# OXYGEN ENHANCED COMBUSTION FOR NOx CONTROL

# FINAL REPORT

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**Principal Authors:**

**Program Manager and Business Officer: David R. Thompson**
**Principal Investigator, Combustion Development: Lawrence E. Bool**
**Principal Investigator, OTM Development: Jack C. Chen**



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**Submitted by:**

**Praxair, Inc.**
**175 East Park Drive**
**Tonawanda, NY 14150**



**Prepared for:**

**U.S. Department of Energy**
**National Energy Technology Laboratory**
**626 Cochrans Mill Road**
**Pittsburgh, PA 15236**

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## ABSTRACT

Conventional wisdom says adding oxygen to a combustion system enhances product throughput, system efficiency, and, unless special care is taken, increases NOx emissions. This increase in NOx emissions is typically due to elevated flame temperatures associated with oxygen use leading to added thermal NOx formation. Innovative low flame temperature oxy-fuel burner designs have been developed and commercialized to minimize both thermal and fuel NOx formation for gas and oil fired industrial furnaces. To be effective these systems require close to 100% oxy-fuel combustion and the cost of oxygen is paid for by fuel savings and other benefits. For applications to coal-fired utility boilers at the current cost of oxygen, however, it is not economically feasible to use 100% oxygen for NOx control.

In spite of this conventional wisdom, Praxair and its team members, in partnership with the US Department of Energy National Energy Technology Laboratory, have developed a novel way to use oxygen to reduce NOx emissions without resorting to complete oxy-fuel conversion. In this concept oxygen is added to the combustion process to enhance operation of a low NOx combustion system. Only a small fraction of combustion air is replaced with oxygen in the process. By selectively adding oxygen to a low NOx combustion system it is possible to reduce NOx emissions from nitrogen-containing fuels, including pulverized coal, while improving combustion characteristics such as unburned carbon.

A combination of experimental work and modeling was used to define how well oxygen enhanced combustion could reduce NOx emissions. The results of this work suggest that small amounts of oxygen replacement can reduce the NOx emissions as compared to the air-alone system. NOx emissions significantly below 0.15 lbs/MMBtu were measured. Oxygen addition was also shown to reduce carbon in ash. Comparison of the costs of using oxygen for NOx control against competing technologies, such as SCR, show that this concept offers substantial savings over SCR and is an economically attractive alternative to purchasing NOx credits or installing other conventional technologies.

In conjunction with the development of oxygen based low NOx technology, Praxair also worked on developing the economically enhancing oxygen transport membrane (OTM) technology which is ideally suited for integration with combustion systems to achieve further significant cost reductions and efficiency improvements. This OTM oxygen production technology is based on ceramic mixed conductor membranes that operate at high temperatures and can be operated in a pressure driven mode to separate oxygen with infinite selectivity and high flux. An OTM material was selected and characterized. OTM elements were successfully fabricated. A single tube OTM reactor was designed and assembled. Testing of dense OTM elements was conducted with promising oxygen flux results of 100% of target flux. However, based on current natural gas prices and stand-alone air separation processes, ceramic membranes do not offer an economic advantage for this application. Under a different DOE-NETL Cooperative Agreement, Praxair is continuing to develop oxygen transport membranes for the Advanced Boiler where the economics appear more attractive.

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## 1.0 INTRODUCTION

Controlling NOx emissions from utility boilers is a major issue facing the power generation community. Current regulations require NOx emissions to be reduced to 0.15 lb/MMBtu, regardless of the fuel being fired, in many boilers. Major changes will have to be made to the existing fleet of coal fired plants to allow coal to remain a viable fuel for power generation. Although technologies such as Selective Catalytic Reduction (SCR) can achieve these low emissions levels, they are often costly to implement and may require major boiler modifications. Low NOx burners (LNB) and Selective Non Catalytic Reduction (SNCR) can substantially reduce NOx emissions, but they typically cannot meet low emission requirements and may cause operational problems such as high carbon content in ash, reduced flame stability, or ammonia/urea slip.

The development of oxygen enhanced combustion and oxygen enhanced secondary control technologies will allow utilities to meet near term NOx limits while at the same time paving the way for the development of advanced combustion technologies that produce low pollutant emissions and facilitate $CO_2$ sequestration. The combustion expertise of the team and novel burners and technologies developed by Praxair were used to develop oxygen enhanced NOx control technologies that can be implemented by utility operators before the stringent NOx limits go into effect. In addition, these technologies can achieve low NOx emissions without major boiler modifications at costs lower than a conventional SCR system, and with enhanced boiler operation.

Oxygen enhanced coal combustion can reduce NOx in several ways. Oxygen enrichment can be used in conventional burners and LNB operated under globally staged conditions for primary combustion control. Oxygen can also be used to enhance the effectiveness of coal based reburning. In burners, the careful addition of oxygen leads to rapid ignition and enhanced coal devolatilization which reduces the flame standoff distance and creates a more fuel rich zone near the burner. The higher temperature achieved by oxygen enriched combustion accelerates NOx reduction kinetics under fuel rich conditions below certain stoichiometric ratios. The advanced oxygen enhanced combustion process can be incorporated air-staged combustion systems utilizing conventional (non-staged) burners or LNB for primary combustion NOx control with relatively minor burner modifications.

Secondary NOx control by coal reburning can also be enhanced through the use of a novel hot oxygen burner developed by Praxair[1]. In this burner rapid ignition and enhanced coal devolatilization can be used to enhance the effectiveness of NOx reduction in coal-based reburning while reducing char yield and promoting lower carbon content in ash. Work by Praxair[2] showed that burnout of both pulverized and granular coal increased significantly when the coal stream mixed with a hot oxygen jet, even at very short (~5 msec) residence times. Another oxygen based technology, Praxair's CoJet® technology[3], can be used to deliver the reburn fuel or air into the center of large boilers.

Unlike many current NOx control techniques, oxygen enrichment improved, rather than degraded, unit operability. For example, flame stability problems and residual carbon in the ash associated with LNB or Ultra Low NOx Burners (ULNB) were virtually eliminated with the judicious use of oxygen. Replacing some small portion of the combustion air with oxygen also slightly improved unit heat rate and regained boiler capacity lost due to boiler balancing problems, such as when a boiler switches from a bituminous coal to a subbituminous coal.

One barrier to oxygen use in boilers, particularly utility boilers, is the current cost of oxygen. To date, full oxygen combustion has been considered too expensive to use in boilers. For example, for 100% oxygen firing, the oxygen cost adds about $15.00 per MWh to the cost of power. However, replacement of part of the combustion air for NOx control is an economically viable option. Oxygen today is produced primarily using cryogenic and vacuum pressure swing adsorption (VPSA) technology. The economic analysis contained in the proposal shows that oxygen enhanced combustion can demonstrate substantial savings over SCR using currently available VPSA technology.

Because of the high operating temperature of ceramic membranes (>700°C), integration with the combustion process can potentially create substantial further cost savings. For air separation using OTM, air can be fed to one side of the OTM at high temperature and elevated pressure. The necessary heat for the OTM to operate can be provided directly, by the combustion reaction, or by the hot exit streams from the combustion chamber. Oxygen will permeate the membrane with 100% selectivity. The hot oxygen can then be fed to a combustion chamber.

## 2.0 EXECUTIVE SUMMARY

The objective of this program was to demonstrate the use of oxygen enhanced combustion as a technical and economical method of meeting the EPA State Implementation Plan for NOx reduction to less than that of 0.15lb/MMBtu for boilers and coal. This program developed both oxygen based low NOx technology and the low cost oxygen transport membrane (OTM) oxygen production technology.

The breakdown of the program work consisted of the following four major tasks:

Task 1.0 Oxygen enhanced combustion (OEC)
Task 2.0 Oxygen transport membranes
Task 3.0 Economic evaluation
Task 4.0 Program management

Task 1 work consisted of computer modeling used to determine the effectiveness of proposed oxygen-based technologies in boiler environments; laboratory-scale, pilot-scale and full-scale testing used to understand the fundamentals of oxygen for NOx emissions control and to illustrate the benefit of oxygen addition to low NOx coal firing systems.

The laboratory-scale experiments at the University of Arizona illustrated two key concepts for the use of OEC for NOx control. First, the data clearly indicate that replacement of a portion of the first stage combustion air can significantly reduce NOx emissions. This finding represented a critical first step towards development of the technology into a commercially viable method of NOx control. The second key factor of OEC use was the impact of the second stage temperature on the NOx emissions. The fact that the second stage temperature, defined as the gas temperature at the OFA injection point, can have a significant impact on the final NOx emissions, even when the temperatures are low enough that thermal NOx formation can be neglected, represents a key parameter for optimizing the use of staged combustion for NOx control.

The primary objective of the experimental work at the University of Utah was to explore the parameters that would allow successful implementation of oxygen-enhanced staging at commercial scale. The experimental work confirmed that the gas temperature at the overfire air injection point has a significant impact on the NOx emissions from staged combustion. As the temperature increases so do the NOx emissions. Residence time in the first, fuel rich, stage was also shown to be important with longer residence times yielding lower NOx emissions. Experiments with oxygen-enhanced staging showed that the use of oxygen enhances the reactions leading to the conversion of fuel nitrogen to molecular nitrogen. At short first stage residence times oxygen can significantly reduce the NOx emissions compared to air alone. At very long residence times, when kinetic limits become less important, oxygen addition has less of an impact. The transport air to fuel ratio, which controls the gas phase stoichiometric ratio in the flame core, and the method used to introduce oxygen were also shown to have an impact on both NOx reduction from staging and the effectiveness of oxygen-enhanced staging. The experimental work also showed that air preheating and oxygen purity have a minimal impact on oxygen effectiveness.

The successful demonstration of oxygen enhanced combustion for NOx control at the pilot and full-scale single burner levels led to an agreement between Praxair and City Utilities of Springfield, Missouri to test oxygen enhanced combustion at full scale (separately funded). The results from the full-scale demonstration project at the James River Power Station indicated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants.

Task 2 work focused on the development and testing of an OTM system for use with the proposed technologies. Material characterization of the selected OTM composition, designated PSO1, was completed. Permeation test results of a thin dense PSO1 disk at 1050°C resulted in an oxygen flux of > 100% of target. It was determined that an improved materials system with greater oxygen ion conductivity needs to be developed. Therefore, efforts focused on the study of modified PSO1 compositions to improve mechanical properties such as creep and fracture toughness. Significant improvement in mechanical properties was made with modified PSO1d compositions over PSO1. OTM elements were fabricated successfully by several different methods. Elements were characterized and tested in QC both destructively and non-destructively. Process optimizations were made to increase element quality and yield.

The single tube reactor was assembled and operated successfully. The production of oxygen with a purity better than 99.5% was demonstrated for 150 hours. Testing of dense PSO1d element was conducted with promising preliminary oxygen flux results of 100% of the target flux. Long-term testing of an architecturally modified PSO1d element was completed with no dimensional changes after >600 hours of continuous operation. This lack of deformation is an important milestone in the long-term development of the OTM technology.

Task 3 work confirmed the economic advantages of oxygen enhancement based on beta site test results. This work demonstrated that the technology could be economically applied successfully to a utility boiler. Comparison of the costs of using oxygen for NOx control against competing technologies, such as SCR, show that this concept offers substantial savings over SCR and is an economically attractive alternative to purchasing NOx credits or installing other conventional technologies. OTM processes do not show an economic advantage based on the current processes, natural gas prices, and technology status.

Program management (Task 4) was consistent throughout the program. All major milestones were met. The program was completed under budget. All subcontracts and amendments to subcontracts were negotiated and executed. Project documentation was prepared and delivered to the US DOE in accordance with the cooperative agreement. Program reviews were conducted as scheduled.

The objectives and major accomplishments of this program are summarized in Table 2-1.

**Table 2-1 Oxygen Enhanced Combustion for NOx Control Program Objectives**

| ID | Task | Milestone | Accomplishments |
|---|---|---|---|
| 1 | 1.1.1 | Praxair combustion modeling complete | Praxair combustion modeling was conducted. |
| 2 | 1.1.1 | REI combustion modeling complete | REI combustion modeling was conducted. Combustion modeling with Keystone boiler was completed. CFD model of potential beta site boiler was conducted. Combustion models of two O2 injection lance designs completed. |
| 3 | 1.1.2 | Preliminary lab-scale staged combustion tests complete | Preliminary lab-scale staged combustion tests were completed indicating 30-40% reduction in NOx emissions with modest oxygen additions. |
| 4 | 1.1.2 | Lab-scale experiments complete | Lab-scale experiments complete |
| 5 | 1.2 | Hot oxygen and coherent jet tests complete | Hot oxygen tests complete. Coherent jet tests eliminated from scope of program. |
| 6 | 1.3.1 | Pilot-scale testing of staged combustion complete | Pilot-scale testing of staged combustion complete |
| 7 | 1.3.2 | Pilot-scale testing of reburning complete | Objective eliminated from scope of program |
| 8 | 1.4.1 | Selection of equipment to be tested complete (burner type) | An 'off the shelf' RSFC Burner selected to use in these tests |
| 9 | 1.4.1 | Design of full scale equipment complete | Design of full scale equipment complete |
| 10 | 1.4.2 | Modifications of full scale burner complete | Modifications of full scale burner complete |
| 11 | 1.4.2 | Equipment procured and installed for full-scale tests | Equipment procured and installed for full-scale tests |
| 12 | 1.4.3 | Burner test at full scale complete | Burner testing at full scale complete. The results from the full-scale demonstration project at the James River Power Station indicated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants. |
| 13 | 2.1.1 | Selection of OTM material | PSO1 was selected as OTM material. |
| 14 | 2.1.2 | Optimization of OTM material complete | Optimization of OTM material PSO1 and PSO1d complete |
| 15 | 2.1.3 | Characterization of OTM material | OTM material characterization of PSO1 has been completed. |
| 16,17,18 | 2.2.1 | 50,75,100% of commercial target flux demonstrated with disks | 100% of commercial target flux was demonstrated with disks. |
| 19 | 2.3.1.1 | Performance modeling complete | Phenomenological model for dense tube completed |
| 20 | 2.3.1.2 | Reactor modeling complete | Single tube reactor modeling complete |
| 21 | 2.3.2.1 | Single tube reactor design complete | The single tube reactor design was completed. |
| 22 | 2.3.2.1 | Single tube reactor construction complete | The single tube high pressure reactor was assembled and operated. |
| 23 | 2.3.2.2 | 50% of commercial target flux demonstrated with small tubes | 50% of commercial target flux was demonstrated under no purge conditions with small PSO1 tube. The production of oxygen with a purity of 99.5% was demonstrated. |
| 24 | 2.3.2.2 | 75% of commercial target flux demonstrated with small tubes | 75% of commercial target flux demonstrated under no purge conditions with small PSO1 tubes; Production of oxygen with >99.999% purity demonstrated |

**Table 2-1 Oxygen Enhanced Combustion for NOx Control Program Objectives (continued)**

| ID | Task | Milestone | Accomplishments |
|---|---|---|---|
| 25 | 2.4.1 | Multi-tube reactor conceptual design complete | Objective eliminated from scope of program |
| 26 | 2.4.2 | Multi-tube reactor detailed design complete | Objective eliminated from scope of program |
| 27 | 2.4.3 | Construction of multi-tube reactor complete | Objective eliminated from scope of program |
| 28 | 2.4.4 | 50% of commercial target flux demonstrated with large tubes | Objective eliminated from scope of program |
| 29 | 2.4.4 | Start-up of multi-tube reactor | Objective eliminated from scope of program |
| 30 | 3.1 | Baseline economic verification complete | $O_2$ advantage versus SCR/SNCR confirmed with utilities |
| 31 | 3.2 | Confirmation of economics complete | Economic advantages of $O_2$ confirmed based on pilot and commercial burner performance tests |
| 32 | 3.3 | Market segment definition complete | Market segmentation complete; Target utilities, boilers identified |
| 33 | 3.4 | Host site identified | Two host sites identified |
| 34 | 3.5 | Site specific economics complete | Site visits conducted. Detailed customer estimates conducted. The economic advantage of oxygen enhancement was confirmed. Market segmentation was completed with target utilities and boilers identified. Discussions were held with utilities to confirm economics and identify issues limiting the commercialization of the technology. Additional beta site proposals and commercial proposals have been submitted. |
| 35 | 4.1 | Program review meetings | Six month project review meeting was held 9/25/00 with team members present. Annual program review meeting held on May 23, 2001 at the US DOE and on May 31, 2001 at REI. Update meeting held at US DOE on December 6, 2001. Annual program review meeting held on May 15, 2002 at the US DOE. Teleconferences for combustion review were conducted throughout the program. Program was extended through March 30, 2004 to allow additional time for the final project report and program closeout. |
| 36 | 4.1 | Project final report completed | Project final report completed and submitted in March 2004 to US DOE |

# 3.0 STATEMENT OF WORK

## 3.1 Program Definition

### 3.1.1 Work Breakdown Structure, Schedule, and Milestones

The program work breakdown structure (WBS) is presented in Figure 3-1. The program schedule is presented in Figure 3-2. The major program milestones and accomplishments were summarized in Table 2-1 of the Executive Summary. The combustion portion of the program, Task 1, was completed by the end of the third year. Task 2, OTM Development, also continued until the end of year three. The economic evaluation, Task 3, was primarily completed by the end of year two, and evaluations of the OTM continued through the end of year three. Program management, Task 4, took place throughout the program.

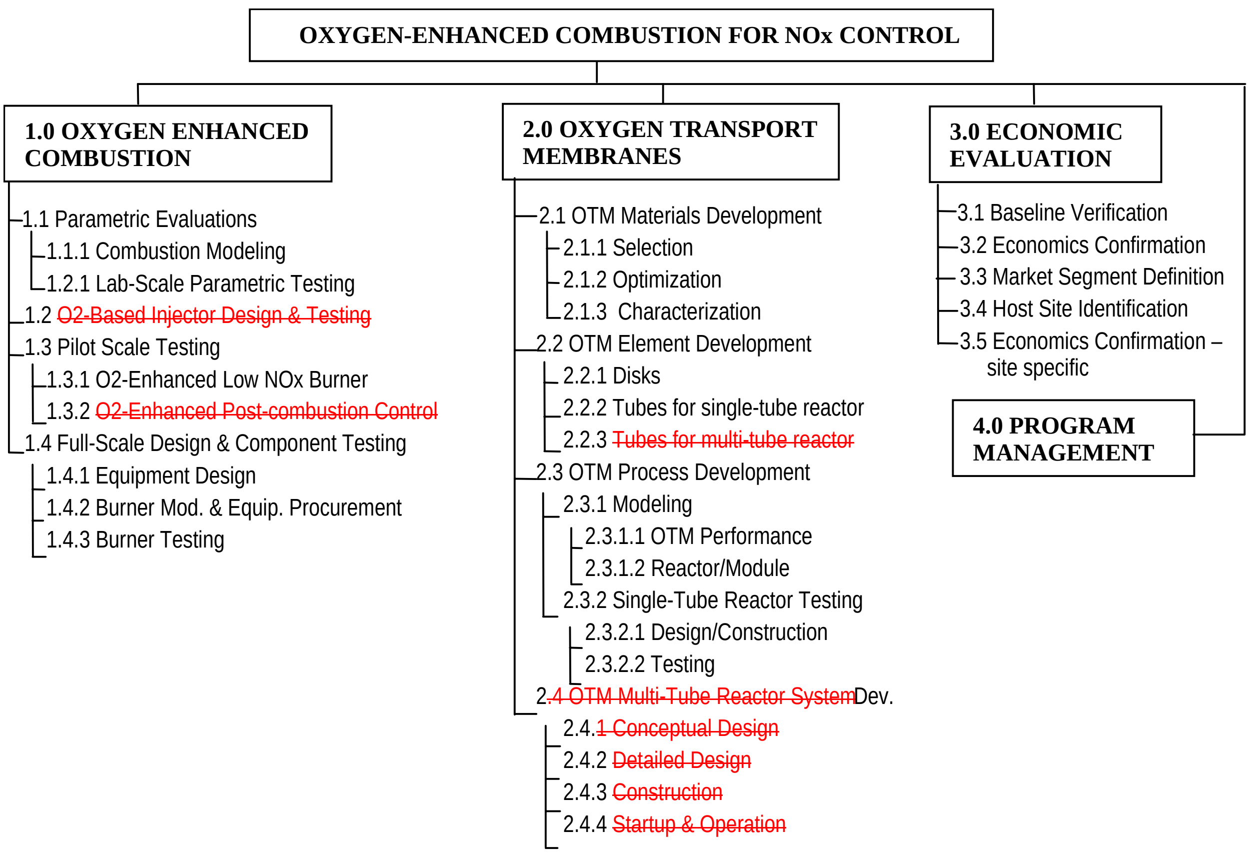


**Figure 3-1 Work Breakdown Structure**

| TASK | YEAR 1 | YEAR 2 | YEAR 3 | RESPONSIBILITY |
|---|---|---|---|---|
| **1.0 OXYGEN ENHANCED COMBUSTION** | | | | |
| **1.1 Parametric Evaluations** | | | | |
| 1.1.1 Combustion Modeling | | | | PX, REI |
| 1.1.2 Lab-Scale Parametric Testing | | | | UA |
| **1.2** | | | | PX |
| **1.3 Pilot-Scale Testing** | | | | |
| 1.3.1 O2-Enhanced Low-Nox Burner | | | | REI, PX, ABB |
| ~~1.3.2 O2-Enhanced Post-Combustion Control~~ | | | | REI, PX, ABB |
| **1.4 Full Scale Design & Component Testing** | | | | |
| 1.4.1 Equipment Design | | | | ABB, PX |
| 1.4.2 Burner Mod. & Equip. Procurement | | | | ABB, PX |
| 1.4.3 Burner Testing | | | | ABB, PX |
| **2.0 OXYGEN TRANSPORT MEMBRANES** | | | | |
| **2.1 OTM Materials Development** | | | | |
| 2.1.1 Selection | | | | PX |
| 2.1.2 Optimization | | | | PX, UMR |
| 2.1.3 Characterization | | | | PX, UMR |
| **2.2 OTM Element Development** | | | | |
| 2.2.1 Disks | | | | PX |
| 2.2.2 Tubes for single-tube reactor | | | | PX |
| 2.2.3 Tubes for multi-tube reactor | | | | PX |
| **2.3 OTM Process Development** | | | | |
| 2.3.1 Modeling | | | | |
| 2.3.1.1 OTM Performance | | | | PX |
| 2.3.1.2 Reactor/Module | | | | PX |
| 2.3.2 Single-Tube Reactor Testing | | | | |
| 2.3.2.1 Design/Construction | | | | PX |
| 2.3.2.2 Testing | | | | PX |
| ~~**2.4 OTM Multi-Tube Reactor System Development**~~ | | | | |
| ~~2.4.1 Conceptual Design~~ | | | | PX |
| ~~2.4.2 Detailed Design~~ | | | | PX |
| ~~2.4.3 Construction~~ | | | | PX |
| ~~2.4.4 Startup & Operation~~ | | | | PX |
| **3.0 ECONOMIC EVALUATION** | | | | |
| **3.1 Baseline Verification** | | | | PX, ABB, UAP* |
| **3.2 Economics Confirmation** | | | | PX, ABB, UAP |
| **3.3 Market Segment Definition** | | | | PX, ABB, UAP |
| **3.4 Host Site Identification** | | | | PX, ABB, UAP |
| **3.5 Economics Confirmation - Site Specific** | | | | PX, ABB, UAP |
| **4.0 PROGRAM MANAGEMENT** | | | | PX |

*Utility Advisory Panel

**Figure 3-2 Program Schedule – Oxygen Enhanced Combustion for NOx Control**

### 3.1.2 Resource Application and Labor Distribution Plan

Praxair has a group headed by Dr. D. Bonaquist that has developed an OTM-based industrial gas technology. This group developed OTM technology for oxygen production as defined in the original proposal. Dr. J. Chen served as the Principal Investigator for the OTM work. Mr. D. R. Thompson, Manager-Business Development for Ceramic Membranes, focused on the business aspects of the program. Dr. B. A. Van Hassel was responsible for modeling and process demonstration/ development. Dr. P. Apte manufactured OTM elements. Praxair has existing facilities for manufacturing OTM disks and tubes, and testing the OTM elements in disk reactors, single-tube reactors, and multi-tube pilot-scale reactors.

The combustion effort was led by members of Praxair's Combustion R&D group. Dr. L. Bool was the Principal Investigator for the combustion portion and coordinated the effort between the subcontractors. Dr. H. Kobayashi provided technical guidance on oxygen for NOx control throughout the program. Existing hot oxygen burners, coherent jet burners, combustion models, and test facilities were used in the program.

Professor J. Wendt of the University of Arizona led a combustion research group that used existing laboratory scale coal combustors to parametrically evaluate oxygen addition for NOx control.

Professor H. U. Anderson of the University of Missouri at Rolla (UMR) led a research group dedicated to the study of electronic and physical properties of mixed oxides. He oversees the materials characterization and OTM preparation studies at UMR.

Dr. B. Adams and Dr. M. Cremer were responsible for the REI subcontract and also participated in modeling of oxygen enhanced coal combustion in corner-, wall- and cyclone-fired boiler furnaces. Dr. E. Eddings was responsible for the University of Utah Subcontract, pilot scale testing and modeling using an existing pilot scale facility.

Dr. N. Nsakala was project manager for the Alstom portion of the program. He led the effort at Alstom's existing burner test facility. Mr. C. Maney performed the burner design portion of the program based on Alstom and Praxair supplied technology.

## 3.2 Task Descriptions

### TASK 1 OXYGEN ENHANCED COAL COMBUSTION

### Task 1.1 Parametric Evaluations

**Task 1.1.1 Combustion Modeling -** Existing models at Praxair and REI were used to explore oxygen in staged low NOx burners (LNB) and the impact of burners on boiler operation.

REI illustrated the benefits of oxygen enhanced coal combustion using existing burner and boiler models. These models included three different wall fired boilers. The results provided important comparisons with other NOx control alternatives which have been evaluated extensively. For the wall fired boiler two burner conditions were modeled. Output from these cases was used in the boiler simulation. Multiple injection strategies and $O_2$ use rates were simulated for each burner. Oxygen injection with a coal blend was evaluated. Furnace emissions, LOI, water wall wastage potential, and furnace heat absorption were used to compare cases.

Additional combustion modeling work included the development of a CFD model of a potential beta site boiler to predict case specific performance of oxygen addition. Also $O_2$ injection lance work continued with the development of combustion models of two lance designs.

**Task 1.1.2 Laboratory-scale Parametric Testing -** Researchers at UA used a small-scale combustor to explore the impact of oxygen enrichment on NOx formation and on the standoff distance of coal flames. Staged combustion experiments utilized an existing 17 kW downfired self-sustained combustor which provides time-temperature histories typical of full-scale utility boilers. NOx concentration measurements were made for a wide range of first stage stoichiometric ratios and oxygen replacements. Experiments were performed concurrently with pilot-scale experiments to elucidate the NOx emissions observed in these tests.

**Task 1.2 Oxygen Based Injector Design and Testing -** A prototype hot oxygen burner was modified to handle pulverized coal and operated with stoichiometric ratios from 0.3-0.8, and temperatures from 2000$^{o}$F to 3000$^{o}$F to identify issues such as chamber slagging and composition of the gaseous reburn fuel. All experiments were performed in Praxair's outdoor burner test facility.

### Task 1.3 Pilot Scale Testing

**Task 1.3.1 Oxygen Enhanced Low NOx Burner –** The University of Utah's pilot-scale facility and existing pilot scale LNB were used extensively to explore the effect of oxygen injection on NOx emissions from various burner types. The furnace is a nominal 15 MMBtu/hr pilot-scale furnace designed to simulate commercial combustion conditions. Baseline low NOx data (without oxygen addition) were taken for each burner condition. Oxygen addition was systematically explored. Important variables are the interactions between oxygen enhancement and burner characteristics to minimize NOx formation. Praxair and Alstom provided input and performed data analysis for this task.

### Task 1.4 Full Scale Design and Component Testing

**Task 1.4.1 Equipment Design -** Praxair, REI, and Alstom designed a conceptual oxygen enhanced secondary NOx control system. They also designed a low NOx burner based on Alstom's RSFC™ burner for full scale testing in Alstom's Industrial Scale Burner Test Facility (ISBF). Design modifications were based on data from earlier tasks and Alstom's commercial design experience.

**Task 1.4.2 Burner Modifications and Equipment Procurement -** An existing Alstom 30 MMBtu/hr burner was modified for installation into the ISBF. Alstom Power Plant Laboratories' ISBF is a balanced draft, front wall fired combustion test facility designed to replicate the combustion environment of a typical industrial design boiler. All major aspects of an industrial boiler are duplicated in the ISBF. Four thermocouples were installed at the burner face to monitor the burner face temperatures. An oxygen control skid and liquid oxygen tank were provided by Praxair.

**Task 1.4.3 Burner Testing -** The modified RSFC™ burner was installed and tested in Alstom's ISBF to demonstrate that an optimized oxygen-enhanced coal combustion system can meet the emissions target of 0.15 lb/MMBtu with minimal impact on unburned carbon, CO emissions, and furnace performance. Test parameters included primary staged stoichiometry and residence time, combustion air temperature, overall stoichiometry, oxygen enrichment, and pure oxygen injection location. Fuels included an eastern bituminous, Illinois 6 and a PRB coal.

## TASK 2. OXYGEN TRANSPORT MEMBRANES (OTM)

### Task 2.1 OTM Materials Development

**Task 2.1.1 Selection -** Praxair has identified candidate materials that meet many of the requirements for the OTM. A candidate material, designated PSO1, was selected based on previous experience.

**Task 2.1.2 Optimization -** Praxair optimized the material composition by making small changes to improve properties. Testing continued until a suitable composition, designated PSO1d, was completely defined.

**Task 2.1.3 Characterization -** Praxair measured the physical and chemical properties of candidate materials. Ionic conductivity was measured by measuring oxygen diffusion. Electronic conductivity was measured directly. The decomposition threshold was measured by post mortem analysis of samples which were exposed to different environments. Strength under operating conditions was measured by extrapolating data from burst tests done under ambient conditions. Thermal expansion and compositional expansion were measured by dilatometry. Compatibility with other reactor materials was analyzed using microscopy and spectroscopy. Phase stability was measured by testing under operating conditions and post mortem examination by microscopy and spectroscopy.

### Task 2.2 OTM Element Development

**Task 2.2.1 Disks –** Disks and small tubes were fabricated from the OTM material using proprietary methods developed outside of this program. Sintered disks were measured for shrinkage and density, and phase composition by x-ray diffraction. Disks that demonstrated 100% of the commercial target flux were produced.

**Task 2.2.2 Tubes for Single-Tube Reactor -** Membrane tubes were fabricated using proprietary methods developed outside of this program. Powders were prepared by Praxair Specialty Ceramics. The green body of the OTM elements were densified by using an optimized sintering condition. The dimension change and the weight loss of the sintered tubes were monitored to control tube quality.

### Task 2.3 OTM Process Development

### Task 2.3.1 Modeling

**Task 2.3.1.1 OTM Performance -** The diffusion of oxygen through the membrane was modeled with the ambipolar diffusion equation. The result was an expression for the oxygen flux as a function of temperature and oxygen partial pressure difference. The model calculations were validated using data from the disk and single tube tests.

**Task 2.3.1.2 Reactor/Module –** The single tube reactor modeling was completed.

**Task 2.3.2 Single-Tube Reactor Testing**

**Task 2.3.2.1 Design/Construction -** The single-tube reactor for high-pressure operation was designed, built, and operated. The OTM, seal, and pressure vessel had to be capable of withstanding a high differential pressure. The OTM was pressurized from the outside to take advantage of the fact that ceramics are stronger under compression than under tension. The high-pressure reactor was heated externally by an electric furnace.

**Task 2.3.2.2 Testing -** The membrane process was demonstrated in two steps: 1) Oxygen flux measurements at atmospheric pressure with simulated compressed air and an inert sweep gas to provide a sufficient driving force for oxygen permeation, and 2) Oxygen flux measurements at elevated pressure. At least 75% of the commercial target flux was demonstrated under no purge conditions with small PSO1 tubes.

## TASK 3. ECONOMIC EVALUATION

**Task 3.1 Baseline Verification -** Baseline economics have been developed based on literature data and discussions with members of the Utility Board and commercial equipment suppliers. Additional information was acquired to confirm these economics.

**Task 3.2 Economics Confirmation -** The initial pilot testing provided data necessary to improve the quality of the market and cost estimates. The burner modification costs were updated and the quantity of oxygen required and the NOx reduction results achieved along with the costs were used to update the cost analysis. The data was reviewed with the Utility Advisory Board. Any burner requirements that potentially limit the market were used to restate the market size.

**Task 3.3 Market Segment Definition -** The effect of boiler size and type on relative cost and economic performance was calculated using data from the pilot scale work.

**Task 3.4 Host Site Identification -** To facilitate commercialization, Praxair identified a site for demonstration of oxygen enhanced NOx control technologies. Operators of this site have strong interest in implementing the technologies and have qualifications to maximize the chance of success.

**Task 3.5 Confirmation – Site Specific -** Based on the selected host site, a more detailed cost estimate was developed to confirm the installation costs and better estimate the O&M costs. These costs were confirmed during a beta site test conducted outside this program. Upon future completion of the OTM development, the impact of OTM cost savings will be better known.

## TASK 4 PROGRAM MANAGEMENT

**Task 4.1 Program Direction, Coordination, and Control –** The program manager provided a single point of contact with DOE for contractual matters, ensured that contract terms and conditions were complied with, and ensured that necessary skills and resources were provided and assigned effectively to perform project activities. He maintained the lines of authority necessary for ensuring that individual activities were performed in accordance with the overall program goals, and the controls necessary to complete the project on schedule and within budget. He also was responsible for ensuring that Praxair technical management and business management were aware of program progress, and coordinated pre-commercialization activities within Praxair.

Project documentation was prepared and delivered to DOE in accordance with mutually established requirements; oral reviews covering the progress and status of the program were conducted as scheduled.

**Task 4.2 Collaboration with Advisory Panel -** Praxair communicated with the Advisory Panel to solicit comments and guidance on the technical, economic, and market acceptability of the oxygen enhanced NOx reduction technologies developed in the program.

# 4.0 OXYGEN ENHANCED COMBUSTION (TASK 1)

## 4.1 Parametric Evaluations (Task 1.1)

### 4.1.1 Combustion Modeling (Task 1.1.1)

#### *4.1.1.1 Experimental – Task 1.1.1*

Reaction Engineering International's (REI) existing burner and boiler models were used to explore the benefit of oxygen-enhanced combustion. These models were used to evaluate different oxygen mixing strategies on both the small pilot-scale burner at the University of Utah and in three different full-scale utility boilers. The full-scale modeling was designed to determine whether oxygen-enhanced combustion would reduce NOx emissions under staged conditions at these plants. Issues such as unburned carbon and waterwall wastage were also addressed using the CFD tools.

Also, an existing Praxair kinetics model was used to explore the impact of using oxygen on NOx formation during the combustion process. The objective of the modeling was to better understand both the kinetics of NOx formation when oxygen enrichment is used and the impact of mixing on the formation rate.

Model Description

The computational tools used by REI are based on software developed over the last two decades at REI, the University of Utah, and Brigham Young University. The current software simulates reacting and non-reacting flow of gases and particles, including gaseous diffusion flames, pulverized-coal flames, liquid sprays, coal slurries, isothermal and reacting two-phase flows, injected sorbents, and other oxidation/reduction systems. *BANFF* is REI's three-dimensional, gas-phase turbulent reacting flow code, and *GLACIER* adds physical models to treat two-phase flows. These software tools have been applied to a wide variety of industrial systems encompassing utility boilers, pyrolysis furnaces, gas turbine combustors, rotary kilns, waste incinerators, smelting cyclones and others. These applications have been used for basic design, problem solving, pollution control, etc. using many different fuels including natural gas, coal, and waste.

The computational approach involves numerical discretization of the partial differential equation set which describes the physics of the system, including equations for conservation of mass, momentum, and energy. Typically $10^5$ - $10^6$ discrete computational nodes are needed to resolve the most relevant features of a three-dimensional combustion process. Around 60 variables (representing, e.g., gas velocity, temperature, concentration of various chemical species) are tracked at each node.

Turbulence can be modeled using various traditional methods of moment closure including Prandtl's mixing length model, the two-equation k-$\varepsilon$ model[4] and the nonlinear k-$\varepsilon$ model[5]. In all simulations discussed in this report, the standard k-$\varepsilon$ model was used due to its general applicability in modeling the mean velocity field in reacting flows.

Within the model, the rate at which the primary combustion reactions occur is assumed to be limited by the rate of mixing between the fuel and the oxidizer. That is, the rate of chemical reactions is assumed to be fast compared to the rate of mixing (i.e. full chemical equilibrium is assumed), which is a reasonable assumption for the chemical reactions governing heat release. So, the thermochemical state at each spatial position is a function of the degree of mixing (parameterized by the mixture fraction, *f*), the mass fraction of coal particle off-gas ($\eta$), and the enthalpy (parameterized by the degree of heat loss, HL). The effect of turbulence on the mean chemical composition is incorporated by assuming that the mixture fraction, obtained using the k-$\varepsilon$ model, is described by a "clipped-gaussian" probability density function having spatially varying mean, and variance *g*. Mean chemical species concentrations are obtained by convolution over this assumed probability density function (PDF). Chemical reactions that are kinetically controlled, such as those involved in NOx formation and destruction, are handled differently to account for the effects of their relatively slow reaction rates in comparison to the mixing rates.

Particle-phase mechanics are solved by following the mean path or trajectory for a discretized group or ensemble of particles in a Lagrangian frame of reference. Particle mass and momentum sources are converted from a Lagrangian to an Eulerian reference frame where they are coupled with gas phase fluid mechanics. The dispersion of the particle cloud is based on statistics gathered from the turbulent flow field. Heat, mass, and momentum transport effects are included for each particle cloud.

Particle reaction processes include coal devolatilization, char oxidation and gas-particle interchange. Particle swelling is accounted for empirically. The particles are assumed to be isothermal. Particle reaction rates are characterized by multiple parallel reaction rates with fixed activation energies. The parameters that describe the particle reaction rates are part of the input to the code. Particles are defined to consist of coal, char, ash and moisture. Ash is inert by definition; volatile mineral matter is considered as part of the volatile matter of the coal. The offgas from particle reactions is assumed to be of constant elemental composition. Turbulent fluctuations and complete, local, chemical equilibrium are included in the particle reactions.

Since radiation is typically the most significant mode of heat transfer in a large boiler, it is critical that the radiation field be accurately represented. Accurately simulating radiative transfer to specific regions in a system requires a model that can account for both absorbing-emitting radiation processes and complex system geometries, including arbitrary structures such as convective tube pass. Additionally, it is desirable that any radiative model selected be computationally efficient in terms of execution time and storage to allow coupling with other routines in a comprehensive combustion model. REI's model utilizes the discrete-ordinates method, which has been shown to be a viable choice for modeling radiation in combustion systems, both in terms of computational efficiency and accuracy. This method retains the directional dependency of the radiation intensity in a way that other flux models are unable to achieve, yet provides for a finite-difference or finite-volume solution that is more computationally efficient than zone methods and more deterministic than Monte Carlo methods. The development of the discrete-ordinates method and its application to a number of complex geometry's have been presented in the literature and serve to validate the use of this method in accurately modeling radiative heat transfer in coal-fired boilers[6-8].

#### *4.1.1.2 Results and Discussion – Task 1.1.1*

<u>Modeling of the L1500 facility</u>

As part of the overall CFD modeling effort specific models were developed and run of the L1500 furnace at the University of Utah. These models were designed to provide insight on both the experimental work and on the concept as a whole. The L1500 is nominally a 5 MMBtu/hr pilot-scale furnace designed to simulate commercial combustion conditions. The pulverized coal burner used in the L1500 combustion facility is a dual concentric swirl burner designed to provide excellent flame stability and offer a wide range of swirl stabilized flames. The L1500 furnace walls have multiple-layered insulation to reduce the temperature from about 1925 K on the fireside to below 330 K on the shell-side.

The L1500 facility was originally designed to represent a wet bottom boiler. In the CFD simulations, wall resistance (heat extraction) was varied to represent time/temperature history in a "typical" dry bottom boiler. Figure 4-1 shows comparison of model simulations previously carried out in Georgia Power Company's Hammond Unit 4, a 500 MW opposed wall-fired furnace, with those of the L1500 for a range of wall thermal resistances. The average wall thermal resistance in the L1500 facility is 0.4 K·m$^2$/W. It appears that simulation results, using a wall thermal resistance of 0.08 K·m$^2$/W, reasonably represent the time/temperature histories previously predicted in the Hammond furnace. Results, not shown here, also indicate that the calculated mass-weighted average gas temperatures along the furnace length are in good agreement with predictions obtained in Hammond Unit 4. Figures 4-2 and 4-3 show coal burnout and heat extraction as functions of wall thermal resistance, respectively. It can be seen that with a wall thermal resistance of 0.08 K·m$^2$/W, coal burnout is complete. It can also be found from Figure 4-3 that heat loss in the furnace is mainly due to radiation; convective heat transfer only makes up a small portion of the total heat loss.

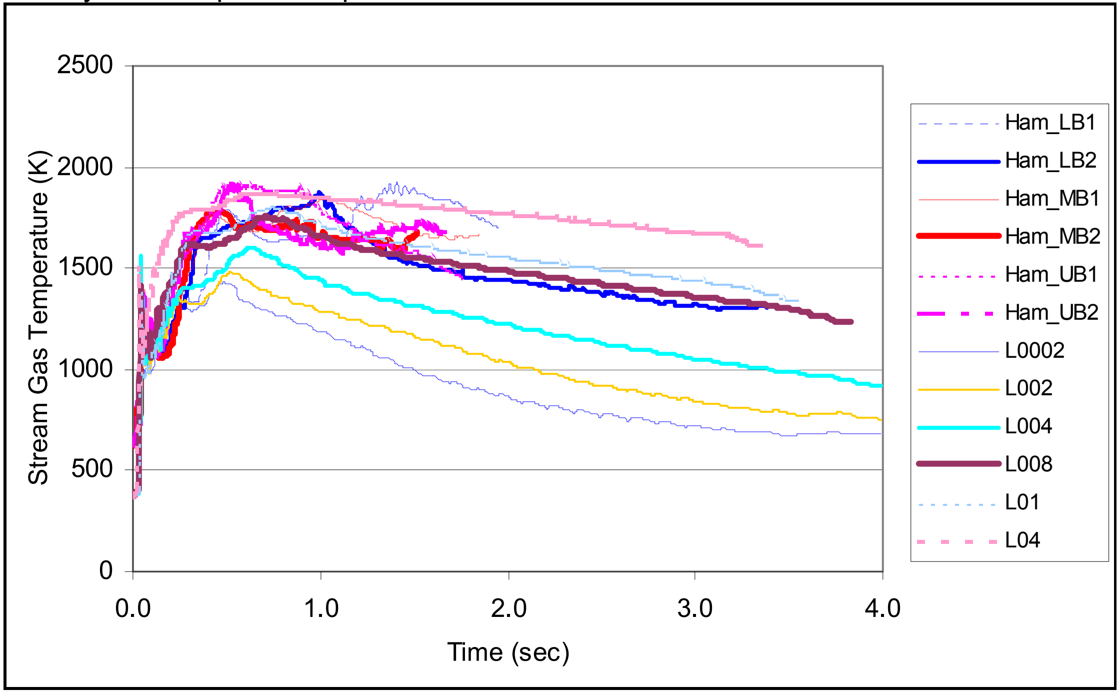


**Figure 4-1. Time/temperature histories along streamlines comparing Hammond Unit 4 and L1500 cases with different wall thermal resistances. All streamlines begin in the primary air region of the burner. Labels LB, MB, and UB refer to lower level burner, middle level burner, and upper level burner in Hammond Unit 4, respectively. L0002 to L04 represent L1500 cases with wall thermal resistance of 0.002 to 0.4 K·m$^2$/W.**

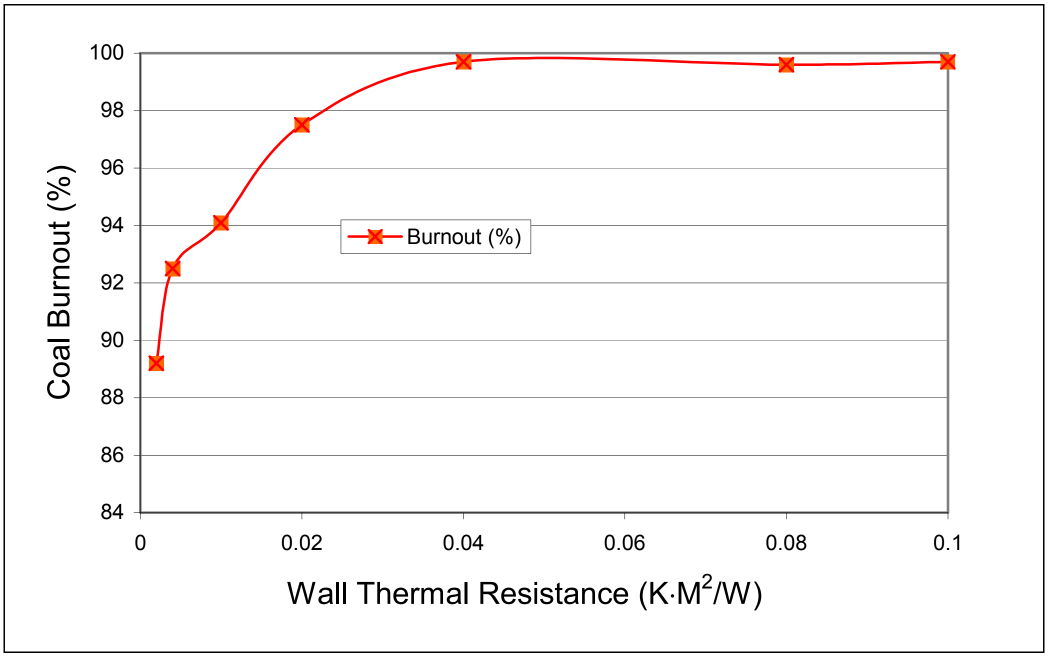


**Figure 4-2. Coal burnout as a function of wall thermal resistance of the furnace**

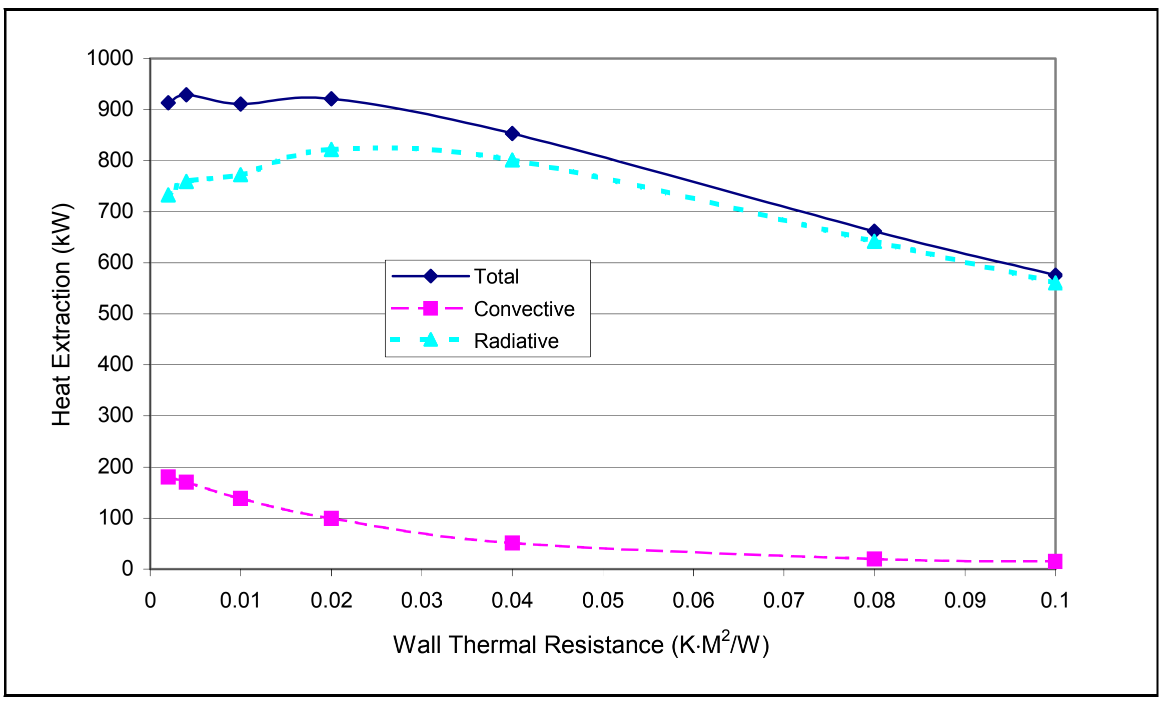


**Figure 4-3. Heat extraction as a function of wall thermal resistance of the furnace**

Investigation into the effect of wall thermal resistance on the time/temperature history of the streamline and the average gas temperatures indicates that model calculations using a wall resistance of 0.08 K·m$^2$/W closely represent that obtained in Hammond Unit 4. Thus, in all subsequent simulations, a wall thermal resistance of 0.08 K·m$^2$/W was employed.

An Illinois No. 6 coal was used for the simulations and the typical firing rate tested at this facility, 4 MMBtu/hr, was assumed. The coal properties are listed in Table 4-1. The L1500 modeling effort was broken into two parts. In Part 1 the focus was to evaluate different methods of introducing oxygen into a low NOx burner. These simulations also evaluated the impact of removing air, for oxygen replacement, from the different burner air streams. In Part 2 the focus was on near field evaluation of oxygen injection into a staged low NOx burner. For these simulations it was assumed that the air was removed from the windbox (secondary and tertiary air streams) as would be typical of a commercial installation of the technology.

**Table 4-1. Firing Conditions and Coal Properties for the Base Case**

| **Proximate Analysis, as received** | |
|---|---|
| % Moisture | 15.82 |
| % Ash | 8.33 |
| % Volatile | 37.26 |
| % Fixed Carbon | 38.59 |
| HHV, Btu/lb (daf) | 14155 |
| **Ultimate Analysis, as received** | |
| % Carbon | 60.16 |
| % Hydrogen | 4.56 |
| % Nitrogen | 0.98 |
| % Sulfur | 3.41 |
| % Oxygen | 6.74 |
| % Moisture | 15.82 |
| % Ash | 8.33 |
| **Coal Particle Size Distribution** | |
| Size (micron) | Mass Fraction |
| 16.5 | 0.017 |
| 26.4 | 0.063 |
| 40.4 | 0.283 |
| 59.4 | 0.284 |
| 86.8 | 0.233 |
| 122.6 | 0.072 |
| 169.6 | 0.043 |
| 278.5 | 0.005 |
| **Coal particle Mass-weighted Average Diameter: 68.0 micron** | |

In general the modeling of the L1500 showed that adding oxygen to a conventional low NOx burner without global staging would likely cause an increase in the NOx emissions due to increased flame temperatures and thermal NOx formation. However, when the furnace is globally staged adding oxygen to the burner leads to lower NOx emissions and potentially lower unburned carbon. These results are consistent with the experimental data obtained with at the L1500.

Modeling of the "Generic" utility boiler

Although both the experimental work and the modeling of the L1500 suggested that significant reductions in NOx emissions can be obtained through oxygen enhancement in low-NOx burners, it is important to also evaluate the potential for increased rates of waterwall wastage and unburned carbon in the fly ash. CFD modeling has been used to evaluate these impacts in a 180 MW front wall fired boiler equipped with low-NOx burners and overfire air. Waterwall wastage involving both gas phase and particle phase corrosion mechanisms has been considered. The predictions have indicated that oxygen enhancement for NOx control in this unit will likely result in unchanged rates of waterwall corrosion under low-NOx firing conditions as compared to the case of no oxygen enhancement, and potentially reduced waterwall surface area subject to high rates of corrosion. Predictions of unburned carbon in the fly ash indicate that operation under low-NOx firing conditions with oxygen enhancement will likely have a beneficial effect.

Figure 4-4 shows an outline of the single wall fired coal unit evaluated here. The unit's capacity is approximately 180 MW, it fires an eastern bituminous coal containing 1.4% sulfur, is equipped with a Riley low NOx firing system including 16 Controlled Combustion Venturi (CCV) burners, and front and side wall overfire air and boundary air. As shown in Figure 4-4, one-half of the unit was modeled by placing a symmetry boundary condition through the center of the unit. Both geometrical and operational symmetry about this plane makes this a good assumption and reduces the computational requirements compared to modeling the full furnace.

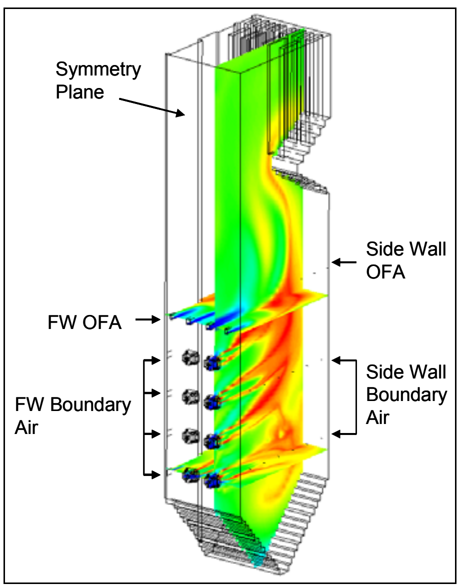


**Figure 4-4. Outline of model for one-half of 180 MW front wall fired coal boiler**

In the furnace model, the secondary air properties (temperature, mass flow rate, and swirl) were specified at the burner throat, and properties of the transport air and coal were specified at the exit of the coal pipe. To accurately represent the coal distribution at the exit of the coal pipe, results from a separate detailed model were utilized as inputs to the furnace model. This predicted dependence of coal mass distribution on particle size was interpolated into the furnace model at the burner throat for each of the burners, preserving the correct swirl directions for each.

A number of the model results are discussed here to show the predicted impact of oxygen enhancement in the 180 MW unit. Although results are shown for NOx emissions and unburned carbon in the fly ash, the emphasis is on the evaluation of waterwall corrosion. Results are shown here for four simulations as described in Table 4-2. Two parameters were evaluated: 1) Burner stoichiometric ratio (SR), and 2) oxygen replacement rate. Case 1 represents baseline operation with no oxygen enhancement and typical OFA flow rates. In the three subsequent cases (2-4), the burner SR was decreased. In cases 2-4, there was 0%, A%, and 2A% replacement where the oxygen replacement is a percentage of the stoichiometric requirement. Thus, the impact of three levels of oxygen replacement at a deeper staged condition compared with baseline operation is evaluated.

**Table 4-2. Summary of simulations completed for 180 MW single wall fired unit**

| **Case** | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| **Burner SR** | 0.9 | 0.9-? | 0.9-? | 0.9-? |
| **$O_2$ Replacement (%)** | 0 | 0 | A | 2A |

Figure 4-5 shows the predicted impact of oxygen injection on the temperature distribution in the 180 MW unit. Temperature profiles are shown for cases 2-4 and illustrate a significant increase in burner zone temperatures with increasing $O_2$ replacement rate. The simulations showed that care must be taken in the method of oxygen injection so that the increased temperature does not cause an increase in thermal NOx formation. The increase in gas temperature for the cases shown here is accompanied by an increase in total volatile yield of 7% for case 4 compared to case 1. The increased gas temperature coupled with the enhanced volatile release in the fuel rich primary combustion zone leads to an increase in NOx reduction rates in this zone. The increased temperature and devolatilization due to oxygen enhancement would also be expected to improve flame stability at reduced burner SRs compared to air alone. Figure 4-6 shows the predicted NOx emissions for the cases. These predictions indicate increasing NOx reduction with increasing $O_2$ replacement rates up to 35% reduction for case 4 compared to case 1. This significant decrease in NOx formation is primarily due to the increased temperature leading to higher $N_2$ formation. The increase in volatile yield means more fuel nitrogen is in the gas phase and can be reduced to $N_2$, which also reduces the overall NOx formation.

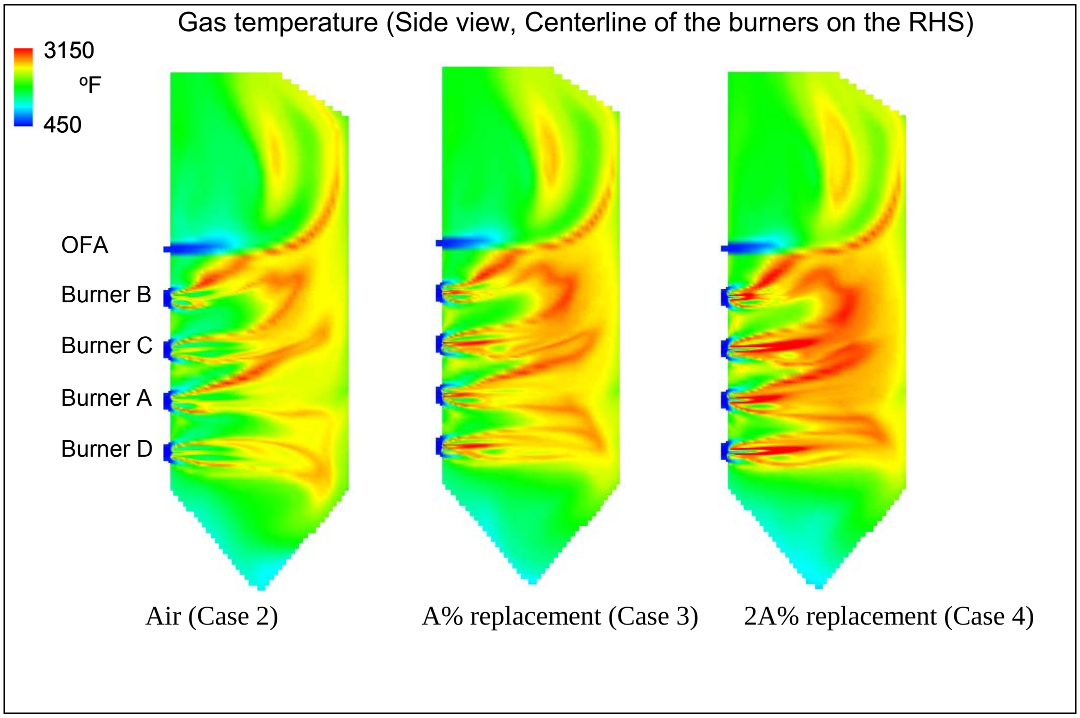


**Figure 4-5. Predicted gas temperature distribution as a function of $O_2$ replacement rate**

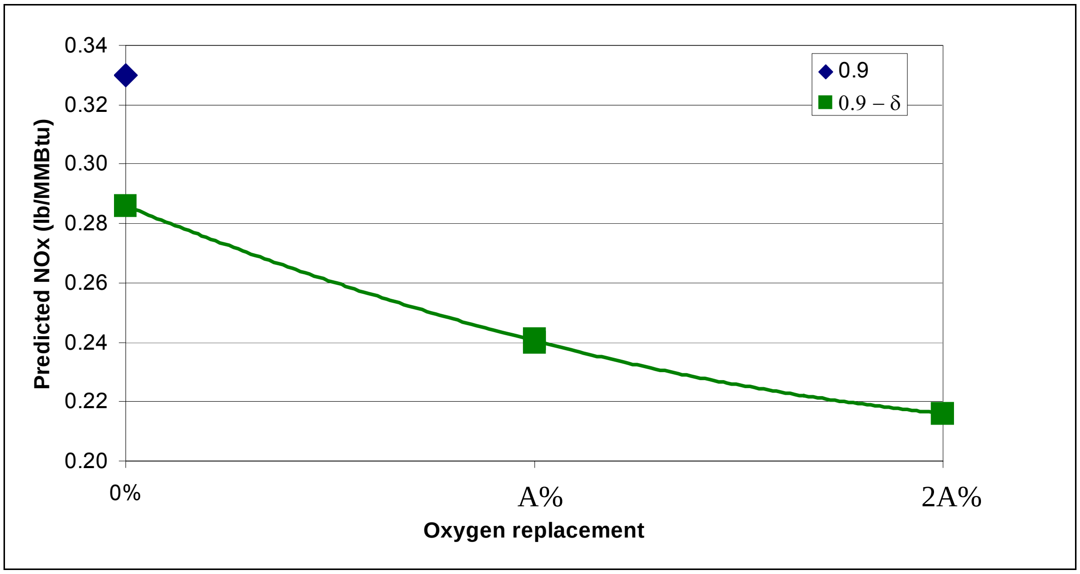


**Figure 4-6. Predicted change in NOx emissions**

Figure 4-7 shows the corresponding predictions of unburned carbon in the fly ash for cases 1-4. In the absence of oxygen enhancement, the unburned carbon is predicted to increase with a reduction in burner SR. However, in both cases with oxygen enhancement, the unburned carbon is predicted to decrease, up to 18% in case 4. The predicted change, in part, is due to the increased devolatilization that occurs in the primary combustion zone, leaving less char to be oxidized downstream of the overfire air addition. These predicted impacts of oxygen enhancement on NOx emissions and unburned carbon in fly ash appear to be consistent results at the James River Unit 3.

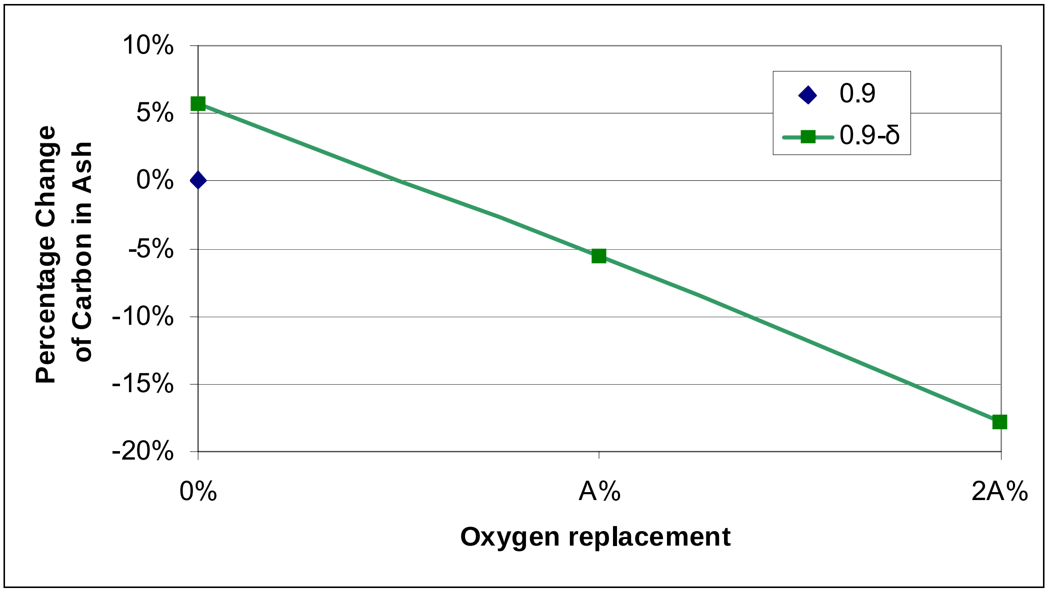


**Figure 4-7. Predicted change in unburned carbon in fly ash**

The same simulations that were completed to evaluate the impact of oxygen enhancement on NOx emissions and unburned carbon in fly ash were utilized to predict waterwall corrosion. The key mechanisms investigated here for contribution to waterwall corrosion were: 1) Gas-phase attack by reduced sulfur species such as $H_2S$, and 2) Deposition of unreacted fuel and resulting sulfur-based attack. The bituminous coal evaluated here precluded a significant corrosion contribution due to chlorine attack because of the extremely low chlorine concentration. Figure 4-8 shows the predicted rate of waterwall corrosion on the rear and sidewalls due to gas phase sulfur attack for cases 1, 2, and 4. Very little difference is predicted for these three cases, with the highest rates being approximately 5 mils/yr.

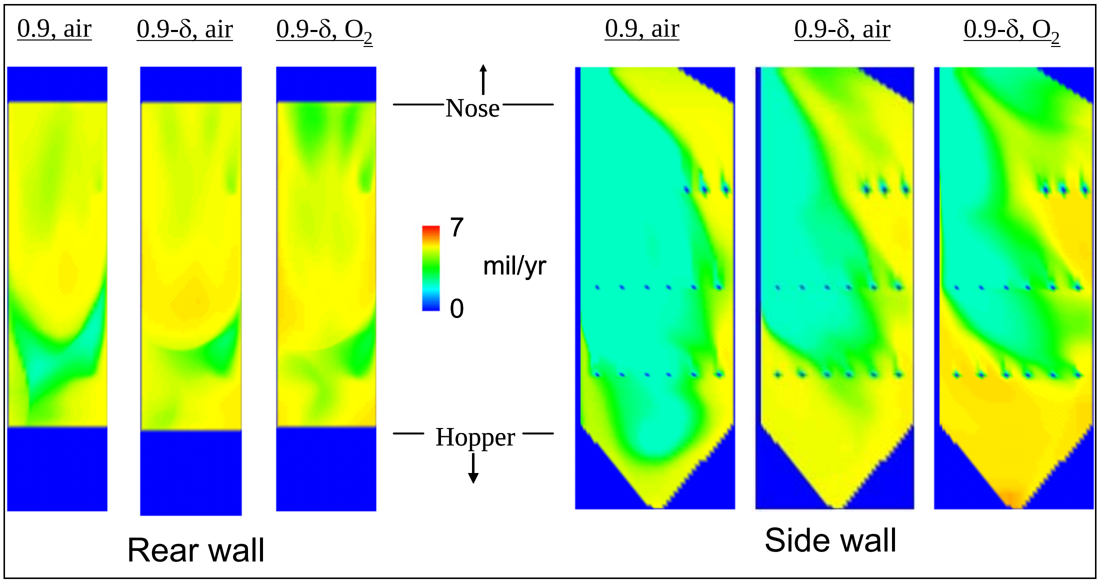


**Figure 4-8. Predicted corrosion rate due to near wall $H_2S$ on the rear and side walls**

Figure 4-9 shows the predicted corrosion rates from sulfur based attack due to deposition of unreacted fuel. In the simulations, particulate deposition is predicted to occur if the particle cloud contacts the waterwall and either the particle or surface temperature exceeds the deformation temperature of coal mineral matter. The corrosion rate is dependent on a number of factors including: 1) the fraction of unburned fuel in the deposited material, 2) the rate of deposition of unburned fuel, 3) the tube metal temperature, and 4) the near wall stoichiometry. The average predicted rates (30 mils/yr) significantly exceed those predicted from gas phase reduced sulfur attack. These predicted average rates for the baseline case are relatively high for a subcritical unit, but are in agreement with plant observations of high corrosion rates. Figure 4-9 shows that for all three cases, the largest fraction of waterwall surface susceptible to FeS based corrosive attack occurs on the rear wall. The average rate of corrosion in all three instances is not predicted to change. However, it can be seen from Figure 4-9 that with oxygen enhancement, the area susceptible to FeS based attack is significantly reduced. This is consistent with the predicted increase in volatile yield and reduced unburned carbon with oxygen enhancement.

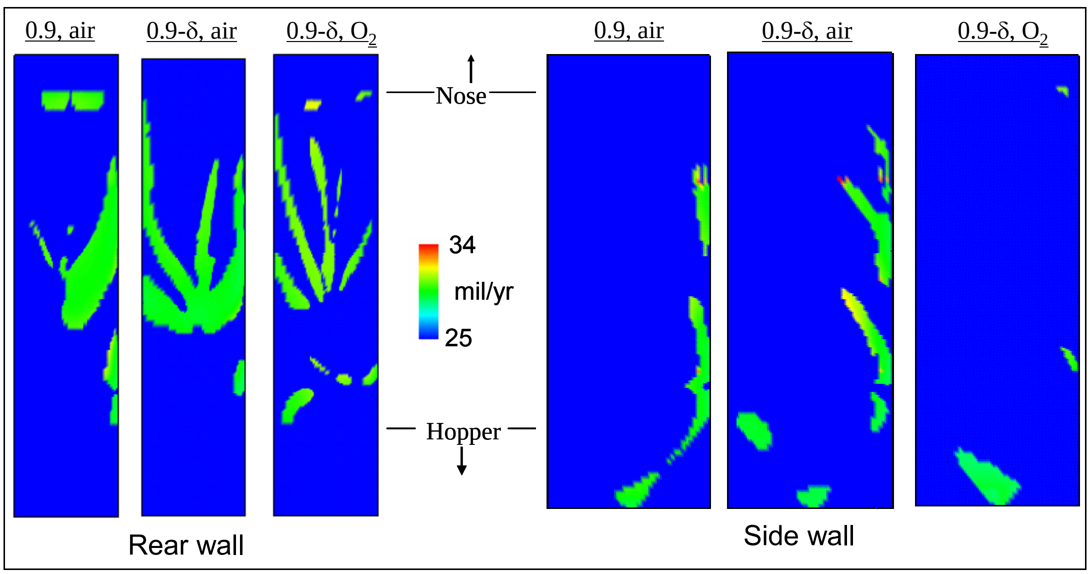


**Figure 4-9. Predicted rates of corrosion due to FeS**

Figure 4-10 summarizes the waterwall surface area below the OFA ports (the region of most significant corrosion) predicted to be susceptible to FeS based attack for cases 1, 2, and 4. As previously indicated, the rear wall is predicted to be most susceptible to corrosion. Compared to the baseline case (case 1), a reduction in burner SR with no oxygen enhancement (case 2) is predicted to yield a significant increase in waterwall area subject to corrosion (increase from 8% to 15%). However, oxygen enhancement, as simulated in case 4 is predicted to significantly reduce the susceptible area not only in comparison to case 2, but also in comparison to the baseline case (case 1). Since the corrosion rates due to deposition of unreacted fuel are significantly higher than those attributed to gas phase sulfur attack, in agreement with previous evaluations (refs), oxygen enhancement is predicted to lead to a significant reduction in waterwall area susceptible to the highest rates of sulfur based corrosion.

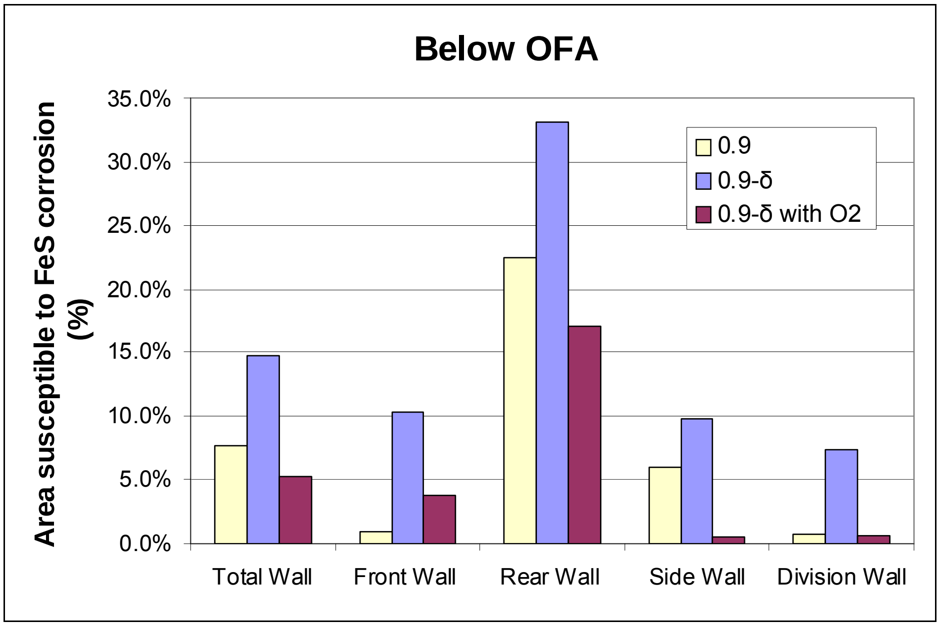


**Figure 4-10. Total waterwall surface area below the OFA ports predicted to be susceptible to FeS based corrosion**

These CFD model results indicate that in a currently operating single wall fired unit equipped with a low NOx firing system with bituminous coal, NOx emissions can be reduced by approximately 35% from baseline emissions of 0.33 lb/MMBtu. These predictions also indicate that the NOx reductions would be accompanied by a decrease in unburned carbon in the fly ash. Since oxygen enhancement for NOx reduction includes burner operation under more deeply staged conditions, a concern is the potential impact on waterwall corrosion. The CFD model evaluation described here indicates that oxygen enhancement would likely reduce the extent of waterwall corrosion due to sulfur based attack. The average and maximum rates of corrosion are predicted to remain unchanged with oxygen enhancement. However, the total area susceptible to significant rates of corrosion is predicted to decrease with oxygen enhancement.

Modeling of City Utilities James River Unit 3

Although modeling of the generic 180 MW unit provided some insight on how oxygen use in pc-fired boilers can reduce NOx emissions, no direct measurements were available to validate the model and its findings. Consequently a CFD model was developed for the first full-scale demonstration at the James River Power Station, Unit 3 both to validate the model and to provide some assurances to the plant that waterwall wastage would be minimized during the test period. This plant is owned by City Utilities and is located in Springfield MO. The unit is a Riley Stoker, pulverized coal, sub-critical steam generator with a capacity of 44 MW. The unit is equipped with 3 Attrita pulverizers. Six D B Riley CCV Low NOx burners are arranged in two elevations on the front wall of the boiler. An overfire air system consisting of 5 ports had previously been installed on a single elevation above the top row of burners. The OFA ducts were designed such that each duct is divided into two ducts in a 1/3-2/3 arrangement. Experimental results from this test are described elsewhere[9].

Results of CFD modeling similar to that described for the generic boiler are shown in Figures 4-11 through 4-13. Both the measured and predicted NOx emissions are shown in Figure 4-11. Although these data show the unit achieving low levels on air alone this was done primarily during the test period. Issues such as opacity limits and flame stability concerns preclude the plant from staging as deeply over longer-term operation. Comparisons of the measured and predicted NOx trends with air alone suggest that the model consistently overpredicts the NOx. However, the trends are similar. Similarly the model shows a reduction between the oxygen-enhanced staging cases and the baseline similar to the measured data. When the data are plotted only in terms of reduction from a baseline, defined as the air case for SR=1.0, as shown in Figure 4-12, there is good agreement between the data and predictions. The LOI data, shown in Figure 4-13, also are in reasonable agreement between the measured and predicted values.

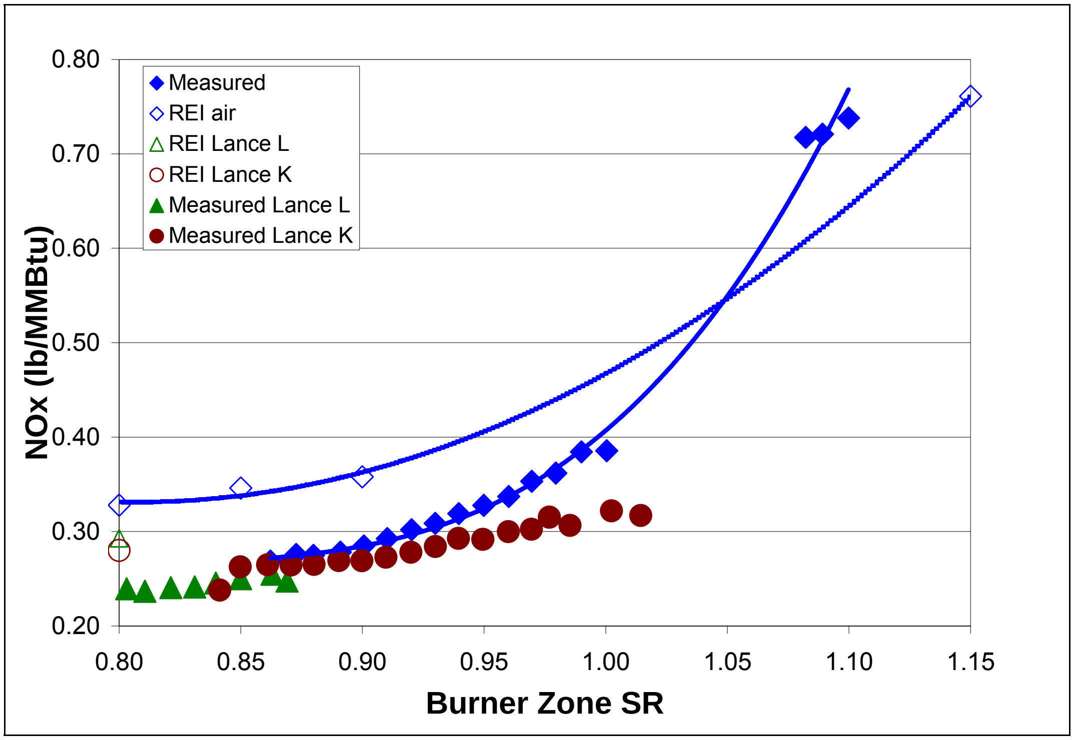


**Figure 4-11. Predicted versus measured NOx emissions from James River Unit 3 firing bituminous coal**

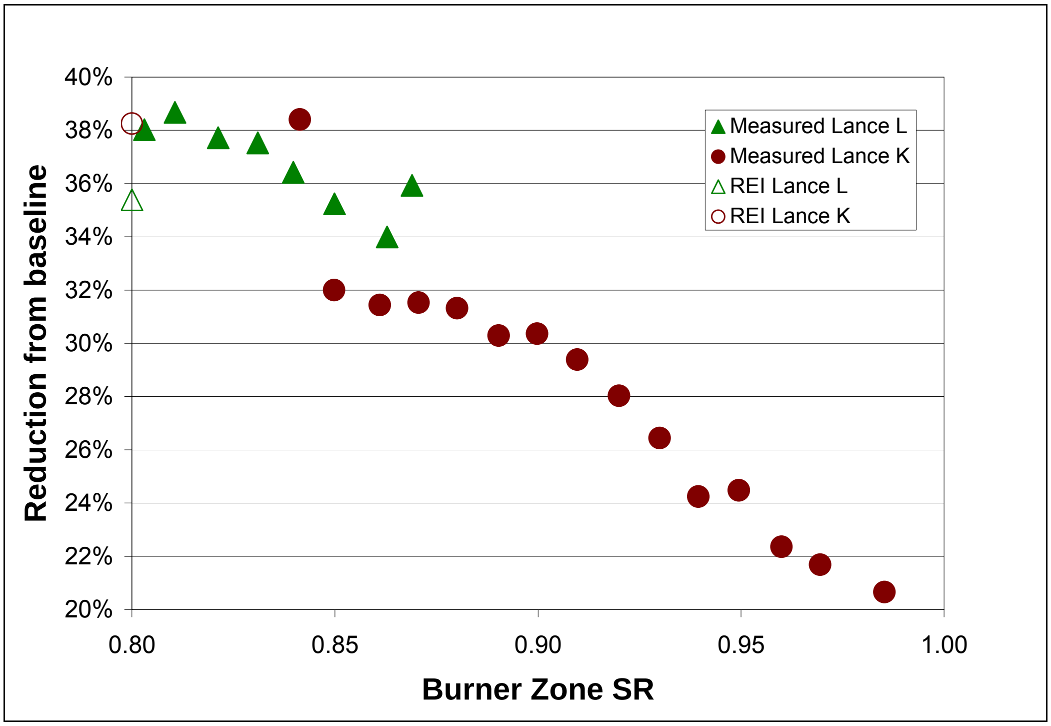


**Figure 4-12. Predicted versus Measured NOx Reductions at James River Unit 3**

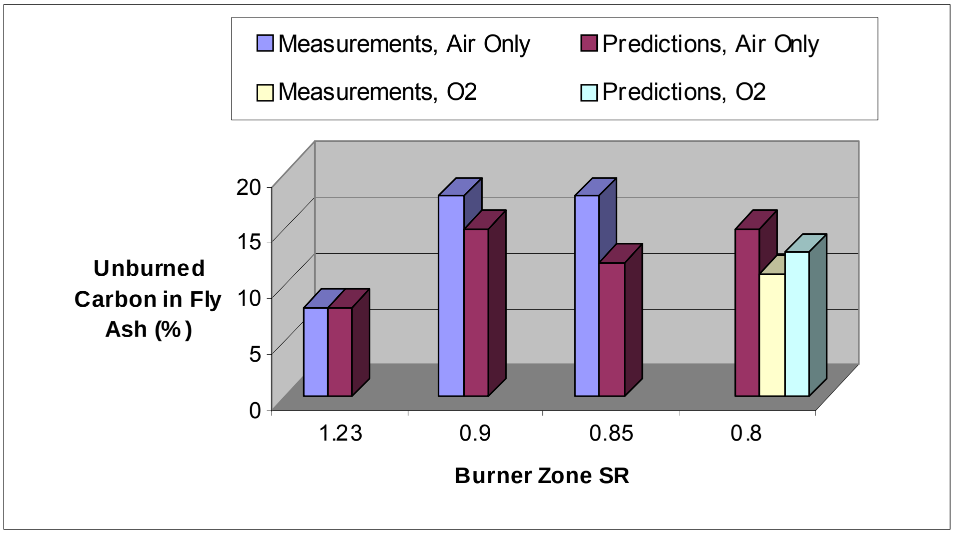


**Figure 4-13. Predicted versus measured LOI at James River Unit 3**

Based on these data the model seems to get the trends and some of the non-NOx data correct, but consistently over predicts the NOx emissions. One possible explanation has to do with the simplified kinetics code used for the NOx determination. Given that oxygen-enhanced combustion typically yields combinations of stoichiometric ratio and flame temperature well outside that found with air combustion it is possible that the initial kinetics need to be expanded. Preliminary work with an expanded kinetics model at the end of the program provided much better agreement with the measurements under staged conditions, but less agreement under lean conditions. Clearly this issue needs to be further addressed to generate a model capable of predicting the absolute NOx emissions and not just the trends.

Another issue that could be limiting the accuracy of the model is the fact the oxygen injection takes place in the near field of the burner. In most full boiler models computational limits preclude fine resolution in the burner region, therefore some key aspects of oxygen-enhanced combustion under staged conditions may be missing.

Corrosion potential modeling was also performed for James River Unit 3. These models suggested that corrosion potential was essentially unchanged when the unit was deeply staged using oxygen-enhanced combustion. These results were similar to those described above for the generic 180 MW boiler.

Modeling of Northeast Utilities Mt Tom Station

In an effort to further refine the modeling capabilities and develop a robust CFD tool for analyzing the potential benefits of oxygen-enhanced combustion in specific boilers experimental data obtained as part of the first commercial installation was also used for model validation. The first commercial installation took place during June of 2003 at the Mt. Tom Generating Station, owned by Northeast Utilities, in Holyoke MA. The Mount Tom Station Unit #1 is a Riley Stoker, pulverized coal, sub-critical steam generator with a nameplate capacity of 125 $MW_g$. The unit is equipped with 4 pulverizers and sixteen Riley CCV low NOx burners arranged in a 4 x 4 configuration. A Riley overfire air system consisting of 6 ports had previously been installed on a single elevation above the top row of burners. The boiler was typically over-fired to provide 147 MW net generating capacity.

During the ’03 ozone season the plant fired different class C and class A bituminous coals, including several non-US coals. Class C bituminous coals have lower heating values (11,500-13,000 Btu/lb) than Class A bituminous coals (>14,000 Btu/lb). Data was collected for a wide range of loads with and without oxygen enrichment and showed that significant NOx reduction could be achieved[10]. NOx emissions below 0.15 lb/MMBtu were achieved with two different coals and oxygen enrichment. Selected conditions, including conditions leading to the <0.15 lb/MMBtu emissions levels, were modeled. Results from several of these conditions are shown in Figure 4-14. As with the James River tests the model initially over predicted, by a significant amount, the NOx. However, when the kinetics package was expanded the agreement was much better, particularly with Cases 4 and 5. This improvement suggests that the expanded kinetics is more appropriate for the oxygen-enhanced conditions. Model simulations with primarily non-domestic coals (Cases 1-3) were not in as good agreement as those simulating use of at least 50% domestic coals. In fact, even with the improved kinetics the model was unable to predict the low NOx emissions observed during testing with a South American class C bituminous coal. Combined with reasonably good agreement between the blend simulations and good agreement with the previous James River Unit 3 results using the expanded kinetics these results suggest the nitrogen partitioning assumptions used in the model may not be appropriate for non-domestic coals. The current kinetics package may also fall short of predicting the very low (100-150 ppm) NOx concentrations measured during the testing.

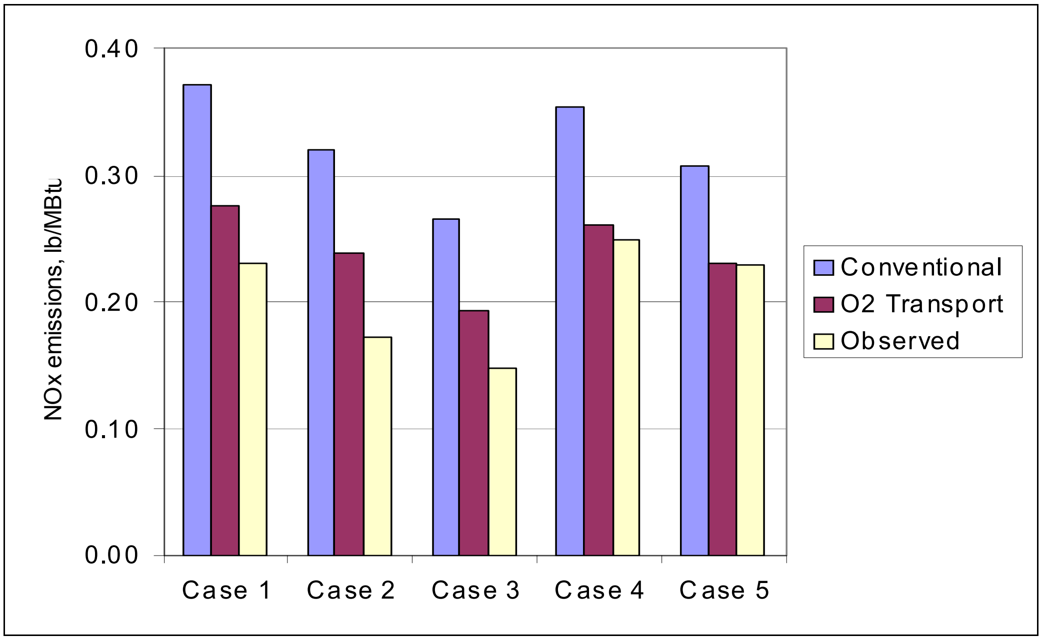


**Figure 4-14. NOx comparison for CFD modeling of the Mt. Tom Generating Station**

<u>Modeling results - Praxair's existing coal combustion model</u>

During this program Praxair's existing coal combustion model was used to explore the impact of adding oxygen to the fuel rich zone of a small combustor. The model uses a proprietary kinetics package, including a detailed coal devolatilization model, coupled with heat transfer calculations to model fairly complex systems. Unlike the more complex CFD modeling performed by Reaction Engineering International, the mixing patterns are imposed on the flows – allowing the effects of kinetics and mixing to be studied independently. By creating a series of well stirred and plug flow reactors it is possible to simulate very complex flow systems. The model's relative simplicity also provides a way to explore a wide range of conditions to better understand how oxygen addition impacts NOx formation.

One critical part of any parametric study is the definition of the baseline case and validation of the model against experimental data. In this program data from the laboratory-scale combustor at the University of Arizona (UA) was used to define the baseline configuration and to validate the model. The initial configuration consisted of a well stirred reactor where all of the flows enter the reactor at the same time followed by a series of plug flow reactors selected to simulate the reaction from one port location to the next. Staging air was added into the $7^{th}$ reactor to simulate the staging point used at port 6. Using literature coal devolatilization rates and the wall temperature, derived from measured gas temperatures, allowed the model to simulate the UA furnace fairly well. As seen in Figure 4-15 the calculated NOx profiles were in good agreement with the data for both the air baseline case and the oxygen enriched case.

In the next mixing concept tested, labeled "Mixing Concept 1" in Figure 4-15, a specific mixing strategy was defined. As can be seen from Figure 4-15 this controlled mixing, which is more representative of a typical low NOx burner operated under a globally staged condition, results in significantly lower NOx. The final mixing concept, labeled "Mixing Concept 2" in Figure 4-15 attempted to mix the oxygen at a rate that was more advantageous for NOx control. Although this simulation provided the lowest predicted NOx emissions of the group, the required oxygen and air mixing rate was much lower than could be achieved in the practical systems. Looking at the model results, including the species compositions at each time step, suggests that adding oxygen in a specific method yields significant NOx reductions. If, in contrast, the oxygen is introduced incorrectly it could lead to the formation of relatively high thermal NOx.

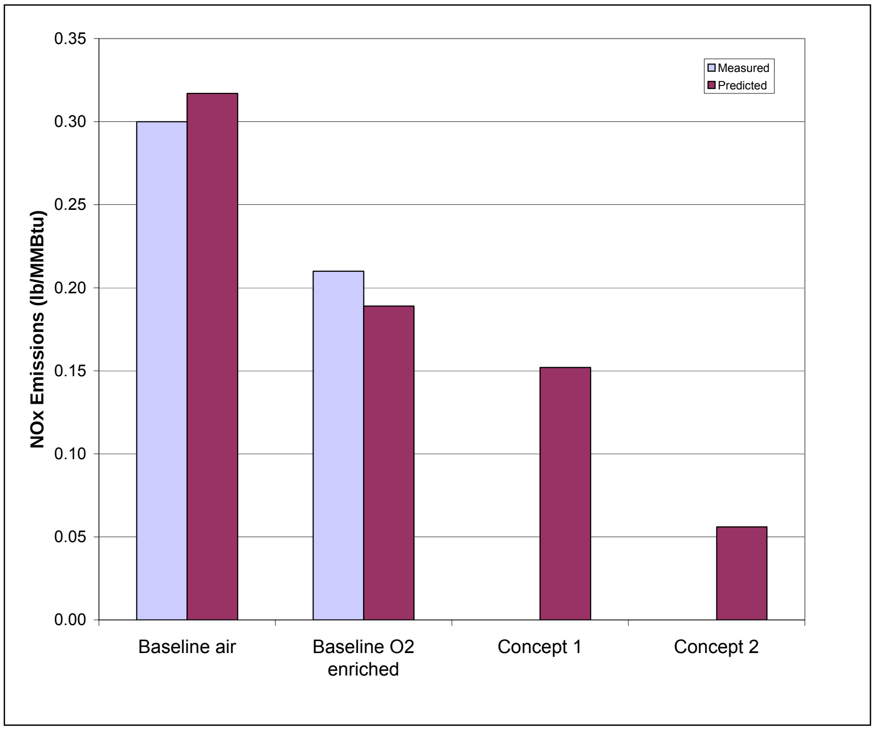


**Figure 4-15. Kinetic modeling results**

#### *4.1.1.3 Conclusion – Task 1.1.1*

Existing CFD models were used to evaluate the effectiveness of oxygen-enhanced combustion for NOx control at a number of scales. In general these models were consistent with the available experimental data in showing that using oxygen-enhanced combustion under staged conditions leads to reduced NOx emissions and typically lower unburned carbon. Modeling of the L1500 provided key insight suggesting that removing air from the windbox and reinjecting the oxygen contained in that air as pure oxygen elsewhere in the burner provided significant NOx reductions, reduced flame standoff distances, and enhanced devolatilization under staged conditions. However, similar injection under unstaged conditions lead to *increased* NOx emissions as the increase in thermal NOx produced due to increased flame temperatures under these conditions was not offset by enhanced NOx destruction elsewhere in the flame. Comparison of the full-scale boiler modeling and experimental data showed the model was not able to reproduce the very low NOx emissions observed with oxygen-enhanced combustion in the field. As mentioned above, poor model resolution in the near burner region coupled kinetics challenges associated with the unique combination of fuel rich conditions and high temperatures found under oxygen-enhanced combustion are the likely causes for the discrepancies. Additional modeling with an enhanced kinetics package was able to better match the observed NOx trends for higher NOx emissions (>0.2 lb/MMBtu). In all cases the model was able to reproduce the lower LOI observed with oxygen-enhanced combustion was used. Corrosion modeling using REI's models also showed that corrosion potential was essentially unchanged with deep staging when oxygen-enhanced combustion was used.

### 4.1.2. Lab-Scale Parametric Testing (Task 1.1.2)

#### *4.1.2.1 Experimental – Task 1.1.2*

Although theory suggests that enriching the first stage of a staged combustion system with oxygen reduces NOx emissions, very little experimental data existed to demonstrate the concept. Therefore, the key objective of the lab-scale experiments at the University of Arizona was to act as a proof of concept test for oxygen-enhanced combustion (OEC) for NOx control. To accomplish this goal several experiments were designed to evaluate the impact of first stage oxygen enrichment on NOx emissions.

These proof of concept experiments utilized the existing laboratory-scale combustor at the University of Arizona. This 17 kW down-fired self-sustained combustor, shown schematically in Figure 4-16, is designed to provide time-temperature histories typical of full-scale utility boilers. Preheated air and coal are premixed upstream of a water-cooled grid, which acts as a flashback preventor. After passing through the water-cooled grid the premixed coal-air stream passes through a simple nozzle forming a classic premixed type 0 (so swirl) flame. The first stage stoichiometric ratio ($SR_1$) is controlled by controlling the airflow into the first stage. Overfire air (OFA), also called second stage air, was injected in port 6 to achieve a nominal overall stoichiometric ratio of 1.2.

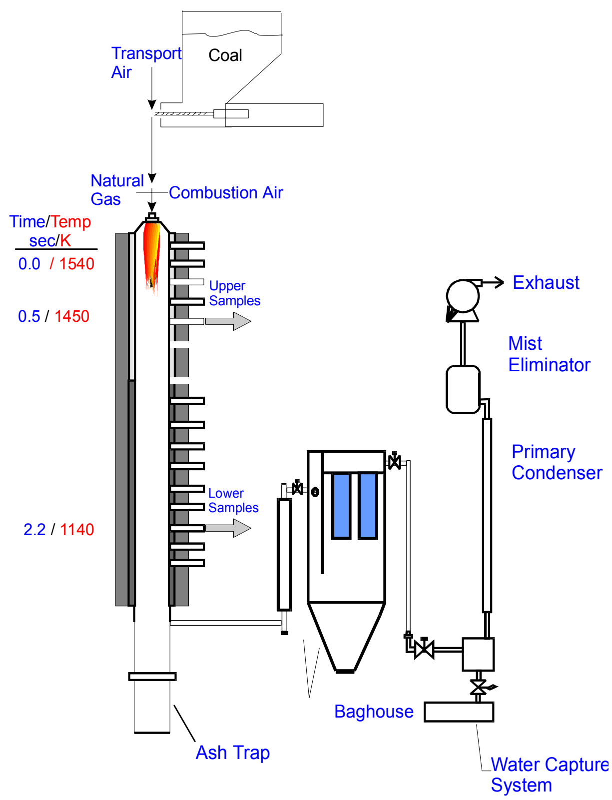


**Figure 4-16. Downfired combustor at the University of Arizona**

### *4.1.2.2 Results and Discussion – Task 1.1.2*

In this program two different samples of coal from the Illinois No. 6 coal seam were burned under a wide range of first stage stoichiometric ratios and oxygen replacement rates. For oxygen enrichment tests pure oxygen was mixed with the combustion air upstream of the water-cooled grid. Approximately 20% of the first stage combustion air was replaced by oxygen yielding an oxygen concentration of 25%. Axial temperature and gas composition profiles were measured for each condition. The resulting data shown in Figure 4-17 show that oxygen addition has a positive impact on NOx emissions.

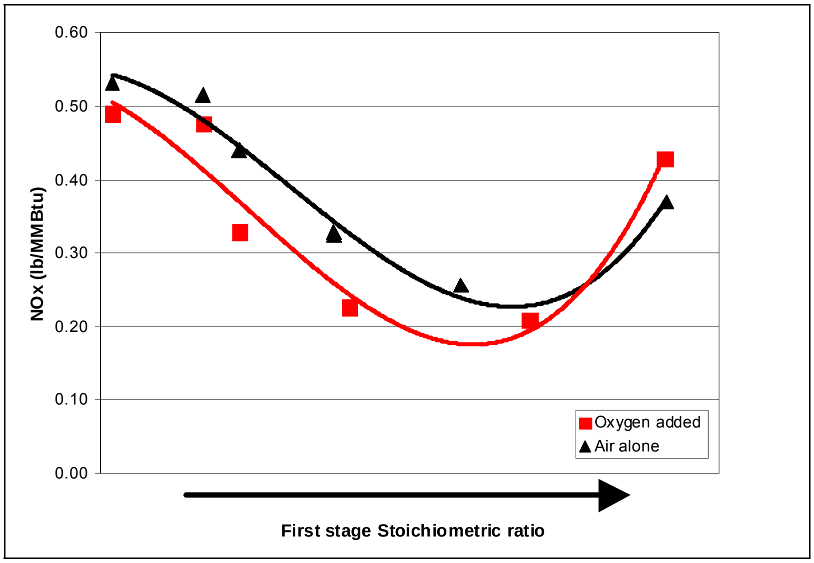


**Figure 4-17. Effect of first stage stoichiometric ratio on NOx emissions**

Initial experiments suggested that there are some differences between the two coal data sets, however both show a general trend of improved NOx emissions with oxygen enrichment. The scatter in the data was due to significantly different second stage temperatures. The effect of the second stage temperature has been described by Johnson[11] and others. Essentially increasing the second stage temperature causes an increase in the net NOx emissions. To avoid this confounding influence oxygen-enhanced and baseline data were compared for those data where the second stage temperature was the same. These data suggest that under fuel rich conditions oxygen addition significantly reduces NOx emissions.

### *4.1.2.3 Conclusion – Task 1.1.2*

The laboratory-scale experiments at the University of Arizona illustrated two key concepts for the use of OEC for NOx control. First, the data clearly indicate that replacement of a portion of the first stage combustion air can significantly reduce NOx emissions. This finding represented a critical first step towards development of the technology into a commercially viable method of NOx control. The second key factor of OEC use was the impact of the second stage temperature on the NOx emissions. The fact that the second stage temperature can have a significant impact on the final NOx emissions, even when the temperatures are low enough that thermal NOx formation can be neglected, represents a key parameter for optimizing the use of staged combustion for NOx control.

## 4.2 Oxygen Based Injector Design and Testing (Task 1.2)

### *4.2.1 Experimental – Task 1.2*

One of the objectives of this program is to evaluate how oxygen can be used to enhance the capabilities of post-combustion NOx control strategies such as reburning and SNCR. One potential oxygen based technology is the patented CoJet$^{TM}$ technology, which could be used to inject reburn fuel or SNCR reagents deep into the upper furnace without the need for long lances. Although promising, this technology was not explored in depth during this program. For example, although coal-based reburning can be effective for NOx control it has the major drawback of increasing the unburned carbon in the ash. This problem is related to the difficulty of burning out the residual char from the reburn fuel in the short space available above the reburn zone. One way to address this problem is to use hot oxygen, which is oxygen that has been preheated by combustion of a gaseous fuel, to enhance devolatilization of the reburn fuel – increasing the amount of gaseous products available for reburning and reducing the amount of residual char that must be combusted. Hot oxygen can be used two ways. One way would be to inject the hot oxygen and the reburn fuel directly into the combustion space. In this way the hot oxygen and reburn fuel would interact in the furnace to enhance the fuel devolatilization. Although this arrangement would simplify the equipment requirements, the hot oxygen would be significantly diluted by flue gas before it interacts with the fuel–thus minimizing the impact of hot oxygen. Alternatively the coal can be reacted with hot oxygen outside of the boiler to maximize the impact and the resulting product stream introduced to act as the reburn fuel. This second strategy was explored in the bench-scale tests as part of this program.

The objective of these bench-scale experiments is to determine the effectiveness of hot oxygen in enhancing coal devolatilization. In these experiments an eastern compliance coal consisting of a mixture from the Elkhorn and Hazard seams was burned under a range of conditions. The coal properties are shown in Table 4-3.

**Table 4-3. Elkhorn/Hazard Coal Properties**

| | Dry Basis | As Received |
|---|---|---|
| <u>Proximate (wt %)</u> | | |
| Fixed Carbon | 57.80 | 56.46 |
| Volatile Matter | 34.61 | 33.80 |
| Moisture | 0.00 | 2.33 |
| Ash | 7.59 | 7.41 |
| Ultimate (wt%) | | |
| Carbon | 76.66 | 74.87 |
| Hydrogen | 4.70 | 4.59 |
| Nitrogen | 1.46 | 1.43 |
| Sulfur | 0.84 | 0.82 |
| Oxygen | 8.58 | 8.38 |
| Chlorine | 0.17 | 0.17 |
| Moisture | 0.00 | 2.33 |
| Ash | 7.59 | 7.41 |

The test rig is shown in Figure 4-18. Coal is fed from an Accurate Model 304 volumetric feeder into a tee where transport air is mixed with the coal at a rate of 3.4 standard cubic feet (scf) per pound of coal. The air-coal mixture is transported to the mixing section through a 3/8 inch copper tube. In the mixing section the coal-air mixture is entrained into the hot oxygen and ignited. The burning mixture then enters a 48 inch long, 12 inch ID refractory lined chamber. Three thermocouples are mounted flush with the inside wall of the refractory to measure wall temperatures. A 6 inch long, 8 inch ID refractory sleeve is inserted into the exit of the combustion chamber to promote internal recirculation of the partial oxidation products. The hot combustibles exit the combustion section and burn with surrounding air.


**Figure 4-18. Photograph of hot oxygen test rig**

The thermal nozzle is used to create a high velocity oxygen enriched stream. Oxygen is fed into the burner and combusted with natural gas fed into the central burner. Combustion of the natural gas consumes a portion of the oxygen and heats the mixture. The hot gas passes through a nozzle, creating a high velocity gas stream, into the mixing chamber. The final gas composition, temperature, and velocity are controlled by the amount of natural gas fed to the burner and the nozzle diameter.

The gas composition leaving the refractory lined combustor is measured by inserting a water cooled gas probe far enough into the combustor to avoid dilution by any surrounding air that might be drawn into the chamber. The gas sample is cooled to ambient temperature and passed through a filter to remove particulate and condensed moisture. The cleaned sample enters the analytical train consisting of a Nova model 7800P five-gas analyzer (CO, $CO_2$, $H_2$, $O_2$, and CH4). The analytical range for oxygen, $CO_2$, $CH_4$ is 0-100%. The range for CO and hydrogen is 0-50%. A typical gas measurement trace is shown below in Figure 4-19. Particle samples were taken using a nitrogen-quench, water-cooled probe. During particulate sampling with the particle probe the gas leaving the filter was sent to the analytical train. This switch to sampling from the particle probe is shown in Figure 4-19 as the time when all the measured gas concentrations drop dramatically. By analyzing the gas from the particle probe it is possible to both measure the amount of sample collected and the dilution ratio. The samples were burned out in a furnace to determine the loss on ignition (LOI), which were then used to determine the conversion of the combustibles.

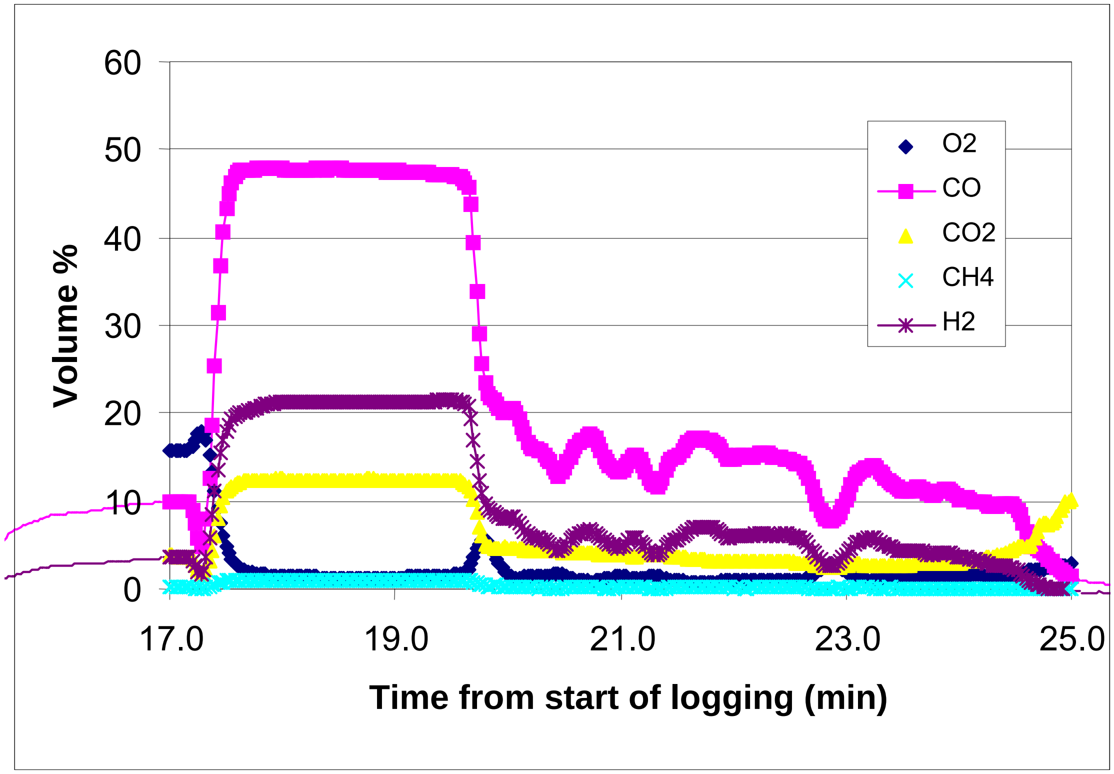


**Figure 4-19. Typical gas composition plot**

### *4.2.2 Results and Discussion – Task 1.2*

Although these experiments were able to successfully obtain data on the effect of hot oxygen on conversion of the coal to gaseous species, there were several operational issues that should be noted. First, a potential problem with the sampling procedure is that soot and tars that formed when the coal is devolatilized will condense in the probe (in the case of tars) and be captured along with the ash. Thus the LOI may be undermeasuring the portion of carbon that actually went into the gas phase. Next, under some conditions there were large slag deposits in the mixing chamber even after short duration runs. This was addressed by changing how the hot oxygen comes into contact with the coal in the mixing section. In addition, under some conditions significant slag deposits formed, often at the inlet portion of the combustor. These could be controlled somewhat by the mixing chamber design, but were not eliminated.

Data was obtained to show the technology can be used to reduce NOx emissions. LOI data, not shown, indicate that conversion of the combustibles to the gas phase decreases as the stoichiometric ratio is reduced, but exceeds 50% in all cases. The data also suggest that the conversion on a dry, ash free, basis shows an asymptotic trend in conversion as the can gets more fuel lean.

#### *4.2.3 Conclusion – Task 1.2*

In general these data support the premise that hot oxygen can be used to enhance coal-based reburning. Even with an unoptimized reactor design mixing hot oxygen with the coal converted the majority of the combustibles to gas phase species that could readily react to reduce NOx. By optimizing the reactor design, it should be possible to increase the coal conversion and minimize the operational problems, such as slagging. Optimizing the hot oxygen composition and temperature, as well as adding other gasses, such as steam, could also enhance the conversion. Clearly the technology shows promise to enhance coal-based reburning but additional work is required before it can be tested at full-scale.

### 4.3 Pilot Scale Testing (Task 1.3)

#### 4.3.1 Experimental – Task 1.3

In order to apply OEC for NOx control in commercial systems it is critical to understand how different operating parameters influence NOx emissions and the effectiveness of OEC. Therefore, the primary objective of the experimental work at the University of Utah was to explore the application of oxygen-enhanced combustion to commercially relevant non-premixed burner systems. First the small pilot-scale test facility was used to demonstrate that OEC is effective for NOx control with commercially relevant burners. Significant NOx reductions and emissions levels below 0.15 lb/MMBtu were demonstrated. Experimental work was also performed to explore how specific operating parameters impact NOx emissions. These parameters include the temperature at the overfire air (OFA) injection point, combustion air preheating, and the first stage residence time. Factors such as the stoichiometric ratio of the primary air, the oxygen injection strategy, and the coal type were also explored to determine their impact on OEC effectiveness.

<u>Description of the L1500 Test Facility</u>

Although the premixed data suggested oxygen addition can reduce NOx formation, more work was needed to evaluate the effect of oxygen under more commercially realistic, non-premixed, burners. This testing took place at the L1500 facility at the University of Utah, shown schematically in Figure 4-20. The University of Utah pilot-scale combustion test furnace referred to as the "L1500" is a nominal 15 MMBtu/hr pilot-scale furnace designed to simulate commercial combustion conditions, particularly the thermal history of operating commercial coal-fired-boilers.

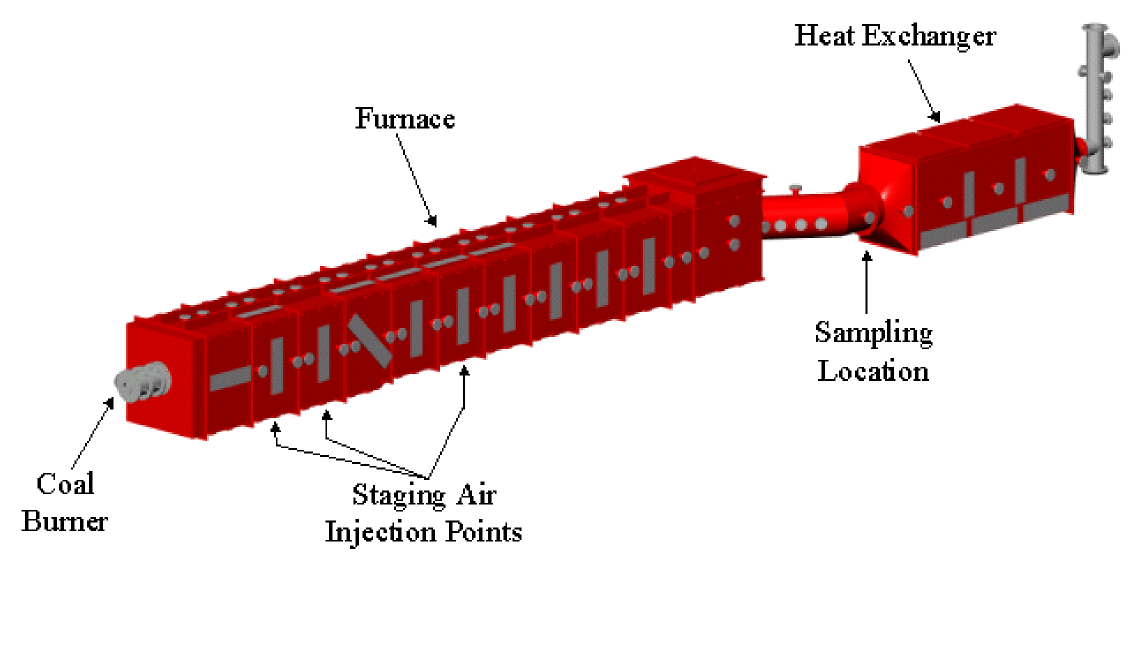


**Figure 4-20. Schematic of the L1500**

The horizontal-fired combustor is 1.1 m x 1.1 m square and nearly 12.5 meters long. The walls have multiple-layered insulation to reduce the temperature from about 1925 K on the fireside to below 330 K on the shell-side. The combustor is modular in design with numerous access ports and optional cooling panels in each section. This allows the flue gas temperature profile to be adjusted to better simulate commercial equipment. The access ports are used for visual observations, fuel and/or air injection, and product sampling. The combustion facility includes the air supply system, water supply and cooling system, L1500 combustor, fuel supply systems, a flue-gas-cooling chamber, scrubber, and induced-draft fan and a stack.

The dual concentric swirl burner used on the L1500, shown in Figure 4-21, is designed to provide excellent flame stability and offer a wide range of swirl stabilized flames. The burner consists of a central bluff body, a concentric coal pipe, a concentric opening for gas firing (if needed) and two concentric secondary air streams.  Each air stream is independently controlled metered and can be varied over a wide range of swirl numbers.

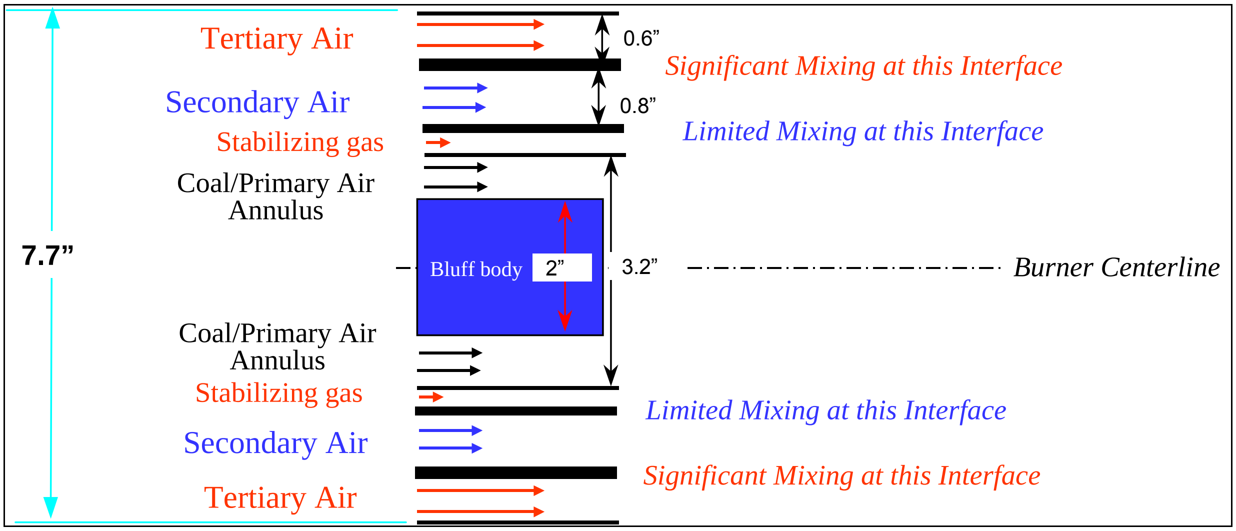


**Figure 4-21. Schematic of the burner in the L1500**

One of the advantages of using the L1500, is the ability to explore the effect of a wide range of parameters on the effectiveness of staged combustion. For example, in this work 2 different bituminous coals and one sub-bituminous coal from the Powder River Basin were used to evaluate the effect of coal characteristics on the effectiveness of oxygen for NOx control. Burner parameters, such as the swirl number, were evaluated, as were the first stage stoichiometric ratio and residence time. Several methods were explored to introduce the oxygen into the first stage.

### 4.3.2 Results and Discussion – Task 1.3

Factors influencing NOx emissions under air-staged combustion conditions

A number of factors influence NOx emissions from coal combustion, with and without oxygen addition. Among these are the gas temperature at the overfire air injection point, preheating of the combustion air, and residence time in the fuel rich stage. A number of experiments were performed to explore the impact of these parameters on NOx emissions in the L1500.

During the initial experiments the scatter in the measured NOx emissions was much higher than expected based on previous work at the facility. The measured NOx emissions often varied significantly for a given stoichiometric ratio and oxygen use. One explanation for the variability was related to the thermal environment of the furnace. During a typical test day the furnace temperature would continue to rise slowly throughout the day. Therefore the NOx data collected at the end of the day may be at a significantly different furnace temperature profile than that collected at the beginning of the day. The realization that the temperature at the OFA injection point can impact the net NOx emissions under deeply staged conditions is not new. This phenomenon was described by Johnson et al[11] who showed that increasing the temperature in the second zone leads to an increase in the net NOx formation. This is likely due to preferential oxidation of the fuel NOx precursors leaving the first zone. When the NOx data was plotted as a function of wall temperature at the OFA injection location, see Figure 4-22, it became clear that a similar increase in NOx as a function of temperature was taking place in the L1500. For these data the first stage and total stoichiometric ratios were held constant. These data also suggested that the temperature dependence depends on the total stoichiometric ratio as shown by the two air trends. Based on these observations changes were incorporated to both the data analysis procedure and the test protocol to ensure that data comparisons were based on constant temperatures.

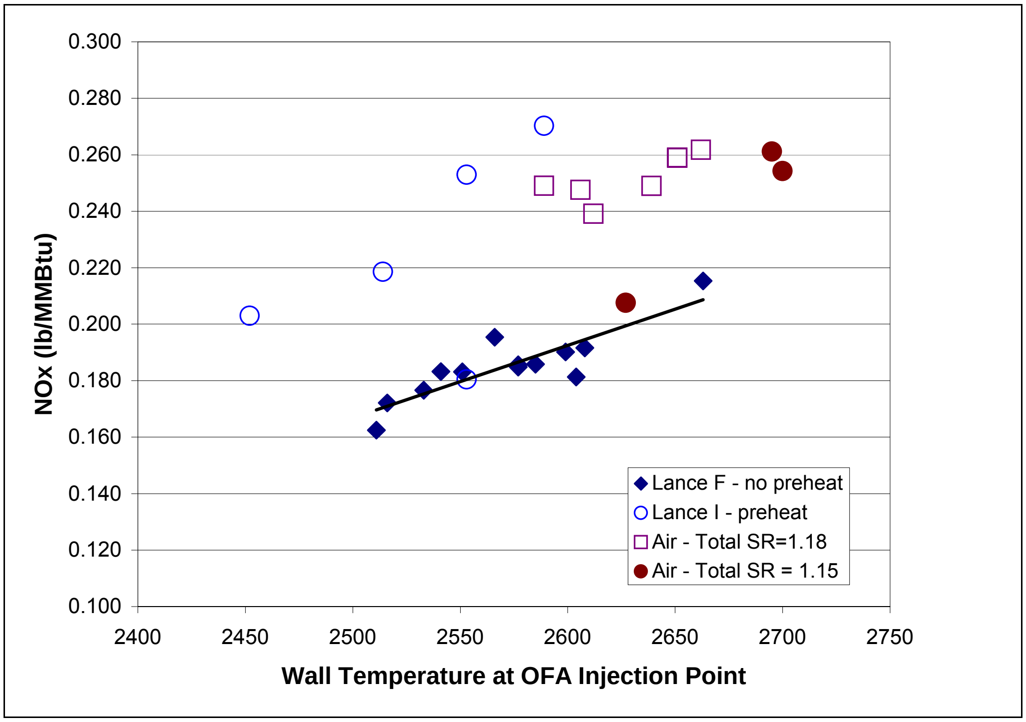


**Figure 4-22. Effect of second stage temperature on NOx emissions**

A number of experiments were also performed to explore whether preheating the combustion air has an impact on the overall NOx emissions. These data indicate the air preheat temperature did not seem to have a significant impact on the NOx emissions.

Finally, since the reactions leading to the conversion of fuel nitrogen to molecular nitrogen are kinetically limited under typical combustion conditions, the residence time under fuel rich conditions controls how much fuel nitrogen reacts. For example, at very short residence times the fuel nitrogen does not have time to react to form molecular nitrogen. When overfire air is added the residual fuel nitrogen is oxidized to form NOx. Replacing a portion of the first stage combustion air with oxygen helps to overcome this problem in two ways. First, when the local flame temperature is increased using oxygen the reaction rates for molecular nitrogen formation are increased. Therefore more of the fuel nitrogen is converted to molecular nitrogen for a given residence time. Also, since the gas volume is reduced when oxygen replaces air the residence time is also slightly increased. Figure 4-23 shows the impact of both residence time and oxygen use on NOx emissions from the L1500. In these experiments the OFA injection point was moved from port 3 (the original injection point) to port 4, then to port 5, and so on to increase the residence time of the first stage. As can be seen from the data increasing the residence time under staged conditions lead to significantly lower NOx emissions. Under short residence times the use of oxygen significantly reduces NOx emissions. However, at longer residence times there is less difference between the oxygen enhanced and baseline NOx emissions. This is consistent with the fact that at long residence times the final NOx reductions (i.e.; nitrogen production) is less kinetically limited and therefore adding oxygen has less impact. However, at short residence times oxygen helps to overcome the kinetic limitation – leading to lower NOx emissions.

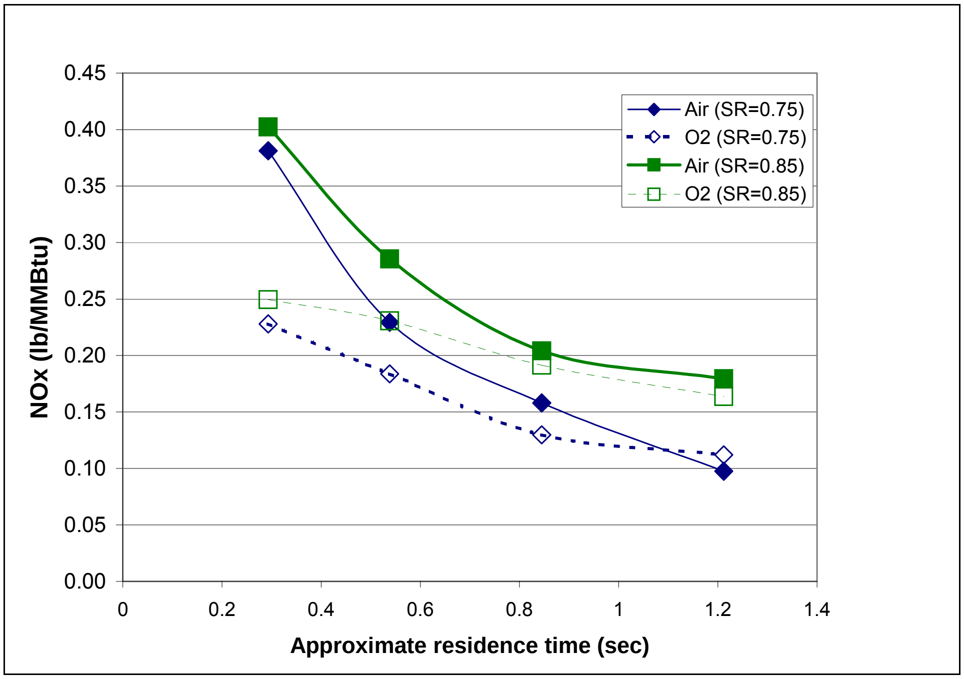


**Figure 4-23. Effect of first stage residence time on NOx emissions**

<u>Factors influencing the effectiveness of OEC for NOx control</u>

One of the primary objectives for the experimental work at the University of Utah was to determine what operating parameters maximize the effectiveness of oxygen enhanced combustion for NOx control. This work suggests there are several major variables that impact oxygen enhanced combustion. The transport air to fuel ratio, the oxygen replacement rate, and the burner zone stoichiometric ratio rank among the most important variables. The oxygen injection method and the coal type also had an impact under some conditions.

By far the most important variable for both NOx emissions and the effectiveness of oxygen enhanced combustion is the main burner zone stoichiometric ratio. Figure 4-24 shows a typical set of staging curves developed as part of this program. These curves clearly show that as the burner zone stoichiometric ratio in reduced the NOx emissions are also reduced, typical of staged combustion. These curves also show that the effectiveness of oxygen addition increases as the burner zone stoichiometric ratio is reduced. In fact, in many cases the use of oxygen under mildly stage combustion conditions actually increases NOx emissions. As discussed above when oxygen is used in the first stage the flame temperature increases. Under mildly staged conditions this increase in flame temperature can increase thermal NOx formation – resulting in an increase in NOx emissions. This tendency to increase thermal NOx when oxygen is used shifts the staging curve towards more fuel rich conditions. However, under deeply staged conditions oxygen use leads to significant NOx reductions compared to the baseline. For commercial implementation of the technology a balance must be struck between the need to deeply stage to achieve significant NOx reductions and boiler design or operational considerations that limit deep staging.

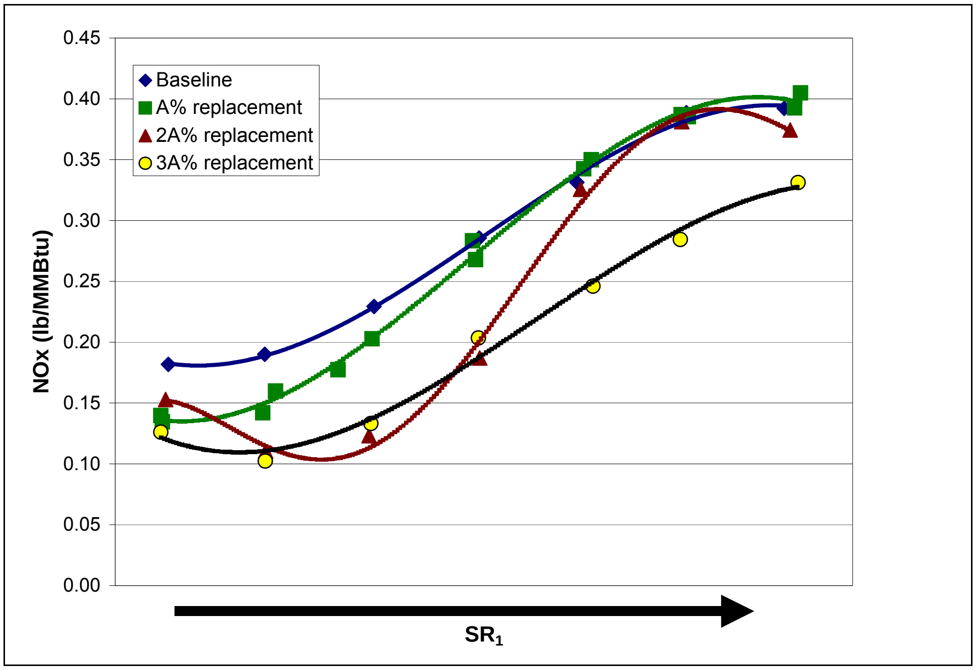


**Figure 4-24. NOx emissions versus burner zone SR, Illinois coal, Lance F**

Another critical variable is the transport air to fuel ratio. Experimental data suggest that under deeply staged conditions as the TaF is increased the NOx emissions increase. As the TaF is increased there is less of a benefit of using oxygen. Both of these observations can be explained by the fact that increasing the TaF changes the burner aerodynamics and internal staging.

Another factor in applying the concept of oxygen enhanced staging to practical systems is how to introduce the oxygen into the first stage. Since this issue is critical to both understanding the fundamentals of oxygen-enhanced staging and successful commercialization of the technology it was the focus of most of the experimental work. For these experiments a wide range of burner conditions, including swirl number and stoichiometric ratio, were explored. These experiments indicated that how the oxygen is introduced into the burner zone is critical to achieve the best results from the technology. In general oxygen injection into specific portions of the flame also provides the best reductions. Other strategies can actually lead to increases in emissions as compared to the air air-only condition.

Experiments were also performed with the Utah coal and the Corderro coal to explore the effect of coal properties on the effectiveness of OEC. Selected coal properties are shown in Table 4-4. Note that no proximate analysis data was available for the Corderro coal. Results from experiments with the Utah coal suggest the baseline NOx profile for the Utah coal is significantly lower than the Illinois 6. These data suggest that while oxygen addition still provides a benefit beyond staging alone, the benefit is slightly less with the Utah coal. One possible reason for both the lower baseline with the Utah coal and the lower impact of oxygen addition is the higher volatility of the Utah coal. The higher volatility typical of PRB coals may also account for the finding that under certain conditions, particularly TaF, oxygen addition to burners firing PRB coals seems to have little or no impact beyond staging alone. Since many utilities are firing blends of bituminous and PRB coals a series of experiments were performed to evaluate the impact of blending the Illinois 6 data with the Corderro coal. Data from these experiments suggest that even when small amounts of a bituminous coal are blended with the PRB coal the addition of oxygen enhances the effectiveness of staging.

**Table 4-4. Coal Properties**

| | Illinois 6 | Utah | Corderro |
|---|---|---|---|
| **Ultimate Analysis** | | | |
| Carbon | 66.10 | 69.65 | 54.00 |
| Hydrogen | 4.61 | 4.42 | 3.90 |
| Nitrogen | 1.13 | 1.25 | 0.90 |
| Chlorine | 0.14 | | 0.00 |
| Sulfur | 3.47 | 0.40 | 0.40 |
| Oxygen | 8.70 | 9.16 | 13.70 |
| Ash | 9.54 | 10.44 | 6.00 |
| Moisture | 6.31 | 4.68 | 21.10 |
| | | | |
| **Proximate Analysis** | | | |
| Fixed carbon | 48.62 | 45.46 | NA |
| Volatile matter | 35.53 | 39.42 | NA |
| Ash | 9.54 | 10.44 | NA |
| Moisture | 6.31 | 4.68 | NA |
| | | | |
| VM/FC | 0.73 | 0.87 | NA |
| lb N/MMBtu | 0.95 | 1.02 | 0.74 |
| | | | |
| **HHV (Btu/lb)** | 11,915 | 12,303 | 12,100 |

Finally, experiments were performed to evaluate the effect of oxygen purity, within the range of current oxygen production methods, on the effectiveness of OEC. The data suggest there is little or no impact of oxygen purity on oxygen enhanced staging. This allows the use of VPSA systems that produce oxygen at lower purity (90-93%) and lower cost for smaller sizes (<300,000 CFH). At larger sizes, lower purity (~95%) cryogenic plants can also provide oxygen cost savings versus high purity (99.5%) plants.

### 4.3.3 Conclusion – Task 1.3

The primary objective of the experimental work at the University of Utah was to explore the parameters that would allow successful implementation of oxygen-enhanced staging at commercial scale. The experimental work confirmed that the gas temperature at the overfire air injection point has a significant impact on the NOx emissions from staged combustion. As the temperature increases so do the NOx emissions. Residence time in the first, fuel rich, stage was also shown to be important with longer residence times yielding lower NOx emissions. Experiments with oxygen-enhanced staging showed that the use of oxygen enhances the reactions leading to the conversion of fuel nitrogen to molecular nitrogen. At short first stage residence times oxygen can significantly reduce the NOx emissions compared to air alone. At very long residence times, when kinetic limits become less important, oxygen addition has less of an impact. The transport air to fuel ratio, which controls the gas phase stoichiometric ratio in the flame core, and the method used to introduce oxygen were also shown to have an impact on both NOx reduction from staging and the effectiveness of oxygen-enhanced staging. The experimental work also showed that air preheating and oxygen purity have a minimal impact on oxygen effectiveness.

## 4.4 Full Scale Design and Component Testing (Task 1.4)

### *4.4.1 Experimental – Task 1.4*

The objective of this task is to design a conceptual oxygen enhanced secondary NOx control system with a modified burner designed to replicate the combustion environment of a typical industrial design boiler. This test facility will then be used to demonstrate that an optimized oxygen-enhanced coal combustion system can meet the emissions target of 0.15 lb/MMBtu with minimal impact on CO emissions and furnace performance.

The experimental work was performed at Alstom Power's Power Plant Laboratory in Windsor, CT. The experiments were designed to demonstrate the concept of oxygen enhanced low NOx firing systems using a well characterized single burner test facility and a commercial burner.

Full-scale experiments were performed in Alstom Power's Industrial Scale Burner Facility (ISBF) in Windsor, CT. The ISBF is a water-cooled tunnel furnace designed to test burners up to 50 MMBtu/h in firing rate with time-temperature histories similar to PC-fired boilers. The unit has two locations for separated over-fire air (SOFA) injection. An 'off the shelf' 25 MMBtu/h commercially available Radially Stratified Flame Core (RSFC™) low NOx burner was used in these experiments. The burner was designed for a firing rate of 26 MMBtu/h and was typically fired at 24 MMBtu/h for these tests. A wide range of burner parameters were evaluated, as were the first stage stoichiometric ratio and residence time. Several methods were explored to introduce the oxygen into the first stage.

The main driver for the development of oxygen enhanced combustion for NOx control is to not only allow utility operators to control NOx emissions but to also avoid or minimize many of the detrimental side effects common to alternative control strategies. The successful demonstration of the concept at the pilot and full-scale single burner levels led to an agreement between Praxair and City Utilities of Springfield, Missouri to test oxygen enhanced combustion at full scale. The demonstration project (separately funded) utilized Unit 3 at the James River Power Station to evaluate the effect of $O_2$ addition during staged combustion on NOx emissions, residual carbon in ash, opacity and plant operation[9].

### *4.4.2 Results and Discussion – Task 1.4*

Full-scale single burner testing at Alstom was completed. Figure 4-25 shows the effect of oxygen replacement under deeply staged conditions. These data further support that under fuel rich conditions oxygen enhanced combustion can significantly reduce NOx formation even with very low oxygen replacement rates[12]. Similar data demonstrated that oxygen can enhance staging for NOx control over a wide range of conditions, and that the method for oxygen introduction is critical to the NOx reduction achieved[12].

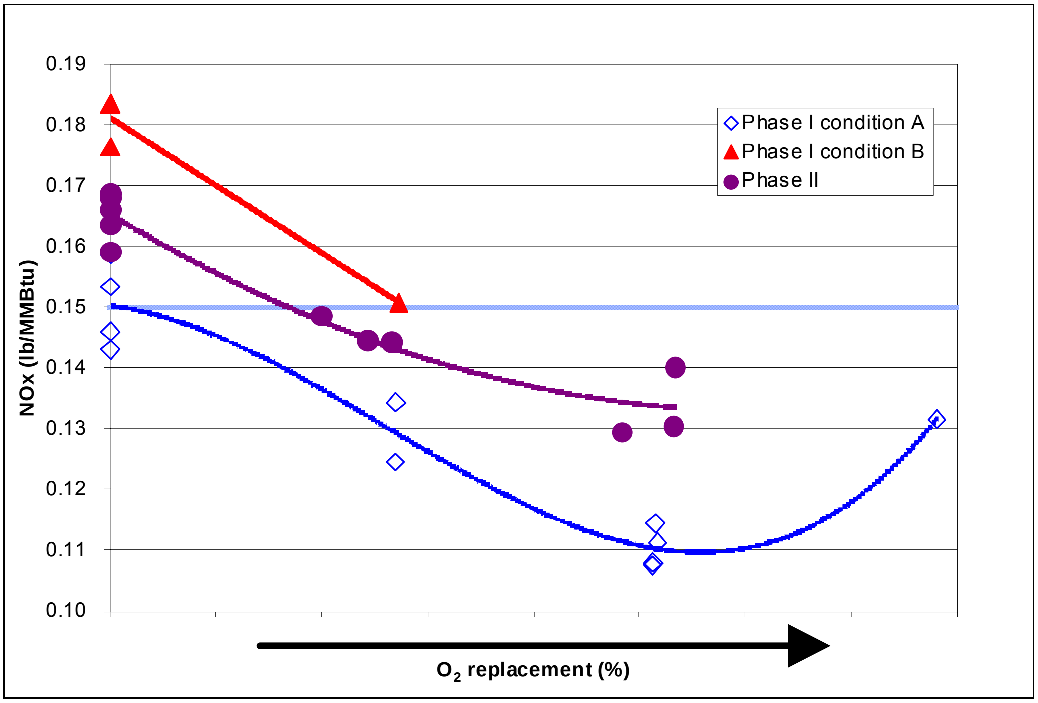


**Figure 4-25. Full-scale single burner results – Alstom Power**

This single burner work demonstrated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants.

Data analysis of the demonstration project at James River Unit 3 also indicated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants. The burner observations indicate that flame stability was dramatically improved with oxygen addition. The use of oxygen also *reduced* LOI and opacity as compared to the air- alone staging, with measured LOI and opacity being comparable or only slightly higher than the unstaged air-only condition. Therefore, this project demonstrated that oxygen enhanced combustion leads to significant reductions in NOx emissions *without* many of the problems typically associated with staged combustion systems.

### *4.4.3 Conclusion – Task 1.4*

The successful demonstration of oxygen enhanced combustion for NOx control at the pilot and full-scale single burner levels led to an agreement between Praxair and City Utilities of Springfield, Missouri to test oxygen enhanced combustion at full scale (separately funded). The results from the full-scale demonstration project at the James River Power Station indicated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants.

## 5.0 OXYGEN TRANSPORT MEMBRANES (OTM) (TASK 2)

### 5.2 5.1 OTM Materials Development (Task 2.1)

#### *5.1.1 Experimental – Task 2.1*

The objective of the materials development program was to obtain a suitable material composition that could be fabricated into dense elements capable of producing the target oxygen flux under the operating conditions. A candidate material was selected prior to this program based on work conducted at Praxair and BP as part of a NIST-ATP program. The material, designated PSO1, was selected due to high oxygen flux values measured on sintered disks at 1000°C.

Material characterization procedures for PSO1 have included flux measurement, electrical conductivity, x-ray diffraction, surface exchange, bulk diffusion, creep measurement and mechanical strength measurement. Some characterization techniques are described as follows:

Flux testing

A permeation cell for measuring the oxygen flux of disks of OTM materials is in place at Praxair as part of a NIST-ATP program. The permeation cell has a feed gas containing oxygen passing over the surface of the membrane where oxygen is removed from the gas stream and incorporated into the OTM sample. On the other side of the disk a helium purge gas stream is passed over the membrane surface and oxygen is extracted from the OTM material at atmospheric pressure. The oxygen flux can be calculated by measuring the fraction of oxygen in the purge gas stream and the flow rate of the gas. Leaks are detected by monitoring nitrogen concentrations in the purge stream. The sample is contained in a furnace allowing temperature dependence measurements.

Mechanical testing

A commercially available unit was used to measure the 4-point flexure strength of bars of OTM materials. The tests were conducted on dense bars of materials in accordance with ASTM Specification C1161-94. The tests were performed at ambient temperatures in air. The breaking load was measured and the flexural strength calculated using Equation [1].

$$S = \frac{3PL}{4BD^2} \qquad \text{Equation [1]}$$

Dilatometry

Dilatometry is used to measure dimension changes as a result of heating or changing gas composition. Dilatometry measurements were carried out using a commercially available dilatometer at ambient pressure using different gas compositions to simulate high-pressure air and low-pressure oxygen.

Creep measurements

A uniaxial compressive creep testing apparatus was constructed at UMR under a separate Praxair program. Creep measurements were carried out at different temperatures and different loads.

Characterization of PSO1 has shown that further improvement of mechanical and electrochemical properties is required for commercial use. Therefore, work focused on the development of modified PSO1 compositions and alternative membrane architecture with improved creep resistance and fracture toughness. Fracture toughness was measured for PSO1d using the Vicker's indentation method.

### *5.1.2 Results and Discussion – Task 2.1*

For commercial robustness, an increase in the mechanical strength of PSO1 is desirable. Creep measurements performed at 1000°C indicated a high creep rate for PSO1. Work has been ongoing to optimize process conditions and material composition to enhance mechanical properties and reduce creep.

Efforts have focused on optimization of the thermo-mechanical and thermo-chemical compatibility of modified PSO1 compositions via improved processing and detailed characterization. The high temperature mechanical properties of the modified composition were investigated. Increased stability of the modified composition's thermal expansion behavior over that of PSO1 was demonstrated. This result is important for integration of system components with the ceramic OTM elements since large differences in thermal expansion behavior can result in the development of significant thermal stresses.

Flux tests were conducted on several new compositions given the designation PxNOx1a through d and PxNOx2a through d. The oxygen flux was measured on dense tubes at atmospheric pressure using an inert gas purge. The highest flux measured for PxNOx1a was 64% of the target flux at 1050°C. In order to meet the flux targets composition improvements and thinner membranes were investigated. The oxygen flux through a dense thin disk of PSO1 was studied as a function of temperature and oxygen partial pressure using a helium purge gas. The temperature range for this experiment was 900-1050°C. At 1050°C, an oxygen flux of > 100% of target was obtained, which is one of the first year milestones for the program. Alternative PSO1 membrane architecture of the thin dense PSO1 disk was investigated. Test results indicate that there is a substantial increase in the oxygen flux over the untreated PSO1.

Optimization of process conditions and material composition to enhance mechanical properties and reduce creep for commercial robustness was conducted. Sintering behavior and chemical interaction of modified PSO1 compositions were investigated.

Creep measurements performed on modified PSO1d compositions showed improvement over PSO1. Two modified compositions yielded promising results, however, some improvements are necessary to reach the target of 1% strain per year. Additional testing of modified PSO1d compositions showed up to 17% improvement in creep rate compared to PSO1d.

The Vicker's indentation method was used to measure fracture toughness for PSO1d and a modified PSO1d composition. The fracture toughness of the modified PSO1d composition was almost twice that of PSO1.

### *5.1.3 Conclusion – Task 2.1*

Material characterization of PSO1 was completed. Permeation test results of a thin dense PSO1 disk at 1050°C resulted in an oxygen flux of > 100% of target. It was determined that an improved materials system with greater oxygen ion conductivity needs to be developed.

Therefore, efforts focused on the study of modified PSO1 compositions to improve mechanical properties such as creep and fracture toughness. Significant improvement in mechanical properties was made with modified PSO1d compositions over PSO1.

## 5.2 OTM Element Development (Task 2.2)

### *5.2.1 Experimental – Task 2.2*

The objective of this task is to fabricate elements from OTM materials for testing. In order to develop high quality OTM tubes, characterization and testing of incoming powders (Powder Quality Control) must be conducted. The following measurement apparatus will be utilized:

- Inductively Coupled Plasma Analysis (ICP) - Stoichiometry and impurities
- X-ray Diffraction (XRD) - Phase purity
- Particle Size Analysis - Particle size distribution
- BET - Surface area
- Scanning electron microscope (SEM) - Particle morphology
- Thermo-gravimetric Analysis (TGA) - Organic content and water loss

After characterization, the powders are mixed into workable pastes and formed into tubular shapes utilizing methods developed in previous Praxair programs. The OTM tubes are then sintered in a controlled atmosphere at a controlled rate of heating in a high temperature muffle furnace. The sintered tubes then undergo tube characterization (Tube Quality Control) where a battery of tests are conducted to determine strength, diameter, straightness, flaws and phase purity.

PSO1 and PSO1d dense elements were manufactured and delivered for high pressure single tube reactor tests. Binder burnout / sintering trials continued on elements with new designs. Process optimization continued with fabrication of dense PSO1d elements.

### *5.2.2 Results and Discussion – Task 2.2*

Initial element development trials resulted in disks and tubes that sinter to ~86% theoretical density. The desired density (95% of the theoretical) was achieved after sintering optimization. PSO1 elements were manufactured according to the high-pressure permeation tester specifications and a minimum of six (6) were delivered each month. OTM element sintering tests were conducted in a single furnace dedicated to this program to prevent sample contamination.

The mean strength of PSO1 calculated from short element burst tests was 40% of target. A visual examination showed a significant number of fractures near the region of minimum wall thickness. Powder specifications for PSO1 base powder were set. A thickness gauge was evaluated for its non-destructive quality control evaluation capabilities and determined to be a valuable quality control tool for element fabrication.

PSO1 and PSO1d elements were manufactured according to the high-pressure permeation tester specifications. PSO1d powder process optimization continued. Sintering optimization of OTM elements was ongoing, and progress was made in the straightness and ovality of the elements. Scale-up to 3ft long PSO1d tubes was successful.

New element designs that may be more resistant to creep were investigated. One OTM element with new architecture was successfully prepared. A modified binder burnout protocol from a previous Praxair program was conducted on various sections of one of this element with moderate success.

Using short sections of a 3ft dense PSO1d tube, the modified binder burnout conditions were optimized, which resulted in average PSO1d burst strength measurements >75% of PSO1 strength measurements.

An alternative proprietary element fabrication method, which may result in lower processing costs, was further investigated using PSO1d composition. Straight green and sintered elements were successfully prepared.

#### *5.2.3 Conclusion – Task 2.2*

The desired density of OTM tubes was achieved after sintering optimization. Required amounts of elements for this program were fabricated and delivered for testing. Elements were characterized and tested in QC both destructively and non-destructively. Process optimizations were made to increase element quality and yield. Elements were fabricated successfully by several different methods.

### 5.3 OTM Process Development (Task 2.3)

#### *5.3.1 Experimental – Task 2.3*

The objective of this task was to design, build and operate a single tube reactor for high pressure operation that can demonstrate at least 75% of the commercial target flux. The single tube high-pressure permeation test facility was constructed and is now in full operation. The first sample tested, a dense PSO1 element, was heated to 900°C and exposed to several pressure cycles for >500 hours continuous operation. Air was the feed gas and an inert gas (nitrogen or helium) was the purge gas. The oxygen product flowrate was measured using a bubble flowmeter. The oxygen product purity was measured using a Servomex oxygen analyzer. Equation 2 was used to calculate the average oxygen flux.

$$J_{O_2} = \frac{y_{O_2} \overline{Q}}{a_{\exp}}$$

$J_{O_2}$ = average oxygen flux [=] sccm/cm$^2$ Equation [2]

$y_{O_2}$ = oxygen product mole fraction (dimensionless)

$\overline{Q}$ = Average oxygen product flowrate [=] sccm

$a_{\exp}$ = exposed OTM surface area [=] cm$^2$

Dense, thin-walled PSO1 elements, modified PSO1 elements, and architecturally modified PSO1d elements were tested in the single tube high-pressure permeation reactor. The maximum operating temperature for these tests was 900-950°C.

### *5.3.2 Results and Discussion – Task 2.3*

Many OTM elements were tested in the single tube high-pressure reactor during this program. The highlights in OTM process development are as follows:

A dense PSO1 element tested in the high-pressure test facility demonstrated production of oxygen with a purity better than 99.5% for 150 hours. After >500 hours, the oxygen purity decreased to 94.8%. The highest average oxygen flux measured during this experiment was 16% of the target flux. The seal performance was very good with a leak rate of 3% of the maximum allowable leak rate.

The same dense PSO1 element was put through a second thermal cycle. The average oxygen flux was 29% greater than the highest flux measured during the first thermal cycle. 96.5% oxygen product purity was the maximum purity observed during the second thermal cycle.

A thin-walled dense PSO1 element was architecturally modified and tested in the single-tube high pressure reactor. Preliminary data suggests that the average oxygen flux at 900ºC under non-commercial purge conditions is 50% of target flux. The oxygen product purity was observed to be as high as 97.6% at 900ºC.

The goal of achieving an oxygen flux 75% of the target flux was achieved with a thin-walled, coated, dense PSO1 element at 950°C under no purge conditions. The data shows that the flux is higher at 950ºC than at 900ºC by an average of about 20%. No evidence of oxygen flux or purity degradation was observed after >390 hours of continuous operation.

A dense PSO1d element was tested in the single-tube high-pressure reactor at 900ºC. The oxygen product purity was observed to be as high as 99.999% and remained above 98% for the duration of the test, which was >190 hours.

A process development milestone was to test an OTM element for five full thermal cycles. Eight thermal cycles were completed with an OTM element. A dense modified PSO1 composition element underwent eight full thermal cycles to 900°C.

A long-term alternative architecture PSO1d element test in the NOx reactor was completed. The element did not experience any dimensional changes after >600 hours of continuous operation.

### *5.3.3 Conclusion – Task 2.3*

As described above, significant progress has been made in OTM Process Development. The single tube reactor was assembled and operated successfully. The production of oxygen with a purity better than 99.5% was demonstrated for 150 hours. Testing of dense PSO1d element was conducted with promising preliminary oxygen flux results of 100% of the commercial target flux. Long-term testing of an architecturally modified PSO1d element was completed with no dimensional changes after >600 hours of continuous operation. This lack of deformation is an important milestone in the long-term development of the OTM technology.

# 6.0 ECONOMIC EVALUATION (TASK 3)

## *6.1 Experimental – Task 3*

The objective of this program was to develop oxygen enhanced combustion technology that could be used to cost effectively reduce NOx emissions to less than 0.15 lb/MMBtu without the use of SCR. As the project developed and as the technology was discussed with potential utility customers, questions of coal type, baseline NOx, burner type and oxygen consumption were some of the key factors affecting the cost effectiveness of the process. Laboratory test results and subsequent field tests confirmed the NOx reductions that were achievable and quantities of oxygen required. The discussion below will show that for wall fired boilers that NOx reductions to less than 0.15 lb/MMBtu can be achieved at costs that are more than 40% less than SCR.

Background

The two major types of pulverized coal boilers in service today are wall and T or corner fired units. A T-Fired or corner fired boiler is called that because of the way in which the coal is injected into the combustion section of the furnace. Pulverized coal and air are injected into a central core where a uniform flame ball is created to combust the coal. Coal and air are injected at multiple levels from all four corners of the boiler to create the central fireball. The coal and air are injected almost tangent to the circular shape of the central fireball. Hence this type of boiler is referred to as corner or T-Fired. NOx control is achieved in T-Fired boilers by controlling the injection of coal and air into the primary combustion zone, by controlling the burner zone stoichiometry and controlling peak temperatures in the fireball. Unstaged T-Fired and wall fired units can achieve similar NOx emissions levels of ~0.4-0.45 lb/MMBtu burning bituminous coal utilizing low NOx burners.

A wall fired boiler consists of numerous individual burners, each with an individual flame firing into the furnace plenum. Low NOx wall fired burners control NOx emissions by controlling the rate at which the air and fuel are mixed. Each burner must be controlled individually to maintain stable combustion and low NOx performance. Low NOx wall fired burners in a furnace are capable of NOx emissions of ~ 0.4-0.45 lb/MMBtu.

As was discussed in section 4 creating a fuel rich zone can result in the fuel bound nitrogen going to $N_2$ versus NO. This is normally accomplished by staging the lower furnace and injecting the remaining air through the OFA ports. In a T-fired boiler because the flows from all of the burners are well mixed in the furnace core, they can operate with a deeper burner zone stoichiometry; T-Fired boilers can operate with SR's of ~0.85. As a result, they can achieve staged NOx emissions of ~0.25 with bituminous coal and <0.15 with PRB coals.

In contrast, because of the individual operation of the burners, wall fired boilers are more limited in their ability to be staged. Among the reasons are high carbon in ash, burner stability, CO, flame monitoring limits, unburned carbon impinging on the walls and burner to burner imbalances. As a result, wall fired units can generally only be staged to lower furnace SR's of 0.9-0.98 without oxygen. This allows them to achieve baseline NOx emission levels of ~0.35 lb/MMBtu with bituminous coals and 0.2-0.25 with PRB coals.

Oxygen allows deeper staging for both wall and T-fired units. Because the potential economic benefits for wall fired units were greater, the focus of the economic analysis, commercial boiler tests, and the commercialization activities have been focused on wall fired boilers. The assumed baseline NOx for this analysis is 0.35 lb/MMBtu at SR of 0.98.

### *6.2 Results and Discussion – Task 3*

The major economic assumptions are listed in the following table. The key sources for the SCR data are Status Report on NOx Control Technologies and Cost Effectiveness for Utility Boilers (Staudt[13]) and Power Engineering[14]. The catalyst price has been reduced to $8000/m3 based on market pricing. SCR removal efficiency has been increased to 90% based on reported operating experience. The capital cost for SCR's has been adjusted based on data reported in Power Engineering, May 2003[14]. The Capital Recovery Factor (IRR) used for evaluation has been increased to 0.145 reflecting a 12% capital cost rate based on feedback from utilities.

**Table 6-1 Economic Assumptions**

| | |
|---|---|
| Generating Capacity | 160/300 MW |
| Boiler Type | Wall Fired |
| Pre-Retrofit NOx | 0.35 lb/MMBtu |
| Pre-Retrofit SR | ~0.98 |
| Capacity Factor | 0.85 |
| Coal Type | Bituminous |
| Plant Heat Rate Btu/kWh | 10500 |
| IRR (capital recovery factor) | 0.145 |
| Capital recovery life | 15 years |
| SCR Capital Cost | $120/kW |
| SCR Removal Efficiency | 90% |
| SCR Catalyst Life | 24000 hours |
| Catalyst Cost | $8000/m3 |
| Ammonia cost | $200/ton |

Tables 6-2 and 6-3 compare the cost oxygen enhanced NOx control with SCR. In both cases it is assumed that low NOx burners and overfire air have been previously installed. Cases are presented here for 160 and 300 MW boilers. The 300 MW boiler is front wall fired with 18 burners; OFA is assumed to have been previously installed. Based on models developed based on pilot and beta site experience, NOx reductions from 0.35 to 0.15 lb/MMBtu are expected with 5% oxygen replacement and from 0.35 to 0.2 lb/MMBtu with 3% replacement. Both of these units have sufficient residence time between the burners and nose to allow for NOx reduction and CO burnout. The oxygen system costs are estimated based on beta site installations. The costs include all equipment and installation. The oxygen equipment includes: VPSA oxygen plant, oxygen flow controls, oxygen injection lances, and all of the associated electrical equipment and controls. The installation includes site preparation, foundations and all necessary piping and wiring. On this cost basis, the cost of NOx reductions is less than $1800/ton and the savings are over 50% when compared with SCR.

SCR's can achieve NOx emissions below 0.15 lb/MMBtu, and as a result allow the sale of emissions allowances. For the 300 MW case shown in Table 6-2, this results in a credit of $1.3 million per year for the SCR. For the case of oxygen enhanced combustion at 3% $O_2$, allowances are assumed to be purchased at an annual cost of $0.6 million. Even allowing for the sales of allowances, oxygen enhanced combustion achieves NOx emissions reductions at a cost less than one-half of SCR: $0.75/Mwhr versus $1.977/Mwhr. For the case of a 160 Mw boiler shown in Table 6-3, similar savings are shown for oxygen enhanced combustion versus SCR: $0.89/Mwhr versus $2.19/Mwhr.

**Table 6-2 Cost Comparison Table for 300 MW Boiler**

| Economic Analysis | SCR vs Oxygen for Boilers with LNB's and OFA | | |
|---|---|---|---|
| | SCR | 3% Oxygen | 5% Oxygen |
| | Cost Impact of Technology Choice | | |
| MW | 300 | 300 | 300 |
| Heat Rate (BTU's/KWH) | 10,300 | 10,300 | 10,300 |
| Fuel Cost, MMBTU | $1.50 | $1.50 | $1.50 |
| Uncontrolled Nox(lb/MMBTU's) | 0.35 | 0.35 | 0.35 |
| Controlled NOx | 0.04 | 0.2 | 0.15 |
| Capital Cost ($/KW) | $ 120 | $ 20 | $ 30 |
| Fixed O&M ($/yr) | $100,000 | $141,750 | $209,790 |
| Catalyst volume, m3 | 300 | 0 | 0 |
| # layers | 2 | NA | NA |
| Hrs between cat addition | 24,000 | | |
| Catalyst price $/m3 | $ 8,000 | NA | NA |
| 100% bypass? Yes/no | no | no | no |
| Catalyst Disposal $/m3 | $1,200 | Na | Na |
| Total Capital | $ 36,000,000 | $ 6,000,000 | $ 8,880,000 |
| **Capital Cost Savings** | **Base** | **0.83** | **0.75** |
| Reagent Price, $/ton | $ 200.00 | $ - | $ - |
| Power ConsumptionKWH | 900.00 | 2,052.00 | 3,420.00 |
| Power Cost ($/KWH) | $ 0.030 | $ 0.030 | $ 0.030 |
| Power Cost ($/Year) | $ 83,768 | $ 190,990 | $ 318,317 |
| Loss/Gain in heat rate | -0.5% | 0.2% | 0.3% |
| Capacity Factor | 0.85 | 0.85 | 0.85 |
| Months deNOx in service | 5 | 5 | 5 |
| Book Life of Project | 15 | 15 | 15 |
| Real cap cost rate, % | 12 | 12 | 12 |
| Cap. Rec. Factor | 0.145 | 0.145 | 0.145 |
| Annual Ammonia | $ 106,393 | $ - | $ - |
| Ann. Catalyst | $ 118,625 | $ - | $ - |
| Catalyst Disposal | $ 32,850 | $ - | $ - |
| Ann. Heat Rate Pen. | $ (71,900) | $ 28,760 | $ 35,950 |
| LOI benefit | $ - | $ 67,652 | $ 96,645 |
| Variable O&M $/yr | $ 413,537 | $ 94,578 | $ 185,721 |
| Fixed O&M ($/yr) | $100,000 | $113,400 | $167,832 |
| **Operating Cost Savings** | **Base** | **0.60** | **0.31** |
| Fixed Chrg Capital | $ 5,220,000 | $ 870,000 | $ 1,287,600 |
| Annual Cost | $ 5,733,537 | $ 1,077,978 | $ 1,641,153 |
| Ann. NOx red'n, tons | 1485.942375 | 719.004375 | 958.6725 |
| Ann. Nox tons to 0.15 | -527.269875 | 239.668125 | 0 |
| Added Cost/Benefit ($2000/ton) | $ (1,318,175) | $ 599,170 | $ - |
| Net Annual Cost | $ 4,415,362 | $ 1,677,149 | $ 1,641,153 |
| **$/ton removed** | **$ 3,859** | **$ 1,499** | **$ 1,712** |
| **% Total Savings** | **Base** | **0.620** | **0.628** |
| $/Mwhr (inc. allow. sales) | $ 1.977 | $ 0.751 | $ 0.735 |

Table 6-3 compares NOx reduction costs with an SCR and those with oxygen enhanced combustion for a 160 MW boiler; this unit has 16 burners and burns bituminous coal. Even at this smaller size the cost of NOx reduction using oxygen is less than $2200/ton with savings of over 40% compared with SCR.

**Table 6-3 Cost Comparison Table for 160 MW Boiler**

| Economic Analysis | SCR vs Oxygen for Boilers with LNB's and OFA | | |
|---|---|---|---|
| | SCR | 3% Oxygen | 5% Oxygen |
| | Cost Impact of Technology Choice | | |
| MW | 160 | 160 | 160 |
| Heat Rate (BTU's/KWH) | 10,300 | 10,300 | 10,300 |
| Fuel Cost, MMBTU | $1.50 | $1.50 | $1.50 |
| Uncontrolled Nox(lb/MMBTU's) | 0.35 | 0.35 | 0.35 |
| Controlled NOx | 0.04 | 0.2 | 0.15 |
| Capital Cost ($/KW) | $ 120 | $ 30 | $ 34 |
| Fixed O&M ($/yr) | $100,000 | $90,720 | $102,816 |
| Catalyst volume, m3 | 300 | 0 | 0 |
| # layers | 2 | NA | NA |
| Hrs between cat addition | 24,000 | | |
| Catalyst price $/m3 | $ 8,000 | NA | NA |
| 100% bypass? Yes/no | no | no | no |
| Catalyst Disposal $/m3 | $1,200 | Na | Na |
| Total Capital | $ 19,200,000 | $ 4,800,000 | $ 5,440,000 |
| **Capital Cost Savings** | **Base** | **0.75** | **0.72** |
| Reagent Price, $/ton | $ 200.00 | $ - | $ - |
| Power ConsumptionKWH | 480.00 | 1,094.40 | 1,824.00 |
| Power Cost ($/KWH) | $ 0.030 | $ 0.030 | $ 0.030 |
| Power Cost ($/Year) | $ 44,676 | $ 101,861 | $ 169,769 |
| Loss/Gain in heat rate | -0.5% | 0.2% | 0.3% |
| Capacity Factor | 0.85 | 0.85 | 0.85 |
| Months deNOx in service | 5 | 5 | 5 |
| Book Life of Project | 15 | 15 | 15 |
| Real cap cost rate, % | 12 | 12 | 12 |
| Cap. Rec. Factor | 0.145 | 0.145 | 0.145 |
| Annual Ammonia | $ 56,743 | $ - | $ - |
| Ann. Catalyst | $ 118,625 | $ - | $ - |
| Catalyst Disposal | $ 32,850 | $ - | $ - |
| Ann. Heat Rate Pen. | $ (38,347) | $ 15,339 | $ 19,173 |
| LOI benefit | $ - | $ 67,652 | $ 96,645 |
| Variable O&M $/yr | $ 291,241 | $ 18,871 | $ 53,950 |
| Fixed O&M ($/yr) | $100,000 | $90,720 | $102,816 |
| **Operating Cost Savings** | **Base** | **0.72** | **0.60** |
| Fixed Chrg Capital | $ 2,784,000 | $ 696,000 | $ 788,800 |
| Annual Cost | $ 3,175,241 | $ 805,591 | $ 945,566 |
| Ann. NOx red'n, tons | 792.5026 | 383.469 | 511.292 |
| Ann. Nox tons to 0.15 | -281.2106 | 127.823 | 0 |
| Added Cost/Benefit ($2000/ton) | $ (562,421) | $ 255,646 | $ - |
| Net Annual Cost | $ 2,612,820 | $ 1,061,237 | $ 945,566 |
| **$/ton removed** | **$ 4,007** | **$ 2,101** | **$ 1,849** |
| **% Total Savings** | **Base** | **0.594** | **0.638** |
| $/Mwhr (inc. allow. sales) | $ 2.193 | $ 0.891 | $ 0.794 |

Commercialization Planning

Based on the work conducted in this program a beta site test was conducted at City Utilities James River 44MW Unit 3 in November of 2002. This work demonstrated that the technology could be applied successfully to a full boiler. Based on the successful testing at James River, a commercial demonstration was conducted at Northeast Utilities 125 MW nameplate Mt. Tom station during the summer of 2003. While specific boiler and overfire air limitations prevented optimum performance, the boiler was able to achieve NOx emissions <0.15 lb/MMBtu at 80% of nameplate burning class C bituminous coal. Further at both Mt. Tom and City Utilities the process demonstrated reduced LOI. Based on these successful demonstrations further commercial activity is planned. Because SCR's are more cost effective on larger boilers, Praxair has focused on commercializing this technology on boilers less than 500 MW. In the SIP Call states there are ~ 500 boilers less than 500 MW with combined generating capacity of over 50,000 MW.

### *6.3 Conclusion – Task 3*

Oxygen enhancement advantage versus SCR was confirmed with utilities. Based on pilot-scales tests, commercial burner performance tests, and the beta site test results, the economic advantage of oxygen enhancement was confirmed.

## 7.0 PROGRAM MANAGEMENT (TASK 4)

### *7.1 Objectives – Task 4*

The program manager will provide a single point of contact with DOE for contractual matters, ensure that contract terms and conditions are complied with, and ensure that necessary skills and resources are provided and assigned effectively to perform project activities. He will maintain the lines of authority necessary for ensuring that individual activities are performed in accordance with the overall program goals, and the controls necessary to complete the project on schedule and within budget. He will also be responsible for ensuring that Praxair technical management and business management are aware of program progress, and will coordinate pre-commercialization activities within Praxair. Project documentation will be prepared and delivered to DOE in accordance with mutually established requirements; oral reviews covering the progress and status of the program will be conducted as scheduled.

### *7.2 Results and Discussion – Task 4*

The Program Management highlights for the US DOE $NO_x$ program are as follows:

- A kick-off meeting was held with all of the Program team members on April 4, 2000 to initiate the work on the Program. Participants, including Reaction Engineering International (REI), University of Missouri, Rolla, University of Arizona, Alstom Power (US Power Plant Laboratory) and Praxair attended in person or via teleconference.
- The Program kick-off meeting was held with the US DOE in Pittsburgh on April 18,2000.
- Sub-Contracts have been executed with the University of Arizona, University of Missouri, Rolla, Alstom Power, Reaction Engineering International (REI) and University of Utah.
- A project review meeting was held on September 25, 2000 with all members of the team present.
- Teleconferences were held among combustion team members throughout the program.
- Monitoring of accounts established within the Praxair accounting system to track labor hours and costs was ongoing.
- Project documentation has been prepared and delivered to the US DOE in accordance with the cooperative agreement including the following documents: Hazardous Substance Plan, request for an Advance Waiver of Patents, quarterly technical progress reports and financial status reports.
- Annual project review meetings were held May 23, 2001 at the US DOE and on May 31, 2001 at REI.
- An update meeting was held on December 6, 2001 at the US DOE.
- Annual project review meeting was held May 15, 2002 at the US DOE.
- An update meeting was held on December 18, 2002 at the US DOE.
- A paper entitled "$O_2$ Enhanced Combustion for NOx Control" was presented by Dr. Lawrence Bool of Praxair at the 2002 Conference on SCR and SNCR for NOx Control, Pittsburgh, PA, May 15-16, 2002.
- A paper entitled "Oxygen for NOx Control – A Step Change Technology?" was presented by Dr. Lawrence Bool of Praxair at the Nineteenth Annual Pittsburgh Coal Conference, Pittsburgh, PA, September 24-26, 2002.
- A presentation entitled "CFD Evaluation of Oxygen Enhanced Combustion in Coal Fired Boilers: Impacts on NOx, Carbon in Ash and Waterwall Corrosion" was co-authored by REI and Praxair and presented by Dr. Brad Adams of REI at the Electric Utilities Environmental Conference, Tucson, AZ, January 27-30, 2003.

- A paper entitled "NOx Reduction from a 44MW Wall-Fired Boiler Utilizing Oxygen Enhanced Combustion" was presented by Dr. Lawrence Bool of Praxair at the 28th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, March 10-13, 2003.
- A paper entitled "CFD Evaluation of Oxygen Enhanced Combustion in Coal Fired Boilers: Impacts on NOx, Carbon in Ash and Waterwall Corrosion" was co-authored by REI and Praxair and presented by Dr. Marc Cremer of REI at the 28th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, March 10-13, 2003.
- A presentation was made at the Pittsburgh Coal Conference based on work from the pilot combustion tests, beta site tests and performance data from the Mt Tom Station in Holyoke, MA.
- A presentation entitled "OEC Technology for NOx Control at Mt. Tom" was co-authored by Praxair and Mt. Tom Station and presented by Ed Kaczenski of Mt. Tom Station at the Electric Utilities Environmental Conference, Tucson, AZ, January 19-22, 2004.
- A paper entitled "Oxygen-Enhanced Combustion Technology for NOx SIP Call Compliance on PC Boilers" was presented by Dr. Lawrence Bool of Praxair at the 29th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, 2004.
- Patent number US 6,565,632 B1 was granted to Praxair on May 20, 2003 for the invention entitled "Ion-Transport Membrane Assembly Incorporating Internal Support". This invention was previously disclosed to the US DOE in a letter dated September 25, 2001, and DOE Case number 98,293 was assigned.

### *7.3 Conclusion – Task 4*

The program manager successfully ensured that Praxair was in compliance with contract terms and conditions, and ensured that necessary skills and resources were provided and assigned effectively to perform project activities within budget. Project documentation was prepared and delivered to DOE in accordance with mutually established requirements. Project reviews were conducted twice a year.

## 8.0 CONCLUSIONS

The DE-FC26-00NT40756 “Oxygen Enhanced Combustion for NOx Control” program was completed successfully and under budget. All major program milestones from the revised statement of work were met.

**Oxygen Enhanced Combustion Tasks:**

The results of the single burner work demonstrated that oxygen enhanced combustion can substantially reduce NOx emissions from coal-fired power plants. The burner observations indicate that flame stability was dramatically improved with oxygen addition. The use of oxygen also *reduced* LOI and opacity as compared to the air- alone staging, with measured LOI and opacity being comparable or only slightly higher than the unstaged air-only condition. Therefore, this project demonstrated that oxygen enhanced combustion leads to significant reductions in NOx emissions *without* many of the problems typically associated with staged combustion systems.

All of the experimental and modeling results generated during this development effort indicate that oxygen addition can significantly reduce NOx emissions from pulverized coal fired boilers. Even when the initial NOx concentrations are low addition of oxygen can drive the NOx emissions even lower, with NOx emissions well below 0.15lb/MMBtu observed during the experimental work.

There are seven patents pending for oxygen enhanced combustion testing work completed under the scope of this program.

**Oxygen Transport Membrane Tasks:**

Praxair developed the economically enhancing oxygen transport membrane (OTM) technology which is ideally suited for integration with combustion systems to achieve further significant cost reductions and efficiency improvements. This OTM oxygen production technology is based on ceramic mixed conductor membranes that operate at high temperatures and can be operated in a pressure driven mode to separate oxygen with infinite selectivity and high flux. An OTM material was selected and characterized. OTM elements were successfully fabricated. A single tube OTM reactor was designed and assembled. Testing of dense OTM elements was conducted with promising oxygen flux results of 100% of target flux.

Patent number US 6,565,632 B1 was granted to Praxair on May 20, 2003 for the invention entitled “Ion-Transport Membrane Assembly Incorporating Internal Support”. This invention was previously disclosed to the US DOE in a letter dated September 25, 2001, and DOE Case number 98,293 was assigned.

**Economic Evaluation:**

Comparison of the costs of using oxygen for NOx control against competing technologies, such as SCR, shows that this concept offers substantial savings over SCR and is an economically attractive alternative to purchasing NOx credits or installing other conventional technologies. Based on successful demonstrations, further commercial activity is planned. Because SCR’s are more cost-effective on larger boilers, Praxair has focused on commercializing this technology on boilers less than 500 MW. In the SIP Call states, there are ~500 boilers less than 500 MW, with a combined generating capacity of over 50,000 MW.

OTM processes do not show an economic advantage based on the current processes, natural gas prices, and technology status.

## 9.0 REFERENCES


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