

## **MEMBRANE DEVICE FOR HYDROGEN FROM COAL**

### **Final Report**

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**Longmont, CO**

**And**

**U.S. Department of Energy**

**National Energy Technology Laboratory**

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**By**

**Western Research Institute**

**Laramie, Wyoming**

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## ABSTRACT

The objectives of the project were to build pilot scale hydrogen separation systems for use in a gasification product stream. This device would demonstrate fabrication and manufacturing techniques for producing commercially ready facilities. The design was a 2 lb/day hydrogen device which included composite hydrogen separation membranes, a water gas shift monolith catalyst, and stainless steel structural components.

Synkera Technologies was to prepare hydrogen separation membranes with metallic rims, and to adjust the alloy composition in their membranes to a palladium-gold composition which is sulfur resistant. Chart was to confirm their brazing technology for bonding the metallic rims of the composite membranes to their structural components and design and build the 2 lbs/day device incorporating membranes and catalysts. WRI prepared the catalysts and completed the testing of the membranes and devices on coal derived syngas.

The reactor incorporated eighteen 2" by 7" composite palladium alloy membranes. These membranes were assembled with three stacks of three paired membranes. Initial vacuum testing and visual inspection indicated that some membranes were cracked, either in transportation or in testing. During replacement of the failed membranes, while pulling a vacuum on the back side of the membranes, folds were formed in the flexible composite membranes. In some instances these folds led to cracks, primarily at the interface between the alumina and the aluminum rim. The design of the 2 lb/day device was compromised by the lack of any membrane isolation. A leak in any membrane failed the entire device. A large number of tests were undertaken to bring the full 2 lb per day hydrogen capacity on line, but no single test lasted more than 48 hours. Subsequent tests to replace the mechanical seals with brazing have been promising, but the technology remains promising but not proven.

## EXECUTIVE SUMMARY

Carbon dioxide emissions during energy production provide a source of global warming. Synthesis gas production results from steam reforming of natural gas, gasification of coal or biomass gasification. Water gas shift catalysis then is used to convert the synthesis gas to carbon dioxide and hydrogen. Hydrogen may be removed from the product stream through a selective membrane leaving a high-pressure carbon dioxide stream that may be compressed for sequestration or chemical applications. Providing there is a sink available to sequester the carbon dioxide, a clean hydrogen fuel has been produced with minimal additional greenhouse gas emissions to the environment. The partial oxidation step consumes energy, and there are compression costs for sequestering the carbon dioxide. Additionally, there is a compression cost associated with the hydrogen so that it can be transported economically. If a high pressure gasifier is employed, efficiencies are increased and this proposed approach provides a high pressure relatively clean carbon dioxide stream that is sequestration ready thus saving energy.

The objectives of the multi-phase project were to build and test several pilot scale hydrogen separation systems for use in a gasification product stream. Based on our previous research to integrate structural water gas shift catalysts with metallic hydrogen separation membranes, this larger scale device would demonstrate fabrication and manufacturing techniques for producing commercially ready facilities. The Phase I objective was a 2 lb/day hydrogen device which includes composite hydrogen separation membranes, a water gas shift monolith catalyst, a transitional aluminum/stainless steel component and stainless steel structural components for maintaining pressure, temperature and correct gas flows. The goal was that if Phase II and III funds were available then the further objectives would be a 100 lb/day hydrogen device and the complete engineering for a 4 ton per day hydrogen system.

This work was conducted by a project team with three members. In Phase I, Synkera Technologies had three subtasks: to prepare blank composite sheets, to prepare hydrogen separation membranes with active surfaces of 1" x 5" with metallic rims, and to adjust the alloy composition in their membranes to a palladium-copper or palladium-gold composition which is sulfur resistant. Chart's responsibilities in Phase I were to confirm their brazing technology for bonding the metallic rims of the composite membranes to their structural components and design and build the 2 lbs/day device incorporating the membranes and the water gas shift monoliths. WRI prepared the WGS catalysts and completed the testing of the membranes and devices on coal derived syngas. WRI also tested methanation technology to improve the value of the off gas carbon dioxide.

The core of the hydrogen separation device is a palladium / alumina composite membrane which was fabricated in two stages: anodization of the aluminum into a porous alumina structure; and electrochemical addition of palladium alloy plugs into the porous structure. Various sizes and shapes of membranes were prepared during Phase I, both as test materials and as design of the 2 lb/day device evolved. Those shapes included 1 inch circles, 2 inch by 7 inch rectangular pieces, and six inch diameter circular membranes with multiple

internal structures. Each of these shapes was prepared both as blank anodized alumina and as fully operational palladium composites. A majority of the membranes were prepared as 2 inch by 7 inch rectangles when that design became finalized for the 2 lb/day device. Approximately 125 of these membranes were produced during Phase I. The smaller active area of each membrane required the overall number of membranes in the 2 lb/day device to be 18. These membranes were assembled in a design with three stacks of three paired membranes. That device was delivered to WRI for testing in May of 2012.

Initial vacuum testing and visual inspection indicated that some membranes were cracked, either in transportation or during the test. During replacement of the failed membranes, it was observed that while pulling a vacuum on the back side of the membranes, they were seen to shift slightly as they were pulled against the support structure. This shift resulted in folds in the flexible composite membranes. In some instances these folds led to cracks forming, primarily at the interface between the alumina and the aluminum rim. Clearly the design of the 2 lb/day device was compromised by the lack of any membrane isolation valving. A leak in any membrane failed the entire device. The mechanical seal system was a compromise that required near perfect execution. A large number of test attempts were undertaken to bring the full 2 lb per day hydrogen capacity on line, but no single test lasted more than 48 hours before failure. Significant subsequent tests to replace the mechanical seals with brazing were promising, but the technology remains promising but not proven.

The methanation work completed as part of the cost share portion of the project was to investigate the catalytic activity for conversion of CO<sub>2</sub> to methane in the presence of hydrogen. The goal was to reproduce conditions after the hydrogen separation step in a carbon dioxide off gas that would have a low level of hydrogen remaining. Methanation of the hydrogen would make the carbon dioxide more effective as an enhanced oil recovery material. Carbon dioxide with a small amount of methane, approximately 3% methane, has a higher solubility in saline aquifers than pure carbon dioxide. A number of methanation catalysts were tested under realistic conditions. Several catalysts including Ni/SiO<sub>2</sub> and Ni-ferrite showed the highest activity for this methanation process. Ni/SiO<sub>2</sub> was found to be stable for a considerable time on-stream. The activity of all the catalysts was evaluated under 300 psi pressure which is indicative of the conditions which would be necessary. To coordinate the hydrogen separation and methanation processes. These results show that this technique and the resulting methanated carbon dioxide would be a valuable co-product in an IGCC plant designed primarily to produce power and hydrogen.

It was clear following experiments to join the aluminum rimmed composite palladium membranes that the thermal expansion differences between the anodized alumina and the aluminum rim contributed to membrane failures during thermal cycles. A series of experiments were completed to join the anodized alumina with no aluminum rim to structural alloys like Kovar. Kovar is a very low thermal expansion alloy that could be used as a transition piece between the higher expansion stainless steel and very low thermal expansion anodized alumina.

Chart worked with three vendors on preparing brazed structures to avoid the thermal expansion issues found using the aluminum rimmed membranes. All of the three vendors were production facilities, and with limited personnel focused on R&D, so could produce only one or two braze assemblies at a time. Chart tried to increase the success rate by contracting multiple vendors, hoping the best brazing practices of at least one of the three vendors would meet our expectations and produce a successful assembly. The experiments to produce anodized alumina and Kovar joints were ultimately successful enough that this method appears promising for eliminating mechanical seals used in the 2 lb/day device.

The pursuit of pure hydrogen for hydrogen based cars and PEM fuel cells came from the top. Administration policy instructed the Department of Energy to research hydrogen separation, hydrogen storage and a hydrogen based energy system that included distributed power and cars that burned hydrogen and emitted only water vapor. IGCC was supposed to be the power plant of the future and local hydrogen stations would fill up your car. All that research pointed out the multiple complications of a hydrogen based energy system. It is not clear if IGCC can compete economically with conventional power generation. There is no evidence that distributed power generation based on fuel cells of any design is in our near future. High issues with hydrogen storage and the absence of the infrastructure for getting hydrogen to consumers means that hydrogen based cars are still unlikely in large numbers. Hydrogen is still a major national commodity product. Large amounts of hydrogen are needed for petroleum refining, fertilizer production and the petrochemical industry. Economically competitive separation technologies are still needed. After nine years researching in the hydrogen separation field, WRI has investigated four classes of membrane materials including vanadium alloys, palladium composites, amorphous alloys and polymer membranes. Of these materials the palladium composites have shown the highest performance, but their reliability has not been proven. Production of very small membranes can be done repeatedly, and those membranes have shown excellent hydrogen flux and fair resistance to carbon monoxide and hydrogen sulfide poisoning. However variability in the aluminum metallurgy in the membrane precursor foils leads to imperfections in the membranes when produced electrochemically. The larger the membrane, the more likely the presence of a fatal defect will occur. There may be techniques available to refine the metallurgy to reduce or eliminate these flaws. The promise of the approach remains, but the proof of the suitability of this technology for commercial scale devices is not yet there.

The work completed in methanation of the small amounts of hydrogen remaining in carbon dioxide after separation has been a very rewarding subtask of this project. The value of carbon dioxide for enhanced oil recovery can be increased by this methane by-product improving the performance of the carbon dioxide through increased solubility in saline aquifers. This is a technology suitable for further study.

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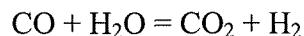
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## BACKGROUND

Carbon dioxide emissions during energy production provide a source of global warming. Synthesis gas production results from steam reforming of natural gas, gasification of coal or biomass gasification. Water gas shift catalysis then is used to convert the synthesis gas to carbon dioxide and hydrogen. Hydrogen may be removed from the product stream through a selective membrane leaving a high-pressure carbon dioxide stream that may be compressed for sequestration or chemical applications. Providing there is a sink available to sequester the carbon dioxide, a clean hydrogen fuel has been produced with minimal additional greenhouse gas emissions to the environment. The partial oxidation step consumes energy, and there are compression costs for sequestration the carbon dioxide. Additionally, there is a compression cost associated with the hydrogen so that it can be transported economically. If a high pressure gasifier is employed, efficiencies are increased and this proposed approach provides a high pressure relatively clean carbon dioxide stream that is sequestration ready thus saving energy.

If we are willing to accept the additional energy costs to make hydrogen as described above, then the areas of scientific and engineering challenges are: 1) optimization of the partial oxidation or gasification step; 2) filter particulates, tars, sulfur, mercury and trace contaminants from the synthesis stream; 3) maximize hydrogen production by performing the water gas shift step on all the carbon monoxide possible, and 4) maximize the hydrogen separation efficiencies of the separation membrane. By combining challenges 3 and 4, conducting the hydrogen separation in the presence of the water gas shift catalyst, the equilibrium of the shift reaction can be pushed towards the right to favor total conversion of the carbon monoxide.



Recent advances in hydrogen separation membranes have made the combined water gas shift/ hydrogen separation operation quite realistic. Commercial scale separation of hydrogen is carried out using pressure swing absorption systems (PSA) or with the use of palladium foil membranes. Neither of those systems is compatible with water gas shift operations due to hardware, pressure or temperature requirements. Hydrogen separation membranes based on a composite of anodic aluminum oxide films have been shown to operate well in the temperature range of high shift water gas shift catalysts (380-440°C). Alloying has improved the resistance of palladium to sulfur and also improved the physical characteristics with respect to embrittlement issues. The integration of the water gas shift catalyst and composite hydrogen membranes at commercial scale remains an achievable goal.

## **PROJECT OBJECTIVES**

The objectives of the multi-phase project were to build and test several pilot scale hydrogen separation systems for use in a gasification product stream. Based on our previous research to integrate structural water gas shift catalysts with metallic hydrogen separation membranes, this larger scale device would demonstrate fabrication and manufacturing techniques for producing commercially ready facilities. The Phase I objective was a 2 lb/day hydrogen device which includes composite hydrogen separation membranes, a water gas shift monolith catalyst, a transitional aluminum/stainless steel component and stainless steel structural components for maintaining pressure, temperature and correct gas flows. The goal was that if Phase II and III funds were available then the further objectives would be a 100 lb/day hydrogen device and the complete engineering for a 4 ton per day hydrogen system.

## **SCOPE OF WORK**

In Phase I, Synkera Technologies had three subtasks: to prepare blank composite sheets, to prepare hydrogen separation membranes with active surfaces of 1" x 5" with metallic rims, and to adjust the alloy composition in their membranes to a palladium-copper or palladium-gold composition which is sulfur resistant. Chart's responsibilities in Phase I were to confirm their brazing technology for bonding the metallic rims of the composite membranes to their structural components and design and build the 2 lbs/day device incorporating the membranes and the water gas shift monoliths. WRI prepared the WGS catalysts and completed the testing of the membranes and devices on coal derived syngas. The distribution of work will be primarily the same for Phase II, though all parties will contribute to overall designs. Much of the engineering for Phase III would be completed in house at Chart with assistance from the other two partners.

The tasks included with project management and proceeded through the technical tasks to be completed during the project. The tasks built on the accomplishments of the previous years in which hydrogen separation membranes based on metallic alloys and monolithic water gas shift catalysts were incorporated into 10,000 l/day devices and tested under coal gasification conditions. The tasks took those concepts and design the next logical scale up to the production of 2lbs/day then 100-lbs/day of hydrogen. Task 1 covered project management operations. Task 2 dealt with the fabrication of the large separation units. Task 3 covered the water gas shift catalyst preparation. Task 4 described the production of composite membranes. Task 5 covered the testing of the devices under NETL protocol and coal gasification conditions. Task 6 dealt with methanation in the retentate stream.

## RESULTS

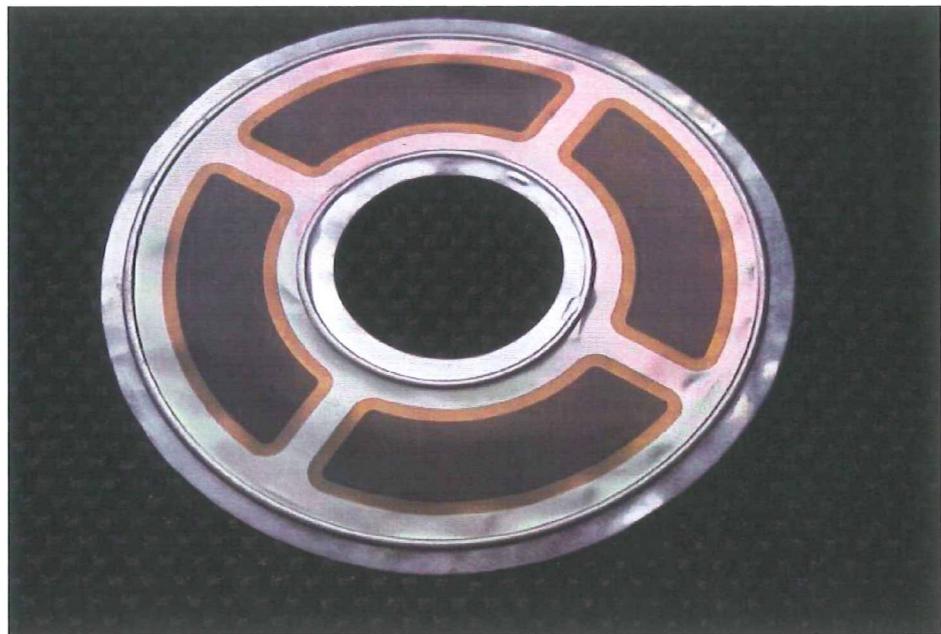
### Membrane Fabrication

The palladium / alumina composite membrane, as described elsewhere in this document, is fabricated in two stages: anodization of the aluminum into a porous alumina structure; and electrochemical addition of palladium alloy plugs into the porous structure. Various sizes and shapes of membranes were prepared during Phase I, both as test materials and as design of the 2 lb/day device evolved. Those shapes included 1 inch circles, 2 inch by 7 inch rectangular pieces, and six inch diameter circular membranes with multiple internal structures. Each of these shapes was prepared both as blank anodized alumina and as fully operational palladium composites. (Figures 1 and 2) A majority of the membranes were prepared as 2 inch by 7 inch rectangles when that design became finalized for the 2 lb/day device. Approximately 125 of these membranes were produced during Phase I.



**Figure 1. Donut membranes of alternate design for thermal expansion issues before Pd addition**

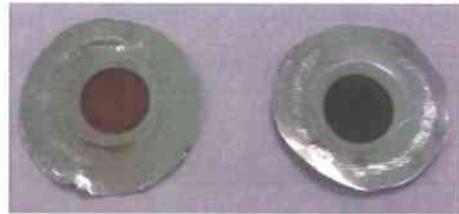
Initial membranes were prepared using an anodized thickness of  $100\mu\text{m}$ , and thus an aluminum thickness of  $100 \mu\text{m}$ . Though these membranes survived heating and pressure tests, the electro-deposition of palladium into the pores was pore resulting in inadequate selectivity. Time was spent on attempting to improve the electro-deposition on these membranes, but we were unable to make selective membranes. It was determined that the ratio of the aluminum thickness to the anodized thickness is important to the survival of the membranes upon heating. Membranes were then made  $50\mu\text{m}$  thick (for optimum electro-deposition), but stripping the aluminum down to  $\sim 80\mu\text{m}$ . These membranes both survived heating and pressure trials, and resulted in near infinite selectivity.



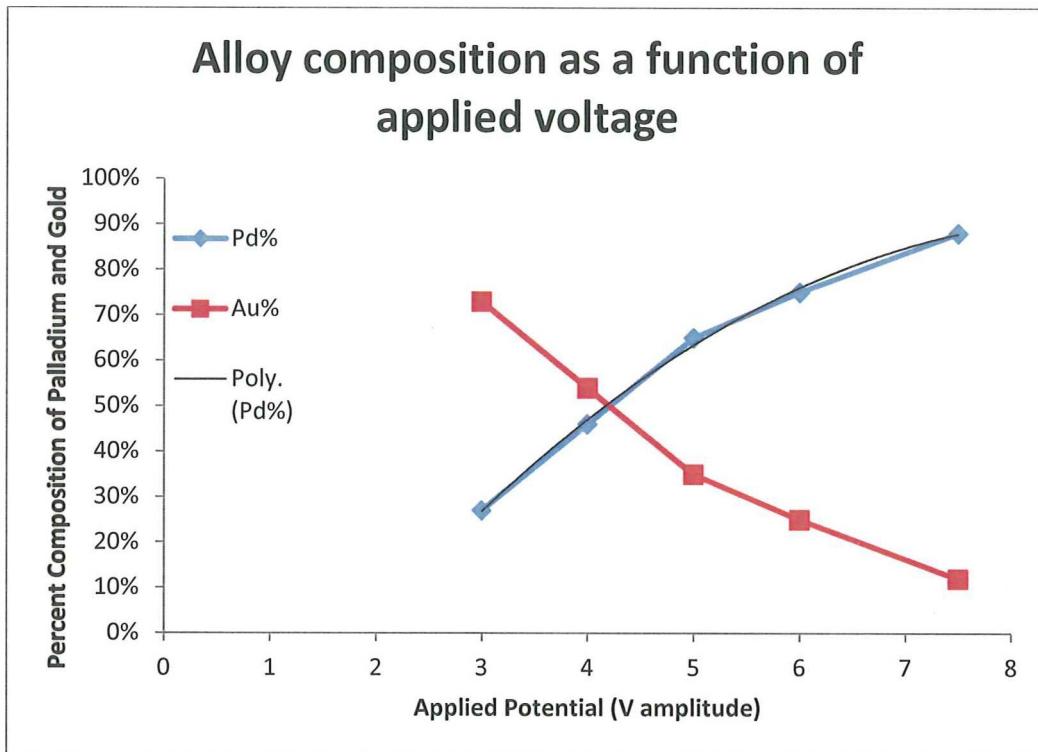
**Figure 2. Pd composite membrane foil with inner and outer diameter seals**

#### Palladium Alloys

It was recognized early that while pure palladium plugs could provide very high flux values due to their inherent minimum thickness, pure palladium would be susceptible to corrosion by high hydrogen sulfide concentrations in coal derived syngas. Testing was conducted to form those plugs as palladium alloys less sensitive to sulfur concentration. Those alloys were identified as palladium – copper, palladium - silver, and palladium – gold. The method to deposit the plugs within the porous alumina is essential an electrochemical process. With pure palladium, that is conducted using a palladium nitrate solution at a given over-voltage. The introduction of a second metal to the alloy is complicated by the difference in reduction potential of the two metals. The controllable variables in the process are the metal salt anions, the relative metal salt concentrations and the deposition over-voltage. While 60% palladium – 40% copper was the alloy of choice for mixed alloy development due to the reduced cost of the materials, the large difference in reduction potential and the incompatibility of several of the metal salt anions made the production of palladium copper alloys possible but problematic. Small membranes with the correct 60% palladium – 40% copper alloy were produced. (Figure 3) The solutions of the metal salts also decomposed rapidly which reduced the working time of the process. A decision was made to focus on the palladium gold alloys. By varying the applied voltage, the distribution between palladium and gold could be adjusted. (Figure 4)



**Figure 3. Left: Cu-Pd Alloy in anodized alumina, Right: Pd in anodized alumina**

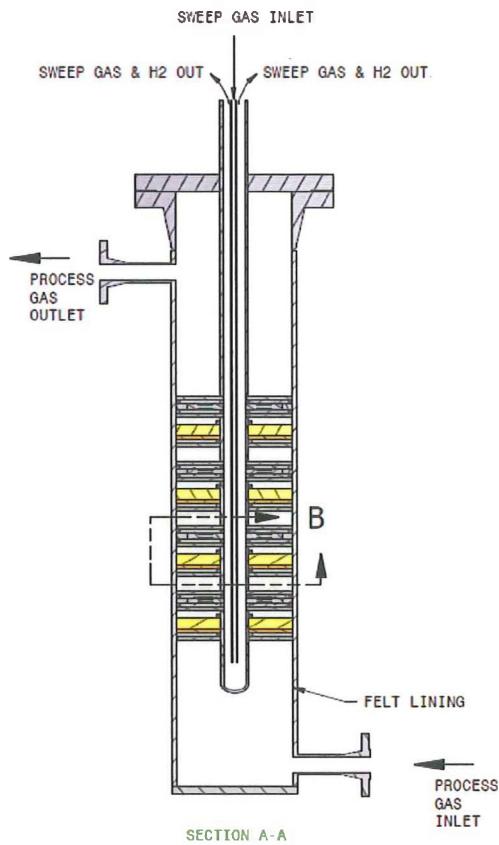


**Figure 4. Pd-Au Alloys by Applied Voltage**

#### Reactor Design and Fabrication

In the work plan submitted with the DOE proposal, the design and fabrication of the 2 lb/day hydrogen separation device, and its testing, was the primary focus of the project. Intrinsic to this goal was the desire to produce a device that was modular in form, scalable and manufactured with methods and practices that were commercially sensible. While the original work plan suggested that this fabrication could be completed within eight to ten months, in actuality this step took considerably longer. The original design called for donut shaped membranes approximately six inches in diameter with a seal that could be made by brazing both the inner diameter and the outer diameter of the donut. (Figure 2) Testing by brazing of these donut shaped membranes into stainless steel structures showed that differential thermal expansion and contraction placed ripples into the membranes after the thermal cycle. The cause

was determined to be a combination of both the thermal expansion differences between the aluminum rims and the stainless steel, but also the aluminum rim and the alumina of the membrane itself. Alternate designs of the donuts using different amounts of alumina and aluminum did not solve the problem. Although additional work since then has shown that a solution is likely to this problem, at the time, with the original 18 month deadline rapidly approaching, the design of the reactor was changed to incorporate mechanical seals similar to those which Synkera had used to test their membranes successfully for several years. The new design incorporated the 2 inch by 7 inch membranes. The smaller active area of each membrane increased the overall number of membranes in the 2 lb/day device to 18. These membranes were then moved from a stacked planar design to a design with three stacks of three paired membranes. (Figures 5, 6 and 7) That device was delivered to WRI for testing in May of 2012, well after the original expected delivery date.



**Figure 5. First 2 lb/day device design using donut shaped membranes**

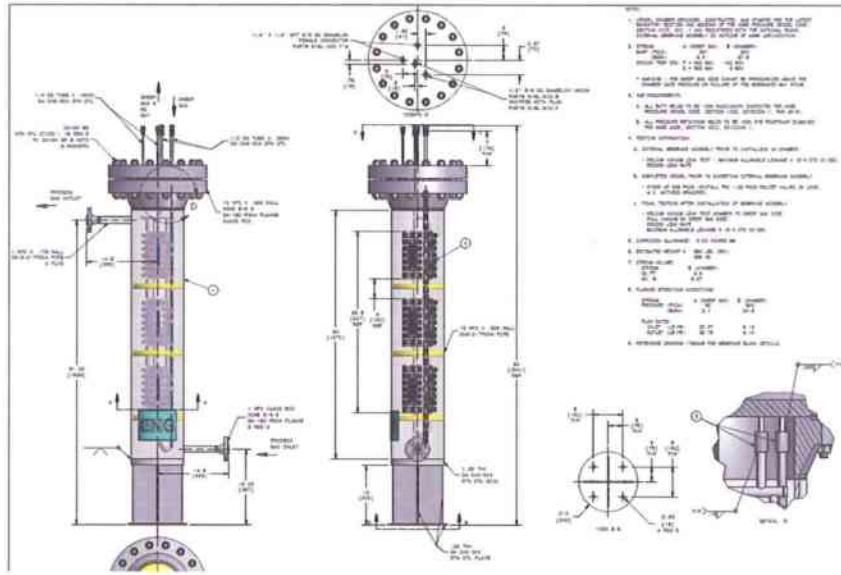


Figure 6. Revised design incorporating eighteen 2 inch by 7 inch membranes

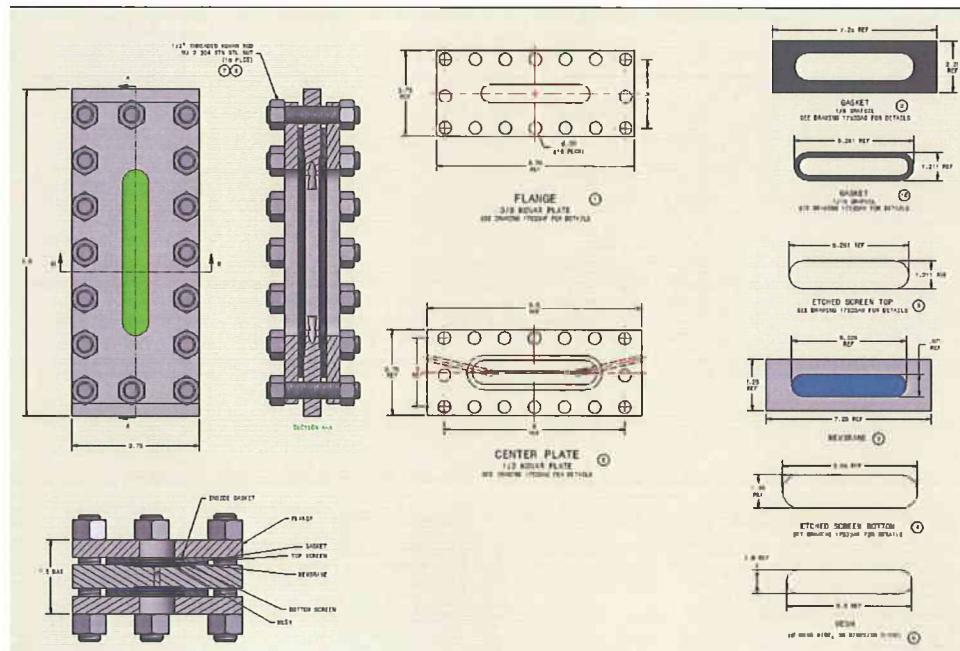
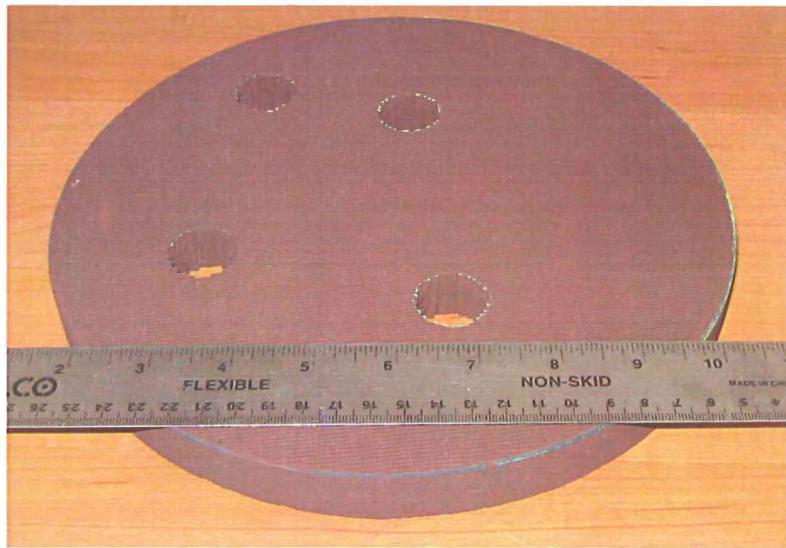


Figure 7. Flanges to hold membrane pairs

### Water Gas Shift Catalyst Monoliths

Water gas shift catalyst is typically used pelletized in fixed beds. In the first 2 lb/day device design, the water gas shift catalyst was to be prepared as porous sheet used to redirect

syngas flows over the membrane surfaces. Some testing of the performance of that catalyst type was completed using a gel deposition method onto porous alumina. Later as the reactor design was altered, the form of the catalyst was transformed into powder sintered onto cordierite honeycomb. This form of the WGS catalyst proved highly active. A stability test was carried out for over 200 hours on the monolith catalyst at 400°C. The CO conversion declined from 88% to about 74%, a 15% loss of activity then seemed stabilized after 200 hours. Current testing under 100 ppm hydrogen sulfide showed no degradation of catalyst performance after 100 hours (Figure 8) Incorporation of a sheet of this catalyst between each membrane stack would be sufficient to shift carbon monoxide to maximize hydrogen production within the reactor. There was a small amount of dead volume at the bottom of the reactor that pelletized WGS catalyst could be added if necessary.

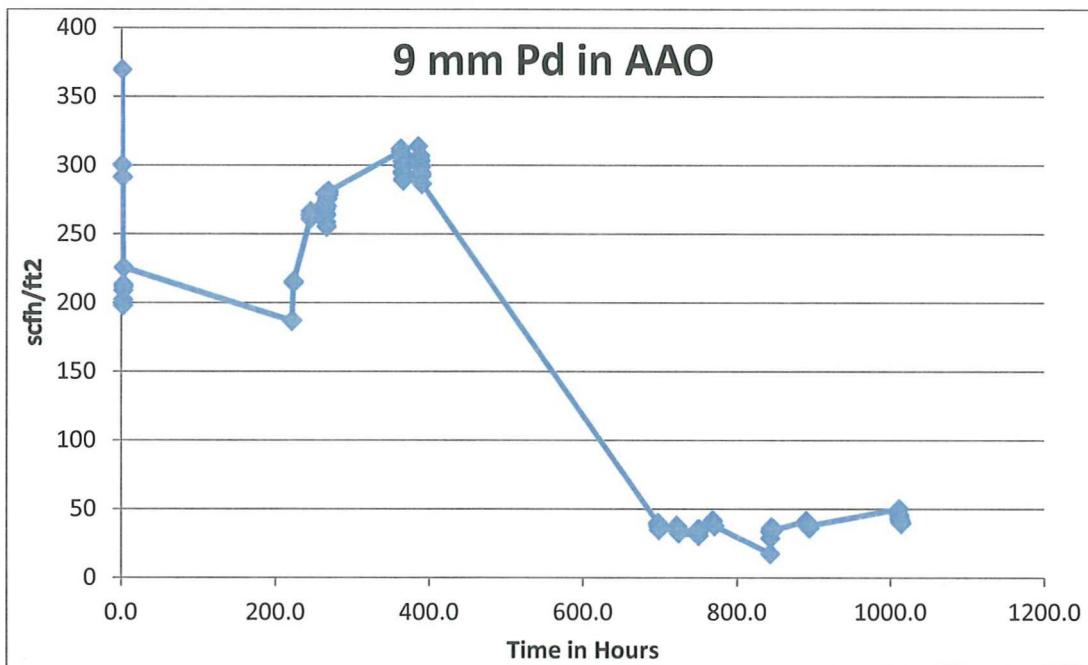


**Figure 8. Monolithic water gas shift catalyst piece to go between membrane stacks**

#### Membrane Testing

Individual membrane testing on hydrogen, NETL protocol mixtures and coal derived syngas were not part of our original work plan. As the solicitation was interpreted, testing of the completed 2 lb/day device was prioritized over testing of components. In the work plan, individual membrane testing was limited to proving suitability for incorporation into the final device. As the project progressed and fabrication of the 2 lb device was delayed, it was pointed out by NETL staff that our team was not reporting membrane performance. A change was made to our work plan and a test added. This test was completed using a palladium composite membrane under pure hydrogen, the NETL protocol mixture and coal derived syngas. The test was operated for just over 1000 hours. (Figure 9) The data has been normalized to a hydrogen partial pressure as if tested at 600 psid. The reason that the data is normalized is that in the four conditions of testing, the partial pressure of hydrogen varied. Normalization was the only method that all of the data could be presented on a single chart so that the effect of testing

condition could be compared. The initial test of the membrane was in pure hydrogen followed by testing in the NETL protocol gas mixture which is primarily hydrogen and carbon dioxide with only 1 % carbon monoxide. The data starting about 700 hours was in coal derived syngas with only 38% hydrogen and 30% carbon monoxide. The carbon monoxide seemed to affect the flux performance greatly. The test data after 800 hours includes 100 ppm of H<sub>2</sub>S in the syngas. The addition of hydrogen sulfide did not change the flux compared to the syngas data. The intention was to return to pure hydrogen to see if the flux performance was recoverable but the membrane failed at 1016 hours.

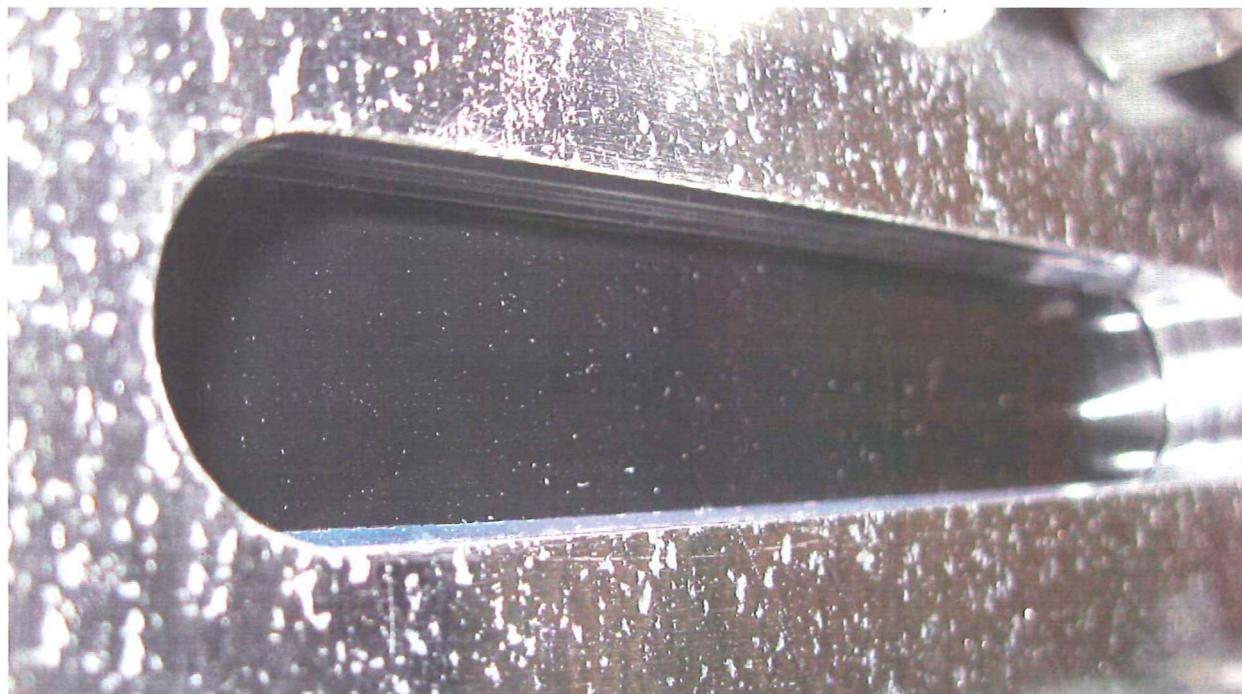


**Figure 9. Flux data for 1000 hour test of Pd composite membrane with various feeds**

#### Reactor Testing

The 2 lb/day hydrogen separation device arrived at WRI with 18 membranes in place. Each pair of membranes was secured with 16 bolted rods sandwiching the membranes with the internal support structure and graphite gaskets. Initial vacuum testing and visual inspection indicated that some membranes were cracked, either in transportation or during the test. During replacement of the failed membranes, it was observed that while pulling a vacuum on the back side of the membranes, they were seen to shift slightly as they were pulled against the support structure. This shift resulted in folds in the flexible composite membranes. In some instances these folds led to cracks forming, primarily at the interface between the alumina and the aluminum rim. (Figure 10) A change in the bolting procedure eliminated the shifting and folding of the membranes during the first application of differential pressure. The whole structure, now proven to be leak tight was moved to the gasifier facility and the heating system attached. With

the thermal mass of the device and the desire to avoid thermal expansion issues, the device was heated to 400°C over 48 hours. When differential pressure was applied, no pressure would build, indicating that once again there was a membrane failure. The device was cooled and opened. Several membranes had failed. Those membranes were replaced with aluminum foils. Twice more the entire procedure was followed with heat up and pressure testing, and twice more failed membranes were replaced with foils. A decision was made then to bring the device up with a single pair of membranes, and that test was successful. Under argon the two membrane system was leak tight. Under pure hydrogen, there was significant hydrogen flux at 50 psig differential pressure for 80 hours. When the hydrogen inlet gas was replaced with the first NETL protocol mixture, the membrane continued to hold pressure, but there was a significant amount of carbon dioxide in the sweep indicating a less than perfect seal system. The test was terminated once again. Clearly the design of the 2 lb/day device was compromised by the lack of any membrane isolation valving. A leak in any membrane fails the entire device. The mechanical seal system is a second compromise that requires near perfect execution.



**Figure 10. The 2 inch by 7 inch membranes produced folds and cracks under differential pressure.**

## Methanation

The main objective of this study was to investigate the catalytic activity for conversion of CO<sub>2</sub> to methane in the presence of hydrogen. The goal was to reproduce conditions after the hydrogen separation step in a carbon dioxide off gas that would have a low level of hydrogen remaining. Methanation of the hydrogen would make the carbon dioxide more effective as an enhanced oil recovery material.

## Experiments

Reaction: CO<sub>2</sub> hydrogenation

Reactor: vertical flow-type

Catalyst amount: 3 g

Pressure: 1 atm

Reactant flows: CO<sub>2</sub>, 5 mL; H<sub>2</sub>, 20 mL; N<sub>2</sub>, 20 mL

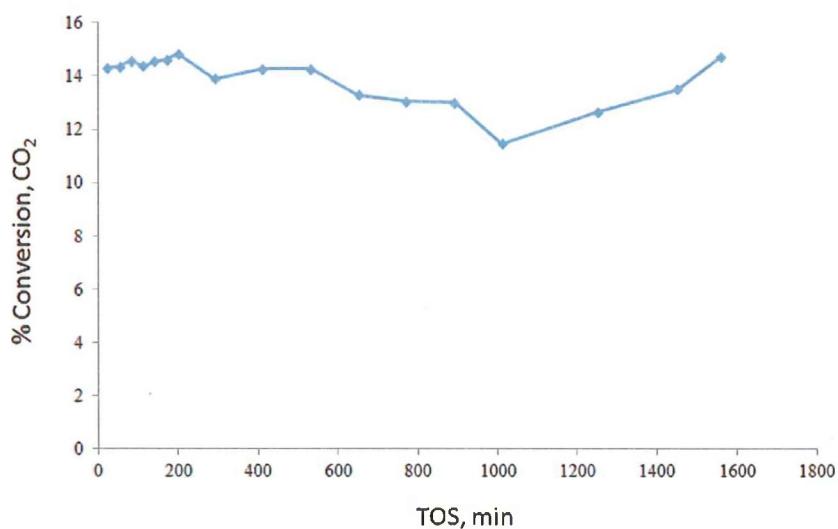
G.H.S.V.: 15 mLg<sup>-1</sup>

300°C

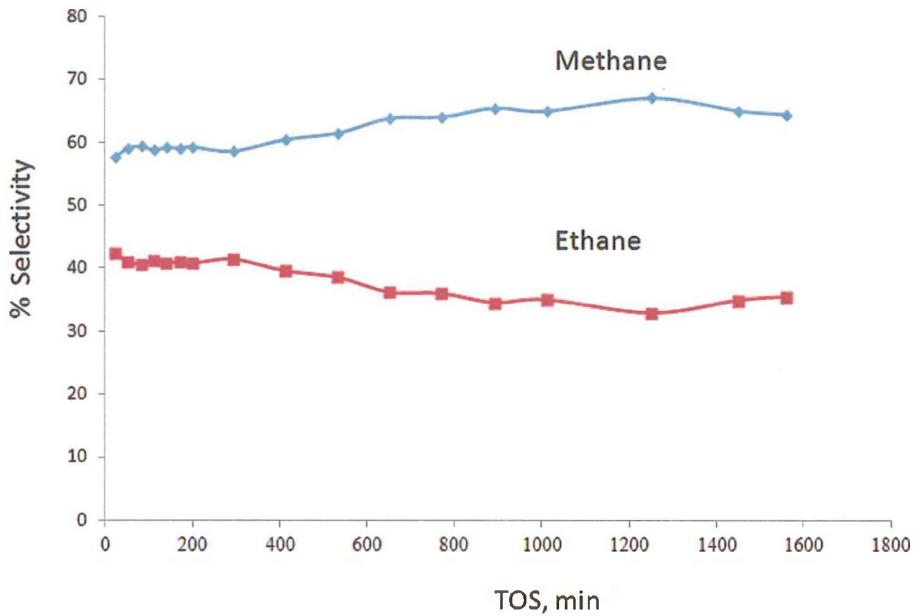
Following four different catalysts were evaluated for their activity.

### 1. 10%Ni-SiO<sub>2</sub>

This catalyst was prepared by a method developed in our laboratory. Calculated amount of nickel precursor and high surface area silica were stirred at room temperature for 24 hours, followed by drying and calcinations. Following is the data for its CO<sub>2</sub> conversion and hydrocarbon selectivity performances.



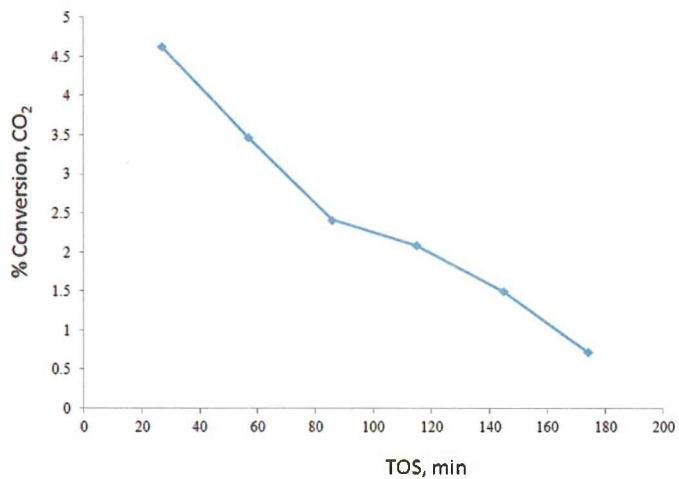
**Figure 11. CO<sub>2</sub> conversion with time on-stream on 10%Ni-SiO<sub>2</sub> catalyst.**



**Figure 12.** Percentage selectivity to methane and ethane with time on-stream on 10%Ni-SiO<sub>2</sub> catalyst.

## 2. 5%Co- 10%Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

This catalyst was prepared by a modified wet impregnation method reported by Riyas et al. (1). A calculated amount of pure hydrous TiO<sub>2</sub> was taken in a 250 ml beaker, then a fixed amounts of ferric nitrate and cobalt nitrate were dissolved in 50 ml distilled water and were added to the TiO<sub>2</sub> slurry. The slurry was stirred at room temperature and made into a paste by mixing thoroughly. It was then dried in an oven for 3 h at 110°C, ground well, and calcined at 450°C in a muffle furnace.

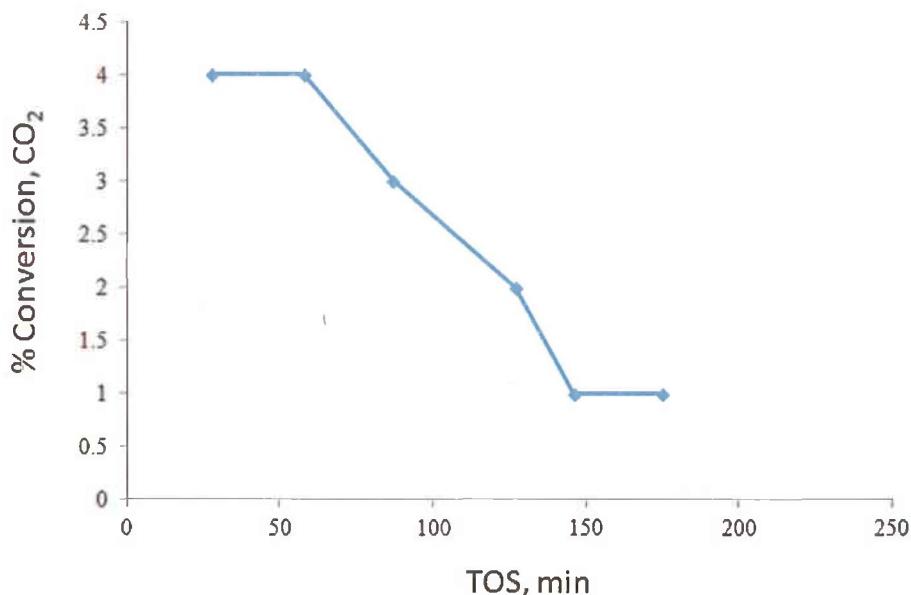


**Figure 13.** CO<sub>2</sub> conversion with time on-stream on 5%Co-10%Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst.

The reaction with this catalyst was discontinued after 3h as the activity was continuously decreasing with time on stream.

### 3. 2%Rh–2.5%Fe/TiO<sub>2</sub>

The catalyst was prepared following the procedure described by Gogate et al. (2). In a small beaker, 0.315 g Rh(NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O and 0.90 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 7.5 mL of deionized water. This solution was then added drop-wise with proper kneading to 5 g of TiO<sub>2</sub> (Degussa P-25) to the point of incipient wetness. The resulting paste was dried overnight in air at 120°C and subsequently calcined in air at 500 °C for 4 h.



**Figure 14.** CO<sub>2</sub> conversion with time on-stream on 2%Rh–2.5%Fe/TiO<sub>2</sub> catalyst.

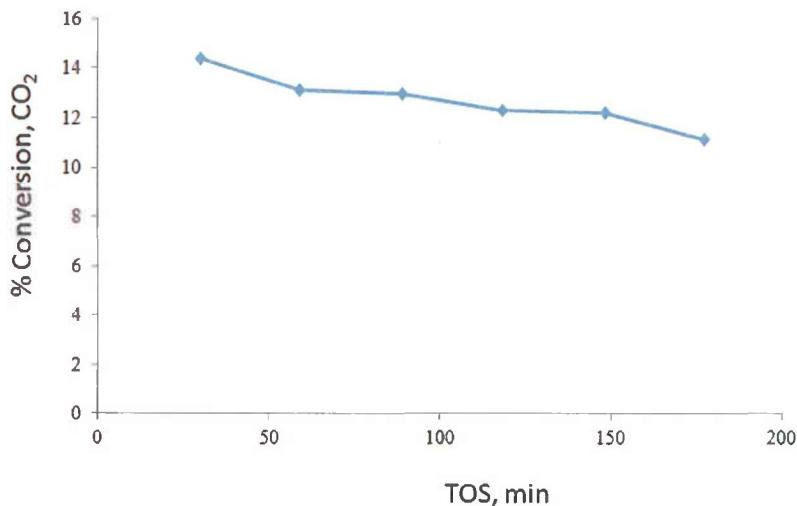
The reaction with this catalyst was discontinued as the activity was continuously decreasing with time on stream.

### 4. Ni-ferrite, Ni(II)/Fe(II) = 0.15 (molar)

The catalyst was prepared by following the method of Tsuji et al. (3).

Appropriate portions of NiCl<sub>2</sub>·6H<sub>2</sub>O (2.09 g), FeCl<sub>2</sub>·4H<sub>2</sub>O (2.68 g), and FeCl<sub>3</sub>·6H<sub>2</sub>O (12.2 g) were dissolved at 60°C in 150 mL of deionized water previously degassed by passing nitrogen gas through it for a few hours. An appropriate amount of NaOH (7.20 g) was separately dissolved in degassed water and the NaOH solution was kept at 60°C. The mixed metal chloride solution was added to the NaOH solution at 60°C, with vigorous stirring for coprecipitation. The formed coprecipitate was aged for 1 h at 60°C by bubbling nitrogen gas in the mother solution. The products thus synthesized were collected by centrifuging at 10,000 rpm. After washing with distilled water and successively with acetone, they were dried in vacuum at 60°C for a day. The

products were then heated in an N<sub>2</sub> gas stream at 300°C for 1–2 h to remove H<sub>2</sub>O and any OH<sup>-</sup> groups incorporated.



**Figure 15. CO<sub>2</sub> conversion with time on-stream on Ni-ferrite catalyst.**

The reaction with this catalyst could not be continued for a longer time on-stream due to some technical difficulty.

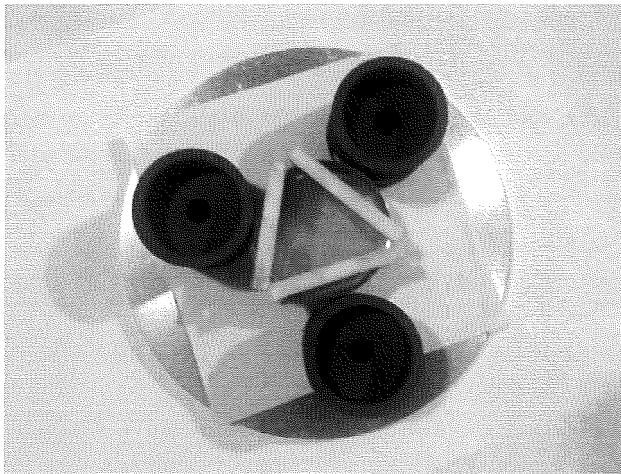
#### Brazing

Chart worked with 3 different vendors on preparing brazed structures to avoid the thermal expansion issues found using the aluminum rimmed membranes. All of the three vendors were production facilities, and with limited personnel focused on R&D, so could produce only one or two braze assemblies at a time. Chart has tried to increase the success rate by contracting multiple vendors, hoping the best brazing practices of at least one of the three vendors would meet our expectations and produce a successful assembly.

First, Chart started our initial efforts with Wesgo's Morgan Technical Ceramics at Hayward, CA. Despite best efforts, Morgan Technical Ceramics couldn't produce a successful braze assembly. In all cases, the alumina membrane cracked into several pieces. The active braze filler alloy did not show adequate melting and wetting of the ceramics that it could be easily pried away. Morgan Technical Ceramics opined a change in joint design. Morgan Technical Ceramics also expressed an inability to procure and machine Kovar for small lots, and asked Chart to supply Kovar, so they would quote only for the brazing trials. Chart is yet to contract Morgan Technical Ceramics for additional braze assemblies.

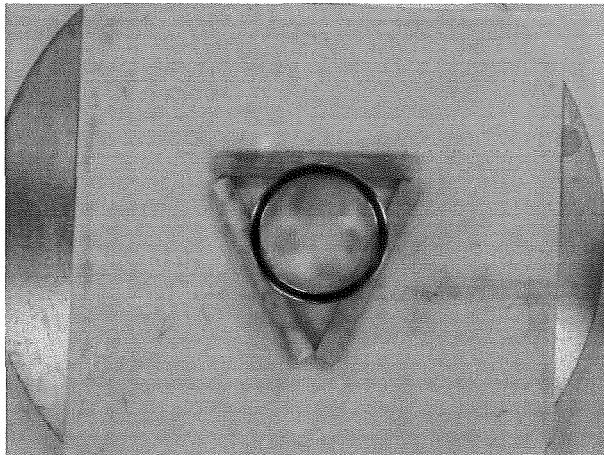
Subsequently, Chart Industries contracted with Altair Technologies, Inc., at Menlo Park, CA and attempted to produce vacuum brazed assemblies on a best effort basis, and used a modified braze joint design doing away with the pair of alumina rings. This effort attempted to join directly the alumina membrane with the kovar base and kovar ring (Figure 16). The initial

brazing effort showed wetting of the kovar base and ring, but did not produce any significant wetting on the alumina membrane. Furthermore, the alumina membrane cracked into several pieces.

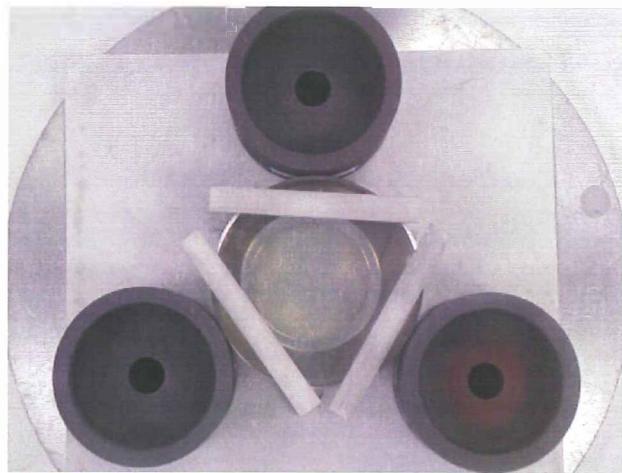


**Figure 16. Initial preparation of braze assembly without kovar support ring.** The figure shows a set of three graphite blocks to eliminate movement of the assembly, and 3 alumina pieces to support placing a graphite block atop (not shown in Figure 16) to ensure adequate contact during brazing.

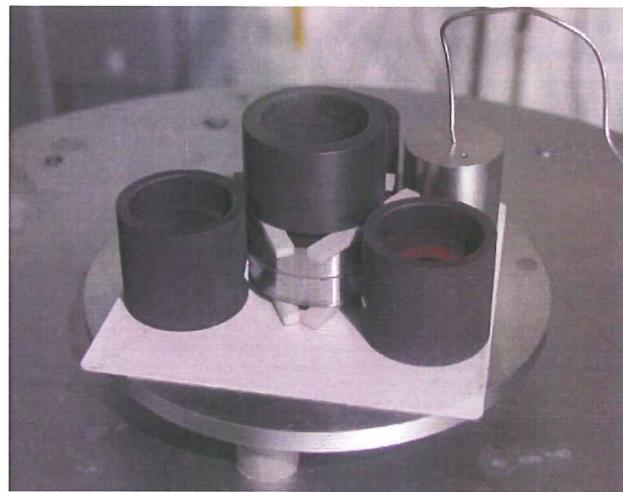
In a second attempt, Altair Technologies, Inc., used a precision-machined kovar support ring to hold the alumina membrane (as shown in Figures 17 thru 19). While the second attempt produced a brazed joint between the kovar rings, the alumina membrane cracked into a couple of pieces (Figure 20).



**Figure 17. A precision-machined kovar ring placed over alumina spacers with the kovar ring serving as a structural support for the alumina membrane.**



**Figure 18. Top view of the assembly prior to brazing.**



**Figure 19. Side views of the assembly ready for brazing**



**Figure 20.** The assembly following brazing, the cracked alumina membrane resting on the kovar support ring. A significant portion of the alumina membrane remained brazed to the kovar rings.

Discussions with Altair Technologies, Inc., revealed that a full support of the membrane using a solid kovar base would be helpful. Furthermore, it appeared that the choice of the braze filler and the form of the braze filler might also be significant. Considering that the alumina membrane is either 50 or 100  $\mu\text{m}$  thick, and residual stresses following the manufacture of the alumina membrane may contribute to cracking during low-temperature brazing, it was proposed that subsequent brazing trials could use a high temperature brazing foil made of Cu-Ti alloy, and the foil could be as thin as 30 to 60  $\mu\text{m}$ . The high temperature vacuum brazing condition may be desirable to relieve significant amount of residual stresses in the membrane, eliminate the cracking of the alumina membrane, and contribute to a successful braze assembly.

Altair produced 2 additional assemblies, trying to ascertain factors that affected the brazeability. Altair held the alumina membrane between two alumina rings, trying to ascertain the brazeability. Altair applied a metallization layer by hand and sintered during the braze run. As a result, the bonding surface was likely not very flat. This similar-materials assembly resulted in discoloration but only a minor-cracking of the alumina membrane (Figure 21).



**Figure 21.** The similar-materials assembly (left) prior to brazing, and (right) following brazing showing discoloration and minor-cracking of the alumina membrane.

To ascertain the cause for the cracking of the alumina membrane, Altair subjected a “free-standing” alumina membrane to the brazing thermal cycle in a dry hydrogen atmosphere. The alumina membrane didn’t survive the brazing thermal cycle (Figure 22). The blackened color of the alumina membrane indicated possible organic contamination in the as-received condition.

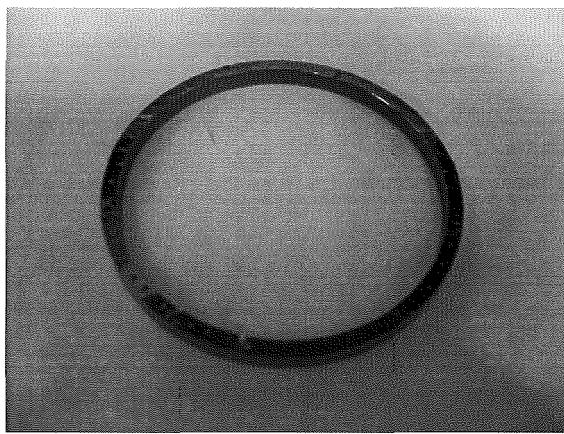


**Figure 22.** The alumina membrane following the brazing thermal cycle in a dry hydrogen atmosphere.

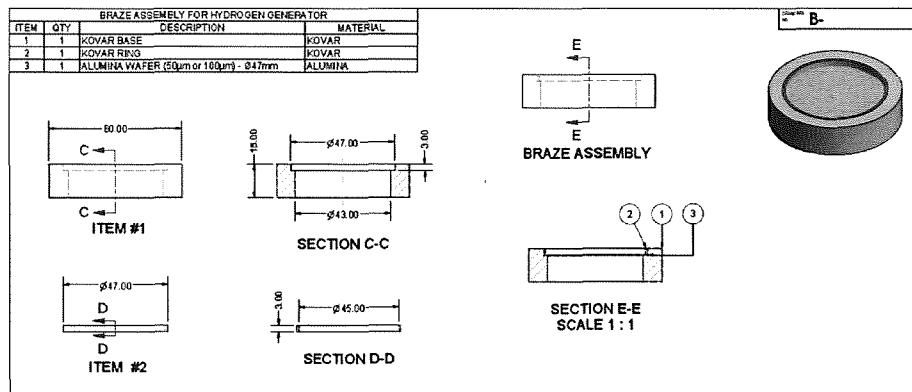
Thus far, Altair has produced one braze assembly that showed only minor cracking of the alumina membrane (Figure 21), and further brazing trials would be necessary.

Chart also worked with Bodycote, Cincinnati, OH to provide brazing services to produce a set of 6 braze assemblies. Chart provided Bodycote all parts – Kovar base, Kovar ring, alumina membranes per Chart drawing Braze Assembly for Hydrogen Generator.

Bodycote, Cincinnati, OH offered to procure the Au95Ti5 active braze filler as perform for use with the assemblies. Each assembly required 2 preform rings, one placed on the step in the Kovar base, and sandwiched between the base and the alumina membrane, and the other sandwiched between the alumina membrane and the Kovar ring. (Figures 23 and 24).



**Figure 23.** The brazing preform is made of 95% gold and 5% titanium.



**Figure 24.** Design of Braze Assembly

## **CONCLUSIONS AND RECOMMENDATIONS**

The pursuit of pure hydrogen for hydrogen based cars and PEM fuel cells came from the top. Administration policy pushed the Department of Energy to spend billions of US dollars to research hydrogen separation, hydrogen storage and a hydrogen based energy system that included distributed power and cars that burned hydrogen and emitted only water vapor. IGCC was supposed to be the power plant of the future and local hydrogen stations would fill up your car. All that research pointed out the multiple complications of a hydrogen based energy system. It is not clear if IGCC can compete economically with conventional power generation. There is no evidence that distributed power generation based on fuels cells of any design is in our near future. Hugh issues with hydrogen storage and the absence of the infrastructure for getting hydrogen to consumers means that hydrogen based cars are still unlikely in large numbers. The DOE has backed significantly away from hydrogen research and focused almost entirely on carbon sequestration in the fossil fuels area.

Hydrogen is still a major national commodity product. Large amounts of hydrogen are needed for petroleum refining, fertilizer production and the petrochemical industry. Economically competitive separation technologies are still needed. After none years researching in the hydrogen separation field, WRI has investigated four classes of membrane materials including vanadium alloys, palladium composites, amorphous alloys and polymer membranes. Of these materials the palladium composites have shown the highest performance, but their reliability has not been proven. Production of very small membranes can be done repeatedly, and those membranes have shown excellent hydrogen flux and fair resistance to carbon monoxide and hydrogen sulfide poisoning. However variability in the aluminum metallurgy in the membrane precursor foils leads to imperfections in the membranes when produced electrochemically. The larger the membrane, the more likely the presence of a fatal defect will occur. There may be techniques available to refine the metallurgy to reduce or eliminate these flaws. The promise of the approach remains, but no proof of the suitability of this technology for commercial scale devices is not yet there.

The work completed in methanation of the small amounts of hydrogen remaining in carbon dioxide after separation has been a very rewarding subtask of this project. The increasing value of carbon dioxide for enhanced oil recovery can be enhanced by this methane by-product improving the performance of the carbon dioxide through increased solubility in saline aquifers. This is a technology suitable for further study.

## BIOGRAPHICAL SKETCH APPENDIX

### **Thomas F. Barton**

Principal Engineer  
Western Research Institute

#### Education

B.S. Chemistry, Purdue University, 1986

PhD Chemistry, Virginia Polytechnic Institute and State University, 1990

Postdoctoral Research Fellow, University of Auckland, New Zealand, 1990-1992

#### Experience

- 2004– present. Principal Engineer, Western Research Institute. Dr. Barton is in the Energy Production and Generation Business Unit, and is responsible for projects concerning oxygen production for oxy-combustion, hydrogen production, coal gasification, biomass gasification and materials for high temperature, energy related plant.
- 1997-2003. Manager for Natural Gas Systems, Eltron Research, Inc. Dr Barton conducted government and client funded contract research concerned with oxygen and hydrogen transport with ceramic membranes, and surface treatments of metals. Those projects included operation of high-pressure reactors for the conversion of methane to synthesis, operation of high-pressure separation units to isolate hydrogen from synthesis gas streams, and gasification of coal and biomass for hydrogen generation.
- 1992-1997. Research Manager for Surface Treatments, Industrial Research Ltd., Auckland, New Zealand. Dr. Barton was the project manager of a large program developing coatings. Several of these coatings led to patents and commercialization of the electrochemical processes. He was the chairman of the Health and Safety committee for 2 years and assisted in the ISO 9001 registration process. His specific research projects concerned: 1) anodization of magnesium, 2) nickel oxide solar coatings, 3) electrochemical zinc oxide coatings, 4) nanoporous coatings as filters, and 5) neural networks for electrochemical noise identification.
- 1990-1992. Postdoctoral Research Fellow, University of Auckland, New Zealand. Dr Barton conducted research involving surface enhanced Raman spectroscopy and the controlled partial electro-oxidation of substituted porphyrins.
- 1986-1990. Graduate Research Assistant, Virginia Tech. Dr. Barton's PhD research on magnetic iron oxides involved aqueous inorganic synthesis followed by surface analysis by numerous techniques.

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### **Education**

PhD in Chemical Engineering, the University of Alabama, 2004

M.S. in Chemical Engineering, Nanjing University of Chemical Engineering and Technology, China, 1988

### **Professional Experience**

2005 –Present Chart Energy & Chemicals, Senior Chemical Applications Engineer

- Developing compact reactors for various chemical applications.

2004 – 2005 Brigham Young University USA

- Developed a method to catalytically produce biomarker and further identify warfare bio-agents, such as Bacillus Anthracis. Invented a small reactor for catalytic generation of biomarkers from spore decomposition. Utilized Pyrolysis and GC/MS to analyze the biomarkers from biological materials

1999 - 2004 The University of Alabama USA

- Developed new catalysts in nano scale for low-CO methanol reforming

1988 - 1998 Jiangnan University China

Senior Engineer and Associate Professor in the Department of Chemical Engineering  
Research and development

- Involved in a nationally important project in 1997 that synthesized a chloronicotinyl-related benzyl compound in the lab and led a team for scale-up operations in pilot plant
- Led a team to synthesize 3-hydroxy-2-methyl-quinoline-4-carboxylic acid in the lab and scaled it up in industrial plant in 1994
- Led a team to design and fabricate semi-conductive inner and outer shielding material for cables in the lab and scaled it up in industrial plant in 1996

Consultant for companies

- Distillation for petroleum refinery; organic synthesis and manufacture for fine chemicals companies, for example, stearate, lactic acid and nitrobenzidine.

### **Patents and Publications**

- Four US patents and one China patents, numerous scientific publications and presentations

### **Affiliations**

- American Institute of Chemical Engineering (AIChE)
- American Chemistry Society (ACS)

## **Dr. Dmitri Routkevitch, Synkera Technologies Inc.**

Dr. Routkevitch received his Ph.D. in Physical Chemistry from the State University of Belarus in 1993. His early research involved fundamental and applied aspects of catalytic heterogeneous charge transfer and new phase formation at nanoscale. In the mid-1990s, as a NATO Postdoctoral Fellow at the University of Toronto, he pioneered templated nanofabrication with self-organized anodic aluminum oxide. This approach has become widely recognized and extensively used by multiple research groups worldwide (three papers he co-authored with Prof. Moskovits has been cited over 700 times).

In 1997 Dr. Routkevitch joined Nanomaterials Research, where he established and led a successful and well-funded research program on the development of advanced materials and devices based on anodic alumina. His research accomplishments include development of advanced nanotemplates with tailored 3-D morphology, functional materials based on integrated nanoarrays, novel Ceramic MEMS technology that enables robust microdevices with functionality derived from the nanoscale.

Dr. Routkevitch is currently a Strategic Business Manager and a Principal Scientist at Synkera Technologies, where he leads the development of new products based on advanced nano- and microfabrication platform enabled by nanostructured ceramics. His efforts resulted in transitioning of this technology into near-, mid- and long-term market opportunities in diverse areas from hydrogen generation and renewable energy, to nanofiltration and water purification, chemical and biological sensing, and bioengineering. As a result, some of these products (ceramic membranes and microsensors) have already entered the marketplace, while others are in the commercialization pipeline.

Dr. Routkevitch is a recipient of multiple research grants from US government agencies. He has numerous invited seminars, has 5 patents and numerous invention disclosures, and authored 27 publications with outstanding citation impact. His background and expertise in nanocomposite ceramic membranes make him ideally suited for this project.