a306870
CPUB

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

Energy Research Laboratories
Laboratoires de recherche sur l'énergie

a306870 CPUB

POROUS MEMBRANES FOR HIGH TEMPERATURE RECOVERY OF HYDROGEN

ERL 90-0100 CPUB

Canada

ERL 90-0100

CPUB

a306870 CPUB

POROUS MEMBRANES FOR HIGH TEMPERATURE RECOVERY OF HYDROGEN

ERL 90-0100 CPUB

Brian Farnand and Craig Fairbridge
January 1990

ENERGY RESEARCH LABORATORIES

THIS REPORT IS CONFIDENTIAL. ACCESS TO IT IS RESTRICTED TO EMPLOYEES OF ENERGY, MINES AND RESOURCES AND TO PERSONS AUTHORIZED BY THE HYDROGEN INDUSTRY COUNCIL.

Porous Membranes for High Temperature Recovery of Hydrogen

Synopsis:

The separation of hydrogen from other gases at high temperature by the use of membranes shall be investigated. Novel membrane materials such as metals, ceramics, high service temperature polymers and glasses shall be investigated. Further, the performance of membranes for the generation of hydrogen by the catalytic decomposition of hydrogen sulphide at the membrane surface shall also be investigated.

Objectives:

1. To test high temperature porous membranes for the separation of hydrogen from other gases.

2. To evaluate new formulations and materials for their performance as membranes in the high temperature separation of hydrogen.

3. To determine the limits of performance for high temperature separations in the presence of corrosive gases.

4. To use membranes as a support for catalysts that cause the dissociation of hydrogen sulphide to elemental sulphur and hydrogen, and to use Knudsen flow to create a purified hydrogen stream.

Benefits/Risks:

\+ A separation of hydrogen at high temperature and low pressure shall improve the economics and safety of hydrogen generation.
\+ Near commercial membrane technology can be exploited for the generation of hydrogen.
\+ Hydrogen is removed without the use of solvents.
\+ The replacement of the Claus process with a process which produces hydrogen as a byproduct.
\+ The replacement of absorption in natural gas sweetening with a membrane reaction process eliminates a pernicious waste stream (stripper sludge).

\- Operation at 500°C and higher may be too challenging for most membranes in the presence of H_2S.
\- Economic benefits may not be adequate for commercial operation or for displacement of proven technology.
\- Porous membranes may not perform as expected at elevated temperatures.
\- Catalysts may not be active enough to exploit the membrane supported catalysts within limiting membrane temperatures.

Background:

A spinoff of nuclear weapons technology is the high temperature membranes developed for nuclear isotope separation which have become commercially available for other processes. While the original use was for the high temperature diffusion separation of isotopes according to Graham's law, advances in ceramics have permitted the preparation of small pore membranes suitable for the separation of elemental gases. These membranes and high operating temperature can be used to exploit the large molecular difference of H_2 and other gases such as H_2S, CO_2, COS, CO, S_2 and CH_4. These are the waste products of natural gas sweetening operations that are currently processed by the Claus process or other similar sulphur reduction processes.

An example of the membranes that have become available is the recently introduced ALCOA Membralox ceramic membranes for food processing and other service to 425°C that take advantage of the inertness of the ceramic membranes, their resistance to thermal stress, and the ruggedness of the membrane for backflushing and cleaning. Their application to the separation of gases is limited to high temperatures where Knudsen flow is dominant because of their large pore size distributions.

Some polymers show excellent temperature resistance to 350°C, such as polybenzimidazole(350°C), polybenzothiazole(300°C), and polyimide(320°C) which are used for jet turbine manufacture because of their light weight. Use of such polymers for membrane manufacture has been reported in the scientific literature, though there are no commercial units available.

Two approaches are considered for a process to recover hydrogen. They are:

1, the use of a membrane process to treat hydrogen rich effluent for the removal of hydrogen and recycle H_2S for further reaction;

2, the use of membranes that combine the catalytic dissociation of H_2S with the selective removal of hydrogen by Knudsen flow.

From a brief review of similar studies, there has not been a comprehensive assessment of the removal of hydrogen from polar gases at the conditions that would be present in an H_2S decomposition reactor effluent rich in hydrogen such as in a thermal diffusion reactor with thermal/catalytic dissociation of H_2S to H_2 and elemental sulphur. The dissociation reaction is favoured by high temperature, which may preclude the use of polymeric membranes even at the temperatures described above. However, the possibility of a membrane surface shift in the decomposition reaction by the immediate permeation of hydrogen with rejection of elemental sulphur and H_2S has not been well investigated. This provides an opportunity for a selective membrane process to remove hydrogen from an H_2S containing natural gas stream.

References:

Al-Shamma,L. and Naman,S.A., "Kinetic study for thermal production of hydrogen from hydrogen sulfide by heterogenous catalysis of vanadium sulfide in a flow system", Int. J. Hydrogen Energy, 14, 173 (1989).

Bandermann,F. and Harder, K.B., "Production of H_2 via thermal decomposition of H_2S and separation of H_2 and H_2S by pressure swing absorption", Int. J. Hydrogen Energy, 7, 471 (1982).

Kameyama,T.; Dokiya,M.; Fujishige,H.; Yokokawa,H.; Fukuda, K., "Production of hydrogen from hydrogen sulfide by means of selective diffusion membranes", Int. J. Hydrogen Energy, 8, 5 (1983).

Work Plan

Task 1 Literature Survey

A survey of the existing gas processing literature shall be made in scientific journals, patent disclosures and technical literature. Producers of candidate membranes and membrane materials shall be contacted for detailed product information. A brief report describing the state of the art shall be prepared along with an assessment of the viability of the project.

Task 2 Polymer Membrane Testing

Preliminary experiments with polymeric membranes shall be performed at temperatures in the range of 100°C. Membranes shall be fabricated by literature methods, obtained from manufacturers, or modified for high temperature operation. The permeation experiments shall be performed with gases that are expected to be in hydrogen rich reactor effluent streams containing mainly H_2 with H_2S, CO_2, COS, CO and CH_4. The goal of this separation is to produce a purified H_2 stream. Special high temperature polymeric membranes shall then be reevaluated at higher temperatures, approaching their limiting service temperatures. These polymers shall include both pure resin and composites of polybenzimidazoles, polybenzothiazoles, and polyimides, as well other high temperature polymer systems identified in the literature survey. These membranes shall be tested with the same gases as before at higher temperatures up to their failure point. A minimum total of 10 experiments shall be performed.

Task 3 Inorganic Membrane Testing

As in Task 2, inorganic membranes shall be evaluated for selective permeation of synthetic hydrogen rich reactor effluent streams with the goal of producing a purified hydrogen stream. The membranes used in this task shall be obtained from manufacturers or made in-house from literature descriptions of methods. These shall first be tested at 100°C for their ability to produce a hydrogen rich product from a blend of the same gases as used in Task 2. They shall then be tested at temperatures approaching their thermal limitations with the same gases. A minimum total of 10 experiments shall be performed.

Task 4 Membrane Reactor Fabrication and Testing

Various catalysts that cause the dissociation of hydrogen and sulphur from H_2S shall be added onto the surface of inorganic membranes. These shall include MoS_2 and other successful catalysts identified in the literature survey or ongoing in-house projects. These shall be evaluated up to the limiting operating temperatures of the membrane supports. Feed gases to be tested shall include synthetic H_2S rich streams representing natural gas sweetening conditions, synthetic gas representing a hydrogen generation reactor effluent with H_2S, and synthetic well head natural gas containing H_2S. A minimum total of 10 experiments shall be performed.

Task 5 Final Report

The experimental results and their interpretation shall be included in a final report. A brief economic assessment based upon textbook values and M&S indices shall be used to evaluate the most promising configuration with a design basis suitable for an operating natural gas sweetening plant. Recommendations for the direction of future work shall be made.

Timetable

Year 1

Task	0	1	2	3	4	5	6	7	8	9	10	11	12
1. Literature Survey	****												
2. Polymer Membrane Test		*************************											
3. Inorganic Membrane Test								********************					
4. Membrane Reactor													
5. Final Report													

Year 2

Task	0	1	2	3	4	5	6	7	8	9	10	11	12
1. Literature Survey	complete												
2. Polymer Membrane Test	complete												
3. Inorganic Membrane Test	*********												
4. Membrane Reactor			************************************										
5. Final Report												****	

Price Proposal

Project Team and Physical Resources:

Dr. Brian Farnand will be the project leader and a principle investigator. Dr. Craig Fairbridge will be the other principle researcher. Mr. Terrance Giddings is the research chemist that will perform most of the experiments.

	Days	$/h	Total	Task Total
Task 1				$15 075
Research Scientist	20	86	12900	
Research Chemist	5	58	2175	
Task 2				$38 685
Research Scientist	33	86	21285	
Research Chemist	40	58	17400	
Task 3				$45 780
Research Scientist	44	86	28380	
Research Chemist	40	58	17400	
Task 4				$79 650
Research Scientist	50	86	32250	
Research Chemist	30	58	13050	
Metal Analyses	25	84	2100	
Task 5				$15 075
Research Scientist	20	86	12900	
Research Chemist	05	58	2175	
Total For Project				$194 265

BRIAN A. FARNAND

CLASSIFICATION

Research Scientist 02

EDUCATION

1978	B.A.Sc.	University of Ottawa (Chemical Engineering)
1983	Ph.D.	University of Ottawa (Chemical Engineering)

EMPLOYMENT

1978-82	University of Ottawa, Dept. Chemical Engineering -Graduate Student
1978-82	National Research Council Canada, Division of Chemistry -Guest Researcher
1982 to present	Energy Mines and Resources Canada, Ottawa, Ont. -Research Scientist

RECENT PROJECTS

1. Processing Sludge Derived Oil
   The oil product of sewage sludge pyrolysis was treated to create raw materials for petroleum refining.

2. Membrane Processing of Petroleum Distillate
   Reverse osmosis and pervaporation were studied for the removal of aromatics from naphtha and middle distillate.

PATENTS AND PUBLICATIONS

2 Patents issued
15 Refereed publications

Craig Fairbridge

CLASSIFICATION	Research Scientist (SE RES 02)

EDUCATION

Ph. D.	Chemistry, University of St. Andrews	1981
M. Sc.	Chemistry, Lakehead University	1976
H.B. Sc.	Chemistry, Lakehead University	1973

EMPLOYMENT

1987-1989

Assistant Program Director, Fuels Technology
CANMET Research Program Office
Energy, Mines and Resources Canada, Ottawa, Ontario

- preparation of policy and program planning documents
- coordination of CANMET Energy Conversion Program
- development of guidelines for communications and marketing
- coordination of all oil and gas contracted-out R&D

1981-1987

Research Scientist, Catalytic Hydroprocessing
CANMET Energy Research Laboratories
Energy, Mines and Resources Canada, Ottawa, Ontario

- evaluation of catalysts for the hydroprocessing of coal-derived distillates
- design of novel catalyst characterization methods

1976-1977

Research Assistant, Chemistry Department
Lakehead University, Thunder Bay, Ontario

- design, fabrication and maintenance of reactor systems for studying gas-solid reactions

1968-1970

Laboratory Technician, Science Instrumentation
Laboratory, Lakehead University, Thunder Bay, Ontario

- chemical analyses

RECENT PROJECTS

- application of fractal geometry to problems in surface chemistry
- review of characterization of porous solids

PUBLICATIONS

21 papers in refereed journals
4 papers in conference proceedings
3 internal reports
18 presentations at conferences

Terrance Giddings

CLASSIFICATION	Research Chemist 02	
EDUCATION		
	1985	B.Sc., Carleton University (Chemistry)
EMPLOYMENT		
	1986-87	Agriculture Canada, Sault Ste.Marie, Ont. -Technician, Pesticide Accountability and Analyses
	1987-88	Agriculture Canada, Ottawa, Ontario -Technician, Pesticide Analyses
	1988-89	Department of National Defence, Hull, Que. -Technician, Textile and Gas Analyses
	1989 to present	Energy Mines and Resources Canada, Ottawa -Research Chemist