Advances in OTM Technology for IGCC

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Abstract

In partnership with the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE), a team led by Praxair is developing advanced Oxygen Transport Membranes (OTM), which can be integrated with Integrated Gasification Combined Cycles (IGCC) power generation cycles to produce significantly lower-cost oxygen for gasification. OTM technology, based on high-temperature, ceramic-mixed conductor membranes, can be operated in a pressure-driven mode to separate oxygen with infinite selectivity and high flux, offering unique opportunities for synergistic integration.

This paper will provide an overview of the OTM development program, and discuss the significant progress made to date. Novel schemes for OTM integration with IGCC will be discussed, along with advances in new materials to improve performance and reliability and enable novel processes. Progress in membrane fabrication, element performance, seal technology, and process tests and pilot plant will be reviewed. Results to date confirm the potential of OTM to achieve high performance and stability in a high-pressure, high-temperature operation to achieve step-change improvement in IGCC oxygen production.

1. Introduction

Integrated Gasification Combined Cycle (IGCC) continues to develop as the technology of choice for clean, efficient base load electric power generation, because IGCC can co-produce a wide variety of commodity and premium products to meet market requirements. This quality makes it an attractive alternative to conventional power generation. Building on operating experience in industrial applications today, gasification-based technologies can be refined and improved, leading to reduced capital and operating costs as well as to improvements in thermal efficiency and superior environmental performance.

One such improvement would be the use of oxygen instead of air for gasification, which would remove the excess nitrogen from the gasifier. This in turn would result in increased efficiency, substantial NOx reduction, and improved gas purity. The removal of nitrogen from the fuel gas could be critical to use of this gas for products other than electricity. However, the use of oxygen instead of air in IGCC processes is impeded by: 1) The high cost of oxygen production, and 2) The loss of thermal efficiency inherent in the low temperatures of the current technology - cryogenic separation.

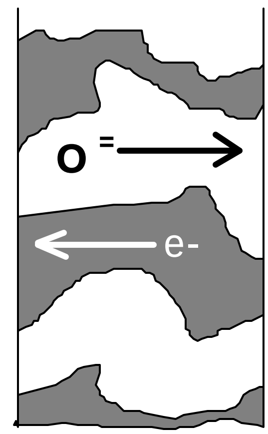
In partnership with the National Energy Technology Laboratory (NETL) of the DOE, Praxair is developing high-temperature, ceramic Oxygen Transport Membranes (OTMs), which are ideally suited for thermal integration with the gasification cycles to achieve major cost reductions and efficiency improvements. The goals of this program are to advance critical technologies for the commercial deployment of OTMs for IGCC oxygen production to enable significant improvements in process economics, efficiency and environmental benefits. This paper discusses the benefits of OTM integration with IGCC, the substantial progress made and several critical performance milestones that have been achieved.

2. OTM – Principle of Operation

OTM technology is based on ceramic materials which can rapidly transport oxygen ions at 600-1000°C. Mixed conductors, which transport both oxygen ions and electrons, can be operated in a pressure driven mode, obviating the need for the costly electrodes and external circuits that are required for purely ionic conductors. Mixed conductors can be a single-phase material, which conducts both electrons and oxygen ions, or “dual phase” materials (Fig.1) wherein two separate phases are used for transporting oxygen ions and electrons.

The oxygen chemical potential difference across the membrane provides the driving force for oxygen transport. Oxygen atoms adsorb on the cathode (high oxygen partial pressure side of the membrane), dissociate into atoms/ions as they pick electrons.. These ions travel from cathode to anode (the low oxygen partial pressure) by jumping through lattice sites and vacancies until they reach the anode side of the membrane. On the anode side, the oxygen ions give up their electrons to become atoms/molecules, which are then desorbed into the gas phase. Electrons from the anode side are carried through the membrane to the cathode side to complete the circuit. The rate of oxygen transport through such membranes is temperature sensitive, and can be very fast at high temperatures.

Figure. 1 Dual Phase OTM



Ideally, the flux through the membrane is inversely proportional to the thickness, hence thin films can enable higher fluxes, leading to compact systems. These membranes also have infinite selectivity for oxygen over other gases, because only oxygen ions can occupy the lattice positions. The ability to produce pure oxygen at high permeation rates combined with the thermal integration enabled by high temperature operation results in significant benefits upon integration with the IGCC cycle.

3. OTM integration with IGCC

As part of a Cooperative Research and Development Agreement (CRADA), Praxair and DOE-NETL have assessed the potential of OTM integration with IGCC processes. Some of the results are summarized herein. The reader is referred to earlier publications for further details [Refs. 1-2]. The following assumptions were made in these studies:

1. Illinois #6 coal was used as the feedstock
2. A Westinghouse 501G gas turbine (GT) was used for power generation.
3. A Shell gasifier was used for coal gasification
4. The anchor point for all cases was a GT power output of ~272 MW.

The "base case" used an advanced cryogenic air separation unit (ASU) tailored for IGCC systems. This case represents future improvements in cryogenic technology and features a high level of integration between the gas turbine and the ASU on both the air and nitrogen sides.

Two OTM-based IGCC concepts were considered. One concept integrates the OTM with the gas turbine (GT). The second concept is based on a proprietary Praxair concept [Ref. 3] in which a solid oxide fuel cell (SOFC) and an OTM are integrated with the GT. Significant synergy is realized in both cases because the OTM, which uses uncooled compressed air from the GT, operates at the same temperature at which the gasifier operates.

Reference 3 shows a process schematic of the OTM-SOFC IGCC process. To maximize the benefits of integration, the maximum amount of gas turbine air flow for oxygen separation in the OTM was extracted. Supplemental air was supplied that not only replaces the oxygen and nitrogen sent to the gasification plant, but also provides additional mass flow through the expander raise the GT output to ~272 MW.

For the OTM-only case (in which no SOFC was used), fuel is used to raise the air temperature to a level that is optimal for the OTM. In the OTM-SOFC case, the waste heat from the SOFC was used to preheat the air. In both OTM cases, high-purity oxygen is recovered at near-atmospheric pressure. Thermal energy is recovered by preheating the boiler feed water. The cooled oxygen is compressed and sent to the gasifier. The oxygen-depleted air is sent to the GT.

Table 1 compares the OTM-integrated IGCC processes with the "base case". Compared to the advanced cryogenic case, OTM oxygen production increases process efficiency and reduces cost of electricity (COE) by 3 mills/kWh. The SOFC-OTM-integrated IGCC case provides further 7-point improvement in thermal efficiency. At a fuel cell cost of $800/kW, the COE is less than the advanced cryogenic case but more than the OTM only case. At the projected Solid State Energy Conversion Alliance (SECA) target of $400/kW, the COE is reduced to 44.9 mills/kWh.

Table 1- IGCC Process Parameters and Cost/Performance

Case	"Base Case" Advanced Cryo	OTM	SOFC/OTM @ $800/kW	SOFC/OTM @ $400/kW
Gas Turbine	W501G	W501G	W501G	W501G
Gasifier	Shell	Shell	Shell	Shell
Gas Clean-Up	Mdea	Rectisol	Rectisol	Rectisol
Oxygen (100%, TPD)	2423	2448	3429	3429
Oxygen Purity (%)	95%	>99%	>99%	>99%
Coal (TPD)	3173	2312	4489	4489
Gas Turbine Power (MWe)	272	272	272	272
Steam Turbine Power (MWe)	182.9	198.8	217.5	217.5
SOFC Power (MWe)	--	--	240.7	240.7
Misc. Power (MWe)	45.9	50.9	56.1	56.1
Net Power (MWe)	404.9	419.9	674.1	674.1
Efficiency (%, HHV)	44.8%	45.9%	52.7%	52.7%
ASU Cost, relative	100	75	91.7	91.7
IGCC Cost ($MM)	$569	$551.6	$980.8	$840.4
Capital Cost ($/kW)	$1407	$1314	$1455	$1247
COE, current $ (mills/kWh)	51.9	48.9	50.7	44.9

Praxair currently is investigating a variety of process alternatives in which a higher of level of integration between OTM oxygen production and the IGCC process is implemented. Some alternatives are based on proprietary Praxair concepts (e.g. Refs. 4-6) in which a steam purge is swept through the product side of the OTM. Fig. 2 shows a process for producing a gas stream containing oxygen and steam to feed to a coal gasifier. Steam from the steam cycle may be used to provide at least a portion of the purge gas. Although the process in Fig. 2 shows a case using high-pressure (HP) steam as the purge stream, these processes are not limited to such operation. The purge gas pressure (i.e., steam pressure) may be anywhere from 1 to 40 atm. Therefore, the OTM may utilize low-pressure, intermediate-pressure, or high-pressure steam from the steam cycle. The reader is referred to references 4-6 for further details of these processes.

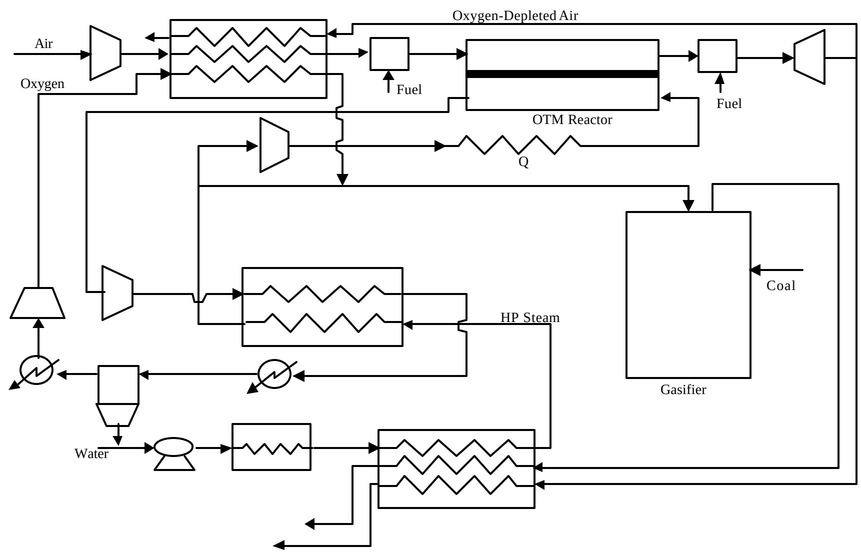


Figure 2. IGCC with Steam-Purged OTM

4. Program Plan

The joint DOE/Praxair program is 50% cost shared, and is comprised of a three-year Phase 1 and a two-year Phase 2. Phase1 is nearing completion and has achieved critical milestones. The major technical tasks in each Phase are:

Phase 1

- **Material Development**: Develop and select OTM membrane and substrate materials for oxygen production in integrated IGCC/OTM cycles. Characterize the materials for their mechanical and thermo-chemical properties, performance and stability under operating environments
- **Composite OTM Development:** Select architecture, materials and fabrication techniques for thin film OTM supported on porous substrates. Design composite OTM to achieve the high flux required at the small driving force available in IGCC cycles. Test single element for performance and stability to provide feedback for required improvements.

- **Manufacturing Development:** Develop technology suitable for large-scale element fabrication and make elements for laboratory and pilot scale reactors. Establish quality control techniques to ensure that performance, stability, and strength targets are met.
- **Process Development:** Conduct laboratory in single-element, high-pressure reactors under simulated IGCC process conditions to map the operating characteristics of composite OTM. Develop and validate models using experimental data and use to optimize element performance, reactor design and operation.
- **Proof-of-Concept in a Multi-Element Lab Reactor:** Build and operate a multi-element laboratory reactor to demonstrate proof of concept of the process, control strategy, design of key components and progress towards commercialization. Develop specialized components for the reactor including high temperature cyclable seals.

Phase 2

- Key components of Phase2 activity will include advancing element reliability to ensure 10-year life, manufacturing of full-size elements for the pilot plant, development of critical components required for efficient thermal and power integration, assessment of advanced process integration concepts, economic modeling and business and marketing studies. A multi-element pilot reactor sufficiently large to confirm scale-up issues will be designed, built, and operated, and will feature the elements and design concepts anticipated in the commercial design. It will validate the engineering design basis, startup and shutdown protocols and demonstrate safety, and provide cost data to verify that economic targets are met when scaled to full size.

5. Technology Advances:

5.1 Materials Development

OTM materials for applications such as IGCC require extremely good oxygen transport properties. In a previous paper [Ref.1], the oxygen transport properties of the initial lead OTM material (OTM1) were outlined. Improvements to that material were achieved in a new OTM material (OTM2). High oxygen fluxes have been achieved with OTM2, and an additional modification of OTM2 provided further improvement. The impact of this modification on the flux of OTM2 flux is shown in Fig. 3. Using the current OTM materials developed at Praxair, commercial flux targets have been obtained under conditions similar to those anticipated under IGCC operation.

The mechanical strength of the membrane material is critical since the OTM elements are subjected to large pressure gradients and possible thermal gradients during transients. Typically, OTM materials that have high oxygen ion conductivity have poor mechanical properties. The mechanical properties of the initial OTM1 and OTM2 materials, while adequate for tests lasting several thousand hours, were insufficient for 10-year commercial life. Through numerous improvements to OTM2, its fracture toughness has been doubled and its 4-point bend strength has been increased by close to 50% (see Figs. 4 & 5). Figure 5 also shows a recently discovered material, OTM3, which has even higher strength than the improved OTM2 along with improved flux performance.

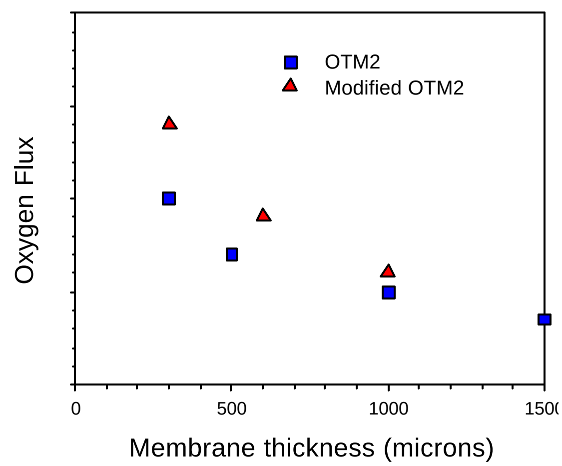


Figure 3. Flux of unmodified & modified OTM2

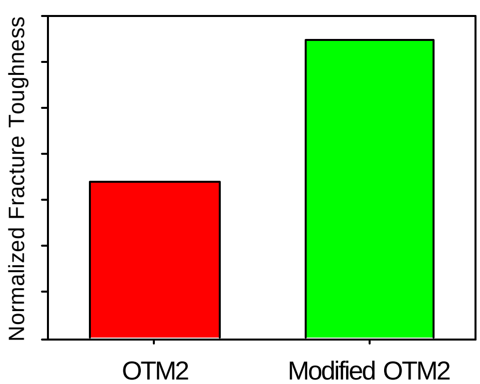


Figure 4. Improvements in the fracture toughness of OTM materials.

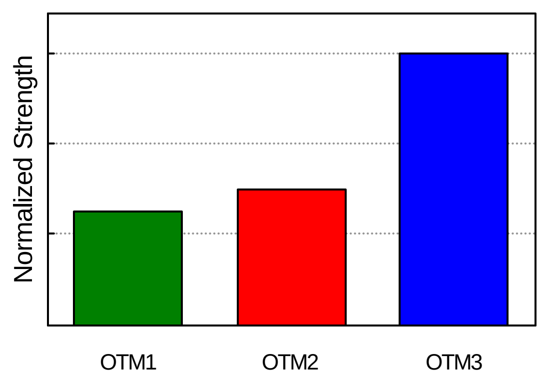


Figure 5. Improvement in the strength of OTM materials.

Achieving these substantial improvements in mechanical properties without sacrificing any flux performance of the membrane is a major achievement of the Phase 1 program.

5.2 Composite OTM Development

The IGCC application of OTM is characterized by the need to achieve very high fluxes with only a small driving force across the membrane. Even with the high-flux OTM materials, a composite OTM element with a thin OTM film supported on a porous substrate is needed. Hence there has been significant effort on the development of thin, dense films and high quality porous supports.

Several novel fabrication technologies have been developed in Phase 1 to produce high quality composite elements with the film thickness in the range of 25-100μm. One of these has been selected as the primary technology for manufacturing process scale-up. The technology was selected based on its suitability for large-scale fabrication of OTM elements with the required geometry, cost, and quality. A critical aspect of quality has been the ability to ensure that the OTM elements have low leak rate and high oxygen flux. Through careful optimization of the fabrication process, major reductions in leak rate have been achieved (Fig. 6). ***At present, high quality composite OTM elements with a leak rate of ~10^{-9} cc/sec can be routinely made by this process.*** The process has also been successfully scaled up for composite OTM elements of different sizes and architectures.

Figure 7 shows the improvement in oxygen flux achieved during the course of Phase 1. Through improvements in the architecture of the composite OTM elements, ~120% of commercial flux target can now be attained at 900ºC (a 150ºC reduction in operating temperature from initial target). Furthermore, these high flux elements are capable of producing oxygen with a purity exceeding 99% in unpurged operation. ***Demonstrating the ability to produce pure oxygen at fluxes exceeding the very high commercial flux target and at a temperature 150°C below our original target is another major accomplishment of the Phase1 program.***.

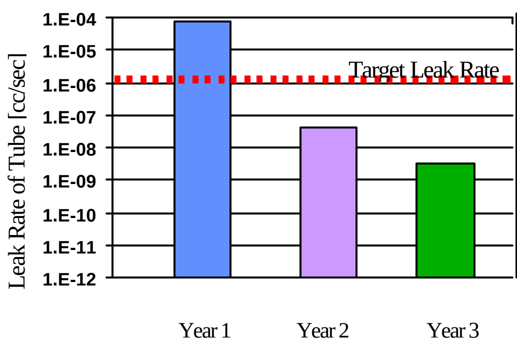


Figure 6. Leak rate improvement in composite OTM elements.

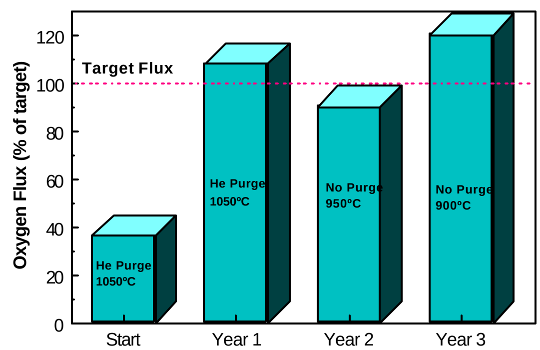


Figure 7. Progress in flux performance of composite OTM elements during Phase 1.

5.3 Manufacturing development

The materials used for the separation layer in the OTM elements are synthetic inorganic compounds that have been formulated within the last few years. The laboratory scale work is generally performed with powders that are adequate for small scale testing. Manufacturing development therefore involves development of a manufacturing protocol for scaling up powder production and subsequent processing of the powder into membrane elements. Praxair has established a one-of-a-kind semi-works facility to accomplish this and accelerate commercial manufacturing development.
Some important steps are outlined below.

1. *Powder Synthesis*. The lead candidate material is a multi-component, mixed oxide mixed conductor. The route selected for manufacture of the powder is a patented Praxair process based on a solution precursor technique. This process yields the desired chemistry and the composition is locked in to provide high compositional

homogeneity. Scale up then involves development of the appropriate processing cycles to ensure that the proper chemistry can be maintained. Careful development has resulted in a viable manufacturing protocol .

2. *Powder Conditioning*. The synthesized powder is treated thermally to control the surface area and mechanically attrited to the desired particle size according to the fabrication process. The powder is then mixed with the appropriate amount of binder, plasticizer, and/or other additives for the specific green forming process in which it will be used. Powder properties such as particle size, surface area, crystal structure, flow properties, and sinterability are measured.
3. *Green Forming*. As described above, Praxair has developed several proprietary green forming processes capable of producing high quality dense membranes on porous substrates for a variety of architectures and element geometry. A critical step in manufacturing has been the scale-up of the green forming technique.
4. *Removal of Organic Additives.* The organic additives are removed by thermal treatment in which the temperature, heating rate, and atmosphere are controlled to avoid physical or chemical damage to the membranes. During this period the membranes are extremely fragile prone to damage.
5. *Sintering.* The membranes are sintered at >1100°C in a controlled atmosphere and then cooled at a controlled rate.
6. *Inspection*. Each element is inspected both visually and via optical magnification for major flaws, measured for compliance with geometrical tolerances, and checked for leaks. Mechanical testing is also performed on a fraction of the elements to identify strength limiting defects (type and size), monitor consistency in processing, and develop a protocol for proof testing

Praxair's semi-works has successfully produced OTM elements up to several meters in length with burst strengths many times the expected operating pressure. A key feature of Praxair's manufacturing process is the ability to make specialized architecture elements which can be integrated into our advanced seal technology to yield ultra low leak rates in operation.

5.4 Process Development

The oxygen transport membranes developed in this project were subjected to simulated IGCC operating conditions such as high differential pressure at elevated temperature for over a 1000 hrs. **Several major milestones were demonstrated, such as reaching the oxygen flux target, demonstrating oxygen purity, showing 1000 hrs of stable operation, and demonstrating cyclability.**

A logarithmic dependence of the oxygen flux on the oxygen partial pressure ratio was clearly demonstrated, as shown in Fig. 8. The mass transfer resistance of this membrane element had been significantly reduced and thereby allowed the very high commercial flux target to be exceeded at the low driving force available in IGCC applications.

The dependence of the oxygen flux on oxygen recovery and various temperatures has been mapped. Besides the demonstration of commercial flux target, a major achievement was the high fluxes achieved at temperatures as low as 750°C. Operation at such low temperatures is expected to significantly reduce reactor costs, permit greater flexibility in the selection of materials of construction and enhance life and robustness.

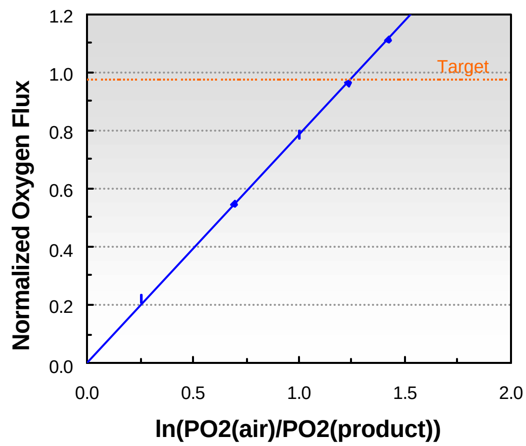


Figure 8. Normalized oxygen flux versus driving force at 900°C.

Figure 9 shows the stability of the oxygen flux over 1000 hrs of operation at 275 psid and 900°C. The oxygen purity dropped during the test due to a seal issue which has since been identified and resolved. ***The membrane did not show a significant increase in the helium leak rate before and after this life test demonstrating the integrity of the composite OTM during the life test***. ***Another major milestone was achieved when an OTM element with an improved seal was cycled >10 times between room temperature and 900°C at 275psig with minimum loss in either oxygen purity or oxygen flux*** (Fig. 10).

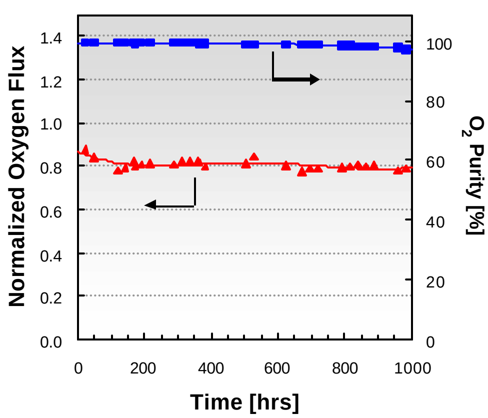


Figure 9. Results of OTM life test at 900°C and 275 psid.

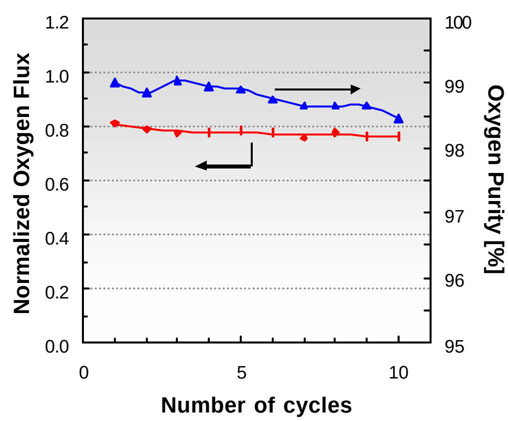


Figure 10. Stability of oxygen flux and purity during cycling.

5.5 Systems Development

5.5.1 Pilot Plant Operations

The oxygen production pilot plant (O-1) has focused on four areas of systems development: thermal design, materials of construction, system design, and operations. The O-1 reactor, shown in Figure 11, is designed to operate at high-temperature (950°C) and high-pressures (375 psig). At these elevated conditions, the heat generation, heat transfer, and material issues become a major design concern. Praxair has implemented a number of novel concepts to address heat management issues, and several metal and ceramic materials that appear sufficiently robust have been identified. Evaluation of these materials in actual operation will continue through the remainder of the program.

Figure 11: O-1 Reactor System

Initial reactor testing proved that the control system was reliable and that the ceramic OTM element/metal seal fixture was adequate to meet project goals for oxygen purity. Moreover, initial and subsequent attempts to operate with OTM elements have clearly demonstrated oxygen production.

5.5.2 Seal Technology Development

A critical component technology is the high temperature, high differential pressure seal required between the ceramic OTM element and the metal manifold inside the reactor. OTM seals must operate under relatively rigorous conditions that include steady state temperatures up to 1000°C, large pressure differentials up to 300psid, and multiple thermal cycles during the life of the plant. Praxair has been able to steadily advance seal technologies to a point where leak rates are significantly below the commercial target for IGCC application.

Several of the seal technologies developed by Praxair have demonstrated the ability to survive extended operation and multiple cycles from ambient temperature up to 1000°C. However, adverse interaction between the OTM and sealant materials has been problematic for maintaining product purity over time. Praxair has recently advanced the seal technology further to provide the same or better sealing capability than previous sealants and a much

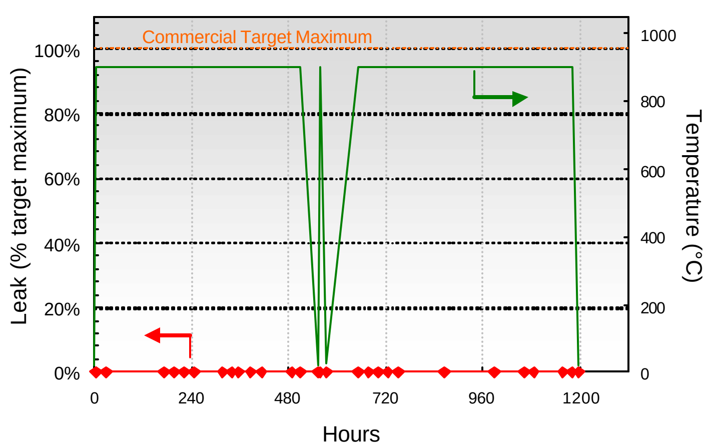


Figure 12. Leak rate over time with the improved seal

more stable OTM/sealant interface. Leak rates well below the commercial target can be readily achieved and maintained for extended periods (Fig. 12).

To date, no adverse reactions between the OTM and the improved sealant materials have been observed in *in-situ* laboratory experiments lasting up to 1000h. The improved seals have also been subjected to over 20 thermal cycles (ambient to 900°C) without an increase in leak rate or other deleterious effects. The current seal materials are considered to have excellent potential for commercial application. Effort is now underway to optimize seal deployment in order to maximize reliability and minimize cost.

6. Conclusion:

Significant progress has been made in Phase 1 of the Praxair-DOE cooperative program aimed at developing advanced OTM technology for IGCC oxygen production. A new, high-performance material has been invented which greatly improves the mechanical properties of the OTM element while maintaining the superior flux performance of the earlier lead candidate. Composite OTM technology capable of high-performance, gas-tight composite OTM membranes capable of sustained operation at 900°C and high-pressure differential has been developed. These elements have demonstrated the production of >99% pure oxygen at fluxes 120% of commercial target in tests conducted at 900°C with a 275 psi pressure differential. A 1000 hr life test and >10 complete thermal cycles were demonstrated on such elements under simulated IGCC conditions with virtually no membrane degradation. Significant progress is being made in scaling up the manufacturing of the elements. Seal technology has advanced to the point where leak rates are much below commercial target and adverse interactions with the OTM membrane are absent. A multi-element pilot reactor is operational and is being used to understand operational characteristics of the OTM reactor module and validate design concepts for scale-up.

Acknowledgement

The authors wish to acknowledge the contributions of Ted McMahon and Jenny Tenant, NETL program managers of the Praxair-DOE Cooperative Program #DE-FC26-99FT404237, in guiding the overall program. The authors also wish to thank the entire Praxair OTM team whose hard work and dedication to excellence had made possible the substantial advances reported in this paper.

References:

1. "OTM- A novel technology for integrated oxygen production in IGCC", Ravi Prasad, Minish Shah, Ray Drnevich, Dave Thompson, 17th Annual International Pittsburgh Coal Conference, Sept. 12-15, 2000, Pittsburgh, Pa.
2. "Advances in Oxygen Transport Membrane Technology for Integrated Oxygen Production in IGCC", Ravi Prasad, Jack Chen, Bart VanHassel, John Sirman, James White, 18th Annual Pittsburgh Coal Conference, Dec. 3-7, 2001, Newcastle, Australia.

3. “Process integrating a solid oxide fuel cell and an ion transport reactor”, Ravi Prasad, Christian Gottzmann, Nitin Keskar, US Patent 6,017,646
4. “Solid Electrolyte Ionic Conductor With Adjustable Steam-Oxygen Production”, Nitin Keskar, Ravi Prasad, Christian Gottzmann, US Patent 5,964,922
5. “Solid Electrolyte Ionic Conductor Oxygen Production With Power Generation”, Nitin Keskar, Ravi Prasad, Christian Gottzmann, US Patent 5,954,859
6. “Solid Electrolyte Ionic Conductor Oxygen Production With Steam Purge”, Ravi Prasad, Christian Gottzmann, US Patent 5,935,298