



Separation of H_2S from N_2 by selective permeation through polymeric membranes
by Robert Leo Heyd

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
Montana State University
© Copyright by Robert Leo Heyd (1976)

Abstract:

Vinylidene fluoride films modified with several different chemicals, and several commercially available films were tested for the separation of H_2S from H_2S-N_2 mixtures. Flux and separation factor values were obtained over a temperature range from $23^\circ C$ to $125^\circ C$ with an operating pressure of 500 psig.

Microscopic examination of the surfaces of modified vinylidene fluoride membranes indicated that uniform polymer films could be produced by allowing polymer solutions to stand for 15 days to insure complete dispersion of the polymer along with de-gassing the solution before pouring it onto a flat plate to form membrane films.

The following chemicals were added as modifiers to vinylidene fluoride: sulfolene, 3-methyl sulfolene, 1-methyl-2-pyrrolidinone, morpholine, monoethanol amine, triethanolamine, diisopropanol amine, and monoisopropanol amine. Good separation of H_2S from a 5% mixture of H_2S in N_2 was obtained using 3-methyl sulfolene, morpholene, monoisopropanol amine, and diisopropanol amine. For example, a film modified with 10% 3-methyl sulfolene gave a permeate, containing 33% H_2S at $50^\circ C$.

The commercially available polymer films tested included: dimethyl silicone, silicone polycarbonate copolymer, poly vinyl fluoride, polyamide, heat stabilized polyamide, polysulfone and polyethersulfone. Very high flux values and good separation were found with several of these polymers.

Strong trends toward increasing flux with increasing temperature, and an increasing percentage of H_2S in the permeate gas with increasing temperature were observed.

Separation factor values for H_2S , determined using a 5% mixture of H_2S in N_2 , ranged from less than .1 to 12.9. Flux values ranged from less than $10^{-5} \text{ m}^3(\text{STP})/\text{m}^2 \text{ hr}$ to $.727 \text{ m}^3(\text{STP})/\text{m}^2\text{hr}$.

Tests conducted with a feed gas containing .27% H_2S in a H_2S/N_2 mixture showed that permeate flux decreased as the percentage of H_2S in the feed gas decreased. No definite trend in the change of separation factor with feed gas composition was observed.

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature Robert L. Heyd

Date December 3, 1976

SEPARATION OF H₂S FROM N₂ BY SELECTIVE PERMEATION
THROUGH POLYMERIC MEMBRANES

by

ROBERT LEO HEYD

A thesis submitted in partial fulfillment of
the requirements for the degree

of

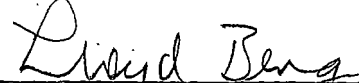
MASTER OF SCIENCE

in

Chemical Engineering

Approved:


Chairperson, Graduate Committee


Head, Major Department


Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1976

ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department at Montana State University for their criticisms and suggestions which led to the completion of this project.

Special thanks goes to Dr. F. P. McCandless for his advice, assistance, and encouragement throughout this investigation. Also, thanks are extended to Mr. Silas Huso and Mr. James Tillery for their help in tracking down various equipment pieces needed during the course of this research work.

The author is indebted to the National Science Foundation for the financial support which helped to make this research project possible.

The author wishes to thank his parents for their encouragement and support.

Finally, thanks goes to Sherry Greene for typing this thesis.

TABLE OF CONTENTS

	<u>Page</u>
VITA	ii
ACKNOWLEDGMENTS.	iii
LIST OF TABLES	viii
LIST OF FIGURES.	ix
ABSTRACT	xii
I. INTRODUCTION AND PURPOSE.	1
II. REVIEW OF THE LITERATURE.	3
COMMERCIAL PROCESSES FOR CONCENTRATING H ₂ S.	3
COMMERCIAL PROCESSES FOR CONVERTING H ₂ S TO ELEMENTAL SULFUR.	5
LABORATORY SCALE H ₂ S REMOVAL PROCESSES.	7
USE OF MEMBRANES FOR GAS SEPARATIONS.	10
MEMBRANES FOR SEPARATING H ₂ S FROM GAS MIXTURES.	12
III. THEORETICAL BACKGROUND.	14
NATURE OF THE TRANSPORT PROCESS	14
TRANSPORT THROUGH A GASEOUS FILM.	14
TRANSPORT THROUGH A POLYMERIC MEMBRANE.	14
POLYMER CHEMISTRY ASPECTS	18
TEMPERATURE EFFECTS	20
DEFINITION OF THE SEPARATION FACTOR	22
IV. EXPERIMENTAL EQUIPMENT, MATERIALS AND PROCEDURES.	23
DESCRIPTION OF EQUIPMENT.	23

TABLE OF CONTENTS (Cont)

	<u>Page</u>
1. PERMEATION CELL.	23
2. CONSTANT TEMPERATURE ENCLOSURE AND TEMPERATURE MEASURING EQUIPMENT.	26
3. GAS MIXTURE STORAGE AND FEEDING EQUIPMENT.	27
4. PURGE GAS SYSTEM COMPONENTS.	29
5. PERMEATE RATE MEASUREMENT EQUIPMENT.	29
6. GAS COMPOSITION ANALYSIS EQUIPMENT	30
7. MEMBRANE SURFACE AND COMPOSITION ANALYSIS EQUIPMENT.	30
MATERIALS.	31
EXPERIMENTAL PROCEDURE	34
1. PREPARATION OF GAS MIXTURES.	34
2. CALIBRATION OF GAS CHROMATOGRAPH	34
3. CALIBRATION OF EXHAUST GAS ROTAMETER	35
4. MEMBRANE MANUFACTURE	35
5. MICROSCOPIC EXAMINATION OF MEMBRANE SURFACES	40
6. TEST FOR THE PRESENCE OF RESIDUAL SOLVENT USING INFRARED SPECTROSCOPY.	41
7. PREPARATION FOR A TEST RUN	41
8. TEST RUN PROCEDURE	42
V. EXPERIMENTAL RESULTS AND DISCUSSION.	44
MODIFIED VINYLIDENE FLUORIDE FILMS	44
1. MATERIALS TESTED	44

TABLE OF CONTENTS (Cont)

	<u>Page</u>
2. RESULTS OF MICROSCOPIC ANALYSIS.	45
3. THE DATA	60
4. DISCUSSION - FILMS WITH NO MODIFIER ADDED.	69
5. DISCUSSION - FILMS WITH MODIFIER ADDED.	74
6. EFFECT OF TEMPERATURE.	79
COMMERCIALY AVAILABLE POLYMER FILMS	80
1. MATERIALS TESTED	80
2. THE DATA	81
3. DISCUSSION	81
4. EFFECT OF TEMPERATURE.	88
EFFECT OF FEED GAS COMPOSITION	90
1. MATERIALS TESTED	90
2. THE DATA	90
3. DISCUSSION	91
SUMMARY OF BEST RESULTS.	97
ANALYSIS OF ERRORS	99
VI. CONCLUSIONS AND RECOMMENDATIONS.	101
CONCLUSIONS.	101
RECOMMENDATIONS.	102
1. MODIFIED VINYLIDENE FLUORIDE FILMS	102
2. COMMERCIAL FILMS	103

TABLE OF CONTENTS (Cont.)

	<u>Page</u>
3. ALL FILMS.	104
VII. REFERENCE FOOTNOTES.	106
VIII. APPENDIX.	110
TABLE OF NOMENCLATURE.	111
IX. BIBLIOGRAPHY	113

LIST OF TABLES

<u>Table</u>		<u>Page</u>
V-1	Summary of Test Results for Modified Vinylidene Fluoride Films	61
V-2	Summary of Test Results for Commercially Available Polymer Films.	82
V-3	Comparison of Flux and Separation Values for Two Different Feed Gas Compositions.	92
V-4	Summary of Best Separation Results	98

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
III-1	Concentration Profiles of Component a in the Membrane and its Vicinity.	15
IV-1	Simplified Diagram of Permeation Equipment	24
IV-2	Permeation Cell Diagram.	25
IV-3	Constant Temperature Enclosure - High Temperature.	28
IV-4	Calibration of Gas Chromatograph - Sample Volume vs. Peak Weight x Attenuation for Nitrogen and Hydrogen Sulfide.	36
IV-5	Calibration Curve for Gas Chromatograph - Area Percent of H ₂ S vs. Volume Percent of H ₂ S	37
IV-6	Rotameter Calibration Curve - Flow Rate (STP) vs. Rotameter Reading.	38
V-1	Surface View of Membrane Containing 15% Sulfolene at 500x Magnification - Membrane Formed Immediately from Polymer Solution.	46
V-2	Cross Section of Membrane Containing 15% Sulfolene at 600x Magnification - Membrane Formed Immediately from Polymer Solution.	47
V-3	Surface View of Membrane Modified with 12% Sulfolene at 400x Magnification - Polymer Solution De-gassed Following a 24 Hour Solution Period.	50
V-4	Surface View of Membrane Modified with 10% Diisopropanolamine at 700x Magnification - Polymer Solution De-gassed Following a 24 Hour Solution Period.	51
V-5	Surface View of Membrane Modified with 10% 1-Methyl-2-Pyrrolidinone at 400x Magnification - Polymer Solution De-gassed Following a 24 Hour Solution Period	52

LIST OF FIGURES (Cont)

<u>Figure</u>		<u>Page</u>
V-6	Surface View of Membrane Modified with 5% Triethanolamine at 700x Magnification - Polymer Solution De-gassed Following a 24 Hour Solution Period.	53
V-7	Surface View of Membrane Modified with 10% Triethanolamine at 400x Magnification - Polymer Solution De-gassed Following a 15 Day Solution Period.	55
V-8	Surface View of Membrane Modified with 10% Morpholine at 400x Magnification - Polymer Solution De-gassed Following a 15 Day Solution Period.	56
V-9	Surface View of Membrane Modified with 10% Triethanolamine at 400x Magnification - Polymer Solution De-gassed Following a 15 Day Solution Period.	57
V-10	Surface View of Membrane Modified with 10% Mono-isopropanolamine at 400x Magnification - Polymer Solution De-gassed Following a 15 Day Solution Period.	58
V-11	Surface View of Membrane Modified with 10% Mono-isopropanolamine at 1000x Magnification - Polymer Solution De-gassed Following a 15 Day Solution Period . .	59
V-12	Separation Factor vs. Temperature for Some Modified Vinylidene Fluoride Films	65
V-13	Separation Factor vs. Temperature for Alkanolamine Modifiers in Vinylidene Fluoride.	66
V-14	Flux vs. Temperature for Some Modified Vinylidene Fluoride Films.	67
V-15	Flux vs. Temperature for Alkanolamine Modifiers in Vinylidene Fluoride	68
V-16	Results of Infrared Spectrophotometer Tests on Unmodified Vinylidene Fluoride Films.	70

LIST OF FIGURES (Cont)

<u>Figure</u>		<u>Page</u>
V-17	Separation Factor vs. Temperature for Unmodified Vinylidene Fluoride Films	72
V-18	Flux vs. Temperature for Unmodified Vinylidene Fluoride Films	73
V-19	Separation Factor vs. Temperature for Commercially Available Films	84
V-20	Flux vs. Temperature for Commercially Available Films	85
V-21	Effect of Feed Gas Composition on Separation For Vinylidene Fluoride with 10% 3-Methyl Sulfolene Modifier	93
V-22	Effect of Feed Gas Composition on Flux For Vinylidene Fluoride with 10% 3-Methyl Sulfolene Modifier	94
V-23	Effect of Feed Gas Composition on Separation for Silicone Polycarbonate Copolymer	95
V-24	Effect of Feed Gas Composition on Flux for Silicone Polycarbonate Copolymer	96

ABSTRACT

Vinylidene fluoride films modified with several different chemicals, and several commercially available films were tested for the separation of H_2S from H_2S-N_2 mixtures. Flux and separation factor values were obtained over a temperature range from $23^\circ C$ to $125^\circ C$ with an operating pressure of 500 psig.

Microscopic examination of the surfaces of modified vinylidene fluoride membranes indicated that uniform polymer films could be produced by allowing polymer solutions to stand for 15 days to insure complete dispersion of the polymer along with de-gassing the solution before pouring it onto a flat plate to form membrane films.

The following chemicals were added as modifiers to vinylidene fluoride: sulfolene, 3-methyl sulfolene, 1-methyl-2-pyrrolidinone, morpholine, monoethanolamine, triethanolamine, diisopropanolamine, and monoisopropanolamine. Good separation of H_2S from a 5% mixture of H_2S in N_2 was obtained using 3-methyl sulfolene, morpholine, monoisopropanolamine, and diisopropanolamine. For example, a film modified with 10% 3-methyl sulfolene gave a permeate containing 33% H_2S at $50^\circ C$.

The commercially available polymer films tested included: dimethyl silicone, silicone polycarbonate copolymer, poly vinyl fluoride, polyamide, heat stabilized polyamide, polysulfone and polyethersulfone. Very high flux values and good separation were found with several of these polymers.

Strong trends toward increasing flux with increasing temperature, and an increasing percentage of H_2S in the permeate gas with increasing temperature were observed.

Separation factor values for H_2S , determined using a 5% mixture of H_2S in N_2 , ranged from less than .1 to 12.9. Flux values ranged from less than $10^{-5} m^3(STP)/m^2 hr$ to $.727 m^3(STP)/m^2 hr$.

Tests conducted with a feed gas containing .27% H_2S in a H_2S/N_2 mixture showed that permeate flux decreased as the percentage of H_2S in the feed gas decreased. No definite trend in the change of separation factor with feed gas composition was observed.

INTRODUCTION AND PURPOSE

The separation of H_2S from other components in a gas stream is important in a number of areas, particularly in the utilization of the fossil fuels natural gas, petroleum, and coal.

Hydrogen sulfide gas is highly toxic, corrosive, and a catalyst poison. These properties necessitate its removal from gas streams.

Natural gas must be "sweetened", that is, hydrogen sulfide must be removed before it can be distributed by pipeline.

Hydrogen sulfide produced during refining from the sulfur present in crude oil is removed to prevent catalyst poisoning and corrosion.

When coal is gasified, regardless of the specific process used, most of the sulfur in the coal is converted to hydrogen sulfide. This hydrogen sulfide must be removed from the gasifier exit gas because it quickly destroys the activity of methanation catalysts.

As petroleum supplies become more scarce, coal gasification is expected to become a major industry. It has been estimated (1) that to produce clean fuel equivalent to 20% of current U. S. oil consumption from coal will require 80 gasification plants each producing 250 million ft^3 /day of gas. Each plant would consume about 12,000 tons/day of high quality eastern coal and produce about 400 tons/day (8.4×10^6 SCF/day) of hydrogen sulfide.

Because most of the coal gasification processes currently under development operate to produce a product gas under pressure, the driving force for a membrane separation process is already present.

This is a big advantage of a membrane separation process over conventional liquid absorption hydrogen sulfide removal processes. Membrane separation processes also have the advantage of requiring much less equipment than liquid absorption processes.

In an attempt to contribute to the ultimate goal of a membrane separation system for hydrogen sulfide removal this work was conducted.

The specific objectives of this research were as follows:

1. To test a number of different plasticizers in vinylidene fluoride to determine permeation rate and selectivity for H_2S .
2. To test various commercially available polymeric films to determine permeation rate and selectivity for H_2S .
3. To determine the effect of temperature on selectivity for H_2S in the various membranes.
4. To determine the effect of temperature on permeation rate in the various membranes.
5. To determine the effect of feed gas composition on permeation rate and selectivity for H_2S for materials which appear promising.

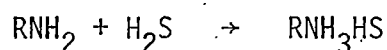
REVIEW OF THE LITERATURE

Hydrogen sulfide removal technology includes a large number of commercial processes along with several recent laboratory developments. Much work has been done on membranes for gas separations, including some studies dealing with hydrogen sulfide.

A. COMMERCIAL PROCESSES FOR CONCENTRATING H₂S

The largest number of commercial processes for concentrating hydrogen sulfide gas involve absorption of H₂S into solution followed by a regeneration step which separates the H₂S from the absorbing solution.

Alkanolamine solutions are used as the absorbent in many processes. The Girbotal Process (2) and the Adip Process (3) use aqueous solutions of monoethanolamine, diethanolamine or triethanolamine as absorbents. The H₂S reacts with the amines to form compounds which may be broken down by heat. The reaction form is:



The solutions are regenerated by being heated. This drives off the H₂S to form a concentrated H₂S stream and an amine solution which is recycled. The SNPA-DEA (4) Process uses a concentrated aqueous solution of diethanolamine as the solvent.

Two commercial processes have been developed which use an alkanolamine combined with other chemicals as the absorbent solution. In the Amisol Process (5) the solvent consists of methanol, an additive,

and an organic base (diethanolamine or triethanolamine). This solvent has the advantage of high loading capacity and a low regeneration temperature. The Sulfinol Process (6) makes use of an organic solvent, sulfolane (tetrahydrothiophene dioxide), mixed with an alkanolamine and water. Simultaneous chemical and physical absorption of H_2S takes place using this solvent.

An aqueous solution of the primary alkanolamine $HO-C_2H_4-O-C_2H_4-NH_2$ (trade named diglycolamine) is the solvent used in the Fluor Econamine Process (7).

A number of processes have been developed which use carbonate solutions for H_2S absorption. The most widely used process of this type is the Benfield Process (8). Hydrogen sulfide is removed by contact with a potassium carbonate solution containing Benfield additives at high pressure (100 - 2000 psig). The solution is regenerated by stripping at atmospheric pressure. A modification of the Benfield Process, known as the Hi-Pure Process (9) uses two different carbonate solutions in series. The advantage of this process is that it produces a product gas containing an extremely low concentration of H_2S (1-20 PPM). The Fluor Solvent Process (10) uses an anhydrous organic compound, propylene carbonate, for H_2S removal. This solvent is regenerated simply by pressure letdown of the rich solvent, without the application of heat.

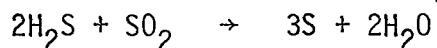
Two processes are available which use a potassium salt solution

to absorb H_2S . In the Alkazid Process (11) two types of absorbents are used. Alkazid 'DIK' (potassium salt of dimethyl amino acetic acid) is used for the selective absorption of H_2S . Alkazid 'M' (potassium salt of methyl amino propionic acid) is used for simultaneous removal of CO_2 and H_2S . A potassium salt solution containing a stable catalyst is used for absorption of H_2S in the Catacarb Process (12).

Other commercial absorption processes include the Purisol Process, the Rectisol Process and the Selexol Solvent Process. Physical absorption of H_2S in N-methyl-pyrrolidone is used in the Purisol Process (13). The Rectisol Process (14) uses absorption in cooled methanol, and the Selexol Solvent Process (15) is based on the absorption of H_2S in dimethyl ether of polyethylene glycol.

B. COMMERCIAL PROCESSES FOR CONVERTING H_2S TO ELEMENTAL SULFUR

The most common method for converting H_2S to sulfur is the Claus Process (16). In this process, gas containing hydrogen sulfide is fed to a reaction furnace where it is burned with air. Part of the H_2S is oxidized to SO_2 which reacts with the remaining H_2S to form elemental sulfur according to the Claus reaction:



This process can only be used on a gas stream with a high concentration of H_2S (minimum H_2S concentration is about 15%). Therefore, Claus units are often used to treat the concentrated gas streams produced in liquid

absorption H_2S removal units.

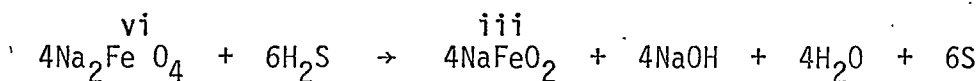
The exit gas leaving a Claus unit contains more H_2S than recent environmental regulations allow (17). Therefore, a large number of add-on systems for removing the H_2S from Claus Process tail gas have been developed. The major tail gas cleanup systems are: the Beavon Process (18) which uses hydrogenation followed by treatment with sodium carbonate solution, the IFP Process (19) in which H_2S and SO_2 are reacted stoichiometrically to elemental sulfur, the SCOT Process (20) in which all sulfur compounds are catalytically converted to H_2S and then removed by absorption with an alkanolamine solution, the Sulfreen Process (21, 22) which uses an activated carbon or alumina catalyst to convert H_2S to elemental sulfur, the CBA Process (23) which also uses a catalytic process to convert H_2S to sulfur, the Trencor M Process (24) which uses a proprietary aqueous solution of methyldiethanolamine to absorb H_2S , and the Catabon Process (25) in which a complexed polyvalent metal ion oxidizes H_2S to sulfur.

In the Holmes-Stretford Process (26) H_2S is converted to elemental sulfur by being scrubbed with an alkaline solution containing a vanadium salt and an anthraquinone derivative. The H_2S is converted to elemental sulfur while the vanadium salt is reduced.

The Takahax Process (27) uses an alkaline sodium carbonate solution (pH = 8.5) containing 1,4-naphthoquinone, 2-sulfonate as a redox catalyst. Hydrogen sulfide reacts with sodium carbonate to

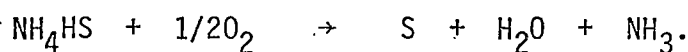
form sodium bisulfide and sodium bicarbonate. The bisulfide is oxidized by the catalyst to produce fine particles of solid sulfur.

The Konox Process (28) is based on the absorption of hydrogen sulfide with a strong iron oxide oxidizing agent. Sulfur is produced according to the following reaction:



An alkali arsenates and arsenites solution is used to scrub H_2S from feed gas in the Giammarco Vetrocoke Process (29). Sodium thioarsenite is produced in the absorption step. The thioarsenite is converted to monothioarsenate in an oxidizing column. An air-blown oxidizing column is used to decompose the monothioarsenate to elemental sulfur and arsenite.

The Sulfox Process (30) uses an aqueous ammonia solution to scrub H_2S from the feed gas stream. The rich solution is warmed, mixed with air and passed over a catalyst which directs the oxidation of the mixture to yield mostly sulfur, according to the reaction:

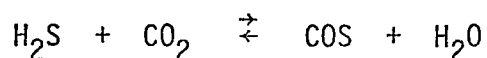


The sulfur forms a separate molten phase which is withdrawn as product.

C. LABORATORY SCALE H_2S REMOVAL PROCESSES.

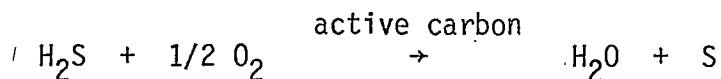
Phillips Petroleum Company has tested molecular sieves for H_2S

removal (31). In a molecular sieve desulfurizer H_2S is adsorbed and a simultaneous rate-limited, adsorbent-catalyzed reaction of H_2S with any available CO_2 to form carbonyl sulfide occurs. The reversible reaction involved is:



When carbonyl sulfide appears in the exit gas, the molecular sieve unit must be regenerated. Five commercially available molecular sieves were tested using feed gas containing 30-160 PPM H_2S . The sieve which gave the best results had a true H_2S loading of .88 lb H_2S /lb sieve.

Adsorption of H_2S on solid surfaces has been studied by a number of investigators. Activated carbon acts as a catalyst as well as an adsorbent (32). In the presence of free oxygen H_2S is catalyzed to elemental sulfur according to the following reaction:



Adsorption of H_2S on manganese dioxide and activated carbon has been studied at the University of Illinois (33). Several activated carbons were tested along with manganese dioxide impregnated on sawdust. Both the efficiency and capacity of the MnO_2 -sawdust were found to be better than those of any of the activated carbons tested. Adsorption of hydrogen sulfide on Amberlyst A26 ion exchange resin has been studied (34). Rate curves and sorption isotherms were determined for this

system.

Removal of H_2S using an organic solution which converts the H_2S to crystalline sulfur has been studied at the University of New Brunswick (35). It was found that the best liquid phase system consisted of a mixture of 83 volume percent ethylene glycol monoethyl ether (Cellosolve), 15% water and, 2% dibutylamine. The water was found to act as a catalyst, since no reaction occurred in water-free mixtures. The dibutylamine allowed nucleation to proceed to produce granular sulfur.

The U. S. Bureau of Mines has developed three sintered materials capable of removing H_2S from producer gas at $1000^\circ F$ to $1500^\circ F$ (36). The absorbents are mixtures of ferric oxide and flyash, ferric oxide and pumice stone, and red mud (a ferric oxide - containing residue from bauxite processing). Red mud has the greatest capacity, absorbing 16 weight percent sulfur at $1000^\circ F$, 24% at $1250^\circ F$ and 45.1% at $1500^\circ F$.

A number of H_2S removal processes have recently been patented. U. S. 3,502,428 (37) covers H_2S removal with N-methylethanolamine in 2,2dimethyl-1,3-dioxolane-4-methanol. U. S. 3,716,620 (38) describes a process for purifying a gas containing H_2S or a mercaptan, wherein the gas is contacted with a solution of iodine and an amine in an organic solvent. Removal of acid gases from mixtures by washing with N-substituted ϵ -caprolactams is described in U. S. 3,653,809 (39). U. S. 3,409,520 (40) describes an electrolysis process for removing

H₂S from a hydrocarbon gas mixture.

D. USE OF MEMBRANES FOR GAS SEPARATIONS

A large number of membrane systems have been developed for gas separations. In order to effect a separation the membrane material allows one component of a mixture to permeate at a greater rate than the others. The source of membrane selectivity is usually either preferential solubility of the desired component or a lower resistance to transfer for one component than for others, or both (41).

A commercial installation for the recovery of hydrogen from a refinery gas mixture using hollow fibers of dacron polyester has been in operation since 1969 (42).

The use of a membrane systems to separate helium from natural gas has received considerable attention. Stern et. al. (43) studied a large number of polymer materials with helium, nitrogen, and methane mixtures. Separation factors for He-N₂ and He-CH₄ systems were reported for 16 polymers including silicone rubber, teflon FEP, polystyrene, polyvinyl chloride, polyethylene, polyvinyl fluoride, mylar and saran. Large scale tests have also been conducted on the use of cellulose acetate films for the separation of helium from natural gas (44).

The separation of oxygen from air using an ethyl cellulose film has been studied (45). In a one-stage process oxygen could be enriched to 32.6%.

Laboratory scale separation information has been reported for a large number of polymer systems.. Brubaker and Kammermeyer (46) presented data for polyethylene with four gas systems (He-O₂, CO₂-H₂-O₂-N₂, SO₂-O₂-N₂, NH₃-H₂-N₂), Trifluoromonochloroethylene with two gas systems (CO₂-H₂-O₂-N₂, NH₃-H₂-N₂) and cellulose acetate butyrate with one gas system (CO₂-H₂-O₂-N₂).. McCandless (47) tested four polymer materials (caprolactam, dacron, parylene C poly (monochloro-para-xylylene) and polyimide) with a binary gas system of carbon monoxide and hydrogen.

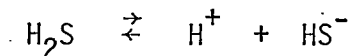
Tajar and Miller (48) reported data for the permeation of CO₂, O₂ and N₂ in a four component membrane system composed of polyethyl-imine, polyvinylbutyral, epoxy and water. This membrane system was found to be quite selective for CO₂ over O₂ and N₂. Permeability coefficient ratios on the order of 30:1 or greater were reported.

Modified vinylidene fluoride membranes have been used in two studies. Seibel and McCandless (49) used vinylidene fluoride modified with sulfolane for the separation of SO₂ from N₂. Separation factors ranging from 30 to 100 were obtained. Zavaleta (50) studied a number of chemical modifiers for vinylidene fluoride in order to effect the separation of SO₂ from N₂. The modifiers tested included: sulfolene, 3-methyl sulfolene, p-amino sulfolene, phenyl sulfone, 4,4-sulfonyl diphenol, and tetrahydro-3-thiophenamine 1,1-dioxide. Membranes containing 18 weight percent sulfolene gave the best results. Membranes

of this composition allowed a permeate stream containing 95.5 volume percent SO_2 to be obtained from a feed stream containing 5.6% SO_2 .

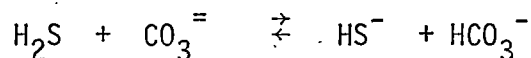
E. MEMBRANES FOR SEPARATING H_2S FROM GAS MIXTURES

There is some information in the literature concerning membrane separations of H_2S . U. S. 3,819,806 (51) has been awarded to Ward, Salemme and Mayer for an immobilized liquid membrane which is used to separate H_2S from a gas mixture. The dissociation of H_2S in water proceeds according to the following reaction:



By forming an immobilized liquid membrane from an aqueous solution containing specific anions, the acid to HS^- transfer so provided greatly increases the transport of H_2S across the membrane from the value expected based on diffusivity and solubility.

A recent paper presented by Matson and Kimura (52) discussed highly permeable and selective polymeric membranes for H_2S removal which are based on the principle of facilitated transport. Chemical reaction augments the diffusion process through the following reaction:



Robb (53) reported the permeabilities of a number of gases, including hydrogen sulfide, in a dimethyl-silicone rubber consisting of dimethyl

siloxane plus 33% by weight silica filler. The permeability of H_2S in the film was significantly greater than that of the atmospheric gases nitrogen and oxygen. The value of the permeability constant for H_2S is 1000×10^{-9} ccgas (RTP) cm/sec $cm^2cmHg\Delta P$ compared to 28×10^{-9} ccgas (RTP)cm/sec $cm^2cmHg\Delta P$ for nitrogen and 6×10^{-9} ccgas(RTP)cm/sec $cm^2cmHg\Delta P$ for oxygen (RTP indicates room temperature and pressure).

Dimethyl silicone membranes which have much greater permeability to H_2S than atmospheric gases have been developed by General Electric (54). Permeability of H_2S is reported as 840×10^{-9} ccgas(RTP)cm/sec $cm^2cmHg\Delta P$ compared to 25×10^{-9} ccgas (RTP)cm/sec $cm^2cmHg\Delta P$ for nitrogen and 50×10^{-9} ccgas (RTP) cm/sec $cm^2cmHg\Delta P$ for oxygen.

The permeability of several commercial films to hydrogen sulfide gas was studied by Heilman, et. al (55). The films tested included Nylon 6 polyamide, cellulose acetate, rubber hydrochloride, cellulose, polyethylene, poly vinyl butyral, polyvinyl trifluoroacetate, mylar, polyvinylidene chloride and ethylcellulose.

THEORETICAL BACKGROUND

A. NATURE OF THE TRANSPORT PROCESS

The permeation of a gaseous mixture through a polymeric material involves three transport stages (Figure III-1).

These stages are:

- (1) Transport from the gas mixture to the membrane surface.
- (2) Transport through the membrane.
- (3) Transport from the membrane to the permeate stream.

B. TRANSPORT THROUGH A GASEOUS FILM

In gas-phase permeation, transport to the membrane surface and from the membrane surface provides negligible resistance compared to that of transport through the membrane (56). The concentration gradient between the high pressure side of the membrane and the bulk gas can be greatly reduced by maintaining a high gas flow rate across the high pressure side of the membrane, as was done in this study.

C. TRANSPORT THROUGH A POLYMERIC MEMBRANE

The basic equation describing membrane diffusion transport at steady state is (57):

$$N_a = -D \frac{\partial C_a}{\partial Z} - \frac{D}{2C_m} \frac{\partial^2 C_a}{\partial Z^2} \quad (1)$$

This equation differs from the Fick's first law equation by addition of the second term due to the presence of the membrane. In

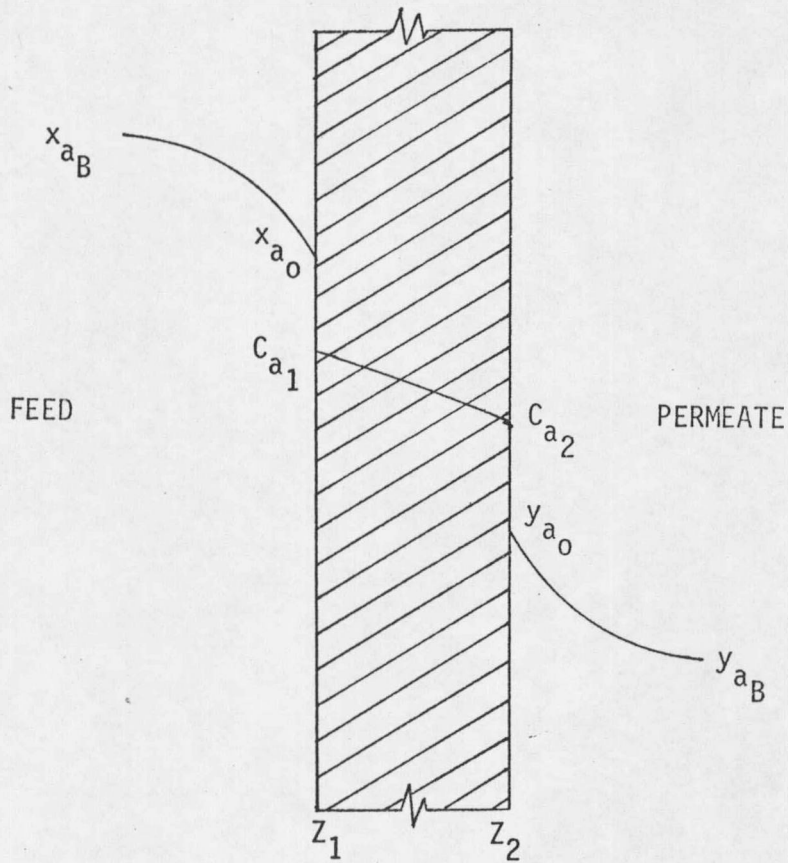


FIGURE III-1. CONCENTRATION PROFILES OF COMPONENT a IN THE MEMBRANE AND ITS VICINITY

gaseous diffusion the second term is usually negligible (58).

Neglecting this term yields

$$N_a = -D \frac{\partial C_a}{\partial Z} \quad (2)$$

which is the mathematical expression of Fick's first law for steady state diffusion.

Since the concentration is a function only of distance through the membrane, whole derivatives can be used.

$$N_a = -D \frac{dC_a}{dZ} \quad (3)$$

If an average value of the diffusivity is used, Equation 3 can be integrated subject to the following boundary conditions:

$$\begin{aligned} Z = Z_1 & \quad C_a = C_{a1} \\ Z = Z_2 & \quad C_a = C_{a2} \end{aligned} \quad (4)$$

to give

$$N_a \int_{Z_2}^{Z_1} dZ = -D \int_{C_{a2}}^{C_{a1}} dC_a \quad (5)$$

doing the integration results in the expression

$$-N_a (Z_1 - Z_2) = -D (C_{a1} - C_{a2}) \quad (6)$$

$(Z_2 - Z_1)$ represents the thickness of the membrane, L , so the following equations can be written:

$$-N_a = \frac{-D}{L} (C_{a_1} - C_{a_2}) \quad (7)$$

or

$$N_a = \frac{D}{L} (C_{a_1} - C_{a_2}) \quad (8)$$

The solubility of a gas in a polymer at equilibrium can be described by a Henry's Law expression, where the constant S represents the solubility of the gas in the polymer.

$$C_a = S p_a \quad (9)$$

Since the permeation process is generally slow, the use of this equilibrium relationship between the concentration of sorbed gas and the partial pressure at the interface can be used.

Substituting the Henry's Law expression into equation 8 results in the expression:

$$N_a = \frac{D}{L} (S_1(p_{a_1})_o - S_2(p_{a_2})_o) \quad (10)$$

If solubility is assumed to be a function only of temperature, and both membrane surfaces are at the same temperature, then

$$S_1 = S_2 = S \quad (11)$$

and,

$$N_a = \frac{DS}{L} [(p_{a_1})_o - (p_{a_2})_o] \quad (12)$$

The partial pressures at the interfaces can be expressed in terms of the total pressures:

$$p_{a_1} = P_1 x_{a_1} \quad (13)$$

$$p_{a_2} = P_2 y_{a_2}$$

Making this substitution yields:

$$N_a = \frac{DS (P_1(x_{a_1})_o - P_2(y_{a_2})_o)}{L} \quad (14)$$

From this expression it is clearly seen that the flux of gas through a membrane is dependent on solubility and diffusivity of the gas in the membrane. One of the objectives of this research is to add plasticizers to polymeric membranes in order to increase solubility and thereby increase the flux of the desired component (H_2S).

D. POLYMER CHEMISTRY ASPECTS

Gases are transported through a polymeric nonporous membrane by means of diffusion. As can be seen from Equation 14 the process depends on the solubility of the penetrant in the membrane as well as the mobility of the penetrant molecule in the polymer matrix.

At a given moment a penetrant molecule can be visualized as occupying a vacant site existing between adjacent polymer chains. The penetrant proceeds, under the influence of a concentration gradient, from one position to another and eventually achieves a finite jump in

the direction imposed by the concentration gradient. The overall motion of a particle consists of a series of steps or diffusional jumps.

Gases are unable to permeate through crystalline regions of a polymer because polymer chains in these regions are tightly linked, leaving no vacant sites for gas molecules to move into. Crystalline regions have several other negative effects on the rate of gaseous diffusion through a polymer. The three principle effects are: the reduction in the available polymer volume for diffusion, the tortuosity involved in by-passing crystalline areas, and the decrease in the mobility of amorphous chain segments as a result of the presence of crystalline regions which may act as crosslinks.

At the glass transition temperature of a polymer there is a change in physical properties of the polymer. Above the glass transition temperature there is increased molecular freedom. That is, molecular chain segments are free to vibrate and twist. Movement of penetrant molecules through the polymer is much easier above the glass transition temperature.

The addition of plasticizers or modifiers to a polymer has several effects. Plasticizers increase the diffusivity of a given gas or vapor. The increase is attributed to the increase in polymer segmental mobility as a result of lower cohesive forces between chains (59). Modifiers also lower the glass transition temperature by allowing for increased mobility of polymer chain segments. Solubility of gases or

vapors may also be greatly increased by the addition of modifiers, particularly when the gas or vapor is soluble in the modifier. The net effect of modifier addition is a marked increase in the gas permeation rate.

E. TEMPERATURE EFFECTS

As can be seen from Equation 14:

$$N_a = \frac{DS(P_1(x_{a_1})_o - P_2(y_{a_2})_o)}{L}$$

the effect of temperature on permeation flux will depend primarily on the manner in which diffusivity (D) and solubility (S) depend on temperature if the operating pressures remain constant.

The temperature dependence of diffusivity conforms with an Arrhenius-type relationship (60),

$$D = D^0 e^{-E/RT} \quad (15)$$

By measuring diffusivities at several temperatures an Arrhenius plot of $\ln D$ vs $1/T$ yields the activation energy for diffusion of the penetrant in the polymer (61).

It is clear, then, that increasing the temperature of a permeation system will cause the diffusivity to increase exponentially with absolute temperature.

For sorption of gases into solid polymer systems, solubility also follows an Arrhenius-type relationship (62),

$$S = S^0 e^{-\Delta h/RT} \quad (16)$$

where Δh is the apparent heat of solution. Another means of expressing this dependence on temperature is in terms of the Henry's Law constant (63),

$$H = H^0 e^{-\Delta h/RT} \quad (17)$$

Thus, increasing temperature increases gas solubility in an unmodified polymer film.

However, for modified films to which liquid modifiers have been added, the temperature effect on solubility is more complicated.

The solubility of gases in liquid modifiers usually decreases as temperature is increased. Since the gases are much more soluble in the modifier than in the base polymer, it is possible that this effect outweighs the increased solubility of gases in the polymer. Therefore, flux could actually decrease with increasing temperature.

For a modified polymer film, diffusivity increases as temperature increases, while the solubility term is acted on by opposing effects.

For unmodified films, diffusivity increases as temperature increases and the solubility of the gases in the polymer also increases.

However, studies with polyethylene (64) have shown that both solubility and diffusivity are dependent on crystallinity. Solubility was found to be directly proportional to the volume percent amorphous material present. It is reasonable to assume that this crystallinity

