Appendix IV

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

ANNUAL TECHNICAL PROGRESS REPORT

Reporting Period Start Date October 1999
Reporting Period End Date October 2000

Principal Author: Ravi Prasad

DOE Program Manager: Ted McMahon

Date Report was Issued: October 2000

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

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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.

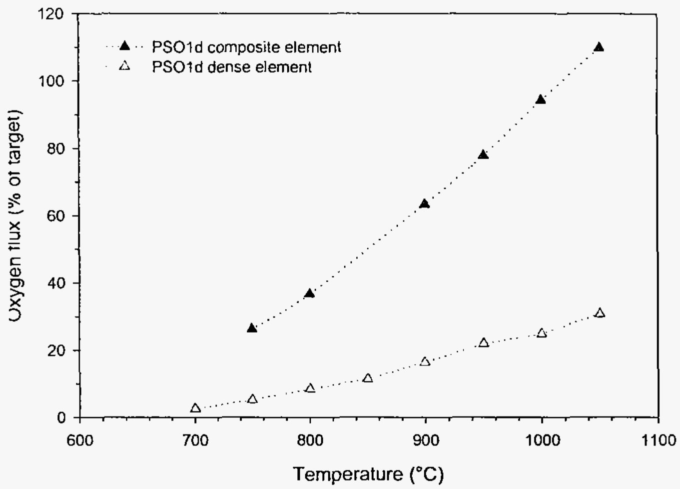

Figure 1. Oxygen flux through elements of PSO1d at ambient pressure using a helium purge gas stream

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.

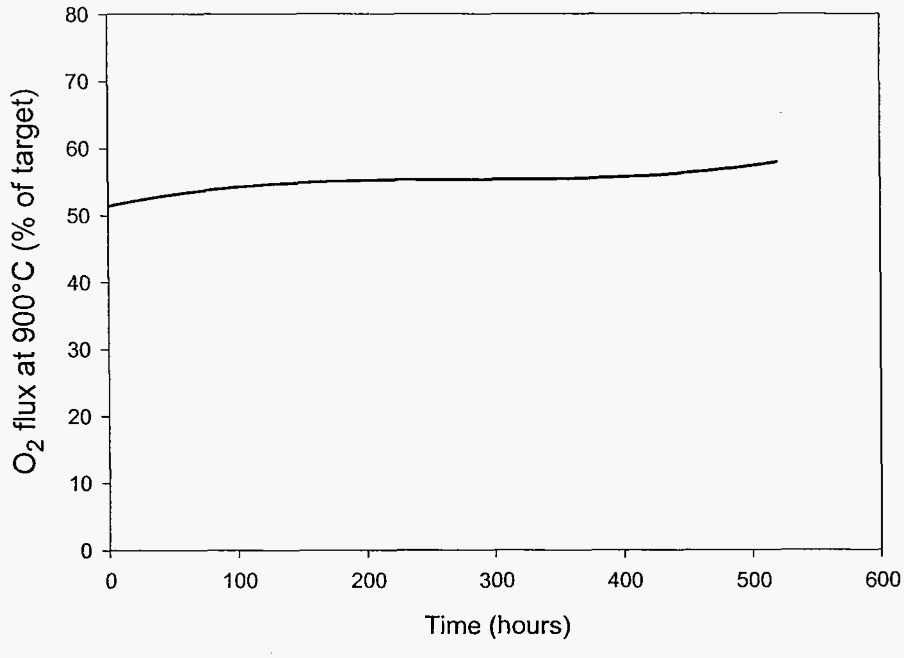

Figure 2. Oxygen flux of composite PSO1 as a function of time.

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 PSO1d on porous PSO1d 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 NOx 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.

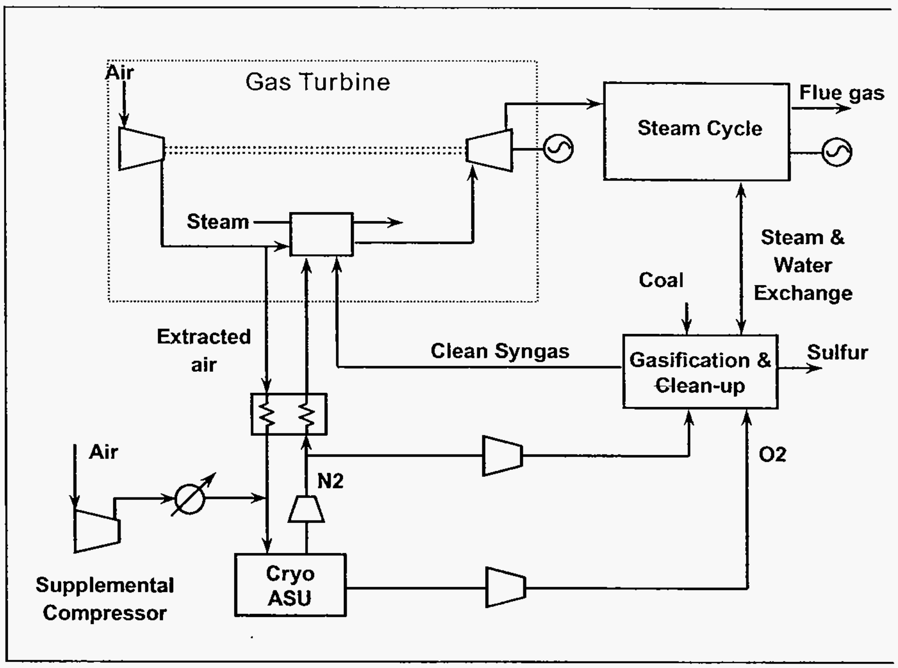

Figure 3. IGCC with Advanced Cryogenic ASU

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.

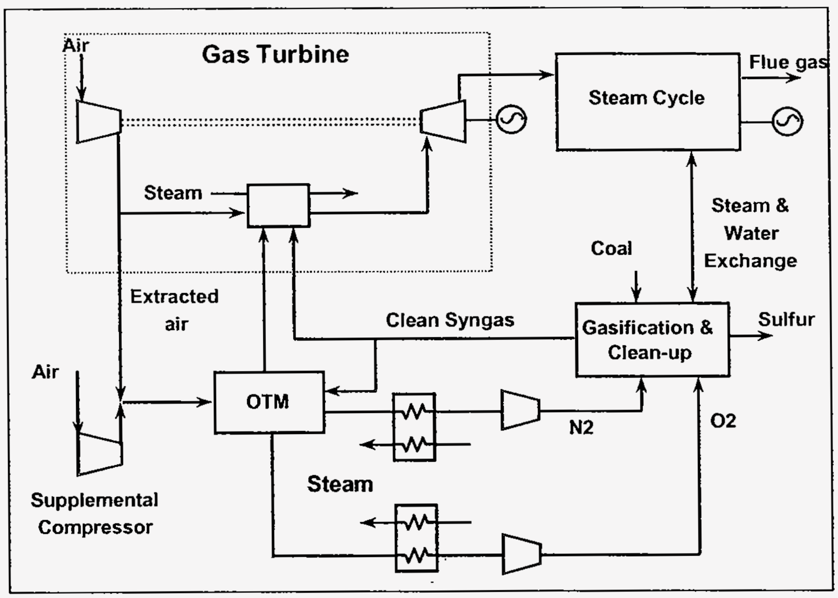

Figure 4. IGCC with Oxygen Production by OTM

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.

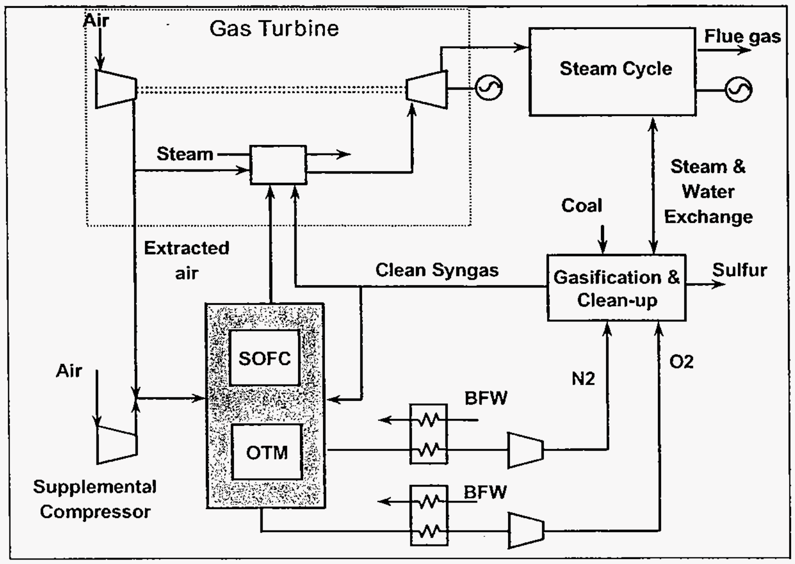

Figure 5. IGCC with OTM and SOFC

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 approxiamtely 8%.

- Achieving these performance targets requires achieving an OTM performance target (Flux/cost) >4 $scc.cm^{-2}sec^{-1}$/\$/cm2.
- 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.

Appendix V

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period Start Date: October 2000
Reporting Period End Date: December 2000

Principal Investigator: Ravi Prasad
DOE Program Manager: Ted McMahon

Date Report was Issued: January 2001

DOE AWARD NO. DE-FC26-99FT40437

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DISCLAIMER:

ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter October to December 2000. In task 1 careful modification of the processing conditions of the OTM has improved the properties of the final element. In addition, finite element modeling has been used to predict the mechanical behavior of OTM tubes and to identify strategies for improving OTM robustness. In task 2, composite elements of PSO1d have been prepared and tested for over 800 hours without degradation in oxygen flux. Alternative materials for composite OTM and architectures have been examined with success. In task 3, modification of fabrication routes has resulted in a substantial increase in the yield of PSO1d composite elements. The work in task 4 has demonstrated that composite OTM elements can produce oxygen at atmospheric pressure of greater than 95% purity from a high-pressure air feed gas. The work in task 5 to construct a multi-tube OTM reactor has begun.

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A. Executive Summary

The objectives of the second year of the program are to define a material composition and composite architecture that enable the oxygen flux and stability targets to be obtained in high-pressure flux tests. Composite development technology will be developed to enable the production of high-quality, dense membranes of a thickness that allows the oxygen flux target to be obtained. The fabrication technology will be scaled up to produce three feet composite tubes with the desired leak rate. A laboratory scale, multi-tube pilot reactor will be designed and constructed to produce oxygen.

In the first quarter of the second year of the program, work has focussed on materials optimization, composite and manufacturing development and oxygen flux testing at high pressures. This work has led to several major achievements, summarized below.

- **Oxygen has been produced from a composite OTM tube at the target purity level of greater than 95%.**
- Finite element analysis has predicted the mechanical behavior of OTM tubes and has suggested several strategies for increasing OTM robustness.
- Thin films of PSO1 have been successfully deposited on porous substrates of more commercially viable materials

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].

B.5. O-1 Pilot Reactor Development Experimental Methods

Commercial software has been used to determine mechanical stress and heat balance of the pilot scale reactor.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

Careful modification of powder processing has enabled the manufacture of OTM materials coupled with more traditional ceramics that are of commercial interest. The sintering temperature and shrinkage of these advanced powders can be controlled to minimize residual stresses. FEM has accurately predicted the mechanical behavior of OTM tubes and suggested new strategies for increasing OTM robustness.

Thermodynamic modeling has suggested that under the majority of IGCC process conditions PSO1d is sufficiently stable. In addition, new compositions have been prepared that have improved stability in certain conditions that may arise in alternative IGCC process options.

C.2. Composite OTM Development Results and Discussion

High quality composite elements of PSO1d on PSO1d can be routinely prepared using a variety of processing methods. Composite elements are gas tight and have been tested for over 800 hours with no degradation in flux performance. Thin films of PSO1 have also been successfully deposited on substrates of other commercially viable materials. These samples have been tested for oxygen flux and have exhibited promising fluxes.

Methods for producing substrates with an improved porous structure have been developed. These substrates can be routinely prepared and thin films have been successfully deposited. These substrates have a permeation rate almost twice that of conventional substrates.

C.3. Manufacturing Development Results and Discussion

Initial fabrication of composite elements of PSO1d on PSO1d had a poor yield, with many samples exhibiting significant cracking. Modifications to the fabrication process were developed that has increased the yield of composite OTM elements, and the final strength of the sintered body. This process will be employed to fabricate elements up to three feet in length.

C.4. Process Development Results and Discussion

A composite tube comprising of PSO1 on a suitable substrate was tested in the high-pressure permeation tester at 900°C for over 300hrs. **The membrane was subjected to feed pressures in excess of 200psig and oxygen was produced at atmospheric pressure with a purity of greater than 95%.** Further experimentation on composite OTM elements with improved architecture are expected to yield higher flux performance. Post analysis of the composite OTM element has identified areas of improvement to meet commercial requirements.

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

An initial OTM element assembly design was selected to enable the construction of a multi-tube pilot reactor that will produce oxygen under process conditions simulating IGCC operation. The feed gas heating system was designed based on the results of process simulation models. The selected design is flexible and allows substantially different flow rates of the feed gas to be used during the experimental test program.

D. Conclusion

Good progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, improved powder processing has enabled the production of elements that incorporate OTM films and substrates of commercial interest. In task 2, multiple fabrication processes have been developed that have been used to create stable OTM membranes and to deposit these on commercially relevant substrates. In task 3 modifications to the processing of OTM elements has led to an increase in the production yield of composite samples. In task 4, **oxygen has been produced at atmospheric pressure with a purity of greater than 95% in high pressure operation**. The work in task 5 has identified an OTM module design to meet the target oxygen production rate of the O1 pilot 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.**

Appendix VI

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period Starting January 1, 2001 and Ending March 31, 2001

Principal Investigator: Ravi Prasad
DOE Program Manager: Ted McMahon

Report Issue Date: April 2001

DOE AWARD NO. DE-FC26-99FT40437

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter January to March 2001. In task 1 careful modification of the composition and processing conditions of the OTM has enabled manufacture of high quality OTM elements. In addition, finite element modeling has been used to identify a suitable composition and geometry for successful pilot plant operation. In task 2, composite elements of materials with improved mechanical properties have been developed. In task 3, development of preferred fabrication methods has resulted in production of pilot plant scale composite elements. The work in task 4 has demonstrated that composite OTM elements can produce oxygen at atmospheric pressure of greater than 95% purity from a high-pressure air feed gas. The work in task 5 to construct a multi-tube OTM reactor is ongoing.

TABLE OF CONTENTS

A. Executive Summary

The objectives of the second year of the program are to define a material composition and composite architecture that enable the oxygen flux and stability targets to be obtained in high-pressure flux tests. Composite development technology will be developed to enable the production of high-quality, dense membranes of a thickness that allows the oxygen flux target to be obtained. The fabrication technology will be scaled up to produce three feet composite tubes with the desired leak rate. A laboratory scale, multi-tube pilot reactor will be designed and constructed to produce oxygen.

In the second quarter of the second year of the program, work has focussed on materials optimization, composite and manufacturing development and oxygen flux testing at high pressures. This work has led to several major achievements, summarized below.

- Finite element analysis has identified a composition and architecture that enables successful operation of the O1 pilot plant.
- Oxygen can be routinely produced from a composite OTM tube at the target purity level of greater than 95%.
- Composite OTM elements have demonstrated stable operation at $\Delta P > 200$ psi
- Pilot plant scale OTM composite elements have been successfully produced.

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].

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B.5. O-1 Pilot Reactor Development Experimental Methods

Commercial software has been used to determine mechanical stress and heat balance of the pilot scale reactor.

C. Results and Discussion

C.1. OTM Materials Development Results and Discussion

Optimization of OTM materials is ongoing with the view to improving properties required for commercial operation. In addition, FEM has been used to identify OTM element architectures suitable for successful O1 pilot plant operation using the current OTM materials.

New compositions with significant benefits in certain IGCC process conditions are being characterized. These compositions show substantial improvement over PSO1d in certain areas. Further work to improve other critical requirements is ongoing.

C.2. Composite OTM Development Results and Discussion

High quality composite elements of PSO1d on PSO1d can be routinely prepared using a variety of processing methods. These composite elements are gas tight and have enabled the production of high purity oxygen in the permeation testers. Composite elements comprising improved compositions have also been manufactured.

C.3. Manufacturing Development Results and Discussion

Improvements to the fabrication process were developed that has enabled the production O1 pilot plant scale composite OTM elements. Complementary technology is also being developed. Issues in batch to batch variations in powder quality are being addressed.

C.4. Process Development Results and Discussion

Composite tubes have routinely produced oxygen at atmospheric pressure with a purity greater than 95% under a large pressure differential of > 250 psi. Further experimentation on composite OTM elements with improved architecture are expected to yield higher flux performance.

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

The P&I diagram for the O1 pilot plant was completed. Materials with suitable oxygen compatibility have been selected for fabrication of the OTM vessel. Details of the analytical system are being completed.

D. Conclusion

Good progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, the materials and architecture required for O1 pilot plant operation were defined. In task 2, multiple fabrication processes have been developed that have enable gas tight composite membranes to be produced, resulting in high purity oxygen production. In task 3 improvements to the processing of OTM elements has led to the fabrication of pilot plant scale tubes. In task 4, can be routinely produced at a purity of >95%. In task 5 the P&I diagram has been finalized and materials have been selected for fabrication of the OTM vessel.

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 VII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period Starting April 1, 2001 and Ending June 30, 2001

Principal Investigator: Ravi Prasad
DOE Program Manager: Ted McMahon

Report Issue Date: August 2001

DOE AWARD NO. DE-FC26-99FT40437

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ABSTRACT:

This quarterly technical progress report will summarize work accomplished for Phase 1 Program during the quarter April to June 2001. In task 1 optimization of the membrane architecture has showed the potential for significant improvements to membrane performance. In task 2, **improved composite elements have been prepared that have demonstrated 75% of the commercial target flux**. In task 3, control of fabrication steps has resulted in a significant increase in yield of OTN elements. The work in task 4 has demonstrated that composite OTM elements can produce oxygen at greater than 95% purity and 75% of the target flux. In task 5 work the design of a multi-tube OTM reactor is completed and construction will begin next quarter.

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A. Executive Summary

The objectives of the second year of the program are to define a material composition and composite architecture that enable the oxygen flux and stability targets to be obtained in high-pressure flux tests. Composite technology will be developed to enable the production of high-quality, defect free membranes of a thickness that allows the oxygen flux target to be obtained. The fabrication technology will be scaled up to produce three feet composite tubes with the desired leak rate. A laboratory scale, multi-tube pilot reactor will be designed and constructed to produce oxygen.

In the third quarter of the second year of the program, work has focussed on materials optimization, composite and manufacturing development and oxygen flux testing at high pressures. This work has led to several major achievements, summarized below.

- **Oxygen has been produced under conditions similar to IGCC operation using composite OTM elements at a flux greater than the 2001 target.** Under conditions with a greater driving force the commercial target flux has been met.
- Methods to significantly increase the oxygen flux without compromise to its mechanical integrity have been identified.
- Composite OTM elements have demonstrated stable operation at $\Delta P > 250$ psi
- Design of the pilot plant is complete and construction will begin next quarter.

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 the surface properties of the OTM material have shown that significant improvement can be made to the oxygen flux without compromise to the mechanical integrity of the element.

Work has continued on new compositions that have significant benefits in certain IGCC process conditions. Larger batches of powder have been ordered to enable composite development of these materials.

C.2. Composite OTM Development Results and Discussion

High quality composite elements of PSO1d can be 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. Composite elements comprising improved compositions and structures have also been manufactured.

C.3. Manufacturing Development Results and Discussion

Improvements to the fabrication process were developed that have significantly improved the yield of OTM elements. Further modification to the process is continuing to ensure this increased yield applies to larger OTM elements.

C.4. Process Development Results and Discussion

Composite tubes have routinely produced oxygen under conditions similar to IGCC operation with a **flux greater than 75% of the commercial target and purity greater than 95%**. Under conditions with an increased driving force the commercial target flux has been obtained.

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

Design of the OTM pilot plant has been completed. Parts have been ordered and contracts awarded. Construction will begin next quarter.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, a method of increasing the oxygen flux without compromise to the mechanical integrity was identified. In task 2, composite elements have been produced that meet the 2001 oxygen flux target. In task 3 improvements to the processing of OTM elements has led to an increase in the yield of OTM elements. In task 4, **an oxygen flux greater than 75% of the commercial flux target was met under conditions similar to the IGCC process**. The commercial target flux was obtained under conditions with an increased driving force. In task 5 the design of the O-1 reactor was completed. Construction will begin next quarter.

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 VIII

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

ANNUAL TECHNICAL PROGRESS REPORT

Reporting Period Start Date October 2000
Reporting Period End Date October 2001

Principal Author: Ravi Prasad

DOE Program Manager: Ted McMahon

Date Report was Issued: October 2001

DOE AWARD NO. DE-FC26-99FT40437

Submitted by:

Praxair, Inc.
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ABSTRACT:

This yearly technical progress report will summarize work accomplished for Phase 1 Program during the program year 2000 / 2001. In task 1, the lead material composition was modified to enable superior fluxes and its mechanical properties improved. In task 2, composite OTM elements were fabricated that enable oxygen production at the commercial target purity and 75% of the target flux. In task 3, manufacturing development demonstrated the technology to fabricate an OTM tube of the size required for the multi-tube tester. The work in task 4 has enabled a preferred composite architecture and process conditions to be predicted. In task 5, the multi-tube reactor is designed and fabrication almost complete.

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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

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 3 is to demonstrate large-scale production of OTM composite elements. 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. The objectives of task 5 are to design, construct and operate a multi-tube laboratory tester.

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

- optimize a material composition that has high performance as a composite membrane for IGCC applications,
- demonstrate oxygen transport through composite OTM elements at 75% of the commercial target under simulated IGCC conditions
- demonstrate oxygen purity > 95% from composite OTM
- demonstrate technology to fabricate a tube of the size required for the laboratory reactor
- design and construct a multi-tube laboratory reactor

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

- The lead material, PSO1d, was modified to improve the surface exchange coefficient enabling the flux target to be obtained.
- 75% of the commercial oxygen flux target has been exceeded under simulated IGCC conditions using composite tubes of modified PSO1d.

- The program oxygen purity target was exceeded under simulated IGCC conditions using composite tubes of modified PSO1d.
- A composite tube of PSO1d of the required size was manufactured.

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

Modification of the OTM material has shown that significant improvement can be made to the oxygen flux without compromise to the mechanical integrity of the element. Figure 1 shows the flux enhancements possible with this modification.

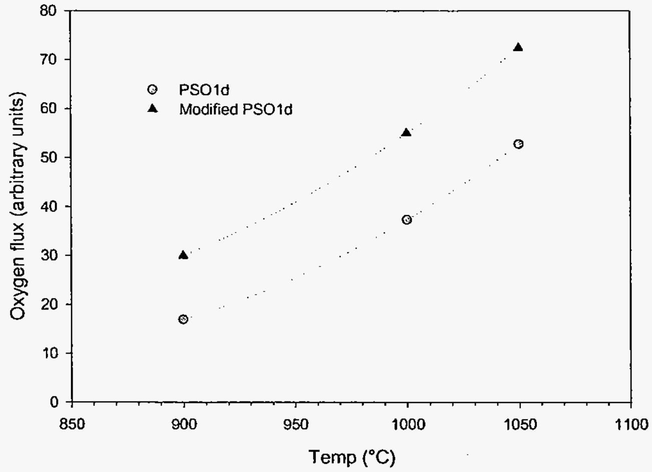

Figure 1. Oxygen flux of unmodified and modified PSO1d using a helium purge.

C.2. Composite OTM Development Results and Discussion

Composite OTM tubes have demonstrated that oxygen can be produced at the commercial purity target. They have also demonstrated oxygen production at 70% of the commercial flux target under simulated IGCC conditions. This is an extremely encouraging result and demonstrates that OTM technology is viable for commercial operation.

C.3. Manufacturing Development Results and Discussion

Improvements to the fabrication process were developed that have significantly improved the yield of OTM elements. Further modification to the process is continuing to ensure this increased yield applies to larger OTM elements. Fabrication technology has been demonstrated that enables the production of pre-commercial length tubes.

C.4. Process Development Results and Discussion

Composite tubes have routinely produced oxygen under conditions similar to IGCC operation with a **flux greater than 75% of the commercial target and purity greater than 95%**. Figure 2 illustrates the oxygen flux obtained under simulated IGCC conditions. Under conditions with an increased driving force the commercial target flux has been obtained. Stable operation has been demonstrated at greater than 250 psi.

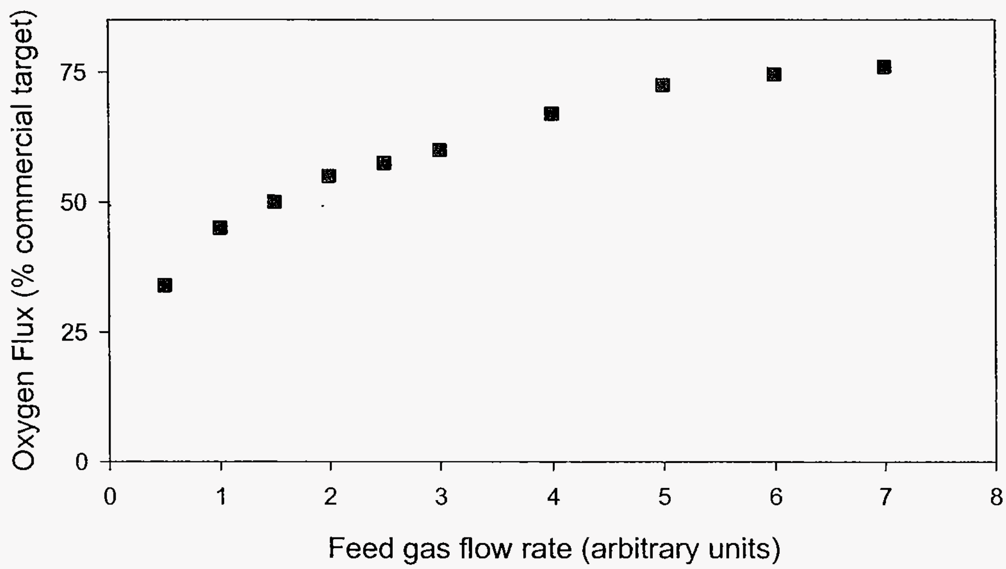

Figure 2. Oxygen flux of composite OTM tube at 900°C as
a function of feed flow rate at a pressure differential of 275 psi.

A high temperature seal has been developed that allows oxygen to be produced at the commercial target purity.

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

Design of the OTM multi tube pilot plant has been completed. Construction is underway and is expected to be completed in October.

D. Conclusion

Good progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, the lead material, PSO1d, has been modified to improve the surface exchange coefficient. This has enabled significant improvement to the oxygen flux. In task 2, fabrication processes have been developed, from which tubes have been produced that allow oxygen production at the commercial purity target and 75% of the commercial flux target. In task 3, fabrication technology has been demonstrated that enables the production of pre-commercial length tubes. In task 4, process conditions have been determined that allow oxygen production at 75% of the commercial flux target. Stable operation at a pressure differential of 250 psi was demonstrated. In task 5, a laboratory scale, multi-tube tester has been designed and construction almost completed.

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 IX

CERAMIC MEMBRANE ENABLING TECHNOLOGY FOR IMPROVED IGCC EFFICIENCY

QUARTERLY TECHNICAL PROGRESS REPORT

For Reporting Period starting October 1, 2001 and ending December 31, 2001

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

Report Issue Date: February 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 October to December 2001. In task 1 optimization of the substrate material has yielded substantial improvements to membrane life. In task 2, composite development has enabled 50% of the target flux under Type 1B process conditions. In task 3, manufacturing development has demonstrated that 36" long tubes can be produced. The work in task 4 has demonstrated that composite OTM elements can produce oxygen at greater than 95% purity for more than 500 hours of the target flux. In task 5 construction of the multi-tube OTM reactor is completed and initial startup testing was carried out.

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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 first quarter of the third year of the program, work has focussed on improving the mechanical properties of OTM substrate materials, fabricating 36" long composite tubes for the pilot reactor, demonstrating stable operation of PSO1d OTM membranes and initializing the O1 reactor for operation. The major accomplishments this quarter were

- **500 hour life was demonstrated on a PSO1d OTM tube with an oxygen flux of 80% of the commercial target at greater than the purity target under high pressure operation.**
- 36 " long composite PSO1d tubes were fabricated
- O1 pilot reactor operation was started

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 the properties of the substrate material have shown that substantial increase in the mechanical integrity of the element is achievable. This development indicates that commercial life can be obtained.

Work has continued on subtle doping of PSO1d to increase its oxygen transport properties. Initial tests on dense discs indicate that flux improvements greater than 20% are possible.

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 were developed that have enabled fabrication of 36" long composite elements of PSO1d. These elements will be used in the O1 pilot reactor.

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 500 hours**.

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

Construction of the OTM pilot plant has been completed. Initial startup procedures have been carried out. Testing of PSO1d tubes will begin next quarter.

D. Conclusion

Progress has been made in all tasks toward achieving the DOE-IGCC program objectives. In task 1, improvements to the substrate material indicate that commercial life can be achieved. In task 2, composite elements of larger size have been produced to the same high quality as smaller tubes that obtained the 2001 oxygen flux target. In task 3 improvements to the processing of OTM elements has enabled fabrication of 36" long composite PSO1d elements. 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 500 hours**. In task 5 construction of the O-1 reactor was completed and initial startup procedures were carried out.

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.