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Facilitated Transport Ceramic Membranes for High-Temperature Gas Cleanup

**Final Report
February 1990 - April 1994**

**R. Quinn
E. Minford
A. S. Damle
S. K. Gangwal
B. A. Hart**

April 1994

Work Performed Under Interagency Agreement No.: DE-AC21-90MC26038

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

MASTER

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High-Temperature Gas Cleanup

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Morgantown, West Virginia 26507-0880**

**By
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April 1994

Table of Contents

	<u>Page</u>
List of Tables	iv
List of Figures	v
Executive Summary	vi
1.0 Background	1
2.0 Objectives and Project Description	5
2.1 Objectives	5
2.2 Project Description	5
3.0 Experimental Section	6
3.1 Salt Mixture Preparation and Characterization	6
3.1.1 Methods	6
3.1.2 Materials	6
3.2 Absorption Experiments	7
3.3 Membrane Preparation and Testing	13
3.3.1 Membrane Testing	13
3.3.2 Membrane Preparation	16
4.0 Results and Discussion	17
4.1 Development of Molten Carbonate Salts	17
4.1.1 Survey of H ₂ S Reactivity of Pure Carbonate Salts	17
4.1.2 Characterization of Pure Carbonate Salts	18
4.1.3 Preparation and Characterization of Carbonate Mixtures	26
4.1.4 Preparation and Characterization of Sulfide-Containing Carbonate Mixtures	30
4.1.5 Determination of Equilibrium Constants for the Reaction of H ₂ S with Molten Carbonate Mixtures	32
4.1.5.1 Gas Phase Reactivity	33
4.1.5.2 H ₂ S Absorption Experiments	34
4.1.5.3 H ₂ S-Metal Reactivity	36
4.2 Ceramic Materials Development	36
4.2.1 Materials Selection	37
4.2.2 Wetting Behavior	39
4.2.3 Ceramic Substrate Development	41
4.2.4 Ceramic Membrane Infiltration	45
4.3 Membrane Testing	49
4.3.1 Molten Carbonate/Gold Frit Membranes	50
4.3.2 Planar Molten Carbonate/Ceramic Membranes	51
4.3.2.1 Membrane Sealing	52
4.3.2.2 Testing with H ₂ S Containing Feeds	52
4.3.2.3 Testing with non-H ₂ S Containing Feeds	57
4.3.3 Alternative Materials of Construction for Membrane Cells	60
4.3.4 Planar and Tubular Molten Carbonate/Ceramic Membranes. Testing at RTI	61
4.3.5 Modeling of Membrane Performance	61

5.0	Summary and Conclusions	65
6.0	References	68
7.0	Appendix	70

List of Tables

Number		Page
3.1.1	Compositions and melting temperatures of carbonate mixtures prepared	6
4.1	Log K values for reactions 1-3 at 627°C for pure alkali and alkaline earth carbonates	18
4.2	Metal ion content of alkali and alkaline earth carbonates	20
4.3	High temperature weight losses for pure carbonate salts	24
4.4	Endotherms for pure metal carbonate salts between 30 and 100°C under a N ₂ atmosphere.	26
4.5	Compositions and melting temperatures of carbonate mixtures.	27
4.6	TGA results for carbonate salt mixtures. High temperature weight losses for mixtures under N ₂ or CO ₂ atmospheres	28
4.7	DTA results for carbonate mixtures. Observed endotherm temperatures between 30 and 1000°C for samples under N ₂ or CO ₂ atmospheres	30
4.8	DTA results for carbonate mixtures. Observed exotherm temperatures between 30 and 1000°C for samples under N ₂ or CO ₂ atmospheres	30
4.9	Composition of carbonate salt mixtures containing added sulfide ion.	31
4.10	DTA exotherm and endotherm temperatures for sulfide ion containing carbonate mixtures	32
4.11	Equilibrium constant values for gas phase reactions	34
4.12	Headspace analysis of gases at equilibrium in absorption experiment 12666-2	35
4.13	ESCA surface analysis of AlN samples	41
4.14	Capillary force as a function of support pore radius	44
4.15	Phase analysis of long term salt retention samples	45
4.16	Planar disc support infiltration results	48
4.17	Tubular support infiltration results	49
4.18	Calculated permeabilities of CO, CO ₂ , and H ₂ in a molten carbonate membrane.	50
4.19	Permselective properties of molten carbonate /gold frit membranes at 560°C	51
4.20	Listing of molten carbonate/ceramic planar membranes tested	52
4.21	Permselective properties of molten carbonate/ceramic membranes at 560°C using H ₂ S containing feeds	54
4.22	Elements present as determined by EDS in the membrane cell after evaluation of membrane 12496-2-3	55
4.23	Analysis of H ₂ S gas mixtures passed through a gold plated membrane cell at 560°C	55
4.24	Permselective properties of molten salt/ceramic membranes at 560°C using non-H ₂ S containing feeds	58
4.25	Permselective properties of molten carbonate/ceramic membranes at 560°C using non-H ₂ S containing feeds.	59
4.26	Analysis of 6% H ₂ S in N ₂ feed after passage through quartz or alumina tubes at the indicated temperatures	60
4.27	Input and output data for the program CMEM	64

List of Figures

Number		Page
1.1	Removal of contaminant gases from IGCC gases using a high temperature membrane.	2
1.2	Mechanism of facilitated transport of H ₂ S in a molten carbonate membrane	4
3.1	Schematic diagram of high temperature, high pressure absorption and membrane system	9
3.2	Schematic diagrams of membrane test cells.	15
4.1	Log K plots for reactions of pure carbonate salts	19
4.2	TGA traces of Na ₂ CO ₃ obtained upon heating under a N ₂ atmosphere.	21
4.3	TGA traces of La ₂ (CO ₃) ₃	22
4.4	TGA traces of Eu ₂ (CO ₃) ₃	23
4.5	DTA trace of Cs ₂ CO ₃ upon heated under a N ₂ atmosphere	25
4.6	DTA traces of base composition carbonate mixture 30-A	29
4.7	Weight loss of ceramic powders after 24 hour exposure to molten carbonates	38
4.8	Sessile drop test system	40
4.9	Effect of sulfide ion content of mixed alkali carbonates on the contact angle on AlN	42
4.10	Effect of long term exposure on the contact angle of mixed alkali carbonates on AlN	43
4.11	Long term salt retention of aluminum nitride and lithium aluminate porous samples	46

Executive Summary

The successful development of advanced power generation systems such as Integrated Gasification Combined Cycle (IGCC) requires that practical methods for removal of gaseous and other contaminants be developed. Among numerous alternatives, membranes supply a method for the removal of contaminant gases.

A preferred gaseous separation scheme would involve removal of contaminant gases such as H_2S , HCl , NH_3 and others from the hot, high pressure fuel gas. Thus, the useful fuel gases such as H_2 , CO , and CH_4 would be recovered hot and at high pressure. Neither conventional polymeric membranes or microporous ceramic membranes can be used to accomplish the desired separation. Polymeric membranes are unstable at the high temperatures of IGCC gas mixtures and, in addition, generally permeate permanent gases, particularly H_2 , more readily than most contaminant gases. Microporous ceramic membranes likewise permeate H_2 more readily than contaminant gases.

The objective of this program was to demonstrate the feasibility of developing high temperature, high pressure, facilitated transport ceramic membranes to control gaseous contaminants in Integrated Gasification Combined Cycle (IGCC) power generation systems. Meeting this objective requires that the contaminant gas H_2S be removed from an IGCC gas mixture without a substantial loss of the other gaseous components, specifically H_2 and CH_4 . As described above, this requires consideration of other, nonconventional types of membranes. The solution evaluated in this program involved the use of facilitated transport membranes consisting of molten mixtures of alkali and alkaline earth carbonate salts immobilized in a microporous ceramic support.

To accomplish this objective, Air Products and Chemicals, Inc., Golden Technologies Company Inc., and Research Triangle Institute worked together to develop and test high temperature facilitated membranes for the removal of H_2S from IGCC gas mixtures. Three basic experimental activities were pursued:

- (1) evaluation of the H_2S chemistry of a variety of alkali and alkaline earth carbonate salt mixtures
- (2) development of microporous ceramic materials which were chemically and physically compatible with molten carbonate salt mixtures under IGCC conditions and which could function as a host to support a molten carbonate mixture and
- (3) fabrication of molten carbonate/ceramic immobilized liquid membranes and evaluation of these membranes under conditions approximating those found in the intended application.

Results of these activities are summarized below.

A series of mixtures consisting of alkali and alkaline earth carbonate salts were prepared and characterized by a variety of techniques including thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). Seven of these exhibited properties suitable for use in a high temperature immobilized liquid membranes, melting points below 600°C and nonvolatility under CO₂ at temperatures to 840°C. It was further shown that incorporation of sulfide ion in concentrations as high as 25 mole % resulted in molten mixtures at 600°C or lower. That sulfide-containing mixtures are liquid at reasonable temperatures is critical to the success of molten carbonate membranes for removal of H₂S. Partial solidification of the melt could result in membrane failure.

Since carbonate membranes permeate H₂S by a facilitated transport mechanism, a knowledge of the reactivity of H₂S with the carbonate mixtures was required for choice of the optimal membrane material. For this reason, an evaluation of the equilibrium constant for the reaction of H₂S with molten carbonate mixtures was carried out by a series of absorption experiments. This activity was complicated by several experimental difficulties. The most serious of these was the reactivity of H₂S with the metal test apparatus at the high temperatures used.

Such reactivity made collection of meaningful information quite difficult.

However, a reasonable equilibrium constant for the reaction of H₂S with one carbonate melt was determined, 0.235 atm at 560°C.

Through a process involving literature searches and screening experiments, it was determined that aluminum nitride and lithium aluminate were the best candidate ceramics for use as microporous supports for immobilized molten carbonate membranes.

Aluminum nitride discs and tubes with pore sizes in the range 0.38-0.42 μm with 45-50% open porosity were successfully produced. These discs and tubes were infiltrated with a molten carbonate mixture using techniques developed for this program. In the course of this work, it was determined that boron nitride can be used as a coating to help control the infiltration process of these materials. While lithium aluminate had better long term stability than aluminum nitride in contact with the molten carbonates, fabrication of discs of this material with pore sizes in the range required to contain the molten carbonate mixtures was unsuccessful. This was because of limited source suppliers of lithium aluminate powders and the inability to reduce the starting particle size of commercially available powders without introducing excessive mill/media contamination.

Three types of molten carbonate membranes were prepared. These consisted of a carbonate mixture immobilized in a microporous gold frit, in a planar microporous ceramic support, or in a tubular microporous ceramic support. A significant problem relating to membrane testing involved the tendency of planar ceramic membranes to crack upon sealing in the membrane cell. Membrane cracking was minimized by sealing using a graphite tape technique. Testing of molten carbonate membranes at 560°C and using H₂S containing feeds at relatively low flow rates was complicated greatly by the reactivity of H₂S with the membrane cell. As for the absorption experiments above, consumption of H₂S by reaction with metal led to unreliable determinations of H₂S permeabilities. This is a serious problem which would need to be addressed in future

work. Membrane cells could be constructed of quartz or alumina which were shown to be inert with respect to H_2S at temperature to 700°C .

Due to the problem of H_2S -metal reactivity, molten carbonate/planar ceramic membranes were evaluated using feeds which contained no H_2S . For most of the membranes so examined, gas permeance were quite high indicative of defects in the molten carbonate layer. This is, of course, a serious problem that would need to be addressed further. However, for a few membranes, reasonable, but still somewhat high, CO_2 permeabilities; for example 1,200 Barrers, were obtained suggesting that the fabrication of largely defect-free membranes is possible.

Some of the difficulties of H_2S -metal reactivity were minimized through testing at significantly higher gas flow rates. Permselective testing was performed using membranes consisting of a molten carbonate mixture in planar and tubular ceramic supports. Erratic membrane performance was observed. Often, H_2 or helium permeabilities were much higher than those predicted based on a solution-diffusion mechanism indicative of defects in the molten carbonate layer. However, in some instances H_2S to H_2 or He selectivities greater than one were observed. Based on fairly limited data, an observed decrease in H_2S permeability with increasing feed pressure was consistent with facilitated transport of H_2S . Examination of membranes after testing revealed that there apparently is a tendency for the melt to migrate in or out of the support. This was particularly apparent for tubular membranes where the salt appeared to have migrated downward along the tube. Planar ceramic membranes examined after testing showed evidence of regions of unfilled pores near the middle of the discs. In addition, for one unused planar ceramic membrane, similar unfilled regions were observed as well.

1.0 Background

The successful development of advanced power generation systems such as Integrated Gasification Combined Cycle (IGCC) requires that practical methods for removal of gaseous and other contaminants be developed. Among numerous alternatives, membranes supply a method for the removal of contaminant gases. As illustrated in Figure 1.1, the preferred gaseous separation scheme would involve removal of contaminant gases such as H_2S , HCl , NH_3 and others from the hot, high pressure fuel gas.¹ Thus, the useful fuel gases such as H_2 , CO , and CH_4 , would be recovered hot and at high pressure.

Application of conventional gas separating membranes to such a separation scheme is impractical. Generally, such membranes consist of organic polymers which cannot be used at the high temperatures of IGCC gas mixtures. Further, conventional polymeric membranes generally permeate permanent gases, particularly H_2 , more readily than most contaminant gases.² Thus, the permselective properties of conventional polymeric membranes are unsuitable for removal of a contaminant such as H_2S from a gas mixture rich in H_2 .

Microporous ceramic membranes, unlike polymeric membranes, are stable at the high IGCC temperatures. However, the permselective properties of these membranes are also not suited to the separation scheme illustrated in Figure 1.1. Microporous ceramic membranes permeate gases such as H_2 more readily than contaminants such as H_2S and the desired separation is not obtained.³

The specific problem addressed in this program was the development of membranes which selectively permeate H_2S from hot fuel gas while leaving the other gases in the stream largely unaffected. Development of such a membrane requires consideration of other, nonconventional types of membranes. The solution evaluated in this program involved the use of facilitated transport membranes. Facilitated transport membranes are systems in which permeation of a specific gas is augmented by means of a reversible chemical reaction or interaction with the membrane material. Other gases do not react with the membrane and, hence, are far less permeable. Generally speaking, facilitated transport membranes have historically consisted of a reactive liquid immobilized in a porous support.⁴ For example, Air Products has developed a family of facilitated transport membranes which selectively permeate acid gases at ambient temperatures.⁵ These membranes consisted of an acid gas reactive liquid immobilized in the pores of a microporous polymeric support. The reversible reactivity of the liquid with CO_2 or H_2S resulted in high permeabilities of these gases. Gases such as H_2 or CH_4 have low solubilities in the membrane liquid and, since they permeate by a solution-diffusion pathway, their permeabilities are quite low. Thus, an effective separation of acid gases from H_2 or CH_4 can be obtained. Such membranes, although useful at room temperature, are of no value at the high temperatures and pressures found in fuel gas separations. Nonetheless, the concept can be applied successfully if the "right" reactive liquid and support can be found.

Figure 1.1 Removal of contaminant gases from IGCC gases using a high temperature membrane.

The requirements for the right materials are fairly stringent. The reactive liquid must be stable and involatile at high temperature, 500-800°C. In addition, the liquid must react reversibly with H₂S at the pressures found in fuel gases. The support must be inert with respect to the reactive liquid and the fuel gas at elevated temperature and be relatively thin. It must have sufficiently small pores to maintain thin liquid films at high pressures. After examination of the available literature, carbonate salt mixtures were chosen as the reactive liquid and microporous ceramics were chosen as the support.

It is known that carbonate salts react reversibly with H₂S as represented by reaction (1) where M represents a monovalent metal cation and n is 1 or 2:⁶

In addition, although most pure carbonate salts are not molten at a temperature reasonable (e.g. K₂CO₃, mp. 898°C⁷) for use in an immobilized liquid membrane, many examples of relatively low melting mixtures of alkali and alkaline earth carbonates are known. For example, a mixture containing 44.1 mole% Li₂CO₃, 29.8 mole% Na₂CO₃, and 26.1 mole% K₂CO₃ melts at 393°C.⁷ Mixtures of carbonate salts possess the reversible H₂S reactivity and melting points required for a successful facilitated transport membrane.

Various carbonates and carbonate mixtures have been extensively evaluated as absorbents for H₂S. Moore,⁸ Stegen,⁹ and Lyke¹⁰ and their coworkers have shown carbonate melts to be effective absorbents of H₂S from hot fuel gas mixtures and at least two US patents claiming the use of carbonate melts as H₂S absorbents have appeared.^{11,12} Absorption occurs by the chemistry of reaction (1). Equilibrium constants and enthalpies of reaction for reaction (1) involving carbonate melts containing lithium, sodium, potassium, and calcium cations were determined and at 750°C ranged from 1.6 to 2.0 atm. Regeneration of the H₂S free absorbent is accomplished by exposure to CO₂ and steam which results in reaction (1) proceeding in the reverse direction.

The mechanism of permeation of H₂S in a molten carbonate membrane is shown schematically in Figure 1.2. At the feed interface, where the pressure of H₂S is relatively high, H₂S reacts with carbonate ions as in reaction (1) to form sulfide ions in the melt and H₂O and CO₂ which are liberated into the gas phase. The sulfide ions diffuse in a concentration gradient to the low pressure side (permeate) of the membrane. Here, a sweep gas containing CO₂ and H₂O causes reaction (1) to occur in the reverse direction. H₂S is formed, released into the gas phase and removed from the permeate interface by the sweep gas. This is accompanied by "regeneration" of the melt to the carbonate form. The other gases in the feed fuel gas, H₂, CO, CH₄ and others, do not react chemically with the melt. Permeation of these gases can only occur by a solution-diffusion mechanism in which gases physically dissolve as discrete molecules and diffuse from the high to the low pressure side of the membrane. Since the solubility of gases such as H₂ are expected to be low in the highly ionic carbonate melts, permeabilities of these gases

are likewise expected to be low. Thus, in principle, a selective removal of H_2S without substantial loss of other fuel gases can be achieved.

Figure 1.2 Mechanism of facilitated transport of H_2S in a molten carbonate membrane. Membrane is viewed in cross-section.

The high operating temperatures (500-800°C) combined with the range of oxidative conditions (very low on feed side and moderate on the sweep side of the membrane) present a significant challenge for selection of the microporous support material. The highly corrosive nature of the molten alkali carbonates makes that selection even more difficult. Metals and metallic alloys, especially in the very high surface area form required in a microporous support, will not be suitable due to their tendency toward oxidation and corrosion. Ceramic materials, on the other hand, possess the desirable combination of high temperature strength, corrosion resistance, and the ability to form high void fraction microporous supports. Crystalline ceramics are known to maintain their strength and elastic stiffness to near their melting temperature, which for most ceramics of interest to this program is greater than 1200°C. The corrosion resistance of ceramics is also well documented, with ceramics used in the processing of molten metals and glasses and in such severe environments as molten cryolite. In addition, substantial progress has been made in recent years to develop microporous ceramics for use as membranes for the separation of liquids and gases.

2. Objectives and Project Description

2.1 Objectives

The objective of this project was to demonstrate the feasibility of developing high temperature, high pressure, facilitated transport ceramic membranes to control gaseous contaminants in Integrated Gasification Combined Cycle (IGCC) power generation systems. Meeting this objective requires that the contaminant gas hydrogen sulfide, H_2S , be removed from an IGCC gas mixture without substantial loss of the other gaseous components, specifically hydrogen, carbon monoxide, and methane.

2.2 Program Description

To accomplish the above objectives, Air Products and Chemicals, Inc., Golden Technologies and Research Triangle Institute worked together to develop and test high temperature facilitated membranes for the removal of H_2S from IGCC gas mixtures. The work involved in this program can be grouped into four tasks: (1) test plan preparation (2) concept evaluation, development and testing (3) feasibility demonstration and (4) process performance, evaluation and economics. The test plan formulated was reported previously. Due to some very serious experimental problems, limited work relating to Tasks 3 and 4 was completed and the current report describes largely the results of Task 2 activities.

Task 2 consisted of three basic activities. The first of these involved the determination of equilibrium constants for the reaction of H_2S with various molten alkali and alkaline earth carbonate salt mixtures. In addition, immobilized molten carbonate membranes were to be prepared and evaluated for the removal of H_2S from gas mixtures. Further, a model to predict the permselective properties of molten carbonate membranes was to be developed with the intent of determining the required H_2S -molten carbonate reactivity for optimal permselective properties.

A second activity pursued in parallel involved the development of ceramic materials which were chemically and physically compatible with molten carbonate salt mixtures under IGCC conditions. A microporous ceramic host capable of supporting a molten carbonate mixture was to be developed and appropriate immobilized liquid membranes were to be fabricated.

Thirdly, the permselective properties of these molten carbonate/ceramic immobilized liquid membranes were to be evaluated under conditions approximating those found in the intended application. The results of this evaluation would then provide a basis for assessing the technical feasibility of the concept.

3.0 Experimental Section

3.1 Salt mixture preparation and characterization

3.1.1 Methods

Differential thermal analysis (DTA) data was obtained using a DuPont 1600 differential thermal analysis analyzer. The sample was contained in a platinum cup. The reference cup was filled with alumina. The sample chamber was purged with CO₂ or N₂ as indicated as a flow rate of 100 cc/min. Data was collected from ambient to 1000°C at a heating rate of 20°C/min.

Thermal gravimetric analysis (TGA) data was obtained using a Perkin-Elmer 7 Series Thermal Analysis System. Samples were contained in a platinum pan and the sample compartment was purged with CO₂ or N₂ as indicated at a flow rate of 50 cc/min. Generally, data was collected from between 30 and 830°C at a heating rate of 40°C/min. Exceptions are noted in the text.

3.1.2 Materials

Prior to use, as received carbonate salts were heated under flowing CO₂ for 18 hours at 300°C in dense alumina crucibles. Following heating, the aluminum ion content of each salt was quite low, <0.04%, confirming that no contamination from the crucible had occurred.

Mixture preparation. Each mixture was prepared using the following general procedure. Weighed quantities of the appropriate salts were ground into a mixture of fine powders using a mortar and pestle. The mixture was transferred into a gold crucible and was heated under an atmosphere of CO₂ at 300°C for 4 hours and 550°C for 4 hours. The molten mixture was poured from the hot crucible into an aluminum pan at room temperature, causing immediate solidification. The solid was ground into a fine powder and heated to 300°C under CO₂ to remove absorbed water. It was subsequently stored under a dry, inert atmosphere. Exceptions to this general procedure and other information specific to the preparation of individual mixtures are noted below. Mixture compositions are listed in Table 3.1.1 below.

Table 3.1.1. Compositions and melting temperatures of carbonate mixtures prepared.

	<u>Composition, mole %</u>									
<u>Components</u>	30-A	34-1	27-1	23-2	31-1	32-1	34-2	25-2	26-1	40-1
Li ₂ CO ₃	49.0	37.36	35.29	32.98	32.87	33.27	35.34	34.67	36.42	
K ₂ CO ₃	25.2	19.26	21.82	22.38	22.22	22.40	21.74	22.19	22.59	33.23
CaCO ₃	25.7	20.06	23.71	25.06	25.01	24.73	23.69	23.42	22.81	
Na ₂ CO ₃		23.30								33.09
Rb ₂ CO ₃			19.59							

Cs ₂ CO ₃				19.19						33.68
SrCO ₃					19.89					
BaCO ₃						19.60				
MnCO ₃							19.23			
La ₂ (CO ₃) ₃								19.72		
Eu ₂ (CO ₃) ₃									18.18	
MP(°C)	485	405, 449	447, 482	426, 443	481	469	*	*	*	429, 546

* Unstable at or below melting point

Prior to heating at elevated temperatures, mixture 23-2 was heated overnight under CO₂ at 130°C.

When mixture 32-1 was heated to 550°C, some solid remained. Additional heating at 650°C for 4 hours resulted in a fully molten sample.

Mixtures 25-2 and 26-1 were heated under flowing CO₂ at 300°C for 4h and 550°C for 2h. Neither sample appeared to be molten at 550°C. Heating to 600°C for 1.5h did not result in melting for either mixture. After cooling under CO₂, it was determined that mixture 25-2 had lost 7.1% of its initial weight and mixture 26-1 had lost 54.1%.

For mixture 40-1, additional heating at 600°C for 2h was required to obtain a fully molten sample. To transfer the liquid from the crucible, the temperature was raised to 650°C briefly.

Mixture 34-2, which contained MnCO₃, was heated to 300°C for 4h and then to 550°C. The mixture formed a deep brown/red liquid which appeared to be evolve gas. Heating was ended.

Preparation of mixtures containing sulfide ions. Sulfide-containing mixtures were prepared by a procedure similar to that described above. Weighed quantities of Li₂CO₃, K₂CO₃, CaCO₃, and CaS (Matthey Electronics, 99.99%) were ground into a fine powder using a mortar and pestle. The amount of CaCO₃ was adjusted to keep the Li/K/Ca molar ratio the same as that of the base composition. For mixtures containing about 25% CaS, no CaCO₃ was used. Mixtures were transferred into gold crucibles and heated under flowing CO₂ at 300°C for 1h, 550°C for 1/2h and 600°C for 3h. All the samples appeared to be liquid at this temperature but each were somewhat colored with a small amount of a gold colored solid, most likely iron sulfide, floating on the surface. The molten mixtures were poured into aluminum pans at room temperature, which resulted in immediate solidification. The samples were ground into a powder under an inert atmosphere.

Mixtures 46-1 and 46-2 were prepared by heating to 100°C overnight, 550°C for 2 h, and 600°C for 2 h under flowing CO₂ rather than at the above cited temperatures.

3.2 Absorption Experiments.

The apparatus used to perform absorption experiments is shown schematically in Figure 3.2. A detailed drawing of this apparatus and listing of the components can be found in the Appendix. Details of each individual absorption experiment are listed below.

Feed mixtures were prepared by transferring known pressures of gas into an initially evacuated mixing vessel. H_2S was transferred into the vessel first, followed by CO_2 and then other permanent gases. Prior to initiating experimental work, it had been intended to introduce water vapor by adding liquid water to the evacuated mixing vessel and heating to vaporization. However, experiments using water containing gas mixtures were not performed. When the addition of gases was complete, the mixing vessels were heated to 70°C and the contents were stirred with a paddle stirrer. All gas lines leading from the mixing vessels were heat traced and maintained at 70°C . The dosing and sampling containers were stainless steel vessels which were also heat traced. The volumes of the dosing volume and sample volume were determined by expansion of gas from a calibrated volume and were 0.5124L and 0.1857 L, respectively. Molar quantities of gases transferred or absorbed were calculated based on the assumption that all gases are ideal.

Figure 3.1 Schematic diagram of high temperature, high pressure absorption and membrane system.

The absorption vessel consisted of a one liter Parr reactor designed for operation at pressures and temperatures to 1000 psi and 800°C. The reactor body, head, and thermowells were constructed of Incoloy 800 HT. The contents of the reactor were heated by cartridge heaters inserted into the exterior of the thermowells. The internal surface of the reactor was lined with a ceramic tube with a wall thickness of about 0.2 in. The bottom of the reactor was lined with a ceramic disc of about the same thickness. Inside the ceramic lining was placed a cylindrical gold vessel. The purpose of the gold vessel was to provide an inert container for the carbonate melts upon exposure to H₂S.

To analyze the gas phase of the absorption vessel, an aliquot of gas was withdrawn into the sampling volume. Following pressurization with N₂, the sample was analyzed in a Hewlett Packard GC operating at an oven temperature of 80°C. Columns and configurations as listed in Appendix. This configuration of the GC permitted detection and quantification of H₂, CO, CO₂, H₂S, COS, and CH₄.

Absorption experiment 12666-2. The intent of the experiment was to expose the base composition carbonate mixture to a gas mixture containing only H₂S and CH₄. However, due to a mechanical problem or back contamination of gases of unknown origin, the feed mixture used contained H₂ as well. The composition of the feed mixture as determined by GC was 10.7% H₂S, 6.40% CO₂, 81.1% CH₄, and 1.8% H₂. The absorption vessel was loaded with 124.81 g (1.2899 mole CO₃²⁻) of the base carbonate mixture 30-A. The absorption vessel was heated to 560°C and stirring of the melt was begun. The dosing and sample volumes were maintained at 75°C.

The volume of the absorption vessel available to gas was determined by helium expansion from the dosing volume and was 0.7636 L. The volumes of the dosing volume and sample volume, as determined previously using a calibrated gas volume, were 0.5124 and 0.1857 L, respectively. The feed gas mixture was added to the evacuated dosing volume to a pressure of 402.3 psia. A portion of this gas was added to the absorption vessel such that the final pressure of the dosing volume was 287.5 psia. This pressure change corresponds to 0.1401 moles of gas transferred into the absorption vessel. After 12 hrs, the pressure in the reactor dropped from 248.8 psia initially to 240.6 psia at equilibrium. A portion of the headspace gases was withdrawn into the evacuated sample volume to a pressure of 51.8 psia (0.0229 moles). This mixture was pressurized with N₂ to a total pressure of 616.0 psia and analyzed by GC revealing the following gas concentrations in ppm:

	<u>ppm</u>	<u>mole fraction</u> <u>(see below)</u>
H ₂ S	80.8	9.608x10 ⁻⁴
CO ₂	2,678	3.185x10 ⁻²
CH ₄	64,665	7.692x10 ⁻¹
CO	7,567	8.998x10 ⁻²
COS	8.3	9.809x10 ⁻⁵
H ₂	5,941	7.065x10 ⁻²
H ₂ O	-	3.726x10 ⁻²

Using the above values of gas concentration, the quantity in moles of each component withdrawn into the sample volume were calculated and summed. Assuming that water is only gas which was present and not quantified by GC, the concentration of water is given by the difference between the above sum and the quantity of gas as determined by the ideal gas law. Mole fractions corresponding to the gas composition at equilibrium were calculated and are displayed above.

The quantity of H₂S absorbed at equilibrium corresponds to the quantity of H₂S added to the absorption vessel minus that remaining at equilibrium or 1.48x10⁻² moles.¹² Hence, at equilibrium the salt mixture contains 1.48x10⁻² moles of S²⁻. The quantity of CO₃²⁻ is given the initial quantity of CO₃²⁻ minus the quantity of sulfide at equilibrium or 1.249 mole CO₃²⁻. Substituting the appropriate values in equation (12) yields K = 3.448 psia or 0.235 atm:

$$K = P \cdot \frac{x_{H_2O} \cdot x_{CO_2}}{x_{H_2S}} \cdot \frac{n(S^{2-})}{n(CO_3^{2-})}$$

Absorption experiment 12666-6. A gas mixture of the composition 8.382% H₂S, 40.36% CO₂, 51.28% CH₄, as determined by GC, was used to perform a second absorption experiment. To the absorption vessel was added 134.2 g of the base carbonate mixture (1.3869 mole CO₃²⁻), which was heated to 560°C. The dosing volume was pressurized to 420.3 psia with the feed gas mixture. A portion of this was transferred into the absorption vessel such that the final pressure of the dosing volume was 275.7 psia or 0.17642 moles of gas were transferred. After standing overnight, the pressure in the absorption vessel was 225.0 psia. A portion of the gas phase was transferred to the sample volume (74.1 psia) and pressurized with N₂ to a total pressure of 798.6 psia. Analysis by GC gave the following composition:

Gas	conc. (ppm)
H ₂ S	475.1
CO ₂	30163
CH ₄	51120
CO	25789
COS	64.8
H ₂	4072
H ₂ O	-

When the quantities of gases in the above table were used to calculate quantities in moles and were summed, the value obtained was greater than the number of moles of gas withdrawn into the sample volume. Hence, a quantity of H₂O, and thus an equilibrium constant, could not be calculated. Presumably, this arises from the relatively larger error in the sum of the individual gases.

Absorption experiment 12666-15. The absorption properties of the base carbonate mixture were determined using a feed gas containing only H₂S and CO₂. Although an inadvertent valve switch precluded a quantitative treatment, the data were provided a basis for comparison. A 126.9 g sample of the base composition carbonate mixture was heated to 560°C in the absorption vessel. The melt was then exposed to a gas mixture containing 15.0% H₂S in CO₂. After standing overnight, a portion of the headspace gases was withdrawn into the sample volume to a pressure of 102.9 psia, pressurized with N₂ to a total pressure of 803.1 psia, and analyzed by GC. The following gases were detected in the indicated quantities:

Gas	conc (ppm)
H ₂ S	2,710
CO ₂	116,600
CO	25,060
COS	130
H ₂	2,690

Absorption experiment 12923-32. One additional absorption experiment was performed following gold plating of the various components of the absorption vessel. Feed gas containing 0.5% H₂S in N₂ was added to 125.8 g of the base carbonate mixture 30-A at 550°C. This was dosed into the reactor, and the system was allowed to come to equilibrium. Some gas was removed into the sampling volume (69.8 psia) and pressurized to 805.9 psia with N₂. Analysis of this gas revealed the following gas concentrations: CO₂, 2419 ppm; CO, 1306 ppm; CH₄, 1063 ppm; H₂, 1121 ppm. H₂S and COS were not detected. Assuming that no water is present in the gas phase, the concentration of gases at equilibrium were: CO₂, 2.82%; CO, 1.52%; CH₄, 1.24%; H₂, 1.30%.

Gas phase reactivity in the absence of a molten carbonate mixture. The absorption vessel with the gold liner was partially filled with sand as a thermal sink and heated to 550°C. The absorption vessel was pressurized to 111.9 psia with a mixture containing 32.1% CO₂, 46.5% H₂, and 21.4% CH₄. After standing overnight, the pressure dropped slightly to 107.0 psia. A portion of the gas phase was removed, pressurized with N₂, analyzed by GC and found to contain CO in addition to the three original gases. Assuming that no other gases were present with the exception of the diluent N₂, the following concentrations of gases were present in the absorption vessel: 20.9% CO; 16.5% CO₂; 40.0% H₂; 22.6% CH₄. It is likely that H₂O was also present but it was not quantified. Following cooling to room temperature, visual examination of the absorption vessel revealed no black deposits.

Estimation of errors in the determination of quantities of gas. To establish the accuracy with which quantities of gas absorbed could be determined, a blank experiment involving helium gas at 27°C was performed. Following determination of the absorption vessel volume by expansion of gas from the dosing volume, the absorption vessel was pressurized with helium to 100.1 psia which corresponded to 0.258 mole of gas.

Transfer of a portion of this gas into the evacuated sample volume resulted in an absorption vessel pressure of 92.1 psia or 0.237 mole remained. The pressure of the sample vessel was 34.3 psia which corresponded to 0.0176 moles. Based on this value, the quantity of gas remaining in the absorption vessel should be 0.240 moles or a 0.0034 mole discrepancy or about a 1.5% error. Realistically, this is a minimum error and larger errors can be expected at the actual operating temperature of the unit.

3.3. Membrane preparation and testing

3.3.1 Membrane testing. The apparatus used to evaluate the permselective properties of molten carbonate membranes is shown schematically in Figure 3.1. A detailed drawing of this apparatus and a listing of the components is in the Appendix. Two gas mixtures, a feed and a sweep gas, were prepared in the mixing vessel as described above. Initially, it had been intended to add liquid water to the mixing vessels and heat to vaporization, but it was subsequently decided to humidify the feed and sweep gases by passage through bubblers containing water, usually at 60°C. These bubblers are not shown in Figure 3.1. After the mixing, all gas line vessels were heat traced and maintained at 80°C. Feed and sweep gas flows were set using mass flow controllers. However, it was found that exposure of these controllers to corrosive gases at 80°C resulted in numerous instances of controller failure, and they were replaced with needle valves. The membrane to be tested was held in a membrane cell constructed of stainless steel and illustrated in Figure 3.2. Different cells were used for molten carbonate/gold frit and planar molten carbonate/ ceramic membranes and both are shown in Figure 3.2. Some membranes were examined using the same holder following gold plating of surfaces exposed to gas. The membrane cell was heated to the operating temperature, usually 560°C, in a furnace. Downstream from the membrane unit were back pressure regulators which could be set to obtain either feed or sweep pressures greater than ambient. Pressures of both gases were determined by the use of pressure transducers. Either the feed or sweep gas could be directed to the GC for analysis as described in Section 3.2.

Ceramic based membranes were sealed in the membrane cell using either a gold plated O-ring or C-ring. Sealing was accomplished by contact of the O- or C-ring with the surface of the membranes. The use of a C-ring resulted in a greater frequency of crack-free membranes. For later membranes, an alternative approach utilized graphite tape. In an initial attempt, 3/8" wide, 0.005" thick graphite tape was applied to the edges and part of the faces of an AlN/salt membrane. An inner C-ring was not used. Examination of the membrane after testing suggested that removal of the inner C-ring groove would supply more appropriate surfaces for sealing to graphite tape. This was done and subsequent membranes were sealed by the use of circular graphite gaskets which were laid on the faces of the membrane.

Permeabilities of molten carbonate/gold frit membranes were calculated assuming that the membrane area and thickness are those of the gold frit, 1.13 cm² and 0.1639 cm. No correction for porosity or tortuosity was applied.

Permeabilities of carbonate/ceramic membranes were calculated assuming that the membrane area and thickness were those of the ceramic support: 4.31 cm² and 0.254 cm. A porosity of 50% was assumed. No correction for tortuosity was applied.

Figure 3.2 Schematic diagrams of membrane test cells.
 Top: Cell used for molten carbonate/gold frit membranes.
 Bottom: Cell used for planar molten carbonate/ceramic membranes.

3.3.2 Membrane preparation

Preparation of molten salt membranes supported in gold frits. A weighed quantity of the base carbonate mixture 30-A was placed on the surface of a gold frit containing $0.5\mu\text{m}$ pores and was heated to 550°C under flowing CO_2 . After cooling to room temperature, no salt was observed on the bottom surface of the frit. A small residue of salt was observed on the top surface, and it was removed by scrapping it off. Several membranes were prepared in this manner. Two were used for testing: membrane 11818-47-2 containing 0.0755g of the base composition and membrane 11818-54-2 containing 0.0655 g.

Preparation of molten salt membranes supported in microporous ceramic planar discs. The infiltration process for planar discs involved placing the porous ceramic disc into a boat fashioned out of gold foil. Powdered salt was then added. The amount of salt added was calculated to be 25% in excess of that needed to completely fill the open pore volume of the ceramic disc. The foil boat containing the disc and salt were then placed in a retort furnace. The furnace was evacuated and backfilled to 1atm with CO_2 twice. The furnace was heated to $\sim 700^{\circ}\text{C}$ under flowing CO_2 at which point the furnace was again evacuated and backfilled with CO_2 twice. The furnace was then cooled to room temperature under flowing CO_2 . In some cases, the ceramic disc was coated with a colloidal boron nitride (BN) spray prior to infiltration in an attempt to better control the infiltration (as discussed in Section 4.2.4). The principle underlying this method is that gases in the open pores are removed by evacuating the furnace. When the furnace chamber is then repressurized, the atmospheric pressure forces the molten salt into the pore volume of the ceramic. In addition, capillary forces ensure that the salt fills the smallest pores in the microstructure.

Preparation of molten salt membranes supported in microporous ceramic tubular supports. The infiltration of tubular membrane supports was performed in a way similar to that for discs; however, care had to be taken to prevent complete filling of the bore of the tube with the molten salts as this could lead to problems in removing the salts. This fixturing problem was resolved by placing a graphite rod slightly smaller than the tube ID down the bore of the tube. The end of the rod was wrapped with graphite tape to form a snug fit into the ends of the tube. This tube assembly was then placed into a boat fashioned from gold foil. The powdered salt was then added. In the case of the tubes, the amount of salt added was calculated to be 50% in excess of that needed to fill the open porosity, due to the larger surface area of the tubes. The actual infiltration was then accomplished in the same way as described above for the planar discs.

4.0 Results and Discussion

4.1 Development of molten carbonate salts.

The objective in the area of development of molten carbonate salts was to identify mixtures of carbonate salts which react reversibly with H₂S, CO₂ and H₂O under IGCC conditions. Such salts would then be used to fabricate immobilized liquid membranes which would selectively permeate H₂S from hot fuel gas streams. As described in Section 1.0, mixtures of carbonate salts were considered since the melting points of pure alkali or alkaline earth metal carbonates are generally higher than the expected temperature of membrane use, 500 to 850°C.

Efforts associated with development of molten carbonate mixtures involved an examination of available literature involving: (1) the reactivity of pure carbonates with H₂S, (2) the synthesis of new carbonate mixtures, and (3) the characterization of the physical and chemical properties of these mixtures. Chemical characterization involved a determination of the equilibrium constant for reaction (1) which occurs upon exposure of molten carbonates to H₂S. The value of K₁ can be determined by an absorption experiment which is discussed below.

M = alkali or alkaline earth metal cation

n = 1 or 2

K₁ is the equilibrium constant of the reaction (1)

4.1.1 Survey of the H₂S reactivity of pure carbonate salts.

Before setting out on the synthesis of new carbonate melts, the thermodynamics of the reaction of pure carbonate salts with H₂S as in reaction (1) were examined. Reaction (1) can be thought of as occurring in two steps. The first, reaction (2), involved decomposition of the carbonate to yield the oxide and CO₂ gas. The oxide thus generated reacts with H₂S in an acid-base reaction, reaction (3).

The extent of reaction (1) depends on the equilibrium constants K₂ and K₃ since K₁ = K₂K₃. Hence, the less stable the carbonate (large K₂) and the more basic the oxide (large K₃), the greater will be the value of K₁. The available thermodynamic data (527-827°C) for alkali (Li, Na, K, Rb) and alkaline earth (Ca, Sr, Ba) salts were used to obtain log K

values which are plotted as a function of temperature in Figure 4.1.¹³ Values of K_2 and K_1 increase with increasing temperature while K_3 decreases. For illustrative purposes, $\log K$ at 627°C are listed below in Table 4.1.

Table 4.1. $\log K$ values for reactions 1-3 at 627°C for pure alkali and alkaline earth carbonates.

metal cation	$\log K_2$	$\log K_3$	$\log K_1$
Li	-4.84	4.47	-0.37
Na	-10.99	9.79	-1.20
K	-14.86	15.58	0.72
Rb	-15.70	-	-
Ca	-1.96	3.64	1.68
Sr	-4.78	4.64	-0.14
Ba	-6.84	6.92	0.076

The above data suggests that Group I (alkali) carbonates are more stable than the corresponding Group II (alkaline earth) salts and stability increases down a group. Similarly, the basicity of oxides increases down a group and Group I oxides are more basic than Group II. The values of K_1 are less periodic in nature. Nonetheless, in the absence of literature data, it would appear that evaluation of Rb_2CO_3 or Cs_2CO_3 in carbonate mixtures would be worthwhile if larger K_1 values are required, especially at higher temperatures. It is reasonable to predict that Rb_2O and Cs_2O are among the most basic oxides and the presence of either carbonate in melts is expected to lead to large K_1 values.

4.1.2 Characterization of pure carbonate salts.

Prior to use in mixture preparation, the pure carbonate salts used were characterized by a variety of techniques. As received carbonate salts were heated under flowing CO_2 for 18 hr prior to use. To confirm the expected composition, the metal ion content of many of the salts was determined using atomic absorption analysis. These results are listed in Table 4.2 along with those for the as received salts. In general, agreement between theoretical metal ion content and that determined after heating were good. Satisfactory elemental analysis could not be obtained for $MgCO_3$. This coupled with its unusual thermal gravimetric properties led to discontinuation of its use.

Figure 4.1. Log K versus temperature for reactions of pure carbonate salts.
 Top: $\log K_1$. Middle: $\log K_2$. Bottom: $\log K_3$

Table 4.2. Metal ion content of alkali and alkaline earth carbonate salts.

Salt	Metal ion content, weight percent		
	<u>theoretical</u>	<u>observed</u> as received	after heating
Li_2CO_3	18.78	16.37	18.69
Na_2CO_3	43.38	38.82	43.75
K_2CO_3	56.58	52.47	57.96
Rb_2CO_3	74.02	68.18	nd
Cs_2CO_3	81.58	33.25	79.16
CaCO_3	40.04	40.33	nd
SrCO_3	59.35	61.36	nd
BaCO_3	69.59	65.69	70.67

Thermal gravimetric analysis (TGA) was used to determine the water content of the various carbonate salts and, more importantly, to determine their stability with respect to oxide formation and their volatility. In general, TGA data was collected under an N_2 atmosphere or a CO_2 atmosphere. Samples were heated from 30 to 830°C at a rate of $40^\circ\text{C}/\text{min}$. The temperature was maintained at 830°C for 10 min prior to cooling to room temperature. In general, it was found that heating of as received salts under N_2 led to a weight loss at relatively low temperature attributable to desorption of bound water from the sample. This is illustrated, for example, by the TGA trace (Figure 4.2) of as received Na_2CO_3 which exhibits a 20.05% weight loss ending at 230°C . The heat treatment of carbonate salts described above generally reduced the water content of the salts to near zero. Again, this is illustrated by the TGA trace for Na_2CO_3 after heating (Figure 4.2) which shows no water desorption. Exceptions were the salts Rb_2CO_3 and Cs_2CO_3 . The salts Rb_2CO_3 and Cs_2CO_3 were heated a second time as above. TGA traces of both salts after heating as above showed that bound water was still present, suggesting that these salts readily absorb water when handled even briefly in the air.

In addition to the relatively low temperature weight loss ascribed to water, a few of the carbonate salts exhibited a high temperature weight loss when heated under a N_2 atmosphere (Table 4.3). This can be assigned to loss of CO_2 via oxide formation as in reaction (2) above. With the exceptions noted below, a high temperature weight loss was not observed when salt samples were heated under flowing CO_2 (15 psia), which is consistent with the chemistry of reaction (2) and with the fact that most carbonate salts were nonvolatile to temperatures of 830°C .

Compared with the other salts, MgCO_3 , $\text{La}_2(\text{CO}_3)_3$, and $\text{Eu}_2(\text{CO}_3)_3$ are unusual. MgCO_3 ¹⁴ heated under N_2 or CO_2 exhibited the same TGA trace, which was characterized by a continuous weight loss over the entire heating range. The rare earth carbonates $\text{La}_2(\text{CO}_3)_3$ and $\text{Eu}_2(\text{CO}_3)_3$ apparently decompose to oxides in the presence or absence of CO_2 (Figures 4.3 and 4.4). Under N_2 , both salts exhibited two high temperature weight losses beginning at 430°C and at 650°C . Under CO_2 , $\text{La}_2(\text{CO}_3)_3$ exhibited one weight loss starting at 470°C while $\text{Eu}_2(\text{CO}_3)_3$ exhibited two at 490°C and 690°C .

Figure 4.2 TGA traces of Na₂CO₃ obtained upon heating under a N₂ atmosphere. 30°C to 830°C at 40°C/min.
 Top: As received salt.
 Bottom: After heating under a CO₂ atmosphere.

Figure 4.3 TGA traces of $\text{La}_2(\text{CO}_3)_3$.
 30°C to 830°C at 40°C/min.
 Top: Sample heated under a N_2 atmosphere.
 Bottom: Sample heated under a CO_2 atmosphere.

Figure 4.4 TGA traces of $\text{Eu}_2(\text{CO}_3)_3$.
 30°C to 830°C at 40°C/min.
 Top: Sample heated under a N_2 atmosphere.
 Bottom: Sample heated under a CO_2 atmosphere.

Carbonate salts were also characterized using differential thermal analysis (DTA). DTA data were most often collected under an N₂ atmosphere between 30 and 1000°C for as received salts and for salt after heat treatment. Table 4.4 summarizes the observed endotherm temperatures and a representative DTA trace is illustrated in Figure 4.5. For the as received samples, endotherms below 300°C correspond to desorption of bound water, consistent with the above TGA data. Higher temperature endotherms correspond either to melting or decomposition to the oxide and CO₂ as in reaction (2). For reference, literature melting points of various pure carbonates are listed in Table 4.4. Additional DTA information for pure carbonate salts is available in the literature.¹⁴ Endotherms for La₂(CO₃)₃ and Eu₂(CO₃)₃ are probably the result of decompositions to oxides since weight losses at comparable temperatures were observed in the TGA. Literature DTA results for La₂(CO₃)₃ show endotherms as 460°C and 915°C reportedly due to reactions 4 and 5 respectively:¹⁴

where La₂O₃•CO₂ is the mixed oxide-carbonate salt La₂O₂(CO₃).

Table 4.3. High temperature weight losses for pure carbonate salts.

Salt	under N ₂	under CO ₂
Li ₂ CO ₃	570	none
Na ₂ CO ₃	none	none
K ₂ CO ₃	none	none
Rb ₂ CO ₃	none	none
Cs ₂ CO ₃	none	none
MgCO ₃	continuous*	continuous*
CaCO ₃	650	none
SrCO ₃	590**	610**
BaCO ₃	none	none
La ₂ (CO ₃) ₃	430, 650	470
Eu ₂ (CO ₃) ₃	430, 650	490, 690

*continuous weight loss over entire temperature range, 30 - 830°C.

**relatively small weight loss, perhaps water.

Figure 4.5 DTA trace of Cs_2CO_3 upon heating under a N_2 atmosphere.

Table 4.4. Endotherms for pure metal carbonate salts between 30 and 1000°C under a N₂ atmosphere.

Salt	Endotherm temperature, °C		lit. mp(°C) ^{a, 7,15}
	as received	after heating under CO ₂	
Li ₂ CO ₃	742	741	723
Na ₂ CO ₃	130, 849	459, 861	858
K ₂ CO ₃	147, 305, 896	785, 913	898
Rb ₂ CO ₃	509, 865	885	837
Cs ₂ CO ₃	105, 233, 785	798	-
MgCO ₃	283, 476	94, 340, 450	-
CaCO ₃	851	849	1339
SrCO ₃	937	936	1497
BaCO ₃	823	815	1740
La ₂ (CO ₃) ₃	not done	509, 776	-
Eu ₂ (CO ₃) ₃	not done	554, 660	-

a. some literature melting points were for salt at higher than ambient pressure

4.1.3. Preparation and characterization of carbonate mixtures.

A series of carbonate salt mixtures for subsequent evaluation in H₂S-selective membranes were prepared and characterized. Details concerning the preparation of these mixtures can be found in the Section 3.0. A typical procedure was as follows. Weighed quantities of the appropriate salts were ground into a mixture of fine powder using a mortar and pestle. The mixture was transferred to a gold crucible and heated under an atmosphere of CO₂ until it was molten, typically 550°C. Following rapid cooling to room temperature, the mixture was ground into a fine powder, dried at moderate temperatures under CO₂, and subsequently protected from atmospheric moisture.

The compositions of various mixtures prepared are listed in Table 4.5. The first of these, mixture 30-A, a ternary mixture of Li₂CO₃, K₂CO₃, and CaCO₃, was designated as the "base composition." The H₂S reactivity of this composition has been reported in the literature.⁹ Most of the other mixtures were prepared by addition of roughly 20 mole percent of a fourth carbonate to the base composition. One mixture, 40-1, was a ternary mixture which did not contain Li₂CO₃ and was prepared in an attempt to improve ceramic/carbonate salt compatibility. The literature has few references to low melting carbonate mixtures which do not contain Li⁺ and most of these have relatively high melting points, for example, 56 mole % Na₂CO₃/44 mole % K₂CO₃ which melts at 710°C.³ Mixture 40-1, which contained about equimolar quantities of Na₂CO₃, K₂CO₃, and Cs₂CO₃ was molten at 550°C. One additional quaternary mixture, 34-1, was prepared for which H₂S reactivity data is available.⁹

Table 4.5. Compositions and melting temperatures of carbonate mixtures prepared.

Components	Composition, mole %									
	30-A	34-1	27-1	23-2	31-1	32-1	34-2	25-2	26-1	40-1
Li ₂ CO ₃	49.0	37.36	35.29	32.98	32.87	33.27	35.34	34.67	36.42	
K ₂ CO ₃	25.2	19.26	21.82	22.38	22.22	22.40	21.74	22.19	22.59	33.23
CaCO ₃	25.7	20.06	23.71	25.06	25.01	24.73	23.69	23.42	22.81	
Na ₂ CO ₃		23.30								33.09
Rb ₂ CO ₃			19.59							
Cs ₂ CO ₃				19.19						33.68
SrCO ₃					19.89					
BaCO ₃						19.60				
MnCO ₃							19.23			
La ₂ (CO ₃) ₃								19.72		
Eu ₂ (CO ₃) ₃									18.18	
MP(°C)	485	405, 449	447, 482	426, 443	481 482	469 443	*	*	*	429, 546

* Unstable at or below melting point

The melting points of the various carbonates mixtures, as determined by DTA and described in more detail below, are also listed in Table 4.5. Three of the mixtures were found to be unstable at or below their melting points. One of these, mixture 34-2, contained Mn(II)CO₃ in an attempt to produce a transition metal containing melt. Heating of this mixture to 550°C resulted in a deep brown/red liquid which appeared to evolve gas. Subsequently, a literature reference¹⁶ was found which reported that MnCO₃ is unstable in a Li₂CO₃-Na₂CO₃-K₂CO₃ eutectic above 400°C and that CO₂ and CO are liberated as in reaction (6):

This points out the potential difficulty using metal ions with more than one readily accessible oxidation state to prepare molten carbonate mixtures.

Also unsuccessful were attempts to prepare carbonate mixtures containing the rare earth elements La(III) and Eu(III). Heating of mixtures 25-2 (La) and 26-1 (Eu) to 550°C and subsequently to 600°C did not result in a molten product. After cooling to room temperature under CO₂, it was determined that the mixtures had lost 7.1% (25-2) and 54.1% (26-1) of their initial weights, implying decomposition of significant quantities of salt to oxides. This can be traced to the instability of La₂(CO₃)₃ and Eu₂(CO₃)₃ even in the presence of CO₂ as demonstrated by the TGA data for the pure salts (see above). The thermal instability of these two salts makes their use in H₂S selective membranes unlikely.

TGA data for carbonate salt mixtures were obtained at temperatures of 30 to 830°C. As for the pure salts, some carbonate mixtures exhibited relatively low temperature, below

400°C, weight losses attributable to desorption of bound water. High temperature weight losses were observed when mixtures were heated under N₂ (Table 4.6). These losses correspond to decomposition of some carbonate to oxide (reaction (2)). Decomposition to the oxide was largely eliminated when the various mixtures were heated under CO₂ and high temperature weight losses were generally not observed (see Table 4.6). Results of additional TGA experiments at elevated temperatures demonstrated that carbonate salt mixtures were largely nonvolatile under a CO₂ atmosphere. A sample of the base composition (30-A) under CO₂ showed no change in the sample weight after 5.5 hours at 650°C. Similarly, the Cs⁺ containing mixture 27-1 showed no weight loss under CO₂ when held at 550°C for 110 min.

The melting points of the carbonate salt mixtures were of particular importance since these must fall within the range of temperatures amenable to membrane testing, 400 to 800°C. As shown above for pure salts, DTA is particularly useful in this regard. DTA data, which is summarized in Tables 4.7 and 4.8, were obtained for the mixtures under a N₂ and/or CO₂ atmospheres at between 30 to 1000°C. Representative of the DTA traces for the various mixtures are provided for mixture 30-A in Figure 4.6.

Table 4.6. TGA results for carbonate salt mixtures. High temperature weight losses for mixtures under N₂ or CO₂ atmospheres.

Mixture	metal ions present ^a	T(°C) of weight loss	
		under N ₂	under CO ₂
30-A	Li, K, Ca	700	none
34-1	Li, K, Ca, Na	675	none
23-2	Li, K, Ca, Rb	700	none
27-1	Li, K, Ca, Cs	640	none
31-1	Li, K, Ca, Sr	660	730*
32-1	Li, K, Ca, Ba	630	none**
40-1	K, Na, Cs	720	800*

a. Refer to Table 4.5 for exact compositions.

* very slight weight loss

** slight weight increase beginning at 510°C

Each mixture exhibited one or more endotherms below 550°C which can reasonably be attributed to melting. This assignment is supported by the similarity of the endotherm temperature for a mixture obtained under N₂ and CO₂. Further, the absence of weight loss in the TGA below 550°C imply that these endotherm are not the result of sample decomposition. For two samples under CO₂, 30-A and 40-1, an endotherm at higher temperatures, 895°C and 738°C respectively, may result from slight decomposition to oxide. Low temperature endotherms, less than 400°C, attributable to desorption of bound water, were not observed, with the exception of sample 40-1, implying that the mixtures were anhydrous. Some samples exhibit exotherms at temperatures below 400°C (Table 4.8) which are most reasonably assigned to a crystallization process.

Figure 4.6 DTA traces of the base composition carbonate mixture 30-A.
Top: Sample heated under a N₂ atmosphere.
Bottom: Sample heated under a CO₂ atmosphere.

Table 4.7. DTA results for carbonate mixtures. Observed endotherm temperatures between 30 and 1000°C for samples under N₂ or CO₂ atmospheres.

Mixture	metal ions present	Endotherm T (°C)	
		under N ₂	under CO ₂
30-A	Li, K, Ca	488	485, 895
34-1	Li, K, Ca, Na	405, 459	405, 449
23-2	Li, K, Ca, Rb	456, 491	447, 482
27-1	Li, K, Ca, Cs	433, 457	426, 443
31-1	Li, K, Ca, Sr	483	481
32-1	Li, K, Ca, Ba	470	469
40-1	K, Na, Cs	-	247, 426, 551, 738

Table 4.8. DTA results for carbonate mixtures. Observed exotherm temperatures between 30 and 1000°C for sample under N₂ or CO₂ atmospheres.

Mixture	metal ions present	Exotherm T (°C)	
		under N ₂	under CO ₂
30-A	Li, K, Ca	-	329
34-1	Li, K, Ca, Na	332	332
23-2	Li, K, Ca, Rb	-	-
27-1	Li, K, Ca, Cs	-	-
31-1	Li, K, Ca, Sr	394	390
32-1	Li, K, Ca, Ba	357	355
40-1	K, Na, Cs	-	-

4.1.4. Preparation and characterization of sulfide-containing carbonate mixtures.

Little literature data is available concerning the melting points of carbonate salt mixtures containing added sulfide ions.¹⁷ Therefore, to mimic the salt compositions that might be expected upon exposure to H₂S and to determine the melting points of these compositions, a series of carbonate mixtures containing added sulfide ion were prepared. Sulfide ion was added to the base composition 30-A by replacing some CaCO₃ with CaS. The sulfide ion content ranged from 5 to 25 mol percent. Compositions are listed in Table 4.9. Each sample was contaminated with colored impurities along with a gold colored solid believed to be iron sulfide (see Section 3.0 for details).

DTA results for sulfide-containing salt mixtures are listed in Table 4.10. Samples were heated from 30 to 1000°C under a CO₂ atmosphere. Each mixture exhibited one or two endotherms below 550°C which can be attributed to melting. That sulfide-containing carbonate mixtures are liquids at reasonable temperatures is critical to the success of molten carbonate membranes for removal of H₂S. Partial solidification of the melt during membrane operation could lead to membrane failure. DTA data suggest that,

even at sulfide ion concentrations as high as 25 mole percent, the base composition mixture will remain molten at a reasonable minimum temperature of 600°C.

Two of the mixtures listed in Table 4.9, 38-1 and 38-2, were characterized by TGA. Samples were heated under CO₂ from 30 to 830°C which resulted in a slight weight increase beginning at about 325°C and totaling about 0.9 weight percent by 830°C. The weight increase presumably corresponds to reaction of CO₂ and trace water with sulfide in the melts as in reaction (7):

or by reaction of CO₂ with the sulfide as in reaction (8):¹⁸

Subsequent reaction with additional CO₂ to COS and carbonate, as in reaction (9), is reasonable:

It should be noted that the above sulfide containing melts most likely contained some sulfate in addition to sulfide. The infrared (IR) spectra of the mixtures listed in Table 4.9 were obtained as KBr pellets. Each exhibited bands in addition to those expected for carbonate. The IR spectrum of the base carbonate mixture 30-A containing no added sulfide exhibited bands at 1480, 1420, 868, 713 and 496 cm⁻¹. In contrast, the spectrum of mixture 46-2 which contained 24.69 mole % sulfide exhibited the above bands and additional bands at 1265, 1113, 1091, 619, and 488 cm⁻¹. At least two of these bands, 1113 and 619 cm⁻¹, can be assigned to free sulfate¹⁹ which exhibits bands at 1104(vs) and 613(s) cm⁻¹. The spectra of the other sulfide ion containing mixtures had similar bands. The IR spectrum of the CaS used for sample preparation was featureless and eliminated it as a source of sulfate. The most likely source is air oxidation of sulfide either during heating of the mixture under flowing CO₂ or during the rapid cooling of the hot mixture, which was done in air.

Table 4.9. Composition of carbonate salt mixtures containing added sulfide ion.

Salt	Composition, mole %				
	38-1	46-1	38-2	43-1	46-2
Li ₂ CO ₃	49.02	49.11	48.34	49.35	50.90
K ₂ CO ₃	25.32	24.96	24.93	25.88	24.40
CaCO ₃	20.67	15.13	15.57	-	-
CaS	5.00	10.80	11.16	24.77	24.69

Table 4.10 DTA exotherm and endotherm temperatures for sulfide ion containing carbonate mixtures.

Mixture ^a	mole % CaS present	Exotherm, T(°C)	Endotherm, T(°C)
38-1	5.00	342, 914	489
38-2	11.16	356	479, 528
46-1	10.80	356	477, 550
46-2	24.69	368	474, 545

a. See Table 4.9 for exact compositions.

4.1.5. Determination of equilibrium constants for reaction of H₂S with molten carbonate mixtures.

To carry out the experiments necessary to obtain equilibrium constant values for reaction (1), a test facility to determine the H₂S absorption properties of carbonate salt mixtures under IGCC conditions was designed and constructed. This facility was also equipped to determine the permselective properties of molten carbonate membranes as described in a subsequent section. Because of the high temperatures and pressures of operation and the use of toxic and reactive gases, the test facility was designed for remote operation and was housed in a process development cell.

The facility consisted of three units which are illustrated schematically in Figure 3.1: a gas supply unit, an absorption unit and a membrane test unit. The gas supply unit consisted of a gas manifold and two gas mixing vessels. Each mixing vessel was equipped with a paddle-type stirrer to insure well blended mixtures. Water vapor was obtained by addition of liquid water to the mixing vessel and heating to complete vaporization, while other gases were added by pressure. Gas mixtures were analyzed by gas chromatography (GC) prior to use.

The absorption unit consisted of a reactor and dosing and sampling volumes. The reactor was a high pressure and temperature stainless steel Parr reactor. The inside wall of the reactor was insulated with an alumina liner, which was lined in turn with a gold vessel. The carbonate melt to be examined was contained in the gold vessel. The dosing volume was used to supply a known quantity of a gas mixture to the reactor, and the sampling volume was used to remove a portion of the gas above the melt for analysis by GC.

Detailed procedures for conducting absorption experiments are in Section 3.2. A summary of a typical procedure follows. In one of the mixing vessels, an H₂S containing feed gas mixture was prepared and analyzed by GC. A weighed quantity of the carbonate mixture was added to the absorption vessel and gradually heated to the operating temperature, usually 560°C. A quantity of feed gas was transferred into the dosing volume. The molten salt was then exposed to a known quantity of the feed gas mixture delivered from the dosing volume. Once equilibrium was attained, a portion of the gas above the salt was withdrawn into the sampling volume and analyzed by GC. As described below, a knowledge of pressures and the composition of the gas phase at

equilibrium along with the quantity of H₂S absorbed permitted calculation of an equilibrium constant. Minimum errors of 1.5% are associated with the determination of molar quantities of gases (see Section 3.2 for details).

Excluding the cations for simplicity, reaction (1) can be rewritten as reaction (10):

The equilibrium constant for reaction (10), K, is given by the expression:

$$K = \frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{P_{\text{H}_2\text{S}}} \cdot \frac{[\text{S}^{2-}]}{[\text{CO}_3^{2-}]} \quad (11)$$

where P_i are partial pressures and $[X]$ are molar concentrations. Equation (11) can be simplified to equation (12):

$$K = P \cdot \frac{x_{\text{H}_2\text{O}} x_{\text{CO}_2}}{x_{\text{H}_2\text{S}}} \cdot \frac{n(\text{S}^{2-})}{n(\text{CO}_3^{2-})} \quad (12)$$

where x_i are mole fractions, n_i are moles and P is the total pressure. Thus, calculation of K , requires a knowledge of the equilibrium mole fractions of CO₂, H₂O, and H₂S and the amount of H₂S absorbed by the melt.

Although the above experimental procedure in principle may appear straightforward, several significant problems made determination of accurate equilibrium constants very difficult. These included gas phase reactivity at high temperatures, quantification of gaseous water, and, more critically, H₂S-metal reactivity. These issues are addressed below.

4.1.5.1 Gas phase reactivity. A "blank" experiment, in which no salt was present, clearly indicated that feed gas mixtures were reactive at elevated temperatures. The absorption vessel containing a mixture of 32.1% CO₂, 46.5% H₂, and 21.4% CH₄ at 111.9 psia was heated to 550°C. After standing overnight, the pressure dropped slightly to 107.0 psia. GC analysis of the gas phase revealed the presence of CO in addition to the three original gases. Assuming that no other gases were present in the headspace,²⁰ individual concentrations were: 20.9% CO; 16.5% CO₂; 40.0% H₂; 22.6% CH₄. That the pressure in the absorption vessel remained nearly constant suggests that elemental carbon was not formed. In fact, when the absorption vessel was opened, no black residue was observed. It is reasonable to postulate that CO arises from the water gas shift reaction (13):

The value of K at 527°C calculated from literature data^{13,21} is 0.237. The above experimental partial pressures of CO₂, H₂, and CO, coupled with the assumption that the concentration of water and of CO were identical, result in a value of K of 0.66. Considering the crudity of the experiment, agreement between the calculated and experimental values of K are sufficient to imply the presence of water gas shift chemistry. In addition, it should be noted that various metal oxides, particularly those of iron, copper, cobalt, and molybdenum, have been shown to catalyze the water gas shift reaction, and at least for one particular catalyst, the presence of Cs₂CO₃ or K₂CO₃ led to enhanced catalytic activity.²¹ Such conditions might be encountered in a typical absorption experiment.

Observation of such gas phase reactivity prompted a consideration of other possible gas phase reactions. Table 4.11 lists some equilibrium constants calculated from literature thermodynamic data¹³ for such gas phase reactions over the temperature range of 527°C to 827°C.

Table 4.11. Equilibrium constant values for gas phase reactions.¹³

Reaction ^a	527°C	627°C	727°C	827°C
(a) CO ₂ + H ₂ = H ₂ O + CO	0.237	0.437	0.701	1.026
(b) CO ₂ + H ₂ S = COS + H ₂ O	0.0126	0.0213	0.0323	0.0455
(c) CO ₂ + CH ₄ = 2CO + 2H ₂	0.0069	0.542	17.86	313.0
(d) CO + H ₂ = C + H ₂ O	24.03	2.478	0.400	0.0901
(e) 2CO = C + CO ₂	101.5	5.666	0.571	0.0878
(f) CH ₄ + H ₂ O = CO + H ₂	0.0293	1.240	25.45	305.0
(g) H ₂ S + CO = COS + H ₂	0.053	0.049	0.046	0.044
(h) CO + 3H ₂ = CH ₄ + H ₂ O	34	1.24	0.0398	0.00334
(i) 2CO + 2H ₂ = CO ₂ + CH ₄	141	1.84	0.0566	0.00326

a: All species are gases, except C which is a solid.

At the lowest temperatures at which absorption experiments would be run, 560°C, other than reaction (a), only reactions (d) and (e) occur to an appreciable extent. However, at higher temperatures reactions (c) and (f) involving CH₄ become favorable. The gas phase reactivity of CO₂ with H₂S forming COS (reaction b) is relatively unfavorable over the temperature range of 527 to 827°C. The CH₄ forming reactions are thermodynamically favorable at lower than 527°C but become unfavorable at higher temperatures. The potential variety of reactions, of course, complicates analysis of absorption data.

4.1.5.2 H₂S absorption experiments. A series of absorption experiments involving the base composition carbonate mixture 30-A and H₂S containing feed gases were performed. Details of these experiments can be found in the Section 3.0. In the first experiment, 12666-2, the base composition carbonate mixture 30-A at 560°C was

exposed to a gas mixture containing 10.7% H₂S, 6.40% CO₂, 81.1% CH₄, and 1.8% H₂. Once equilibrium was achieved, GC analysis of the headspace gases revealed the presence and concentrations of CO and COS in addition to H₂S, CO₂, H₂ and CH₄ as listed in Table 4.12. The quantity of water in the gas phase was calculated by assuming that it was the difference between the sum of the above gases and the total quantity of gas present at equilibrium.

Table 4.12. Headspace analysis of gases at equilibrium in absorption experiment 12666-2

gas	concentration in	
	ppm	mole fraction
H ₂ S	80.8	9.608x10 ⁻⁴
CO ₂	2,678	3.185x10 ⁻²
CH ₄	64,665	7.692x10 ⁻¹
CO	7,567	8.998x10 ⁻²
COS	8.3	9.809x10 ⁻⁵
H ₂	5,941	7.065x10 ⁻²
H ₂ O	-	3.726x10 ⁻²

Using the above mole fractions of CO₂, H₂S, and H₂O and the calculated quantities of sulfide and carbonate ions present in the melt at equilibrium, a value of K₁ of 0.235 atm was obtained. Although to the best of our knowledge, literature data at 560°C is unavailable, the value of K₁ at 750°C for this salt mixture is 1.7 atm.⁹ Equilibrium constants for the reaction of interest increase with increasing temperature so that 0.2atm is a reasonable but perhaps somewhat high value for 560°C.

When the above run was completed, stirring of the melt was stopped and the absorption vessel was cooled to room temperature. Examination of the contents of the vessel revealed a black powder, presumed to be carbon, on the surface of a white solid. This observation implies that the black solid was generated upon cooling otherwise it would have been dispersed throughout the white solid phase. Such reactivity is consistent with the thermodynamics of carbon formation (see Table 4.11). In addition to the black solid, gold-colored solid deposits were observed on various metal surfaces, indicative of metal-H₂S reactivity. Energy dispersive X-ray spectroscopy (EDS) of deposits on the thermowells of the absorption vessel indicated the presence of the elements Fe, Ni, Cr, O, and S, consistent with the formation of metal sulfides. The identification of such deposits calls into question the value of K₁ obtained, since some of the H₂S thought to have been absorbed by the molten salt was actually consumed in formation of metal sulfides.

In a second absorption experiment, 12666-6, the base composition carbonate mixture at 560°C was exposed to a gas mixture containing 8.382% H₂S, 40.36% CO₂, 51.28% CH₄. At equilibrium, analysis of the headspace above the melt revealed the presence of CO, H₂, and COS in addition to H₂S, CO₂, and CH₄. Treating the absorption data as above resulted in an unrealistic value for the quantity of water vapor present at equilibrium and, thus, a value for the equilibrium constant could not be calculated. This points out the difficulty in determining relatively small amounts of water gas by difference. The sum

of the errors in the individual concentrations is likely to be large with respect to the concentration of water.

Absorption experiment 12666-15 involved 126.9 g of the base composition carbonate mixture 30-A at 560°C that was then exposed to a gas mixture consisting of 15.0% H₂S in CO₂. Although an inadvertent valve switch precluded a quantitative treatment, the data was qualitatively enlightening. After standing overnight, a portion of the headspace gases was withdrawn and analyzed by GC. Surprisingly, in addition to H₂S and CO₂, CO, H₂ and COS were detected. The ratio of gases with H₂S set equal to one were: H₂S, 1; CO₂, 43.0; CO, 9.2; COS, 0.045; H₂, 0.99. It is highly unlikely that H₂ resulted from reaction of H₂S with CO₂ (see Table 4.11 above). A more likely source of the observed H₂, and hence CO, is the oxidation-reduction reaction of H₂S with the non-gold metal components of the absorption vessel as in reaction (14):

Such consumption of H₂S makes the determination of an accurate equilibrium constant for the reaction of carbonate with H₂S quite difficult.

4.1.5.3 H₂S-metal reactivity. In an attempt to overcome the problems associated with the metal reactivity of H₂S, the various components of the absorption vessel were gold plated. Another absorption experiment, 12923-32, was performed using 125.8 g of the base carbonate mixture 30-A at 550°C. A feed gas containing only 0.5% H₂S in N₂ was dosed into the reactor and the system was allowed to come to equilibrium. A headspace analysis of the gas phase revealed the presence of CO₂, CH₄, CO, and H₂, but not H₂S or COS. Based on the assumption that no water is present in the gas phase, the gas concentrations at equilibrium were: CO₂, 2.82%; CO, 1.52%; CH₄, 1.24%; H₂, 1.30%. Such concentrations would appear to be unrealistically high considering that the feed gas contained only 0.5% H₂S. In any case, the presence of the above gases strongly implies that H₂ was formed by reaction of H₂S with metal. This was supported by visual examination after the run which revealed that much of the gold plating, especially on the thermowells, was no longer present. Some H₂S was apparently absorbed by the carbonate melt as well. This was the source of the CO₂ and H₂O (unobserved). CH₄ could arise from reaction of CO and H₂ as in reaction (15) and/or (16) below for which the calculated equilibrium constants at 527°C are relatively large (see also Table 4.11).

4.2 Ceramic Materials Development

The development of the porous ceramic membrane supports was broken down into a series of subtasks. Initially, a literature search was implemented to identify candidate

ceramic compounds. This search concentrated on the molten carbonate fuel cell literature. Candidate compounds identified via this search were then screened for chemical compatibility using a mixed powder screening protocol developed for this program. Those materials determined most suitable were then obtained in the form of dense coupons and the wetting behavior of the candidate salt mixtures was determined using a high temperature sessile drop test system. Containment strategies were then developed based on the observed wetting behavior. In conjunction with Golden Technologies, techniques were developed to produce the candidate ceramic materials in the form of porous disc membrane substrates with the desired pore size distribution. Methods were developed to impregnate these porous supports with the molten alkali carbonate salt mixtures identified in Section 4.1. These membranes were then submitted for membrane performance testing as described in Section 4.3.

4.2.1 Materials Selection

A literature survey was implemented, concentrating on the molten carbonate fuel cell (MCFC) literature. From this basis²²⁻²⁴ it was determined that silicon-based ceramics (SiC , Si_3N_4 , SiO_2 , etc.) react with molten carbonates to form low melting alkali silicates. Alumina, zirconia, and titania all react to form mixed oxides with the alkali from the carbonates, and MgO and CaO are soluble in the carbonate melts. However, AlN and TiB_2 are known to be stable in molten cryolite and some molten salts, spinel (MgAl_2O_4) is expected to be stable, and LiAlO_2 is known to be stable in MCFC environments; however, it is polymorphic and not used as a structural material. On this basis, in conjunction with discussions with Golden Technologies, five compounds were chosen for initial screening evaluation. Those were: titanium diboride (TiB_2), tungsten carbide (WC), calcium aluminate (CaAl_2O_4), magnesium aluminate (MgAl_2O_4), and aluminum nitride (AlN).

A series of experiments were performed to determine qualitatively the chemical compatibility of the selected ceramics with the base composition carbonate mixture 30-A (see Table 4.5). The experiments were performed by mixing a known weight of the ceramic powder with a 10:1 excess of the salt mixture in a gold crucible, placing the crucible in a furnace with a flowing CO_2 atmosphere, and heat treating the mixture for 24 hours at 600, 700, or 800°C. Results were evaluated by visual observation, weight change, and X-ray powder diffraction.

The TiB_2 was eliminated from further consideration due to excessive reaction with the molten salts. WC was observed to change color and to gain weight, indicating oxidation, and was also eliminated.

The weight loss results for CaAl_2O_4 , MgAl_2O_4 , and AlN are shown in Figure 4.7. Little or no weight loss was observed after the 24 hour heat treatment at 600°C. CaAl_2O_4 exhibited excessive weight loss (~98%) at 700 and 800°C. X-ray analysis indicated that the CaAl_2O_4 reacted at 700°C to form $\text{Ca}_3\text{Al}_2\text{O}_6$ and lithium aluminate (LiAlO_2) and at

Figure 4.7 Weight loss of ceramic powders after 24 hour exposure to molten alkali carbonates

800°C to form LiAlO_2 and some $\text{Ca}_3\text{Al}_2\text{O}_6$. Based on these results CaAl_2O_4 was eliminated from further consideration. MgAl_2O_4 and AlN were observed to be more resistant to weight loss within the data scatter at 600 and 700°C. The AlN lost ~50% of its initial weight after salt exposure at 800°C while the MgAl_2O_4 lost ~20%. The X-ray analysis indicated that the AlN phase remained stable in contact with the molten salt while the MgAl_2O_4 at 800°C was converted to LiAlO_2 . Based on these results it was decided to continue evaluation of AlN and MgAl_2O_4 in wetting studies and to further investigate LiAlO_2 .

4.2.2. Wetting Behavior

Sessile drop experiments were conducted using the apparatus shown schematically in Figure 4.8. Contact angles are defined such that angles greater than 90° are considered non-wetting and angles less than 90° are considered wetting. AlN and MgAl_2O_4 samples were obtained from Golden Technologies in the form of dense plates which were cleaned in a two step procedure using chlorinated solvents. Tests were run in a tube furnace with a flowing CO_2 atmosphere. The hold time at temperature ranged from one-half to six hours. In addition, a series of long term tests was carried out with a maximum exposure time of 500 hours. A sessile drop test was also performed on gold to provide data needed to specify the desired pore size for fritted gold discs to be used, if needed, for initial membrane tests. The measured contact angle of the base composition carbonate mixture on gold was 52°.

Initial sessile drop experiments were performed using the molten salt composition listed above on samples of AlN previously obtained from a vendor other than Golden Technologies. In this case, a very low contact angle was observed (2-4°) indicating good wetting. Comparable wetting behavior was observed with the MgAl_2O_4 materials obtained from GTC with a measured contact angle of 6°. However, the contact angle measured with the same salt composition on the AlN material obtained from GTC was 130-134° indicating very poor wetting of the surface by the salt. Surface analysis of the two AlN materials using ESCA sputter depth profiling indicated that the surface of the GTC AlN was primarily composed of boron nitride as a consequence of the fact that the AlN plates were fired on BN setters. Table 4.13 compares the ESCA results for the two materials. Also included is the ESCA results for the GTC material after mechanically removing the BN surface layer using tumbling. When this BN surface layer was removed mechanically, the measured contact angle was 5-8°, in good agreement with the results from the other AlN material. It was further determined that a colloidal spray of BN applied to the surface of MgAl_2O_4 could result in an increase of the measured contact angle from 5-6° to 94-145°.

Figure 4.8 Sessile Drop Test System

Table 4.13. ESCA Surface Analysis of AlN Samples

Rel. Depth	TCL AlN		GTC AlN		GTC AlN (t)	
	B/N	Al/N	B/N	Al/N	B/N	Al/N
surface	-	1.1	0.53	0.09	-	1.03
cycle 1	-	1.4	0.54	0.08	-	0.94
cycle 2	-	1.5	0.51	0.08	-	0.84
cycle 3	-	0.81	0.46	0.20	-	0.78
cycle 4	-	0.81	0.45	0.20	-	0.82
cycle 5	-	0.89	0.49	0.30	-	0.86
cycle 6	-	0.86	0.46	0.35	-	0.85
cycle 7	-	0.89	0.42	0.38	-	0.90

The effect of the sulfide ion content of the salt melt on wetting of AlN (from GTC in the as-received condition) was also studied. Three S²⁻-containing salts were examined (see Table 4.9). The results are shown in Figure 4.9. As can be seen, the S²⁻ content has little effect except at the high (25%) level. In preliminary tests on MgAl₂O₄, the measured contact angles were 6° and 1° for the base mixture and the 11% S²⁻-containing mixture, respectively.

The results of long term tests of the wetting of AlN by sulfide ion containing salts are shown in Figure 4.10. In all cases, the contact angles are observed to decrease with exposure time. This could be the result of oxidation of the substrate, reaction between the salt and the substrate, or a combination of the two. Implications are that with time and contact with H₂S, the melt may creep.

4.2.3 Ceramic Substrate Development

Aluminum nitride and lithium aluminate were determined to be the best choices for further development as ceramic membrane supports. This determination was based on results from a series of initial screening experiments which indicated that AlN and LiAlO₂ were the ceramic materials with the best chemical stability in the presence of the molten mixed alkali carbonates. Work with MgAl₂O₄ was discontinued due to its reactivity with lithium containing salts at high temperatures as compared to AlN.

Wetting studies were used as a basis for the design of the desired microstructures for salt containment. This was particularly true in the case of AlN. It was not possible to obtain or fabricate dense samples of LiAlO₂ for use in wetting studies; however, it is known that LiAlO₂ is wet by the salt compositions of interest. In order to estimate the transmembrane pressure which the membrane could sustain without the loss of the salt, the capillary force equation was used:

$$\Delta P = 2 \gamma \cos \theta / r \quad (17)$$

where ΔP is the transmembrane pressure, γ is the surface tension of the molten salt, θ is the contact angle of the molten salt with the ceramic, and r is the radius of the pore in which the molten salt is immobilized. A typical value²³ of γ for a mixed alkali carbonate

Figure 4.9 Effect of sulfide ion content of mixed alkali carbonates on the contact angle on AlN

Figure 4.10 Effect of long term exposure on the contact angle of mixed alkali carbonates on AlN

at 600°C is ~225 mN/m and the contact angle for the salt on AlN is ~5°. Using these values and equation (17), the transmembrane pressure can be estimated as a function of membrane support pore radius. As can be seen in Table 4.14, at pore sizes less than 1 µm a significant pressure differential can be tolerated.

Table 4.14. Capillary Force as a Function of Support Pore Radius

Pore Radius, µm	ΔP, psi
0.1	653
1.0	65
5.0	13

GTC developed fabrication techniques to produce porous aluminum nitride. Using a standard starting aluminum nitride powder composition, GTC examined the effects of consolidation pressure and sintering temperature on pore size, pore size distribution, and pore volume fraction. In the case of material sintered at 1600°C, the porosity values ranged from a pore diameter of 0.58 µm with a pore volume fraction of 53.4% when consolidated at 2.5 kpsi to a pore diameter of 0.44 µm with a pore volume fraction of 45.1% when consolidated at 20 kpsi. For material fired at 1650°C, the values ranged from 0.6 µm/51.7% to 0.38 µm/42.3% for consolidation pressures of 2.5 to 20 kpsi. The fabrication conditions chosen to produce substrates for evaluation as membrane supports were 10 kpsi consolidation pressure fired at 1600°C and 2.5 kpsi consolidation pressure fired at 1650°C. These conditions resulted in membrane supports with a pore size of 0.34 µm with a pore volume fraction of 57.7% for the 1600/10 samples and a pore size of 0.52 µm with a pore volume fraction of 53.2% for the 1650/2.5 samples. Samples prepared using these process variables were infiltrated with the base composition carbonate mixture 30-A and used in experiments to evaluate the salt retention behavior of the supports as well as to produce supported salt membranes for membrane testing.

A similar fabrication study was undertaken at Air Products to develop porous lithium aluminate. Commercial lithium aluminate powders were mixed with an organic binder (polyethylene glycol) and a sintering aide (lithium fluoride). Initially, the level of binder and sintering aide were varied in an effort to fabricate dense lithium aluminate. When high density samples could not be produced, efforts were concentrated on fabricating material with controlled pore size. The early fabrication attempts resulted in samples consisting of primarily the higher alumina form of lithium aluminate (LiAl₅O₈) due to too high a firing temperature. These samples also had a bi-modal pore size distribution with pores at one and three microns diameter. Further refinement of the processing resulted in single phase LiAlO₂ with a narrow pore size distribution centered on ~3 µm. Results of the lithium aluminate fabrication study were transferred to GTC for continuation and production of membrane substrates.

Techniques, described in more detail in Section 3.3, were developed to infiltrate the molten carbonate salt mixtures into the porous aluminum nitride and lithium aluminate substrates. The long term salt retention behavior of these infiltrated substrates were then

examined through a series of heat treatments at 600°C in flowing CO₂. The samples were infiltrated using the technique described previously, surfaces were cleaned to remove excess salt, and initial weight was measured. The samples were then heat treated for 100 hr intervals between which they were cooled to room temperature and re-weighed. The results of the exposure testing are shown in Figure 4.11.

The aluminum nitride samples exhibited an initial weight loss over the first 500 hours and then stabilized at a loss equivalent to ~15-20% of the initial salt content. In contrast, the lithium aluminate samples exhibited virtually no loss of weight for up to 2000 hr of exposure. Based on TGA results described in Section 4.1.3, the salt mixture itself was stable against vaporization under these conditions. Part of the observed weight losses may be due to reactions between the salt and the ceramic. This is supported by the X-ray phase analysis of the infiltrated samples before and after exposure for 2000 hr as shown in Table 4.15.

Table 4.15. Phase Analysis of Long-term Salt Retention Samples

Substrate	Initial Phases	Phases after 2000 hr
AlN	AlN, salts	AlN, LiAlO ₂ , salts
Lithium Aluminate	LiAl ₅ O ₈ , salts	LiAlO ₂ , LiAl ₅ O ₈ , salts
Lithium Aluminate	LiAlO ₂ , salts	LiAlO ₂ , salts

As can be seen in Table 4.15, both the aluminum nitride and the LiAl₅O₈ phase of lithium aluminate show some degree of reaction with the Li₂CO₃ portion of the alkali carbonate melt. Possible reactions to explain these results are:

These results indicate that there could be some long term stability questions for the use of aluminum nitride as a membrane support; however, since the weight loss stabilized after ~500 hr, it is likely that reaction (18) resulted in the formation of a passivating layer of LiAlO₂ on the surface of the AlN. The results in Table 4.15 also indicate the desirability of starting with phase pure LiAlO₂ as the substrate in the case of lithium aluminate. The lithium aluminate fabrication processes were directed to that end. The details of the LiAlO₂ development effort can be found in the report from GTC which is appended.

4.2.4 Ceramic Membrane Infiltration

A technique was developed to infiltrate the porous ceramic membranes with the molten carbonate salt mixtures. The process developed consisted of a vacuum infiltration technique in which the substrate was immersed in an excess of the salt powder, heated to a temperature greater than the anticipated test temperature under flowing CO₂, the furnace chamber was then repeatedly evacuated and back-filled with CO₂ to force the salt

Figure 4.11 Long term salt retention of aluminum nitride and lithium aluminate porous samples

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Table 4.16. Planar Disc Support Infiltration Results

Sample #	Material	% Infiltrated	Sample #	Material	% Infiltrated
12496-13-1	AlN	80	12496-14-1	LiAlO ₂	65
12496-13-2	AlN	70	12496-14-2	LiAlO ₂	93
12496-13-3	AlN	82	12496-14-3	LiAlO ₂	97
12496-13-4	AlN	80	12496-14-4	LiAlO ₂	66
12496-15-1	AlN	83, cracked	12496-16-1	LiAlO ₂	80
12496-15-2	AlN	84	12496-16-2	LiAlO ₂	90
12496-15-3	AlN	77, cracked	12496-16-3	LiAlO ₂	100
12496-15-4	AlN	81	12496-16-4	LiAlO ₂	87
12496-17-1	AlN	83, cracked			
12496-17-4	AlN	88, cracked			
12496-17-5	AlN	83, cracked			
12496-17-6	AlN	76, cracked			
12496-17-7	AlN	78			
12496-18-1	AlN	68, cracked			
12496-18-2	AlN	69			
12496-18-3	AlN	61			
12496-19-3	AlN	62			
12496-19-4	AlN	63			
12496-20-2	AlN	66			
12496-21-1	AlN	66			
12496-21-2	AlN	72			
12496-21-3	AlN	68			
12496-21-4	AlN	75			
12496-21-5	AlN	72			
12496-21-6	AlN	73			
12496-23-1	AlN	76			
12496-23-2	AlN	65			
12496-23-5	AlN	68			
12496-23-6	AlN	72			
12496-23-7	AlN	74			
12496-23-8	AlN	67			
12496-24-1	AlN, thin	69			
12496-24-3	AlN, thick	34			
12496-24-4	AlN, thick	40			
12496-24-5	AlN	65			
12496-24-6	AlN	66			
12496-24-7	AlN	67			
12496-24-8	AlN	63			
12496-24-9	AlN	64			
12496-24-10	AlN	64			

Table 4.17. Tubular Support Infiltration Results

Sample #	Material	% Infiltrated
12496-25-T1	AlN Tube	80
12496-25-T2	AlN Tube	74
12496-25-T3	AlN Tube	82
12496-25-T4	AlN Tube	83

4.3 Membrane Testing

To evaluate membranes at high temperatures and pressures, a membrane test unit was constructed which is shown schematically in Figure 3.1. This unit was used in conjunction with the gas delivery system described in more detail previously (Section 4.1.3). Details of the membrane test unit and its operation can be found in Section 3.3. A brief description follows.

The membrane to be tested was sealed in a high temperature and pressure membrane cell constructed of stainless steel. The cell and membrane were heated to the required temperature in a furnace, usually 560°C. Gas lines from the mixing vessels carried gases across the two surfaces of the membrane. The feed gas mixture contained H₂S and other IGCC gases. The sweep gas consisted of H₂O and CO₂ in an inert gas. Gases from the feed which permeated the membrane were collected by the sweep gas and were analyzed by GC. The membranes examined consisted of the base composition carbonate mixture 30-A supported in a gold frit or a planar or tubular ceramic support.

Although the concept of a facilitated transport membrane for removal of H₂S at high temperatures is straightforward, a demonstration of its practicality is not. Numerous very significant problems were encountered during this effort, the most troublesome being H₂S-metal reactivity and the inability to obtain defect-free membranes. H₂S-metal reactivity is troublesome but solvable by methods discussed below. Defect-free membranes present a major challenge since, as described below, molten carbonate membranes are barriers to gases other than H₂S; defects permit permeation of relatively large quantities of these gases and an effective removal of H₂S is not obtained.

The concept of separation of H₂S from an IGCC gas mixture is illustrated in Figure 1.2. (p. 5) A feed gas mixture consisting of H₂S, CO₂, H₂ and other IGCC gases is passed across one surface of the membrane. From the feed side, the membrane can be viewed largely as a barrier to all gases except H₂S. These gases have relatively low physical solubilities in molten carbonates and, hence, relatively low permeabilities are expected. In contrast, the "solubility" of H₂S in the membrane is relatively high arising from its chemical reaction with the carbonate melt (reaction (1)). The sulfide formed at the feed interface diffuses across the membrane to the permeate side. There a sweep gas containing CO₂ and H₂O drives reaction (1) to the left reforming H₂S which is liberated into the sweep gas.

Estimates of the permeabilities of gases other than H₂S can be obtained from literature solubility and diffusivity data. For such gases which permeate by a solution-diffusion mechanism, P₀ is given by the equation (20) where S is the solubility and D is the diffusivity of a gas in the membrane medium, the molten carbonate mixture in the present case.

$$P_0 = S \cdot D \quad (20)$$

Literature data for H₂, CO, and CO₂ in molten carbonates were obtained from Selman and Maru.²³ Solubilities were calculated using an expression of the form $S = Ae^{-E/RT}$ for a ternary carbonate mixture at 560°C. Although the temperature of interest is outside the temperature range of the expressions for CO and CO₂, the errors are probably not large. Listed in Table 4.18 are calculated solubilities in units of mol(gas)/cc(melt)•atm and cc(g)/cc(melt)•cmHg. Estimates of diffusivities are less reliable. Experimental values for the D(H₂), e.g. 62x10⁻⁵ cm²/s at 560°C, are probably too large.²³ Alternatively, diffusivities can be calculated using the Wilke-Chang equation and values are available at 600°C for CO, CO₂, and H₂.²³ For the calculation of P₀, it was assumed that diffusivities at 600°C and 560°C were the same.

Table 4.18. Calculated permeabilities of CO, CO₂, and H₂ in a molten carbonate membrane.

Gas	S(mol/cc•atm) 560°C	S(cc/cc•cmHg) 560°C	D(cm ² /s) 600°C	P ₀ (Barrers)
CO	1.70x10 ⁻⁶	5.01x10 ⁻⁴	0.70x10 ⁻⁵	35
CO ₂	1.19x10 ⁻⁵	3.51x10 ⁻³	0.66x10 ⁻⁵	232
H ₂	6.29x10 ⁻⁶	1.85x10 ⁻³	1.12x10 ⁻⁶	210

4.3.1. Molten carbonate/gold frit membranes

Prior to availability of microporous ceramic supports, membranes consisting of molten carbonate salt mixtures immobilized in porous gold fritted discs were evaluated. In preliminary work, it was shown that a membrane consisting of molten mixture 30-A immobilized in a stainless steel fritted disc with 0.5 μm diameter pores could support a 40 psi pressure differential. Thus, gold frits with pore diameters of 0.5 μm were utilized initially. Two such membranes were evaluated at a temperature of 550°C and results are listed in Table 4.19. For both membranes, only H₂ was detected in the permeate when comparable feed and sweep pressures were used. H₂ permeabilities were 1600 and 3400 Barrers. These values are large compared with the theoretical H₂ permeability of 210 Barrers for a molten carbonate membrane (see Table 4.18), implying that the membranes have defects in the molten layer or that the molten layer was thinner than believed. For both membranes, increasing the feed pressure above those reported in Table 4.19 resulted in salt blow-through as indicated by the detection of large quantities of permeating gases. For membrane 11818-47-2, large amounts of CH₄ and H₂ along with some CO were detected in the sweep gas. This coupled with the observation of carbon powder deposits,

as confirmed EDS, in the membrane cell following the run, are consistent with reaction of CO₂ and H₂, possibly by the reactions listed below.

For membrane 11818-54-2, increased feed pressure resulted in detection of large quantities of H₂S, CH₄, COS, CO, and H₂ in the sweep. When examined at the end of the run, a rather large quantity of a yellow, metallic-appearing solid was found on the inner surface of the membrane holder. An analysis of this solid by EDS showed that it contained the elements Fe, Ni, and S. Clearly, the membrane cell and/or the gas lines leading to the cell had reacted with H₂S to yield nickel and iron sulfides.

The transmembrane pressure, ΔP, withstood by the above membranes, is far lower than that predicted for a molten carbonate salt/ceramic membrane by equation (17). For a pore of diameter 0.5 μm and an experimental contact angle of 52° for mixture 30-A, ΔP from equation (17) is 161 psi. Perhaps, some plugging of gas lines by carbon or metal sulfide led to an increase in pressure beyond this limit.

Table 4.19. Permselective properties of molten carbonate/gold frit membranes at 560°C.

Membrane	conditions (see below)	Feed P (psia)	Sweep P (psia)	gas	ppm in permeate	P _o (Barrers)
11818-47-2	a	29.1	22.2	H ₂	120	1600
				CO ₂	nd	-
				CH ₄	nd	-
11818-54-2	b	15.0	15.0	H ₂	130	3400
				H ₂ S	nd	
				CO ₂	nd	
				CH ₄	nd	

Conditions: a. Feed: 32.1% CO₂ and 21.4% CH₄ in H₂; sweep: 50.8% CO₂ in N₂;
feed and sweep flows: 30 sccm, 40 sccm.

b. Feed: 5.5% H₂S, 32.4% CO₂, and 16.2% CH₄ in H₂; ; sweep: 50.8%
CO₂ in N₂; feed and sweep flows: 30 sccm, 40 sccm.

4.3.2. Planar molten carbonate/ceramic membranes

With the availability of a microporous ceramic, attention was shifted to examination of membranes consisting of the molten base carbonate composition 30-A immobilized in planar microporous ceramic support consisting of AlN or LiAlO₂. A summary listing of the membranes tested is provided in Table 4.20.

4.3.2.1. Membrane Sealing. Sealing of AlN/salt membranes in the membrane cell often proved to be difficult. Many membranes cracked upon sealing. It was found that the use of a sealing C-ring in place of an O-ring resulted in membranes which were more often crack-free. Somewhat later it was found that elimination of the C-ring and sealing using a graphite tape proved to be more reliable. See Section 3.3 for details.

4.3.2.2 Testing with H₂S containing feeds. The most significant problem associated with testing of molten salt/ceramic membranes was the reactivity of H₂S with the metal of the membrane holder and cell. This is illustrated by the results for a molten carbonate/AlN membrane (12334-92-1) evaluated at a membrane temperature of 560°C. Using humidified feed (2% H₂S, 2% CO₂, 10% CH₄, 26% H₂ in N₂) and sweep gases (10% CO₂ in N₂), no permeating gases were detected in the sweep during the first hour of operation. In addition, feed and sweep pressures were independent of one other. These observations are consistent with a membrane which was largely defect free under the experimental conditions. Subsequently, relatively large quantities of CH₄, H₂ and CO were detected in the sweep suggestive of formation of defects in the molten salt layer.

Table 4.20. Listing of molten carbonate/ceramic planar membranes tested.

Membrane	Support	Comments
12334-92-1	AlN	Membrane cracked
12334-91	AlN	Withstood brief ΔP of 70 psia; intact membrane; data in Table 4.16
12334-92-2	AlN	Membrane cracked
12344-92-4	AlN	Membrane cracked
12344-92-5	AlN	Operated briefly at 560°C before a hole developed; data in Table 4.19
12496-2-5	AlN	Membrane cracked.
12496-2-4	AlN	Membrane cracked
12496-2-2	AlN	Data in Table 4.23
12496-2-3	AlN	Data in Table 4.21
12496-2-1	AlN	Membrane cracked after initial data at ambient pressure
12496-2-6	AlN	Membrane cracked
12496-5-6	AlN	Membrane cracked after initial data at ambient pressure
12496-5-2	AlN	Membrane cracked
12496-5-1	AlN	Data in Table 4.21; cracked upon raising pressure above ambient
12496-11-2	LiAlO ₂	Large and variable concentrations of permeating gas due to failed flow controller
12496-11-1	LiAlO ₂	Pressure differential could not be maintained; cracked?
12496-14-3	LiAlO ₂	Data in Table 4.23; unrealistically large CO ₂ P _O ; cracked at higher feed pressures.
12496-15-4	AlN	Data in table 4.23
12832-15-2	AlN	Data in Table 4.24
12496-16-3	LiAlO ₂	Data in Table 4.24
12496-16-4	LiAlO ₂	Data in Table 4.24
12496-18-2	AlN	Data in Table 4.24
12496-18-3	AlN	Data in Table 4.24
12496-17-7	AlN	Data in Table 4.24
12496-19-4	AlN	Data in Table 4.24

Almost no H_2S was detected in the sweep probably due to reaction of H_2S with the Inconel membrane cell. Upon examination after the run, the membrane was found to have cracked. In addition, relatively large amounts of black, gray, and gold colored solids were observed throughout the cell. Some of these deposits resulted in blockage of gas lines. This evidently led to a plugging of the gas line which may have resulted in cracking of the membrane. EDS analysis of the various deposits indicated the presence of the following elements: O, S, K, Ca, Cr, Fe, Ni. The presence of K, Ca, O can be ascribed to the carbonate mixture while S, Cr, Fe, and Ni are the result of metal sulfide formation from reaction of H_2S with the Inconel membrane cell.

Somewhat less metal- H_2S reactivity was observed when the molten salt/ AlN membrane 12334-91 was evaluated using dry feed (H_2S , CO_2 in N_2) and sweep (CO_2 in N_2) gases and a stainless steel 304-membrane cell. Results are listed in Table 4.21. Feed and sweep back pressures were adjusted to keep the transmembrane pressure (ΔP), relatively small, approximately 5 psia. However, during adjustment to reach the final set of pressures, a ΔP of about 70 psi occurred but the membrane apparently suffered no cracking or salt blow-through as implied by the relatively small concentration of permeating gases. As listed in Table 4.14, the calculated ΔP for a AlN membrane with 1 μm pores is 65 psi. Since water was absent from the sweep gas, facilitated transport of H_2S was not expected. At the feed pressure examined, 26.8 psia, no H_2S was detected in the permeate but at two higher pressures, H_2S permeabilities of 10,900 and 2,270 Barrers were obtained. However, it is clear that reaction of H_2S with the metal membrane cell had occurred. At all three feed pressures, significant quantities of H_2 and CO were observed in the permeate. H_2 is a result of an H_2S /metal reaction as in reaction (14) and CO arises from a subsequent reaction of H_2 and CO_2 (reaction (13)).

It was clear that obtaining meaningful H_2S permeation data at the low flows and elevated temperature using stainless steel components, and at relatively low gas flow rates, would be virtually hopeless. Since the absolute quantity of H_2S permeating the relatively thick salt/ceramic membranes was small, loss of H_2S due to reactivity with metal had a major impact on the H_2S permeabilities obtained. Although materials which are inert with respect to H_2S are available (see later), construction and testing of membrane cells composed of these would have required a long time. A shorter term alternative was to render inert the metal surface exposed to H_2S . Two possible techniques considered were gold plating and alonizing. Alonizing gave a membrane cell with fairly rough surfaces which prevented successful sealing of membranes in the cell. Gold plating, of course, gave smooth surfaces; therefore, membranes could be successfully sealed in the cell making it possible to evaluate the membranes.

Table 4.21. Permselective properties of molten carbonate/ceramic membranes at 560°C using H₂S containing feeds.

Support	Membrane	Conditions (see below)	Feed P (psia)	Sweep P (psia)	gas	ppm in permeate	P _O (Barrers)
AlN	12334-91	a	26.8	20.1	H ₂ S	nd	-
					H ₂	187	-
					CO	406	-
					COS	nd	-
		a	46.4	48.4	H ₂ S	162	10,900
					H ₂	26	-
					CO	268	-
					COS	22	-
		a	207.3	204.0	H ₂ S	151	2270
					H ₂	13	-
					CO	670	-
					COS	181	-
AlN	12496-5-1	b	15.0	15.0	H ₂ S	nd	-
					CO	3800	149,000
					COS	nd	-
					H ₂	2700	181,000
AlN	12496-2-3	c	16.6	16.5	CO	9000	-
					H ₂	793	-
					H ₂ S	nd	-

Test conditions:

- Feed: 6.1% H₂S, 5.7% CO₂ in N₂; sweep: 11.3% CO₂ in N₂; both dry; flow rates, 50 sccm.
- Feed: 0.62% H₂S, 5.52% CO₂, 15.84% CO, 9.52% H₂ in N₂ or 0.59% H₂S, 5.64% CO₂, 16.10% CO, 9.43% H₂ in N₂; sweep: 20% CO₂ in N₂; both humidified by passage through 60°C water bubblers; flow rate, 25 sccm.
- Feed: 10% CO₂, 10% H₂S in N₂; sweep: 20% CO₂ in N₂; both gases through 60°C water bubblers at 25 sccm.

The molten carbonate/AlN membrane 12496-2-3 in a gold plated holder was evaluated at 560°C using feed (10% H₂S and 10% CO₂ in N₂) and sweep (20% CO₂ in N₂) gases humidified by passage through water bubblers at 60°C. As indicated in Table 4.21, no H₂S was detected in the sweep but 9000 ppm CO, 800 ppm H₂ and a trace of COS were. These results imply H₂ formation by reaction of H₂S with metal. In fact, examination of the cell upon completion of the run revealed solid deposits on the sealing C-ring surfaces, the feed and sweep side flanges and on the membrane surface. Two visually different deposits were observed on the sweep side flange and on the AlN surface. Elemental compositions of these deposits were determined by EDS and are listed below in Table 4.22.

Table 4.22. Elements present as determined by EDS in the membrane cell after evaluation of membrane 12496-2-3.

Location	elements present
feed side flange	O, S, K, Si, Cr, Fe, Ni
sweep side flange	1. O, S, K, Fe, Ni 2. O, S, K, Ca
AlN surface	1. Black - O, S, K., Al 2. Gold - K, Au
C-ring feed side	O, S, K, Si, Ti, Cr, Fe, Ni

Presumably, the elements S, Si, Ti, Cr, Fe, and Ni arise from reaction of the base metal of the membrane cell or the tubing with H₂S while O, K, and Ca are from the carbonate mixture. These results clearly indicate that gold plating was unsuccessful in producing an H₂S-inert surface, at least at the relatively low flow rates, 25 sccm, used in these experiments.

Two additional membranes were examined using gold plated membrane cells. For one of these (molten salt/LiAlO₂ membrane 12496-11-2), equipment failure prohibited collection of permselective data but solid deposits like those described above were observed. The molten carbonate/AlN membrane 12496-5-1 exhibited no detectable permeation of H₂S; however, very high permeabilities of CO and H₂ were observed when a feed containing H₂S, CO₂, CO and H₂ was used. This indicates substantial reactivity of H₂S with metal and some defects in the membrane. A slight increase in the feed pressure resulted in cracking of the membrane.

A gold plated membrane cell in the absence of a membrane was examined to insure that the membrane was not responsible for decomposition of H₂S. The sweep side of a holder was sealed off so that gas could exit only through the feed reject, which was analyzed by GC. Data was collected at 560°C using feeds containing about 11 to 0.4% H₂S in N₂ and for a feed containing about 0.5% H₂S and 5% H₂ in N₂. Average or final concentrations of H₂S and H₂ in the feed reject are listed in Table 4.23.

Table 4.23. Analysis of H₂S gas mixtures passed through a gold plated membrane cell at 560°C.

Feed #	Feed composition, %		gas conc., % in feed reject		% H ₂ S decomposition	value of K (see equation 25 below)
	H ₂ S	H ₂	H ₂ S	H ₂		
1	10.98	-	10.93	0.200	0.6	3.3x10 ⁻⁷
2	5.18	-	5.11	0.116	1.4	3.0x10 ⁻⁷
3	2.72	-	2.62	0.0794	3.7	3.7x10 ⁻⁷
4	0.428	-	0.395	0.0412	7.7	2.3x10 ⁻⁶
5	0.526	4.92	0.451	4.96	14.3	4.7x10 ⁻²

For each of the above feeds, some H₂S decomposed upon passage through the membrane holder. Except for feed number 1, the amount of H₂S consumed and H₂ generated were comparable. The percent decomposition of H₂S based on the initial concentration of H₂S and that in the feed reject are listed above.

One possible fate of H₂S upon passage through a hot membrane cell is thermal decomposition as in reaction (24) below. Thermal decomposition of H₂S at elevated temperatures is well known and, in fact, has been proposed as a method to dispose of H₂S or to produce H₂.^{25,26} Various catalysts have been evaluated in an attempt to make decomposition of H₂S practical.²⁷ In addition, composite-platinum membranes have recently been used to promote thermal decomposition of H₂S by permeation of product H₂.²⁸

Using a simple free energy calculation,¹³ ΔG° for reaction (24) at 527°C is 24.4 kcal/mole or $K = 2.1 \times 10^{-7}$.

$$K = \frac{[\text{H}_2]^2 \cdot [\text{S}_2]}{[\text{H}_2\text{S}]^2} \quad (25)$$

Values of the above equilibrium constant expression were calculated for feeds 1-4 by assuming that the S₂ concentration was one half that of the H₂ concentration. For feed 5, the concentration of S₂ was assumed to be one half of the H₂S consumed. The calculated values of K are each greater than that expected for simple thermal decomposition of H₂S and implies an additional source of H₂S decomposition and H₂ production. This is particularly apparent at low feed concentrations of H₂S (feeds 4 and 5). In addition, the presence of H₂ in feed 5 should suppress thermal decomposition of H₂S. Decomposition of only $9 \times 10^{-5}\%$ H₂S or 0.005 ppm is expected for the initial concentrations of feed 5 listed in Table 4.23, significantly lower than the observed value of 14.7%. The above data is consistent with two modes of H₂S decomposition: (1) thermal (2) reaction with metal. For feeds with relatively high H₂S concentrations, thermal decomposition predominates. At lower feed concentrations, proportionally less thermal decomposition occurs and decomposition by reaction with metal becomes more apparent.

It is worth noting that extended exposure of a gold plated membrane cell to H₂S containing feeds at elevated temperatures resulted in the deposition of a dull, crystal-like layer on the gold surface. The elemental composition by EDS (S, Cr, Mn, Fe, Ni, Cu, Zn, and Au) confirmed the presence of metal sulfides. This layer may result in some passivation with respect to H₂S. Exposure of the gold plated cell to H₂S containing feeds for an extended time at 560°C resulted in a decrease in H₂S decomposition from 37% initially to about 2.3% after seven days.

4.3.2.3 Testing with non-H₂S containing feeds. As a result of H₂S-metal reactivity, molten salt/ceramic membranes were evaluated using feeds which contained no H₂S. Results for the various membranes examined are listed in Table 4.24. For these membranes, the feed compositions, which were determined at ambient temperature, were assumed to be unchanged by heating to a membrane temperature of 560°C. This is not, of course, the case when H₂ and CO₂ are present in the feed since CO was observed in the permeate of these membranes. Nonetheless, the permselective data reported in Table 4.24 is at least qualitatively useful. For example, membrane 12344-92-5 exhibited very large CO₂ and H₂ permeabilities. Such results are typical of a membrane with holes or defects which permit Knudsen flow of gases but which are small enough to maintain a transmembrane pressure of greater than 20 psia. Substantial quantities of CO were observed in the permeate even though none was present in the feed. It presumably resulted from reaction of CO₂ and H₂ (reaction (13)).

Complications associated with the presence of both CO₂ and H₂ at elevated temperatures were eliminated by using feeds consisting only of CO₂ and an inert gas. Using such feeds, a series of membranes were examined. Some resulted in very large permeabilities of CO₂ and the inert gas, suggestive of holes or defects in these membranes (12496-14-3, 12495-15-4). Others gave lower permeabilities due to lower defect rates. However, the CO₂ permeabilities of none of these membranes were comparable to the theoretical CO₂ permeability of a molten carbonate membrane, 232 Barrers, (see Table 4.18). For some membranes (e.g. 12496-2-2), significant amounts of CO were detected in the sweep, even when only CO₂ and an inert gas were present in the feed. Apparently the membrane and/or the membrane cell provide reactive surfaces at which reduction of CO₂ occurs.

For membrane 12496-2-2, using a CO₂/Ar feed and initial feed and sweep pressures of 37.8 psia and 20.0 psia, a large quantity of CO₂ was detected in the sweep. This is suggestive of pinholes or other defects in the membrane. However, over the period of several hours these defects apparently sealed and the data listed in Table 4.24 was obtained.

As mentioned previously, an alternative membrane sealing technique using graphite tape in place of the gold C-rings proved to be more successful. In general, it appeared that the use of graphite tape resulted in fewer cracked membranes. The permselective properties of membranes sealed using this technique and using non-H₂S containing feeds are listed in Table 4.25. For one such membrane, the molten carbonate/LiAlO₂ membrane 12496-16-3, a bench top pressure check was performed at room temperature using 20 psia. No gas flow across the membrane was detected. Membranes examined using dry feed and sweep gases exhibited CO₂ permeances in the range of about 1,200 to 10,000 Barrers. In each case, permeabilities of the inert gases N₂ or Ar were greater than that of CO₂. Visual examination of the above membranes revealed no evidence of cracking or other defects, but there appears to have been some migration of salt in the AlN membranes.

Table 4.24. Permselective properties of molten salt/ceramic membranes at 560°C using non-H₂S containing feeds.

Support	Membrane*	Conditions (see below)	Feed P (psia)	Sweep P (psia)	gas	ppm in permeate	P _o (Barrers)
AlN	12344-92-5	a	18.9	20.4	CO ₂	1397	38,000
					H ₂	25599	834,000
					CO	14225	-
			35.8	27.8	CO ₂	55903	906,000
					H ₂	58113	1,060,000
					CO	39972	-
			58.6	31.7	CO ₂	116230	1,220,000
					H ₂	97091	1,110,000
					CO	82888	-
LiAlO ₂	12496-14-3	d	15.0	15.0	CO ₂	5922	234,000
					N ₂	15431	131,000
AlN	12496-15-4	d	16.0	15.6	CO ₂	801	19,000
					N ₂	2189	17,400
AlN	12496-2-2	b	20.4	15.7	CO ₂	1772	6,640
					Ar	**	-
					CO	453	-
			41.0	15.9	CO ₂	3104	5760
					Ar	**	-
					CO	428	-

Test conditions

- a. feed: 37.1% CO₂, 33.6% H₂ in N₂; N₂ sweep; both gases passed through 60°C water bubblers; flow rates 50 sccm.
- b. Feed: 50.0% CO₂ in Ar, He sweep; both dry, flow rates 10 sccm
unknown sources were also detected in the permeate.
- d. Feed: 25.3% CO₂ in N₂; sweep: helium; both dry; 25 sccm sweep flow.

Notes:

- * all membranes sealed in membrane cell using a C-ring.
- ** Ar detected but not quantified.

Table 4.25. Permselective properties of molten carbonate/ceramic membranes at 560°C using non-H₂S containing feeds. Dry feed and sweep gases unless stated otherwise.

Support	Membrane***	Conditions (see below)	Feed P (psia)	Sweep P (psia)	gas	ppm in permeate	P _o (Barrers)
AlN	12832-15-2	a	16.5	15.1	CO ₂	344	9740
					Ar	**	-
LiAlO ₂	12496-16-3	a	16.4	15.5	CO ₂	199	5670
					Ar	trace**	-
AlN	12496-19-4	b	53.3	15.5	CO ₂	213	5290
					CO	24	1200
					N ₂	554	9200
		b-wet	59.2	15.7	CO ₂	507	11300
					CO	116	5130
					N ₂	634	9480
AlN	12496-17-7	c	54.3	15.5	CO ₂	87	3480
					Ar	216	2020
		c-wet	52.1	15.5	CO ₂	7685	320,000
					Ar	29,925	292,000
		d	55.6	15.3	CO ₂	17,412	386,000
					CO	7,604	328,000
					He	**	-
AlN	12496-18-3	e	37.7	15.5	CO ₂	187	9570
					Ar	802	12400
		e	44.9	15.5	CO ₂	39	1670
					Ar	344	3040
		e	62.4	15.5	CO ₂	62	1900
					CO	71	-
					Ar	441	4050
LiAlO ₂	12496-16-4	f	16.5	15.5	CO ₂	58	6190
					Ar	491	14400
		g	49.0	15.5	CO ₂	11	*
					Ar	199	*
AlN	12496-18-2	h	41.4	15.5	CO ₂	12	1400
					Ar	182	5450
		i	64.5	15.5	CO ₂	9	1190
					Ar	208	7070

Test conditions: dry = dry feed and sweep; wet = feed and sweep gases passed through 60°C water bubblers.

a. feed: 20.5% CO₂ in Ar; sweep: N₂; both dry. Small quantities of CH₄ and H₂ in sweep.

b. feed: 31.0% CO₂, 15.7% CO in N₂; sweep, helium; feed flow 112 sccm, sweep flow 109 sccm.

c. feed: 9.0% CO₂ in Ar; sweep, helium; feed flow 112 sccm, sweep flow 109 sccm.

d. feed: 33.4% CO₂, 17.2% CO in He; sweep, N₂; feed flow, 112 sccm; sweep flow, 109 sccm.

e. feed: 23.2% CO₂ in Ar; sweep, helium; feed flow, 120 sccm; sweep flow, 118 sccm

f. feed - 21.8% CO₂ in Ar; feed flow rate 100 sccm; sweep flow rate, 101 sccm.

g. same as f but sweep flow rate undetermined.

h. feed: 20.4% CO₂ in Ar; feed and sweep flow rates, 260 sccm.

i. feed: 20.4% CO₂ in Ar; feed and sweep flow rates, 460 sccm.

Notes: *permeability could not be calculated since sweep flow rate was not determined; **helium detected but not quantified; ***all membranes sealed in cell using graphite tape.

The effect of the feed pressure of CO₂ on its permeability was evaluated for two different membranes. For membrane 12496-18-2, CO₂ permeabilities were roughly the same at the two different pressures evaluated. This is consistent with permeation of CO₂ by a solution-diffusion mechanism, as is expected. Membrane 12496-18-3 was examined using a CO₂/Ar feed at three different feed pressures. At the lowest pressure examined, the CO₂ permeability was the largest which might suggest facilitated transport of CO₂. However, the permeability of N₂ was also large compared to values at higher pressures. A more reasonable explanation is that small defects were present initially which subsequently sealed.

Humidification of feed and sweep gases apparently has a substantial effect on gas permeabilities. For example, the CO₂ permeabilities of membrane 12496-17-7 increased 100-fold upon humidification of feed and sweep gases. Such large permeabilities are suggestive of defects in the membrane. Upon returning to dry gases, CO₂ and other permeabilities remained large. The effect of gas stream humidification on the performance of membrane 12496-19-4 was quite different. Humidification resulted in an approximate doubling of the CO₂ permeability and a four-fold increase in the CO permeability, but the N₂ permeability was unchanged.

4.3.3 Alternative materials of construction for membrane cells

Although the time involved in fabrication and testing of membrane cells consisting of materials other than stainless steel or related metals would likely be quite long, some preliminary investigations of alternative materials were pursued. Two such materials were quartz and alumina. The reactivity of H₂S with these materials was evaluated by passing a stream of approximately 6% H₂S in N₂ at 25 sccm through tubes of either material. The exit stream was analyzed by GC and data for various temperatures are listed in Table 4.26.

Table 4.26. Analysis of 6% H₂S in N₂ feed after passage through quartz or alumina tubes at the indicated temperatures.

Material	T(°C)	gas conc (ppm)	
		H ₂ S	H ₂
Quartz	23	61840	nd
	560	63660	nd
	600	64530	23
	650	63650	60
	700	63450	203
Alumina	23	60010	nd
	500	60680	nd
	550	61070	nd
	600	60190	nd
	650	61180	nd
	700	61650	12

In addition, small quantities of CO₂, 50-60 ppm, were detected in the exit from the quartz tube at 560-700°C. It is presumed that this corresponds to a slight leakage at the sealing gasket. No CO₂ was detected in the exit from the alumina tube. It would appear that both quartz and alumina are essentially inert with respect to H₂S at flow rates comparable to those used in membrane experiments. Hence, either material could be used to fabricate an H₂S-inert membrane cell.

4.3.4 Planar and tubular molten carbonate/ceramic membranes. Testing at Research Triangle Institute.

A series of membranes consisting of the molten base composition mixture 30-A immobilized in planar or tubular microporous ceramic supports were evaluated at Research Triangle Institute (RTI). Through the use of fairly high flow rates of gases, liters per minute rather than milliliters per minute, much of the difficulties associated with H₂S-metal reactivity were minimized. The permselective properties of the membranes tested by RTI are detailed in a separate report which is in the Appendix.

4.3.5 Modeling of membrane performance

A model designated CMEM was developed which predicts the permselective properties of a molten carbonate membrane. The model is also useful for testing the effect of any of a number of physical parameters that affect membrane performance. The most important of which are the equilibrium constant of the facilitating reaction (reaction (1)) and the sweep and feed stream pressures and compositions. The central premise of the model is that only H₂S is solubilized in the membrane by reaction with the carbonate melt as in reaction (1). Other gases, including H₂S, permeate the membrane by physically dissolving as discrete molecules and diffusing. The model was designed to evaluate membranes in a counterflow configuration.

If it is assumed that the chemical equilibrium between H₂S and the melt as in reaction (1) exist, and without specifying or having knowledge of the forward or reverse rates of reaction, the assumption must be made that the reaction occurs only at the gas-membrane interface. The additional assumption that mass transfer resistance in the gas phase is negligible means that the partial pressures of H₂S, CO₂, and H₂O at the membrane interface can be set equal to the gas stream partial pressures. If the only anions present in the melt are sulfide and carbonate, the concentration of sulfide ion is given by:

$$[S^{2-}] = \frac{C_T K_1 P_{H_2S}}{P_{H_2O} P_{CO_2} + K_1 P_{H_2S}} \quad (26)$$

where C_T is the sum of the concentration of S²⁻ and CO₃²⁻ ions at equilibrium. The flux of H₂S across the membrane is taken to be equal to the flux of sulfide ion following Fickian diffusion:

$$\text{Flux}_{\text{H}_2\text{S}} = \frac{D_{\text{S}^{2-}}}{\delta} ([\text{S}^{2-}]_1 - [\text{S}^{2-}]_2) \quad (27)$$

where δ is the thickness of the membrane, $D_{\text{S}^{2-}}$ is the diffusivity of the sulfide ion, and $[\text{S}^{2-}]$ is the concentration of sulfide ion on the feed ($i=1$) or sweep ($i=2$) side of the membrane. By the stoichiometry of reaction (1), the fluxes of CO_2 and H_2O are equal to that of H_2S but permeate from the sweep to feed side of the membrane rather than from feed to sweep as for H_2S . Transport of H_2O and CO_2 are assumed to occur by the reaction mechanism alone and transport by solution/diffusion is neglected. For the "inert" gases such as H_2 and CO , transport by a solution-diffusion mechanism was presumed. The flux of these gases was obtained from an expression analogous to equation (27) but where concentrations were those of physically dissolved gases at the feed and sweep interfaces.

The input required to run the program included the diffusivity and solubility of each inert gas, the diffusivity of the sulfide ion, and the equilibrium constant, K_1 . Each of these is sensitive to temperature and composition of the molten salt mixture. CMEM will prompt for the diffusivity and solubility of each inert beginning with N_2 . Given a value for N_2 diffusivity, CMEM provides an estimate for the diffusivity of the remaining inert gases based on the Wilke-Chang equation and tabulated molar volumes (cc/gmole).²³ The diffusivity of the sulfide ion may be estimated from the value for sodium ion. The diffusivity of S^{2-} is typically about 0.3 times that of Na^+ , based on ionic volumes.²³

CMEM also requires the molten salt anion concentration, C_T , and the membrane thickness, δ . The anion concentration is the liquid density divided by the average molecular weight of salt species present. The membrane thickness is the actual thickness of the molten salt barrier unless a tortuosity factor is required for a given porous support. Since experimental tortuosities were not determined, no tortuosity corrections were applied.

Process parameters required by CMEM are the ratio of sweep to feed flow rates, feed and sweep compositions, and the total pressure of each stream. The pressure drop from module inlet to outlet on either side of the membrane is assumed to be negligible. A target concentration of H_2S in the clean outlet stream (feed reject) is required.

Input and output for a run of CMEM are illustrated in Table 4.27. The input file lists the information required to run the program. The composition of the feed and sweep streams, as mole fractions, are specified in lines 3 and 5 in the following order: H_2S , H_2O , CO_2 , N_2 , CO , H_2 , NH_3 , and CH_4 . Line 7 is the mole fraction of H_2S in the feed reject. Membrane thickness in cm is listed in line 8. Other parameters are self explanatory.

Using the input parameters, CMEM first estimates the performance of a counter-flow module based on 'log-mean driving force' assumptions. These simplifications are well suited to streams dilute in the active gases, and permits an initial check as to whether

target outlet concentration of H_2S is achievable. A more rigorous calculation, involving an integration along the membrane surface and calculation of fluxes and gas phase compositions at each point, is then performed. An example of the results of such a calculation are listed in the output file in Table 4.27. Reported are the H_2S flux, the area required to achieve the target concentration of H_2S in the feed reject, H_2S permeance, selectivity, and fractional conversion to S^{2-} at the feed and sweep interfaces.

Table 4.27. Input and output data for the program CMEM.

Example Input File INPUT.PAR

```

1.0          | Specific Feed Rate must be 1.0
1.0          | Q2i, moles Sweep per mole Feed
0.5      1.0      5.0      48.0      21.0      20.0      0.30      4.20      | Y1i
20.0        | P Feed (atm)
0.0      5.0      10.0     80.0      5.0      0.0      0.0      0.0      | Y2i
15.0        | P Sweep (atm)
0.001       | Y H2S Reject
1.0         | delta (cm)
.20000E-03 .10000E-03 | Diff., Solub of N2 (cm*cm/sec and mmole/cc/atm)
.20000E-03 .20000E-02 | Diff., Solub of CO (cm*cm/sec and mmole/cc/atm)
.32000E-03 .50000E-02 | Diff., Solub of H2 (cm*cm/sec and mmole/cc/atm)
.22000E-03 .10000E-02 | Diff., Solub of NH3 (cm*cm/sec and mmole/cc/atm)
.21000E-03 .10000E-02 | Diff., Solub of CH4 (cm*cm/sec and mmole/cc/atm)
.30000E-05 | Diffusivity of Sulfide Ion (cm*cm/sec)
2.0         | Equilibrium Const K1 (atm)
20.0        | CO3 Anion Concentration (mmole/cc)

```

Example Output File OUTPUT.DAT

```

RUN NUMBER          1
-----
Module Performance:

Flux of H2S          0.14E-04 (mmoles/sec/cm^2)
Area required        0.28E+03 * Feed Rate (cm^2 open area)
                      (Feed Rate in mmoles/sec)
*Permeance of H2S    0.14E-03 (mmole/sec-sq.cm-atm)
                      0.46E-04 (scc/sec-sq.cm-cmHg)
*Selectivity H2S/Inerts 0.11E+03
Fractional Conv. to S--
- Feed Side          0.12E+00
- Sweep Side         0.91E-05

```

---

*Based on Feed/Sweep pressure drop

5.0 Summary and Conclusions

To develop high temperature facilitated membranes for the removal of H_2S from IGCC gas mixtures, three basic experimental activities were pursued:

- (1) evaluation of the H_2S chemistry of a variety of alkali and alkaline earth carbonate salt mixtures
- (2) development of microporous ceramic materials which were chemically and physically compatible with molten carbonate salt mixtures under IGCC conditions and which could function as a host to support a molten carbonate mixture and
- (3) fabrication of molten carbonate/ceramic immobilized liquid membranes and evaluation of these membranes under conditions approximating those found in the intended application.

A variety of carbonate mixtures consisting of alkali and alkaline earth carbonate salts could be prepared. Characterization by TGA and DTA have shown that seven of these have melting points below 600°C and are essentially nonvolatile under CO_2 at temperatures to 840°C . Of these, four mixtures containing Rb_2CO_3 , Cs_2CO_3 , SrCO_3 , or BaCO_3 have apparently not been prepared or characterized previously. The low melting points of the above mixtures relative to pure carbonate salts and their involatility at high temperature make them potentially useful for fabrication of immobilized liquid membranes which selectively permeate H_2S . In addition, the wide variety of carbonate compositions prepared offers the potential for a range of reactivities with H_2S .

The properties of one mixture, designated as the base composition (25.2 mole % K_2CO_3 , 25.7 mole % CaCO_3 in Li_2CO_3), were further evaluated. Incorporation of up to 25 mole % sulfide ion into the base composition carbonate mixture resulted in mixtures which were molten at 600°C or lower. That sulfide-containing mixtures are liquid at reasonable temperatures is critical to the success of molten carbonate membranes for removal of H_2S . Partial solidification of the melt could result in membrane failure. It would appear that the base composition mixture will not suffer from such membrane failure.

Since carbonate membranes permeate H_2S by a facilitated transport mechanism, a knowledge of the reactivity of H_2S with the carbonate mixtures described above was required for choice of the optimal membrane material. For this reason, an evaluation of the equilibrium constant for the reaction of the base composition carbonate mixture with H_2S was carried out by a series of absorption experiments. This activity was complicated by several experimental difficulties. These included gas phase reactivity and the accurate determination of the concentration of water in the gas phase. In addition, at the high temperatures of these experiments, significant reactivity between H_2S and the absorption vessel and its internal components was observed. This is a very serious problem since some of the H_2S thought to be absorbed by the melt was actually consumed by reaction with metal. It is unlikely that accurate equilibrium constants were

obtained under such conditions. However, in one experiment, an equilibrium constant for H_2S absorption was determined, 0.235 atm at 560°C , which was reasonable when compared with literature data.

Through a process involving literature searches and screening experiments, it was determined that aluminum nitride and lithium aluminate were the best candidate ceramics for use as microporous supports for immobilized molten alkali carbonate membranes. Golden Technologies Company, Inc. was successful in producing aluminum nitride discs and tubes with pore sizes in the range $0.38\text{--}0.42\ \mu\text{m}$ with 45-50% open porosity. These discs and tubes were infiltrated with molten alkali carbonates at APCI using techniques developed for this program. In the course of this work, it was determined that boron nitride can be used as a coating to help control the infiltration process of these materials. While lithium aluminate has better long term stability than aluminum nitride in contact with the molten alkali carbonates, neither APCI nor Golden Technologies were able to fabricate discs of this material with pore sizes in the range required to contain the molten salts. This was because of limited source suppliers of lithium aluminate powders and the inability to reduce the starting particle size of commercially available powders without introducing excessive mill/media contamination.

Three types of molten carbonate membranes were prepared. These consisted of the base composition carbonate mixture immobilized in a microporous gold frit, a planar microporous ceramic support, or a tubular microporous ceramic support. A significant problem in membrane testing was the tendency of planar ceramic membranes to crack upon sealing in the membrane cell. Membrane cracking was minimized by sealing using a graphite tape technique developed at RTI. Testing of molten carbonate membranes at 560°C and using H_2S containing feeds at relatively low flow rates was complicated greatly by the reactivity of H_2S with the membrane cell. As for the absorption experiments above, consumption of H_2S by reaction with metal led to unreliable determinations of H_2S permeabilities. This is a serious problem which should be addressed in future work. Membrane cells could be constructed of quartz or alumina which were shown to be inert with respect to H_2S at temperatures to 700°C . Finally, to be practical, thinner ceramic supports need to be constructed to produce membranes with higher H_2S fluxes.

Due to the problem of H_2S -metal reactivity, molten carbonate/planar ceramic membranes were evaluated using feeds which contained no H_2S . For most of the membranes so examined, gas permeances were quite high indicative of defects in the molten carbonate layer. This is, of course, a serious problem which needs to be addressed further. However, for a few membranes, reasonable, but still somewhat high, CO_2 permeabilities; for example 1,200 Barrers, were obtained suggesting that the fabrication of largely defect free membranes is possible.

Some of the difficulties of H_2S -metal reactivity were minimized through testing at RTI carried out at significantly higher gas flow rates. Permselective testing was performed using membranes containing the base composition carbonate mixture in planar and

tubular ceramic supports. A more detailed listing of conclusions is provided in the attached RTI final report. The most significant points are summarized below.

Erratic membrane performance was observed. Often, H_2 or He permeabilities were much higher than those predicted based on a solution-diffusion mechanism indicative of defects in the molten carbonate layer. However, in some instances H_2S to H_2 or He selectivities greater than one were observed. Based on fairly limited data, an observed decrease in H_2S permeability with increasing feed pressure was consistent with facilitated transport of H_2S . Examination of membranes after testing revealed that there apparently is a tendency for the melt to migrate in or out of the support. This was particularly apparent for tubular membranes where the salt appeared to have migrated downward along the tube. Planar ceramic membranes examined after testing showed evidence of regions of unfilled pores near the middle of the discs. In addition, for one unused planar ceramic membrane, similar unfilled regions were also observed. Although the experimental information described in this report has not resulted in a demonstration of the use of molten carbonate membrane for removal of H_2S from fuel gas mixtures, it has shown some success on the way to this goal and has identified the significant problems would need to be addressed by future efforts. These are:

- Minimize or eliminate the reactivity of H_2S with membrane testing apparatus by using materials of construction (eg. alumina, quartz) which are inert with respect to H_2S .
- Fabricate ceramic supports which are at least an order of magnitude thinner, or larger in area, than the current ones.
- Address the question of salt migration within the ceramic support.
- Develop techniques for fabricating largely defect-free molten carbonate membranes (e.g. porous structure of support).
- Conduct absorption experiments to evaluate the reactivity of H_2S with the molten carbonate mixtures identified in this study by using an H_2S - inert apparatus.
- Develop improved ceramic support materials (e.g. $LiAlO_2$) and fabrication methods (to ensure appropriate pore size distribution).

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7.0 APPENDIX

7.1 Detailed schematic diagram of absorption and membrane test apparatus and a listing of components.

HIGH TEMPERATURE MEMBRANE SYSTEM FLOW DIAGRAM		PRODUCTS AIR CRSD / IEAS	
DRAWN	J.ZAPP	CHECKED	
FIRST USED ON	6/29/90		
ART-507895-03-00		IEAS-90531B	
		SHEET 1 OF 2	

DUGANBYSYS1 02/07/91 REV.G

HIGH TEMPERATURE MEMBRANE SYSTEM FLOW DIAGRAM

AIR PRODUCTS
CRSD / IEAS

DRAWN J.ZAPP 6/29/80

CHECKED

FIRST USED ON
ART-507695-03-00

IEAS-90531B
SHEET 2 OF 2

DVG MEMB SYS2 02/07/91

REV.G

USE NO.	REV.	DATE	REVISION DESCRIPTION				DATE	BY	CHECK	APPROV.
VALVE IDENTIFICATION NUMBER			DATE	TIME	FILE	MIXING VESSEL (12 LITER) HIGH TEMPERATURE MEMBRANE SYSTEM 				
FRACITION NUMBER, JAVEL			02/08	12:30 PM						
1 2.00 1.00										
HALE LAMINATE HALE SIZE										
1.00 2.00										
ART-807695-03-00			02/08							
			FILE	REVIEW	PLANT	END NO.	IEAS-92021			
			DATE	TIME	BY	CHECK				

PRODUCTS

**Materials List for High Pressure High Temperature Membrane and Absorption Unit
Cell 410**

Page 1

Drawing Designation	Model # Manufacturer	Description	Material of Construction	Pressure Rating (psi)	Temperature Rating (C)
V1, V2, V3, V4, V5, V6, V7, V8, V9, V10, V11, V12, V13, V14, V16, V17, V26, V31	SS-0VS2 Whitey	Integral Bonnet Needle Valve	316 SS	5000	232
V27, V28, V33, V34, V35, V36, V37, V38, V39, V40	SS-0KS2 Whitey	Integral Bonnet Needle Valve	316 SS	5000	93
V15	SS-0RS2 Whitey	Integral Bonnet Needle Valve	316 SS	5000	232
V22, V23	SS-83XF4 Whitey	Valve	SS	1500	232
V18, V19, V20, V21	SS-83XTF4 Whitey	3-way valve	316 SS	1500	232
V24, V25	SS-SS2-D-KZ-S Nupro	Metering Valve	316 SS	2000	149
V2A	SS1VF4 Whitey	Valve	SS	5000	232
V29, V30	SS-44S6 Whitey	Ball Valve	SS	2500	65
CV1, CV2, CV3, CV4, CV5, CV6, CV7, CV8, CV9, CV10, CV11, CV12, CV13, CV14, CV15, CV19, CV20, CV21, CV22, CV23, CV24, CV25, CV26, CV29, CV30	SS-2C-10 Nupro	Check Valve	316 SS	3000	121
CV27, CV28	SS-2C-1/3 Nupro	Check Valve	316 SS	3000	121

Drawing Designation	Model # Manufacturer	Description	Material of Construction	Pressure Rating (psi)	Temperature Rating (C)
AV1, AV2, AV3, AV4, AV5, AV6, AV7, AV8, AV9, AV10, AV11, AV12, AV13, AV14, AV15, AV16, AV17, AV18, AV19, AV20, AV30, AV31, AV32, AV33, AV34, AV35, AV36, AV37	SS-41S2-31C Whitey	Ball Valve	316 SS	2500	65
AV21, AV22, AV23, AV24, AV25, AV26, AV27, AV28, AV29	SS-33VF4-31C Whitey	Ball Valve	316 SS	6000	232
PCV-3	26-1016-24-002 Tescom	Regulator	SS	10000	74
PCV4, PCV12, PCV16, PCV17	44-1114-24 Tescom	Regulator	SS	10000	75
PCV7, PCV10	102-601 GO	Regulator	SS	3000	90
PCV5, PCV6, PCV11, PCV12,	11486P2A Grove	Dome Loaded Regulator	SS	5000	74
PCV13	1Z838D Speedaire	Regulator		250	80
PCV8, PCV9	101-063 GO	Regulator	SS	6000	175
PCV14, PCV15	E11-E-E444 APCI	Regulator	SS	10000	75
SC1	304L-HDF4-500 Whitey	Sample Cylinder	304 SS	1800	N/A
SC2	304L-HDF4-150 Whitey	Sample Cylinder	304 SS	1800	N/A
CT1, CT2	APCI	Water Trap	SS	N/A	N/A
ABV1	Parr HP/HT Custom	Absorption Vessel	Incoloy 800HT	800 WP	800
MV1, MV2	APCI Manuf.	Mix Vessel	304SS	2200	150

Drawing Designation	Model # Manufacturer	Description	Material of Construction	Pressure Rating (psi)	Temperature Rating (C)
RV1, RV2	SS-4R3A Nupro	Relief Valve 2200 psi SP	SS	6000	121
RV3	SS-4R3A Nupro	Relief Valve 900 psi SP	316 SS	6000	121
BPR1, BPR2	101-181 GO	Back- pressure regulator	SS	3000	175
BPR3, BPR4	BPR21U22542 Circle Seal	Back- pressure regulator	SS	6000	200
FI1, FI2	APCI 150mm	Rotameter	SS/Glass	200	120
PT1, PT2, PT3, PT4, PT5, PT6, PT7, PT8	1151GP-8-E-22 Rosemont	Pressure Transducer	SS	6000	71
FCV3	EVA-1XA1-6A Badger Meter	Research Control Valve	SS	5000	65
MFC1, MFC2	201 Porter	Mass Flow Controller	SS	1000	70
PI21, PI26	McDaniel Gauge 0-100 psi	Gauge	SS	300	100
PI12, PI12A	McDaniel Gauge 0-600 psi	Gauge	SS	1800	100
PI6, PI8, PI15, PI16, PI17, PI18	McDaniel Gauge 0-1500 psi	Gauge	SS	4500	100
PI22, PI23, PI24, PI25, PI27	McDaniel Gauge 0-800 pis	Gauge	SS	2400	100
PI1, PI2, PI3	McDaniel Gauge 0-5000 pis	Gauge	SS	15000	100
PI4, PI5	McDaniel Gauge 0-3000 pis	Gauge	SS	9000	100
PI22, PI23, PI24, PI25, PI27	McDaniel Gauge 0-800 pis	Gauge	SS	2400	100
PI7, PI9	McDaniel Gauge 0-300 pis	Gauge	SS	900	100

Drawing Designation	Model # Manufacturer	Description	Material of Construction	Pressure Rating (psi)	Temperature Rating (C)
PI11	Model K 0-3000 psi Gauge	Gauge	SS	9000	100
TIC1, TIC2, TIC3, TIC4	UT-30 Yokogawa	Controller	N/A	N/A	N/A
PIC1	UT-30 Yokogawa	Controller	N/A	N/A	N/A
PI14, PI19, PI20	Red Lion	Digital Panel Meter	N/A	N/A	N/A
TE1, TE2, TE3, TE4		Thermo- couple	316 SS	N/A	850
V41, V42	SS-43S4 Whitey	Ball Valve	316 SS	3000	65

7.2 Information relating to the gas chromatograph used in absorption and membrane experiments

SUPPLEMENTAL INFORMATION FOR ARNEL JOB NO. 1245

GC Operational Parameters

Method #1: Analysis of H₂, O₂, N₂, CO, CH₄, CO₂, H₂S, and COS

Temperatures:

Injection Port A:	120°C
Injection Port B:	120°C
Detector A:	200°C
Detector B:	200°C
Aux. Temp (Valve Oven):	100°C
Oven Maximum:	150°C

Temperature Program:

Initial Oven Temp:	80°C
Initial Time:	25
Rate:	0
Final Temp:	80°C

Detector Signal:

Detector A:	Low Sens,	(+)
Time:	N/A	
Detector B:	Low Sens,	(-)
Time:	N/A	
Signal 1:	A	
Range:	0	
Attn:	0	
Zero:	2.8	
Signal 2:	B	
Range:	0	
Attn:	0	
Zero:	11.0	

SUPPLEMENTAL INFORMATION FOR ARNEL JOB NO. 1245

Method #1: Analysis of H₂, O₂, N₂, CO, CH₄, CO₂, H₂S, and COS

Flows & Pressures: GC Ready at Injection Temperature

Injection Port A	Packed (He)
Pressure	45 psi
Carrier Flow	30 ml/min. @ Det A
Injection Port B	Packed N ₂
Pressure	41 psi
Carrier Flow	30 ml/min. @ Det B
Aux.1	40 psi He
Flow	35 ml/min. @ BF vent #1
Aux. 2	48 psi N ₂
Flow	30 ml/min. @ BF vent #3
Detector A	TCD He
Reference	40 ml/min. @ TCD A
Total & Carrier	70 ml/min. @ TCD A
Detector B	TCD N ₂
Reference	40 ml/min. @ TCD B
Total & Carrier	70 ml/min. @ TCD B

AIR PRODUCTS & CHEMICALS, ARNEL JOB 1245

ARNEL ARNEL INCORPORATED

DESIGNER

UPDATED BY: /DATE

FILE NAME

DATE

DRAFTSMAN

REF

T.J.M:5/30/91

1245

4/18/91

THOMAS MASTERHOUSE

SUPPLEMENTAL INFORMATION FOR ARNEL JOB NO. 1245

APPENDIX A

Column Temperature Limits:

Molecular Sieve	-	350°C
Hayesep N	-	165°C

COLUMN INFORMATION

<u>Column No.</u>	<u>Length</u>	<u>Description</u>
1	9'	Hayesep N 80/100
2	9'	Molecular Sieve 5A 45/60
3A	4'	Hayesep N 80/100
3B	9'	Molecular Sieve 5A 80/100
PTA's	3'	Chromosorb P aw 60/80

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2 of 3

7.3 Research Triangle Institute Final Report

DEVELOPMENT OF FACILITATED TRANSPORT CERAMIC MEMBRANES — EXPERIMENTAL TESTING

FINAL REPORT

**Work performed under a subcontract with
prime contract No.: DE-AC21-89MC26038**

Prepared by

**A.S. Damle
S.K. Gangwal
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194**

Prepared for

**Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501**

January 1994

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Table of Contents

Section	Page
List of Figures	iv
List of Tables	vi
Executive Summary	vii
1 Introduction	1
1.1 Facilitated Transport Process Concept/Chemistry	1
2 Experimental	4
2.1 Experimental System	4
2.1.1 Preliminary Disk Membrane Apparatus	4
2.1.2 Continuous Long-term Disk Membrane Test Apparatus	5
2.1.3 Continuous Long-term Tubular Membrane Test Apparatus ...	9
2.1.4 Simulated Coal Gas and Sweep Gas Compositions	9
2.1.5 Experimental Procedure	11
2.2 Experimental Matrix	11
3 Results and Discussion	13
3.1 Preliminary Disc Membrane Testing	13
3.1.1 Run No. 1	13
3.1.2 Run No. 2	16
3.1.3 Run No. 4	17
3.1.4 Run No. 5	17
3.1.5 Summary and Discussion	17
3.2 Continuous Long-term Disc Membrane Testing	19
3.2.1 Run No. 6	19
3.2.2 Run No. 7	25
3.2.3 Run No. 8	25
3.2.4 Run No. 9	26
3.2.5 Run No. 10	26
3.2.6 Run No. 11	28
3.2.7 Run No. 12	28
3.2.8 Run No. 13	29
3.2.9 Run No. 14	29
3.2.10 Summary and Discussion	29
3.3 Continuous Long-term Tubular Membrane Testing	37
3.3.1 Run No. T-2	37
3.3.2 Run No. T-3	39
3.3.3 Run No. T-4	44
3.3.4 Run No. T-5	44
3.3.5 Summary and Discussion	51

Table of Contents (con.)

Section	Page
4 Theoretical Modeling of Facilitated Transport	52
4.1 Analysis of Steady-state Data	52
4.2 Estimation of K and $D_{s..}$ from Steady-state Experimental Permeation Data	55
4.2.1 Data from Run No. 6	55
4.2.2 Data from Run No. 14	57
4.3 Analysis of Transient Data	58
4.3.1 Estimation of Diffusion Coefficient from Experimental Data	60
4.4 Maximum Achievable H_2S Concentration in Permeate	62
5 Process Evaluation	65
5.1 Estimation of Membrane Module Size for a 100-MW IGCC Plant ...	66
6 Conclusions and Recommendations	67
7 References	69

List of Figures

Number		Page
1-1	Cross-sectional view of the active molten salt film in an IMS membrane for the separation of H_2S	3
2-1	Test apparatus used in preliminary disc membrane studies	6
2-2	Schematic drawing of membrane test cell design	7
2-3	Schematic of a continuous condensate drain system	8
2-4	Schematic of a symmetrical half of the tubular membrane reactor assembly	10
3-1	Helium and H_2S concentration with time (Run #6, 5/3/93, 50 psig, 556 °C)	21
3-2	Helium, hydrogen, and H_2S concentrations with time (Run #6, 5/4/93, 50 psig, 556 °C)	22
3-3	Helium, hydrogen, and H_2S concentrations with time (Run #6, 5/5/93, 50 psig, 556 °C)	23
3-4	Helium, hydrogen, and H_2S concentrations with time (Run #8, 6/4-6/6/93, 50 psig, 615 °C)	24
3-5	Helium, hydrogen, and H_2S concentrations with time (Run #9, 6/23/93, 50 psig, 600 °C)	27
3-6	H_2S , helium, and hydrogen concentrations with time (Run #14, 8/30-9/1/93, 50, 100, 200 psig, 560 °C)	30
3-7	H_2S , helium, and hydrogen concentrations with time (Run #14, 9/1-9/4/93, 50, 100, 200 psig, 560 °C)	31
3-8	Cross section of an unused thicker membrane	33
3-9	Cross section of a membrane used in Run No. 10	34
3-10	Cross section of a membrane used in Run No. 6	35
3-11	Cross section of a membrane used in Run No. 8	36
3-12	H_2S concentration with time (Run #T-2, 11/17-11/22/93, 50, 100 psig, 500-560 °C)	40

List of Figures (con.)

Number		Page
3-13	Helium and hydrogen concentration with time (Run #T-2, 11/17-11/22/93, 50, 100 psig, 500-560 °C)	41
3-14	H ₂ S/He selectivity with time (Run #T-2, 11/17-11/22/93, 50, 100 psig, 500-560 °C)	42
3-15	Used tubular membrane showing downward salt movement	43
3-16	H ₂ S concentration with time (Run #T-4, 12/15-12/22/93, 50 psig, 510-520 °C)	45
3-17	Helium and hydrogen concentration with time (Run #T-4, 12/15-12/22/93, 50 psig, 510-520°C).	46
3-18	H ₂ S/He and H ₂ /He with time (Run #T-4, 12/15-12/22/93, 50 psig, 510-520 °C)	47
3-19	H ₂ S concentration with time (Run #T-5, 12/27-12/31/93, 50 psig, 515 °C)	48
3-20	Helium and hydrogen concentration with time (Run #T-5, 12/27-12/31/93, 50 psig, 515 °C)	49
3-21	H ₂ S/He and H ₂ /He selectivities with time (Run #T-5, 12/27-12/31/93, 50 psig, 515 °C)	50
4-1	Schematic of concentration gradients in the molten salt	54
4-2	Variation of flux rate with time—diffusion through a plane sheet	61

List of Tables

Number		Page
3-1	Percent Salt Infiltrations in the Membranes Used	14
3-2	Experimental Results of Preliminary Disc Membrane Experiments	15
3-3	Experimental Results of Continuous Long-term Disc Membrane Experiments	20
3-4	Experimental Results of Continuous Long-term Tabular Membrane Experiments	38

EXECUTIVE SUMMARY

The economic viability of advanced power generation concepts such as Integrated Gasification Combined Cycle (IGCC) and Direct Coal-Fired Turbines (DCFT) technologies depends on efficient removal of contaminants at the high temperature-high pressure (HTHP) operating conditions. Molten salt impregnated ceramic membranes provide a novel potential technique for removal of contaminant gases such as H_2S , NH_3 , SO_2 and NO_x based on facilitated transport mechanism for the contaminant species. In recent years, microporous ceramic membranes have been investigated for gas separation applications based upon passive mechanisms such as Knudson diffusion and molecular sieving. However, such passive separations cannot remove low concentration contaminants efficiently. Facilitated transport mechanism allows selective removal of such contaminants based on their chemical reactivity toward suitable reagents.

In this project, the technical feasibility of molten salt impregnated ceramic membranes, provided by Air Products and Chemicals, Inc., was investigated experimentally for removal of H_2S from coal gas at HTHP conditions. Both the disc and tubular membrane geometries were investigated, although the bulk of the membrane testing was conducted with membrane discs. Alkali carbonate salts were impregnated in microporous aluminum nitride discs/tubes to prepare these membranes. The microporous substrates were fabricated by Golden Technologies, Inc., and were infiltrated with molten salts by Air Products and Chemicals, Inc.

The experimental testing of membranes was conducted in three distinct phases. In the first phase, preliminary short-term experiments were conducted with disc membranes to verify enhanced transport of H_2S . These experiments determined experimental conditions under which measurable H_2S permeation rates could be obtained, and established the facilitated transport mode for H_2S permeation. These experiments, conducted at temperatures of 560 to 600 °C and pressures of 50 to 200 psig, also identified a need for a long-term stable operation to obtain steady-state permeation data. During this first phase, permeation data were obtained from a total of four membranes.

The experimental system used during the preliminary experiments was successfully modified to allow long-term, continuous, unattended testing of membranes. During the second phase long-term experiments were conducted using a total of nine disc membranes. These experiments confirmed the enhanced transport of H_2S with H_2S permeabilities in the range of 13,000 to 200,000 Barrers and H_2S to helium selectivities as high as 18. These membranes also indicated high permeabilities for hydrogen and helium indicating substantial leakage flow across a membrane. Similar to the first phase, the second phase studies were also conducted at 560 to 600 °C and 50 to 200 psig pressure. The results obtained with these membranes were inconsistent with some membranes not showing any H_2S permeation at all. The inconsistencies in the performance of different membranes are thought to be due to nonuniform or incomplete salt infiltration in the ceramic porous matrix. For the membranes showing enhanced H_2S transport, long periods of time, of the order of several hours, were needed to achieve steady-state permeation conditions indicating slow liquid phase diffusion process.

The long-term disc membrane tests indicated several key trends expected with facilitated transport: (1) lower permeabilities at higher pressures, (2) greater permeabilities at higher temperatures, (3) gradual increase in H_2S permeation across membrane, and (4) >1 selectivity

for species permeated by facilitated transport. All of the above trends were observed in spite of substantial porous leakage flow.

The observed H_2S selectivities in the long-term disc membrane testing were strongly affected by large leakage flow of helium and hydrogen. To increase the membrane surface area and to reduce overall contribution by leakage at seals, long-term experiments were conducted using three tubular membranes during the third phase of the experimental program. Testing at a temperature of 560 °C, typically used for disc membrane studies, indicated rapid increase in leakage flow with time indicating downward movement of salt within the ceramic matrix due to gravity. Further testing indicated that the membrane temperature can be increased only 10 to 20 °C above salt melting point without a quick increase in leakage flow. The lower operating temperature coupled with a greater thickness as compared to disc membranes resulted in significantly lower H_2S permeabilities with tubular membranes. The time required for steady-state operation was also found to be considerably longer with tubular membranes as steady state was not observed even after several days of operation.

Theoretical analysis of the facilitated transport process indicated that uphill transport of H_2S is possible, and that up to 13 percent H_2S permeate stream could be obtained, with 0.5 percent H_2S coal gas, without any transmembrane pressure differential. However, the above analysis assumed no mass transfer resistance. The membrane studies indicated a slow liquid phase diffusion process. For practical application of this concept, the observed H_2S flux rates need to be increased by an order of magnitude and the time requirement to achieve steady-state operation needs to be reduced by two orders of magnitude. The salt retention in the porous matrix is essential for this concept to work. Thus, the mean pore size of the ceramic matrix needs to be reduced with elimination of large pores $>1\ \mu m$ to improve the ability of the ceramic matrix to hold molten salt in place by capillary suction.

SECTION 1

INTRODUCTION

The successful development of advanced power generation systems such as Integrated Gasification Combined Cycle (IGCC) and Direct Coal Fired Turbines (DCFT) technologies depends on an economically viable and environmentally acceptable removal of contaminant gases. Facilitated transport membranes that can operate under the high-temperature, high-pressure (HTHP) conditions within these processes offer a potential technique for removal of contaminant gases such as H_2S , NH_3 , SO_2 , and NO_x . In recent years, microporous ceramic membranes have been investigated for gas separation applications based on Knudsen diffusion and molecular sieving mechanisms. However, such passive separations will not be able to remove low concentration contaminants. Facilitated transport mechanism offers a novel technique for selective removal of such contaminants based on their reactivity toward suitable reagents. In this project, the technical feasibility of molten salt impregnated ceramic membranes, developed by Air Products and Chemicals, Inc., was experimentally investigated for removal of H_2S from coal gas.

Both the disc and tubular membrane geometries were investigated, although the bulk of the membrane testing was conducted with the membrane discs. Alkali carbonate salts were impregnated in microporous aluminum nitride discs/tubes to prepare these membranes. The aluminum nitride microporous disc and tubular membrane substrates were fabricated by Golden Technologies, Inc., and were infiltrated with molten carbonate salt by Air Products & Chemicals, Inc. Permeation rates of H_2S along with other gas species across the membrane were measured under different operating conditions to determine the effectiveness of these membranes for separating H_2S from coal gas. Experiments were conducted over a period of 1 year from October 1992 through December 1993. A brief description of the facilitated transport concept and process chemistry involved is given below.

The experimental systems used are described in Section 2 and the experimental results are discussed in Section 3. Section 4 provides theoretical estimation of important parameters governing facilitated transport of H_2S and Section 5 provides a brief process evaluation.

1.1 FACILITATED TRANSPORT PROCESS CONCEPT/CHEMISTRY

In the facilitated transport concept, an active reagent, capable of reacting reversibly with the desired contaminant, is incorporated in the pores of a microporous membrane. This concept combines the absorption/reaction of the contaminant species in the reagent and subsequent stripping of the contaminant species with regeneration of the reagent, in one unit. A number of alkali metal carbonates are liquids in the range of 400 and 900 °C and are capable of reacting reversibly with H_2S and thus are excellent candidates for the facilitated separation of H_2S from coal gas under HTHP conditions. The reaction of carbonate melts with H_2S in the presence of H_2O and CO_2 has been studied by several investigators (Moore, et al., 1980; Stegen, 1982; and Lyke et al., 1985a, 1985b) to develop a hot gas cleanup system for IGCC/molten carbonate fuel cell power plants.

Figure 1-1 illustrates the process chemistry involved in the H₂S removal from coal gas by the molten carbonate salt impregnated in a microporous membrane. The membrane is exposed on the feed side to a high-pressure coal gas stream predominantly containing H₂, CO, CO₂, H₂O, CH₄, and H₂S, while the permeate side membrane/gas interface is swept by a gas mixture containing CO₂ and H₂O. At the feed membrane/gas interface, H₂S reacts with the alkali carbonate melt to produce water, carbon dioxide, and alkali sulfide:

Since free H₂O and CO₂ have a very low physical solubility in the molten salt, they will be largely liberated into the gas phase and go into the feed reject stream. Sulfide ions, the major product remaining in the melt, will diffuse to the permeate membrane/gas interface where it will react with the CO₂ and H₂O in the sweep gas stream by the same reversible reaction (1-1) to form H₂S and regenerate carbonate salt (CO₃²⁻). The hydrogen sulfide is liberated into the permeate stream, and with back diffusion of CO₃²⁻ ions to the feed side the overall transport cycle is completed.

This overall cycle amounts to a carrier-mediated transport of H₂S from the feed to permeate, coupled with a flow of steam and CO₂ in the opposite direction (i.e., from permeate to feed). According to the stoichiometry of Equation (1-1), for each mole of H₂S that is removed from the IGCC hot-gas stream, 1 mol of H₂O and CO₂ is introduced. Because of the coupled nature of this transport process, the H₂S flux is determined by the partial pressure gradients of all three permeating gases (H₂S, CO₂, and H₂O) across the membrane. Thus, it would be possible to transport H₂S across the membrane against its own concentration gradient, i.e., uphill transport, by setting appropriate gradients for the other two species. Such uphill transport would also allow near-complete removal of H₂S from coal gas. Since the transport of H₂S depends on its reaction, a highly selective separation of H₂S from coal gas can be achieved.

The mechanism of transport of H_2S , with a coupled transport of H_2O and CO_2 in the reverse direction is indicated.

Figure 1-1. Cross-sectional view of the active molten salt film in an IMS membrane for the separation of H_2S .

SECTION 2

EXPERIMENTAL

The experimental testing of the membranes supplied by Air Products and Chemicals, Inc., was conducted in three distinct phases. In the first phase preliminary short-term experiments were conducted with disc membranes to determine the experimental conditions under which measurable H_2S permeation rates could be obtained. These runs also provided an indication of permeation of other gas species, system stability, time requirement for achieving a steady state, and requirements for gas chromatographs (GCs) for adequate analytical resolution. During these experiments, a set of operating conditions was held constant for periods of only 1 to 4 hours. A total of four membranes were tested in this phase. The disc membranes were approximately 1 in. dia and 0.1 in. thick. The mean pore size was estimated to be $<1\ \mu\text{m}$. The percent by weight of salt infiltration in these four membranes was estimated to be from 72 to 82 percent.

In the second phase, disc membranes were tested in continuous long-term experiments to determine permeation of H_2S and other species over a long period of time as a function of operating conditions. A total of nine membranes were used in this phase, with the test durations for different membranes ranging from a period of one to several days. Seven of these membranes were similar to the ones used in the preliminary experiments, i.e., approximately 1 in. dia, and 0.1 in. thick. One disc membrane tested was slightly thicker, about 0.12 in. thick and one membrane was thinner with 0.06 in. thick. The mean pore size was again estimated to be $<1\ \mu\text{m}$. The percent by weight of salt infiltration in these membranes was estimated to be from 65 to 74 percent except for the one thicker membrane for which the percent salt infiltration was estimated to be only 34 percent.

In the third phase, tubular membranes were tested in continuous long-term experiments to determine the permeation characteristics as a function of operating conditions. A total of three tubular membranes were used in this phase, with the test durations for these membranes ranging over several days. The mean pore size of the tubular membranes was also expected to be $<1\ \mu\text{m}$. The tubes were approximately 15-mm OD, 8-mm ID, and 3.5-mm thick. The percent of salt infiltration in the tubular membranes was estimated to be from 74 to 82 percent by weight. The ceramic tubes ranged from 8 in. to 10 in. in length.

2.1 EXPERIMENTAL SYSTEM

Experimental systems used during the three testing phases were slightly different and are described below. The simulated coal gas and sweep gas compositions as well as experimental procedures are also outlined below.

2.1.1 Preliminary Disc Membrane Test Apparatus

The HTHP disc membrane testing facility used in the preliminary studies is shown schematically in Figure 2-1. The gas delivery system can supply the simulated coal gas composition or an inert 5 percent CO_2 in N_2 purge gas to the feed side of the membrane as well as a 30 percent CO_2 in N_2 sweep gas composition to the permeate side of the membrane. The flow rate of the gases is controlled by calibrated mass flow controllers (MFCs). The water vapor required for both the feed and sweep gases is generated by high pressure positive displacement

pumps and heating tapes wrapped around the stainless steel supply tubings. The water vapors are mixed with the preheated feed and sweep gases prior to introduction in the membrane test cell. The membrane is housed in a stainless steel holder which is maintained at a controlled temperature in a tubular furnace. The exit feed and sweep gas streams are cooled in condensers to remove water vapor and then combined before they exit through a dryer, filter, and a back pressure regulator (BPR). The single BPR controls the pressure on both sides of the membrane with a minimal transmembrane pressure drop. The pressure drop across the membrane is monitored by a differential pressure gauge. The transmembrane pressure drop can be adjusted to a small extent by changing the ratio of the feed and sweep gas flow rates. The feed and sweep gas exit streams are analyzed by on-line GCs.

The membrane holder used in these tests was provided by Air Products & Chemicals, Inc., and is shown schematically in Figure 2-2. In the original design a gold-plated metal "C" ring was used to seal the membrane against the holder. However, this sealing method led to frequent cracking of the membranes during loading. Therefore, a graphite tape was wrapped around the circular disc membrane in these preliminary experiments. Part of the tape also extended on the flat portion of the membrane along its periphery which acted as a seal against the membrane holder. This procedure reduced the probability of cracking the membranes. Since the graphite tape covered part of the flat portion of the disc membrane, the effective surface area exposed to feed gas was reduced from 5 to about 2.3 cm².

Because of relatively high water vapor rates used, the condensers needed frequent manual draining to prevent buildup and carryover into the exit gas streams. The positive displacement pumps also required occasional fillups during an experimental run. Because of the limitations imposed by condenser draining and pump fillup requirements, the experiments in this phase could not be run unattended for an extended period of time.

2.1.2 Continuous Long-term Disc Membrane Test Apparatus

In the second phase of the membrane testing, the system used in the preliminary studies was modified to allow for continuous long-term unattended operation. Helium was substituted for a part of inert nitrogen in the coal gas to provide an unambiguous quantitative detection of leak flow through unfilled membrane pores or around the graphite seal. Annular graphite gaskets were used for sealing the membrane instead of wrapping a graphite tape around the membrane. In addition, GCs with higher resolution detectors were used to provide simultaneous measurements of H₂S, He, and H₂ in the permeate stream.

To allow for continuous long-term unattended operation, a modified condensate drain system was installed on both the feed and sweep side condensers. The drain system is shown schematically in Figure 2-3. A small continuous gas flow is maintained through the drain system to force the accumulated condensate in a large reservoir continuously. Tests indicated that these systems could be operated successfully with as little as 200 cc/min vent gas flow rate.

The positive displacement pumps were replaced by high-pressure liquid pumps which could withdraw water continuously from a large reservoir increasing its capacity substantially. A flow control valve was installed in the sweep gas exit line prior to its merging with the feed gas exit stream. This valve allowed adjustment of the transmembrane differential pressure drop without changing the feed and sweep gas flow rates. Two cylinder manifolds were installed for both the feed gas and sweep gas continuous supply. Each manifold is connected to two gas cylinders of the same composition, which allows replacing an empty cylinder without interrupting system flows.

Figure 2-1. Test apparatus used in preliminary disc membrane studies.

Figure 2-2. Schematic of membrane test cell design.

Figure 2-3. Schematic of a continuous condensate drain system.

2.1.3 Continuous Long-term Tubular Membrane Test Apparatus

For testing the tubular membranes, the membrane disc holder was replaced by a 1.5-in. dia, 18-in. long stainless-steel reactor tube closed by 1.5 in. caps. Weld fitting joints were used to allow for feed and sweep inlet and outlet connections. The ceramic membrane tubes were approximately 15 mm in outside diameter. A tube was connected to 1/4 in. stainless-steel tubing using 15 mm to 1/2 in. and 1/2 in. to 1/4 in. stainless-steel reducing unions as shown in the reactor schematic in Figure 2-4. Custom-designed 15-mm graphite ferrules were used for sealing a membrane tube in the reducing unions on both ends. The existing furnace was large enough to house the tubular membrane reactor assembly. All other system components were the same as used in the continuous long-term disc membrane testing.

2.1.4 Simulated Coal Gas and Sweep Gas Compositions

For bulk of the experimental runs, gas composition similar to the KRW gasifier coal gas composition was used as the membrane feed gas. KRW coal gas typically consists of 10 percent hydrogen, 15 percent carbon monoxide, 5 percent carbon dioxide, 0.5 percent hydrogen sulfide, 54.5 percent nitrogen, and 15 percent water vapor. Dry gas mixture consisting of 12 percent hydrogen, 18 percent carbon monoxide, 6 percent carbon dioxide, 0.6 percent hydrogen sulfide with balance nitrogen was therefore used as feed gas in the preliminary disc experiments. During these experiments, it became apparent that it would be desirable to include a unique inert gas species in the feed gas to quantitatively determine the contribution of leak to the overall permeation. Six percent helium was therefore substituted for nitrogen as a tracer gas for the long-term disc and tubular membrane experiments. The exact gas composition used in each individual experiment was somewhat different due to the variability in the gas received from suppliers and was noted for all runs. In some experiments, a 2 percent hydrogen sulfide in nitrogen gas mixture was used as a feed gas to maximize H_2S , CO_2 , as well as H_2O concentration gradients for greater facilitation of H_2S transport.

In all experiments 30 percent CO_2 in N_2 was used as a dry sweep gas. The water vapor concentration in the sweep stream was always kept slightly greater than that in the feed stream. For the preliminary disc membrane experiments and earlier long-term disc membrane experiments, 15 percent water vapor was used in the feed stream as being typical of the KRW coal gas. The water vapor concentration in the sweep gas in these runs was kept about 16 percent. During the earlier long-term membrane experiments it became apparent that carbon deposition may become a problem for longer duration runs. Therefore, in subsequent runs, the water vapor concentration in the feed gas was increased to 25 percent to prevent carbon formation. The water vapor concentration in the sweep gas was kept at 26 percent in these experiments.

During the initial heating of the membrane to the desired temperature, a 5 percent CO_2 in N_2 gas was used as a purge gas instead of actual coal gas. Also, during the preliminary disc membrane experiments, a membrane was often kept molten during nontesting hours while maintaining a small purge gas and sweep gas flows on the two sides of the membrane.

Figure 2-4. Schematic of a symmetrical half of the tubular membrane reactor assembly.

2.1.5 Experimental Procedure

Generally, the same experimental procedure was used for all runs. A disc or tubular membrane was loaded in a holder or a tubular reactor, respectively, using graphite tape (preliminary disc membrane experiments), annular graphite gaskets (long-term disc membrane experiments), or graphite ferrules (tubular membranes) for sealing the membrane against the housing. The membrane holder is then leak tested at room temperature by pressurizing the feed side with nitrogen and monitoring the leak flow by bubble flow meter. For tubular membranes the membrane tube was pressurized on the inside. The bolts on the holder or the fittings in the tubular membranes were then tightened until the leak rate was minimized at 20 psig feed pressure. For disc membranes it was often possible to stop the leak completely. All tubular membranes, however, were found to be porous enough to permit a very small leak flow of the order of 0.2 to 0.4 cm³/min at 20 psig pressure differential. The maximum transmembrane pressure drop imposed in actual runs was about 20 in. of water. Thus, the expected leak rate in the case of tubular membranes was still very small. The leak rate by porous flow in actual experiments was determined from the helium permeation rates during the long-term experiments.

The loaded membrane holder or the tubular reactor is then installed in the furnace and connected to the respective feed and sweep lines. The membrane is then heated gradually, in stages, to the desired temperature while flowing the purge gas on the feed side and the sweep gas on the permeate side at the desired flow rates. Upon reaching the target temperature, the system pressure is raised to the appropriate level. Both the feed and sweep side high pressure water pumps are then turned on to inject the appropriate amount of water vapor. Deionized water was used as the source of water. During the early preliminary disc membrane experiments it became apparent that the dissolved oxygen in the deionized water may be contributing to some extent to the membrane deactivation by oxidizing the alkali salt to sulfates. To eliminate this possibility, the water supply was aerated continuously by nitrogen to remove dissolved oxygen. The transmembrane pressure drop across the membrane was usually adjusted to 10 to 20 in. of water on the sweep side to reduce the viscous flow contribution.

After allowing enough time for the steam to reach condensers, the flow on the feed side was switched from the purge gas to the coal gas. The exit sweep stream was continuously monitored by GCs to determine H₂S, H₂, and He concentrations. Since the permeation rates of all species were fairly small, no measurable change in the feed gas composition was anticipated. Therefore, the feed gas exit stream was monitored only periodically with another on-line GC.

2.2 EXPERIMENTAL MATRIX

The primary operating variables during testing of a membrane were membrane temperature and system pressure. In bulk of the experiments, KRW coal gas was used as a feed gas. In some experiments, a 2 percent hydrogen sulfide in nitrogen gas mixture was used as a feed gas to maximize H₂S transport. The membrane temperatures during the disc experiments ranged from 555 to 660 °C and the system pressures ranged from 50 to 200 psig. The bulk of the experiments were conducted at about 560 °C and 50 psig system pressure. During the long-term tubular membrane experiments the membrane temperatures ranged from 490 to 560 °C and the system pressure ranged from 50 to 100 psig. The bulk of the tubular membrane experiments were conducted at 50 psig pressure.

The dry sweep gas flow rate for the preliminary disc membrane experiments ranged from 1.3 to 2 std. L/min, whereas, during the long term continuous experiments approximately 1 std. L/min of dry sweep gas flow rate was used. The dry feed gas flow rate for all experiments was approximately 1 std. L/min.

In all the preliminary disc membrane experiments and in early long-term continuous disc membrane experiments, approximately 15 percent water vapor was used on the feed side as being typical of the KRW coal gas. In the latter part of the long-term disc membrane experiments and in all of the tubular membrane experiments, the feed side water vapor content was increased to 25 percent to minimize carbon deposition. The corresponding sweep side water vapor contents were 16 and 26 percent, respectively.

SECTION 3

RESULTS AND DISCUSSION

Permeation data collected in all three experimental phases were analyzed to determine the membrane permeability for H_2S as well as other gases and the membrane selectivity with respect to H_2S as a function of operating conditions. Since the experimental setups were somewhat different in the three phases of the membrane testing the results obtained in each phase are discussed separately. The membranes used in all of the experiments and their respective percent salt infiltrations are given in Table 3-1.

3.1 PRELIMINARY DISC MEMBRANE TESTING

The objective of the preliminary disc membrane experiments was to verify the transport of H_2S across the molten salt impregnated ceramic membranes and to determine the order of magnitude of H_2S permeation and selectivity with respect to other gases. The focus was on confirming the facilitated transport mechanism involving H_2S reaction with the alkali carbonates and to determine the operating conditions under which measurable H_2S permeation could be obtained. A total of four membranes were investigated in this phase, each membrane being tested over a period of several days. The amount of salt infiltration in these membranes ranged from 72 to 82 percent by weight. Since this phase was more of a scoping study, only short-term experiments were conducted, i.e., a set of operating conditions was held constant only for a period of 1 to 4 hours. These membranes were kept molten during nontesting hours with a small flow of CO_2/N_2 purge and sweep gases on both sides of the membranes. In general, membranes were found to be very dynamic in nature with small pressure fluctuations in the feed or sweep side causing immediate surges in concentrations of permeating species on the sweep side. A steady state was therefore found to be difficult to achieve during these short-term experiments. The permeation data collected during reasonably steady-state operations in these four runs are given in Table 3-2 along with the respective operating conditions.

Hydrogen and carbon monoxide concentrations were measured in the permeate stream along with H_2S concentrations to provide an indication of permeation across the membrane by porous viscous and diffusive flow mechanisms. Any H_2S transport in excess of that accounted by the porous viscous flow and diffusion mechanisms was considered to provide an indication of an enhanced facilitated transport of H_2S .

In all preliminary disc membrane experiments, dry feed gas composition corresponding to KRW coal gas was used which typically consisted of 18 percent CO , 12 percent H_2 , 6 percent CO_2 , 0.6 percent H_2S with balance N_2 . The sweep gas consisted of 30 percent CO_2 in N_2 .

3.1.1 Run No. 1

During loading of the first membrane to be tested in the membrane holder, a graphite tape wrapped around the ceramic membrane disc was found to provide a better seal than the "C" rings in the original membrane holder design (see Figure 2-2). This membrane was found to be very susceptible to small pressure fluctuations, e.g., those caused by draining of the condensate from the condensate separator catch-pot. Small changes in the transmembrane pressure drop were found to have a strong effect on the permeate concentrations indicating significant viscous flow contribution.

Table 3-1. Percent Salt Infiltrations in the Membranes Used

Run No.	Membrane No.	Percent salt Infiltration by weight
1	12496-13-1	80
2	12496-15-4	81
3	12496-13-3	82
4	12496-21-2	72
5	12496-21-5	72
6	12496-21-3	68
7	12496-23-5	68
8	12496-23-6	72
9	12496-23-8	67
10	12496-23-7	74
11	12496-24-5	65
12	12496-24-3	34
13	12496-24-1	69
14	12496-24-6	66
T-2	12496-26-T2	74
T-3	12496-26-T3	82
T-4	12496-26-T4	87.3

Table 3-2. Experimental Results of Preliminary Disc Membrane Experiments

Run No.	Date	Temp. (°C)	Pressure (psig)	Sweep gas flow rate dry scc/sec	Permeate conc. (ppm)				Permeability (Barrer x 10 ⁻⁴)				Selectivity	
					H ₂ S	COS	H ₂	CO	H ₂ S	COS	H ₂	CO	H ₂ S/H ₂ (COS/H ₂)	H ₂ S/CO (COS/CO)
1	10/28/92	570	50	21.7	30	0	NM	NM	82.9	—	—	—	—	—
	10/28/92	570	200	21.7	55	0	150	NM	45.8	—	6.4	—	7.2	—
	10/28/92	650	50	21.7	58	0	230	NM	60.2	—	32.4	—	4.9	—
	10/30/92	660	50	21.7	10	0	85	9	27.6	—	12.0	0.9	2.3	30.7
2	12/11/92	570	50	37.2	—	2.3	28	NM	—	11.1	6.9	—	1.6	—
	12/14/92	570	50	37.2	—	0.8	ND	NM	—	3.9	<0.7 ^a	—	>5.5	—
	12/14/92	605	50	37.2	—	1.1	ND	NM	—	5.3	<0.7 ^a	—	>7.6	—
	12/15/92	570	50	21.7	1.9	—	57	32	5.3	—	8.2	3.0	0.65	1.8
	12/15/92	570	100	21.7	3.6	—	94	28	5.7	—	7.7	1.5	0.74	3.8
4	1/27/93	560	53	33.1	0.45	—	ND	ND	1.9	—	<0.6 ^a	<1.4	>3.2	>1.4
	1/28/93	560	51	33.1	0.80	—	ND	ND	3.5	—	<0.7 ^a	<1.5	>5.0	>2.3
	1/28/93	560	200	39.1	1.0	—	ND	ND	1.6	—	<0.2 ^a	<0.5	>8.0	>3.2
	1/29/93	560	54	33.1	1.0	—	9	ND	4.0	—	1.8	<1.4	2.2	>2.9
	1/29/93	606	54	33.1	2.0	—	14	ND	8.2	—	3.0	<1.4	2.7	>5.9
5	2/4/93	560	52	33.1	0.51	—	ND	ND	2.0	—	<0.6 ^a	<1.4	>3.3	>1.4
	2/4/93	560	200	39.1	0.46	—	ND	ND	0.7	—	<0.2 ^a	<0.5	>3.5	>1.4

NM = Not measured.

ND = Not detected.

^a Hydrogen and CO concentrations were assumed to be 3 and 10 ppm, respectively, equal to detection limits.

the transmembrane pressure drop were found to have a strong effect on the permeate concentrations indicating significant viscous flow contribution.

During the course of testing this membrane, it was discovered that in the absence of steam on the sweep side, carbonyl sulfide is liberated instead of H₂S. This fact was easily explained by the reaction of CO₂ alone with the sulfide (S²⁻) ions in the melt instead of reaction given in Equation (1-1):

Gradual increase in H₂S (or COS) concentrations was also often observed consistent with the reaction pathway and establishment of S²⁻ ion concentration gradient across the membrane. Reasonably steady-state data were collected on only four occasions as shown in Table 3-2. In general, increasing system pressure was found to increase H₂S concentration in the permeate stream; however, as data in Table 3-2 indicate, the permeability actually decreased with pressure consistent with the facilitated transport behavior. Increasing temperature was also found to increase the membrane permeability for H₂S. The membrane performance, however, was found to degrade with time as seen from the second set of data obtained at the higher temperature.

The membrane permeability for H₂S was quite high and ranged from 2.7x10⁵ to 1.6x10⁶ Barrers (1 Barrer = 10⁻¹⁰ cm³-cm/cm²-s-cm of Hg). The measured H₂ permeabilities were also high and ranged from 6x10⁴ to 1.2x10⁵ Barrer units. The measured permeability for CO was about 9,000 Barrers. The expected permeability of hydrogen based on solution diffusion mechanism is of the order of only 200 Barrers. Thus, the high permeability for H₂ and CO indicates substantial leakage. The membrane still exhibited significantly higher selectivity for H₂S when compared with H₂ and CO, indicating transport of H₂S in excess of that accounted by leakage.

3.1.2 Run No. 2

The membrane used in this run was also found to be very dynamic and susceptible to small differential pressure changes. In the early part of this run, no gradual increase in H₂S was observed on the permeate side with H₂S containing coal gas on the feed side and 30 percent CO₂ sweep gas with steam on the permeate side. Similar to Run No. 1, steam was then turned off on the sweep side. After about 2 hours, at 570 °C and 50 psig conditions, COS was detected on the permeate side which began rising with time. Data collected after leveling off of permeate concentrations are shown in Table 3-2. Hydrogen concentrations in the permeate were also significant as seen from these data. On the next day, the effect of temperature was investigated on COS formation. Incidentally, on this day, hydrogen concentrations were below detection limit unlike the previous day. It appeared that, by keeping the membrane in purge gas, CO₂ atmosphere with negligible flows may seal any pores exposed during the flow testing conditions. Higher temperature operation increased the COS permeation. In general, the H₂S and other permeabilities were much lower than those observed in Run No. 1 perhaps due to less leakage. H₂S selectivities were also lower, except for the data collected on 12/14/92 when both H₂ and CO concentrations were found to be below detection limit.

On subsequent days, additional data were collected in the presence of steam on the sweep side with H₂S being formed instead of COS. Significant CO and H₂ concentrations, however, were also observed as seen from data presented in Table 3-2. Eventually, H₂S

concentrations in the permeate appeared to decrease with time, indicating degradation of membrane performance. One potential reason for membrane degradation is sulfate formation in the molten salt which reduces the amount of active species in the melt. Possible sources of oxygen include trace amounts in the sweep gas cylinders and dissolved oxygen in the water used to form steam. Oxygen-free sweep gases were used in the subsequent runs. Also the water reservoir was aerated with nitrogen in subsequent runs to remove dissolved oxygen from the deionized water.

3.1.3 Run No. 4

Run No. 3 was aborted because of the carbon formation during startup leading to plugging and no data were collected. The steady-state data obtained in Run No. 4 are shown in Table 3-2. KRW coal gas was used as feed gas and data were collected at two pressures and two temperatures. Operating conditions were kept constant for about 2 hours (by avoiding draining of condensate) before collecting steady-state data. The data collected for identical operating conditions on subsequent days appeared to be different, e.g., those on 1/27/93 and 1/28/93, indicating a need for a long-term continuous operation. During the overnight conditions of low purge and sweep CO_2 gas flows, the sulfide and carbonate ion concentrations within the melt apparently redistribute to achieve uniform concentrations. Thus, at the beginning of the next day, owing to the greater sulfide concentration on the permeate side of the membrane, the H_2S concentration in the permeate is always found to be greater than that at the end of the previous day.

The data collected at 50 and 200 psig system pressures indicated reduction in H_2S permeability at the higher pressure. This is generally consistent with the facilitated transport mechanism. Increasing membrane temperature was found to increase the H_2S permeability significantly. The CO concentrations in the permeate were below detection limit throughout the duration of this run indicating good sealing of the membrane. Hydrogen concentrations were also below detection limit for the first few days. Run No. 4 was the first good run indicating H_2S transport in the absence of any significant CO and H_2 transport, thus emphasizing the potential for significant H_2S selectivity over H_2 in these membrane systems. Membrane degradation observed in Runs No. 1 and 2 appeared to be reduced in Run No. 4. The measured H_2S permeabilities ranged from 16,000 to 82,000 Barrers well in excess of those expected by the solution diffusion mechanism.

3.1.4 Run No. 5

This run attempted to reproduce the results obtained in Run No. 4, using a new membrane. Steady-state data obtained at 50 and 200 psig system pressure at 560 °C are shown in Table 3-2. H_2S permeation observed at 50 psig condition was similar to that observed in Run No. 4, whereas H_2S permeation observed at 200 psig pressure was lower than in the previous run. Both the hydrogen and CO concentrations in the permeate was below the detection limit, thus indicating potentially high H_2S selectivities for this membrane.

3.1.5 Summary and Discussion

The preliminary disc membrane experiments indicated significant H_2S transport across the membrane and identified several interesting trends as summarized below:

- Permeability of the molten salt impregnated ceramic membranes was often greater for H_2S than that for H_2 and CO , indicating enhancement of H_2S transport over the porous viscous and diffusive flow mechanisms.
- Concentration of H_2S in the permeate increases gradually before apparent leveling off. This fact is consistent with the reaction pathway for H_2S transport and the time needed for diffusion of sulfide ions (S^{2-}) within the liquid phase to establish a concentration gradient.
- In the absence of steam on the sweep side, COS is liberated instead of H_2S . The concentration of COS was also seen to increase gradually with time. These observations are consistent with establishment of S^{2-} ion concentration gradient in the liquid phase and subsequent reaction of S^{2-} ions with CO_2 on the permeate side.
- Permeability of H_2S was found to decrease with increasing feed pressure, consistent with facilitated transport of H_2S . For conventional, solution diffusion mechanism, the permeability is expected to increase with the feed pressure.
- Permeability of H_2S was found to increase with increasing temperature, presumably due to increased diffusivity of the S^{2-} ions in the liquid phase.
- The susceptibility of the disc membranes to small changes in the transmembrane differential pressure, of the order of 1 to 2 psi, indicates either failure of the graphite seal at higher temperature or the presence of unfilled and/or relatively large pores in the ceramic membrane matrix which allow leakage of gases. (Approximate calculations indicate that 1 μm pores should be able to hold salt by capillary suction against 70 psi pressure differential.) The pressure fluctuations usually occurred with draining of the condensate. Thus, a continuous condensate draining system would be desirable to prevent system pressure upsets.
- The membrane often exhibited different steady states on subsequent days after keeping the membrane molten with low purge and sweep gas flow rates without steam. The H_2S concentration in the permeate, in the presence of steam, was also usually higher at the beginning of a day as compared to that at the end of the previous day. During the overnight conditions of low purge and sweep CO_2 gas flows, the sulfide and carbonate ion concentrations within the melt apparently redistribute to achieve uniform concentrations. Thus, at the beginning of the next day, owing to the greater sulfide concentration on the permeate side of the membrane, the H_2S concentration in the permeate is always greater than that at the end of the previous day. This observation indirectly corroborates the facilitated transport mechanism and identifies a need for a long-term continuous operation.
- In general, H_2S concentrations in the permeate were low, less than a few parts per million. The H_2 and CO concentrations were often below detection limits of the detectors used. Thus, these preliminary experiments indicated a need for greater resolution in the GC analysis.

3.2 CONTINUOUS LONG-TERM DISC MEMBRANE TESTING

The purpose of the long-term disc membrane testing was to further substantiate facilitated transport mechanism for H_2S permeation and to investigate membrane stability and performance over a long period of time. In these tests, the experimental system used during preliminary studies was modified to allow continuous operation as described in Section 2.1.2. In the preliminary experiments, permeation of H_2S was compared with the permeation of H_2 and CO to determine the membrane selectivity with respect to H_2S . However, both of these gas species may have alternative sources in addition to permeation through the membrane, e.g., H_2 may be formed by reaction of steam with the metallic parts of the membrane holder on the permeate side or even by decomposition of permeated H_2S . Similarly, CO may be formed by reverse water gas shift reaction on the permeate side. In order to obtain quantitative determination of permeation due to porous viscous or diffusive flow mechanism, an inert gas, helium, was added to the coal gas in all of the long-term membrane experiments.

A total of nine disc membranes were tested in continuous long-term operation mode. The amount of salt infiltration in these membranes ranged from 65 to 74 weight percent except for a thicker membrane used in Run No. 12 which had only 34 percent salt infiltration. The modifications made to the condensate drain system virtually eliminated system pressure fluctuations, allowing operation at small controllable transmembrane differential pressures of 0 to 2 psi. More sensitive detectors were used in the GCs with a detection limit of 0.1 ppm for H_2S and 2 ppm for both helium and hydrogen. With the system modifications, it was possible to maintain the same operating conditions over a period of days instead of a few hours as in the case of the preliminary experiments. The steady-state data obtained in the continuous long-term disc membrane tests are summarized in Table 3-3. The results obtained in each experiment are described below separately.

3.2.1 Run No. 6

During this first long-term run, steady-state membrane permeation data were obtained using two feed gas compositions: (1) similar to KRW coal gas with steam and (2) 2 percent H_2S in N_2 without steam. The operating conditions were 50 psig pressure and 560 °C temperature and the corresponding data are presented in Table 3-3. Early on during this run, it became evident that a long time of several hours was needed to achieve steady-state membrane operation in contrast to the preliminary experiments. The primary difference in the long-term experiments and the preliminary experiments was the lack of pressure upsets in the long-term runs which usually caused sudden bursts of high H_2S and other gas species concentrations in the preliminary experiments. Perhaps, these occasional high concentration leaks helped more rapid sulfidation of the salt layer and allowed a steady state in a shorter time in the preliminary experiments.

Both the steady-state data and the transient time dependent data could be used to determine the reaction equilibrium constant and the liquid phase diffusion coefficient as described in Section 4. After collecting the initial data, the molten salt in the membrane was accidentally solidified because of power failure which turned off the furnace. The salt was remelted and data were collected under conditions similar to the initial data as shown in Table 3-3. The membrane's ability to permeate H_2S was found to be reduced as indicated by the higher temperature needed to obtain similar H_2S permeation rate using coal gas as feed. The membrane degradation may be due to freezing and remelting process.

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**Figure 3-1. Helium and H₂S concentrations with time
(Run #6, 5/3/93, 50 psig, 556 °C).**

**Figure 3-2. Helium, hydrogen, and H_2S concentrations with time
(Run #6, 5/4/93, 50 psig, 556 °C).**

**Figure 3-3. Helium, hydrogen, and H_2S concentrations with time
(Run #6, 5/5/93, 50 psig, 556 °C).**

Figure 3-4. Helium, hydrogen, and H₂S concentrations with time (Run #8, 6/4/93 – 6/6/93, 50 psig, 615 °C).

The membrane permeability for H_2S ranged from 40,000 to 60,000 Barrers and the H_2S selectivities with respect to hydrogen and helium were found to be 3.4 and 6.1, respectively. Both the helium and hydrogen concentrations were found to increase slowly with time in this run as seen in the concentration/time plots shown in Figures 3-1, 3-2, and 3-3 indicating a slow increase in the leakage rate with time. The transient H_2S concentration data, e.g., that seen in Figure 3-1 may be used to estimate the liquid phase diffusion coefficient.

3.2.2 Run No. 7

This experiment was conducted with KRW coal gas with steam as feed gas and 30 percent CO_2 in N_2 as sweep gas. The system pressure and temperature were 50 psig and 560 °C, similar to the last run. This membrane did not indicate any H_2S permeation over 6 hours, although helium and hydrogen concentrations in the permeate were significant. This run was therefore terminated. The reasons for the membrane inactivity were not clear. Incomplete salt penetration into the ceramic matrix leading to an inner zone of no salt is a possibility.

3.2.3 Run No. 8

This experiment was carried out with the feed gas composition similar to the KRW coal gas and was continued for almost 4 days from 6/4/93 to 6/7/93. The sweep gas composition and the steam flow rates were the same as in the previous runs. The membrane conditions were kept at 50 psig pressure and 615 °C for about 2½ days. As seen from the concentration/time plot shown in Figure 3-4, for the first 4 to 5 hours both helium and H_2S concentrations in the permeate were negligible, and hydrogen concentrations were below 4 ppm. All three concentrations began rising in the permeate for the next 7 to 8 hours. The permeate H_2S concentration went through a peak of about 6 ppm and then leveled off to about 2.7 ppm. The helium and hydrogen concentrations went through peaks of 10 and 30 ppm with mean concentrations of 8 and 26 ppm during the leveling off period for the H_2S concentrations. The resulting selectivities of H_2S permeation with respect to helium and hydrogen were about 3.4 and 1.04 respectively. The H_2S selectivities at peak concentrations were about 5.9 and 2.4, respectively.

The reasons for much higher hydrogen concentrations than helium concentrations were not clear. Decomposition of permeated H_2S may partially account for the higher hydrogen concentrations. It is interesting that the peaking of hydrogen and helium concentrations occurred soon after the peaking of H_2S concentration.

At the end of the 2½ day run, it was apparent that there was significantly more pressure drop on the sweep side of the membrane holder. At this time the temperature was reduced to 575 °C; however, the pressure drop continued to increase with time. An attempt was made to obtain permeation data at a higher system pressure of 200 psig. However, a leak was developed in the membrane during pressurization on both sides of the membrane. By the time the membrane was stabilized the sweep side pressure drop had become excessive and the run was aborted. Upon disassembly of the membrane, the sweep side pressure drop was attributed to oozing of the molten salt on the sweep side (which was also the bottom side) and blocking the gas flow in the small gas flow clearance space. The oozing of the salt from the membrane pores due to gravity indicates presence of some pores much greater than 1 μm . In order to prevent such blockage in future experiments, the gas flow clearance on the sweep (bottom) side of the membrane holder was increased by increasing the depth of the recessed space in the membrane holder.

3.2.4 Run No. 9

This run was carried out on 6/23/93 to 2/4/93, with experimental parameters of 600 °C temperature and 50 psig pressure. The experimental conditions were maintained constant for about 5 hours until the end of the day, and the testing was continued overnight. H₂S and helium concentrations began to appear in the sweep gas after about 3 hours. For the next 6 to 7 hours H₂S and H₂ concentrations increased continuously to about 9 and 20 ppm, respectively, whereas helium concentrations stabilized to about 3 to 4 ppm. At this point, apparently a leak was developed in the membrane resulting in very high concentrations of permeating species in the sweep gas. Although the run continued, the measured concentrations were erratic. The next morning, the system pressure was found to have increased to about 140 psig (from 50 psig). A filter before the BPR was found to be clogged causing the pressure increase. This run was therefore aborted, although the membrane was kept molten with purge CO₂/N₂ gas mixtures flowing on both sides. The clogged filter element was removed. All the filter elements made for 1/8 in. tube fittings were replaced with larger filter elements made for 1/4 in. tube fittings.

The concentrations prior to the system upset are shown in Figure 3-5. The final concentrations in this plot were used to estimate the membrane permeabilities and selectivities. As seen from the Table 3-3, the H₂S permeability at this point was about 2×10^5 Barrers. The membrane selectivities for H₂S with respect to helium and hydrogen were about 18 and 11.

The membrane used in the previous run was reused on 6/28/93 with identical experimental conditions. However, within the first 3 hours it became apparent that on the test side of the membrane holder there was an excessive pressure drop and it was impossible to balance the pressures on both sides of the membrane. The run was therefore aborted. Upon disassembly of the membrane, the feed side pressure drop was attributed to carbon deposits on the membrane near the inlet feed gas opening blocking the gas flow. Carbon may form if the steam concentration is not adequate to prevent reverse gasification reactions. In order to determine the effect of feed side steam concentration on carbon formation, a dummy run was made on June 30 using a stainless-steel disc instead of the membrane and a feed side steam concentration of 25 percent by volume. All other conditions were the same as in this run. The membrane differential pressure gauge was monitored for any evidence of increased pressure drop on the feed side. The differential pressure remained constant over a 6-hour period indicating a stable system operation. No helium or hydrogen was detected in the sweep outlet gas.

3.2.5 Run No. 10

This run was carried out on 7/6/93 to 7/9/93 with experimental parameters of 600 to 640 °C temperature and 50 psig pressure. Thirty percent CO₂ in N₂ was used as sweep gas. The steam content in sweep gas was about 16.7 percent. Due to high CO and H₂ concentrations in the coal gas used, steam concentration in the membrane feed gas was maintained at about 25 percent to minimize carbon formation. The temperature was initially maintained at 600 °C. This membrane did not indicate any significant H₂S permeation for first 24 hours except for a brief period of H₂S concentrations in sweep gas of 0.2 ppm. The temperature was, therefore, increased to about 640 °C to increase membrane activity. The helium concentration in the sweep gas was negligible for first 16 hours indicating good sealing of the membrane. The helium concentration then increased to about 5 ppm in the next 8 hours. After raising the membrane temperature, H₂S concentration reached a steady-state level of 0.54 ppm in sweep gas in about 5 hours. The H₂S concentrations remained at this level for about 5 hours and then declined to

Figure 3-5. Helium, hydrogen, and H₂S concentrations with time (Run #9, 6/23/93, 50 psig, 600 °C).

about 0.3 ppm in next 6 to 7 hours. At this point the steam concentration on the feed side was decreased to 15 percent which increased the H₂S concentration to another steady-state level of 0.66 ppm where it remained for about 4 hours. Helium concentrations in the sweep gas, however, also increased at the same time to about 12 ppm. The membrane temperature was then decreased to 600 °C to determine the effect of temperature on membrane performance. The sweep gas H₂S concentration decreased to about 0.4 ppm and remained at this level for next 3 hours and then decreased to less than 0.1 ppm in next 3 hours. During the same time helium concentrations increased to about 20 ppm.

The observed H₂S selectivity of the membrane with respect to helium was only 1.3 during the 5 hour steady-state period at 640 °C with H₂S permeability of 13,000 Barrers. The hydrogen concentrations in the sweep gas were consistently higher than helium with a hydrogen selectivity with respect to helium of about 1.9 during the latter half of the experimental run.

3.2.6 Run No. 11

This run was conducted on 8/4/93 to 8/7/93. A mixed coal gas composition consisting of 24.6 percent H₂, 29.3 percent CO, 10.4 percent CO₂, 6.6 percent He, 0.9 percent H₂S, and balance N₂ was used as feed gas. The membrane was maintained at 607 °C and the system pressure was varied from 50 to 150 psig. Thirty percent CO₂ in N₂ was used as sweep gas. The steam content in sweep gas was about 26 percent. Due to high CO and H₂ concentrations in the coal gas used, steam concentration in the membrane feed gas was maintained at about 25 percent to minimize carbon formation. At the initially 50 psig system pressure, a steady state was observed after about 19 hours with steady concentrations of H₂S, helium, and H₂ of 1.4 ppm, 19 ppm, and 135 ppm, respectively. The selectivity of H₂S with respect to helium was about 0.6 with H₂S permeability of 23,000 Barrers. After increasing the system pressure to 100 psig, the H₂S concentrations first reached an apparent steady-state level of 2.1 ppm which held for several hours, resulting in H₂S permeability of 19,000 Barrers. The H₂S concentration then declined continuously. The helium and hydrogen concentrations were stable at approximately 20 ppm and 150 ppm, respectively. Upon increasing the system pressure to 150 psig, both the helium and hydrogen concentrations in the permeate increased, whereas the H₂S concentration declined continuously. The membrane was believed to be slowly deactivating, and the run was terminated after 75 hours of total operation.

3.2.7 Run No. 12

This run was conducted with one of the thicker membranes on 8/16/93 to 8/19/93. KRW coal gas composition consisting of 12.3 percent H₂, 6.4 percent He, 17.6 percent CO, 6.2 percent CO₂, 0.67 percent H₂S, and balance N₂ was used as feed gas. 30 percent CO₂ in N₂ was used as sweep gas. The steam content in sweep gas was about 26 percent. The steam concentration in the membrane feed gas was maintained at about 25 percent to minimize carbon formation. The temperature was maintained at 605 °C and the system pressure was maintained at 50 psig. No H₂S was detected in the permeate during a 60-hour run although significant amounts of helium and hydrogen were found in the permeate. The run was terminated after 60 hours. The membrane used in this run cracked during disassembly. The exposed cross section of this membrane indicated incomplete penetration of salt into the membrane.

3.2.8 Run No. 13

This experimental run was conducted with the thin membrane with identical conditions as in Run No. 12 on 8/24/93 to 8/25/93. In this run also, no H₂S was detected in the permeate although a significant concentration of helium and hydrogen was present in the permeate. This run was terminated after 24 hours.

3.2.9 Run No. 14

This run was conducted on 8/30/93 to 9/4/93. Due to the lack of H₂S permeation in the last two runs using coal gas, this run was begun with 2.9 percent H₂S in nitrogen as feed gas. The membrane temperature was maintained at 560 °C and no steam was added to the feed gas. Thirty percent CO₂ in N₂ was used as sweep gas with about 15 percent steam. The system pressure was initially maintained at 50 psig. The first trace of H₂S appeared in the permeate after about 8 hours. The H₂S concentration then steadily increased to reach a steady-state level of about 17 ppm. The system pressure was then raised to 100 psig. The same level of the steady-state concentration was again reached. The system pressure was then increased to 200 psig. The H₂S concentration again appeared to be steady at about 17 ppm, consistent with facilitated transport mechanism. These data are shown in Table 3-3.

The feed gas was then changed to the typical KRW coal gas composition. The steam content on the test side was about 25 percent and that on the sweep side was about 26 percent. The membrane temperature was again maintained at 560 °C and the system pressure was decreased to 50 psig. H₂S concentration in the permeate decreased to a new steady-state level of 4.3 ppm with helium and H₂ concentrations of 5.5 ppm and 35 ppm, respectively. The H₂S selectivity with respect to helium was about 7 and that with respect to hydrogen was about 2.5. The H₂S permeability was about 92,000 Barrers. The system pressure was then raised to 100 psig. The new apparent steady-state concentrations of H₂S, helium, and H₂ were about 3 ppm, 7.5 ppm, and 47 ppm, respectively. The selectivity of H₂S with respect to helium decreased to about 4 and that with respect to hydrogen to only 1.1. The concentration/time for this run are shown in Figures 3-6 and 3-7.

Finally, the system pressure was then raised to 200 psig. After several hours, the transmembrane pressure drop increased substantially indicating an obstruction to gas flow on the sweep side of the membrane holder. No steady-state data could therefore be obtained at 200 psig condition. The run was terminated after 110 hours of operation. Upon disassembly of the membrane holder, the gas flow blockage was attributed to oozing of the molten salt from the membrane around the gas flow opening.

3.2.10 Summary and Discussion

The long-term testing of the disc membranes in Runs No. 6 through 14 produced mixed results. Enhanced H₂S transport was observed in Runs No. 6, 8, 9, and 14, as evidenced by H₂S selectivities of greater than unity with respect to helium and hydrogen. Membranes used in Runs No. 7, 12, and 13 did not indicate any H₂S transport at all, whereas those used in Runs No. 10 and 11 produced poor selectivity. As seen in Table 3-1, all of these membranes had about the same amount of salt infiltration in the range of 65 to 74 percent by weight except for the thicker membrane used in Run 12 with only 34 percent by weight salt infiltration. Inspection of the cross section of the membrane used in Run No. 12 indicated an inner continuous zone of no salt

**Figure 3-6. Helium, hydrogen, and H₂S concentrations with time
(Run #14, 8/30/93 – 9/1/93, 50, 100, 200 psig, 560 °C).**

Figure 3-7. Helium, hydrogen, and H₂S concentrations with time (Run #14, 9/1/93 – 9/4/93, 50, 100, 200 psig, 560 °C).

infiltration. Figures 3-8(a) and 3-8(b) clearly show an inner zone of no salt infiltration in a cross section of an unused thicker membrane which had cracked during the loading process. A similar zone of incomplete salt infiltration is also evident, as seen in Figures 3-9(a) and 3-9(b), in the cross section of a membrane used in Run No. 10 which had exhibited poor H₂S selectivity. The cross sections of membranes used in Runs No. 6 and 8, which had shown enhanced H₂S transport, also indicate non-uniform salt infiltration as seen by pockets of no salt infiltrations in Figures 3-10(a), 3-10(b), 3-11(a), and 3-11(b).

For enhanced facilitated H₂S transport it is essential to have a continuous liquid phase exposed to feed and sweep gases on the two sides of a membrane. Any zones of discontinuity will obviously hinder the facilitated transport of H₂S by the reaction pathway. The extreme case of a continuous inner zone of no salt infiltration will completely prevent the facilitated transport of H₂S. In such an extreme case, the molten carbonate salt on the sweep side of the membrane will simply act as a scavenger for any H₂S leaking through the porous flow, thus explaining the presence of significant helium and hydrogen permeate concentrations without any measurable permeate H₂S concentrations in Run No. 12.

The nonuniformities in salt infiltration will also reduce the effective membrane cross-sectional area for H₂S transport, thus affecting the calculated membrane permeabilities. The membrane H₂S permeabilities observed in Runs No. 6, 8, 9, 10, 11, and 14 reflect a broad range in the calculated permeabilities that were based on a fixed membrane cross-sectional area. The calculated permeabilities for H₂S ranged from 13,000 to 200,000 Barrers. On the other hand, the observed helium permeabilities, which essentially provide an indication of leakage flow, ranged from 10,000 to 40,000 Barrers with most of the values about 10,000 Barrers. The H₂S to He selectivities for these runs were greater than unity except for Run No. 11 and ranged from 0.6 to 18. Hydrogen permeabilities were greater than those for helium, generally by a factor of two or more, and ranged from 18,000 to 79,000 Barrers. The corresponding H₂S selectivities with respect to hydrogen were lower and ranged from 0.3 to 11.

The overall results obtained in the long-term membrane testing are summarized below:

- Enhanced transport of H₂S was observed in several of the membranes tested with H₂S permeabilities in the range of 13,000 to 200,000 Barrers and H₂S to helium selectivities ranging from 0.6 to 18.
- Hydrogen permeabilities were greater than those for helium, generally by a factor of two, and ranged from 18,000 to 79,000 Barrers. The corresponding H₂S selectivities with respect to hydrogen were lower and ranged from 0.3 to 11.
- Unlike the preliminary disc membrane experiments, the relatively stable operating conditions in the long-term experiments required much longer time, of the order of several hours, to achieve steady-state permeate concentrations. This time requirement indicates a very slow liquid phase diffusion process which also limits the observed H₂S flux rates.
- The gradual increase in the permeate H₂S concentrations is consistent with the reaction pathway for H₂S transport and the time needed for diffusion of sulfide ions (S²⁻) within the liquid phase to establish a concentration gradient.

(a)

(b)

Figure 3-8. Cross section of an unused thicker membrane.

(a)

(b)

Figure 3-9. Cross section of a membrane used in Run No. 10.

(a)

(b)

Figure 3-10. Cross section of a membrane used in Run No. 6.

(a)

(b)

Figure 3-11. Cross section of a membrane used in Run No. 8.

- Increasing system pressure was consistently shown to reduce H₂S permeability, corroborating a facilitated transport process.
- The inconsistencies in the performance of different membranes may be explained by incomplete or nonuniform salt infiltration in the ceramic porous matrix.
- Helium and hydrogen concentrations generally increased over a long period of operation at a given temperature. This fact coupled with the observations of salt oozing from the membrane by gravity indicates the presence of large pores in the ceramic matrix unable to hold the salt in pores by capillary suction.

3.3 CONTINUOUS LONG-TERM TUBULAR MEMBRANE TESTING

The observed permeate H₂S concentrations in the long-term disc membrane experiments were low, ranging from 0.5 ppm to 9 ppm for coal gas conditions. Therefore, leakage due to the porous flow (viscous and diffusion) can have a substantial effect on the observed membrane performance. One source of leak is the graphite seals. The effect of leakage on the observed membrane performance can be minimized by increasing the membrane surface area. A tubular membrane offers a large membrane surface area while limiting the contribution by leakage at the seals. Membrane experiments with a tubular geometry that can increase the H₂S flux rates while minimizing leakage are thus desirable to assess the performance of the molten salt membranes.

The tubular membranes used in these studies were about 15-mm dia and 3.5-mm thick and ranged from 8 to 10 in. in length. During salt infiltration, the inside of the tube was blocked from the salt by graphite rods, i.e., the molten salt was infiltrated only from outside of these tubes. Custom-made 15-mm graphite ferrules allowed sealing the tube ends in 15 mm to 1/2 in. reducing unions. A total of three membrane tubes were tested for membrane performance in continuous long-term tests. The membrane permeability and selectivity data collected in these tests are shown in Table 3-4.

3.3.1 Run No. T-2

Shakedown tests (Run No. T-1) were first conducted using a blank, unimpregnated membrane tube to test the tubular membrane reactor assembly. Run No. T-2 was the first test conducted with a salt-impregnated membrane tube and was carried out over 5 days on 11/17/93 to 11/22/93. A small leak flow through the tube was observed at 20 psi pressure differential during the cold pressure test. The test run began with 30 percent CO₂ on both sides of the membrane at 50 psig pressure and 560 °C temperature. The initial hydrogen leak rate through the tube was determined by using a KRW clean coal gas (without H₂S) as a feed gas and was found to produce about 35-ppm concentration in the sweep outlet gas. The feed gas was then switched to the KRW coal gas with H₂S. During the first 24 hours, the hydrogen, helium, and H₂S concentrations increased substantially. The increase in sweep outlet concentrations was thought to be due to the downward gravitational flow of molten salt within the tube leading to opening of pores in the upper section of the tube. The temperature was then decreased to 500 °C. Relatively stable sweep outlet gas concentrations were observed during the next 16 hours. The H₂S selectivity with respect to helium was about 1.6 during this period. The selectivity with respect to hydrogen was about 1 during the same period. The system pressure was then increased to 100 psig. For the next 9 hours the sweep outlet helium and hydrogen concentrations began to increase, whereas H₂S concentration decreased slightly. At this point, during the over-

Table 3-4. Experimental Results of Continuous Long-term Tubular Membrane Experiments

Run No.	Date	Temp. (°C)	Pressure (psig)	Sweep gas flow rate dry scc/sec	Permeate conc. (ppm)				Permeability (Barrer x 10 ⁻⁴)				Selectivity	
					H ₂ S	H ₂	He		H ₂ S	H ₂	He		H ₂ S/H ₂	H ₂ S/He
T-2	11/18/93	560	50	16.7	34	590	210		2.7	2.35	1.67		1.15	1.62
	11/19/93	500	50	16.7	20	400	130		1.62	1.59	1.03		1.02	1.57
	11/21/93	500	50	16.7	12	840	270		0.95	3.34	2.14		0.28	0.44
	11/22/93 ^a	530	50	16.7	20	1,930	620		1.62	7.68	4.92		0.21	0.33
T-3	12/4/93	500	50	16.7	1.8	50	22		0.18	0.24	0.21		0.75	0.86
	12/6/93	516	50	16.7	2.6	85	38		0.25	0.42	0.37		0.6	0.68
T-4	12/16/93	510	50	16.7	0.3	40	15		0.02	0.15	0.11		0.13	0.18
	12/22/93	515	50	16.7	4.4	170	60		0.33	0.64	0.45		0.52	0.73
T-5	12/29/93	515	50	16.7	37	80	22		2.76	0.3	0.16		9.2	17.3
	12/30/93	515	50	16.7	31	85	25		2.31	0.32	0.19		7.22	12.2
	12/30/93 ^a	515	50	16.7	31	112	32		2.31	0.42	0.24		5.5	9.6

^aAt the end of the run.

Coal Gas ~12% H₂, 6% He, 6% CO₂, 18% CO, 0.6% H₂S, and balance N₂.

night operation, a leak developed in the membrane leading to very high sweep outlet concentrations. The next day the system pressure was reduced to 50 psig returning concentrations to stable levels for the next 20 hours. The H₂S selectivities with respect to helium and hydrogen were much lower during this period and were about 0.4 and 0.3, respectively. The membrane temperature was then increased from 500 to 530 °C. All the sweep outlet concentrations again began to increase; however, there was not any significant change in the H₂S selectivities with respect to other gases. The observed H₂S permeabilities were somewhat lower than those in disc membrane experiments and ranged from 9,500 to 27,000 Barrers.

The concentration and selectivity data collected during this continuous run of over 100 hours are shown in Figures 3-12, 3-13, and 3-14. The continuous rapid increase in the sweep outlet concentrations of both helium and hydrogen at 560 °C as well as 530 °C indicates that above 530 °C molten salt flows downward by gravity within the tube opening up pores in the upper section of the tube. Upon disassembly, salt deposits were observed on both inside and outside of the lower section of the tube, as seen in Figure 3-15(a) and 3-15(b), confirming the salt flow within the tube. The salt is much less mobile at 500 °C, as indicated by relatively stable permeate concentrations of helium and hydrogen. The H₂S selectivity with respect to helium and hydrogen was low indicating smaller contribution of diffusional H₂S transport to the overall permeate flow. The potential reasons for the poorer performance of the tubular membranes, as opposed to disc membranes, include (1) downward migration of salt, thereby opening up pores; (2) greater thickness of the tube, thus offering greater liquid phase diffusional resistance; and (3) unimpregnated part of the thickness on the inner side of the tubular membrane which provides additional gas phase mass transfer resistance.

3.3.2 Run No. T-3

This run was conducted from 11/30/93 to 12/7/93. During the previous run, rapid increase in helium and hydrogen concentrations was observed indicating downward salt movement within the membrane creating unfilled pores for leakage. Therefore, in this run, the effect of temperature on the molten salt mobility was determined by increasing the temperature gradually in stages starting at 490 °C, just above the salt melting point. A small leak flow through the tube was again observed at 20 psi pressure differential during the cold pressure test. The run began with 30 percent CO₂ on both sides of the membrane at 50 psig pressure. The initial hydrogen leak rate through the tube was determined using a KRW clean coal gas as a feed gas and was found to produce about 45 ppm hydrogen concentration and about 18 ppm helium concentration in the sweep outlet gas. The KRW coal gas with H₂S was started next. The H₂S concentration began appearing in the permeate after about 4 hours. Although the operating conditions were stable, frequent surges in all the three concentrations were observed. The temperature was increased to 500 °C over 4 days, with relatively little change in the H₂S, He, and H₂ concentrations. The H₂S to helium selectivity reached a maximum of 0.9, eventually leveling off at 0.6. The temperature was then increased to 530 °C in stages to increase the reactivity of H₂S and salt. The helium and hydrogen concentrations increased steadily with time for temperatures greater than 505 °C. The rate of increase was even greater at temperatures greater than 515 °C indicating downward movement of salt due to gravity. Although the H₂S concentrations also increased with higher temperatures, the H₂S to helium selectivity increased very slowly indicating that bulk of H₂S permeation was associated with the leakage flow.

Although there were frequent surges in the permeate concentrations, because of the lower membrane temperature the baseline permeate concentrations were lower than those observed

Figure 3-12. H₂S concentration with time
(Run T-2, 11/17/93 – 11/22/93, 50, 100 psig, 500 – 560 °C).

**Figure 3-13. Helium and hydrogen concentration with time
(Run T-2, 11/17/93 – 11/22/93, 50, 100 psig, 500 – 560 °C).**

Figure 3-14. H₂S/He selectivity with time
(Run T-2, 11/17/93 – 11/22/93, 50, 100 psig, 500 – 560 °C).

Figure 3-15. Used tubular membrane showing downward salt movement.

in Run No. T-2. The H_2S permeability at the membrane temperatures of 500 to 515 °C ranged only from 1,800 to 2,500 Barrers. The helium and hydrogen permeabilities were also lower than in Run No. T-2.

3.3.3 Run No. T-4

This run, with a new membrane, began with 50 psig pressure, 510 °C temperature and KRW clean coal gas on the test side. This run was carried out from 12/15/93 to 12/22/93. The initial porous leak flow produced about 45 ppm hydrogen and 17 ppm helium in the sweep gas. The feed gas was then switched to KRW coal gas with H_2S . The helium and hydrogen permeate concentrations were very stable initially, while H_2S concentrations rose very slowly. The selectivity for H_2S was well below 1, although rising slowly. The temperature was then increased to 520 °C and then decreased to 515 °C to prevent rapid increase in helium and hydrogen permeate concentrations which leveled off at 60 ppm and 170 ppm, respectively. The H_2S to helium selectivity increased from 0.2 to 0.7 over the 7 days of this run, which indicated substantial leakage flow along with an increasing contribution of the facilitated transport of H_2S . Similar to Run No. T-3, the H_2S permeabilities were low because of lower membrane temperatures and ranged from 200 to 3,300 Barrers. The helium and hydrogen permeabilities were also low compared to Run No. T-2, indicating lesser salt movement in the membrane. The continuous increase in the selectivity also indicates that steady state with respect to H_2S transport had not been reached even after 7 days of this run. The concentrations and selectivities with time during this period are shown in Figures 3-16, 3-17, and 3-18.

At the end of Run No. T-4, the membrane test system was sealed up with 2.9 percent H_2S in N_2 on the test side and 30 percent CO_2 in N_2 on the sweep side. The steam was turned off on both sides of the membrane. The membrane was then maintained at 510 °C during the 4-day holiday period.

3.3.4 Run No. T-5

This run was conducted with the same membrane tube used in Run No. T-4 with coal gas on the test side, 50 psig pressure, and 515 °C temperature; the same conditions at the end of the T-4 run. This run was carried out for 4 days on 12/27-12/31/93. The sealing of the membrane tube at the end of the previous run allowed sulfidation of the salt by the 2.9 percent H_2S sealed on the test side of the membrane similar to the disc membrane Run No. 6-4. Thus, at the start of this run, H_2S concentrations in excess of 100 ppm were observed. The H_2S concentration in the permeate then decreased continuously, eventually leveling off at about 31 ppm. Interestingly H_2 concentration also decreased initially and leveled off before rising again.

This observation indicates some dependence of H_2 transport on H_2S transport, e.g., decomposition of H_2S . The helium concentration, on the other hand, first increased slowly, leveled off, and then began rising along with hydrogen concentration. This run was aborted due to a power failure which shut off the furnace. The membrane tube was found to be cracked due to rapid cooling and the membrane run could not be continued. The concentrations and selectivities observed in this run are shown in Figures 3-19, 3-20, and 3-21.

The H_2S to He selectivity decreased continuously with time from over 100 at the beginning to about 9 at the end of this run. During the same time, the membrane selectivity for H_2S with respect to hydrogen decreased from about 14 to 6. At the end, although the H_2S concentration

**Figure 3-16. H₂S concentration with time
(Run T-4, 12/15/93 – 12/22/93, 50 psig, 510 – 520 °C).**

**Figure 3-17. Helium and hydrogen concentration with time
(Run T-4, 12/15/93 – 12/22/93, 50 psig, 510 – 520 °C).**

Figure 3-18. H_2S/He and H_2/He selectivities with time (Run T-4, 12/15/93 – 12/22/93, 50 psig, 510 – 520 °C).

**Figure 3-19. H₂S concentration with time
(Run T-5, 12/27/93 – 12/31/93, 50 psig, 515 °C).**

**Figure 3-20. Helium and hydrogen concentration with time
(Run T-5, 12/27/93 – 12/31/93, 50 psig, 515 °C).**

**Figure 3-21. H_2S/He and H_2/He selectivities with time
(Run T-5, 12/27/93 – 12/31/93, 50 psig, 515 °C).**

had leveled off, the selectivity was still decreasing because of the increasing helium concentration with leakage flow. This run, however, clearly indicated reaction pathway for enhanced H_2S transport as evidenced by the membrane selectivities for H_2S , with respect to helium and hydrogen, considerably greater than 1. The H_2S permeabilities were almost an order of magnitude greater than those observed in Run No. T-4 with the same membrane. At the same time, the helium and hydrogen permeabilities were similar to those in Run No. T-4.

3.3.5 Summary and Discussion

Initial experiments (Run No. T-2) with the tubular membranes at a temperature of 560 °C, which was typically used during disc membrane experiments, indicated substantial downward migration of salt by gravity with subsequent opening of pores in the upper section of the tubular membrane. Subsequent testing (Run No. T-3) at lower temperatures indicated that membrane temperature needs to be less than 520 °C to prevent rapid increase in inert gas permeation by leakage. The permeability of the tubular membranes for H_2S was found to be much lower than those observed in the disc membrane experiments. Possible reasons for the lower H_2S permeabilities include lower temperatures used in Runs No. T-3 and T-4, larger thickness of the tubular membranes as compared to the disc membranes, and the unimpregnated part of the thickness on the inner side of the tubular membrane which provides additional gas-phase mass transfer resistance.

In Run No. T-4, the membrane selectivity for H_2S increased continuously over 7 days, which indicated that a steady state had not reached by the end of the 7-day run. Both the membrane permeability and selectivity for H_2S increased dramatically upon sulfidation of the salt in sealed conditions. Apparently, sulfidation of salt in static conditions helped establish S^{2-} concentration gradient within the liquid phase. At the end of Run No. T-5, the concentrations of helium and hydrogen were again on the rise indicative of pore opening with the downward salt movement even at 515 °C membrane temperature. The apparent leveling of H_2S concentrations resulted from two contrasting factors — increase in H_2S permeation with porous leakage flow and decrease in permeation due to decreasing S^{2-} ion concentrations on the sweep side of the membrane due to continued stripping. Again the relatively long time needed for stripping of the S^{2-} from the sweep side of the membrane indicates slow reaction rate and low liquid phase diffusivities at the lower temperatures used in the tubular membrane studies.

SECTION 4

THEORETICAL MODELING OF FACILITATED TRANSPORT

The steady-state data collected during the membrane experiments may be used to estimate parameters governing the facilitated transport of H_2S through the molten salt. A brief description of the facilitated transport concept and the process chemistry involved was provided in Section 1.1. Based on this understanding of the concept, approximate relationships may be developed to predict the flux rate of H_2S transport through a molten salt.

4.1 ANALYSIS OF STEADY-STATE DATA

The H_2S absorption and stripping reactions occurring on the two sides of a molten salt impregnated ceramic membrane are expressed by the reversible reaction given in Equation (4-1).

where K is a chemical equilibrium constant for the above reaction and is given by

$$K = \frac{[S^{--}] [H_2O] [CO_2]}{[H_2S] [CO_3^{--}]} \quad (4-2)$$

where

S^{--} = Molar concentration of S^{--} ions in the liquid phase (gmole/cm³)

CO_3^{--} = Molar concentration of CO_3^{--} ions in the liquid phase (gmole/cm³)

H_2O = Molar concentration of water vapor in the gas phase expressed as partial pressure in atm

CO_2 = Molar concentration of CO_2 in the gas phase expressed as partial pressure in atm

H_2S = Molar concentration of H_2S in the gas phase expressed as partial pressure in atm

K = Reaction equilibrium constant in atm.

The equilibrium constant, K , is a function of reaction temperature, T . Since the partial pressures of the reacting species, H_2O , CO_2 , and H_2S , are different on the feed and sweep sides of the membrane, the concentrations of the sulfide and carbonate ions on the respective membrane

surfaces will be different at steady-state chemical equilibrium conditions. The differences in liquid phase concentrations on the two sides of a membrane will establish a concentration gradient within the liquid phase as shown schematically in Figure 4-1.

Since 1 mol of carbonate ion $[\text{CO}_3^{--}]$ produces 1 mol of sulfide ion $[\text{S}^{--}]$ by reacting with H_2S , according to Equation (4-1), the total molar concentration in the liquid phase is expected to be the same, regardless of the extent of reaction. For pure carbonate melt to begin with, the total molar concentration, C_T , gmoles/cm³, is given by

$$C_T = [\text{S}^{--}] + [\text{CO}_3^{--}]. \quad (4-3)$$

Any loss of salt by evaporation and presence of impurities in the salt is ignored in the above equation. The fraction of the sulfide ions $[\text{S}^{--}]$ at any position in the liquid phase may be expressed by X

$$X = [\text{S}^{--}] / C_T. \quad (4-4)$$

The corresponding fraction of carbonate ions is given by

$$1 - X = [\text{CO}_3^{--}] / C_T. \quad (4-5)$$

The equilibrium constant, K, may be expressed in terms of X and gas phase partial pressures

$$K = \frac{X \cdot p(\text{H}_2\text{O}) \cdot p(\text{CO}_2)}{(1-X) p(\text{H}_2\text{S})}. \quad (4-6)$$

The sulfide ion fraction in the melt at the feed side and sweep side membrane surfaces is then given by

$$X = \frac{K p(\text{H}_2\text{S})}{K p(\text{H}_2\text{S}) + p(\text{H}_2\text{O}) p(\text{CO}_2)}. \quad (4-7)$$

By substituting appropriate gas phase partial pressure values, Equation (4-7) can provide the sulfide ion fraction on the two sides of the membrane, x_{feed} and x_{sweep} .

The flux rate of sulfide ions, S^{--} , across the liquid phase depends on the diffusivity of sulfide ions in the liquid phase and the sulfide ion concentration gradient. The molar flux rate of gas phase H_2S across the liquid phase membrane by the reaction pathway is, in effect, provided by the molar flux rate of the sulfide ions across the liquid phase.

$$J_{\text{H}_2\text{S}} = \frac{D_{(\text{S}^{--})}}{l} \cdot A \cdot C_T \cdot (X_{\text{feed}} - X_{\text{sweep}}) \quad (4-8)$$

Figure 4-1. Schematic of concentration gradients in the molten salt.

where

- J_{H_2S} = Flux rate of H_2S (gmole/sec)
 D_{S--} = Diffusivity of $S--$ in liquid phase (cm^2/s)
 l = Membrane thickness (cm)
 A = Membrane surface area (cm^2)

substituting for X

$$J_{H_2S} = \frac{D_{S--} A C_T}{l} \left[\frac{K p(H_2S)}{K p(H_2S) + p(H_2O) p(CO_2)} \Big|_{feed} - \frac{K p(H_2S)}{K p(H_2S) + p(H_2O) p(CO_2)} \Big|_{sweep} \right] \quad (4-9)$$

Since 1 mol of H_2S transport from feed side to sweep side produces transport of 1 mol of CO_2 and H_2O in the opposite direction,

$$J_{H_2O} = J_{CO_2} = J_{H_2S} \quad (4-10)$$

4.2 ESTIMATION OF K AND D_{S--} FROM STEADY-STATE EXPERIMENTAL PERMEATION DATA

Equation (4-9) contains two unknown parameters, K and D_{S--} , which must be determined from the experimental data. Since the number of unknowns in the above equation is 2, steady-state H_2S permeation data are need at two different partial pressures of H_2S . As seen from Table 3-3, such data were collected in Runs No. 6 and 14.

4.2.1 Data from Run No. 6

One set of permeation data was collected using 2 percent H_2S in N_2 as feed gas at 50 psig system pressure. No steam or CO_2 were present in feed gas. Thirty percent CO_2 in N_2 was used as sweep gas with approximately 16.8 percent water vapor. The measured dry H_2S permeate concentration was 9.5 ppm with a dry sweep gas flow rate of 994 std. cm^3/min .

Thus, $p(H_2S)$ on feed side ~ 0.088 atm
 $p(H_2O)$ on sweep side ~ 0.737 atm
 $p(CO_2)$ on sweep side ~ 1.1 atm.

H_2S concentration on sweep side ~ 9.5 ppm dry
 ~ 7.9 ppm wet
 $p(H_2S)$ on sweep side ~ 3.48×10^{-5} atm.

The H_2S flux rate is $\sim 7.03 \times 10^{-9}$ gmol/sec. Since 1 mol of H_2S transport from feed side to sweep side results in 1 mol of CO_2 and H_2O transport, the concentrations of CO_2 and H_2O on feed side can be estimated using H_2S flux rate:

$$\begin{aligned} p(\text{H}_2\text{O}) \text{ on feed side} &\sim 3.52 \times 10^{-5} \text{ atm} \\ p(\text{CO}_2) \text{ on feed side} &\sim 3.52 \times 10^{-5} \text{ atm.} \end{aligned}$$

Substituting the above values in Equation (4-9):

$$7.03 \times 10^{-9} = \left(\frac{D_s - A C_T}{l} \right) \left[\frac{0.088 K}{0.088 K + (3.52 \times 10^{-5}) \cdot (3.52 \times 10^{-5})} - \frac{3.48 \times 10^{-5} \cdot K}{(3.48 \times 10^{-5}) \cdot K + 0.737 \times 1.1} \right] \quad (4-11)$$

In Run No. 6, another set of permeation data was collected using 0.6 percent H_2S in the feed gas. The feed gas contained 9 percent CO and 6 percent H_2 ; however, it did not contain any CO_2 . The steam used on the test side was approximately 15.9 percent. The water gas shift reaction between H_2O and CO is likely to produce some CO_2 at the experimental temperatures. The analysis of feed exit gas indicated presence of about 0.25 percent CO_2 .

$$\begin{aligned} \text{Thus, } p(\text{H}_2\text{S}) \text{ on feed side} &\sim 0.022 \text{ atm} \\ p(\text{H}_2\text{O}) \text{ on feed side} &\sim 0.7 \text{ atm} \\ p(\text{CO}_2) \text{ on feed side} &\sim 0.011 \text{ atm.} \end{aligned}$$

Thirty percent CO_2 in N_2 was again used as sweep gas with 16.8 percent steam.

$$\begin{aligned} \text{Thus, } p(\text{H}_2\text{O}) \text{ on sweep side} &\sim 0.737 \text{ atm} \\ p(\text{CO}_2) \text{ on sweep side} &\sim 1.1 \text{ atm.} \end{aligned}$$

$$\begin{aligned} \text{The } \text{H}_2\text{S} \text{ concentration on sweep side} &\sim 2.8 \text{ ppm dry} \\ &\sim 2.33 \text{ ppm wet} \\ p(\text{H}_2\text{S}) \text{ on sweep side} &\sim 1.03 \times 10^{-5} \text{ atm.} \end{aligned}$$

The H_2S flux rate was $\sim 2.07 \times 10^{-9}$ gmol/sec. Substituting the above set of values in Equation (4-9):

$$2.07 \times 10^{-9} = \left(\frac{D_s - A C_T}{l} \right) \left[\frac{0.022 K}{0.022 K + 0.011 \times 0.7} - \frac{1.03 \times 10^{-5} \cdot K}{1.03 \times 10^{-5} \cdot K + 0.737 \times 1.1} \right] \quad (4-12)$$

Solving Equations (4-11) and (4-12):

$$\text{Equilibrium constant, } K \sim 0.15 \text{ atm at } 560^\circ \text{C, and}$$

$$\frac{D_{S^{--}} \cdot C_T \cdot A}{l} \sim 7.03 \times 10^{-9} \text{ gmol/sec} .$$

For 49 percent Li_2CO_3 , 25 percent K_2CO_3 , and 26 percent CaCO_3 mixture, the liquid salt density is $\sim 2.54 \times 10^{-2} \text{ gmol/cm}^3$. The percent salt infiltration for membrane used in Run No. 6 was 68 percent. Assuming ceramic matrix porosity of 0.5 the molar salt concentration in the membrane, C_T , was $\sim 8.64 \times 10^{-3} \text{ gmol/cm}^3$. The membrane thickness was $\sim 0.25 \text{ cm}$ and the effective membrane surface area was estimated to be 2.3 cm^2 .

Thus, $D_{S^{--}} \sim 8.84 \times 10^{-8} \text{ cm}^2/\text{sec}$
 $\sim$ Diffusivity of S^{--} in molten salt at 560°C .

4.2.2 Data from Run No. 14

During this run, one set of permeation data was collected using 2.9 percent H_2S in N_2 as feed gas at 50 psig system pressure. No steam or CO_2 were present in feed gas. Thirty percent CO_2 in N_2 was used as sweep gas with approximately 16.8 percent steam. The measured dry H_2S permeate concentration was 16.3 ppm with a dry sweep gas flow rate of $1,000 \text{ std. cm}^3/\text{min}$.

Thus, $p(\text{H}_2\text{S})$ on feed side = 0.13 atm
 $p(\text{H}_2\text{O})$ on sweep side = 0.737 atm
 $p(\text{CO}_2)$ on sweep side = 1.1 atm
 $p(\text{H}_2\text{S})$ on sweep side = $6 \times 10^{-5} \text{ atm}$
 H_2S flux rate = $1.21 \times 10^{-8} \text{ gmol/sec}$
 $p(\text{H}_2\text{O})$ on feed side = $7.2 \times 10^{-5} \text{ atm}$.
 $p(\text{CO}_2)$ on feed side = $7.2 \times 10^{-5} \text{ atm}$.

Substituting the above values in Equation (4-9)

$$1.21 \times 10^{-8} = \left(\frac{D_{S^{--}} A C_T}{l} \right) \left[\frac{0.13 K}{0.13 K + 7.2 \times 10^{-5} \times 7.2 \times 10^{-5}} - \frac{6 \times 10^{-5} K}{6 \times 10^{-5} + 0.737 \times 1.1} \right] . \quad (4-13)$$

Solving the above equation

$$\frac{D_{S^{--}} A C_T}{l} \sim 1.21 \times 10^{-8} \text{ gmol/sec} . \quad (4-14)$$

Data were also obtained at 100 and 200 psig system pressure and the same gas compositions. The corresponding H_2S permeation rates observed were 16.5 and 17.1 ppm, respectively. These steady-state values were not significantly different than those obtained at 50 psig pressure conditions. Inspection of Equation (4-13) indicates that these results are consistent, since pressure does not have a significant effect on liquid phase diffusivity.

In Run No. 14, another set of permeation data was collected using 0.6 H₂S in feed gas with 6 percent CO₂. The steam used on feed side was about 25.2 percent. Thirty percent CO₂ in N₂ was used as sweep gas with 25.9 percent water vapor. The steady-state H₂S concentrations were obtained at two system pressures of 50 and 100 psig and were 4.3 and 3.0 ppm, respectively. The dry sweep gas flow rate in both cases was 1,000 std. cm³/min.

Thus, for 50 psig system operation,

$$\begin{aligned} p(\text{H}_2\text{S}) \text{ on feed side} &= 0.021 \text{ atm} \\ p(\text{CO}_2) \text{ on feed side} &= 0.21 \text{ atm} \\ p(\text{H}_2\text{O}) \text{ on feed side} &= 1.11 \text{ atm} \\ p(\text{H}_2\text{O}) \text{ on sweep side} &= 1.14 \text{ atm} \\ p(\text{CO}_2) \text{ on sweep side} &= 1.05 \text{ atm} \\ p(\text{H}_2\text{S}) \text{ on sweep side} &= 1.5 \times 10^{-5} \text{ atm} \end{aligned}$$

$$\text{and H}_2\text{S flux rate} = 3.2 \times 10^{-9} \text{ gmol/sec.}$$

Substituting the above values in Equation (4-9), using Equation (4-12) and solving

$$K = 3.98 \text{ atm.}$$

At 100 psig system operation,

$$\begin{aligned} p(\text{H}_2\text{S}) \text{ on feed side} &= 0.037 \text{ atm} \\ p(\text{CO}_2) \text{ on feed side} &= 0.37 \text{ atm} \\ p(\text{H}_2\text{O}) \text{ on feed side} &= 1.97 \text{ atm} \\ p(\text{H}_2\text{O}) \text{ on sweep side} &= 2.02 \text{ atm} \\ p(\text{CO}_2) \text{ on sweep side} &= 1.86 \text{ atm} \\ p(\text{H}_2\text{S}) \text{ on sweep side} &= 1.86 \times 10^{-5} \text{ atm.} \end{aligned}$$

Substituting the above values in Equation (4-9), using Equation (4-12) and solving

$$K = 4.47 \text{ atm.}$$

The above value of K is close to that calculated from data collected at 50 psig pressure. Thus, these data are consistent with facilitated transport mechanism for H₂S. This value of K is, however, much higher than that obtained in Run No. 6. One important difference in these two runs was the lack of CO₂ in the feed gas used in Run No. 6. The feed side CO₂ concentration in that case was measured by a GC. Any error in that measurement can have a substantial effect in calculations. The liquid phase diffusivity, based on data in Run No. 14, is estimated to be $1.56 \times 10^{-7} \text{ cm}^2/\text{sec}$. This value for D_{S--} is very close to that obtained from Run No. 6 data.

4.3 ANALYSIS OF TRANSIENT DATA

Analysis of the H₂S transport process as given in Section 4-1 allows estimation of the reaction equilibrium constant and liquid phase diffusivity using steady-state permeation data. Almost all of the membrane experiments have indicated a gradual rise in H₂S concentrations with time. Referring to Figure 4-1, this time requirement may be considered as that required for development of the concentration gradients in the liquid phase.

Starting with a fresh molten salt membrane, the sulfide ion $[S^{2-}]$ concentrations would be zero initially throughout the liquid phase. As the feed side of the molten salt membrane is exposed to a gas containing H_2S , the concentration of the S^{2-} ion on the feed side surface of the membrane may be assumed to reach the equilibrium concentration instantaneously. The development of the concentration gradient in the liquid phase of the membrane may be considered to be diffusion of the S^{2-} ions within the liquid film, similar to diffusion in an infinite length slab. The diffusion of S^{2-} ions in a semi-infinite membrane of thickness l may be expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial \chi^2} \quad (4-15)$$

where

C = concentration of S^{2-} ions in the liquid phase at time t and position χ (gmole/cm³)

t = time (sec)

D = Diffusivity of S^{2-} ions in the liquid phase (cm²/sec)

χ = Distance across a membrane from the sweep side of the membrane (cm).

The initial condition is given as

$$C(\chi, t) = 0 \text{ for } t=0 \text{ and } 0 < \chi < l.$$

Since there is no H_2S in the sweep gas, the sulfide ion concentration on the sweep side surface of the membrane may be assumed to be zero.

The sulfide ion concentration at the feed side surface of the membrane is assumed to be that given by the reaction equilibrium, C_o , which would be constant with time for constant feed gas composition. Thus, the boundary conditions are

$$\begin{aligned} C &= 0, \text{ for } \chi = 0, t \geq 0 \text{ and} \\ C &= C_o, \text{ for } \chi = l, t \geq 0. \end{aligned}$$

The development of concentration profile with t and X is given by solution of Equation (4-13) (Crank, 1964):

$$C(\chi, t) = C_o \frac{\chi}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} C_o \frac{\cos(n\pi)}{n} \cdot \sin \frac{(n\pi\chi)}{l} \cdot e^{-Dn^2\pi^2 t/l^2} \quad (4-16)$$

The above solution indicates that steady state is practically achieved in dimensionless time, $\frac{Dt}{l^2}$, of 0.45. A cumulative amount of the species permeated is obtained by integrating

the above solution and is given by Crank (1964) as:

$$\frac{Q_t}{l C_o} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-Dn^2\pi^2 t/l^2} \quad (4-17)$$

where Q_t is a cumulative permeated amount of the diffusing species (gmole/cm²). The flux rate at any given time is obtained by differentiating Q_t with time in Equation (4-15)

$$\frac{d \left[\frac{Q_t}{l C_o} \right]}{dt} = \frac{D}{l^2} + \frac{2D}{l^2} \sum_{n=1}^{\infty} (-1)^n e^{-\frac{Dn^2\pi^2 t}{l^2}} \quad (4-18)$$

or

$$\frac{\frac{dQ_t}{dt}}{\left[\frac{DC_o}{l} \right]} = \frac{(\text{Flux})_t}{(\text{Flux})_{\text{maximum}}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2\pi^2 \left[\frac{Dt}{l^2} \right]} \quad (4-19)$$

The right side of the above equation was evaluated numerically for different values of dimensionless time, $\frac{Dt}{l^2}$, and is plotted in Figure 4-2. The H₂S flux rate through the molten

salt membrane is directly proportional to the measured H₂S concentration in the sweep outlet gas. Thus, Figure 4-2 simulates a gradual increase in permeate H₂S concentration with time. This figure may be compared with the observed gradual increase in H₂S concentration to determine the diffusion coefficient of S²⁻ ions in the liquid phase. For example, the initial transient data obtained with fresh membrane in Runs No. 6, 8, and 14 as seen in Figures 3-1, 3-4, and 3-6 may be used to estimate the diffusion coefficient.

4.3.1 Estimates of Diffusion Coefficient from Experimental Data

As seen in Figure 3-4, the time required to reach the peak H₂S concentration in Run No. 8 was about 800 min, although H₂S concentration actually stabilized after about 1,300 min. In Run No. 14, also the time required to reach steady state at 50 psi conditions was found to be about 1,300 min. Since the dimensionless time needed to achieve a practical steady state is about 0.45 and the membrane thickness is about 0.25 cm, the liquid phase diffusivity is estimated to be

$$\begin{aligned} D &\sim \frac{0.45 \cdot l^2}{t} \sim \frac{0.45 \times 0.25 \times 0.25}{1,300 \times 60} \\ &\sim 3.6 \times 10^{-7} \text{ cm}^2/\text{sec} \end{aligned} \quad (4-20)$$

Figure 4-2. Variation of flux rate with time—diffusion through a plane sheet.

From Figure 4-2 it can be seen that a more reliable estimate of diffusivity may be obtained by comparing time required to reach 50 percent of the steady-state level, since this point would be in the zone of steeper rise in concentrations. From Figure 4-2, a dimensionless time of 0.15 would be needed to reach 50 percent of the steady-state concentration level. In Run No. 6 the steady-state H_2S concentration with coal gas at 50 psig condition was about 2.5 ppm. From Figure 3-1, the time required to reach half of this level was about 300 min. In Figure 3-4 the time required to reach half of the peak H_2S concentration of 6 ppm in Run No. 8 was about 600 min, whereas half of the ultimate steady-state concentration of 2.5 ppm was reached in about 400 min. In Run No. 14 the time required to reach half of the peak concentration was much longer, on the order of 1,000 min. The theoretical analysis assumes that the H_2S reaction with salt and diffusion of S^{--} ions in liquid phase is the only possible mechanism for H_2S transport. Whereas, in actual cases, porous viscous and diffusive flow contributed significantly to the overall H_2S transport, thus contributing to the observed variability in the times required to reach half of the apparent steady-state levels. Also, it is interesting to note that the onset time required for first measurable H_2S detection was also significantly different in all three runs ranging from 180 min to 500 min. As discussed in Section 3.2.10, the observed nonuniformities in salt infiltration in the membranes can substantially affect the permeation characteristics. The time required to reach half of the apparent steady-state varied from 300 to 1,000 min. The corresponding calculated diffusivity values range from 5×10^{-7} to 2×10^{-7} cm^2/sec . The value of liquid phase $[\text{S}^{--}]$ diffusion coefficient based upon transient analysis (2 to 5×10^{-7} cm^2/sec) compares fairly well with 8.8×10^{-8} cm^2/sec calculated from one set of steady-state permeation data.

4.4 MAXIMUM ACHIEVABLE H_2S CONCENTRATION IN PERMEATE

One of the requirements for a successful application of a facilitated transport membrane is its ability to transport H_2S in uphill direction against the H_2S concentration gradient across a membrane. The membrane permeation data collected in tests with disc membranes thus far indicate substantial diffusional resistance in the present membrane configuration. Theoretical analysis was therefore conducted to determine the maximum achievable H_2S concentration in the sweep gas in a hypothetical case of no diffusional resistance. In such a case, the H_2S concentration in the permeate would be dictated solely by the reaction equilibrium. The data collected in Run No. 6, indicated an equilibrium constant for H_2S -carbonate salt reaction of about 0.15 atm. This equilibrium constant may be used to determine the maximum possible H_2S transport across a membrane for a given set of operating conditions.

The equilibrium constant, which is estimated to be 0.15 atm, based on Run No. 6, is expressed as

$$\frac{[\text{S}^{--}] [\text{H}_2\text{O}] [\text{CO}_2]}{[\text{CO}_3^{--}] [\text{H}_2\text{S}]} = 0.15 \quad (4-21)$$

where $[\text{S}^{--}]$ and $[\text{CO}_3^{--}]$ are ionic concentrations in the molten salt (gmole/cm^3) and $[\text{H}_2\text{O}]$, $[\text{CO}_2]$, and $[\text{H}_2\text{S}]$ are the partial pressures, atmospheres, of the respective species in the gas phase in contact with the molten salt surface. This equilibrium constant would be applicable to both the feed and permeate sides of the membrane. Within the liquid phase molten salt, the S^{--} and CO_3^{--} ions migrate according to the concentration gradient for the respective ionic species. Therefore, the criterion for H_2S transport across the molten salt membrane is that there should be a positive gradient for $[\text{S}^{--}]$ ions from the feed side to the permeate side of a membrane. For a KRW

gasifier, the coal gas typically consists of 0.5 percent H_2S , 5 percent CO_2 , and 15 percent steam. Thus, for a pressure of P atmospheres on the feed side, the ratio of S^{--} and CO_3^{--} concentrations on the feed side of the membrane is given by

$$\frac{[\text{S}^{--}]}{[\text{CO}_3^{--}]} = \frac{0.15 \cdot P \cdot \frac{0.5}{100}}{P \cdot \frac{15}{100} \cdot P \cdot \frac{5}{100}} \quad (4-22)$$

$$\frac{[\text{S}^{--}]}{[\text{CO}_3^{--}]} = \frac{0.1}{P_{\text{feed}}} \text{ or } \frac{0.2 \cdot (X_{\text{H}_2\text{S}})_{\text{feed}}}{P_{\text{feed}}}$$

where $(X_{\text{H}_2\text{S}})_{\text{feed}}$ is the percent of H_2S on the feed side gas.

On the sweep side the maximum CO_2 and H_2O concentrations would be 50 percent with no H_2S in the sweep gas, 49 percent with 2 percent H_2S in the sweep gas and $(100 - X_{\text{H}_2\text{S}}/2)$ where, $X_{\text{H}_2\text{S}}$ is the sweep (permeate) gas percent H_2S .

Thus, for a pressure of P_{sweep} atmospheres on the sweep side, the ratio of the ionic concentrations of S^{--} and CO_3^{--} in the molten salt on the permeate side of the surface is given by

$$\frac{[\text{S}^{--}]}{[\text{CO}_3^{--}]} \Big|_{\text{sweep}} = \frac{0.15 \cdot 400 \cdot X_{\text{H}_2\text{S}}}{(100 - X_{\text{H}_2\text{S}}) \cdot (100 - X_{\text{H}_2\text{S}}) \cdot P_{\text{sweep}}} \quad (4-23)$$

For positive S^{--} gradient from the feed side to the permeate side across the membrane:

$$\begin{aligned} \frac{[\text{S}^{--}]}{[\text{CO}_3^{--}]} \Big|_{\text{feed}} &> \frac{[\text{S}^{--}]}{[\text{CO}_3^{--}]} \Big|_{\text{sweep}} \\ \frac{0.1}{P_{\text{feed}}} &> \frac{60}{P_{\text{sweep}}} \frac{X_{\text{H}_2\text{S}}}{(100 - X_{\text{H}_2\text{S}})^2} \end{aligned} \quad (4-24)$$

For maximum permeate $X_{\text{H}_2\text{S}}$

$$\frac{0.1}{P_{\text{feed}}} = \frac{60}{P_{\text{sweep}}} \frac{X_{\text{H}_2\text{S}}}{(100 - X_{\text{H}_2\text{S}})^2} \quad (4-25)$$

Thus, for a pressure ratio of $[P_{\text{feed}} / P_{\text{sweep}}]$ equal to one, the maximum H_2S concentration on the permeate sweep side would be 12.75 percent. With a feed pressure to sweep pressure ratio of 3, the maximum possible H_2S concentration in the permeate would be limited to 5 percent, whereas with a sweep pressure to feed pressure ratio of 3, up to 27 percent H_2S concentration in the permeate could be possible. This apparently anomalous behavior is a result of the coupled transport of H_2O and CO_2 in the molten salt in the opposite direction of the H_2S transport.

SECTION 5

PROCESS EVALUATION

The data collected in long-term disc and tubular membrane experiments indicated permeability of molten salt impregnated ceramic membranes for H_2S of 10,000 to 200,000 Barrers. The maximum membrane selectivity for H_2S with respect to helium was about 18. The membranes tested exhibited substantial permeation for both helium and hydrogen, with helium permeabilities ranging from 10,000 to 40,000 Barrers. Such a large permeability for an inert gas like helium indicates substantial porous leakage flow across the molten salt membranes.

The tubular membranes exhibited substantial movement of the molten salt within the membrane at temperatures of 530 °C or higher which is only 30 °C above the salt melting point. The downward flow of salt was also observed in the long-term disc membrane experiments. These observations indicate that the porous aluminum nitride matrix is unable to hold salt in pores by capillary action due to presence of large pores. Calculations indicate that 1 μm pores should be able to hold salt in place by capillary action at up to 70 psi pressure differentials across the membrane. Thus pores considerably greater than 1 μm may be present in the ceramic matrix.

For practical application of the facilitated transport membranes in coal gas environment, the membranes must be able to concentrate the H_2S permeated to sweep side. The process analysis presented in Section 4.4 suggested that with no pressure differential across the membrane, i.e., $[P_{feed}/P_{sweep}]$ equal to one, it would be possible to concentrate H_2S from 0.6 percent H_2S coal gas on feed side to almost 13 percent (or by a factor of 20) on the permeate side. The H_2S concentration in the sweep gas can be increased even more by increasing sweep side pressure. With a sweep pressure to feed pressure ratio of 3, H_2S can be concentrated to 27 percent in the permeate. These theoretical calculations obviously indicate that this concept is promising.

Above theoretical analysis of the membrane process assumed an instantaneous establishment of the liquid phase concentration gradients. The membrane experiments with 0.25-cm thick disks indicated that up to 1300 minutes may be needed to achieve steady state permeation. For tubular membranes the time needed to achieve steady state appears to be even longer with 0.35-cm thickness membrane tubes.

For practical applications of molten salt impregnated ceramic membranes the time needed to achieve a steady-state operation needs to be much shorter, i.e., <1 hour. From the analysis of a transient diffusion process presented in Section 4.3, the time required to achieve steady state is inversely proportional to the liquid phase diffusion coefficient and is directly proportional to the square of the membrane thickness. Liquid phase diffusion coefficient is a function of temperature which cannot be changed significantly for the molten salt membrane operations. Thus, for faster steady-state operation within <1 hour, the membrane thickness needs to be reduced by an order of magnitude.

5.1 ESTIMATION OF MEMBRANE MODULE SIZE FOR A 100-MW IGCC PLANT

For a 100-MW IGCC plant using a KRW gasifier the approximate coal feed gas composition would consist of 10 percent H_2 , 15 percent CO , 5 percent CO_2 , 15 percent H_2O , 0.5 percent H_2S , 0.3 percent NH_3 with balance of N_2 . For a pressurized gasifier like the KRW gasifier, the pressure is typically 25 atm and temperature is 600 °C. The approximate gas flow rate at 25 atm and 600 °C is estimated to be 6.7×10^5 ft³/h. To reduce the H_2S content of the feed gas from 5,000 ppmv to 100 ppmv the amount of H_2S that needs to be removed would be

$$\begin{aligned} \frac{H_2S \text{ Removal Rate}}{H_2S \text{ Removal Rate}} &= \frac{6.7 \times 10^5 \cdot (5 \times 10^{-3} - 1 \times 10^{-4}) \cdot 25 \cdot 273}{(600 + 273) \cdot 359} \\ &= 71.5 \text{ lb mol/h} . \end{aligned}$$

The observed H_2S flux rates with long-term disc membranes conducted with 0.5 percent coal gas as feed gas were of the order of 2 to 3×10^{-9} gmole/sec, as shown in Section 4.2. Although the disc membranes were approximately 1 in. in dia, the effective surface area exposed to feed gas was estimated to be about 2.3 cm². Thus, the observed H_2S flux rates at 50 psig and 560 °C membrane conditions with coal feed gas were about 1.1×10^{-9} gmol/cm²/sec or about 8×10^{-6} lb mol/ft²/h. Assuming that the same flux rate is observed at 25 atm and 600 °C conditions, the membrane surface area needed to remove the required 71.5 lb mol/h of H_2S is estimated to be 9×10^6 ft².

An existing Coors Ceramics membrane unit used for filtration can pack a membrane surface area to volume of 870 ft²/ft³. With this packing density, about 10,000 ft³ of membrane volume would be needed to provide the required surface area. Nine vessels, each 10 ft in diameter and 15 ft long, would thus be needed to provide the required membrane surface area to remove 98 percent H_2S from coal feed gas for 100-MW IGCC plant.

The H_2S flux rate by facilitated transport is expected to be inversely proportional to the membrane thickness. Thus, by reducing the membrane thickness by an order of magnitude would reduce the module volume requirement to 1,000 ft³, in addition to reducing the time required for steady operation within practical limits.

The membrane operational data collected in this experimental program are of preliminary nature. The experiments also identified several practical problems such as salt movement within porous matrix and extremely long time requirement for steady-state operation. Further improvements are therefore needed for such membranes to become practical. No detailed process evaluation as well as meaningful economic evaluation can therefore be carried out at this time.

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

Molten salt impregnated ceramic disc and tubular membranes were successfully tested during this experimental program to determine their permeation characteristics for H_2S and other gases such as hydrogen. The following conclusions and recommendations can be made based on the experimental results:

- Enhanced H_2S transport with membrane selectiveness with respect to H_2S greater than unity was observed in both disc and tubular membrane studies.
- The membranes also exhibited high permeabilities for other gases, hydrogen and helium, in much excess of those expected from solution diffusion mechanism, indicating substantial porous leakage flow.
- Limited data collected at different pressures with otherwise similar conditions indicated lower H_2S permeabilities at higher pressures consistent with facilitated transport mechanism for H_2S .
- Increasing temperature produced greater H_2S permeabilities consistent with increased diffusion rate.
- Both disc and tubular membranes were successfully tested in long-term, continuous, unattended operations indicating successful experimental procedures.
- Observed membrane selectivity for H_2S with respect to helium ranged from 0.6 to 18 with bulk of values >1 . The membrane selectivities for H_2S with respect to hydrogen were about half of those observed with respect to helium.
- Permeabilities of disc membranes for H_2S ranged from 13,000 to 200,000 Barrers. H_2S permeabilities of tubular membranes were substantially lower and ranged from 200 to 28,000 Barrers.
- A gradual increase in H_2S concentration was observed in most of the experiments. Such gradual increase is consistent with reaction pathway and facilitated transport mechanism for H_2S .
- The time required to achieve steady-state operation was of the order of several hours ($\sim 1,000$ min) in the case of disc membrane experiments. For tubular membranes, steady-state operation was not observed even after several days.
- The molten salt was found to be highly mobile within the ceramic matrix at temperatures over 530°C . This fact was readily evident in tubular membrane experiments due to rapid increase in helium and hydrogen concentration with time. Oozing of molten salt was also observed during disc membrane experiments. These observations indicate that the ceramic matrix pores were unable to hold salt by capillary suction.

- The performance of disc membranes was found to be inconsistent with a large variation in observed permeabilities. Inspection of cross section of these membranes indicated nonuniform and/or incomplete infiltration of salt within the matrix.
- For practical application of the molten salt impregnated ceramic membranes the observed H₂S flux rates need to be increased by an order of magnitude and the time requirement to achieve steady-state operation needs to be reduced by two orders of magnitude.
- The mean pore size of the ceramic matrix needs to be reduced with elimination of presence of large pores (>1 µm) to improve retention of molten salt in the ceramic matrix.

SECTION 7

REFERENCES

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Lyke, S.E. et al. 1985a. Development of a Hot Gas Cleanup System for Integrated Coal Gasification/Molten Carbonate Fuel Cell Power Plants. Final Report DOE/MC/19077-1830.

Lyke, S.E., et al. 1985b. Prepr. Pap., *Am. Chem. Soc., Div. Fuel Chem*, 30(4):26-35.

Moore, R.H., et al. 1980 Molten Salt Scrubbing Process for Removal of Particles and Sulfur Compounds from Low Btu Fuel Gases. BNWL-SA-6030, Pacific Northwest Lab., Richland, WA.

Stegen, G.E., et al. 1982. Development of a Solid Absorption Process for Removal of Sulfur from Fuel Gas. DOE/ET/11028-9.

7.4 Golden Technologies Final report

Air Products & Chemicals Inc.

Facilitate Transport Ceramic Membranes for High Temperature Gas Clean-up

Final Report

Program Goal:

The goal of this project is to demonstrate the feasibility of developing high-temperature, high-pressure facilitated transport gas separation ceramic membranes in order to control gaseous contaminants in integrated Gasification Combined Cycle (IGCC) systems. These membranes will selectively and effectively remove hydrogen sulfide (H_2S) from hot gas streams in the hostile process environment encountered in IGCC systems, at temperatures ranging from 1,000°F to 1600°F, and pressures between 200 and 700 psig.

The gaseous components to be tested shall include, at a minimum, hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, ammonia, methane, nitrogen, carbonyl sulfide, and water.

Program Objectives

- Provide Air Products & Chemicals Inc. with a porous substrate of a defined composition as determined by their molten salt infiltration requirements.
- Prepare parts from Aluminum Nitride and Lithium Aluminate, that have a pore size of 0.3μ - 0.5μ and a porosity of 30%.
- Demonstrate repeatability of ceramic process and configuration capabilities

Statement of Work - Tasks:

<u>TASK DESCRIPTION</u>	<u>STATUS</u>
<u>Task 1.0: Test Plan Preparation</u> Prepare a test plan to develop and evaluate facilitated transport ceramic membranes for reducing representative gas compositions.	Completed Attached
<u>Task 2.2: Ceramic Membrane Substrate and Metal Seal Development</u> Based on information and recommendations from Air Products, fabricate a ceramic membrane substrate, support system, and metal seal system capable of withstanding the high temperature and pressure requirements in Integrated Gasification Combined Cycle systems.	Completed Delivered systems and samples to APCI
<u>Task 2.3: Membrane Fabrication and Conceptual Testing</u> Fabricate Disc Membranes for testing using the membrane materials selected in Tasks 2.1 & 2.2. Parts will be tested at Air Products.	Completed Delivered to APCI
<u>Task 3.1: Preparation of High Temperature, High Pressure Test Plan</u> Assist Air Products & Chemicals Inc. in developing a test plan to demonstrate the feasibility of the molten salt membrane concepts developed in Task 2.	Completed
<u>Task 3.2: Fabrication of H₂S Membrane</u> Fabricate a series of molten salt membrane samples as identified in the test plan (Task 3.1).	Completed Delivered to APCI

Project Highlights:

- Both flat discs of varying thicknesses and single bore tubes were prepared from Aluminum Nitride as requested by Air Products & Chemicals Inc.
- Tests showed that both pore diameter and porosity were controllable by specific firing profiles.
- A suitable Lithium Aluminate (LiAlO₂) raw material powder could not be found to yield the pore size and porosity required. Available powder was found with a particle size that gave pore size of 1 to 3 μ . Wet Grinding produced the correct particle size to yield the 0.5 μ pore size in the fired structure, but caused a shift to LiAl₅O₈. Dry grinding did not change the particle size to the required diameter, although the composition remained LiAlO₂.

Discussion of the Project:

Based on the literature reviews and initial test & conceptual test plans, we were requested to produce membranes of varying thicknesses out of two key materials: Aluminum Nitride, and Lithium Aluminate. Due to the pore and particle size requirements for suitable membranes, Lithium Aluminate powder of sufficiently fine particle size was *not* commercially available. Attempts to mill available raw Lithium Aluminate powders to appropriate particle sizes remains a technical difficulty as discussed below.

The Aluminum Nitride that was used for parts is a commercial available product from Dow Chemical. It was used for both the dry and iso-pressing of parts. We were unable to get discs to a thickness of 0.025" as requested without secondary forming processes. Discs at 0.100" and 0.050" thickness could be pressed and directly fired without additional forming. Best results for firing were found to be on setter covered with Boron Nitride powder. It is necessary to fire these parts in a Nitrogen Atmosphere. We found no limit to part size or configuration with the samples. When additional forming is necessary, either green forming and/or finish grinding can be performed. The most effective finish grinding method involves using a double face lab grinder to avoid "cupping" of very thin components.

The Lithium Aluminate powder was purchased from FMC corporation, Cypress Goote Mineral Co., and Johnson Matthey Catalog Co. The particle size of all these powders proved to be too large to yield the 0.5 μ pore size upon firing. Tests using both wet and dry grinding were used to reduce the particles size of raw materials to achieve the correct pore size upon firing. A wet grind of 24 hours did yield the particles size desired, but the material was contaminated by the high alumina mill and grinding media. This contamination changed the material from LiAlO₂ to LiAl₅O₈. The resultant LiAl₅O₈ changed the wetting angle of the molten salt which impeded the salt infiltration. Work was discontinued on the Lithium Aluminate material and re-focused on Aluminum Nitride.

The following tables illustrate the relationship between raw material surface area, firing temperature, and yielded porosity and pore size:

Aluminum Nitride

Firing Temperature	% Porosity	Pore Size
1550	48	0.38μ
1600	47	0.39μ
1650	46	0.42μ

Lithium Aluminate (LiAlO₂)

Firing Temperature	% Porosity	Pore Size
1350	48	4.2μ
1400	50	4.0μ

Surface Area Affects on Lithium Aluminate (LiAlO₂)

Surface Area	% Porosity Fired at 1350°C	Pore Size
0.69 M ² /gm	46	4μ
① 1.40 M ² /gm	44	2.8μ
② 2.10 M ² /gm	40	2.0μ
* 4.00 M ² /gm	38	1.2μ
* 5.60 M ² /gm	38	0.7μ

① High Intensity dry grind 4 hours

② High Intensity dry grind 8 hours

* These were achieved by wet grinding. However, it caused the chemical to change from LiAlO₂ to LiAl₅O₈ due to the ball/mill wear from 48 hour grind time.

The resulting microstructures and performance graphs are attached.

Final Analysis & Cost of Aluminum Nitride Parts:

- Discs 0.100" thick x 1.00" in diameter \$2.00 Each
- Tubes 0.500" diameter x 6" long x 0.100" wall \$4.00 Each

From a final cost, manufacturability, and ease of handling perspective, the best thickness membrane to perform this level of separation seems to be either the 0.100" to 0.075" thicknesses. The thinner level membranes offer relatively little performance improvement at a significantly high manufacturing cost, and are more fragile to handle.

TASK 2.2 -- CERAMIC AND SEAL DEVELOPMENT -- FY 91/92 -- CONCEPT EVALUATION, DEVELOPMENT AND TESTING -- COORS CERAMICS

TASK	APRIL		MAY				JUNE
	21	28	05	12	19	26	02
1. ALUMINUM NITRIDE DEVELOPMENT							
1. RECEIVE INPUT FROM APCI	**						
2. DETERMINE TEST MATRIX	***						
3. PREPARE AlN SPECIMENS	*****						
4. CHARACTERIZE GREEN AlN		*****					
5. DETERMINE FIRING SCHEDULES			*****				
6. INITIAL FIRING (HP/MOLY)			*****				
7. CHARACTERIZE FIRED AlN				*****			
8. PERFORM ADDITIONAL FIRINGS				*****			
9. CHARACTERIZE ALL FIRINGS				*****			
10. DETERMINE VARIABLE RELATIONS					*****	*****	
11. Hg POROSIMETRY EVALUATIONS					*****	*****	
12. SAMPLES TO APCI						*****	
13. POROUS DEVELOPMENT							
14. CONTROLLED POROSITY EXP'TS							
15. POROUS SAMPLES TO APCI							
16. MONTHLY PROGRESS REPORT			**				**
17. ALUMINUM TITANATE TO APCI	**						
18. MEETING IN CINCINNATI		**					

APCI MEMBRANE DEVELOPMENT

ID	Name	April	May	June	July	August	September	October	November	December	J
1	LITHIUM ALUMINATE										
2	milling experiment										
3	apci replication										
4	process study										
5	initial samples										
6	membrane production										
7	ALUMINUM NITRIDE										
8	1600/10ksi samples										
9	coarse material										
10	bi-layer material										
11	MEETING AT COORS										
12	REPORTS										

Project: APCI MEMBRANE
Date: 4/10/92

Critical

Progress

Summary

Noncritical

Milestone

APCI/COORS SHORT TERM WORK PLAN

10/04/91

=====			
TASK	OCTOBER 1991	NOVEMBER 1991	DECEMBER 1991
=====	=====	=====	=====
AIN MEMBRANES	XXXXXXXXXXXXXXXX	XXXXXXXXXXXXX	
LIPID REPRO/MEM	XXXXXXXXXXXXXXXX	XXXXXXXXXXXXXXXXXXXXXXXXXXXX	XXXXXXXXXXXXXXXXXXXXXXXXXXXX
COARSE AIN	XXXXXXXXXXXXXXXX	XXXXXXXXXXXXXXXXXXXXXXXXXXXX	XXXXXX
BILAYER AIN			XXXXXXXXXXXXXXXXXXXXXXX
AIN/BN HYBRIDS			XXXXXXXXXX
=====			

APCI FACILITATED TRANSPORT CONTRACT -- 1992-93

Project: APCI CONTRACT 92-93
Date: 6/11/92

Critical Progress Summary
Noncritical Milestone

APCI FACILITATED TRANSPORT CONTRACT - 1992-93										
March Mar	April Apr	May May	June Jun	July Jul	August Aug	September Sep	October Oct	November Nov	December Dec	January Jan
Project: APCI CONTRACT 92-93 Date: 6/11/92 Critical Progress Summary Noncritical Milestone										

Critical

Noncritical

Summary

AIN DELTECH FIRING 1600 C/1 HR

POROUS ALUMINUM NITRIDE

FIRING: 1600 C, DELTECH/CRUCIBLE

LOT #: 71

PRESSURE: 10 KPSI

MAGNIFICATION: 10,000 X

SAMPLE PREP: FRACTURE SURFACE

DATE: 06/01/91

AIN DELTECH FIRING 1650 C/1 HR

175

POROUS ALUMINUM NITRIDE

FIRING: 1650 C, DELTECH/CRUCIBLE

LOT #: 71

PRESSURE: 10 KPSI

MAGNIFICATION: 10,000 X

SAMPLE PREP: FRACTURE SURFACE

DATE: 06/01/91

LITHIUM ALUMINATE MILLING STUDY W/ 10% LITHIUM FLUORIDE

PORE & PARTICLE SIZE VS. MILLING TIME
LiAlO₂ & 10% LiF • 10KPSI/1300 C

AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

3 of 3

PARTICLE SIZE DISTRIBUTION

CI 2204

SAMPLE IDENTIFICATION *21 A1*

Density *2.55* g/cc LIQUID

Preparation

K-616 3c (ug) 1 A-51 3c (ug)

Density g/cc Viscosity cp

DATE *6-3-72*

BY *h. S. Schmitt*

TEMPERATURE *28* °C

RALE *1/0-1* START DIA *380* μ m

EQUIVALENT SPHERICAL DIAMETER, μ m

PARTICLE SIZE DISTRIBUTION

CL-2204

SAMPLE IDENTIFICATION *L: A1*

Density *2.558* g/cc LIQUID

Preparation *05 Solplex 270*

15 min K-616 - 8.11%₂

Density

g/cc

Viscosity

cp

DATE

6-16-92

BY

D. Hunt

TEMPERATURE

28

°C

TIME

10:41

DATE

6-16-92

TIME

10:41

EQUIVALENT SPHERICAL DIAMETER μm

**DATE
FILMED**

10/18/94

END