



THE ENGINEERING SCALE-UP OF HYDROGEN SEPARATION FACILITIES

Executive Summary

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**For
The State of Wyoming Clean Coal Initiative
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**And
U.S. Department of Energy
National Energy Technology Laboratory
Morgantown, West Virginia**

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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.

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.

WORK SCOPE

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.

RESULTS

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. (Figure 1) 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 shaped membranes of alternate design for thermal expansion issues

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. (Figures 2, 3 and 4)

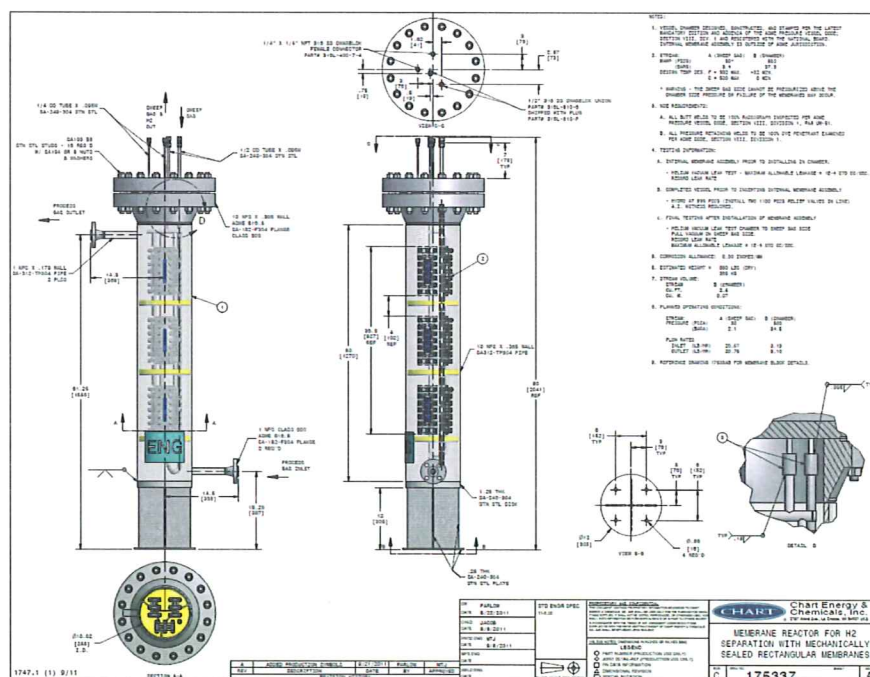


Figure 2. Revised design incorporating eighteen 2 inch by 7 inch membranes

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.

METHANATION

The main objective of this study was to investigate the catalytic activity for conversion of CO₂ 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/SiO₂ and Ni-ferrite showed the highest activity for this methanation process. Ni/SiO₂ 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.

BRAZING OF ANODIZED ALUMINA

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.

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. 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. 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 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.