

## Task 6.5 - Gas Separation and Hot-Gas Cleanup

**Semi-Annual Report  
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By  
**John P. Hurley  
Donald P. McCollor**

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U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
P.O. Box 880  
Morgantown, West Virginia 26507-0880

By  
Energy and Environmental Research Center  
University of North Dakota  
P. O. Box 9018  
Grand Forks, North Dakota 58202-9018

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## TASK 6.5 - GAS SEPARATION AND HOT-GAS CLEANUP

### 1.0 BACKGROUND

Catalytic gasification of coal to produce H<sub>2</sub>- and CH<sub>4</sub>-rich gases for consumption in molten carbonate fuel cells is currently under development. To optimize the fuel cell performance and extend its operating life, it is desired to separate as much of the inerts (i.e., CO<sub>2</sub> and N<sub>2</sub>) and impurities (i.e., H<sub>2</sub>S and NH<sub>3</sub>) as possible from the fuel gas before they enter the fuel cell. In addition, the economics of the integrated gasification combined cycle (IGCC) can be improved by separating as much of the hydrogen as possible from the fuel, since hydrogen is a high-value product. One process currently under development by the Energy & Environmental Research Center (EERC) for accomplishing this gas separation and hot-gas cleanup involves gas separation membranes. These membranes are operated at temperatures as high as 800°C and pressures up to 300 psig. Hydrogen separation is dependent on the temperature, pressure, pressure ratio across the membrane, and ratio of permeate flow to total flow. Some of these membranes can have very small pores (30–50 Å), which inefficiently separate the undesired gases by operating in the Knudsen diffusion region of mass transport. Other membranes with smaller pore sizes (<5 Å) operate in the molecular-sieving region of mass transport phenomena. The EERC is concentrating on separating impurities with a ceramic membrane, possibly followed by purification by dissolution of atomic hydrogen into thin metallic membranes made of platinum and palladium alloys.

Technological and economic issues that must be resolved before gas separation membranes are commercially viable include improved gas separation efficiency, membrane optimization, sealing of membranes in pressure vessels, high burst strength of the ceramic material, pore thermal stability, and material chemical stability.

### 2.0 OBJECTIVES

The objective of Subtask 6.5 is to develop and test superior gas separation membranes. Several methods are to be tested to prepare new membrane materials, including physical vapor deposition via electron beam evaporation. The selectivity of these membrane materials for separating undesired gases was to be determined. Selectivity will be measured by feeding the gases to the membrane and sampling the inlet, permeate, and raffinate streams for gas composition and volumetric flow rate.

Specific questions to be answered during the year include the following:

- What are the effects of ceramic membrane properties (i.e., surface area, pore size, coating thickness) on permeability and selectivity of the desired gases?
- What are the effects of operating conditions (i.e., temperature, pressure, and flow rate) on permeability and selectivity?

### **3.0 STATEMENT OF WORK**

#### **3.1 Activity 1**

Several methods for preparing an inorganic membrane material, including physical vapor deposition via electron beam evaporation, are to be tested. Other ceramic filter materials utilized in hot-gas particulate filters will be obtained from selected suppliers as substrates to develop a thin-film membrane selective to hydrogen permeation. This thin-film membrane will be prepared by a modified EERC proprietary process. The base filter materials will already have been characterized for hydrothermal and chemical stability and pore size.

#### **3.2 Activity 2**

A bench-scale (4-lb/hr) continuous fluid-bed reactor is available to test bottled gas mixtures or to provide an actual coal-derived fuel gas stream for the testing of selected membranes. A Foxboro 931C process gas chromatograph or a HP 5880 gas chromatograph will be utilized to determine gas composition of all gas streams.

### **4.0 ACCOMPLISHMENTS**

A literature review conducted in the first part of the project year suggested that the most likely chance for a successful high-temperature membrane for hydrogen separation from a gasification product stream would be a ceramic analog of a dense metal membrane, where the hydrogen would dissolve into and diffuse through the membrane structure. Work on development of a thin-film membrane was begun. The electron beam coating instrument for producing potential separation membrane thin films has been made fully operational. Initial metal film coating tests have been performed using the instrument, with zinc films successfully applied to glass substrates. Preliminary experiments to test the feasibility of reacting zinc thin films with sulfur to form zinc sulfide were performed.

#### **4.1 Research Directions Suggested by the Literature Review of Membrane Gas Separation Technology**

##### ***4.1.1 Summary of Membrane Technology Related to Hydrogen Separation***

###### **Organic membranes**

- Technology is mature.
- Good separations are possible.
- Temperature limitations make organic membranes unsuitable.

###### **Metal membranes**

- Technology is mature.
- Good resistance to temperature.
- Problems with strength, fatigue, and poisoning.
- Cost is a major problem.

#### Ceramic membranes (Knudsen diffusion)

- Technology is in the research stage.
- Good resistance to temperature and corrosive atmospheres.
- Problems with reproducibility, fragility and surface cracking.
- Pure Knudsen diffusion is unsuitable for separation.

#### Ceramic membranes (molecular sieve)

- Technology is in the early research stage.
- Good resistance to temperature and corrosive atmosphere.
- Problems with fabrication and stability.
- Separations rely on very small size differences.

#### Graphitic membranes

- Technology is in the research/commercial stage.
- Good resistance to temperature and atmospheres.
- Problems with fragility and probable problems with swelling.
- Currently relying on pores; may not be highly selective.

#### Dichalcogenide membranes

- Technology is in the early research stage.
- Uncertainties as to robustness, selectivity and temperature resistance.
- Probably not as highly selective as graphites.

#### Active ceramic membranes

- No reference found for H<sub>2</sub> selectivity.
- Potential good resistance to temperature and atmospheres.
- Potential high selectivity.
- No examples are known.

#### Supported liquid (ceramic) membranes

- No reference found for high-temperature applications.
- Potential good resistance to temperature and atmosphere.
- Potential problems with stability and performance degradation.
- No examples are known.

### ***4.1.2 Research Directions Related to Hydrogen Separation***

A supported liquid ceramic membrane is not likely to succeed. In concept, a microporous (pore diameter 10–40 Å) ceramic substrate would have the pores flooded with a second ceramic material that 1) becomes liquid at the membrane operating temperature, 2) is immiscible with the solid substrate phase, and 3) has an affinity for hydrogen and/or in which hydrogen has a high solubility. No such membrane appears to have yet been proposed and may not be possible.

Also not likely to succeed is the zeolite-type molecular sieve membrane. A sodalite-type structure appears to have the best chance, with the pore size approaching that needed for passing only hydrogen. Uncertainties exist in the approach to fabrication, the selectivity and diffusion rate, and the stability. Other aluminosilicate materials may be suitable if the lattice structure expands on

heating to operating temperature to approach the  $2.97 \text{ \AA}$   $\text{H}_2$  diameter. Again, the membrane itself would likely have to be very thin.

Also, ceramic membranes employing Knudsen diffusion are unlikely to succeed because of low separation factors, unless a means can be found to significantly enhance the surface diffusion of hydrogen or to discourage the other gas components. Dense metal membranes are at a commercial stage, with the known problems being cost and engineering issues, e.g., poisoning by gas contaminants such as hydrogen sulfide.

Therefore, we believe the most likely successful high-temperature membrane for hydrogen separation from a gasification product stream would be a ceramic analog of a dense metal membrane, where the hydrogen would dissolve into and diffuse through the membrane structure. An oxygen-deficient aluminosilicate membrane or a variant thereof appears to be sound, since an  $n$ -type semiconductor such as  $\text{ZnO}$  is favorable for the chemisorption of  $\text{H}_2$  (1). The membrane layer would likely have to be very thin for appreciable amounts of hydrogen to diffuse through.

## 4.2 Membrane Development Activities

### 4.2.1 Description and Operation of the Electron Beam Coating Instrument

The coating instrument is a CHA Industries high-vacuum deposition and pumping station designed for both research or production electron beam coating applications. A schematic of the system is shown in Figure 1. The heart of the instrument is an 18-inch-diameter  $\times$  26-inch-high vacuum bell containing a Sloan Technology Corporation  $270^\circ$  electron beam gun able to operate at power levels up to 12 kilowatts, with the beam directed into a water-cooled hearth containing the material to be evaporated and deposited. Substrates to be coated are held in a CHA Industries

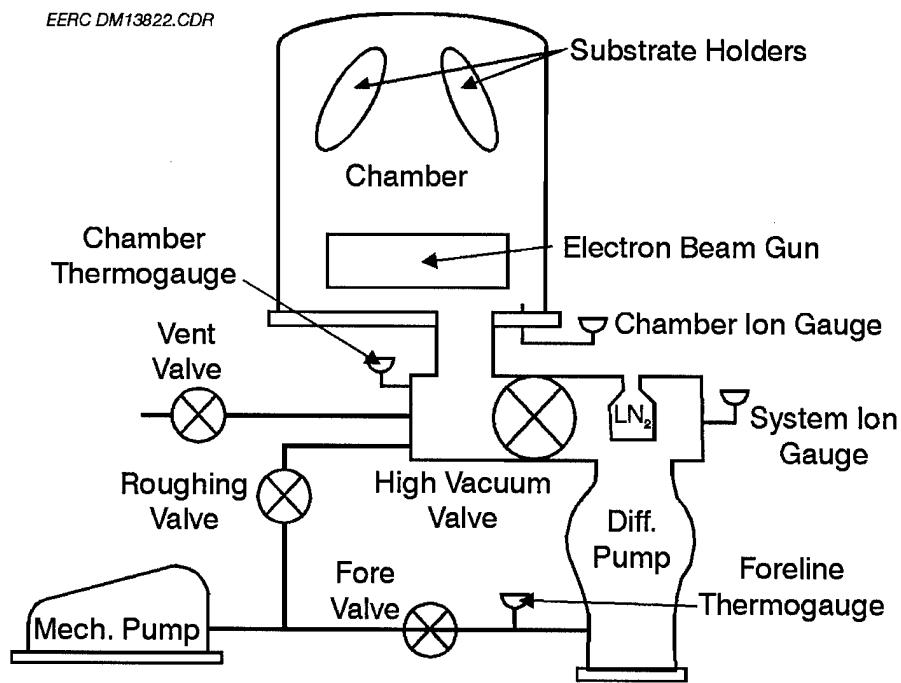


Figure 1. Schematic of the electron beam coating instrument.

rotary planetary fixture which permits a controlled, even film deposition. Quartz lamps around the periphery of the fixture track allow controlled heating of the substrates. A mechanical roughing pump and a diffusion pump along with associated valving provide the high vacuum necessary for operation.

Two modifications to the instrument have been made, the first being a holder containing four microscope slides positioned inside the bell in front of the observation window. The disposable slides provide a sacrificial surface, considerably reducing the amount of deposition on the viewport glass itself. A second modification was the provision for purging the bell with dry nitrogen prior to vacuum pumpdown and while being brought up to atmospheric pressure after deposition tests. This reduces possible reaction of the films produced with air, as well as preventing moisture condensation on the walls of the water-cooled vacuum bell.

In operation, the material to be deposited is loaded into a crucible fitted in the electron gun hearth. Substrate plates to be coated are mounted to the rotary fixture. After verification that cooling water flows are adequate, the vacuum bell is lowered onto the baseplate over the gun-and-fixture assembly. The bell is purged with a flow of nitrogen for approximately 10–15 minutes prior to starting the mechanical roughing pump. The system is pumped down to approximately  $1 \times 10^{-1}$  torr (vacuum bell) to  $8 \times 10^{-2}$  torr (forechamber and diffusion pump), and the mechanical pump stopped briefly to check for leakage. Significant vacuum deterioration requires repressurizing and reseating the vacuum bell to improve the seal as well as cycling the fore valve and high-vacuum valve to improve sealing. When satisfactory sealing has been achieved, the diffusion pump is started and allowed to warm for approximately 1 hour with the large high-vacuum valve into the chamber closed. At this time, the liquid nitrogen trap serving the diffusion pump is filled. The mechanical roughing pump remains on-drawing from both the vacuum bell chamber and the exhaust (fore chamber) of the diffusion pump. The roughing valve is then closed, isolating the roughing pump from the bell chamber, and the high-vacuum valve is opened. This allows the diffusion pump to draw from the bell chamber, with the roughing pump drawing only on the diffusion pump exhaust. The diffusion pump is operated for 1 hour, with the two thermogauge vacuum readings generally in the  $8 \times 10^{-2}$  range. The ion gauge is then turned on to verify that high vacuum is present in the bell chamber (a pressure greater than  $1 \times 10^{-3}$  torr will cause the ion gauge to immediately turn off). The ion gauge is switched to the "degas" setting for approximately 15 minutes before switching back to the measurement position. Normal bell chamber pressures are in the range of  $1 \times 10^{-6}$  to  $5 \times 10^{-6}$  torr.

With the bell chamber at a stable high vacuum, deposition tests using the electron beam coater are ready to commence. The power connection to the electron gun is plugged in, and the control unit is activated. Operation will only occur when safety interlocks verifying cooling water pressure, air pressure, high bell chamber vacuum, and instrument cabinet panel closures are correct. At this time, the quartz heat lamps may be turned on and the rotary fixture started, bringing the substrates uniformly to the desired temperature. The electron beam is kept at minimum power and directed to the center of the crucible containing the material to be evaporated using the x- and y-position controls. The beam appears as a dull violet fluorescence on the material surface. Beam power is increased, with adjustments to the position as needed while the material is heated (in the case of a metal to the melting point). An indication of material evaporation is provided by the clouding of the sacrificial microscope slides protecting the viewport. In the future, a quartz film thickness monitor will be installed to accurately measure film deposition rates. The metal shutters



shielding the substrates from the evaporating material in the electron beam gun crucible are then opened for a timed interval for deposition to occur. The shutters are then closed, the electron beam reduced to minimum power, the control unit switched off, the gun system unplugged, and the quartz heaters and rotation motor turned off.

Before bringing the bell chamber back to ambient pressure, the ion gauge and the diffusion pump are turned off. The diffusion pump is allowed to cool to ambient temperature with the roughing vacuum pump on and the high-vacuum valve closed before the chamber is vented to atmosphere. The roughing pump is then turned off and dry nitrogen introduced by opening the vent valve into the bell chamber. When the chamber is at atmospheric pressure, the bell is raised to remove the coated substrates. Other instrument components, such as the thermopressure gauges, are turned off, and the water and air supplies are closed.

#### **4.2.2 Metal Deposition Tests**

The initial metal thin-film deposition tests were performed using metallic zinc as the material to be evaporated, with conventional glass microscope slides as substrates. These tests were planned to gain experience with the operation of the electron beam coating instrument as well as provide thin films to test the feasibility of conversion of the zinc film to zinc sulfide by deposition of a sulfur overlayer with subsequent reaction of the two materials.

Fisher-certified ACS zinc metal (mossy zinc, 99.995% purity) was placed in a graphite crucible (UNOCAL EB-9M) fitting into the electron gun hearth. Glass substrates were mounted in a custom-built holder mounted on the rotary substrate fixture at the top front of the bell chamber. The chamber was pumped down to high vacuum following the procedures described in the previous section. Chamber pressures were normally in the range of  $2 \times 10^{-5}$  torr when the electron beam was turned on, rising to  $4 \times 10^{-5}$  torr because of outgasing from the zinc as the metal was melted and evaporated. Because of the relatively low melting point of zinc metal ( $419.6^\circ\text{C}$ ), melting and evaporation were rapid at low electron beam power.

The slides serving as substrate were uniformly coated with a relatively thick, mirrored silver-grey film of zinc which adhered well to the glass. An overcoating of sulfur was applied to the zinc film of test slides under low vacuum ( $1 \times 10^{-1}$  torr) by sublimation at approximately  $110^\circ\text{C}$ . A uniform overcoating of sulfur was rapidly deposited and the coated slide allowed to slowly cool under vacuum. The excess sulfur was wiped free and the film examined under an optical microscope. Although some dulling of the film was noted, along with a small increase in electrical resistance, there appeared to be little reaction of the zinc with the sulfur overcoating. Subsequent additional tests produced essentially the same results. The next alternative method to be attempted will be to produce zinc sulfide thin films by direct sublimation and deposition of zinc sulfide onto substrates.

## **5.0 CONCLUSIONS AND FUTURE PLANS**

The most likely ceramic membrane for future testing of high-temperature hydrogen separation from a gasification product stream has been targeted as a ceramic analog of a dense-metal membrane, where the hydrogen would dissolve into and diffuse through the membrane

structure. An oxygen-deficient amorphous membrane such as an aluminosilicate or other material appears to be promising.

Initial metal film coating tests have been performed using the instrument, with zinc films successfully applied to glass substrates. Preliminary experiments to test the feasibility of reacting zinc thin films with sulfur to form zinc sulfide were performed. Initial observations indicated little or no reaction occurred at the relatively mild conditions employed. As an alternative, production of zinc sulfide thin films by direct evaporation and deposition of zinc sulfide onto substrate surfaces will be tested. Their stability in a gasification atmosphere at elevated temperature will be determined, as well as permeability to the components of a gasification atmosphere determined.

## 6.0 REFERENCES

1. Laidler, K.J. *Chemical Kinetics*; McGraw-Hill: New York, 2nd ed., 1965; pp 310-317.

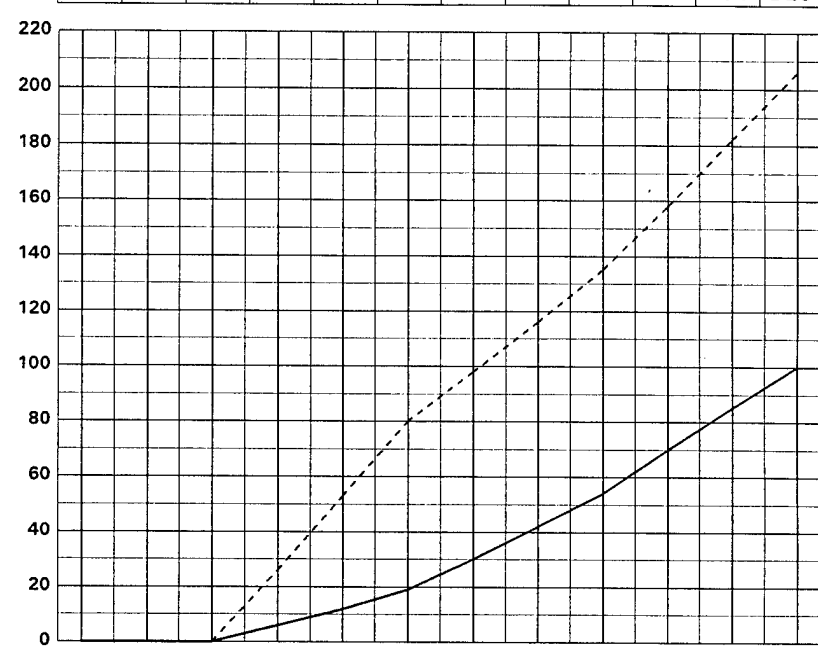
**U.S. DEPARTMENT OF ENERGY  
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT**

1. Program/Project Identification No. <b>DE-FC21-93MC30097</b>	2. Program/Project Title <b>TASK 6.0 HIGH-TEMPERATURE MATERIALS</b>	3. Reporting Period 10-1-96 through 12-31-96
4. Name and Address Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000		5. Program Start Date 01-12-93
		6. Completion Date 12-31-97

7. FY <b>96/97</b>	8. Months or Quarters Quarters	b. Dollar Scale	1st	2nd	3rd	4th								
			JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC

9. Cost Status      a. Dollars Expressed In Thousands

Fund Source		Quarter				Cum. to Date	Tot. Plan
		1st	2nd	3rd	4th		
DOE	P	0	80	55	71	206	206
	A	0	19	35	46	100	
	P						
	A						
	P						
	A						
	P						
	A						
<b>Total P</b>		<b>0</b>	<b>80</b>	<b>55</b>	<b>71</b>	<b>206</b>	<b>206</b>
<b>Total A</b>		<b>0</b>	<b>19</b>	<b>35</b>	<b>46</b>	<b>100</b>	
<b>Variance</b>		<b>0</b>	<b>61</b>	<b>20</b>	<b>25</b>	<b>106</b>	



P = Planned    A = Actual

Total Planned Costs for Program/Project \$206	Planned			0			80			135			206
	Actual			0			19			54			100
	Variance			0			61			81			106

11. Major Milestone Status	Units Planned	
	Units Complete	
6.3 Engineering Performance of Advanced Materials	P	
	C	
6.5 Materials for Gas Separation	P	
	C	
6.6 SiAlON Coatings for Alkali-Resistant Silicon Nitride	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

12. Remarks  
The remainder of Year 3 , Task 6.3 -\$16,000 was transferred to Year 4, Task 6.3.

13. Signature of Recipient and Date <i>[Signature]</i> 2/13/97	14. Signature of DOE Reviewing Representative and Date
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**U.S. DEPARTMENT OF ENERGY  
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT**

1. Program/Project Identification No. <b>DE-FC21-93MC30097</b>		2. Program/Project Title <b>TASK 6.0 HIGH-TEMPERATURE MATERIALS</b>		3. Reporting Period 10-1-96 through 12-31-96	
4. Name and Address Energy & Environmental Research Center University of North Dakota PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000			5. Program Start Date 01-12-93		6. Completion Date 12-31-97
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Subtask 6.3	Engineering Performance of Advanced Materials			All milestones should be moved back 3 months to reflect the late start of the work.	
a	Complete joining tests of silicon carbide using Joule heating	9/96			
b	Complete joining tests of silicon nitride with SiAION	9/96	9/96		*
c	Complete corrosion tests of ceramic joints	12/96			
d	Complete corrosion tests of high-temperature alloys	12/96			
Subtask 6.5	Materials for Gas Separation				
a	Complete preparation of substoichiometric aluminosilicate membranes with the electron-beam coater	9/96			
b	Complete testing of hydrogen and hydrogen disulfide permeability of the substoichiometric aluminosilicate membrane	12/96			
Subtask 6.6	SiAION Coatings for Alkali Resistant Silicon Nitride				
a	Determine morphologic and mechanical properties of alkali vapor-corroded SiAION	9/96	12/96		
b	Determine morphologic and mechanical properties of coal slag-corroded SiAION	12/96	12/96		
* Moved to Subtask 6.6 for reporting					