

# THERMAL CYCLING STABILITY OF SILICA MEMBRANES FOR GAS SEPARATION

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## ABSTRACT

Hydrogen is being seen as an alternative energy carrier to conventional hydrocarbons to reduce greenhouse gas emissions. High efficiency separation technologies to remove hydrogen from the greenhouse gas, carbon dioxide, are therefore in growing demand. Traditional thermodynamic separation systems utilise distillation, absorption and adsorption, but are limited in efficiency at compact scales. Molecular sieve silica (MSS) membranes can perform this separation as they have high permselectivity of hydrogen to carbon dioxide, but their stability under thermal cycling is not well reported. In this work we exposed a standard MSS membrane and a carbonised template MSS (CTMSS) membrane to thermal cycling from 100 to 450°C. The standard MSS and carbonised template CTMSS membranes both showed permselectivity of helium to nitrogen dropping from around 10 to 6 in the first set of cycles, remaining stable until the last test. The permselectivity drop was due to small micropore collapse, which occurred via structure movement during cycling. Simulating single stage membrane separation with a 50:50 molar feed of H<sub>2</sub>:CO<sub>2</sub>, H<sub>2</sub> exiting the permeate stream would start at 79% and stabilise at 67%. Higher selectivity membranes showed less of a purity drop, indicating the margin at which to design a stable membrane separation unit for CO<sub>2</sub> capture.

## INTRODUCTION

The global consumption of energy has been increasing since the industrial revolution. With this consumption, the emissions of carbon dioxide have also increased which is now accepted to account for 50% of the global warming effect (Lee and Yik 2004). Industry and transport are the major sources of CO<sub>2</sub>, estimated to be responsible for 62% of greenhouse gas emissions in Australia (AGO 2004), 80% of which comes from electricity generation as it is mostly sourced from coal (Dicks et al. 2004). Governments around the world are aiming to prevent higher than sustainable increases in global greenhouse gas reduction, so research is targeting H<sub>2</sub> as a clean fuel carrier. Only 5% of Australia's total energy supply comes from renewable sources which means supply of clean H<sub>2</sub> at this stage must come from fossil fuels. Effective means to remove it from gas streams to capture the CO<sub>2</sub> are therefore needed. The purified H<sub>2</sub> can then be used to harness zero emission energy with fuel cells, while the captured CO<sub>2</sub> can be stored by sequestration. Distillation, absorption and adsorption are common methods for continuous CO<sub>2</sub> removal from H<sub>2</sub>. For example a pressure swing adsorption (PSA) unit can supply continuous pure H<sub>2</sub> from a H<sub>2</sub>/CO<sub>2</sub> mixture (Stoecker et al. 1998), however PSA systems are complex (need for moving parts), bulky and energy intensive processes.

A technology which offers separation in a compact single stage unit with minimal process control is membranes. Simply by controlling the operation temperature and pressure drop, membranes can remove hydrogen from carbon dioxide in a single stage. Three membrane types are available for this separation:

1. Mixed conduction or perovskite;
2. Pd composite; and
3. Microporous silica.

The first two types operate by allowing proton conduction or atomic hydrogen diffusion only through the membrane, allowing for very high purity (> 99%) H<sub>2</sub> streams (Ledjeff-Hey et al. 1998; Alberti and Casciola 2001). Perovskite membranes however only begin to conduct at high temperatures (>600°C) and require further research to improve electron conductivity, leading to higher flux (Balachandran et al. 2004). Pd membranes and their composites (Pd/Ag, Pd/Cu) must also be operated at high temperature (> 300°), especially in the presence

of CO, which inhibits hydrogen surface dissolution and transport. The Pd membrane concept has been around for almost a century now yet the technology still faces problems such as cost of the precious metal (Pd) as well as film stability when exposed to thermal cycles (Armor 1992; Tosti et al. 2003).

Molecular sieve silica (MSS) membranes are an emerging technology for gas, and even liquid separation. The silica structure is synthesised by hydrolysis and condensation reactions, resulting in the formation of silanol (Si-OH) and siloxane (Si-O-Si) groups, respectively. These membranes undergo micropore formation at 500°C resulting in pore diameters in the range of 3Å. The first high selectivities started to appear in the early 90's, for example de Lange and co-workers (1995a) reported H<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> permselectivity at 5.3 and 23 respectively with H<sub>2</sub> permeance of 1.6 x 10<sup>-6</sup> mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup> (200°C). Since then groups have improved permselectivity with Nair's group (2004), reporting H<sub>2</sub>/N<sub>2</sub> permselectivity in the region of 1000. Such selectivity improvements could significantly reduce stage numbers and complexity, making MSS membranes an efficient alternative to fundamentally complex systems such as PSA. Transport mechanisms of gases within MSS membranes are described as an activated diffusion process through the micropores coupled with size exclusion which gives the membrane its permselectivity (de Lange et al. 1995b). Their hydrothermal stability was identified as a problem but has recently been addressed, in particular with carbonised template MSS (CTMSS) membranes developed by this group (Duke et al. 2004). Despite research promoting high flux, permselectivity and hydrothermal stability, there is little work contributing to their performance under thermal cycles, which are likely to be experienced in a real hydrogen separation unit. For instance in potential applications such as automobiles, it is important to know how technologies perform under heating/cooling stresses. This work therefore investigates the thermal cycling of MSS and CTMSS membranes. Gas permeation was used to measure the changes to the flux and permselectivity as an indication of the thermal cycling effect.

## EXPERIMENTAL

MSS and CTMS silica derived membranes were synthesised on α-Al<sub>2</sub>O<sub>3</sub> platelets. The synthesis procedures are now becoming standardised and are described in more detail by several research groups (de Vos and Verweij 1998; Tsai et al. 2000; Diniz da Costa et al. 2002; Duke et al. 2004). Standard permeation was measured at 200°C using a dead end permeation apparatus where the feed gas, He or N<sub>2</sub>, was feed at 1 bar(abs) to the feed side of the membrane. After an initial vacuum was established on the permeate side, the pressure build up with time after closing the vacuum valve was recorded. This was then converted to permeance constant, a function of the permeate gas, cell temperature and pressure drop, by the equation:

$$\ln\left(\frac{P_H - P_0}{P_H - P_t}\right) = \left(\frac{P}{l}\right) \frac{ART_V}{V} t \quad (1)$$

where  $P_H$  is the feed pressure (1 bar(abs)),  $P_0$  is the pressure on the permeate side at  $t = 0$  (~0 bar(abs)),  $P_t$  is the permeate pressure at time  $t$ ,  $(P/l)$  is the permeance constant (mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>),  $A$  is the active membrane area (m<sup>2</sup>),  $V$  is the dead end volume,  $T_V$  is the temperature of the dead end volume (K) and  $R$  is the ideal gas constant.

He and N<sub>2</sub> were chosen as the permeate gases which are cost effective and safer to handle experimentally. Our past work has shown that He permeance is comparable to H<sub>2</sub>, and permselectivity to N<sub>2</sub> can indicate the potential permselectivity of H<sub>2</sub>/CO<sub>2</sub> (Duke et al. 2001; Duke et al. 2004). He/N<sub>2</sub> permselectivity was calculated as the quotient of He to N<sub>2</sub> permeance, which provided a useful indicator to structural changes over the test period. Thermal cycling was performed on the membranes by programming the temperature controller of the Lindberg Blue type HTF55432C tube furnace. All membranes were placed in the tube and N<sub>2</sub> (99.9%) was allowed to flow through the tube to maintain a non-oxidising atmosphere to replicate real membrane operation. Cycles were programmed to ramp at 5°C per minute to 450°C. After a hold period of 2 hours, the furnace was then cooled at the same rate to 100°C and held at 30 mins before the next cycle. The high temperature represents the safe extreme limit of MSS membranes (500°C). Permeation tests after thermal cycles indicated changes to membranes. The test program is outlined in Table 1.

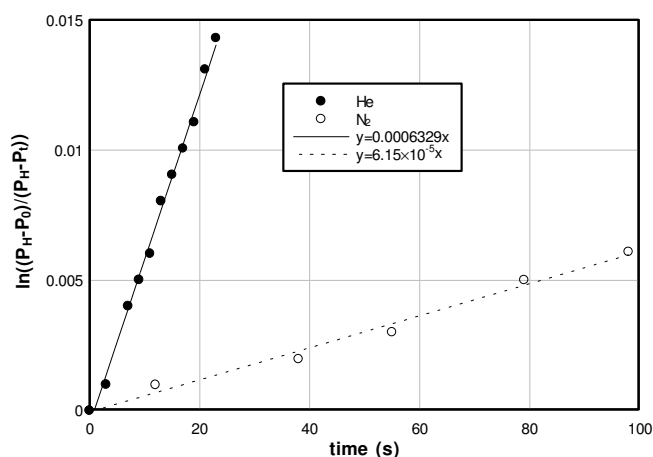
**Table 1: Thermal cycling test program for MSS and CTMSS membranes**

Permeation test number	Prior membrane treatment
1	Initial
2	8 thermal cycles
3	4 thermal cycles
4	Storage in atmospheric conditions for 11 days
5	4 thermal cycles

The CTMSS membrane was initially grey in colour due to the presence of carbon templates and can be useful for indicating changes to the membrane. Photos of the membranes were taken using a Nikon Coolpix 995 (3.34 megapixel) digital camera to record these changes.

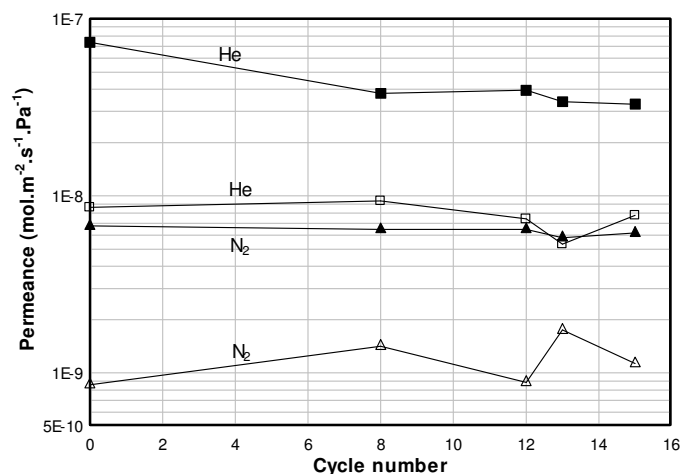
## RESULTS AND DISCUSSION

Figure 1 shows the linear plot from Equation 1 for the CTMSS membrane experimental results. The slope was then used to calculate the permeance constant. It is observed that the permeation of the smaller molecule (He) is faster than the large molecule (N<sub>2</sub>). This result clearly showed the ability of these membranes to separate gases based on molecular size.



**Figure 1: Permeance constant determination from transient data using Equation 1. Permeance measured at 200°C, 1 bar  $\Delta P$ .**

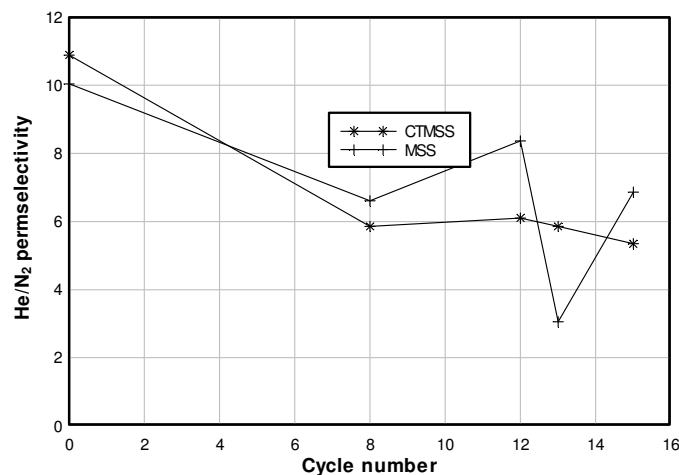
The permeation of He and N<sub>2</sub> with respect to thermal cycles are shown in Figure 2. Thermal cycling appeared to reduce initial permeance of gases in the CTMSS membrane only, while from the 8<sup>th</sup> cycle remained stable. Meanwhile the MSS membrane showed some He permeance loss after the 8<sup>th</sup> cycle. N<sub>2</sub> permeances of both membranes remained mostly stable over the whole cycling period although the MSS membrane showed a slight increase in permeation. This can be attributed to a very fractional pore size enlargement of the membrane structure.



**Figure 2: Permeance of He and N<sub>2</sub> through CTMSS (solid symbols) and MSS (hollow symbols) membrane after thermal cycling to 450°C. Permeance measured at 200°C and 1 atm  $\Delta P$ .**

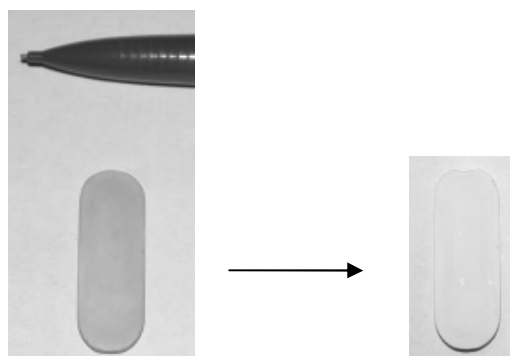
Exploring the performance in more detail is shown by the He/N<sub>2</sub> permselectivity depicted in Figure 3. Permselectivity appeared to drop from around 11 to around 6, almost 50% of the original value. However as shown more clearly on the CTMSS membrane, the effect of thermal cycling appeared to stabilise after the first

set of cycles. The MSS membrane showed some variation in permselectivity, especially on the test after the 13<sup>th</sup> cycle. It is likely that may be due to some experimental error arising from handling of the membrane during removal and installation in the test cell.



**Figure 3: He/N<sub>2</sub> permselectivity with respect to thermal cycle to 450°C for both CTMSS and MSS membranes (200°C, 1 atm ΔP).**

Overall, there appeared to be little difference between MSS and CTMSS membranes in terms of thermal cycling stability. However on visual inspection of the CTMSS membrane shown in Figure 4, there appeared to be some colour loss. If the membrane changed colour from grey to white over the test period, it is likely that the carbon templates may have left the silica micropores, leaving behind a MSS-like membrane. If this is the case, the true advantage of CTMSS membranes under thermal cycling was not seen. The loss of carbon is likely to have been caused by reaction with oxygen picked up during exchange from the membrane cell to the furnace or small leaks in both unit operations. This is an issue of importance, in particular that engineering processes always tend to present leaks caused by heat stresses in flanges and connections.

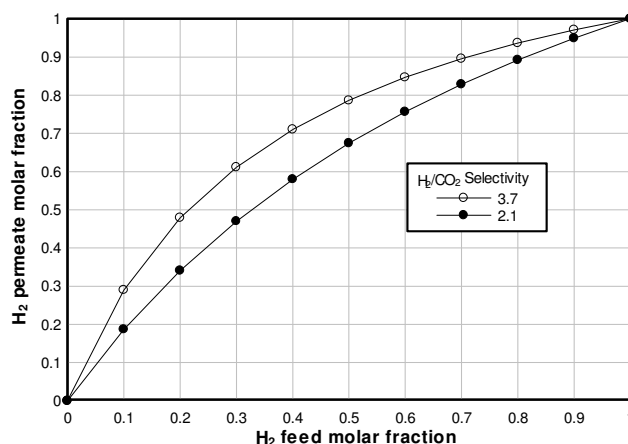


**Figure 4: Images taken of CTMSS membrane showing change in colour from grey (test 1) to white (test 5).**

The He and N<sub>2</sub> results can be translated to H<sub>2</sub> and CO<sub>2</sub> performance assuming permselectivity drop for all gases is uniform. Our past work showed H<sub>2</sub> permeance is around 92% that of He, and H<sub>2</sub>/CO<sub>2</sub> selectivity is around 36% of the He/N<sub>2</sub> selectivity for this type of membrane at 200°C (Duke et al. 2004). Using the forecasted H<sub>2</sub>/CO<sub>2</sub> selectivity drop calculated to be from 3.7 to 2.1 with this assumption, the performance in terms of outlet purity can be simulated. For example if the feed of H<sub>2</sub> in a binary H<sub>2</sub>/CO<sub>2</sub> mixture was 50 mol%, then the exit concentration from a single membrane stage operating at 200°C with vacuum on the permeate side and 1 bar(abs) on the feed would start at 79 mol% and drop to 67 mol%. Figure 5 shows this simulation over a range of inlet feed fractions of H<sub>2</sub>.

With higher selectivity, this difference becomes less significant. For example under the same conditions a H<sub>2</sub>/CO<sub>2</sub> selectivity drop from 20 to 10 would translate to a H<sub>2</sub> fraction drop from 95 to 91 mol%. A membrane system designed to handle at most a 10% drop in H<sub>2</sub> purity should operate stably in a CO<sub>2</sub> capture operation.

Thermal cycling of standard silica membranes causing some loss of permselectivity could be addressed by designing either larger membrane modules, or further research to improve cycling stability of the silica material.



**Figure 5: Simulated single stage membrane separation of H<sub>2</sub> assuming binary H<sub>2</sub>/CO<sub>2</sub> mixture as a function of H<sub>2</sub> feed fraction and selectivity change due to thermal cycling exposure to 450°C. Values simulated using data from this work at 200°C, and 1 bar ΔP with vacuum on the permeate side.**

## CONCLUSION

Standard MSS and hydrostable CTMSS membranes were tested for dry thermal cycling stability. The results clearly indicated that thermal cycling affected the silica microstructure of these membranes, as observed by changes in permeation and permselectivity. The permeation of all gases reduced from the initial cycle and became stable at around the 8<sup>th</sup> heating cycle. Permselectivity loss was observed after the first set of thermal cycles for both membranes, but remained fairly stable at 55% of the original permselectivity. Translated to separation of a 50:50 mixture of H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub> purity in a single stage declined from 79 to 67 mol%, with less of a drop predicted for higher selectivity. Air leaks were a cause of concern for the CTMSS membrane, which requires non-oxidative gas streams.

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