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## Recent development in the HMR pre-combustion gas power cycle

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### Abstract

The focus area of the current HMR phase has been HMR process engineering and fabrication and testing of a small-scale monolith module. A new, less complicated HMR gas power cycle has been developed and benchmarked. The efficiency loss and CO<sub>2</sub> capture are typically 8 %-point and 85 %, respectively, but more than 90 % of the installed membrane area of the original concepts is rendered superfluous. Small-scale monolith modules have been fabricated and tested under real HMR process conditions, demonstrating promising hydrogen flux and steam reforming according to equilibrium.

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### 1. Introduction

The Hydrogen Membrane Reformer (HMR) gas power cycle is a pre-combustion Carbon Capture and Storage (CCS) technology under development in StatoilHydro. Since the start up in 2001, the development of the HMR gas power cycle has been financed by the Carbon Capture Project (CCP), which is currently in its second phase, with co-funding from the Research Council of Norway. The core of the HMR technology is a syngas reactor based on a hydrogen selective membrane. In the early years of the HMR project the focus areas were design of a first generation power cycle and selection of membrane material [1,2]. Recent development includes improvements in the process design, reactor design and scale-up and testing of membrane modules.

### 2. The HMR reactor

The HMR reactor concept is based on a square channel monolith structure with chess patterned distribution of the process and sweep gas (Figure 1) [3]. A complete module is made of the monolith together with two end manifolds.

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The monolith has porous walls, and serves as a mechanical support to the thin membrane (30-50  $\mu\text{m}$ ), which is coated in each second channel according to the chess pattern. The manifolds are sealed to the monolith by a specially developed glass ceramic sealing material, and serves to convert the process and sweep gases from two single channel streams into two checkerboard patterned multi channel streams. The monolith configuration secures a compact reactor design, i.e. high membrane surface area to reactor volume ratio, and is ideal for integrated transfer of ions and heat. The dimension of the full scale HMR monolith modules will typically be  $15 \times 15 \times 70 \text{ cm}^3$  with 2300 channels. For full scale applications several membrane modules will need to be stacked together to reach the necessary reactor capacity. An illustration of a full scale reactor is shown in Figure 2. This reactor may have capacity for reforming 800 – 900 MW (LHV) natural gas to syngas sufficient for a 400 MW Pre-Combustion Power plant.

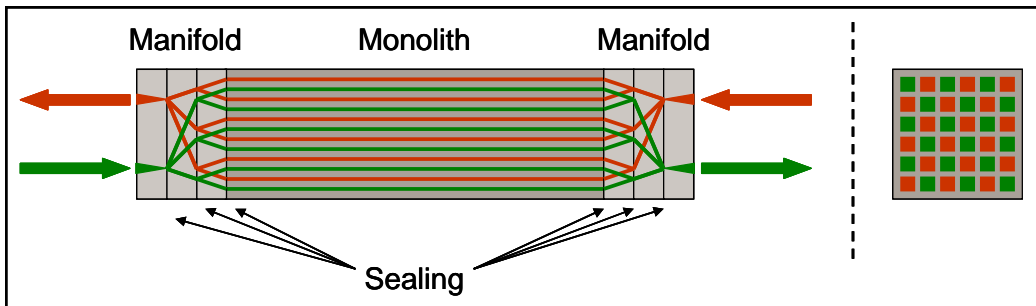


Figure 1: The HMR module design based on a square channelled monolith with gas distribution manifolds at each end.

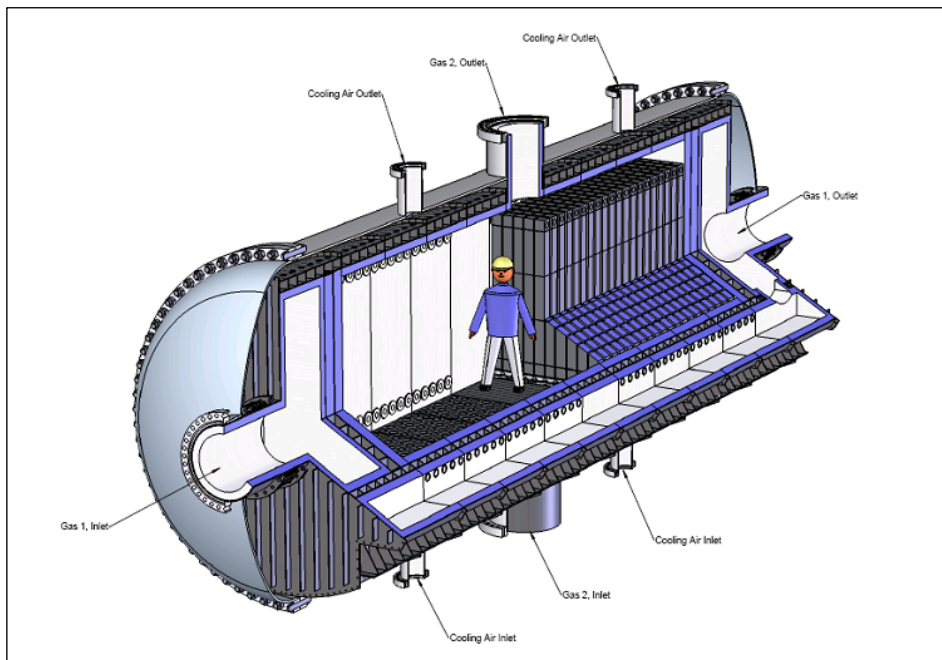


Figure 2: Illustration of the full scale HMR reactor with capacity for a 400 MW pre-combustion gas power plant.

### 3. The HMR gas power cycle

The original HMR reactor system (Figure 3) shows reduced potential compared with the results from CCP1 caused by a significantly higher membrane reactor cost. This is mainly due to better knowledge and insight in how to design a monolith based membrane reactor learned by parallel in-house ceramic membrane projects.

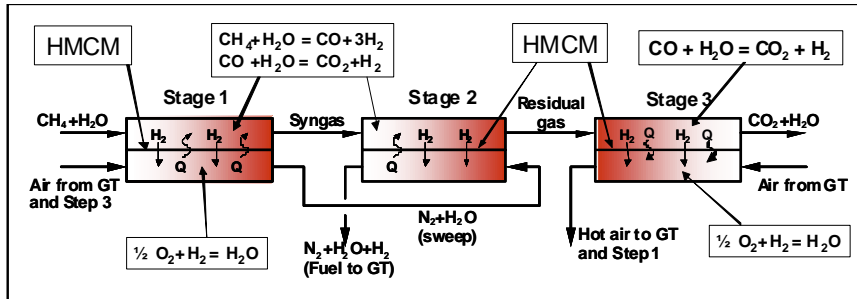


Figure 3: The original HMR reactor system.

Stage 2 and 3 become very expensive due to the large membrane area needed in these stages. It has therefore been a target to develop a more simple HMR process by significantly reducing the number of membrane units (Table 1). It has also been a target to develop a HMR concept using a more conventional gas turbine setup with an air extraction ratio below 15%. Several new process concepts were evaluated. The process finally selected is shown in Figure 4. Only the syngas generation stage remains, and supplementary  $CO_2$  removal, e.g. by using a conventional absorption process is needed. Methane is reformed with steam on the retentate side of the membrane and  $CO$  is shifted to  $H_2$  in downstream shift reactors. A limited amount of air is supplied to the permeate side to combust all permeated hydrogen, generating “ $CO_2$  free” heat for the endothermic steam methane reactions. Approximately all oxygen in the air stream is consumed and the resulting gas containing mainly  $H_2O$  and  $N_2$  is used to dilute the hydrogen fuel recovered in the  $CO_2$  removal process. This will generate a fuel containing less than 50% hydrogen securing full control of the  $NO_x$  emissions. To achieve about  $1000\text{ }^\circ C$  exit the HMR reactor, about 11% gas turbine air extraction is needed. This is well within proven ratios. An air booster is needed to secure sufficient fuel pressure.

Since syngas and air is processed separately the heat recovery will be very efficient. In addition the higher  $CO_2$  concentration will allow a more efficient  $CO_2$  separation. This gives an overall efficiency including compression of  $CO_2$  to 150 bar close to 50%. This is below what can be achieved in the original process (Table 2), but due to lower investment costs (due to the significant lower membrane area) the new process has a  $CO_2$  avoided cost about 20% below the original process.

Table 1: Membrane volumes for the new and original HMR gas power cycles.

HMR Process	Stage 1 (m3)	Stage 2 (m3)	Stage 3 (m3)	Total (m3)
New	16.9	-	-	16.9
Original	15.9	124.6	67.5	208.0

Table 2: Performance of the new HMR process compared with the original HMR process.



#### 4. Scale-up and testing of HMR membrane modules

Until now, the only HMR membranes which have been tested under realistic process conditions are small tubes with approximately 15 cm<sup>2</sup> membrane area. In the current phase of the project, the first multi channel monolith modules have been fabricated and tested. The modules were made of a circular monolith (length = 9 cm, diameter = 1.8 cm) with 21 process and 16 sweep channels (1.5 mm square). The membrane area of the monolith modules was 90 cm<sup>2</sup>, i.e. the up-scaling factor is 6 compared to the tube modules tested earlier.

The monoliths were made by extrusion of a plastic mixture of the ceramic membrane powder, water and organic material like pore former, binder and plasticizer. After extrusion the green monoliths were dried, and the organics were removed by heating the modules to 500 °C. These steps were critical for the quality of the monoliths, yielding cracks if they were too rapid. To apply the membrane coating, the monoliths were pre-sintered at 1300 °C to secure the necessary strength. After pre-sintering each second monolith channel was blocked according to the chess pattern, and the monoliths were dip-coated by immersion in a slip of membrane powder, binder and ethyl acetate. For dip-coating, the thickness of the membrane is proportional to the amount of powder precipitating from the slip, which again is influenced by the porosity of the substrate and the dipping time. After dip-coating, the monoliths were finally sintered at 1700 °C in moisturized dilute hydrogen (4%). Figure 5 shows an example of a cross-sectioned sintered monolith with the dense membrane in each second channel. The membrane is 50 µm thick, and located in the sweep channels. The steam reforming catalyst was deposited directly in the process channels by impregnation of the porous monolith walls with a catalyst nitrate solution followed by calcination at 1000 °C.

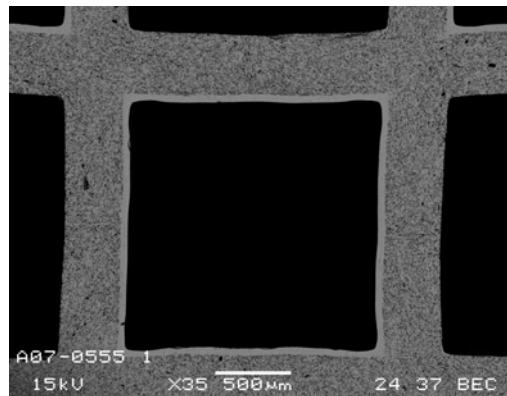


Figure 5: Scanning electron microscope picture of a cross sectioned monolith. The porous monolith has membrane coating (50 µm thickness) in each second channel.

Besides the sintered monolith, the small-scale monolith modules were made of two choke plates, two flow distributor plates and two top hats (Figure 6). The role of the choke plates was to create the necessary pressure drop along the module to secure gas supply to every channel. The flow distributor plates converted the process and sweep gas streams into the multi-channel checkerboard flow pattern. Both choke plates and flow distributor plates were made of sintered, dense disks of the membrane material where the patterns were made by mechanical machining. The top hats were made of stabilized ZrO<sub>2</sub>, and connected each test module to the rig. The different parts were assembled and sealed to each other by a special glass ceramic sealing material developed in-house. The process channels were available from the inside of the top hat, whereas the sweep channels were available from the outside, i.e. the sweep gas entered the module through the holes in the edge/side of the flow distributor. As seen from Figure 6, the modules also had two rings around the monolith. These were gas baffles, forcing the sweep gas through the module rather than passing outside, and centering the module in the reactor during testing.

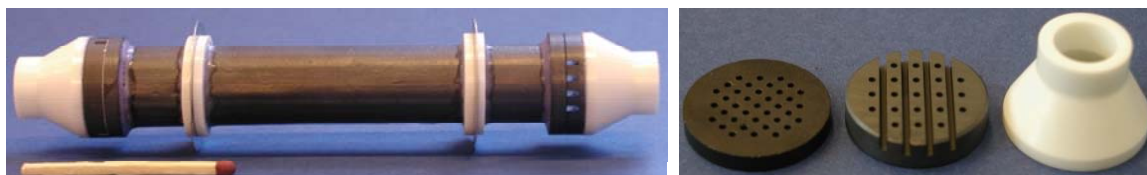


Figure 6: HMR small-scale test module, and a separate choke plate, flow distributor and top hat before module assembly.

The hydrogen flux and steam reforming activity of the membrane modules were tested at 800-1000 °C and 20 bar pressure, i.e. no difference in total pressure between the process and sweep side of the membrane, according to the test matrices in Table 3. At each side, the total gas feeding rate was 1000 ml min<sup>-1</sup>. The sweep gas composition was identical for all tests, whereas 3 different gas mixtures were used for the process side. The composition of the process and sweep gas after passing through the module was determined by gas chromatography analysis, and used for calculating the hydrogen flux and steam reforming activity. To detect any leakage across the membrane, nitrogen was added to the process gas, i.e. the hydrogen leakage was calculated from the final concentration of nitrogen in the sweep gas.

Table 3: Membrane module test matrices.

	<u>Condition1-Process side:</u>	<u>Cond2-Process side (3:1):</u>	<u>Cond3-Process side (2:1):</u>
	<ul style="list-style-type: none"> <li>• 700 ml/min H<sub>2</sub></li> <li>• 200 ml/min H<sub>2</sub>O</li> <li>• 100 ml/min N<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>• 225 ml/min CH<sub>4</sub></li> <li>• 675 ml/min H<sub>2</sub>O</li> <li>• 100 ml/min N<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>• 300 ml/min CH<sub>4</sub></li> <li>• 600 ml/min H<sub>2</sub>O</li> <li>• 100 ml/min N<sub>2</sub></li> </ul>
<u>Sweep side:</u>			
<ul style="list-style-type: none"> <li>• 800 ml/min Ar</li> <li>• 200 ml/min H<sub>2</sub>O</li> </ul>	√	√	√

Figure 7 shows the measured hydrogen flux of a monolith module. At 1000 °C it was 1.7 ml cm<sup>-2</sup> min<sup>-1</sup>. The figure also shows the modeled hydrogen flux according to the test conditions. The measured flux was approximately 50 % of the model predictions, i.e. the agreement is reasonable. The hydrogen flux model is based on the Wagner equation and earlier flux measurements, and was developed during the first phase of the HMR project [1].

The experimental hydrogen flux of the small-scale monolith modules are below the target flux for the HMR technology (5 ml cm<sup>-2</sup> min<sup>-1</sup> at 1000 °C), and also below earlier measurements with the smaller tube modules, where typically fluxes of 15 ml cm<sup>-2</sup> min<sup>-1</sup> have been demonstrated. The deviation may be explained from the experimental setup. For the earlier measurements with the tube modules, the gas feeding rate was 3000 ml min<sup>-1</sup> at each side, with 80 % hydrogen in the process gas (2400 ml min<sup>-1</sup> H<sub>2</sub>). The membrane area was only 15 cm<sup>2</sup>, and the main fraction of

hydrogen passed through the module at the process side, i.e. without being transported across the membrane, maintaining a high driving force for hydrogen transport throughout the module. For the small-scale monolith modules, the gas feeding rate was  $1000 \text{ ml min}^{-1}$ . With 70 % hydrogen in the process gas only  $700 \text{ ml min}^{-1}$  hydrogen was supplied to the monolith modules. Taking the larger membrane area into account ( $90 \text{ cm}^2$ ), the driving force for hydrogen transport rapidly decreased and at the module outlet it was more or less lost entirely.

The low hydrogen flux for the small-scale monolith modules should thereby not be taken as an indication of failure to reach the target flux. The measured fluxes agree with model predictions, which for other more favorable boundary conditions yield fluxes well above target. The low hydrogen flux is thereby rather a measure of the importance of maintaining a high driving force throughout the module when aiming for high hydrogen fluxes.

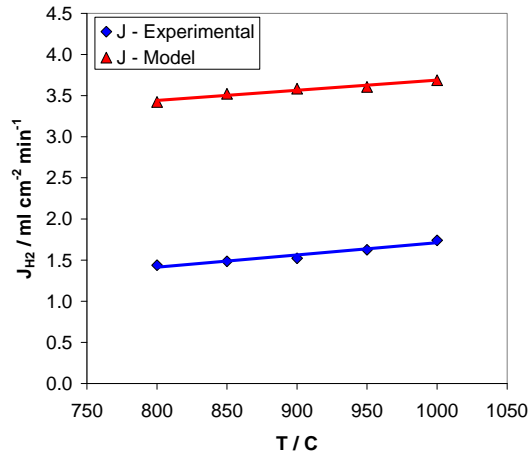


Figure 7: The experimental hydrogen flux (♦) of a monolith module tested with 70% hydrogen in the process gas (Condition1). The measured flux is approximately 50 % of the modelled hydrogen flux (▲).

The steam reforming at 20 bar was tested for 3:1 and 2:1 steam to carbon ratio (condition 2 and 3, respectively, Table 3). The steam reforming activity of a monolith module is illustrated in Figure 8. The parameters  $R$  and  $S$  are measures of the methane conversion and water gas shift, respectively. The conversion of methane increased with increasing temperature and steam to methane ratio, and was near equilibrium for the entire temperature test range. The water gas shift, i.e. the degree of carbon monoxide to carbon dioxide conversion, was favoured by low temperature and decreased with increasing temperature just as predicted from equilibrium calculations.

During the steam reforming testing the leakage across the membrane increased abruptly when methane was introduced at the process side. Inspection of the membrane module after ending the experimental testing showed severe cracking in the inlet manifold and monolith. Analysis with powder X-ray diffraction detected only the membrane phase and coke, i.e. the cracking was not due to decomposition. Another explanation may be temperature gradients introduced by the endothermic steam reforming, suggesting that methane should be added stepwise. The coke was probably formed during testing with the 2:1 steam to carbon process gas mixture, as the tendency for coke formation increases with decreasing steam to methane ratio.

After testing the small-scale monolith modules, especially two questions remained. The co-performance of the hydrogen membrane and steam reforming catalysis had not been evaluated since the membrane module fractured, and no reliable flux data were obtained for the steam reforming measurements. It is also questionable whether the porous monolith walls are suitable catalyst carriers, or if other carrier systems need to be introduced in the module, e.g. a porous coating of a catalyst/carrier washcoat. The two gas mixtures tested reached equilibrium, but the residence time was high (1.2 s) and the modules contained up to 2.5 wt% steam reforming catalyst. Further testing is therefore necessary to optimise the catalyst for the modules.

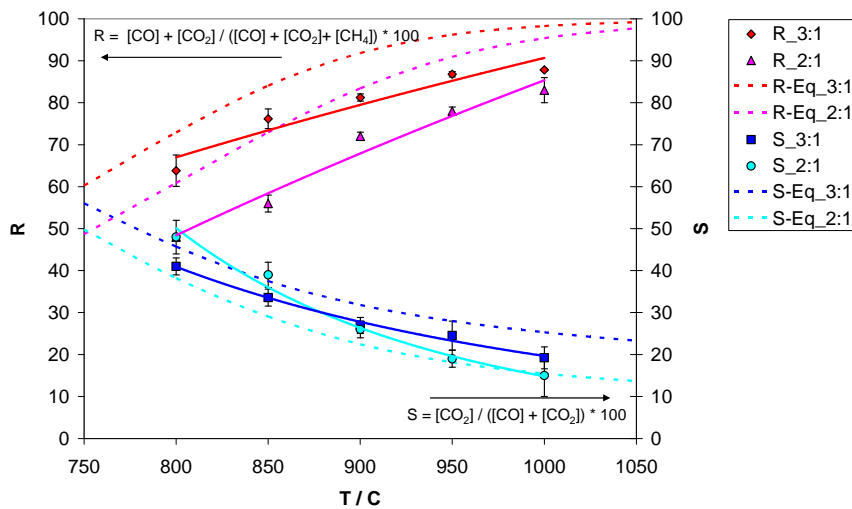


Figure 8: The steam reforming activity ( $R$ ) and water gas shift activity ( $S$ ) of a membrane module at 20 bar pressure and steam to methane ratio 3:1 and 2:1. Dotted curves represent equilibrium conditions. The residence time is 1.2 s.



## 5. Conclusion

A new, less complicated HMR gas power cycle has been developed and benchmarked. The efficiency loss and CO<sub>2</sub> capture are typically 8 %-point and 85 %, respectively. This is below what can be achieved by the original HMR process, but due to lower investment costs, i.e. more than 90 % of the earlier membrane area is rendered superfluous, the new process has a CO<sub>2</sub> avoidance cost approximately 20 % below the original concept.

Small-scale monolith modules have been fabricated and tested under realistic HMR process conditions, i.e. 20 bar total pressure and 800-1000 °C. At 1000 °C the hydrogen flux was 1.7 ml cm<sup>-2</sup> min<sup>-1</sup>, which is approximately 50 % of model predictions. The low hydrogen flux was mainly due to unfavorable boundary conditions, i.e. rapid decrease in driving force along the module length. If a higher driving force is maintained throughout the module it is expected that the target flux (5 ml cm<sup>-2</sup> min<sup>-1</sup> at 1000 °C) will be met. The measurements also demonstrated methane steam reforming according to equilibrium, but the co-performance of the hydrogen membrane and steam reforming catalysis still needs to be evaluated in a latter phase of the HMR project.

## Acknowledgements

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