CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting January 1, 2002 and ending March 31, 2002

Praxair Program Manager: **Ravi Prasad**
DOE Program Manager: **Ted McMahon**

Report Issue Date: May 2002

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
175 East Park Drive
Tonawanda, NY 14150

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter January to March 2002. In task 1 improvements to the membrane material have shown increased flux, and high temperature mechanical properties are being measured. In task 2, composite development has shown that alternative fabrication routes of the substrate can improve membrane performance under certain conditions. In task 3, scale-up issues associated with manufacturing large tubes have been identified and are being addressed. The work in task 4 has demonstrated that composite OTM elements can produce oxygen at greater than 95% purity for more than 1000 hours of the target flux under simulated IGCC operating conditions. In task 5 the multi-tube OTM reactor has been operated and produced oxygen.

TABLE OF CONTENTS

A.	Executive Summary	Page 3
B.	Experimental Methods	Page 3
	B.1. OTM Materials Development	Page 3
	B.2. Composite OTM Development	Page 3
	B.3. Manufacturing Development	Page 3
	B.4. Process Development	Page 4
C.	Results and Discussion	Page 4
	C.1. OTM Materials Development	Page 4
	C.2. Composite OTM Development	Page 4
	C.3. Manufacturing Development	Page 4
	C.4. Process Development	Page 4
	C.5. O-1 Pilot Reactor Development	Page 4
D.	Conclusion	Page 5
E.	References	Page 5
F.	List of Publications	Page 5
G.	Appendix – Limited Rights Data	Page A1

A. Executive Summary

The objectives of the third year of the program are to operate a laboratory scale pilot reactor that can produce 200-300 CFH oxygen. Manufacturing technology will be developed to demonstrate that commercial size tubes can be fabricated using methods that can become economically viable. Material and composite development are required to produce OTM tubes that are capable of a commercial flux and that have sufficient mechanical robustness for commercial life. The target flux will be demonstrated on 6" tubes of a material that can be used for pilot plant demonstration.

In the second quarter of the third year of the program, work has focussed on demonstrating stable operation of PSO1d composite tubes under simulated Type 1A IGCC conditions, and operating the O1 reactor. The major accomplishments this quarter were

- **1000 hour continuous operation with a pressure differential of 275psig at 900^{o}C was achieved using a composite PSO1d tube. The oxygen purity was > 95% and the flux > 75% of commercial target.**
- **O1 pilot reactor was operated using two dense PSO1d tubes. Oxygen production was recorded during the test**.

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 oxygen permeation testers were used to measure the oxygen flux of OTM discs. The permeation test facility was described in the DOE IGCC first annual report [1].

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. Manufacturing Development Experimental Methods

Fabrication routes developed in task 2 have been used for the manufacture of OTM elements for testing in the high-pressure permeation testers used in task 4.

B.4. 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 high-pressure test facility and method previously described in the DOE IGCC first annual report [1]. A method of increasing the driving force for oxygen transport has been added to the flux tester.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

Improvements to PSO1d to increase its oxygen transport properties continued. The next composition, labeled PSO1x, shows significant improvement to oxygen flux under a variety of processing conditions.

High temperature mechanical strength measurements have been made on PSO1d. There is minimal impact on the 4-point bending strength of PSO1d between room temperature and the IGCC operating temperature.

C.2. Composite OTM Development Results and Discussion

High quality composite elements of PSO1d have been routinely prepared using a variety of processing methods. These composite elements are gas tight and have enabled the 2001 target oxygen flux to be obtained. This technology has now been applied to larger tubes.

C.3. Manufacturing Development Results and Discussion

Improvements to the manufacturing process have been used to fabricate 36" long composite elements of PSO1d. Issues associated with scale-up are being addressed.

C.4. Process Development Results and Discussion

A composite tube has produced oxygen under conditions similar to IGCC operation with a **flux greater than 75% of the commercial target and purity greater than 95% for more than 1000 hours**.

C.5. O-1 Pilot Reactor Development Results and Discussion

PSO1d tubes have been tested in the O-1 reactor and have produced oxygen. This is the first multi-tube OTM reactor to produce oxygen. Issues with heat control are being examined.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, improvements to the membrane material indicate that oxygen flux can be further increased. In task 2, composite elements of capable of producing the 2001 oxygen flux target can be routinely prepared. In task 3, 36" long composite PSO1d OTM elements can be fabricated. In task 4, a composite tube has produced oxygen under conditions similar to IGCC operation with a **flux greater than 75% of the commercial target and purity greater than 95% for more than 1000 hours**. In task5 oxygen was produced in the multi-tube O-1 reactor.

E. References

[1] Prasad, Ravi, "Ceramic Membrane Enabling Technology for Improved IGCC Efficiency" 1st Annual Technical Progress Report for US DOE Award No DE-FC26-99FT40437, October 2000.

F. List of Publications

Prasad, R., Chen, J., van Hassel, B., Sirman, J., White, J., "Advances in Oxygen Transport Membrane Technology for Integrated Oxygen Production in IGCC", copyright 2001, presented at the 18th Pittsburgh Coal Conference, December 2001.