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 first quarter April – June 2000 in the following task areas:

Task 1 Oxygen Enhanced Coal Combustion

Task 2 Oxygen Transport Membranes

Task 4 Program Management

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A. Introduction

Increased environmental regulations will require utility boilers to reduce NO_x emissions to less than 0.15lb/MMBtu in the near term. Conventional technologies such as Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) are unable to achieve these lowered emission levels without substantially higher costs and major operating problems. Oxygen enhanced combustion is a novel technology that allows utilities to meet the NO_x emission requirements without the operational problems that occur with SCR and SNCR. Furthermore, oxygen enhanced combustion can achieve these NO_x limits at costs lower than conventional technologies. 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 0.15lb/MMBtu for a wide range of boilers and coal.

The oxygen enhanced coal combustion program (Task 1) focussed this quarter on the specific objective of exploration of the impact of oxygen enrichment on NO_x formation utilizing small-scale combustors for parametric testing. Research efforts toward understanding any limitations to the applicability of the technology to different burners and fuels such as different types of coal are underway.

The objective of the oxygen transport membrane (OTM) materials development program (Task 2.1) is to ascertain a suitable material composition that can be fabricated into dense tubes capable of producing the target oxygen flux under the operating conditions. This requires that the material have sufficient oxygen permeation resulting from high oxygen ion conductivity, high electronic conductivity and high oxygen surface exchange rate.

The OTM element development program (Task 2.2) objective is to develop, fabricate and characterize OTM elements for laboratory and pilot reactors utilizing quality control parameters to ensure reproducibility and superior performance. A specific goal is to achieve a material that will sinter to desired density without compromising other variables such as reaction to binder systems or phase purity.

Oxygen-enhanced combustion requires a facility which is capable of supplying high purity oxygen (>99.5%) at low costs. This goal can be achieved through the thermal integration of high temperature air separation with ceramic OTM. The objective of the OTM process development program (Task 2.3) is to demonstrate successfully the program objectives on a lab-scale single OTM tube reactor under process conditions comparable to those of an optimum large-scale oxygen facility.

B. Executive Summary

During the reporting period the efforts under Task 1 focussed primarily on procuring, fabricating, and testing the experimental equipment to be used in this program. The down-fired combustor at the University of Arizona underwent refurbishing in preparation for the upcoming parametric tests (Task 1.1.2). The test equipment for combustion tests at Praxair (Task 1.2) was designed and required parts procured. Finally, a suitable test coal for the program was selected and will be procured and prepared by Alstom Power. Combustion experiments at both the University of Arizona and Praxair are planned for the next quarter. Modeling at REI is also planned for the next quarter.

Regarding OTM materials development program (Task 2.1), a candidate OTM 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 discs at 1000°C using a helium purge gas and air feed gas. In the first quarter of this program the thermo-mechanical stability of PSO1 was determined. Apparatus to determine oxygen diffusion and surface exchange rates, oxygen flux and creep rates were designed and construction is underway. Initial results indicate that the mechanical strength and creep resistance of PSO1 need to be improved to meet commercial targets. Efforts are underway to fully interpret the results and develop processing routes or new materials to improve properties. It is expected that a thinner membrane will be required in order to produce sufficient oxygen flux.

Activities are under way in the OTM element development program (Task 2.2) to develop OTM tubes. These activities may be divided into the following categories: Characterization and testing of incoming powders or Powder Quality Control; mixing of the powders into a workable paste; tube formation; sintering of the tubes; and tube characterization or Tube Quality Control. Pressing, extrusion and sintering trials of the lead candidate material PSO1 resulted in disks and tubes sintered to 86 % of theoretical density, where >95% of theoretical density is the desired value. A finer particle size PSO1 will be tested next quarter. Mixing and extrusion trials of PSO1 are in the preliminary stages.

Significant progress was made in the first quarter for OTM process development (Task 2.3). The single-tube test facility is near completion, and will be operational next quarter. Four dense OTM tubes (1 mm thick) have been tested as potential candidates for this program. Flux performance on dense membranes still needs to be improved and OTM modifications will take place next quarter.

Program management (Task 4) is on track since the Program team member kick-off meeting on April 4, 2000 and the Program kick-off meeting with the US DOE on April 18, 2000. Two sub-contracts have been executed, and a third sub-contract has been drafted. Project documentation has been prepared and delivered to the US DOE in accordance with the cooperative agreement.

C. Experimental Data

C.1. Oxygen Enhanced Coal Combustion Program (Task 1) Experimental Data

C.1.1. Facilities and Equipment

Before initiating either the parametric evaluation (Task 1.1.2) or the oxygen-based injector design and testing (Task 1.2) several pieces of experimental equipment had to be either fabricated or refurbished. These components included the down-fired combustor at the University of Arizona, flow measurement equipment at Praxair, and the experimental device for the oxygen enhanced coal reburning testing. The goal of the fabrication and refurbishment efforts was to ensure that the equipment operates safely and effectively, and to ensure that the data collected is both representative and reliable.

During May and June the upper and middle sections of the down-fired combustor at the University of Arizona, shown in Figure 1, were dismantled and rebuilt. The lining of the middle section was replaced, and the entire upper section was rebuilt. New sample ports, in the same location as the existing ports, were installed. The rebuilt was required to prevent air in-leakage into the furnace to allow better furnace control under fuel rich combustion conditions. The rebuilt system was also designed to minimize slagging on the walls. Reconstruction of the furnace was completed on June 29. A shakedown experiment was performed using natural gas as the fuel after construction was complete.

For the oxygen-based injector design and testing several pieces of equipment had to be fabricated, purchased, or identified from existing experimental equipment. First, fabrication was begun on a water-cooled pitot tube table. This table consists of a 2 axis mount holding a pitot tube and a rail system that allows the 2 axis mount to be moved along the third axis. An identical assembly, which has been used extensively to characterize various types of jets, is being used as a pattern. Conflicts with previously scheduled experiments preclude use of the existing system in the current program.

Figure 1. Down-fired Combustor at the University of Arizona

A jet device to deliver natural gas into the center of large boilers was also identified and procured during the last quarter. This small-scale device, capable of delivering approximately 400 scfh of natural gas, was fabricated as part of an earlier program and will be available for testing in this program.

Test equipment for the oxygen-enhanced coal-based reburning was also acquired during this timeframe. The basic test equipment consists of a novel burner that is mounted on a refractory lined steel can, approximately 4 feet long and 12 inches in diameter. An Accurate powder feeder was purchased feed coal to the burner, and new refractory liners were purchased for the steel can. A series of shakedown experiments were performed with the system. In addition, a particle probe, based on a design used in earlier US DOE programs¹ was fabricated. This probe will be used to collect particulate samples from the outlet of the can to determine the degree of devolatilization.

C.1.2. Coal Selection

One of the goals of this program is to develop effective NO_x control technologies that can be rapidly introduced to the market. One way to facilitate use of the technology in the market is to use conventionally available coals during the development process. For this program two coals were selected, based on discussions with one of the Utility Advisory Panel members. The first is a low sulfur subbituminous coal. The second is a high sulfur bituminous coal.

Samples of each coal will be procured and prepared by Alstom power and distributed to the University of Arizona and REI. Although both coals will be used in the parametric studies, time and resource constraints may limit the pilot-scale testing to a single coal. Prior to the large scale testing one of the two coals will be selected for the large-scale tests and a new sample will be procured from the mine. Although the ideal case would be to use exactly the same coal sample in the large-scale test as was used in the smaller-scales, the requirement to store large quantities of coal on site, along with weathering concerns for the coal, make this option unattractive. Instead, a second coal sample will be obtained from the same mine. Although variations will exist between the earlier coal samples and the later coal samples, obtaining the coal from the same coal mine will help limit the variability.

C.2. OTM Materials Development (Task 2.1) Experimental Data

C.2.1. Flux testing

A permeation cell for measuring the oxygen flux of discs 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 disc 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. A new permeation cell is being constructed as part of a separate Praxair program but will be available for use in this program.

C.2.2. Mechanical Testing

A commercially available unit is 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].

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

C.2.3. 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.

C.2.4. Creep Measurements

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

C.3. OTM Element Development (Task 2.2) Experimental Data

C.3.1. Experimental Apparatus and Activities:

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
- Microtrac - 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.

C.4. OTM Process Development (Task 2.3) Experimental Data

C.4.1. Single-Tube Reactor Experimental Design

The OTM single tube test facility has been constructed. A three-zone furnace is used to heat the OTM to the operating temperature, between 800 and 1050°C. The process consists of a gas manifold that delivers oxygen, nitrogen, air, and mixtures thereof to the OTM. Backpressure regulators are used to control the pressure both at the air side and at the oxygen product side of the membrane. A paramagnetic oxygen analyzer is used to determine the level of oxygen depletion from the air stream and the oxygen product purity.

The flux of oxygen through the OTM tube, J_{O_2} , is determined using Equation [2]:

$$J_{O_2} = \frac{y_{O_2} F_{purge}}{A_{OTM}} \quad \text{Equation [2]}$$

where:

J_{O_2} = Average oxygen flux (sccm/cm²)

y_{O_2} = Oxygen mole fraction in the purge gas as measured by the oxygen analyzer

F_{purge} = Volumetric flow rate of the purge gas as measured by the Flowmeter

A_{OTM} = OTM Area (cm²)

C.4.2. Dense Ceramic OTM Membranes

Four dense OTM tubes (1 mm thick) have been tested as potential candidates for this program ^[2-5]: PSO1a, PSO1b, PSO2a, and PSO3a. PSO3a achieved the highest flux at 900°C.

D. Results and Discussion

D.1. Oxygen Enhanced Coal Combustion Program (Task 1) Results and Discussion

D.1.1. Shakedown experiments with down-fired combustor

After the reconstruction of the furnace was completed a shakedown test was performed on the system. The furnace was heated on natural gas and air until the furnace temperature was similar to the planned experiments. No discrepancies were reported.

D.1.2. Shakedown experiments with oxygen-enhanced coal reburn equipment

Several experiments were performed with the oxygen-enhanced coal-reburn equipment to ensure that the burner could be operated safely. First a set of experiments were made to assess the impact of feeding transport air into the burner portion. As expected, the data suggests feeding significant amounts of transport air would adversely affect the burner performance. Second, experiments were made to ensure that the burner could operate safely at much lower gas flowrates that it was originally designed for. These tests showed that the burner could easily operate at the lower flowrates. In fact, some operational problems, such as noise from the burner, were actually avoided by operating at the lower flowrates.

D.2. OTM Materials Development (Task 2.1) Results and Discussion

Permeation measurements were performed at 900°C for a dense PSO1 disk. The effect of thermally cycling PSO1 through the phase transition temperature was investigated by cooling and re-heating the sample between 200°C and 900°C and measuring the oxygen flux after repeated cycles at 900°C. The flux is not affected by thermal cycling, however, the leak rate systematically increased. Post mortem inspection of the sample showed a large crack in the sample. In this case the sample was constrained by seals on both sides of the membrane. A single seal design may prevent this fracture of the OTM. However, this result indicates a detailed study of thermal cycling of PSO1 is required before larger scale manufacturing occurs.

For commercial robustness, it is desirable to increase the mechanical strength of PSO1. Tests completed on different perovskites systems conducted outside of this program produced four point bend strengths of the order twice that of PSO1. Improved processing routes are expected to improve the strength. Creep measurements performed at 1000°C indicate a high creep rate for PSO1. This may be due in part to liquid phases at the grain boundaries. Further work is ongoing to optimize process conditions and material composition to enhance mechanical properties and reduce creep.

Thermal expansion measurements show the large non-linearity of PSO1 in the phase transition temperature range, which is undesirable. Modification to the composition can remove this transition.

D.3. OTM Element Development (Task 2.2) Results and Discussion

D.3.1. Powder Specifications:

Element development trials have resulted in disks and tubes that sinter to ~86% theoretical density. Our desired density is > 95% of the theoretical. Discussions with the powder manufacturer (Praxair Specialty Ceramics) on this subject indicate that a finer material with higher surface area is required. This new "super-grind" PSO1 was received and will be tested next quarter. A process of tightening up and locking in a standard PSO1 specification is expected in the next quarter. The powder optimization will involve changing process variables such as the calcination temperature. Our goal is to achieve a material that will sinter to desired density without compromising other variables such as reaction to binder systems or phase purity.

D.3.2. Mixing & Production:

Surprising results were encountered in the trial PSO1 mixing and production runs. A reaction was initially expected between the powder and binder system, however all mixing trials indicated that any reaction if present was negligible.

The mixing and production trials using binder and PSO1 are in the preliminary stage. This is compounded by the use of new equipment. The most noteworthy problem is that of air pockets seen on the surface of the extruded tubes. Optimization of OTM tube development will continue.

D.4. OTM Process Development (Task 2.3) Results and Discussion

The procurement and fabrication of the single tube OTM test facility was completed this quarter. A new reactor and seal assembly will be tested next quarter.

In order for the OTM process to be economically competitive with cryogenic O₂ production or vacuum pressure swing adsorption (VPSA), the OTM area (and subsequently, the number of OTM tubes) must be minimized to the greatest extent possible. Also, a high O₂ flux is desired. Four dense OTM tubes (1 mm thick) have been tested as potential candidates for this program^[2-5]: PSO1a, PSO1b, PSO2a, and PSO3a. The flux data for these 4 tubes has been obtained at 900°C, a 20.9% inlet O₂ mole fraction, and a helium purge. PSO3a achieved the highest flux at 900°C, but still needs improvement to reach the commercial target. Reducing the membrane thickness is one method for improving the flux. If the thickness were reduced, the flux would increase substantially, because the O²⁻ ions would be transported across a shorter distance. However, the mechanical stability would be compromised greatly at a smaller tube thickness. Improved structural design is necessary to enhance the mechanical integrity of a thinner membrane for our application.

D.5. Program Management (Task 4) Results and Discussion

The Program Management highlights for the first of the quarter 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 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 and the University of Missouri, Rolla.
- A draft sub-contract has been submitted to Alstom Power.
- Accounts have been established within the Praxair accounting system to track labor hours and costs.
- The Hazardous Substance Plan was submitted to the US DOE.
- The request for an Advance Waiver of Patents has been submitted to the US DOE.

E. Conclusion

Significant progress has been made toward US DOE NO_x program objectives in the first quarter. The experimental portion of Tasks 1.1 and 1.2 are proceeding as planned. The furnace rebuild is complete at the University of Arizona, and the equipment is ready for use in the coming months. Test equipment for the oxygen-enhanced coal-based reburning concept has been assembled and preliminary shakedown tests completed. This equipment is ready for use in the coming quarter.

In the next quarter a number of parametric experiments will be performed at the University of Arizona. These experiments should provide key information on the effectiveness of the general concept of oxygen enhanced combustion for Low NO_x burners as a means of lowering NO_x emissions. Experiments will also be performed at the Praxair site in Tarrytown, NY to evaluate the effectiveness of the oxygen enhanced coal-based reburning concept. Computational Fluid Dynamics (CFD) modeling under Task 1.1.1 will also begin in the next quarter.

Task 2.1 OTM materials development is on schedule. Flux measurements conducted at ambient pressure on disc specimens indicate that a thinner membrane is required to achieve the commercial flux target. Modification of the PSO1 composition has produced significant fluxes at temperatures less than 850°C, but have not produced a substantial increase in the oxygen flux at temperatures greater than 900°C. Therefore either an improved materials system with greater oxygen ion conductivity needs to be developed, or the use of thinner membranes is required in order to meet the flux targets.

Efforts need to focus on identifying materials that have improved mechanical and thermo-mechanical properties or improving the structural design of the thinner membrane to maintain its mechanical integrity under high temperature and high pressure applications.

In the next quarter material characterization efforts will focus on materials with high flux and no phase transition, as well as with improved creep resistance. Fabrication and initial operation of new permeation test apparatus will be conducted. A simple creep test facility that will increase the number of specimens to be examined will be designed and constructed.

Considerable progress has been made in the OTM element development work of Task 2.2. Powder quality control, mixing, element production and tube quality control methods are in place. PSO1 density falls >9 % short of the desired density, therefore, sintering work will continue using a PSO1 powder exhibiting a finer particle size distribution. Mixing and production trials using binder and PSO1 for OTM tube optimization will continue.

OTM process development work in Task 2.3 is on schedule. The single-tube test facility is near completion, and will be operational in the next quarter. The process development for the DOE-NO_x program is at schedule. The OTM single-tube test facility has been constructed and will be operational in the next quarter. This will allow the study of OTM performance under higher absolute pressure differences. The seal assembly was delivered and currently is being Alonized™.

F. References

1. Helble et. al, "Transformations of Inorganic Coal Constituents in Combustion Systems", Final Report for US DOE Contract DE-AC22-86PC90751, 1992
2. Makuch, D.M. and B.A. van Hassel, Internal Praxair Report, 2000.
3. Ibid
4. Ibid
5. Ibid