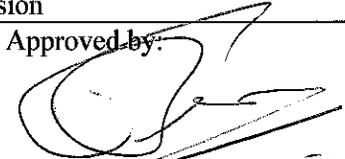
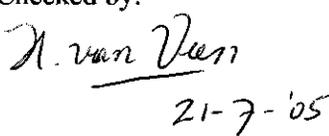
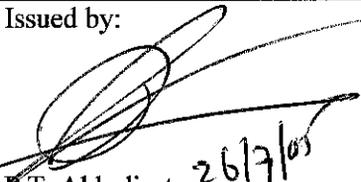


# Silica Membranes for Hydrogen Fuel Production by Membrane Water Gas Shift Reaction and Development of a Mathematical Model for a Membrane Reactor

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## Abstract

One of the technologies for Pre-Combustion Decarbonisation is the production of hydrogen rich fuel gas from fossil fuel feed stock by means of a water gas shift membrane reactor system. A study to develop and test hydrogen selective membranes for use in a water gas shift membrane reactor operating with sour synthesis gas has been sponsored by the CO<sub>2</sub> Capture Project. The aim of the project was to demonstrate a proof of concept water gas shift membrane reactor for this purpose.

As one of the potential membrane options in such a membrane reactor tubular micro porous silica membranes have been made for testing with a simulated water gas shift mixture. With standard silica membranes the flux criteria can be met when no water is present in the feed. However, with water in the feed the flux drops to a value, which is a factor 3 below the target. At the start of the project it was clear that the perm selectivity criterion of 100 was too high for micro porous membranes, because a maximum H<sub>2</sub>/CO<sub>2</sub> perm selectivity of 39 was thus far measured for standard silica membranes. Selectivity improvement was focused on higher sintering temperatures, but increase of the H<sub>2</sub>/CO<sub>2</sub> selectivity has not been experimentally proven. It was shown that H<sub>2</sub>S has no detrimental effect on a standard silica membrane and the H<sub>2</sub>/H<sub>2</sub>S selectivity is very high. Under the process conditions, so including a relative high water concentration, the stability of the silica membrane is limited to days as expected. The hydrothermal stability has been improved by incorporating alkyl-groups in the silica structure (ECN patent pending). The modified silica membrane is stable for more than 1000 hours under simulated steam atmosphere testing.

A software model of the water gas shift membrane reactor has been developed. The model simulates a counter current water gas shift membrane reactor with micro porous membranes (silica and zeolite) and dense (palladium and proton conducting) membranes and copes with the isothermal and non-isothermal operation of the membrane reactor. The model is implemented as an Aspen Plus User Model (Aspen Plus, version 11.1) and is written in FORTRAN.

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## 1. Introduction

The CO<sub>2</sub> Capture Project (CCP) is an initiative of eight major energy and oil companies to develop cost effective technologies for the capture and geologic storage of carbon dioxide.

CCP has sponsored a study on the development of technology to produce hydrogen rich fuel gas from fossil fuel feedstock by means of a water gas shift (WGS) membrane reactor system. The hydrogen rich fuel can be used as a carbon-free fuel in refinery heaters, gas turbines and for power generation. The envisioned application of a water gas shift membrane reactor is to convert the CO in the syngas from a gasifier to produce a hydrogen rich fuel gas stream and a CO<sub>2</sub> rich stream, which can be compressed for geological sequestration with minimum further treatment.

The aim of the project is to develop the water gas shift membrane reactor technology to proof of concept. The system is to be designed for operation with sour synthesis gas. The study was divided into two phases. Phase 1 (12 month activity) involved membrane development and testing on four different membrane materials. Preliminary process calculations have set membrane targets on a hydrogen selectivity >100 and a hydrogen permeance > 0.1 mol/m<sup>2</sup>sbar. The results from this work will be used to estimate membrane and reactor performances, and to determine which of the four membrane types will be selected for further development and application in a laboratory reactor system during phase 2.

The development and testing of tubular micro porous silica membranes for use in the reactor, and the development of a computer simulation model of the membrane reactor are described in this paper.



## 2. Experimental

### 2.1 Silica membrane preparation

To get an overview of the performance and the stability of the membrane under WGS conditions several batches of tubular silica membranes have been made according to current standard recipes [1]. The silica membranes are made in a batch process, with a maximum of 10 tubes each time. Alumina substrate tubes with a maximum length of 1 meter were coated on the outside with porous intermediate layers in order to overcome the surface roughness. A so-called polymeric silica sol was made and coated on top of the intermediate layer [2]. After calcining the membranes are ready for use. The pore size of the membranes is about 5Å and can be optimised for certain applications by e.g. modifying the silica sol or the calcining procedure. The separation layer of these membranes consists of a very thin (<200 nm) hydrophilic amorphous silica film on the outside of a multi-layer alumina support tube (see Figure 2.1).

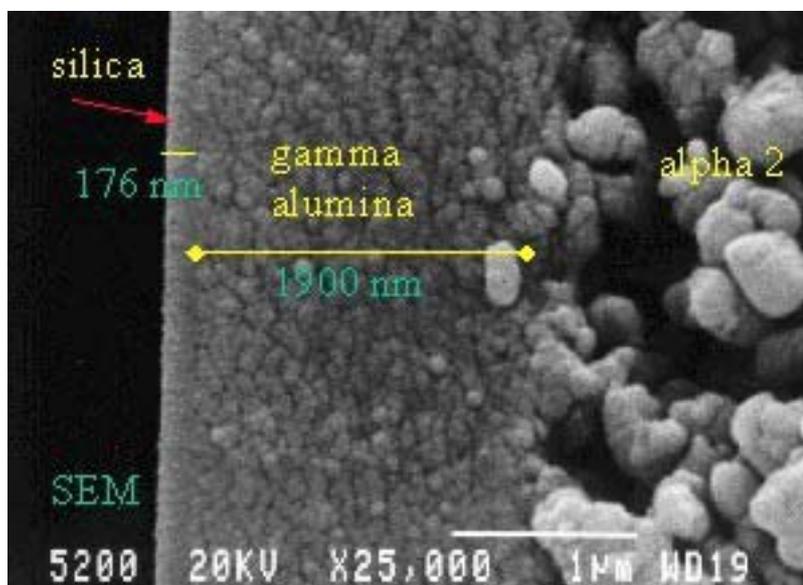


Figure 2.1 Scanning Electron Micrograph of a high-selective silica membrane

The membrane tubes are made at a length of 1 meter, an ID/OD of 8/14 mm and as a batch containing 12 tubes. Pieces of 10 cm have been cut from these tubes for use in the test programme. An overview of properties of the support and membrane layer is given in Table 2.1.

Table 2.1 Overview of properties of the support and membrane layer

Layer	Coating type	Name	Compound	Thickness	porosity	Pore $d_{50}/nm$
1	-	Extruded tube	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3000 $\mu m$	0.35	4000
2	suspension	alpha 1	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30-50 $\mu m$	0.22	180
3	suspension	alpha 2	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30-40 $\mu m$	0.34	170
4	Sol-gel	gamma	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1.5-2.0 $\mu m$	0.5	3-5
5	Sol-gel	silica	SiO <sub>2</sub>	50- 120 nm	0.5	<1

The silica membrane batch quality has been checked by our so-called Helium-1-point test. The Helium-1-point test gives an indication of the defect density of the membrane. By comparing the results of the He-1-point test with gas permeation tests we found that the probability for sufficient gas separation properties is high enough when the 1-point He value is below 100 ml

He/min.10cm.3bar. Silica membrane pieces for use in the test programme have been selected based upon the He value. Gas permeation tests have been performed with silica membranes with a He-value below 100 units.

Specifically for the separation of hydrogen from CO<sub>2</sub>/CO/H<sub>2</sub>O it is foreseen that further membrane development is necessary to improve the hydrothermal stability. For this stability improvement modified silica structures, which incorporates alkyl-groups (ECN patent pending) have been prepared. Small batches of tubular modified silica membranes with built in methyl groups have been made according to available recipes [3]. Addition of methyl groups in the silica structure has been done by the addition of and reaction with methyltriethoxysilane (MTES), see Figure 2.2. Calcinations temperatures (250 or 400°C), calcinations atmosphere (air or nitrogen) and pre-treatment procedures have been varied during fabrication to determine the effect of these processing parameters on the gas separation performance. Pieces of 10 cm have been cut from these tubes for use in the test programme. The modified silica membranes have been checked for their suitability in hydrogen separation and the gas separation performance has been compared with the standard membranes.

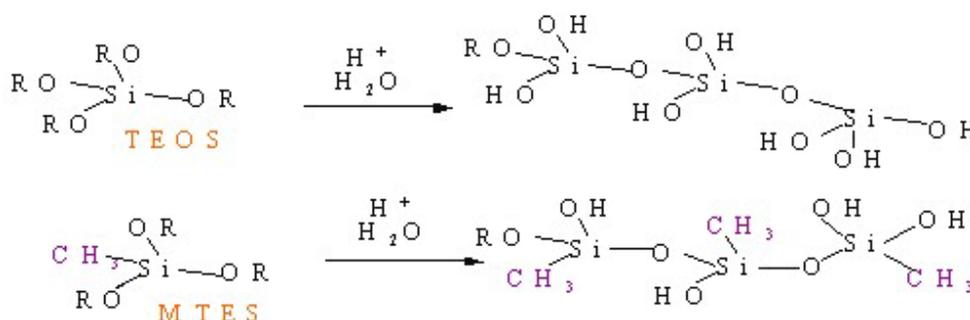


Figure 2.2 *Simplified reaction scheme for silica and modified silica membranes*

## 2.2 Equipment

### 2.2.1 Low-pressure gas permeation equipment

The low-pressure (LP) gas permeation equipment, used for single gas permeation tests, is an automated set-up, which can measure gas flows through a membrane (dead-end mode) for a programmed sequence of gases, temperatures, feed pressures and average pressures. An overview of the set-up is given in Figure 2.3.

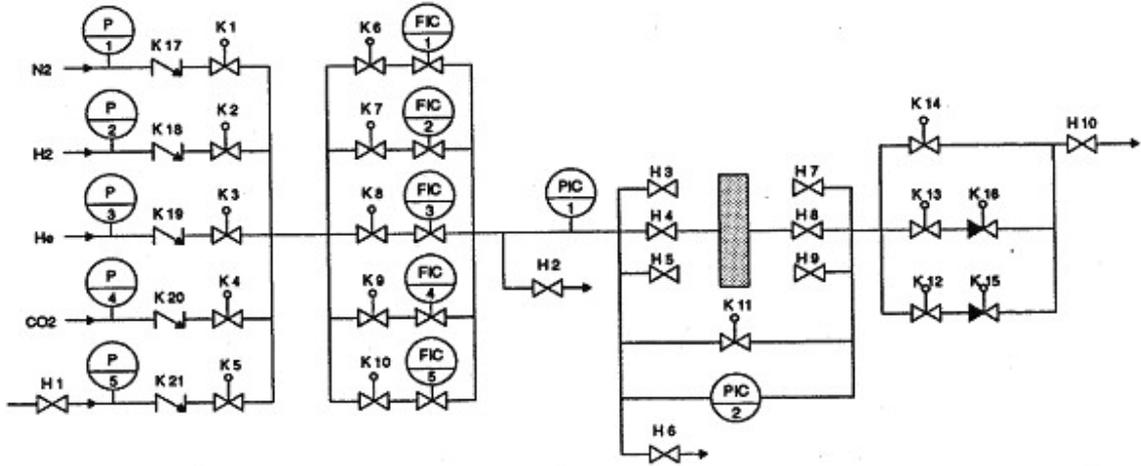


Figure 2.3 *Low-pressure gas permeation set-up*

The flow meters and control valves of the mass flow controllers operate independently to control the feed pressure and measure the flow. The feed pressure is measured with PIC1. The pressure difference across the membrane is measured by PIC2. The signal of this differential pressure meter controls valves K16 or K15 to keep the pressure difference at the level set. The temperature is measured and controlled by a thermocouple placed in the membrane module. The set-up is suitable for pressures up to 10 bar and temperatures up to 600°C (restricted by the stainless steel module).

### 2.2.2 High pressure gas separation equipment

A high-pressure, high temperature facility for testing membranes under realistic process conditions (feed pressures up to 70 bar, temperatures up to 600°C) has been used for separation tests. A simplified flow sheet of the installation is shown in Figure 2.4.

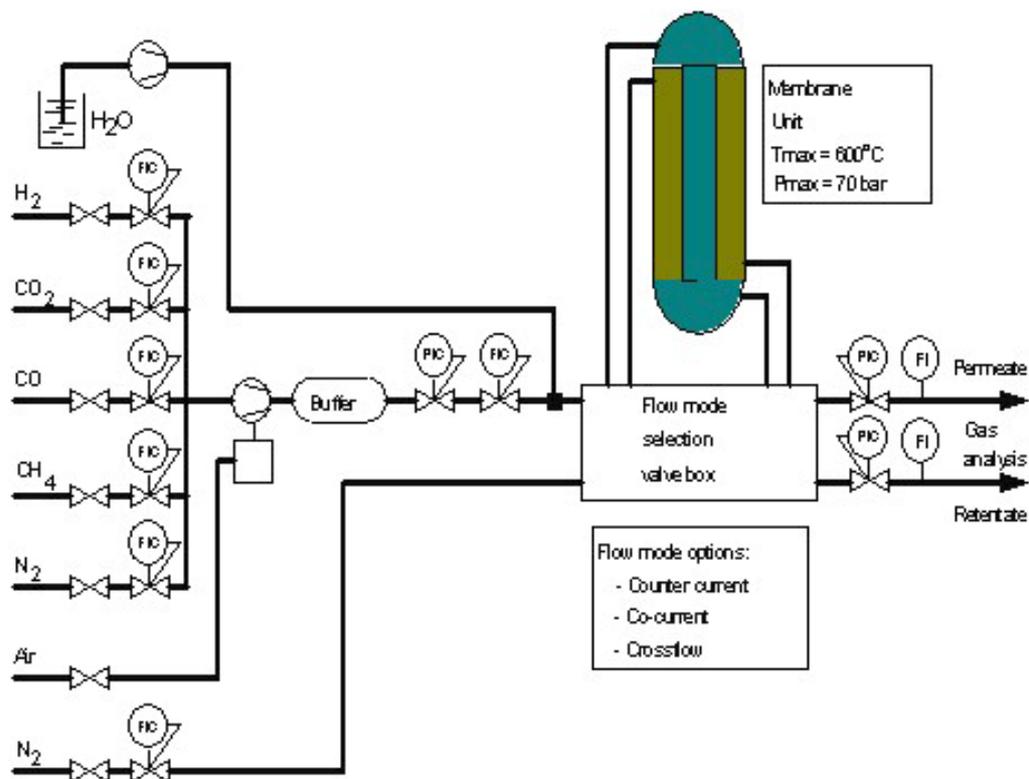


Figure 2.4 *Simplified flowsheet of the high-pressure gas separation equipment*

The installation is laid out for use of gas mixtures without trace contaminants. Pure gases ( $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $N_2$ ) enter the system through mass flow controllers (MFC). Mixtures with variable compositions can be obtained by adjusting the ratio of flows through the MFC's. The gases, delivered to the installation at a pressure of approximately 5 bar, are compressed by a booster to a maximum pressure of 70 bar and are stored (temporarily) in a small storage drum (5 l.). The drum is emptied through a pressure controller, which determines the feed pressure to a MFC. This MFC determines the feed flow through the reactor/to the membrane. The feed flow through the reactor is mainly limited by the capacity of the booster. A typical value for the flow of the chosen booster at high pressure is 15 Nl/min and at moderate pressures the maximum flow is 27 Nl/min. After the booster, the stream is first heated to  $200^\circ C$  and steam injection can take place. Feed and sweep gas are fed to the membrane module. The module is placed in an oven that can be heated to a maximum temperature of  $600^\circ C$ . After the membrane the retentate and permeate pressure drops to atmospheric pressure and the flow in both streams is measured using a flow indicator. Finally the gas flows to a gas analysis device in which the composition can be determined.

### 2.2.3 Membrane steam exposition equipment

The effect of water vapour on the permeances of gases through a silica membrane is measured with set-up for steam/water vapour exposition, which is shown in Figure 2.5.

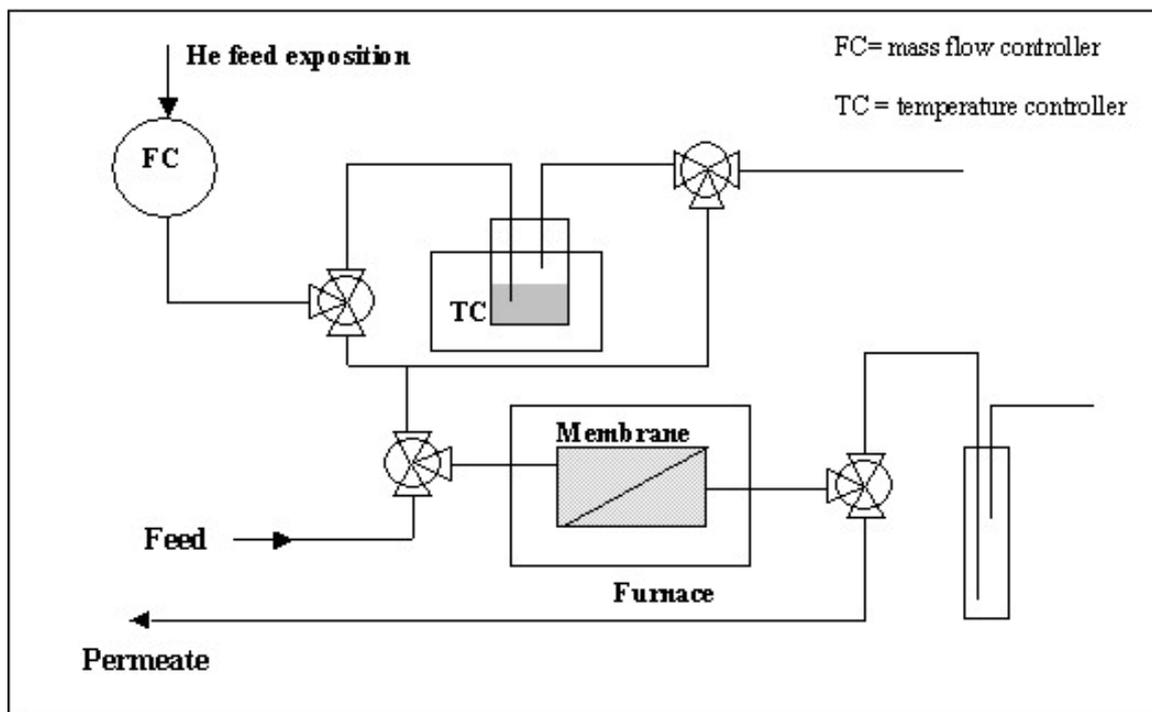


Figure 2.5 Set-up for steam/water vapour exposition experiments

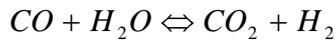
A helium stream controlled by a mass flow controller (0-200 ml/min) is sent to a water bubbler, set at a temperature between  $\sim 20^{\circ}\text{C}$  and  $95^{\circ}\text{C}$ . The wetted gas stream is fed to the membrane module placed in a furnace that is set at the desired temperature, usually in the range  $100\text{-}350^{\circ}\text{C}$ . After a certain exposition time the valves are switched to the dry gas permeance mode and the membrane is dried at the desired temperature. Then the permeances of desired gases, usually helium, can be measured. In this way a plot of the “dry” permeance as function of the exposition time can be made and the quality of the membrane can be monitored in-situ. In some cases the wet helium flux directly after exposition is measured by measuring with a separate flux tester in order to follow the relaxation of the permeance during drying of the membrane.



### 3. Water gas shift membrane reactor simulation model

A computer model of the water gas shift membrane reactor was developed to evaluate the performance of different membrane types under development in the CCP project. The water gas shift membrane reactor model simulates a counter-current water gas-shift membrane reactor and describes the non-isothermal and isothermal operation of the membrane reactor. The membrane reactor model is implemented as an Aspen Plus User Model (Aspen Plus, version 11.1).

In the membrane reactor hydrogen and carbon dioxide is produced in the reaction of carbon monoxide and steam; the water gas shift reaction. The reaction is a gas phase equilibrium reaction according to reaction scheme:



The reaction is moderately exothermic ( $\Delta H = -41.1$  kJ/mol). The equilibrium constant  $K_p$  is

defined by: 
$$K_p = \frac{c_{H_2} c_{CO_2}}{c_{CO} c_{H_2O}} \quad [-]$$

with  $c_i$  the concentration of component  $i$  [mol/m<sup>3</sup>].  $K_p$  decreases with increasing temperature, which means that less product will be formed as the temperature rises. A simple expression for the equilibrium constant is [4]:

$$K_p = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad [-]$$

A FeCr catalyst is chosen as a starting point for the kinetic expression in this model [5, 6]. The catalyst is active in the temperature range of interest (300-450°C). Furthermore it can tolerate small amounts of sulphuric components. The reaction rate is described by [7] using a power law expression:

$$R_{CO} = -k_1 c_{CO}^{0.73} c_{H_2O}^{0.55} (1 - \beta) \quad [\text{mol/m}^3\text{s}]$$

with  $\beta$ , the reversibility factor: 
$$\beta = \frac{c_{CO_2} c_{H_2}}{K_p c_{CO} c_{H_2O}} \quad [-]$$

The hydrogen transport through the membrane is described by:

$$J_{H_2} = Q_{H_2}^0 e^{-E_a/RT} (P_{f,H_2}^n - P_{p,H_2}^n)$$

in which:

$J_{H_2}$	hydrogen flux through the membrane [mol/m <sup>2</sup> s]
$Q_{H_2}(T)$	temperature dependent hydrogen permeance [mol/m <sup>2</sup> sPa <sup>n</sup> ]
$P_{H_2}$	partial hydrogen pressure on feed (f) and permeate (p) side [Pa]
$n$	exponent on partial pressure [-]
$Q_{H_2}^0$	temperature independent constant [mol/m <sup>2</sup> sPa]
$E_a$	activation energy for transport [J/mol]
$T$	absolute temperature [K]
$R$	gas constant [J/molK]

The active temperature range of the water gas shift catalyst makes this equation suitable for both porous and dense membrane under investigation in the overall project. The Pd-alloy membrane and the ceramic-metal composite membrane typically work with  $n=0.5 - 1$  and for the silica and the zeolite membrane,  $n=1$ . Similar equations were developed for other components than hydrogen. The membrane reactor model was used to calculate a CO<sub>2</sub> capture model plant as described in [8] and works well.



## 4. Results and Discussion

### 4.1 Single gas permeance

Standard and modified silica membranes have been tested in single gas ( $H_2$ ,  $CO_2$ ,  $N_2$ ,  $CH_4$ ) permeation tests at  $350^\circ C$  and a maximum feed pressure of 10 bar. The performance at  $350^\circ C$ , 10 bar feed pressure and a pressure difference of 1 bar for the silica membranes is given in the Table 4.1. Silica membranes with a lower selectivity have a high  $H_2$  flux.

Table 4.1 *Performance of standard and modified silica membranes*

Temperature	350°C		450°C	
Membrane type	$H_2$ flux [mol/m <sup>2</sup> sbar]	$H_2/CO_2$ permsel.	$H_2$ flux [mol/m <sup>2</sup> sbar]	$H_2/CO_2$ permsel.
Modified silica ( $N_2$ calcined)	0.2	7	0.3	9
Modified silica (Air calcined)	0.2-0.8	4-8	0.1-0.9	5
Standard silica	0.1-0.3	5-15	-	-

#### 4.1.1 Maximum selectivity and selectivity improvement

Standard silica membranes all made according to the same recipe show a variation in hydrogen permeance and  $H_2/CO_2$  perm selectivity. In order to know the range of variation an inventory has been made of the twenty-two membranes made and tested in a period of two years. Only two of these membranes had a  $H_2/CO_2$  selectivity between 30 and 40 (see Figure 4.1) showing that it is extremely difficult for these membrane to reach a reproducible performance well above these values. One should also consider that the membrane test samples are taken from membrane tubes made at an industrial scale of 1-meter length.

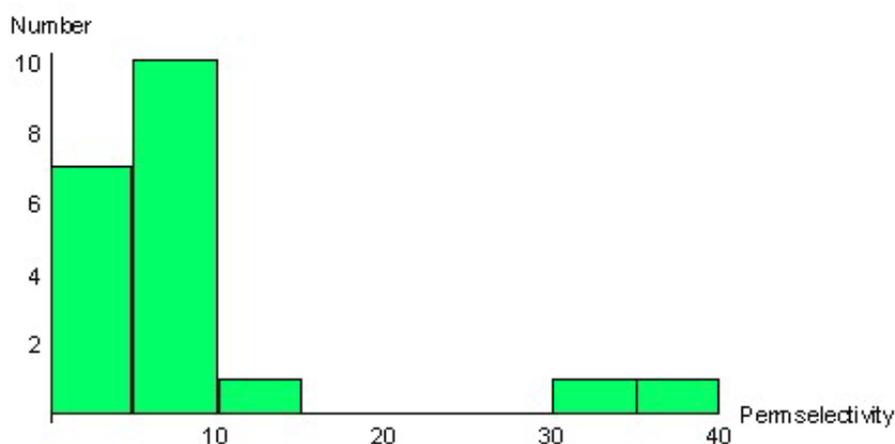


Figure 4.1 *Number histogram of  $H_2/CO_2$  perm selectivity's at  $350^\circ C$  and  $P_{av}=9.5$  bar*

The average  $H_2/CO_2$  perm selectivity was between 5 and 15. The membrane used in the hydrothermal test had a  $H_2/CO_2$  perm selectivity higher than average (= 29.7). An overview of the performance of three standard silica membranes with increased selectivity is given in Table 4.2. When the membranes have a  $H_2/CO_2$  permselectivity, which is a factor 3 to 4 higher than, standard they have a hydrogen flux that is a factor 5 to 10 lower. From this data it is

expected that the hydrogen permeance of a silica membrane with a H<sub>2</sub>/CO<sub>2</sub> selectivity of 50 would be in the range of 0.01 to 0.005 mol/m<sup>2</sup>sbar, which is well below the target permeance of 0.1 mol/m<sup>2</sup>sbar for this application. Increasing the selectivity will cause definitely a decrease of the flux through the membrane, which is without doubt detrimental to the economic feasibility.

Table 4.2 *Overview performance standard silica membranes*

Temperature	350°C	
Membrane type	H <sub>2</sub> flux [mol/m <sup>2</sup> sbar]	H <sub>2</sub> /CO <sub>2</sub> permsel.
Average	0.1-0.3	5-15
X2M62Si07	0.041	39
X65Si02	0.016	33
XT51Si53	0.037	29.7

A possibility for increasing the selectivity of the silica membranes would be calcinations at 600°C. In the PhD work of R. de Vos [9] it was reported that the H<sub>2</sub>/CO<sub>2</sub> selectivity increases with at least a factor of 10 when the sintering temperature is increased from 400 to 600°C. The hydrogen permeance measured at higher temperature (300 in stead of 200°C) decreased with at least a factor of 3 (see Table 4.3).

Table 4.3 *Hydrogen permeance and H<sub>2</sub>/CO<sub>2</sub> selectivity of silica membranes*

Membrane	Avg H <sub>2</sub> permeance [mol/m <sup>2</sup> sPa]	H <sub>2</sub> /CO <sub>2</sub> selectivity
Si400 (200°C) R. de Vos	1.64 10 <sup>-6</sup>	7.5
Si600 (300°C) R. de Vos	6 10 <sup>-7</sup>	70 - 139
Si400 (200°C) ECN	5.4 10 <sup>-7</sup>	9 - 13.6
Si600 (200°C) ECN	5.1 10 <sup>-7</sup>	7.7
Modified Si250 (350°C) ECN	7.6 - 3.1 10 <sup>-6</sup>	4.1 - 4.5
Modified Si450 (350°C) ECN	3.9 - 9.3 10 <sup>-6</sup>	4.2 - 5

Several silica membranes have been made and were sintered at 400 and 600°C. However, as shown in Table 4.3 both silica membrane types as made by ECN gave the same hydrogen permeance and H<sub>2</sub>/CO<sub>2</sub> selectivity. Also increasing the sintering temperature of the modified silica membranes did not show an increase of selectivity.

#### 4.1.2 H<sub>2</sub>S permeation

A standard silica membrane has been tested with pure H<sub>2</sub>S at different temperatures (up to 100°C) to determine the permeance and the selectivity of the membrane in feeds containing H<sub>2</sub>S. The H<sub>2</sub>S permeance is very low (5-6 10<sup>-4</sup> mol/m<sup>2</sup>sbar at 50°C), which gives a H<sub>2</sub>/H<sub>2</sub>S permselectivity of more than 400. After three days of testing with H<sub>2</sub>S the single gas helium flux test indicates no detrimental effect on the silica when exposed to H<sub>2</sub>S.

## 4.2 Gas separation

### 4.2.1 Gas separation tests without water

Gas separation tests with a simulated water gas shift mixture (H<sub>2</sub>:CO<sub>2</sub>:CO:N<sub>2</sub>= 35:22:2.5:40.5) have been performed with a standard silica membrane. With pure gases this membrane had a hydrogen permeance of 0.1 mol/m<sup>2</sup>sbar and a H<sub>2</sub>/CO<sub>2</sub> permselectivity of 13.6 at 350°C. First measurements are performed **without** water to see the effect of a gas mixture on the hydrogen permeance and the selectivity. The water is balanced in these tests with nitrogen.

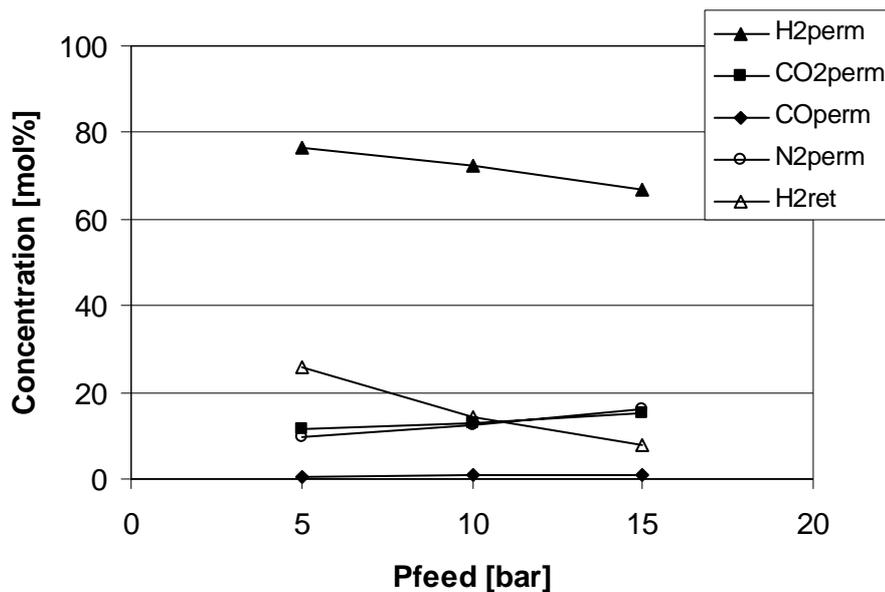


Figure 4.2 Permeate and retentate concentrations as a function of feed pressure at 450°C

In Figure 4.2 it can be observed that the membrane is capable of producing a hydrogen rich stream containing about 75% hydrogen from a feed stream containing only 35% hydrogen. Carbon monoxide and nitrogen permeate hardly through the membrane. From the retentate composition it can be observed that there is a significant depletion of hydrogen in the feed. Especially when the driving force is high ( $dP=14$  bar) the feed is depleted in hydrogen from 35% to 8% over a membrane of only 10 cm length. In other words: the hydrogen recovery increases with an increase of the driving force. However, one should consider that this is offset by a decrease in the hydrogen concentration in the permeate.

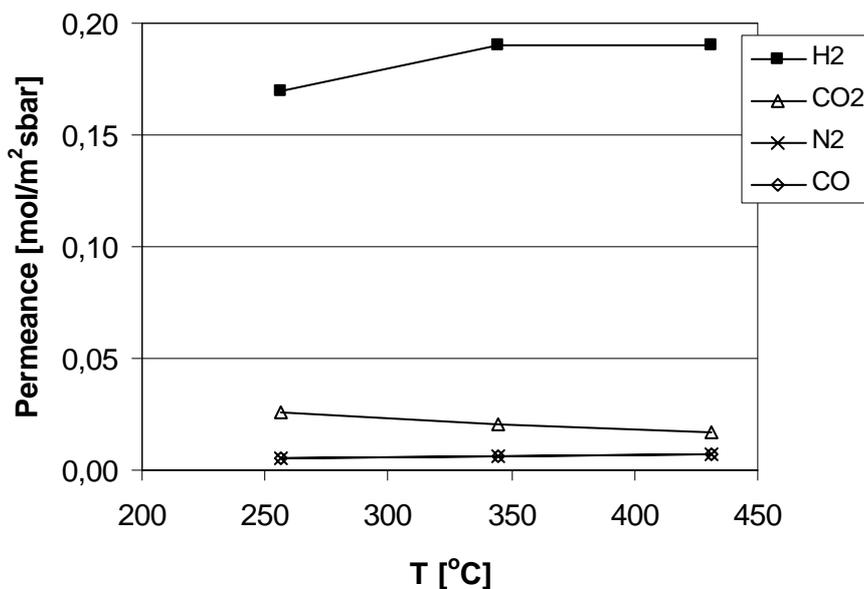


Figure 4.3 Permeances as a function of temperature ( $P_{feed} = 5$  bar,  $P_p = 1$  bar)

The membrane data (see Figure 4.3) show that the hydrogen permeance increases slightly with temperature. Also the nitrogen and carbon monoxide permeance increase with temperature,

which indicates for these molecules the main transport is through small pores and not through defects, as defect flow is governed by Knudsen diffusion and/or viscous flow and thus decreases with a temperature increase. The carbon dioxide permeance decreases with temperature probably because of the fact that this molecule strongly adsorbs on the surface and it is commonly known that this surface adsorption (and flow) decreases with an increase in temperature.

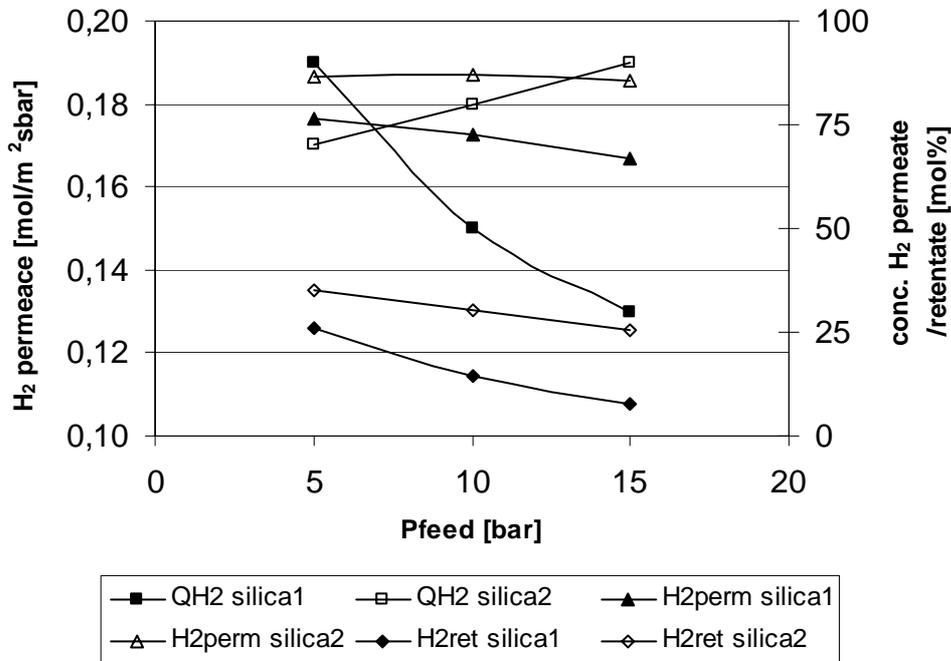


Figure 4.4 *Hydrogen permeance, permeate and retentate concentrations for two silica membranes at 450 °C*

Gas separation experiments **without** water were repeated with a comparable silica membrane. With pure gases this membrane had a hydrogen permeance of 0.17 mol/m<sup>2</sup>sbar and a H<sub>2</sub>/CO<sub>2</sub> permselectivity of 7.5 at 350°C. This membrane is also capable of producing a hydrogen rich stream containing about 85% hydrogen from a feed stream containing only 37% hydrogen (see Figure 4.4). Carbon monoxide and nitrogen permeate hardly through the membrane. These results compare well with the previous membrane. The hydrogen concentration in the permeate is even higher now, as less depletion of hydrogen on the feed side occurs at the higher feed flow rate used now (15 NI/min in stead of 5NI/min). From these separation measurements a maximum selectivity of 18 is obtained for H<sub>2</sub>/CO<sub>2</sub>. The hydrogen permeance, derived from the hydrogen partial pressure driving force is for both silica membranes well above 0.1 mol/s.m<sup>2</sup>bar, which is the target permeance for the application.

#### 4.2.2 Gas separation tests with water

Experiments with the second membrane were continued, now **with** water added to the feed (H<sub>2</sub>:CO<sub>2</sub>:CO:H<sub>2</sub>O=29.3:15.2:1.8:53.7). The measurements have started at 350°C, then 250°C and finally 450°C measurements have been performed.

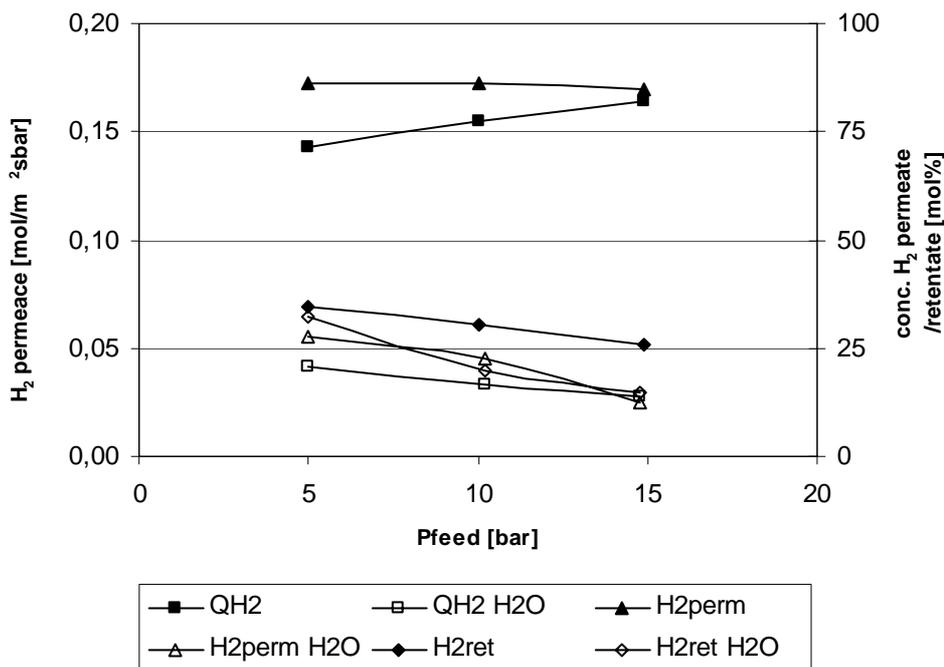


Figure 4.5 Hydrogen permeance, permeate and retentate concentrations with and without water in feed mixture at 350 °C

From these measurements and checking of the membrane performance between these temperatures it is clear that the membrane quality (pure silica membrane) decreased already during the measurements at 250°C. When comparing the measurements at 350°C without water with the measurements with water in the feed it is clear that both the hydrogen purity in the permeate and the hydrogen permeance are decreased by the water present in the feed stream (see Figure 4.5). The hydrogen permeance, derived from the hydrogen partial pressure driving force has a maximum value of 0.031 mol/s.m<sup>2</sup>bar, which is below the target permeance of 0.1 mol/m<sup>2</sup>sbar.

### 4.3 Hydrothermal stability testing

Before hydrothermal testing the prolonged exposition to elevated temperatures was investigated. Thermal cycling of a standard silica membrane from 50 to 350°C under dry helium flow shows a slow increase in helium permeance in time. The hydrothermal stability for both silica and modified silica membranes has been tested. In these tests the membranes are exposed to a helium water vapour mixture (70 kPa water with 80 ml/min He) at 350°C. During exposition the He and CH<sub>4</sub> permeability have been measured at certain time intervals to monitor the change in membrane performance.

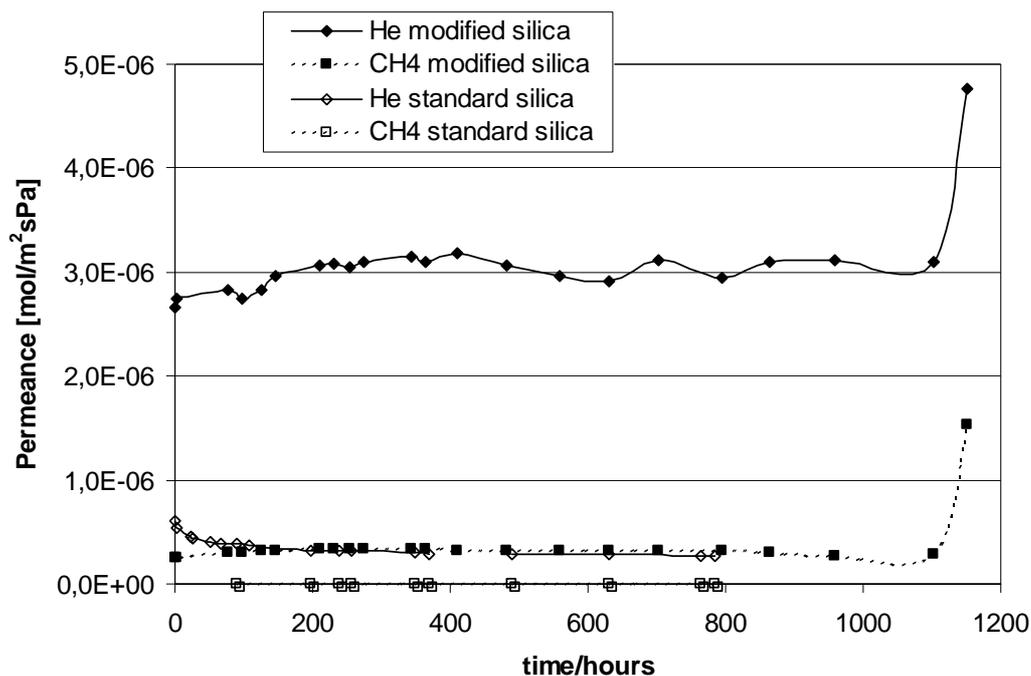


Figure 4.6 *He and CH<sub>4</sub> permeance as a function of time for a standard and a modified silica membrane at 350°C*

The results of the measurements are given in Figure 4.6. In the first 200 hours the standard silica membrane shows a decrease in the helium and methane permeance of a factor 2. After this period of time the flux is more or less constant. There is hardly any change in selectivity (48 at the start and 41 after 874 hours for He/CH<sub>4</sub>) as both fluxes have decreased.

The modified silica membrane shows a slight increase in the permeance after the start of the measurement and after about 200 hours this value is constant. The selectivity He/CH<sub>4</sub> is always 10±1. After about 1150 hours on stream both the helium and methane flux increased and the selectivity dropped. Post-test analysis of the sample revealed that the sudden flux increase is probably due to crack formation and not by change of the pore system.

## 5. Conclusions

The maximum  $H_2/CO_2$  perm selectivity measured at 350°C for standard silica membranes calcined at 400°C is 39. At a  $H_2/CO_2$  perm selectivity of 50 the hydrogen permeance is expected to be between 0.01 and 0.005 mol/m<sup>2</sup>sbar. Increase of the  $H_2/CO_2$  selectivity by increasing the sintering temperature of the silica membranes could not be experimentally proven at ECN. It is hardly expected that  $H_2/CO_2$  selectivity's above 100 can be achieved reproducibly with this type of membrane, certainly if produced at large scale.

$H_2/H_2S$  selectivity was measured to be at 400. This indicates that only undetectable trace amounts of  $H_2S$  will permeate through the membrane. Three days testing with  $H_2S$  has no detrimental effect on a standard silica membrane. Exposition of a standard silica membrane to steam at 350°C shows as expected a decline in permeance and selectivity. In 15 days the  $H_2/CO_2$  selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. A silica membrane modified by building in methyl groups has been on stream in wet gas stability testing for 1000 hours and shows stable and reproducible performance. However the modified silica membrane has systematically lower selectivity's due to larger pores because of the modification.

Gas separation with a dry gas mixture showed that from a feed stream containing 35% hydrogen a permeate stream containing 75% hydrogen could be derived. This performance is achieved with a membrane with a  $H_2/CO_2$  selectivity of 13.6, which is far below the target of 100. The hydrogen permeance, derived from the hydrogen partial pressure driving force during gas separation testing with a dry gas mixture is well above 0.1 mol/s.m<sup>2</sup>bar, which is the target permeance for the application. The presence of water in the feed mixture reduces the hydrogen permeance and thus hydrogen purity in the permeate compared to the tests without water.

The final conclusion is that silica membranes can meet the flux criteria when no water is present in the feed, but the  $H_2/CO_2$  selectivity criterion of 100 is too high for porous silica membranes. A value of 9 has been reached for the silica membrane under simulated process conditions. Under these process conditions, so including water, the stability of this silica membrane is limited to several days. Modified silica membranes have an improved hydrothermal stability, but a systematically lower selectivity. Summarising it can be concluded that porous silica membranes are not suitable for this application.



## 6. Recommendations

Although it seems almost utopia to reach the economic selectivity and flux targets for a water gas shift reactor application of sol/gel silica membranes, future research should at least concentrate on significantly increasing the  $H_2/CO_2$  selectivity while maintaining the flux also in environments containing water. As the molecular sizing of  $H_2$  and  $CO_2$  are very near this will be an utmost challenge. If this challenge could be beaten then also the long-term stability in water containing environments needs to be improved significantly. Following this the final hurdle of reproducible large scale manufacturing should be taken. Based on these observations it is obvious to recommend not pursuing currently the path for silica membranes in water gas shift membrane reactor applications. However in other applications where no water is present such as hydrocarbon separation this membrane can be a good candidate.

More promising candidates for this application are dense membranes like thin layer palladium alloy membranes, which can produce very high purity hydrogen at high flux. Although the hydrogen flux of these membranes has been improved in the last years, higher productivity at high permselectivities is still needed to become economically feasible for large-scale applications. Also for these membranes other important issues need to be resolved like long term material stability and membrane performance in realistic environments, development of feasible manufacturing processes suitable for large scale production and reliable seals, fittings, module and reactor designs.

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## List of Acronyms and Abbreviations

WGS	Water gas shift
ECN	Energy research Centre of the Netherlands
CCP	CO <sub>2</sub> capture project
PIC	Pressure indicator and controller
MFC	Mass flow controller