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Evaluation and Characterization of Membranes for HI/H_2O/I_2 Water Separation for the S-I Cycle

FY 2005 Report for Project: Sulfur Cycles – Acid Concentration Membranes Nuclear Hydrogen Initiative

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Abstract

In the Sulfur-Iodine (S-I) thermochemical cycle, iodine is added to the product of the Bunsen reaction to facilitate the separation of sulfuric acid (H_2SO_4) from hydriodic acid (HI). The amount of iodine can be as high as 83% of the overall mass load of the Bunsen product stream, which potentially introduces a large burden on the cycle's efficiency. Removal of water from the HI and I_2 mixture would substantially reduce the amount of required additional iodine. In this work, Nafion® membranes have been studied for their use as de-watering membranes. Specifically, two thicknesses of Nafion membranes have been found to be effective in this application. The thicker membrane, Nafion-117®, produces moderate fluxes of water with very high separation factors. On the other hand, the thinner membrane, Nafion-112®, yielded very large fluxes of water, however with smaller separation factors. All membranes were found to be durable and did not degrade in contact with the feed stream over periods of time up to three months.

Introduction

Thermochemical water splitting cycles are methods that have been proposed to generate hydrogen on a commercial scale. Most commonly, hydrogen today is formed from the steam reforming of natural gas. Hydrogen generated using this method is generally consumed in industrial processes. Considerable interest now exists in using hydrogen as an energy carrier for transportation and other applications where fossil fuels are used today. For the conversion from a fossil fuel based economy to a hydrogen-based economy, the amount of hydrogen produced must be significantly increased from alternative resources. Even if a fossil based economy is maintained for the longer term, lower grade sources of oil will have to be exploited through upgrading, which requires increasing the hydrogen to carbon ratio through added hydrogen. Regardless of which way the nation turns, hydrogen will play a central role.

Formation of hydrogen from thermochemical cycles has been proposed using nuclear reactor supplied thermal energy.[1] Thermochemical cycles are processes in which hydrogen is produced through a series of chemical reactions where all reactants are recycled. Thus, the only chemical input is water and the only effluent is oxygen. Heat, in the range of 750 °C – 1000 °C, is provided to drive endothermic reactions.

Thermochemical cycles were principally investigated from the 1960's through the 1980's. Interest waned with the drop in crude oil prices in the 1980's. Recent energy price increases have renewed interest in hydrogen production from non-fossil based resources

Advantages of nuclear driven hydrogen production include hydrogen's inherent renewable nature, a reliance of the process on domestic resources, and an absence of CO_2 emissions. Similar advantages can be obtained through the use of high temperature solar concentrators. More than 100 thermochemical cycles have been proposed in the literature.[2] The sulfur-iodine process (SI), which has been shown to be one of the more promising cycles using flowsheet development processes[3], is comprised of three chemical reactions. Water enters the cycle as a reactant in the Bunsen reaction[4], as shown in Eq 1.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \qquad \text{eq 1}$$

In Eq 1, hydriodic acid (HI) is formed from the reduction of I_2 at an approximate temperature of 400 °C. HI is then decomposed to generate H_2 at 350 °C to 400 °C, Eq 2, and the co-generated I_2 is recycled. To re-generate SO_2, H_2SO_4 is decomposed at temperatures as high as 1200 °C, see Eq 3.

$$2HI \rightarrow H_2 + I_2 \qquad \text{eq 2}$$

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \qquad \text{eq 3}$$

Key to the operation of this proposed cycle is the Bunsen reaction. Separation of the HI from the H_2SO_4 is accomplished by the addition of a large excess of I_2, which causes the product mixture to separate into two phases. Water and H_2SO_4 comprise the lighter phase, while the lower phase is a mixture of HI, water, and I_2 at an approximate ratio of 2:10:8, respectively. To facilitate this phase separation, a dehydration loop employing concentrated phosphoric acid is added to the system to remove water from the HI/I_2 mixture. In the current flowsheets, additional water could be removed and the HI would be decomposed using reactive distillation.[5] However, removal of water is limited by the HI/water azeotrope at 57% HI, distillation will not yield a more concentrated acid product. Direct removal of water using a membrane process would allow both the elimination of the phosphoric acid system and a large reduction in the amount of iodine, thus increasing the efficiency of the cycle by lowering the recycle ratio per Kg of hydrogen generated. However, membrane concentration of HI/I_2 mixtures has not been demonstrated. Thus, this research was required to identify and study potential membrane candidates that could fill this role. For these studies, we have focused on Nafion-117® and Nafion-112® membranes in the pervaporation of water from a water/HI and water/HI/I_2 feeds.

Accomplishments

During FY 2005, the performance of Nafion-117® and Nafion-112® membranes was assessed for the removal of water from HI/water and HI/water/I_2 mixtures at temperatures as high as 135 °C. Prior to collection of data, considerable effort was dedicated to upgrading a laboratory-scale instrument capable of performing the experiments at temperatures above 120 °C under extremely corrosive conditions.

System upgrade. A cartoon of a typical pervaporation apparatus is shown in Figure 1. The heart of the system is the membrane cell. At the inception of this work, a 47 mm stainless steel filtration cell modified for feed side flow was used to secure the membrane. Upstream of the membrane cell is tubing and a pump to ensure feed flow across the membrane surface. Pumping was provided by a peristaltic pump using a Teflon® pumping tube. One-eighth inch Teflon® tubing was used to connect the cell to the pump and the feed reservoir. Initial experiments using the HI/water feeds indicated that this arrangement worked well, although there was a degree of corrosion inside the cell housing and the Teflon® pumping tube showed limited pumping life, necessitating periodic replacement. Application of this system to the HI/water/I_2 feed was not satisfactory due to the high density of the solution and the tendency of elemental iodine to precipitate from solution at lower temperatures clogging the narrow feed lines and fittings. To eliminate these problems, the entire feed flow system was replaced with Viton® rubber peristaltic pump assembly and Teflon® bayonet fittings for attaching the lines to the cell. This new configuration allows for considerably higher flow rates at temperatures up to 150 °C without choke points or fittings that can leak with time. The only downside of this system has been the limited pumping life of the Viton® tubing, which requires periodic replacement.

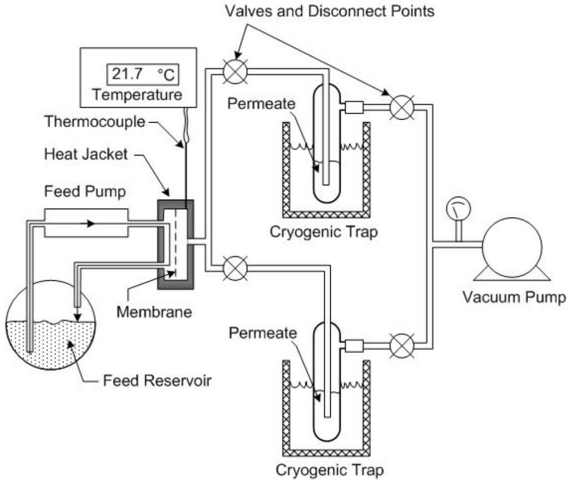

Figure 1. Pervaporation System.

Maintenance of cell temperatures was another technical hurdle that was addressed during FY 2005. Previous work employed electrically operated heat tape applied directly to the cell with external shielding of aluminum foil to maintain stable cell temperatures. This configuration worked well up to 100 °C, but not higher. As a part of this year's instrumental upgrade task, the bulk of the system was enclosed in an oven in that only the pump and the downstream trapping assembly remained outside. Cell temperatures in the 120-140 °C range were difficult to achieve using only the oven because of cell cooling due to feed flow and evaporation of permeates off the backside of the membrane. To achieve the desired cell temperatures, the oven often had to be heated to temperatures as high as 160-170 °C, which was too high for some of the Teflon® components and also caused the feed solutions to spatter. This situation was remedied by use of heat tape on the cell in addition to the oven. For experiments at or above 120 °C, the oven was maintained at 100-110 °C, while the heat tape provided localized heat to the cell to boost it to the desired temperature.

Task Summary. At the end of FY 2005, we have upgraded two pervaporation systems, one set up for HI/water feeds, and the other designed to handle the more dense and corrosive HI/water/I_2 feeds. Both of these systems will be utilized to screen other membrane materials during FY 2006 to provide the enabling data for inclusion of a membrane system into the S-I process. Additionally, these systems should operate well for the sulfuric acid de-watering experiments set to commence in 2006.

Membrane Testing and Evaluation. To characterize any particular membrane's performance, two central factors must be determined. First, is the flux across the membrane, which is the amount of permeate that can be collected off the backside of the membrane per unit membrane area per unit time. Units for flux used in this work are g/m^2h (grams of flux per square meter of membrane area per hour). Secondly, the separation factor must be measured. The separation factor is a relative measure of the membrane's ability to effect the desired separation and is calculated according to equation 4:

$$\text{Separation factor } (\alpha) = \frac{[H_2O]_p / [HI]_p}{[H_2O]_f / [HI]_f} \qquad \text{eq 4}$$

where $[H_2O]_p$ and $[H_2O]_f$ are concentrations of water in the permeate and feed, respectively, as weight percents. Likewise, $[HI]_p$ and $[HI]_f$ refer to the HI concentrations. Larger separation factors equate to a better separation. For the HI/water/I_2 feed experiments, the acid term encompasses both the HI and I_2 concentrations. Concentrations of HI were determined through titration of both feed and permeate samples using standardized sodium hydroxide to a phenolphthalein endpoint. Feeds with added I_2 yielded homogenous solutions and the added I_2 was accounted for by consideration of the HI-I_2 complexes typically referred to as HI_x, where the HI_x concentration was the sum of the HI and I_2 concentrations in terms of weight percent.

The target temperature range for the de-watering process is between 120-350 °C. For organic-based pervaporation membranes, the practical temperature range is toward the lower end of this range. For example, Nafion-type membranes have a useful upper temperature limit of 150 °C. However, the advantage of organic membranes is that selectivity can be influenced by both diffusional and solubility interactions. The permeability coefficient of any membrane is a product of the diffusion and solubility coefficients. Pervaporation, as opposed to reverse osmosis, which is commonly performed using porous membranes, is driven by polymer-permeant solubility and permeant volatility. Membranes in which the diffusion component is dominant are facilitated by large differences in molecular size between feed components. For this particular application, HI, I_2 and water have similar molecular sizes, thus membranes that rely more on solubility behaviors may have better applicability for this separation. Nafion® membranes are known to be ionically conductive, chemically stable, and physically durable and have been extensively investigated for use in proton exchange membrane (PEM) fuel cells. One of their disadvantages is that they pass too much water. However, this disadvantage is an advantage for this project where chemically durable water passing membranes were of interest.

During FY 2005, two Nafion membrane formulations were studied for their performance in removing water from HI/water and HI/water/I_2 systems at temperatures as high as 135 °C. These results and summary conclusions are discussed below.

Nafion-117® Membranes. Nafion-117® is a commercially available perfluoroethylene sulfonate membrane with an ion exchange capacity of 1100 g/EW (grams per equivalent weight) and a thickness of 0.007" (180 µm). It is a durable plastic material that is easy to install into a pervaporation system. However, its structure is far more complex with a porous, phase-separated nature that results in both hydrophilic and hydrophobic regions. The hydrophobic portions of the polymer consist of Teflon-like perfluoroethylene units, while the hydrophilic sulfonates, which are attached to the polymer backbone through perfluorinated chains, tend to form inverse micelles giving tortuous pathway pore structures through which water can pass.

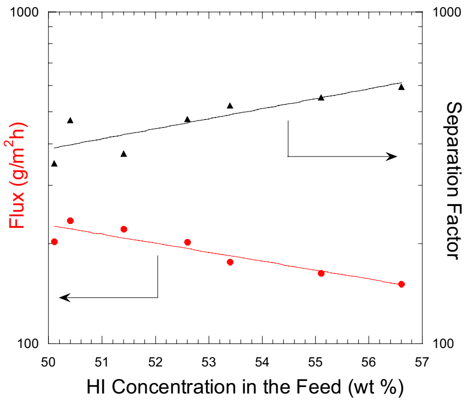

Figure 2. Nafion-117® membrane performance as a factor of feed HI concentration at 132 °C and a flow rate of 10 mL/min.

Testing of Nafion-117® membranes were conducted at 132 °C as shown in Figure 2. Both fluxes and separation factors were determined using an HI/water feed. Flux of water ranged from 151 – 235 g/m^2h and decreased with increasing HI concentration, which also corresponds with decreasing water concentration. Separation factors ranged from 350 – 595, which are commercially competitive. With respect to increasing HI concentration, fluxes were observed to decrease and separations factors increased. This behavior is typical of membrane processes in which a trade-off is observed between flux and separation factor. Decreasing fluxes with decreasing water concentration also is typical of membrane processes.

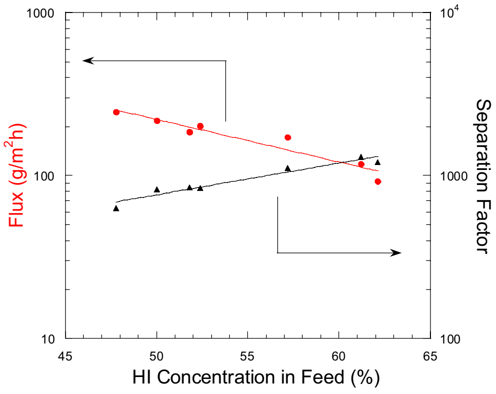

Figure 3. Nafion-117® performance at 134 °C and a flow rate of 28 mL/min using an HI/water feed as a factor of HI concentration.

An additional aspect that was addressed in this particular experiment was the feed flow rate. Flux changes with changes in flow rate across the surface of the membrane can be indicative of the presence of a boundary layer. A boundary layer is a permeant depleted zone at the surface of the membrane that inhibits further permeation. In Figure 2, the flow rate was 10 mL per minute. Increasing the flow rate as shown in Figure 3 to 28 mL/min revealed no significant difference in membrane flux performance suggesting that, at least at the flow rates examined, a boundary layer does not appear to inhibit water transport.

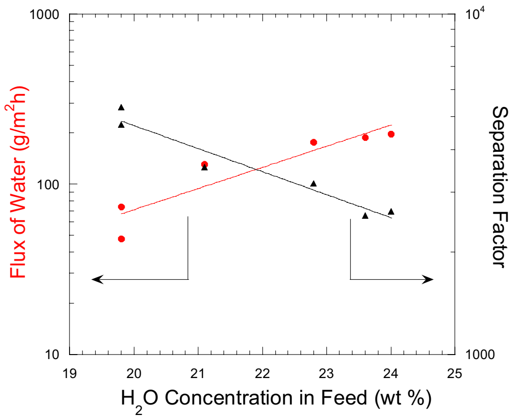

Figure 4. Performance of a Nafion-117® membrane using HI/water/I_2 feed at 85 °C in terms of the feed water concentration.

Experiments using a HI/water/I_2 feed were found to require a slight re-engineering of the test system, as discussed earlier. The most significant modification was the replacement of a half of the membrane cell with a Teflon component. The membrane cells used in this work consist of two halves that are bolted together; a feed side and a permeate side with the membrane mounted as a separator. In this work, the feed side was duplicated by the INL machine shop using a Teflon block. The permeate side was retained because of the rigidity that it provided to the cell as a whole and due to the membrane's ability to perform the separation, the permeate side did not experience any significant corrosion.

Due to the use of the hybrid cell configuration, experiments were conducted first at 85 °C and then at 125 °C using a feed that consisted of a 1:6:1 molar ratio of HI, water and I_2, respectively. As shown in Figure 4, the data at 85 °C is plotted in terms of the water concentration, however the data is consistent with the above experiments in which higher fluxes of water are observed from feeds that have a higher water concentration. Fluxes of water range from 48-197 g/m^{2}h, depending on feed concentration. Separation factors, likewise, were observed to increase with decreasing feed water concentration, ranging from 2636 to 5330, which are significantly higher than the previous experiments, which could be due to the extremely low concentration of HI_x in the permeate. However, the relative difference in separation factors from previous experiments shown above to this experiment should not be considered overly significant due to the mathematical implications of dividing large numbers by small numbers. Slight deviances in the smaller terms, such as permeate HI_x concentrations in the 10^{-3} – 10^{-4} range, can cause inordinately large swings in the measured separation factor. The more meaningful conclusion that can be drawn from this experiment is that the permeate of both HI/water and HI/water/I_2 experiments are virtually the same in terms of their composition.

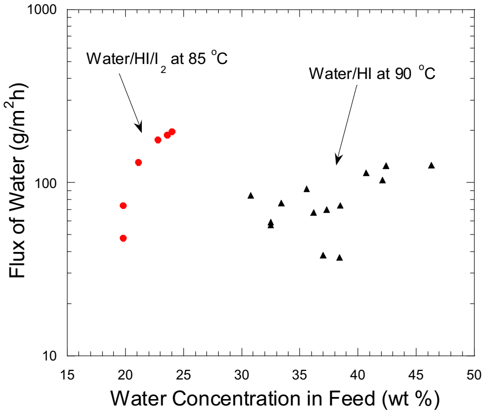

Figure 5. A comparison of the flux of water with the two feed types with respect to feed water concentration.

A comparison of flux data for the two differing feeds steams revealed an unexpected comparison. Typically, the flux is a function of the permeant content in the feed. In this instance this relationship was not observed, see Figure 5. Fluxes of water from iodine-enhanced feeds are roughly similar to that of the HI/water feeds although there is significantly lower water content in the iodine-added samples. This phenomenon has not been further studied in this work, however a potential explanation involves the fact that the molar ratios of HI/water and HI_x/water is nearly the same in these two experiments, thus yielding similar water fluxes.

Pervaporation experiments were also conducted at 125 °C on the HI/water/I_2 feed. In this experiment, a solution was prepared using additional water for an initial molar ratio of 1:12:1 for HI, water, and iodine, respectively. This was done due to a tendency for the I_2 to precipitate from more concentrated (water content < 20%) solutions of HI_x upon removal of water. Precipitated iodine clogs the pumping system and also fouls the membrane. This behavior could be alleviated by maintaining high system temperatures since the precipitation appears to occur during the cool down cycle between daylong experiments. Complete system shut down between experiments is performed because of safety concerns for fear of leaving an unattended system hot for extended periods of time. The additional water in the feed allows for several days operating time on a single batch of feed without precipitation concerns.

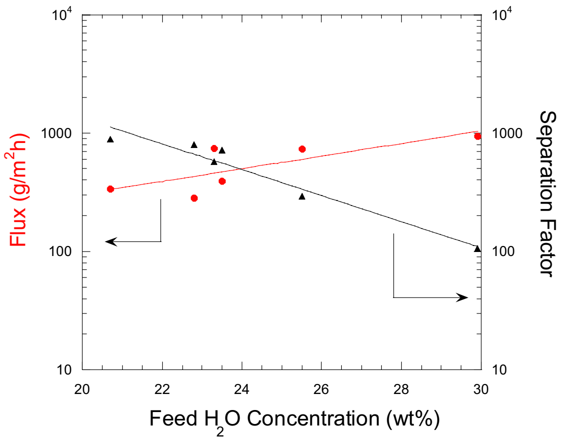

Figure 6. Nafion –117® performance using an HI/Water/I_2 feed at 125 °C.

Results for this experiment yielded high initial fluxes, up to 900 g/m^{2}h, which was expected due to the higher water content of the feed (~30%), see Figure 6. These flux rates rapidly fell to 282 as water as was removed from the system. In comparison to the corresponding experiment at 85 °C, higher system operating temperatures yielded significantly higher flux rates. Also observed was the expected increasing trend in the separation factor from 106 to 885, consistent with the previous experiments. The actual magnitudes of the separation factors were considerably less than data measured at 85 °C, however these values, in general, are large for commercial membrane processes.

Nafion-112® Membranes. Nafion-112® has the same equivalent weight of ion carrier as does the Nafion-117®. The only difference is the material thickness. Nafion-112® is substantially thinner at 0.002" (50 μm). Thinner membranes are expected to yield far higher permeant fluxes and lower separation factors. This was of interest because the Nafion-117® membranes yielded potentially greater separation than what should be required for the S-I process, so this provided an opportunity to take advantage of the "excess" separation capability to increase permeant fluxes. Permeant fluxes are directly reflected by the membrane area in that lower flux processes require larger membranes per unit volume of feedstream. Conversely, higher flux processes result in lower membrane area requirements, which, in turn, significantly lower the membrane process capital, operations, and maintenance costs.

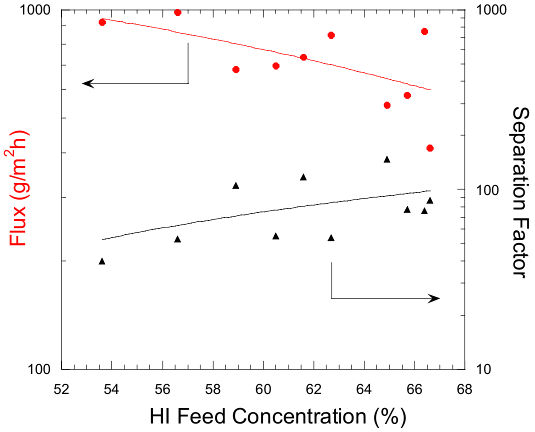

Figure 7. Performance of a Nafion-112® membrane at 133 °C using an HI/water feed.

At 133 °C, both fluxes and separation factors were measured as shown in Figure 7. With respect to feed HI concentration, the trade-off between flux rate and separation factor was again observed. However, the magnitude of each parameter was significantly different. For example, permeant fluxes ranged from 400 – 1000 g/m^2h, depending on feed concentration where lower water concentrations (higher HI concentrations) yielded lower fluxes. More significantly, it was noted that these flux rates were substantially higher than those derived from Nafion-117®, thus validating the expected relationship between flux rates and membrane thickness. Providing additional support were the separation factors, which ranged from 50 – 150. These values are much lower than the Nafion-117® data, as expected. An additional feature of this work that is worth noting is the concentration of the acid. During this experiment, the initial acid concentration was measured to be 53% HI. As the experiment was conducted, the acid was concentrated to approximately 67% HI. HI and water form a low boiling azeotrope at 57% HI. Thus, this is a clear demonstration of the use of pervaporation to “break” the HI/water azeotrope and yield a higher acid concentration than would be possible using distillation.

Task Summary. During FY 2005, two membrane materials were identified for their ability to pass water with a high degree of separation from both concentrated HI and HI_x feed streams. Both Nafion-117® and Nafion-112® were shown to be effective in the removal of water from these feeds and showed no degradation, even upon testing at temperature as high as 135 °C. Typical in the transport behavior of these membranes was the trade-off between flux and separation performance. With lower water concentrations in the feeds, flux rates tended to decrease while the separation performance increased. Nafion-117®, the thicker membrane (0.007"), was characterized by more modest water fluxes and high separation factors. Nafion-112® membranes, which are thinner at 0.002", were characterized with substantially higher fluxes, however the separation factors were considerably lower.

Project Summary

During FY 2005, two membrane systems were upgraded to address the unique chemical and physical characteristics of concentrated HI and HI_x feed streams. Furthermore, we have developed the methodology for performing these experiments and gaining scientifically useful information in a timely manner. This will allow for evaluation of other membrane materials that can be compared to the data discussed in this report to evaluate the applicability of membranes for acid concentration. Discussed throughout this report are transmembrane fluxes and separation factors. The interplay between these parameters is significant because they dictate the physical requirements of a plant for the treatment of a given amount of feed. Also, it is important to know how well a separation needs to be for the desired application. For the S-I process, acid concentration on the HI loop is a relatively new concept, and thus there are no established requirements. However, at this point, it is clear that membrane throughput (flux) is probably a more important parameter than the separation factor. Thus, the goal of this work is to maximize flux while still retaining a majority of the acid in the feed.

Membrane plant configuration can be used to address this situation. For example, the performance of the more permeable Nafion-112® can be compared to Nafion-117®, the better separator using an HI/water feed for simplicity. For a desired plant scale throughput of 1000 Kg/ day at 135 °C, a single pass by a Nafion-117® pervaporation system would yield flux of 121 g/m^{2}h and a separation factor of 1195, see Table 1. This system would produce a permeate with a concentration of 0.13% HI. A similar system with a Nafion-112® membrane gives far higher flux of 775 g/m^{2}h, however with a separation factor of only 75. Using these parameters, the membrane area needed to perform these separations is 54 m^2 for Nafion-112®, while for Nafion-117®, over six times the membrane area is required. Thus, if a permeate with 2% HI is sufficient, Nafion-112® would represent a significant savings in terms of capital equipment, operations, and maintenance costs.

Table 1. Calculated performance for Nafion-117® and Nafion-112® single stage and a Nafion-112® double stage pervaporation systems using a 60% HI/water feed at 135 °C.

Parameter	Nafion-117® Single Stage	Nafion-112® Single Stage	Nafion-112® Dual Stage
Flux (g/m^{2}h)	121	775	2328 (second stage)
Separation Factor	1195	75	3.5 (second stage)
Product HI Concentration (%)	0.13	2	0.6
Membrane Area Required for 1000 Kg/day of Flux (m^2)	343	54	54 + 18

A dual stage application can also be considered in which the permeate from the first stage can be processed through a second membrane for additional acid concentration. The flux from a Nafion-112® membrane applied to the permeate of a single stage unit would result in substantially higher flux rates with concurrent loss of separation factor down to 3.5. Using these parameters, a product HI concentration of 0.6% was calculated. However, due to the higher flux rates, only an additional 18 m^2 of membrane area would be required to reduce the HI concentration from 2% to 0.6%.

The performance aspect of two Nafion membranes is shown in this work. Further optimization and determination of the maximum in membrane performance requires additional work to identify and evaluate other membrane materials that may produce higher fluxes without significant losses in separation factor. During this year's effort, we have determined the general method by which other membranes may be evaluated and compared to the Nafion data. Once other materials are evaluated, process modeling may be used to determine the most effective and economically advantageous membrane system for application to an S-I plant.

Publication and Presentations During FY 2005

1. Christopher J. Orme, Michael G. Jones, and Frederick F. Stewart, "Pervaporation of Water from Aqueous HI using Nafion®-117 Membranes for the Sulfur-Iodine Thermochemical Water Splitting Process", *Journal of Membrane Science* **2005** 252 (1-2), 245-252.

2. Frederick F. Stewart, Christopher J. Orme, and Michael G. Jones, "Membrane Processes for the Sulfur-Iodine Thermochemical Cycle", *AICHE Proceedings* as a part of the Spring Meeting, Atlanta, GA, Paper 75c, **2005**.

3. Frederick F. Stewart, Christopher J. Orme, and Michael G. Jones, "Membrane Processes for the Sulfur-Iodine Thermochemical Cycle", Submitted to the *International Journal of Hydrogen Energy*", 2005.

4. Frederick F. Stewart and Christopher J. Orme, "Stability and Performance of Nafion-117 Membranes for the Concentration of HI/Water and HI/Water/Iodine Mixtures" *To be presented to the Annual AICHE Meeting, Nuclear Engineering Division, Cincinnati, OH, November 2005.*

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