SECOND GENERATION ADVANCED REBURNING  
FOR HIGH EFFICIENCY NOx CONTROL

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July 1 - September 30, 1997

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ABSTRACT

This project is designed to develop a family of novel NO\textsubscript{x} control technologies, called Second Generation Advanced Reburning which has the potential to achieve 90+\% NO\textsubscript{x} control in coal fired boilers at a significantly lower cost than SCR. The eighth reporting period (July 1 - September 30, 1997) included experimental and final report preparation activities. Experiments on high-temperature reactions of sodium carbonate were completed at the University of Texas in Austin. This study revealed that sodium can affect NO concentrations under both fuel-rich and fuel-lean conditions. The engineering design conducted during the previous reporting period was converted into retrofit hardware for the AR-Lean system and initial test results are presented and discussed. All information presented in this report is in summary form since a Draft Final project report was submitted to DOE FETC by July 31, 1997.
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EXECUTIVE SUMMARY

This project is designed to develop a family of novel NO\textsubscript{x} control technologies, called Second Generation Advanced Reburning, which has the potential to achieve 90+\% NO\textsubscript{x} control in coal fired boilers at a significantly lower cost than SCR. The eighth reporting period (July 1 - September 30, 1997) included final Phase I experimental activities, as well as preparation of the Phase I Final Report and the Phase II proposal.

A literature search on thermodynamic data for Na\textsubscript{2}CO\textsubscript{3} confirmed that extensive reliable data are available for the solid and liquid phases of the compound, but not for the gas phase. New experimental data for high-temperature reactions of sodium carbonate were obtained in a flow reactor at the University of Texas in Austin. The flow system was used to determine the influence of Na\textsubscript{2}CO\textsubscript{3} additive on NO removal in the SNCR process. Without sodium carbonate, the efficiency of NH\textsubscript{3} as NO removing agent varies from 26 to 49\%. Sodium carbonate additive increases the efficiency of NH\textsubscript{3} as NO removing agent with efficiency approaching a constant value of about 63 \% at high concentrations of Na\textsubscript{2}CO\textsubscript{3}. These results will be used for comparing the efficiency of Na additives with that of other metals in Phase II of this work.

The process design presented in the previous quarterly report was converted into retrofit hardware for the AR-Lean system. The results of initial AR-Lean tests as well as tests of some of the SGAR components are discussed. The unit is Greenidge Unit 4, which is owned and operated by New York State Electric and Gas (NYSEG). EER installed the gas reburning system as part of a commercial project with guaranteed performance. The upgrade to AR-Lean was conducted as a cooperatively funded demonstration project with the support of NYSEG and a number of cofunding organizations. The Greenidge tests have revealed an important AR issue: the uniformity of conditions in the reburning zone is important to the optimization of the AR process. In small scale tests, the furnace flow is fairly well mixed so that this stratification effect is not significant. However, stratification may be the limiting factor in full scale applications. Once this stratification effect was understood, additional tests were conducted at Greenidge to improve performance. The focus of testing in summer 1997 was on adjusting the AR-Lean system to provide more uniform reburn zone conditions. This included: (1) burner balancing, (2) modification of the gas injectors to reduce stratification and enhance the micro-mixing of the fuel and air so as to avoid regions of excessively rich or lean conditions, and (3) reduction of leakage air through the furnace overfire air ports. In addition, the N-agent injectors were modified to allow the tailoring of the distribution of the N-agent among the convective pass overfire air injectors. These changes have resulted in improved performance and additional NO\textsubscript{x} reduction with lower NH\textsubscript{3} slip.

In addition to these AR-Lean tests, opportunity was taken to obtain larger scale data on several of the SGAR components: N-agent injection downstream of the overfire air, N-agent injection into the reburn zone, and multiple N-agent injection. All these tests did not represent optimum AR configurations, however, they allowed a preliminary evaluation of multiple injection and the ability to stratify the N-agent injection for the stratified furnace flow conditions.

If this project proceeds to Phase II, these large scale tests will continue in summer 1998. Alternate injection arrangements and promoters are expected to be tested.
1.0 Introduction

This project is designed to develop a family of novel NO\textsubscript{x} control technologies, called Second Generation Advanced Reburning (SGAR), which has the potential to achieve 90+% NO\textsubscript{x} control in coal fired boilers at a significantly lower cost than SCR. Phase I consists of six tasks:

- Task 1.1 Project Coordination and Reporting/Deliverables
- Task 1.2 Kinetics of Na\textsubscript{2}CO\textsubscript{3} Reactions with Flue Gas Components
- Task 1.3 0.1 x 10\textsuperscript{6} Btu/hr Optimization Studies
- Task 1.4 1.0 x 10\textsuperscript{6} Btu/hr Process Development Tests
- Task 1.5 Mechanism Development and Modeling
- Task 1.6 Design Methodology and Application

During the period (October 1, 1995 - June 30, 1997), flow system experiments were conducted at the University of Texas in Austin on experimental evaluation of sodium carbonate kinetics (Task 1.2). The bench-scale 0.1 MMBtu/hr combustion tests were completed on different variants of the AR technology (Task 1.3). The pilot-scale combustion tests in 1.0 MMBtu/hr Boiler Simulator Facility (BSF) were completed (Task 1.4). A C-H-O-N-Na-S-Cl chemical mechanism for description of the process chemistry was developed, and kinetic calculations were conducted to evaluate the effects of interaction of ammonia with NO in the reburning and overfire air (OFA) zones (Task 1.5). The effect of various additives to promote NO-NH\textsubscript{3} interaction in the reburning zone was also evaluated by modeling. Engineering design studies were conducted to evaluate the application of AR technologies to a 100 MW utility boiler.

The eighth reporting period (July 1 - September 30, 1997) included final Phase I experimental activities, as well as preparation of the final report and Phase II proposal.
This Section of the report was prepared by W.C. Gardiner and V.V. Lissianski of the University of Texas at Austin.

Our work from July 1 to September 30 concentrated on preparing a proposal for Phase II of this research and experimental determination of the efficiency of NO removal in the SNCR process in the presence of Na$_2$CO$_3$. We also continued research on the thermochemistry of Na$_2$CO$_3$, in different physical states, and related compounds.

A literature search on thermodynamic data for Na$_2$CO$_3$ confirmed that extensive reliable data [1, 2, 3] are available for the solid and liquid phases of the compound. Some of them [2, 3] are expressed in the NASA polynomial format used by Chemkin II. However, the only thermodynamic data suggested for the gas phase Na$_2$CO$_3$ [2] showed serious contradictions with thermodynamic theory. Table 2-1 shows the enthalpies and entropies of formation of Na$_2$CO$_3$ in different physical states as functions of temperature as calculated using NASA polynomials from EER's data base [2].

Table 2-1. Thermodynamic properties of Na$_2$CO$_3$ in solid, liquid and gas phases as calculated from NASA polynomials [2].

<table>
<thead>
<tr>
<th>T, K</th>
<th>$H^0_{T-H_f^0_{298}}$, kcal/mol</th>
<th>$S^0$, cal/deg mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid</td>
<td>Liquid</td>
</tr>
<tr>
<td>700</td>
<td>11.7</td>
<td>18.5</td>
</tr>
<tr>
<td>900</td>
<td>19.1</td>
<td>27.7</td>
</tr>
<tr>
<td>1100</td>
<td>27.4</td>
<td>36.3</td>
</tr>
<tr>
<td>1300</td>
<td>37.0</td>
<td>44.8</td>
</tr>
<tr>
<td>1500</td>
<td>48.3</td>
<td>54.1</td>
</tr>
</tbody>
</table>

The enthalpy of formation data show that $H^0_{T-H_f^0_{298}}$ for the liquid phase is consistently higher than that for solid phase, because the transition from solid to liquid phases requires input of the
heat of fusion. However, $H^0_T - H^0_f$ for the gas phase in Table 2-1 are smaller than that for liquid phase even though transition from liquid to gas phases also requires input of energy, this time the enthalpy of vaporization. A second contradiction is that the entropy of any substance increases as it is transformed from solid to liquid and then gas phases. Table 2-1 shows that for the temperature interval from 700 to 1100 K it is not the case for the liquid-gas transition. We conclude that the available thermodynamic data for gas phase Na$_2$CO$_3$ are wrong and that further research is needed.

The flow system was used to determine the influence of Na$_2$CO$_3$ additive on NO removal in the SNCR process. The experiments were done in mixture containing 270 ppm NO, 270 ppm NH$_3$, 4% O$_2$, 8% H$_2$O in N$_2$ at 1175 K, which approximately corresponds to the lowest temperature in the SNCR process [4] without NH$_3$ slip. Sodium carbonate was injected in form of an aqueous 5% Na$_2$CO$_3$ solution with a variable rate of injection that provided a concentration range from 270 to 2300 ppm of Na$_2$CO$_3$. Results are shown in Figure 2-1. Without sodium carbonate, the efficiency of NH$_3$ as NO removing agent varies from 26 to 49 % depending on the run. The scatter is probably due to the fact that ammonia was injected in pure form into the stream of pre-made NO + O$_2$ + N$_2$ mixture with many associated difficulties of maintaining a steady flow of NH$_3$. Sodium carbonate additive increases the efficiency of NH$_3$ as NO removing agent with efficiency approaching a constant value of about 63 % at high concentrations of Na$_2$CO$_3$.

These results will be used for comparing the efficiency of Na additives with that of other metals in Phase II of this work.

References for Section 2:

Figure 2-1. Dependence of NO removal efficiency determined as $\frac{[NO]}{[NO]_0}$ (100% in the SNCR process on amount of $Na_2CO_3$ in the mixture). $T = 1175K$, $P = 1$ atm, residence time 0.15 s.
3.0 Advanced Reburning Application

This section discusses the conversion of the process design presented in the previous quarterly report into retrofit hardware for the AR-Lean system and discusses the results of initial AR-Lean tests as well as tests of some of the SGAR components.

The unit is Greenidge Unit 4, which is owned and operated by New York State Electric and Gas (NYSEG). All of NYSEG’s units are located within the North East Ozone Transport Region (NEOTR) and as a result are subject to Title 1 NOx control requirements. NYSEG’s compliance plan involves a system-wide daily cap on NOx emissions. After considering a number of alternatives, NYSEG decided to utilize reburning and AR-Lean for NOx control at Greenidge. EER installed the gas reburning system as part of a commercial project with guaranteed performance. The upgrade to AR-Lean was conducted as a cooperatively funded demonstration project with the support of NYSEG and a number of cofunding organizations including the Electric Power Research Institute, Empire State Electric Energy Research Corporation, Gas Research Institute, Gaz de France, New York State Energy Research & Development Authority, and Orange & Rockland Utilities.

The AR-Lean process design specifications for the location and size of the reburning gas, furnace overfire air, and convective pass overfire air were utilized to prepare an engineering retrofit design. Figure 3-1 is an isometric view of the unit showing the arrangement of the gas reburning and AR-Lean components external to the furnace. The gas injectors were corner mounted and consisted of multiple injectors in each corner with a surrounding cooling air passage. The multiple gas injector approach allows independent control of the quantity of reburn fuel and the injection velocity. The natural gas valve train included pressure reduction, double block and bleed shutoff control, and flowrate control valves. The furnace OFA ports were corner mounted above the reburn injectors but below the furnace nose. The OFA for these ports was supplied by takeoffs from the top of the burner windbox. Although this tangentially fired unit operates at a relatively low windbox to furnace pressure differential, the differential was sufficient to achieve the design air injection velocities. The overfire air flow was controlled by dampers.
Figure 3-1. Isometric view of Greenridge Unit 4 showing gas reburning and AR-Lean components external to the boiler.
To achieve the required rapid and complete mixing of the convective pass OFA with the furnace gases in the narrow space between the convective surfaces, air was injected from side wall ports as well as a header in the center extending downward from the boiler penthouse. The windbox to furnace pressure differential was insufficient to produce the design point velocity. To boost the pressure, two fans were installed between the windbox and the convective pass overfire air supply headers.

Aqueous ammonia was used for the N-agent. It was produced on site from anhydrous ammonia. A variable speed positive displacement pump provided flow control. The N-agent was piped to pressure atomizers located in the convective pass overfire air headers on each side of the unit downstream of the booster fans. To provide enhanced control of the N-agent injection distribution, this system was subsequently modified with separate injectors in each wall port and in each air supply duct feeding the central header.

The gas reburning and AR-Lean components were integrated with the unit’s WDPF Level 4 control system. This includes 140 input/outputs fully integrated with the combustion control system. The gas reburning and AR-Lean systems can be controlled remotely from the boiler control room and are fully automated. A series of permissives and trips ensure safe operation.

The gas reburning and AR-Lean systems were designed to provide the flexibility to adjust NOx to meet NYSEG’s system-wide NOx cap. The initial NOx reduction is from leakage air through the furnace and convective pass overfire air ports which provides a degree of staging.

The gas reburning system is brought into operation for the second increment of NOx reduction. This involves, (1) ramping up the gas injection rate, (2) reducing the coal firing rate to compensate for the gas, (3) decreasing the combustion air supplied to the burners to maintain lower furnace stoichiometry, and (4) injecting combustion air through the furnace overfire air ports to maintain the overall stoichiometry at near baseline. The gas injection rate is the primary variable controlling NOx reduction. The coal firing rate and air flows are adjusted to the design point burner and overall stoichiometries. NOx is decreased as the gas injection rate is ramped up.

A transition is made to AR-Lean for the final increment of NOx reduction. This involves (1) decreasing the gas injection rate, (2) increasing the coal firing rate, (3) increasing the combustion air supplied to the burners to maintain lower furnace stoichiometry, (4) switching the OFA from
the furnace to the convective pass ports, (5) adjusting the OFA flowrate to maintain the overall stoichiometry at near baseline, and (6) injecting the N-agent through the convective pass overfire air ports. The N-agent injection rate is the primary variable controlling NO\textsubscript{x} reduction. The gas, coal and combustion air flow rates are adjusted to produce near stoichiometric conditions in the reburn zone and design point burner and overall stoichiometries. NO\textsubscript{x} is decreased as the N-agent injection rate is ramped up.

NO\textsubscript{x} emissions for gas reburning and AR-Lean are shown in Figure 3-2 as a function of the reburning gas percentage. The baseline NO\textsubscript{x} emissions for the unit prior to the equipment retrofit were 0.62 lb/10\textsuperscript{6} Btu. Leakage air through the furnace and convective pass overfire air ports provided air staging and reduced NO\textsubscript{x} to 0.46 lb/10\textsuperscript{6} Btu. In the normal gas reburning mode, additional overfire air was added through the furnace overfire air ports as the reburning gas was injected. As shown in Figure 3-2, NO\textsubscript{x} decreased as the gas injection rate increased down to 0.22 lb/10\textsuperscript{6} Btu which represents a NO\textsubscript{x} control level of 62 percent. CO emissions were typically under 30 ppm.

Since the gas reburning portion of the system was a commercial system, a guarantee test was conducted with the following result at 15% gas injection:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measured Performance</th>
<th>Commercial Guarantee</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>0.286</td>
<td>0.300</td>
<td>lb/10\textsuperscript{6} Btu</td>
</tr>
<tr>
<td>CO</td>
<td>17</td>
<td>60</td>
<td>ppm</td>
</tr>
</tbody>
</table>

Initial testing of AR-Lean was conducted in summer 1996. The initial tests focused on establishing the operating conditions without ammonia injection. This involved the first five steps listed above. The system was set up to control the CO level at the point of convective pass overfire air introduction. Under these conditions, NO\textsubscript{x} was reduced slightly to about 0.30 lb/10\textsuperscript{6} Btu. This was a consequence of the moving the overfire air injection to the convective pass which extended the reburning zone. The convective pass overfire air system was effective in controlling stack CO emissions to levels comparable to baseline.
Figure 3-2. Gas reburning and AR-Lean NOx data, Greenridge Unit 4.
The next test series involved ramping up the N-agent injection (step six in the list above). As the N-agent injection was increased, NO\textsubscript{x} decreased, as expected. Figure 3-2 shows the AR-Lean NO\textsubscript{x} data superimposed on the gas reburning data illustrating the lower NO\textsubscript{x} emissions achieved at nominally 10% gas firing. In these AR-Lean tests, minimum NO\textsubscript{x} was constrained by NH\textsubscript{3} emissions to 0.19 lb/10\textsuperscript{6} Btu. This was unexpected and was traced to non-uniform conditions in the reburning zone as discussed below.

In conventional N-agent injection without reburning, the temperature window is narrow: injection within the window reduces NO\textsubscript{x} with minimum NH\textsubscript{3} emissions; injection on the hot side of the temperature window may increase NO\textsubscript{x} but with minimal NH\textsubscript{3} emissions; injection on the cold side of the temperature window achieves less NO\textsubscript{x} reduction and produces NH\textsubscript{3} emissions. With AR-Lean, CO oxidation occurs in parallel with the NH\textsubscript{3} reactions effectively broadening the temperature window on the cold side. During these AR-Lean tests, the CO level in the reburning zone was in the range expected to broaden the temperature window to lower temperatures, on the order of several thousand ppm. CO measured in the boiler exhaust was typically less than 50 ppm indicating excellent CO burnout. While the overall CO levels and burnout were on design, probe measurements in the upper furnace showed considerable CO stratification. In some regions the furnace gases had low CO and excess O\textsubscript{2}. In other areas while CO was on design, O\textsubscript{2} was also present indicating streamwise stratification or poor micro-mixing. This stratification accounts for the NO\textsubscript{x} emission reduction and NH\textsubscript{3} emissions. That portion of the furnace flow with low CO and excess O\textsubscript{2} was not producing the temperature window broadening and this resulted in excess NH\textsubscript{3} emissions limiting the maximum NH\textsubscript{3} injection rate and hence NO\textsubscript{x} reduction.

These Greenidge tests have revealed an important AR issue: the uniformity of conditions in the reburning zone is important to the optimization of the AR process. In small scale tests, the furnace flow is fairly well mixed so that this stratification effect is not significant. However, stratification may be the limiting factor in full scale applications.

Once this stratification effect was understood, additional tests were conducted at Greenidge to improve performance. The focus of testing in summer 1997 was on adjusting the AR-Lean system to provide more uniform reburn zone conditions. This included: (1) burner balancing, (2) modification of the gas injectors to reduce stratification and enhance the micro-mixing of the fuel and air so as to avoid regions of excessively rich or lean conditions, and (3) reduction of leakage.
air through the furnace overfire air ports. In addition, the N-agent injectors were modified to allow
the tailoring of the distribution of the N-agent among the convective pass overfire air injectors.
These changes have resulted in improved performance and additional NOx reduction with lower
NH₃ slip.

In addition to these AR-Lean tests, opportunity was taken to obtain larger scale data on several of
the SGAR components. It should be noted that the Greenidge unit was set up only for AR-Lean
and the furnace penetrations available in the unit were not optimum for the other SGAR
configurations. A series of tests were conducted in Summer 1997 to evaluate the following SGAR
components:

- N-agent injection downstream of the overfire air  In these tests, the gas reburning
  system was operated in the normal mode using the furnace overfire air. The
  N-agent was injected through a series of lances on the front wall above the overfire
  air ports. Based on the process design studies, it was expected that these temporary
  N-agent injectors would not produce a uniform distribution of N-agent across the
  furnace and that the furnace temperature would be too hot for effective SNCR
  operation. The tests confirmed these predictions. Only modest NOₓ reduction was
  achieved and NH₃ slip was minimal.

- N-agent Injection into the reburn zone  This SGAR component was tested by
  operating the system in the AR-Lean configuration using the convective pass
  overfire air ports. The N-agent was injected through the same furnace lances
  described above. While this injection location was not optimum, it provided some
  initial data on AR-Rich conditions.

- Multiple N-agent injection  Limited tests were also conducted with injection both
  through the furnace lances and through the convective pass injectors. Again, the
  tests do not represent an optimum MIAR configuration. However, they allow a
  preliminary evaluation of multiple injection and the ability to stratify the N-agent
  injection for the stratified furnace flow conditions.

If this project proceeds to Phase II, these large scale tests will continue in summer 1998. Alternate
injection arrangements and promoters are expected to be tested.