DEVELOPMENT OF INORGANIC MEMBRANES FOR HYDROGEN SEPARATION

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ABSTRACT

For over fifteen years, significant research and development on potentially useful commercial inorganic membranes has been performed at the Inorganic Membrane Technology Laboratory (IMTL). During the past ten years, or more, the knowledge base about inorganic membranes with pore diameters less than 2 nanometers for separating gases based on molecular size has been greatly expanded. Much of that research has been focused on the separation of hydrogen from other gases. This research has recently led to the commencement of a new project sponsored by the Office of Fossil Energy's Coal Gasification and Fuels Programs to scale-up these membranes for testing in a coal gasification plant. This document provides the status of the hydrogen separation membrane development effort. The physical, flow and separation performance properties will be presented for the best candidate membranes to date.

INTRODUCTION AND BACKGROUND

This research has benefited from previous research and development on the barrier used in the U.S. Gaseous Diffusion Program for separating uranium isotopes. Because of the legacy classification issues, membranes that are developed at IMTL are initially handled as classified pending a review. However, a process has been instituted by DOE for reviewing membranes/filters that have been developed for potential commercial use for classification and non-proliferation concerns. When the review process concludes that there are no classification concerns and the manufactured membrane/filter is not a proliferation risk, the membrane can be declared unclassified and approved for commercial manufacture. To date, 17 membranes/filters have been approved for commercial manufacture. At present, Pall Corporation is the only company licensed to manufacture the membranes/filters that have been approved.

There are several transport mechanisms that can govern the flow of gas molecules through membranes. Viscous flow occurs when the gases flow through a membrane as a fluid without any differentiation between gases and results in no separation. Molecular sieving occurs when a membrane's pores are sized such that the smaller gas molecules can pass through the membrane while the larger ones do not fit through the pores and are thus rejected. Knudsen separation occurs by taking advantage of differences in molecular velocities. Lighter molecules transport faster through pores than heavier molecules resulting in an enhancement of the lighter molecules product stream. Lastly, surface diffusion occurs when one of the gas molecules is adsorbed on the surface of the pores and travels along the surface rather than in the gas phase. The adsorbed molecules can block the pores so that the flow of other gas molecules are impeded resulting in an enhancement of the concentration of adsorbable molecules in the permeate stream.

For gas separations by molecular sieving, the effective mean pore diameter must be on the order of the diameter of the gas molecules, normally 2 nanometers or less. In order to get perfect separation, the pore size must be larger than the smaller molecule but smaller than the larger molecule. If an inorganic membrane is homogeneous, its permeance is inversely proportional to the membrane thickness. Permeance is defined as volumetric flow rate per unit area per unit pressure drop across the membrane. With such small pores, if the membrane is to be commercially useful, it must be very thin, no more than one-to-two micrometers thick, and preferably less. In order for such a thin membrane to be useful, it must

be layered on a strong porous support material, either metal or ceramic. Metal is preferred because modules can be more easily and less expensively constructed. The separative membrane layer can be applied directly to the support material or on top of an intermediate layer. The intermediate layer with an intermediate pore size allows the application of a thinner and more uniform separative membrane layer. The separative layer should have a mean effective pore diameter of 10 nanometers or less and preferably as small as 2 nanometers. Once the separative layer is in place various chemical treatments can be used to reduce the effective pore diameter to the desired value, as low as 0.5 nanometers.

Early work funded through the ARM program focused on developing a hydrogen separation membrane that could operate at temperatures of 600-800 °C. Few conventional metals are stable in long term use at these temperatures, especially in a sulfidizing environment typical of coal gasification systems. For operation under these conditions, a porous aluminum oxide (alumina) tube was developed to be used as a support for application of the ceramic separative layers. It was determined that in order to maximize the permeance the separative layer needs to be a thin as possible. However, an extremely thin separative layer requires an intermediate layer having a pore size much smaller than the support tube. The thin separative layer was then applied on top of the intermediate layer. Over 100 ceramic supported hydrogen separation membrane prototypes were fabricated during this development effort. This work formed the basis for fabrication protocols used today. Also by analyzing the flow data of air, nitrogen, and helium gas through these membranes over a range of total pressures and transmembrane pressures, the Hard Sphere Model[1] was developed as a tool to determine the percentage of flow through the defects (oversized pores) and what effect that will have on the separation factor.

Recently, coal gasification research has shown that high efficiency can still be achieved with gas cleaning at lower temperatures than previously considered necessary and now the target temperature is in the range of 250-500 °C. At these temperatures, an alumina support tube can still operate without degradation. However, many metals, including some stainless steels might be stable under long-term use. Metal support tubes offer many advantages. They are more robust. Ceramic tubes can be fragile and are more easily broken. Metal tubes are more flexible and will not break when minor stresses are applied. If a ceramic tube fails during operation, a cascading effect can take place where pieces of the broken tube can cause the breakage of adjacent tubes leading to a catastrophic failure. Lastly, it is much easier to seal metal tubes into large modules for scaling up. The porous metal tubes can have non-porous end fittings welded on the ends, thus providing connection fittings for integration into a gas separation module. These tube end fittings can be welded into tube sheets for installation into the modules. Ceramic tubes require either that metal end fittings be brazed onto them using special ceramic to metal brazing techniques or the use a glass glaze to make the ends non-porous. These glazed ends require high temperature seals to make them gas-tight.

CURRENT WORK

The lower target temperature for synthesis gas cleaning has prompted the development of metal supports for the current hydrogen separation membranes. The criteria used for materials selection for both the support tube and separative layer included known compatibility issues with a sulfidizing environment and the target operating temperature. Under typical coal gasification, conditions many stainless steels and other iron based alloys are stable. At higher temperature and increased sulfur levels, an alumina forming alloy such as iron aluminide is known to be stable.

The development of metal supported hydrogen separation membranes was initiated in 2001 using the fabrication protocols acquired during the work on the ceramic supported hydrogen separation membranes. The first step was the fabrication of suitable support tubes. The porous tubes used for the first metal supported prototypes were developed under a CRADA with Pall Corporation. They were made from 316L stainless steel having a pore diameter between 3 and 5 micrometers.

The early metal supported membranes were fabricated by first applying an intermediate porous layer having an average pore size of approximately 70 Å followed by the separative layer with a pore size less than 10 Å. Figure 1 shows the progress that was made during the transition to metallic supports in 2002. Each point on the graphs represents a unique metal supported membrane that was evaluated for flow

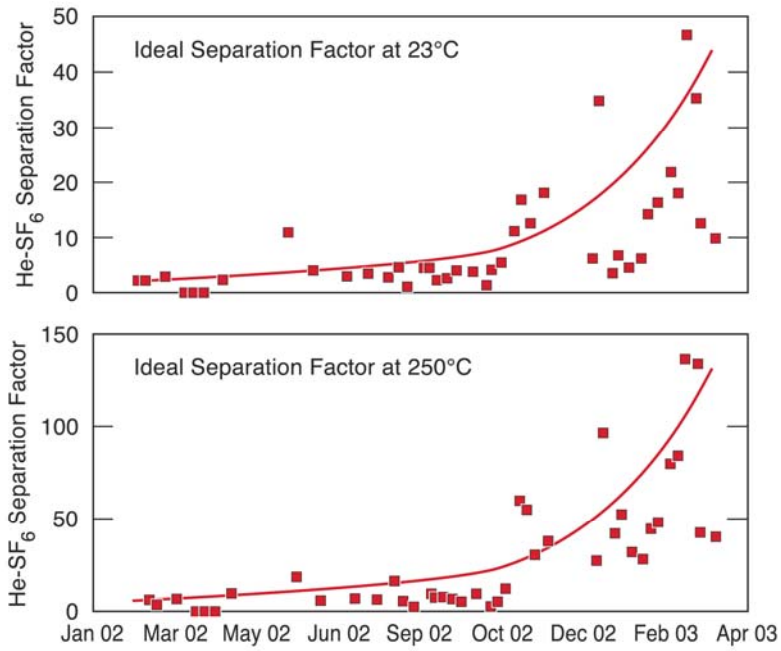

Figure 1. Graph showing the progress of the development of metal supported hydrogen separation membranes.

using both helium and sulfur hexafluoride at both room temperature and 250 °C. Only those membranes that showed promise were even evaluated using these tests. During this phase of work porous tubes made from several different particle sizes and morphologies of stainless steel and iron based alloys were evaluated as possible supports. As shown in Figure 1, gas flow data using early prototypes of the metal supported tubes showed separation factors less than 10 for helium from sulfur hexafluoride (this gas pair was used because helium is a good surrogate for hydrogen and sulfur hexafluoride is a very large and stable molecule that offers the potential for molecular sieving of helium). Analysis of the tubes throughout the fabrication revealed that the intermediate layer had a high number of leaks. Application of the separative layer did not eliminate all of the leaks resulting in separation factors not much higher than would be expected from Knudsen diffusion.

Since the intermediate porous layer was applied using the same techniques as the ceramic supported membranes, it was determined that the problem must lie in the metal support tubes. Either the quality of the tube was the problem or there was an incompatibility between the metal support and the ceramic intermediate layer. The tubes were fabricated from water atomized powder. Scanning electron micrographs of water atomized powder show the powder to be irregular in shape as shown in Figure 2 while gas atomized powder is more spherical as shown in Figures 3 and 4.

Based on the higher than desired leak rate for the membranes made using water atomized powder, the next generation porous support tubes were fabricated from gas atomized powder. The membranes made using these supports showed higher separation factors for He from SF_6 as shown in Figure 1 starting in late 2002. Helium and sulfur hexafluoride have been used often as surrogates for separations instead of using hydrogen and other flammable gases. However, because of the desire to evaluate the membranes for their performance with hydrogen, the systems were evaluated by the ORNL Environmental, Safety,

and Health Organization for the use of flammable gases such as hydrogen and hydrocarbons such as propane. After minor modifications and installation of flammable gas monitors an operations procedure was approved for these gases in the IMTL test systems. In order to compare new data to historical data, the flow of helium will continue to be evaluated with new membranes in addition to the flammable gases.

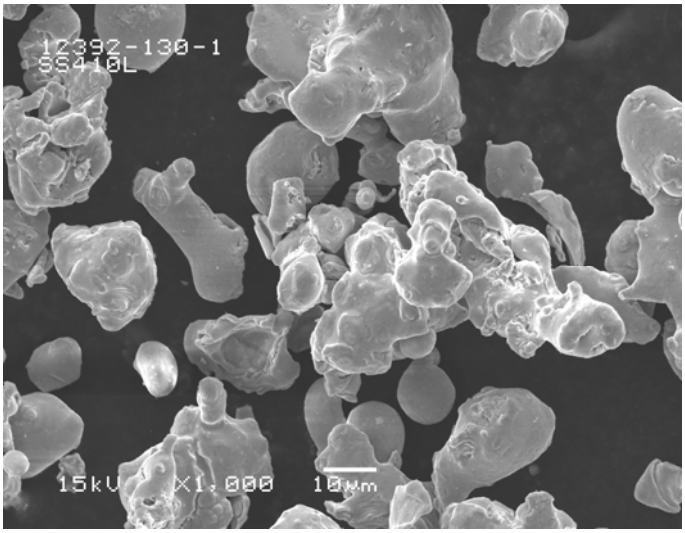

Figure 2 Scanning electron micrograph of water atomized 400 series stainless

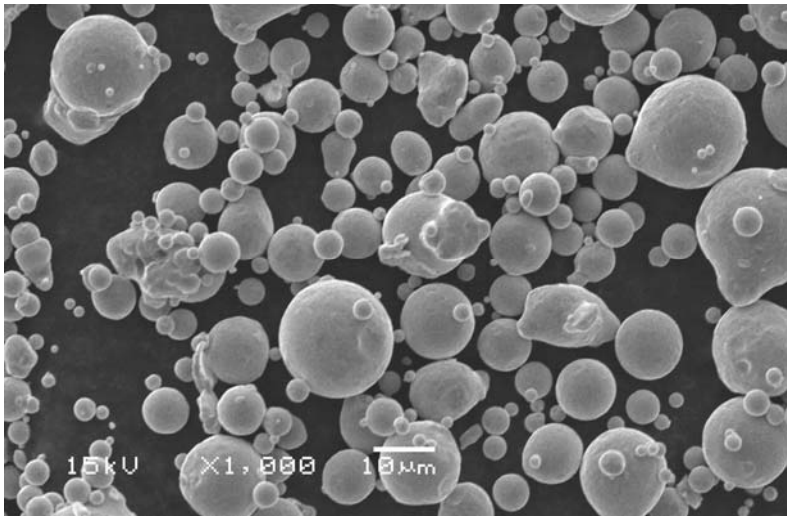

Figure 3 Scanning electron micrograph of gas atomized 400 series stainless steel powder.

Another interesting feature of Figure 1 is that the ideal separation factors are higher at 250 °C than they are at room temperature. In order to determine the cause of this phenomenon, several membranes were evaluated for gas flow at several temperatures using a series of gases. The results are shown in Figure 5. The permeance for all of the gases increased as the temperature was increased but the permeance of hydrogen and helium increased at a much higher rate than the larger/heavier molecules of carbon dioxide and propane. The result is an increase in separation factor (Figure 6) as the temperature is increased. The separation factor initially increased until a membrane seal developed a leak on the last set of data at the highest temperature. This problem is indicative of problems encountered trying to seal developmental prototypes into test systems for high temperature evaluations. When constructing a module for large scale testing or industrial applications, the membranes can be welded into the module permanently, eliminating

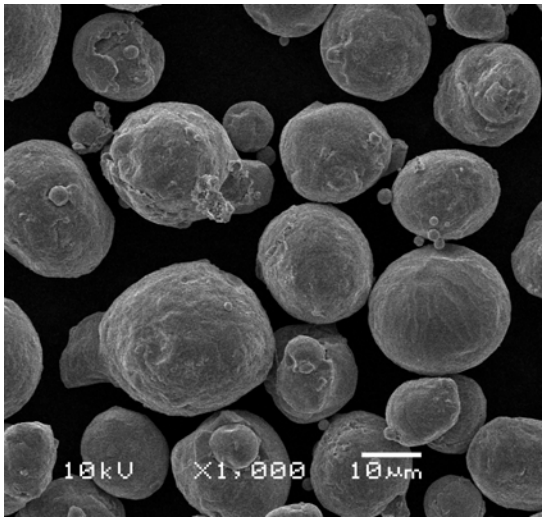

Figure 4 Scanning electron micrograph of gas atomized 400 series stainless steel powder produced by Ames Laboratory.

this problem. The increase in permeance is contrary to expectations for Knudsen flow alone. It should be emphasized that if Knudsen diffusion were the dominant mechanism in operation the permeances would decrease as the inverse square root of temperature. It can also be shown that the permeance for mechanisms that operate by adsorption followed by surface diffusion decreases with increasing temperature. The progressive increase with temperature of permeance for all the gases shown in Figure 5 indicates the possibility of thermally activated behavior. This thermally activated characteristic is similar to the diffusion of defects or atoms in the solid state in the presence of traps2, with activation energy Ed. Physically this is plausible, because delay time in negotiating the pore and activation energy have a one-to-one correspondence in the sense that they can be directly related to each other in a trapping model. Here now the jump distance is determined by the pore diameter rather than being constrained to a crystal lattice dimension, however, the lower limit on size of a pore must correspond to interatomic spacing in the solid state.

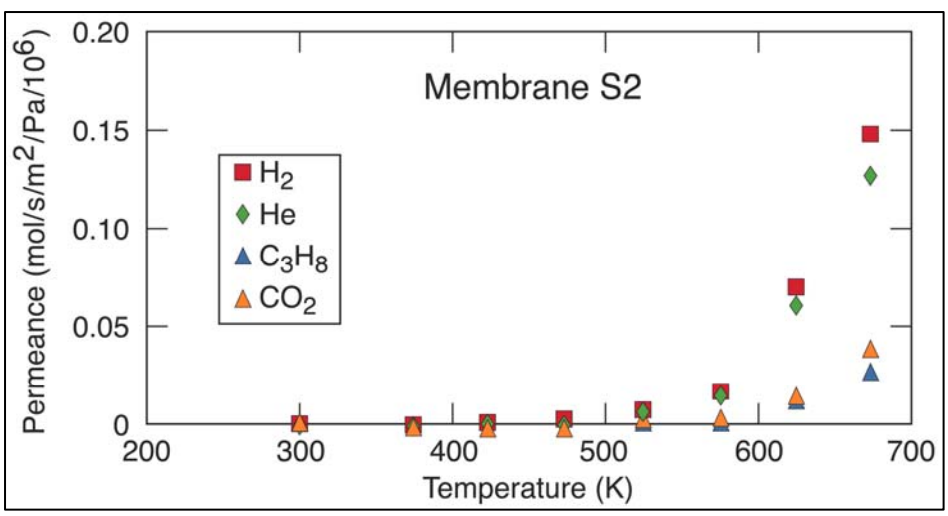

Figure 5 Permeance of several gases as a function of temperature

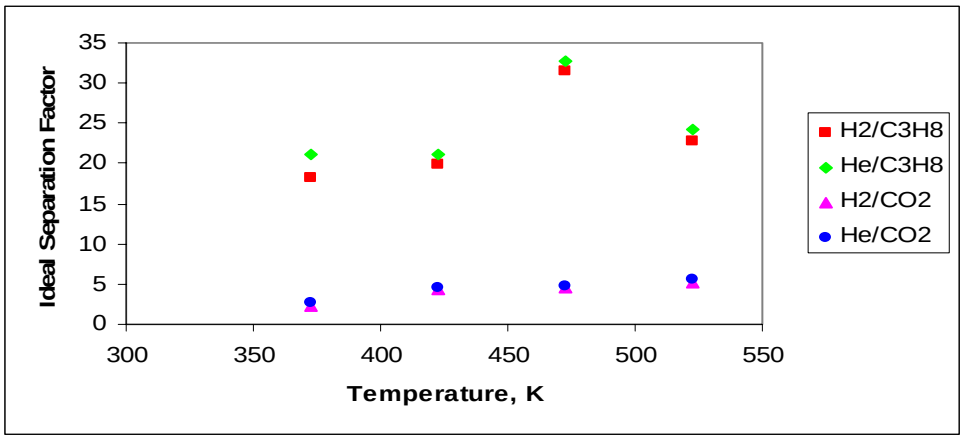

Figure 6 Ideal separation factor for several gas pairs as a function of temperature

With a general procedure developed for the fabrication of metal supported hydrogen separation membranes, a prototype was submitted for a Classification and Non-proliferation Review (NPR) in January of 2004. In July 2004 approval was received from DOE for the unrestricted development and testing of a series of prototype membranes. The support for the approved membranes can be made from any 300 series or 400 series stainless steel, Hastelloy X, or iron aluminide. The intermediate porous layer is made of aluminum oxide with the separative layer made from any one or a combination of any of the oxides of silicon, aluminum, zirconium, or titanium. A proprietary leak repair technique can be used to eliminate oversized pores to eliminate non-separative flow through the membranes. The approval also provided for any pore size less than 20 Å, which allows the pore size to be adjusted in order to balance the separation factor with the permeance to achieve the best overall performance. Membranes can be fabricated in diameters ranging from 0.4 inches to 1 inch and in lengths up to eight feet long. Transmission electron micrographs are shown in Figures 7 and 8. Figure 7 shows the surface of the membrane showing the separative layer which is mostly silica layer in this case. Figure 8 shows the cross section where the white material is the aluminum oxide intermediate layer, with a pore size of approximately 70 Å and a thickness between 2 and 3 micrometers. The thin darker layer, the separative layer, has a thickness much less than 1 micrometer thick, probably less than 0.1 µM thick.

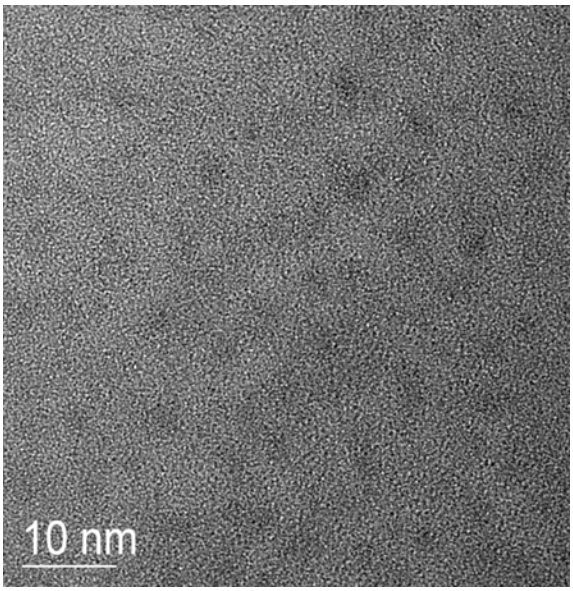

Figure 7 Transmission electron micrograph of surface of metal supported membrane

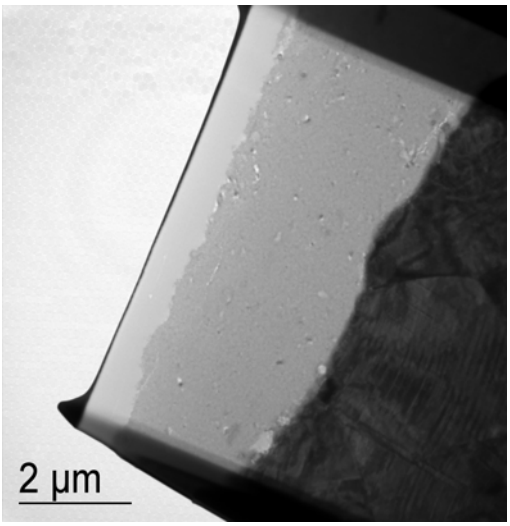

Figure 8 Transmission electron micrograph of cross section of metal supported membrane.

FUTURE WORK

Future work in the ARM Program project will concentrate on making improvements to the membrane fabrication process that will provide the best balance of separation performance and permeance. The work is currently concentrated in two areas; improved support tubes and improved leak repair methods. It was shown previously that the membranes had fewer leaks when applied to the support tubes made from gas atomized powder. For supported palladium membranes, the thickness required depends on the largest pore (or defect) that has to be bridged by the palladium layer. Similarly for microporous membranes, the quality (number and severity of leaks) of the membranes appears to depend on the quality of the support tube. The surface of a support tube produced from gas atomized powders is apparently much smoother than the surface of a tube produced from the very irregular shaped water atomized powder.

Based on the improvements in membrane performance achieved when switching to spherical powders for the support tubes, further work is planned to study the effect that powder size distribution can have on the uniformity of pores in the support tubes and ultimately on the quality of the membrane layers. The powders shown in the Figures 2 and 3 were obtained from commercial suppliers while the powder shown in the micrograph in Figure 4 was made using a high shear atomization process developed at Ames Laboratory. The commercial powders have a broader particle size distribution (Figures 9 and 10) while the particle size distribution for the powder produced by Ames has a much narrower particle size distribution (Figure 11). A larger quantity of powder is being obtained from Ames so that the next support tubes can be made from this powder and evaluated for surface roughness and how the powder affects the quality of the intermediate layer. The uniformity of pores may be an important factor in determining the quality of the intermediate layer. Data has shown that if the intermediate layer has leaks, the final membrane will also have leaks. The thin separative layer is not able to cover up these leaks. Therefore, effort is underway to better evaluate the quality of the support tubes and the intermediate layer. It is also important to understand what processing parameters affect the quality of these surfaces for application of the next layer. The quality of the support tube and intermediate layer will be evaluated using flow tests, microscopy, and profilometry. Promising leak repair methods will also continue to be investigated, especially those that have shown promise to date. This study will be invaluable in determining the most effective point to repair any membrane defects during the fabrication process. Lastly, data will continue to be evaluated to develop a better predictive tool to correlate simple gas flow measurements with ultimate membrane quality.

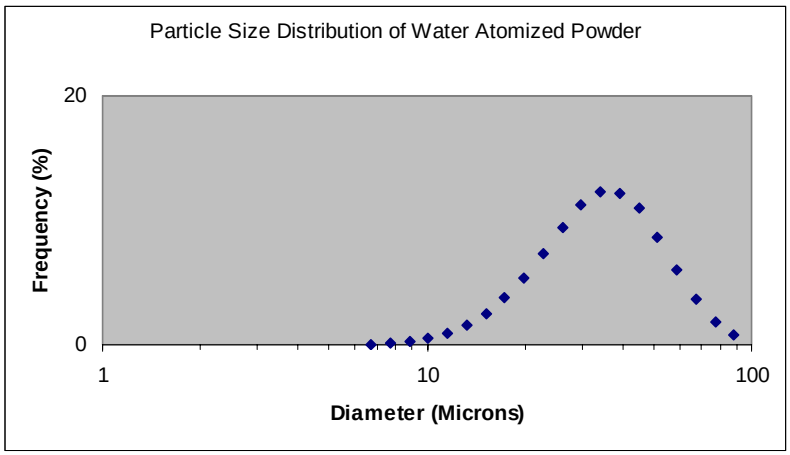

Figure 9 Particle size distribution of water atomized 400 series stainless steel powder obtained by light scattering

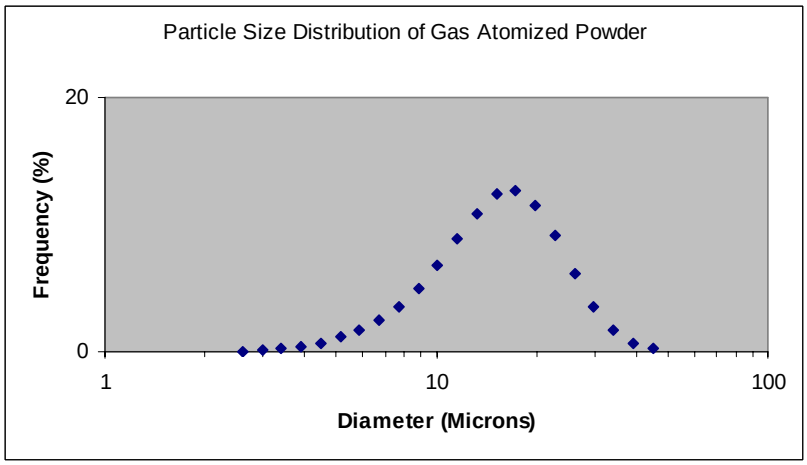

Figure 10 Particle size distribution of gas atomized 400 series stainless steel powder obtained by light scattering.

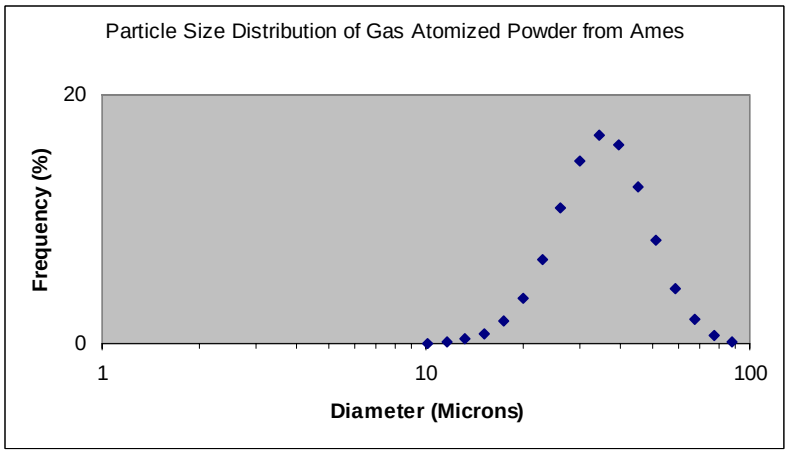

Figure 11 Particle size distribution of gas atomized 400 series stainless steel powder from Ames Laboratory

SUMMARY

It is important to note that although the fabrication techniques have been established to achieve relatively high permeances while also having separation factors well above what would be expected from Knudsen diffusion alone, work is still continuing in the ARM Program to improve the performance of the membranes. The fabrication parameters are still being adjusted which often results in improvements to the membrane performance but also results in many membranes where the performance has decreased. Any improvements in fabrication techniques learned as a result of the ARM Program project will greatly benefit the scale-up project also sponsored by the Office of Fossil Energy.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Office of Fossil Energy's Advance Materials Program for financial support. We would also like to thank Curtis Miller and Gordon Sutton for support fabrication and Bruce Marshall for technical input.

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