OXYGEN ENHANCED COMBUSTION FOR NOx CONTROL

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period Starting January 1, 2001 and Ending March 31, 2001

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for the Program through the fourth quarter January-March 2001 in the following task areas: Task 1 - Oxygen Enhanced Combustion, Task 2 - Oxygen Transport Membranes and Task 4 - Program Management. This report will also recap the results of the past year.

The program is proceeding in accordance with the objectives for the first year. OTM material characterization was completed. 100% of commercial target flux was demonstrated with OTM disks.

The design and assembly of Praxair's single tube high-pressure test facility was completed. The production of oxygen with a purity of better than 99.5% was demonstrated.

Coal combustion testing was conducted at the University of Arizona. Modest oxygen enhancement resulted in NOx emissions reduction. The injector for oxygen enhanced coal based reburning was conducted at Praxair.

Combustion modeling with Keystone boiler was completed. Pilot-scale combustion test furnace simulations continued this quarter.

Pilot scale testing was initiated at the University of Utah this quarter.

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Executive Summary

The objective of this program is 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 will develop both oxygen based low NOx technology and the new low cost oxygen transport membrane (OTM) oxygen production technology.

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

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

The work for the first year of the program focused on Tasks 1, 2 and 4. Task 1 work consists of laboratory scale testing used to understand the fundamentals of oxygen for NOx emissions control, and computer modeling used to determine the effectiveness of proposed oxygen-based technologies in boiler environments. Task 2 work focuses on the development and testing of an OTM system for use with the proposed technologies. The objectives and major accomplishments of the first year of the program are summarized in Table 1 below.

Table 1. Oxygen Enhanced Combustion for NOx Control Program Objectives - Year 1

ID	Milestone	Accomplishments
1	Praxair combustion modeling complete	Praxair combustion modeling was conducted.
2	REI combustion modeling complete	REI combustion modeling was conducted. Combustion modeling with Keystone boiler was completed.
3	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	Lab-scale experiments complete	Lab-scale experiments are in progress.
5	Hot oxygen and coherent jet tests complete	Hot oxygen tests were conducted and testing is in progress.
6	Pilot-scale testing of stage combustion complete	Pilot-scale testing of stage combustion is in progress.
7	Pilot-scale testing of reburning complete	Pilot-scale testing of reburning is in progress.
13	Selection of OTM material	PSO1 was selected as OTM material.
15	Characterization of OTM material	OTM material characterization of PSO1 has been completed.
16,17,18	50,75,100% of commercial target flux demonstrated with disks	100% of commercial target flux was demonstrated with disks.
21	Single tube reactor design complete	The single tube reactor design was completed.
22	Single tube reactor construction complete	The single tube high pressure reactor was assembled and is in operation.
28	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.
35	Program review meetings	Six month project review meeting was held 9/25/00 with team members present.

A. Experimental Methods

B.1. Combustion Modeling (Task 1.1.1) Experimental Methods

The objective of this task is to illustrate the benefit of oxygen enhanced coal combustion to low NOx firing systems. The expected benefits include: 1) reduced NOx emissions, 2) reduced unburned carbon (UBC), 3) decreased water wall wastage potential, and 4) improved system operability.

The modeling activities in this task focused on computational fluid dynamics (CFD) modeling of O_2 enhanced combustion in a corner fired boiler (the Keystone boiler) and on modeling O_2 enhanced combustion in the University of Utah's 1500 kW pilot-scale test facility. Details on the computational tools were described in the third quarterly technical progress report[1].

Combustion modeling simulations using the L1500 combustion facility were conducted this quarter. An Illinois No. 6 coal was used for the simulations

B.2. Laboratory-Scale Parametric Testing (Task 1.1.2) Experimental Methods

The objective of this task is to explore the impact of oxygen enrichment on NOx formation and on the standoff distance of coal flames using a down-fired combustor which was previously described in the first quarterly report[2]. Initially, there were delays due to coal handling issues. Preliminary testing of oxygen enrichment in the fuel rich zone of a pulverized coal staged combustion system was completed. Ten runs were successfully completed at various fuel rich zone stoichiometries. Staged combustion experiments with oxygen enriched atmosphere continued this quarter.

B.3. Oxygen-based Injector Design and Testing (Task 1.2) Experimental Methods

The objective of this task is to explore the impact of oxygen on post combustion control strategies. During the last quarter work continued on two strategies: reburning and SNCR (Selective Non Catalytic Reduction). The hot oxygen test rig, described in the last quarterly report[1], was run successfully utilizing a solid fuel. Testing with the oxygen injection test rig indicated several modifications that were required for stable operation. These modifications are ongoing. A separate test rig was designed and fabricated to explore methods for oxygen enhanced reburning and SNCR.

The objective of the reburning bench-scale experiments is to determine the effectiveness of hot oxygen in enhancing coal devolatilization. In the reburning experiments conducted this quarter, an eastern compliance coal was reacted with hot oxygen outside of the boiler to maximize the impact and the resulting product stream introduced to act as the reburn fuel.

B.4. OTM Materials Development (Task 2.1) Experimental Methods

The objective of this task is to determine a suitable material composition that can be fabricated into elements capable of producing the target oxygen flux under the operating conditions. A candidate material designated PSO1 was selected prior to this program. Material characterization procedures for PSO1 have included flux measurement[2], electrical conductivity, x-ray diffraction, surface exchange, bulk diffusion, creep measurement and mechanical strength measurement[2]. Characterization of PSO1 has shown that further improvement of mechanical and electrochemical properties is required for commercial use.

Efforts are in progress to improve the OTM mechanical and electrochemical properties required for commercial use via improved processing and improved compositions. Modified PSO1 compositions have been characterized. Alternative membrane architecture was investigated last quarter.

B.5. OTM Element Development (Task 2.2) Experimental Methods

The objective of this task is to fabricate elements from OTM materials for testing. Powder characterization techniques and element manufacturing equipment were described in the first quarter technical progress report[2]. Six (6) or more PSO1 dense elements were manufactured and delivered each month for high pressure single tube reactor tests. Burst strength was measured on short element sections[1]. Optimization of element sintering was ongoing. A thickness gauge was evaluated for its non-destructive quality control evaluation capabilities.

B.6. OTM Process Development (Task 2.3) Experimental Methods

The objective of this task is to design, build and operate a single tube reactor for high pressure operation that can demonstrate at least 75% of the commercial target flux in year 2 of the program. The single tube high-pressure permeation test facility was constructed[3] and is now in full operation. The first sample tested, a dense PSO1 element, was heated to 900^{o}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 1 was used to calculate the average oxygen flux.

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

$$J_{O_2} = \text{average oxygen flux [=] sccm/cm}^2 \qquad [1]$$

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

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

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

Last quarter two modified PSO1 elements were tested in the single tube high-pressure permeation reactor.

B. Results and Discussion

C.1. Combustion Modeling (Task 1.1.1) Results and Discussion

The Keystone boiler is a 900 MW supercritical twin furnace with a shared center wall and is a corner-fired boiler fitted with an ABB Low-NOx Concentric Firing System (LNCFS) level III. The LNCFS Level III system utilizes both Close Coupled Over-Fire Air (CCOFA) and Separated Over-Fire Air (SOFA). The Keystone boiler was previously modeled by REI and the "base case" utilized an existing setup. Two cases were performed to evaluate oxygen enrichment without boiler modifications. The overall excess O_2 and burner design in the boiler remained the same in all simulations. The results obtained suggest that without modification of the burner/boiler oxygen addition can lead to increased unburned carbon, NOx and CO emissions in the furnace.

The University of Utah pilot-scale combustion test furnace referred to as the L1500 is a nominal 5 MMBtu/hr pilot-scale furnace designed to simulate commercial combustion conditions. A major objective of this combustion facility is to study pollutant formation and control, carbon utilization, and ash management in a system which operates similar to commercial boilers. The pulverized coal burner used on 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^{o}K on the fire-side to below 330^{o}K on the shell-side. A series of simulations were initiated using an Illinois No. 6 coal and the typical firing rate tested at this facility, 4 MMBtu/hr. Preliminary calculations assuming a high wall temperature, yielding much lower heat removal rates that found in a typical boiler, were completed. These results were used to define more simulations with more realistic heat removal rates.

A series of simulations were then performed, using the appropriate heat removal pattern, to provide a preliminary evaluation of the impact of various methods of using oxygen from NOx control. These simulations suggested a minimum oxygen replacement to have an impact, positive or negative on NOx emissions versus baseline conditions. Various oxygen replacement rates and utilization methods resulted in changes from an *increase* in NOx to a significant (22%) reduction in NOx emissions. The reductions were achieved with very modest replacement rates. These simulations are ongoing. The results of all the L1500 simulations will be reported when all the calculations are complete.

C.2. Laboratory-Scale Parametric Testing (Task 1.1.2) Results and Discussion

Experimental difficulties were experienced early in the program with the pulverized coal combustor. Problems involving the air compressor coal feeder were resolved and testing with coal was initiated. Oxygen enhanced coal combustion testing in the fuel rich zone of the pulverized coal staged combustion system was conducted with the completion of ten successful runs. The data from these experiments indicate that oxygen addition has a significant impact on NOx emissions. Even modest oxygen enrichment yielded NOx emissions reductions in the range of 30% to 40% from the baseline (air) case.

C.3. Oxygen-based Injector Design and Testing (Task 1.2) Results and Discussion

The oxygen injector test apparatus assembly was been completed and shakedown testing was conducted. The hot oxygen burner was run successfully on a solid fuel. Several experiments were attempted to explore the impact of oxygen on coal-based reburning. In these experiments, using the test rig discussed in Section B.3 of the third quarterly progress report[1], an oxygen-based burner was used to fire coal into a small test combustor. A gas probe was inserted into the end of the combustion chamber to sample the combustion gases before they mixed with surrounding air. Although the results are generally encouraging, operating problems such as plugging of the burner or gas sample probe have hampered progress.

Bench-scale experiments were conducted to determine the effectiveness of hot oxygen in enhancing coal devolatilization. For the use of hot oxygen to promote coal-based reburning it is critical that the coal is devolatilized/gasified rather than simply combusted with the hot oxygen. Experimental data show that as the combustion conditions become more fuel rich the fraction of carbon in the gas phase as combustibles (CO and methane) that may play a role in reburning increases.

Another method oxygen has been proposed to enhance post combustion NOx control strategies is to use a coherent jet to deliver either reburn fuel or SNCR reagents into the center of the furnace. A series of calculations were performed to evaluate the economic feasibility of the concept and technical problems that might arise from the use of conventional CoJet™ for this application. Although technically feasible, the modifications required to ensure the process was economically attractive would require significant experimentation. However, since this effort would be largely outside the scope of the current program, and the oxygen enhanced low NOx burner approach is the most promising approach it was decided that the remaining resources for this task will be refocused on the burner effort.

C.4. OTM Materials Development (Task 2.1) Results and Discussion

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.

C.5. OTM Element Development (Task 2.2) Results and Discussion

Element development trials resulted in disks and tubes that sinter to ~86% theoretical density. The desired density is > 95% of the theoretical. PSO1 elements were manufactured according to the high-pressure permeation tester specifications and a minimum of six (6) were delivered each month. Sintering optimization of elements has been ongoing. 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. Manufacturing optimization will continue next quarter.

C.6. OTM Process Development (Task 2.3) Results and Discussion

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. This study is still in progress, however, 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. Flux performance under a helium purge currently is in progress. Complete results from this study will be included in the next quarterly report.

As described above, significant progress has been made in OTM Process Development. The single tube reactor was assembled and is now in operation. The production of oxygen with a purity better than 99.5% was demonstrated for 150 hours. Testing of an architecturally modified PSO1 element is in progress with promising preliminary oxygen flux results of 50% of the commercial target flux. Process development optimization will continue next quarter.

C.7. Program Management (Task 4) Results and Discussion

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 among combustion team members were held in November and December 2000.
- Accounts have been established within the Praxair accounting system to track labor hours and costs. Monitoring of these accounts is 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 will be held May 23, 2001 at the US DOE and on May 31, 2001 at REI.

C. Conclusion

Significant progress was made in all tasks toward achieving the DOE NOx program objectives. In Task 1.1.1 modeling oxygen-enhance combustion in the Keystone boiler was completed. Results indicated that boiler modifications were necessary to prevent increased unburned coal, NOx and CO emissions with addition of oxygen in the furnace. L1500 pilot-scale combustion facility simulations are ongoing and complete results will be reported next quarter. In Task 1.1.2, laboratory-scale parametric testing results showed significant NOx emissions reduction (30-40%) with modest oxygen addition. Lab-scale testing will continue next quarter. In Task 1.2, the hot oxygen burner was run successfully utilizing a solid fuel. Calculations were performed that determined that, although technically feasible, the modifications required to ensure the process was economically attractive would require significant experimentation. In 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. Modified PSO1 composition characterization will continue next quarter. In Task 2.2, element fabrication and sintering optimization is ongoing resulting in manufacturing and delivery of a minimum of six PSO1 elements each month. In Task 2.3, the production of oxygen with purity better than 99.5% was demonstrated testing in the single-tube high pressure permeation test facility. Preliminary test data of a thin-walled dense architecturally modified PSO1 element suggests that the average oxygen flux at 1000ºC under no purge conditions is 50% of target flux. Complete results will be reported next quarter.

D. References

1. Thompson et. al, “Oxygen Enhanced Combustion for NOx Control”, Quarterly Technical Progress Report for US DOE Award No. DE-FC26-00NT40756, January 2001

2. Thompson et. al, “Oxygen Enhanced Combustion for NOx Control”, Quarterly Technical Progress Report for US DOE Award No. DE-FC26-00NT40756, July 2000

3. Thompson et. al, “Oxygen Enhanced Combustion for NOx Control”, Quarterly Technical Progress Report for US DOE Award No. DE-FC26-00NT40756, October 2000