

# Hydrogen Membrane Selection for a Water Gas Shift Reactor – Phase II

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### 1 Summary

The CO<sub>2</sub> Capture Project with the support from the US Department of Energy sponsored a study to develop and test hydrogen transport membranes for incorporation into a sulfur-tolerant membrane water gas shift (MWGS) reactor operating with sour synthesis gas. The goals of the project were to demonstrate a proof-of-concept MWGS reactor and to determine the CO<sub>2</sub> capture cost savings.

In Phase I, four membrane types were tested with pure component mixtures of hydrogen and inert gases (no H<sub>2</sub>S). Three out of the four membranes failed to demonstrate sufficient H<sub>2</sub>:CO<sub>2</sub> selectivity to meet the target requirements on carbon recovery. The fourth membrane achieved infinite H<sub>2</sub>:CO<sub>2</sub> selectivity, but when this membrane was subjected to sour syngas, the hydrogen permeance drastically decreased.

In Phase II, the process scheme for the capture plant was modified so that sweet syngas is supplied to the MWGS reactor. A metal alloy membrane was developed and tested. Results indicated outstanding performance in terms of hydrogen flux and H<sub>2</sub>:CO<sub>2</sub> selectivity. A conceptual commercial scale MWGS reactor was designed and cost estimated.

This paper summarizes the work that took place in Phase II.

### 2 Background - CO<sub>2</sub> Capture Project

The CO<sub>2</sub> Capture Project (CCP) is an international effort funded by eight of the world's leading energy companies. This project intends to address the issue of reducing emissions in a manner that will contribute to an environmentally acceptable and competitively priced continuous energy supply for the world. The CO<sub>2</sub> Capture Project:

- Aims to reduce the cost of CO<sub>2</sub> capture from combustion sources.
- Is developing methods for safely storing CO<sub>2</sub> underground.
- Is working together with governments, non-government organizations, and other stakeholders to deliver technology that is cost-effective and meets the needs of society.

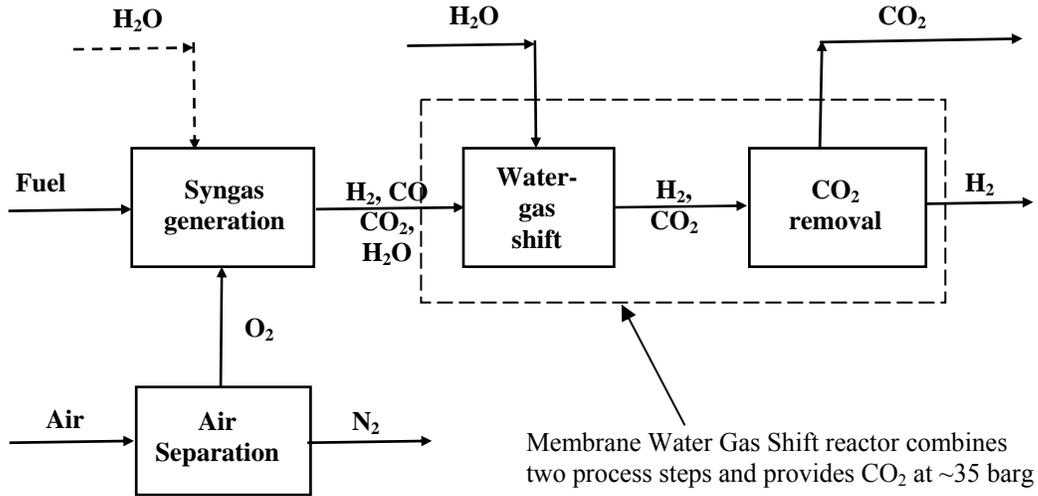
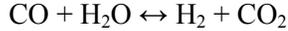
The project is studying three routes for CO<sub>2</sub> capture, as well as the sequestration of CO<sub>2</sub>. The three areas of CO<sub>2</sub> capture are:

- Post-Combustion Scrubbing - CO<sub>2</sub> is removed from the exhaust gas from furnaces, boilers, gas turbines, etc. This technology is commercially proven and can be retrofitted to existing equipment.
- Oxy firing - Oxygen is separated from air and then used to combust hydrocarbons to produce an exhaust containing CO<sub>2</sub> and water (no nitrogen). The H<sub>2</sub>O can be easily condensed, leaving a highly concentrated CO<sub>2</sub> stream for storage.
- Pre-Combustion Decarbonization (PCDC) – A description is provided in Section 3.

The Membrane Water Gas Shift study is part of a wide range of PCDC research and development projects and engineering studies that is sponsored by the CO<sub>2</sub> Capture Project.

### 3 Basic PCDC process

The basic concept for pre-combustion decarbonization is shown in Figure 1. Hydrocarbon-based gas, liquid or solids are converted into synthesis gas or syngas (primarily CO and hydrogen) in a reformer or partial combustion unit. The CO and H<sub>2</sub>O are further converted into CO<sub>2</sub> and H<sub>2</sub> in one or two reactors via the equilibrium-limited water gas shift reaction.



CO<sub>2</sub> is recovered by a solvent absorption system and is then compressed from near atmospheric pressure to the elevated pressures required for underground storage. The hydrogen fuel is available for use in boilers, furnaces, fuel cells, and gas turbines.

The focus of the MWGS study is to develop a system which will combine the shift reaction and CO<sub>2</sub> removal process steps.

Figure 1 – Basic Pre-combustion Decarbonization

### 4 MWGS reactor concept

The MWGS concept is to place a hydrogen transport membrane inside of a water gas shift reactor (Figure 2). Hydrogen in the syngas as well as the hydrogen that is produced via the WGS reaction will permeate through the membrane

allowing the shift reaction to move further toward the desired product, H<sub>2</sub>. The retentate

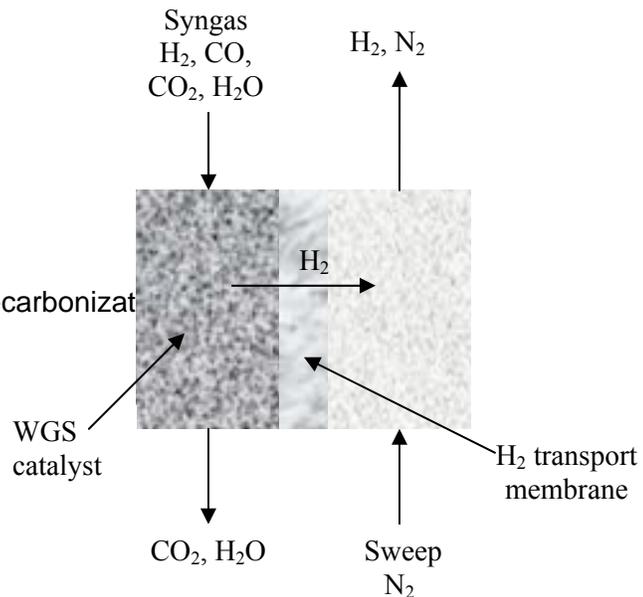


Figure 2 - Schematic for a Membrane Water-Gas Shift Reactor

stream consists primarily of CO<sub>2</sub>, non-recovered H<sub>2</sub>, and water. The end result is separate H<sub>2</sub>-rich and CO<sub>2</sub>-rich streams.

For CO<sub>2</sub> capture and sequestration purposes, a clear advantage of this concept is that the CO<sub>2</sub>-rich retentate stream is maintained at near syngas generation pressures (~35 barg). This results in lower sequestration compression costs.

## 5 Scenarios

The CCP has chosen to evaluate CO<sub>2</sub> capture technologies in four different scenarios. In this way, technologies are evaluated under “real” conditions, and the capability of a technology to handle a variety of situations/conditions can be identified.

- Norcap – Natural gas fired 385 MW combined cycle power plant
- Alaska – Multiple, distributed simple cycle gas turbines driving process compressors
- Canadian tarsands complex – Petroleum coke gasifier supplying hydrogen, steam and power
- European refinery – Multiple furnaces and boilers fired with fuel gas, natural gas, and/or sulfur containing fuel oil

The MWGS reactor concept was evaluated for the European refinery scenario. The primary fuel source was sulfur-containing fuel oil, with supplementary fuel gas and natural gas utilized as required. After the gasification step, facilities are provided to remove H<sub>2</sub>S from the synthesis gas. The MWGS concept fits especially well in the European refinery scenario because the boilers and furnaces can accept a low pressure fuel source, such as the MWGS hydrogen permeate stream.

## 6 Study objectives/work plan

The overall objective of the study is 1) to provide a proof-of-concept MWGS reactor and 2) to estimate the avoided CO<sub>2</sub> capture costs in a process incorporating a MWGS reactor.

The study was divided into two phases. In Phase I (3/02-2/03), the following tasks were undertaken.

- Development and testing of hydrogen transfer membranes in a sour syngas environment
- Development of a computer simulation model of the membrane water gas shift reactor
- Development of a computer simulation model of a CO<sub>2</sub> capture plant based on MWGS technology
- Evaluation of the performance of each type of membrane in a CO<sub>2</sub> capture environment

In Phase II (3/03-12/03), the following tasks were completed. The CO<sub>2</sub> capture plant process scheme was modified to remove H<sub>2</sub>S before the MWGS reactor.

- Testing a lab scale membrane water gas shift reactor
- Development of equipment specifications for the CO<sub>2</sub> capture plant
- Design and cost estimate of a commercial scale membrane water gas shift reactor

The deliverables from the last two items were submitted to a CCP cost estimator. The cost estimator provided opex and capex estimations that were consistent for all capture technologies that are being considered by the CCP. Cost estimation was not part of the MWGS study.

## 7 Phase II membrane development

In Phase II, the membrane development effort was conducted by Eltron Research Inc. in Boulder, CO.

The overall work scope focused on conducting performance tests on the metal alloy membrane that was developed in Phase I. The testing used both ambient pressure and high pressure test rigs with both ideal gas mixtures (e.g. hydrogen and helium) and simulated syngas mixtures. Key highlights from the test program were as follows:

- Very high hydrogen flux and permeance values were achieved (see following section)
- As expected with a dense membrane, essentially infinite H<sub>2</sub>:CO<sub>2</sub> selectivity was demonstrated

- Gas diffusion limitations initially limited hydrogen flux. Modifications to the test rigs reduced the gas diffusion limitation effect
- Guard beds were required to capture 1) wall contaminants and 2) sulfur evolving from the upstream water gas shift catalyst beds
- High pressure tests with wet, syngas feed were completed with full structural integrity intact
- A proof-of-concept test rig consisting of a series of shift reactors and hydrogen membranes was constructed. The results from this rig showed that the membrane does, in fact, increase the equilibrium limited shift reaction toward the production of hydrogen

## 7.1 Performance results

The most successful membranes tested used Group IVB and VB elements (Nb, Ta, V, Zr, etc.) and their alloys. These elements have the highest known permeabilities for hydrogen of any known substances while retaining essentially 100% selectivity for hydrogen. Membrane materials were selected for compatibility with operating conditions of commercial high-temperature water-gas shift reactors which typically run in the temperature range of 340-440°C at 35 bar and use catalysts containing 90 wt % Fe<sub>3</sub>O<sub>4</sub>/10 wt % Cr<sub>2</sub>O<sub>3</sub>, with additives of Cu and graphite.

### 7.1.1 High pressure testing

One milestone achieved in the project was to demonstrate that membrane disks, 16 mm in diameter and 127 microns thick could resist a differential pressure of at least 30 bar (3.0 MPa or 435 psi) while maintaining exceptionally high flux of hydrogen at essentially 100 % hydrogen selectivity.

- Membranes were successfully tested for over 300 hours at 673 K (400°C) at an absolute pressure on the feed side of 3.23 MPa (32.3 bar or 468 psi) and a differential pressure of 3.13 MPa (31.3 bar or 454 psi).
- Tests used a feed containing 37.3 mol % steam, 17.8 mol % CO<sub>2</sub>, 41.4 mol % H<sub>2</sub>, 3.3 mol % CO with balance of nitrogen.

### 7.1.2 Proof of concept testing

The removal of hydrogen by membranes produced the expected shift in the reaction as predicted when the hydrogen-depleted gas was passed over beds of water-gas shift catalyst.

### 7.1.3 Ideal gas testing

After eliminating rate limiting steps due to adsorption of impurities on both sides of the membrane and rate limiting steps due to gas phase diffusion, a hydrogen flux of 280 mL·min<sup>-1</sup>·cm<sup>-2</sup> (STP) was achieved for a 127 micron thick metal membrane at 440°C, using the target partial pressure of H<sub>2</sub> of 13.1 bar, an ideal H<sub>2</sub>/He mixture in the gas feed, and a differential pressure of 31.0 bar. The flux was increased to 346 mL·min<sup>-1</sup>·cm<sup>-2</sup> (STP) using H<sub>2</sub> partial pressure in the feed of 29.0 bar in an ideal H<sub>2</sub>/He mixture.

### 7.1.4 Gas diffusion issues

Membranes 127 and 75 microns thick showed identical values of hydrogen flux, demonstrating that flux is limited by surface effects for the thinnest membranes. For the 127 micron thick membrane, the maximum measured permeability at 31.0 bar feed pressure, 13.1 bar H<sub>2</sub> partial pressure, and 440°C was  $2.4 \times 10^{-7} \text{ mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$  yielding a permeance of  $1.9 \times 10^{-3} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ .

Hydrogen flux through membranes 250 microns and thicker showed limitations due to diffusion of hydrogen through the bulk metal material. The maximum measured permeability at 440°C was  $3.2 \times 10^{-7} \text{ mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ , yielding a permeance of  $1.28 \times 10^{-3} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$ .

## 8 Commercial scale MWGS reactor design

The commercial reactor design effort was conducted by SOFCo-EFS of Alliance, OH. The primary objective of this work task was to design a conceptual commercial scale MWGS reactor and to estimate its cost.

Three feasible MWGS reactor designs were developed which use either a planar or a tubular hydrogen separation membrane. Two reactor designs used a planar membrane composed of a curved membrane supported by a corrugated Type 430 stainless steel sheet. Finite element analysis which considered the pressure, gravity, and differential thermal expansion loadings indicates that it is structurally adequate for 41.1 bar (600 psid) pressure loading at 450°C (842°F). A third MWGS reactor concept is based on a tubular membrane sized appropriately to contain high pressure inside the tubes.

An analysis tool was developed to permit examination of different arrangements for the MWGS reactor and bench-marked against the membrane simulation model developed in Phase I. This analysis tool determined the membrane area required for the planar and tubular reactor concepts.

The baseline planar design places the membrane internals inside of a conventional pressure vessel. An alternative planar design uses an externally stayed structure to house the membrane panels. The planar membrane reactors have the following characteristics:

- A multi-pass cross flow arrangement to meet the performance and pressure drop requirements
- Catalyst placement in a catalyst gap of 0.15 meters (6 inches) between each membrane stack
- 40 stacks of 159 membrane wafer panels, 2 meters (6.55 ft) long by 3.05 meters (10 ft) tall by 0.305 meters (1 ft) wide
- Total active membrane surface area of 5357 m<sup>2</sup> (57,662 ft<sup>2</sup>)
- Length is approximately 26.8 meters (88 feet)

The baseline reactor design is shown in Figure 3.

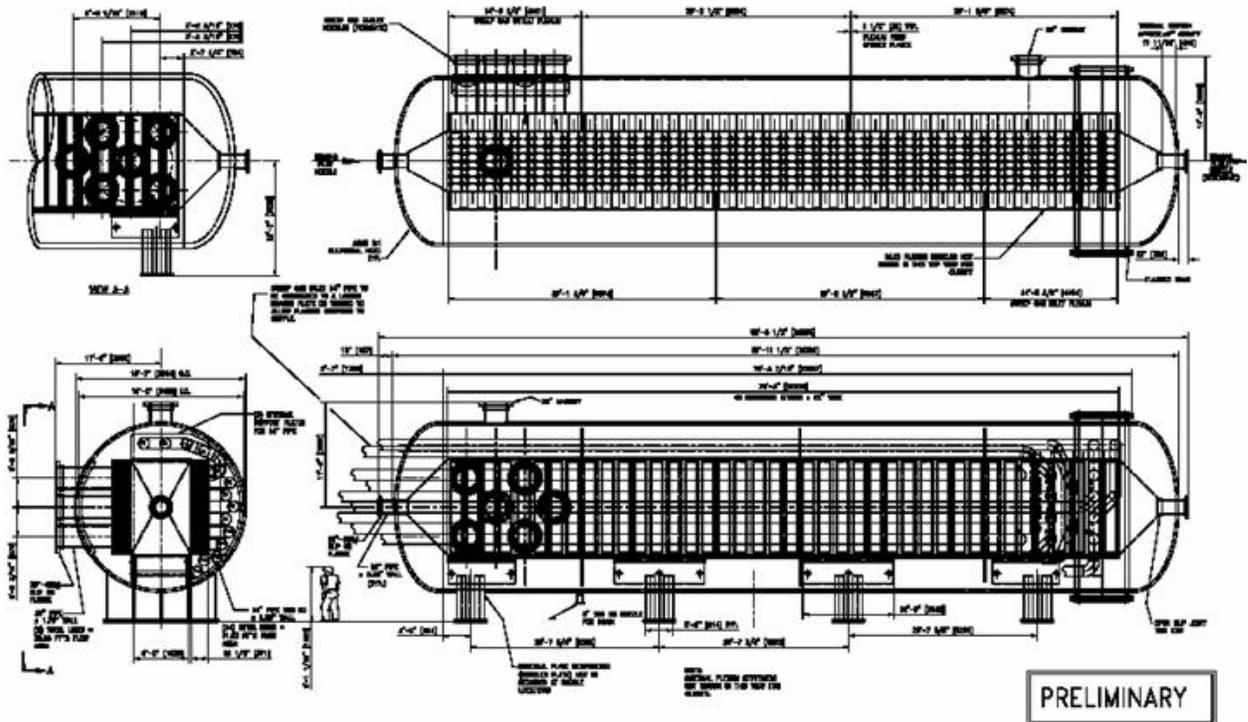


Figure 3 - Baseline Reactor

The tubular membrane reactor concept has the high pressure feed gas inside the tubes and the sweep gas flowing across the tube bank. The tubular membrane reactor concept, which was not designed as rigorously as the planar options, was based on standard shell and tube construction. The tube length was set to meet the feed-side pressure drop constraint for a given tube diameter, and the tube pitch and baffle arrangement were set to meet the sweep-side pressure drop constraint. The characteristics of the tubular arrangement include:

- 4 separate membrane reactors interstaged with catalyst reactors
- Each membrane reactor has 9730 U-tubes, 1.07 cm (0.424 inch) ID, 4.2 m (13.8 feet) long
- Total active membrane surface area of 5685 m<sup>2</sup> (61,193 ft<sup>2</sup>)
- Each membrane reactor is about 7.6 m (25 feet) long and 3.2 m (10.5 feet) diameter

### 8.1 Reactor cost estimation

The estimated order-of-magnitude cost to fabricate the reactor vessel for the baseline design is approximately \$19 million. A breakdown of the costs is given in Figure 4. The estimate is based on input from suppliers of materials and services, as well as manufacturers specializing in the fabrication of components specified for the reactor. In many cases, where detailed information was not developed, rough cost estimates were provided by vendors based on similar work and standard cost models. The vessels are designed according to Section VIII, Division 1 of the ASME Boiler and Pressure Vessel Code, for an

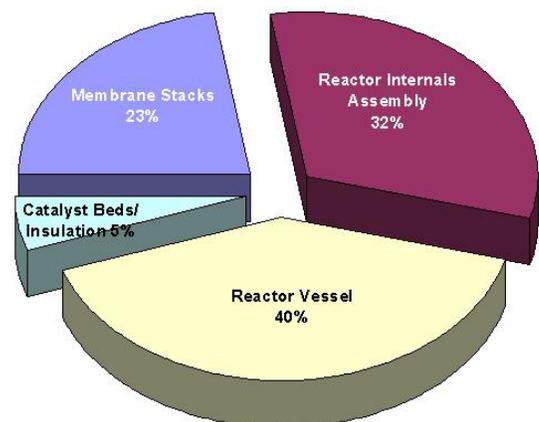


Figure 4 - Breakdown of Reactor Costs

internal pressure of 41.1 bar (600 psig) and temperature of 454°C (850°F).

The alternate planar MWGS reactor option which eliminated the external pressure vessel in favor of an externally stayed feed gas flow duct was estimated to reduce the total cost down to approximately \$12 million. The tubular membrane MWGS reactor was estimated with 3 sub-options in which vessels were combined. The alternate arrangement cost estimates are summarized below in Table 1.

**Table 1 - MWGS Reactor Estimate Summary**

Vessel Option	Estimated Cost, MMS
Baseline Planar Concept, Separate Internals and Pressure Vessel	19.05
Externally Stayed Rectangular Vessel (Planar Membrane)	11.97
Shell and Tube Vessel with Tubular Membranes	
4 Membrane Vessels + 4 Catalyst Vessels	11.81
2 Membrane + 4 Catalyst	11.69
2 Membrane + 1 Catalyst	11.19

## 9 CO<sub>2</sub> capture plant simulation model

The design of the CO<sub>2</sub> capture plant was provided by Fluor Federal Services Inc. in Aliso Viejo, CA. The objective of the work was to provide a detailed equipment specifications list, which could be used by others to develop a cost estimate of the plant.

Fuel oil and fuel gas are fed to an oxygen-blown gasifier to produce syngas. After scrubbing and cooling, the gas is sent to acid gas removal unit to remove H<sub>2</sub>S. The sweet syngas is then routed to a bulk high temperature shift reactor where about 85% of the shift reaction takes place. The remaining portion of the reaction takes place in the MWGS reactor. The hydrogen permeate is sent to the refinery furnaces and boilers, while the CO<sub>2</sub>-rich retentate is cooled, compressed, and sent to sequestration.

The electrical power and steam required by the gasification plant are supplied by a natural gas fired combined cycle system.

Table 2 summarizes the overall performance of the capture plant.

<b>Table 2 - Gasification Plant Performance</b> Metal Alloy Membrane	
Gasifier feed (41% fuel oil/59% refinery fuel gas)	3802.8 GJ/hr (LHV)
Natural gas for power generation	755.8 GJ/hr (LHV)
Total fuel to plant	4558.6 GJ/hr (LHV)
Hydrogen fuel return to existing boilers	2812.3 GJ/hr (LHV)
Overall thermal efficiency for hydrogen fuel	62%
Pure carbon dioxide to sequestration	1.98 million tonnes/yr
Total carbon recovery (including power generation)	84%
Power Generation	MWe
Combustion Turbine	72
Steam Turbine	45
Auxiliary Power Consumption	76
Net Power Export	42

## 10 Phase II conclusions

- A hydrogen transfer membrane was developed which showed outstanding flux and selectivity performance.
- The membrane was able to withstand high differential pressures when subjected to simulated synthesis gas mixtures.
- Proof of concept testing demonstrated that the integration of the hydrogen membrane into a water gas shift reactor furthers the shift reaction toward the production of hydrogen.
- A feasible design of a commercial scale reactor was developed and cost estimated.
- The membrane water gas shift reactor was integrated into a CO<sub>2</sub> capture plant. A detailed equipment specification list was developed for the plant.

## 11 Acknowledgements

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