Pd-membranes on their way towards application for CO_2-capture

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Abstract

Pd-membranes in combination with water gas shift (WGS) reactors are considered as a cost and energy efficient technology for CO_2 capture in natural gas or coal-fired power stations. An important step towards realization of a full-scale membrane reactor is the demonstration of a scaled-down version. This paper describes the realization of a scaled-down membrane module, which is able to generate a hydrogen flux of approximately 12 Nm^3/m^2.hr at a hydrogen recovery of 95% and an operating temperature of 400°C under 30 bar of NGCC-gas composition as feed stream and 6 bar N_2 sweep stream.

Keywords: Pd-membranes; carbon capture; NGCC; membrane module; demonstration; hydrogen flux

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1. Introduction

In the European FP6 research project CACHET, palladium-based hydrogen membrane reactors for pre-combustion CO_2 capture from natural gas combined cycles have been developed. In the project both the electroless plating method used by the Dalian Institute of Chemistry and Physics DICP (Dalian, China) and two-stage membrane preparation method based on magnetron sputtering by SINTEF (Oslo, Norway) have been successfully scaled up to produce membrane tubes at a length of 50 cm. The membranes have been tested extensively with hydrogen/nitrogen gas mixtures and with simulated feed gas for reforming and watergas shift conditions. Process design studies showed that both the Integrated Reformer Combined Cycle (MREF) and the Integrated Membrane Water Gas Shift Reactor Combined Cycle (MWGS) are able to capture virtually 100% of CO_2. However, due to economic benefits the current concepts have been designed to operate at 92% capture of the CO_2 having power generation efficiencies of 46.2% and 47.1%, respectively [1].

In 2010 a follow up of the CACHET project was formulated with the acronym CACHET 2 (Carbon Capture and Hydrogen Production with Membranes) [2] being funded within the European FP7 framework. The aim of the project is to demonstrate larger than 50% net electric efficiency for a natural gas combined cycle (NGCC) power plant with CO_2 capture by using the Pd-membrane technology in combination with the WGS-reaction and to demonstrate the feasibility of further scale-up to a full-scale membrane module design. An important step towards the realization of such large-scale membrane module is to show the feasibility of a scaled-down version. The demonstration of such scaled-down membrane module is one of the prime goals of the project. This down-scaled membrane module should include one meter long Pd membranes equipped with robust sealing and has to demonstrate a long-term stability over a testing period of 1000 hours under realistic conditions as encountered in the NGCC-case.

The following steps are of importance to achieve this demonstration (See figure 1):

- Step 1: The scale-up of high-flux Pd-membranes to a length of one meter plus the development of sealing technology, aiming for compact seals with minimized leakage rates;
- Step 2: Characterization of the membrane performance in terms of permeance and stability of performance over extensive periods of time.
- Step 3: The design of a full-scale membrane module with lowest amount of required membrane area , aiming for cost efficiency.
- Step 4: Construction and testing of a scaled-down 1 m length membrane module on basis of the full scale design. A 1000 hours test with this module will be performed under realistic NGCC-conditions.

This paper will highlight the most relevant results obtained during the first two and a half project years of CACHET 2, following above mentioned steps.

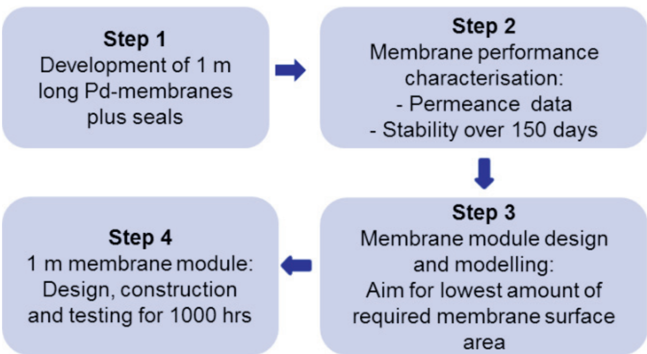

Figure 1: Schematic description of the approach towards the scaled-down membrane module.

2. Step 1: Development of 1 m long membranes and seals

2.1. Development of 1 m long membranes

An essential step towards the scaled-down membrane module is the demonstration of the manufacturing of longer membranes and the demonstration of robust seals, which form the connection between membranes and module hardware. At the start of the CACHET 2-project the initial length scale of the membranes was in the order of 10-50 cm with a diameter of 14 mm. The aim was to scale-up to a length of 1 m. The manufacturing of the Pd-membranes consists of several steps which are described in the following. The preparation of the alumina support is performed by ECN. Alumina membrane supports were obtained from a proprietary commercial company. These supports have a length of 1 m, a diameter of 14 mm and a porosity in the range of 30-40% (See table 1). In order to obtain a better surface quality for Pd-deposition these support tubes were dip coated with a suspension containing fine alumina particles, followed by a sintering step [3]. The resulting intermediate layer has a thickness of 240 μm and small pore sizes on the surface (< 0.2 μm), which makes it suitable for Pd-deposition by electro-less plating. In order to guarantee a well-defined plating deposition of palladium at the rear ends of the tube, at which the dip-coated layers show some irregularities, a small part is being cut off at the rear ends resulting in an effective membrane length of 0.95 m. The final step was to provide a Pd-layer on top of these 1 m supports, as being performed by DICP as previously described [4].

Table 1. Properties of the porous alumina support tube and the intermediate layer in terms of diameter, wall thickness, porosity and pore size.

Properties	Values
Outer diameter	14 mm
Length	0.95 m
Wall thickness	2 mm
Porosity	43 vol/o
Average pore diameter	3.5 micron
Surface coating thickness	~240 μm
Surface coating porosity	~35 vol/o
Surface coating pore size	< 0.2 μm

2.2 Development of membrane seals

Two different membrane seal concepts have been used within the CACHET 2 project, namely a seal based on direct ceramic-to-metal connection and a compression graphite based seal. See figure 2 for an impression of both seals. IMR has developed seals based on direct ceramic-to-metal connections, which has the benefit of a small seal footprint in the order of the cross-section of the membrane, enabling a reduction of the distance between membrane surface and reactor wall, which has its benefit for reducing mass transport losses and thus optimizing the required amount of membrane surface in the final membrane module. This type of seal has been established by firstly realize the connection between the ceramic support tube and the metal seal, using a brazing technology after which brazing step the Pd-layer is deposited by electro-less plating.

ECN has prepared seals, based on their already established graphite based compression seal with an emphasis on the prevention of the possibility of mechanical slip of the seal after capping the membrane and thus ensuring a more robust behavior of the seal. The seal consists of a graphite ring in direct contact with the membrane which is compressed tightly around the membrane by pressing it into a circumventing metal bus. A more in-depth description is given in reference [5]. This graphite-base seal is being applied after Pd-deposition. After sealing, typical N_2-leak rates at 100 kPa pressure difference and operating

temperature of 400°C are in the order of 1 x10^{-5} mol/m^2.s for 0.5 m length membranes. This number is a sufficient low leak rate as shown in the next chapter.
A picture of the two resulting 0.95 m long Pd membranes with IMR's direct ceramic-to-metal seal and ECN's compression seal are shown in Figure 3.

3. Step 2: Membrane performance characterisation

Performance characterization of the Pd membranes, equipped with both type of seals, have been carried out in areas of pure H_2 and N_2 permeance and apparent H_2 permeance under NGCC syngas conditions. Its long term behavior over 150 days has also been assessed. The resulting apparent hydrogen permeance values are of importance for estimating the required membrane surface area. Higher hydrogen permeance values result in lower required membrane areas and thus reduced membrane module costs. The selectivity is of importance for the resulting purity of either the CO_2-stream at the retentate, which should contain less than 4% of non-condensables in order to be stored at high pressures, or the cross-over of CO_2 to the permeate, which has an impact on the resulting CO_2-capture ratio, which should be preferably at least 90% of all the carbon in the feed stream being captured as CO_2. In order to fulfil these requirements, it was calculated that the resulting H_2/N_2 permselectivity, i.e. the ratio between pure H_2- and N_2 permeance, of the membrane needs to be higher than 1000.

The membrane performance characteristics were obtained by measuring in first instance 0.5 m long membranes in a bench scale multi-tube Process Development Unit (PDU) at ECN. With the PDU, experiments can be conducted that demonstrate the concept of membrane reactors on a multi-tube scale, and that provide data for reactor and process development [6,7].

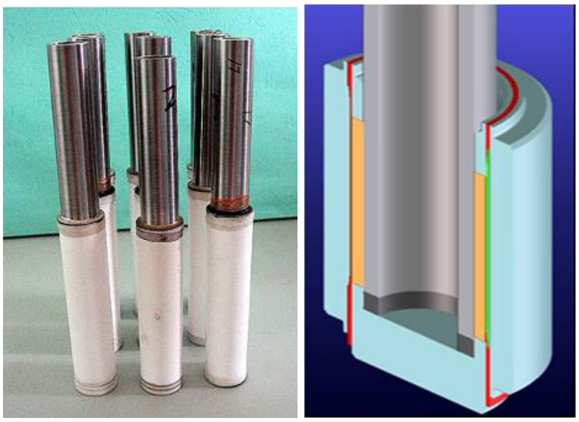

Figure 2. Impression of the ceramic-to-metal connection (left) and the graphite-based compression seal (right).

Figure 3. Picture of the two 0.95 m membranes, where the bottom one has been equipped with the compression seal and the top one has been equipped with the direct ceramic-to-metal seal.

Pure hydrogen and pure nitrogen permeation experiments were performed at 400°C/673K and at a feed and permeate pressures of 2/1 bar respectively, see table 2. The membranes with either type of seal showed an ideal H_2/N_2 permselectivity in the range of 3000-35000, fulfilling the minimum permselectivity requirement of 1000.

Table 2. Typical hydrogen fluxes and permselectivity values for 0.5 m long membranes equipped with either graphite compression seals or ceramic-to-metal connections. Feed/permeate pressure 2/1 bara.

Membrane-seal combination	Parallel membranes	Typical pure H_2 flux at 2 bar feed / 1 bar permeate	Typical pure N_2-flux at 2 bar feed / 1 bar permeate	H_2/N_2 permselectivity
	#	mol/m^2.s	mol/m^2.s	-
Graphite compression seal	3	0.3	0.6 – 1.2*10^{-5}	25000 – 35000
Ceramic-to-metal connection	2	0.28	5 – 9*10^{-5}	3000 – 6000

Dual gas (H_2/N_2 mixture) experiments with N_2 sweep gas were performed in order to obtain information on the impact of the mass transfer resistance in the feed and sweep gas compartment, and on the support mass transfer resistance [8,9]. These resistances will lead to a lower permeance (apparent permeance) when using these mixtures at the feed side and sweep at the permeate side, compared to the pure hydrogen permeance measured using a pure hydrogen feed and no sweep. The impact on the (apparent) flux at 400°C/673K is seen from the first two columns of table 3. Higher pressures were used in order to have data that are representative for full-scale applications. There is a reduction in (apparent) flux of approximately 60% when using a 50/50 H_2/N_2-mixture at the feed side and N_2-sweep at the permeate side. This indicates that mass transfer limitations have a significant impact on the permeance and that this should be taken into account in the membrane module design, as described in the next chapter.

Table 3. Typical pure and apparent hydrogen fluxes going from pure H_2 to H_2/N_2 and syngas for indicated feed/permeate pressures at 400 °C/673K.

Gas	Pure H_2	H_2/N_2	Syngas-mixture
Non-Integrated	0.8 mol/m^2.s	0.3 mol/m^2.s	0.25 mol/m^2.s
Total pressure(feed/permeate)	15/5 bar(a)	31/15 bar(a)	31/15 bar(a)

Hydrogen separation experiments using synthesis gas feed mixtures were conducted at 400ºC/673K in order to obtain information on both the impact of the mass transfer losses in the feed gas compartment on the permeance, and on the additional impact of inhibition on the permeance by the presence of syngas components, for which predominantly CO is known to have the largest contribution [9]. This is reflected in the third column of table 3 (syngas mixture) in which the apparent flux of a syngas mixture shows a slightly further reduction in apparent permeance compared to the H_2/N_2-case. The syngas composition was taken from process design modeling on integration of membranes in a natural gas combined cycle (NGCC) power plant equipped with CO_2 capture [10]. The test under the syngas-mixture was also used to demonstrate the ability to obtain the relatively high hydrogen recovery required for applying membranes in CO_2 capture applications, see figure 4. A hydrogen recovery of 95% is reached at a feed flow of 14 NL/min at 26 bar and a permeate pressure of 2 bar. This feed flow corresponds with a load/surface ratio of approximately 30 Nml/min.cm^2, which results in a hydrogen production rate of approximately 9.3 Nm^3/m^2/hr.

The acquisition of the aforementioned data on pure hydrogen, H_2/N_2-mixtures and the use of syngas was carried out on the PDU over a period of approximately 1000 to 1600 hours. Over this time period the stability of the performance of the membrane was monitored by measuring frequently the pure hydrogen permeance over time at different feed and permeate pressures. Figure 5 shows an example of the hydrogen permeance as a function of time, showing constant pure hydrogen permeance over a period of 1500 hours for a feed and permeate pressure of resp. 2 and 1 bar.

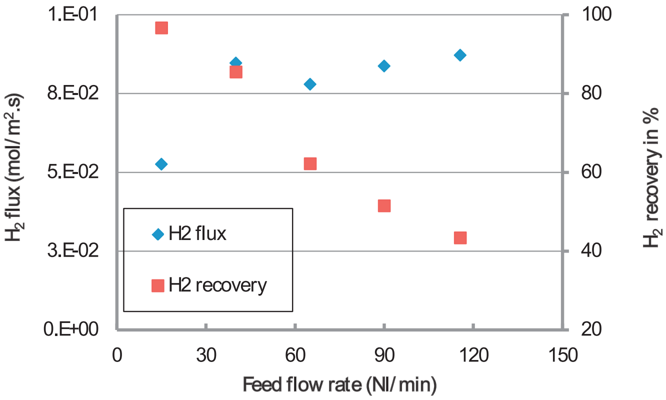

Figure 4. Hydrogen recovery and flux as function of feed flow rate in syngas (0.4% CO, 16.1% CO_2, 30% H_2O and 51.5% H_2, 400°C, N_2 sweep gas).

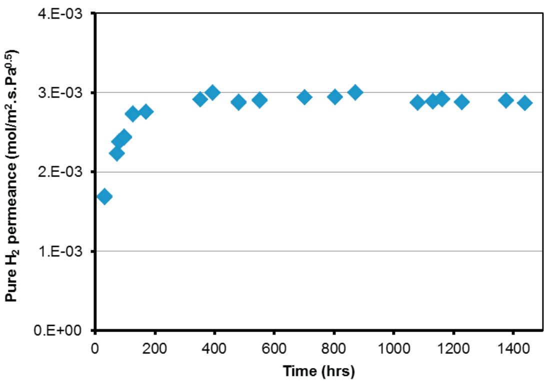

Figure 5. Pure hydrogen permeance at feed and permeate pressures of resp. 2 and 1 bar as function of testing time at 400°C.

4. Step 3: Membrane module modeling and design

A combination of system modeling and membrane modeling was used to select between two possible concepts. In the integrated membrane reactor concept, a water gas shift (WGS) catalyst is inserted at the feed side of the membrane module. In the non-integrated concept the WGS catalyst is moved from the feed side to a separate catalytic reactor in front of the membrane unit; and 2 or 3 of these reactor/separator combinations are placed in series. The membrane module consists of two concentric tubes, where the tubular palladium membrane is deposited on the outside of the inner support tube. The feed side is the annular space between the tubes, which may be filled with WGS catalyst. The sweep gas is in the core, and may flow either co- or counter-currently (See figure 6).

The membrane model is developed by SINTEF, and is a 2-dimensional model calculating the feed and permeate side mass transfer resistance, the support mass transfer resistance and the membrane separation layer resistance based on the permeability and membrane thickness both experimentally derived in CACHET 2. The membrane tube diameter was equal to that of the standard 14 mm diameter membrane supports. For the outer tube diameter, sensitivity studies were performed that indicated that it is essential to reduce the diameter to the lowest value possible, but limited to have sufficient space for membrane seals. The diameter selected was based on a standard pipe dimensions.

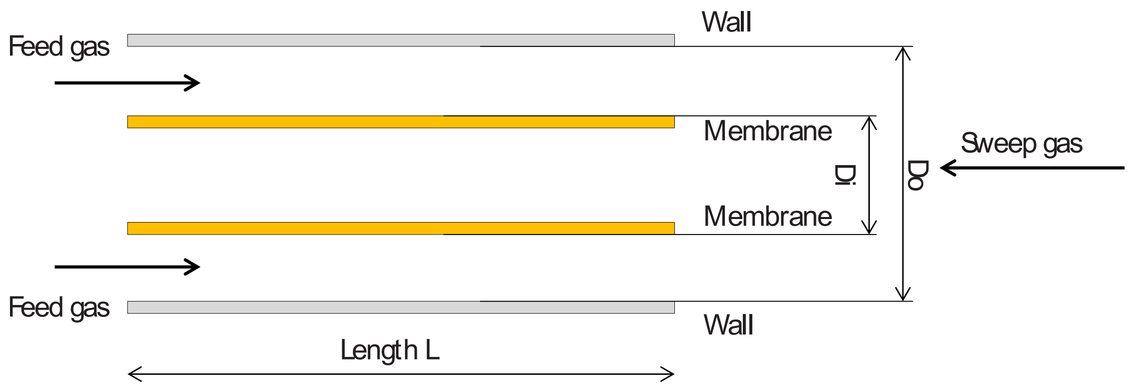

Figure 6. Schematic drawing of the membrane configuration used in the modeling tool.

The simulations at a 95% hydrogen recovery factor shows that the integrated concept does not necessary have a higher required membrane surface area, compared to the non-integrated concept. The cause is the higher mass transfer resistance in the laminar catalyst bed compared to the feed side turbulent or transitional flow regime in the non-integrated concept. The higher average feed H_2 concentration in the integrated case proved to be of lower importance for surface area.

Based on evaluation of the geometry with SINTEF's 2-dimensional model, a full scale module design has been prepared by Technip**.** The full scale design consist of a vessel of 6 m long which can include 7 membrane tubes at a diameter of 14 mm, resulting in a total membrane area of 1.8 m^2 (See table 4). This full scale design has been used as a starting point for the construction of the down-scaled membrane module, as described in the next chapter. A further enhanced full scale membrane module is envisaged in which the diameter of the membranes is increased to 1 inch and the number of membranes to 19, bringing the total membrane area to a value of 9 m^2.

Table 4. Relevant parameters of both the full-scale, enhanced full scale and scaled-down membrane modules. For the scaled-down membrane module the number and the length of the membranes have been brought down.

		Full scale module	Enhanced full scale module	Down-scaled module
Diameter membrane	m	0.0140	0.0254	0.0140
Membrane length	m	6	6	0.9
Amount of tubes	#	7	19	3
Membrane surface area	m^2	1.8	9	0.12

5. Step 4: One meter membrane module design, construction and testing

The full-scale concept has been used to prepare the scaled-down unit, for which the main characteristics are also shown in table 4. A schematic drawing is shown in figure 7. This scaled-down membrane module is currently being tested at ECN with respect to membrane performance in terms of flux vs. feed and permeate gas compositions and pressures. The first experiments at the time of writing indicates that this module can generate about 12 Nm^3/m^2.hr of hydrogen at an operating temperature of 400^oC under 30 bar of NGCC-gas composition and 6 bar N_2 sweep pressure at a H_2-recovery of approximately 95%. The retentate composition results in dry CO_2-levels well above 80% balanced by remaining CO and H_2. The further removal of CO and hydrogen has to take place in the actual system by WGS-reactors and membrane modules placed in series with the current membrane module. The presence of non-condensables in the retentate is lower than 1%, which should be good enough for CO_2-storage. The first long term measurement data is being collected at the time of writing.

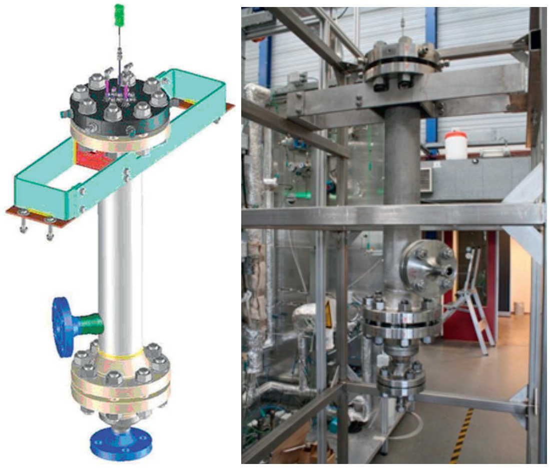

Figure 7. Drawing and picture of the down-scaled membrane module.

6. Conclusions

The aim of the CACHET 2 project is to demonstrate larger than 50% net electric efficiency for a natural gas combined cycle (NGCC) power plant with CO_2 capture by using the Pd-membrane technology in combination with the WGS-reaction and to demonstrate the feasibility of further scale-up to a full-scale membrane module design. An important step towards the realization of large-scale membrane modules is to show the feasibility of a scaled-down version, which includes one meter long Pd membranes equipped with robust sealing and which has to demonstrate a long-term stability over a testing period of 1000 hours under realistic conditions as encountered in the NGCC-case. In order to realize this scaled down membrane module the following steps have been realized:

- The manufacturing of membranes with a length of 1 meter on basis of porous alumina supports with a diameter of 14 mm has been demonstrated.

- Two seals have been developed, one on basis of a ceramic-to-metal connection and one on basis of a graphite compression seal. For both seal types it has been shown that the leakage rate of these seals is sufficiently low to fulfil the requirement of a H_2/N_2 perm selectivity of 1000.
- Characterization of the membrane-seal combinations under NGCC-case conditions reveal hydrogen flux values in the range of 0.25 mol/m^2.s at 31 bar feed (0.4% CO, 16.1% CO_2, 30% H_2O and 51.5% H_2) and 15 bar permeate. The introduction of mixed gas compositions and sweep gas introduces additional mass transfer losses reducing the overall permeance-value compared to the pure hydrogen case.
- A membrane 2D-model tool has been developed. This model takes into account the feed and permeate side mass transfer resistance, the support mass transfer resistance and the membrane separation layer resistance based on the permeability and membrane thickness. The model was used to calculate the optimum dimensions for a membrane-module. The optimised numbers formed input for the design of a full-scale membrane module.
- On basis of the full scale membrane module a scaled-down membrane module was designed and constructed for testing of one meter membranes. The first experiments at the time of writing indicates that this module can generate about 12 Nm^3/m^2.hr of hydrogen at an operating temperature of 400^{o}C under 30 bar of NGCC-gas composition and 6 bar N_2 sweep pressure at a H_2-recovery of approximately 95%.

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