Appendix X

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
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DISCLAIMER:

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

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°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 18^{th} Pittsburgh Coal Conference, December 2001.

Appendix XI

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting April 1, 2002 and ending June 30, 2002

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Ted McMahon/Jenny Tennant

Report Issue Date: August 2002

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter April to June 2002. In task 1 improvements to the membrane material have shown increased flux, stability and strength. In task 2, composite development has demonstrated the ability to cycle membranes. In task 3, scale-up issues associated with manufacturing large elements 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 after 10 thermal and pressure cycles. In task 5 the multi-tube OTM reactor has been operated and produced oxygen.

TABLE OF CONTENTS

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 elements can be fabricated using methods that can become economically viable. Material and composite development are required to produce OTM elements that are capable of a commercial flux and that have sufficient mechanical robustness for commercial life. The target flux will be demonstrated on 6" elements of a material that can be used for pilot plant demonstration.

In the third quarter of the third year of the program, work has focussed on improving the properties of the OTM material, demonstrating cyclability of PSO1d composite elements under simulated Type 1A IGCC conditions, and operating the O1 reactor. The major accomplishments this quarter were

- **A new material, PSO1x has been demonstrated to have superior flux, mechanical strength and stability than PSO1d.**
- **10 complete cycles were achieved using a composite PSO1d element between room temperature with no pressure differential to 275psig at 900°C. The oxygen purity was > 95% after every cycle.**
- **Three tests were completed in the O1 pilot reactor using two dense PSO1d elements. Oxygen production was recorded during each 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. PSO1x also shows substantial (>40%) improvement to the mechanical strength and is more stable in conditions that are present under certain IGCC process cycles.

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, life and thermal and pressure cycling to be obtained. This technology has now been applied to larger elements.

C.3. Manufacturing Development Results and Discussion

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

C.4. Process Development Results and Discussion

A composite element has produced oxygen under conditions similar to IGCC operation with **flux greater than 75% of the commercial target and purity greater than 95% O_2 after 10 thermal and pressure cycles.**

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

Three tests have been completed in the O-1 reactor using PSO1d elements. In each test oxygen has been produced. This is the first multi-element OTM reactor to produce oxygen.

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, stability and strength can be further increased. In task 2, composite elements of capable of producing 10 thermal cycles have been prepared. In task 3, 36" long composite PSO1d OTM elements can be fabricated. In task 4, a composite element has produced oxygen under conditions similar to IGCC operation with a **flux greater than 75% of the commercial target and purity greater than 95% after 10 thermal cycles**. In task 5 oxygen was produced in the multi-element O-1 reactor during three separate tests.

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 18^{th} Pittsburgh Coal Conference, December 2001.

Appendix XII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting July 1, 2002 and ending September 30, 2002

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: March 2003

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter October to December 2002. In task 1 improvements to PSO1x have shown increased performance in strength and stability. In task 2, PSO1d and PSO1x elements have been fabricated for testing in the pilot reactor . In task 3, the lab-scale pilot reactor has been operated for 1000 hours. In task 6 initial power recovery simulation has begun. In task 7, HYSIS models have been developed to optimize the process for a 50 ton per day demonstration unit.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the first year of phase 2 of the program are to construct and operate an engineering pilot reactor that can produce 2-5 TPD oxygen. Manufacturing technology will be developed to demonstrate that commercial size elements can be fabricated using methods that can become economically viable. Material and composite development are required to produce OTM elements that are capable of a commercial flux and that have sufficient mechanical robustness for commercial life. The target flux will be demonstrated on composite elements of a material that can be used for pilot plant demonstration.

In the fourth quarter of the third year of the program, work has focussed on characterizing the new OTM, PSO1x, and operating the O1 reactor. The major accomplishments this quarter were

- **High temperature strength of PSO1x is as high as the room temperature strength**

- **The O1 reactor was operated at target flux and target purity using shorter composite tubes.**

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 longer single element tester has been designed and constructed.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

Characterization of PSO1x continued. The material has high temperature strength similar to the room temperature strength. Samples exposed to conditions similar to expected operation for 50 hours also showed no decrease in strength.

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, life and thermal and pressure cycling to be obtained. These elements have been used successfully in O-1 to yield target flux and purity.

C.3. Manufacturing Development Results and Discussion

Improvements to the manufacturing process have been used to fabricate 20" long composite elements of PSO1d, and shorter elements of PSO1x.

C.4. Process Development Results and Discussion

A composite element of PSO1x has produced oxygen under conditions similar to IGCC operation with target purity for greater than 500 hours.

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

The O-1 reactor has been operated using high flux, composite PSO1d elements. The reactor is being operated at 900°C with a pressure differential of 275 psi across the membrane. The target flux per tube was exceeded and >95% oxygen purity were obtained and the reactor continues to operate.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, improvements to the membrane material show the strength of PSO1x is as high at high temperature as at room temperature. In task 2, composite elements of PSO1d and PSO1x can be routinely prepared. In task 3, longer composite PSO1d OTM elements and short PSO1x composite elements can be fabricated using the technology developed in task 2. In task 4, a composite element of PSO1x has produced oxygen at purity greater than 95% after 500 hours. In task 5, oxygen was produced in the multi-tube O-1 reactor at greater than target purity and target flux per tube.

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

[1] "Advances in OTM Technology for IGCC", Ravi Prasad, Jack Chen, Bart van Hassel, John Sirman, James White, Prasad Apte, Tim Aaron, Eric Shreiber, Presented at the 19th Annual International Pittsburgh Coal Conference, Pittsburgh, 9/26/02.

Appendix XIII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting October 1, 2002 and ending December 31, 2002

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: March 2003

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter October to December 2002. In task 1 improvements to PSO1x have shown increased performance in strength and stability. In task 2, PSO1d and PSO1x elements have been fabricated for testing in the pilot reactor. In task 3, the lab-scale pilot reactor has been operated for 1000 hours. In task 6 initial power recovery simulation has begun. In task 7, HYSIS models have been developed to optimize the process for a future demonstration unit.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the first year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Methods to improve the strength and stability of PSO1x were identified.**

- **The O1 reactor was operated at target flux and target purity for 1000 hours.**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation are proprietary information and included in the Appendix.

B.4. Power Recovery Experimental Methods

HYSIS simulations are used to model power recovery options.

B.5. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

Improvements to the strength and stability of PSO1x continued. Modifications to processing and other additions haven produced a 20% increase in strength and improved tolerance to various process gases and contaminants.

C.2. Element Manufacturing Results and Discussion

High quality composite elements of PSO1d and PSO1x have been routinely prepared These elements have been used successfully in O-1 to yield target flux and purity.

C.3. Systems Technology Results and Discussion

The O-1 reactor has been operated for 1000 hours at the operating temperature and pressure, producing the target oxygen flux and purity.

C.4. Power Recovery Results and Discussion

A HYSIS model has been generated and a preliminary design established based on one of the processes considered for a future demonstration plant.

C.5. Process Analysis and Economics Results and Discussion

Two models have been developed for a future demonstration plant to begin optimization of heat integration and power recovery.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, improvements to the membrane material have increased the strength and stability of PSO1x. In task 2, composite elements of PSO1d and PSO1x can be routinely prepared. In task 3, the O-1 reactor has been operated for 1000 hours. In task 6, initial power recovery work has begun. In task 7, initial process analysis has begun to optimize heat integration and power recovery for a future demonstration plant.

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

[1] "OTM – An Advanced Oxygen Technology for IGCC", Ravi Prasad, Jack Chen, Bart van Hassel, John Sirman, James White, Eric Shreiber, Joe Corpus, Joshua Harnanto, Presented at the Gasification Technologies 2002 Conference, San Franciso, October 30, 2002.

Appendix XIV

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting January 1, 2003 and ending March 31, 2003

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: April 2003

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter January to March 2003. In task 1 detailed modeling has identified preferred architectures. In task 2, PSO1d and PSO1x elements have been fabricated for testing in the pilot reactor. In task 3, the lab-scale pilot reactor has been operated for 1000 hours with improved success. In task 6, power recovery simulation has identified preliminary machine configurations. In task 7, HYSIS models continue to be developed to optimize the process for a future demonstration unit.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the first year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Preferred OTM architectures have been identified through stress analysis.**
- **The O1 reactor was operated at target flux and target purity for 1000 hours.**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation are proprietary information and included in the Appendix.

B.4. Power Recovery Experimental Methods

HYSIS simulations are used to model power recovery options.

B.5. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

Modeling of the OTM elements and conditions has produced a preferred range of architectures to use for commercial operation.

C.2. Element Manufacturing Results and Discussion

High quality composite elements of PSO1d and PSO1x have been routinely prepared in large numbers. These elements have been used successfully in O-1 to yield target flux and purity.

C.3. Systems Technology Results and Discussion

The O-1 reactor has been operated for 1000 hours for the third time at the operating temperature and pressure, producing the target oxygen flux and purity.

C.4. Power Recovery Results and Discussion

A HYSIS model has been generated and preliminary machine configurations have been designed.

C.5. Process Analysis and Economics Results and Discussion

Development of two process models continues to enable heat and power integration of a future demonstration unit.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, modeling has produced a preferred range of architectures to use for commercial operation. In task 2, composite elements of PSO1d and PSO1x can be routinely prepared in large numbers. In task 3, the O-1 reactor has been operated for 1000 hours. In task 6, power recovery work has enabled design of preliminary machine configurations. In task 7, process analysis continues to optimize heat integration and power recovery for a future demonstration plant.

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.

Appendix XV

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting April 1, 2003 and ending June 30, 2003

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: July 2003

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter April to June 2003. In task 1 OTM development has led to improved flux and strength performance. In task 2, robust PSO1d elements have been fabricated for testing in the pilot reactor. In task 3, the lab-scale pilot reactor has been operated for 1000 hours with improved success. In task 7, economic models substantial benefit of OTM IGCC over CRYO based oxygen production.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the first year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Robust elements are being produced at Praxair's manufacturing facility**
- **The O1 reactor was operated at target flux and target purity for 1000 hours.**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation are proprietary information and included in the Appendix.

B.4. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

Improvements to composite element design have yielded 25% improvement in flux performance. Continued development of the OTM has resulted in large increases in mechanical strength and robustness.

C.2. Element Manufacturing Results and Discussion

High quality, robust composite elements of PSO1d have been prepared. These elements are expected to pass life cycle requirements.

C.3. Systems Technology Results and Discussion

The O-1 reactor has been operated for 1000 hours for the fourth time at the operating temperature and pressure, producing the target oxygen flux and purity.

C.4. Process Analysis and Economics Results and Discussion

Economic analysis has shown considerable cost of electricity advantage of OTM-IGCC over CRYO based systems. Opportunities for further improvement were identified.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, flux and strength improvements to the OTM have been made. In task 2, robust composite elements of PSO1d have been prepared. In task 3, the O-1 reactor has been operated for 1000 hours. In task 7, modeling shows cost advantages of OTM-IGCC over CRYO based separation.

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.

Appendix XVI

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting July 1, 2003 and ending September 30, 2003

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: November 2003

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter July to September 2003. In task 1 OTM development has led to improved strength and composite design. In task 2, the manufacture of robust PSO1d elements has been scaled up. In task 3, operational improvements in the lab-scale pilot reactor have reduced turn-around time and increased product purity. In task 7, economic models show substantial benefit of OTM IGCC over CRYO based oxygen production.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the first year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Element production at Praxair's manufacturing facility is being scaled up**

- **Substantial improvements to the OTM high temperature strength have been made.**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation are proprietary information and included in the Appendix.

B.4. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

Improvements to composite element design have yielded improvement in strength. Continued development of the OTM has resulted in large increases in high temperature mechanical strength and robustness.

C.2. Element Manufacturing Results and Discussion

Production of high quality, robust composite elements of PSO1d has been scaled up at Praxair's manufacturing facility.

C.3. Systems Technology Results and Discussion

O-1 reactor testing has continued. Operational improvements have been made to decrease turnaround time and improve product purity.

C.4. Process Analysis and Economics Results and Discussion

Economic analysis has shown considerable cost of electricity advantage of OTM-IGCC over CRYO based systems.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, high temperature strength improvements to the OTM have been made. In task 2, manufacture of robust composite PSO1d elements has been scaled up. In task 3, the operation of the O-1 reactor has been improved. In task 7, modeling shows cost advantages of OTM-IGCC over CRYO based separation.

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

[1] "Oxygen Transport Membranes for Future IGCC Power Plants", Ravi Prasad, Jack Chen, Hancun Chen, Jonathan Lane, James White, Joseph Corpus, Eric Shreiber, John Spero and Bart A. van Hassel. Presented at Session 19, Gasification-Advanced Technologies-1, Proceedings of the Twentieth Annual International Pittsburgh Coal Conference, September 15-19, 2003, Pittsburgh, Pennsylvania, USA, Copyright Pittsburgh Coal Conference, ISBN 1-890977-20-9.

Appendix XVII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting October 1, 2003 and ending December 31, 2003

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: February 2004

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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

DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter October to December 2003. In task 1 OTM development has led to improved strength and composite design for lower temperatures. In task 2, the yield of a large batch of OTM elements improved. In task 3, operational improvements in the lab-scale pilot reactor have reduced turn-around time and increased product purity. In task 7, IGCC economics were updated to reflect state-of-the-art OTM and cryogenic air separation processes.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Long term life and process cycle tests have been completed**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation and advanced reactor design are proprietary information and included in the Appendix.

B.4. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

OTM life and process cycle tests have been completed. Improvements to the OTM material continue to be made.

C.2. Element Manufacturing Results and Discussion

Production of high quality, robust composite elements of PSO1d has been scaled up at Praxair's manufacturing facility. The batch size OTM element production was increased.

C.3. Systems Technology Results and Discussion

O-1 reactor testing has continued. Operational improvements continue to decrease turnaround time and stabilize oxygen flux and purity.

C.4. Process Analysis and Economics Results and Discussion

IGCC economics were updated to reflect state-of-the-art OTM and cryogenic air separation processes. Methods to operational costs have been identified.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, more robust OTM elements have been tested in life and process cycle tests. In task 2, manufacture of robust composite PSO1d elements has been scaled up with improvement in yields. In task 3, the operation of the O-1 reactor has been improved, and the advanced reactor design was finalized. In task 7, alternate OTM-IGCC processes were developed and process economics were evaluated.

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.

Appendix XVIII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting January 1, 2004 and ending March 31, 2004

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: June 2004

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
175 East Park Drive
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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter January to March 2004. In task 1 OTM development has led to improved strength and composite design for lower temperatures. In task 2, the measurement system of OTM element dimensions was improved. In task 3, a 10-cycle test of a three-tube sub-module was reproduced successfully. In task 5, sizing of several potential heat recovery systems was initiated. In task 7, advanced OTM and cryogenic IGCC cases for near-term integration were developed.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- Systems technology
- High temperature heat exchange
- Power recovery
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Long term life test of OTM element passed six months**
- **Process cycle tests have been completed and reproduced successfully**

B. Experimental Methods

B.1. OTM Element Reliability 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 elements. The permeation test facility was described in the DOE IGCC first annual report [1].

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used are proprietary information and included in the Appendix.

B.3. Systems Technology Experimental Methods

Details of the O-1 pilot reactor operation and advanced reactor design are proprietary information and included in the Appendix.

B.4. High Temperature Heat Exchange Experimental Methods

The design and engineering methods utilized are proprietary information.

B.5. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

OTM life tests continued with one life test passing the six-month mark. Improvements to the OTM material continue to be made.

C.2. Element Manufacturing Results and Discussion

Consistency of both the powder and the element manufacturing process was demonstrated at Praxair's manufacturing facility. The measurement system of the OTM element dimensions was improved.

C.3. Systems Technology Results and Discussion

Testing of a three-tube sub-module has continued with the successful reproduction of a 10-cycle test. Operational improvements continue to decrease turnaround time and stabilize oxygen flux and purity. Sources of variation that affect the O-1 reactor seal performance were identified as part of a six sigma project.

C.4. High Temperature Heat Exchange Results and Discussion

A kick-off meeting was conducted for the heat recovery task of the Foster Wheeler subcontract. Sizing of several potential heat recovery systems was initiated.

C.5. Process Analysis and Economics Results and Discussion

OTM processes were developed and cryogenic processes for integration with near-term IGCC processes were updated.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, OTM development has led to improved strength and composite design for lower temperatures. In task 2, the measurement system of OTM element dimensions was improved, and consistency of the powder and element manufacturing process was demonstrated. In task 3, a 10-cycle test of a three-tube sub-module was reproduced successfully, and sources affecting O-1 seal performance were identified. In task 5, sizing of several potential heat recovery systems was initiated. In task 7, advanced OTM and cryogenic IGCC cases for near-term integration were developed.

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.

Appendix XIX

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting April 1, 2004 and ending June 30, 2004

Praxair Program Manager: Ravi Prasad
DOE Program Manager: Jenny Tennant

Report Issue Date: September 2004

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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

DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter April to June 2004. In task 1, long term testing of OTM elements at different temperatures and process conditions continued. In task 2, OTM elements were manufactured as necessary for task1. In task 7, advanced OTM and cryogenic IGCC cases for near-term integration were developed, leading to cost requirements for commercial viability. In task 9, discussion with DOE regarding restructuring the program for subsequent phases were initiated.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- Element reliability
- Element fabrication
- IGCC process analysis and economics

The major accomplishments this quarter were

- **Long term life test of OTM element passed nine months at different testing conditions**

B. Experimental Methods

B.1. OTM Element Reliability 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. In addition oxygen permeation testers were used to collect oxygen and measure the oxygen flux of OTM elements.

B.2. Element Manufacturing Experimental Methods

Various fabrication routes have been developed to prepare composite OTM samples. The fabrication routes used have been discussed previously.

B.3. Process Analysis and Economics Experimental Methods

HYSIS simulations are used to model various process options.

C. Results and Discussion

C.1. OTM Element Reliability Results and Discussion

OTM life tests continued with multiple life tests passing the six-month mark and one test passing nine months. Element reliability at higher testing temperatures (900°C+) indicates commercial reliability of the OTM will be hard to obtain at such temperatures.

C.2. Element Manufacturing Results and Discussion

Elements for life and cycle testing were produced as required for testing in task 1.

C.3. Process Analysis and Economics Results and Discussion

OTM processes were developed and cryogenic processes for integration with near-term IGCC processes were updated to produce cost targets for the OTM.

C.4. Program Management

Negotiations were initiated to restructure the program for the next phase of the program. Full communication of technical and economic hurdles was presented to DOE at NETL on June 7th, 2004.

D. Conclusion

Progress has been made toward achieving the DOE-IGCC program objectives. In task 1, life tests at < 900C have passed 9 months, and element reliability testing at higher temperatures indicates that at temperatures 900C and higher commercial reliability will be difficulty to obtain. In task 2, elements were produced as necessary for task 1. In task 7, advanced OTM and cryogenic IGCC cases for near-term integration were developed that provide cost targets for the OTM modules.

Appendix XX

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting July 1, 2004 and ending September 30, 2004

Praxair Program Manager: John Sirman
DOE Program Manager: Jenny Tennant

Report Issue Date: January 2005

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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

DISCLAIMER:

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter April to June 2004. In task 7, reactor cost analysis was performed to determine whether OTM technology when integrated with IGCC provides a commercially attractive process. In task 9, discussions with DOE regarding restructuring the program continued.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- IGCC process analysis and economics

B. Experimental Methods

No experimental work was conducted during this period.

C. Results and Discussion

C.1. Process Analysis and Economics Results and Discussion

Using updated to produce cost targets for the packaged OTM, studies to determine actual cost of packaging ceramic OTM tubular and non-tubular elements were conducted. Initial results show that the costs of packaging tubular OTM elements does not meet the cost requirements. Work is also continuing on non-tubular geometries. A topical report will be prepared that will detail these results separately.

C.2. Program Management

Negotiations continued to determine the best method for the program to continue or be terminated.

D. Conclusion

Economic analysis of OTM-IGCC appears unattractive. Further work will continue to verify this initial conclusion. If the analysis is verified, the program will be terminated at the mutual agreement of DOE and Praxair, Inc.

Appendix XXI

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting October 1, 2004 and ending December 31, 2004

Praxair Program Manager: John Sirman
DOE Program Manager: Jenny Tennant

Report Issue Date: January 2005

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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

DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 2 Program during the quarter April to June 2004. In task 7, reactor cost analysis continued to determine whether OTM technology when integrated with IGCC provides a commercially attractive process. In task 9, discussions with DOE regarding restructuring the program continued. The DOE were verbally notified that the cost targets to enable OTM-IGCC integration could not be met using the technology developed within this program.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of phase 2 of the program are to construct and operate an engineering pilot reactor for OTM oxygen. Work to support this objective is being undertaken in the following areas in this quarter:

- IGCC process analysis and economics

B. Experimental Methods

No experimental work was conducted during this period.

C. Results and Discussion

C.1. Process Analysis and Economics Results and Discussion

Process studies to produce cost targets for the packaged OTM, studies to determine actual cost of packaging ceramic OTM tubular and non-tubular elements were completed. The results show that the costs of packaging tubular OTM elements does not meet the cost requirements, predominately due to the relatively high cost of manufacturing tubular OTM materials, in conjunction with the low packing density that resulted in high reactor costs. Analysis of stacked planar geometries showed lower unit cost per surface area of membrane both in terms of the ceramic component and the packaging cost. However, the flow characteristics of such devices reduce the oxygen flux per unit area such that much of the cost benefit from such architectures is eliminated. The cost of stacked planar geometries is also not competitive with state-of-the-art cryogenic technology. A topical report will be prepared that will detail these results separately.

C.2. Program Management

Discussions with DOE on how to close out the program effectively were initiated. Offers to present the full finding of the data at NETL were made.

D. Conclusion

Economic analysis of OTM-IGCC is unattractive due to the high cost of the ceramic component and the cost of packaging the OTM's in a reactor. A detailed report will be prepared that demonstrates the various cases examined. The program will be closed out in the most appropriate manner at the mutual agreement of DOE and Praxair, Inc.