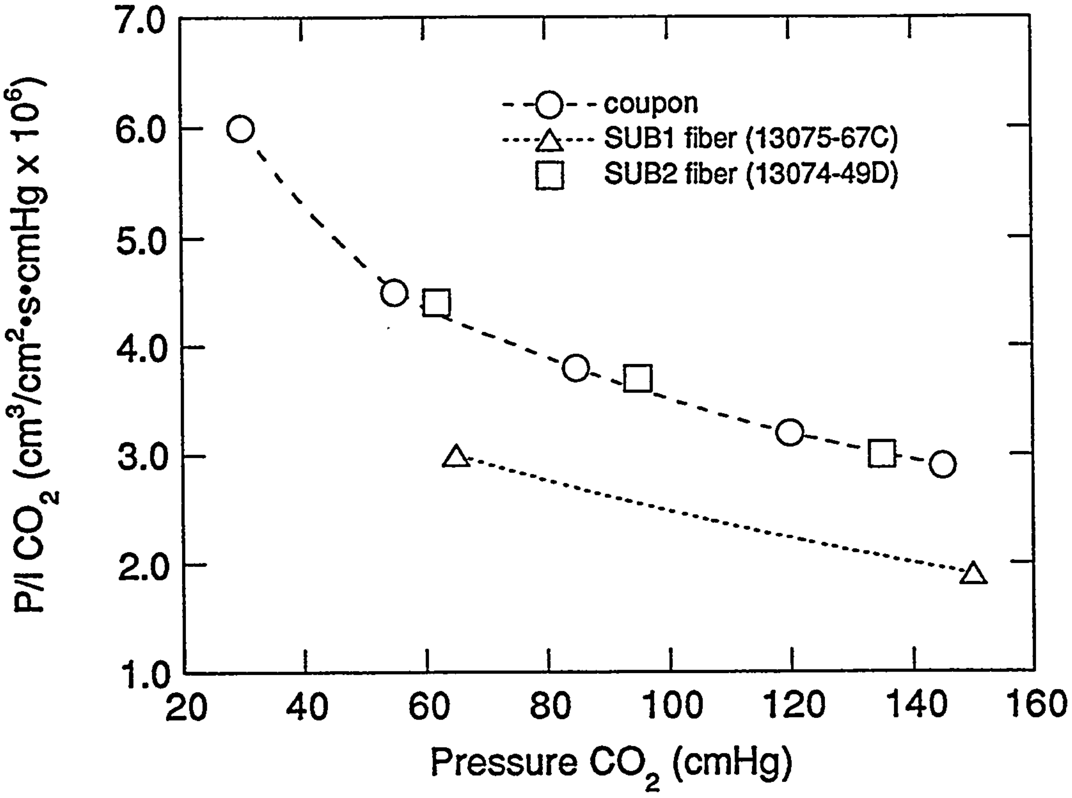
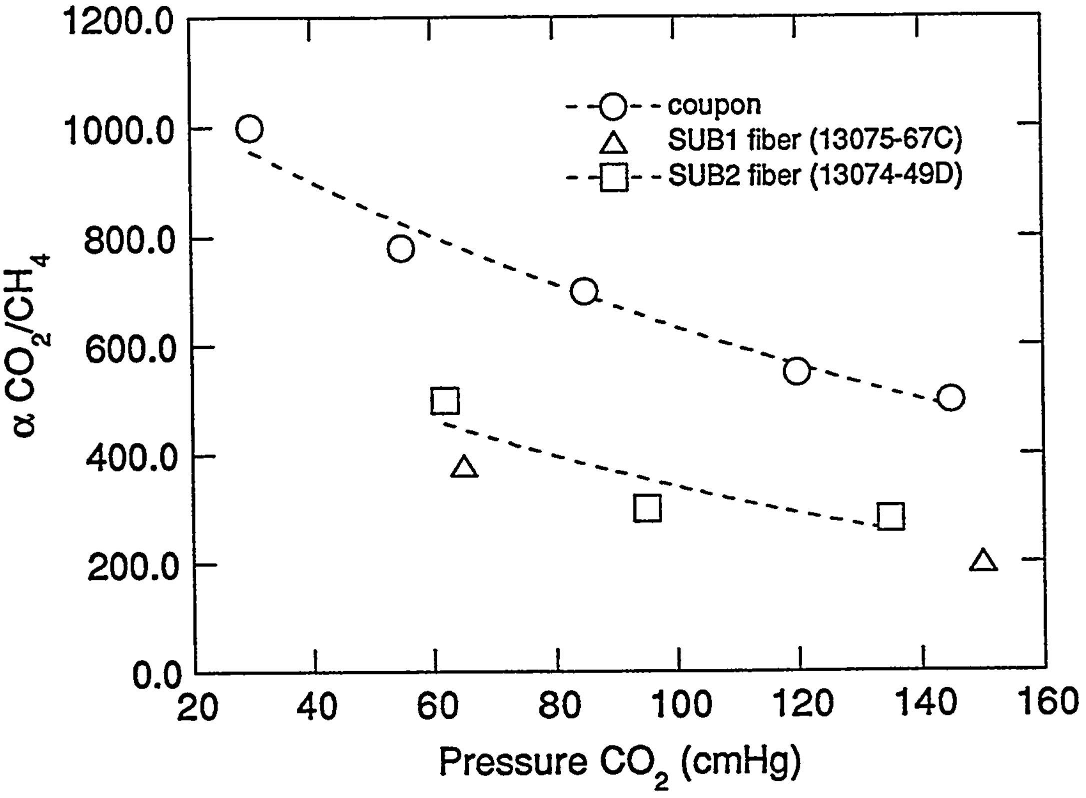
Figure 4-15A

Comparison of Polysulfone-Supported PVBTAF Planar Coupons and Hollow Fiber Lab Modules



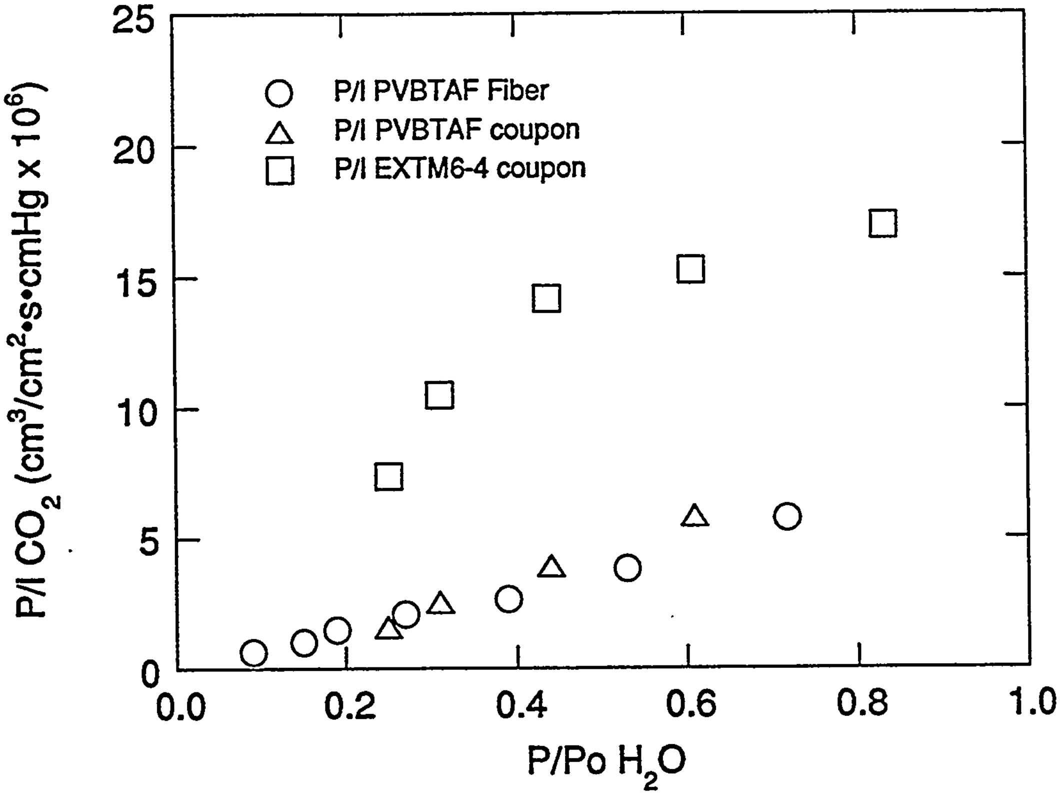
DOE4/F4-15A

Figure 4-15B



DOE4/F4-15B

Figure 4-15C



DOE4/F4-15C

V. Recent Advances in the Development of Active Transport Materials

1.0 Influence of H_2O Vapor on ATM Permeation Properties

NMR results[38] support the following acid-base chemistry for the reaction of CO_2 with TMAF and PVBTAF:

$$2F^- + H_2O = HF_2^- + OH^- \tag{1}$$

$$OH^- + CO_2 = HCO_3^- \tag{2}$$

$$\text{net rxn:} \quad 2F^- + H_2O + CO_2 = HF_2^- + HCO_3^- \tag{3}$$

Water enters directly into CO_2 complexation as one of the reactants. It is believed that the complexation reaction uses water solubilized within the membrane [H_2O]; that is, dissolved water in equilibrium with water vapor in the feed stream. From the above equations, an increase in [H_2O] is expected to drive the reaction forward, however, increasing [H_2O] also increases the solvation sphere of F^- and hence decreases its basicity. Thus, the net effect of increasing [H_2O] at constant temperature is to decrease the equilibrium constant, $K_{eq}CO_2$, for reaction 3; i.e. less CO_2 is dissolved in the membrane as HCO_3^-. This model has been verified experimentally for TMAF and by analogy for PVBTAF (Figure 5-1).

The equilibrium constant for CO_2 complexation is highest for TMAF•$2H_2O$ (n=2)* and decreases as the hydration state is increased. Thus, CO_2 ATMs are expected to have the maximum loading of chemically bound CO_2 at feed stream dew points which produce low hydration state AT material. It is therefore essential to know how the hydration state of the AT material varies with feed stream dew point.

1.1 Measurement of H_2O Absorption Isotherms

Aqueous PVBTAF and EXTM6-4** solutions were prepared as described previously.[29] "Dry" films were prepared by evaporating the solutions to dryness under nitrogen followed by vacuum at 25°C. Before an H_2O absorption isotherm could be measured, the composition of the starting material had to be identified; that is, the hydration state of the "dry"

---

[38] R. Quinn, Air Products internal memorandum, 1991.

* TMAF•1H_2O absorbs CO_2 irreversibly.

** EXTM6-4 is a proprietary blend of AT polymer and AT salt.

Figure 5-1

Chemical Complexation of CO_2 by TMAF • nH_2O

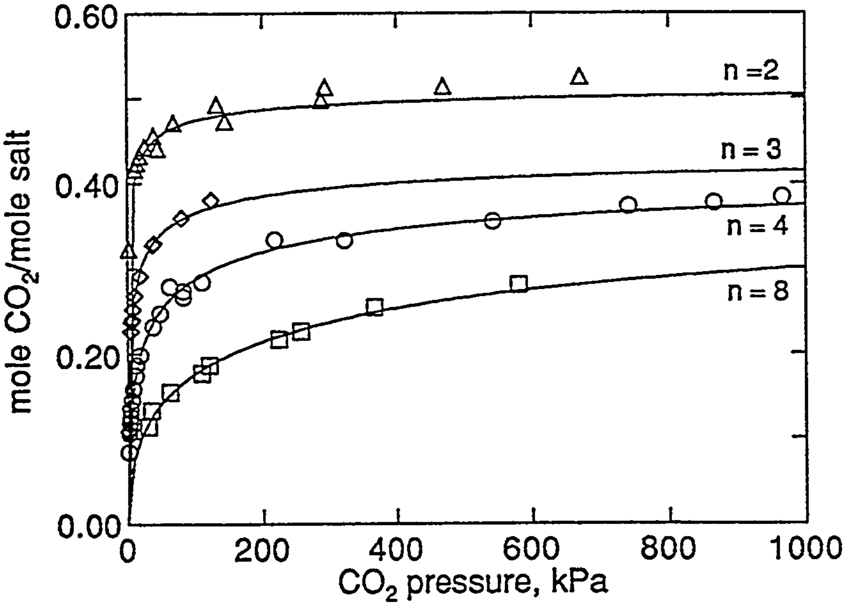


Table 5-1
NMR Peak Assignments

		# of protons	
Proton	chemical shift	PVBTAF	EXTM6-4
a	1.3 ppm	2.6	2.5
b	6.4,6.9 ppm	3.6	3.6
c	4.0 ppm	1.6	1.6
d	2.7 ppm	9.0	6.4
e	4.6 ppm	2.6	3.8

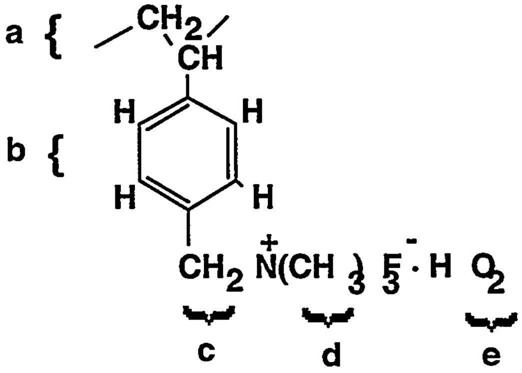


Figure 5-2

Thermal Decomposition of PVBTAF and EXTM6-4

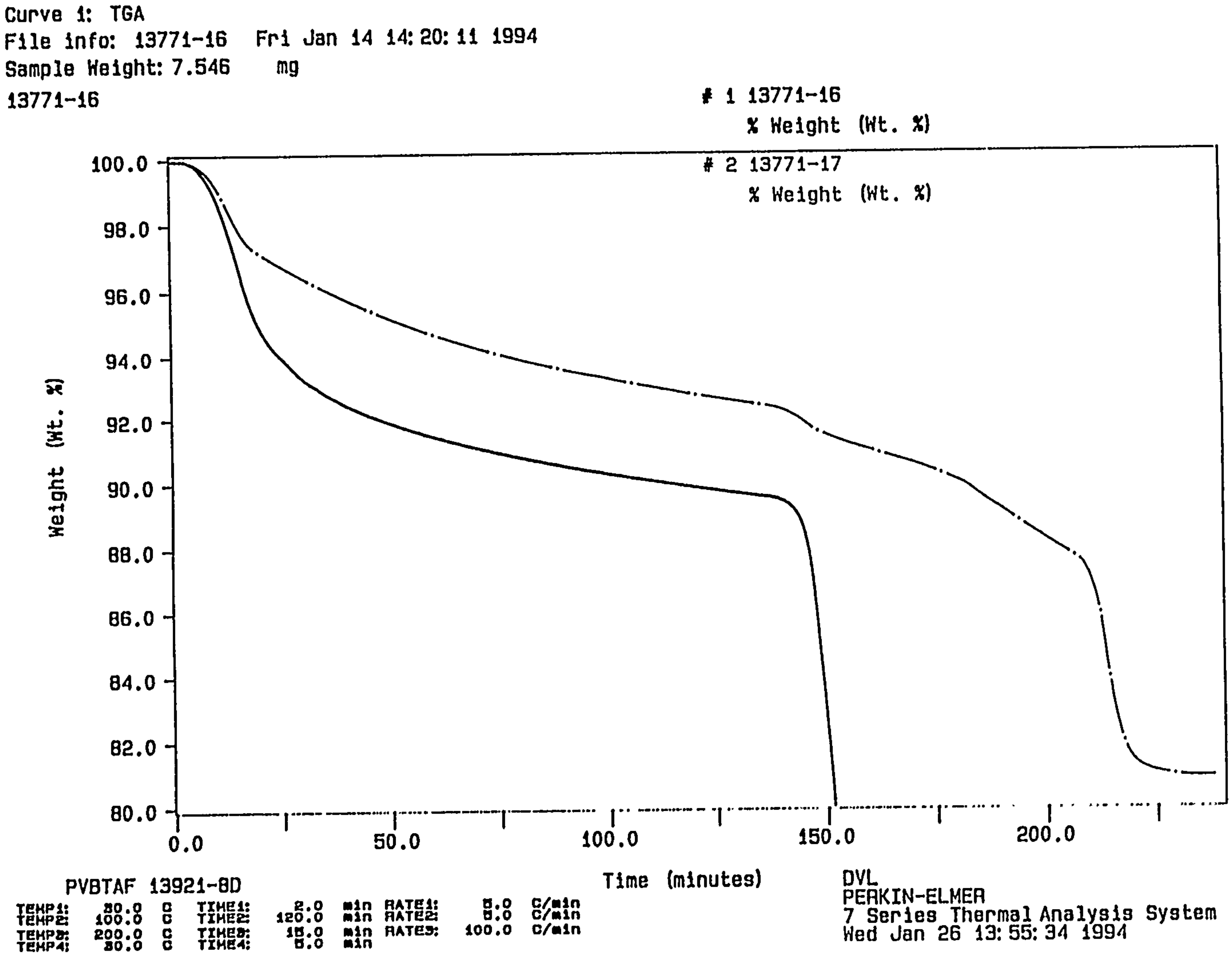
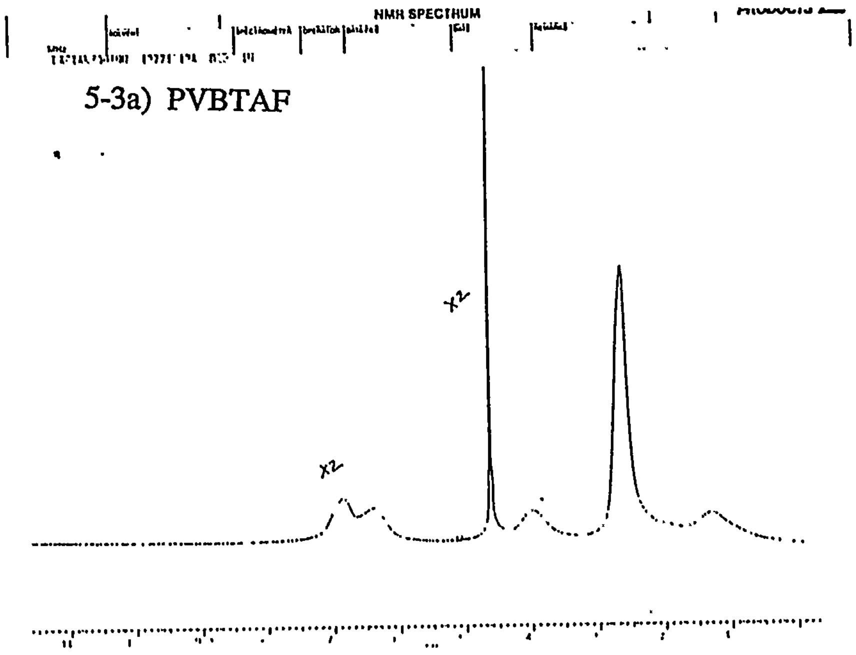
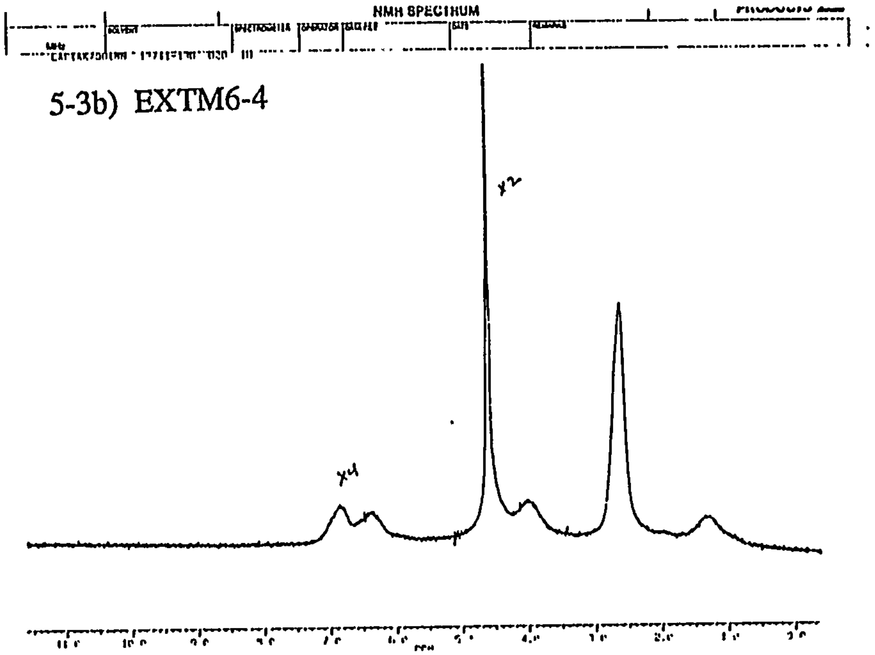


Figure 5-3
^{1}H nmr of PVBTAF and EXTM6-4

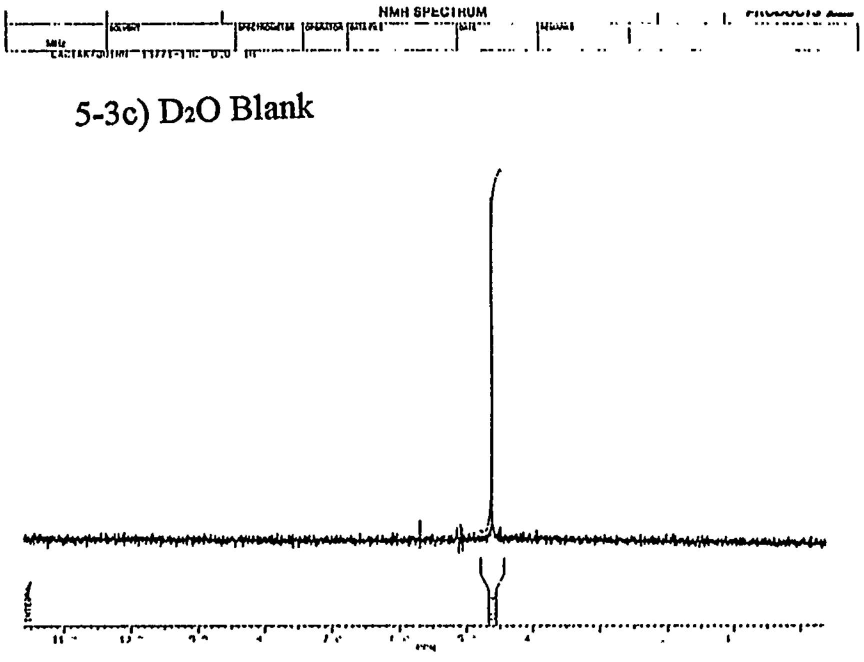
5-3a) PVBTAF



5-3b) EXTM6-4



5-3c) D_2O Blank



Results of the TGA and NMR experiments are summarized and compared in Table 5-2. Agreement between the methods is excellent. The composition of the "dry" polyelectrolytes can best be expressed as PVBTAF•$1H_2O$ and EXTM6-4• $5H_2O$. It is interesting to note that both samples contain $1H_2O/1F^-$.

Table 5-2: Water Content of "Dry" PVBTAF and EXTM6-4

			wt% H_2O		
Material	Sample Ref.	Source Ref.	TGA	NMR	Hydrate #
PVBTAF	13771-16	13921-8D	9.7	10.7	0.98
EXTM6-4	13771-17	13921-8E	7.5	6.7	4.88

The H_2O absorption isotherms for PVBTAF and EXTM6-4 were determined using a McBain microbalance. Table 5-3 and Figures 5-4 and 5-5 relate the partial pressure of H_2O in the feed stream to the hydration state of PVBTAF and EXTM6-4. Some interesting points to note about the isotherms include:

1) Consistent with the addition of the AT salt, on a "molar" basis EXTM6-4 absorbs much more H_2O than does PVBTAF (Figure 5-4), however

2) On a fluoride ion basis (Figure 5-5), there is no significant difference in the amount of water absorbed by the two polymers. This suggests that solvating the F^- ion is the driving force behind the water affinity of both these materials.

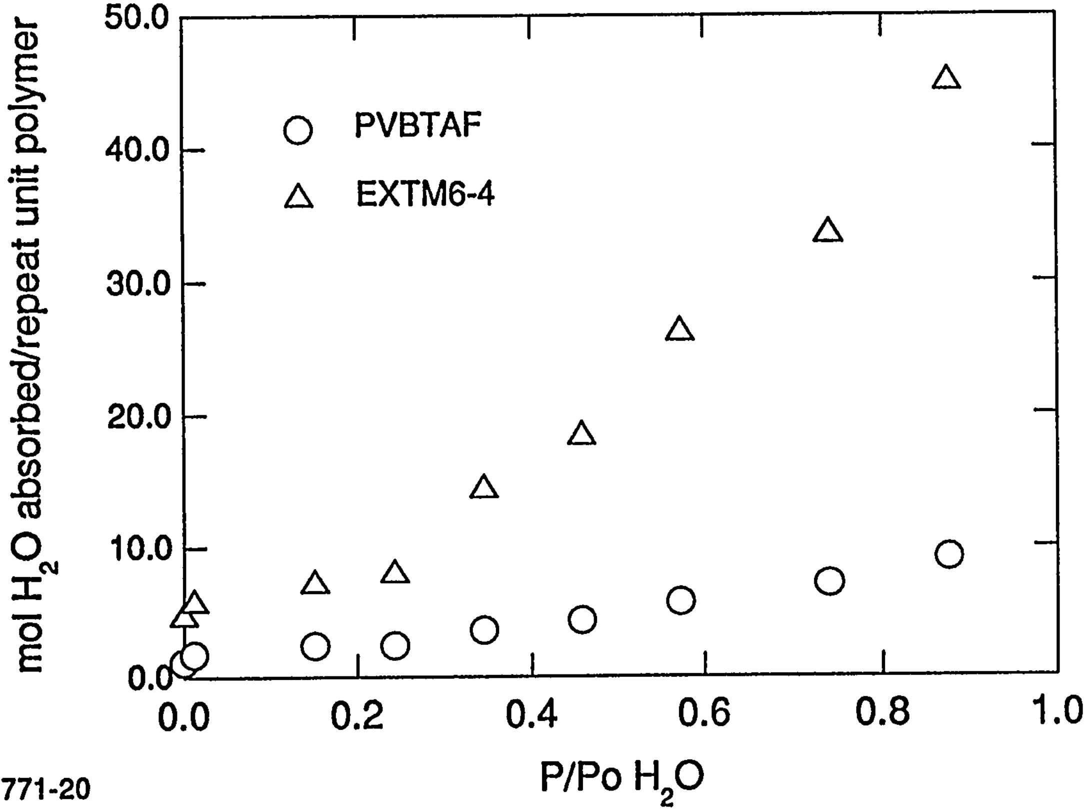
3) Both isotherms contain an inflection point at P/Po ≈ 0.3. At lower values of P/Po, the slope of the isotherm is almost flat. As P/Po passes through ≈ 0.3, the slope changes and there is a marked increase in the amount of H_2O absorbed.

Table 5-3

H_2O Absorption by PVBTAF and EXTM6-4 at 25° C

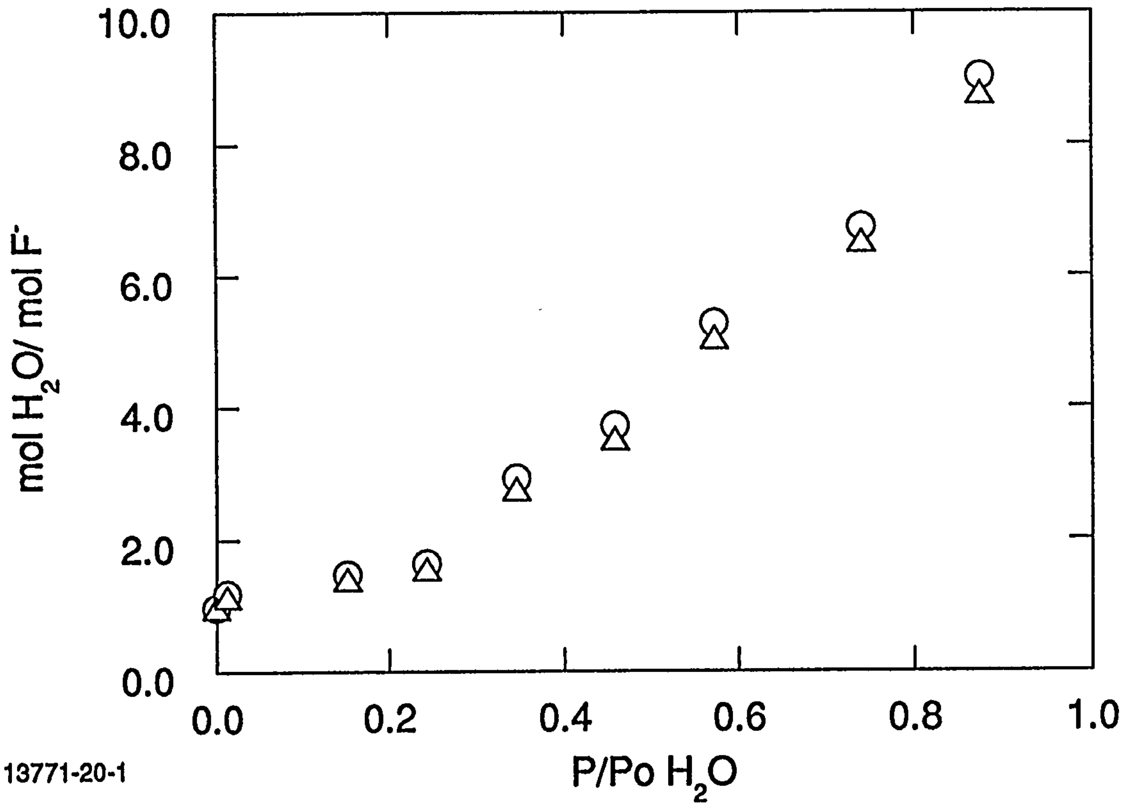
PVBTAF P/Po	mmol H_2O / g sample	sample #1 mol H_2O / repeat unit	mol H_2O / mol F	mmol H_2O / g sample	sample #2 mol H_2O / repeat unit	mol H_2O/ mol F
0.000	0	1.17	1.17	0	1.17	1.17
0.123	2.83	1.78	1.78	2.89	1.80	1.80
0.152	6.04	2.47	2.47	5.80	2.42	2.42
0.243	5.98	2.46	2.46	2.91	2.45	2.45
0.345	11.27	3.61	3.61	10.95	3.54	3.54
0.459	14.75	4.36	4.36	14.53	4.31	4.31
0.573	21.35	5.78	5.78	21.05	5.72	5.72
0.741	27.75	7.17	7.17	27.64	7.14	7.14
0.876	37.06	9.18	9.18	36.89	9.14	9.14

EXTM6-4 P/Po	mmolH_2O/g sample	sampe #1 mol H_2O/ repeat unit	mol H_2O / mol F	mmol H_2O/g sample	sample #2 mol H_2O / repeat unit	mol H_2O / mol F
0.000	0	4.88	0.98	0	4.88	0.98
0.123	1.18	5.92	1.19	0.90	5.68	1.14
0.152	2.83	7.38	1.48	2.41	7.01	1.40
0.243	3.75	8.19	1.64	3.29	7.79	1.56
0.345	10.99	14.59	2.92	10.05	13.76	2.75
0.459	15.52	18.59	3.72	14.37	17.57	3.51
0.573	24.39	26.42	5.28	23.10	25.28	5.06
0.741	32.68	33.74	6.75	31.40	32.62	6.52
0.876	45.66	45.20	9.04	44.13	43.85	8.77



13771-20
DOE4/F5-4

Figure 5-4
H2O Absorption by PVBTAF and EXTM6-4 at 25°C Repeat Unit Basis



13771-20-1
DOE4/F5-5

Figure 5-5
H_2O Absorption by PVBTAF and EXTM6-4 at 25°C Fluoride Basis

1.2 Correlation of H_2O Absorption with Permselectivity

This information can be used to rationalize the observed properties of PVBTAF and EXTM6-4 composite membranes. Typical results for a CO_2/CH_4 separation as function of P/Po are plotted in Figure 5-4. The increasing permeance of both gases at higher P/Po suggests that the increasing quantity of water absorbed under these conditions acts to "loosen" the polymer network, making diffusion more facile. Since this is a nonselective process, it stands to reason that the flux of all components increases. This hypothesis is being verified experimentally using PGSE-NMR.

We observe experimentally that while P/l of all gases increases with increasing P/Po, the selectivity passes through a maximum. The curve of $\alpha CO_2/CH_4$ vs P/Po for a PVBTAF/Sub1 polysulfone hollow fiber membrane is, in Figure 5-6, superimposed on a graph of H_2O absorption. Clearly the maximum in the selectivity coincides with the flat portion of the isotherm. At very low P/Po it is likely that diffusion is limited because the polymer network, being ionic and having little absorbed water, is very "tight" and diffusion is slow. At P/Po greater than ≈0.35, there is a substantial decrease in selectivity. The reason for this is two-fold:

1) As described earlier, higher P/Po decreases the concentration of complexed CO_2

2) The ionic strength of the medium is lower at higher values of P/Po thus making the ionic barrier to CH_4 less effective, i.e. a diminishing of the "salting-out" effect.

The CO_2/H_2 selectivity of a EXTM6-4 polysulfone planar membrane is superimposed on the graph of H_2O absorption in Figure 5-8. Here however, the maximum selectivity is shifted to slightly higher P/Po. To rationalize this feature one need only consider the differences in ionic strength of the two polyelectrolyte solutions as shown in Figure 5-9. The curve of the ionic strength is nearly flat until P/Po≈0.3 at which point it decreases rapidly. It is interesting to note that the ionic strength of PVBTAF at it optimum P/Po (≈ 0.25) is equal to that of EXTM6-4 at P/Po≈0.45.

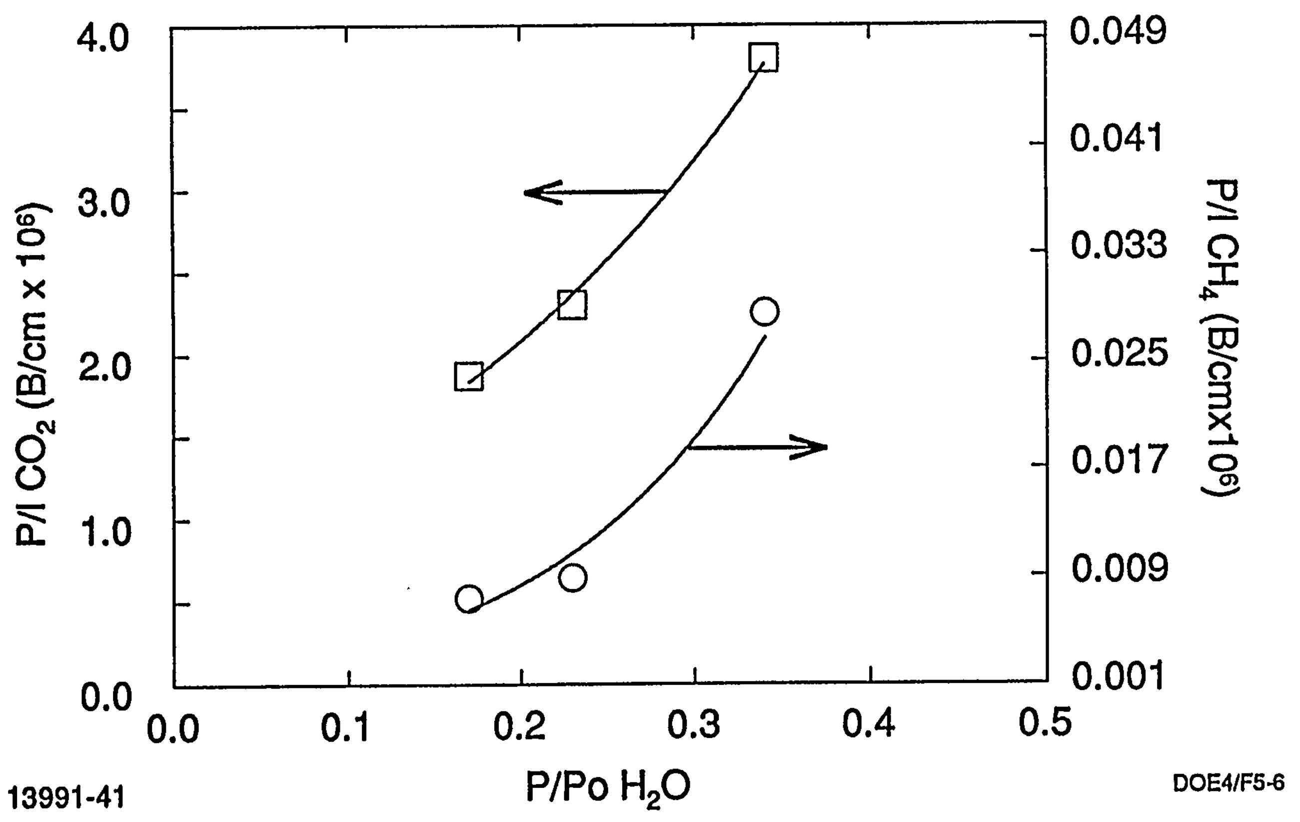


Figure 5-6

Permselectivity of a PVBTAF/Polysulfone Membrane as a Function P/Po

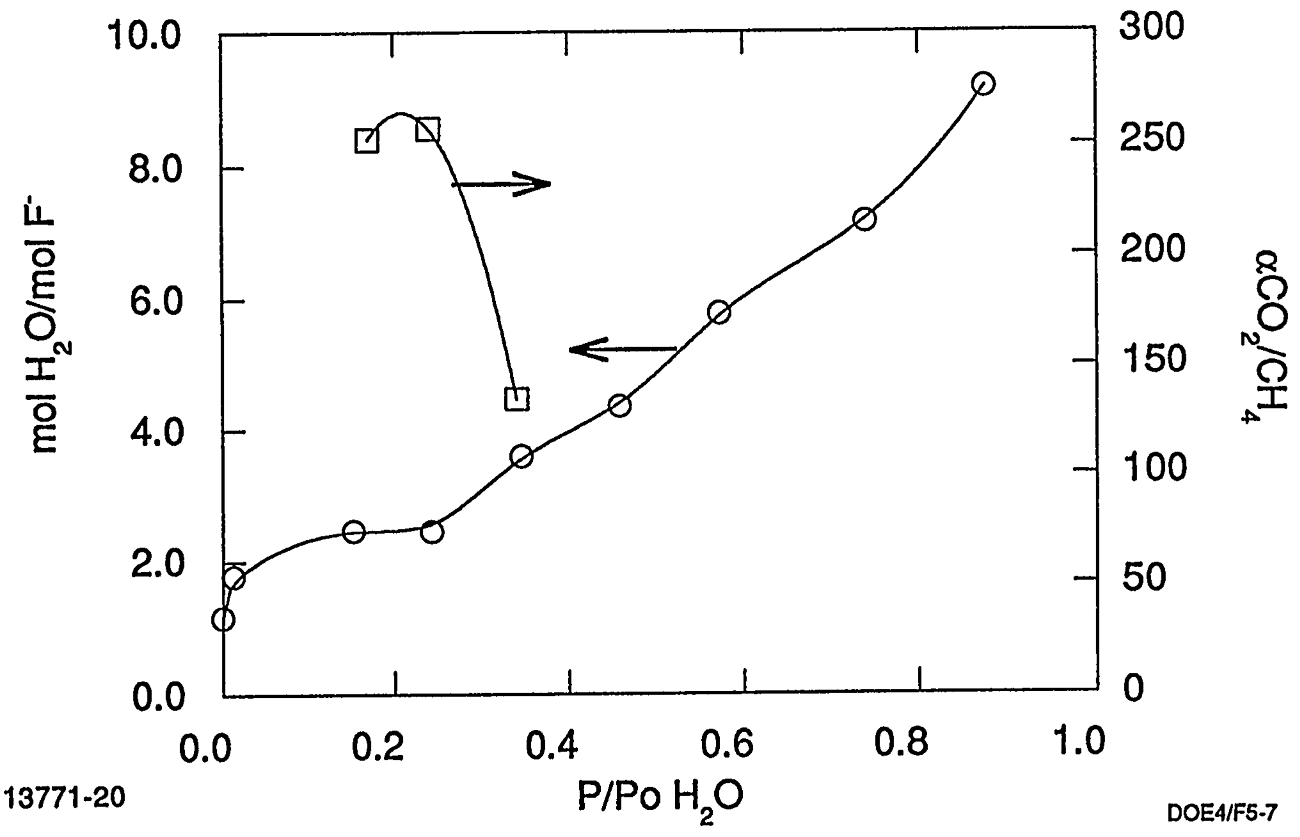


Figure 5-7
Selectivity and H2O Absorption of PVBTAF

Figure 5-8

Selectivity and H_2O Absorption of EXTM6-4

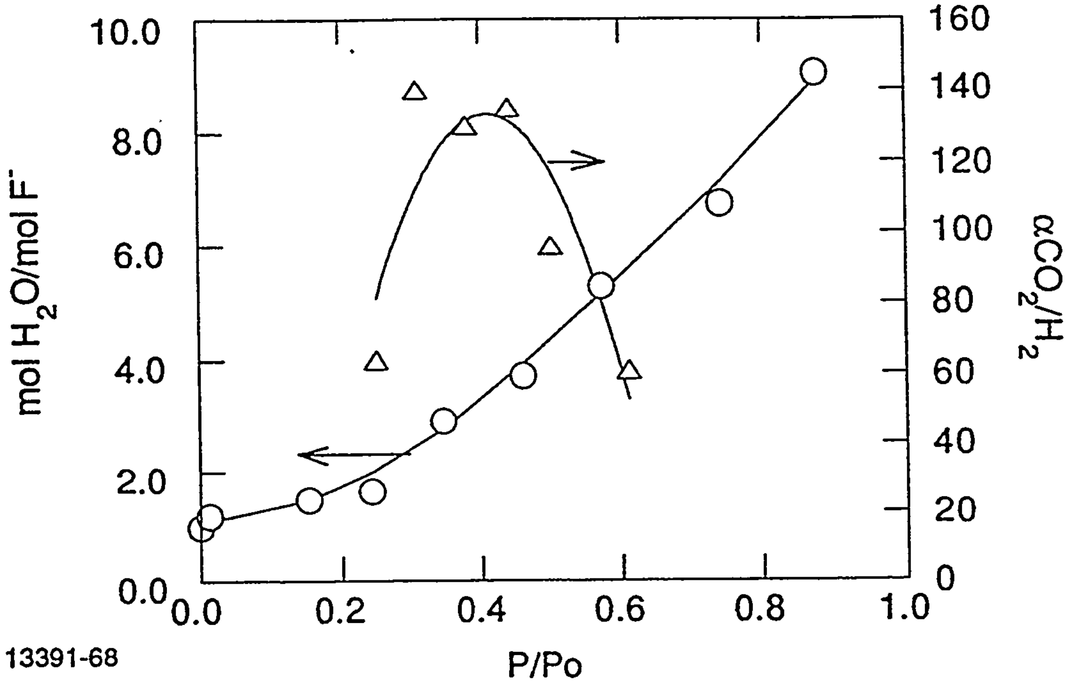
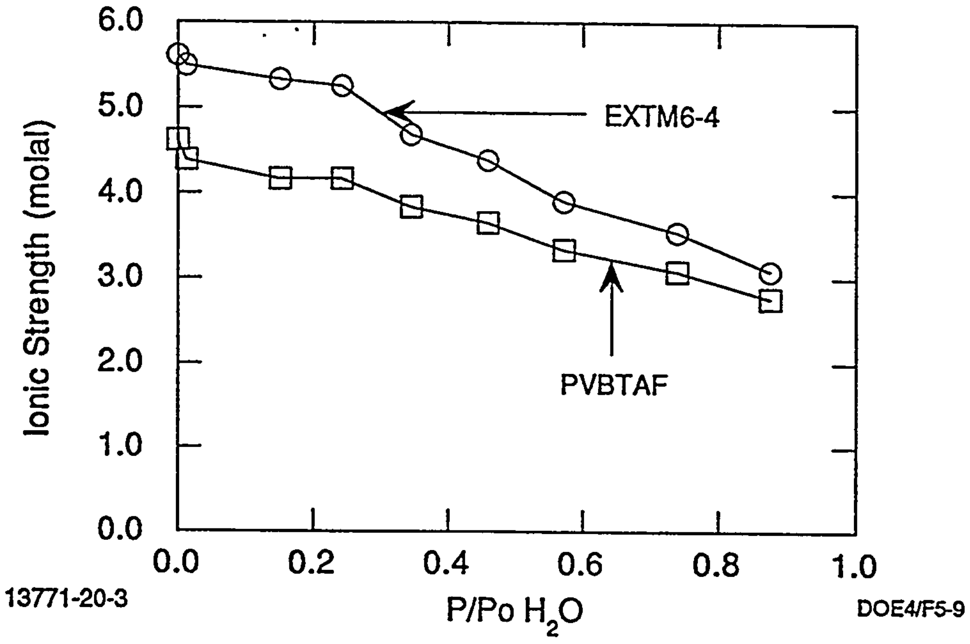


Figure 5-9

Ionic Strength of PVBTAF and EXTM6-4



1.3 Conclusions

The dew point-dependent permselectivity of CO_2-selective Active Transport membranes fabricated from poly(vinylbenzyltrimethylammoniumfluoride) [PVBTAF] or blends of polymers with AT salts can be related to the equilibrium water absorption of the materials. An inflection point in the isotherm correlates with the observed decrease in the selectivity of PVBTAF composite membranes. Differences in performance between PVBTAF and EXTM6-4 can be attributed to differences in ionic strength. Because extremes of dew point result in either delamination of the AT layer or loss of permselectivity it will be necessary to control the level of water in the feed stream to Active Transport membranes.

2.0 Assessment of H_2S Reactivity of ATM Membranes

2.1 H_2S Permselectivity

PVBTAF composite membranes also selectively permeate H_2S. Typical gas permeation properties of PVBTAF composite membranes are listed in Table 5-4. The H_2S permeance varies from 28 - 10 x 10^{-6} $cm^3/cm^2{\bullet}s{\bullet}cmHg$ [12582-40B1] over the pressure range studied indicating facilitated transport of that gas. The selectivity of >1000 to CH_4 is impressive.

The H_2S and CO_2 permselective properties of PVBTAF membranes depend on the composition of the feed gas. Both H_2S and CO_2 are acid gases and should compete for the same permeation sites. The H_2S permeance decreased by 15-40% when CO_2 was admitted to the feed gas at an equal partial pressure ([12582-40B2] and Figure 5-10). Similarly, the presence of H_2S in the feed suppress permeation of CO_2. Under comparable experimental conditions, addition of H_2S to the feed decreased the CO_2 permeance by approximately an order of magnitude (Figure 5-11).

H_2S/CO_2 selectivities ranged from 11 to 8. In this regard, PVBTAF membranes are unique and potentially useful for the separation of H_2S from CO_2-containing mixtures. Typical polymer membranes show little selectivity for H_2S over CO_2 with selectivities of 2 or less.

Table 5-4

H_2S Permselective Properties of PVBTAF Membranes at 22°C

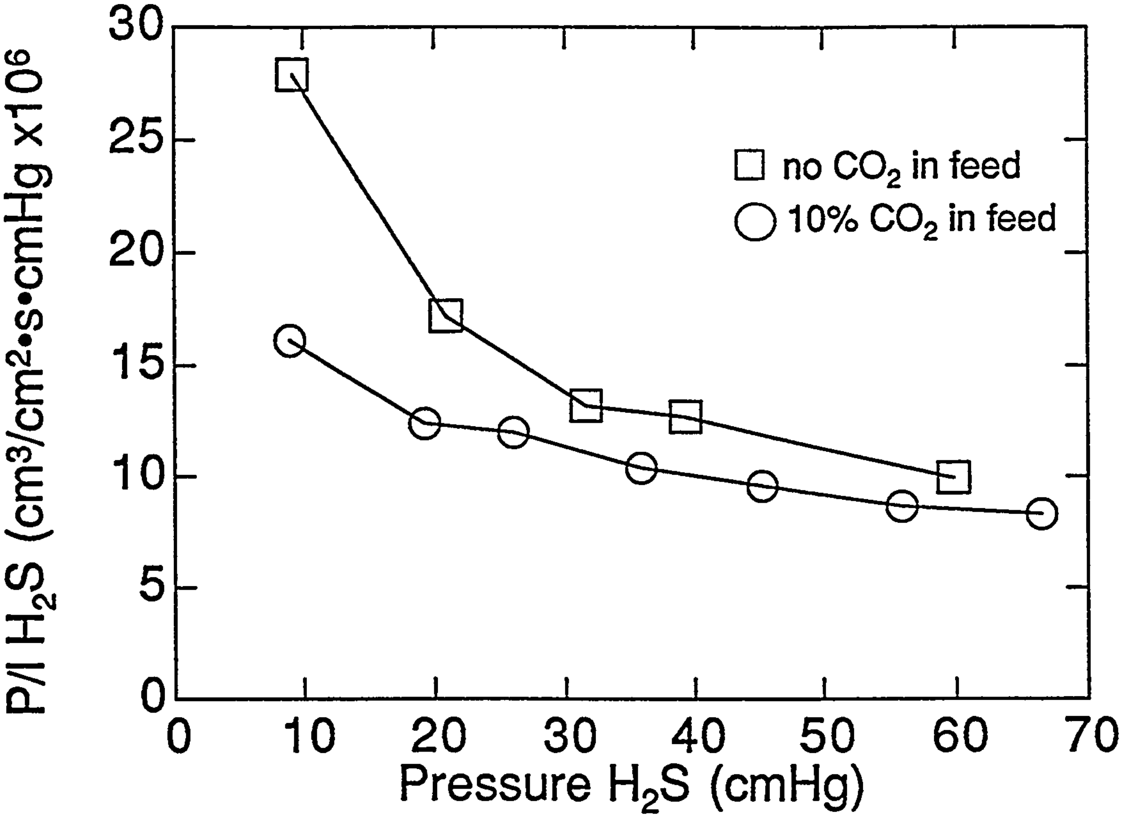
membrane	feed	H_2S	CO_2	$(P_o/l)\cdot10^6$ cc/cm$^2\cdot$s$\cdot$cmHg			selectivity	
	P(psig)	P(cmHg)	P(cmHg)	H_2S	CO_2	CH_4	H_2S/CO_2	H_2S/CH_4
12582-40-B1*	2.4	9.2	0	27.9	-	nd	-	7000$^{\#}$
	24.1	20.9	0	17.2	-	nd	-	1290$^{\#}$
	44.1	31.6	0	13.2	-	nd	-	990$^{\#}$
	58.4	39.3	0	12.7	-	nd	-	950$^{\#}$
	96.6	59.8	0	9.95	-	0.00388	-	2500
12582-40-B2**	2.1	8.95	8.67	16.1	1.49	nd	10.8	3300$^{\#}$
	21.5	19.3	18.7	12.4	1.33	nd	9.3	2600$^{\#}$
	34.0	25.9	25.1	12.0	1.41	nd	8.5	2500$^{\#}$
	52.7	35.9	34.8	10.4	1.24	nd	8.4	2200$^{\#}$
	70.4	45.3	43.9	9.60	1.18	0.00530	8.1	1920
	90.3	55.9	54.2	8.70	0.953	0.00476	9.1	1730
	110.1	66.7	64.4	8.30	0.949	0.00436	8.7	2100
return to:	41.7	30.0	29.1	12.4	1.11	nd	11.1	n.o.

* Feed Gas: 10.5% H_2S in CH_4; P/Po=0.3

** Feed Gas: 10.3% H_2S, 10% CO_2 in CH_4; P/Po=0.3

\# no CH_4 was detected. Selectivity based on observed CH_4 permeance at higher pressures

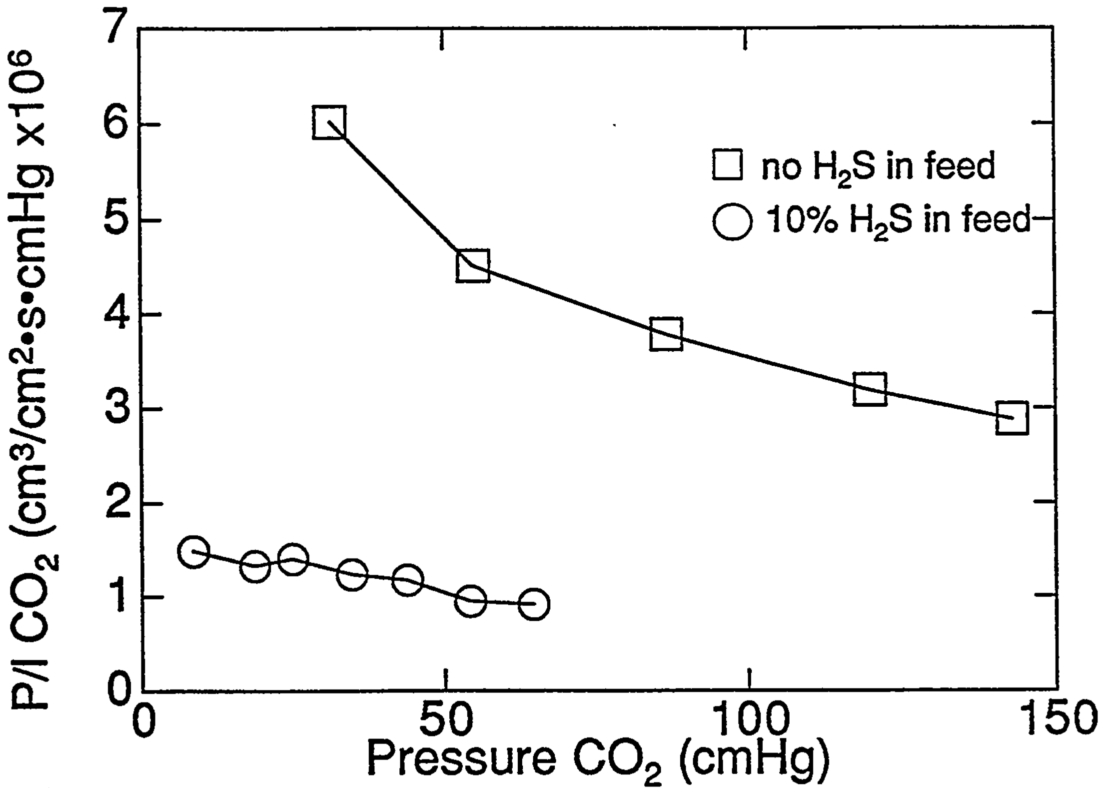
Figure 5-10
H_2S Permeance of a PVBTAF Composite as a Function of H_2S Pressure



12582-40-B

DOE4/F5-10

Figure 5-11
CO_2 Permeance of a PVBTAF Composite as a Function of CO_2 Pressure



12484-76B
12582-40-B

DOE4/5-11

2.2 Membrane stability

Membrane stability was investigated by measuring the permselectivity of planar PVBTAF composite membranes as a function of time. The data was collected under one of two set of conditions: (1) helium was used to sweep permeating gases from permeate and (2) no sweep gas was used. The latter represents the harsher condition since the permeate pressure of H_2S was significantly greater than zero. Permeance as a function of time is graphed Figure 5-12. A membrane (13095-1-9) operating with a helium sweep exhibited a 34% decline in H_2S permeance over a 19.5 day period (Table 5-5). Near the end of the run, the H_2S permeance appeared to have leveled off. H_2S/CO_2 selectivities remained constant or increased slightly throughout the run. CH_4 was not detected in the permeate but the estimated minimum H_2S/CH_4 selectivities are high - 6500 to 2200. Under harsher conditions, the decline of H_2S permeance with time was more pronounced. For example, a similar membrane (13095-1-3) evaluated without a helium sweep gas and at higher feed partial pressures than above exhibited a 70% H_2S permeance decline over 7 days, at which time a steady state permeance had apparently been reached (Table 5-6).

To evaluate the chemical stability of PVBTAF in the presence of CO_2 and particularly H_2S, samples of solid polymer were exposed to each gas for an extended period and subsequently characterized by NMR. Exposure of solid PVBTAF to CO_2 at 480kPa and 23°C for three weeks resulted in absorption of 0.70 mole CO_2/mole repeat unit. A portion of the sample containing absorbed CO_2 was dissolved in D_2O, resulting in evolution of gas. The ^1H, ^{13}C, and ^{19}F spectra of this sample and of PVBTAF in D_2O were identical (Figure 5-13) implying that PVBTAF is not degraded by CO_2.

An H_2S containing sample was prepared in a similar manner and, after a three week exposure, solid PVBTAF absorbed 2.0 mole H_2S/mole repeat unit at 476 kPa and 23°C. The H_2S-containing sample was brittle and almost insoluble in water and other common solvents (e.g. methanol , acetone, and acetonitrile). The solid was also insoluble in 1M HCl which would appear to eliminate the possibility of an S^{2-} crosslinked structure. Clearly, however, exposure to H_2S caused some chemical change to the polymer.

Solid state NMR spectra of pure PVBTAF and PVBTAF containing absorbed H_2S and CO_2 were obtained (Figure 5-14). The solid state ^{13}C NMR spectra of PVBTAF and PVBTAF exposed to CO_2 or H_2S are identical with the exception of the intensity of the methyl

Table 5-5
H_2S Permselectivity vs. Time for a PVBTAF Composite at 30°C
(13095-1-9)

Feed P (psig)	**H_2S** P(cmHg)	time, min.	Average P_o/l H_2S	CO_2	CH_4	Average α H_2S/CO_2	H_2S/CH_4
30.4[a]	23.2	5760-6540	38.4	3.71	nd	10.3	6500[c]
		10080-11160	35.6	3.46	nd	10.3	6000[c]
		14400-15480	34.1	3.22	nd	10.6	5800[c]
4.0[b]	29.0	17280-18360	29.4	2.56	nd	11.5	5000[c]
		20640-21720	27.4	2.36	nd	11.6	4600[c]
		24480-25560	25.5	2.15	nd	11.8	4300[c]
30.6[b]	70.4	27000-28080	12.9	1.20	nd	10.7	2200[c]

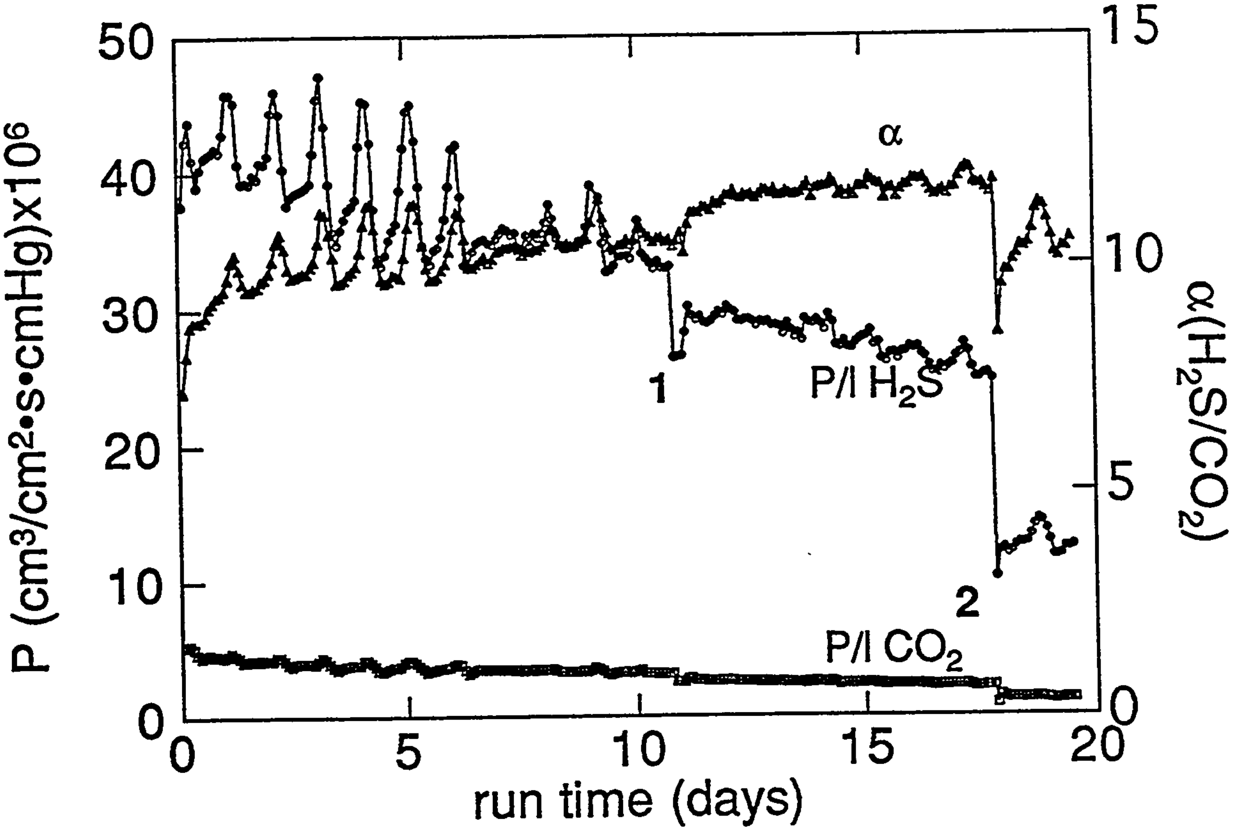
c. No CH_4 detected; estimated minimum selectivity based on a calculated maximum CH_4 permeance of 0.0059.
Sweep: helium;
feed: (a)9.9% H_2S, 10.0% CO_2 in CH_4 or
(b)30.0% H_2S, 30.0% CO_2 in CH_4;
P/Po=0.3

Table 5-6
H_2S Permselectivity vs. Time for a PVBTAF Composite Membrane at 30°C

membrane	Feed P* (psig)	run time (min)	$(Po/l) \cdot 10^6$ cc/cm^2•s•cmHg H_2S	CO_2	CH_4	Selectivity H_2S/CO_2	H_2S/CH_4
13095-1-3[b]	54.4	960-1440	11.5	2.25	0.0352	5.1	326
		2340-2820	9.51	1.90	0.0274	5.0	348
		5700-7140	4.95	0.817	0.0157	6.1	315
		8040-8520	3.55	0.639	0.0145	5.6	245
		9600-10080	3.45	0.564	0.0140	6.1	247

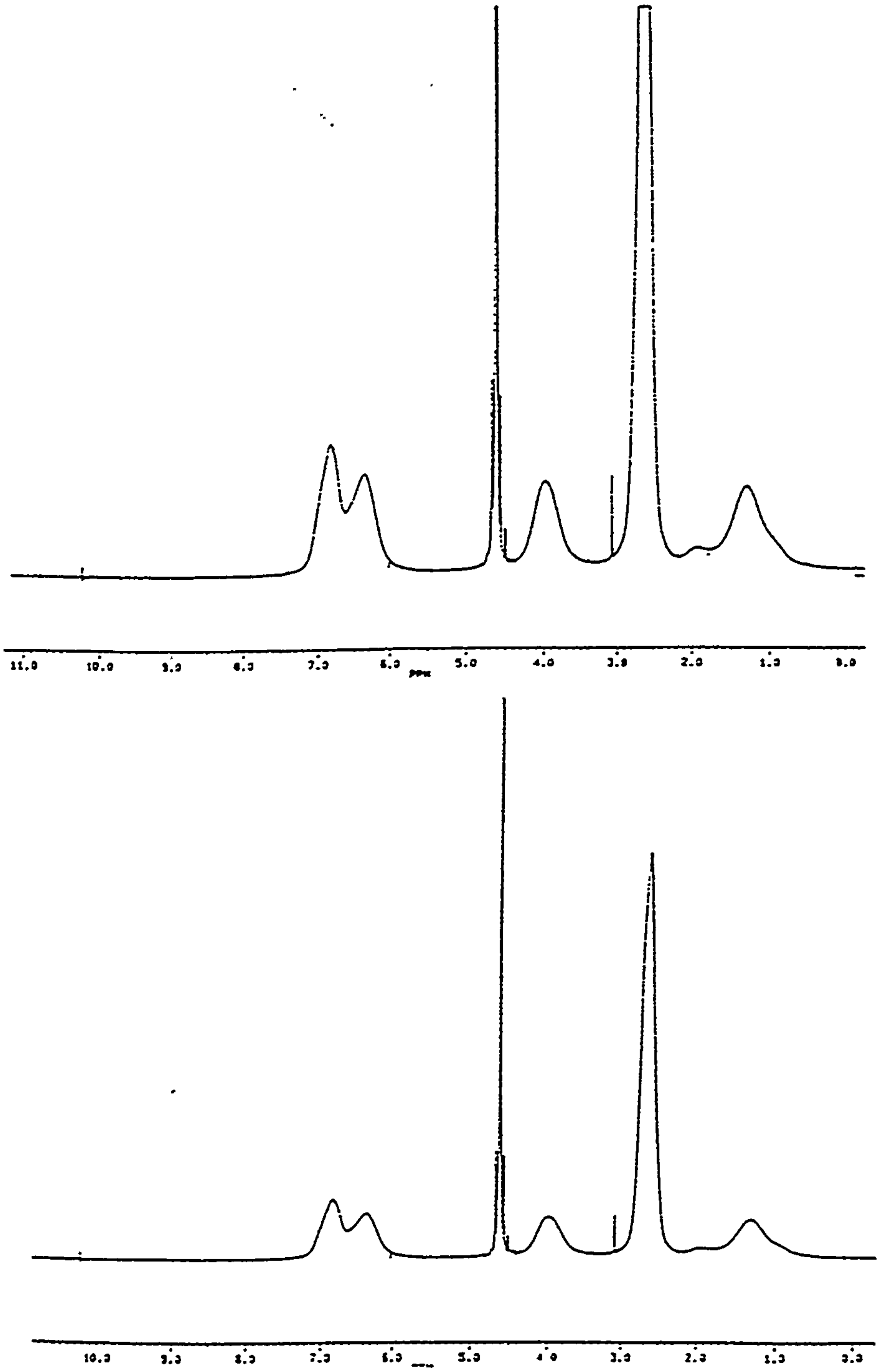
*Feed: 27.4% H_2S, 30.0 % CO_2 in CH_4; P/Po=0.4
permeate pressure, 1.0-1.4 psig;

Figure 5-12
Lifetime of a PVBTAF Composite Membrane



13095-1-9
13230-84

DOE4/F5-12



<u>Figure 5-13</u>
^1H NMR spectra of D_2O solutions of PVBTAF before (top) and after (bottom) exposure to CO_2.

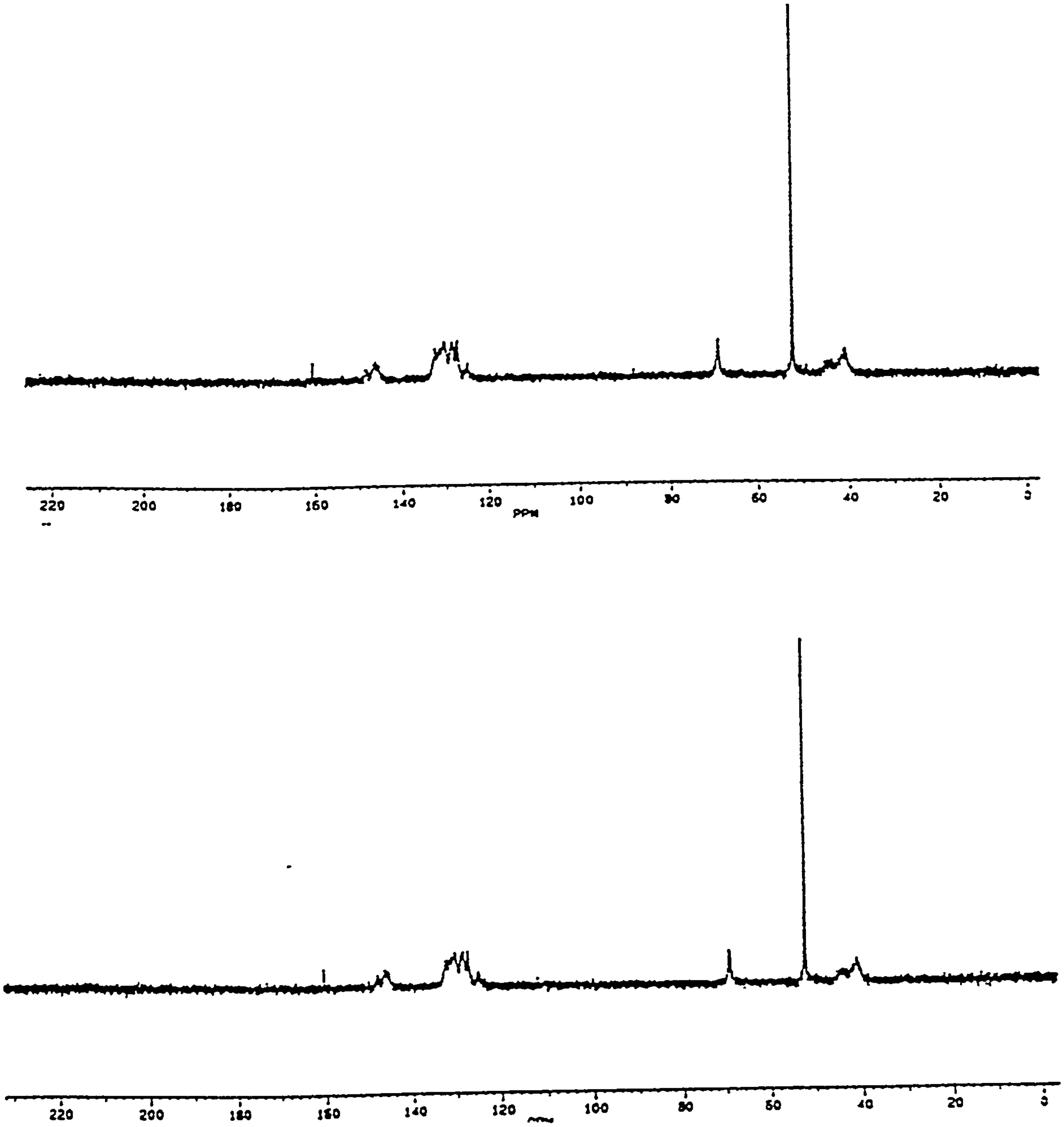


Figure 5-13 (continued)
^{13}C NMR spectra of D_2O solutions of PVBTAF before (top) and after (bottom) exposure to CO_2.

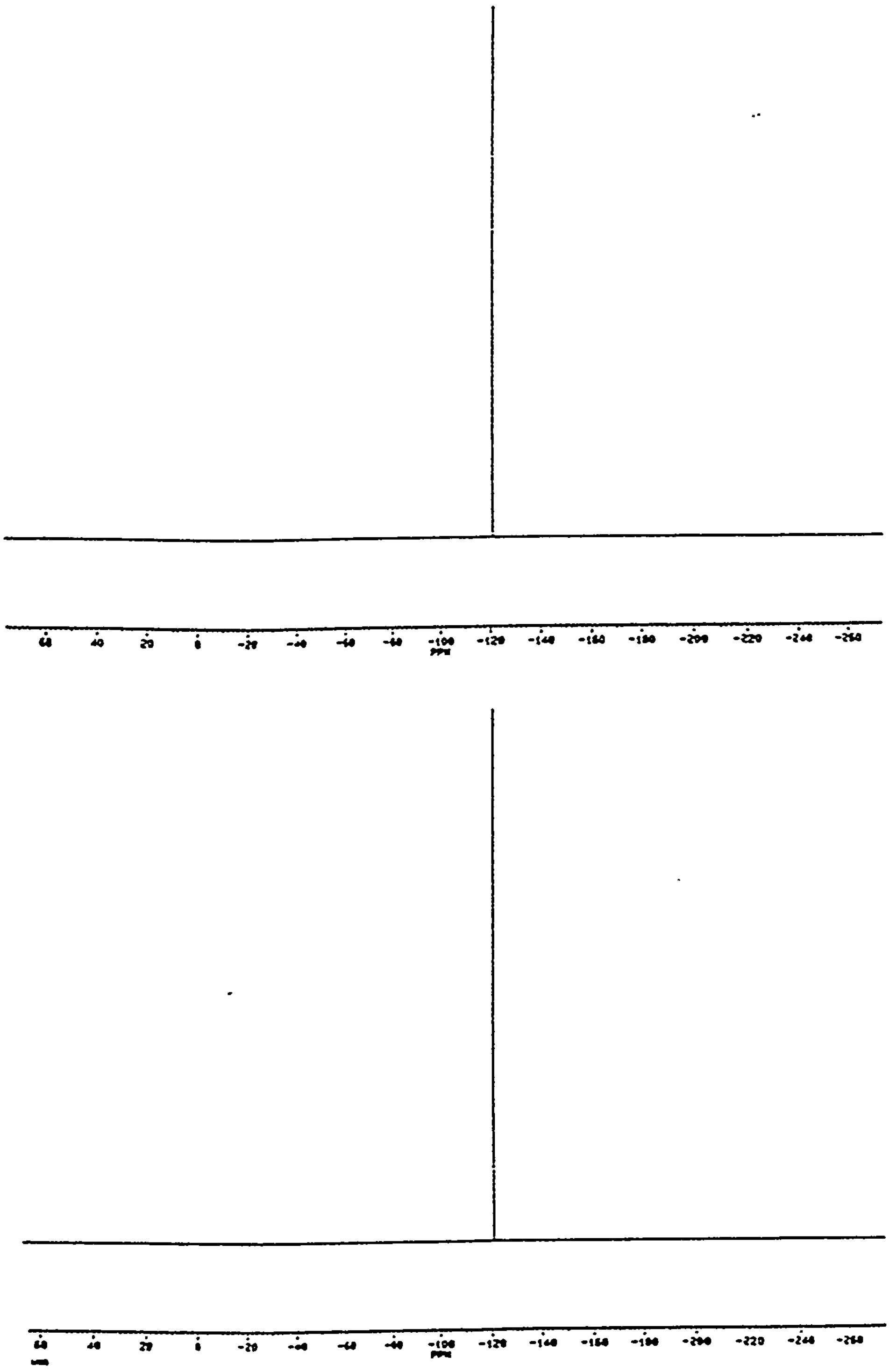


Figure 5-13 (continued)

^{19}F NMR spectra of D_2O solutions of PVBTAF before (top) and after (bottom) exposure to CO_2.

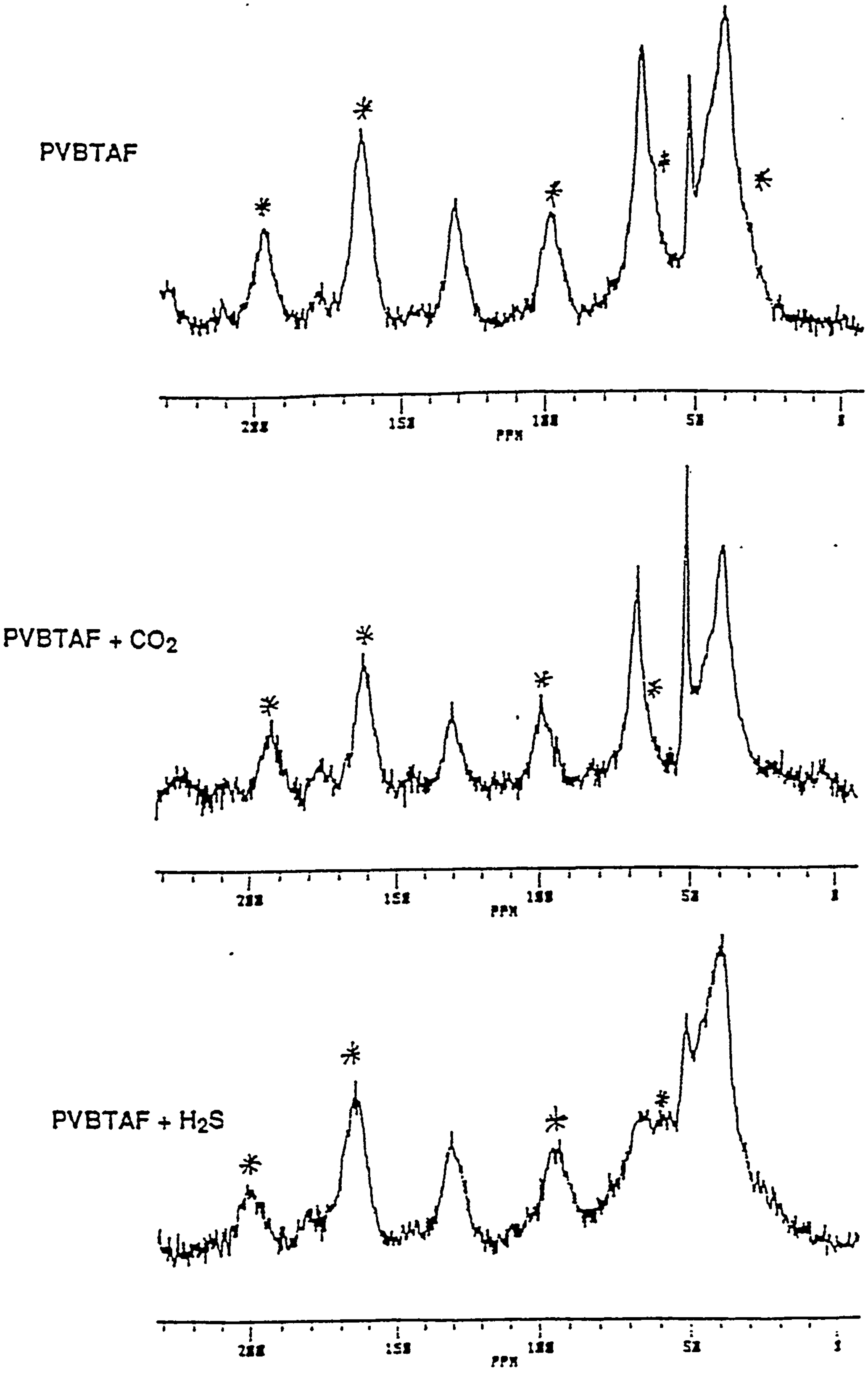


Figure 5-14
Solid state CP MAS ^{13}C NMR spectra of PVBTAF and PVBTAF after exposure to CO_2 or H_2S. Top: PVBTAF. Middle: PVBTAF + CO_2. Bottom: PVBTAF + H_2S. Spinning side bands indicated by *

resonances. The intensity of the methyl resonances can vary with the number of methyl groups in the sample or with its proximity to neighboring H atoms (i.e. the rigidity of the structure about the methyl group). That no resonances different from those of PVBTAF are observed in the spectrum of PVBTAF containing absorbed H_2S or CO_2 implies that no appreciable cleavage and loss of methyl groups occurs upon exposure to either gas. Hence, based on solid state NMR evidence, the organic portion of PVBTAF is inert with respect to degradation by H_2S or CO_2.

Analysis of the H_2S source gas indicated the presence of numerous components in addition to H_2S including COS, several hydrocarbons, methanol, methylformate, CH_3SH, 2-chloropropane, propane-2-thiol, t-butane thiol, propane thiol, CH_3CCl_3, CH_3SSH, H_2S_2, diisopropylthioether, and S_8. The headspace of the absorption reactor contained H_2S, air and only these same contaminants. This implies that exposure of PVBTAF to H_2S does not result in the formation of volatile components. Additional mass spec data provided no positive evidence for the liberation of HF upon exposure of PVBTAF to H_2S. Although this does not rule out the possibility of HF formation, it is thought to be unlikely.

The above GCMS and NMR data implies that PVBTAF is not reacting with H_2S nonetheless something clearly happens when the polymer is exposed to H_2S. Based on the change in solubility of PVBTAF, the above spectroscopic evidence, and the fact that many of the contaminants found in the source gas are more reactive than H_2S, we believe that an impurity in H_2S reacts to crosslink a relatively small portion of the polymer. Efforts are continuing to understand this phenomenon.

3.0 Discovery of New "High Performance" ATMs

Air Products has discovered a new class of proprietary AT materials. They consist of blends of AT polymers and AT salts. Planar composite membranes of these materials met preliminary CO_2 flux and CO_2/CH_4 selectivity targets. Much to our surprise, these blends were clear, apparently homogeneous (by eye) films and could be cast from aqueous or methanlic solutions. Unexpectedly large amounts of the AT salt could be incorporated into the blend, 0.25 to 4 mol per mol of polymer repeat unit. It is rare that equal molar quantities of a salt can be added to a polymer and that apparently homogeneous films can be obtained. Membranes examined visually after permeation testing generally showed no sign of salt crystallization. Two membranes examined by SEM after permeation testing revealed a largely homogeneous surface with some areas of widely scattered crystals and a few regions of crystal clusters.

Permselective properties of one such ATM blend, EXTM6-4, are listed in Table 5-7 in order of increasing AT salt concentration. It can clearly be seen (Figure 5-15) that incorporation of the AT salt significantly increases the CO_2 permeance while maintaining the exceptional selectivity. CO_2 permeances ranged from 25.7×10^{-6} at low pressure to 13.0×10^{-6} at high pressure. Compared with a PVBTAF at similar feed pressures, these represent a 400 to 600% increase in CO_2 permeance. For three different EXTM6-4 compositions, permeance data was collected as a function of feed pressure and this data is plotted in Figure 5-16. As expected, CO_2 permeances increase with decreasing feed pressure.

In much the same way that ATM blends increased CO_2 permeances with no sacrifice of selectivity, increased acid gas permeances were observed when H_2S-containing feeds were used. Membranes containing 0.5, 1, 2, and 4 mole AT salt per mole of AT polymer repeat unit were evaluated with feeds consisting of H_2S, CO_2, and CH_4 and the results are listed in Table 5-8. For each composition, H_2S permeances decrease with increasing pressure. The blend exhibits a 200-700% higher H_2S flux than does PVBTAF (Figure 5-17).

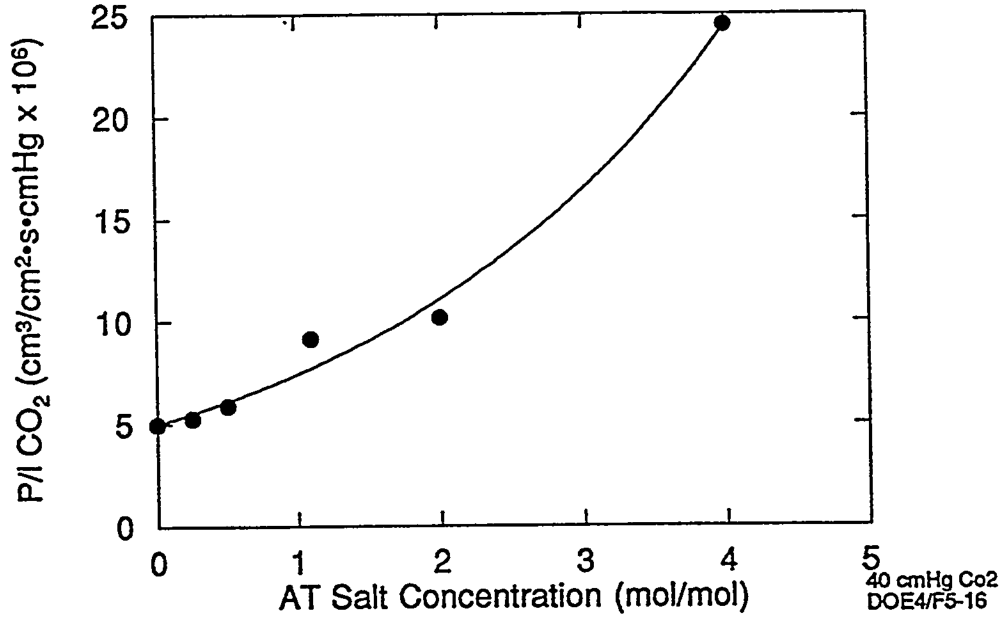
Table 5-7
CO_2 Permselective Properties of EXTM6-4 Composites at 23°C

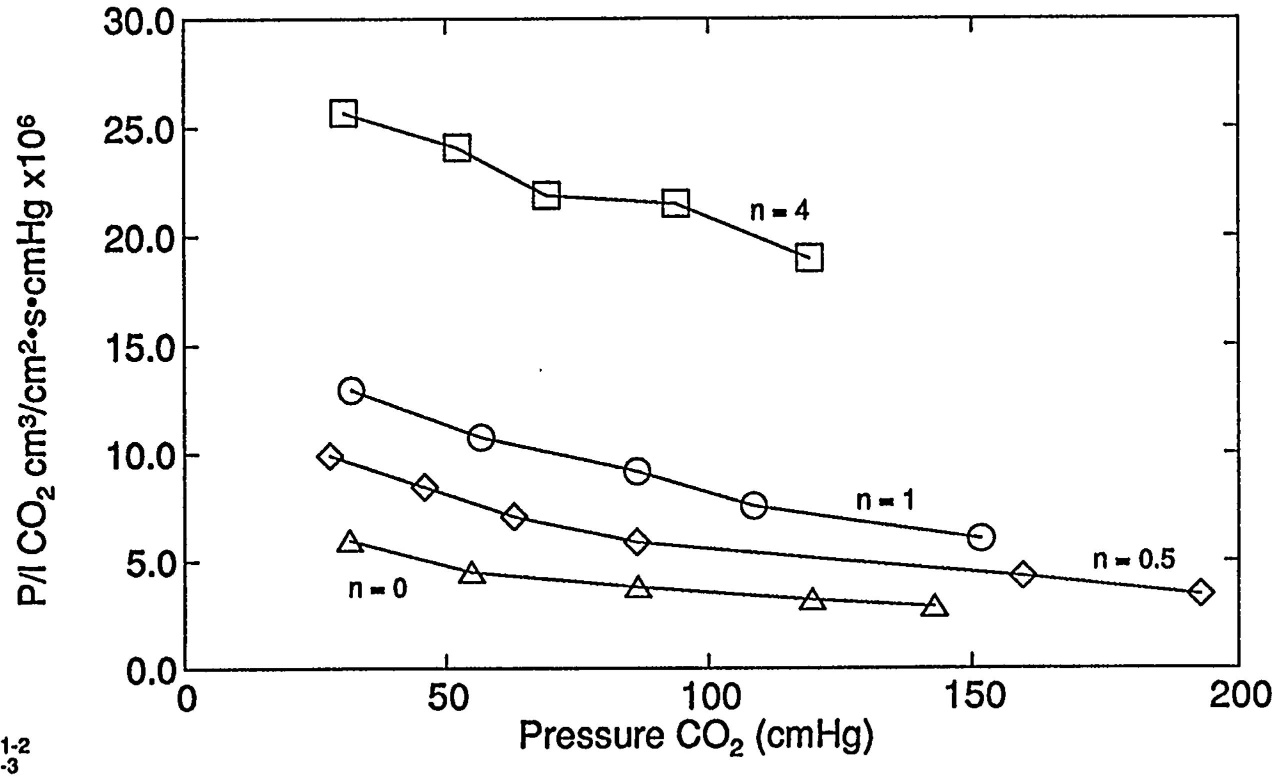
AT salt	feed	CO_2	$(P_o/l)\cdot10^6$ cc/$cm^2\cdot$s$\cdot$cmHg			Selectivity	
(mol/mol)	P(psig)	P(cmHg)	CO_2	H_2	CH_4	CO_2/H_2	CO_2/CH_4
0.25	2.6*	29.4	8.78	0.0644	nd	136	-
(12836-14-4)	17.8*	55.3	6.58	0.0625	nd	105	-
	29.9*	76.0	5.87	0.0646	nd	91	-
	39.8*	92.8	5.30	0.0647	0.00325	82	1630
	77.7*	157.4	3.75	0.0620	0.00325	60	1150
0.5	2.8	27.7	9.94	0.0296	nd	335	-
(12575-93-2)	14.3	45.9	8.46	0.0290	nd	291	-
	25.0	62.9	7.10	0.0273	0.00413	260	1720
	39.7	86.2	5.92	0.0249	0.00337	238	1760
	85.9	159.4	4.30	0.0329	0.00361	131	1191
	107.0	192.9	3.45	0.0350	0.00399	99	866
1.1	5.5	32.0	13.0	0.107	nd	122	-
(12836-3-3)	21.1	56.7	10.8	0.102	nd	106	-
	39.8	86.4	9.18	0.102	0.00864	90	1060
	53.5	108.7	7.57	0.0888	0.00421	85	1800
	81.0	151.7	6.05	0.0831	0.00524	73	1150
return to	37.4	82.6	8.96	0.0934	0.00626	96	1430
2.0							
(12836-22-3)	39.7*	92.7	10.2	0.0973	0.00764	105	1340
4.0	3.2**	30.6	25.7	0.203	0.0438	127	588
(13100-41-2)	15.9**	52.4	24.1	0.228	0.0535	106	450
	26.0**	69.7	21.9	0.218	0.0469	100	466
	40.0**	93.8	21.5	0.238	0.0511	90	420
	54.9**	119.3	19.1	0.248	0.0425	77	449
	94.6**	187.4	13.0	0.299	0.0350	43	370
return to	40.2**	94.1	15.9	0.306	0.0560	52	284

feed: 30.6% CO_2, 34.4 % CH_4 in H_2 or (x)
* 32.9% CO_2, 32.6% CH_4, in H_2 or
** 33.1% CO_2, 33.1% CH_4 in H_2;
P/Po=0.3

Figure 5-15

Effect of ATM-AT Salt Blends on CO_2 Permeance





13100-41-2
12836-3-3
12575-93-2
12484-76B

DOE4/F5-16

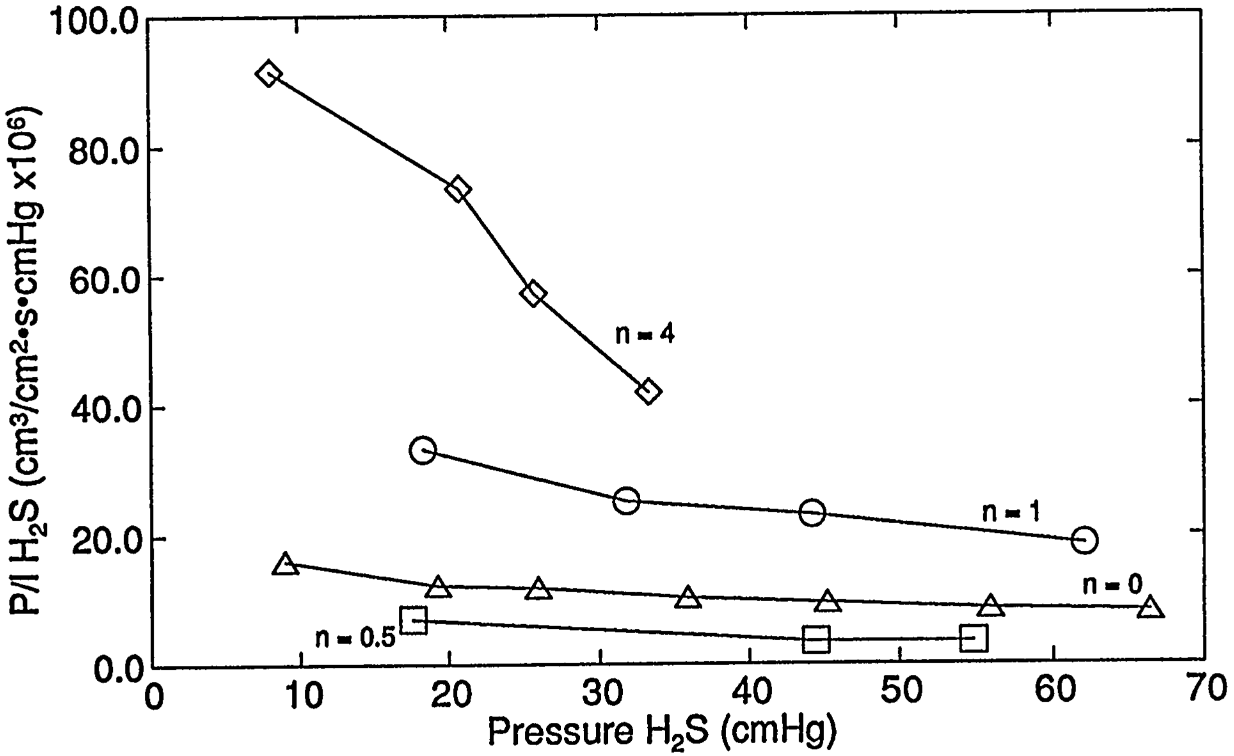
Figure 5-16
CO_2 Permeance of EXTM6-4 Composite Membranes
as a FunctionAT Salt Concentration
(n= mol salt/mol polymer)

Table 5-8

H_2S Permselective Properties of EXTM6-4 Membranes at 30°C

	feed	H_2S	CO_2	$(P_o/l)\cdot 10^6$ cc/cm^2•s•cmHg			Selectivity	
membrane	P(psig)	P(cmHg)	P(cmHg)	H_2S	CO_2	CH_4	H_2S/CO_2	H_2S/CH_4
0.5	19.6	17.6	17.7	7.06	1.41	nd	5.0	700#
(12836-11-3)	72.3	44.5	45.0	3.50	0.767	nd	4.6	700#
	91.2	54.2	54.8	3.55	0.496	nd	7.2	700#
1.0	20.6	18.1	18.3	33.2	6.77	0.0637	4.9	521
(12836-3-4)	46.8	31.5	31.8	25.3	5.14	0.0550	4.9	460
	70.9	43.8	44.3	23.2	4.06	0.0551	5.7	420
	105.5	61.5	62.1	18.6	3.86	0.0509	4.8	364
2.0	40.7	28.5	28.6	4.44	0.513	nd	8.7	500^a
(12836-22-3)	48.1	32.3	32.5	4.17	0.260	nd	16.1	500^a
	39.7*	0	92.7	-	10.2		-	-
4.0	1.1	8.1	8.2	91.6	8.91	nd	10.3	-
(13100-41-2)	25.7	20.8	20.9	73.6	8.83	nd	8.3	-
	35.4	25.7	25.9	57.3	8.30	nd	6.9	-
	50.2	33.3	33.6	42.0	9.03	nd	4.7	4200^a
(13100-41-4)	1.6	8.4	8.4	155.0	17.8	nd	8.7	nd
	19.6	17.6	17.8	101.0	16.0	0.0457	6.3	222

feed: 9.9% H_2S, 10.0% CO_2 in CH_4 or
* 32.9% CO_2, 32.6% CH_4 in H_2
P/Po=0.2
No CH_4 detected; selectivity based on calculated maximum CH_4 P_o/l of 0.0098



membranes: 12582-40, 12836-11-3,
12836-3-4, 13100-41-2

Figure 5-17
H2S Permeance of EXTM6-4 Composite Membranes
as a Function of AT SAlt Concentration
(n=mol salt/mol polymer)

VI. Process Application Development and Technology Benefits - Upgrading Subquality Natural Gas

The objective of this task was to determine the technology benefit that could be derived by applying ATM technology to natural gas processing. This effort comprises the development of a semi-empirical computer model of the gas permeation mechanism and development and evaluation of a process flowsheet.

1.0 Computer Modeling of Active Transport Membranes

The permeation mechanism of ATMs is significantly different from that of conventional (solution-diffusion) polymeric membranes. The mathematical models describing gas permeation through polymeric membranes cannot be applied to AT systems. Like traditional facilitated transport systems, ATM involves coupled chemical reaction and diffusion. However, the current mathematical models of gas transport through facilitated transport systems require detailed knowledge of the chemical complexation products, the kinetics of reaction, and the diffusion coefficients of all chemical species. The fundamental chemistry of ATM has not been developed to the extent necessary to use these models. Therefore, the first element of this task was to develop a semi-empirical computer model of gas permeation in Active Transport membranes. Using laboratory data measured on planar membrane coupons, correlations were derived between the key experimental variables (CO_2 and H_2S partial pressure and gas stream humidity). This model formed the basis for estimating ATM performance, setting preliminary performance targets, calculating the membrane area required for a separation, determining product recovery, and estimating the separation cost. A more rigorous model will eventually have to be developed.

1.1 Model Development

The ATM permeation model assumes reaction equilibria and then correlates permselectivity at various values of P/Po. Details of the model can be found in Appendix A. Briefly, the model is of the form:

$$N = P/\ell \bullet \Delta P \bullet R \bullet F$$

where N = local CO_2 flux
P/ℓ = CO_2 permeance
ΔP = partial pressure driving force
R = semi-empirical P/Po correlation factor
F = facilitation factor ($F>1$ for CO_2 and H_2S; $F<1$ for CH_4)

As indicated earlier, R and F were derived from experimental data. It is important to note that when this model was derived only limited information was available on the P/Po dependence of $\alpha(CO_2/CH_4)$ and, thus, the results described below are tentative and, in this respect, need further verification. The model will be updated early in the next phase of this work.

1.2 Results

The model predicted CO_2 permeance is compared to the experimental data in Figure 6-1. The model adequately represents the experimental data as a function of CO_2 partial pressure in the range 100-400 cmHg and P/Po 0.16-0.45. In Figure 6-2 the predicted CO_2 and CH_4 permeance is compared to experimental values as a function of P/Po for a constant CO_2 partial pressure. Again, the fit is good within the range of experimental data. Additional experimental data outside this range is needed to extend the range of operating variables and increase confidence in using the model as a predictive tool.

Figure 6-1

Experimental and Model Predicted CO_2 Permeance of PVBTAF MLC at 34° C

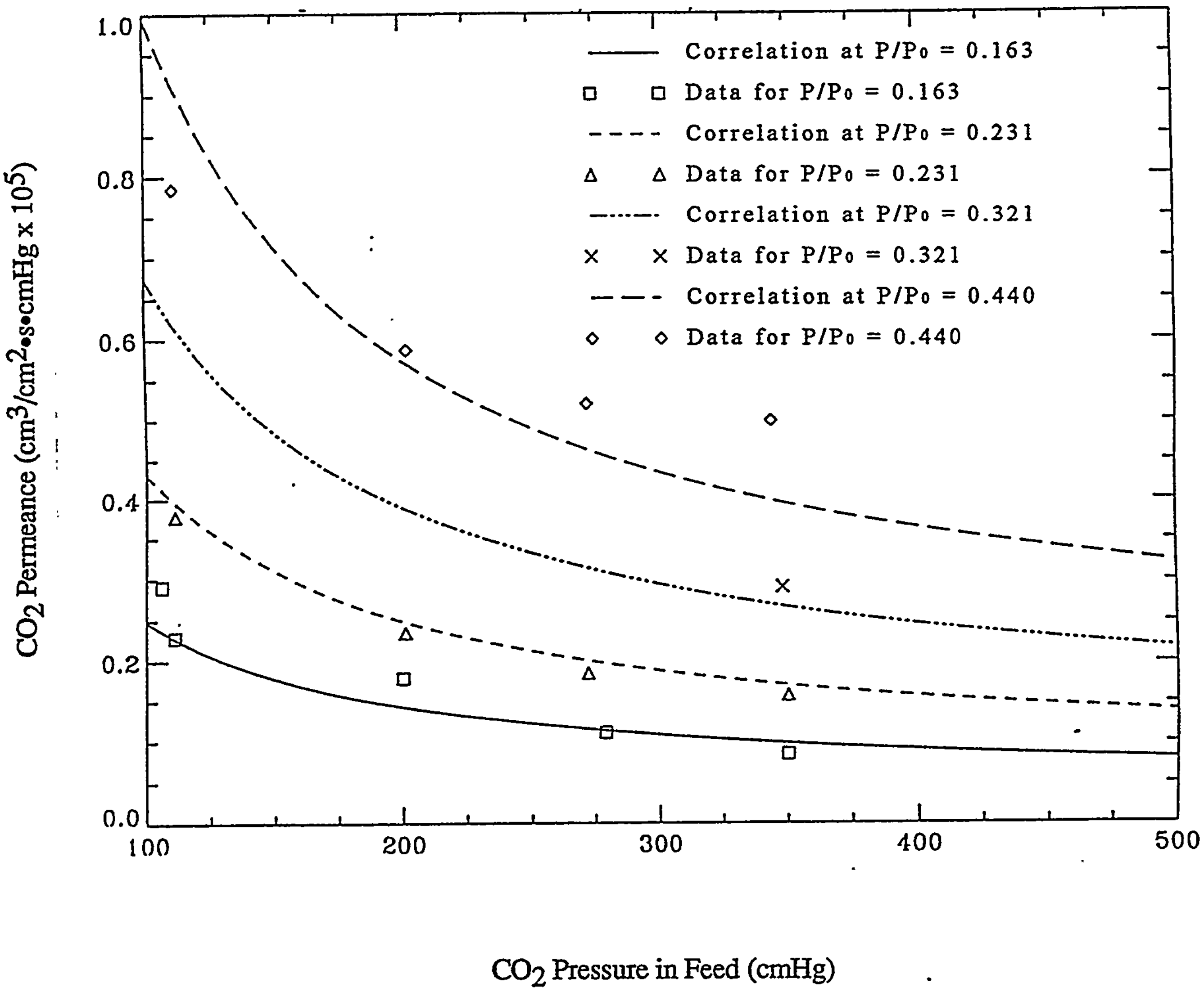
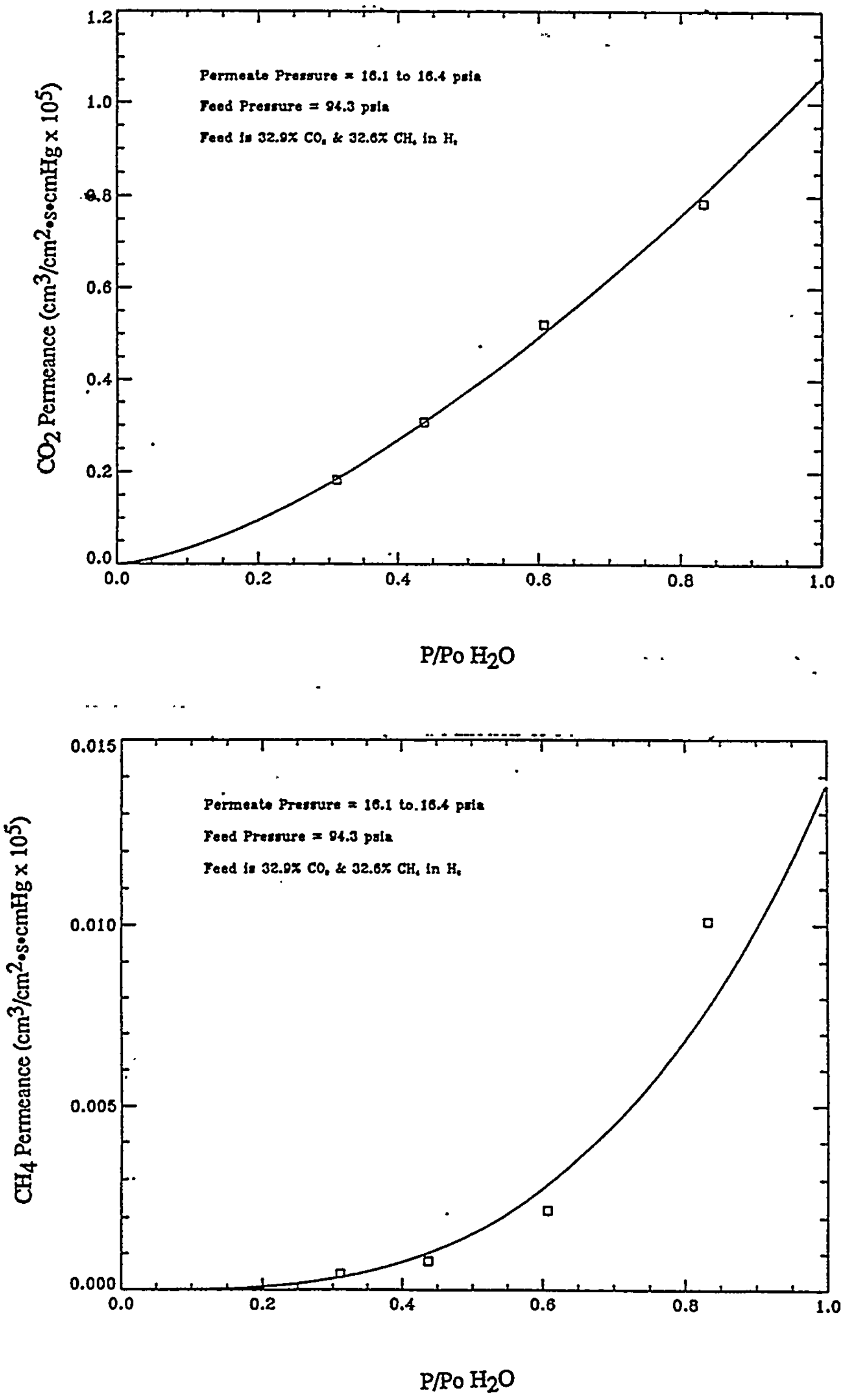


Figure 6-2

Experimental and Model Predicted CO_2 and CH_4 Permeance as a Function of P/Po



2.0 ATM Process for Upgrading Natural Gas

2.1 Test Case: Upgrading 6.5% CO_2 in CH_4

The simulation used the model described above. Two additions to the model were necessary:

1) The feed gas to the membrane was saturated with H_2O. The H_2O permeability of the ATM was assumed to be 250×10^{-6} $cm^3/cm^2 \bullet s \bullet cmHg$ and independent of pressure.

2) The model was expanded to vary the concentration of CO_2, CH_4 and H_2O in the feed and permeate gas as function of position in the module.

The test case used a natural gas feed containing 6.5% CO_2 at 800-1000 psig at 150 MMSCFD. The goal was to provide at least 20% lower gas processing costs than competing technologies. Additional design specifications were to maintain hydrocarbon losses at less than 1% and power at less than 25 BHP per MMSCFD. The natural gas product specification was 2% CO_2. Module productivity was assumed to be > 0.5 MMSCFD per module.

The process flowsheet is shown in Figure 6-3. After removing condensable components, gas is fed to the ATM at 834 psia. The nonpermeate stream is pipeline quality CH_4 at 822 psia. The membrane permeate is further processed to recover CH_4. It is recompressed from 17 to 864 psia and fed to a second, much smaller, membrane. Permeating CO_2 is vented and the CH_4 - enriched permeate is recycled.

We have found a number of advantages of the idealized ATM-based process:

- **Fewer modules.** Figure 6-4 shows that the optimized ATM requires ≈50% fewer modules than conventional membranes.

- **Less energy**. Figure 6-5 compares the power requirements for the current membrane technology and ATM. An optimized ATM would require about one-half the energy of other membrane systems.

Figure 6-3

Process Flow Diagram: CO_2 Separation from Natural Gas by ATMs

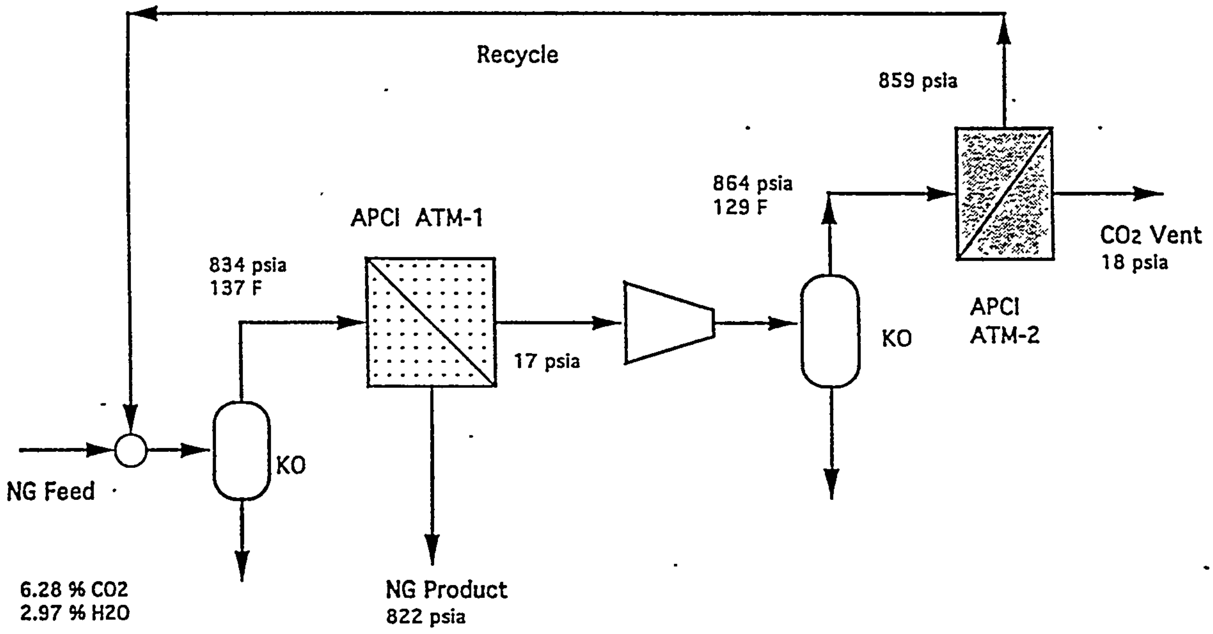


Figure 6-4

Number of Modules

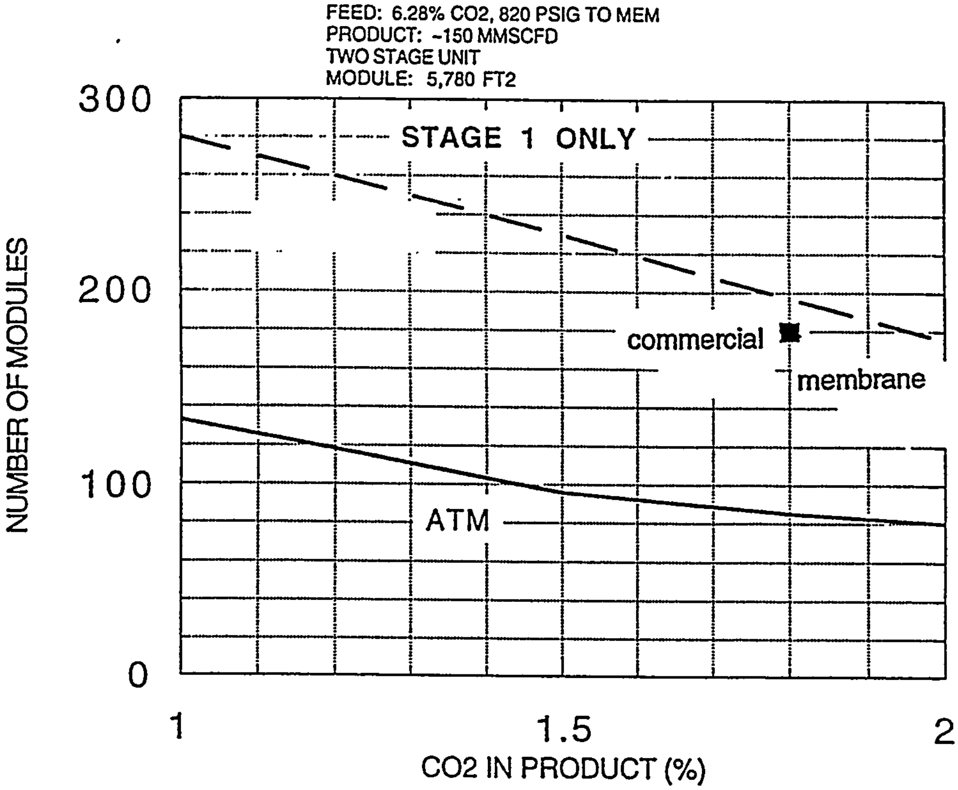
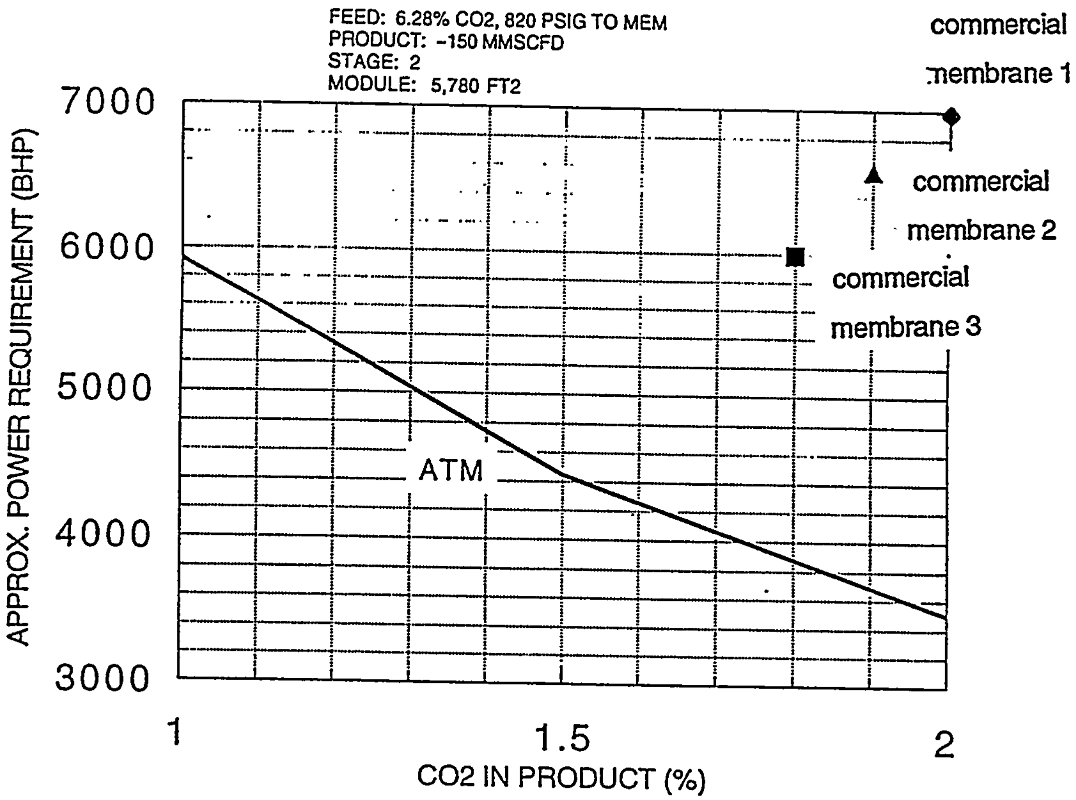


Figure 6-5

Compressor Power



- **Lower product loss.** The inherently high selectivity of the ATM manifests itself as low CH_4 loss (Figure 6-6). Thus, the ATM system has a high CH_4 recovery.

The gas processing costs of the ATM system are compared to diethanolamine (DEA) as a function of capacity in Figure 6-7. An ATM system would be an attractive option for a wide variety of feed rates. By contrast, the market niche for conventional membranes is generally considered to be less than about 10 MMSCFD[39]

2.2 Preliminary ATM Targets

Based on computer modeling to date and the above test case, preliminary permeance targets have been set for the ATM. Since ATM performance is a function of several process variables, this target is not a simple P/ℓ, α combination as it would be for a conventional polymeric membrane. The preliminary ATM permeance target is shown as the solid curve in Figure 6-8. Also shown in Figure 6-8 is the laboratory performance of ATM coupons and hollow fiber modules. Currently, neither PVBTAF planar coupons nor hollow fiber modules meet the performance target, however, it is anticipated that further improvements in membrane fabrication (e.g. thinning the ATM layer) will improve their CO_2 permeance. An attractive ATM material option is the recently discovered EXTM6-4. Planar composite coupons of this ATM do meet the preliminary permeance target. It will interesting to see if hollow fiber modules also exhibit this improved performance.

3.0 Recommendations

The results to date demonstrate the effectiveness of an optimized ATM system. It is important to note that certain assumptions were made in this analysis. It will be critical to verify these assumptions in the next segment of this program. Such a program should address:

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[39] R.W. Spillman et.al., "Gas Membrane Process Optimization", presented at the AIChE mtg., New Orleans, LA, March 9, 1988.

Figure 6-6

Hydrocarbon Loss

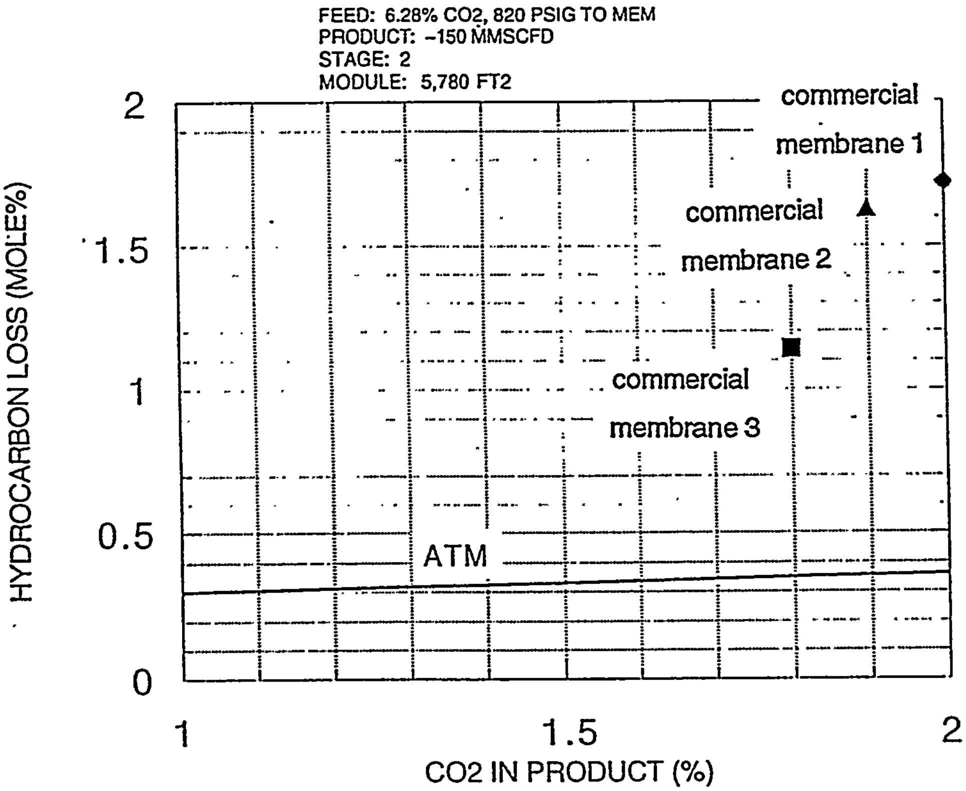


Figure 6-7
Economics of ATM and DEA Systems for CO_2 Separation from Natural Gas

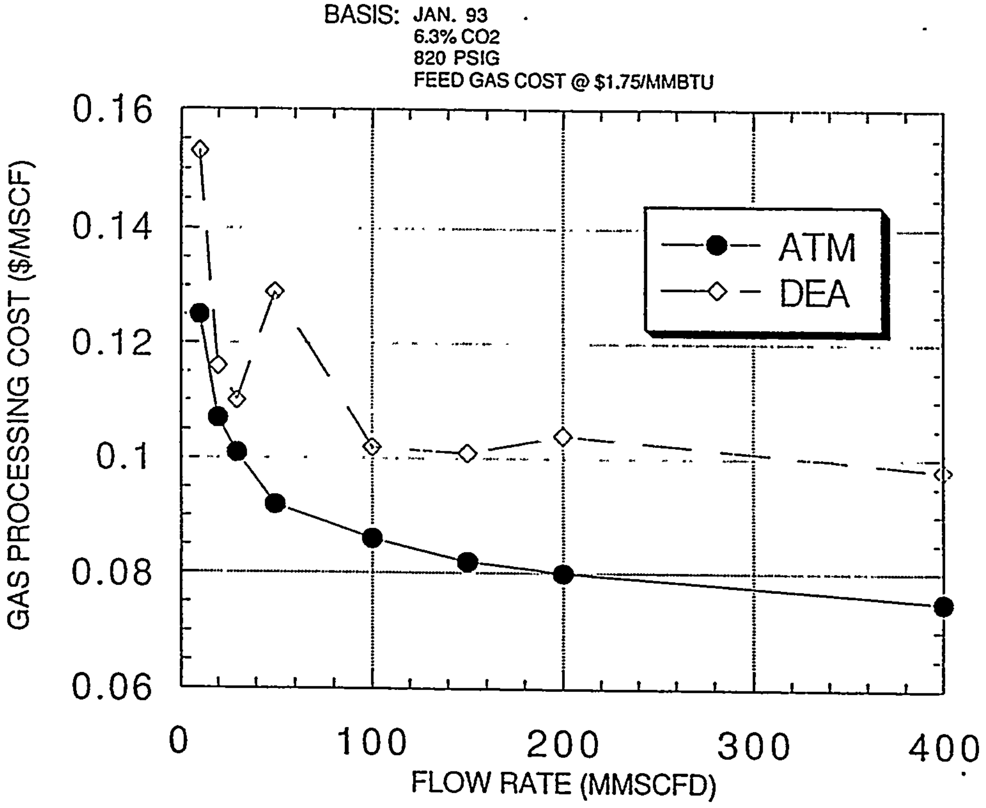
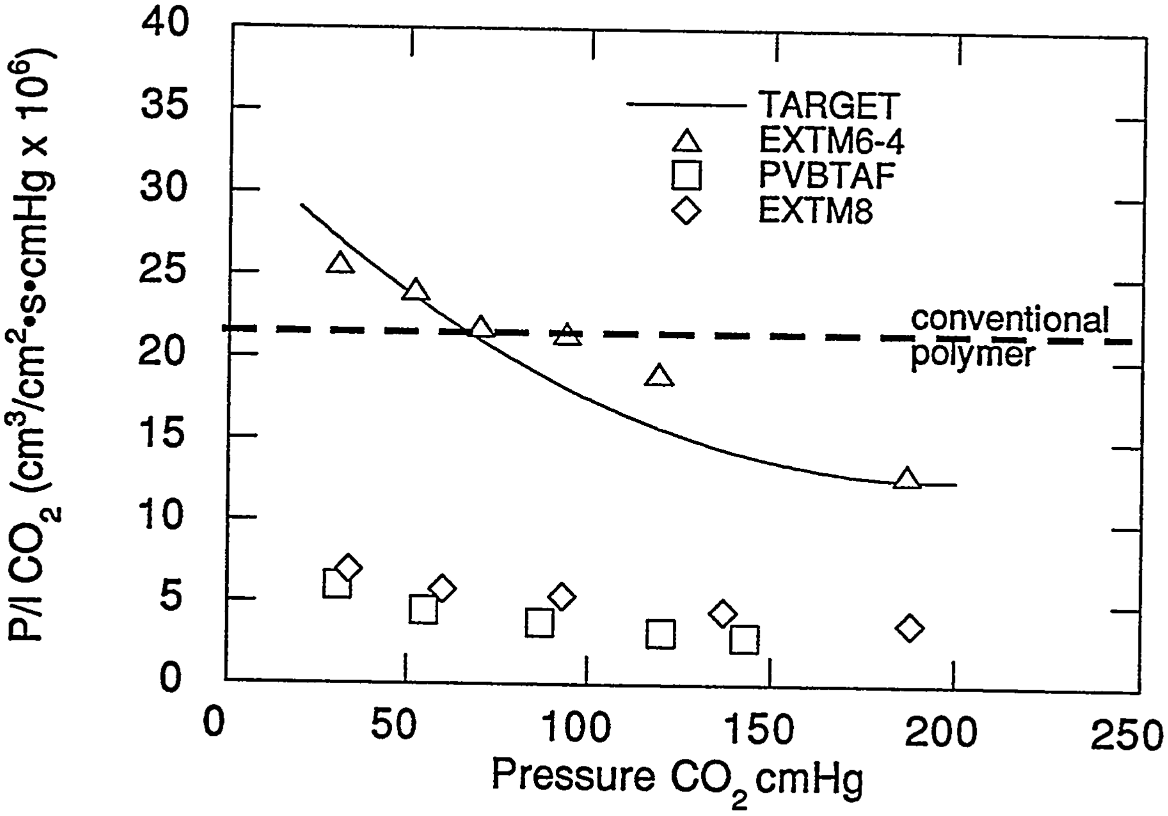


Figure 6-8
Comparison of Laboratory Properties to Targets



- **Experimentally determine the H_2O permeance of the ATM.** Since water plays a critical role determining ATM permselectivity, it will be essential to have an experimental value for this parameter. The rate at which the ATM permeates water from the gas stream may have a large effect on the membrane area and, hence, gas processing costs.

- **Experimentally determine ATM performance at extremes of P/Po and incorporate into model.** Work to date has focused on ATM performance in the P/Po range 0.2 to 0.6. An ATM module will also have to function outside this range. The current ATM computer model extrapolates into this range from the current dataset. It will therefore be essential to experimentally measure these properties.

- **Examine process variable sensitivity to processing costs.** A follow-on program should address the impact of gas composition, flowrate and membrane selectivity on the natural gas processing cost. Additionally, that analysis should compare the cost of using conventional amine scrubbing and membrane technology.

VII. Commercial Opportunities

Air Products researchers have identified AT membranes which selectively permeate CO_2 from CH_4 and H_2, H_2S from CH_4 and H_2, and NH_3 from N_2 and H_2. Throughout this program commercial development activities have focused on identifying and evaluating industrial applications for ATM, understanding market needs and forces, and setting ATM performance criteria. The following sections describe potential large-scale commercial opportunities for ATM technology.

1.0 Upgrading Subquality Natural Gas

1.1 Recent Market Trends

Background information on the natural gas industry, including size and competition for gas treating, was detailed in a previous report.[29] An update is summarized below.

- *US Consumption and domestic production growing.* Table 7-1 summarizes US natural gas consumption, domestic production and import data since 1987.[40] US consumption is expected to increase nearly 4% in 1994 to 21.1 trillion cubic feet (60,285 MMSCFD). This is the highest consumption level since 1974. Domestic production is expected to increase by 2% in 1994 to 18.8 trillion cubic feet (53,715 MMSCFD). Since 1986, domestic production has been growing at about 2.4% each year, or between 1000 and 1500 MMSCFD. Increased domestic production is expected to meet only about one-half of the increase in demand. The balance will be made up by new imports. Canadian imports will account for roughly 11% of US consumption in 1994.

- *"Gas Bubble" (in capacity) is over.* Figure 7-1 shows US production capacity and utilization rates for the last 8 years. Domestic production capacity surpassed production for this period. The low utilization rate period was commonly termed the

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[40] U.S. Chemical Outlook, U.S. Dept. of Energy, Energy Information Administration, 1994.

gas bubble. Recent data estimate utilization rates will near 100%; projected growth in production will require construction of new processing plants.[41]

Table 7-1
U.S. Natural Gas Consumption and Production
(Dry Gas Basis)

	Consumption		Production	
Year	Trillion CFY	MMSCFD	Trillion CFY	MMSCFD
1987	17.21	47,151	16.62	45,534
1988	18.03	49,397	17.10	46,849
1989	18.80	51,507	17.31	47,425
1990	18.72	51,288	17.81	48,795
1991	19.13	52,411	17.75	48,630
1992	19.75	54,110	17.78	48,712
1993*	20.36	55,781	18.41	50,438
1994**	21.10	57,808	18.78	51,452

* estimate
** forecast

1.2 Natural Gas Impurities

Natural gas is obtained from three types of wells: 1) oil wells in which natural gas is associated with oil (associated gas), 2) wet gas wells, which are predominantly natural gas but also produce natural gas liquids (NGLs), and 3) "dry" gas wells which contain low concentrations of heavy hydrocarbons (though the gas is still H_2O saturated). Sources 2 and 3 are collectively termed non-associated gas production. In the US, non-associated gas accounts for 80 to 85% of domestic production. Wellhead gas contains various impurities that must be removed before transmission by pipeline including:

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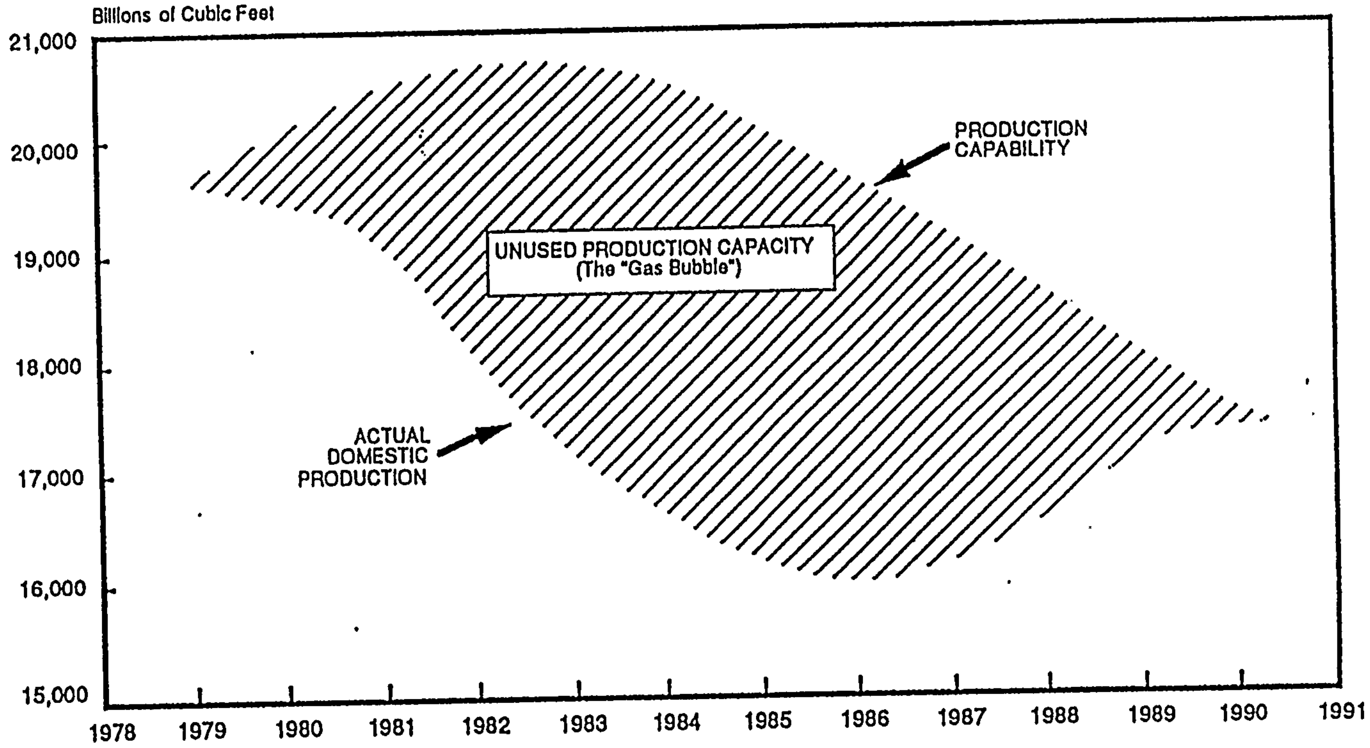
[41] SRI, International, Chemical Economics Handbook, CEH Product Review, Natural Gas, June 1993.

Figure 7.1

U.S. Utilization of Natural Gas Production Capability



Source: Reference 43

H_2O: Wellhead gas is saturated with water. Gas dehydration is necessary to prevent hydrate formation and corrosion in transmission pipelines. The industry standard is 4 - 7 lbs H_2O per MMSCF of natural gas ($\approx$ 85 - 150 ppm H_2O). The lower specification is typical for northern pipelines due to lower temperatures.

CO_2: The concentration of CO_2 in transmission pipelines is controlled to prevent corrosion and to maintain a high heat value. The most common CO_2 specification is <3 vol%, however, some pipelines limit CO_2 to less than 2 vol%.

H_2S: Most pipeline companies specify a maximum concentration of 4 ppm H_2S. There is also a limit on mercaptans and total sulfur content of the treated gas. Gas treating plants at highly contaminated wells employ a method to convert H_2S to elemental sulfur which can then be sold or disposed.

In 1994, the Gas Research Institute (GRI)[42] estimated gas treating needs for non-associated gas production and reserves using 1988 data (Table 7-2). A large fraction of natural gas (nearly 75% of non-associated 1988 production) required only dehydration. Only 15% of 1988 non-associated gas production needed CO_2 removal. However, by comparing the GRI data for production vs. reserves, it can be seen that the fraction of raw gas needing acid gas removal is expected to increase as the US begins to consume lower quality reserves.

The GRI report did not consider H_2S-containing sources. We met with representatives from GRI to estimate the fraction of gas likely to require H_2S removal. Table 7-3 contains our estimates for the 1988 proven reserves. The data can be summarized as follows:

62% of non-associated gas reserves will require dehydration only.
3% of the gas will require both H_2S treating and dehydration.
10% of the gas will require only CO_2 treating and dehydration.
7% of the gas requires CO_2 and H_2S treating, and dehydration.
18% of the gas is high in N_2 and/or CO_2 and H_2S.

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[42] "Chemical Composition of Discovered and Undiscovered Natural Gas in the Lower-48", Gas Research Institute, 1994.

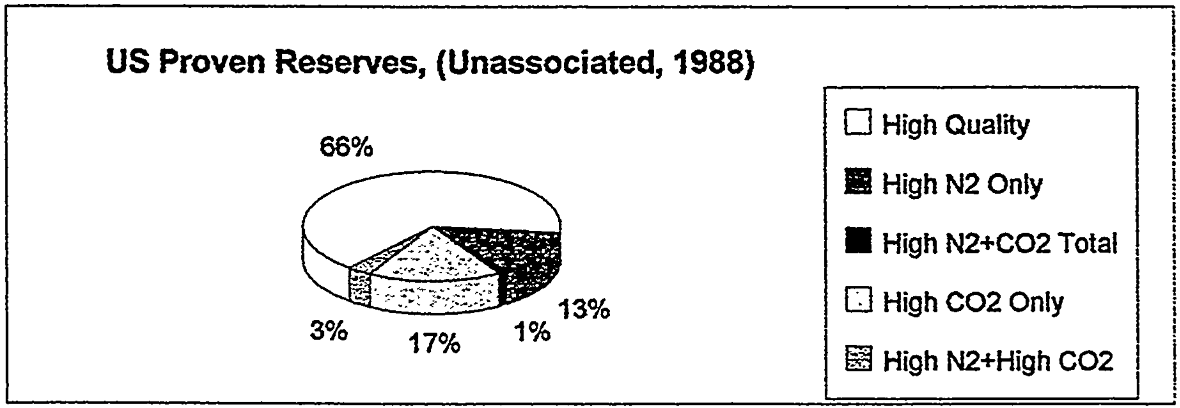
Table 7.2

US Natural Gas Production and Reserves Data

	1988 Proven Reserves	1988 Production	Undiscovered and Undeveloped Gas Resource	Discovered / Non-Producing Low Quality Gas Resource
	– All numbers in Trillion SCF –			
High Quality	95.1	10.81	376.9	0
High N2 Only	19.25	1.32	35.2	0
High CO2 Only	24.05	2.18	167.6	1
High N2+High CO2	4.12	0.31	16.6	134
High N2+CO2 Total	1.44	0.09	3.1	0
Totals	**144**	**14.7**	**599.4**	**135**

Definitions:

1. High Quality gas contains less than 2%CO2, and less than 4% N2.
2. High N2 ONLY gas contains more than 4%N2, and less than 2% CO2.
3. High CO2 ONLY gas contains less than 4%N2, and more than 2% CO2.
4. High N2 + High CO2 gas contains more than 4%N2, and more than 2% CO2.
5. For High N2 + CO2 Total gas, % N2 + % CO2 is more than 4.


US Proven Reserves, (Unassociated, 1988)

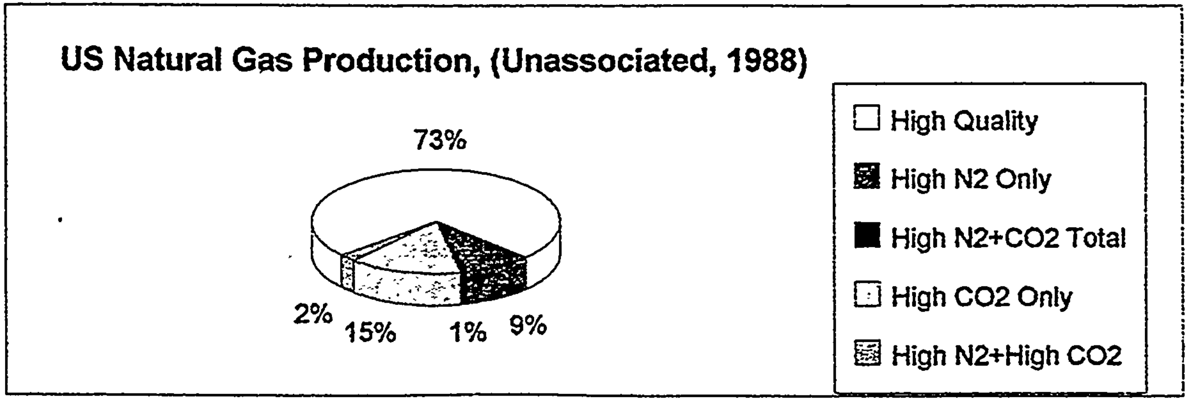
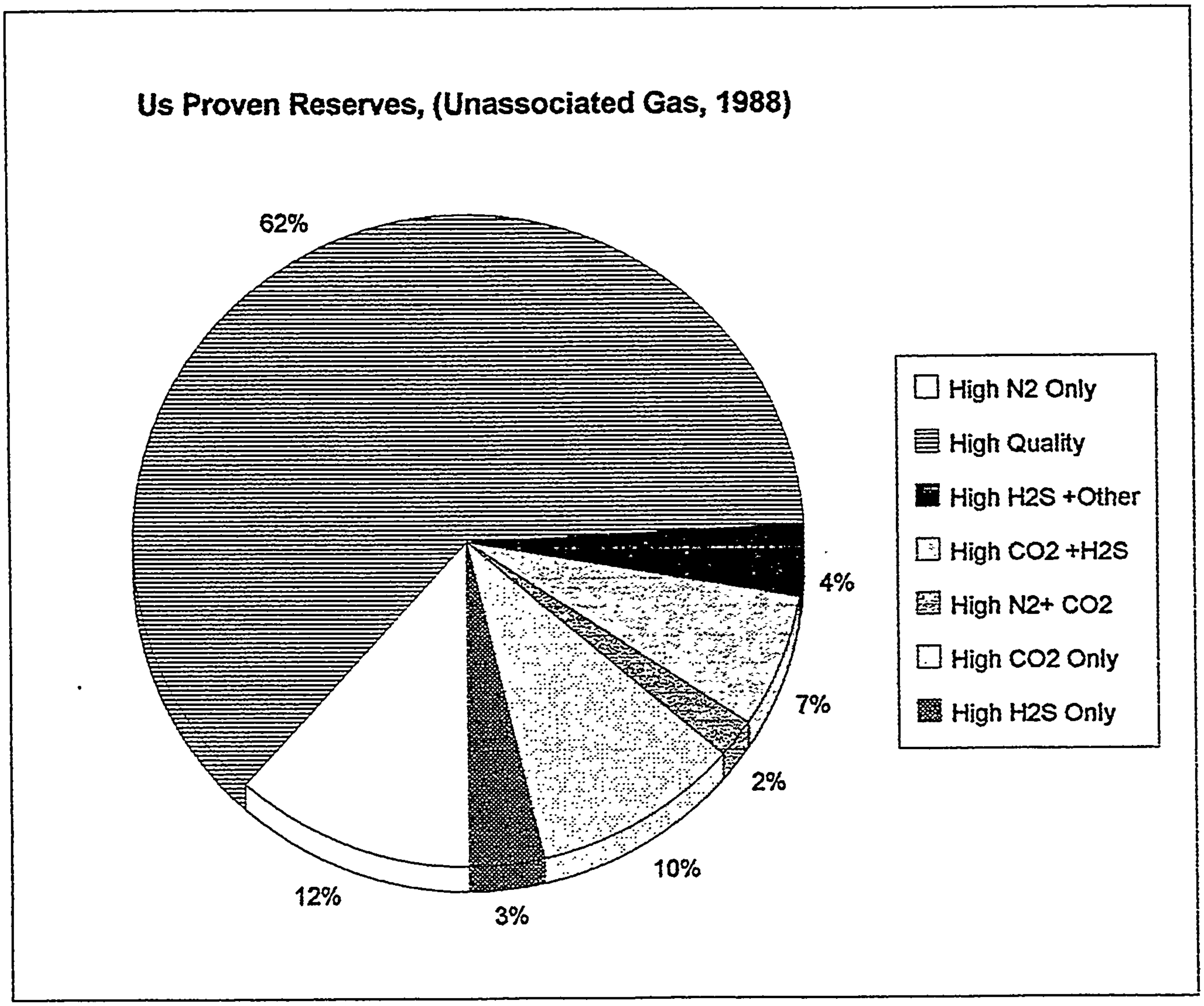

US Natural Gas Production, (Unassociated, 1988)

Table 7.3

Non-Hydrocarbon Impurities Estimate for US Natural Gas Reserves

Gas Type	1988 Production	1988 Proven Reserves Total	1988 Reserves H2S Treating Needed	1988 Reserves No H2S Treating
	– All numbers in Trillion SCF –			
High Quality	10.81	95.1	5	90.1
High N2 Only	1.32	19.25	2.4	16.85
High CO2 Only	2.18	24.05	9.6	14.45
High N2+High CO2	0.31	4.12	2.2	1.92
High N2+CO2 Total	0.09	1.44	0.5	0.94
Totals	**14.7**	**144**	**19.7**	**124.3**



1.3 Natural gas treatment costs

Figure 7-2[43] shows how the price of natural gas increases as it passes from producer to consumer. In 1991, the composite well head price for natural gas was around $1.59 per MSCF. Today it is ≈ $1.65 per MSCF. Some portion of the price is related to the cost of upgrading raw gas to pipeline specifications. A recent presentation at the 73rd Annual Gas Producers Association Conference,[44] estimated gas treating costs for commonly used acid gas treating processes. A summary of the total treatment cost (operating + recovered capital) is provided in Table 7-4.

Table 7-4
Natural Gas Treatment Costs at 10 MMSCFD

Impurity	Treatment Process	Treatment Cost in $/MSCF
H_2O	Glycol Dehydration	0.04 (@ >10 MMSCFD) 0.09 (@ <1 MMSCFD)
CO_2 (2-7%), H_2O	Amine Scrubbing (DEA) + glycol dehydration	0.20 (10 MMSCFD)
CO_2, (6%) H_2S (1%), H_2O	Amine Scrubbing + Liquid Oxidation + Glycol Dehydration	0.50 (10 MMSCFD)
CO_2 (3%), H_2S(3%), H_2O	Amine Scrubbing + Claus Process + Glycol Dehydration	0.47 (10 MMSCFD)
N_2	Cryogenic + Glycol Dehydration	0.85 (10 MMSCFD)

Source: reference no. 44

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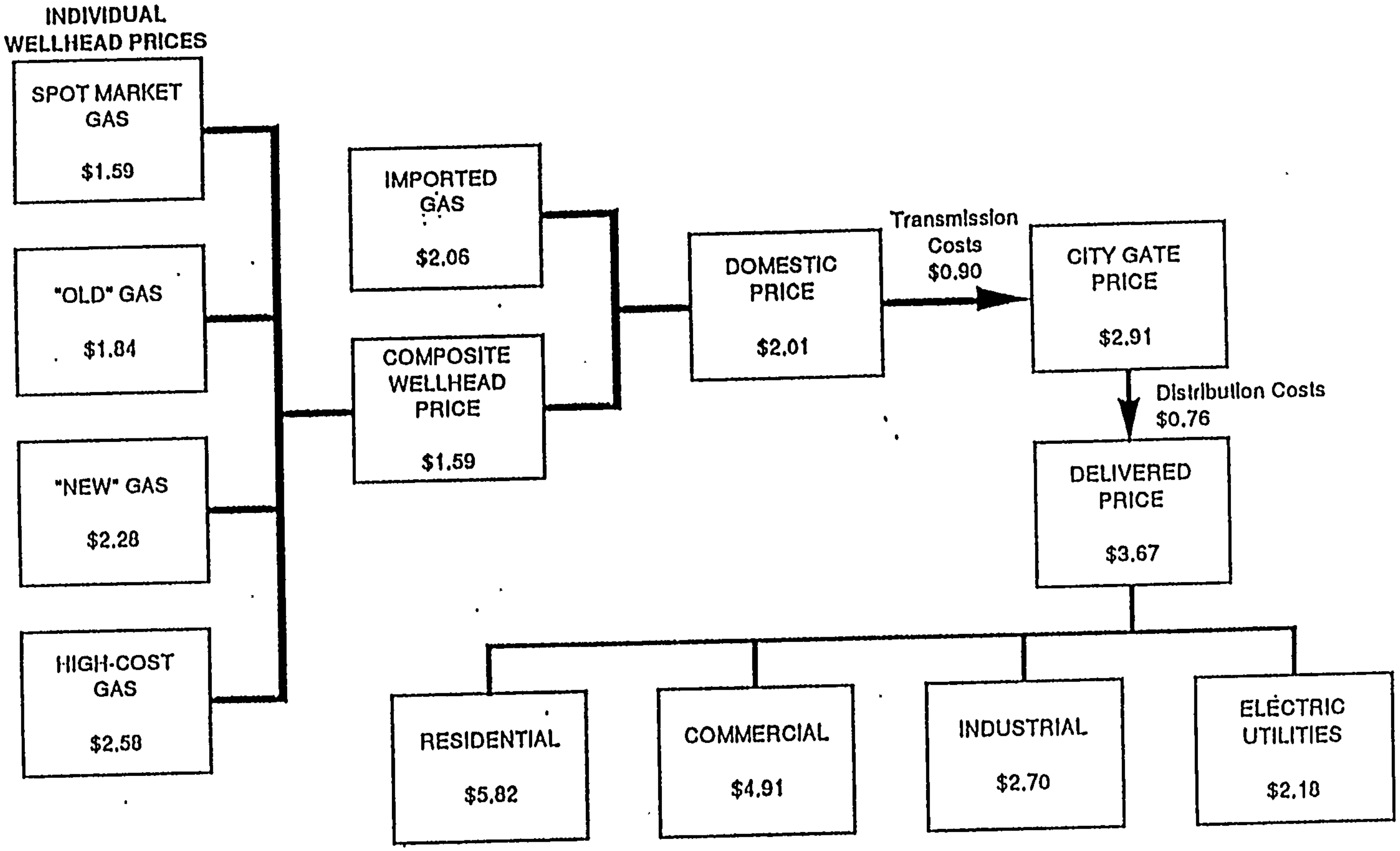
[43] Natural Gas Monthly, U.S. Department of Energy, Energy Information Administration, March 1992, in "Chemical Economics Handbook", SRI International, (June 1993.)

[44] Tannehill et. al. "Cost of Conditioning your Natural Gas for Market" presented at 73rd Annual GPA Convention, March 1994.

Figure 7.2

Natural Gas Prices In the United States—1991
(national average price per thousand cubic feet)



Source: Reference 43

1.4 Amenable U.S. Market

The information in Tables 7-2 and 7-3 was used to estimate the amenable U.S. market segments for the CO_2 ATM. Unassociated production was ~15 trillion ft^3, while the total active reserves are estimated at 144 trillion ft^3. The estimate for the discovered/non-producing low quality resource is comparable to that of the reserves for active wells and the undiscovered/undeveloped resource is estimated to be >4 times that of the current reserves. The portions of low quality gas, as seen, are substantially higher for the latter categories of the resources.

Of the segments identified in the report, two segments are amenable for CO_2 removal technologies: high CO_2 only (>2%), and high CO_2 and high H_2S (>4 ppm). Based on this assumption, the total amenable production and reserve segments (1988) are estimated to be about 2.2 trillion CFY and 24 trillion CF, or 15% and 17% of the total production rate and reserve, respectively. Assuming the ATM technology will capture 5-10% of the amenable production rates, or 0.8-1.7% of the total U.S. production, the market size projected for ATM is 400-800 million CFD/YR. To reiterate, the amenable segment in the discovered/non-producing low quality resource is comparable to the active reserve and the undiscovered/undeveloped resource is about 6 times that of the active reserve.

1.5 ATM Product Differentiation and Technology Benefits

The acid gas removal market is highly competitive as shown by the number of major vendors listed in Table 7-5. As shown in Table 7-6, the most commonly used technologies are absorption systems based on chemical or physical solvents. Major characteristics of amine versus general membrane technologies are compared in Table 7-7. Diethanolamine (DEA) and methyl diethanolamine (MDEA) systems have captured greater than 50% of the AGR market. An increase in market share for membranes and adsorption technologies is forecast if expected improvements to current generation products are realized. Indeed, this is projected to be the fastest growing market segment.

Table 7-5
Acid Gas Removal Market Players

Vendor	Technology Type*	Process Name
Shell	AC, AP	Sulfinol, -M, etc.
	AC	ADIP
Union Carbide	AC	AmineGuard
	AC	HS
	AC	Benfield
	AC	PSA
Dow	AC	GasSpec, ST-1, FT-1
Exxon	AC	Flexsorb -SE, PE, HP, PS
BASF	AC	MDEA
	AC	TEA
	AC	Alkazid
	AC	Sepasolv
Lurgi	AP	Rectisol
	AP	Amisol
Parsons	AP	Purisol
Koch	CR	Ryan-Holmes
Permea	M	Prism
Grace Membrane Systems	M	Grace Membranes
Separex	M	Separex
Delta Engineering	M	DELSEP
Peabody Holmes	DC	Stretford
ARI-Technolgies	DC	LO-CAT

* A=Absorption; C=chemical solvent; P=physical solvent; CR=cryogenic; M=membrane
PSA=pressure swing adsorption; DC=direct conversion

Table 7-6
Acid Gas Removal - Dominant Technologies, U.S. 1984-1995

Technology	Current Market Share	Projected Market Share
DEA (diethanolamine)	29	43
MEA (monoethanolamine)	25	2
Sulfinol (Mixed Solvents)	9	9
DEGA (diethyleneglycolamine)	6	2
Potassium Carbonate	4	0
MDEA (methyl diethanolamine)	4	19
Selexol (glycol derivatives)	2	5
Membranes	<1	3
Ryan-Holmes (cryogenic)	<1	2
Other	20	15
TOTAL	100%	100%

* all existing units
** new units only
from "North American Gas Treating Market Study", Purvin and Gertz, Inc., for Air Products and Chemicals, Inc., May 1984.

Table 7-7
Technology Comparison of Amine and Membrane Technologies

	Amine Technology	Membrane Technology
Pros:	long-term proven technology	active since early 1980s
	know-how in engineering contractors	easier field operation
	H_2S/CO_2 handling*	enhanced flexibility in meeting gas production criteria (flow rate)
	good economy of scale	attractive characteristics for off-shore markets (weight, size, no chemicals, modular design, etc.)
	low hydrocarbon losses*	short start-up time
Cons:	liquid processing/inventory	limited operating temperatures
	maintenance	tolerance to trace contaminants (performance & life)
	waste disposal	
	energy consumption increases as CO_2 in feed increases	

* These benefits will diminish in the event of a commercialized ATM technology.

There is some disagreement in the literature concerning the exact fit of membrane technology to this market, however, it is generally held that even currently available membrane systems are preferred over amine systems for production capacity of less than ≈20-30 MMSCFD.[45] In fact, Grace Membrane Systems claims to be competitive up to 60 MMSCFD.[46] It is also generally true that membrane technology is favored as the CO_2 concentration of the gas increases. As shown in Table 7-6, the market share currently held by membrane technology is <1%; but increasing. Membrane technology is becoming more attractive at remote wells, off-shore platforms, etc. Furthermore, the new U.S. energy initiative emphasizing natural gas will encourage future production of discovered but non-producing subquality wells and undeveloped resources.

Key suppliers of polymeric membranes are Grace, Hoechst Celanese (Separex), and Dow Cynara. Dow has been active in EOR application and markets an "own-and-operate" concept. Their overall activities in this application are[47] outlined below.

GRACE:

- spiral-wound technology originally developed by Bend Research
- active since 1984
- large research efforts in CO_2 membranes
- mainly sale-of equipment
- ~100 small plants
- unattended at well head & remote areas
- <1,500 psia

HOECHST CELANESE/SEPAREX:

- spiral-wound technology
- active since early 1980s
- ~20 plants, generally <3.5 mmscfd
- <1,400 psia

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[45] .K. Changela et. al., "Technical Evaluation of Hybrid Membrane/DEA Modeling", Topical Report, GRI (1990).

[46] R.E. Babcock et. al., "Natural Gas Cleanup: A Comparsion of Membrane and Amine Treatment Processes", presented at the AIChE Spring National Mtg., March 1988.

[47] Torleiv et. al., "CO_2/HC Membrane Separation: A Mature Technology", presented at the AIChE Spring National Meeting, March 1992.

CYNARA/DOW:

- hollow fiber technology
- mainly own-and-operate concept
- primary focus in EOR ($C0_2$ flooding)
- SACROC operation (80 mmscfd) start-up in 1983, 240 membrane elements
- a few other small plants

Based on our analyses to date, we believe that a successful ATM technology will be significantly differentiated from current membrane technology and will lead to a number of technology benefits:

DIFFERENTIATION:

- High selectivity with a CO_2 permeance at least comparable to conventional CO_2 membranes
- Light gas (CH_4, etc.) recovery at high pressure
- Outstanding performance characteristics in the low partial pressure region

TECHNOLOGY BENEFITS:

- Higher product recovery
- Lower energy consumption
- Simpler process (number of stages) and less equipment
- Greater market penetration

2.0 CO_2- Selective ATM: Other Opportunities

In addition to the natural gas application, several large volume markets with good growth opportunities have been identified for ATM materials that will selectively permeate CO_2 from synthesis gas or process gas streams in chemical manufacturing plants. Because the applications and treating specifications vary, we have quantified the size of the amenable market by estimating the gas handling volumes.

As discussed above, roughly, 5100 MMSCFD of natural gas is treated for CO_2 removal in the US. This represents about 10% of current US production. Another 3500 MMSCFD of natural gas is treated for CO_2 and H_2S impurities. This portion of the amenable market requires AT materials that can withstand some exposure to H_2S. This area is an ongoing part of our Active Transport materials development program.

Chemical manufacturing operations treat large volumes of gas to remove CO_2. They include SYNGAS treating for H_2 and ammonia production; ethylene manufacturing , and selective oxidation processes for ethylene oxide, vinyl acetate monomer, and other chemicals. Since the 1950's, the chemical industry has used selective oxidation routes for key commodity chemicals. Some oxidation processes have evolved from using air to using pure oxygen ($> 95\%$ O_2). The oxygen based processes generally remove CO_2 from gases that are recycled to the main reactor. This trend is continuing as evidenced by incorporation of such technology into new processes being developed for maleic anhydride and acrylonitrile. In general, the chemical manufacturing plants require very selective CO_2 removal because they cannot afford to lose high valve feedstocks or products to the permeate.

2.1 Synthesis Gas Treating

Our last interim report provided some background on the use of ATM's for removing CO_2 from synthesis gas in ammonia and hydrogen manufacturing plants. We presented process schemes using hybrid CO_2 removal systems - ATM and MEA combinations for ammonia manufacturing, and ATM-PSA combinations for hydrogen manufacturing.

Ammonia Plants

For ammonia plants, the acid gas treating is for CO_2 removal only. If H_2S is present in the natural gas feed to the plant, it is usually removed by adsorption ahead of the natural gas reformer. The synthesis gas feed to the acid gas removal step contains from 16-19 mole per cent CO_2. It is processed to less than 0.05 mol % CO_2. The tight CO_2 product spec would normally rule out a stand-alone membrane system. The total synthesis gas volumes treated for ammonia manufacturing in the US and the world are 7500 and 30,000 MMSCFD, respectively[29]. The US volume assumes 100% capacity utilization. The world volume assumes 75% capacity utilization.

As discussed earlier,[29] growth in the US ammonia market will occur mainly through retrofits rather than new construction. We concluded from discussion with ammonia producers that the industry is not likely to replace sunk AGR capital with other technologies. In specific plants, ATMs used ahead of an existing AGR system might be considered for retrofits in connection with capacity increases. At the same time, new inhibitors and additives are being introduced that allow higher MEA concentration solutions be used. This reduces the required solvent recirculation rates (allowing some room for debottlenecking) and the steam needed for solvent regeneration.

Hydrogen Manufacturing

Synthesis gas treating for hydrogen manufacture requires the removal of several impurities - N_2, CO, CO_2, and H_2O. Roughly 3400 MMSCFD of synthesis gas needs to be treated for hydrogen plants serving refineries and chemical plants in the US. (This figure excludes ammonia, methanol, and acetic acid manufacturing.)

The hybrid ATM-MEA combination, discussed above for ammonia plants, can also be used for older hydrogen or carbon monoxide plants using MEA for CO_2 removal. Newer hydrogen plants have adopted PSA technology for synthesis gas purification. The advantages of PSA are 1) the H_2 product is retained at high pressure; 2) the PSA can remove all impurities in one step. (Older methods required MEA (for CO_2 removal), a drier, and then a cold box for high purity H_2 or CO plants; or a MEA -methanator combination for lower purity hydrogen used in refineries and ammonia plants.)

Air Products is the world's largest producer of merchant hydrogen (more than 25 plants) and produces over 400 MMSCFD of hydrogen. We reviewed ATM integration schemes with PSA or MEA systems for CO_2 removal with our HYCO (hydrogen-carbon monoxide) plant process engineering group. If ATMs were commercially available, they could have limited use for older plants using MEA. Some benefits may be derived from ATM-PSA combinations in new plants. At first pass, the HYCO designers estimate there will not be a downsizing significant of the PSA. PSA size is set more by the N_2 and CO removal requirements, rather than CO_2, however, this application is still under review. A perceived drawback to the ATM system is the potential return to multiple process steps for hydrogen clean-up.

2.2 Chemicals Manufacturing by Selective Oxidation Processes

In addition to synthesis gas treating, CO_2 removal is used in chemicals manufacturing for selective oxidation processes. These include ethylene oxide, vinyl acetate monomer, vinyl chloride monomer, and new routes being developed for acrylonitrile and maleic anhydride.

Most of the oxidation processes requiring CO_2 removal use pure O_2 instead of air. They recycle a large volume of gas around a reactor loop to help with reactor temperature control and to avoid flammable conditions since oxygen is being reacted with a hydrocarbon feed. CO_2 is produced in the reactor through nonselective, by-product reactions and must be removed from the recycle gas, usually to optimize catalyst performance. Grouped together, the gases treated for CO_2 removal in the selective oxidation plants represent a large market, comparable to the natural gas treated for CO_2 removal in the US.

Generally, these processes require very selective removal of CO_2 to avoid costly losses of chemical feedstock, e.g., ethylene. The standard technology for the industry is the Benfield process because of its high selectivity and its ability to process gas streams that contain oxygen. Most amine based absorption systems and physical solvents can not be used. Polymer membranes have not been used to remove CO_2 in any of these applications because of their poor selectivity, but they have been used in some plants for purge gas treating.

We met with Scientific Design, a leading licensor for ethylene oxide technology. They expressed interest in an all membrane process to replace the Benfield process in their ethylene oxide plants (Figure 7-4). They stressed high selectivity would be required. Table 7-8 lists typical stream compositions for a CO_2 removal unit in an ethylene oxide plant. The flows are for a 300 MM pound per year plant. Complete CO_2 removal is not required (treated gas CO_2 specification is $\approx$1 mol%). Also, the recycle gas does not need to be dehydrated, as in natural gas treating. On first pass the ethylene oxide process conditions are well suited for an ATM. In addition, because it is an attended plant, humidity control schemes, if required, would be more readily accepted.

3.0 Ammonia-Selective ATM Materials

Marketing activities for ammonia applications were completed in 1992. The details are documented in the latest interim report, "Development of Active Transport Membrane Devices - Interim Report" (issued January 1993). The highlights are presented here.

Table 7-8

Ethylene Oxide Plant - CO2 Removal Service

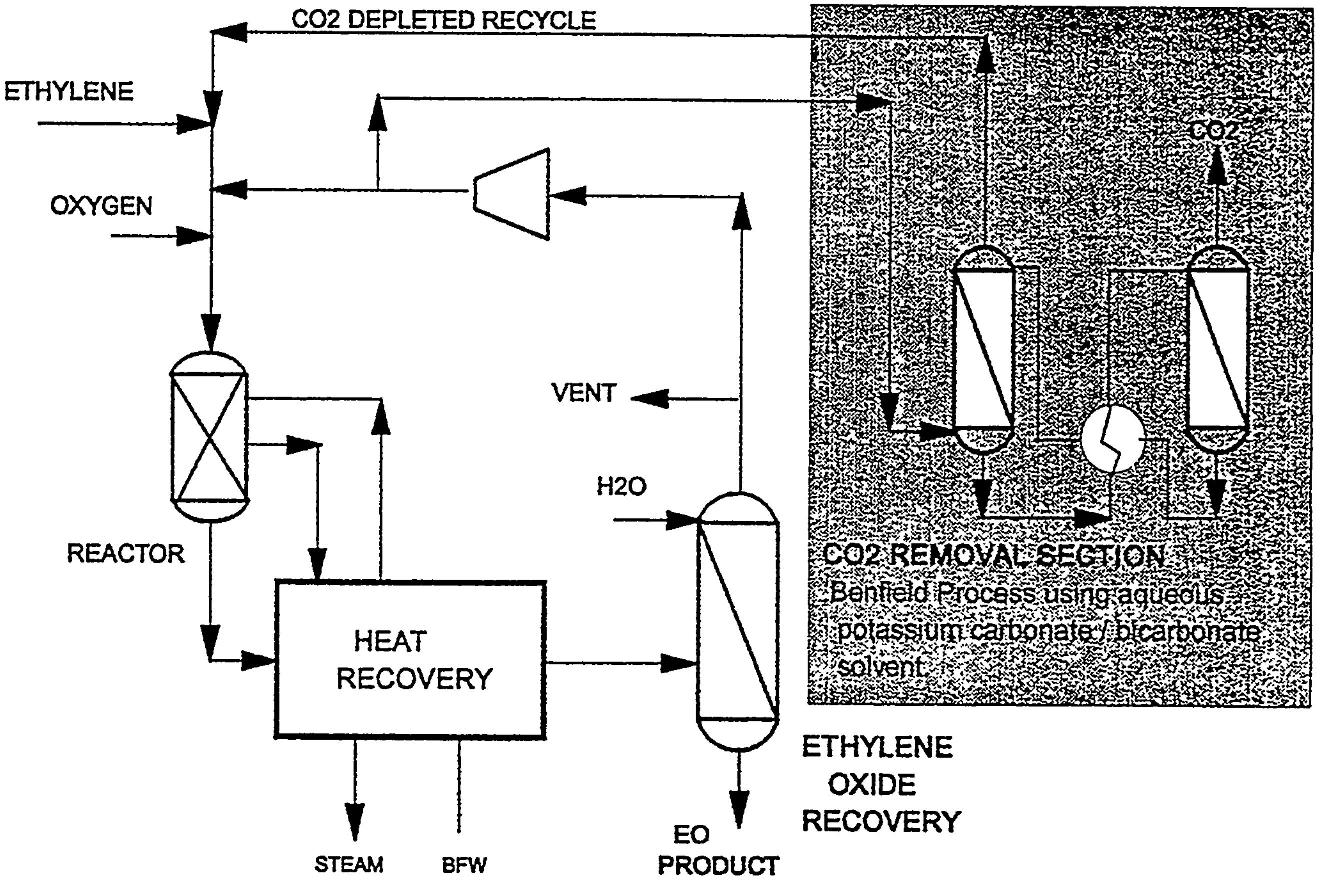
Component	MWT	Feed to CO2 Removal.		Treated Gas
		mol %		mol %
Ethylene	28	20.50		20.89
Oxygen	32	3.54		3.60
Carbon Dioxide	**44**	**3.94**	(a)	**0.78**
Argon	39.95	9.72		9.91
Methane	16	59.95		61.34
Ethane	30	2.10		2.14
Ethylene Oxide	44	20 - 100 ppm	(b)	20 - 100 ppm
Acetalhyde	44	0.00		0.00
Formaldehyde	30	0.00		0.00
Water	18	0.27		1.34
Ethylene Dichloride	99	2- 3 ppm	(b)	2- 3 ppm
Potassium Carbonate	138	0.00		0.00
TOTAL		100.00		100.00
GAS TREATED, MMSCFD		**140**	(c)	

Notes:

a) Calculated from SRI report. SRI confirms range is from 4 to 7 mole% CO2.
b) Provided by Scientific Design.
c) Gas treated for a 300 MM lb/yr EO Plant (136.1 M MTPA)

Rule of thumb : Gas treated (expressed in MM SCFD) equals about half of EO plant nameplate capacity expressed in MM lb/yr, or equal to nameplate capacity, expressed in M MTPA.

Figure 7-3
Generic Ethylene Oxide Process



3.1 Technology Status

Air Products researchers fabricated and tested multi-layer composite membranes for NH_3 removal from mixtures of NH_3, H_2 and N_2. These materials exhibited high NH_3 permeance and selectivity over N_2 and H_2. The membranes were stable at pressures up to 1000 psi. The permselectivity at these pressures, while less than at low pressure, was acceptable. Process simulations were completed for several membrane applications in an ammonia synthesis plant. (This analysis assumed that commercial modules could achieve the high permselectivity of laboratory membranes and that concentration polarization effects were not dominant.) The results were encouraging and showed

- Ammonia selective ATMs could be used to increase product recovery and debottleneck existing plant capacity by 25% without major revamps to the refrigeration system.
- For new plants, ammonia selective ATMs could be used with much smaller refrigeration equipment and yield substantial capital and operating savings.
- Ammonia selective ATMs could be used to recover NH_3 product from an existing plant purge gas by sweeping with a low pressure slipstream of syngas. This would compete with water wash systems used in today's operations.

3.2 Marketing

Macro world market conditions were assessed and discussions were held with four major ammonia producers (The producers we contacted account for almost 36% of US production). The findings are summarized below.

World Market Conditions

The world ammonia industry is undergoing a period of restructuring that began in the early 1980's. The industry is recovering from a period of stagnant growth, overcapacity, and relocation of major production facilities to less developed regions with low natural gas feedstock costs. The interim report referenced earlier presents details for ammonia production and consumption by geographic area. The data includes 1990 actuals and projections for 1995. New plant capacity is anticipated for less developed regions - SW Asia, Africa, South America, and the Middle East.

US Industry

Between 1980 and 1990, US ammonia consumption remained essentially flat, between 14,000 and 15,000 Metric Tons per year. Imports grew 52% and domestic production fell 13%. 34 plants were shutdown. Retrofits for better efficiency and some debottlenecking capacity projects are the only on-going activities. No new capacity is forecast for 1995. Imports are forecast to increase.

3.3 Contacts with Ammonia Producers

Air Products reviewed the potential membrane applications for ammonia manufacturing with four US producers. Most of the producers also manufacture urea; and they discussed membrane uses for both chemical processes.

We presented two process schemes using ATMs for ammonia recovery from the converter effluent gas. One used ATMs to recover bulk NH_3. (This would displace existing equipment.) The second scheme used ATMs before or after the deep level refrigeration stage (last stage) to get higher product recovery. This process would reduce the ammonia content of the gas recycled to the ammonia converter section, and increase conversion per pass.

The producers put a low priority on the bulk removal scheme; however, they thought the second scheme would be useful for their debottlenecking and efficiency improvement programs if we could attain the membrane performance assumed for the process simulation work.

Ammonia recovery from the plant purge gas was also considered. Most existing plants use membranes for H_2 recovery and a water wash operation for ammonia. Producers were interested in an all membrane purge gas treating system. However, it is unlikely that producers would replace existing water wash units with ATM's because operating savings may not be large enough to justify replacement of existing capital.

3.4 Competition

There are no competing membrane technologies for NH_3 removal from N_2 or H_2 containing gases. ATM's would however need to out perform conventional ammonia separation technologies including refrigeration and water wash systems. New catalysts for NH_3 converters that enhance conversion per pass would also compete with the debottlenecking process schemes developed.

4.0 Conclusions

Phase 1 commercial development activities have focused on identifying and evaluating potential ATM applications, understanding market needs and forces, and in setting performance criteria for new gas separation technologies based on active transport membranes.

- Several large volume markets with good growth have identified for AT materials that selectively remove CO_2 from natural gas or process gases in chemical manufacturing plants.

- CO_2 removal from natural gas has been selected as the first target application. Between 15 and 20% of US production and proven gas reserves require treatment to reduce the concentration of CO_2 or CO_2 and H_2S to pipeline specifications. U.S. production is growing at ≈4% per year and capacity utilization rates are high; forecasted growth will require construction of new plants. An H_2S tolerant membrane will be required to capture portions of the market.

- CO_2 removal from natural gas is a highly competitive market. Membrane technology is gaining acceptance, and is now competing with solvent based absorption technologies in small capacity installations. AT materials will need to outperform existing membranes.

- CO_2 removal from process gases in chemical plants represents a potential market as large as natural gas treating (on a volume of gas treating basis). Specific applications include synthesis gas treating for ammonia, hydrogen, and carbon monoxide manufacturing, and CO_2 removal from process gases in chemical plants using oxygen based selective oxidation technologies (e.g. ethylene oxide).

- CO_2 removal services in selective oxidation plants represent an attractive potential market for CO_2 AT materials. Treated gas volumes and projected growth are good, and the service requires very selective CO_2 removal. The competition is limited down to Benfield systems, since the processed gases contained oxygen. On first pass, these applications appear well suited for AT membranes. The treated gas can contain water and some residual CO_2. The operations are attended, so humidity control systems, if required for AT membranes, would be more readily accepted.

- Ammonia manufacturing offers limited market opportunities for new ammonia selective AT materials (especially in the U.S.). Membrane performance targets were established.

We have assigned a low priority to the ammonia selective AT materials, and stopped R&D efforts in order to pursue better opportunities for CO_2 selective membranes in natural gas applications.

VIII. Technology Development Status and Overall Recommendations

ATM developmental efforts have thus far focused on identifying ATM and substrate materials, spinning support fiber, and fabricating and evaluating thin film composite hollow fiber lab modules for the natural gas application. Other work focused on developing a computer model of the permeation mechanism in ATMs.

A number of ATM materials have been identified as candidates for the CO_2 separating layer. These materials are based on polyelectrolytes and have been tested in flatsheet or hollow fiber forms. In general, they exhibited a high selectivity (>>100) but a relatively low permeance rate ($<30 \times 10^{-6}$ scc/cm^2•sec•cm-Hg). EXTM6-4 is the leading candidate ATM material. The CO_2 flux of planar EXTM6-4 composite membranes meets the preliminary flux target. Since the economics (and competitiveness) of the ATM system in large natural gas applications are determined mainly by membrane investment (area / permeance), it would be highly desirable to maximize the CO_2 flux.

In addition to the attractiveness of obtaining an optimized permeance, it is also highly desirable to minimize the impact of H_2O vapor on polyelectrolyte ATMs. If the permeance rate of H_2O is very high, the H_2O level in the latter half of the ATM module may become very low and consequently the ATM performance and stability may become issues.

The best support material is PAI, which shows a high tolerance to hydrocarbon solvents and is processable into a microporous hollow fiber substrate. However, the ultimate compatibility and coatability of this support material to the ATM remain to be determined.

Future efforts in ATM should address following development issues:

- Maximizing the CO_2 permeance
- Maintaining high $\alpha(CO_2/CH_4)$, $\alpha(H_2S/CO_2)$ and $\alpha(CO_2/H_2)$ over the range of process conditions
- Establishing the relationship of CO_2 permeance and selectivity to ATM thickness

- Verifying reproducibility and reversibility of the CO_2 permeance versus CO_2 partial pressure and relative humidity

- Further investigate the effect of temperature on performance

- Measuring the H_2O permeance and assessing the impact of feed H_2O level on ATM performance

- Assess the impact of sulfur impurities on process economics and seek material modifications if required

- Extending lifetime and stability studies to real process streams

As these issues are addressed, two key objectives must be accomplished:

1) Achieve the flatsheet EXTM6-4 permeation characteristics (selectivity and intrinsic CO_2 permeability) in a thin hollow fiber membrane form using a substrate material that meets our selection criteria (hydrocarbon tolerance, etc.) such as PAI.

2) Develop a ATM-based thin film composite membrane and its continuous fabrication technologies that require minimal modifications to Air Products' commercial fabrication facilities.

Finally, in addition to developing the ATM technology, one should continue to monitor and assess new conventional polymeric membranes being developed and determine if any of these new polymeric membranes may offer an attractive interim product or overall superior system.

Appendix A - Derivation of ATM Computer Model

A semi-empirical model is proposed for estimating the acid gas flux through active-transport membranes. The flux equation is similar to standard facilitated transport expressions with the exception that the effective permeance is corrected for relative humidity and, if applicable, for carrier facilitation:

$$N_i = P/\ell_i \bullet (p_{if} - p_{iL}) \bullet R_i \bullet F_i \tag{1}$$

where, N_i = flux of component **i**

p_{if} = partial pressure of component **i** on feed side

p_{iL} = partial pressure of component **i** on permeate side

P/ℓ_i = permeance of component **i** as dissolved free gas at reference humidity $\Re^*$

R_i = relative humidity correction factor for permeance of component **i**:

$$R_i = 1 + \frac{\delta_i (\Re_f - \Re^*)}{\Pi_{i*}} \tag{2}$$

δ_i = change in permeance of component **i** per unit change in humidity

$\Re_f$ = relative humidity of vapor on feed side

$\Re^*$ = reference relative humidity

F_i = facilitation factor, which is unity for non-reactive components

For an acid gas, the facilitation factor is given by the following expression, which is based on the assumption of reaction equilibrium throughout the membrane.

$$F_i = 1 + \frac{\alpha_i \beta_i}{\Pi_i^*} \left\{ \frac{\dfrac{p_{if}}{(p_{if} - p_{iL})}}{1 + \beta_i p_{if} + \beta_j p_{jf}} - \frac{\dfrac{p_{iL}}{(p_{if} - p_{iL})}}{1 + \beta_i p_{iL} + \beta_j p_{jL}} \right\} \quad (3)$$

where, α_i = product of diffusivity of carrier-solute complex and total carrier concentration divided by the effective thickness of the membrane. This parameter is factor a_4 if the solute is CO_2 or factor a_6 if the solute is H_2S. They are determined by curve-fitting performance data as discussed below.

β_i = product of equilibrium constant of carrier-solute reaction and Henry's Law solubility constant for the solute; factor a_1 or a_2. These parameters are also based on curve-fitting performance data.

The subscript 'j' refers to the second acid gas if present.

The following reactions are assumed to occur within the polyelectrolyte membrane:

$$H_2O + 2F^- \leftrightarrow HF_2^- + OH^- \quad (R1)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (R2)$$

$$H_2S + OH^- \leftrightarrow HS^- + H_2O\uparrow \quad (R3)$$

For simplicity, we will use the following symbols to denote the various species:

$A = CO_2$

$B = OH^-$

$AB = HCO_3^-$

$E = H_2S$

$S = HS^-$

$W = H_2O$

$F = F^-$

$G = HF_2^-$

At equilibrium, the flux of any volatile component through the membrane is simply[#] :

$$N_j = \frac{1}{L} \sum_{i=1}^{M} v_{ij} D_i (C_{io} - C_{iL}) \quad (4)$$

[#] J.S. Schultz et.al.,"Facilitated Transport via Carrier Mediated Diffusion in Membranes," ***AIChE Journal*** 20 (1974).

where, N_j = flux of volatile species **j** through membrane of thickness **L**

D_i = diffusion coefficient of species **i**

v_{ij} = number of molecules of species **j** contained in species **i**

C_{io} = concentration of species **i** in membrane at feed interface

C_{iL} = concentration of species **i** in membrane at permeate interface

M = total number of species

We are assuming that mass transfer resistance between the bulk gas and the membrane interface is negligible and the PDMS coating and microporous support contribute no mass transfer resistance.

Thus for carbon dioxide,

$$N_A = \frac{D_A(C_{Ao} - C_{AL})}{L} + \frac{D_{AB}(C_{ABo} - C_{ABL})}{L} \tag{5}$$

Likewise for hydrogen sulfide,

$$N_E = \frac{D_E(C_{Eo} - C_{EL})}{L} + \frac{D_S(C_{So} - C_{SL})}{L} \tag{6}$$

Assuming that the solubility of the dissolved acid gases can be described adequately by Henry's Law, we have

$$C_A = H_A p_A \tag{8}$$

$$C_E = H_E p_E \tag{9}$$

where, p_i = partial pressure of species **i**

H_i = Henry constant for species **i**, assumed to be a function of temperature only

The concentrations of the non-volatile species are derived from the reaction equilibrium relationships:

$$K_1 = \frac{C_B C_G}{C_W C_F^2} \tag{10}$$

$$K_2 = \frac{C_{AB}}{C_A C_B} \tag{11}$$

and $$K_3 = \frac{C_S}{C_E C_B} \tag{12}$$

where, K_i = equilibrium constant for reaction **i**, which is assumed to be a function of temperature only.

For HCO_3^- we have,

$$C_{AB} = K_2 C_A C_B = \frac{K_2 C_A C_T}{1 + K_2 C_A + K_3 C_E} \tag{13}$$

where, C_T = total concentration of carrier, the hydroxyl ion, given by

$$C_T = C_B + C_{AB} + C_S = C_B\,(1 + K_2 C_A + K_3 C_E) \tag{14}$$

Since the fluoride loading is fixed, then C_T is fixed if the water loading is also fixed. Thus most experiments can be analyzed without the need to incorporate the total fluoride concentration, given by

$$C_{TF} = 2C_G + C_F$$

which is a true system invariant.

Likewise for HS⁻ we have

$$C_S = \frac{K_3 C_E C_T}{1 + K_2 C_A + K_3 C_E} \tag{15}$$

$$N_A = \frac{D_A H_A (p_{Ao} - p_{AL})}{L} + \frac{D_{AB} C_T K_2 H_A}{L} \left\{ \frac{p_{Ao}}{1 + K_2 H_A p_{Ao} + K_3 H_E p_{Eo}} - \frac{p_{AL}}{1 + K_2 H_A p_{AL} + K_3 H_E p_{EL}} \right\} \tag{16}$$

$$N_E = \frac{D_E H_E (p_{Eo} - p_{EL})}{L} + \frac{D_S C_T K3 H_E}{L} \left\{ \frac{p_{Eo}}{1 + K_2 H_A p_{AL} + K_3 H_E p_{EL}} - \frac{p_{EL}}{1 + K_2 H_A p_{AL} + K_3 H_E p_{EL}} \right\} \tag{17}$$

With a sweep stream, the permeate pressures become negligible,

$$N_A = \left\{ D_A + \frac{D_{AB} C_T K_2}{1 + K_2 H_A p_{Ao} + K_3 H_E p_{Eo}} \right\} \frac{H_A p_{Ao}}{L} \tag{18}$$

$$N_E = \left\{ D_E + \frac{D_S C_T K_3}{1 + K_2 H_A p_{Ao} + K_3 H_E p_{Eo}} \right\} \frac{H_E p_{Eo}}{L} \tag{20}$$

In terms of permeance

Table A-1

CO_2 Partial Press (cmHg)	CO_2 Permeance scc/(cm^2-s-cmHg)	H_2S Partial Press (cmHg)	H_2S Permeance scc/(cm^2-s-cmHg)
4.2	0.140	4.2	0.98
5.3	0.11	5.4	0.84
9.5	0.10	9.6	0.76
13.6	0.09	13.8	0.64
17.7	0.08	17.9	0.59
21.2	0.06	21.5	0.49
29.1	0.05	29.5	0.36
34.5	0.04	36.1	0.33
46.9	0.06	49.2	0.39
54.5	0.05	57.1	0.33
29.82	0.183		
48.74	0.155		
66.58	0.145		
99.05	0.12		
146.74	0.087		

Values obtained for the six parameters were:

Parameter index - i	Value of Parameter - a(i)
1	0.0166308
2	0.245230
3	0.0289735
4	13.6300
5	0.218506
6	6.80230

The sum-square relative error was 0.3334. The overall quality of the curve-fits is quite good as may be seen in Figures A-1 and A-2.

For this example, the selectivity of H_2S over CO_2 is shown in Figure A-3. The amount of scatter in the data is typical. In Figure A-4, the predicted facilitation factors are presented as functions of the feed partial pressures for an equimolar mixture of H_2S and CO_2. As expected, the best enhancement in mass transfer occurs at the lowest compositions.

The effect of relative humidity on the permeance of CO_2 for the same membrane was also investigated. In this series of tests, the objective was to measure the permeance of water so a dry sweep gas was used. Thus the CO_2 permeances are not directly comparable to those above where the sweep gas was humidified. Nonetheless, the CO_2 permeance is a linear function of the relative humidity as shown in Figure A-5.

Data for a PDMS/PVBTAF membrane also indicated that the permeance of CO_2 is linearly dependent upon the relative humidity.

The data were fit to the following function:

Table A-2

CO_2 Partial Press (cmHg)	CO_2 Permeance scc/(cm^2-s-cmHg)	Relative Humidity
111.0	0.229	0.163
106.0	0.291	0.163
200.0	0.179	0.163
279.0	0.111	0.163
350.0	0.085	0.163
111.0	0.378	0.231
201.0	0.235	0.231
272.0	0.185	0.231
350.0	0.158	0.231
348.0	0.291	0.321
111.0	0.785	0.440
202.0	0.587	0.440
272.0	0.520	0.440
344.0	0.499	0.440

$$P/\ell_{CO_2} = \left[a_3 + a_4\left(\Re_f - \Re^*\right)\right]\left\{1 + \frac{a_2}{a_3 p_{CO_2}}\right\} \qquad (23)$$

Note that the term in brackets is the facilitation factor when the term $a_1 p_{CO_2} >> 1$, which is true in this case. In order to accurately determine a_1, data at lower partial pressures of CO_2 are required.

Using a reference humidity of 0.163, values obtained for the 3 parameters were:

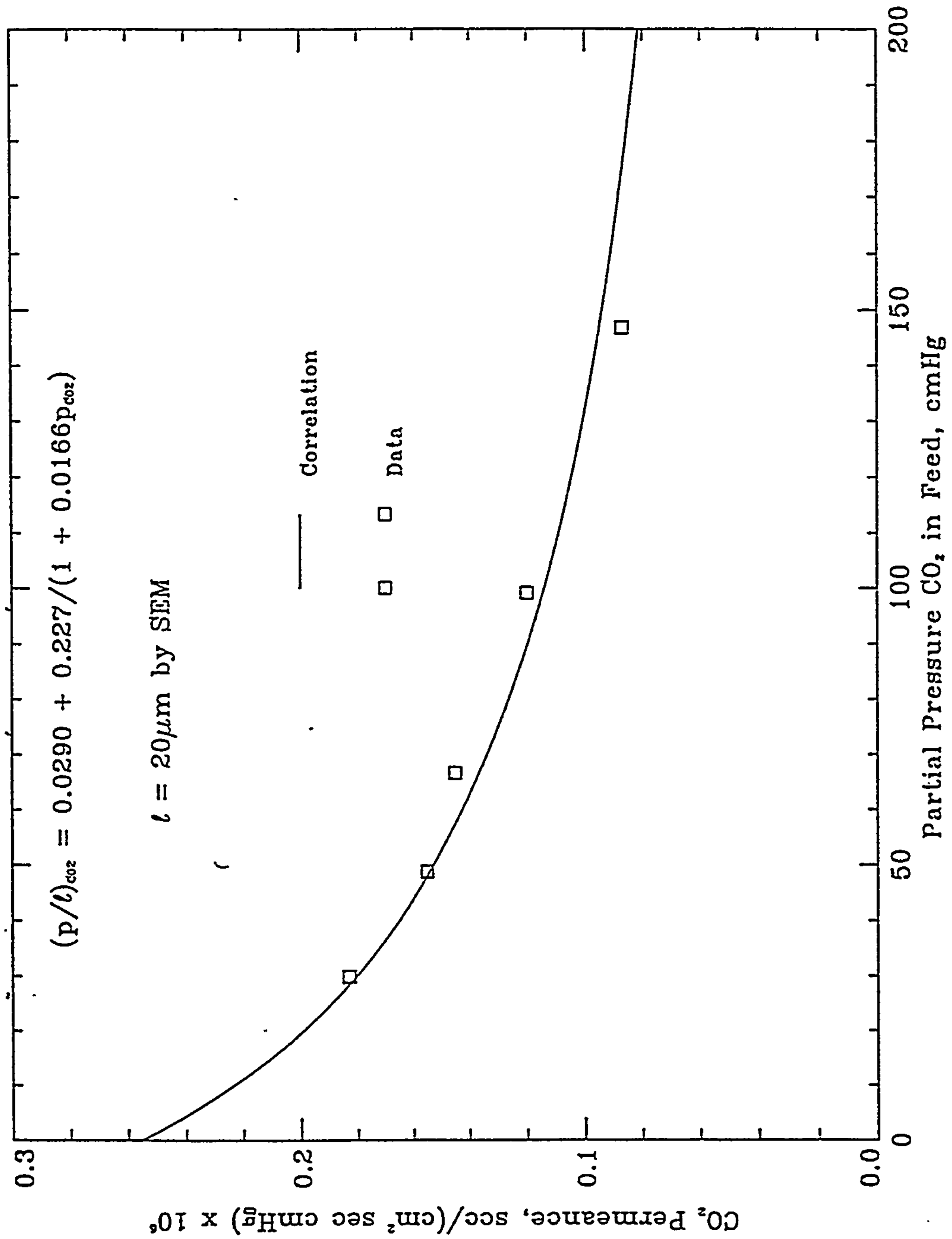
$a_2 = 20.99$

$a_3 = 0.03838$

$a_4 = 0.4165$

and the sum-square relative error was 0.2053. As shown in Figure A-6, the data correlate fairly well, with the worst deviation between data and model occurring at the highest relative humidity tested.

Figure A-1



$(p/\ell)_{co_2} = 0.0290 + 0.227/(1 + 0.0166p_{co_2})$
ℓ = 20μm by SEM
Correlation
Data
0.3
0.2
0.1
0.0
CO_2 Permeance, scc/(cm² sec cmHg) x 10⁶
0
50
100
150
200
Partial Pressure CO_2 in Feed, cmHg

Figure A-2

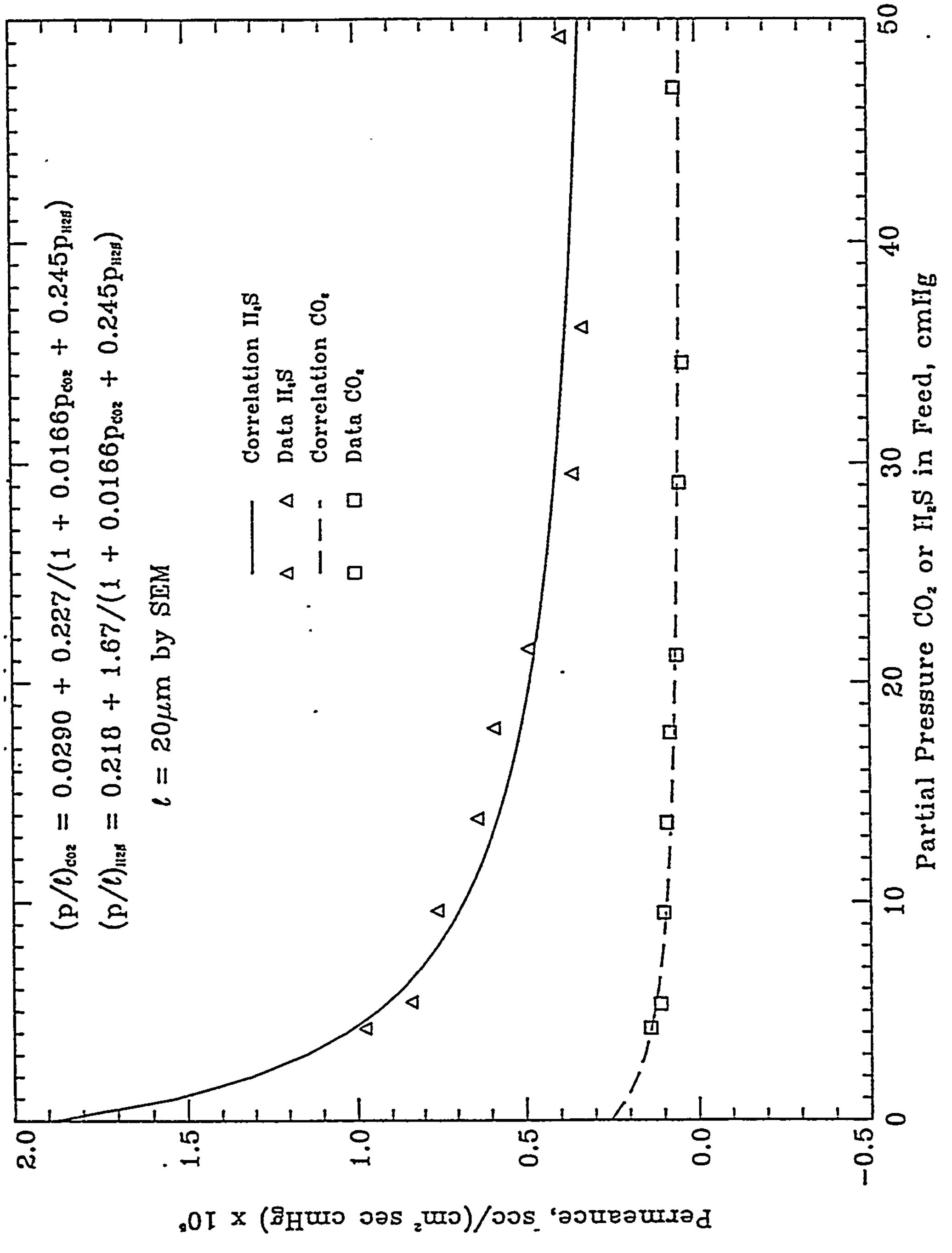

$(p/\ell)_{CO2} = 0.0290 + 0.227/(1 + 0.0166p_{CO2} + 0.245p_{H2S})$
$(p/\ell)_{H2S} = 0.218 + 1.67/(1 + 0.0166p_{CO2} + 0.245p_{H2S})$
$\ell = 20\mu m$ by SEM
Correlation H₂S
Data H₂S
Correlation CO₂
Data CO₂
Permeance, scc/(cm² sec cmHg) x 10⁶
2.0
1.5
1.0
0.5
0.0
−0.5
Partial Pressure CO₂ or H₂S in Feed, cmHg
0
10
20
30
40
50

Figure A-3

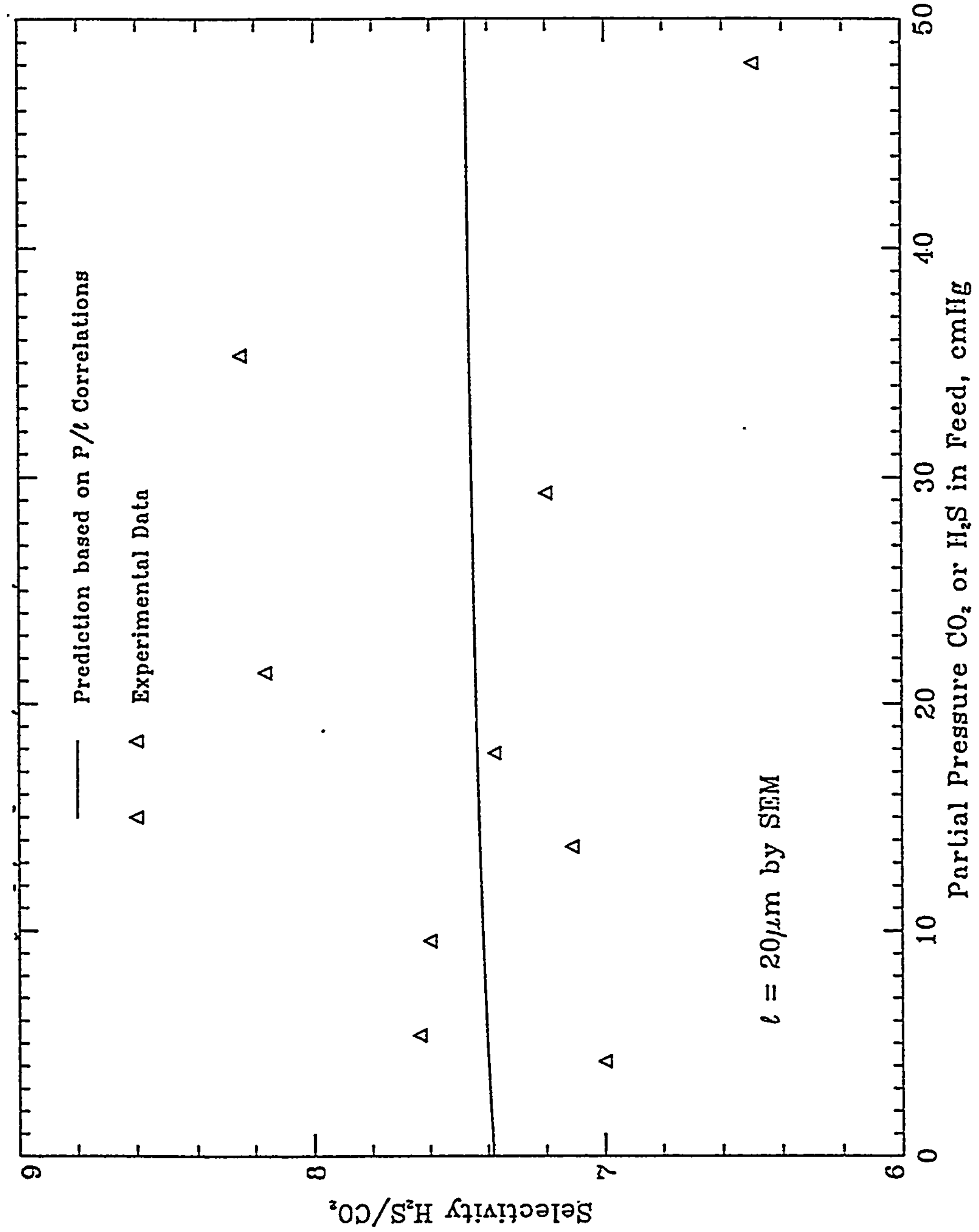

Prediction based on P/ℓ Correlations
Experimental Data
ℓ = 20μm by SEM
Selectivity H_2S/CO_2
Partial Pressure CO_2 or H_2S in Feed, cmHg
0
10
20
30
40
50
6
7
8
9

Figure A-4

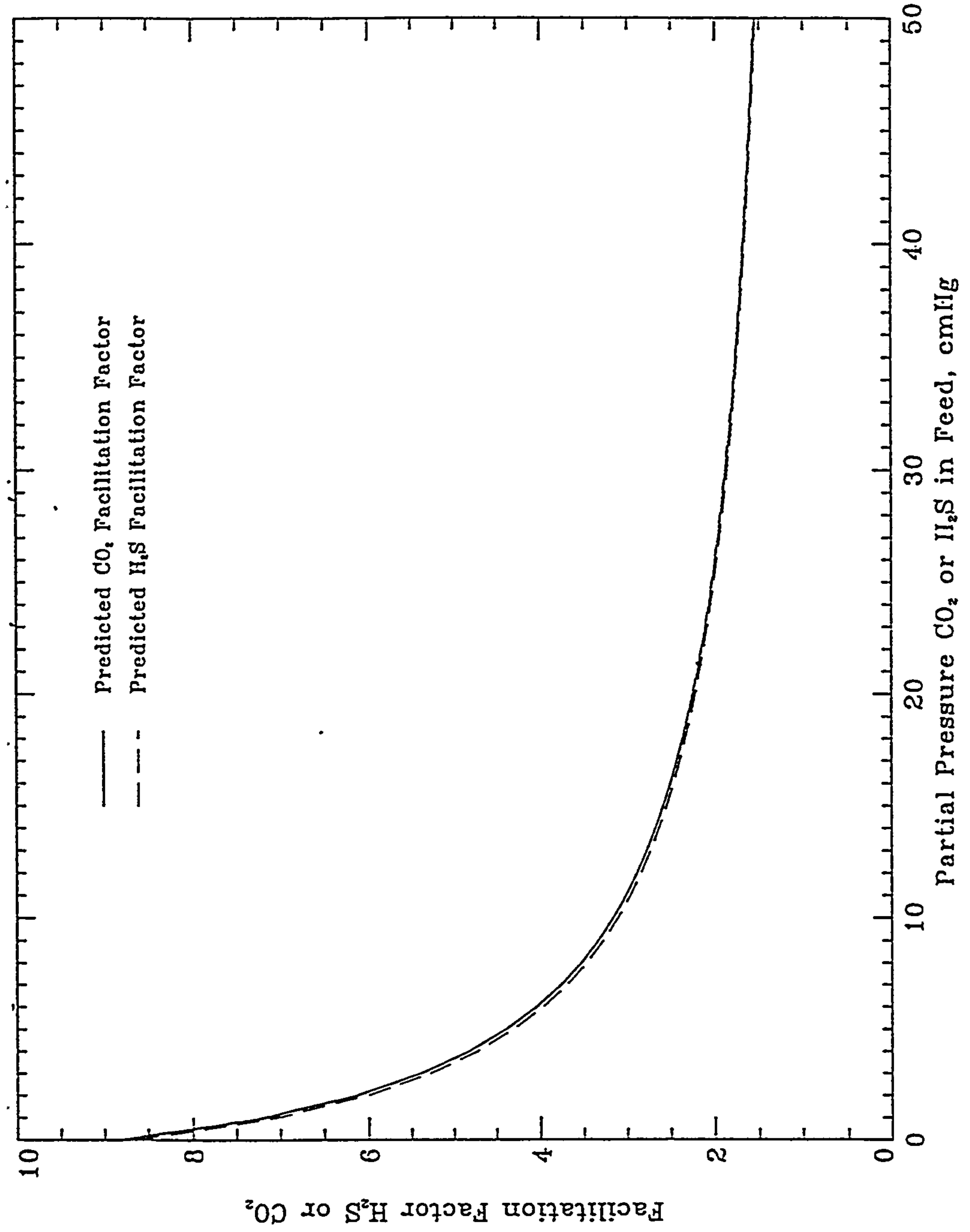

Predicted CO₂ Facilitation Factor
Predicted H₂S Facilitation Factor
Facilitation Factor H₂S or CO₂
10
8
6
4
2
0
0
10
20
30
40
50
Partial Pressure CO₂ or H₂S in Feed, cmHg

Figure A-5

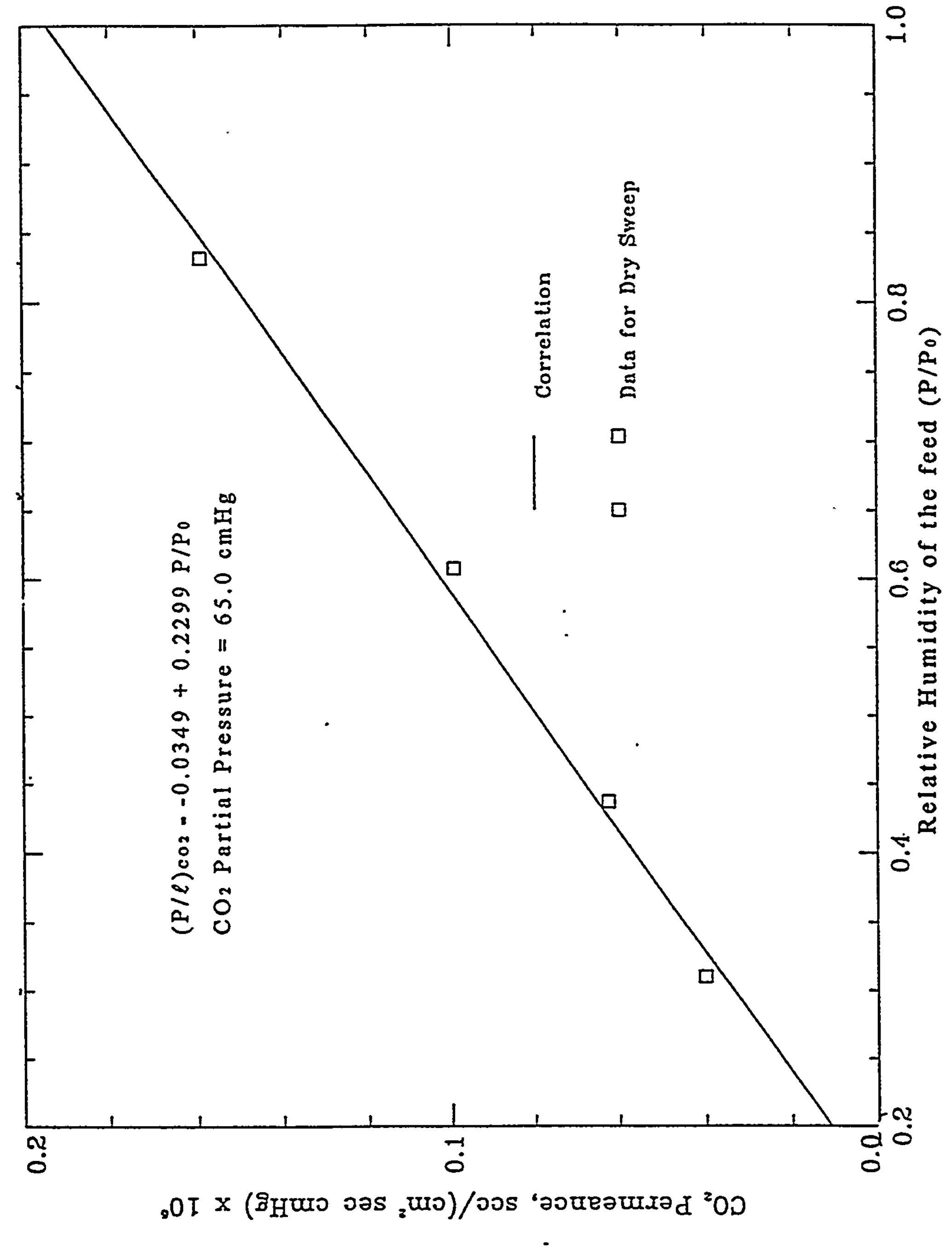
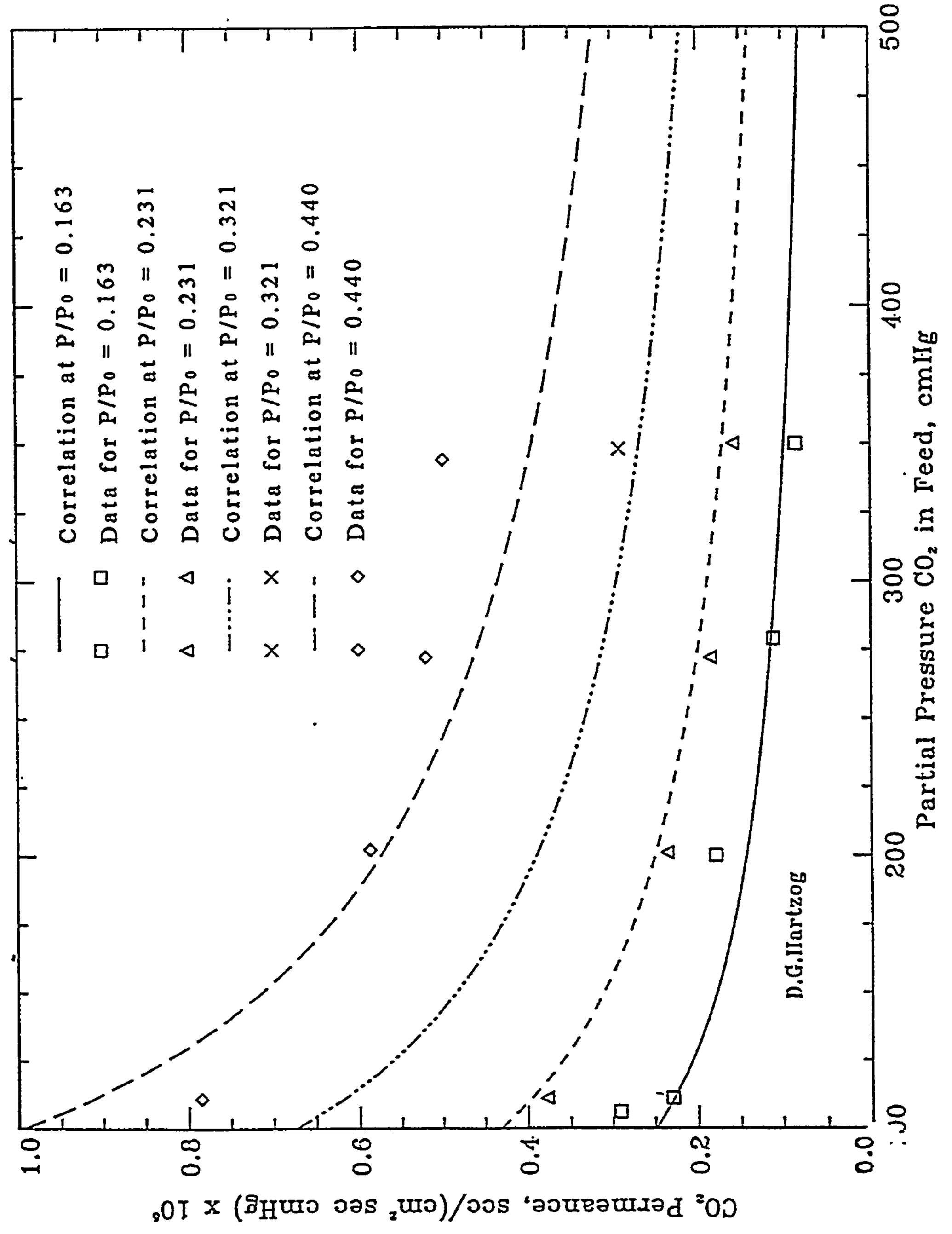

$(P/\ell)_{CO_2}$ = -0.0349 + 0.2299 P/P$_0$
CO$_2$ Partial Pressure = 65.0 cmHg
Correlation
Data for Dry Sweep
Relative Humidity of the feed (P/P$_0$)
0.2
0.4
0.6
0.8
1.0
CO$_2$ Permeance, scc/(cm^2 sec cmHg) x 10^6
0.0
0.1
0.2

Figure A-6


Correlation at P/Po = 0.163
Data for P/Po = 0.163
Correlation at P/Po = 0.231
Data for P/Po = 0.231
Correlation at P/Po = 0.321
Data for P/Po = 0.321
Correlation at P/Po = 0.440
Data for P/Po = 0.440
D.G.Hartzog
Partial Pressure CO_2 in Feed, cmHg
0
200
300
400
500
CO_2 Permeance, scc/(cm² sec cmHg) x 10^6
0.0
0.2
0.4
0.6
0.8
1.0