CERAMIC MEMBRANE ENABLING TECHNOLOGY
FOR IMPROVED IGCC EFFICIENCY

ANNUAL TECHNICAL PROGRESS REPORT

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Principal Author: Ravi Prasad

DOE Program Manager: Ted McMahon

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Submitted by:

Praxair, Inc.
175 East Park Drive
Tonawanda, NY 14151

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ABSTRACT:

This yearly technical progress report will summarize work accomplished for Phase 1 Program during the program year 1999 / 2000. In task 1 a new material composition has been developed (PSO1d) that has superior properties to the initial lead candidate material. PSO1d has now been selected as the new lead candidate for the OTM. In task 2, several fabrication processes have been developed that enable the manufacture of composite OTM elements. Two methods have been selected for scale up to large element manufacturing. The work in task 4 has enabled a preferred composite architecture to be predicted through the use of an oxygen transport model and a reliability model. In task 6 process simulations of OTM and cryogenic IGCC process schemes have been completed to determine the viability of an integrated IGCC-OTM process. The performance requirements of the OTM to produce 25% capital cost savings over a cryogenic air separation unit have been identified.

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A. Executive Summary

The objective of this program is to improve process economics and efficiency and to reduce waste for coal-based IGCC power generation by advancing the development and commercial deployment of ceramic membrane systems that produce oxygen at lower cost than conventional systems.

The work undertaken in phase 1 of this program has been divided into 7 development tasks. These development tasks are,

- 1) Materials development
- 2) Composite development
- 3) Manufacturing development
- 4) Process development
- 5) Lab-scale reactor system
- 6) Preliminary business development
- 7) Program management and reporting

The work this year has focussed on tasks 1, 2, 4 and 6. Tasks 3 and 5 will start in the next quarter. Task 1 involves the development of a materials system that has the desired oxygen transport properties combined with the required stability to meet commercial targets. Task 2 focuses on defining the desired composite and substrate architecture, producing an effective interface layer and developing suitable fabrication techniques for the manufacture of composite OTM elements necessary for tasks 4 and 5. The work in task 4 involves experimental testing of OTM elements in single element flux testers at ambient and high pressures, and the development of oxygen transport models for single element composite OTM and multi-element OTM systems, and a reliability model. In task 6 a preliminary market study assessing potential products and markets, economic comparisons with competing technologies and identifying ancillary technologies required for successful commercialization will be completed. Task 6 will also focus on obtaining preliminary assessments of IGCC-OTM process schemes to establish OTM target properties and to determine the viability of integrated IGCC-OTM processes.

The objectives of the first year of the program are to:

- develop a material composition that has high performance as a composite membrane for IGCC applications,
- perform a detailed study of potential fabrication routes and composite architecture to enable selection of a manufacturing process for pilot plant OTM elements,
- demonstrate oxygen transport through composite OTM elements at 50% of the commercial target
- complete oxygen transport model for composite OTM elements to define composite architecture and process temperature
- define the performance and cost targets required to penetrate key markets

The work to achieve these objectives has led to several major accomplishments, summarized below.

- A new composition, PSO1d, has been selected as the new lead material for the gas separation layer.
- The initial target oxygen flux has been exceeded using composite OTM elements of a new composition, PSO1d.
- New fabrication routes allow thinner membranes of high quality to be deposited on various porous substrates. Two fabrication processes have been selected for the development of large composite elements.
- A combination of data from the oxygen transport model and reliability model have been used to predict preferred architectures for flux and robustness of the OTM.
- Direction for further improvement of OTM materials to permit integration with new process cycles has been identified.
- Strategies to enhance commercial operability and life have been defined.
- A paper entitled : "OTM – A Novel Technology for Integrated Oxygen Production in IGCC" reporting progress made in the current program was published at the Pittsburgh Coal Conference.

B. Experimental Methods

B.1. OTM Materials Development Experimental Methods

Characterization of OTM and substrate materials has been undertaken using many different experimental procedures. These include permeation, crystallographic, thermomechanical, thermochemical and electrochemical measurements. Standard equipment such as XRD, SEM, dilatometry and TGA/DSC were used. In addition an oxygen permeation tester was used to measure the oxygen flux of OTM discs.

The permeation test facility was described in the DOE IGCC second quarterly report ¹. This facility has been modified to enable the use of alternative gas mixtures in the purge gas stream. An additional test facility has also been designed for flux testing. This equipment will be used in the IGCC program.

B.2. Composite OTM Development Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. Small samples are first prepared and the fabrication routes that are most promising are further refined to enable larger OTM elements to be prepared. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Process Development Experimental Methods

Composite OTM elements of the required geometry prepared using methods developed in prior work have been tested for high temperature permeation utilizing the test facility and method previously described in the DOE IGCC second quarterly report ¹. Oxygen transport models and reliability models have been created using commercially available software.

B.4. Business Development Experimental Methods

Process simulations were modeled using commercial software and software provided by the DOE. The power generation section was modeled using Thermoflow GT Pro software. The process models of the gasification section were provided by the DOE NETL under CRADA 99-F032. The models for the cryogenic ASU were generated in HYSIS.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

The initial lead material for the OTM, PSO1 was characterized in detail. The results from the characterization indicate that the oxygen transport performance of this material is excellent. However, a number of shortfalls in this material were identified. The thermal expansion behavior and the chemical reactivity with certain gas compositions were not desirable. Furthermore, improved mechanical properties are desirable for long operating life under IGCC conditions. Therefore a more robust structure to support the membrane is required. A new material, PSO1d, was developed that has superior thermal expansion behavior and also has increased oxygen transport rates. Composite elements of PSO1d have routinely exceeded the initial target flux at ambient pressure using a helium purge. The oxygen flux of PSO1d composite elements is shown in figure 1. Also shown are the results from a PSO1d dense element to illustrate the benefit of the composite architecture. As a result, **PSO1d has been selected as the new lead candidate for the dense gas separation layer.** The properties of PSO1d are also expected to permit a wider selection of supporting structures enabling long life.

Figure 1. Oxygen flux through elements of PSO1d at ambient pressure using a helium purge gas stream

A material with improved high temperature mechanical properties was developed for use as the support. The high temperature mechanical properties of this material have been characterized and show substantial improvements. The chemical reactivity of the support material with PSO1d has also been investigated. At the process operating temperature, no chemical interaction was observed.

C.2. Composite OTM Development Results and Discussion

Initial experiments involved the development of composite OTM structures using OTM films with the same composition as the porous substrate to avoid chemical and mechanical incompatibility between the OTM film and substrate material. The majority of this work was completed using PSO1. Using this material system a variety of fabrication routes were developed, from which two have been selected for scaling up to large element manufacturing. The selection was based on the ease of large-scale fabrication of elements that have the required geometry with respect to the product yield and quality; the costs associated with the process; the leak rates obtainable and the oxygen fluxes obtainable. Several fabrication routes were used to make composite OTM elements that met the initial flux and leak targets so the final selections were based on the ease and cost of scale up.

Composite OTM samples have been tested for oxygen flux at 900°C for over 500 hours using an inert purging gas to generate the driving force without showing a decrease in oxygen flux. The results are shown in figure 2. This is encouraging as it shows that the gas separation membrane is not deteriorating at these temperatures. Under these conditions the oxygen flux was about 50% of the target flux. Results from the oxygen transport model developed in task 4 indicate that under IGCC process conditions the flux will be significantly higher for the same membrane geometry.

Figure 2. Oxygen flux of composite PSO1 as a function of time.

The effects of the thickness of the dense membrane, the thickness of the porous support and the porosity of the porous support on the oxygen flux were all studied independently. The results agreed well with modeling results from task 4. From this, **a preferred membrane architecture for IGCC operation has been determined.**

C.3. Process Development Results and Discussion

Oxygen permeation tests have been conducted on composite OTM elements fabricated using a variety of processes at ambient pressure using a helium purge gas. The flux measurements from these tests have routinely demonstrated the initial target flux at 1050°C. Composite OTM elements comprising PS01d on porous PS01d exceed the target flux.

An oxygen transport model has been developed and validated with experimental results at ambient pressure using a helium purge gas. The model has been used in conjunction with experiments in task 2 to determine the preferred architecture of the composite membrane given the properties of the OTM materials.

A reliability model has been created to determine stress concentrations within the composite membrane for given composite architectures and process conditions. The results from this model and the oxygen transport model have been used in conjunction with experimental results from task 2 to select the preferred composite architecture for OTM operation.

C.4. Business Development Results and Discussion

The following assumptions were used as a basis for the analysis:

1. Illinois #6 coal was used as a feedstock.
2. A Westinghouse 501G gas turbine (GT) was used for power generation and Shell technology was used for gasification.
3. The IGCC system utilizing cryogenic air separation was based on advanced cryogenic technology tailored for IGCC application. This cryogenic case was used as the base case for the comparison with OTM technology.

The base case IGCC was compared with two OTM-based IGCC concepts. In one IGCC concept, the OTM and gas turbine were integrated. In the other IGCC concept, a solid oxide fuel cell (SOFC) and an OTM were integrated with the GT. The anchor point for all cases was power output from gas turbine at ~272 MW. The gas turbine components sizes are fixed for a given model, and the power output from the unit depends on the design characteristics of individual components. The design power output will move with the changes in design of the gas turbine hardware. The steam cycle used was a 3 pressure reheat cycle (1800/330/50 psig).

Cryogenic Based System

The major process areas in these IGCC systems include a gasification plant, a combined cycle power plant, and a cryogenic air separation unit (ASU). The advanced base case IGCC involves a higher level of integration between the gas turbine and the ASU on both the air and nitrogen sides. The higher level of integration is facilitated by

cryogenic processes that are more easily intergrated with modern gas turbines. The nominal power output from the plant is ~400 MW. Figure 3 shows a simplified schematic of the base case IGCC.

Air for the ASU is obtained in part from the gas turbine compressor and in part from a supplemental compressor. Since the gas turbine compressor does not have intercooling, the discharge air is quite hot. The thermal energy in the extracted air is used to heat nitrogen from the ASU, and the remainder of the low-level heat in the air is used to preheat the boiler feed water (not shown). The cooled extracted air is combined with the supplemental air and sent to the cryogenic ASU. The ASU operates at elevated pressure set by the pressure of extracted air, and supplies oxygen at 95% purity to the gasifier. All residual nitrogen remaining after the oxygen and nitrogen requirements for the gasification plant have been met is returned to the gas turbine. Nitrogen injection into the gas turbine reduces NO_x production and increases power production due to an increased flow rate through the gas turbine expander. The quantity of extracted air is adjusted to maximize the gas turbine power output to ~272 MW.

Figure 3. IGCC with Advanced Cryogenic ASU

The gasification plant produces clean syngas from coal and oxygen. The clean syngas is injected into the gas turbine combustor along with nitrogen from the ASU. High pressure steam from the gasification plant is sent to the steam cycle. Additionally, low quality heat from various parts of the gasification plant is used to preheat the boiler feed water. To keep the combustor components cool, medium pressure steam from the steam cycle is

passed around it. The resulting superheated medium pressure steam is returned to the steam cycle.

OTM IGCC

Oxygen transport membrane-based IGCC exploits the synergy between the OTM and the gas turbine. The OTM operates at 900° C and requires high-pressure air to separate oxygen. The operating pressure of the Westinghouse 501G gas turbine is 275 psia, which is suitable for OTM. In addition, the air flow in the gas turbine is usually at least twice the quantity that is needed for complete combustion of the fuel. As a result, OTM and GT offer an excellent opportunity for integration. To maximize the benefit of this synergy, it is necessary to extract the maximum amount of GT air flow for oxygen separation in the OTM. Supplemental air is also supplied that not only replaces the amounts of oxygen and nitrogen sent to the gasification plant, but also serves as additional mass flowing through the expander to maximize the gas turbine output to ~272 MW. As shown in Figure 4, the GT air is combined with the supplemental air and sent to the OTM section.

Figure 4. IGCC with Oxygen Production by OTM

OTM/SOFC IGCC

This concept, shown in Figure 5, takes advantage of the similarity in operating temperature between the OTM and the SOFC to create a step-change improvement in efficiency. The nominal power output from this design is 670-700 MW due to additional power generation from the SOFC. The SOFC produces power with much higher

efficiency than the gas turbine. The SOFC also rejects waste heat at high temperature which can be efficiently used in a combined cycle; the waste heat is used to preheat air to the operating temperature of the SOFC and OTM units. Significant efficiency improvement is achieved as a result. Fuel from the gasification unit and the combined air stream from the gas turbine and supplemental compressor are sent to the SOFC/OTM section. The SOFC is assumed to produce power at 50% efficiency.

Figure 5. IGCC with OTM and SOFC

A portion of oxygen contained in the air stream is consumed in the SOFC and another portion is recovered in the OTM. High-purity nitrogen generation is integrated with oxygen generation. The lean air stream from the SOFC/OTM section is sent to the gas turbine combustor along with additional fuel.

The results of the analysis for the cases completed to date are shown in the following table.

IGCC Key Process Parameters and Cost/Performance				
CASE	Standard Cryogenic Case	Base Case Adv. Cryo	OTM	SOFC / OTM
Gas Clean-up	Mdea	Mdea	Rectisol	Rectisol
Oxygen (100%,TPD)	2403	2405	2411	3419
Oxygen purity, %	95	95	>99%	>99%
Coal (TPD)	3150	3153	3192	4516
Gas Turbine (MWe)	273	272.2	272.8	272.7
Steam Turbine (MWe)	188.3	186.6	193.9	223.4
SOFC (MWe)	—	—	—	257.8
Misc. Power (MWe)	54.3	43.2	40.0	50.9
Net Power (MWe)	407.1	415.6	426.7	703
Efficiency: % HHV	45.4	46.3	46.9	54.6
ASU cost, relative	142	100	85	114
IGCC cost, \$MM	\$597	\$559	\$552	\$966
Capital cost, \$/kW	\$1467	\$1344	\$1294	\$1374
SOFC costs, \$/kW				\$600,\$1000
COE in current \$, mils/kWh	53.4	49.7	48.1	46.5, 52.5

The results show a 25% reduction in the cost of the ASU and 1.04% efficiency improvement in the overall efficiency of power production. For the SOFC/OTM the efficiency improvement is approximately 8%.

- Achieving these performance targets requires achieving an OTM performance target (Flux/cost) $>4 \text{ scc.cm}^{-2}\text{sec}^{-1}/\$/\text{cm}^2$.
- The best processes require the capability for full air extraction from the gas turbine.
- This analysis does not reflect the inclusion of advanced processes which will be analyzed during the next quarter.
- A further review of the data suggests that a more detailed analysis of the “balance of plant costs” need to be further reviewed.
- The results of this analysis are different from the Work conducted under an earlier under CRADA 99-F032 due to differences in gas turbine performance and the addition of an DC/AC conversion efficiency to the SOFC/OTM case.

D. Conclusion

Good progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, a new lead material for the dense gas separation layer, PSO1d, has been selected based on superior oxygen transport and thermo-mechanical properties. The initial oxygen flux target has been exceeded using PSO1d. In task 2, several fabrication processes have been developed, from which two have been selected for scale up to large element manufacturing. The effect of the architecture of the composite on the oxygen flux has also been determined. In task 4, an oxygen transport model has been developed which has been validated with experimental results. A reliability model has been developed to predict stress concentrations within the OTM element for given composite architecture and process conditions. Using the data from the oxygen transport model and the reliability model, in conjunction with experimental flux data from task 2, a preferred composite architecture has been determined. The work in Task 6 identified the OTM performance requirements for Type 1A IGCC operation that enable a 25% reduction in the capital cost of an IGCC plant based on cryogenic separation of oxygen.

E. References

1. **Prasad, Ravi, "Ceramic Membrane Enabling Technology for Improved IGCC Efficiency" Quarterly Technical Progress Report for US DOE Award No. DE-FC26-99FT40437, April 2000.**

F. List of Publications

Prasad, R., Shah, M., Drnevich, R., Thompson, D., "OTM – A Novel Technology for Integrated Oxygen Production in IGCC", copyright 2000, presented at the 2000 Pittsburgh Coal Conference.