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Development of Ceramic Membrane Reactors for High Temperature Gas Cleanup

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Contractor:

SRI International  
333 Ravenswood Avenue  
Menlo Park, CA 94025

Contract Number:

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# Development of Ceramic Membrane Reactors for High Temperature Gas Cleanup

## CONTRACT INFORMATION

**Contract Number** DE-AC21-89MC26373

**Contractor** SRI International  
333 Ravenswood Avenue  
Menlo Park, CA 94025  
Phone: 415/859-6224

**Contractor Project Manager** Dr. Daryl L. Roberts

**Principal Investigator** Dr. Daryl L. Roberts  
Dr. J. Douglas Way (Oregon State University)

**METC Project Manager** Dr. Venkat Venkataraman

**Period of Performance** September 27, 1989 to September 26, 1992

## Schedule and Milestones

The schedule of performance of the five tasks is shown in Figure 1. The project tasks have been largely accomplished, but final experiments and performance modeling calculations are being concluded currently.

## OBJECTIVES

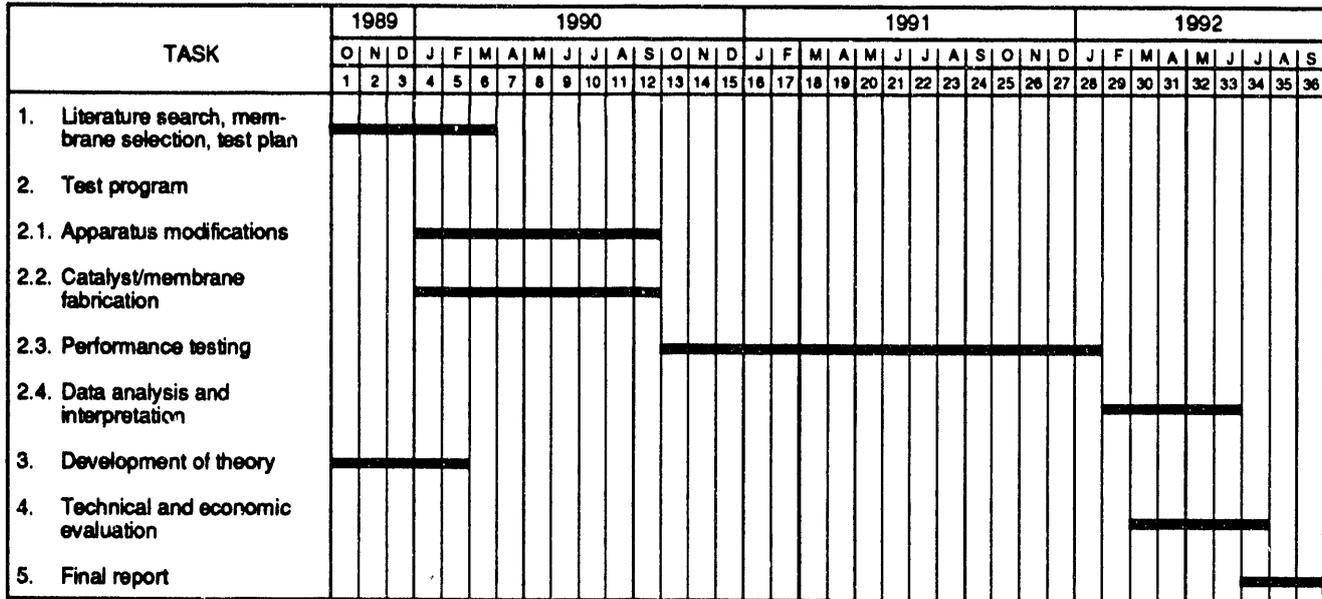
The objective of this project is to develop high-temperature, high-pressure catalytic ceramic membrane reactors and to demonstrate the feasibility of using these membrane reactors to control gaseous contaminants in Integrated Gasification Combined Cycle (IGCC) systems. These catalytic membrane reactors will decompose hydrogen sulfide ( $H_2S$ ) and ammonia ( $NH_3$ ) and separate the reaction products. The reactors will be designed to operate in the hostile process environment encountered in IGCC systems, including temperatures ranging from 1,000 to 2,000°F and pressures from 200 to 1,000 psia. The research involves novel catalytic materials, modification of commercially available inorganic membranes, and the making of laboratory membrane reactors from these catalysts and modified membranes.

## BACKGROUND INFORMATION

DOE is seeking to develop high temperature, high pressure ceramic membrane technology to perform a variety of gas separation processes to improve the efficiency and economics of advanced power generation systems such as direct coal-fueled turbines (DCFT) and the IGCC process. The temperatures encountered in these power generation systems are far above the temperature range for organic membrane materials which is typically 150-200°C for polymers such as silicone rubber, polysulfone, and cellulose esters. Inorganic materials such as ceramics are therefore the most likely membrane materials for use in advanced power generation systems. The focus of this project is IGCC systems wherein control of  $H_2S$  and  $NH_3$  is a key element of the overall system. The IGCC process consists basically of a gasifier to produce synthetic gas that is then fed to a gas turbine generator. The temperature and pressure ranges encountered under IGCC conditions are 1,000° to 2,000°F and 200 to 1,000 psia. There are several potential applications for a high temperature membrane reactor process in the IGCC flowsheet. Downstream of the hot particle removal device, for example, both  $H_2S$  and  $NH_3$  could be removed and catalytically decomposed, leaving the fuel value of the gasifier stream intact. If the contaminants  $H_2S$  and  $NH_3$  are decomposed before they

**Task 1**

Literature Survey	11/15/89
Test Plan	2/1/90
Revised Test Plan	3/31/90



**Figure 1. Project Schedule Based on Start Date of September 27, 1989**

are removed, some hydrogen loss will occur in which case the permeate stream might be useful in the molten carbonate fuel cell. Overall, the technology of membrane reactors is likely to impact several DOE program areas.

**PROJECT DESCRIPTION**

SRI's approach is to combine novel catalytic materials with modified, commercially available inorganic membranes to make membrane reactors capable of decomposing H<sub>2</sub>S and NH<sub>3</sub>. The research also involves developing a theoretical basis for reactor performance and evaluating the economics of the performance at conditions typical of IGCC conditions. The work was conducted in the following five tasks:

- Task 1: Literature Search, Membrane Selection, Test
- Task 2: Experimental Test Program
- Task 3: Development of Theory
- Task 4: Technical and Economic Evaluation
- Task 5: Final Report.

The experimental test program (Task 2) included coating inorganic pre-ceramic polymers onto commercially-available inorganic membranes to try to make a hydrogen selective membrane that withstands IGCC conditions. It also included synthesis of appropriate catalysts for decomposing H<sub>2</sub>S or NH<sub>3</sub>.

## RESULTS

Early in the project, we developed a computer code of the membrane reactor process and developed catalysts capable of decomposing  $H_2S$  and  $NH_3$  separately.

The more difficult part of developing a membrane reactor was making a membrane with suitable permselectivity. Since both the ammonia and  $H_2S$  decomposition reactions produce  $H_2$ , we want a membrane that selectively permeates hydrogen. We have taken the approach of coating a substrate that has fine pores (a microfilter or ultrafilter) with a completely dense layer and then (except for palladium coatings) making super fine pores in the dense layer by leaching or pyrolysis.

We used four different substrates (Norton 0.2  $\mu m$  alumina monolith, Refractron alumina microfilters, Vycor glass, Alcoa ultrafilter) and five different coating materials (Poly N-methyl silazane, Aremco 617 alumina-based glaze, Polycyclohydridomethyl silazane, Aluminum phosphorus oxides, palladium). Only the palladium films on an alumina ultrafilter could be made regularly with a negligible defect population. The other approaches were plagued with cracks and poor reproducibility.

As an example of results with the inorganic polymer coatings, Figure 2 shows hydrogen and nitrogen permeation test results at room temperature for the Aremco 617 glaze coated onto an alumina microfilter (Refractron Corporation, Newark, NY). Most of the selectivities were below 3.74, the value predicted for a Knudsen barrier. There were two results where the selectivity exceeded the Knudsen value, indicating the feasibility of achieving the "molecular sieving" properties that we are trying to produce. We suspect, however, that unselective surface defects in most cases swamp the total permeation rate, leading to low selectivities.

We made palladium films on a tubular alumina ultrafilter (U.S. Filter, Warrendale, PA) by electroless plating from a platinum amine complex solution in hydrazine (Rhoda, 1959). The best results were achieved with an ultrafilter pore size of 100 angstroms and with pretreatment of the surface in a stannic/stannous chloride solution. The films were

about 5 microns thick and appeared defect free under electron microscopy. We have not succeeded yet with permeation measurements with these films at high temperature because of problems making a seal on the membrane that withstands temperatures above 1000°F. Because defect-free palladium films are infinitely selective to hydrogen with respect to the other components of gasifier product gas, we expect that the selectivity of our palladium films will exceed 1000 even with the inevitable defects that accompany real membranes.

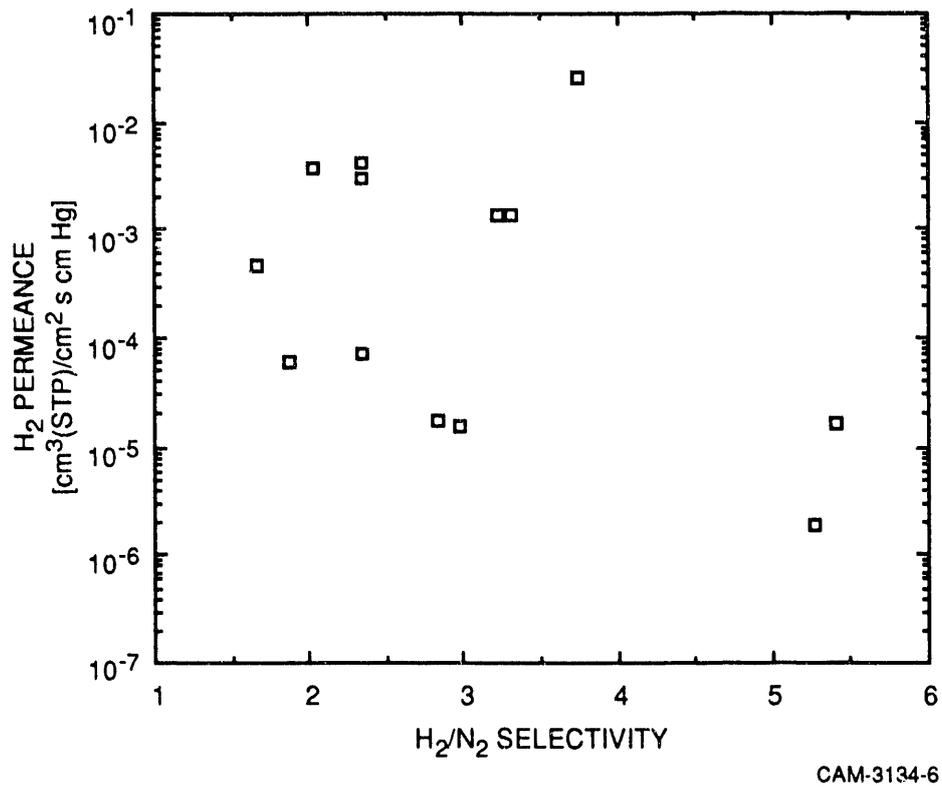
We have analyzed the performance and economics of membrane reactors for  $H_2S$  and  $NH_3$  decomposition using the reaction rates determined experimentally in our catalyst development work and using the permeation behavior of palladium films reported in the literature (Uemiya, et al., 1988). Our results show that membrane reactors for  $H_2S$  decomposition cannot remove  $H_2S$  to as low a level as the zinc ferrite systems (99.3% removal) even though the membrane reactor decomposes  $H_2S$  more efficiently than an ordinary reactor (Figure 3). Further, the feed concentrations of  $H_2S$  and  $NH_3$  are so low (3110 ppm and 750 ppm, respectively, in our base case taken from DOE/MC/26019-3004, December 1990) that the hydrogen losses from the feed gas through the membrane wall are unacceptable. Only if the  $H_2S$  or  $NH_3$  is preconcentrated, such as by permeation through a molten salt membrane, can the cost of the membrane reactor system become reasonable (Figure 4).

## FUTURE WORK

In the remaining time, we intend to acquire representative  $H_2$  permeation data at high temperatures for the palladium films on the alumina ultrafilters. We will use these data in a few representative runs in our performance/economics computer code.

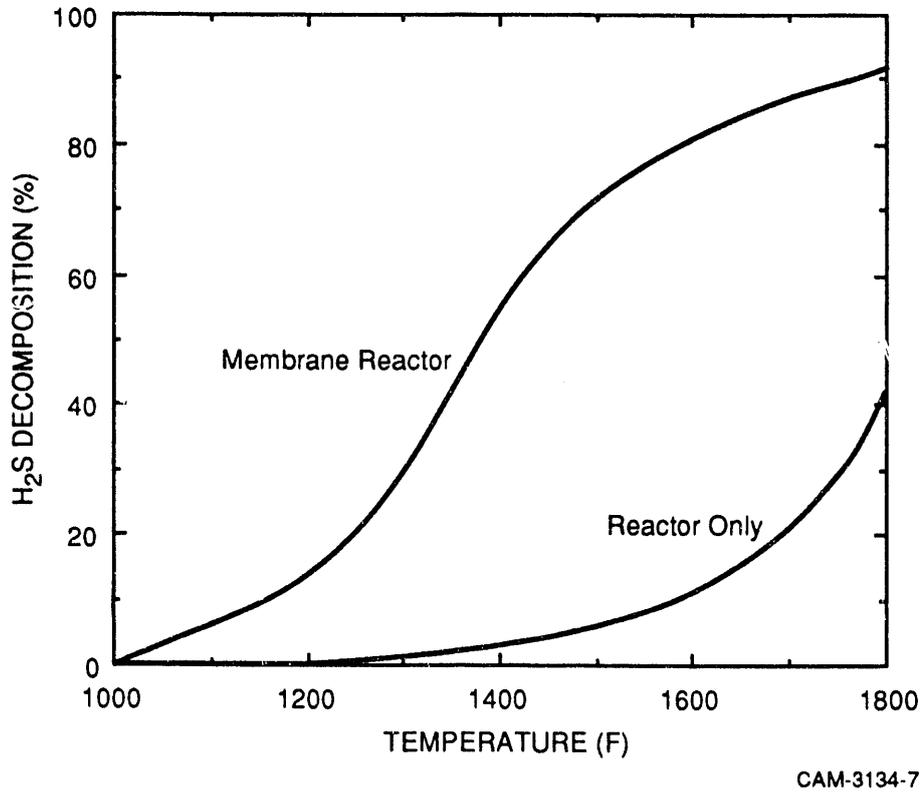
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- Uemiya, S., Y. Kude, K. Sugino, N. Sato, T. Matsuda, E. Kikuchi, "A Palladium/Porous-Glass Composite Membrane for Hydrogen Separation," *Chem. Lett.*, pg. 1687-90 (1988).



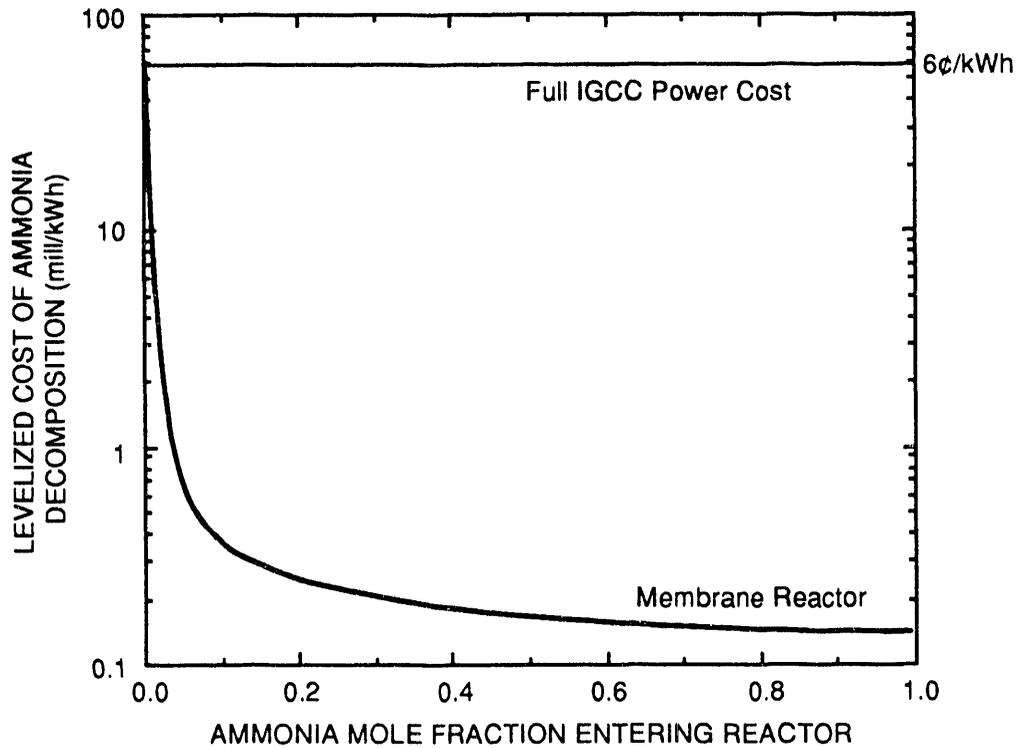
**Figure 2. Alumina Glaze on Refractron Microfilter**

Selectivity greater than that given by the Knudsen mechanism (3.74) was rarely achieved.



**Figure 3. Effect of Reactor Temperature on Decomposition of H<sub>2</sub>S**

Temperatures above 1500°F are necessary for reasonable fractional decomposition of H<sub>2</sub>S even with a membrane reactor.



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**Figure 4. Effect of Ammonia Preconcentration on Total System Cost**

If the  $\text{NH}_3$  can be preconcentrated to 5% to 10%, decomposition costs can be reasonable.

**END**

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