Gas Separations using Ceramic Membranes

Final Project Report

Paul K. T. Liu
Project Director

MEDIA AND PROCESS TECHNOLOGY, INC.
1155 William Pitt Way
Pittsburgh, PA 15238

Date Published – January 5, 2006

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Cooperative Agreement
No. DE-FG36-93CH10561

Subcontractor
University of Southern California
GC Environmental Corp.

EXECUTIVE SUMMARY

This project has been oriented toward the development of a commercially viable ceramic membrane for high temperature gas separations. A technically and commercially viable high temperature gas separation membrane and process has been developed under this project. The lab and field tests have demonstrated the operational stability, both performance and material, of the gas separation thin film, deposited upon the ceramic membrane developed. This performance reliability is built upon the ceramic membrane developed under this project as a substrate for elevated temperature operation. A comprehensive product development approach has been taken to produce an economically viable ceramic substrate, gas selective thin film and the module required to house the innovative membranes for the elevated temperature operation. Field tests have been performed to demonstrate the technical and commercial viability for (i) energy and water recovery from boiler flue gases, and (ii) hydrogen recovery from refinery waste streams using the membrane/module product developed under this project. Active commercializations effort teaming with key industrial OEM's and end users is currently underway for these applications. In addition, the gas separation membrane developed under this project has demonstrated its economical viability for the CO_2 removal from subquality natural gas and landfill gas, although performance stability at the elevated temperature remains to be confirmed in the field.

KEYWORDS
ceramic membranes, gas separations, flue gas energy recovery, subquality natural gas upgrading, landfill gas upgrading, hydrogen separation, high temperature gas separations.

TABLE OF CONTENTS

List of Tables

1. PROJECT OVERVIEW

1.1. Existing Ceramic Membranes as Substrate for Gas Separation Applications

Although ceramic micro- and ultra-filtration membranes were developed over half a century ago, they have always been considered a niche product. Due to their high cost (e.g., =$1,000/m^2 versus $100's/m^2 for polymeric counterparts), their use has been limited primarily to food, beverage and pharmaceutical industry applications traditionally. Recently, most of the development activities have been concentrated in gas separations, particularly as ionic conductors for oxygen transport and as molecular sieve membranes for hydrogen and CO_2 separations. Existing ceramic membranes are not suitable for most gas separation applications since their pore sizes are at least one order-of-magnitude larger than the gas molecular size. However, due to their material stability, particularly temperature stability, existing porous ceramic membrane could be ideal substrate for gas separation membranes. Nevertheless, their high cost and their low packing density per module have prevented their wide use for gas separations. Although the objective of our project is to develop a high temperature gas separation membrane, we have invested substantial effort and resources to develop a new generation of ceramic membrane to meet the cost and the packing density requirement for high temperature gas separations.

1.2. Unique Features of The New Generation of Ceramic Membranes

Under this project, Media and Process Technology Inc. (M&P) has focused on the development of low cost high performance ceramic membranes and their use in cost sensitive applications [1]. The product that has evolved is based upon single ceramic tubular elements potted into large high surface area bundles as Figure 1.1 illustrates. In this configuration, the membrane cost is less than 1/3 of that of existing monolithic ceramic membrane. However, it still retains the high purity materials of construction and controlled pore size distribution of the more expensive counterparts. Further, the robust nature of the technology has been demonstrated in both field tests and commercial installations for operating times of over 3 years with no significant mechanical failure. Finally, to meet the application requirements, the individual tubes as well as the tube bundles can be prepared in various sizes. This flexibility is simply unavailable using conventional monoliths. Numerous industrial liquid streams, both large and small scale, have been identified, which can benefit from this low cost high performance ceramic membrane technology. In this project we have focused on the development of this new generation of ceramic membrane for gas separations.

The advantages of using ceramic membranes as substrate for gas separation membranes include:

- Narrow and well defined pore size distribution in comparison with their polymeric counterparts. Figure 1.2 presents the pore size distribution for our commercial ceramic membranes with various nominal pore sizes covering the micro- and ultra-filtration range. The uniform pore size distribution of the ceramic membrane as substrate is essential for the deposition of a defect free, ultra-thin film for gas separations.

- Material stability in harsh environments. Since most gas separations utilizing inorganic membranes involve higher than room temperature, the high temperature stability of the ceramic membrane is essential as a substrate for gas separation inorganic membranes.

Our new generation of the ceramic membrane offers specific advantages as substrate for gas separations, including

- Manufacturing flexibility for thin film deposition. Promising gas separation thin films encompass a wide array of materials, such as zeolite, metallic, metal oxide, carbon, high temperature polymer, etc. During the manufacturing development phase, a single tube deposition provides the convenience for R&D. However, to reduce the manufacturing cost, deposition and preparation on a module basis is ideal. Our ceramic membrane configuration permits deposition-in-module, as opposed to existing ceramic membranes limiting to the multiple channel element as a preparation unit.

- Module fabrication flexibility. Potential gas separation applications involve a wide array of application environment. Pressure drop, available space, stream size are all important factors to determine the module geometry, dimension (i.e., both cross section and length), and configuration for a given application. Our product offers an unique flexibility to accommodate these factors. Module size of 20 to 40 m^2/module or module length as short as 15” has been designed and/or constructed for application requirements.

- Seal between housing and membrane elements has been a major technical barrier to prevent the use of the ceramic membrane for high temperature applications. In our module configuration, the sealing mechanism and material suitable for both intermediate and high temperature have been developed.

In summary, our new generation of ceramic membrane has addressed cost, technical and engineering issues hampering the use of existing ceramic membranes for gas separations. In the next chapter, we will present a unique application of the use of our new generation of ceramic membrane (without additional thin film deposition) for gas separations. As mentioned earlier, the pore size of existing ceramic membranes is inadequate for most meaningful gas separations. Under this project, through our effort in collaboration with Gas Technology Institute (GTI), we have successfully developed a commercial application using this new generation of ceramic membrane for energy and water recovery from flue gas. In Chapter III and IV, carbon molecular sieve thin film deposited on this ceramic membrane for hydrogen and CO_2 separations respectively are presented.

Tube OD x ID [mm]	Surface Area per Volume [m^2/m^3]	
	ID	OD
3.0 x 1.5	470	940
4.0 x 2.0	400	800
5.5 x 3.5	325	510

Figure 1.1 M&P ceramic membrane tubes and four-inch commercial element. Also given is the packing density of the various standard tubes based upon the inside and outside surface area.

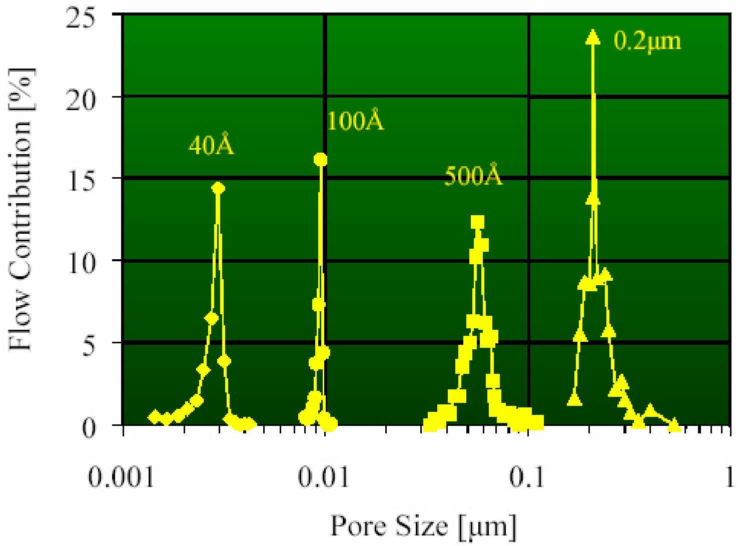


Figure 1.2 . Pore size distributions of various M&P ceramic membranes.

Reference

1. Ciora, R. J., Jr., P. K.T. Liu, “Ceramic membranes for environmental related applications”, Fluid/Particle Sep. *J.*, 15, ,51 (2003*)*

2. ENERGY AND WATER RECOVERY FROM BOILER FLUE GASES

2.1. Introduction/Application Background

An innovative transport membrane condenser (TMC) concept has been demonstrated by the Gas Technology Institute (GTI) for efficient energy and water recovery from low temperature and low pressure boiler flue gases using our new generation of ceramic membranes. The TMC can selectively extract the low pressure water vapor from flue gas into the membrane micropores in the liquid form via the pore condensation mechanism. The recovered ultra-pure hot water is then transported away from the membrane in liquid form for recovery and reuse. This innovative process concept has been demonstrated by GTI to be far superior to conventional condensing economizers. Specifically, due to the low temperature gradient across conventional heat exchanger surfaces, heat transfer is inefficient leading to large condensing economizer surface area requirement. These factors make it cost prohibitive, so that condensing economizers are not commonly used in the North American market [1] and the energy and water contained in the boiler flue is usually not recovered [2].

If energy recovery from flue gas can be efficiently achieved, the energy savings potential is enormous. U.S. industry is the largest single energy consuming sector in the nation, accounting for 35% (about 35 quads, 1 quad=10^{15} Btu=1.055×10^{15} kJ) annually, of which about 15 quads is used for on-site fuel combustion by boilers/steam systems and process heating. Flue gas heat recovery and water reuse via the proposed TMC can increase the boiler efficiency by about 5% for state-of-the-art boilers (energy efficiency boost from ~89% to ~94%, HHV basis, based upon our feasibility test results) and will be significantly higher for lower efficiency older installed boiler capacity. Annual savings well in excess of one quad can be expected. In addition, this proposed TMC concept is not limited to boiler applications; it can also economically recover a wide range of the “low grade” waste heat available in industrial processing streams, such as high humidity drying process exhaust in the paper industry. The total waste energy available in this industry is ~1.8 quad/year [2]. Finally, the fuel consumption reduction realized by the proposed process concept leads directly to a significant reduction in CO_2, CO, and NOx emissions.

2.2. Conventional Technologies, Their Problems and Our Solution

2.2.1. Conventional Technologies

Flue gas is typically available at low pressure, low temperature, and high volume; recovery of water vapor (and its latent heat) in the flue via conventional gas separation technologies, such as membranes or pressure swing adsorption (PSA), is not economical at all. The commercially available condensing economizer offers an avenue to recover this water vapor via condensation (as opposed to gas separation); however, the recovered water is contaminated with the particulate matter (PM) present in the flue. More importantly, it relies on a 2nd fluid as a coolant, to transfer the latent heat away from the condensate. Due to the inefficient conductive heat transfer through the limited temperature gradient, excessive heat transfer surface area required leads to large units that are very expensive, therefore the condensing economizer simply has not achieved any appreciable acceptance and hence market penetration in the US.

Although water vapor separation via pore condensation with a porous membrane as an interphase has been discussed in the literature [3], the technology was explored for a dehumidification. Thus no net gain in energy or water is readily available for practical reuse. In summary, the tremendous energy and water resources available in the flue cannot be recovered economically, practically and "greenly" with conventional gas separation or condensing devices [3]. With our novel process concept, the TMC is capable of recovering "low grade" waste energy efficiently and effectively in an environment where the water vapor pressure and temperature gradient is too low to be practical for conventional technology.

2.2.2. Our Proposed Solution – Transport Membrane Condenser (TMC)

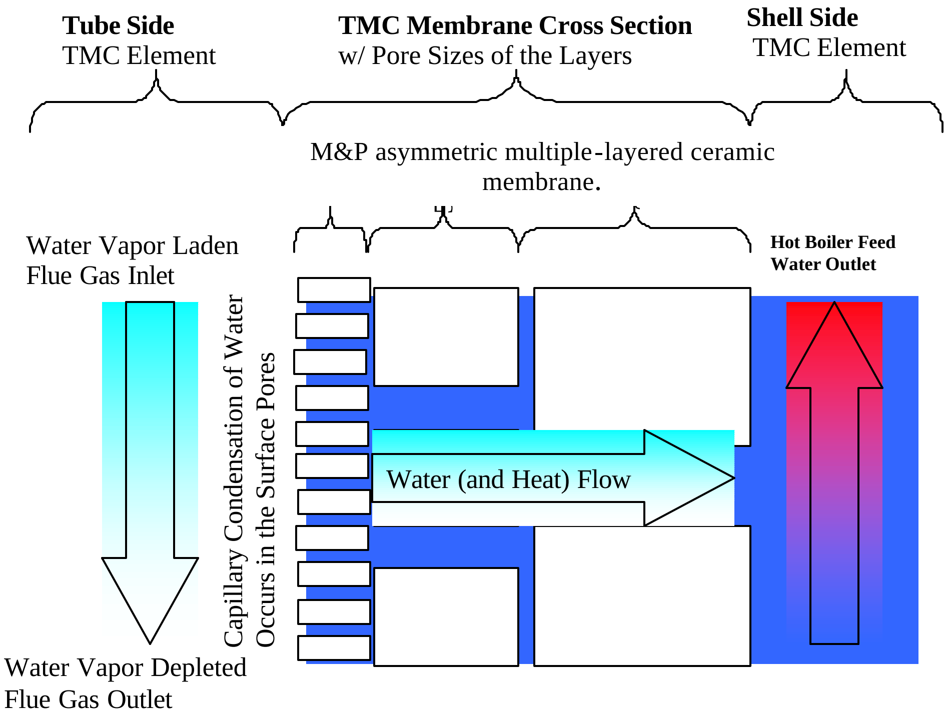


Figure 2.1 - The Transport Membrane Condenser concept. Schematic shows the cross section of a membrane tube in a TMC bundle

GTI has recently demonstrated a new unit operation concept for latent heat recovery from the flue gas of packaged boilers, the TMC as shown in Figure 2.1. Figure 2.2 shows standard M&P ceramic membrane elements configured as prototype TMC elements. Water-vapor-laden flue gas near its dew point is passed through the tubes of the TMC and condensed in the pores of the membrane surface layer. The water is then convected away from the surface under a small negative pressure applied to the water on the shell side of the elements. Condensation results from two sources, namely, (i) the cooling effect of the cold water on the shell side and (ii) capillary condensation in the micropores at the surface of the membrane. Capillary condensation is important here because the water vapor can be condensed in the pores of the membrane even if its vapor pressure is below the saturation pressure at the same temperature (based upon Kelvin equation). Hence, by using the TMC membrane, it is possible to extract water from flue gas that is well above its dew point via enhanced condensation.
In contrast, using the membrane to selectively separate water vapor in the flue via a conventional pressure driven process is practically impossible due to the low vapor pressure difference across the membrane. There are two primary advantages of the TMC over the conventional condensing economizer, specifically, (i) heat transfer between the hot and cold streams occurs not only via conventional heat conduction but also more importantly via convective heat transfer by the condensed water through the membrane and (ii) the water vapor in the emission stream is condensed directly into the unit. These advantages greatly enhance the heat transfer performance and yield a significant reduction in the size of the unit relative to the condensing economizer.

Figure 2.2 - Photo of several prototype TMC elements

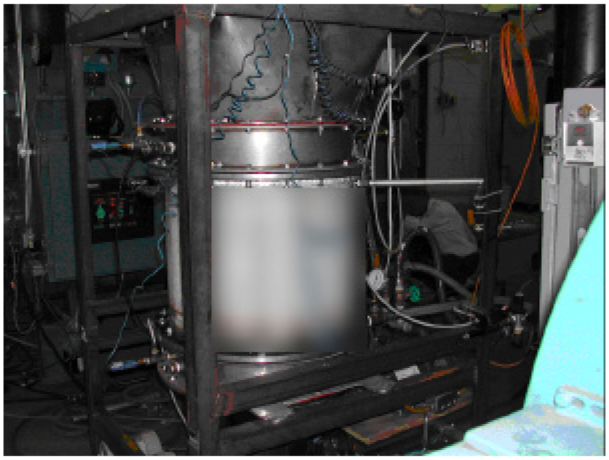


Figure 2.3 – Installed TMC elements for water vapor removal from the flue gas of an 880 kW boiler.

In addition, the flue gas exiting the TMC unit will always be below its dew point so that it is unnecessary to worry about stack corrosion due to condensation and the unfavorable perception of the plume. Practically speaking, a plastic pipe is all you need as a stack, since the flue gas exit from the TMC is lower than 50°C. The TMC concept has been demonstrated successfully at the GTI lab with the prototype unit as presented in Sec. 2.4

2.3. Experimental Methods

The membrane development activities were carried out by Media and Process Technology Inc. while the performance evaluation was mainly performed by GTI. The activities of each party are briefly described below:

- ***Ceramic Membrane Module Fabrication…*** As stated in Chpater I, the unique advantages of our ceramic membrane is its manufacturing flexibility in module configuration. Through iterative effort between GTI (our collaborator) and us, we provided membrane products with various dimensions, pore sizes, and tube spacings for GTI to perform treatability study. Based upon the results, a membrane configuration with a suitable pore size was selected as a first generation product for manufacturing the prototype unit and several commercial units.
- ***Membrane Performance Evaluation…*** Through the joint development effort, GTI was responsible for the evaluation of the performance of the membrane candidates. Using the boiler facility available at GTI, the membrane performance was monitored in terms of its inlet and outlet temperatures and dew points for calculation of energy and water recovery, and then estimate the boiler efficiency improvement.

The test results using the prototype unit are presented in Section 2.4.

2.4. Experimental Results and Discussion

A prototype TMC unit has been fabricated using M&P ceramic membrane products described in Chapter I. This prototype unit was installed (see Figure 2.3) and tested at GTI's facility on an 880 kW industrial boiler. A typical test result is illustrated in Figure 2.5.

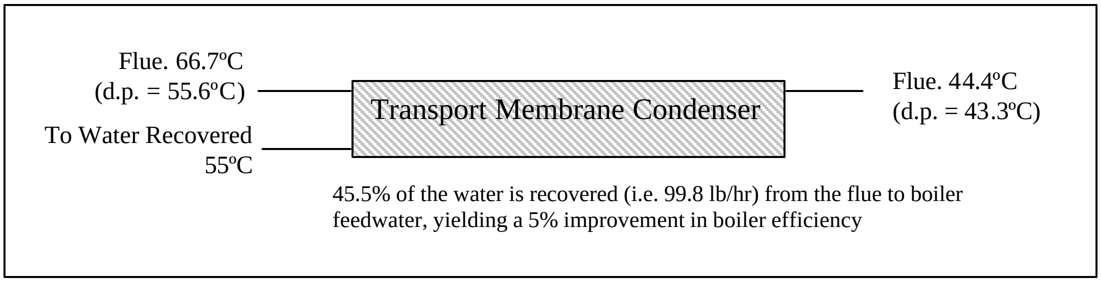


Figure 2.4 - Feed and Exit Stream Temperatures of Flue, and Water through the Proposed Transport Membrane Condenser. A pilot scale testing unit contains a total of 9.75 m^2 of membrane surface area was used here.

About 45% of the water vapor in the flue gas was recovered. This results in a thermal efficiency improvement from ~89% (current state of the art boiler efficiency with economizer, HHV basis) to ~94%. Based upon the % water recovered, we believe that the efficiency improvement could be significantly higher or the required membrane surface area significantly reduced with improved membrane properties. In summary, our preliminary testing has demonstrated the technical feasibility of the TMC to recover energy and water from a low temperature flue gas stream, but the TMC performance using an existing M&P commercial water filtration ceramic membrane was well below the potential performance of the proposed technology. Presently, we have worked closely with GTI for the development of the 2nd generation of the product to maximize the potential offered by this new generation of ceramic membranes.

2.5. Economic Analysis

Since water is recovered via condensation and transport through an ultrafiltration (UF) membrane, the recovered water is ultra pure and can be reused for most of industrial process. As a result of the vapor latent heat recovered from the flue gas, = 5% boiler efficiency improvement can be achieved besides savings in water consumption and treatment in a state of the art boiler. Higher savings can be realized for less efficient installed (legacy) boilers. Our new generation of ceramic membrane, although not originally developed for this specific applications, has been evaluated in a prototype, demonstrating its technical and process viability. Presently, we are working actively with GTI and a commercialization partner to optimize the unit performance via a theoretical and empirical approach for membrane/modules design uniquely suited for this selected application. According to the economic analysis by our commercialization partner, payback period of less than one year is achievable.

References

1. “A Market Assessment for Condensing Boilers in Commercial Heating Applications”, Consortium for Energy Efficiency, 2001.
2. “Energy Use, Loss and Opportunities Analysis: US manufacturing & Mining”, Report prepared by E3M, Inc., December 2004, for US DOE.
3. Scovazzo, P., J. Burgos, A. Hoehn and P. Todd, “Hydrophilic membrane-based humidity control, J. Memb. Sci., 149, 69 (1998).

3. HYDROGEN RECOVERY FROM REFINERY WASTE STREAMS

3.1. Introduction/Application Background

Worldwide hydrogen demand in refineries is expected to grow significantly. Current regulatory and economic trends in the petroleum refining industry will require an estimated 9% average per year increase in worldwide hydrogen production in the coming decades. Presently, the hydrogen in off-gases is burned as fuel, which represents only about 1/3 of its value as a chemical feedstock. If a significant fraction of this hydrogen can be recovered for reuse, then the expected H_2 demand could be delivered without adding hydrogen production capacity. Recovery of hydrogen from waste streams will represent a low-capital and short lead-time, but economically attractive solution. The chemical and petroleum industries in the United States produce large volumes of hydrogen containing off-gas streams in excess of 1,800 million SCFD. The gas streams consist primarily of light hydrocarbons and contain hydrogen at relatively low concentrations 20 to 50%. Currently, recovery of hydrogen from the mixed gas streams is not economical using existing conventional technologies and, therefore, the mixed gas stream is burned as fuel.

3.2. Existing Technologies, Their Limitations and Our Solution.

There are several potential solutions for hydrogen production and recovery to meet the hydrogen demand in refineries. It can be outsourced from over-the-fence suppliers. New hydrogen plants can be built onsite, but this option will involve substantial investment and many years to realize a return. Another attractive option for refiners, who have an existing hydrogen plant, is retrofitting this unit with advanced processing technologies and catalyst systems that can incrementally raise hydrogen capacity. However, this option is not as economically attractive due to the consumption of feedstock and production energy as opposed to a simple filtration process. Alternative non-membrane hydrogen recovery technologies include cryogenic distillation and pressure swing adsorption (PSA). Distillation requires a large capital investment and is most suitable for high purity, large scale applications. In addition, the cryogenic process is highly energy intensive. PSA is more economically suitable for the smaller scale; however, the economics are poor for off-gas streams containing <50% hydrogen, commonly found in waste streams. The membrane-based technology is a nice fit for localized operations.

Recovery via existing polymeric membranes are unacceptable due to fouling and damage by heavy hydrocarbon condensable vapors contained in the off-gas. M&P inorganic membranes resist fouling and can be tailored for the operating temperature, i.e., >80 to 100°C to <250°C. Metallic membranes, such as palladium alloy-based, can deliver very high purity hydrogen. However, elevated temperatures in excess of 400°C are required to be practical. Further, these membranes are highly susceptible to poisoning by carbon monoxide, sulfur, and water at high temperature. In this project, hydrogen-selective CMS membrane, made of carbon, which is known for its inertness, are chosen over the palladium membranes for the selected application.

3.3. Experimental Methods

3.3.1. Preparation of CMS Membranes.

Several polymeric precursors have been selected for the pyrolysis study to deposit a CMS thin film on our ceramic membranes as substrate. Our goal here is to deposit an ultra thin, defect free carbonaceous thin film on our commercial ceramic membrane substrate for hydrogen separations. Numerous polymeric precursors have been explored for a wide pyrolysis temperature range, i.e., 500 to 900ºC, and under various atmosphere. Our tubular commercial ceramic membrane with 3.5 mm ID and 4.5 mm OD with 10" L was used during the developmental stage. During the manufacturing phase of the project, we employed 30" L tube for the manufacture of the full-scale membrane.

3.3.2. Characterization of CMS Membranes with Single Components.

The single tubular CMS membranes were then characterized with single components, including N_2, He, H_2, and CH_4 at room temperature to >300ºC. The tubular membrane was mounted in a stainless steel housing with O-ring or graphite for sealing, depending upon the temperature range studied. Although the permeances of the higher chain hydrocarbons were performed occasionally, generally their permeances were too low for meaningful measurement.

3.3.3. Performance Evaluation with Mixtures.

Some of the CMS membranes after characterization with single components were subject to the mixture separation study. The mixtures selected for this study are composed of hydrogen, nitrogen, CO, methane, and other trace impurities, such as H_2S, simulating reformate. The mixture separation was performed in terms of hydrogen purity vs hydrogen recovery (%) at a given temperature. In addition, the separation results were compared with the mathematical prediction we developed in-house. H_2S content at ppm's levels were determined with the Drager tube. The concentrations of hydrogen, CO, CO_2 and N_2 were determined with GC using the CTR I GC column (Supelco; parallel 5A zeolite and Poropak) with a TCD detector.

3.3.4. Chemical and Storage Stability.

The objective of the chemical stability study was to determine the minimum operating temperature required at which stable membrane performance can be obtained in the presence of non-hydrogen organic vapors as poisons. Based upon previous experience in our H_2 selective CMS membrane program, the long term stability potential of a CMS membrane can be inferred relatively quickly in short term challenge tests (see Sec.3.4) conducted over 20 to 50-hours. Hydrogen or helium was doped with selected contaminants, which was then sent to the membrane at various elevated temperatures (120 to 220°C) for determination of the permeance versus exposure time. In addition, the storage stability of the CMS membrane was evaluated under this study. Finally, the regenerability of the CMS membrane was also experimentally confirmed by thermal regeneration at >200°C with an inert gas. The complete regenerability of the CMS membrane is indicative of the reversibility of poisoning, which offers an insurance policy in the field operation.

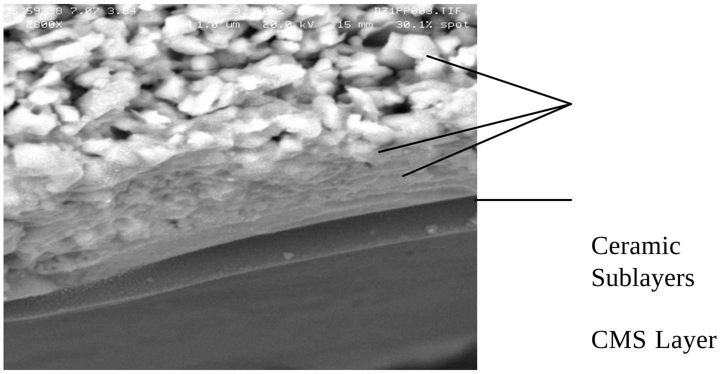


Figure 3.1. SEM photomicrograph of a CMS layer on an M&P commercial ceramic ultrafiltration membrane (as a substrate).

3.3.5. CMS Membrane Manufacturing Development

In addition to the preparation of single tubular membranes under various pyrolysis conditions, we have also performed the manufacturing development for a selected manufacturing condition. A batch of the ceramic membranes were set aside for the deposition and pyrolysis under an identical condition. These membranes were then characterized in terms of their hydrogen (or helium) and nitrogen permeance at a given temperature to determine its manufacturing reproducibility.

3.3.6. Membrane Bundle and Housing Development

The tubular CMS membranes were then potted together with organic or inorganic potting materials to become a multiple tube bundle as a pilot or a full-scale bundle. In addition, stainless steel housing was designed and fabricated for the hydrogen recovery applications. Each bundle was characterized using single components as described above to verify the performance under the bundle configuration.

3.4. Experimental Results and Discussion

3.4.1. M&P CMS Membranes

Our CMS membranes are prepared via deposition and pyrolysis of a polymeric precursor on our commercial ceramic membrane substrates as shown in (carbon layer). Considerable testing has been conducted to verify the performance and stability of the membranes in a variety of gases, vapors, and operating environments. Our in-house evaluation results are summarized in the following subsections.

3.4.2. *Performance of M&P's CMS-based Hydrogen Selective Membrane:*

Membrane H_2 permeances ranging from 0.8 to >5 m^3/m^2/hr/bar (27 to 168 scfh/ft^2, at 10 bar) have been demonstrated by M&P. Selectivities for H_2 to N_2[1] are 25 to >100, even at temperatures up to ~400ºC. A typical permeance vs. temperature for H_2 and N_2 is presented in Figure 3.2. The H_2 permeance increase is consistent with activated diffusion via molecular sieving. The maximum in selectivity is due to the N_2 permeance, which at low temperatures displays Knudsen type diffusivity (i.e., decreases with temperature), but at higher temperatures becomes activated as molecular sieving begins to dominate (about 150 – 400 ºC for this membrane).

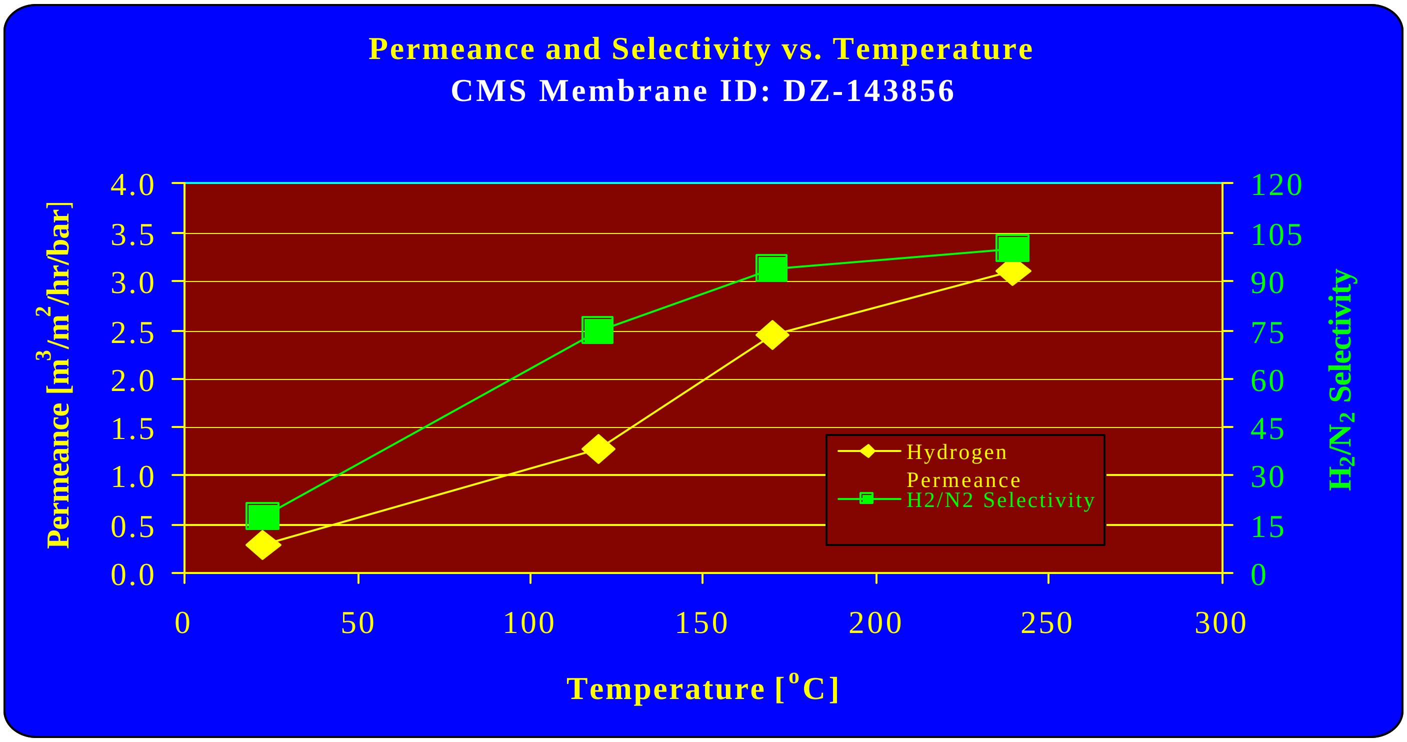


Figure 3.2:Temperature dependence of the permeance and selectivity of an M&P CMS membrane (targeting 50 to 250ºC applications).

---

[1] Nitrogen is used here to represent gas components rejected by this CMS membrane, including CO_2 and CO. and light hydrocarbons.

3.4.3. *Hydrothermal Stability of M&P's CMS-based Hydrogen Selective Membrane*

As is well-known, carbon (particularly microporous carbon) will react with steam at sufficiently high temperatures. The 350 to 400 °C temperature range is, generally, considered low for carbon-steam gasification, particularly in the presence of not so high pressure steam; nevertheless, long-term thermal and hydrothermal stability testing has been conducted at M&P to demonstrate the CMS membrane's suitability for the selected application environment. Figure 3.3 shows the H_2 permeance, and the H_2/N_2 selectivity of one of the M&P membranes in a hydrothermal stability test conducted at 220-300 ºC, in a ca. 25-day test run. The test results demonstrate the hydrothermal stability of the CMS membranes. In addition, though porous carbon poisoning by organic vapors is well-known, it can be prevented by operation at high temperatures, e.g., >200 ^{o}C as shown in the next subsection.

3.4.4. Stability in the Presence of Concentrated Organic Vapors

Beyond membrane permeance and selectivity, membrane performance stability in the proposed operating environment is *the critical factor that determines the commercial viability*. We have found through years of development that CMS based membranes suffer severe performance decay in the presence of water and organic vapors when operated at near ambient temperature. To overcome this problem, elevated temperatures are always necessary to maintain performance stability. As an example, Figure 3.4 shows the results of an organic vapor challenge test of a H_2 selective CMS membrane at 80, 150, and 180ºC using He saturated with hexane at room temperature. At 80 and even 150ºC, significant and rapid He permeance decay is observed. This effect is significantly

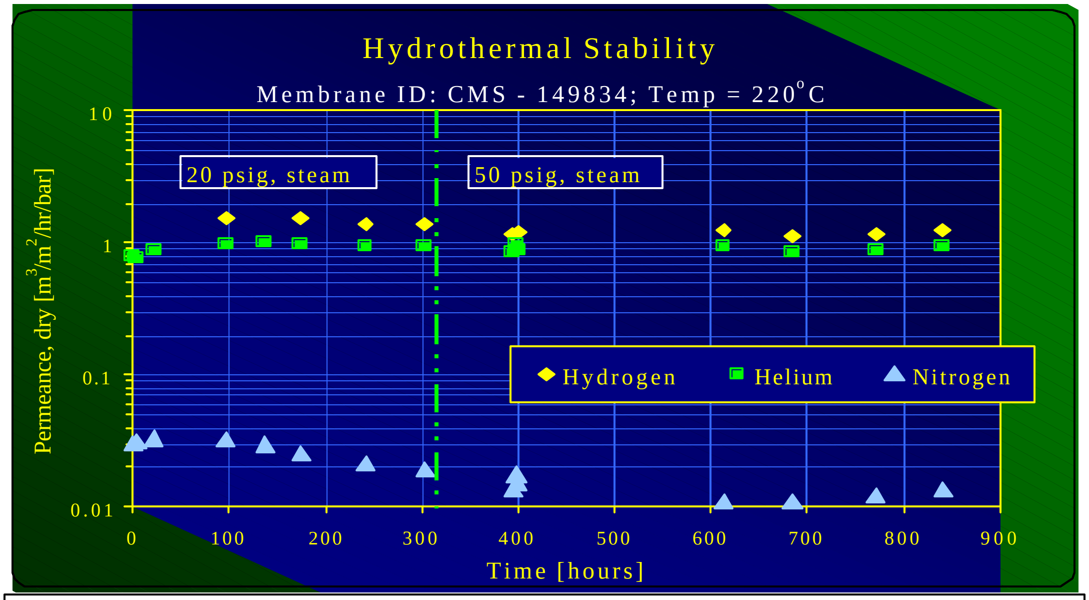


Figure 3.3: Hydrothermal stability test of the CMS membrane at 30 to 50 psig steam and 220ºC.

reduced at 180ºC and in our experience typically disappears above 200ºC. Further and, as importantly, the membrane permeance is easily recovered following thermal cycling of the membrane to 180ºC in pure He. Finally, similar results have been obtained in tests conducted using toluene and trichloroethylene.

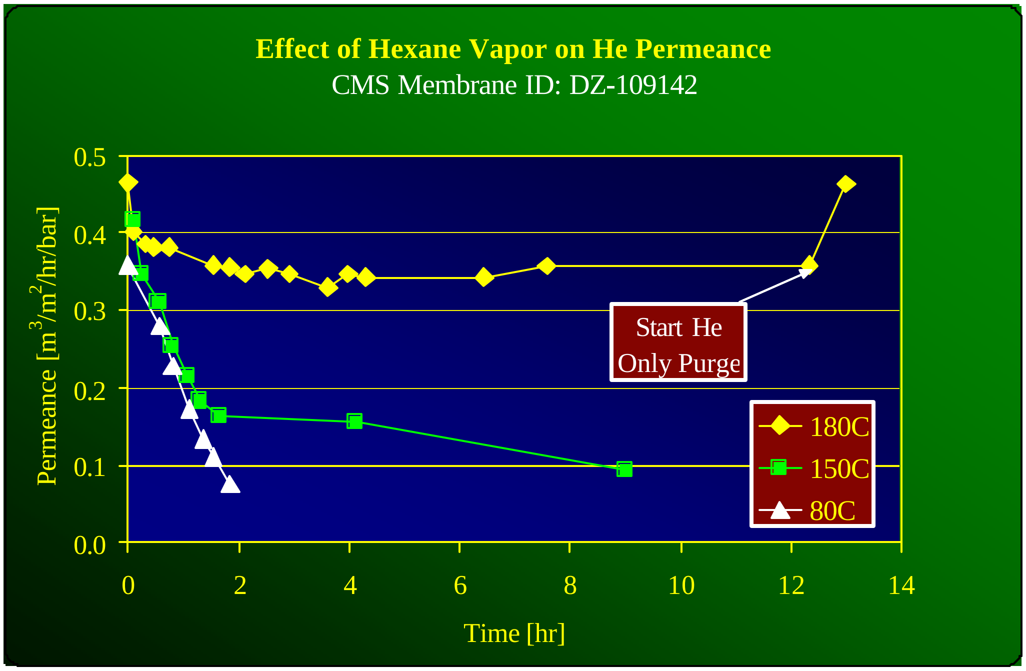
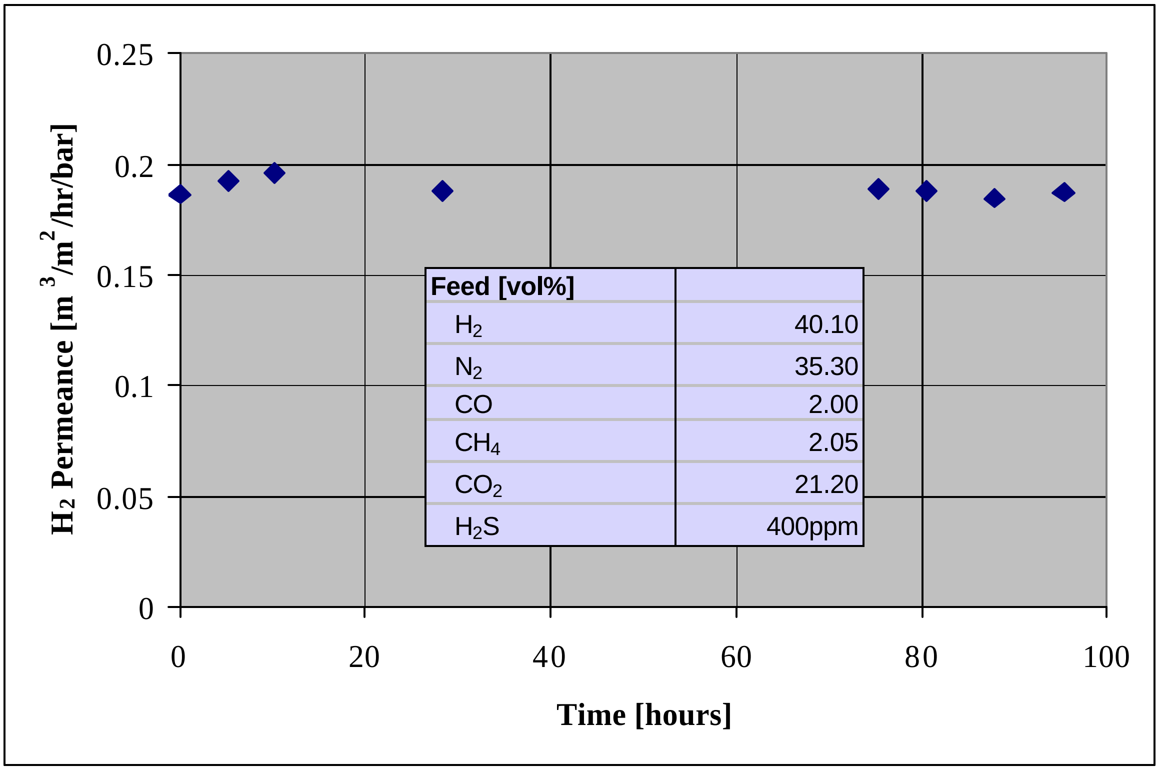


Figure 3.4. Organic vapor stability of a CMS membrane versus temperature.

3.4.5. Stability in the Presence of H_2S, CO and CH_4

Although our previous experience indicates that our CMS membrane is chemically stable in the presence of H_2S, CO and CH_4 an experimental evaluation using the synthetic reformate was performed to confirm its long term operational stability. We conducted over 100 hours of long term performance stability testing of our membranes in the presence of the synthetic feedstock composed of 44% H_2, 31% N_2, 2% CO, 2% CH_4, 21% CO_2 and 400 ppm H_2S. Figure 3.5 shows the results of this test. As can be seen the H_2 permeance is stable over the entire test period.



Feed [vol%]	
H_2	40.10
N_2	35.30
CO	2.00
CH_4	2.05
CO_2	21.20
H_2S	400ppm

Figure 3.5. H_2 permeance versus time for the CMS membrane NN-234 in a 100 hour long term stability test conducted in the presence of synthetic reformate.

In conclusion, comprehensive lab and field tests have been performed by us to demonstrate the performance stability of our CMS membrane in the presence of H_2S, etc. when the CMS membrane was operated at elevated temperature as we recommended.

3.4.6. Performance of M&P CMS Membrane for Mixture Separations

Our hydrogen selective membrane was evaluated here for (i) the removal of poisonous contaminants present in the reformate, primarily hydrogen sulfide and CO, and (ii) enrichment of hydrogen from the reformate mixture. Experimental study on H_2S and CO removal from the synthetic reformate was completed and the result is presented below in Table 3.1:

The mixture separation result using the M&P hydrogen selective membrane is presented in Figure 3.6. Hydrogen purity of the recovered hydrogen can reach ~95% at 75% hydrogen recovery for the feed containing 44% hydrogen. The removal of CO, H_2S vs the % hydrogen recovered is presented in Figure 3.7 and 3.8. In addition, the mathematical simulation was performed based upon the single component permeance. The simulated results can be correlated well with the simulated results for the hydrogen purity, and the removal of H_2S and CO, indicating the mathematical model developed by us can predict the separation reliably.

Table 3.1. CO and H_2S removal vs H_2 recovery using CMS membrane (NN-234) at 220ºC and 150psi.

Stage Cut [%]	Estimated H_2 Recovery [%]	CO Removal		H_2S Removal	
		In [%]	Out [%]	In [ppm]	Out [ppm]
13.2	28	2.0	0.102	400	21
24.5	53	2.0	0.105	400	24
35.4	76	2.0	0.140	400	29

Table 3.2. Composition analysis of mixture separations and their operating conditions

	Run #1	**Run#2**	**Run#3**
Stage Cut [%]	13.5	18.4	24.8
H_2 Recovery [%]	32.6	44.1	58.9
Feed [vol%]			
H_2	*40.1*	*Feed Press*	*164.7 psia*
N_2	35.3	Permeate Press	14.7 psia
CO	2.00	Temperature	220ºC
CH_4	2.05		
CO_2	21.2		
Reject [vol%]			
H_2	30.5	27.8	22.0
N_2	40.6	42.4	44.6
CO	2.37	2.49	2.61
CH_4	2.44	2.56	2.67
CO_2	23.9	24.6	28.0
Permeate [vol%]			
H_2	94.6	93.7	93.0
N_2	3.09	3.51	3.50
CO	0.17	0.18	0.19
CH_4	0.16	0.17	0.18
CO_2	1.94	2.23	3.02

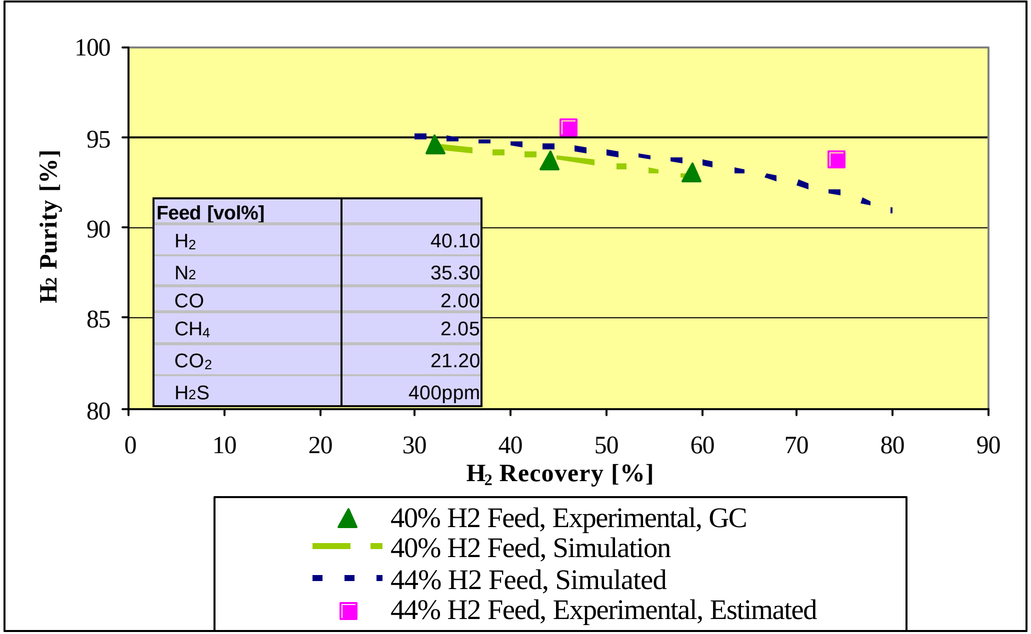


Figure 3.6 Experimental and simulated hydrogen purity vs % hydrogen recovery via M&P Hydrogen Selective Membrane, see Table 3.2 for the experimental condition.

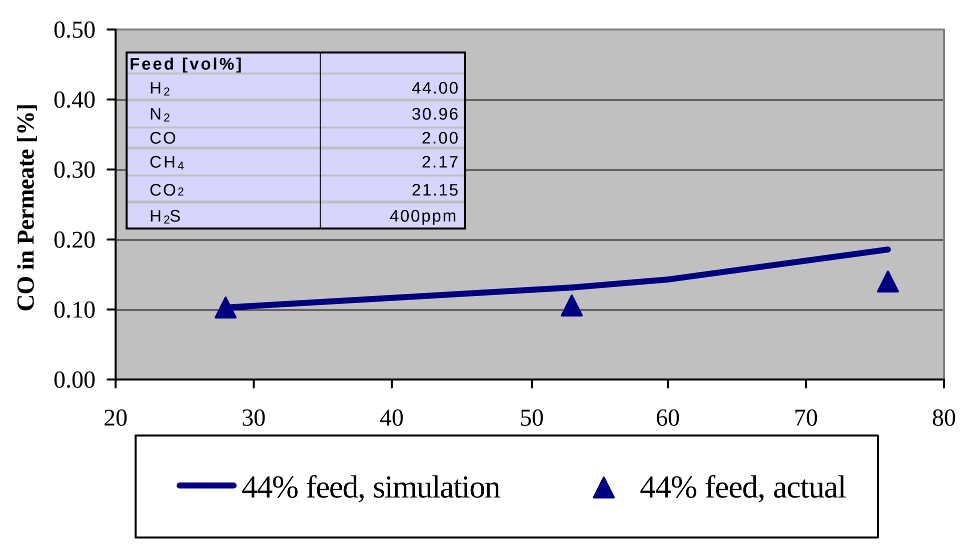
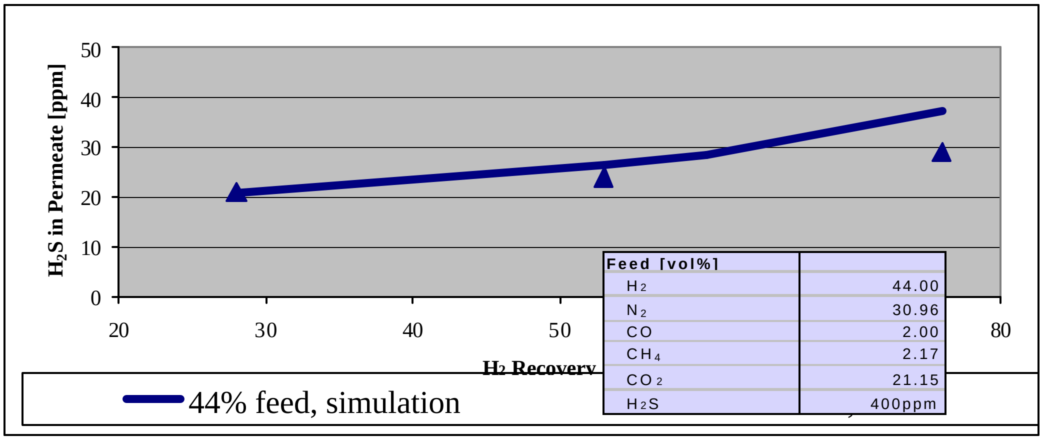


Figure 3.7 Experimental and simulated CO concentration in permeate vs % hydrogen recovery via M&P hydrogen selective membrane, see Table 3.2 for the experimental condition.



Feed [vol%]	
H_2	44.00
N_2	30.96
CO	2.00
CH_4	2.17
CO_2	21.15
H_2S	400ppm

Figure 3.8 Experimental and simulated H_2S concentration in permeate vs % hydrogen recovered via M&P hydrogen selective CMS membrane (NN-234), see Table 3.2 for experimental condition.

3.5. Full Scale Membrane and Module Production

To prepare the CMS membranes for the field tests planned in this project, we actively pursued as prt of the project activities the manufacturing of the full size membrane element (30"L) and the conceptual design of the full-scale module. This production run would produce enough inventory for the membrane requirement for the field test. More importantly, based upon the on-spec ratio of the full-scale membrane production run, the product cost can be estimated realistically.

Figure 3.9. M&P Hydrogen Recovery CMS based Membrane – Pilot Unit

The full-scale membranes were prepared according to the protocol we developed previously. Once prepared, the membrane permeances were determined at 120ºC for its He, H_2, and N_2 permeance. Nitrogen was used as a surrogate gas for CO. In addition, we packaged the individual tubes together as a bundle using ceramic potting material. The bundle was then used for the field tests.

*Quantities Produced and On-Spec Ratio…*A total of 98 membrane tubes have been produced thus far. We set our spec at a H_2 permeance of >0.35 m^3/m^2/hr and H_2/N_2 selectivity of >50 selectivity at 120ºC. This would translate into a H_2 permeance of >0.5 m^3/m^2/hr/bar and H_2/N_2 selectivity of >75 at the target operating temperature of 250ºC. About 23 out of 98 tubes failed to meet this spec during the first production trial, which leads to >75% on-spec ratio. Please refer to Figure 3.10 and Table 3.3 for details.

Full-Scale Module Fabrication… One of the major challenges for ceramic based membranes is its scale up potential. During this reporting period, we have come out with a flexible design, which allows us to fabricate membrane modules with >30 m^2/module without using exotic engineering or materials. This would qualify the ceramic membrane and module for mega-scale applications, such as the application selected in this section, which usually requires several hundred square meters. With the availability of our innovative module design, ceramic membranes no longer suffer this scale-up disadvantage.

Table 3.3 **Characterization of Full-scale Hydrogen Selective Membrane (30"L) produced during this period**

Tube #	Temp	Permeance [m3/m2/hr/bar]		Selectivity		Fail to meet Spec.*
	[C]	He	H2	He/N2	H2/N2	
113	120	0.188	0.524	19	53	
114	120	0.306	0.765	32	80	
128	120	0.753	1.390	39	72	
129	120	0.382	0.974	20	51	
130	120	0.278	0.649	42	98	
132	120	0.523	1.068	47	96	
135	120	0.899	2.055	35	80	
137	120	0.454	0.856	87	164	
140	120	0.303	0.598	73	144	
141	120	0.279	0.728	59	154	
143	120	0.557	1.346	24	58	
145	120	0.293	0.760	27	70	
147	120	0.271	0.690	33	84	
148	120	0.548	1.370	34	85	
153	120	0.319	0.775	28	68	
156	120	0.220	0.436	88	175	
163	120	0.244	0.397	56	91	
164	120	0.204	0.345	28	47	x
168	120	0.132	0.157	43	51	x
169	120	0.177	0.253	150	214	x
171	120	0.118	0.146	38	47	x
175	120	0.225	0.500	68	152	
177	120	0.278	0.666	31	73	
178	120	0.259	0.604	21	49	x
180	120	0.684	1.683	28	70	
182	120	0.413	0.897	19	40	
183	120	0.203	0.371	178	324	
184	120	0.306	0.638	73	151	
185	120	0.246	0.604	30	74	
187	120	0.142	0.266	25	46	x
188	120	0.544	1.265	28	64	
190	120	0.399	0.977	44	109	
196	120	0.370	0.763	79	163	
197	120	0.204	0.353	237	409	
198	120	0.679	1.531	25	56	
200	120	0.678	1.356	30	60	
201	120	0.147	0.254	307	532	x
202	120	0.699	1.625	18	42	x
203	120	0.318	0.641	112	225	
204	120	0.170	0.308	119	215	x
205	120	0.323	0.690	30	64	
206	120	0.416	0.707	59	100	
207	120	0.425	0.773	54	99	
208	120	0.241	0.444	31	58	
210	120	0.310	0.637	91	187	
211	120	0.302	0.659	73	160	
214	120	0.297	0.523	214	377	
215	120	0.232	0.355	75	114	
216	120	0.239	0.349	122	178	
218	120	0.253	0.389	150	230	
219	120	0.234	0.347	41	61	
220	120	0.203	0.285	155	217	x
221	120	0.236	0.359	57	86	
223	120	0.246	0.480	24	46	
226	120	0.151	0.282	43	80	x
227	120	0.200	0.320	178	285	x
228	120	0.367	0.697	26	50	
229	120	0.218	0.321	125	183	

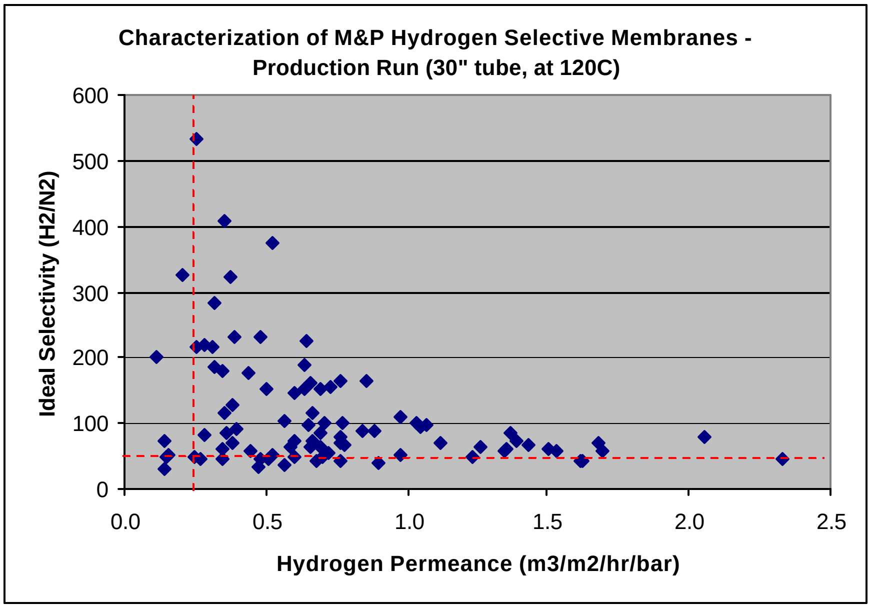


Figure 3.10. H_2 permeance vs. selectivity of full scale membrane tubes prepared during this period.

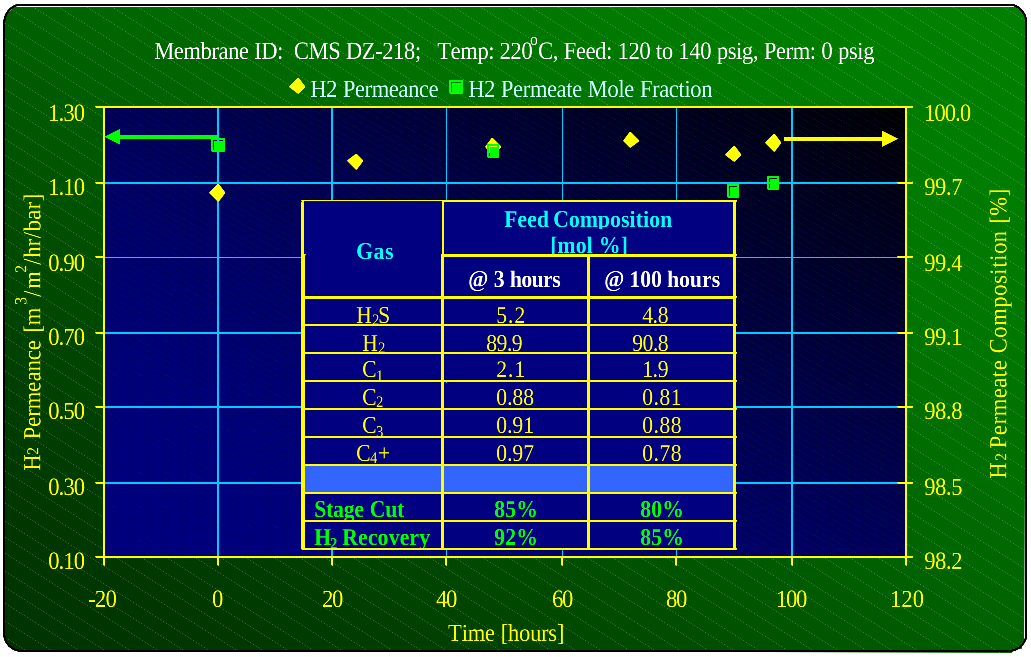
3.6. Field Test

The membrane developed from this project was field tested at an US refinery pilot test facility for hydrogen recovery from a refinery waste stream (hydrocracker purge gas). In addition to confirming the separation efficiency, these field tests provided opportunities to evaluate the membrane stability operated under harsh industrial environment, such as the presence of sulfur, ammonia and heavy hydrocarbons, which are commonly encountered in refinery and waste process applications.

*Membrane Performance Stability in Presence of Concentrated H_2S…*The field test results generated at the refinery pilot test facility are summarized in Figure 3.11. At 220°C and 10 bar, a stable hydrogen permeance of 1.1 m^3/m^2/hr/bar was obtained throughout the test period of about 120 hrs. Hydrogen purity was enriched from ~90% to 99.9% with the hydrogen recovery ratio of 85 to 92%. In addition, the H_2S concentration was reduced from 5.2% in the feed to =0.16% in the permeate. More importantly, no membrane permeance degradation was observed under this concentrated H_2S environment.

*Membrane Challenge Test…*Finally our hydrogen selective membrane was subject to a challenge test at the end of this field test. The membrane was exposed to dead-end gas separation (i.e., exposed to the enriched contaminants) for about 17 hours in the field. The permeance was recorded before the challenge test, at the end of the dead-end test, and after the regeneration to determine the degree of permeance poison and its restoration.

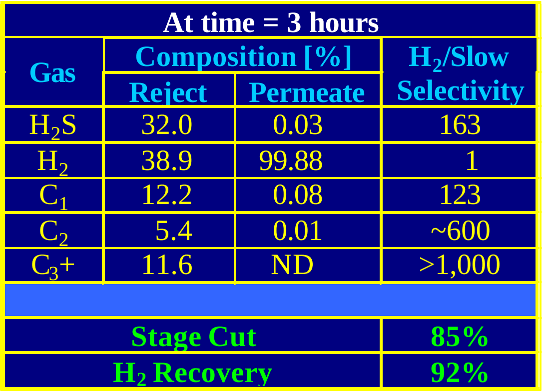
*Membrane Regeneration after Challenge Test…*The aggressive "dead-head" (no reject flow) challenge test reduced the permeance substantially; however, our regeneration restored the original permeance as presented in Table 3.4. Hydrogen permeance of 1.27 m^3/m^2/hr/bar and the selectivity of ~75 for hydrogen over nitrogen at 220°C were obtained before the challenge test. The dead head challenge test was conducted for 17 hours so that the contaminant levels far exceeded those in the standard run, including >>30% H_2S and heavy hydrocarbons. As a result, the membrane was poisoned and its permeance was reduced by ~50% to 0.62 m^3/m^2/hr/bar. However, this permeance loss was restored via our proprietary regeneration technique to nearly the original level, i.e., 1.26 m^3/m^2/hr/bar and the selectivity of 67. Based upon the results from the poison study in the field and its regeneration, we believe that our CMS membrane can be regenerated in case the membrane is accidentally poisoned.



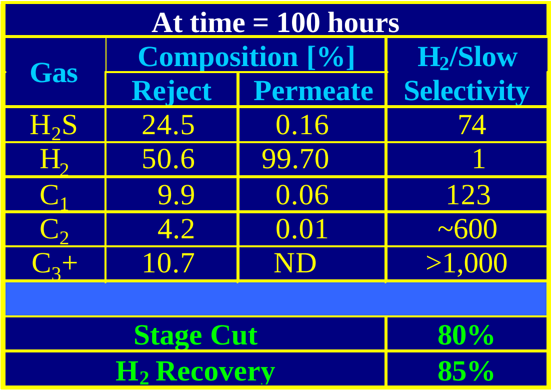
Gas	Feed Composition [mol %]	
	@ 3 hours	@ 100 hours
H_2S	5.2	4.8
H_2	89.9	90.8
C_1	2.1	1.9
C_2	0.88	0.81
C_3	0.91	0.88
C_4+	0.97	0.78
Stage Cut	85%	80%
H_2 Recovery	92%	85%

Permeance and Feed & Permeate Composition 3 and 100 hours

Reject and Permeate Composition at 3 and 100 hours



At time = 3 hours			
Gas	Composition [%]		H_2/Slow Selectivity
	Reject	Permeate	
H_2S	32.0	0.03	163
H_2	38.9	99.88	1
C_1	12.2	0.08	123
C_2	5.4	0.01	~600
C_3+	11.6	ND	>1,000
Stage Cut			85%
H_2 Recovery			92%



At time = 100 hours			
Gas	Composition [%]		H_2/Slow Selectivity
	Reject	Permeate	
H_2S	24.5	0.16	74
H_2	50.6	99.70	1
C_1	9.9	0.06	123
C_2	4.2	0.01	~600
C_3+	10.7	ND	>1,000
Stage Cut			80%
H_2 Recovery			85%

Figure 3.11. CMS membrane stability in the presence of high concentrations of H_2S, NH_3, and various organic vapors as demonstrated in the recovery of H_2 from a VGO hydrocracker off-gas in tests conducted at a refinery pilot plant.

Table 3.4 Degradation of the carbon molecular sieve membrane challenged by the dead-end operation and the restoration of the original permeance via regeneration.

Membrane Regeneration

Pure Component Permeance and Selectivity

Test Conditions: 220ºC @ ~120 psig

Test Phase	**H_2 [$m^3/m^2/hr/bar$]**	**H_2/N_2 [-]**
Before Hydrocracker Testing	**1.27**	**75**
After Hydrocracker Testing	**1.22**	**ND**
After Dead Head Hydrocracker Challenge Test **>> ~17 hrs w/NO Reject Flow (100% Stage Cut)** **>> Permeate flow falls from ~450 to ~3 cc/min**	**0.62**	**53**
After Regeneration	**1.26**	**67**

In addition, we have produced pilot testing membrane modules (i.e., 1.5" dia and 30"L) as shown in Figure 3.9, which are currently being field tested by Startech Environmental Company (Bristle, CT) for hydrogen recovery from the plasma converter off-gas in the system shown in Figure 3.12. Startech has completed the low temperature shakedown testing at 60 to 70ºC; our membrane has performed well thus far. The system is currently under modification enabling the operation at 200ºC. Along with the test reported previously at a refinery hydrotreating facility, our membranes have been evaluated and performed satisfactorily in the field under harsh environment.

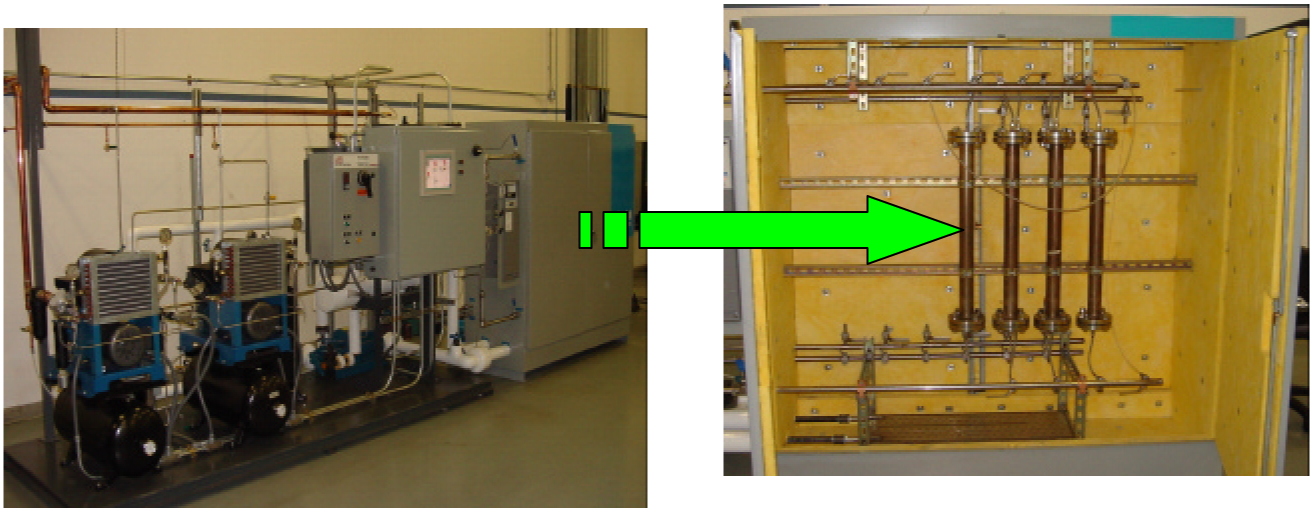


Figure 3.12. Starcell Unit at Startech Environmental Corporation incorporating M&P CMS membranes for hydrogen recovery from plasma converted gas.

3.7. Economic Analysis

Thus far, no other membrane has offered a similar functional performance in this intermediate temperature range (180 to 400 ºC). This temperature range is too high for even the most advanced polymeric-based membranes. This economic analysis here is based upon M&P's low-cost ceramic substrate (with a cost of ~$400/m^2, as opposed to >~$1,000/m^2 for stainless steel substrates) with surface areas of 2 ~20 m^2/module in the shell-and-tube configuration. A finished product, including SS housing, CMS membrane element, and seals, costs =$1,000/m^2 (=$80/ft^2). For small-scale applications, such as distributed and on-board hydrogen production, which are sensitive to the capital cost, the use of the low-cost ceramic substrate will minimize the capital costs per unit hydrogen production. For large scale hydrogen recovery applications, we have designed the module with 20 to 40 m^2/module.

In addition, under this project, we have performed exploratory research to deposit the CMS thin film on the commercial porous stainless substrate as an alternative to our ceramic membrane. The membrane separation for permeance based upon the single component permeation results show positive and promising. However, additional R&D work is required to deliver H_2 permeance and selectivity comparable to the CMS membrane with ceramic substrate.

Based upon the above ceramic membrane substrate and CMS membrane, we have performed economic analysis for two applications for hydrogen recovery in refinery streams as follows:

Applications	**Ethylene Cracker**	**Hydrotreater/ Fluid Cat Cracker**
Stream Compositions	mol%	mol%
H_2	15	35
CH_4, N_2, CO, CO_2	22.5	34
C2's	39.4	7
C_3, C_{4+}	23	4
H_2S	0	0
Total Flowrate [m^3/hr]	166,667	29,500
Temp [C]	60	40
Total Pressure [bar]	30.63	14.98
H_2 Pressure [bar]	4.6	5.24
H_2 Recovered [%]	70	70
H_2 Purity [%]	>97	>97
Membrane area [m^2]	2,800	1,068
Membrane Cost ($)	5,600,000	2,136,000
Total Capital Cost [$]	6,272,000	2,392,320
Value of Recovered H_2	9,215,478	3,798,774
Payback [months]	**8.2**	**7.6**

As shown above, the projected payback period for a refining is less than one year. In summary, the M&P membrane-based hydrogen recovery process represents a simple and economically attractive option to meet the increased hydrogen demand in a refinery.

4. CMS MEMBRANES FOR CO_2 SEPARATION

4.1 Introduction/Application Background

Around 40% of the approximately 54 trillion standard cubic feet of gas reserves in the lower 48 states are not being developed due to the high cost of gas treating [18]. These resources are (i) available from small or remote wells and/or (ii) considered subquality due to the large amount of nonmethane gases present, such as CO_2, H_2S, moisture, nitrogen, and natural gas liquids**.** In this project, we developed a membrane-based sour gas removal process using a new class of membrane material, a carbon molecular sieve (CMS) composite membrane, i.e., CMS membranes supported on commercial porous inorganic membranes as substrates. CMS membranes have been demonstrated in a variety of laboratory studies to be superior to polymeric membranes in terms of permeability, selectivity, and robustness [2-15,20-24]. In comparison to competing membrane technologies for natural gas upgrading, the CMS composite membranes have the potential to reduce both capital and operating costs. Thus, this innovative membrane process can be used to upgrade subquality NG cost effectively and can be implemented practically at remote and/or small wells.

In addition to the sour gas removal, the membrane developed can also be used for landfill gas upgrading. Landfill gas (LFG) emission is a key contributor (i.e., ~1/3) to the total anthropogenic methane emission in the US, amounting to approximately 30 MM tons in 2001 [19]. Overall, LFG emissions contribute to about 3.5%, or 240 MM ton CO_2 equivalent, of the annual greenhouse gas (GHG) emission in US. On the other hand, if the LFG-methane is fully utilized as fuel, it could off-set 462 MM barrels of fossil oil usage in the US and avoid 23 MM ton CO_2 emission due to the use of this renewable energy [25]. In addition, (i) methane is about 21 times more potent than CO_2 in terms of its GHG effect, and (ii) LFG can be captured efficiently, i.e., 60 to 90% [19], the LFG emission reduction and its utilization becomes a technically, economically and practically attractive avenue for mitigating GHG emission in the short term. Other than some specialty uses, power generation [27] is the main technology that has been adopted for LFG utilization, since it can accommodate low quality LFG with little clean-up. However, power generation does not offer significant economic incentive [16]. Thus, a more economical solution [30] is needed to promote the recovery and reutilization of LFG. In this project, we explored the use of our CMS membrane for LFG upgrading to pipeline quality.

4.2. Existing Technologies Available and Their Problems

Traditionally, sour gas removal for NG upgrading has been accomplished via absorption. However, this method is not economical for subquality NG because the operating cost is proportional to the amount of the sour gas contamination. A relatively new and innovative technology is membrane separation used alone or in conjunction with absorption [1]. The hybrid process has demonstrated the potential to reduce treatment costs and can be implemented in a relatively simple and compact system. However, this process thus far has limited penetration in the NG industry and is not considered viable for small/remote wells for the reasons below:

- Inadequate Membrane Selectivity Yields Significant Methane Loss. From 40 to >70% of the operating cost [1] in the existing commercial membrane process results from CH_4 losses due to the low CO_2/CH_4 selectivity (~18 to <25) of existing commercial polymeric membranes. Further, in this work, the value of CH_4 is assumed to be $2/MSCF, well below current and projected future prices.
- Membrane Degradation as a Result of Plasticization. Existing polymeric membranes will plasticize in the presence of high pressure CO_2, H_2S, and water, as found in subquality NG [17] yielding reduced membrane selectivity and hence higher CH_4 losses.
- Attack by Natural Gas Liquids. Polymeric membranes are susceptible to condensable organic liquids [17], so that comprehensive pretreatment is required.
- Marginal Economic Incentive. With current membrane technology, the advantage in operating cost savings is not attractive enough to outweigh the up front capital investment in the case of the hybrid process.

Therefore, a new membrane material was needed that overcame the material stability and selectivity problems of current membrane technology without sacrificing permeability.

LFG upgrading to pipeline quality natural gas (NG) is timely in light of the projected shortage and increasing price of NG. Although R&D has been conducted to enrich the methane content of LFG (i.e., 50 to 60%) via CO_2 and N_2 removal, thus far, no commercially viable process has been offered, primarily due to (i) the high concentration of CO_2, which limits the economical viability of existing technologies, such as pressure swing adsorption (PSA), and (ii) the relatively small scale and limited life (~20 yrs) of LFG sites, which prevent the use of conventional CO_2 removal technology, such as scrubbers (absorption), due to its high capital cost. Also the excessive CO_2 content yields high operating costs. On the other hand, membrane-based CO_2 separation is ideally suited for bulk separations of CO_2 and a small-scale application. However, the high CO_2 loading, miscellaneous sulfur and halogen contaminants, and heavy organics in LFG cause severe membrane material degradation/poison [1]. Hence, there are no commercial membrane installations for LFG upgrading, although the membrane separation is the ideal choice. In this report, we present a robust and low cost inorganic membrane-based CO_2 removal technology, which can overcome the material stability-related barriers of existing membranes for LFG upgrading.

In summary, for CO2 removal in both applications, a robust, stable and efficient membrane, like the CMS-based inorganic, provides a promising solution.

4.3. Experimental methods

Details of the experimental methods employed in this project are given below.

4.3.1. Membrane Preparation…Precursor Selection and Their Pyrolysis Conditions

We have selected several candidate polymers from our H_2 selective CMS membrane program database that show promise in CO_2 separations. These polymeric precursors formed the precursor pool for the preparation of our membrane candidates. Using the original pyrolysis condition for each precursor candidate as a stepping-off point, we examined different pyrolysis conditions including primarily temperature (500 to ~800°C), and possibly pressure (vacuum to ~50psi), and inert environment (vacuum, He, Ar). The pyrolysis conditions suggested here are less aggressive than those necessary to prepare H_2 selective CMS membranes (=850°C), where a denser carbon structure and hence smaller pore size are required. The membrane candidates prepared under the proposed alternative pyrolysis conditions represent a range of pore size distributions, which are expected to critically influence the CO_2 permeance and selectivity vs temperature. Please refer to our publication present in Appendix I [29] for details of the membrane preparation.

4.3.2. Characterization of Membrane Performance at Elevated Temperature

CMS membranes prepared were assessed at the elevated temperature with two primary goals, namely, (i) screening membrane performance with a number of molecular probe gases (i.e., He, N_2, CH_4, Ar, etc.) and (ii) identifying CO_2 selective membrane candidates for further screening. Each membrane candidate was evaluated in terms of the single component permeance at 25, 100, 150 and 200°C. This data was used as basis to fine tune the next pyrolysis condition for iterative study.

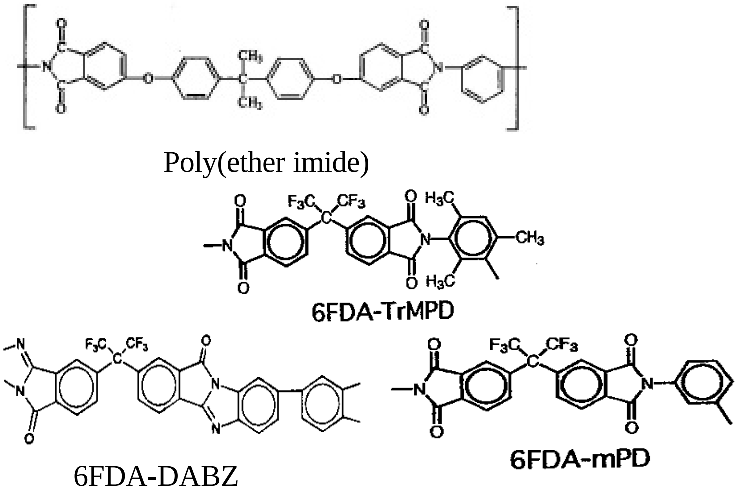
4.3.3. Challenge Testing in the Presence of Potential Poison Surrogates

The primary goal was to determine the minimum operating temperature required at which stable membrane performance can be obtained in the presence of non-methane organic vapors as poisons. Based upon previous experience in our H_2 selective CMS membrane program, the long term stability potential of a CMS membrane can be inferred relatively quickly in short term challenge tests (see Sec.4.4) conducted over 20 to 50-hours. He gas was saturated at room temperature with non-methane LFG organic vapor surrogates, then sent to the membrane at various elevated temperatures (120 to 220°C) for determination of the permeance versus exposure time. The regenerability of the CMS membrane was also experimentally confirmed by thermal regeneration at >200°C with an inert gas. The complete regenerability of the CMS membrane is indicative of the reversibility of poisoning, which offers an insurance policy in the field operation.

4.4. Experimental Results and Discussion

Our CMS membranes are prepared via deposition and pyrolysis of a polymeric precursor on our commercial ceramic membrane substrates as shown in Figure 3.1 (carbon layer) and Figure 2.2 (commercial ceramic bundles). In this section we will focus on the performance characterization of our CMS membrane for CO2-related applications.

4.4.1. Performance of Our CMS Membranes for CO_2 Removal



Poly(ether imide)

6FDA-TrMPD

6FDA-DABZ

6FDA-mPD

Figure 4.1. Polymeric precursors for CMS membranes to be prepared during the Phase I program.

Over the past several years we have had a program in place first to identify H_2 selective CMS membrane candidate materials and more recently to improve/optimize the performance of these materials. During this program, a number of “outlier” membranes have been prepared that would make relatively poor choices as H_2 selective membranes. However, these membranes demonstrate potential as suitable candidates for further study as CO_2 selective membranes for NG and LFG upgrading. The performance of four CMS membranes prepared from the precursors shown in Figure 4.1 is given in Table 4.1. Table 4.1 highlights the performance of four polymeric precursors that emerged from our H_2 selective membrane program that displayed significant potential as candidates for high performance CO_2 selective CMS membranes. Although not prepared under ideal conditions, the performance demonstrates that it is possible to prepare membranes with relatively high flux, reasonable selectivity, and as importantly the potential to be used effectively at elevated temperatures.

Table 4.1 Performance of various CMS membranes prepared from the polymer precursors

Polymer Precursor	Test Temperature	Permeance [$m^3/m^2/hr/bar$]			Selectivity [-]		Comments
		N_2	CO_2	CH_4	CO_2/CH_4	CO_2/N_2	
6FDA-DABZ.01	@27°C	0.295	4.55	0.202	22.5	15.4	
	@46°C		4.28	0.233	18.4		
	@120°C	0.694	4.59	0.531	8.6	6.6	
6FDA-DABZ.02	@ 25°C	0.031	0.299	0.0099	30.0	9.6	N_2/CH_4 ~ 3.1
6FDA-mPD	@123°C	0.303					
	@29°C	0.015	0.26	0.0076	34.2	17.3	N_2/CH_4 ~ 2
6FDA-mPD	@66°C	0.025	0.44			17.5	
	@100°C	0.044	0.75	0.038	19.7	17.1	N_2/CH_4 ~ 1.2
	@24°C	0.028	0.38	0.0103	36.9	13.6	N_2/CH_4 ~ 2.5
6FDA-TrmPD	@28°C	1.1	9.5	0.82	11.6	8.8	High permeance, modest selectivity.

Table 4.2 Performance of various CMS membranes prepared from the polymer precursor, PEI

Polymer Precursor	Gas Permeance Test Temperature	Permeance [$m^3/m^2/hr/bar$]		Selectivity [-]
		CO_2	CH_4	CO_2/CH_4
PEI-2	@20°C	0.92	0.011	83.6
	@50ºC	0.95	0.014	67.8
	@100ºC	0.82	0.019	43.2
	@150ºC	0.65	0.027	24.1

These promising CMS membrane candidates were prepared from the four polymeric precursors shown in Figure 4.1. Three of these precursors were synthesized in our laboratory (the 6FDA-based materials). The fourth was a poly(ether imide) [PEI], Ultem 1000, commercially available from General Electric. As typical, the membranes were prepared via slip casting from dilute solvents onto our ceramic substrate (typical pore size ca. 40 to 100Å) yielding ultra-thin membranes with thicknesses ranging from <0.3 to ~1µm (see Figure 3.1 in Section 3). Following precursor deposition, the membranes were pyrolyzed at high temperature in an inert environment. The specifics of the pyrolysis conditions varied somewhat for each precursor with temperatures in the range of 500 to 750ºC and inert atmospheres of either vacuum or He.

Our existing in-house data have demonstrated that CMS membranes can be prepared with superior performance at room temperature, such as the PEI and 6FDA-mPD based membranes. Even at elevated temperatures, excellent CO_2 permeances can be maintained, although the CO_2/CH_4 selectivities are much more modest.

Based upon the effect of operating temperature on the permeance and selectivity from our preliminary results as presented in Figure 4.2, we can decipher the underlying mechanisms for CO_2 transport through the CMS membrane. It is striking that the variability in membrane performance can be achieved with regard to the temperature dependence of the CO_2 permeance. As the data in Table 4.1 shows, the –DABZ based membrane shows little change in CO_2 permeance with temperature. In contrast, the CO_2 permeance of the –mPD material increases with temperature, while on the other hand, the PEI based membrane CO_2 permeance is inserted to decreases with temperature. Hence, we believe that two transport mechanisms dictate the permeance and selectivity as follows:

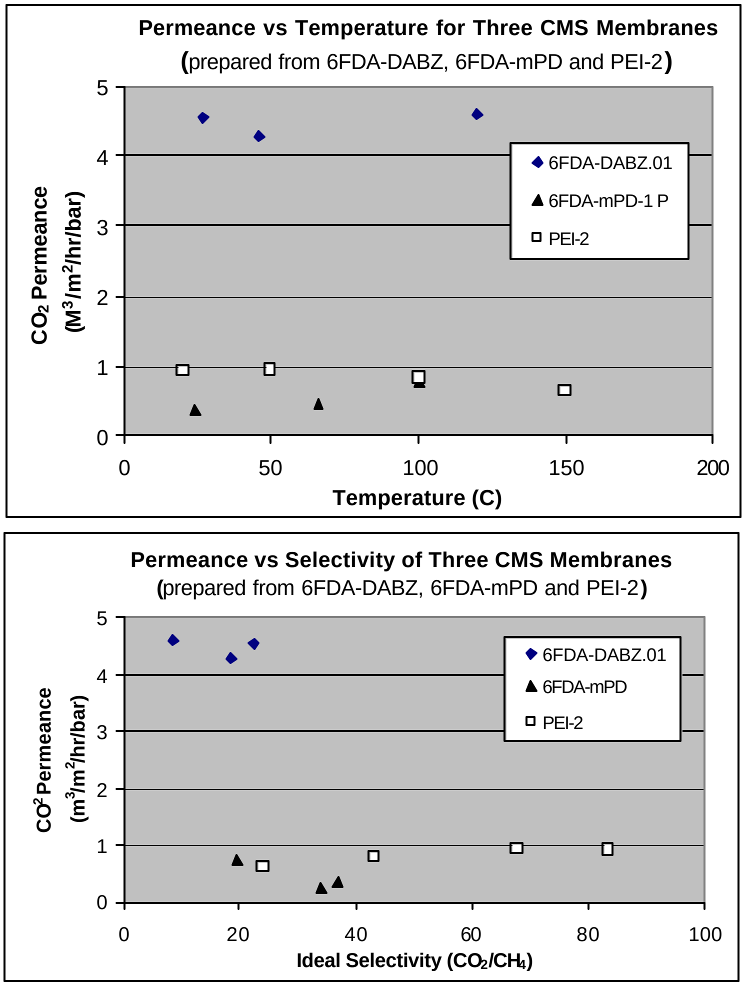


Figure 4.2 CO_2 permeance and CO_2/CH_4 selectivity for candidate LFG upgrading CMS membranes.

- *Interaction between the CMS pore surface and the CO_2 molecule…*Most carbon adsorption experts suggest such an interaction through p-bonding between the rod like CO_2 molecule which is compatible with the "slit" shaped pore unique to porous carbon materials. The strength of this interaction is inversely proportional to the temperature, since it is a physical, not chemical, type attraction.
- *Pore Size Effect on Molecule Transport and Molecular Exclusion…*When the pore size in the CMS membrane is small enough, the constriction exerted by the pore size on the molecule becomes significant and eventually leads to molecular sieving and finally molecular exclusion. If the pore size is within the influence of molecular sieving range for CO_2 and molecular exclusion for CH_4, its selectivity would increase with temperature.

Based upon the above opposing mechanisms, it is not difficult to explain that the CO_2 permeation through (i) the PEI based membranes is likely dominated by the surface interaction mechanism, (ii) the –mPD-based membrane is dominated by molecular sieving, and finally (iii) the -DABZ-based membranes likely result from a mix of the two mechanisms. Although the effect of polymer precursor materials is not taken into consideration but is expected to be important, the above analysis clearly points to the critical role of the resultant pore size after pyrolysis.

If one takes into account the difference between the molecular kinetic diameters of CO_2 vs CH_4 (3.3 vs 3.8?) and the geometry difference (rod vs sphere), it is not difficult to recommend the future work in the membrane development strategy for us: *fine tuning of the pore size of the resultant CMS membrane to enhance the molecular sieving mechanism of CO_2, which can simultaneously enhance the molecular exclusion of CH_4.* However, the price one pays for the pore size reduction is the loss of the permeance due to molecular constriction. Thus an optimum pyrolysis temperature, i.e., optimized pore size, for a given polymer may exist for the proposed application temperature.

4.4.2. Chemical Stability of Our CMS Membranes

Considerable testing has been conducted to verify the performance and stability of the membranes in a variety of gases, vapors, and operating environments. The membrane stability results summarized in Section 3 for water and organic vapors are applicable here. Our in-house results support the elevated operating temperature requirement for the selected NG and LFG application.

In conclusion, comprehensive lab and field tests have been performed by us to demonstrate the performance stability of our CMS membrane in the presence of organic vapors, H_2S, H_2O, NH_3, etc. when the CMS membrane was operated at elevated temperature as we recommended.

4.5. Field Test

A field test was performed by our subcontractor, GC Environmental Co., for the CO_2 removal from LFG. Since the LFG stream size is much smaller than the NG size, we chose to evaluate our membrane performance for LFG for cost and operation consideration. Once the technology was demonstrated, then, an NG site will be identified for future testing. The field test unit assembled by GC Environmental is presented in Figure 4.3, which was installed at a landfill site in California.

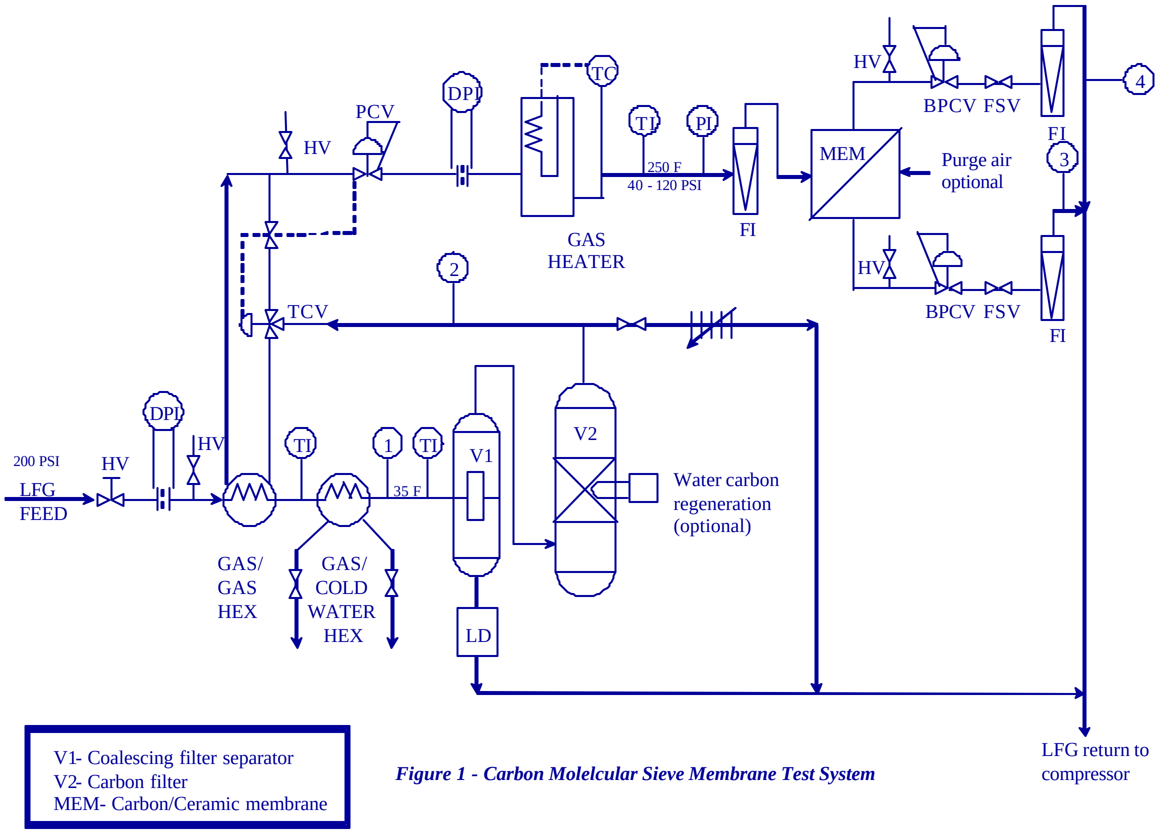


Figure 1 - Carbon Molelcular Sieve Membrane Test System

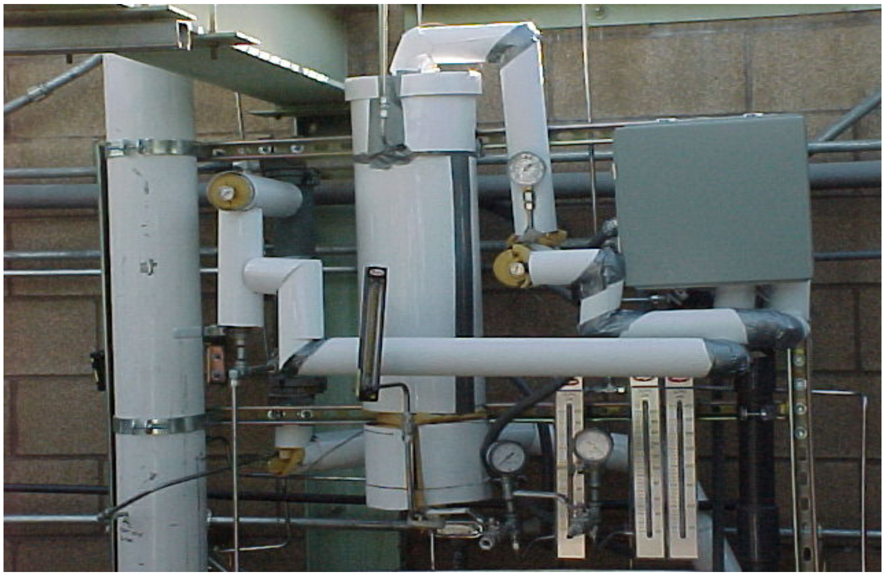


Figure 4.3 Pilot testing facility for CO_2 removal from landfill gas (LFG) at a landfill site in Mountainview, CA, owned and operated by GC Environmental Inc.

Unfortunately, the CMS membrane permeance declined continuously since the startup of the field test. Since this field test was perfomed during the early phase of this project. The test was performed at room temperature . With the addition experience at the elevated temperature as described in section 3, we believed that the elevated temperature operation would overcome the decay issue.

4.6. Economic Analysis

The economics of NG/LFG upgrading were developed in the early stage of the project which was subsequently updated based upon the manufacturing experience obtained from this project. Specifically,

- The CMS/C membrane cost to the end user was determined to be ca. \$750/m^2. This cost is based upon the costs for production of our commercial ceramic ultra- and micro-filtration products, the polymer synthesis, and the polymer deposition/pyrolysis.

- The commercial cellulose acetate membrane is used as a performance benchmark to compare our CMS/C membranes (see Ref. 1 & 26 for cost details). The membrane cost is ca. \$100/m^2. Given a typical CO_2 permeance of ca. 0.24 m^3/m^2/hr/bar, the membrane cost per unit of CO_2 throughput is ca. \$415 per m^3/hr/bar (= \$100/m^2 divided by 0.24 m^3/m^2/hr/bar). The CO_2/CH_4 selectivity is ca. 30 depending upon the CO_2 pressure and the presence of other plasticizing gases such as water, H_2S, and organic vapors which reduce the selectivity. (Interestingly, anecdotal evidence from two cellulose acetate membranes operating on LFG suggest that in actual service, selectivities are as low as 15).

- The CMS/C membrane delivered the best overall performance of the membranes studied with CO_2 permeances is ca. 1.0 to 2.4 m^3/m^2/hr/bar and CO_2/CH_4 selectivity of ~50 to 80, although several deposition/pyrolysis cycles were necessary.

Based upon the above input parameters, we have performed the economic analysis in the following sections.

4.6.1. Economic Analysis for NG Upgrading

Capital Investment Savings: Based upon the permeance above and our estimated production cost (\$750/m^2), the membrane cost per unit CO_2 throughput for our CMS/C membrane is estimated to be ca. \$750 to \$12 per m^3/hr/bar. This is within the target cost range defined by the commercial benchmark (cellulose acetate) of \$415 per m^3/hr/bar. Based upon our economic model developed from several literature studies [1,26], in a hypothetical NG upgrading system treating 35 MMSCFD at 25% CO_2, the cellulose acetate membrane cost represents about 30 to 40% of the total capital investment. Using the higher permeance CMS/C membrane data, the TCI could be reduced by about 12%.

Operating Cost Savings: More importantly, the more highly selective CMS membrane would yield a reduction in NG upgrading costs on the order of 50 to 60% due almost exclusively to the reduced CH_4 losses associated with the significantly higher selectivity membrane (this estimate assumes an NG value of $2/MSCF which is low by recent historical standards[3]). It should be noted that selectivities above 50 as we targeted yield very little further improvement in the operating cost savings.

Overall, with the membranes developed from this project we have demonstrated the potential of the CMS membranes to meet the operating economics. Specifically, we have prepared a CMS/C membrane that delivers equivalent or better cost per unit throughput of CO_2 but at significantly elevated CO_2/CH_4 selectivities =30 in comparison with the commercial benchmark polymer, cellulose acetate. With additional R&D in product optimization, it is expected that our CMS membrane would outperform existing polymeric based membranes for this selected application.

4.6.2. *Economic Analysis for LFG Upgrading*

Two applications for LFG upgrading have been selected under this project. They include:

- ***Internal Combustion Engine Power Generation***

Power project economics dictate that minimal gas processing be performed. LFG from the interior of a landfill may not require CO_2 removal to be a viable fuel. In this case the value added would be to utilize perimeter gas or poor quality interior gas, that may otherwise be flared, by treating it to the point that it is an acceptable fuel. In arid climates, LFG collected even from the interior part of a landfill may not be suitable for use in an engine. The value added in this case is to treat the entire gas stream to a level that is acceptable to the engines.

- ***Upgrade Landfill Gas to Pipeline Quality***

Upgrading the LFG for injection into a natural gas (NG) pipeline is the second application. With the use of the CMS membrane, this application may be economical even for smaller landfills (i.e., 1 to 5 million tons of MSW). One advantage of cleaning LFG to pipeline quality is that no modifications will be required to the end users' natural gas-fired equipment. This application requires relatively extensive treatment of landfill gas to remove CO_2 and impurities. Additionally, when gas is injected into a NG pipeline, there are strict specifications that can impose additional quality control and compression requirements. However, this may be an attractive option for some landfill owners, since it is possible to sell all high BTU LFG that is produced [28].

In this section, we focus on the upgrading to pipeline quality gas. The economic analysis for the IC engine application can be found in Appendix II. For upgrading LFG to pipeline quality gas, the feed and reject pressures are assumed to be 120 psig and the permeate pressure 0 psig. The quality of the LFG entering the membrane is 57% CH_4, 42% CO_2, and 1% O_2 and N_2. The processed gas quality is assumed to be 96% CH_4, 2% CO_2, and 2% N_2 and O_2. The CH_4 yield is 82.5%. The selectivity assumed for CO_2 over CH_4 is

---

[3] According to the Energy Information Administration, average natural gas prices for 2000, 2001, and 2002 were $3.50, $4.27, and $2.87/MSCF [ref. 27].

30. The same selectivity is assumed for CO_2 over O_2 and N_2. The permeance of the CO_2 at this selectivity is 0.59 m^3/m^2/hr/bar. A high separation factor was used to reduce methane losses through the membrane and due to the high methane concentration required in the product gas. Membrane performance calculation results are shown in **Table 4.3.**

Table 4.3: Membrane Simulation Results for Upgrading LFG for Pipeline Quality

	1MM Ton	5MM Ton
Feed Pressure (psig)	120	120
Reject Pressure (psig	120	120
Permeat Pressure (psig)	0	0
Feed, X_{CO2}	0.57	0.57
Feed, X_{CH4}	0.42	0.42
Feed, $X_{N2, O2}$	0.01	0.01
Reject, X_{CO2}	0.02	0.02
Reject, X_{CH4}	0.96	0.96
Reject, $_{XN2,O2}$	0.02	0.02
Permeat, X_{CO2}	0.88	0.88
Permeat, X_{CH4}	0.117	0.117
Permeat, $X_{N2,O2}$	0.003	0.003
Overall Yield (%)	36.1	36.1
CH_4 Yield (%)	82.5	82.5
Area (m^2)	280	1420
Selectivity	30	30
Permeance, CO_2, (m^3/m^2/hr/bar)	0.588	0.588
BTUs Out (MMBTU/hr) (1)	6.66 HHV	33.3 HHV
Gross kW Output-Engine at 12,500 (BTU LHV/kWh)	-	-
Net kW Output (kW)	-	-
Net BTUs Produced (MMBTU/day)	160	800
Annual Capacity Factor	0.9	0.9
Net Energy Sold (kWh/yr.)	-	-
Net Energy Sold (MMBTU HHV/yr)	52,500	262,500

(1) BTUs are reported higher heating value for pipeline quality gas applications.

Since many landfills are now required to implement gas collection systems and flares, the costs of these systems are not included in the analyses. Only the treatment systems and equipment required to compress the gas to pipeline standards will be evaluated. To simplify the analysis in this paper, it is assumed that all collected LFG is processed by the membranes.

Upgrading gas to pipeline quality can be relatively expensive, because of the substantial processing requirements to remove CO_2 and other constituents from raw LFG. This option was previously viable only at larger landfills (i.e., more than 4 million cfd), where significant economies of scale could be achieved. To determine the revenues from the sale of pipeline quality gas, the BTUs available for sale must be evaluated. This has been done for the 1 and 5 million ton example landfills, **Table 4.3**. The annual BTUs produced are approximately 52,500 and 262,500 MMBTU HHV/yr.

Table 4.4 lists the components of the treatment system and their estimated costs. The components fall into six main categories, which are civil, mechanical, electrical, engineering, construction, and contingency.

Table 4.4 Treatment System Component Cost Estimates

Category	Equipment/ Part	Function	Cost Estimate ($)	
Waste in Place (million tons)			1	5
Civil Construction	Grading, Foundations, Drainage		30,000	40,000
Mechanical	Compressor	Compresses LFG to 120 psig	65,000	125,000
	Scrubber	Water Removal	15,000	25,000
	Contaminant removal and dehydration	Removes chlorinated hydrocarbons and water	100,000	200,000
	Waste gas incinerator	Burns waste gas from membranes and removes contaminants	75,000	115,000
	Fin/Fan Cooler	Removes heat	25,000	30,000
	Coalescing Filter Separator	Removes oil from LFG	10,000	20,000
	Membrane	Removes CO_2 from LFG	142,000	709,000
	Liquid Handling System	Handles condensate from system	20,000	30,000
Electrical	Controls		50,000	65,000
Engineering		System design	100,000	150,000
Construction		Build system	150,000	200,000
Contingency	20 %	Uncertainty and soft costs	156,400	341,800
Total (PW)			938,400	2,050,800

O&M expenses for LFG treatment systems vary depending on the system components, sizing, design, and percentage of on-time. The O&M expenses for the 1 and 5 million ton landfills are estimated to be $142,000/yr. and $314,000/yr. respectively. These costs include the cost of power to compress the gas at 6 cents/kW. In order to amortize the initial capital costs of a treatment system for upgrading LFG to pipeline quality gas, the initial capital costs have been analyzed as installment loans, and annual payments based on 5 % and 8 % annual interest rates have been calculated in **Table 4.5**. The annual annuity payment for a present worth principal is given in the following expression:

$$AP = PW * ((I * ((1+I)^n))/(((1+I)^n)-1))$$

Where AP is the annual annuity payment ($), PW is the present worth of the loan or the installed capital costs ($), I is the interest rate per annual payment, and n is the number of annual payments (assume a 10 year payback).

Based on the costs of generating the pipeline quality gas, it is apparent that the projects will be economically feasible if the price of such gas is greater than $4.89/MMBTU and $4.58/MMBTU at annual interest rates of 8 and 5 % for the 1 million ton landfill, and $2.15/MMBTU and $2.01/MMBTU at annual interest rates of 8 and 5 % for the 5 million ton landfill. The economy of scale is clearly demonstrated by these examples. In addition, tax credits and/or incentives may be available for upgrading landfill gas to pipeline quality gas projects.

Table 4.5: Cost Pipeline Quality Gas Generated

Waste in Place (million tons)	1		5	
Installed Capital Costs ($)	938,400	938,400	2,050,800	2,050,800
Annual Interest Rate	0.08	0.05	0.08	0.05
Number of Annual Payments	10	10	10	10
Annual Annuity Payment ($)	139,850	121,500	305,600	265,600
Annual O&M Expenses ($)	142,000	142,000	314,000	314,000
Value of Pipeline Gas Generated ($/yr)	281,850	263,500	619,600	579,600
Annual Energy Content (MMBTU/yr)	57,600	57,600	288,000	288,000
Cost of Pipeline Gas Generated ($/MMBTU)	4.89	4.58	2.15	2.01

Note: Costs do not include pipeline distribution costs.

The carbon molecular sieve (CMS) membrane shows significant promise as a future technology to remove carbon dioxide from landfill gas. Advantages this membrane will offer over other technologies include excellent separation factor while maintaining good permeance, high stability in hot, damp, or corrosive environments, and low cost. With the economic analysis performed above, we conclude that it is possible to utilize landfill gas from sites that are not currently considered for development because of poor quality gas. This technology may open opportunities to upgrade LFG to pipeline quality gas in addition to IC engine applications.

References Cited

1. Bhide, D. and S.A. Stern, “Membrane Processes for the Removal of Acid Gases From Natural Effect. I. Effects of Operating Conditions, Economic Parameters, and Membrane Properties”, J.Memb. Sci., 81, 239 (1993).
2. Hayashi, J., H. Mizuta, M. Yamaoto, K. Kusakabe, and S. Morooka, “Separation of Ethane/Ethylene and Propane/Propylene Systems with a Carbonized BPDA-pp’ODA Polyimide Membrane”, Ind. Eng, Chem. Res., 35, 4176 (1996).
3. Hayashi, J., M. Yamaoto, K. Kusakabe, and S. Morooka, “Simultaneous Improvement of Permeance and Permselectivity of 3,3',4,4'-Biphenyletracarboxylic Dianhydride-4,4'-Oxydianiline Polyimide Membrane by Carbonization”, Ind. Eng. Chem. Res, 34, No 12 (1995).

4. Jones, C., and W. Koros, “Carbon Molecule Sieve Gas Separation Membranes-I. Preparation and Characterization Based on Polyimide Precursors, Carbon, 32, No. 8, 1419-1425 (1994).
5. Jones, C., and W. Koros, “Carbon Molecule Sieve Gas Separation Membranes-II Regeneration Following Organic Exposure, Carbon, 32, No. 8, 1427-1432 (1994).
6. Jones, C., and W. Koros, “Characterization of Ultramicroporous Carbon Membranes with Humidified Feeds”, Ind. Eng. Chem. Res., 34. 158 (1995).
7. Jones, C., and W. Koros, “Carbon Composite Membranes: A Solution to Adverse Humidity Effects”, Ind. Eng. Chem. Res., 34. 164-167 (1995).
8. Kita, H., H. Maeda, K. Tanaka, and K. Okamoto, “Carbon Molecular Sieve Membrane Prepared from Phenolic Resin”, Chemistry Letters, 179-180 (1997).
9. Kusakabe, K., M. Yamamoto, and S. Morooka, “Gas Permeation and Micropore Structure of Carbon Molecular Sieving Membranes Modified by Oxidation”, J. Memb. Sc., 149, 59(1998).
10. Sidigh, M., M. Jahangir, P. Liu, T, Tsotsis, M. Sahimi, “Structural Characterization of Polyetherimide-Based Carbon Molecular Sieve Membrane”, AIChEJ, 46, No. 11 (2000).
11. Sidigh, M., L. Xu., T, Tsotsis, M. Sahimi, “Transport and Morphological Characteristics of Polyetherimide-Based Carbon Molecular Sieve Membranes”, Ind. Eng, Chem. Res., 38, 3367 (1999).
12. Sedigh, M., W. Onstot, L. Xu, L. Peng. T, Tsotsis, and M. Sahimi, “Experiments and Simulation of Transport and Separation of Gas Mixtures in Carbon Molecular Sieve Membranes”, J. Phys. Chem. A, 102, 8580 (1998).
13. Humphery, J. L, A. F. Seibert, and R. A. Koort, Separation Technologies -Advances and Priorities, DOE/ID/12920-1, Feb 1991
14. Ciora, C., P. K.T. Liu, “Carbon Molecular Sieve Membrane - Perspective from a Membrane Manufacturer,” Proceeding of 2000 Membrane Tech & Planning Conf., Dec. 4-5, 2000.
15. Bos, A., I.C.M. Punt, W. Wessling, H. Strathmann, “Suppression of CO2-plasticization by Semiinterpenetrating Penetrating Polymer Network Formation,” J. Membrane Sci., 16,1547(1998)
16. Prosser, D., M. J. Ackerman, P. KT Liu, M. G., Sedigh, T. T. Tsotsis, M Sahim, “an economic evaluation of carbon molecular sieve memrbranes in landfill gas applications”, BCC Membrane Busines and Planning Conf., Dec. 17, 1999.
17. Stern. S.A., B. Krishnakumar, S. G. Chanati, W. S. Amato, A. A. Friedman, D. J. Finess, “Performance of a Bench-scale Membrane Pilot Plant for the Upgrading of Biogas in a Wastewater Treatment Plant,” J. Membrane Sci., 151,63(1998).
18. Koros, W., R. Mahajan, “Pushing the Limits on Possibilitiess for Large Scale Gas Separation; Which Strategies?,” J. Membrane Sci., 175, 181(2000).
19. “Methane Sources and Emissions”, www.USEPA
20. K. Tanaka, H. Kita, M. Okano, and K. Okamoto, “Permeability and permselectivity of gases in fluorinated and non-fluorinated polyimides”, Polymer, 33, 585 (1992).
21. K. Tanaka, M. Okano, H. Toshino, H. Kita, and K. Okamoto, “Effect of Methyl Substituents on Permeability and Permselectivity of Gases in Polyimides Prepared from Methyl-Substituted Phenylenediamines”, J. Polym. Sci. Part B, Polym. Phys., 33, 1907 (1995).

22. K. Tanaka, Y. Osada, H. Kita, and K. Okamoto, “Gas Permeability and Permselectivity of Polyimides with Large Aromatic Rings”, J. Polym. Sci. Part B, Polym. Phys., 33, 1907 (1995).
23. J. Hayashi, H. Mizuta, M. Yamamoto, K. Kusakabe, and S. Morooka, Ind. Eng. Chem Res., 35, 4176 (1996).
24. J. Hayashi, H. Mizuta, M. Yamamoto, K. Kusakabe, and S. Morooka,, J. Membr. Sci., 124, 243 (1997).
25. “Emission Reductions and Environmental and Energy Benefits for Landfill Gas Energy Projects”, www.USEPA- LMOP Calculator,htm
26. Vu, De Q., Koros, W.J., and Miller, S.J., “Effect of Condensable Impurities in CO2/CH4 Gas Feeds on Carbon Molecular Sieve Hollow-Fiber Membranes”, Ind. Eng. Chem. Res., 2003, 42, 1064-1075
27. Bove, R., P. Lunghi, “Electric power generation from landfill gs using traditional and innovative technologies”, Energy Conversion & Management, in press (2005).
28. Landfill Methane Outreach Program (LMOP), Turning a Liability into an Asset: A Landfill Gas-to-Energy Project Development Handbook, U.S. Environmental Protection Agency, September 1996.
29. Sedigh M. G., Xu L., Tsotsis T. T., Sahimi M., Transport and Morphological Characteristics of Polyetherimide-based Carbon Molecular Sieve Membranes, Ind. Eng. Chem. Res. 1999, 38, 3367.
30. Wheless, E. J. Cosulich, and A. Wang, “Converting landfill gas to vehicle fuel: the results of over 30 months of operation”

5. CONCLUSIONS

This project has been oriented toward the development of a commercially viable ceramic membrane for gas separations. Key conclusions obtained from this project are summarized below:

Porous Ceramic Membrane as Substrate for Gas Separation Membranes…A low cost high performance porous ceramic membrane has been developed as a substrate for the deposition of an inorganic thin film for high temperature gas separations. Our innovative substrate is about 1/3 the cost of existing ceramic membranes, and is highly flexible in module configuration, geometry and dimension. More importantly, the module seal has been developed specifically for gas separations at high and intermediate temperature. Surface area/module ranging from 4 m^2 to >20m^2 has been designed and/or constructed. These unique features form essential attributes for an ideal membrane substrate for gas separation.

Energy Recovery from Boiler Flue Gases using Ceramic Membranes…In collaboration with Gas Technology Institute (GTI), a transport membrane condenser (TMC) product based upon the above ceramic substrate has been developed for energy recovery from boiler flue gas. =5% improvement in boiler efficiency has been achieved in a pilot scale unit. Presently, several full scale commercial units have been under construction/installation. Annual energy savings in US well in excess of one quad can be expected.

Carbon Molecular Sieve Thin Film Deposited on the Porous Ceramic Substrate… An ultra-thin, defect free carbon molecular sieve (CMS) membrane has been successfully deposited on the above ceramic substrate. Membrane hydrogen permeances ranging from 0.8 to >5 m^3/m^2/hr/bar (i.e., 27 to 168 scfh/ft^2 at 10 bar pressure drop) have been demonstrated. Selectivities for H_2 to N_2 are 25 to >100 even at temperatures up to ~400°C. The membrane has demonstrated thermal, hydrothermal, organic vapor and H_2S stability at the operating temperature range recommended. Further, hydrogen can be enriched from 40% to ~95% with 75% hydrogen recovery from a stream containing 40% hydrogen. The rejection efficiency for CH_4, CO and H_2S is comparable to or higher than N_2. This hydrogen selective membrane with the above performance and stability is ideal for hydrogen recovery/separations in refinery applications.

Manufacturing of CMS-based Gas Separation Membranes/Modules…Full-scale hydrogen selective membranes were produced. With the spec of 0.5 m^3/m^2/hr/bar and the selectivity of H_2/N_2>75 at 120°C, >75% on-spec ratio was achieved in our first manufacturing campaign . Also pilot scale modules prepared with the full scale membranes have been fabricated and tested successfully and are currently under evaluation in a field test for hydrogen recovery from gasifier off gas.

Field Tests for Hydrogen Recovery Applications… Two field tests have been performed to verify the separation efficiency and the material stability of the hydrogen selective membrane under the actual field operating conditions. Hydrogen recovery from a VGO hydrocracker off-gas at a refinery site was performed with this hydrogen selective membrane. At 220°C and 10 bar, a stable hydrogen permeance of 1.1 m^3/m^2/hr/bar was obtained throughout the test period of about 120 hrs. Hydrogen purity was enriched from ~90% to 99.9% with the hydrogen recovery ratio of 85 to 92%. In addition, the H_2S concentration was reduced from 5.2% in the feed to =0.16% in the permeate. More importantly, no membrane permeance degradation was observed under this environment with concentrated H_2S and heavy hydrocarbons. Another field test involving hydrogen recovery from a waste gasification stream is currently in progress.

Economic Analysis for Hydrogen Recovery Applications…Waste stream in excess of 1,800MM SCFD is estimated to be available in refineries for hydrogen recovery. Economic analyses for the hydrogen recovery from two cases: ethylene cracker and hydrotreater, show that the payback period of <1 year can be achieved. The performance stability of our CMS membrane under the harsh environment, such as concentrated H_2S, and the presence of heavy hydrocarbons, uniquely qualify it for application in hydrogen recovery from refinery waste streams.

CMS Membrane with CO_2 Affinity… Our CMS membrane was also explored for CO_2 removal from methane for upgrading of subquality natural gas (NG) and landfill gas (LFG). The CMS membrane with CO_2/CH_4 selectivity of >80 and the CO_2 permeance of 0.92 m^3/m^2/hr/bar at 25°C have been identified from the "outliers" of the hydrogen selective membranes prepared. The selectivity was reduced to ~25 and the permeance to 0.65 m^3/m^2/hr/bar when the temperature increased to 150°C. Experimental results obtained from the properly selected precursors and pyrolysis conditions indicate the potential to develop a CMS membrane with improved selectivity and permeance at elevated temperature, e.g., =150°C. Due to time constraints no optimization study was performed to develop and manufacture such membranes.

Field Test for CO_2 Selective CMS Membrane for Landfill Gas …A field test was performed using the above CO_2 selective CMS membrane for LFG upgrading in CA during the early phase of the project. The membrane performance deteriorated throughout the test run at room temperature, possibly caused by miscellaneous contaminants present in LFG. It is believed that the operation at the elevated temperature as demonstrated for the hydrogen recovery application would have corrected this performance decay problem. Additional lab testing is presently underway to demonstrate its permeance stability at the elevated temperature operation. Once verified, an additional field test will be planned.

Economic Analysis for Upgrading Subquality Natural Gas (NG) and Landfill Gas (LFG)… Unlike polymeric membranes, the CMS membrane does not degrade as a result of plasticization or attack by natural gas liquid and/or miscellaneous contaminants. Thus, the CMS membrane is ideal for upgrading subquality NG and LFG. Our economic analysis based upon the preliminary performance result shows that the TCI and the operating cost could be reduced by about 12% and 50-60% respectively over existing polymeric membranes for NG upgrading. As far as the LFG upgrading to pipeline quality is concerned, the NG produced would cost at $2.15 to 4.89/MM Btu for 5 to 1

MM ton landfill sites respectively, which are highly attractive under current NG market price. Overall, the CMS membrane has demonstrated both technical and economical potential for NG and LFG upgrading.

In summary, this project has demonstrated the technical and economical feasibility of using ceramic membranes for gas separation applications. Further, the lab and field tests have demonstrated the operational stability, both performance and material, of the gas separation thin film deposited upon the ceramic membrane developed under this project. This performance reliability is built upon the ceramic membrane developed under this project as substrate coupled with the elevated temperature operation. A comprehensive product development approach has been taken to produce an economically viable ceramic substrate, gas selective thin film and the module required to house the innovative membranes for the elevated temperature operation. Field tests have been performed to demonstrate the technical and commercial viability for (i) water and energy recovery from boiler flue gases, and (ii) hydrogen recovery from refinery waste streams using the membrane/module product developed under this project. Active commercialization effort teaming with key industrial OEM’s and end users is currently underway for these applications. In addition, the CMS membrane has demonstrated its economical viability for the CO_2 removal from subquality natural gas and landfill gas although performance stability at the elevated temperature remains to be confirmed in the field.

Appendix

Publications resulted from this project include:

1. Sidigh, M., M. Jahangir, P. Liu, T, Tsotsis, M. Sahimi, "Structural Characterization of Polyetherimide-Based Carbon Molecular Sieve Membrane", AIChEJ, 46, No. 11 (2000).
2. Ciora, R. J., and P. K.T. Liu, "Carbon Membranes – Perspective from a Membrane Manufacturer", 2000 18th Annual Membrane/Separations Technology and Planning Conference, Newton, MA.
3. Prosser, D., Ackerman, M.J., Liu, P.KT., Sedigh, M.G., "An Economic Evaluation of Carbon Molecular Sieve Membranes in Landfill Gas Applications", 2002 20th Annual Membrane/Separations Technology and Planning Conference, Newton, MA.
4. Ciora, R. J., Jr., P. K.T. Liu, "Ceramic membranes for environmental related applications", Fluid/Particle Sep. *J.*, 15, ,51 (2003*)*