OXYGEN ENHANCED COMBUSTION **FOR NO_x CONTROL**

QUARTERLY TECHNICAL PROGRESS REPORT

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for the Program through the fourth quarter January-March 2002 in the following task areas: Task 1 - Oxygen Enhanced Combustion, Task 2 - Oxygen Transport Membranes, Task 3 - Economic Evaluation 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 second year. The first round of pilot scale testing with 3 bituminous coals was completed at the University of Utah.

Full-scale testing equipment is in place and experiments are underway.

Coal combustion lab-scale testing was completed at the University of Arizona. Modest oxygen enhancement resulted in NO_x emissions reduction.

Combustion modeling activities continued with pilot-scale combustion test furnace simulations.

75% of target oxygen flux was demonstrated with small PSO1 tube in Praxair's single tube high-pressure test facility. The production of oxygen with a purity of better than 99.999% was demonstrated.

Economic evaluation has confirmed the advantage of oxygen-enhanced combustion. Two potential host sites have been identified.

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A. 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 NO_x reduction to less than that of 0.15lb/MMBtu for boilers and coal. This program will develop both oxygen based low NO_x 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 second year of the program focused on all four tasks. Task 1 work consisted of laboratory-scale, pilot-scale and full-scale testing and computer modeling used to better understand the fundamentals of oxygen for NO_x emissions control and to illustrate the benefit of oxygen addition to low NO_x coal firing systems. Task 2 work focused on the optimization and testing of an OTM system for use with the proposed technologies. Task 3 work confirmed the advantages of oxygen enhancement and identified target boiler utilities. The major objectives and accomplishments of the second year of the program are summarized in Table 1 below.

Table 1. Major Program Objectives for Year 2 - "Oxygen Enhanced Combustion for NO_x Control"

ID	Task	Milestone	Accomplishments
4	1.1.2	Lab-scale experiments complete	Lab-scale experiments complete
5	1.2	Hot oxygen and coherent jet tests complete	Hot oxygen and coherent jet tests complete
6	1.3.1	Pilot-scale testing of staged combustion complete	First round of pilot-scale testing of staged combustion on 3 bituminous coals complete
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	Two weeks of burner testing at full scale complete
14	2.1.2	Optimization of OTM material complete	Optimization of OTM material PSO1 and PSO1d in progress
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
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 underway
35	4.1	Program review meetings	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; Teleconferences conducted throughout the year for combustion review

B. Experimental Methods

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

Computational fluid dynamic (CFD) modeling activities were performed by Reaction Engineering International (REI) for Praxair's United States Department of Energy (US DOE) program entitled "Oxygen Enhanced Coal Combustion for NO_x Control". The objective of this work was to illustrate the benefit of oxygen addition to low NO_x coal firing systems. Simulations performed during the last reporting period were designed to evaluate the effectiveness of oxygen enhanced low NO_x burners in a full-scale unit.

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 NO_x formation and on the standoff distance of coal flames using a down-fired combustor which was previously described in the first quarterly report ¹. Staged combustion experiments with oxygen enriched atmosphere were completed.

B.3. Pilot-Scale Testing (Task 1.3) Experimental Methods

The objective of this task is to demonstrate the effectiveness of oxygen enhanced combustion for NO_x control on a typical wall-fired burner configuration. During the last year significant work was done to explore the impact of adding oxygen to a typical wall-fired burner. The testing took place at the L1500 facility at the University of Utah. 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. A major objective of this combustion facility is to study pollutant formation and control, and carbon utilization in a system that imitates the thermal history of operating commercial coal-fired-boilers. Additional pilot-scale furnace details may be found in the fifth quarterly report ².

B.4. Full-Scale Testing (Task 1.4) Experimental Methods

The objective of this task is to design a conceptual oxygen enhanced secondary NO_x 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 NO_x firing systems using a well characterized single burner test facility and a commercial burner.

Two separate test campaigns were performed using Alstom Power's Industrial Boiler Simulation Facility (ISBF). 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' RSFC burner, Alstom's commercial low NO_x 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.

B.5. 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. Efforts this year focused on optimization of OTM mechanical and electrochemical properties required for commercial use via improved processing and improved compositions. Specifically, work focused on the further 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.

B.6. 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 ¹. PSO1 or 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 in preparation of commercial scale-up.

B.7. 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. Details of the design and operation of the single tube high-pressure permeation test facility can be found in the second and third quarterly reports ^{4,5}.

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

C. Results and Discussion

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

During the last quarter REI used one of their existing coal fired utility boiler models to explore the effect of oxygen enhanced combustion under staged conditions on NO_x and LOI emissions. The burners in this particular unit were slightly different than those explored experimentally to date, with different coal spreader concepts used. Thus one goal of the modeling was to evaluate whether oxygen would work even with a different burner type that those explored experimentally. A number of oxygen injection techniques were explored.

The results from these calculations show significant NO_x reduction with oxygen addition, depending on how oxygen is added and the amount of oxygen used. These results are comparable to those seen from both the University of Utah results and the Alstom Power results. These data also suggest the coal spreader type has very little effect on the calculated NO_x reduction. This suggests that the concept is fairly robust and burner independent.

In the next quarter REI will continue modeling other burners and boilers to explore the effect of oxygen injection on NO_x formation, and LOI.

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

During the second year of the program several experiments were performed at the University of Arizona to explore the impact of oxygen addition on NO_x control. In the test series an older sample of an Illinois No. 6 coal was used. As would be expected for two coals from the same seam, both coals were generally similar; however, some differences were noted between the two data sets. The largest difference seems to be the lack of any discernable impact of oxygen addition on NO_x emissions, which is in contrast to data from Year 1 which indicated a clear impact of oxygen addition. One potentially confounding influence is the potential for reburning in the second stage as discussed in earlier reports. When the impact of this effect is removed, the data suggest that in most cases oxygen addition significantly reduces NO_x emissions.

The laboratory-scale testing task of this program was completed this year.

C.3. Pilot-Scale Testing (Task 1.3) Results and Discussion

The program coal, Illinois No. 6, and two other bituminous coals, Illinois No. 5 and Utah, were used in the University of Utah's experiments to optimize the O₂ injection strategy in the L1500, a typical wall fired burner. The experiments ranged from simple oxygen addition with various injection strategies under the 'baseline' burner configurations to more detailed optimization for swirl at each burner stoichiometry. For a consistent basis of comparison between coal data a curve fit was made to describe the baseline air as a function of both first stage stoichiometric ratio (SR) and the wall temperature. From this data almost all oxygen addition methods and replacement rates tried yielded significant reductions in NO_x emissions. Reductions in NO_x emissions ranged from 18-37%, with one condition achieving <120 ppm (corrected to 3% O₂) with small amounts of oxygen addition. These experiments demonstrated that oxygen enhanced combustion can lead to significantly lower NO_x emissions, with some conditions leading to NO_x emissions well below the 0.15 lb/MMBtu limit even under commercially viable staging conditions. Finally all of the experimental results are consistent with both the theory and the CFD modeling, enhancing the confidence in the results. Based on the similarity of these results and the full-scale testing described below, additional work is now planned for the University of Utah.

C.4. Full-Scale Testing (Task 1.4) Results and Discussion

In the first full-scale test campaign, denoted Phase I, the Illinois No. 6 coal was used to demonstrate the concept with a full-scale commercial burner. Initial tests were performed to shake down the furnace and to obtain baseline NO_x data for this facility, burner, and coal combination. A series of experiments were then performed to explore the effect of oxygen addition on NO_x emissions.

In the second test campaign, denoted Phase II, selected experiments were repeated with the Illinois NO. 6 coal. An eastern bituminous coal, the Mingo Logan, was then used to evaluate both the effect of a lower volatile coal and the effect of oxygen addition method.

Data from the Illinois No. 6 experiments show that even when the baseline (air only) emissions are very low oxygen addition can drive the NO_x emissions even further. The data further show that the reductions are relatively independent of the initial NO_x concentration. These data are very comparable both qualitatively and quantitatively to those reported earlier from the University of Utah. Data from the Mingo Logan experiments show that the concept works even with the lower volatile coal, and how the oxygen is mixed has a large impact on NO_x reduction.

One final test campaign is scheduled for the next quarter. This test period will use a PRB coal to explore the effect of coal type on NO_x emissions with oxygen addition.

C.5. OTM Materials Development (Task 2.1) Results and Discussion

Work has been ongoing to optimize process conditions and material composition to enhance mechanical properties and reduce creep for commercial robustness. Sintering behavior and chemical interaction of modified PSO1 compositions were investigated.

Creep measurements performed on modified PSO1d compositions show improvement over PSO1. Two modified compositions have 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.

The OTM materials development task of this program was completed this year.

C.6. OTM Element Development (Task 2.2) Results and Discussion

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.

Powder optimization will continue next quarter. Another new element design will be investigated using PSO1d composition.

C.7. OTM Process Development (Task 2.3) Results and Discussion

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

The year 2 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 950°C than at 900°C 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 900°C. 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 as detailed in the sixth quarterly report ⁶.

Future OTM process development work will focus on element thermal cycling and enhancement of oxygen flux by architecture modifications.

C.8. Economic Evaluation (Task 3) Results and Discussion

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

The market segmentation was completed with target boiler utilities identified. Two potential host sites have also been identified.

C.9. Program Management (Task 4) Results and Discussion

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

- 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.
- Teleconferences were held among combustion team members throughout the year.
- 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 quarterly technical progress reports and financial status reports.

D. Conclusion

Significant progress was made in all tasks toward achieving the DOE NO_x program objectives.

Oxygen Enhanced Combustion Tasks:

The first round of pilot scale testing with 3 bituminous coals was completed at the University of Utah. These experiments demonstrated that oxygen enhanced combustion can lead to significantly lower NO_x emissions, with some conditions leading to NO_x emissions well below the 0.15 lb/MMBtu limit even under commercially viable staging conditions. These experimental results are consistent with both the theory and the CFD modeling. The laboratory-scale testing was completed this year and data from this testing also suggest that in most cases oxygen addition significantly reduces NO_x emissions. Phase I and Phase II of the full-scale test campaign were completed and the data are comparable both qualitatively and quantitatively to the pilot-scale data. One final test campaign is planned for the full-scale test facility next quarter. Additional work is now planned for the pilot-scale reactor.

Oxygen Transport Membrane Tasks:

75% of target oxygen flux was demonstrated with a small PSO1 tube in Praxair's single tube high-pressure test facility. The production of oxygen with a purity of better than 99.999% was demonstrated with a dense PSO1d tube. A dense modified PSO1 composition element underwent eight full thermal cycles to 900°C. Material and process optimization progressed, with improvements observed in creep resistance and burst strength of PSO1d. Process optimization will continue and new element design and architecture will be investigated next quarter.

Economic Evaluation:

The advantage of oxygen enhancement versus SCR/SNCR was confirmed with utilities. Based on pilot-scales tests and commercial burner performance tests, the economic advantage of oxygen enhancement was confirmed. Also, market segmentation was completed with target utilities and boilers identified. Two host sites have also been identified.

E. References

1. Thompson et. al, "Oxygen Enhanced Combustion for NO_x Control", Quarterly Technical Progress Report for US DOE Award No. DE-FC26-00NT40756, July 2000
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4. Thompson et. al, "Oxygen Enhanced Combustion for NO_x Control", Quarterly Technical Progress Report for US DOE Award No. DE-FC26-00NT40756, October 2000
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