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Ion-Exchange Membranes for Bulk Separation of H_2S and CO_2

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DISCLAIMER

Ion-Exchange Membranes for Bulk Separation of H_2S and CO_2 from Natural Gas Streams

CONTRACT INFORMATION

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Schedule and Milestones

FY91-92 Program Schedule

Task		Title	A M J J A S O N D J F M A M J J A S
1		Composite Membrane Preparation	
		Screening Studies	
		Optimization	
		Field Test	
2		Membrane Characterization	
		Screening Studies	
		Optimization	
		Field Test	
3		Field Test Characterization	
	3.1	Assemble Test Module	
	3.2	Perform Extended Performance Tests	
4		Comprehensive Topical Report	

OBJECTIVES

The overall goal of this program is to investigate the use of ion exchange membranes in the removal of acid gases during processing of natural gas or during production of H_2 from synthesis gas. As part of this goal we are running a field test of candidate membranes on a natural gas stream to obtain extended performance data on acid gas transport. Additionally we are working on strategies for increasing the productivity and lifetime of these types of membranes. The specific objectives include:

- Evaluate candidate membranes, carriers, solvents, treatments and the effects of process conditions for separation of the acid gases CO_2 and H_2S from H_2, CO and CH_4.

- Develop mathematical models to guide experimental work and for interpretation of results.

- Construct and operate an extended-use test facility to evaluate the long term stability and productivity of various membrane forms relative to acid gases.

- Develop thin film composite membranes as a possible route to higher productivity and lower cost membranes.

- Develop preliminary process design and economic analysis for the use of these membranes in gas cleanup.

BACKGROUND INFORMATION

Membrane gas separations are receiving more attention because of their use in many applications including CO_2 removal in natural gas processing, N_2 generation and H_2 recovery. Economic studies of polymer membranes versus conventional technologies (Schell, 1985, Spillman, 1989) have shown cost advantages for membrane systems from 20 to 80%.

Polymeric membrane processes have already found a niche in CO_2 removal and reinjection in the oil field and in the cleanup of natural gas. Process configurations including combination with existing gas-liquid contacting technologies have been considered for removal of H_2S (McKee, et al, 1991).

Polyperfluorosulfonic acid (PFSA - Nafion®) is an ion-exchange polymer based on fluorocarbon chemistry. The backbone is essentially teflon and there are side groups with covalently-bound sulfonate ions. The sulfonate groups cluster into regions which absorb large quantities of polar solvents. Thus this polymer can imbibe solvents and swell allowing for diffusion rates higher than are typically found in dense polymer films. Due to the chemical nature of the fluorocarbon, films of this polymer can be used at temperatures at least up to 423 K (150°C) and in highly acidic and basic environments without damage. Commercial films (Nafion® N117) are available, with a thickness of approximately 200 μm (7 mils), having been designed primarily for chloralkali cell applications.

Prior work by our group has shown that liquid membrane/facilitated transport with ion exchange membranes can achieve very high selectivity for the removal of CO_2 and H_2S from mixtures containing H_2, CO, CH_4 and higher hydrocarbons at ambient temperatures. We refer to these membranes as enhanced transport, ion-exchange membranes or ET-IEX. The productivity of the ET-IEX membranes, on a per unit thickness basis, can be greater than or equivalent to the best of the passive membranes and more selective.

The use of an ion-exchange membrane (IEM) as a support for chemical and physical solvents alleviates some functional problems of conventional supported liquid membranes. The IEM is non-porous so no "short-circuiting" occurs if there is solvent loss. Ionic species are held in the membrane by electrostatic forces which can help prevent loss and deactivation of added complexing agents. Early investigation of this polymer as a gas separation membrane was conducted by Way, et al (1986). They studied the separation of CO_2 and H_2S from CH_4 using the commercial film (N117) mentioned above.

The N117 was used as a support for a solution containing a physical and chemical solvent for the gases which were being transported through the membrane. In their studies ethylenediamine

(EDA) is the carrier for CO_2 and H_2S, and water is the physical solvent. CH_4 has low solubility in the H_2O and is therefore transported through the membrane at a lower rate. Some key results are presented in the following Table 1.

Table 1. Permeation Rates for a Tri-Component Mixture using N117 Membrane with Water as the Solvent and Ethylenediamine as the Carrier

H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
feed gas mole fraction			relative permeation rate†		
0.00479	0.0778	0.774	0.181	20.6	0.408
0.0079	0.0376	0.723	0.557	14.7	0.389
0.0046	0.0349	0.82	0.24	15.2	0.441
0.0106	0.0138	0.644	1.18	8.29	0.375
0.00449	0.0136	0.839	0.475	8.61	0.453

† 10^{-10} mol/cm^2 s

It should be noted that CO_2 couples with the EDA more favorably than the H_2S does and is therefore transported selectively. The separation factor between CO_2 and CH_4 varied between 500 and 1000. Note that these experiments were conducted at low pressure (84 kPa) where chemical facilitation would be the most efficient.

As promising as these results were, the productivity of the N117 membrane is very low. At 200 μm, the membrane is simply too thick to provide sufficient mass transfer rates for an economic processes. By comparison the "skin" layer on asymmetric membranes is ≤ 1 μm.

Investigations of PFSA continued with a focus on separation of CO_2 and H_2S from mixtures containing H_2 and CO. A developmental form of PFSA (NE111) was made available to us from duPont Co. It is approximately 30 μm (1 mil) thick. CO_2 flux measurements showed the expected improvement, i.e., with 100% CO_2 at 84 kPa, N117 permeated ~2 nanomoles/cm^2 s while NE111 permeated ~10 nanomoles/cm^2 s (Noble, et al. 1988). This productivity is still not sufficient for commercial use.

Gel-PFSA

We then developed a heat-treatment solvent-swelling approach which dramatically increased the productivity of the membranes (Pellegrino et al, 1988 and Heaney and Pellegrino, 1989). Not only did the permeance of the membranes increase dramatically but so did the permeability. Some sample data is presented in Figure 1.

Membranes treated with this technique were identified as GT (gel treatment). Further experiments on ternary mixtures of H_2, CO_2 and H_2S, using a variety of chemical carriers indicated that larger carriers could effectively be used to vary selectively between H_2S and CO_2 (Pellegrino et al, 1990). These results are shown in Figure 2.

These results showed that the intrinsic productivity of the GT-NE111 membranes and its selectivities (the ratio of permeabilities) were extremely high. For example, silicone rubber is one of the most productive membrane materials. The CO_2 and H_2S permeability through silicone is on the order of 2000 and 8500 barrer respectively. The GT-NE111 is intrinsically as permeable as silicone, but with higher selectivity. Unfortunately, it is also much thicker than a silicone film can be made and is therefore less productive

Composite Membranes

Figures 3 presents permeation of a binary mixture of CO_2 and H_2 through microporous teflon (PTFE) coated with PFSA solution (Pellegrino, et al, 1990). These membranes (GTX) were developed because the productivity improvement obtained with the gel-swollen PFSA was still not high enough to be commercially viable. The

experiments were run at a total pressure of 84 kPA with n-methylpyrrolidone (NMP) as the chemical solvent/carrier.

The CO_2 - H_2 selectivity is between 10 and 20. The PFSA in these experiments was in the Na counterion form. A single tri-component mixture was run with a composition of 50% H_2, 40% CO_2 and 10% CO. The permeation results yielded separation factors of 14 for CO_2 - H_2, 28 for CO_2 - CO and 2 for H_2 - CO. This data confirmed reasonable correspondence between the selectivities measured for binary mixtures in a ternary system.

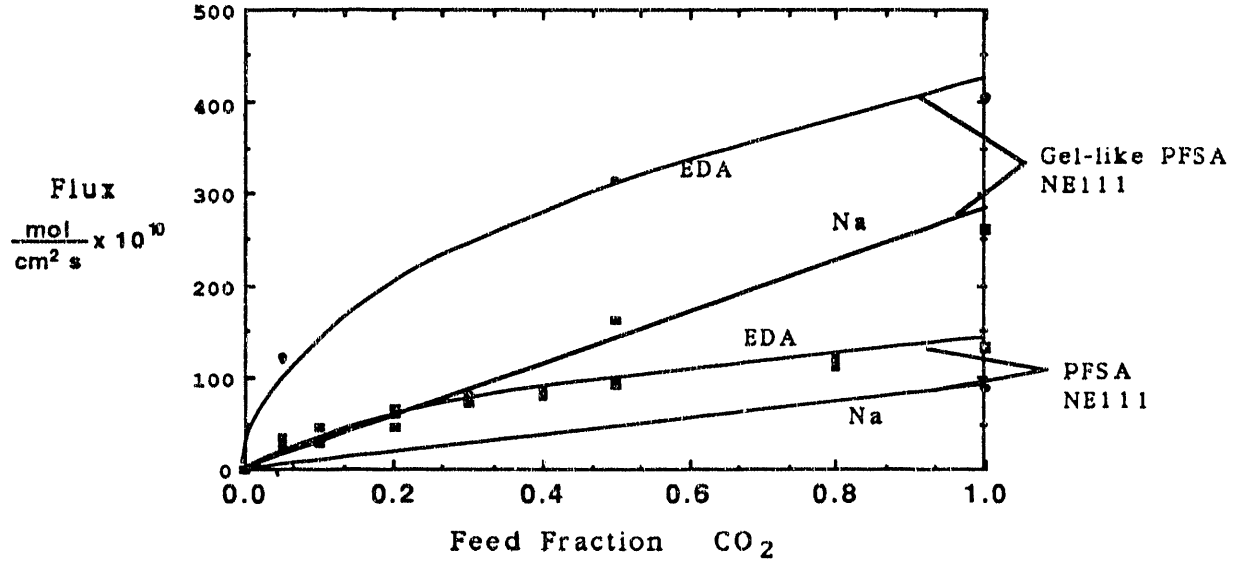

Figure 1. CO_2 flux vs CO_2 feed fraction at 84 kPA total pressure for standard and gel treated NE111 membranes. The Na form is unfacilitated transport.

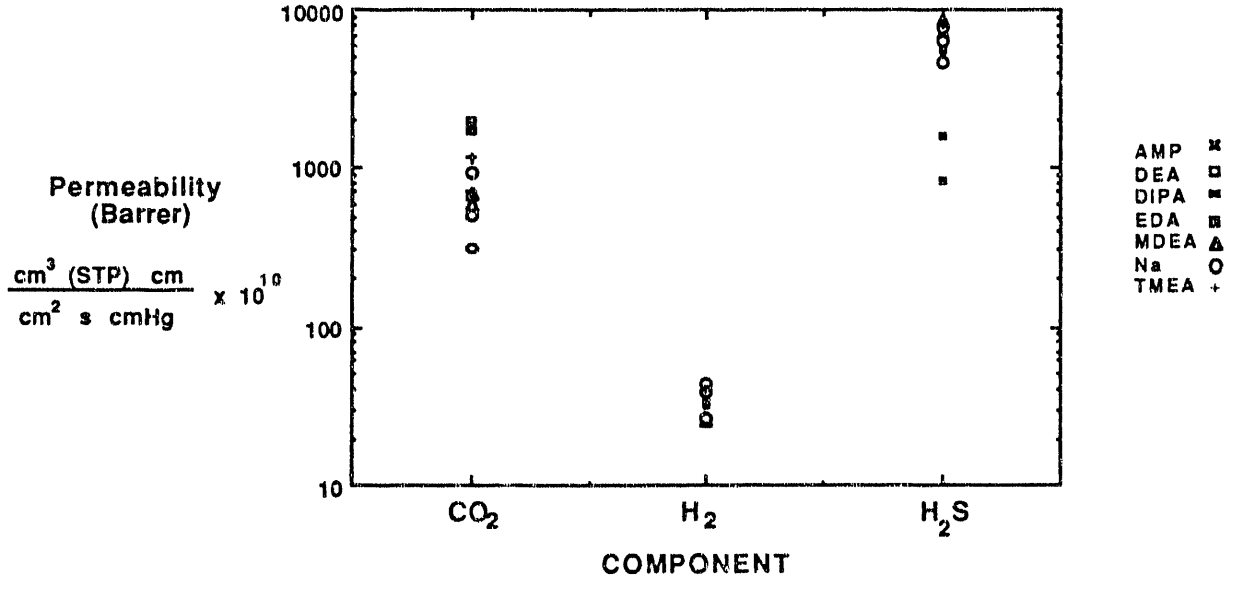

Figure 2. Ternary system containing 70% H_2, 10% CO_2, 1% H_2S and 19% He at 84 kPA total pressure. Gel treated NE111 is the membrane and water is the solvent.

The GTX membranes have not been optimized for thickness or composition, nor have they been characterized completely. Nonetheless, the progression of CO_2 productivity has gone from 2 to 100 nanomoles/cm^2 s (at 84 kPA total pressure) between the commercial N117 PFSA and our GTX films. This 50-fold increase in productivity encourages further development of the thin film membranes.

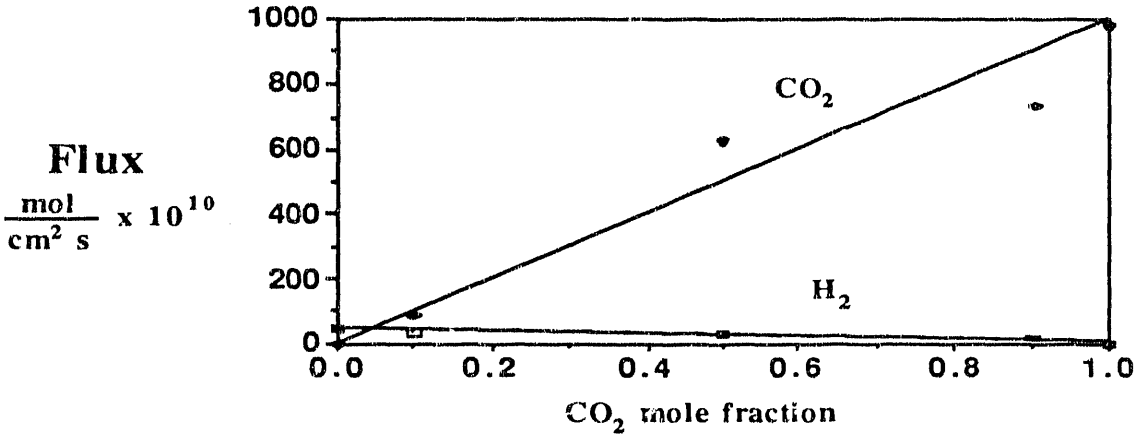

Figure 3. Binary Mixture of CO_2 and H_2 with Composite Membrane (PFSA on PTFE)

Long Term Testing

Our project has also included a task to evaluate the long term performance of the membrane. We implemented this task as a study of membrane stability and transport performance on a "real" process stream taken from a natural gas processing facility. The test is focusing on permeation of CO_2 and H_2S from a feed stream containing natural gas hydrocarbons (CH_4 and up) and potentially small levels of CO. We consider this field test a major step in defining suitable enhanced- transport, liquid membranes for energy production processes.

A great deal of time has been spent on constructing a suitable test rig and trying to develop a tight module which will hold flat sheet membranes (irregularly textured and liquid-laden) and provide at least 0.1 m^2 (1-2 ft^2) of membrane area. We decided to initially start up the system using a module which contains a single membrane sheet until we define an optimum membrane form and chemistry. In a sense the field test site is an extension of our laboratory with additional development capability.

The first field test was a partially gel treated NE111 with H_2O as the solvent and methyldiethanolamine (MDEA) as the chemical carrier. This membrane is meant to promote H_2S transport relative to CH_4 and other hydrocarbons.The gas feed stream is taken off a medium pressure line and fed to the membrane at ~ 800 kPa (~100 psig). The results are presented in Figure 4 which shows the CO_2/CH_4 and H_2S/CH_4 separation factor over time. The H_2S/CH_4 separation factor (~50) is significantly higher than those obtained with current gas membranes 10-30, (Funk and Li, 1990). This membrane is not productive enough to be commercially viable but demonstrated that the high acid gas selectivities could be maintained on a real process stream over extended periods.The stability of the solvent in the membrane is enhanced by the fact that the stream being treated is saturated with water.

Figure 5 depicts results obtained in our lab, 16 months later, using the exact same membrane, and feed pressure and a gas mixture with similar composition (16.9% N_2, 41.3% CH_4, 14.1% H_2S, 6.9% CO_2, 5.5% C_2-C_6's, sat'd H_2O). These results indicate correspondence between experiments in the lab environment and the field test.

At the gas feed pressures of our field test we are unlikely to have significant facilitated

transport with the membrane. Therefore the implication is that the solvent imbibed PFSA is still capable of providing high selectivities. We have dubbed this characteristic, enhanced transport. Additionally, at the point that the feed stream becomes very lean in the transporting species, the reactive transport pathway would be available to keep the selectivity high. The combination of the ionic character of the matrix and a suitable solvent system seems to provide an effective separation medium even at elevated pressures.

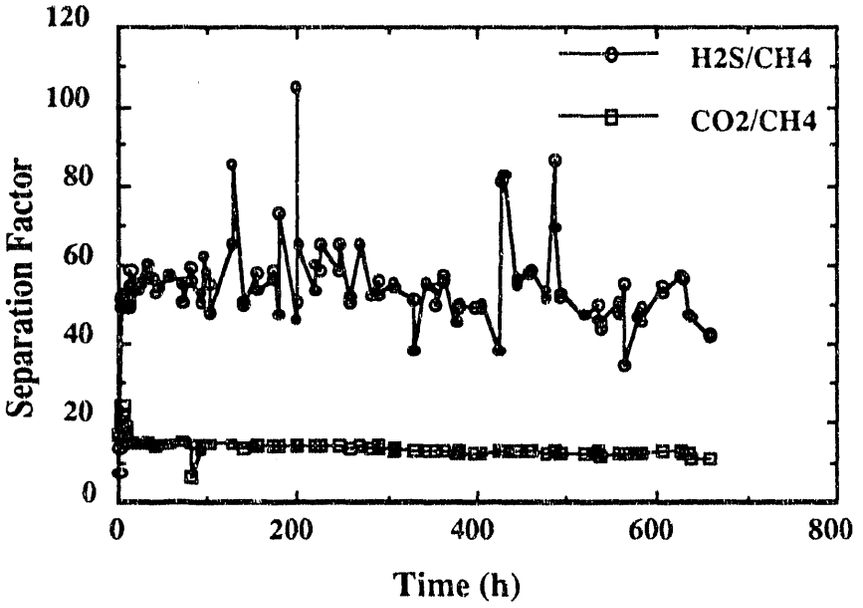

Figure 4. Separation factor for CO_2/CH_4 and H_2S/CH_4 (Carter Creek Field Test 20 Jul -16 Aug 1990, gel-NE111)

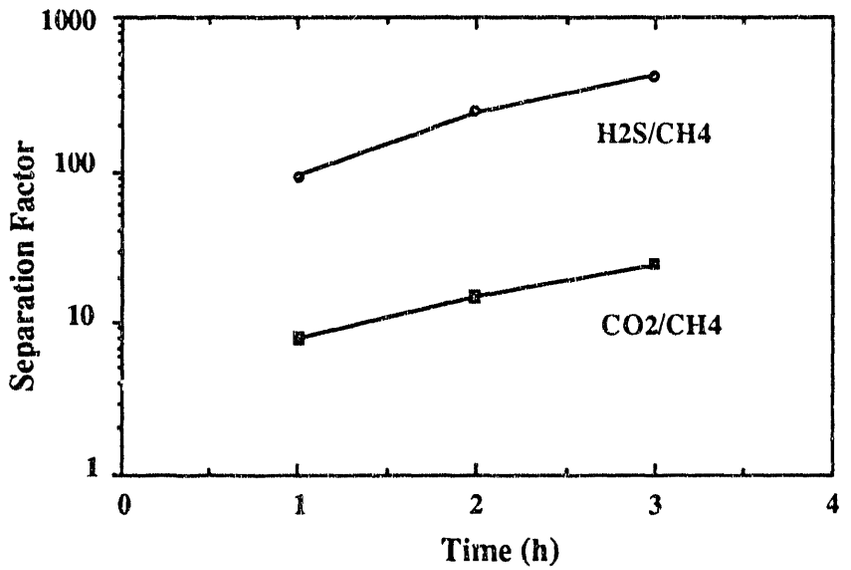

Figure 5. Separation factor for CO_2/CH_4 and H_2S/CH_4 (NIST Jan 1992, gel-NE111)

PROJECT DESCRIPTION

The technical work in the current project is intended to identify film forming conditions which can consistently be used to prepare defect-free, enhanced transport-ion exchange (ET-IEX), composite membranes, and to evaluate their performance in acid gas separations in lab and field tests. The composite membranes are defined as thin films (<10 μm thick) of polyperfluorosulfonic acid (PFSA) coated on a microporous substrate. Since a small amount (ca. 10^{-6} of the available surface area) of defects (i.e., uncoated pores) can render the composite membrane useless for performing gas separations we are stressing the objective of minimizing or eliminating defects.

RESULTS

Field Test

The field test has continued with PFSA composite membranes. The substrates have been a microporous polypropylene supplied by 3M Co. The membranes have been imbibed with either aqueous solutions of methyldiethanolamine (MDEA) or n-methylpyrrolidone (NMP). Data from five composite membranes have thusfar been obtained and are presented in the following Figure 6.

The composite1 membrane gave erratic performance before it mechanically failed, but most of the observed separation factors were high enough (>35) to be consistent with the initial results from the gel-NE111 membrane. The separation factor for the other four composites have been consistently low (between 13 and 3). The main difference is that between composite1 and the rest we installed an inertial separator to remove excess moisture from the feed stream. This separator may be too efficient and the membranes may be drying out. Another possibility is that the membranes may just not be made well enough and sufficient uncoated pores may exist to subvert the separation efficiency. We tested a membrane which had been removed from the field test rig in our laboratory permeation equipment. Those results are presented in Figures 7 and 8. Again good agreement between the field test and our lab experiments.

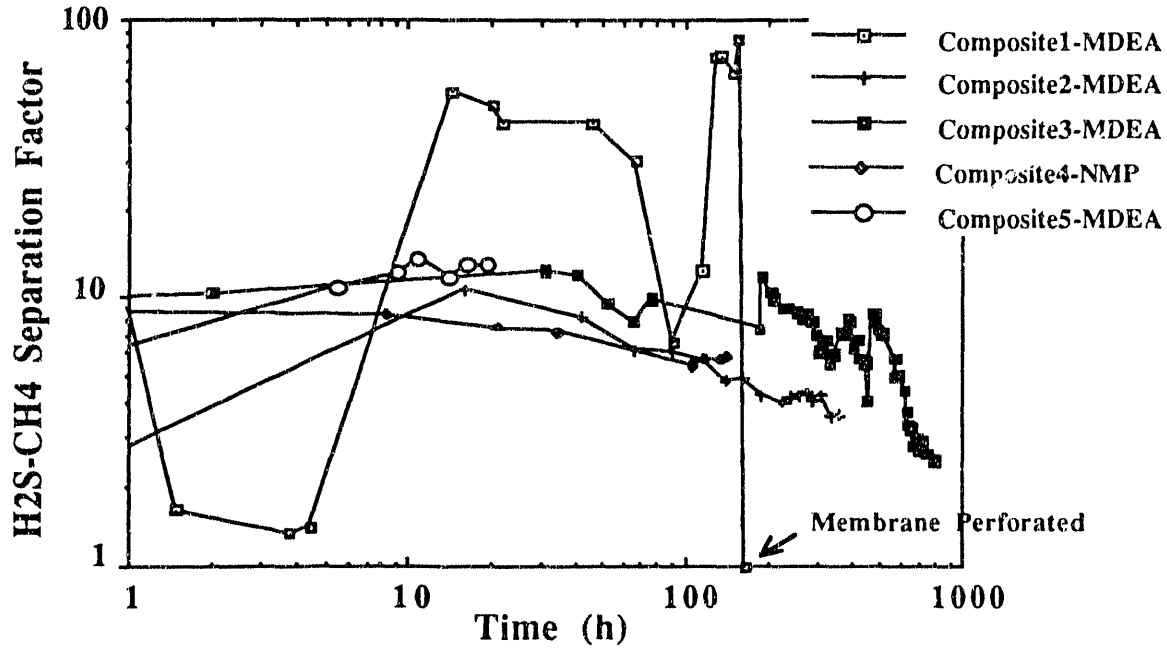

Figure 6. Separation Factor Between H_2S and CH_4 For All the Composite Membranes

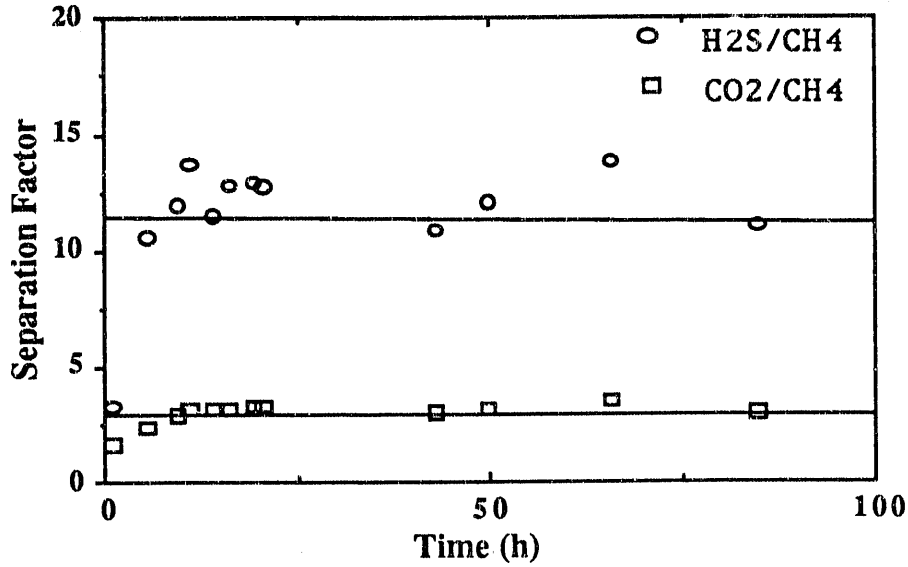

Figure 7. Separation factor for CO_2/CH_4 and H_2S/CH_4 (Carter Creek Field Test 17 Jul -24 Sep 1991-intermittent, Composite No. 5)

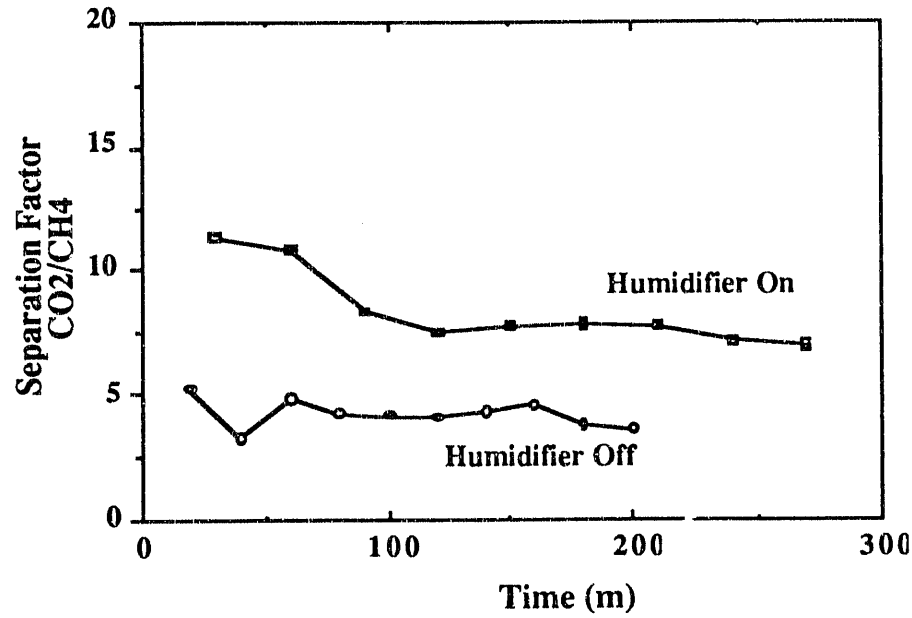

Figure 8. Separation factor for CO_2/CH_4 and H_2S/CH_4 (NIST Dec 1991, Composite No. 5)

It has become clear that casting PFSA films from solution probably results in membranes with significantly different morphologies than the commercial films. To verify this we ran tests of cast films (no support) and NE111 in both Na^+ and EDA^+ forms. A mixture (10% CO_2, 70% CH_4 in He) was run at increasing total pressures. The separation factor for these experiments are presented in Figure 9. These results exhibit the facilitated transport behavior for both types of

membranes at low CO_2 partial pressure and the separation factor seems to converge at high pressures. When we run a cast composite film the difference between it and the NE111 seems to become more significant. This is shown in Figure 10.

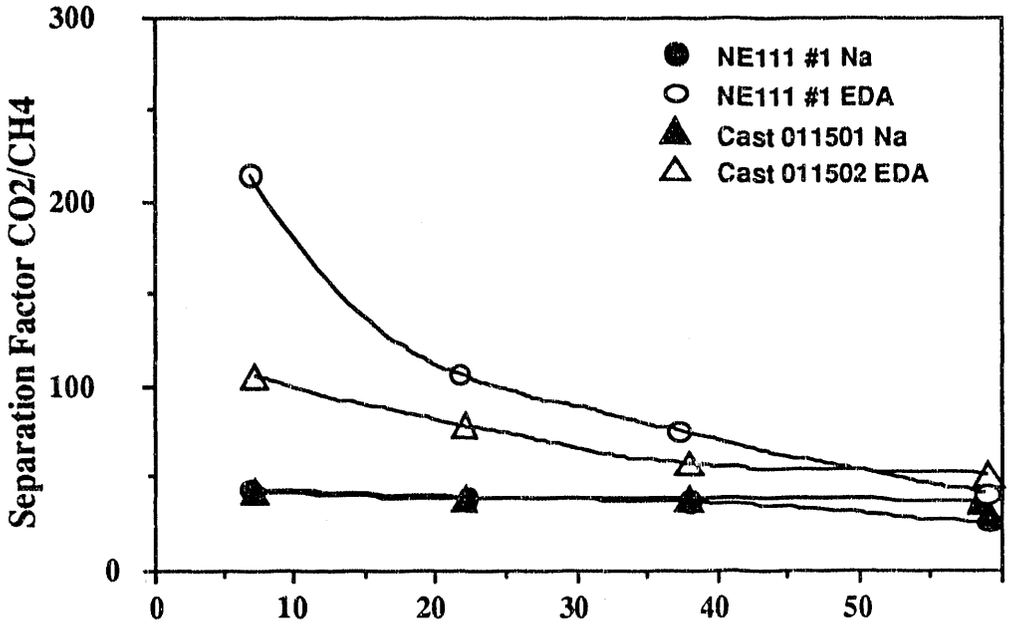

Figure 9. Separation factor for CO_2/CH_4 NE111 and cast films of PFSA

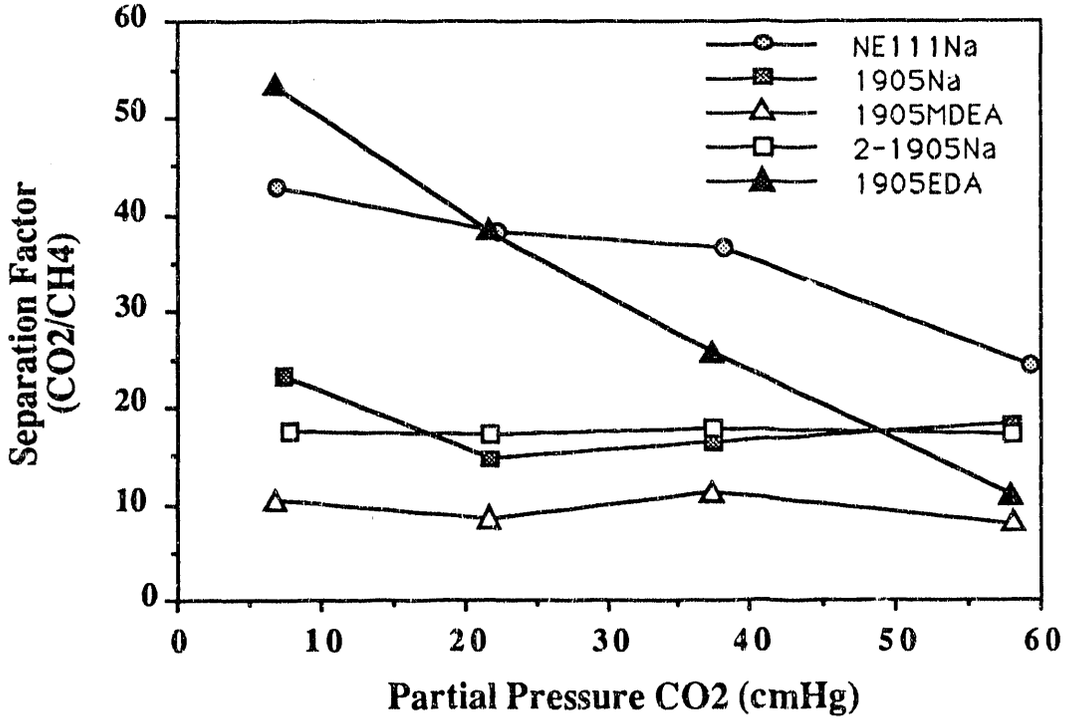

Figure 10. Separation factor for CO_2/CH_4 NE111 and cast composite films of PFSA

The designation 1905 refers to the cast composite. The order of the experiments is as listed in the key. The replicate of the Na^+ form was done after the MDEA form and there may have been incomplete removal of the MDEA.

The results presented herein, and others not discussed, leads us to believe that cast membranes cannot effectively imbibe the MDEA because they have a tighter morphology. Therefore Na^+ form would probably be superior for H_2S removal and EDA for CO_2. The NE111 continues to be a more productive membrane than the cast (composite or unsupported) films. We need to better understand why this occurs before we can make economically productive membranes.

FUTURE WORK

We will continue to make composite membranes using (polypropylene) and teflon (PTFE) substrates. These membranes will be evaluated in time-lag experiments (with H_2O as the solvent and Na^+ as the carrier) with CO_2 and/or N_2 to determine whether defects exist. This will also help identify the thinnest membranes. The most optimal membranes will be reproduced in larger areas and their permeation properties will be characterized with respect to pure and binary gas mixtures from the following list: CO_2, CO, H_2S, CH_2 and H_2.

Testing will be at ambient temperature (288 - 303 K) and pressures up to 3.4 MPa (500 psig). Field test characterization will be done on a test module, containing at least 0.1 m^2 of membrane area based on the best composites from the above. The module will be evaluated in laboratory studies prior to being introduced to the field test site.

A final report detailing coating techniques, permeability characterization tests and extended field test results will be prepared. An engineering analysis of the membrane transport results will be used to develop a process design for treating a typical commercial stream. This engineering analysis will include an assessment of combining unit operations, i.e., membrane devices and gas absorption and adsorption. A simple cost evaluation will be developed based on this process design.

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