ADVANCED OXYFUEL BOILERS AND PROCESS HEATERS FOR COST EFFECTIVE CO_2 CAPTURE AND SEQUESTRATION

ANNUAL TECHNICAL PROGRESS REPORT

For Reporting Period Starting January 1, 2005 and Ending December 31, 2005

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ABSTRACT:

This annual technical progress report summarizes the work accomplished during the third year of the program, January-December 2005, in the following task areas: Task 1 – Conceptual Design, Task 2 – Laboratory Scale Evaluations, Task 3 – OTM Development, Task 4 - Economic Evaluation and Commercialization Planning and Task 5 - Program Management.

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A. Executive summary

The primary objective of this program is to determine the feasibility of integrating Oxygen Transport Membranes (OTM) into combustion processes such as industrial boilers or process heaters. The aim is develop a novel oxy-fuel combustion process that will significantly reduce the complexity CO_2 capture and reduce the cost of carbon sequestration to less that $10/ton.

The breakdown of the program work consists of the following five major tasks; work carried out in 2005 is summarized on a task per task basis below:

Task 1: Conceptual Design
Task 2: Laboratory Scale Evaluation
Task 3: OTM Development
Task 4: Economic Evaluation and Commercialization Planning
Task 5: Program Management

In Task 1, ALSTOM Power developed conceptual designs for an OTM combustor in a 100,000 lb.hr-1 steam boiler. OTM tubes are inter-dispersed with steam tubes in such a manner that that the OTM element temperatures are controlled to within the targeted operating range of 900-1100°C.

In task 2, Praxair commissioned two single-tube OTM reactors and a multi-tube OTM reactor that operates on natural gas fuel. Praxair developed and demonstrated a robust oxygen transport membrane material that is suitable for separating oxygen from air while making the oxygen available to support a combustion process. In excess of 12,000 hrs of failure free membrane operation has been demonstrated, the reliability of the membranes is seen as a significant achievement. The transport rates for oxygen flux through the ceramic membranes have shown steady improvement throughout the year. The current status is that OTM elements achieve ~50% of the target oxygen flux with H_2/CO_2 mixtures at high fuel utilization and ~30% of the oxygen flux target with CO/CO_2 gas mixtures at low fuel utilization. Complete combustion of methane and natural gas has been demonstrated in the multi-tube reactor. At complete combustion the measured oxygen flux was only 10-20% of target however the dried exhaust gas contained only CO_2 and a small amount of residual O_2. Both material, membrane architecture and process development options have been identified as a path forward to drive-up the O_2 transport rates to target values.

The ceramic OTM membranes are developed in Task 3. During 2005, materials selection was finalized and work focused on the development of manufacturing techniques that resulted in membrane architectures that retained mechanical reliability whilst improving oxygen flux. Work focused on providing the appropriate level of porosity in the membrane support tube and reducing the resistance to oxygen ion transport through the membrane gas separation layer.

A preliminary economic analysis of the Advanced Boiler concept was undertaken in Task 4, pending the results of design work being carried out by ALSTOM Power.

Results and Discussion

B.1 Conceptual Design (Task 1)

ALSTOM Power developed conceptual designs of the combustor for an advanced boiler that generates 100,000 lbs/hr of steam with natural gas as the fuel. The conceptual designs are based on arranging the OTM elements between steam tubes in such a way that the temperature of the OTM elements is maintained between 900-1100°C by both convective and radiative heat transfer to the steam tubes. Important design parameters were the OTM tube diameter and length, steam tube diameter, the need for extended surface area on steam tubes and the spacing of the OTM and steam tubes. ALSTOM Power down-selected one conceptual design, a detailed cost estimate of an industrial boiler based on the down-selected OTM-combustor concept shall be completed by the second quarter of the 2006 calendar year. An important design consideration in the conceptual design task for the boiler is fuel flexibility and how coal combustion would be facilitated in such an OTM boiler. Design considerations for OTM coal combustion have been included as Energy Policy Act (EPACT) data in a separate appendix to this report.

B.2 Laboratory scale evaluations (Task 2)

Oxygen flux measurements have been performed both on disc and tube samples. A photograph of a disc reactor is shown in Figure 1a. It consists of a split tube furnace in which the disc is being clamped between two tubes, as shown in Figure 1b. In each tube there is a lance tube that feeds the air and fuel to the opposite sides of the disc.

a)

b)

Figure 1, a) Experimental setup for disc reactor, b) Close-up of the actual disc reactor in which the OTM disc gets clamped between two tubes.

A single tube reactor is shown in Figure 2. The reactor consists of an Al_2O_3 tube partially contained within a split-tube furnace. An OTM tube, seal and gas manifold are supported inside the Al_2O_3 tube reactor shell at the mid-point of the furnace. A fuel gas mixture flows on one side of the membrane while air flows on the opposite side. The inlet and outlet gas composition are determined by means of gas chromatography and outlet flows are measured with mass flow meters and bubble flow meters. Single tube reactors are automated in order to facilitate data collection and reactor control.

Figure 2, Single tube reactor.

A schematic drawing of a multi tube reactor is shown in Figure 3; a photograph of the completed installation is shown in Figure 4. The multi-tube reactor is being used to determine how much fuel can be completely oxidized with six laboratory-scale OTM tubes. The reactor consists of a flue-gas generator, a mixing section for adding fuel to the simulated flue-gas and an OTM section in which the fuel is completely combusted with oxygen in order to form an exhaust gas that contains predominantly carbon dioxide and steam.

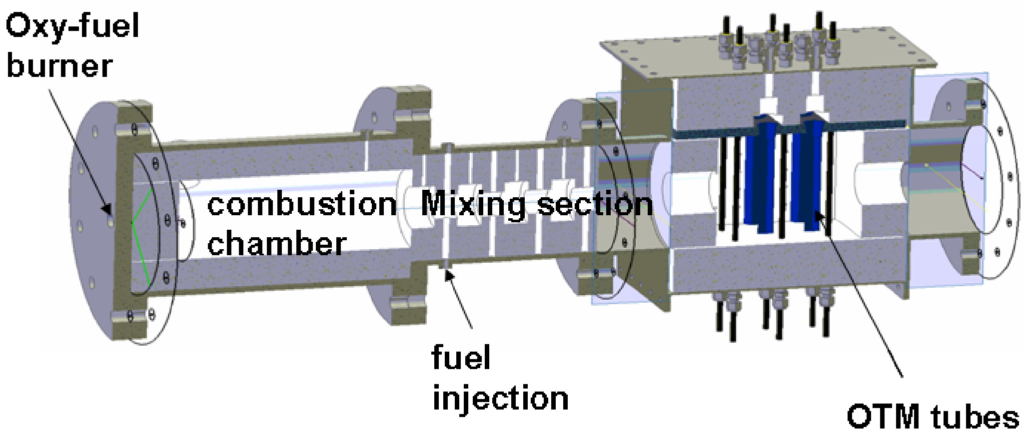

Figure 3, Schematic of the multi-tube reactor.

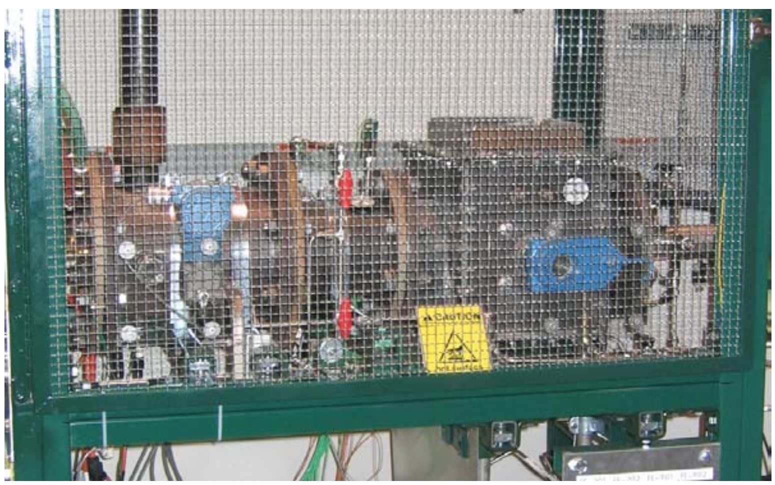

Figure 4, Photograph of the multi-tube reactor.

A change to the membrane architecture in order to improve the oxygen flux is usually first made to discs and if the change has the desired flux improvement then it is applied to tubes that are tested in single tube reactors. The technology is then transferred to R&D personnel located at the Praxair Surface Technologies site in Indianapolis. In Indianapolis, tubes are manufactured in a pilot-scale manufacturing facility as opposed to the Tonawanda laboratory and are subsequently returned to Tonawanda, NY for testing in the multi tube combustion reactor. This development process is illustrated in Table 1. Disc tests will always use the latest generation of membrane material and porous support but the fuel utilization is low due to the small membrane area. This makes the reported oxygen flux for disc higher than the reported oxygen flux for tubes as the fuel utilization in a single tube test is substantially higher. Once proven on discs, a new material or manufacturing methodology will be transferred to tubes and tested in single tube reactors. Finally, when proven in single tube reactors the technology is transferred to Indianapolis and a small series of tubes are manufactured for testing in the multi-tube reactor. The time for a technology change to pass though disc, single tube and finally multi-tube testing can be at least ¼ year. For that reason, the tubes tested in the multi-tube reactor never have the latest innovations that drive-up the oxygen flux and oxygen flux data from the multi-tube reactor are lower than that reported for single tube. Furthermore, the multi-tube reactor is used for complete combustion testing, there is often excess oxygen in the flue gas and therefore a much reduced driving force for oxygen transport as compared to single tube tests. This is a major contributor to the apparent discrepancy in flux observed between single tube reactor and multi-tube reactor test data.

Table 1, Development path from disc to multi-tube reactor.

	Disk	Single Tube Reactor	Multi-Tube Reactor
Materials	Latest	2nd Generation	1st Generation
Degree of Oxidation	Partial	Partial	Complete
O_2 Flux As % of Target	80%	60%	<20%

Oxygen flux measurements in single tube reactors initially showed an oxygen flux that was strongly dependent on temperature and well below the preliminary oxygen flux target. Some of the factors that contributed to this result were the composition of the membrane (chemical reaction with membrane support materials) and the membrane architecture (e.g. porous support porosity). Changes were made to both these variables along with many other parameters in order to manufacture membranes with substantially higher oxygen flux. The progress made in driving-up the rates of oxygen transport through the ceramic membrane structures is summarized in Figure 5.

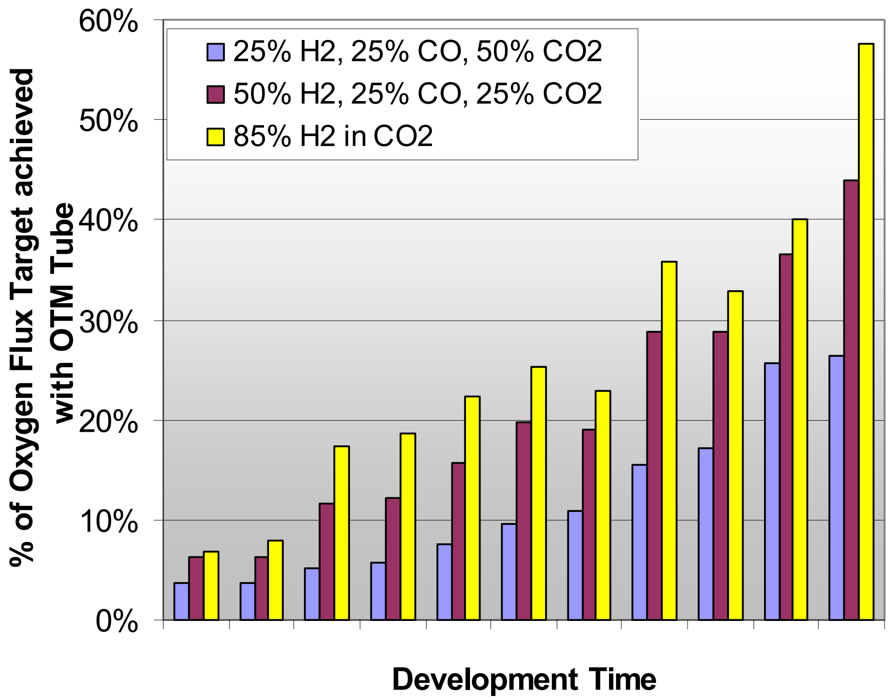

Figure 5, Oxygen flux improvement from 2004-2006 (Single tube reactor data).

The oxygen flux was measured with various fuel gas mixtures. The results are shown in Figure 6. A fuel with a significant amount of hydrogen yields a high oxygen flux as hydrogen is a fast diffusing molecule inside the porous support and burns easily with the oxygen that is permeating through the dense separation layer.

Figure 7 shows the performance of the oxygen transport membrane as a function of temperature and fuel gas composition. The fraction of the fuel that is oxidized at low temperature is small due to the low oxygen flux but this fraction increases substantially up to about 60% at 1000°C when using the H_2/CO_2 mixture with 85% hydrogen.

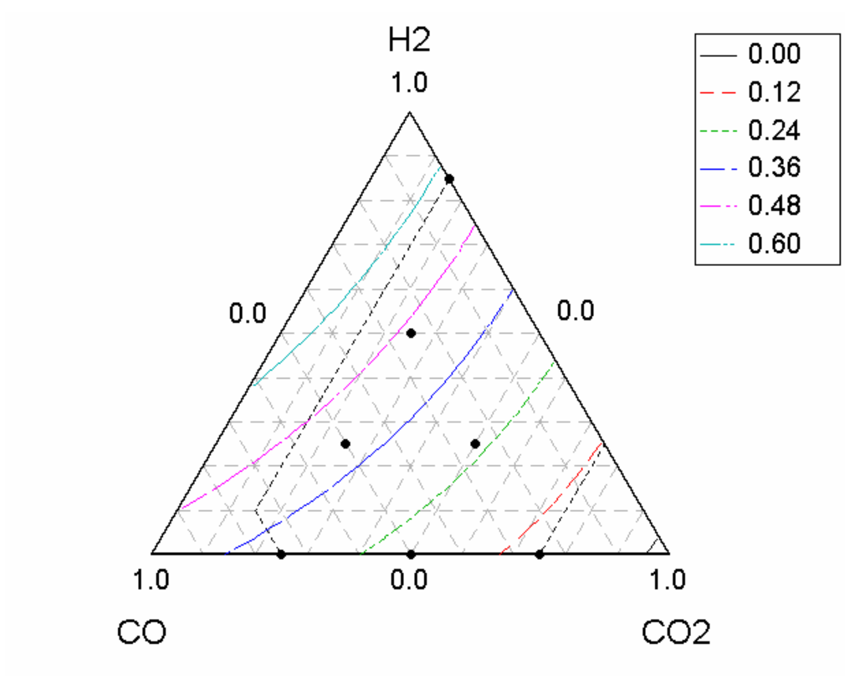

Figure 6, Mixture Contour plot of flux. Fraction of oxygen flux target versus fuel gas composition at a furnace set-point of 900°C.

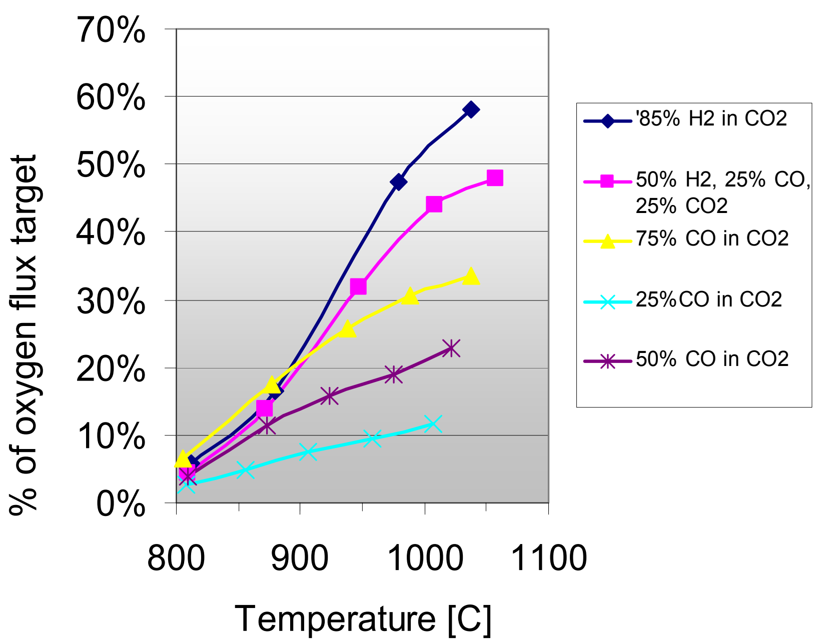

Figure 7, Oxygen flux versus temperature for various fuel gas mixtures, as measured in a single tube reactor.

Figure 7 shows that the oxygen flux through the current state-of-the-art oxygen transport membrane has a strong temperature dependence between 750-1000°C and then flattens off to almost temperature independent values of the oxygen flux. The explanation for this temperature dependence is that the oxygen flux through the membrane becomes mass transport limited in the porous support at high temperature. The porous support simply does not allow methane, hydrogen, or carbon monoxide to diffuse into the porous support towards the gas separation layer at a faster rate than the mass transport limit. The mass transport limited oxygen flux depends on the fuel gas composition due to differences in the effective molecular diffusion coefficient in the different gas mixtures.

Mass transport limitation is illustrated in Figure 8 for a case in which the porous support of the membrane is exposed to a mixture of H_2, CO, CH_4 and H_2O. Figure 8 shows diffusion of the reactants against their oxidation products (H_2O and CO_2). The mole fraction of the fuel gas species drops to near zero values at the interface between the porous support and gas separation layer due to the mass transport limitation.

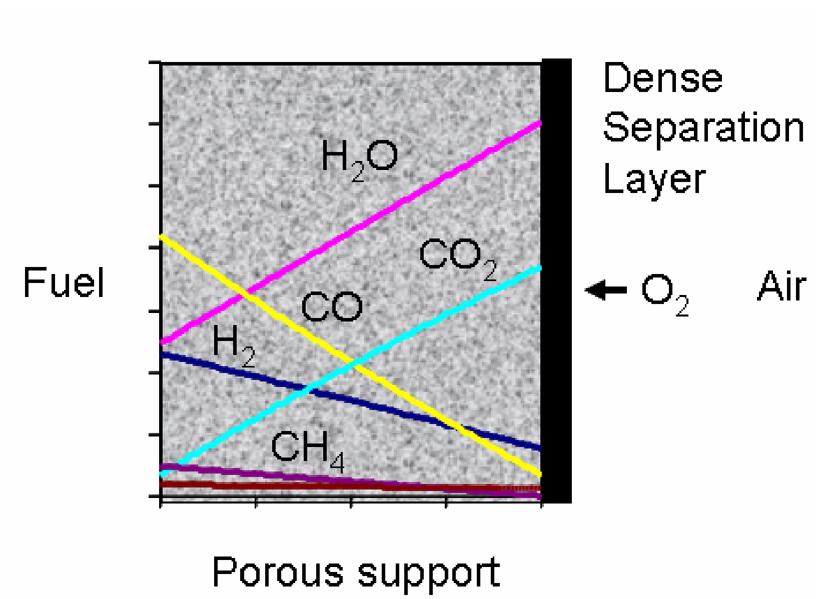

Figure 8, Mass transport limitation in porous support.

The mass transport limiting effect of the porous support is critical for stable operation of the OTM tubes in the boiler. It prevents the issue of thermal runaway of the OTM temperature that can occur in the absence of the porous support when an increase in the oxygen flux would increase the OTM wall temperature, which could cause a further increase in oxygen flux when there would be no heat sink. However, the mass transport limited oxygen flux values that have been reported in Figure 7 are below the oxygen flux performance target for commercialization of the technology.

An oxygen transport model has been developed to assist in developing target parameters for OTM specifications and to provide guidance on what changes need to be made to both the OTM and operating environments in order to reach the oxygen flux target. The model has been used to analyze various cases the results of such specific cases are presented and discussed in the EPACT appendix to this report. Specifically, oxygen flux gradients along the length of the tube and the average oxygen flux as a function of the degree of combustion have been considered and are discussed in the EPACT appendix.

Complete combustion of fuel has been difficult to demonstrate in single tube reactors due to limitations in terms of the oxygen flux of the membrane and the range of mass flow controllers that had been installed. It was therefore decided to only demonstrate complete oxidation of the fuel in the multi-tube reactor. During 2005, Praxair was successful in demonstrating complete oxidation of both methane and natural gas. Figure 9 shows data from a sample of the multi-tube reactor flue gas which has been dried and then analyzed using a gas chromatograph. Figure 10 shows three OTM elements in the multi-tube combustion reactor at a temperature of about 1000°C. In Figure 9, only peaks corresponding to CO_2, Ar/O_2 and N_2 are observed, no residual fuel peaks are generated. To date, the average oxygen flux measured in the multi-tube reactor under complete oxidation conditions is only about 10-20% of the oxygen flux target for the project. Dilution of the fuel in a relatively large volume of simulated re-circulated flue gas plays an important role in reducing the oxygen flux that can be demonstrated. Another factor is the relatively high mass transfer resistance of the membrane.

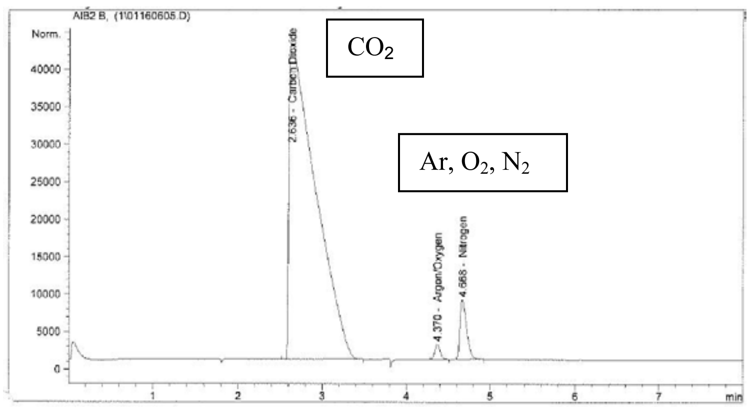

Figure 9, Complete combustion of natural gas in multi-tube combustion reactor.

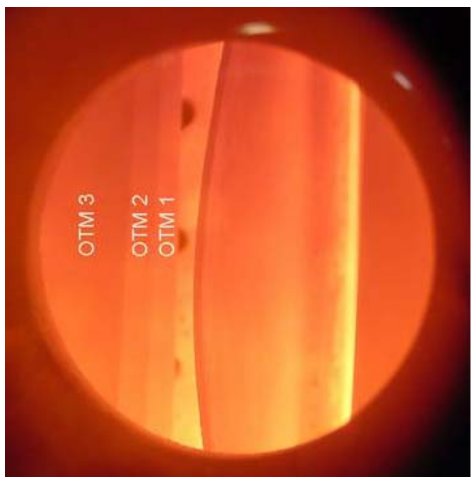

Figure 10, Picture of the three OTM tubes inside the multi-tube reactor at an operating temperature of about 1000°C.

B.3 OTM development (Task 3)

Materials development

Materials selection and development strategy was defined and finalized in 2004. 2005 was used to develop manufacturing techniques, further implement changes in membrane material and architecture and most importantly to demonstrate the robustness of the oxygen transport membrane in a combustion environment. During 2005, substantial progress was made in improving the rate of oxygen transport through the ceramic membranes. Membrane material development is business confidential information, patents are currently being prepared and filed on the developed membrane system, for that reason the data to be presented under this task has been included as EPACT data in the appendix to this report.

The data in the EPACT appendix includes electrical conductivity measurements that characterize the total conductivity of the gas separation layer material as a function of temperature and oxygen partial pressure. The influence of sintering conditions on electrical conductivity of the separation layer material is also reported. The electrical conductivity measurement apparatus is shown in Figure 11.

Figure 11, Apparatus for measuring electrical conductivity of our membrane materials as a function of temperature and oxygen partial pressure.

Oxygen transfer through an oxygen transport membrane under combustion conditions is a multi step process. In the first step oxygen diffuses through a boundary layer and adsorbs on the membrane surface where electron transfer occurs. Current understanding is that the gas separation layer needs to be provided with a porous mixed conducting oxide layer with a high surface area per unit of volume. An increase in oxygen flux is expected by optimizing the porosity, particle size, thickness and composition of the cathode. The cathode will only be exposed to air and can hence be of a material that is less stable in a reducing environment than the material in the gas separation layer and anode. The cathode material needs to have a microstructural stability in order to generate a stable oxygen flux for the combustion process over a long period of time. This imposes some limitations on the particle size and composition of the cathode. The oxygen transport model predicts that improving the rate of fuel oxidation at the porous support / gas separation layer interface will also result in an improvement of the oxygen flux.

The oxygen transport model predicts that a substantial improvement in oxygen flux will result from increasing the porosity and reducing the tortuosity or thickness of the porous support. Increasing the porosity and reducing the thickness of the porous support will result in a decrease of the tube strength and care has to be taken that this will not result in OTM tubes that cannot withstand the conditions during manufacturing (low yield) or the operating conditions in the boiler (short time to failure). Reducing the tortuosity of the porous support should only reduce the mass transfer resistance and have no effect on strength. Substantial progress has been made in reducing the mass transport resistance of the porous support however More work on improving the porous support appears to be warranted. Preliminary measurements of the oxygen flux of oxygen transport membranes with a more open porous support confirm the model prediction.

It is expected that continued development of the composite membrane architecture and composition will result in an increase of the oxygen flux towards values that result in an economically viable oxy-fuel combustion process for a number of combustion applications including boilers for power generation from coal. This is illustrated in Figure 12, the lower curve illustrates the oxygen flux of our current OTM element as a function of temperature when exposed to the predicted fuel composition from one of a number of process integration cycles that have been considered. The upper curve indicates the anticipated oxygen flux after making the improvements to the cathode, separation layer, anode and porous support in order to enable complete oxidation of the fuel close to the target oxygen flux value.

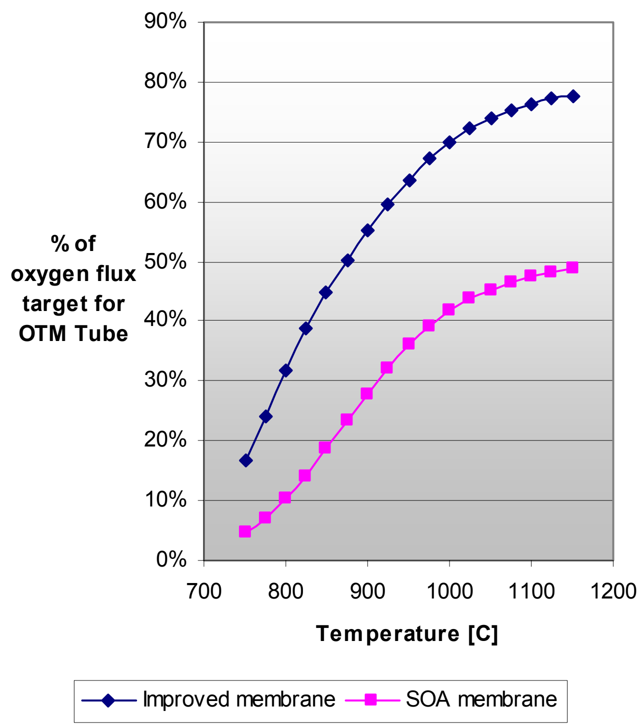

Figure 12, Potential for oxygen flux improvement over state of the art membrane by optimizing the OTM architecture and composition.

Tube Manufacturing

Steps were taken to evaluate the capability of the selected process for fabricating OTM elements that closely resembled the OTM elements that ALSTOM Power identified in the conceptual design task of the advanced boiler. Figure 13 shows some of the infrastructure available at the Praxair Surface Technologies site in Indianapolis for scaling up of the OTM elements.

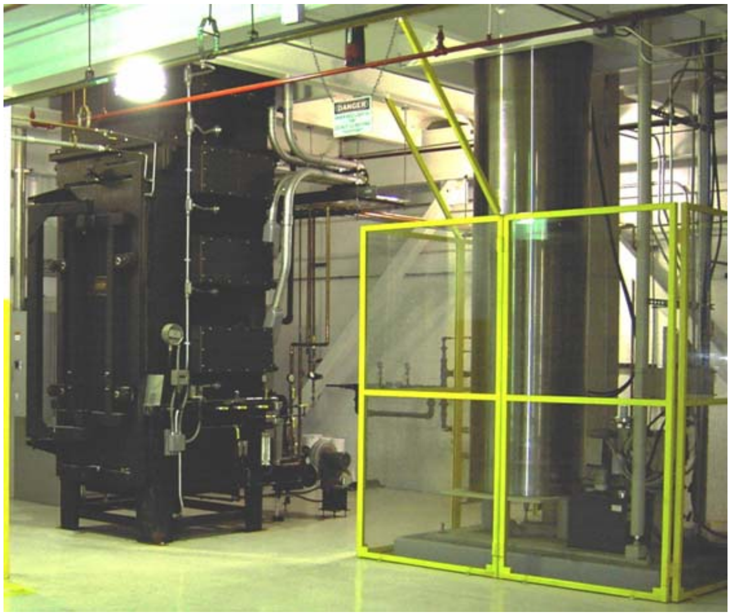

Figure 13, Infrastructure for scale-up of the OTM elements in diameter and length (Left: Hang-fire Furnace. Right: Cold Isostatic Press).

B.4 Economic evaluation and commercialization planning (Task 4)

A preliminary economic analysis of the advanced boiler concept (natural gas fired) was performed in anticipation of more detailed results of the system cost by ALSTOM Power that will become available in June 2006. The results of the preliminary analysis for an industrial boiler are considered to be business confidential information and have therefore been included in as EPACT data in the appendix to this report.

B.5 Program Management (Task 5)

The advanced boiler project [1] developed considerable momentum after the identification of a robust membrane material and after developing a suitable cofiring process.

Figure 14 shows how much was spent on the advanced boiler project between 2002 and 2005. About 80% of the project deliverables have been accomplished, which is in line with the spending on the project. The major accomplishments for 2005 are: Demonstrated a robust membrane material, >12,000 hrs of failure free operation, demonstrated complete combustion in multi-tube reactor and selected a conceptual design for the combustor of the advanced boiler.

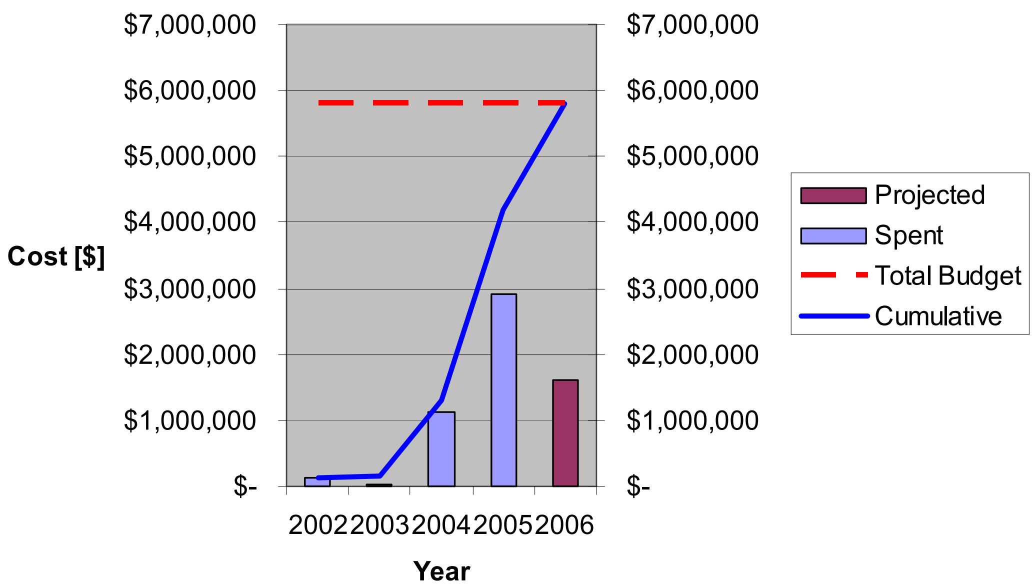

Figure 24, Actual spending versus budget.

There were no recordable injuries or lost work days. Presentations were made at several conferences [2-4].

C. Conclusions

Praxair firmly pushed forward on the development of a robust membrane material system and the demonstration of complete combustion of gaseous fuel in a multi-tube combustion reactor. The oxygen transport membrane system has been shown to be reliable in laboratory evaluations as no failures occurred despite multiple planned thermal and chemical cycles and unplanned reactor shutdowns due to power outages. More progress needs to be made in terms of the oxygen flux under complete combustion conditions in order to obtain the goal of an advanced boiler that is commercially viable and that enables capture of carbon dioxide at a much lower cost than conventional technology can. The development focus is high performance, low cost, reliability, modularity and fuel flexibility.

D. Future Work

The results that were obtained in 2005 illustrated that the mass transfer resistance of the oxygen transport membrane was high and an analysis of the results indicated which processes appeared to be limiting the oxygen flux. The first two quarters of the 2006 calendar year will be used to address these issues without sacrificing the robustness of the membrane (able to withstand process cycles and durability). The single tube reactors will be used to evaluate how these steps contribute to an increase of the oxygen flux. The multi-tube combustion reactor will be used to perform a 1,000 hrs life test under complete combustion conditions providing information about the stability of the oxygen transport membranes versus time. ALSTOM Power will complete the development of a cost estimate of the advanced boiler and these results will be used in a technical and economical evaluation of the advanced boiler concept.

E. References

[1] D.R. Thompson, L.E. Bool III and B.A. van Hassel, United States Department of Energy Technical Application DE-PS26-99FT40613 (2000).

[2] J. Li, L. Switzer, B.A. van Hassel, G.M. Christie, Thermally Integrated Oxy-fuel Boiler, 30th International Coal Conference, Clearwater, FL, April 20, 2005.

[3] B.A. van Hassel, J. Li, L. Switzer, G.M. Christie, J. Sirman, Advanced Oxy-fuel Boilers for Cost-Effective CO2 Capture, Fourth Annual Conference on Carbon Capture & Sequestration, May 2-5, 2005, Alexandria, Virginia

[4] J. Sirman, B.A. van Hassel, L. Switzer, G.M. Christie, A Comparison of Oxygen Supply Systems for Combustion Applications, Fourth Annual Conference on Carbon Capture & Sequestration, May 2-5, 2005, Alexandria, Virginia