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Gas Separation Using Ion Exchange Membranes for Producing Hydrogen from Synthesis Gas

Quarterly Report 22 Covering the Period October 1, 1991 to December 31, 1991

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This report covers work during the three month period between October 1, 1991 and December 31, 1991. The main goal of this project is to demonstrate the use of facilitated transport membranes to separate gases resulting from the formation of H_2, specifically CO_2 and H_2S from CO and H_2. As part of this goal we are running a field test at a producing natural gas plant (Carter Creek Chevron Natual Gas Plant, Evanston, WY) to evaluate the performance and long term stability of candidate membranes. Laboratory work at NIST leads and parallels the field tests.

Objectives

1. Perform extensive tests in the laboratory on membranes removed from the Carter Creek field test apparatus as well as other potential field test samples prepared in our laboratory and by the DuPont Co. The data obtained are to be used to evaluate the separation and productivity performance of the test samples.

2. Test Dupont-supplied spiral wound gel-swollen Nafion® module.

Carter Creek Membranes/Laboratory Sample Membranes

Through a series of tests in our laboratory and at the Chevron/Carter Creek test rig,we are establishing the apparent separation and productivity capabilities of polymer membranes imbibed with various solvents and chemical carriers. In some samples the membranes are also subjected to solvent-swelling heat treatment (gel-treatment).The polymer material is polyperfluorosufonic acid (PFSA-Nafion). The chemical carriers, e.g. methyldiethanolamine (MDEA) and ethylenediamine (EDA) enhance the transport and selectivity of the membrane. They may be in solution with H_2O, glycerol, ethylene glycol, and n-methylpyrrolidone (NMP). Nafion 117 (N117) is a commercial film, 200 microns thick, which is available from DuPont Co. A developmental polymer film, Nafion 111 (NE111) 30-40 microns thick was made available to us by the DuPont Co.

PFSA can be heat treated to form a gel-like substance and we have found that the new morphology resulting from the treatment results in an enhanced productivity and permeability. However, on a theoretical basis, thinner films promote increased productivity for a given permeability, so we are experimenting with techniques for casting very thin films from solutions of PFSA and various carrier/solvents onto microporous substrates. The combination of polymer material and substrate is termed a composite thin film membrane. All of the above mentioned polymer films have been the subjects of our measurements.

According to theory, the flux (or permeance) of a permeating component is proportional to the driving force, in this case the difference of partial pressure or composition across the film, and is also inversely proportional to the thickness. The constant of proportionality is the permeability of the film. While we do observe this trend, we admit to a sparsity of data within the various classes of membranes tested, both with regard to variable thickness and driving force (ΔP or composition). The gel-treated membranes offer greater separation capability and in fact show greater permeance (permeance is permeability divided by thickness) than that of the composite thin film membranes (PFSA composites). The greater permeance is in conflict with expectations, since the composite PFSA is thinner. The mechanism for enhanced separation observed for GT NE111 and the apparent discrepancy in permeance, compared to the composite thin film membranes should be probed further. Also the thin film morphology and casting "recipe" needs to be correlated with the experimental separation performance. We are currently seeking to resolve these issues.

The humidification of the membrane is also apparently important to maintaining the separation performance. All of our data are consistent in that regard.

The following Figs. 1-5 show that there is a correlation between our laboratory results and the data obtained in the field.

The Carter Creek field test run #1 was a partially, gel-treated NE111 with H_2O as the solvent and methyldiethanolamine (MDEA) as the chemical carrier. This membrane was meant to promote H_2S transport relative to CH_4 and other hydrocarbons. Fig. 1 shows the H_2S/CH_4 and CO_2/CH_4 separation factors over time. The H_2S/CH_4 separation factor (~50) is significantly higher than those obtained with current gas membranes 10-30. This membrane is not productive enough to be commercially viable but it demonstrated that high acid gas selectivities could be obtained and maintained on a real process stream over extended periods.

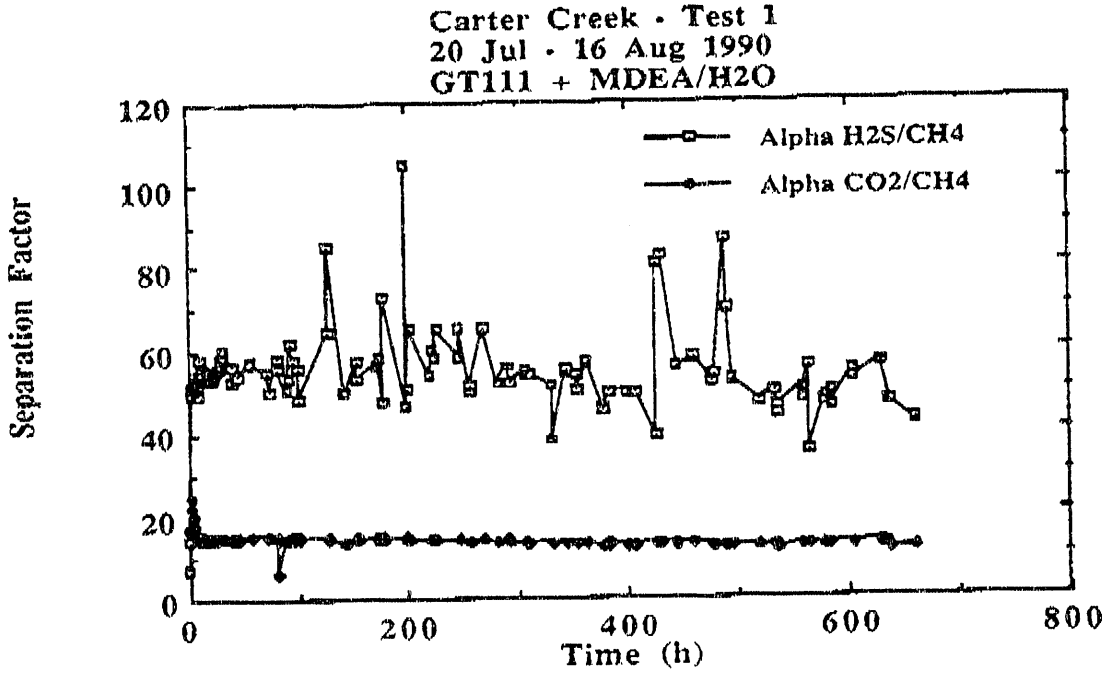

Figure 1. Separation Factor (α) for the acid gases relative to CH_4 for Carter Creek GT111 No. 1.

We also lab-tested the membrane used in this initial Carter Creek test, the GT111 No. 1 (gel-NE111). We have done two replicates using a feed pressure of 100 psig and a feed gas composition of:

10%	CO_2	10%	N_2
2%	CO	5%	C_2H_6
60%	CH_4	3%	C_3H_8
10%	He		

The results for the CO_2/CH_4 separation factor are shown in Fig. 2. The separation factor is at the same level we observed for the H_2S/CH_4 and greater than what we found for CO_2/CH_4 with the same membrane in the field test. We would expect the lab result for the CO_2/CH_4 separation factor to increase, relative to a test with H_2S present, if there is competition between CO_2 and H_2S for the available solute sites in the membrane.

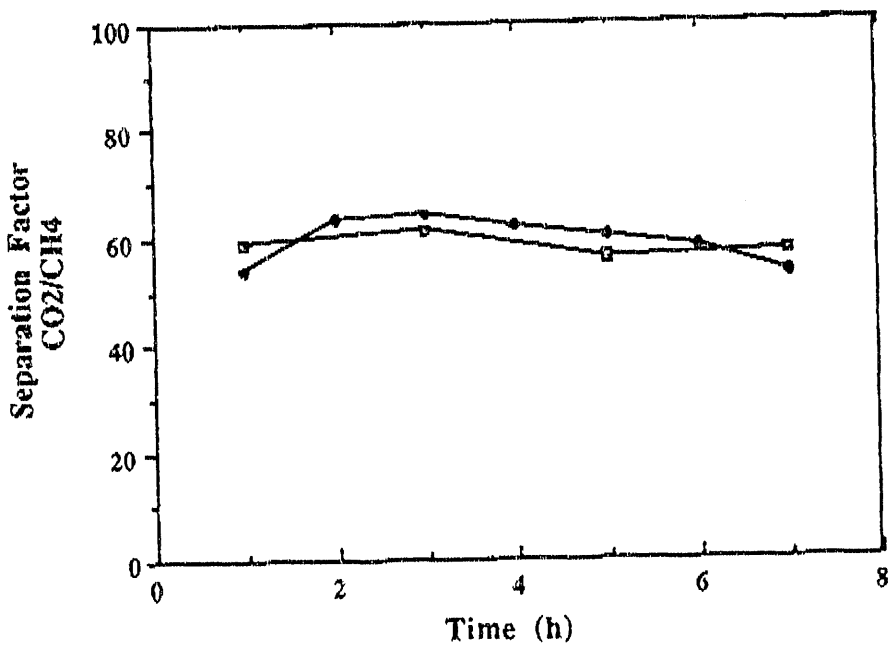

Figure 2. Laboratory Test of Carter Creek GT111 No. 1, CO_2/CH_4 Separation Factor.

We have also completed evaluation of H_2S permeation with this membrane. The experiment was run slightly above atmospheric pressure (~70 cm Hg) and the composition was:

6.89%	CO_2	16.89%	N_2
1.38%	CO	3.44%	C_2H_6
41.31%	CH_4	2.07%	C_3H_8
6.89%	He	14.12%	H_2S

The results are shown in Fig. 3. These results indicate that the membranes had not reached steady-state yet but the separation factors are quite high. At low acid gas feed partial presssures (such as in this experiment) the reactive pathway is most efficient at providing a high separation factor. In general the separation factor results depicted here are consistent with the results we obtained in the Carter Creek experience with this membrane.

The Composite Membrane No.5, a composite thin film PFSA membrane supported by a 3M/817-14G microporous polypropylene substrate and employing MDEA (methyldiethanolamine) as the carrier gave the following mass transfer results in the Carter Creek test rig (Fig. 4). The H_2S/CH_4 separation factor went from an average of 12 to an average of 8 over the course of the evaluation and the CO_2/CH_4 was 3 - 4. This was cut in half to fit our lab module and we ran two experiments with the same half. In one run we fed the feed mixture without humidification and in the second run we humidified the feed by bubbling it through water. The results of these two experiments are shown in Fig. 5. By comparison to Fig. 4 we see that the CO_2/CH_4 separation factor for the unhumidified feed was very similar to that obtained in Carter Creek. And with feed humidification some improvement was obtained.

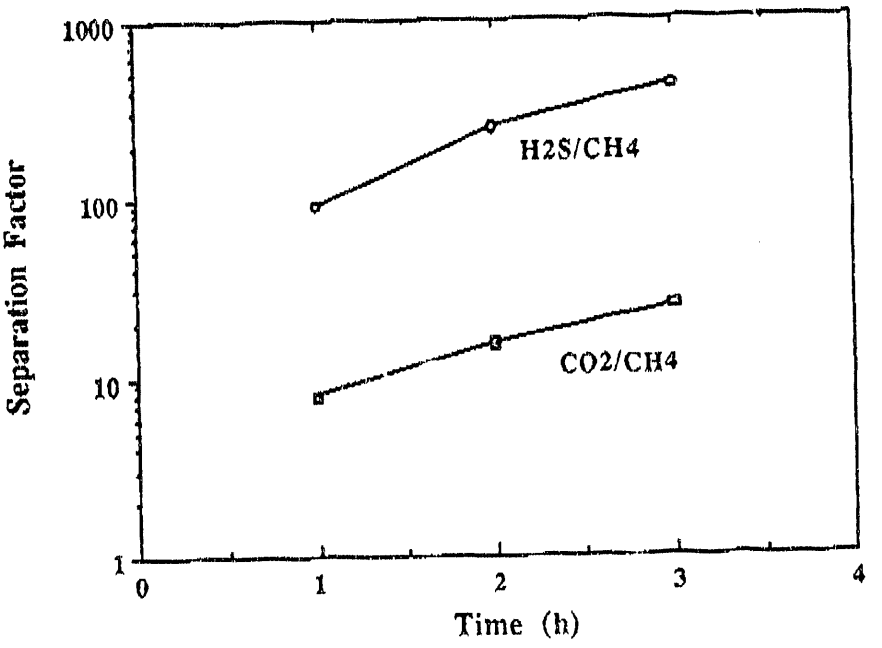

Figure 3. Laboratory Test of Carter Creek GT111 No. 1, CO_2/CH_4 and H_2S/CH_4 Separation Factor.

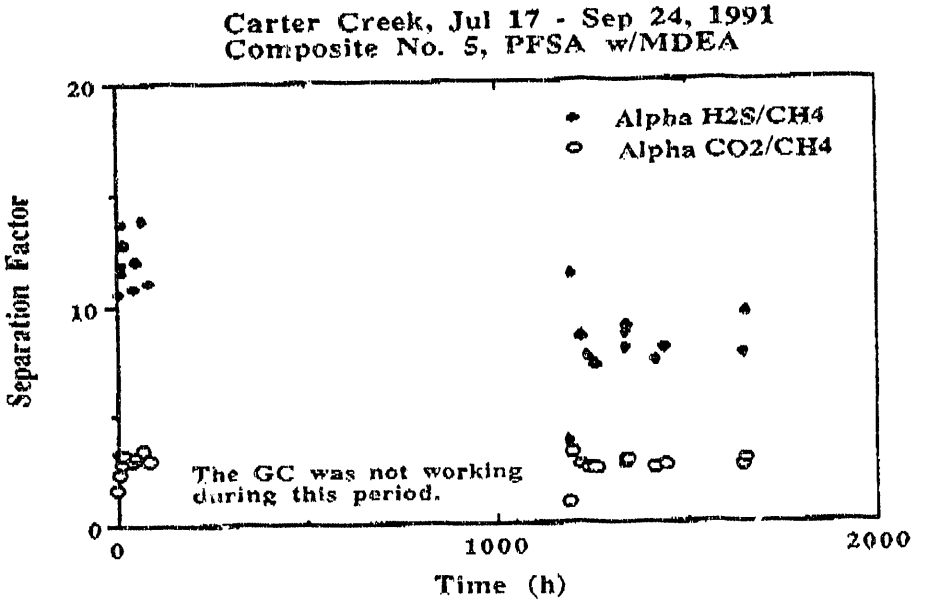

Figure 4. Separation Factor (α) for the acid gases relative to CH_4 at Carter Creek for Composite No. 5.

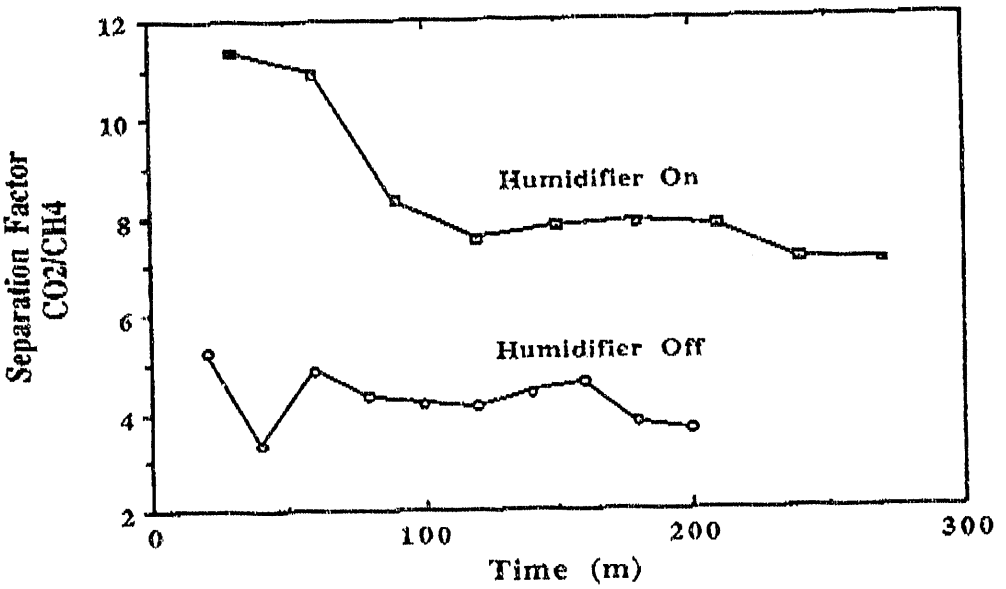

Figure 5. Laboratory Test of Carter Creek Composite No. 5, CO_2/CH_4 Separation Factor.

Dupont spiral wound module

We received a prototype GT NE111 spiral wound module from the Dupont Co. and subjected it to the following tests:

1. Pure component CO_2 and N_2 permeation measurements
2. Liquid water hydrotest
3. Multicomponent gas permeation using our laboratory flow system

The results of the permeation measurements indicated that the module had an internal flaw which allowed convective transport between the feed and permeate sides of the membrane. A flaw of this nature, renders the module unusable for separation. A liquid water hydrotest substantiated the suspicion; a multicomponent gas permeation test, using our laboratory flow system and feed and permeate composition measurement system also confirmed the presence of an internal flaw. Dupont has agreed to supply a new module which we shall test upon arrival.

Conclusions

Our upcoming work will be be focused on obtaining a composite membrane which incorporates the same permeability as the gel-NE111 into a thinner membrane layer. We anticipate the next Quarter's activities to be only in the laboratory with the exception of installing the duPont module when it arrives.

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