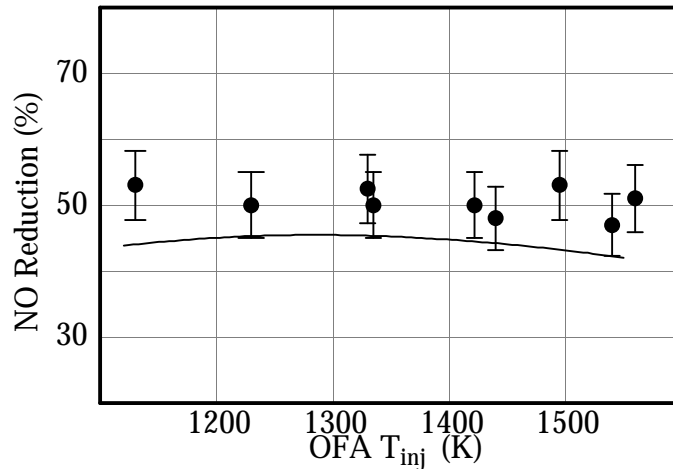


Figure 4-5. Comparison of experimental results on basic reburning with modeling predictions. 10% reburning fuel is added at 1700 K, $[NO]_i = 600$ ppm.

4.3 Parametric Study

There are several adjustable parameters in the model that affect the efficiency of NO reduction. They include fuel stratification in the reburning zone and temperatures of injected reburning fuel and overfire air. Influence of these parameters on modeling predictions is discussed in the following Sections.

4.3.1 Effect of Fuel Stratification in the Reburning Zone

Fuel stratification after reburning fuel injection has a significant effect on modeling predictions. Figure 4-6 shows the effect of fuel stratification coefficient (K) on NO reduction. Value $K = 1$ corresponds to the case with no fuel stratification.

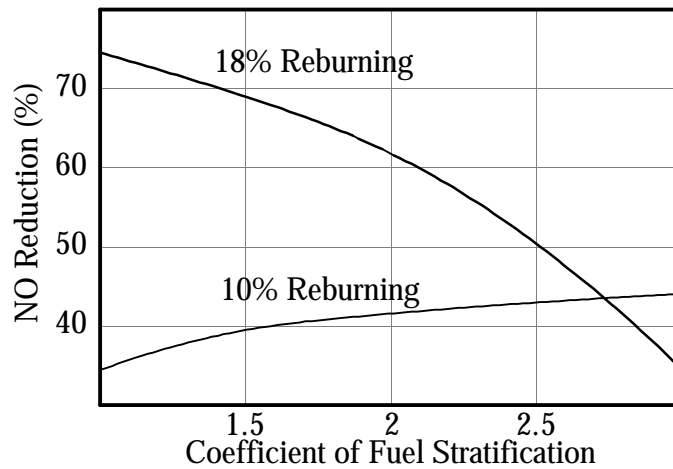


Figure 4-6. Effect of fuel stratification in the mixing area of the reburning zone on modeling predictions. $[\text{NO}]_i = 416$ ppm.

Modeling suggests that non-uniformity of fuel distribution within the reburning zone (increase in K) improves NO reduction for small heat inputs of the reburning fuel and degrades it for large heat inputs. This effect can be explained by the experimental observation (supported by modeling) that there is an optimum amount of the reburning fuel (usually about 20%) that results in maximum NO reduction (Figure 4-3 a-c). For small heat inputs of the reburning fuel, mixture stratification within mixing zone creates areas with a large amount of fuel that is still smaller than the optimum value. NO reduction in such areas significantly exceeds the level of NO reduction at the “average” fuel amount. Therefore, an increase in fuel stratification results in increasing NO reduction. For large heat inputs, due to the existence of the optimum in NO reduction, the efficiency of NO reduction in locally rich areas is lower than that for the “average” amount of fuel. Therefore, in this case, the total efficiency of reburning decreases with increasing fuel stratification.

Variation of the stratification coefficient achieved the best description of the experimental data at $K = 1.8$.

4.3.2 Effect of the Initial Temperature of the Reburning Fuel and Overfire Air

Besides being injected at different locations (which correspond to different temperatures of flue gas at the moment of injection), reburning fuel and overfire air can be injected at different initial temperatures (temperatures of fuel and air streams at the moment of injection). Location of injection is usually determined by the geometry of the boiler and can not be easily changed, but the initial temperature of the injected stream can be regulated, for example, by preheating prior to injection, by mixing with steam or hot flue gases, or by cooling the injector with water.

The ODF code permits two modes for balancing heat in the plug flow reactor: the first mode assumes a fixed temperature profile, the second mode takes into account heat release due to chemical reactions and heat transfer from the reacting gas to reactor walls. Modeling results reported here were obtained using the first mode: temperature decreased with a constant rate of -300 K/s starting from the point of reburning fuel injection (1700 K). In this mode, the temperature of the injected stream is assumed to be the same as the temperature of the main flow. Thus, it is impossible directly to take into account the temperature difference between two flows. Indirectly, however, it is possible. Injection of cold reburning fuel results in temperature decrease in the mixing zone. The higher temperature of the reburning fuel, the closer the temperature history of a gas in the mixing zone follows linear temperature decrease with a constant rate of -300 K/s. Thus, there is a quantitative correlation between the temperature of the injected fuel and the temperature profile in the mixing zone. By changing this profile (for example, by lowering temperature at the beginning of the mixing zone) one can take into account the initial temperature of the injected fuel. The same consideration can be applied to OFA addition.

Figure 4-7 shows the effect of the initial temperature of the reburning fuel on NO reduction. Again, the effect is quite different for small and large heat inputs of the reburning fuel. Preliminary heating of the reburning fuel increases efficiency of the reburning process for large heat inputs of the reburning fuel and decreases it for small heat inputs. Influence of the jet temperature on the reburning performance can be explained by the fact that the initial temperature of the jet affects mixing time: an increase in the jet temperature provides in better jet mixing with the crossflow and as a result the mixing time in the reburning zone decreases.

Figure 4-8 shows the effect of the initial temperature of OFA on NO reduction at 10 and 23% heat input of the reburning fuel. OFA is injected into flue gas at temperatures 1422 K. At 23% reburning, as the initial temperature of OFA decreases, the efficiency of the reburning process increases. At 10% reburning, the initial temperature of OFA does not affect reburning efficiency.

These considerations suggest that initial temperatures of the injected reburning fuel and overfire air are important parameters that affect the efficiency of the reburning process. NO_x reduction can be improved if values of these parameters are optimized.

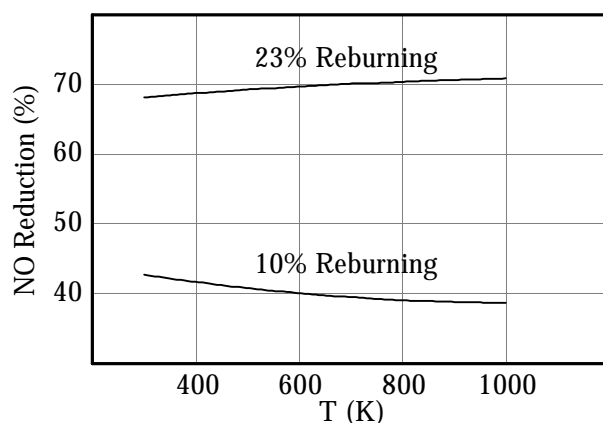


Figure 4-7. Predicted effect of the initial temperature of the reburning fuel on NO reduction. [NO]_i = 416 ppm. Temperature of flue gas at the location of the injection is 1700 K.

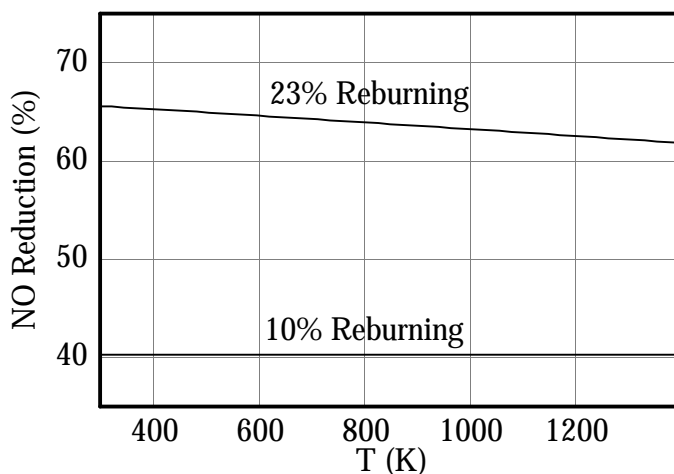


Figure 4-8. Predicted effect of the initial OFA temperature on NO reduction. [NO]_i = 416 ppm.

Figure 4-9 shows comparison of the predicted efficiencies of the reburning process with optimized (dash line) and non-optimized (solid line) initial temperatures of the reburning fuel and overfire air with experimental data. Depending on heat input of the reburning fuel, optimization results in 2-10% increase in NO reduction.

4.3.3 Reactions Responsible for NO Reduction

Figures 4-10 a and b show profiles of the main N-containing species in reburning and burnout zones and main reactions responsible for NO reduction for different heat inputs of the reburning fuel. The concentration profiles clearly show that major NO reduction occurs during addition of the reburning fuel within mixing zone and thus demonstrate that NO reduction is strongly affected by the mixing process.

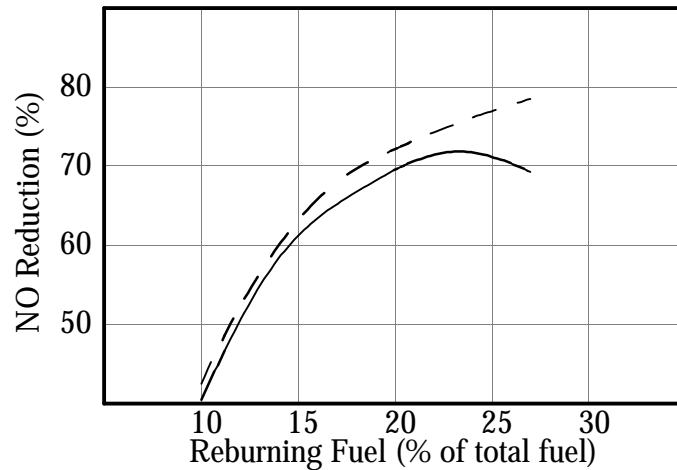


Figure 4-9. Performance of the reburning process for optimized (dash line) and non optimized (solid line) initial temperatures of the injected reburning fuel and overfire air. $[NO]_i = 416$ ppm.

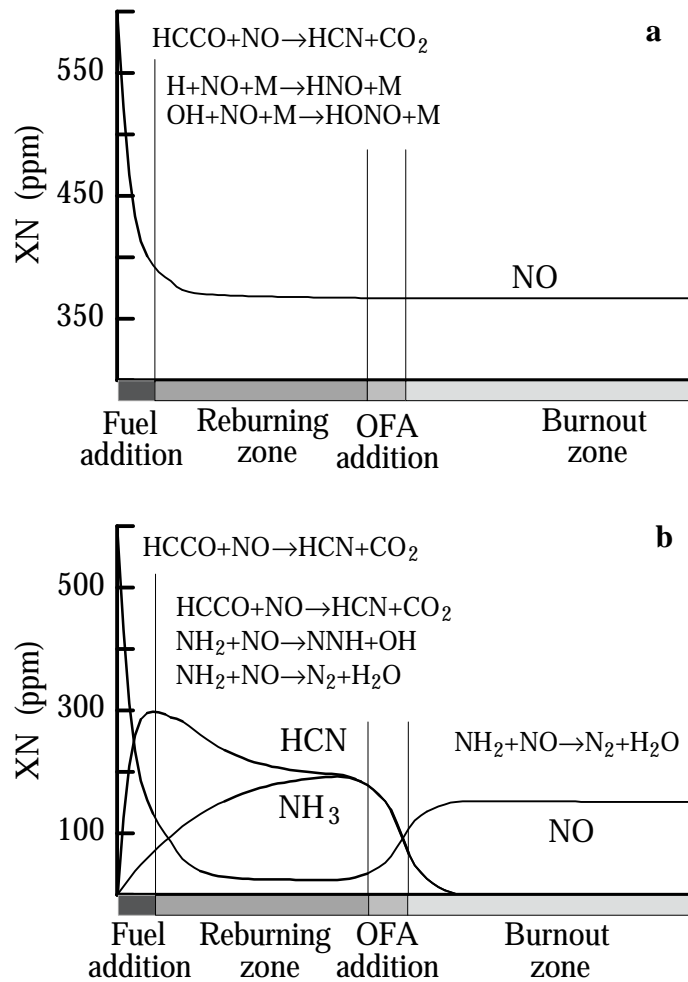


Figure 4-10. Concentrations of N-containing species in reburning and main reactions responsible for NO reduction in different zones. $[\text{NO}]_i = 600$ ppm. a - 10% reburn fuel, b - 27% reburn fuel.

For a small amount of the reburning fuel (Figure 4-10a), main changes in NO concentration occur during fuel fragmentation into CH_i radicals (mixing zone). As soon as fuel is consumed, NO reduction is practically ceased. Additional NO reduction occurs in reactions of NO with H and OH, but this is a minor contribution. Injection of OFA practically does not affect NO concentration.

Figure 4-10b demonstrates the importance of such species as HCN and NH_3 in the reburning

process. Concentrations of these species at the end of the reburning zone (at least for large heat inputs of the reburning fuel) significantly exceed the concentration of NO. Major NO reduction occurs within mixing zone, similar to the case with small heat input of the reburning fuel. NH_2 radicals further reduce NO after mixing is completed. NH_i species play even more important role when OFA is injected. NH_2 radicals, formed in large amount as a result of NH_3 reaction with O_2 , significantly reduce NO formed via HCN oxidation. Reactions of HCN and NH_3 in the burnout zone significantly affect final NO emission, and if conditions in the burnout zone are optimized, can result in lower NO emission.

4.4 Gas Reburning Modeling: Conclusions

The main features of reburning can be described using a detailed chemical mechanism with one-dimensional representation of mixing. Inverse addition of reactants in the mixing area gives much better approximation of fuel rich environment in the reburning zone compared to mixing of reburning fuel into the main stream. Stratification in the mixing zone improves reburning efficiency for small heat inputs of the reburning fuel and degrades reburning efficiency for large heat inputs. Based on modeling observations, it is suggested that design of the injector should be different depending on the amount of the injected reburning fuel. Injection of large amounts of the reburning fuel provides better NO_x reduction if mixing of reactants is fast. Injection of small amounts of the reburning fuel, on the other hand, should result in significant mixture stratification for better NO_x control (as long as complete mixing and burnout is ultimately achieved).

Initial temperatures of the reburning fuel and OFA affect NO reduction and can be optimized for deeper NO control. Optimum temperatures depend on the mixture composition and on the injection location. By optimizing these parameters, NO reduction can be increased by several percentage points.

Reactions of NH_3 in the burnout zone play important role in NO reduction for large heat inputs of the reburning fuel.

5.0 FUTURE PLANS

Experimental evaluation of AR promoters started during the reporting period. These tests are currently continued. Results will be presented in the next quarterly report. The modeling effort will be also continued towards improving the gas reburning model and extending it to advanced reburning applications.

6.0 REFERENCES

- Alzueta, M.U., Bilbao, R., Millera, A., Glarborg, P., Østberg, M., and Dam-Johansen, K. (1998) *Energy & Fuels* 12, 329.
- Broadwell, J.E., and Lutz, A.E. (1998) *Combust. Flame* 115, 319.
- Glarborg, P., Alzueta, M.U., Dam-Johansen, K., and Miller, J.A. (1998) *Combust. Flame* 115, 1.
- Kau, C.J. and Tyson, T.J. (1987) Numerical Model for Two-Phase One-Dimensional Flow Reactor, in *U.S. Environmental Protection Agency Report No. EPA-6000/7-87-027*.
- Kilpinen, P., Glarborg, P., and Hupa, M. (1992) *Ind. Eng. Chem. Res.* 31, 1447.
- Luan, T., Liu, H., Gibbs, B.M., and Hampartsoumian, E. (1996) *The 9th International Symposium on Transport Phenomena in Thermal-Fluids Engineering*, p. 268.
- Lutz, A.E., Kee, R.J., and Miller, J.A. (1987) SENKIN: A Fortran Program for Predicting Gas Phase Chemical Kinetics with Sensitivity Analysis, Sandia National Laboratories, *Report SAND87-8248*.
- Mungal, M., Han, D., Hasselbring, E., Lutz, A., Broadwell, J., Tyson, T., Zamansky, V., Serauskas, R., and Kezerle, J. (1998) *International Gas Research Conference*, San Diego, CA, Paper IPP-25.
- Zamansky, V.M. and Maly, P.M., (1998a) "Second Generation Advanced Reburning", EER Quarterly Report No. 2, DOE Contract No. DE-AC22-95PC95251, Phase II, April 30, 1998.
- Zamansky, V.M., Maly, P.M. and Nguyen, Q., (1998b) "Second Generation Advanced Reburning", EER Quarterly Report No. 3, DOE Contract No. DE-AC22-95PC95251, Phase II, July 30, 1998.