Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

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Chapter 21

GRACE: DEVELOPMENT OF SUPPORTED PALLADIUM ALLOY MEMBRANES

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ABSTRACT

The present study reports development and testing of flat and tubular supported palladium alloy membrane modules at SINTEF. Membranes with thickness in the range of 1 μm have been prepared by a two-stage magnetron sputter process using a single crystal silicon wafer as intermediate support and a wire mesh or porous material as final support. Testing of the hydrogen flux through the tubular membranes at 300°C has shown that permeance values of about 3×10^{-6} mol/(m^2 s Pa) can be attained. For a flat membrane, peak permeance values of about 6.8×10^{-6} mol/(m^2 s Pa) was attained at 300 °C. The membranes are able to separate hydrogen gas from nitrogen gas with 100% selectivity within the detection limits of the equipment. Tubular membrane supports that have been reinforced by a steel insert have been tested up to 14 bar transmembrane pressure. Although the selectivity drops at high pressure, the tests show that the membrane film does not disintegrate at high pressure even at 300 °C. Some of the membranes described have been shipped to ITM-CNR in Italy for catalytic reactor testing as a part of the GRACE program.

INTRODUCTION

The Grangemouth Advanced CO_2 Capture Project (GRACE) was a two-year (2002–2003) research program concerned with the capture of CO_2 from a UK refinery site. One of the technologies that were pursued in the program was the development of hydrogen gas separation by membrane technology. Such technology can be used to enhance the water gas shift reaction for CO_2 capture by pre-combustion decarbonisation of refinery fuel gas.

Palladium alloy membranes for separation and purification of hydrogen gas have been studied world-wide for several decades. The main challenge has been to prepare thin and defect free membranes with sufficient stability. The need for very thin membranes, less than 5 μm thick, is due to the double effect of this parameter on cost. First, the hydrogen flux is inversely proportional to the membrane thickness as long as the transport is limited by diffusion of protons through the metal, and secondly the material costs of the membrane goes drastically down as the thickness is reduced. A large number of different methods have been investigated for preparation of thin membranes supported on either porous substrates or dense highly permeable metal substrates. Even though significant progress has been made during the last 10 years, many problems still exist that hinder up-scaling and broad industrial use. These problems are often linked to the preparation method, support-membrane integration issues and reactions with the ambient atmosphere. While the last problem must be solved by careful control of the operation conditions and development of more stable alloys, the two first problems have been focused in the recent preparation method development that is the subject of this chapter.

Before the GRACE program started, a special technology for preparation of supported palladium alloy membranes had been developed by SINTEF [1]. This work was continued in the GRACE program, leading to the development of three tubular membrane module designs. The objective of the present paper is to report the later stages of SINTEF's own development and testing of a flat supported membrane, as well as the development and testing of the tubular membrane modules prepared for the GRACE program. Some of the membranes described in this paper have been shipped to ITM-CNR in Italy for catalytic reactor testing.

The membrane preparation method is a two stage process. The thin palladium alloy film is first deposited by magnetron sputtering onto the surface of a single crystal silicon wafer. The obtained film, which typically has a thickness between 1 and 5 μm, is defect free. In a second process stage the film is released from the silicon wafer and placed onto the membrane support. The membrane support can be a woven mesh or a porous material.

Membrane thickness in the range of 1 μm can be produced without defects. The film thickness and composition can easily be controlled in the sputter process. The film may be placed on optimised supports that have pore size-to-film thickness ratios in the range 0.5–5. In this way, the film can be much thinner (or the pores much larger) than with other methods typically requiring ratios in the range 0.005–0.01. This limits the mass transport resistance of the support. The design of the support–membrane interface is very flexible because the support properties can be optimised uniquely for supporting the membrane.

EXPERIMENTAL/STUDY METHODOLOGY

Palladium Alloy Film Preparation

The palladium alloy film was prepared by sputter deposition onto a standard single crystal silicon wafer using a DC-magnetron sputter system and a target of the same composition as the film. After deposition, the film had a thickness of 1.3 μm. The film was then removed mechanically from the silicon substrate and transferred by hand to the woven or porous membrane support. The procedure is described in Ref. [1].

Module Assembly

Four different module geometries were assembled. The first geometry was prepared by placing a 1 μm Pd/Ag23% palladium alloy film onto a flat 316L stainless steel woven wire mesh supplied by Fuji Filter (Japan) and sealed with a copper ring as shown in Figure 1.

Figure 1: Application of the palladium alloy membrane film onto a flat stainless steel mesh support.

The mesh of the woven support was very dense; the diameter of the wires was 15 μm and they were separated by 15–30 μm depending on direction. During testing, the foil deformed to follow the shape of the woven wire mesh as shown in Figure 2 without formation of cracks or pin-holes.

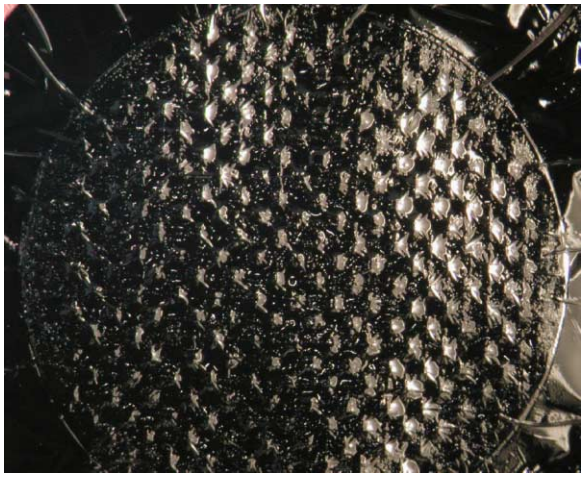

Figure 2: Close-up photograph of the palladium alloy film supported by wire mesh after testing. Although no cracking of the film was observed, considerable deformation has taken place.

This observation indicates that use of substrates with high roughness and surface topography is possible, as long as the size of the open structures of the surface is small. Surface topography may lead to larger surface area that in turn may lead to increased flux.

The second geometry was prepared by wrapping a 1 μm Pd/Ag23% palladium alloy film around a porous "AccuSep" 316-L stainless steel tubular support provided by Pall Corporation (USA). The tube had a length of 20 mm, external diameter 12 mm and wall thickness about 1 mm. Before applying the membrane film, stainless steel tube ends and connections were welded onto the porous tube ends. The membrane foil was wrapped with 5–10 mm overlap. The overlapping foils joined to form a gas-tight seal at around 300 °C by inter-metal diffusion. Several versions of sealing and connection systems were developed. One example is shown in Figure 3, where the membrane is sealed to the stainless steel tube ends by a double set of steel wedge rings.

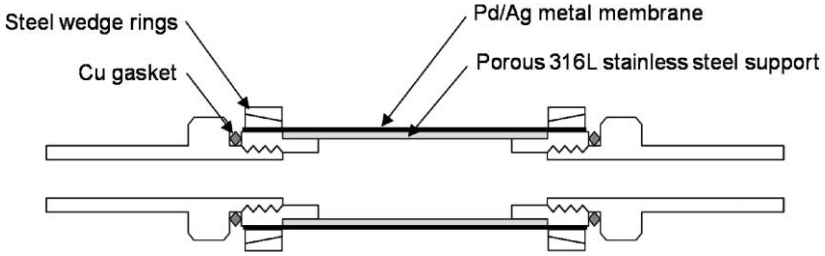

Figure 3: Example of a tubular membrane module shown schematically. The tube diameter is 12 mm and the active length is about 20 mm.

When using a membrane module of this type in a reactor with a heterogeneous catalyst, e.g. in the water gas shift reaction, the solid catalyst is likely to be placed close to the membrane film on the high pressure side of the module. In a configuration like this it may be necessary to protect the membrane from direct mechanical contact with the catalyst to avoid mechanical and chemical interaction. The third geometry module was prepared with this in mind. A cylindrical stainless steel woven mesh tube was placed around the membrane with a distance of about 1 mm between the alloy membrane and the mesh tube, which was fixed to the steel sealing rings. The woven mesh had a thread diameter of about 30 μm. Except for this protective tube, the module was similar to the second geometry module. A photograph of a third geometry module is shown in Figure 4.

Figure 4: Photograph of a tubular module with the external protective wire mesh installed.

The fourth module geometry was designed to withstand transmembrane pressures up to 15 bar. To strengthen the module, an internal reinforcement tube made of stainless steel was inserted inside the porous support tube. To facilitate the flow of hydrogen gas along and through the reinforcement tube, axial and concentric grooves and penetrating holes had been milled into it. Except for this reinforcement tube, the module was similar to the second geometry module. The four module geometries are shown schematically in Figure 5a–d.

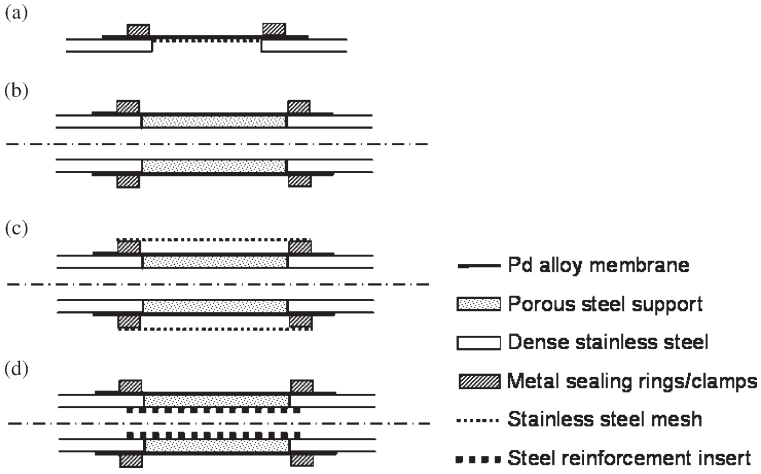

Figure 5: Schematic illustration of the four membrane module geometries; (a) flat, (b) tubular, (c) tubular with external protection tube, and (d) tubular with internal reinforcement for transmembrane pressures up to 15 bar.

Permeation Testing

Figure 6 shows the experimental set-up that was used for permeation testing experiments. The membrane module was mounted in a stainless steel housing inside a furnace that could be heated above 300 °C. The feed side of the membrane could be flushed by single gases or mixtures of H_2, He and N_2. The permeate side could be flushed by Ar. The compositions of the exhaust gases from the permeate and retentate sides were monitored by a quadropole mass spectrometer. Before each experiment, the membranes were tested for leakage at room temperature by supplying He at the feed side and flushing Ar on the permeate side. The membrane was then heated to 300 °C in flowing Ar on the permeate side and N_2 on feed side at 1 bar. In most experiments, pure H_2 at 1 bar was then introduced at one side of the membrane at 300°C. The flow rate of H_2 was measured directly by mass flow meters. He was introduced from time to time at the feed side to check for leakage. After the measurements the membranes were cooled in N_2 and Ar.

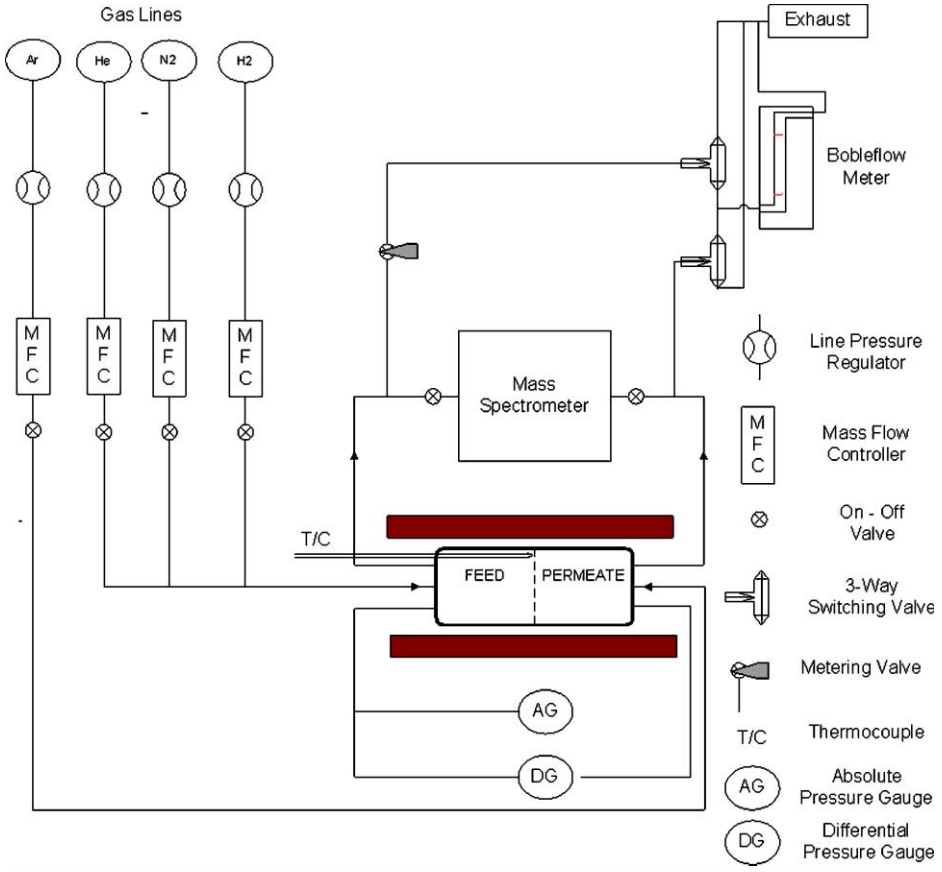

Figure 6: Schematic diagram of the experimental set-up for hydrogen permeation measurements.

RESULTS AND DISCUSSION

Hydrogen permeation measurements of the flat membrane modules showed very high permeance. Values of 6.8×10^{-6} mol/(m^2 s Pa) was attained at 300 °C. At 340 mbar transmembrane pressure difference the H_2 flow through the membrane was 30 ml/(cm^2 min) when 100% H_2 was applied on the feed-side.

With 88%H_2/12%N_2, 14.5 ml/(cm^2 min) was obtained at the same transmembrane pressure difference. The given volumes are with reference to NTP, i.e. 0 °C and 1 atm.

Results from similar measurements of tubular membrane modules (the second geometry) are shown in Figures 7 and 8. Permeance values of about to 3.0×10^{-6} mol/(m^2 s Pa) was attained, and no N_2 leaks were detected. This means that the modules had 100% selectivity within the detection limits of the equipment. Measurements with the protected tubular modules (third geometry) and the reinforced tubular modules (fourth geometry) showed slightly lower maximum permeances, 0.8×10^{-6} and 2.0×10^{-6} mol/(m^2 s Pa), respectively, probably due to mass transport limitations induced by the protective and reinforcement structures.

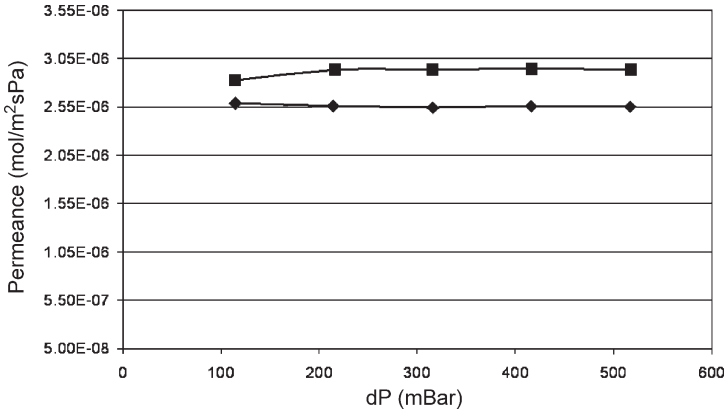

Figure 7: Results from permeation testing of a tubular membrane module of the second geometry: permeance versus pressure at 300 °C for the membrane in pure hydrogen (diamonds), same membrane after cycling to room temperature (squares).

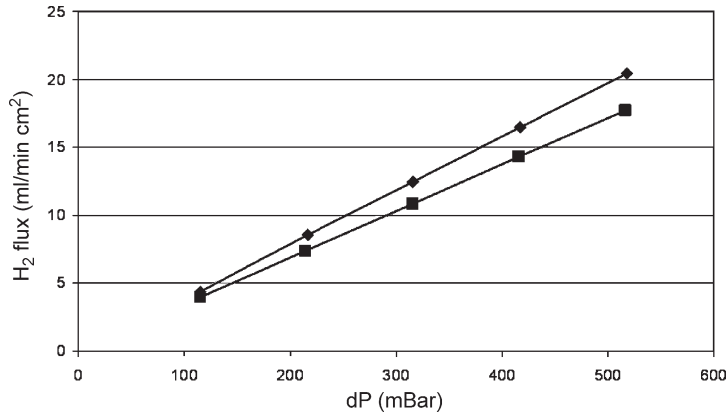

Figure 8: Results from permeation testing of a tubular membrane module of the second geometry: flux versus pressure at 300 °C in pure hyderogen. The same codes are used as in Figure 7.

The tubular membrane modules with internal reinforcement (the forth geometry) was tested up to 14 bar transmembrane pressure. In Figures 9 and 10, the H_2/N_2 separation factor and hydrogen flux is plotted as functions of pressure at 300 °C. In these measurements, the flow of H_2 and N_2 on the feed side was kept constant at 100 ml/min, providing a H_2/N_2 ratio of one and with an argon flow of 100 ml/min on the permeate side. In order to let the palladium alloy film relax and adjust to the porous support before being exposed to hydrogen, the hydrogen was first introduced at 1.5 bar transmembrane pressure. As seen in Figure 9, the separation factor reached a maximum of 30,000 at 3 bar, then a sudden drop to 700 followed by a slow reduction to 125 at 14 bar. The leaks that caused this dramatic reduction in separation was localised by microscopy after the test. The slow increase in the hydrogen flux at higher transmembrane pressure differences shown in Figure 10 may be attributed to depletion of hydrogen on the membrane surface due to limitations on the maximum hydrogen feed rate of the experimental set-up.

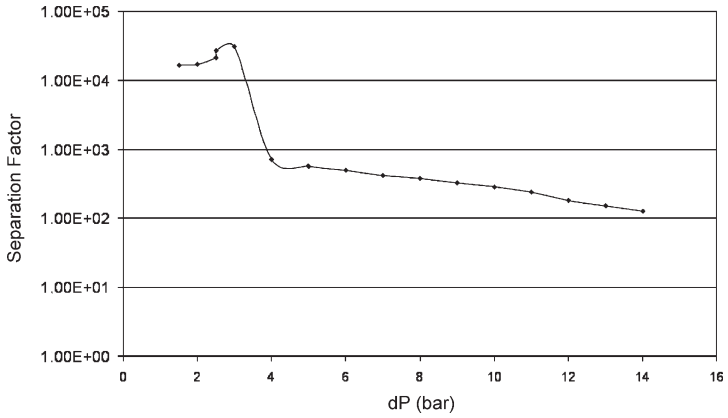

Figure 9: Results from H_2/N_2 separation testing of the reinforced membrane modules (of the fourth geometry) at 300 °C.

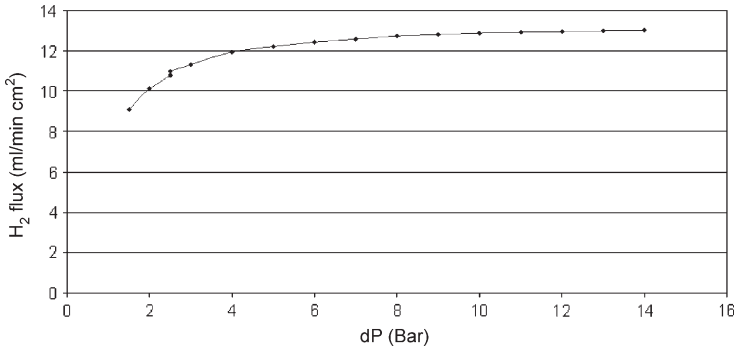

Figure 10: Results from hydrogen permeation testing of a reinforced membrane module (fourth geometry): flux versus pressure at 300 °C. The measurements were carried out with a constant 1:1 mixture of H_2/N_2 on the feed side and a constant flow of argon on the permeate side.

CONCLUSIONS

The present study shows that flat and tubular supported palladium membranes with thickness in the range of 1 μm can be prepared by the two-stage sputter process developed by SINTEF. Testing of the hydrogen flux through the membranes at 300°C has shown that permeance values of about 3×10^{-6} mol/(m^2 s Pa) can be attained. For a flat membrane, peak permeance values of about to 6.8×10^{-6} mol/(m^2 s Pa) was attained at 300 °C. The membranes are able to separate hydrogen gas from nitrogen gas with 100% selectivity within the detection limits of the equipment. Tubular membrane modules reinforced by steel inserts have been tested up to 14 bar transmembrane pressure. Although the selectivity drops at high pressure, the tests show that the membrane film does not disintegrate at high pressure even at 300°C.

RECOMMENDATION

The main challenges in future development of large-scale industrial technology based on the reported palladium alloy membranes are connected to further investigations of the long term stability of the membranes and the modules, and to up-scaling in terms of membrane area and production technology. Therefore, the authors recommend that future work is directed towards verifying and improving the long term stability in realistic reactor environments at high transmembrane pressures, as well as studies on up-scaling of the membrane and module production technology. In parallel to this work, the most important cost driving factors should be identified.

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