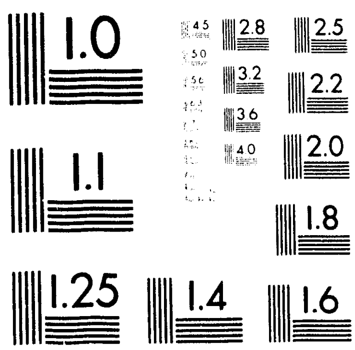
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# High Temperature Size Selective Membranes

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Contractor:
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Contract Number:
DE-AC21-92MC29245

Conference Title:
Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting

Conference Location:
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Conference Sponsor:
Morgantown Energy Technology Center

# High Temperature Size Selective Membranes

## CONTRACT INFORMATION

| | |
|---|---|
| **Contract Number** | DE-AC21-92MC29245 |
| **Contractor** | AlliedSignal, Inc.<br>Box 5016<br>Des Plaines, IL 60017<br>(708) 391-3509 |
| **Contractor Project Manager** | Stephen F. Yates |
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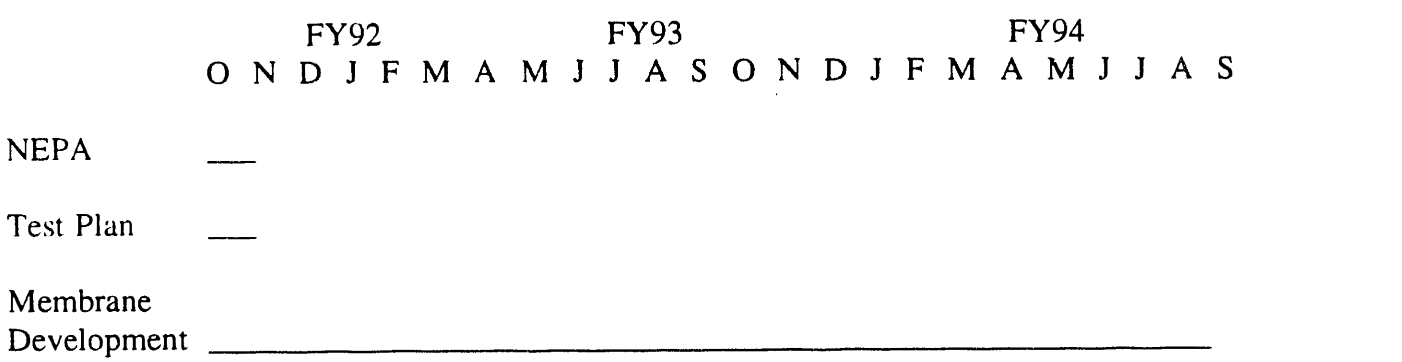
| **METC Project Manager** | Venkat K. Venkataraman |
| **Period of Performance** | September 19, 1992 to September 18, 1994 |

**FY93 Program Schedule**




## OBJECTIVE

The objective of this research is to develop a high temperature size selective membrane which would be capable of separating gas mixture components from each other based on molecular size, using a molecular sieving mechanism. The membrane would be a composite of a carbon molecular sieve (CMS) with a tightly defined pore size distribution between 3 and 4 Å, and a microporous supporting matrix which provides mechanical strength, and resistance to thermal damage. Such a membrane would enable the separation of hydrogen from carbon dioxide.

## BACKGROUND INFORMATION

The high temperature membrane is expected to benefit the Fossil Energy Program. The production of power from coal is one example of an industrial process which would benefit from the availability of the high temperature membrane. For example, separation of hydrogen from the product mixture of a water gas shift reactor at high temperature would allow this hydrogen to be used directly in further reactions. The membrane would replace the technology based on pressure swing adsorption which requires the process gas to be cooled before the separation of hydrogen can be achieved. The membrane, by operating at high temperatures, would save energy and costs.

## PROJECT DESCRIPTION

The high temperature membrane, capable of operation above 550°C, is designed to be a composite membrane composed of a thin layer of a size selective membrane supported by a microporous ceramic support. The kinetic diameters[1] of $H_2$ and $CO_2$ are 2.96 Å and 4.00 Å. The thin layer will be made from CMS whose pore size will be controlled to be less than 4 Å. The membrane will be truly size selective and be impermeable to carbon dioxide. The membrane will have higher selectivity than membranes which operate on Knudsen diffusion mechanism.

The ceramic support will be fabricated from AlliedSignal's proprietary Blackglas™ resin. The ceramic material, noted for its high thermal and oxidative resistance, has a coefficient of thermal expansion which matches closely that of CMS. The close match will insure mechanical integrity when the membrane is subjected to thermal cycles.

The CMS layer will be produced by controlled pyrolysis of polymeric precursors. Pore size will be suitably modified by post-treatments to the carbon.

The composite membrane will be tested for its permeation properties at 550°C or higher. Thermal, mechanical and chemical stability of the membrane will be assessed.

The experimental strategy has been to separately optimize the production of the CMS and the membrane support and then to explore methods of producing the composite membrane.

## RESULTS

We have produced several samples of CMS from polymeric precursors. Figure 1 shows the Horvath-Kawazoe pore size distribution of one set of CMS we have produced. The distribution was obtained from the $CO_2$ adsorption isotherm at 0°C. We post-treated the CMS sample to obtain monodisperse pores.

We have initiated work also on the preparation of microporous supports from Blackglas™ resin. A ceramic fabric support was coated with a known concentration of the resin solution following which the fabric was hot-pressed to obtain a prepreg. The prepreg was then pyrolyzed under nitrogen atmosphere to obtain a porous membrane support. The initial supports had a porosity of approximately 38%. Work is in progress to produce supports with more uniform pore shape and size.

We have completed the design of the high temperature membrane pilot plant. The membrane cell was fabricated out of two kinds of stainless steel. The inner parts are made of SS 316 and the outer ring made of SS 420. The greater thermal expansion of the SS 316 will help obtain a leak free seal at the operating temperatures. The membrane cell is complete with necessary plumbing to allow feed and permeate gases to flow to and from the membrane cell and to allow sweep and purge gases. Thermocouples for monitoring the temperature of the cell are also provided. We have also completed the fabrication of the sample holder used in the carbonization of precursor coated membrane supports. Figure 2 shows a photograph of the retort insert/membrane cell assembly. We have initiated the design and construction of the safety enclosure for the pilot plant.

## FUTURE WORK

Our immediate work will focus on the optimization of the properties of the CMS and the support. Efforts will then be directed to the making of composite membranes in which the CMS forms a gas separating layer. The membranes will be tested in the high temperature membrane pilot plant using pure and mixed gases. In addition to obtaining membrane permeabilities for the various gases, we will obtain information on the stability of the membrane for extended hours of operation at elevated temperatures in the reducing environment of the gases. We will also address the economics of the membrane separation process.

## REFERENCE

1. D. W. Breck, Zeolite Molecular Sieves, p. 636, R. F. Krieger Publishing Co., Malabar, Florida (1974).

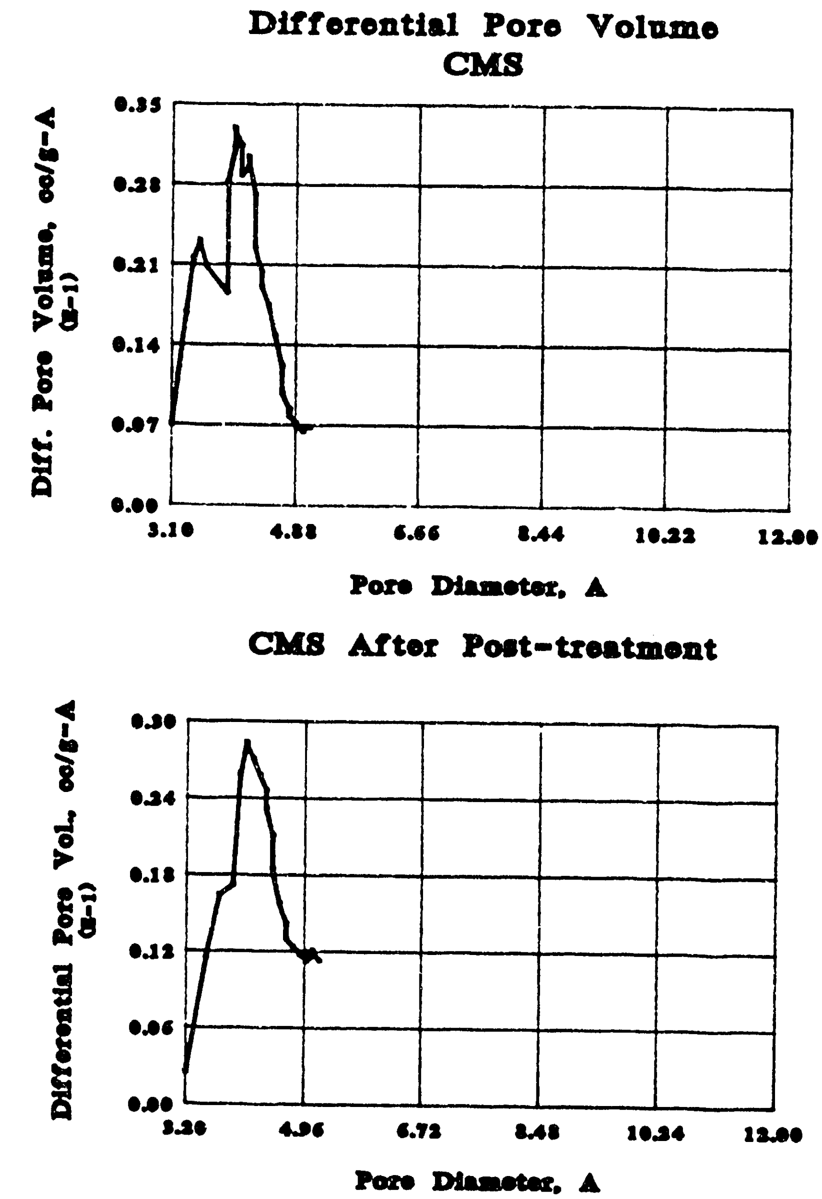



Figure 1. Horvath-Kawazoe Pore Size Distribution of CMS Samples Before and After Post-treatment.

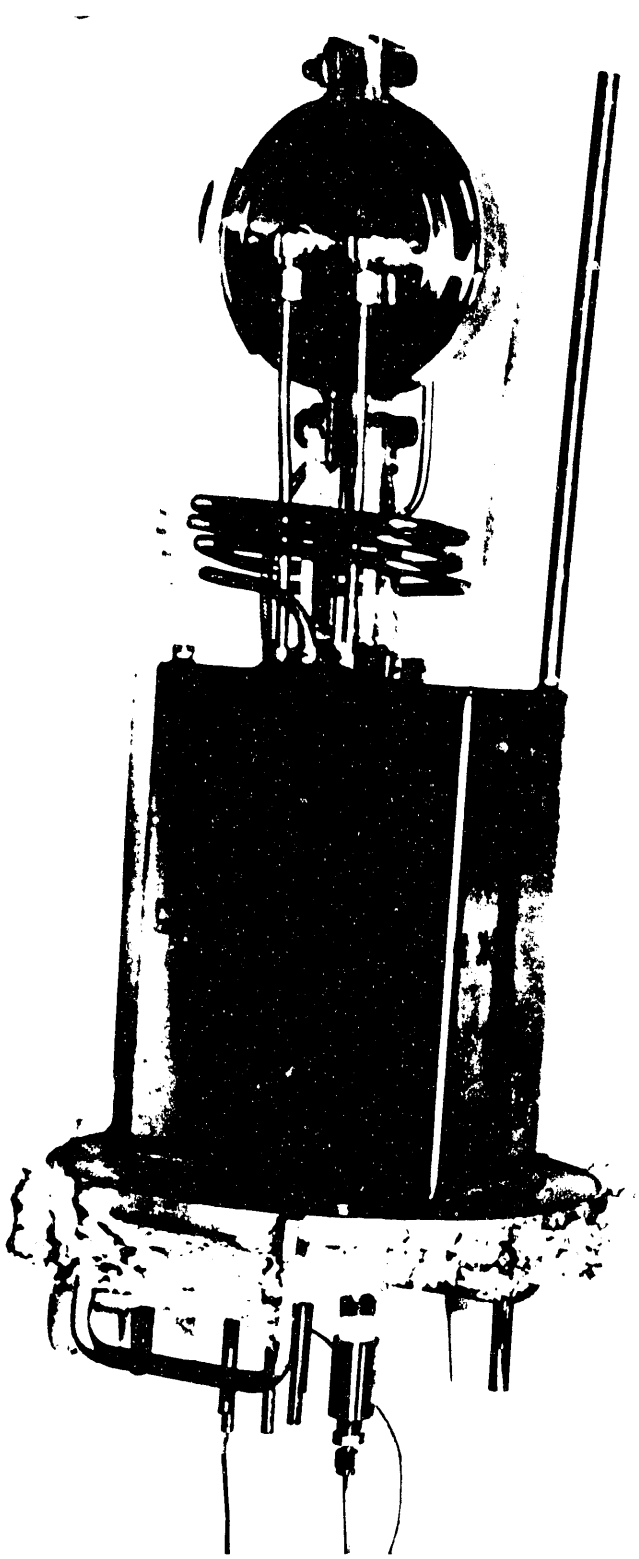


**Figure 2. Photograph of the High Temperature Membrane Cell and the Retort Assembly.**

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