

APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

OXYGEN PRODUCTION

NOVEL SUPPORTS AND MATERIALS FOR OXYGEN SEPARATION AND SUPPLY

Primary Project Goals

Eltron Research is designing and developing a temperature swing adsorption (TSA) system capable of producing high purity (>99%) oxygen (O₂) for use as an air substitute in power plants, reducing waste gas volume and simplifying carbon dioxide (CO₂) capture and containment.

Technical Goals

- Produce materials which provide more O₂/m³•hr than the zeolites currently used in small to mid-size TSA O₂ separation technologies (23 kg O₂/m³•hr).
- Develop materials capable of producing an O₂ with purity comparable to cryogenic O₂ separation (>99+%).

Technical Content

Eltron Research is developing a TSA system that is capable of producing O₂ at purities comparable to those produced by cryogenic methods but at reduced cost.

This program initially focused on the coating of sintered metal fiber filters (SMFFs) with cerium oxide (CeO₂), silicon oxide (SiO₂), and/or aluminum oxide (Al₂O₃). These base-coated fibers were then separately impregnated using a mixed metal oxide nitrate. The SMFFs used were chosen for their high porosity (80%) and permeability (1,500 L/dm²•min), which provided a near-negligible post-reactor pressure drop. Also, due to their high thermal conductivity, the chosen SMFFs had significantly reduced thermal irregularities compared to ceramic monoliths. This feature resulted in near isothermal reactor beds. Cerium- (Ce), silicon- (Si), and aluminum- (Al) based oxides were chosen as base-coating materials for their ability to increase surface area and provide a more ideal binding surface on the SMFFs. Additionally, they also prevent or dramatically decrease agglomeration and its impact on the overall O₂ storage and release capability of the materials. However, based upon an economic analysis, it was determined that the volume needed for the SMFFs was too large, and so the program was then re-focused strictly on fixed beds with no SMFF supports. In addition, the focus was changed from co-precipitated mixed metal oxide materials to perovskite materials produced using ceramic processing methods.

Twelve combinations of materials were selected and produced via ceramic processing methods and calcined at high temperatures (>900 °C). Upon testing, results showed that one of the selected materials (K-12), a perovskite, was capable of producing >132 kg O₂/m³•hr, far surpassing the original mixed metal oxide primary material produced via co-precipitation from nitrate solutions.

Figure 1 compares the O₂ production rates of several leading technologies, including Eltron's primary materials. Figure 2 compares the required reactor volume, based on a 5 ton-per-day (tpd) O₂ system. As indicated, the K-12 sorbent offers significantly improved O₂ production over existing pressure swing adsorption (PSA) zeolite-based sorbents. Utilizing a sorbent capable of such high production rates may significantly reduce the required reactor volume, leading to reduced capital and operational costs.

Technology Maturity:

Laboratory, 5–10 lb oxygen/day

Project Focus:

Materials for Temperature Swing Adsorption Oxygen Separation

Participant:

Eltron Research, Inc.

Project Number:

ER84600.002

NETL Project Manager:

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Partners:

None

Performance Period:

8/8/07 – 8/7/10

Eltron Oxygen Separation Material Advances and Their Comparison to OGSi's Zeolite per Reactor Volume

* - Oxygen Generating Systems, Inc. PSA Zeolite

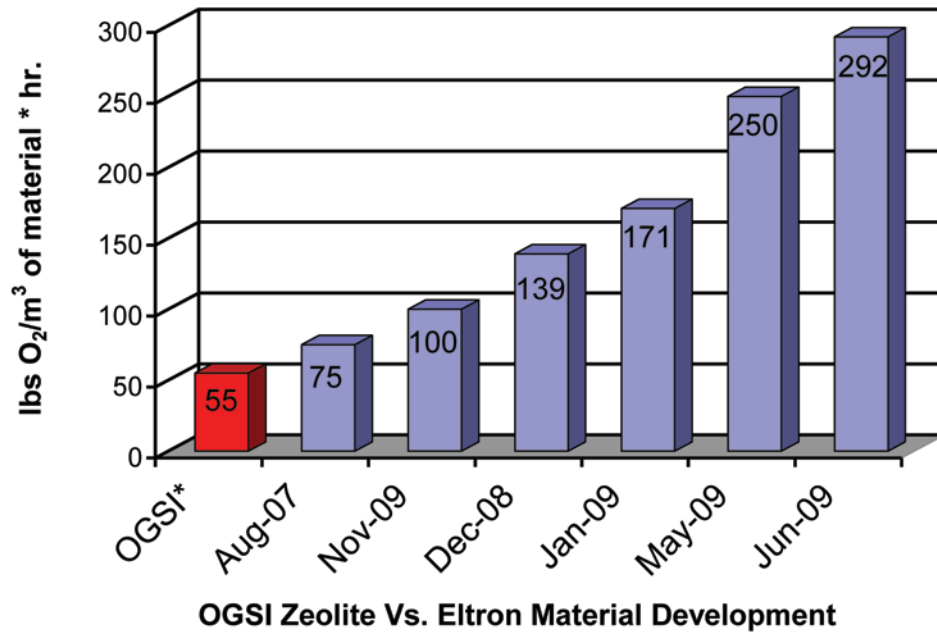


Figure 1: Oxygen Production Comparison

Reactor Volume Required for Five Ton/Day O₂ Plant

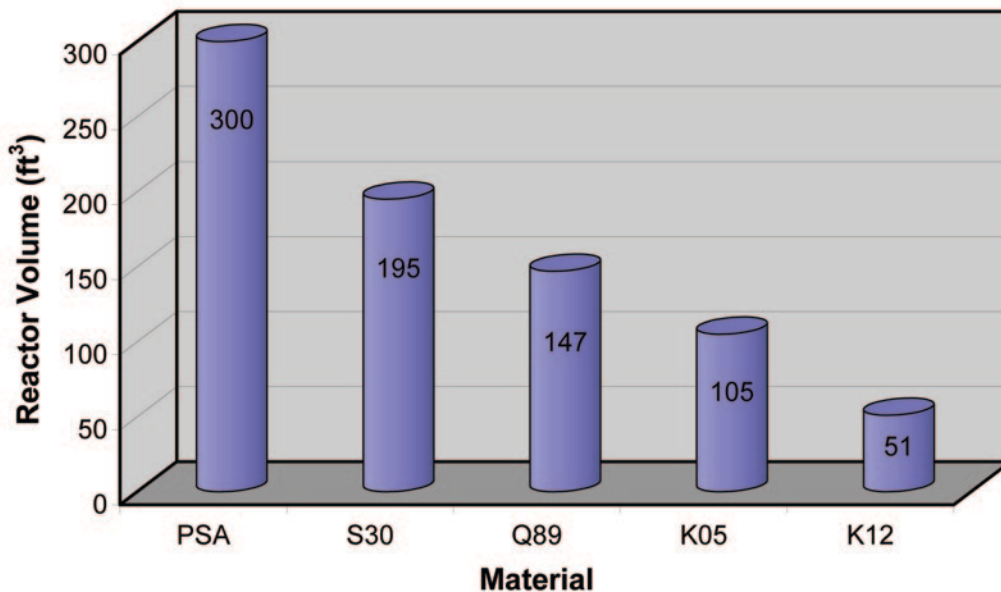


Figure 2: Required Reactor Volume Comparison

Technology Advantages

Materials being researched have superior mechanical strength, durability, and thermal resistance when compared to current TSA materials. They have the capability of producing O₂ at >99% purity, industrially relevant volumes, and at significantly reduced cost in comparison to cryogenic methods.

R&D Challenges

- Heating issues (i.e., how to most effectively heat large amounts of material; how to heat and cool a large amount of material fast; how to make sure heating is even; etc.).
- Scale-up: The central focus of the technology was to compete with cryogenic separation on large scale (>1,000 tpd); however, initial development leaned towards competing with current small-scale PSA systems (1 lb–1,000 tpd), which require additional processes to achieve high O₂ purity >95%.

Results To Date/Accomplishments

- Developed a new primary material (K-12) which yields >132 kg O₂/m³•hr.
- Observed that air flow during calcination is crucial to phase formation.
- Adding polyvinyl butyral (PVB) binder to calcined K-12, pelletizing, and re-firing at calcination temperatures yields a material which produced >130 kg O₂/m³•hr with no drop-off in performance (>16,000 cycles).

Next Steps

- Project complete.
- Engage industrial partner for scale-up and commercialization push.

Available Reports/Technical Papers/Presentations

A.R. Smith and J. Klosek, "A review of air separation technologies and their integration with energy conversion processes," Elsevier, 2001, http://www.airproducts.com/NR/rdonlyres/D29B6AF0-A218-415D-B692-20537B197E7D/0/2_ReviewOfAirSeparationTechnologiesAndTheirIntegrationWithEnergyConversionProcesses2001p.pdf

"Oxygen," Madehow.com, <http://www.madehow.com/Volume-4/Oxygen.html> (accessed September 18, 2007).

"Technology: SeprOx," Trans Ionics Corporation, http://www.transionics.com/tech_seprOx.html

"Vision Fossil Fuel Options for the Future," National Research Council, 2005.

OXYGEN TRANSPORT MEMBRANES FOR INDUSTRIAL APPLICATIONS

Primary Project Goals

Praxair is optimizing oxygen transport membrane (OTM) performance, materials, and process configurations leading to subsequent field testing of OTM technology for both synthesis gas (syngas) production and oxy-combustion applications, providing valuable experience needed to develop commercial OTM technology in industrial applications and, ultimately, future utility-scale power generation applications.

Technical Goals

Phase I:

- Develop more detailed OTM cost and performance estimates based on experiments.
- Develop a preliminary conceptual design and cost models for a pilot plant utilizing OTM technology.
- Identify the rate limiting steps for oxygen (O₂) separation through the OTM and address kinetic or mass transport limitations by appropriate materials selection and membrane architecture.
- Develop procedures to manufacture one-third pilot-size OTM tubes; test them for O₂ flux and durability in carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and water (H₂O) fuel streams with the presence of sulfur impurities.
- Test OTMs in a coal gas OTM reactor.

Phase II:

- Demonstrate ability to produce OTM tubes with the appropriate dimensions and manufacturing yield required to proceed with pilot demonstration.
- Deliver preliminary engineering cost estimate for OTM pilot plant system [OTM partial oxide reactor (POx) and Boiler].

Phase III:

- Demonstrate conversion of natural gas to 1 MM standard cubic feet per day (scfd) of syngas in a skidded OTM integrated pilot-scale system.
- Demonstrate OTM oxy-combustion and heat transfer at high rates of fuel utilization in a developmental-scale 1-MW_{th} system.

Technical Content

As oxy-combustion is currently practiced, a pure stream of O₂ is separated in an air separation unit (ASU) and then delivered to a boiler for combustion. OTM technology integrates O₂ separation and combustion in one unit. An OTM consists of an inert porous support coated with a dense gas separation layer, as illustrated in Figure 1. Air contacts the separation layer where molecular O₂ reacts with O₂ vacancies and electrons on the membrane surface to form O₂ ions, which are transported through O₂ vacancies in the separation layer using a chemical potential difference as

Technology Maturity:

Laboratory, 1–5 liters/minute oxygen

Project Focus:

Oxygen Transport Membrane-Based Oxy-Combustion

Participant:

Praxair, Inc.

Project Number:

NT43088

NETL Project Manager

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Partners:

ENrG, Inc.

The Shaw Group

The University of Utah

Performance Period:

4/30/07 – 9/30/15

the driving force. Fuel species [CO, H₂, methane (CH₄), etc.] located on the porous support side diffuse through the support and react with O₂ ions at the membrane surface to form oxidation products (H₂O, CO₂) and release electrons which are transported back through the separation layer.

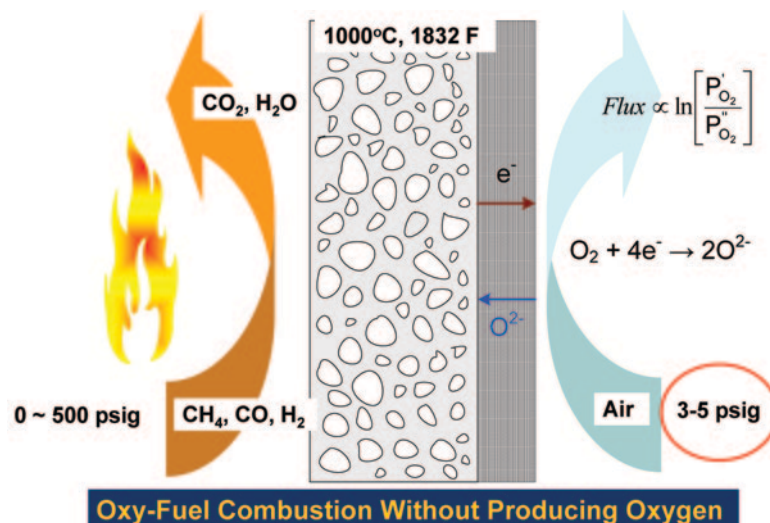


Figure 1: Schematic of Ceramic OTM

Several process concepts incorporating ceramic OTM are being explored to understand their impact on process economics. One process concept under development is shown in Figure 2. In this process, coal is first gasified in an O₂-blown gasifier to generate syngas. The syngas is optionally reacted in an OTM POx to raise its temperature. The hot syngas is expanded to recover power. After the syngas is expanded to ambient pressure, it is sent to the OTM boiler. Within the OTM boiler, syngas is first passed over an array of OTM tubes. Air is preheated by heat exchange with the O₂-depleted air and then passed on to the feed side of the OTM tubes. Oxygen from the air transports across the membrane and reacts with the syngas. Since the rate of O₂ transport is limited by the availability of the membrane area, the oxidation of syngas will take place over a large area (the OTM zone) within the boiler. As the syngas gets oxidized, the driving force for O₂ transport will decrease and the required membrane area will increase. For practical reasons, the OTM will be used to supply O₂ to the fuel side until 80–90% fuel utilization is achieved. The remainder of fuel will be combusted using O₂ supplied from the cryogenic ASU.

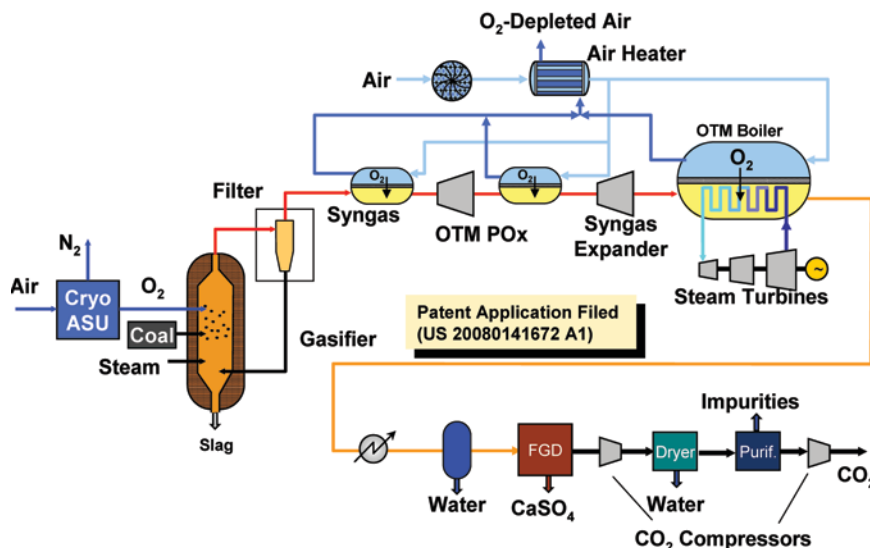


Figure 2: OTM-Based Process for Power Generation with CO₂ Capture

The thermal energy released within the boiler is used for steam generation. In the OTM zone, steam tubes will be interspersed with the OTM tubes such that the temperature is maintained at the optimum level for membrane performance. After the fuel is completely oxidized with externally supplied O₂, the flue gas will pass through a convective section of the boiler for further steam

generation and boiler feed water preheating. The flue gas exiting the boiler is processed according to a purification process proposed for a conventional oxy-fuel technology.

A number of OTM-based power cycles have been simulated for comparison against the DOE Cost of Electricity (COE) targets in 2008 dollars. Table 1 illustrates three OTM cases with different steam cycles (super critical, ultra-supercritical, and advanced ultra-supercritical) and a flue gas desulfurization (FGD) system. The base case for comparison is a DOE pulverized coal air-based combustion power cycle (without CO₂ capture) using a supercritical steam cycle. The table includes data regarding the net efficiency, plant cost, and COE for three different coal prices. The COE increase over the DOE base case is calculated and those cases meeting the DOE target of <35% increase in COE are highlighted in green. The high net efficiency, >36% higher heating value (HHV), seen in the OTM cases is a major contributing factor leading to achievement of the COE increase target.

Table 1: COE Comparison of a Standard DOE Air-Coal Power Cycle with OTM Power Cycles

Case	OTM FGD Process Cases			Air-PC Case
	1 SC	2 USC	3 AdUSC	Praxair/DOE No CCS SC
Net Efficiency (HHV)	36.3	37.2	39.7	39.7
Cost Basis (Year)	3/2008	3/2008	3/2008	3/2008
Plant Cost (\$/kW)	\$2,894	\$2,887	\$2,997	\$1,908
Increase in COE	Coal Price (\$/mMBtu)			
	1.8	39.4%	38.4%	39.7%
	3.0	34.9%	33.8%	33.8%
	4.0	32.1%	30.8%	30.0%

One part within Phase III of the project will focus on the design and construction of a skidded syngas system with O₂ supplied from OTM membranes capable of producing approximately 1 MM scfd of syngas at full capacity. It is anticipated that this system will incorporate a second-generation OTM module that improves on the performance and cost of the initial module. Another part within Phase III of the project will focus on demonstrating the oxy-combustion of a syngas using reactively driven OTM modules operating with high fuel utilization and transferring energy to a thermal load. The unit will be designed to demonstrate heat transfer from the OTM modules to a process stream (Figure 3).

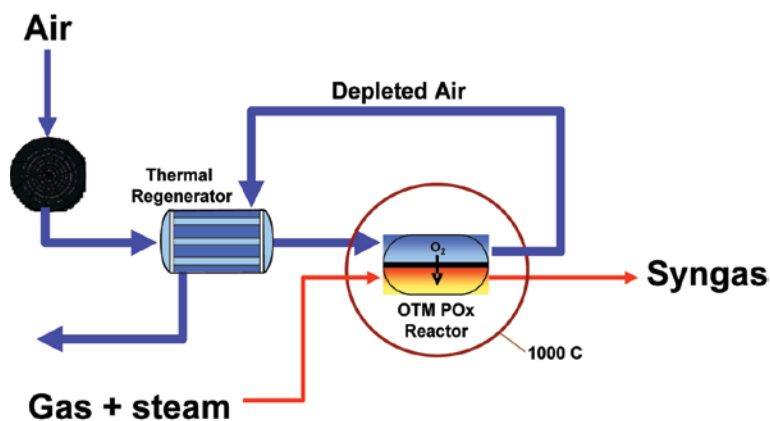


Figure 3: Phase III OTM Syngas System Concept

Technology Advantages

The OTM oxy-combustion system can provide a highly concentrated, sequestration-ready stream of CO₂ without costly cryogenic oxygen production or CO₂ separation processes. The use of reactively driven OTMs is expected to reduce the power associated with oxygen production by 70–80%. This represents a step change in the cost and related CO₂ emissions, and will enable a variety of oxy-combustion technologies, as well as other combustion applications, where CO₂ capture may be required. The development of OTMs will also benefit industrial processes used to produce syngas for subsequent processing into a variety of chemical and/or petrochemical end products by dramatically reducing the power requirements.

R&D Challenges

- Reliability of the OTM tubes at high pressure.
- Achieving membrane cost and performance targets.
- Engineering design of OTM equipment including OTM syngas reactor and boiler.

Results To Date/Accomplishments

- Demonstrated stable OTM performance with sulfur impurities in simulated coal-derived fuel gas.
- Developed pilot plant specifications for OTM oxygen flux and fuel utilization.
- Continued OTM performance improvement through characterization and manufacture of OTM tubes, and preparations for scale-up.
- Demonstrated achievement of flux and performance targets with advanced OTM materials.
- Developed manufacturing protocol for pilot-sized OTM tubes.
- Completed design and construction of the OTM multi-tube reactor at the University of Utah.
- Designed a hot oxygen burner (HOB) coal gasifier to achieve required testing parameters for the OTM system. The HOB was tested at Praxair's facilities and then sent to the OTM reactor at the University of Utah for integration. Testing on coal-derived syngas has been initiated.
- Developed conceptual design of prototype OTM module and methodology for reactor integration.

Next Steps

- Complete a Technology Evaluation Study of the potential uses/benefits of OTM technology. The study will contain projected cost savings, CO₂ reduction potential, CCS capabilities, and other environmental benefits.
- Develop detailed process models of an OTM syngas unit and an OTM combustion unit that, once validated, will be used for development of equipment specifications and to create a detailed process and instrumentation diagram (P&ID).
- Design, optimize, and test first generation OTM modules.
- Design the unit operation process equipment identified in the P&IDs, including the reactors housing the OTM modules, for both the syngas and oxy-combustion units.
- Perform testing on the development-scale syngas system (160,000 scfd), which will validate all required startup and shut-down processes, as well as the overall performance of a fully integrated system.
- Design, construct, and test a skidded pilot-scale syngas system (1 MM scfd) incorporating the second generation OTM module system.
- Develop a 1-MW_{th} oxy-combustion system.

Available Reports/Technical Papers/Presentations

Project webpage: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy-combustion/otm-based.html>

Presentation given at the 2010 NETL CO₂ Capture Technology Meeting (Sep 2010): <http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/tuesday/Maxwell%20Christie%20-%20NT43088.pdf>

Fact sheet: <http://www.netl.doe.gov/publications/factsheets/project/Proj470.pdf>

Presentation at the 2009 American Institute for Chemical Engineers Annual Meeting (Nov 2009): <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/43088%20Praxair%20OTM%20AIChE%20mtg%20ov09.pdf>

Technical paper from the Proceedings of the 34th International Technical Conference on Coal Utilization and Fuel Systems (Jun 2009): <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/43088%20Praxair%20OTM%20presentation%20Clearwater%20jun09.pdf>

Presentation at the CO₂ Capture Technology for Existing Plants Conference in Pittsburgh, PA (March 2009): <http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43088%20Praxair%20oxy-combustion%20OTM%20%28Christie%29%20mar09.pdf>

SORBENTS FOR AIR SEPARATION

Primary Project Goals

TDA Research is designing and developing a new regenerable chemical sorbent to selectively remove oxygen (O₂) from air.

Technical Goals

- Optimize and screen sorbent formulations.
- Scale up sorbent production.
- Perform long-term testing of the sorbent to demonstrate its durability through a minimum of 5,000 absorption/regeneration cycles.
- Design and size a conceptual air separation system based on experimental results.

Technical Content

Air separation units (ASUs) are one of the most expensive components of the integrated gasification combined cycle (IGCC) plant, accounting for approximately 18% of the overall plant cost and more than 14% of the cost of electricity (COE). TDA Research is developing a new, highly efficient, sorbent-based air separation technology that can produce high purity O₂ from air at high temperatures (approximately 800 °C).

By performing the air separation at high temperatures, much of the COE increase is avoided, because much of the energy penalty associated with separating air by cryogenic methods is in cooling the gas to temperatures as low as 80 K. Additionally, some of the capital cost is reduced due to the faster kinetics which permits the use of less material.

TDA's sorbent, a mixed metal oxide, has been found to achieve up to 4 wt% O₂ capacity and maintain its capacity for more than 300 cycles. This sorbent can be regenerated under near isothermal and isobaric conditions by changing O₂ partial pressure between the absorption and regeneration bed. This then demands the use of a minimum of two separate reactors, one for absorption and the other for regeneration. A solid circulation system is being developed to eliminate the use of high temperature valves. Figure 1 is a schematic depiction of this process.

It is estimated that the cost of O₂ could be as low as \$18.5/tonne (\$16.8/ton), which is a significant savings compared to cryogenic methods (\$31–\$35/tonne) and is below the U.S. Department of Energy's (DOE) target of \$22/tonne. Also, capital cost is estimated to be \$85–\$104/kWe, which again is well below cryogenic plants (\$360/tonne) and achieves DOE's target of \$82–\$110/ton.

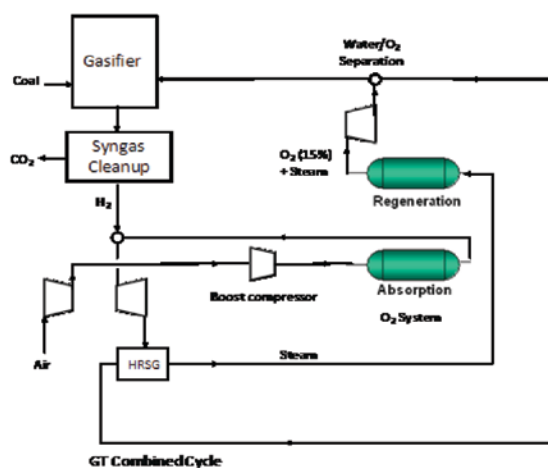


Figure 1: Schematic of Two Reactor Air Separation Unit

Technology Maturity:

Bench-scale

Project Focus:

Sorbents for Air Separation

Participant:

TDA Research, Inc.

Project Number:

ER84216

NETL Project Manager:

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Principal Investigator:

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TDA Research, Inc.

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Partners:

None

Performance Period:

8/7/06 – 8/6/09

Technology Advantages

The process temperature is maintained at 600–800 °C to increase the reaction kinetics. The sorbent is regenerated under an inert gas (e.g., steam) at the same temperature and pressure, eliminating time required for temperature and/or pressure transitions. The oxidized phase is meta-stable and a small change in chemical potential leads to its reduction.

R&D Challenges

Scale up from batch to prototype.

Results To Date/Accomplishments

- Optimized sorbent formulations and screened them under representative IGCC plant conditions.
- Scaled up sorbent production.

Next Steps

Project completed August 2009.

Available Reports/Technical Papers/Presentations

PCC Oxy-Combustion Alptekin, Presentation at the Pittsburgh Coal Conference, September 30, 2008.

Oxygen Sorbents for Oxy-fuel Combustion, Alptekin, Presentation at the 2008 AIChE Annual Meeting. http://www.tda.com/Library/docs/TDA_AIChE-Oxycombustion_111908_v3.pdf

PILOT-SCALE DEMONSTRATION OF A NOVEL, LOW-COST OXYGEN SUPPLY PROCESS AND ITS INTEGRATION WITH OXY-FUEL COAL-FIRED BOILERS

Primary Project Goals

The BOC Group, Inc. (now Linde, LLC) is conducting pilot-scale tests of its Ceramic Auto-Thermal Recovery (CAR) oxygen (O₂) generation process, integrated with a coal-fired combustor, to produce a carbon dioxide (CO₂)-rich flue gas.

Technical Goals

Phase I:

- Evaluate the performance of a 0.7-tonne/day, O₂ pilot-scale CAR system (long- and short-duration), when fully integrated with a pilot-scale coal combustor, and determine the optimum operating conditions of this unit.
- Perform a techno-economic evaluation of a commercial-scale, O₂-fired power plant that utilizes a CAR system to provide the O₂.

Phase II:

- Design and construct a nine-tonne/day, O₂ pilot-scale CAR unit.

Technical Content

In the CAR process, O₂ is separated from an air stream using a perovskite ceramic oxide adsorbent (composed of lanthanum, strontium, cobalt, and iron) at high temperature (800–900 °C). As shown in Figure 1, the process involves two separate beds that are cycled to deliver the O₂ flow (one bed is adsorbing the oxygen, while the other is desorbing). The O₂ is desorbed from the catalyst by a partial pressure swing using a purge gas containing low levels of O₂ in standard runs; CO₂ is used for this purpose. Half cycle times are varied for most efficient operational parameters, but fall in the range of 30 seconds to one minute. Multiple temperatures are monitored in the catalytic bed and are spatially placed to give an accurate representation of the bulk temperatures in the ceramic bed.

Technology Maturity:

Pilot-scale, 0.7 tonnes O₂/day

Project Focus:

Ceramic Auto-Thermal Recovery

Participant:

Linde, LLC (formerly The BOC Group, Inc.)

Project Number:

NT42748

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Partners:

Alstom Power Plant
 Laboratories
 Western Research Institute

Performance Period:

4/1/06 – 9/30/08

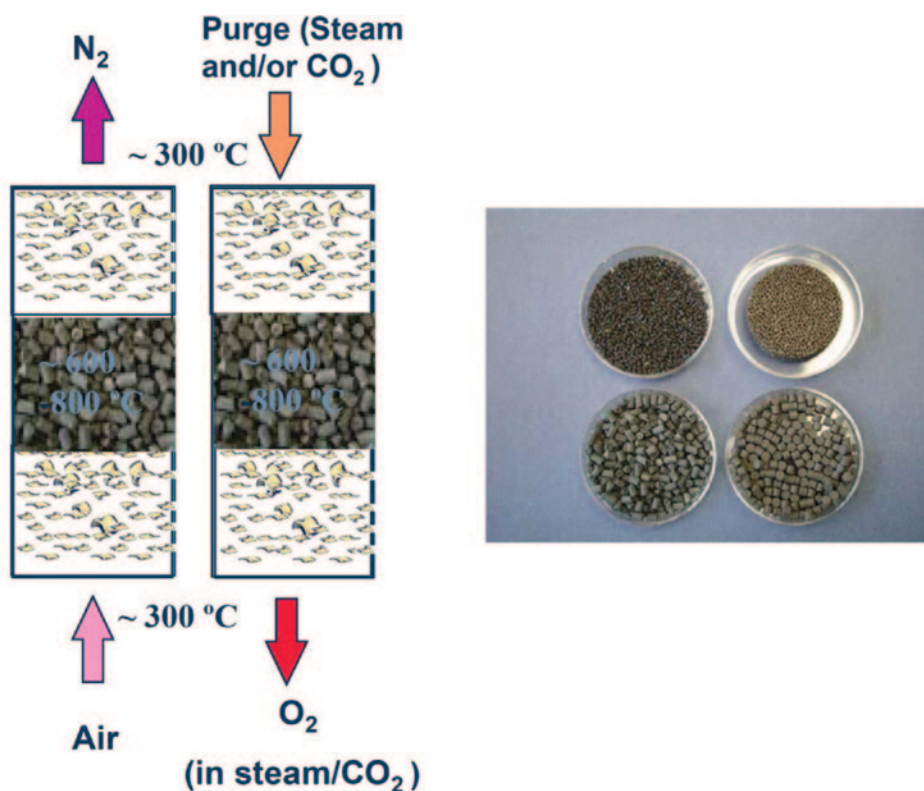


Figure 1: Ceramic Auto-Thermal Recovery (CAR) Two-Bed Oxygen Separation Process

Technology Advantages

The O₂ production process has shown a clear advantage in performance and cost compared to an air separation unit (ASU).

R&D Challenges

Although the CAR process alone compares favorably to an ASU, the techno-economic analysis has shown that overall capital costs, heat losses, and fuel consumption make the CAR process unfavorable compared to an ASU unless the working oxygen capacity of the CAR adsorbent can be increased from the current level of approximately 0.5–1.0 wt%. In addition, long duration tests have shown that the perovskite adsorbent experiences substantial mechanical breakdown and decline in performance when exposed to sulfur dioxide (SO₂).

Results To Date/Accomplishments

Completed Phase I activities include:

- Evaluated the performance of the 0.7-tonne/day, O₂ pilot-scale CAR system (long- and short-duration) and determined the optimum operating conditions of the unit.
- Performed a techno-economic evaluation of a commercial-scale, O₂-fired power plant that utilizes a CAR system to provide the O₂.

Next Steps

Phase I results led to cancellation of Phase II activities; project completed September 2008.

Available Reports/Technical Papers/Presentations

Project webpage: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy-combustion/oxy-fuel.html>

Final Report: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/42748%20BOC%20O2%20supply%20CAR%20Final%20Report_Dec%202008.pdf

Fact Sheet: <http://www.netl.doe.gov/publications/factsheets/project/Proj466.pdf>

May 2007 Presentation, 6th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA.

DEVELOPMENT OF NANOFILLER-MODULATED POLYMERIC OXYGEN ENRICHMENT MEMBRANES FOR REDUCTION OF NITROGEN OXIDES IN COAL COMBUSTION

Primary Project Goals

North Carolina A&T State University (NCATSU) is designing and developing a nanofiller-modulated polymer membrane for the oxygen (O₂)-enrichment of coal combustion and gasification applications. This will reduce the volume of waste gas and increase the concentration of near-capture ready carbon dioxide (CO₂) within the waste gas to simplify capture and reduce related costs.

Technical Goals

- Research and select polymer candidates as well as functional nanofillers.
- Experiment with the selected nanofiller-modulated polymers and document the fundamental microstructure-property relationships.
- Develop models for selected membranes using Material Studio 4.0 and Groningen Machine for Chemical Simulation (GROMACS) 3.3.

Technical Content

NCATSU is researching membrane technology capable of separating O₂ from nitrogen (N₂). The selected membranes must be capable of producing a sufficient volume of high purity O₂ at reasonable operational and capital costs. The primary method of research used to develop a membrane with the required traits has been to vary the amount and type of filler, the type of polymer backbone, and the method of distribution and casting used. The results are used to develop computational models to further study and develop the technology. The membranes evaluated thus far include single-walled carbon nanotube, nanofumed silica polydimethylsiloxane (PDMS), and zeolite-modulated polyimide (a polymer) membranes.

The polyimide selected was Matrimid 5218—chosen for its high glass transition temperature, high structural and thermal stability, and low cost. For example, a mixed matrix membrane utilizing Matrimid 5218 as the polyimide backbone and a zeolite as the filler was fabricated on a porous stainless steel substrate. This membrane was exposed to pure N₂ and pure O₂ at 3.4 atm [50 pounds per square inch (psi)] for two hours. The resulting permeability was 0.114 Barrer and 0.380 Barrer, respectively, with a selectivity for O₂ of 3.33. After 12 hours, the results improved to a permeability of 0.093 for N₂ and 0.460 for O₂, with a selectivity for O₂ of 4.95. While the results are still below required values, they show considerable potential that a mixed matrix polyimide membrane with zeolite nanofiller could meet the requirements necessary for commercial application in the future.

As for nanofumed silica PDMS membranes, the fumed silica chosen was CAB-O-SIL TS-530. The hydrophobic silica was chosen because it had greater potential for proper mixing with the elastomer. However, the fumed silica did not produce good dispersion in the polymer, resulting in limited success. The O₂ selectivity observed for 1% and 2.5% fumed-silica at 4.1 atm (60 psi) was 2.72 and 2.81, respectively. When compared to an O₂ selectivity of 2.54 for pure PDMS, it is apparent that little improvement was achieved through the use of the fumed silica.

Technology Maturity:

Laboratory-scale

Project Focus:

Nanofiller-Modulated Polymeric Membranes

Participant:

North Carolina A&T State University

Project Number:

NT42742

NETL Project Manager:

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Partners:

American Air Liquide
 Babcock & Wilcox
 Battelle Memorial Institute

Performance Period:

2/17/06 – 12/31/10

Lastly, molecular dynamics simulations have been conducted to calculate the theoretical O_2 molecular diffusion coefficient and N_2 molecular coefficient inside single-walled carbon nanotube PDMS membranes, in order to predict the effect of the nanotubes on the gas-separation permeability. A simulated model of these membranes is shown in Figure 1.

The selectivity achieved from experimentation is 0.86 for PDMS filled with single-walled carbon nanotubes. When compared to pure PDMS, with a selectivity of 1.97, it is apparent that this filler is not appropriate for the purpose of this project.

Technology Advantages

The membranes being researched have several desirable properties, including high glass transition temperatures, high thermal and structural stability, high permeability (0.460 Barrers), and high selectivity (4.95). In addition, capital costs are low due to the absence of precious metals found in many other membrane technologies.

R&D Challenges

- The experiments performed thus far have shown that the nanofillers and polymers used have unstable properties over extended periods of time.
- It was found that fumed silica did not produce good dispersion in the polymers tested.
- Insufficient permeability and selectivity for O_2 .

Results To Date/Accomplishments

- Performed permeation and diffusion experiments using polymers with nanosilica particles, nanotubes, and zeolites as fillers.
- Studied the influence of nanofillers on the self diffusion, free volume, glass transition, O_2 diffusion and solubility, and permselectivity of O_2 in polymer membranes.
- Developed molecular models of single-walled carbon nanotube and nanofumed silica PDMS membranes, and zeolites-modulated polyimide membranes.

Next Steps

Project complete.

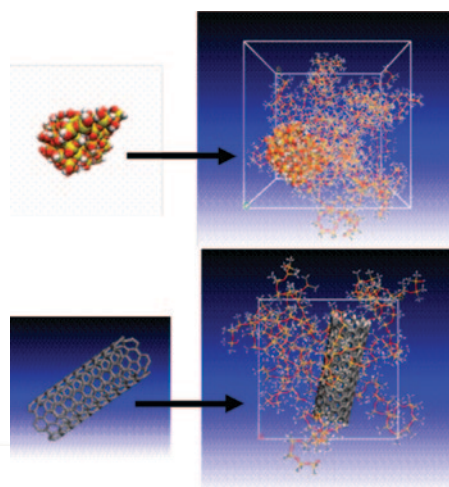


Figure 1: Model of Nanofumed Silica (above) and Single-Walled Carbon Nanotube PDMS Membrane

Available Reports/Technical Papers/Presentations

J. Zhang, J. Lou, S. Ilias, P. Krishnamachari, J. Yan. "Thermal properties of poly(lactic acid) fumed silica nanocomposites: Experiments and molecular dynamics simulations," *Polymer*, **2008**, 49, 2381–2386.

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ITM OXYGEN TECHNOLOGY FOR INTEGRATION IN IGCC AND OTHER ADVANCED POWER GENERATION SYSTEMS

Primary Project Goals

Air Products and Chemicals is designing and developing an ion transport membrane (ITM) based on ceramics that selectively transport oxygen (O_2) ions when operated at high temperature. This high temperature process may be integrated with advanced power generation processes that require O_2 as a feedstock, such as integrated gasification combined cycle (IGCC) and other clean energy and industrial applications.

Technical Goals

- Design, construct, and operate a 0.1-ton/day (TPD) technology development unit (TDU) to validate the ITM technology concept, verify the technology prospects for stand-alone O_2 production plants, and integrate with IGCC and other advanced power generation systems.
- Design and construct a 5-TPD Sub-Scale Engineering Prototype (SEP) facility and produce greater than 95% O_2 purity.
- Increase the scale of the engineering test facility from 5 TPD of O_2 to 100 TPD of O_2 in an intermediate-scale test unit (ISTU).
- Develop the manufacturing capability needed to support ITM technology commercialization.
- Develop preliminary design concepts for a 2,000-TPD ITM O_2 production plant.

Technical Content

Air Products and Chemicals is designing a ceramic ITM that, under high temperatures, separates O_2 from nitrogen (N_2). These non-porous, multi-component metallic oxides have high O_2 flux and selectivity (100%), resulting in high capacity production of high purity O_2 at low cost. Figure 1 illustrates the concept of the ITM.

Technology Maturity:

Prototype, 5 tons oxygen produced/day

Project Focus:

Ion Transport Membrane

Participant:

Air Products and Chemicals, Inc.

Project Number:

FT40343

NETL Project Manager

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Eltron Research

EPRI

GE-Chevron-Texaco

NovelEdge Technologies

Pennsylvania State University

Siemens Power Group

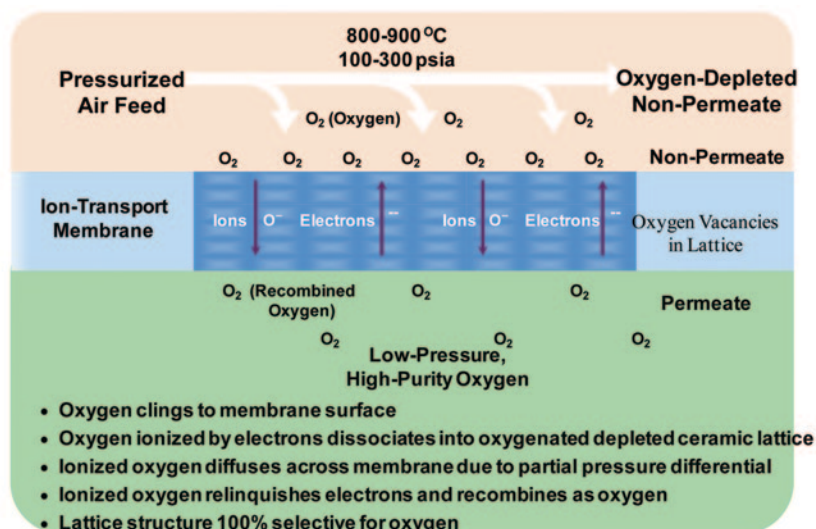
SofCo

University of Pennsylvania

Williams International

Performance Period:

10/1/98 – 9/30/15

Figure 1: Conceptual Schematic of ITM O₂ Technology

The membrane employs a ceramic planar wafer architecture that incorporates a non-porous ITM on supporting porous and slotted layers that typically operate between 800 and 900 °C. The driving force for O₂ separation is determined by the relative O₂ partial pressure gradient across the membrane. Therefore, air is typically supplied at pressures of 7–20 atm, while the product O₂ pressure is typically below ambient (~1 atm). Figure 2 shows a cutaway view of part of a wafer. The wafer consists of two thin outer membrane layers through which the oxygen ions diffuse. The thin layers on the top and bottom of the wafer are supported by a porous layer which is itself supported by a slotted layer. High-temperature, high-pressure air flows over the membrane surface exterior to the wafer. Oxygen passes from the air outside each wafer through the thin outer membrane layer, through the pores of the porous layer and into the slots of the innermost layer, where it is collected. In a typical membrane module, stacks of wafers are joined together, separated by a spacer ring to form a gap for air flow between the wafers. The oxygen is collected in a central region of the module formed by the open center of each wafer and the spacer rings and passes out of the module through a ceramic tube sealed to a metal pipe. The high-pressure air on both sides of each wafer creates compressive stresses within the ceramic, which stabilize the wafer. The planar design also makes for a very compact separation device, while facilitating good gas phase mass transfer. All of the layers are made of the same ceramic material, and therefore expand and contract together during temperature changes.

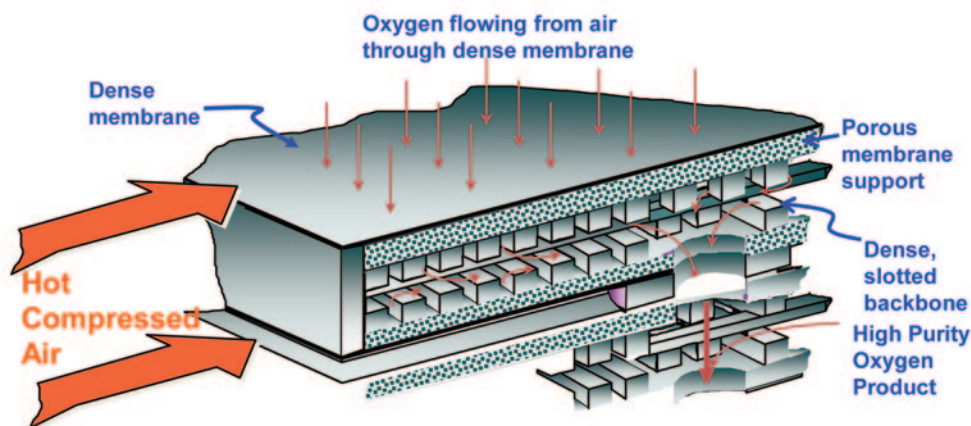
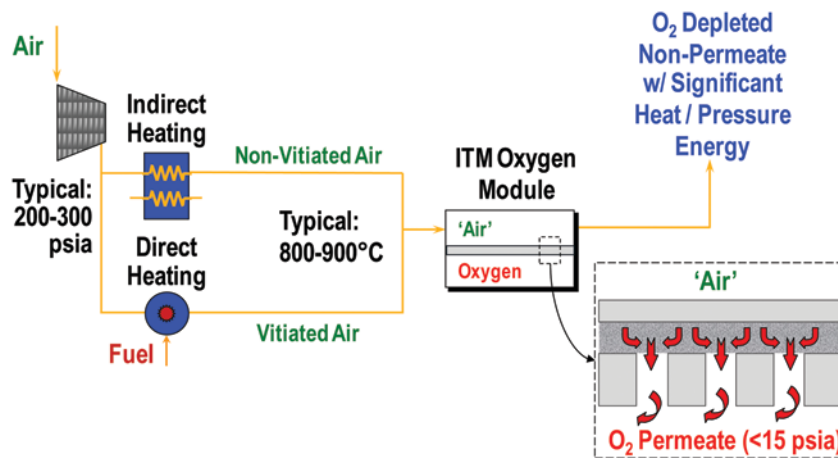


Figure 2: A Portion of an ITM Planar Membrane Wafer Shown in Cutaway View

Figure 3 shows a schematic diagram of an ITM O₂ production plant that includes both indirect and direct heating of the pressurized feed air, in order to satisfy the heating requirement of the thermally activated transport mechanism. While not shown in the schematic, the resulting hot, pressurized, non-permeate stream can be recovered if combined with a gas turbine power generation system.

Figure 3: Diagram of O₂ Production Plant

An ITM O₂ plant is projected to decrease the installed capital cost of air separation equipment by more than one-third and the installed capital cost of an IGCC facility by 7%, while improving efficiency and reducing the power requirement for air separation by approximately 35%. These increases in efficiency and reductions in cost, along with the near-capture ready concentrations of CO₂ in the waste stream, make ITM a technology that may be capable of making CO₂ capture more economically feasible.

Technology Advantages

This technology is capable of producing 95+% O₂ at high flux rates. It is resistant to structural damage and provides consistent performance during thermal and hydraulic cycling. It offers low capital and operating costs, improves efficiency and reduces the power requirement for air separation by approximately 35% relative to cryogenic separation, and reduces capital cost of an IGCC facility by 7%.

R&D Challenges

Scale up from 5 TPD to 100 TPD to 2,000 TPD and obtaining flux rates competitive to other available technologies.

Results To Date/Accomplishments

- Developed a stable, high-flux material; demonstrated stable operation in the 0.1-TPD TDU.
- Demonstrated the commercial flux target under anticipated commercial operating conditions.
- Devised a planar ITM architecture.
- Scaled-up and produced commercial-size wafers in large quantities.
- Built first commercial-scale ITM oxygen modules.
- Completed detailed design, construction, and testing of SEP vessel capable of housing full-size ITM oxygen modules to produce an estimated 5 TPD of 95% pure oxygen at full commercial conditions of 200–300 pounds per square inch gauge (psig) and 800–900 °C.
- Completed subscale wafer flux evaluation studies with feed air impurities and determined the effect of potential impurities on the cost and engineering performance of ITM systems.
- Implemented patented advanced process control techniques during heating and cooling to improve module reliability at the SEP.

- Completed the 100-TPD module conceptual design by including major elements of a commercial ITM oxygen facility.
- Completed economic assessment of carbon capture power plant cases with ITM oxygen that feature carbon capture and sequestration (CCS) technology options.
- The 5-TPD SEP was operated for over 18,000 hours, commercial flux targets were achieved or surpassed, and product purity exceeded 99%.
- Developed and selected a supported getter material that will remove gas phase chromium species upstream of the ITM modules.

Next Steps

- Select one of the proposed designs for a scale up plant and perform a detailed design.
- Construct an ISTU that co-produces electrical power and up to 100 TPD of O₂.
- Develop the manufacturing capability needed to support ITM technology commercialization and preliminary design concepts for a 2,000 TPD ITM oxygen production plant.

Final test results will not be available until the September 2015 project completion date.

Available Reports/Technical Papers/Presentations

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