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

Final Technical Report

For Reporting Period Starting January 1, 2002 and Ending March 31, 2007

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Revised Report Issue Date: December 17, 2007

DOE AWARD NO. DE-FC26-01NT41147

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ABSTRACT:

This Final report documents and summarizes all of the work performed for the DOE award DE-FC26-01NT41147 during the period from January 2002 - March 2007. This report outlines accomplishments for the following tasks: conceptual design and economic analysis, oxygen transport membrane (OTM) development, laboratory scale evaluations, and program management.

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Executive Summary

The purpose of the advanced boilers and process heaters program is to assess the feasibility of integrating Oxygen Transport Membranes (OTM) into combustion processes for cost effective CO_2 capture and sequestration. Introducing CO_2 capture into traditional combustion processes can be expensive, and the pursuit of alternative methods, like the advanced boiler/process heater system, may yield a simple and cost effective solution. In order to assess the integration of an advanced boiler/process heater process, this program addressed the following tasks:

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

For Task 1, ALSTOM Power developed conceptual designs for an OTM reactor incorporated into a steam boiler. The deliverables for task 1 included providing a comparison of performance of the advanced boiler versus a baseline boiler, and providing a detailed conceptual design of the CO_2 capture system integrated with the boiler. The system design integrates an oxyfuel combustion process with air separation via ceramic OTMs where the OTM tubes are inter-dispersed with steam tubes. The following characteristics contribute to high net power available from the advance boiler design:

- Air separation via OTMs – minimal auxiliary power required for cryogenic air separation
- No recirculation of flue gas – integration of steam tubes provides temperature control

- Improved thermal efficiency by latent heat recovery

The task 2 deliverables included providing simplified P&I diagrams and test capabilities of a disc tester, single tube OTM reactor, and multiple tube OTM reactor, providing test matrices along with the data output, descriptive data on combustion and thermal performance, and providing non-dimensional results of the OTM modeling work and conclusions. Two single-tube OTM reactors and one multi-tube OTM reactor that operates on natural gas were built for task 2. Zero membrane failures occurred over the past three years, demonstrating the reliability of the selected materials. The transport rates for oxygen flux through OTMs tested in single tube reactors were below target values, but have shown improvement from < 20% of the target flux in 50% H_2, 25% CO and excess CO_2 at the initiation of this project to ~ 50% of the target flux in 50% H_2, 25% CO and excess CO_2 at the present state of the project, while maintaining reliability. In order to reach target values, and provide adequate combustion in OTM multitube reactors, the oxygen flux must be increased by a factor of three.

An oxygen transport membrane material system for oxyfuel combustion was developed in task 3. The task 3 deliverables included providing oxygen flux as a percentage of target flux, thermal expansion results for coded materials, and operating temperature range. The oxygen transport membrane system included a porous support tube and a dense gas separation layer for oxygen ion transport. Task 3 focused on providing increased porosity in the membrane support tube and reducing the resistance to oxygen ion transport through the membrane gas separation layer, while retaining high membrane reliability. Also for this task, progress has been made towards developing a cost effective manufacturing process.

In task 4, Praxair developed an economic analysis of the advanced boiler system designed in task 1. The task 4 deliverables include providing a comparison of the cost of the advanced boiler versus a baseline boiler, expected CO_2 capture cost, and cost estimates of the most appropriate CO_2 capture system integrated with the boiler. The cost of CO_2 avoided was found to be in the range of \$20-30/ton of CO_2 when applied to large natural gas fired power plants (>250 MWe) owing to a significant economy of scale of the boiler components. The cost of electricity of the proposed power plant that incorporates the advanced boiler/process heater process is approximately \$0.15/kWh for a 1000 MWe power plant. This cost is high, in large part because of its reliance on natural gas as the fossil fuel. This is being addressed in the DOE project awarded in October 2006: “OTM Based OxyCombustion for CO_2 Capture from Coal Power Plants” (DOE Award No. DE-FC26-07NT43088) [1], which will study the feasibility of using coal as the fuel in larger scale (600 MWe) power plants while still providing a large fraction of the oxygen for the combustion process with the oxygen transport membrane system.

1. Introduction

There are two main technologies practiced today for commercial oxygen production; cryogenic distillation and adsorption. Cryogenic plants producing gas and liquid products still represent the bulk of present industrial gas supplies. While the cryogenic technology has been around for almost 100 years and considered a mature technology, there have been a number of significant recent advances. They include larger plants and lower oxygen purities for certain applications. For example 95% oxygen purity, containing mostly argon as an impurity can be supplied at lower cost than high purity oxygen. Another advance is the availability of efficient high pressure oxygen cycles that do not require oxygen compression. There have been continuous, albeit very gradual, reductions in power consumption and overall reductions in oxygen cost. The power consumption of a state-of-the-art large scale cryogenic oxygen plant producing 95% purity oxygen at atmospheric pressure is as low as 220 kWh per metric ton of oxygen.

Adsorption processes for oxygen production became commercially available on a large scale in the early 1970s. For oxygen production, synthetic zeolites are used for selective adsorption of nitrogen from air. The separation is driven by a cyclic pressure fluctuation resulting in a varied adsorption loading capacity for nitrogen. Praxair offers commercial processes that cycle above and below the atmospheric pressure, which are called Vacuum Pressure Swing Adsorption (VPSA). Typical oxygen purities produced are 90 to 95% as argon in air is not separated from oxygen. Early PSA systems had a lower capital cost than cryogenic air separation systems but required relatively a higher power consumption of 450 to 550 kWh per ton of oxygen. There have been dramatic improvements in the performance of the adsorption processes during the last decade. The development of advanced adsorbents, improved process cycles and equipment have simplified the process from three-bed systems to two or one bed systems and the capacity of the plant has increased substantially. The power consumption has been reduced to below 220 kWh per ton of oxygen for the supply of atmospheric pressure oxygen. Improvements of the adsorption technologies are expected to continue further into the future as more advanced adsorbents, process equipment and process cycles are developed.

The current energy consumption to produce oxygen of 220 kWh/ton O_2 represents a severe energy penalty for oxygen combustion. The theoretical energy requirement of oxygen production by the thermodynamically ideal process is less than 40 kWh/ton O_2, which is less than 1/5 of the power requirement of the best current technology. These numbers suggest that air separation technologies are far from mature and there is room for substantial technological improvements in oxygen production. The most exciting new technology for oxygen production is ceramic membranes, which offers a method for substantially reducing the cost of oxygen production in the future. The characteristic that makes ceramic membranes so attractive is their virtually infinite selectivity for oxygen. In other words, the membranes only allow oxygen to pass through. This only occurs at temperatures above about 600°C.

There are two basic types of ceramic membranes, electrically driven and pressure driven. In the case of the electrically driven membranes, only oxygen ions can pass through the membrane. In order to provide the driving force for the separation and to provide a path for the electrons an external circuit and electric power are required. This type of membrane is actively being developed by Praxair. It provides a means to produce high-purity oxygen at high pressure in a single step without the need for compression equipment. Pressure driven membranes have a stream with a high oxygen partial pressure on one side of the membrane and another stream with a low oxygen partial pressure on the other. The oxygen partial pressure ratio across the membrane provides the driving force for the separation. These membranes are called mixed conducting because they allow oxygen ions to flow in one direction and complete the circuit internally by allowing electrons to flow back in the other direction. In order for the process to occur the oxygen molecule must first be adsorbed on the surface, dissociated and converted to an oxygen ion. The higher oxygen partial pressure on one side versus the other provides the driving force to enable the oxygen ion to pass through the membrane. On the other side of the membrane the oxygen ions recombine to form oxygen molecules and release the electrons which then complete the circuit by flowing back through the membrane. These ceramic membranes are also called oxygen transport membrane (OTM). Potential applications for these membranes include oxygen production, oxygen purification, partial oxidation reactions, syngas (H_2 and CO) production, and combustion.

For the production of pure oxygen with OTM, the feed air has to be compressed to a high pressure and heated to a high temperature. Since most of the energy applied to the feed air is carried with the nitrogen rich retentate, it has to be recovered through an expansion step. Thus, an oxygen production system using OTM typically requires integration with a gas turbine cycle, which makes the process capital intensive and the economics complex due to the value of the power produced. A more advantageous application of OTM for oxy-fuel combustion is the direct placement of OTM tubes in a combustion chamber to reduce the partial pressure of oxygen in the permeate side. In such a system the need to compress the feed air is eliminated and the overall process is greatly simplified, as discussed in a separate section. Table 1 shows a comparison of different oxygen production technologies: VPSA, Cryogenic, ceramic membrane and delivered liquid oxygen. [2]

Table 1. Comparison of Oxygen Production Technologies

	VPSA	Cryogenic	OTM	Delivered Liquid
Capacity range (tpd)	<5-200	20-3500	5-200	<30
Oxygen Purity (%)	90-94	95-99.9	99+	99.5+
Co-Products	Difficult	N_2, Ar, Liquids	CO_2	N/A
Power Consumption	Lower	Base	Lowest	Higher
Capital Cost	Lower	Base	Lower	Lowest
Oxygen Cost	Low	Base	Lower	Highest
Operating Temperature	Ambient	-184^oC	> 600^oC	-184^oC
Age of Technology (years)	45	100	20	80

The purpose of carbon dioxide capture and sequestration is to reduce greenhouse gas emissions from burning fossil fuels during industrial and energy-related processes. Emerging R&D technologies attempt to lower the cost of CO_2 avoided. For large natural gas plants (>250 MWe), the cost of carbon dioxide avoided is estimated to be between $40-60/ton of CO_2 with MEA scrubbers, about $40/ton CO_2 with an IGCC scenario, and between $20-30/ton of CO_2 with the advanced boiler system. The primary goal of this project was to develop and commercialize such an efficient advanced boiler that could provide an inexpensive CO_2-rich product stream for sequestration. It required the development of a reliable oxygen transport membrane material and its deposition as a thin film on a porous support. It also required a significant design effort to integrate the membranes in a cost effective way into an industrial boiler. The results were used to determine both the technical and economic viability of this industrial boiler.

The original proposal included a task to evaluate how the OTM elements would integrate with a process heater but this task was discontinued. It was also decided not to spend resources on the conceptual design of a 0.5-1 MMBtu/hr pilot boiler owing to budget constraints. Resources were instead allocated towards completion of the conceptual design and cost estimate of the advanced boiler as it provided insight into the follow-up project which focuses on coal as the fuel instead of natural gas [3].

2. Advanced Boiler Design [Task 1] and Economic Analysis [Task 4]

The oxy-fuel combustion technology that has been developed in this DOE project: “Advanced Oxyfuel Boilers and Process Heaters for Cost Effective CO_2 Capture and Sequestration” [3] is promising. Accomplishments for task 1 and 4 are summarized in this section. It enables the combustion of fuel with pure oxygen obtained from a ceramic oxygen transport membrane and without the large parasitic power load of a vacuum pressure swing or cryogenic air separation unit. The separation of carbon dioxide from the flue gas is achieved by condensing out the water. The latent heat of condensation is available at a higher temperature than in conventional combustion processes that use air and is used in the power plant for heating the condensate from the steam turbine and for preheating the air for the oxygen transport membranes. The power plant can hence make more of its gross power available for distribution while sequestering the carbon dioxide.

The cost of CO_2 avoided for a 90% confidence interval is in the range of \$20-30/ton of CO_2 when applied to large natural gas fired power plants (>250 MWe) due to a significant economy of scale of the boiler components. This is illustrated in Figure 1. It shows the cost of CO_2 avoided of the natural gas fired advanced boiler as a function of the net power from such a power plant. The reference plant was a regular natural gas fired boiler with steam turbine and generator that had the same net power. The cost of electricity of the suggested power plant is approximately \$0.15/kWh for a 1000 MWe power plant. This cost is high, due to its reliance on natural gas as the fossil fuel. This is being addressed in the recently awarded DOE project: "OTM Based OxyCombustion for CO_2 Capture from Coal Power Plants" [1], which will study the feasibility of using coal as the fuel while still providing a large fraction of the oxygen for the combustion process with the oxygen transport membrane system.

Figure 1 also shows the cost of CO_2 avoided of a pulverized coal power plant with an MEA scrubber [4], a super critical pulverized coal power plant that uses oxy-fuel combustion with oxygen supplied from a cryogenic air separation unit and an IGCC power plant with CO_2 sequestration [5]. The lower cost of CO_2 avoided of the advanced boiler system in comparison to the other power plant scenarios with a CO_2 capture system results from using the oxygen chemical potential difference between air and the fuel as the driving force for separation. The need for air compression is therefore minimized. The latent heat of condensation of the steam in the flue gas is available at a higher temperature due to the high dewpoint of the flue gas from an oxyfuel combustion process and is used efficiently in the power cycle. Flue gas recirculation has been eliminated. There is no absorbent that needs to be circulated and regenerated.

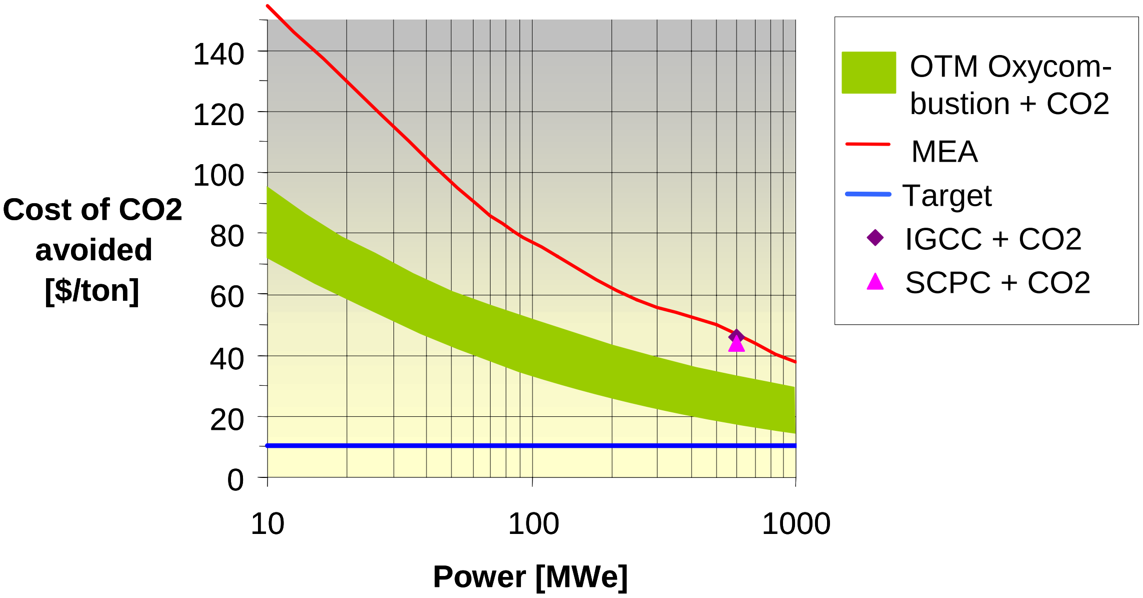


Figure 1, Cost of CO_2 avoided for a 90% confidence interval versus net power for a natural gas fired power plant that is based on the advanced boiler concept in comparison to the cost of CO_2 avoided from coal fired power plants with different CO_2 capture strategies [4,5].

The cost of CO_2 avoided is the final result of a technical-economic analysis of the natural gas fired boiler system with oxygen transport membranes that was conducted by Praxair with ALSTOM Power as a sub-contractor. ALSTOM Power designed the boiler with the oxygen transport membranes as its heating elements and estimated the cost of that system. Praxair developed the membrane materials, estimated the membrane cost and performance under the operating conditions in the boiler, integrated the recovery of the latent heat of condensation with the steam cycle and estimated the cost of the CO_2 compression to 1500 psia. Praxair also performed the final technical and economical evaluation of the concept which will be discussed in more detail below.

2.1 Conceptual design of the advanced boiler system

ALSTOM Power designed a natural gas fired industrial boiler with the system properties that are shown in Table 2. The fuel and flue gas properties are shown in Table 3.

Table 2, Boiler system properties

Steam flow	100,000 lbm/hr	**Heat Fired**	137.71 MBtu/hr
Temperatures		**Heat to Steam**	120.49 MBtu/hr
Inlet	266F	**Efficiency**	87.49%
Outlet	907F	**Excess Air**	28%
Pressures		**Blowdown**	2.2%
Inlet	1731 psig		
Outlet	1688 psig		

Table 3, Fuel and Flue Gas Properties

Fuel Composition (vol. %)		**Flue gas composition (vol. %)**	
Methane	95.45 %	Carbon Dioxide	31.25 %
Ethane	0.37 %	Water vapor	65.5 %
Propane	0.12 %	Nitrogen	1.25 %
Carbon Dioxide	0.1 %	Oxygen	2.0 %
Nitrogen	3.86 %	Dewpoint	89°C(192.4 F)
Fuel Weight	6188 lbm/hr	**Flue gas Weight exiting combustor**	25415
Higher Heating Value	22,253 Btu/lbm		

Figure 2 shows a block diagram of the process in which steam is being generated in the advanced boiler. The steam is expanded in order to generate power in a condensing steam turbine. The condensate and make-up water get preheated in one of the condensing type heat exchangers, which substantially improves the heat to steam efficiency of the boiler. The preheated water feeds into a deaerator. Intermediate steam that has been extracted from the steam turbine is used to heat the boiler feed water to 266F before it gets pumped to 1450 psia and fed into the boiler system. The efficiency of the steam cycle would benefit from reheating the steam after an initial expansion but this would require a change in the boiler and steam turbine design.

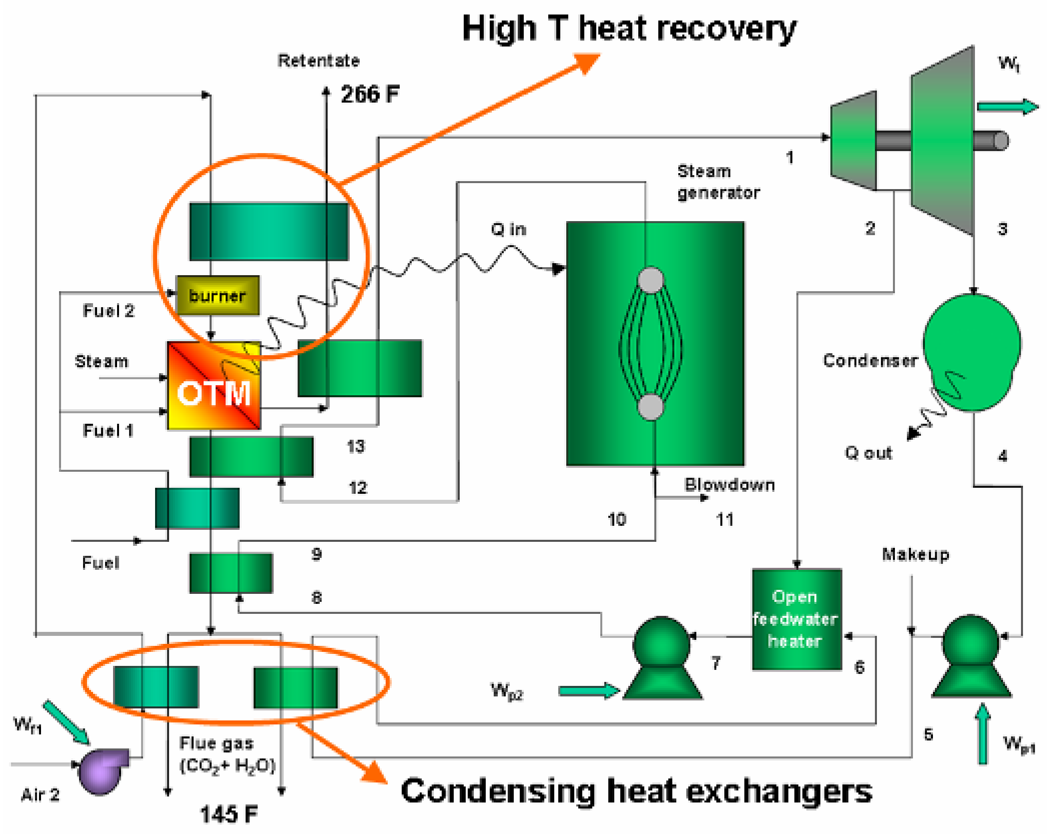


Figure 2, Block diagram of the advanced boiler system.

ALSTOM Power was provided with information about the size of the OTM elements that appeared to be feasible from a ceramic manufacturing point of view. They were also supplied with information about the projected oxygen transport membrane performance as a function of temperature and gas composition. This enabled ALSTOM Power to design the combustor of the boiler. It was decided to position the OTM tubes in between the water tubes of the boiler so that the oxygen transport membrane temperature can be maintained at 1000°C while transferring the heat of combustion to the water tubes [6,7].

Initially 5' long closed-one-end OTM tubes were considered but this would results in an expensive air manifold. It was therefore decided to increase the length of the OTM tube and change from closed-one-end to open-both-end. The layout of the OTM tubes and steam tubes was varied in order to ensure that the temperature of the OTM tubes would not exceed their operating limit while achieving a high energy intensity of the OTM combustor. The steam tube diameter was varied. Some of the cooling tubes were provided with fins in order to improve the convective heat transfer. The orientation of the steam and OTM tubes was varied. This resulted in more than five different design configurations and one was selected for the final design and used for estimating the cost of the advanced boiler. Figure 3 shows the general layout of the combustor that was designed for this project. Figure 4 shows a regular gas fired boiler, which will be used as the reference case for determining the cost of CO_2 avoided.

The air for the oxygen transport membranes needs to be preheated to high temperature in order to enable oxygen transport. This is achieved by first preheating the air in one of the condensing type heat exchangers before recovering the heat of the oxygen depleted retentate stream in a recuperator. In-line combustion of natural gas into the air stream is used to increase the air temperature from 671°C to 973°C. The oxygen depleted retentate stream from the oxygen transport membranes is about 1000°C. Its temperature is reduced to 778°C in a steam superheater before it enters the recuperator in which it is used to preheat the air. This particular combination of recuperator, in-line heating and steam super heater was selected in order to reduce the cost of the heat recovery system at the airside of the oxygen transport membrane system. One could have used a recuperator that would have preheated the air all the way to 950°C with a retentate stream that was available at 1000°C but this would have required the use of expensive alloys.

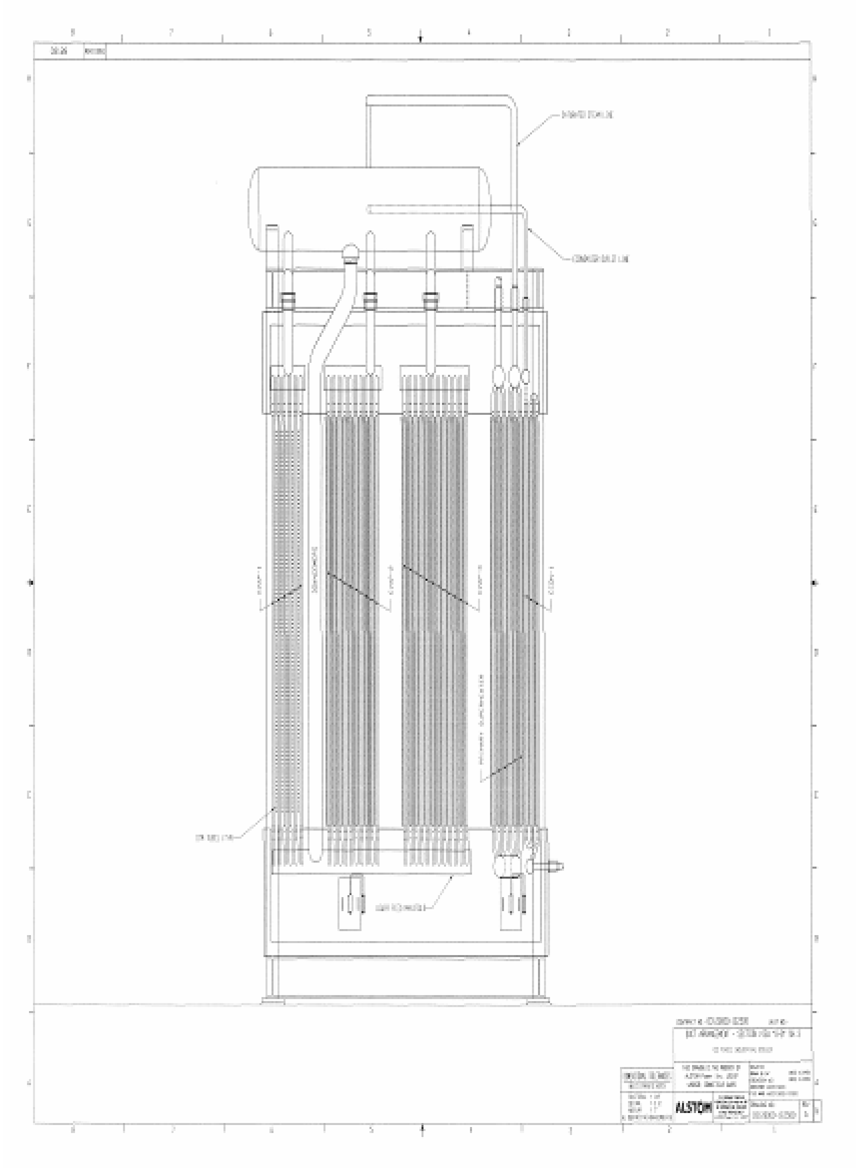


Figure 3, Combustor of the advanced boiler system with OTM tubes positioned in between the water tubes.

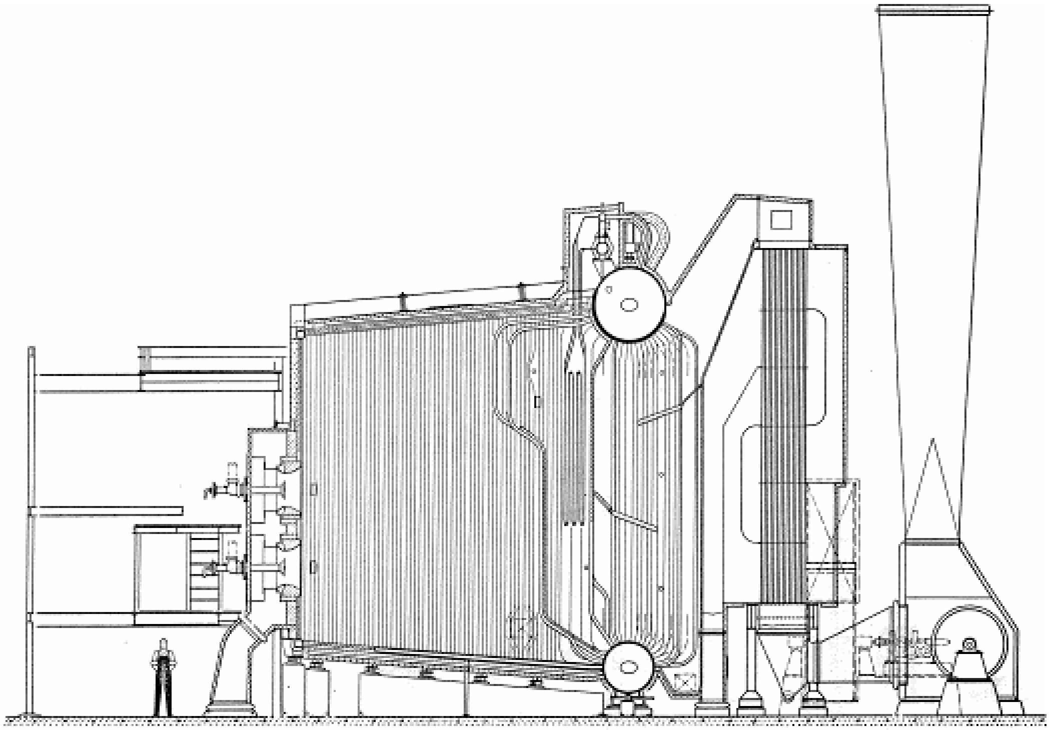


Figure 4, Regular boiler system schematic that shows the water tubes and the mud and steam drum.

The consequence of the current design of the air heating system is that a fraction of the CO_2 generated in the boiler will not be recovered as it is vented in the oxygen depleted retentate stream. The composition and amount of fuel that can be used for in-line heating of the air will be determined by the CO_2 capture target for the particular project. The cooled oxygen depleted air stream still contains a substantial amount of energy that could be used to generate hot water if needed.

A fan is used to force the air through the recuperators, past the in-line heater, OTM tubes and steam superheater before it is being discharged to the atmosphere. This fan is the only auxiliary power load on the advanced boiler system that is related to separating oxygen from air. The system was designed so that the pressure drop of the air stream and oxygen depleted retentate stream would be as small as possible in order to make as much of the gross power of the power plant available for distribution.

The dewpoint of the flue gas generated in this boiler was 89°C (192.4 F), which is about 40°C higher than for a regular boiler in which natural gas is combusted in air. The latent heat of condensation is hence available at a higher temperature and more useful in the power cycle. The three main heat sinks available for this latent heat of condensation are the condensate return from the steam turbine, the make-up water and the air for the oxygen transport membranes. With these heat sinks it was possible to cool the flue gas to 63°C (145 F) and condense out 85% of the water.

The flue gas had to be cooled to a lower temperature (38°C (100F)) and the resulting condensate had to be separated before entering the CO_2 compression system. The CO_2 compression system consisted of two parallel trains in which the CO_2 was compressed from ambient pressure to 1500 psia in four stages. The only integration between the CO_2 capture and compression system is the use of the latent heat of condensation of the steam in the flue gas for preheating the condensate and air for the boiler. Heat recovery in between the compression stages was not pursued and this heat was hence rejected to ambient in a cooling system.

2.2 Performance of the boiler systems

Both the advanced boiler and the air fired boiler were designed for the same steam specifications (100,000 lbs/hr, 907F, 1703 psia). Table 4 shows a comparison of the performance of both systems.

Table 4, Performance of regular and advanced natural gas fired boiler.

	Conventional boiler	**Advanced boiler**
Steam	100,000 lbs/hr 907 F, 1703 psia	100,000 lbs/hr 907 F, 1703 psia
Natural gas	7082 lbs/hr	6188 lbs/hr
Heat input	158 MMBtu/hr	138 MMBtu/hr
Heat to steam	80.3 %	91.9%
Gross power	10.28 Mwe	10.55 Mwe
Steam to power*	27.7%	28.4%
Net power	9.94 Mwe	9.22 Mwe
CO_2 emission	218 tpd	32 tpd (158 tpd captured, 83%)

The advanced boiler required about 8% less natural gas and less steam needed to be extracted from the steam turbine as the latent heat of condensation from the steam in the flue gas was recovered in the process. The net power output from the advanced boiler is lower than that of the regular boiler due to the parasitic power load of the CO_2 compression system.

2.3 Cost comparison

The cost comparison of the regular natural gas fired boiler with the advanced boiler was performed on an installed basis. The installation cost of the boiler components was estimated by ALSTOM Power while different installation factors were used for determining the installed cost of the high temperature heat recovery unit, OTM elements, steam turbine and generator, condensing heat exchangers and CO_2 compression equipment. Figure 5 shows the installed cost of both systems.

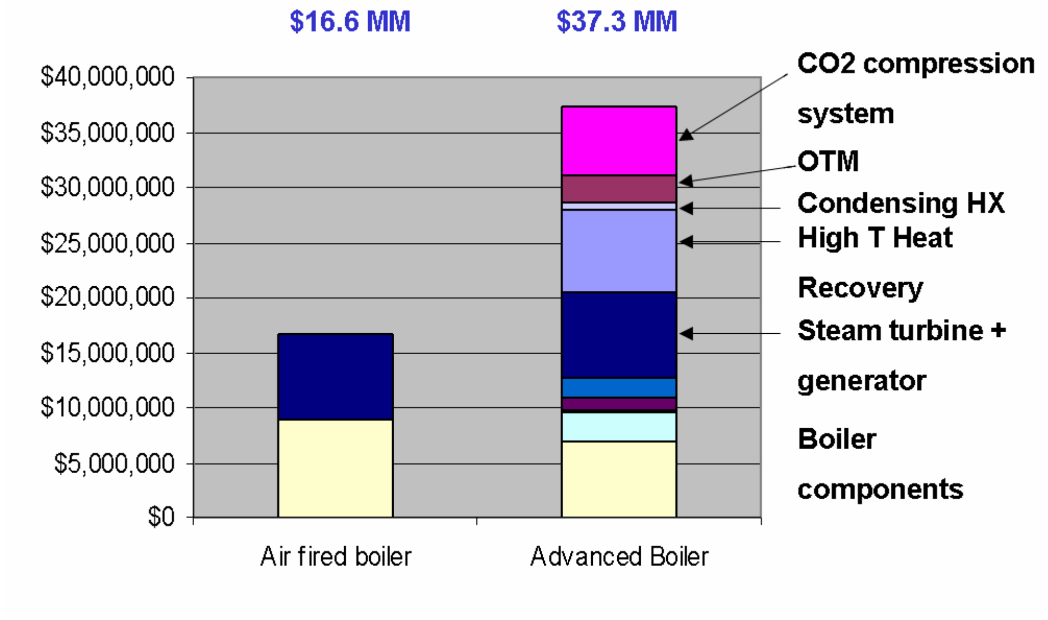


Figure 5, Cost stack comparison between the conventional boiler and the advanced boiler.

The cost of the boiler components for the advanced boiler is very similar to the regular boiler and only increased somewhat due to the additional engineering that is required for the new system. The steam turbine and generator cost is the same as both will be expanding the same amount of steam for generating power.

It was discovered in this project that the cost of the high temperature heat recovery was very high despite limiting the temperature in the recuperator to about 800°C and the use of stainless steel instead of Inconel. This high cost was confirmed by other heat exchanger manufacturers. The heat exchanger manufacturers all complained about the escalating cost of Ni containing materials.

The cost of the condensing heat exchangers was lower than expected. Praxair successfully identified a company that was able to make these heat exchangers at a reasonable cost for this particular industrial boiler size. Several locations were visited where a similar system had been operating for several years without problems. A different company was identified with condensing type heat exchanger technology that would be applicable to large coal fired power plants.

The contribution of the installed cost of the OTM elements to the total installed cost of the advanced boiler is small at this size of the industrial boiler. It is expected that the installed cost of the OTM elements for the power plant will increase almost proportionally to the amount of oxygen that is being transferred. However, the process equipment size exponents for the boiler, heat recovery and CO_2 compression equipment cost are well below one. Therefore it is expected that the cost of the OTM elements as fraction of the installed cost of the power plant will become larger with an increase in the power plant capacity. It will be important to carefully control the manufacturing, installation and maintenance cost (e.g. replacement cost) of the oxygen transport membrane system.

CO_2 compression to 1500 psia is capital intensive and also requires a lot of auxiliary power. However, this cost will be the same for competing CO_2 capture and sequestration processes in which the carbon dioxide is available at atmospheric pressure.

This completes the discussion of the total capital requirement of the regular and air fired boiler systems. It is important to realize that the comparison has been made on an installed cost basis with 2006 dollars. The installation cost of all the components is very substantial and in some cases exceeds the equipment cost despite shop assembling many of the components and then moving them to the customer site. Another aspect of this study is that the footprint of the advanced boiler with CO_2 capture and compression tends to be large due to the presence of a large high temperature heat recovery unit with a lot of duct work and due to the CO_2 compression equipment. This presents a challenge when attempting to replace a regular boiler in an existing facility with the advanced boiler system. Making the system more compact will be important.

2.4 Financial assumptions

The capital charge factor for the advanced boiler was 0.175 and for the conventional boiler system 0.164. The discount period was 20 years. It was assumed that on average the systems would operate at 80% of their capacity for 8,000 hrs per year.

Table 5, Financial assumptions

Capital charge factor advanced boiler	0.175
Capital charge factor regular boiler	0.164
Discount period	20 years
Capacity factor	0.8
Operating hours per year	8000

2.5 Cost of electricity and cost of CO_2 avoided

The cost of all the equipment was aggregated in seven different categories, as shown in Table 6. The resulting cost of each category was given a triangular contribution between -30 to +30 % of that cost. Some costs like engineering, transportation and field support were used as a single value of that cost instead of a cost distribution. Subsequently, the cost of electricity and the cost of CO_2 avoided of the advanced boiler system was simulated with a Monte Carlo method.

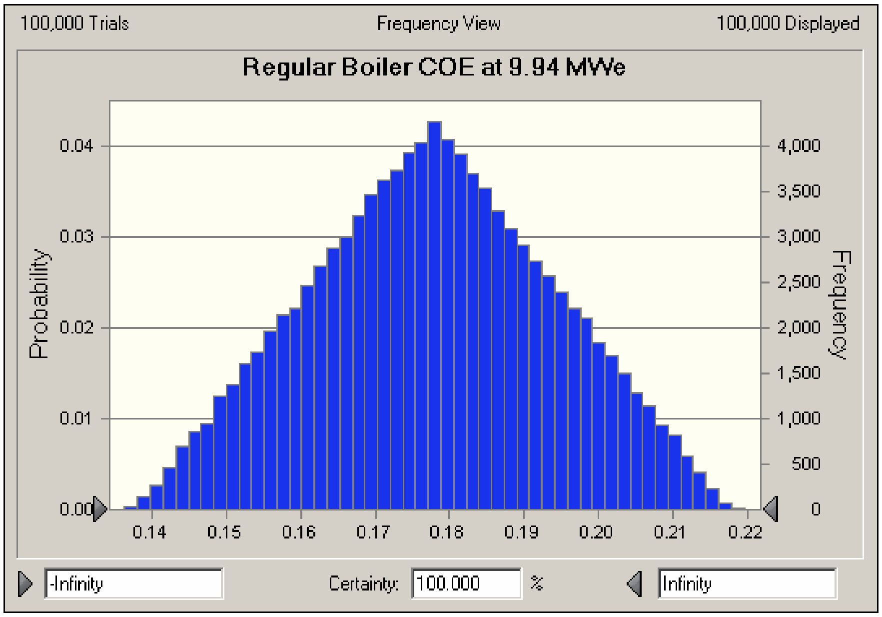
Figure 6 shows the range of the cost of electricity of the regular and advanced boiler systems when the boilers in those systems were generating 100,000 lbs/hr of steam at 1703 psia and 907 F. The CO_2 emission from the regular boiler was 218 tpd and this was reduced to 32 tpd in the advanced boiler. The regular and advanced boiler systems were generating 9.9 MWe and 9.2MWe, respectively. This results in a mean cost of CO_2 avoided of about $87/ton at this small scale of the industrial boiler, as shown in Figure 7.

Table 6, Aggregated cost of key parameters (in million $) that affect the cost of CO_2 avoided of the advanced boiler system.

Assumption	Minimum	Likeliest	Maximum
Regular boiler cost	8.00	9.00	10.00
Boiler components for advanced boiler system	4.82	6.88	8.95
CO_2 compression system	4.38	6.25	8.13
Condensing heat exchanger	0.55	0.78	1.01
High temperature heat recovery	5.21	7.45	9.68
Installed OTM cost	1.67	2.39	3.10
Engineering		2.69	
Transportation		1.06	
Field support		0.29	
Boiler contingency		1.73	
Steam turbine		7.8	

Table 7, Range of other parameters that affect the cost of CO_2 avoided.

Assumption	Minimum	Likeliest	Maximum
Natural gas cost ($/MMBtu)	5	7.5	10
Process Equipment Cost Size Exponent	0.6	0.7	0.8



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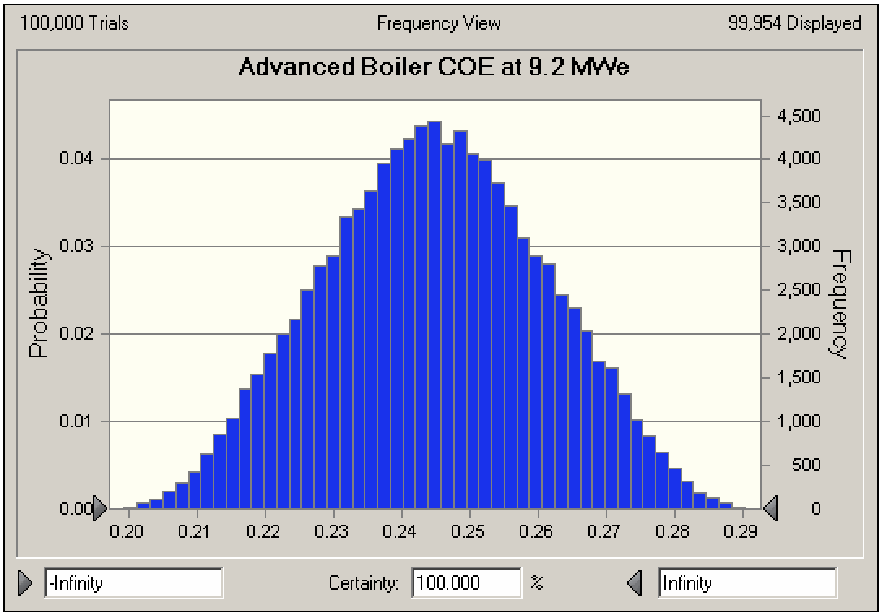
a) Regular boiler



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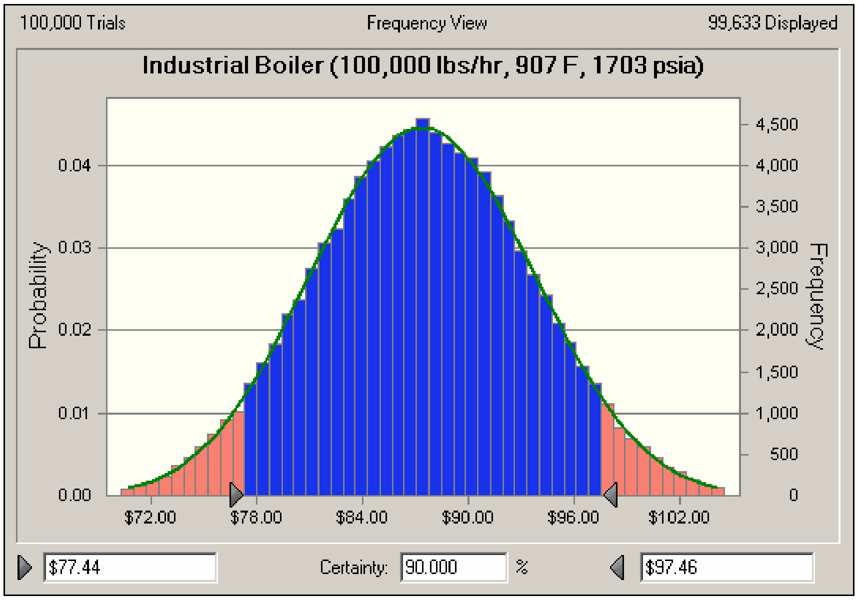
b) Advanced boiler

Figure 6, Cost of electricity


100,000 Trials

Frequency View

99,633 Displayed

$77.44

Certainty: 90.000 %

$97.46

Figure 7, Cost of CO_2 avoided ($/ton of CO_2).

There is a substantial economy of scale in power plants. The process equipment size exponents of Table 7 were applied against the total capital cost requirement in order to determine the cost of CO_2 avoided for a much larger power plant. It was assumed that the OTM installed cost would increase linearly with the total oxygen requirement for the power plant as the analysis would otherwise result in unrealistic membrane cost and performance numbers.

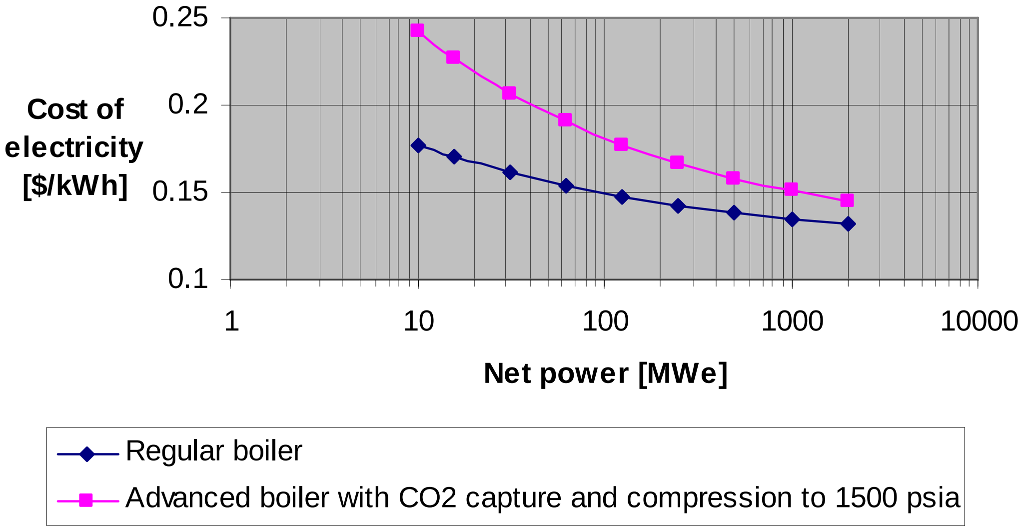


Figure 8, Cost of electricity of the natural gas fired conventional and advanced boiler system with simple steam turbine and generator as a function of the net power from the power plant.

Figure 8 shows the cost of electricity of the regular boiler system and the advanced boiler system versus net power from the power plant. The cost of electricity can be reduced by slightly modifying the boiler and steam turbine in order to allow for a steam reheat in the power cycle. A step change in the cost of electricity can be achieved by switching from natural gas to coal for these power plants. That is the subject of a new DOE project named “OTM Based OxyCombustion for CO_2 Capture from Coal Power Plants” [1], which was recently awarded to Praxair.

2.6 Sensitivity analysis

A high cost of natural gas will make the energy savings of the advanced boiler system more valuable and this will reduce the payback time of the heat recovery equipment and will also reduce the cost of CO_2 avoided of the advanced boiler. An increase in the cost of the conventional boiler will also reduce the cost of CO_2 avoided. An increase in the cost of the high temperature heat recovery, boiler system components, CO_2 compression equipment will all cause an increase in the cost of CO_2 avoided, as shown in Figure 9.

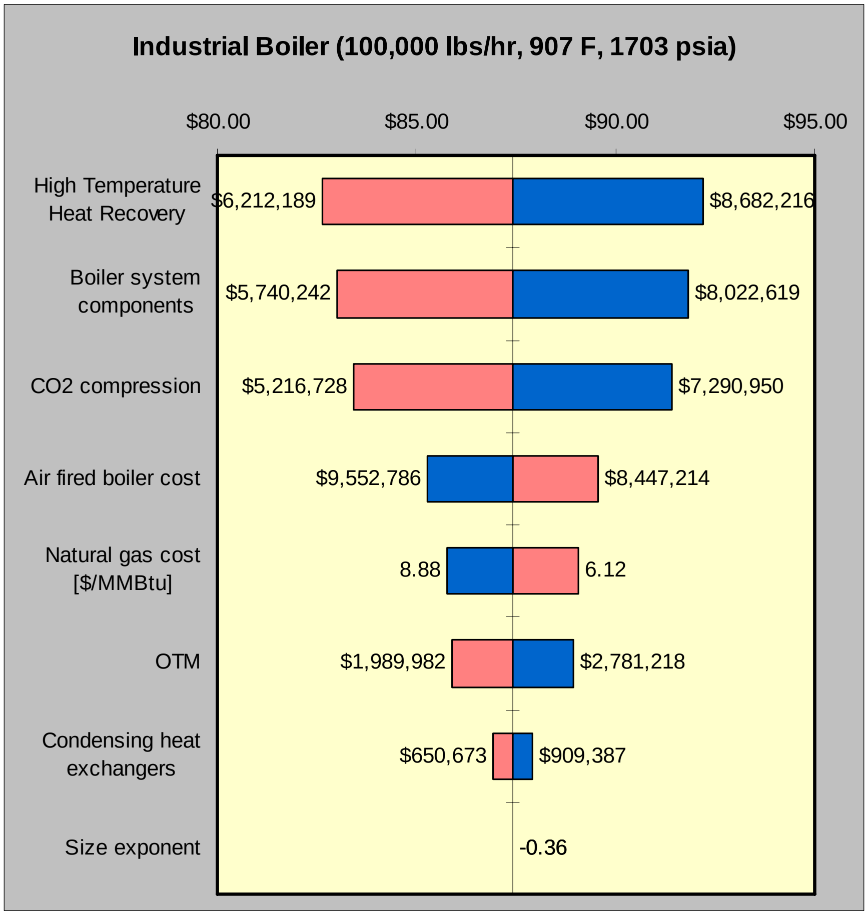


Figure 9, Effect of the cost of process equipment on the cost of CO_2 avoided of the advanced boiler with steam turbine and generator.

The cost of CO_2 avoided is very sensitive to the financial assumptions, as shown in Figure 10. It appears that CO_2 capture and sequestration will require capital funding with a low discount rate if one would like to limit the cost of CO_2 avoided to $10/ton and the increase in the cost of electricity to less than 20%.

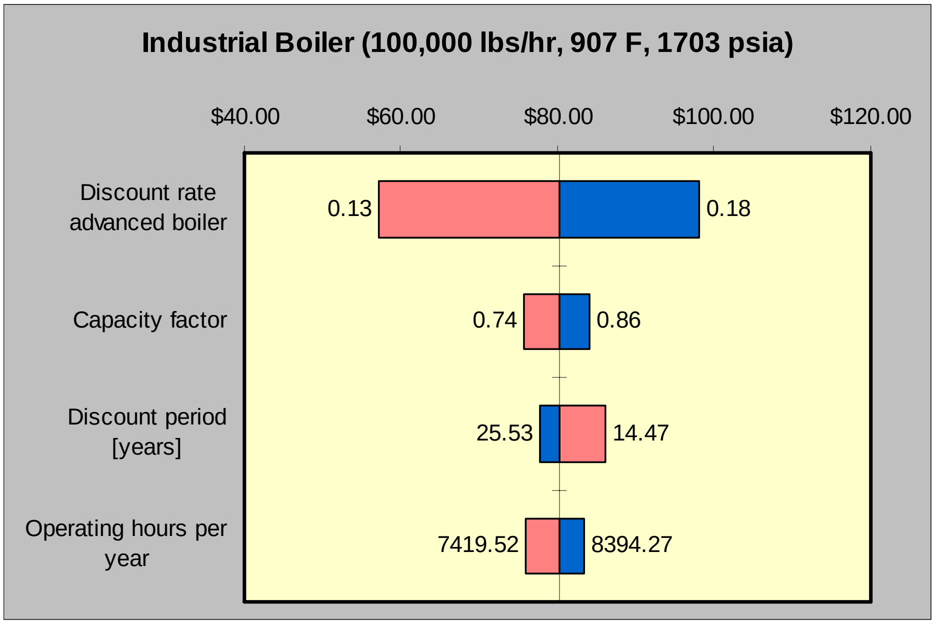


Figure 10, Impact of financial parameters on the cost of CO_2 avoided of the advanced boiler with steam turbine and generator.

2.7 Pilot boiler design

ALSTOM Power informed Praxair that more funds would need to be allocated to their task if the pilot boiler had to be designed. The existing funding was only sufficient for the conceptual design of the advanced boiler and for estimating its cost. Therefore the task of designing the natural gas fired pilot boiler was made contingent on a favorable technical and economic analysis. The result indicated that the natural gas fired boiler was technical feasible but expensive. It was therefore decided not to design the natural gas fired pilot boiler. The

Department of Energy also informed the advanced boiler team that all efforts on developing a new technology for carbon sequestration should be based on coal as the fossil fuel. There was therefore no need to design the natural gas fired pilot boiler anymore.

2.8 Process heaters

The boiler designed in this study has all the characteristics of a process heater. The stream being heated is water. A process heater, unlike a boiler, would however not produce any power. This created a conflict with the request by the DOE that at a minimum they needed to see the % increase in cost of electricity between the air-fired and oxy-combustion cases. Therefore it was decided to focus all efforts on the design of the steam boiler in combination with a steam turbine for power generation. Another reason for this decision was that ALSTOM Power notified Praxair in a progress meeting that they had no business interest in process heaters and that they needed all available resources for their task in order to perform the advanced boiler conceptual design and cost estimation.

2.9 Coal fired concept

A coal fired concept that uses the principle of the advanced boiler system, was developed by Praxair outside of the present Cooperative Agreement (DE-FC26-01NT41147). This concept is the subject of a new DOE project titled “OTM Based OxyCombustion for CO_2 Capture from Coal Power Plants” [1], which was recently awarded to Praxair.

For this system, illustrated in Figure 11, coal is gasified with oxygen from a cryogenic air separation unit. The high pressure synthesis gas is heated in a first oxygen transport membrane module by oxidation of part of the syngas before it gets expanded. The hot syngas expander generates electrical power with a generator. The low pressure synthesis gas is combusted in a second oxygen transport membrane module that has been integrated with a heat recovery steam generator. The steam is used to generate additional power with a steam turbine and generator system.

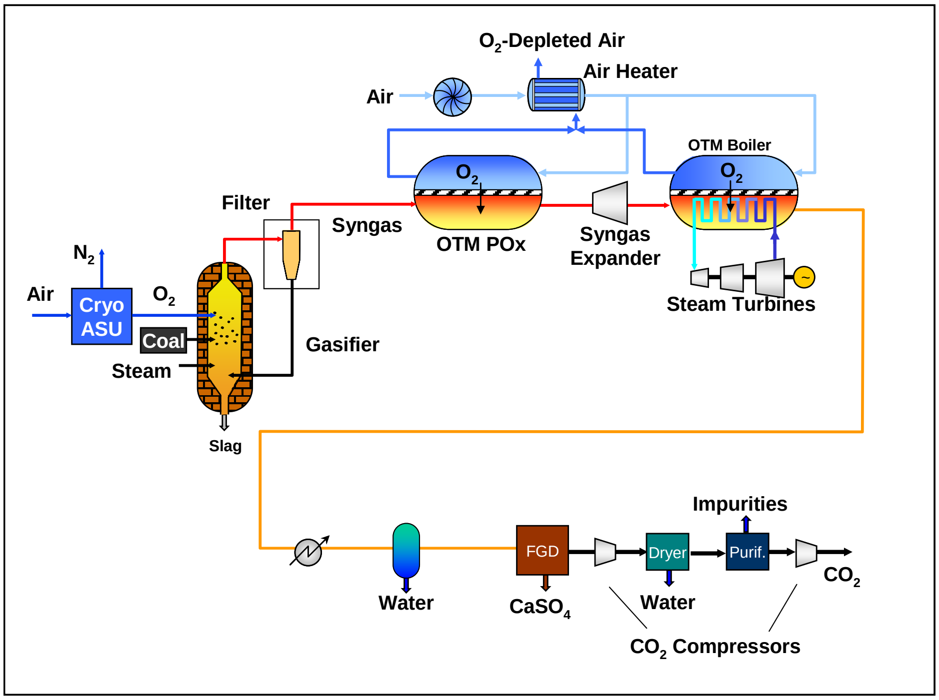


Figure 11, Coal based concept that takes advantage of the low energy requirement for making oxygen available to the combustion process by means of the oxygen transport membranes [1].

3. Oxygen Transport Membrane Development [Task 3]

For task 3, strategies for materials selection and development of oxygen transport membranes were devised and implemented in order to assess and improve OTM reliability, performance, and feasibility of manufacturing. The most important accomplishment of Task 3 was the development and demonstration of an oxygen transport membrane that was robust and reliable in a combustion environment. Work in Task 3 also yielded materials that provided substantial improvement in oxygen transport rates. The OTM system consists of two components: a porous support material (SM), and a dense gas separation layer material. Material selection and characterization of these two components will be discussed.

3.1 Support Material

The primary objective of task 3 was to develop a reliable support material (SM) with high mechanical integrity. The selected SM was also chosen to be stable in a combustion environment, containing carbon dioxide and fuel. Shrinkage upon sintering at 1400°C, median pore diameter, porosity, tortuosity, gas permeability and strength of the porous support materials have been measured, in order gain insight into pathways for improvement.

Fugitive pore formers (PF) were used to meet gas permeability, shrinkage and porosity targets. The pore formers were composed of materials that would burn out at the sintering temperatures and leave in their place pores that facilitate the diffusion and flow of gases through the porous support material. The composition of the pore formers tested will not be disclosed in this document, in accordance with the limited and unlimited rights agreement of this project, but the two pore formers tested will be referred to as PF1 and PF2. Upon sintering at 1400°C the porous support materials with a large increase in pore former quantity yielded a decreased shrinkage rate. Three point bend tests indicated that the porous supports were strong, however a large increase in pore former quantity yielded weak bisque fired tubes.

Gas flow measurements were performed to measure the pressure driven permeability of the support material, and results from these measurements displayed as a normalized permeability for different pore former compositions are shown in Figure 12. The porosity over tortosity ratio also affects the permeability of the support material, and can be considered an important parameter that still requires further improvement. Presently this parameter has been limited to < 0.1 for this porous support generation.

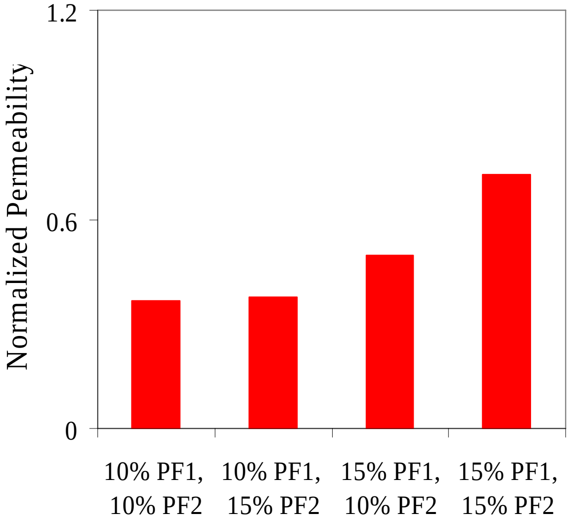


Figure 12, Normalized permeability of porous support materials measured from gas flow measurements

Discs and tubes with the porous supports fabricated from SM, PF1 and PF2 materials were also characterized by SEM analysis, The microstructure of porous substrates indicated a uniform distribution of porosity and a well connected skeleton of the SM material, the images will not be disclosed in this document. However on increasing the pore former size, pinholes were observed in the deposited gas separation layer.

In summary, although increasing the pore former size and quantity in the porous support material should yield a higher oxygen flux, the following problems were encountered under excess poreformer size and quantity: formation of pinholes, decreased shrinkage rate, weak bisque fired tubes, and pore former burn off runaway.

3.2 Gas Separation Layer

The dense gas separation layer was designed to meet the following requirements:

- chemical and thermal expansion match with the porous support materials
- sufficient electronic and ionic conductivity in both fuel and air
- chemical stability in both oxidizing and reducing environments.

A literature review was conducted which yielded a number of electronic conducting (EC) oxides that in principal could meet those requirements. These oxides possessed perovskite structures, low alkaline earth content, specific transition metal oxides incorporated in the B-site and a specific A-site deficiency. A design of experiment was performed involving the above stated criteria in order to identify an optimum composition of the electronic conducting phase that would fulfill all the requirements, including a sufficient ability to sinter. Praxair Surface Technology (PST), Woodinville, WA assisted in the synthesis of the perovskite powders for this design of experiment, as shown in Figure 13. Figure 13 shows 16 compositions of the dense gas separation layer, i.e. electronic conducting phase (EC) that were fabricated and tested.

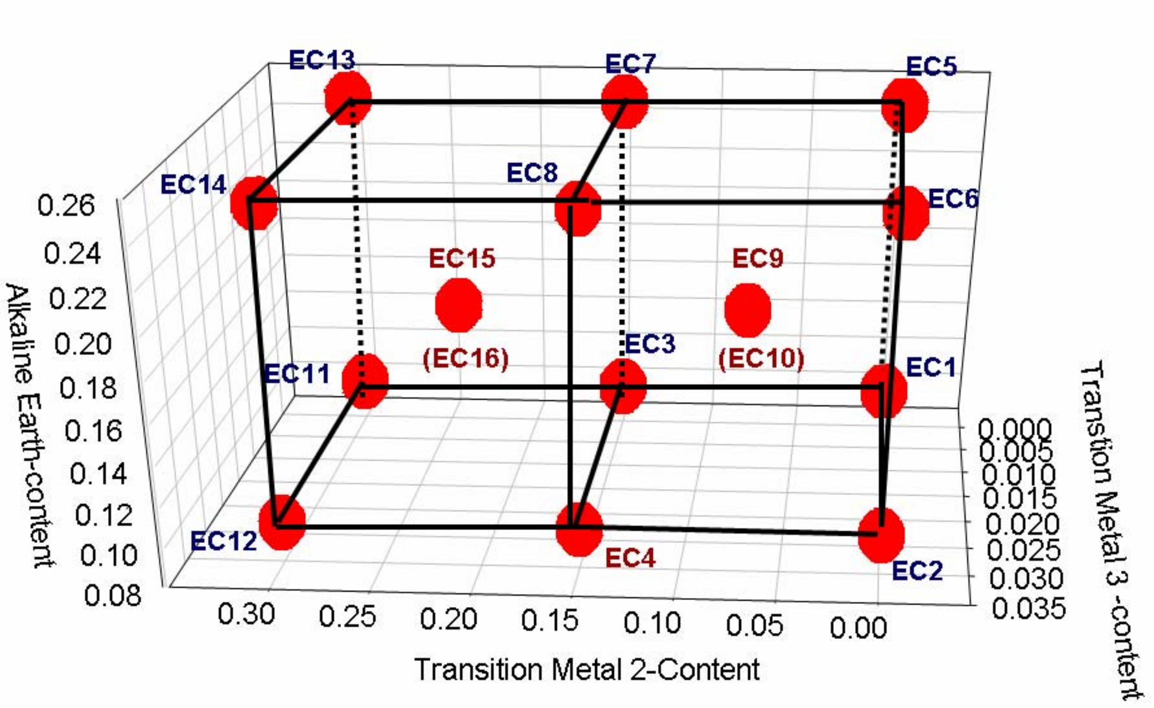


Fig. 13, Design of experiment for identification of a suitable electron conducting phase for the gas separation layer.

The gas separation layer needed to have a thermal expansion coefficient, matching that of the porous support material. This was achieved both by reducing the alkaline earth content and by selecting more stable transition metal oxides. The resulting material was a very stable electronic conductor (EC) but did not possess significant ambipolar conductivity. The gas separation layer material was modified to improve the ambipolar conductivity, by adding an oxygen ion conducting (IC) phase. This resulted in a robust gas separation layer material which incorporated two separate electronic and ionic conducting phases. The IC phase exhibited minimal chemical expansion and had a thermal expansion behavior similar to the EC and SM material. The IC material also proved to have a good chemical compatibility with some of the electronic conducting phases.

Initially, the sintered pellets that were fabricated from the as-received EC and IC powders were porous and the two phases were not well dispersed. The gas separation layer must be dense to prevent air from passing through the gas separation layer, and performance is expected to be enhanced by well dispersed IC and EC phases. The following preparation steps were taken to resolve these issues: ball milling of the EC powder before mixing it with IC powder, increasing the mixing time, using a sintering aid, screening of the powder, controlling the sintering atmosphere, and adjusting the sintering temperature. With these modifications, bars and pellets of the dual phase membrane material could be sintered to almost full density. Base powder and sintered pellets of the EC and IC materials were analyzed by X-ray diffraction in order to determine the crystal constants, phase evolution and bulk density. It was noted that the compositions were all single phase and could be indexed either as a hexagonal or orthorhombic structure. These results correlated well with those reported in literature.

Thermal Expansion Measurements were performed by dilatometry on 4x4x25 mm bars of the sintered EC material, the sintered IC material and the sintered dual phase EC and IC material in air. As illustrated in Table 8, measurements in air in the temperature range of 25-1000ºC indicated a close coefficient of thermal expansion (CTE) match of the EC with IC materials. The sintered OTM bars also had a very close CTE match with that of the support material (SM).

Table 8, Thermal expansion coefficients of EC, IC and dual phase mixtures as measured in Air by dilatometry.

Composition	**EC volume %**	**IC volume %**	**CTE from 100-1000°C**
EC1	100	0	11.3
EC2	100	0	11.7
EC3	100	0	10.4
EC4	100	0	12
EC5	40	60	11.8
EC6	40	60	12
EC7	40	60	11.6
EC8	50	50	11.8
EC9	50	50	11.9
IC	0	100	10.5

Results from x-ray diffraction electrical conductivity, microstructure, electrical and thermal characterization studies are addressed in detail in the EPACT appendix to this report and indicate that the chosen gas separation membrane and porous support materials are stable. Also, a method for depositing the dense gas separation layer is described in the EPACT appendix to this report.

3.3 Manufacturing Process

Powder

Powder for the porous support (SM) was commercially available. Pore former (PF1) was added at Praxair Specialty Ceramics (PSC) facility in Seattle and spray dried with a binder system to a granule size of approximately 25μm. Binder addition is required for adequate green strength after isostatic pressing. Upon receipt of the powder at the Praxair Surface Technology (PST)

Indianapolis manufacturing facility additional pore former (PF4) was added. The addition was accomplished by v-blending the spray dried powder and PF4 for 24hours followed by centrifugal milling to homogenize the mix and inhibit powder separation during mold filling.

EC powder for slurry coating was manufactured at Praxair Specialty Ceramics (PSC). Initial specifications called for a standard off the shelf material with high phase purity. Processing to high phase purity by means of a high calcination temperature resulted in a relatively large particle size of 1.2μm with moderate milling at PSC. The as-received powder was ball milled in the laboratory in order to obtain a particle size with which a dense gas separation layer could be accomplished by sintering at 1400°C. Later powder lots were ordered from PSC with that particle size to eliminate the milling step in Indianapolis.

Green Forming

All tubular substrates for the manufacturing task were formed via cold isostatic pressing (CIP). In this process the substrate powder is vibrated into a mold consisting of a metal mandrel which forms the inside diameter of the tube, a compliant outer bag which forms the outside diameter of the tube, and a plug which forms the closed end of the tube. Filling times were optimized to prevent under filling (too little time) as well as minimize powder/pore former separation (too much time). After filling the mold assembly is placed in a CIP unit and pressurized at pressures ranging from 10-40 kpsi. Various CIP pressures were utilized in order to obtain target sintering shrinkage ratios. Pressed tubes are removed from the mold assembly and stored in an oven held at 80°C until further processing.

Bisque Firing: Binder & pore former removal

Binder and pore former in the tubular substrate are removed via thermal decomposition. Tubes are hang-fired vertically by resting the cone of a tube on a refractory plate. Binder and pore former removal may take up to three days depending on type of pore former and the amount of pore former used. Substrates are thermally processed at temperatures of 850-1050°C to obtain a piece which exhibits enough strength to be further handled. This process is typically known as bisque firing.

Coating

Bisque fired tubes are coated internally by pouring slurry into the substrate, holding for a short amount of time, and carefully pouring out the slurry. A large portion of the manufacturing process development task was devoted to coating development as it was discovered that the coating method may limit the pore former amount, pore former particle size and tube length. Encouraging results were obtained with an alternative coating process which would overcome some of these manufacturing limitations. Further work and exploration is required.

Sintering

Successful sintering of coated substrates occurs in a controlled atmosphere. Lacking an atmosphere controlled furnace for hang firing, substrates are instead placed horizontally on a bed of Zirconia grog and thermally processed in the 1350-1450°C temperature range for several hours. Images of the OTM elements are included in the EPACT attachment to this report.

Quality Control

A run-sheet is created for every tube pressed. The run-sheet documents powder or slurry lot used and various processing parameters such as weights, pressures, temperatures and time. Tubes are visually inspected in the green state after pressing and in the bisque or sintered state after thermal processing. Tubes in various stages of processing are stored in a dry oven at 80°C to prevent outside contamination as well as to control moisture content inside the tubes. Final inspection includes helium leak rate, dimensional measurements, and visual inspection. All tubes exhibit a unique identification code in order to trace the processing history.

Manufacturing Yield & Deliverables

Table 9 lists current manufacturing yield of 6” composite tubes consisting of a porous SM substrate and a dual phase EC/IC separation layer.

Table 9, Yield of 6” composite tubes.

Composition	**0.75" nominal OD**		**1.0" nominal OD**	
	PF1	**PF1 + PF4**	**PF1**	**PF1 + PF4**
EC4	66%	N/A	N/A	N/A
EC10	83%	58%	90%	31%

Composite tube yield is seen to decrease with increasing pore former as well as increasing tube diameter. The majority of tubes failed due to an unacceptable Helium leak rate which is specified to be less than 5.0×10^{-7} cc·atm/sec. Initial experience with manufacturing longer length tubes up to 22” sintered also indicates decreased yield as scale-up issues arise.

Successful coating of long tube of 1" nominal diameter has been elusive. Table 10 lists tubes of length greater than the standard 6" that have been delivered for review.

Table 10: Longer sintered tubes delivered for review

Tube Length (in)	He-leak	Pore Former
12	2.30E-08	PF1
22	Off scale	PF1

Of the tubes listed only the 12" tube met the He-leak rate specification. The 22" tube contained many leaks from small pinholes distributed throughout the internal coating. It is worthy to note that both tubes contained no additional pore former other than PF1.

Scale-up of tube dimensions

The end goal is to manufacture composite tubes of greater than 5 feet of length that meet required specifications and exhibiting acceptable yields. Fabrication methods for scale up are included in the EPACT section of this report.

Manufacturing Cost Development

A cost model was developed for a relative low-volume tube manufacturing process. The model assumes a quantity of 150 tubes per month at approximately 80% yield utilizing the current process (iso-press, bisque fire, intermediate coating, intermediate fire, dense coat, dense fire). Opportunities for cost reduction are using less expensive materials and simplifying the pre-firing & co-firing steps. Reducing material price by half for substrate and slurry powder may reduce the cost to approximately $231.00/ft^2. These material prices can be realized if bulk quantities of powder are ordered and different vendors are chosen. The cost per square foot can be reduced to \$153/ft^2 by advancing the coating process so that firing of the membrane can occur in a single sintering step and by scaling up the manufacturing process.

4. Laboratory Scale Evaluations [Task 2]

4.1 OTM Tube Performance

Oxygen flux measurements have been performed both on disc and tube samples. A photograph of a disc reactor is shown in Figure 14a. It consists of a split tube furnace in which the disc is being clamped between two tubes, as shown in Figure 14b. In each tube there is a lance tube that feeds the air and fuel to the opposite sides of the disc.

a)

b)

Figure 14, 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 15. 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 15, Single tube reactor.

A commercial application of ceramic oxygen transport membranes requires a high reliability and performance and a low manufacturing and installation cost. Task 2 focused on assessing the membrane reliability and performance.

Membrane Reliability

The membrane reliability criteria that were used were the time to failure and the number of cycles to failure. Praxair is pleased to report that no membrane failures occurred in the past three years during which 31 OTM tubes were tested in single tube reactors for up to 1500 hrs each. The membrane and its seal also passed a test with 20 complete process cycles that include heating to 900°C, combusting fuel and cooling down to room temperature. The results of the cycle test are shown in Figure 16. There appears to be a slight decline of the oxygen flux with every cycle and this requires some further investigation. There were no membrane failures by unexpected shutdowns of the reactors as a result of power outages or hood failures.

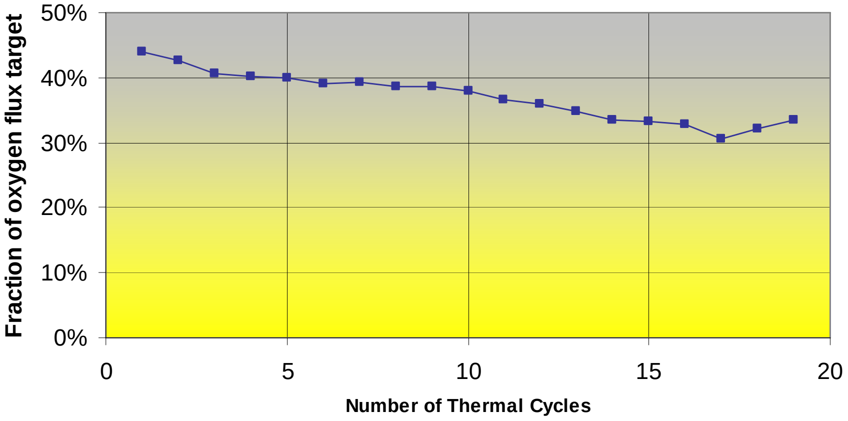


Figure 16, Process cycle test results.

Membrane Performance

The performance of the oxygen transport membrane is strongly dependent on the temperature, fuel gas composition, and the fuel and air flow rates as they impact the degree of fuel combustion and the degree of oxygen utilization from the air stream. Substantial progress was made in increasing the performance of the oxygen transport membrane, as shown in Figure 17. Most of this progress resulted from improving the porous support of the membrane, and by further improvement of activation layers.

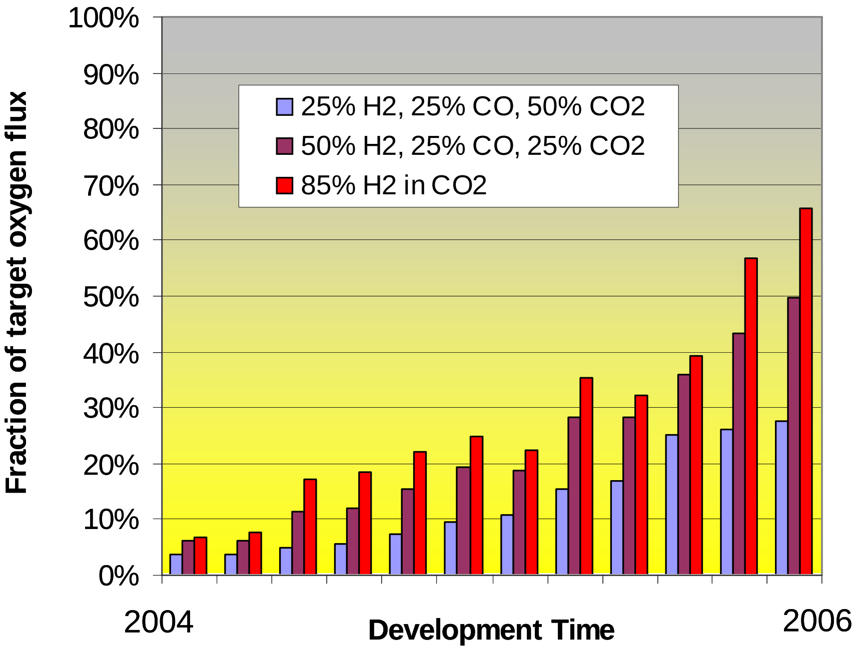


Figure 17, Progress in oxygen flux versus development time

Gas separation

The oxygen transport membranes were gas tight, as determined by the low measured Helium leak rate at room temperature ($< 10^{-7}$ cc-atm/sec).

Fuel gas composition

A design of experiment was developed to determine the dependence of oxygen flux on the fuel mixture with hydrogen, carbon monoxide and carbon dioxide as the components and the air and fuel flow rate as a process variable. Figure 18 shows a contour plot of the percent of target oxygen flux versus gas composition with a furnace setpoint of 900°C, a 1 slpm fuel flow rate and a 2 slpm airflow rate. Figure 18 shows that a higher oxygen flux is obtained when hydrogen is being used instead of carbon monoxide and that a low oxygen flux is obtained when there are no fuel species present (near complete oxidation conditions). The low oxygen flux in the absence of a fuel is a direct consequence of selecting a very stable material for the gas separation layer.

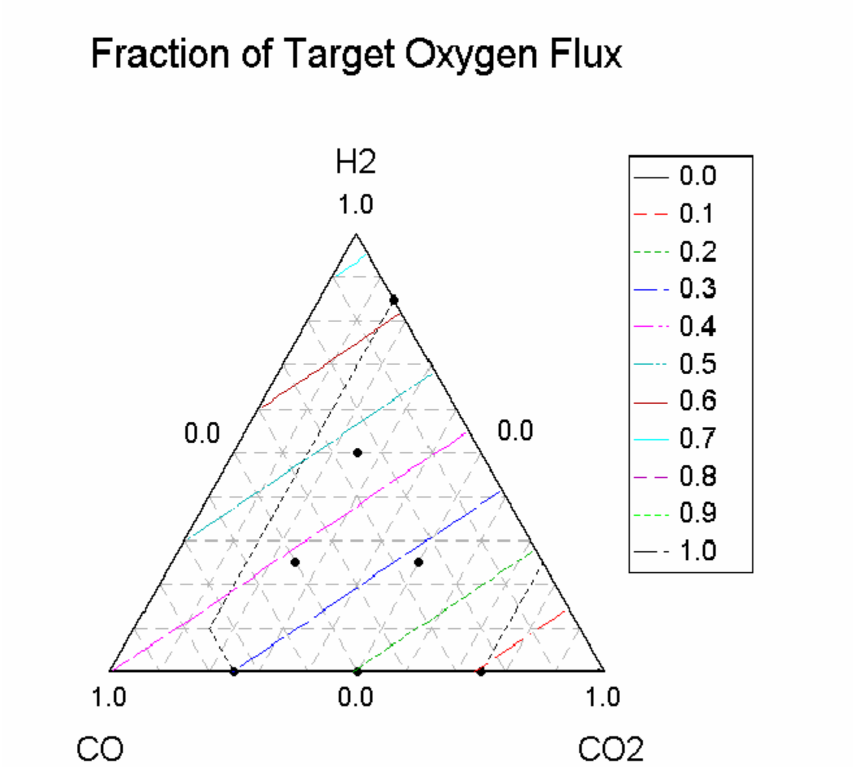


Figure 18, Contour plot of the normalized oxygen flux as a function of the composition of a H_2, CO and CO_2 gas mixture.

Experiments were also performed with methane as one of the components in the fuel, as required for a natural gas fired industrial boiler. The oxygen flux in the presence of methane (40% CH_4 in N_2) was similar to the oxygen flux for a gas mixture with 25% H_2, 50% CO and 25% CO_2. The combustion of methane in the reactor resulted in partial oxidation products by reforming reactions.

Temperature dependence

Figure 19 shows the oxygen flux versus temperature for five different fuel gas compositions. The air flow rate was fixed at 2 slpm and the fuel flow rate was fixed at 1 slpm. The results clearly show a mass transport limitation in the oxygen flux at high temperature when using the CO/CO_2 gas mixtures. The fuel gas composition with the highest hydrogen mole fraction yields the highest oxygen flux. This is because the diffusion coefficient of hydrogen is higher than that of carbon monoxide. The degree of combustion increases from low values (10%) at low temperature for the gas mixture with 75% carbon monoxide in CO_2 to near 80% for the gas mixture with 85% H_2 in CO_2.

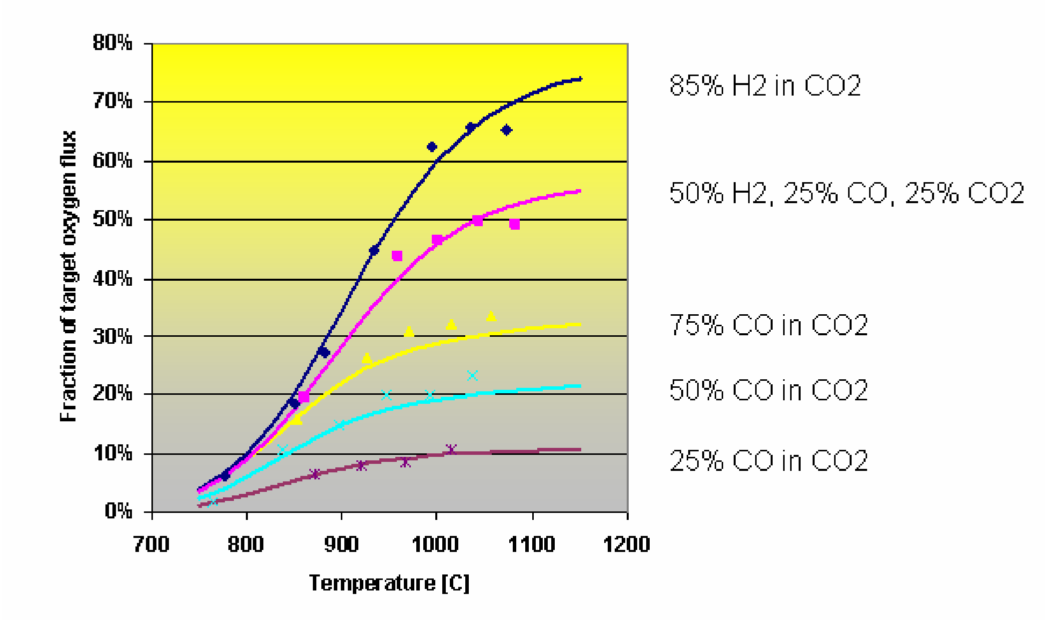


Figure 19, Temperature dependence of the oxygen flux where symbols indicate experimental data and curves indicate the fit to an oxygen transport model.

Flow rate dependence

The flow rates affect the degree of fuel combustion and the degree of oxygen utilization in the air stream. The fuel flow rate had the strongest effect on the oxygen flux while the effect of the air flow rate was weak as long as there was still oxygen in the retentate stream leaving the reactor. The lower the fuel flow rate, the lower the average oxygen flux through the membrane as the degree of combustion increases. The oxygen flux at the inlet of the reactor is still high but it drops to near zero values when all fuel species have been combusted and actual some oxygen is transferred into the combustion atmosphere that contains only carbon dioxide and steam. This was further studied through modeling of the tubular reactor, as discussed in the next section.

Oxygen transport model

The experimental measurements of membrane performance were used to verify and further develop the oxygen transport membrane model. The membrane model takes into account the mass transfer resistance of the airside of the membrane, a limited rate of surface exchange at the air side, the ambipolar diffusion through the gas separation layer, a finite rate of oxidation of fuel species at the interface between the separation layer and the porous support, and the counter diffusion of fuel species and their oxidation products in the porous support. The model provided valuable information about what changes had to be made in the membrane architecture and the composition of the membrane material in order to improve the membrane performance. Results from this model are provided in the EPACT appendix to this report.

4.2 Multi-tube Combustion

Combustion Apparatus

Oxygen transport membranes have been tested in a multi-tube combustion reactor to understand basic combustion phenomena and heat transfer issues in the advanced boiler, such as mechanical and chemical stability of the membranes, change of oxygen flux with fuel composition and temperature control of the OTM tubes.

Figure 20 shows the schematic of the multi-tube reactor, inside which six OTM tubes are installed. Flue gas is generated in an auxiliary combustion chamber to simulate the flue gas recirculation in the advanced boiler and to preheat the incoming fuel. Air is internally preheated to the OTM operating temperature and is sent to the OTM tubes. The flue gas/fuel mixture enters the reactor and passes over the OTM tubes in cross flow. The reactor temperature is controlled by an electric heater inside the reactor. Exhaust gas is sent to a series of analytical equipment to measure its composition. The oxygen depleted air stream is extracted out of the OTM tubes for compositional analysis and oxygen flux calculation. Figure 21 is a picture of the reactor constructed at Praxair in Tonawanda, NY.

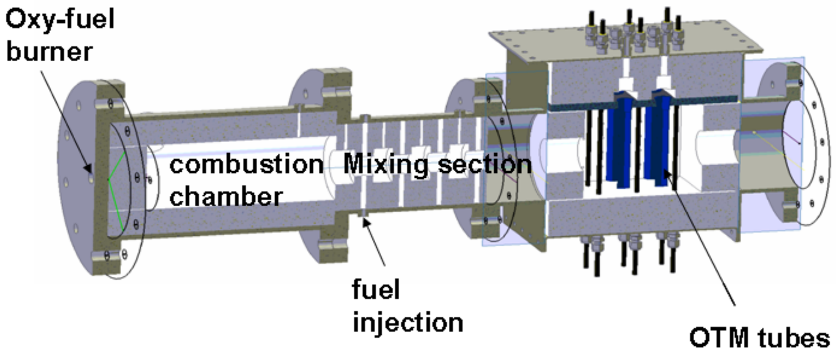


Figure 20, Schematic of the multi-tube reactor.

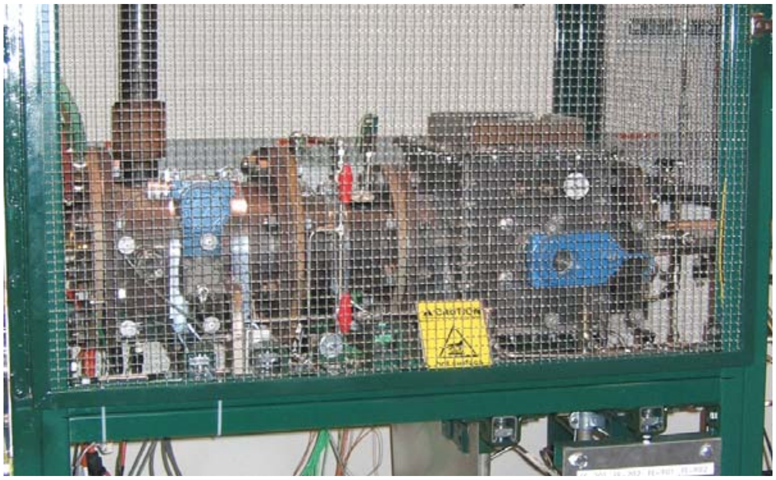


Figure 21, Multi-tube reactor at Praxair, Tonawanda.

Figure 22 shows a picture of the OTM tubes during a combustion test at about 1000°C. As can be seen, the OTM tubes turned red hot in the test. The experiments conducted in the multi-tube reactor are being used to identify the optimal operating conditions and provide background data for the conceptual design of a pilot scale advanced boiler.

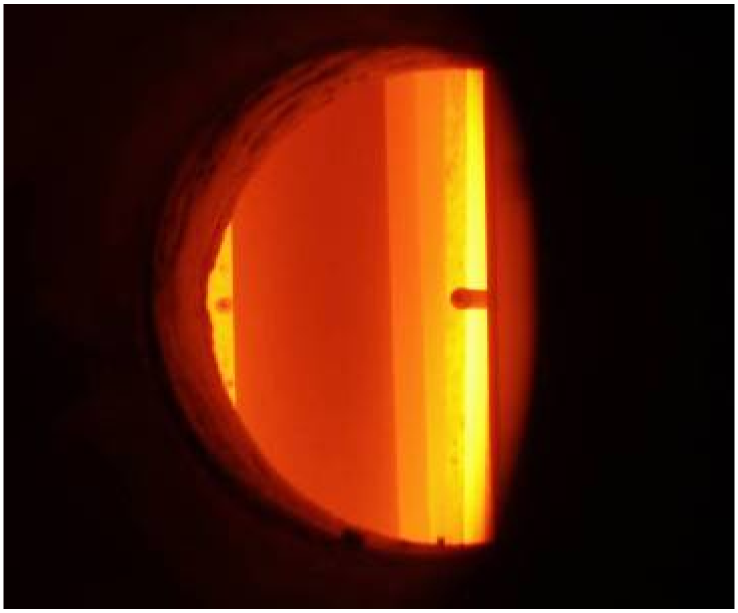


Figure 22, Photograph of OTM tubes during a combustion test in the multi-tube reactor.

Complete combustion

A series of experiments has been conducted to test the OTM tube properties in harsh combustion environments covering fuel-lean to fuel-rich conditions to simulate fuel/flue gas mixture passing over rows of OTM tubes in the advanced boiler. Complete combustion of methane, H_2/CO_2 mixture, and natural gas has been demonstrated in the multi-tube reactor. Figure 23 shows the composition of dried exhaust from the reactor measured by a gas chromatography (GC). In this experiment, natural gas was the fuel and the average temperature of the OTM tubes was approximately 1020^oC. As shown, the dried exhaust mainly consists of CO_2 (~95%), oxygen (~1%), and nitrogen from the natural gas (~4%). The GC measurement illustrates that all fuel species, such as CH_4, CO and H_2, have been completely combusted with the OTM tubes.

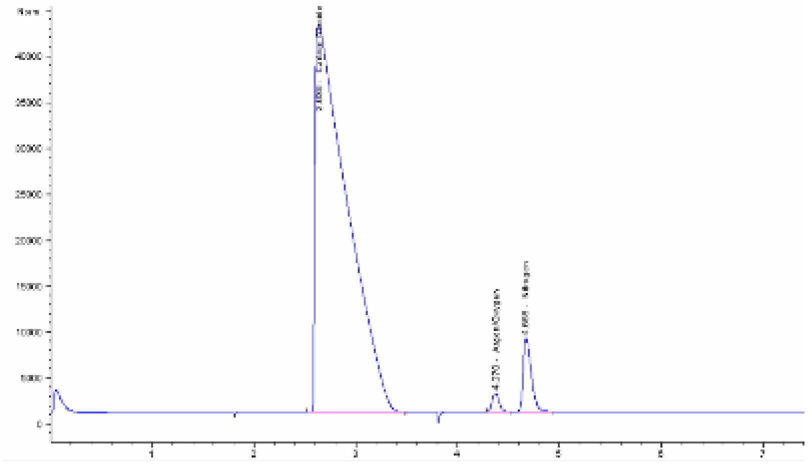


Figure 23. Gas chromatography measurement of dried exhaust from the multi-tube reactor in a natural gas fired experiment with OTM tubes ~ 1020^oC.

NO_x emission

NO_x was measured and found to have a concentration of 30 ppm (i.e. 0.004 lb/MMBTU) in the experiment with complete combustion. The NO_x concentration in the outlet was significantly lower than that in an air-fired system (typically 0.1 lb/MMBTU). In an experiment using CH_4 of high purity (>99%) as the fuel, exhaust NO_x was below 10 ppm. This indicates that the NO_x in the natural gas fired experiment was mainly produced by the reaction of oxygen with trace nitrogen in natural gas. In order to determine whether the NO_x was generated from the oxy-fuel burner or from the OTM tubes, the NO_x concentration in the combustion chamber was measured. The concentration of NO_x was 20 ppm, which demonstrates that the majority of NO_x was generated by the oxy-fuel burner in the auxiliary combustion chamber and not in the OTM section.

Tube Reliability in the Multi-tube Reactor

The OTM tubes tested in the reactor experienced a number of heating and cooling cycles, and chemical reactions with different fuels and at different temperatures (850 – 1050^{o}C). The OTM tubes have been demonstrated to be very robust and no membrane failures have been reported to date throughout the entire test period. This observation corresponds to our experience with testing the OTM tubes in the single tube reactors.

1,000-hour Life Test

A set of OTM tubes of one inch diameter have been tested in the multi-tube reactor for more than 1000 hours under complete combustion conditions. The test was conducted continuously, except for an unplanned shutdown after about 500 hours due to failure of the electric heater. Natural gas was injected into the reactor as the fuel and the OTM tubes were operated at ~ 1000°C in the first 500 hours and 970°C thereafter. The gas composition (vol. %) at the inlet of the OTM tube section was ~ 62.9% H_2O, 31.4% CO_2, and 5.7% CH_4. The gas had a low fuel concentration, which resulted in a low oxygen flux. Low fuel concentrations would be representative of the fuel concentration at the outlet section of the boiler where most of the fuel species would have already been combusted. The oxygen flux under inlet conditions of the boiler would have been significant higher than shown in this life test. Those operating conditions could not be simulated as the heating elements would loose their resistivity when exposed to a high fuel concentration.

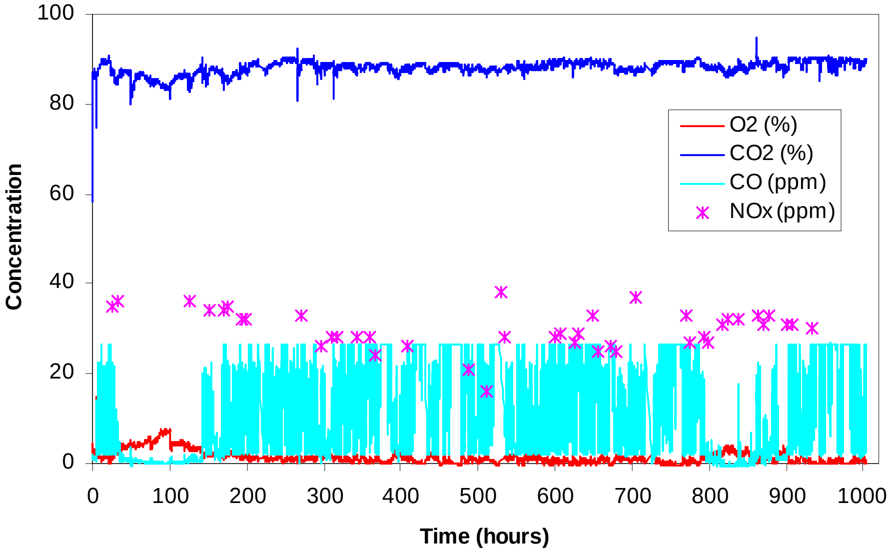


Figure 24, Dry exhaust composition during the 1000-hour life test under complete combustion conditions.

Figure 24 shows the species concentration of the dried exhaust measured by O_2, CO_2, CO, and NO_x on-line analyzers. The dried exhaust mainly consisted of CO_2 (~90%), small amount of oxygen (~1%), and nitrogen (~9%) which came from natural gas (~4%) and air leaking into the reactor and/or sampling line (~5%). The CO and NO_x were measured in ppm units. Analysis shows that at least 95% of the natural gas was completely consumed by the oxygen transported through OTM tubes, and less than 5% by air that leaked through the seals.

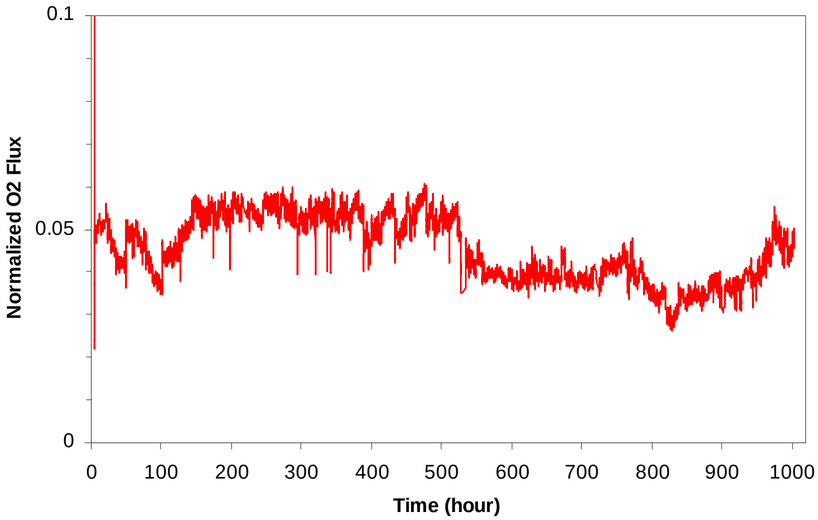


Figure 25. Normalized oxygen flux of OTM tubes during the 1000-hour life test under complete combustion conditions.

Figure 25 shows the normalized oxygen flux of the OTM tubes during the life test. The OTM membrane demonstrated stable performance despite the unplanned shutdown. The decrease of the oxygen flux after 500 hours is mainly due to the lower operating temperature after the shutdown. The average oxygen flux under complete combustion, however, is lower than the target value. Strategies to further improve the membrane performance are under development. One strategy is to use catalysts to convert natural gas to synthesis gas since the oxygen flux of OTM membrane is much higher when hydrogen is present as the fuel. The conversion can occur through stream reforming, CO_2 reforming, and partial oxidation of methane. Another strategy is to reduce or eliminate the simulated flue gas recycle.

After the life test, the air leakage rate of the OTM tubes was verified in order to determine whether any of the tubes broke. One tube was found cracked at the cone which was inside a metal seal holder, while no membrane failure was detected in the section which was inside the reactor and the fuel/flue gas mixture passed over. The crack at the cone is due to high torsion put on the nut of the seal holder which pushes the cone onto a seal gasket in the seal holder. This suggests some strategies to avoid cone failure such as less torsion, the same half-angle of the seal holder as that of the OTM tube cone, and avoiding direct contact of the ceramic tube with the nut of the seal holder.

5. Program Management [Task 5]

Figure 26 shows project spending from year 2002 to 2006, in terms of dollars spent per year, cumulative dollars spent, and the total allotted budget. The project was completed within budget, at the end of 2006. During the early phases of the project, resources were spent designing a mechanically robust and reliable ceramic membrane system. During the time this project allotted for choosing reliable materials, spending on the project was low. As this project matured, and the reliable ceramic membrane materials were developed, spending increased, reflecting confidence in the material development and selection.

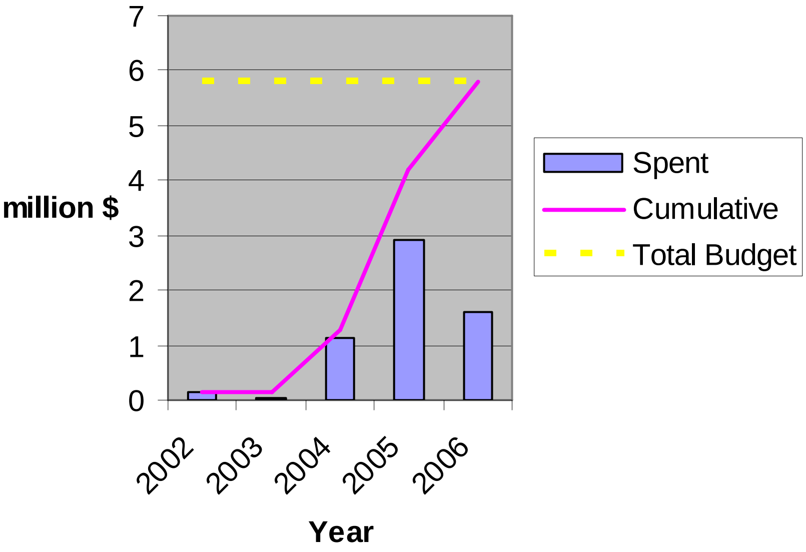


Figure 26, Actual spending versus budget

In past projects, Praxair’s approach focused on selecting high performance membrane materials, which often yielded poor reliability. Two large projects [13, 14] were discontinued as they failed to demonstrate reliability of the oxygen transport membrane system during the same timeframe as the initiation of this project. These prior experiences yielded valuable insight, and influenced Praxair’s current approach toward developing ceramic membranes. Praxair’s current approach involves initially selecting robust and reliable membrane materials and then modifying those materials to improve performance, while maintaining reliability objectives.

The major accomplishments of this project included:

- development and demonstration of a robust membrane material
- zero membrane failures during 2 years of testing in single and multi-tube reactors
- demonstration of complete combustion in a multi-tube reactor
- confirmed feasibility of a combustor design with OTM elements in a boiler

- quantified the cost of CO_2 capture and sequestration from a small natural gas fired boiler that is using an OTM combustor
- conceptual design of a coal fired power plant that incorporates OTM combuster and includes CO_2 capture and sequestration

Praxair informed the DOE about seven inventions or discoveries in the course of or under this contract [6,7]. Presentations were made at several conferences [8-12]. Praxair places a strong emphasis on chemical hygiene and safety. There were no recordable injuries or lost work days as a result of this project.

6. Conclusions

The cost of CO_2 avoided from advanced boilers that use the integration of air separation from OTMs and oxyfuel combustion is competitive with other CO_2 capture processes when applied to large power plants. This results from the low required auxiliary power load of the air separation process, no requirement for flue gas recirculation due to the combustion over a large membrane area, use of the latent heat of condensation of steam out of the flue gas for preheating the condensate return, and make-up water and air for the membrane process.

Durable oxygen transport membranes for oxyfuel combustion can be fabricated to survive and maintain reliability in a fuel environment. It was also determined that integrating the OTMs as heating elements in between the water tubes of a boiler is technically feasible.

During the last two years, we have had a zero percent failure rate, greatly exceeding expectations. However, the highly durable materials selected for the OTM reactors provided a lower performance. Substantial development is required for improving performance by improving the oxygen flux through the OTM system, while maintaining durability, and reducing manufacturing costs.

Reducing the cost of electricity that is produced with the advanced boiler and steam turbine generator system in a large power plant requires a change in fuel from natural gas to coal. Power plant concepts have been developed that use coal as the fuel and the efficiency and cost of electricity needs to be studied in more detail. Membrane materials need to be developed that can tolerate coal impurities.

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