

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Capture and Separation of Carbon Dioxide
from Combustion Sources**

Edited by

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Chapter 15

DEVELOPMENT OF A HYDROGEN MIXED CONDUCTING MEMBRANE BASED CO₂ CAPTURE PROCESS

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ABSTRACT

The aim of this CCP sub-project has been to develop dense hydrogen mixed conducting ceramic membranes (HMCM) with sufficient H₂ transport rates and stability under normal methane steam reforming conditions, and further develop a techno economically viable precombustion de-carbonization (PCDC) power generating process applying said materials. In the novel natural gas to hydrogen process a two step membrane reformer system replaces the traditionally hydrogen production train.

The membrane reformer concept combines steam methane reforming and HMCM. Hydrogen generated in the steam methane reformer sections is transported through the membrane and is in a first step reacted with air extracted from a gas turbine to generate a nitrogen and steam containing sweep gas. This sweep gas is used to recover most of the hydrogen in a membrane reformer step two generating a high pressure (15–20 bar) hydrogen fuel containing about 40% H₂, 40% N₂ and 20% H₂O. The hydrogen fuel mixture is then combusted with air in the gas turbine. The low hydrogen concentration in the fuel is a major advantage since this will depress formation of nitric oxides in the combustion chamber to 15 ppmv or below. The residual synthesis gas containing mainly CO₂, H₂O and CO is further converted to CO₂ and H₂O in a residual gas oxidation section. CO₂ can then be captured simply by condensation of the water vapor.

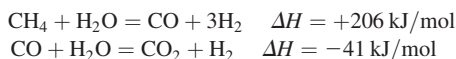
A large number of candidate membrane materials have been synthesized and characterized followed by hydrogen permeability measurements in atmospheric laboratory tests at both SINTEF and University of Oslo (UiO). Based on the measurements and theoretical evaluations, a main candidate materials system, was selected. Theoretical analyses indicate that the membranes will be stable above 700 °C under process conditions.

Supported membrane tubes have been fabricated and tested by Hydro in a pressurized hydrogen flux test rig under relevant process conditions. The measured H₂ flux in the test rig compares favorably with model predictions.

Based on cost estimate from Fluor the CCP CEM team did a cost analysis to evaluate the potential for this technology compared with, e.g. the Norwegian baseline technology. This indicates that the hydrogen membrane reformer process has the potential to reduce the cost of CO₂ capture in a CCGT power plant with at least 50%.

INTRODUCTION

In the PCDC approach fossil fuel is converted to hydrogen fuel and CO₂ is recovered for storage. Traditionally, steam reforming and water gas shift reactions are used in hydrogen production from natural gas:



Existing carbon dioxide separation techniques involve absorption of the CO₂ by an amine or hot potassium carbonate solution or separation of hydrogen by means of pressure swing adsorption (PSA). These techniques give high product purity (>99 mol%), but they are quite energy intensive.

An alternative method is to separate hydrogen from the synthesis gas using hydrogen selective membranes. The steam reforming reaction is favoured by high temperature. It is therefore of technical interest to develop hydrogen membranes which can operate at temperatures above 700 °C. Metal membranes (i.e. Pd-membranes) are expected to have insufficient microstructural stability at such temperatures, due to the high vapor pressure of metal containing gas species and mobility of metal atoms.

Research in high temperature proton conductors has been carried out for more than 20 years. The focus has been on oxides with perovskite structure [4–5]. The challenge has been to develop a material with both high electronic and protonic conductivity [6] (i.e. HMCM) since a mixed conductor can be used as a hydrogen membrane without an outer electric circuit. The transport process requires high temperature (700–1100 °C). Since this transport process is based on ion diffusion and not molecular sieving, the selectivity of the membrane is infinite as long as the membrane is gas impervious, i.e. no cracks or open porosity. The driving force is a difference in hydrogen partial pressure between the permeate and retentate sides of the membrane, see Figure 1.

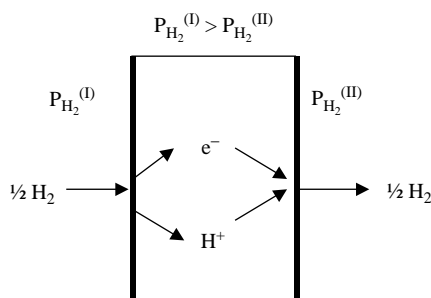


Figure 1: Schematic drawing of the HMCM transport process.

The 1.9 mil US\$ 2.5 year Klimatek funded (52%) CCP sub project started June 2001. The project has been based on Hydro IPR covering: ceramic conducting materials, reactor design and process design [1–3].

EXPERIMENTAL/STUDY METHODOLOGY

Design of the Hydrogen Membrane Reformer System

The two step hydrogen membrane reformer concept combines steam methane reforming and HMCM, see Figure 2. One of the ideas of the novel process was to avoid complicated heat exchange equipment applied to membrane air preheat, and in addition efficient use of the heat value of unconverted residual syngas from the membrane system.

System design

Desulfurised natural gas fuel, mixed with steam and preheated to 700 °C, is fed to the retentate side of the membrane section, and undergoes endothermic steam reforming, producing a hydrogen rich syngas. The retentate side can either be coated with an appropriate methane steam reformer catalyst or designed with interstage adiabatic catalyst beds. Hydrogen is transported through the membrane and is in step 1 reacted with air extracted from the gas turbine compressor to generate a nitrogen and steam containing sweep gas. This sweep gas is used to recover most of the hydrogen in a step 2 membrane reformer generating a high pressure (15–20 bar) hydrogen fuel containing about 40% H₂, 40% N₂ and 20% H₂O. The hydrogen fuel mixture is then combusted with air in the gas turbine. The low hydrogen concentration in the fuel is a major advantage since this will depress formation of nitric oxides in the combustion chamber to 15 ppmv or below.

The pressure of the hydrogen rich permeate fuel to the gas turbine combustion chamber should be higher than the pressure of the air from the gas turbine compressor. If not there would be a great loss of efficiency due to compressed air pressure loss. The most efficient way to compensate for the pressure drop through the

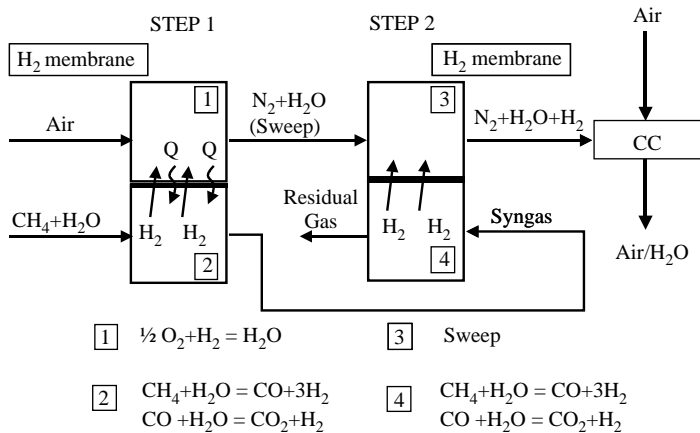


Figure 2: The two step hydrogen membrane reformer (HMR) system.

membrane sections will be to include a booster compressor on the hydrogen rich permeate fuel stream, see Figure 3. This stream is cooled down just above the steam condensation point, in order to save power, and then reheated to a suitable temperature.

The residual synthesis gas containing mainly CO₂, H₂O and CO is converted to CO₂ and H₂O in a residual syngas oxidation section. CO₂ can then be captured at 20–25 bar simply by condensation of the water vapor. CO₂ is further dried, compressed and liquefied and pumped to actual injection pressure. A relatively large portion of the gas turbine compressed air is preheated to 700 °C by means of an inline burner and fed to the residual syngas oxidation unit. By burning off permeated hydrogen, the temperature increases further to 920 °C through this stage. The major part of this hot air stream is returned to the gas turbine. A smaller part is mixed with another small air stream directly from the gas turbine air compressor in order to obtain a mixed temperature of 700 °C prior to entering the first membrane step. Available heat in the exhaust gas streams are recovered as steam that are expanded in the steam turbines to generate electric power.

Reactor Design and Arrangement

Leakage between the air side and the reformer side should be avoided putting very hard demand on sealing and manifolding, bearing in mind that expansion due to temperature increase has to be taken in account. There are connections or couplings ceramic to ceramic and ceramic to metal with need for clever design solutions.

Another aspect of design challenge is the large membrane surface area required. Thus to have compact design solutions, ceramic structures with high surface to volume ratio is needed. All these considerations have been addressed in an ongoing project (AZEP) utilizing oxygen transporting ceramic membranes for gas power production with CO₂ separation [7]. One specific consideration dealt with in AZEP was ceramic structure selection. Plate and pipe or tube solutions were considered, but selection ended up with monolith or honeycomb structures with small channels. Reactor design proposals presented in this paper are based on information generated in the AZEP project.

In a monolithic structure specific surface area per volume is a function of channel or cell diameter. A gas flow distribution of chessboard pattern compared to a linear arrangement of cells for the same gas gives twice as much surface area per volume (given the same cell size and wall thickness) (see Figure 4). Monoliths are made by extrusion and channels are thus parallel. Length is flexible, but width (the cross view sides) is dependant on the extrusion tool (normally below 20 cm).

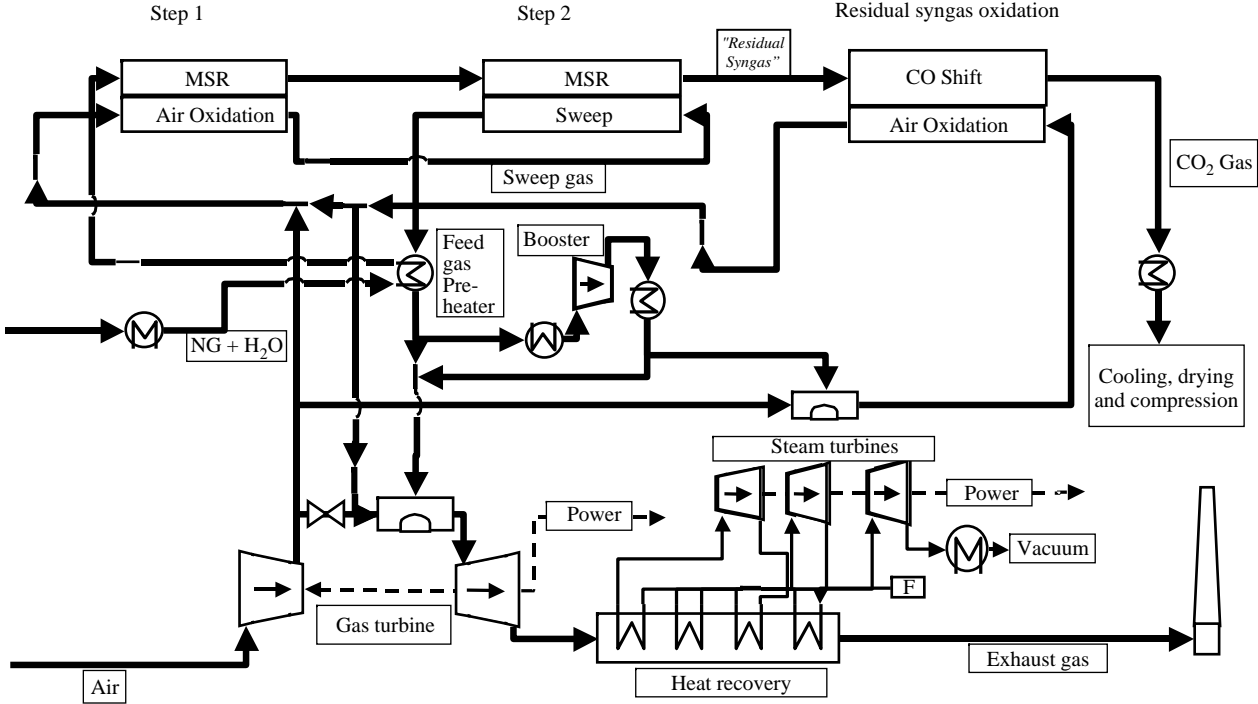


Figure 3: Hydrogen membrane reformer PCDC power plant.

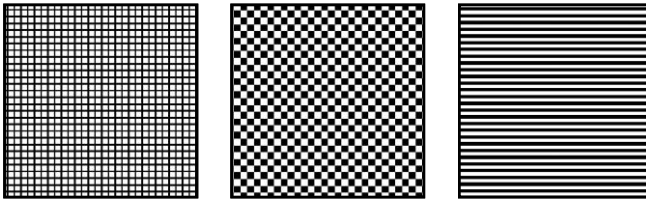


Figure 4: Monolith cell structure (left) with chess (middle) and linear flow (right) distribution.

A major challenge is the manifolding solution enabling feeding the two gases in and out of all the small channels in the monolith. Design solution of manifolding must be designed such that they can withstand the pressure difference between the two gases. The hydrogen membrane reformer design is based on a pressure difference of about 10 bar. A pressure difference of 10 bar is very challenging and puts a strong demand on avoiding large unsupported surfaces for the ceramic structures to survive.

In current design the total height of the monolithic stack is 1 m in step 1, 1.4 m in step 2 and 1 m in the residual syngas oxidation section. The design is based on standard sized monoliths (with side length of ca 15×15 cm and specific surface area per volume of about $700 \text{ m}^2/\text{m}^3$). Based on such a modular system any size of capacity can be performed by simply increasing the number of standard ceramic monolith stacks.

The upper reactor in Figure 5 is for step 1 with co-current operation and the middle two reactors are for step 2 with counter-current operation. Here exemplified with stream 2 entering from top flange and stream A07 from an inlet flange on the side (end cover). The third section (residual syngas oxidation) is arranged below step 2 with stream 18 (residual gas) entering via the top flange. Cooling air (stream A19) entering via flange on the end cover.

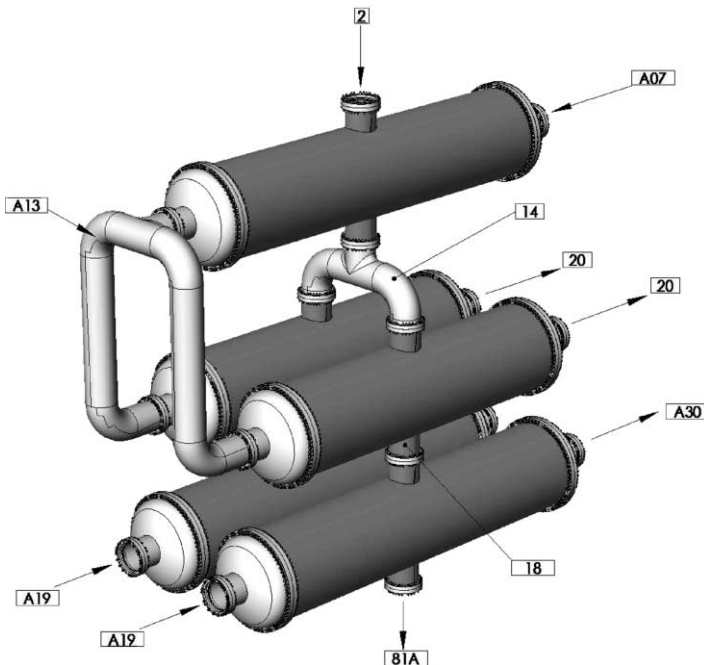


Figure 5: Flow system for steps 1, 2 and 3 connected.

Membrane Preparation and Characterization

Powders for the preparation of mixed conducting membranes were produced either by combustion spray pyrolysis, wet complexing routes (e.g. citric acid) or by conventional solid state reaction using oxides and carbonates. After calcination the powders were milled and uniaxially pressed to disks and in some cases also by cold isostatic pressing. These disks were finally sintered to approximate diameters of either 10 or 20 mm and about 1.5 mm thickness. Sintering studies by dilatometry were regularly employed to select optimum sintering conditions.

All powders and samples were characterized by X-ray diffraction and some by scanning electron microscopy to verify phase purity and to study microstructure. Some powders and samples were also investigated by ICP and XRF to reveal the potential presence of impurity elements, and by TEM and XPS to study grain boundaries. The particle size distribution of the powders were routinely determined.

Prior to flux measurements, the sintered disks were polished and tested for leakage at room temperature by pumping vacuum on one side of the disk.

Hydrogen Flux Measurements at Atmospheric Conditions

The facilities for measuring hydrogen permeability are located at UiO and SINTEF (Oslo). The two locations have essentially identical experimental set-ups.

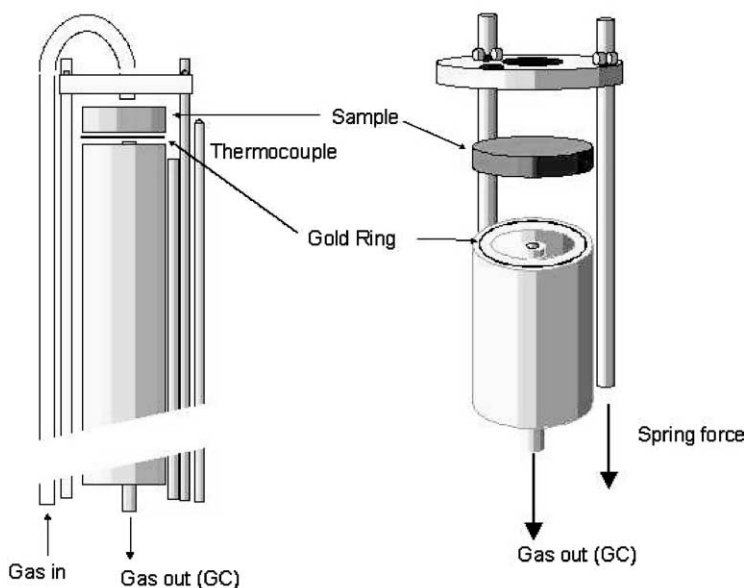


Figure 6: The permeability measurement cell.

The permeability measurement cell contains two chambers separated by the sample placed on the support tube (Figure 6). The sample was pressed onto the tube by a spring-loaded alumina disk. A gold ring was placed between the sample and the alumina tube for sealing. The cell was heated slowly to 1064 °C in order for the gold ring to form a tight seal. Permeation measurements are restricted to temperatures below 1050 °C. A mixture of hydrogen, nitrogen and helium with hydrogen contents of 10, 20, 50 and 100% was used as feed gas. The water vapor pressure in the gas was controlled by bubbling through a saturated solution of KBr, which gives a partial pressure of 0.022 atm. On the secondary side, argon was used as

sweep gas, either dry or humidified to 0.022 atm. The sweep gas exiting the cell was analyzed by a Gas Chromatograph (GC). The GC was also used to monitor the sealing process.

The amount of gas entering and exiting the measurement cell was controlled/measured by flow controllers. By combining the concentration of hydrogen measured by the GC and the amount of gas exiting the cell, the flux of hydrogen through the membrane can be calculated. Leakages were detected and corrected for by measuring the nitrogen and helium content of the exit sweep gas.

Development and Fabrication of Supported Membranes for the Demonstration Unit

For the flux measurements in the demonstration unit tubular supported membranes are used. A porous thick-walled (1–2 mm) tube coated with a thin (20–100 μm) dense layer ensures sufficient mechanical strength combined with high hydrogen flux. The porous support tube is made from the same powder as the thin membrane, but with 40 vol% corn starch admixed to create porosity. Two methods were tried for the manufacturing of the porous tubes, a medium scale and a small scale method.

The medium scale method involved powder production by spray pyrolysis (5 kg/day capacity) followed by extrusion of tubes. By this method more than a hundred high quality 40 cm long green tubes were produced in one day. The small-scale method has a considerably lower capacity (50 g/day). The powder is produced by a wet complexing route, mixed with corn starch, and cold isostatically pressed to 15 cm long tubes.

The porous tubes are coated with slips containing the membrane powder. Binders and corn starch are burnt off in air by slow heating to 500 °C and sintered at 1715 °C.

Reconstruction of Multi Test Reactor System

Hydro possess facilities for testing catalysts at pressure above 20 bar and temperatures above 1000 °C. This test rig, however, could only handle one mixed stream to the reactor system. In order to test membrane tubes the test rig therefore was reconstructed to handle two separate mixed streams, see Figure 7.

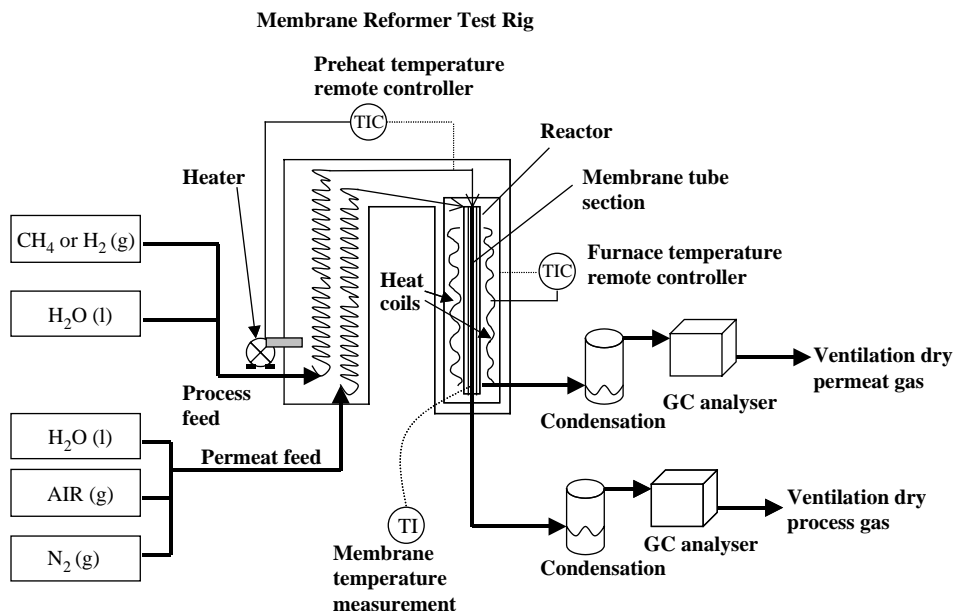


Figure 7: Sketch of the membrane flux test rig at Norsk Hydro Research Centre.

The membrane tube is installed in the middle of the reactor where stable temperature is achieved. Two thermocouples are placed inside the membrane tube (center and outlet) to measure the temperature during the tests. The test rig is equipped with two GC analyzers.

Reactor Modeling

A model of the hydrogen membrane reactor system has been made and implemented in Matlab. The work was done by SINTEF. The modeled reactors consist of small squared channels of reactor and sweep gas compartments with the membrane in between, see Figure 8.

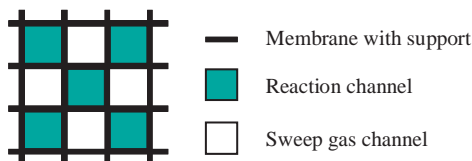


Figure 8: The membrane reactor channels perpendicular to the flow direction.

A kinetic model for methane steam reforming from the literature [8] and a membrane flux equation provided by hydro has been included. The membrane reactor model may be used in both co-current and counter current mode, and the program, combines these to modes into a system of two membrane reactors in series, see Figure 2.

RESULTS AND DISCUSSION

Hydrogen Mixed Conducting Membrane Development

A ceramic hydrogen mixed conducting membrane (HMCM) for use at high temperatures (700–1100 °C) has been developed. The membrane combines good chemical stability with high hydrogen flux rates.

Hydrogen flux measurements and modeling

A total number of 40 candidate membrane materials have been synthesized and characterized and more than 35 hydrogen permeability measurements have been performed. Based on the measurements and theoretical evaluations, a main candidate materials system was selected.

A hydrogen flux model was developed to explore the permeation rates one may expect in actual processes using the selected materials. The purely fundamental model consists of an equilibrium model describing the solution of hydrogen in the solid material and a transport model for the migration of hydrogen through the membrane. The dissolved hydrogen is assumed to associate with oxygen ions in the oxygen lattice of the membrane material, with ideal mixing of oxygen ions and oxygen-hydrogen associated ions. Hence, the equilibrium content of hydrogen is then described by two fundamental parameters, the enthalpy and entropy for the reaction of the non-hydrogen containing material with hydrogen gas to form the hydrogen-saturated material. Hydrogen transport in the membrane is described by the Wagner equation, hence assuming non-limiting solid-gas interface exchange processes. Combination of the two models enables the description of hydrogen flux in terms of four fundamental material parameters, enthalpy and entropy of hydrogen dissolution, and an activation energy and pre-exponential factor related to the hydrogen diffusion coefficient. The model was fitted to the measured flux data of the selected membrane material, see Figure 9. The measured data are shown as symbols, while the curve represents the model fit to the experimental data. The model parameters for the best fit was subsequently used to calculate flux at conditions close to process conditions. These predicted fluxes are orders of magnitude higher than the measured fluxes, partly due to the difference in membrane thickness, partly to the considerably higher solution level of hydrogen in the membranes at the higher hydrogen partial pressures associated with process conditions.

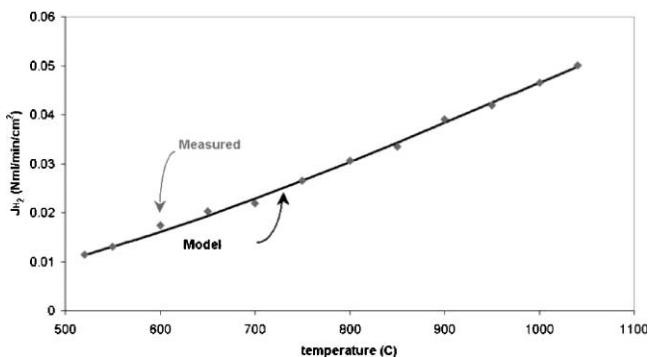


Figure 9: Measured hydrogen flux data of selected candidate material (symbols) and model fit (curve).

A summary of modeled flux for tested materials is shown in Figure 10. For the hydrogen flux given in the figure, the measured values are used as the basis for model calculations corresponding to process conditions for a 20 μm thick supported membrane. Hence, each bar represents an experimentally determined value transformed by use of the model to hydrogen flux under process conditions. Process conditions are here defined by 1000 $^{\circ}\text{C}$, $P_{\text{tot}} = 20$ bar, a steam carbon ratio $S/C = 2$, with 20% hydrogen extracted from the feed gas, and 0.1 bar H_2 in the permeate. The flux model predicts hydrogen flux above target for several materials. However, there are large variations in flux data measured on membranes with similar compositions. This variation may partly be explained by reduced flux due to Zr-contamination in a number of membranes or by the use of dry (non-humified) sweep, but is nevertheless not fully understood.

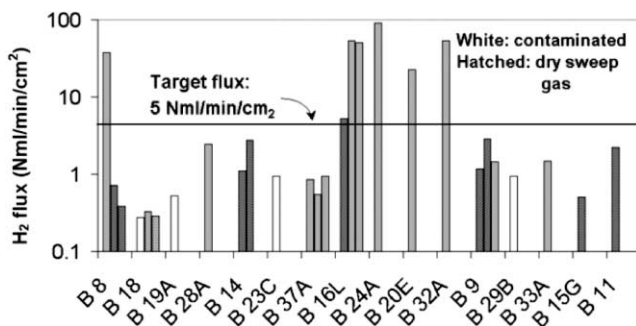


Figure 10: Experimentally determined hydrogen flux transformed to predicted flux under process conditions by use of the model.

Thermodynamic stability modeling

A thermodynamic model was developed which predicts the stability window of the membrane material. The thermodynamics of the membrane compound are described within the framework of a regular solution model, with mixing of ions on sublattices of the compound. The fundamental parameters of the model, enthalpies and entropies of formation for constituent simple compounds and interaction enthalpies, have been obtained by an assessment of available literature. Thermodynamic descriptions of possible decomposition products are included for the evaluation of stability under process conditions characterized by high carbon dioxide and steam pressures, and a wide range of oxygen partial pressures. The high temperature stability of the selected membrane material is excellent (melting temperature of 2000 $^{\circ}\text{C}$). The

stability at low oxygen partial pressure (H_2 , natural gas) is likewise very good. The stability is, however, restricted at low temperatures combined with high partial pressures of oxygen or carbon dioxide. This is illustrated in Figure 11. Under typical process conditions the membrane material is stable provided the temperature is higher than 750 °C. Model predictions show, however, that minor compositional changes may bring down this lower temperature limit. Hence, inlet conditions of 700 °C is probably achievable.

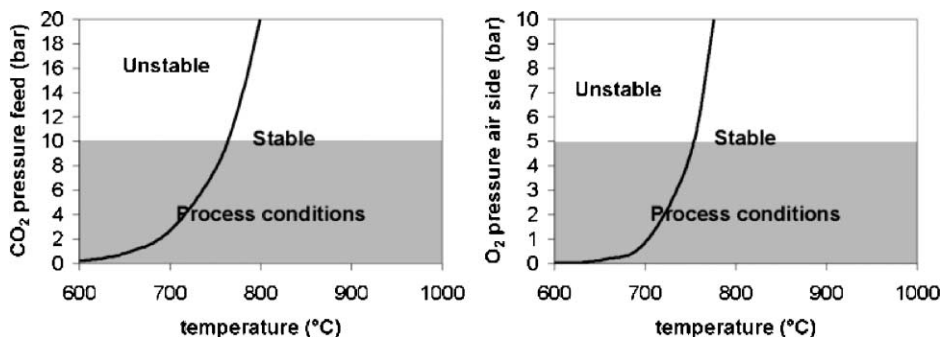


Figure 11: Illustration of membrane material stability.

Test of supported membranes in the demonstration unit

The selected membrane material is difficult to sinter. Disks pressed from very fine powders (0.1–0.2 μm) sinter to gas impervious specimens at 1715 °C under thoroughly controlled atmosphere. Using coarser powder, a lower temperature or less strict atmosphere control gives less shrinkage and samples with open porosity. Despite using these fine powders, a sintering temperature of 1715 °, and strict atmosphere control, the membrane coating of the supported tubes does not fully densify to form gas impervious layers. This is probably due to the lack of a pressure as in the uniaxial pressing of disks. To obtain fully sintered gas impervious coatings, an increase in the sintering temperature without sacrificing atmosphere control is required. This calls for equipment that we do not have access to.

Based on the development and optimization work two membrane tubes with approximately 50 μm thick crack free coatings were made. One of these tubes is shown in Figure 12. The tubes have final dimensions represented by a length of 10 cm, an outer diameter of 8 mm, and a wall thickness of 2 mm. The coatings have some open porosity and are therefore not 100% gas impervious.



Figure 12: Supported HMCM tube.

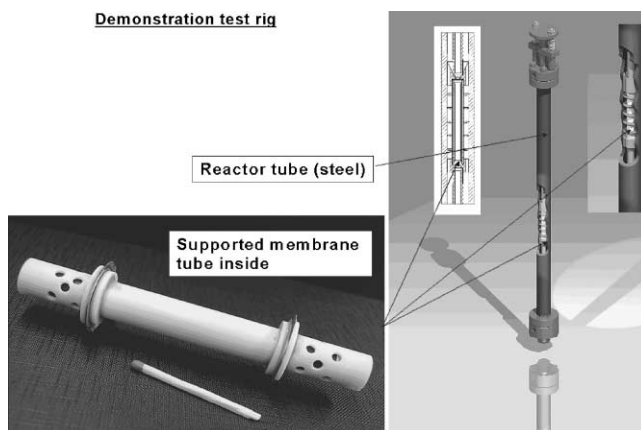


Figure 13: Demonstration test rig and supported membrane tube.

Figure 13 shows a picture of a membrane tube mounted inside a zirconia tube. The zirconia tube acts as a mechanical support. This was installed in the high pressure test reactor tube for hydrogen flux measurements at real process conditions, see Figure 7.

One membrane tube with 50 μm thick membrane coating was tested. The test was performed at a temperature of 1000 $^{\circ}\text{C}$ and a pressure of 20 bar. Initially humidified hydrogen was used at the reactor side (inside of tube) and humidified nitrogen at the sweep side (outside of tube). Since the membrane tube coating was not gas impervious, an overpressure of approximately 50 mbar at the nitrogen side was applied to minimize leakage of hydrogen into the sweep stream. The volume flow data under these conditions calculated from GC data as well as total flow measurements are given in the first part of Table 1. The total transport of nitrogen from the sweep to reactor side is similar to the total transport of hydrogen from the reactor to sweep side. Hence, the total flow at each side is not significantly changed. The total transport of nitrogen is the sum of viscous flow due to the pressure difference and interdiffusion. On the other hand the total transport of hydrogen is the sum of hydrogen flux and interdiffusion. To quantify the contribution of hydrogen flux to the total transport, the interdiffusion must be quantified through estimates or measurements.

TABLE 1
VOLUME FLOW DATA (NmL/MIN) FROM FLUX MEASUREMENTS

Type of measurement	Gas specie	Reactor side		Sweep side	
		Inlet	Outlet	Inlet	Outlet
Flux measurement with hydrogen.	H ₂	2400	1700–1800	0	600–700
GC analyses	N ₂	0	600–700	3000	2300–2400
of both gas streams	H ₂ O	600	Not analyzed	600–800	Not analyzed
Leakage correction measurement.	N ₂	1988	2456 ^a	1896	1428
GC analyses of	CO ₂	337	326 ^a	0	11
sweep side stream	O ₂	0	131 ^a	504	373
Leakage correction measurement.	N ₂	1988	2542	1896	1342 ^(a)
GC analyses of	CO ₂	337	348	0	–11 ^a
reactor side stream	O ₂	0	143	504	361 ^a

^a Calculated from GC analyses of opposite gas stream.

The quantification of interdiffusion was carried out by flowing a gas mixture of 14.5 vol% CO₂ in N₂ at the reactor side and air at the sweep side under otherwise similar conditions to the measurements with hydrogen. Volume flow data are given in the second and third parts of Table 1. The total transport of sweep gas to the reactor side is similar to the run with hydrogen, which is expected when the pressure difference between sweep and reactor side is the same. Also expected is the lower transport of reactor side gas to the sweep gas since there is no flux and since CO₂ and N₂ may diffuse slower than H₂. This difference in transport across the membrane is manifested by a significant increase in total reactor side gas flow and consequently reduction in sweep gas flow. For the quantification of hydrogen diffusion we may use the transport of CO₂ to the sweep side of 11 NmL/min as a basis. This number which is regarded accurate within 30%, is determined from the direct measurement of the CO₂ concentration in the sweep exit gas and the total volume flow of sweep exit gas. The translation of this number to hydrogen diffusion is carried out by the most conservative measure by assuming Knudsen diffusion. In Knudsen diffusion mode the diffusivity of gas molecules are inversely proportional to the square root of their masses. Hence, H₂ is expected to diffuse $\sqrt{(44/2)} = 4.7$ times faster than CO₂. The transport through diffusion is proportional to the difference in partial pressure of the diffusing specie. In the case of hydrogen the average difference is approximately 0.6 bar, while the difference for CO₂ is 0.14 bar. The expected transport of hydrogen through diffusion is therefore $4.7(0.6/0.14 \text{ bar}) \times 11 \text{ NmL/min} = 220 \text{ NmL/min}$.

The average value of total hydrogen transport from reactor side to sweep side in the flux measurements is 660 NmL/min. Correcting for the gas diffusion contribution of 220 NmL/min given above, it appears that 440 NmL/min of hydrogen was transported through the membrane by hydrogen flux. By taking account of the membrane area of 25 sqcm, the measured hydrogen flux was 18 NmL/min/sqcm.

The measured hydrogen flux can be compared to predictions from the flux model. For the inlet conditions of the flux measurements the model prediction is 20 NmL/min/sqcm, while for the outlet conditions a flux of 7 NmL/min/sqcm is calculated. The predicted average flux for the tube would be somewhere between these numbers, but in the lower range. Hence, the measured flux, albeit characterized by a relatively large uncertainty, compares favorably with model predictions.

A failure of gaskets due to insufficient cooling prohibited further measurements at varying temperatures and gas compositions. Furthermore, due to time limitations (project end), the second membrane could not be tested. Nevertheless, and despite the fact that the tested membrane was not gas impervious, the goal of demonstrating the validity of the flux model and verifying the potential of the selected membrane materials as indicated by the lab experiments, is considered reached.

Hydrogen Membrane Reactor Modeling

The reactor model has been used to estimate temperature profiles, concentration profiles, hydrogen flux and required membrane thickness for the different membrane steps.

TABLE 2
MEMBRANE VOLUME FOR DIFFERENT MEMBRANE THICKNESS (STEPS 1 AND 2)

Membrane thickness	Membrane volume (m ³)	
	Stage 1	Stage 2
Target flux (5 NmL/cm ² min)	35	82
25 μm	–	91
30 μm	20	–
50 μm	27	148

Membrane thickness and volume

Initial estimates was done with 50 and 30 μm on step 1 and 50 and 25 μm on step 2. Estimated membrane volume for different membrane thickness is shown in Table 2.

This shows that the average target flux for stage one and two close to 5 $\text{NmL}/\text{cm}^2/\text{min}$ are feasible based on the hydrogen flux model.

Initially the reformer catalyst activity was set to 100% of a nickel based catalyst. The rate constant, however, can be multiplied by an adjustable factor since the catalytic effect of the membrane reaction layer is unknown. A reduced catalyst activity, however, has low effect on the membrane flux and the required membrane volume as can be seen from Table 3. In the modeling it is assumed that the membrane surface is coated with a 50 μm thick porous catalyst layer.

TABLE 3
MEMBRANE VOLUME FOR DIFFERENT CATALYST ACTIVITY

Catalyst activity (%)	Stage 1 (m^3)	Stage 2 (m^3)
100	27.0	91
50	26.7	93
10	26.2	96

Membrane reactor flux modeling

The flux in axial position for steps 1 and 2 is shown in Figure 14. The reformer catalyst activity is set to 50% and membrane thickness is 50 μm on step 1 and 25 μm on step 2.

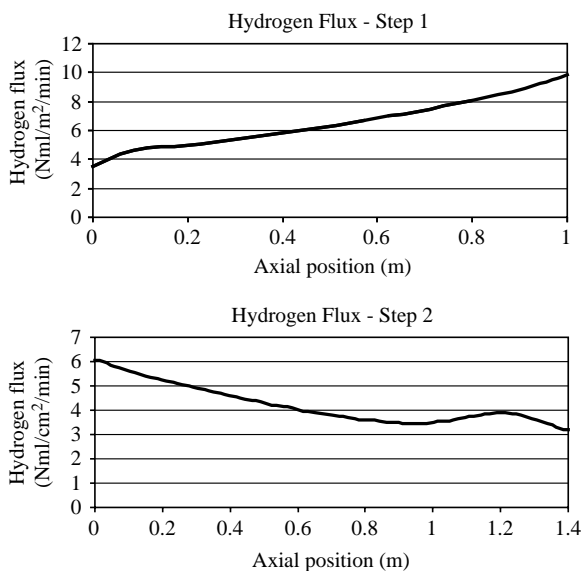


Figure 14: Hydrogen flux hydrogen membrane reformer steps 1 and 2.

Membrane reactor temperature profiles

Temperature profiles is shown in Figure 15. The drop in temperature (in the middle of reactor step 2) is caused by the heat consuming reforming of methane. In order to avoid substantial temperature drop on step 2 the methane slip from step 1 must be controlled.

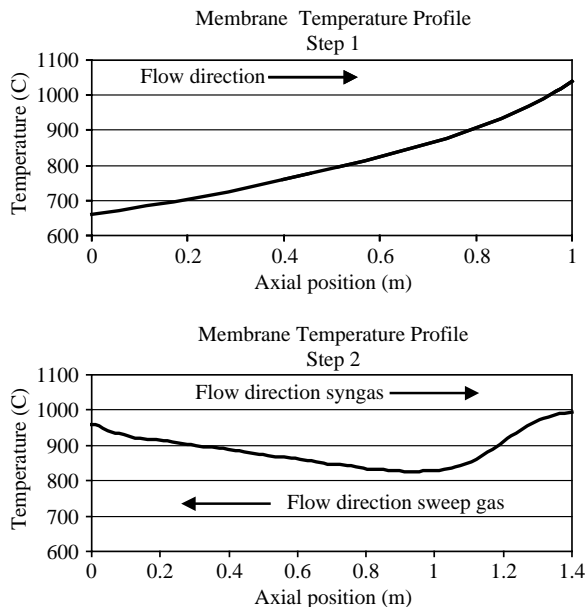


Figure 15: Membrane temperature profiles for steps 1 and 2.

If the reformed gas from step 1 is far from equilibrium it can be fed to an adiabatic steam reformer (equal the catalyst bed in an auto thermal reformer —ATR, that is used in conventional ammonia plants). This will prevent the undesirable temperature drop on stage 2. Any unconverted oxygen in the sweep gas from stage one will also affect the temperature profile on stage 2. The model does not include heat transport in axial direction. Some heat transport is likely which will smooth the temperature profile.

Concentration profiles step 2

Figure 16 showing, e.g. profiles for the reformer/CO-shift side at step 2 indicates that most of the methane is converted after 1.2 m. On the sweep gas side the estimates shows that hydrogen concentration above 40% can be achieved in the sweep gas which is a perfect gas turbine fuel.

Residual syngas oxidation section

The residual syngas oxidation section was simulated using the same geometry as in steps 1 and 2. This was found to be necessary due to the low hydrogen flux in this stage based on the selected process conditions. The modeled hydrogen flux is shown in Figure 17 (left side).

The low flux gives a reactor size similar to the size of step 2. Using Oxygen transport membranes a oxygen flux 5–10 times higher should be possible and it is recommended to further evaluate the oxygen membrane alternative in an eventually next phase.

The concentration profiles (Figure 17 right side) shows that most of the CO are converted to CO₂, but there is still about 2% CO left in the residual gas while about 0.5% is an acceptable level. This could be solved by

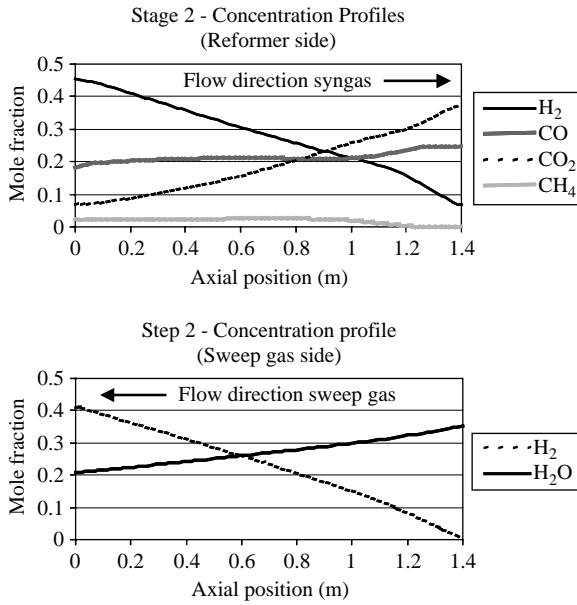


Figure 16: Concentration profiles step 2.

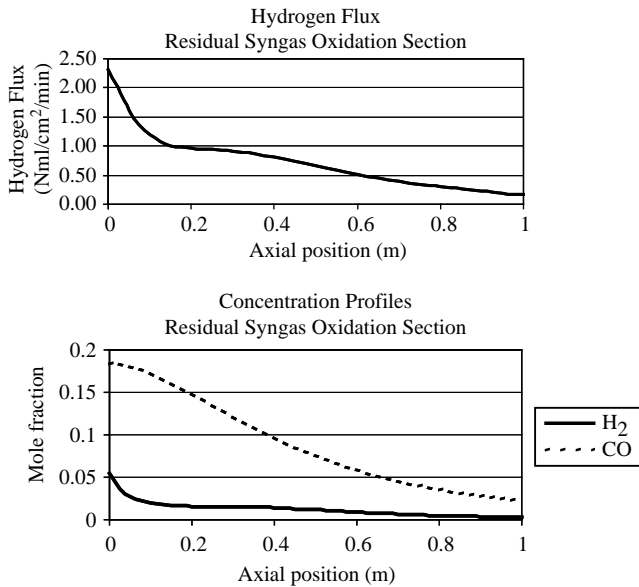


Figure 17: Residual syngas oxidation section. Hydrogen flux and concentration profiles.

oxidation with pure oxygen or the CO could be converted to CO₂ and H₂ in a down stream water gas shift reactor. The alternative using oxygen transport membranes is probably the best solutions to solve this problem.

Process and Cost Evaluation

Loss in efficiency is estimated to be only 5%-points compared with a conventional plant. This includes compression of purified CO₂ to 150 bar. A comparison with conventional CCGT is shown in Table 4.

TABLE 4
POWER PLANT PERFORMANCE SUMMARY

	H2 membrane CCGT	Base case (conventional CCGT)
Total fuel consumption (MW)	681.0	681
Net power output (MW)	361.9	395
Thermal efficiency, inclusive CO ₂	53.1%	58.0%
CO ₂ emission (t/h)	Close to zero	144.1

Based on the final cost estimate from Fluor the CCP CEM team did a cost analysis to evaluate the potential for this technology compared with, e.g. the Norwegian baseline technology. This indicates that the hydrogen membrane reformer process has the potential to reduce the cost of CO₂ capture in a CCGT power plant with at least 50%.

It is questionable if the HMCM based residual syngas oxidation reactor can convert sufficient amount of CO. The reactor model has shown that a quite high CO slippage is likely for a reasonable reactor size and oxygen transport membranes should be evaluated as an alternative. Probably this will work better and cost less. This change in design will therefore not change the CO₂-capture cost reduction potential. The 60% extraction of combustion air from the compressor section of the gas turbine is outside vendor's experience. A next phase of the project should evaluate alternatives that can reduce the amount of extracted air.

CONCLUSIONS

There is significant technical challenge in the membrane development and its integration into a PCDC process. However, promising results have been obtained. Several process alternatives have been evaluated and one process configuration was selected for the final cost evaluation. In the novel natural gas to hydrogen process a membrane reformer system replaces the traditional hydrogen production train. The hydrogen process in this study is integrated with a 390 MW gas fired combined cycle power plant. CO₂ emission is close to zero and NO_x emission below 15 ppmv can be achieved without catalytic NO_x reduction. Loss in efficiency is estimated to be only 5%-points.

A ceramic HMCM for use at high temperatures (600–1100 °C) has been developed. The membrane combines good chemical stability with high hydrogen flux rates. The stability of the membrane material at high temperatures and at low partial pressures of oxygen is excellent. The material melts at around 2000 °C and does not sinter below 1700 °C. The stability is, however, restricted at low temperatures combined with high partial pressures of oxygen or carbon dioxide. A thermodynamic model developed in the project predicts stability in process above 750 °C but this may be further improved and inlet conditions of 700 °C is considered achievable.

A method for manufacturing supported membrane tubes was developed. The tubes consist of a porous tubular support (wall thickness 2 mm) with a thin membrane coating (50 µm). Two such membrane tubes

were made and one was tested under conditions similar to process conditions in a test rig at Norsk Hydro Research Centre.

The measured H_2 flux in the test rig was 18 NmL/min/sqcm, which compares favorably with model predictions. Although the measurement is characterized by a relatively large uncertainty due to the fact that the tested membrane was not totally gas impervious, the goal of verifying target flux is considered reached.

Based on the final cost estimate from Fluor the CCP CEM team did a cost analysis to evaluate the potential for this technology compared with, e.g. the Norwegian baseline technology. This indicates that the hydrogen membrane reformer process has the potential to reduce the cost of CO_2 capture in a CCGT power plant with at least 50%.

RECOMMENDATIONS

Due to the short development phase in this project we had to select material and process design in an early phase. A much more extensive materials work is required to reveal all possibilities and to further optimise proton conducting membranes for application in a PCDC process. Optimization of the process and membrane reactor system is likely achievable.

Tests with combustion of hydrogen with air on the permeate side was not performed. Further tests are therefore needed. Additional flux measurements with gas impervious tubes are also needed and a method to deposit catalyst on the membrane surface must be developed and tested.

It is questionable if the HMCM based residual syngas oxidation reactor can convert sufficient CO. The reactor model has shown that a quite high CO slippage is likely for a reasonable reactor size and oxygen transport membranes should be evaluated as an alternative. Probably this will work better and cost less. This change in design will therefore not change the CO_2 -capture cost reduction potential.

The 60% extraction of combustion air from the compressor section of the gas turbine is outside vendor's experience. A next phase of the project should evaluate alternatives that can reduce the amount of extracted air.

NOMENCLATURE

AZEP	advanced zero emission powerplant
CEM	cost estimation model
CCGT	combined cycle gas turbine
CCP	carbon capture project
GC	gas Chromatograph
ΔH	Enthalpy
HMCM	hydrogen mixed conducting membrane
ICP	inductive coupled plasma
MW	megawatts
p, P	pressure
PCDC	precombustion de-carbonization
ppmv	volume parts per million
T	temperature
TEM	transmission electron microscopy
UiO	University of Oslo
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

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