

CONDUCTING THE HOMOGENEOUS WATER-GAS SHIFT REACTION IN A PALLADIUM/COPPER ALLOY MEMBRANE REACTOR AT HIGH TEMPERATURE AND PRESSURE

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1. Introduction

The US DOE National Energy Technology Laboratory, NETL, is investigating the potential of producing hydrogen from coal in order to fuel the hydrogen economy. One concept under consideration is the use of a palladium-based membrane reactor in a coal gasification facility. The CO-rich gasifier effluent would be directed to the membrane reactor inlet, where it would be combined with high pressure steam. The CO and H₂O would convert to CO₂ and H₂ via the water-gas shift reaction (WGSR). The H₂ would dissociate into atoms at the palladium surface, diffuse through the palladium film, re-associate into H₂ at the opposite palladium surface, and flow into the permeate stream. This removal of hydrogen from the gas-phase reaction mixture would enhance the conversion of CO to levels that would exceed conversion under comparable conditions in a conventional reactor (Enick et al., 2000). Because hydrogen alone would permeate a defect-free, dense palladium film and thereby drive the WGSR to essentially complete conversion, the retentate effluent would be a high pressure CO₂-rich stream suitable for sequestration while the permeate effluent would be a high purity, low pressure hydrogen stream.

The performance of a palladium-based membrane reactor is influenced strongly by temperature. For example, if the membrane reactor is placed in close proximity to the gasifier, it could be expected to operate at very high temperatures of roughly 900°C and pressures of 400 – 1000 psia. Conventional reactors are not considered for such applications because the WGSR is reversible, and the value of the equilibrium constant decreases with temperature. This results in an extremely low and unattractive equilibrium limitation for CO conversion. Although the value of the equilibrium constant remains unchanged in a membrane reactor, the removal of H₂ product from the gas-phase mixture decreases the partial pressure of hydrogen, allowing for high CO conversions to be attained. Assuming that there is sufficient surface area for H₂ mass transfer, the CO conversion is limited only by the H₂ partial pressure in the permeate stream. Hydrogen permeance through bulk Palladium (Morreale et al. 2003) and Palladium-based alloys (Howard et al., 2004) has been reported to be strongly influenced by temperature. This increase in permeance with temperature enhances the flux of hydrogen through the membrane. The kinetics of the WGSR is also favorably influenced by increasing temperature, resulting in an increase of intrinsic reaction rate that may be great enough to eliminate the need for heterogeneous catalyst particles because mass-transport of

hydrogen through the membrane (rather than reaction kinetics) would become the rate-limiting step. Further, the palladium-based alloy surface itself has been shown to exert a significant catalytic influence on the WGS rate at high temperature (Bustamante et al., 2004). US DOE NETL models that incorporate the temperature-dependence of the reaction rate, membrane permeance, and equilibrium constant indicate that it is possible to achieve near-complete conversions of CO and H₂O to H₂ and CO₂ at very high temperatures if a resilient, supported, thin film, Pd membrane is used and the partial pressure of hydrogen in the permeate is maintained at low levels (Enick et al., 2000). Unfortunately, extreme temperature conditions can compromise the integrity of a thin palladium film. Therefore, palladium-based membrane reactors have also been evaluated most extensively at lower temperatures of 300 – 500°C (Kikuchi et al., 1989, Basile et al., 1996), conditions where the membrane is likely to be more robust. Despite the promise of palladium-based membrane reactors over a wide range of temperatures, there are several impediments that prevent this technology from being commercialized in coal gasification plants. Pure palladium undergoes a temperature-induced phase transformation when exposed to hydrogen that results in the failure of membranes due to the density (and hence volume) difference between the α and β phases (Grashoff et al., 1983). Although this problem was addressed by alloying silver and palladium, which enhanced the mechanical properties of the membrane and improved its permeance over a narrow range of alloy composition (Grashoff et al., 1983) several significant problems still remain. Palladium is a precious metal, and economically viable composite membranes need to contain palladium or palladium-alloy films that are on the order of 1-10 microns in thickness. If these films are supported on a porous metal or porous ceramic substrate, they must be defect-free because cracks and pits represent high-permeability, low-selectivity failures if the support is porous. In the case of porous stainless steel supports or dense noble metal supports, intermetallic diffusion with the substrate, favored at high temperatures, must be mitigated in order to maintain the precise alloy composition of the membrane. Further, the effluent stream from coal gasification would contain dilute concentrations of compounds, such as H₂S, COS, NH₃, HCl, and light alkanes, that may poison the palladium or palladium-silver alloy.

In this work, we evaluate the potential of the palladium/copper alloy, Pd/Cu, as a membrane material in a series of tests over a wide range of alloy composition, temperature and pressure. These results will enable us to assess the permeance and H₂S poisoning resistance of a Pd/Cu. The effect of CO on the permeance of the membranes will also be evaluated, along with the effect of oxygen (O₂ may be periodically introduced to remove C deposits or to re-activate membrane surfaces) on the Pd/Cu membrane permeance and morphology. Finally, the potential catalytic effect of Pd/Cu surfaces for the WGS will be examined. Relatively thick, disk-like foil membranes were used because of ease of manufacture and precise control of membrane composition. *We are not proposing that 25-1000 micron thick Pd/Cu membranes are suited for commercial membrane reactors. Rather, it is our objective to gain an understanding of the effects of membrane composition and phase, temperature, pressure, gas composition, and gas impurities on membrane performance.* Our results will enable researchers focusing on the manufacture of composite membranes containing ultra-thin Pd/Cu films on porous ceramic (e.g., J.D. Way - Colorado School of Mines), porous stainless steel

(e.g., Y.H. Ma – Worcester Polytechnic Institute), or dense noble metals (e.g., R.E. Buxbaum - REB Research) to optimize the Pd/Cu alloy composition for the conditions associated with their particular application. The design of a thin-walled, tubular, Pd/Cu membrane reactors currently being fabricated at NETL will also be based on these results.

2. Experimental Apparatus

The Pd and Pd/Cu foils used in this study were 25-1000 microns thick and commercially available in precise composition and thickness. The compositions of interest consisted of 40, 53, 60, 80, and 100wt% Pd (indicated by the red dotted lines in figure 1) and the temperatures of interest were $300 \leq T \leq 900^\circ\text{C}$. These ranges of composition and temperature were sufficient to investigate the bcc (body-centered cubic) and fcc (face-centered cubic) regions of the Pd/Cu phase diagram, Figure 1, the two Pd/Cu crystalline structures present in the temperature range of interest in this study.

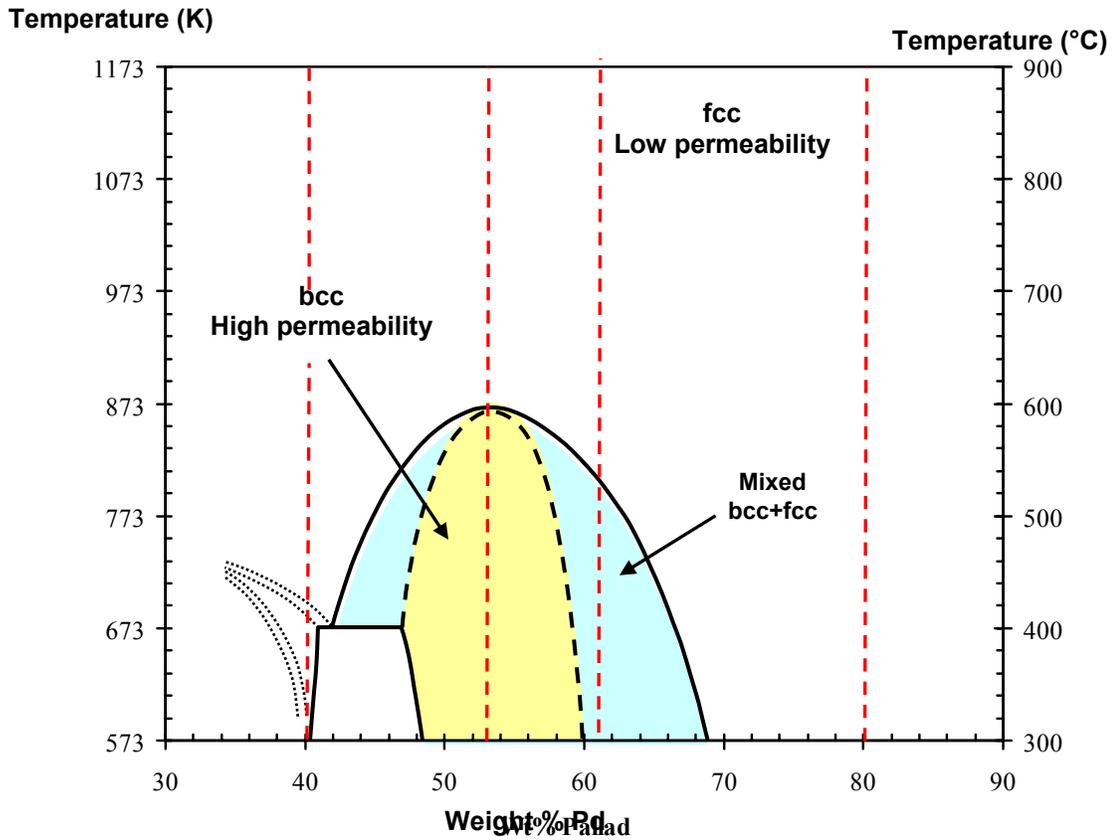


Figure 1. Pd/Cu Phase Diagram (P.R. Subramanian et al., 1990)

During permeance and H_2S poisoning tests, the foils were studied over the $14.7 \leq P \leq 400$ psi pressure range, with a 90% H_2 / 10%He retentate gas mixture. The sweep pressure was maintained at 14.7 psia. Because helium is unable to diffuse through Pd and Pd/Cu membranes, the presence of He in the permeate was evidence of a defect that indicated the membrane needed to be replaced. A H_2S concentration of 1000 ppm was employed

in the “effect of sulfur” tests; a concentration in excess of that found in typical gasifier effluent streams (prior to H₂S removal). Figure 2 illustrates the configuration of the membrane holder. From left (retentate) to right (permeate), it is shown to consist of an Inconel tube, a washer, the Pd/Cu membrane, a porous metal substrate that supports the membrane, and an Inconel tube.

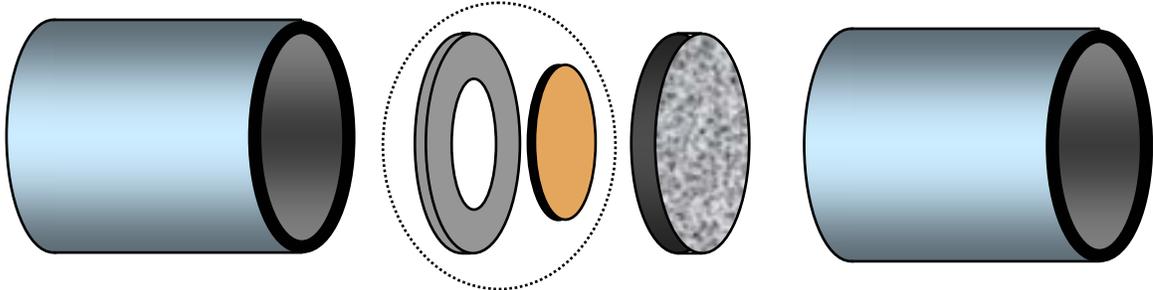


Figure 2. Pd/Cu Membrane Holder for Disk Membranes; retentate (L), permeate I

Three steady-state Hydrogen Membrane Test units, Figure 3, were designed and built at NETL to accommodate disk membranes, spiral-wound tubular membranes, and small plug-flow reactors or membrane reactors. These units are capable of attaining pressures up to 400 psig and temperatures up to 900°C. Further, either clean or H₂S-contaminated H₂ feedstocks, or CO/H₂O can be introduced to the retentate. Online analysis of products is accomplished by GC. An unsteady-state unit was also available for estimating membrane permeance in the presence of H₂S from transient data.



Figure 3. One of three steady-state Hydrogen Membrane Test units

3. The Permeance and Permeability of Pd/Cu Alloys

Transport of hydrogen through a dense palladium alloy membrane consists of dissociation of hydrogen into atoms at the retentate surface, transport of hydrogen atoms through the metal via diffusion, and re-association of hydrogen atoms into molecular

hydrogen on the permeate side. The dependence of hydrogen flux through a Pd/Cu membrane on the hydrogen partial pressure of the retentate and permeate streams was determined. A linear fit of flux vs. the difference in partial pressure raised to an exponent was attained for an exponent value of 0.5, Figure 4. This exponent value confirms that for relatively thick foils, the transport of hydrogen is controlled by the diffusion of hydrogen atoms through the membrane.

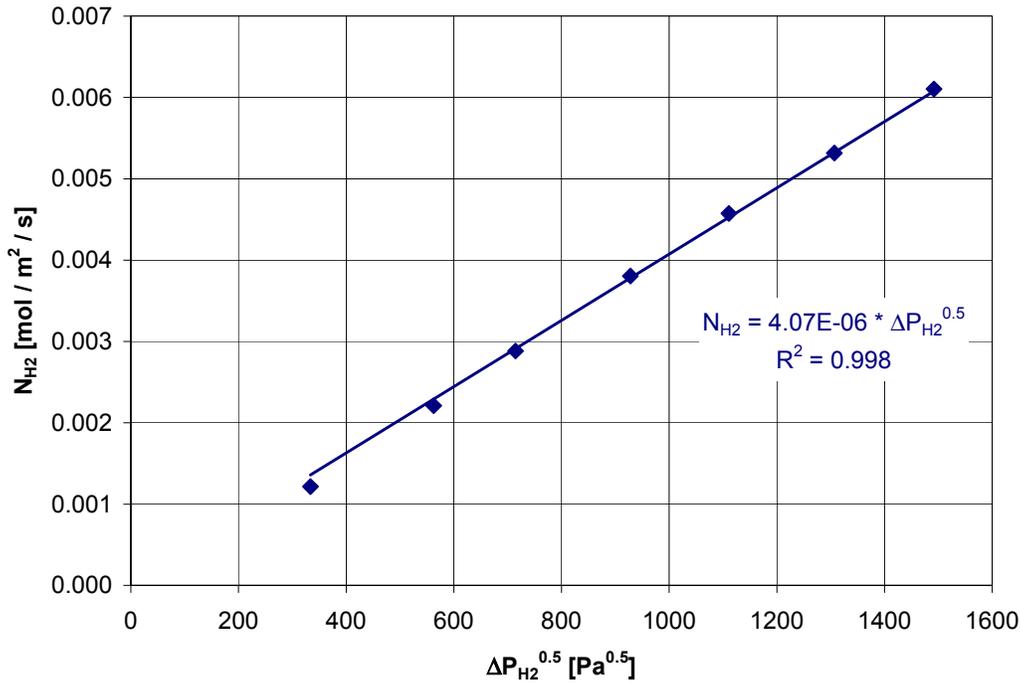


Figure 4. Flux of hydrogen through PdCu is dependent upon ΔP^n , where $n = 0.5$

Therefore, the hydrogen flux can be related to the hydrogen partial pressure in the permeate and retentate streams by using the permeance, k' :

$$N_{H_2} = -k' \left(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5} \right)$$

Flux data was obtained over a wide range of temperature, pressure and membrane composition in the presence of a H₂/He mixture. In all cases, no flux of He through the membrane was detected. The results for 100 micron-thick Pd/Cu foils are illustrated in Figure 5.

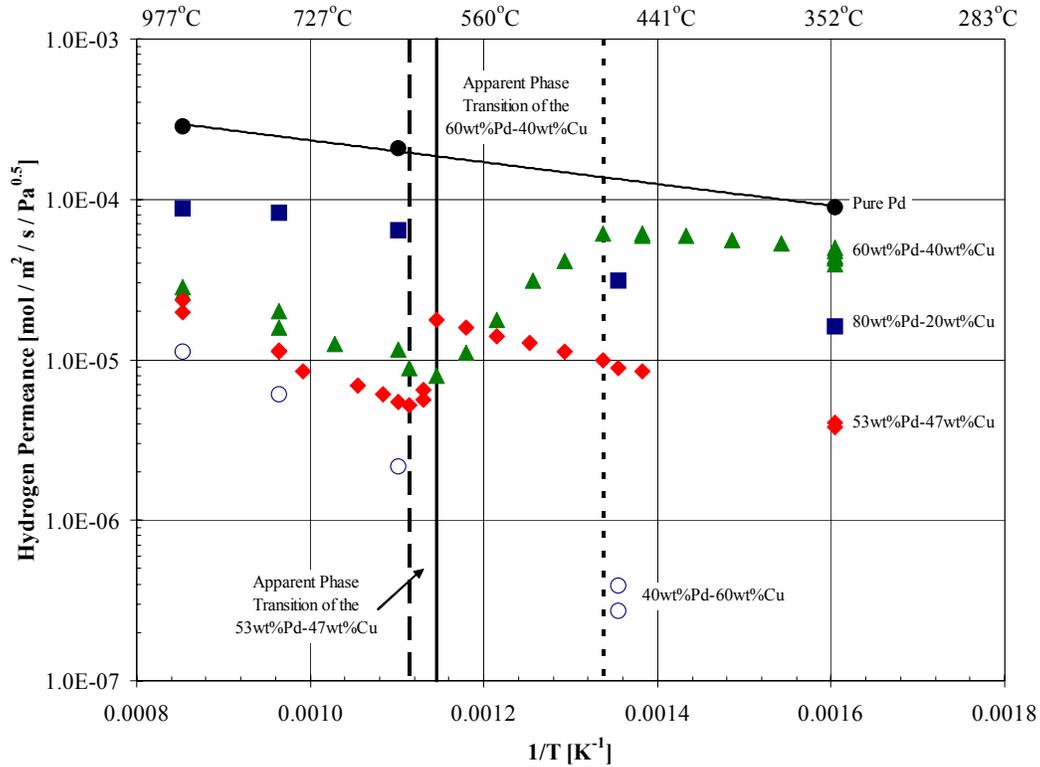


Figure 5. The hydrogen permeance of Pd/Cu membranes of varying composition – the membranes were exposed to 90% H_2 /10%He mixtures.

Permeance of Pd/Cu increases with increasing temperature (decreasing inverse temperature in Fig. 5) for the fcc phase and the bcc phase. If a phase transition from lower temperature bcc or mixed phase bcc+fcc to higher temperature fcc occurs (see Fig. 1), a decrease in permeance will occur because the bcc phase is more permeable than the fcc phase, as shown by the Pd_{53}/Cu_{47} and Pd_{60}/Cu_{40} data in Figure 5. For a given phase, bcc or fcc, an increase in Pd content causes an increase in permeance, approaching that of pure Pd.

4. The H_2S Resistance of Pd/Cu Alloys

There have been a few prior reports of H_2S resistance and H_2S poisoning of Pd/Cu membranes under limited conditions (McKinley 1967, Edlund, 1996). Our results, however, provide a more comprehensive assessment of the effect of temperature, crystal phase, and palladium content on the sulfur-resistance of these membranes (Morreale et al., 2004). Initially, relatively short transient pressure experiments (several hours per test) were used to assess the permeance of the Pd/Cu alloy in the presence of high pressure H_2 on the retentate side and a sweep gas on the permeate side. Permeance was determined by finding the permeance value that provided the best fit of the retentate pressure decline curve (a time-integrated hydrogen mass balance equation). Figure 6 presents the permeance vs. temperature results for 90% H_2 /10%He retentate mixtures (filled symbols) and 90% H_2 /10%He retentate mixtures contaminated with 1000 ppm H_2S (open symbols).

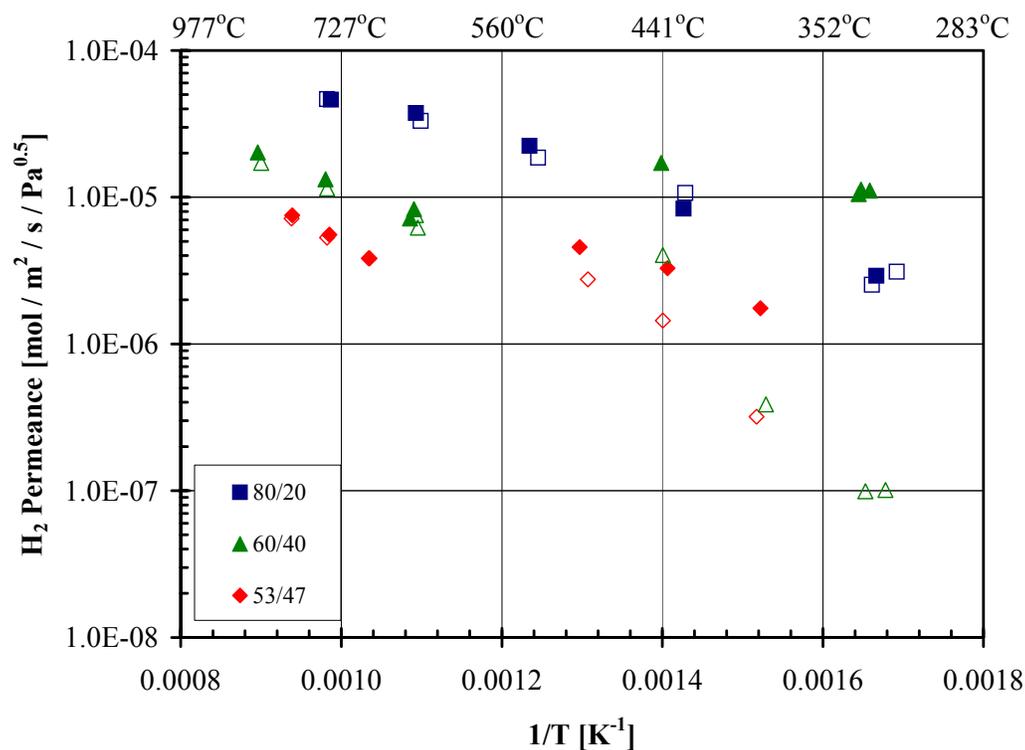


Figure 6. Permeance of Pd/Cu with and without 1000 ppm H₂S present in the 90%H₂/10%He retentate stream; transient pressure decline tests; several hours in duration

These results show that the permeance of the bcc phase (Pd₆₀/Cu₄₀ and Pd₅₇/Cu₄₃ at low temperature, see Fig. 1) decreases dramatically in the presence of H₂S, while the fcc phase of each alloy exhibits no significant decrease in permeance. Longer term testing was then conducted in an HMT unit by exposing the retentate side of the membrane to a flowing stream of hydrogen or H₂S-contaminated hydrogen. The results for the 100 micron-thick Pd₈₀/Cu₂₀ alloy presented in Figure 7 also illustrate that this fcc alloy is H₂S-resistant. The small decrease in permeance is greater than that observed for the shorter transient experimental results shown in Figure 6, perhaps due to the longer exposure of the Pd/Cu surface to the H₂S-contaminated retentate.

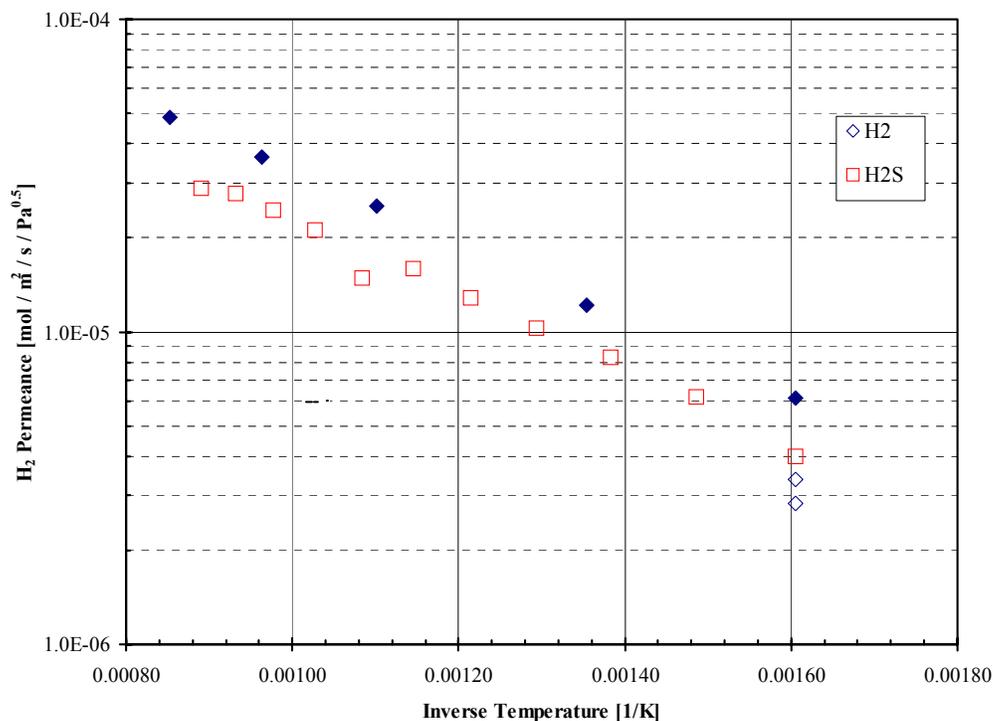


Figure 7. Permeance of Pd/Cu with and without 1000 ppm H₂S present in the 90%H₂/10%He retentate stream; steady state tests; several days in duration

5. The Effect of CO on the Pd/Cu Permeance

The reactants of the water-gas shift reaction, CO and H₂O, have both been reported to affect hydrogen permeance through Pd/stainless steel membranes (Li et al. 2000). Hence, it was important to establish the effect of CO on the permeance of hydrogen through the Pd/Cu alloy membrane. The ultimate goal was to determine if these compounds impeded hydrogen permeation over our experimental range, subsequently affecting hydrogen yield from the WGSR. The permeation tests were conducted using a 1mm thick Pd(80)Cu(20) disk membrane. A 90%H₂-10%He feed stream was used to establish a base line for H₂ flux at the various conditions and then a 50%H₂-50%CO stream was introduced to determine the effect of the presence of CO in the feed stream.

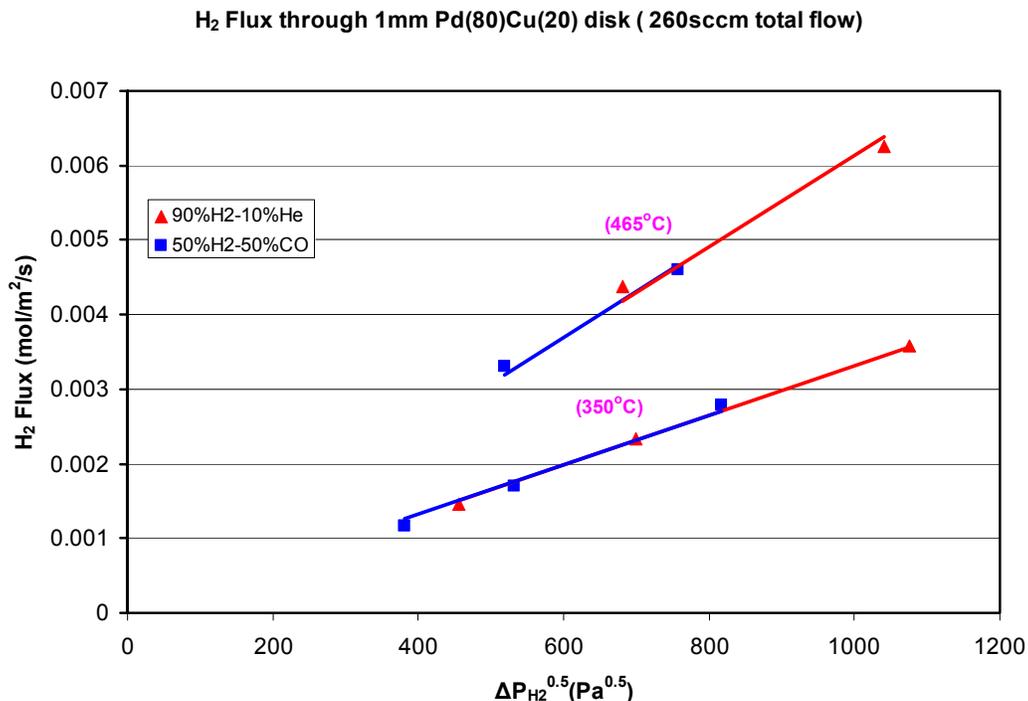


Figure 8. Permeance of Pd/Cu with and without CO present in the 90%H₂/10%He retentate stream

The graph suggests that the presence of CO in the feed stream had no discernable effect on H₂ permeation within our temperature range with pressures up to 210 Psi. This was evident from the plot of H₂ flux versus the hydrogen partial pressure difference between the retentate and the permeate streams for the H₂-He and H₂-CO feed streams respectively. The equivalence of the slopes of each line, which is equivalent to the H₂ permeance for the H₂-He and H₂-CO conditions at a particular temperature suggests a negligible influence of CO on hydrogen permeation.

6. The Effect of O₂ on the Pd/Cu Surface

A gasifier is typically operated at condition corresponding to the incomplete combustion of the fuel; therefore it is unlikely that O₂ will be present in any significant concentration within the membrane reactor. Nonetheless, the Pd and Pd/Cu membranes were exposed to a high concentration of O₂ because such a treatment could be contemplated for the removal of coke deposits from the membrane or the re-activation of the Pd/Cu membrane surface. Although exposure to O₂ at 900°C slightly enhanced the permeance of the membranes, Figure 9 illustrates that this was probably caused by surface roughening. Although the increased surface area of the membrane promotes hydrogen transport in these 100 micron-thick foils, the size of the openings (the scale bar in each figure is 50 microns) would undoubtedly lead to the failure of ultra-thin membranes (1-10 microns in thickness).

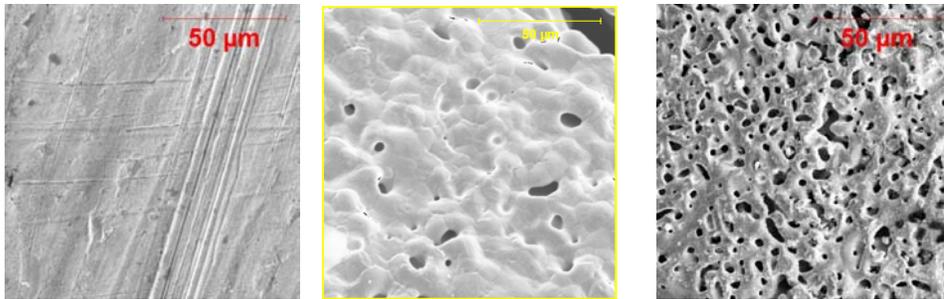


Figure 9. SEM images of membrane surfaces; from left to right; fresh Pd (fresh Pd/Cu is not shown but is similar in appearance), Pd/Cu after exposure to O₂ at 900°C, and Pd after exposure to O₂ at 900°C

7. The Catalytic Effect of Pd/Cu Surface on fWGS Kinetics

We explored the possibility of operating the WGS membrane reactor at elevated temperatures up to 900°C. Previously, we had established that the rate of the high pressure, high temperature WGS reaction in a Inconel reactor was fast enough at these conditions that need for the addition of heterogeneous catalyst particles would be reduced or eliminated (Bustamante et al.2004). In this study, the catalytic influence of the Pd/Cu membrane surface was evaluated at several conditions. In order to isolate the effect of the Pd/Cu surface on reaction kinetics from the effect on kinetics of removing hydrogen from the reaction mixture, these tests were done in an H₂-impermeable quartz reactor packed with Pd/Cu particles (rather than a membrane reactor). Although we could not obtain enough low conversion data to generate a rate expression for the Pd/Cu catalyzed WGS reaction, the results shown in Figure 10 make it obvious that the Pd/Cu membrane surfaces greatly enhance the reaction rate. Conversions without Pd/Cu at these conditions were on the order of 0.1%, and a several order of magnitude increase in conversion was achieved in the presence of Pd/Cu. (Similar results had been previously attained with Pd packed quartz reactors.)

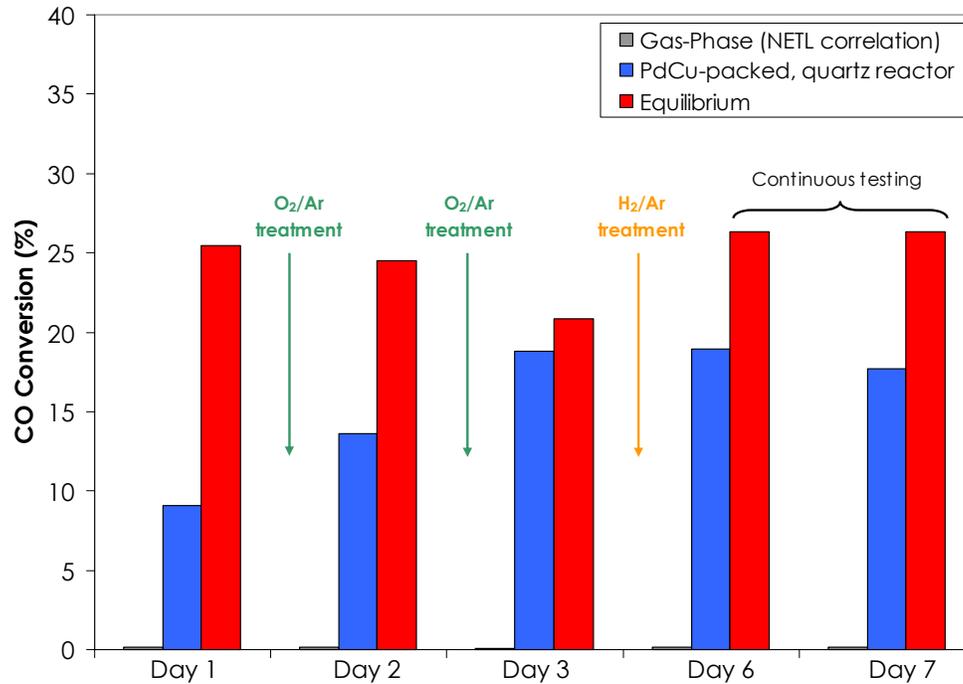


Figure 10. Three measures of CO conversion for WGS reaction in (from left to right) an empty quartz reactor (conversions $\ll 1\%$); a quartz reactor packed with Pd/Cu; thermodynamic equilibrium conversion. Average conditions: $T = 900^\circ\text{C}$, $P = 1$ bar, $t = 0.7$ s, $y_{\text{CO},0} = 0.70$, $y_{\text{H}_2\text{O},0} = 0.30$, each condition represents a day of testing during this 6-day test

8. The Thin-walled Tubular Pd Membrane Reactor

Recently, we constructed a tubular, thin-walled Pd WGS membrane reactor that was operated at 900°C , Figure 11

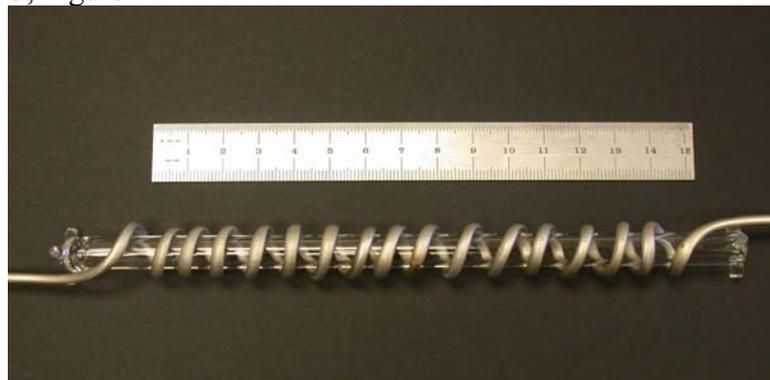


Figure 11. Thin-walled (125 micron) Pd $1/8''$ OD, 2' long, tubular fWGS membrane reactor

This reactor was operated at 900°C with no heterogeneous catalyst particles packed within the retentate (tube) side of the reactor. Figure 12 shows that at the highest permeate sweep flow rate (i.e. lowest H₂ partial pressure), both of the goals of a membrane reactor were realized: CO conversion exceeded the equilibrium conversion of a conventional reactor (no membrane surfaces) operating at identical conditions, and only H₂ was transported through the membrane into the permeate stream. Current research efforts are being directed to implementing and testing a thin-wall Pd/Cu membrane reactor for the hydrogen production via the WGSR.

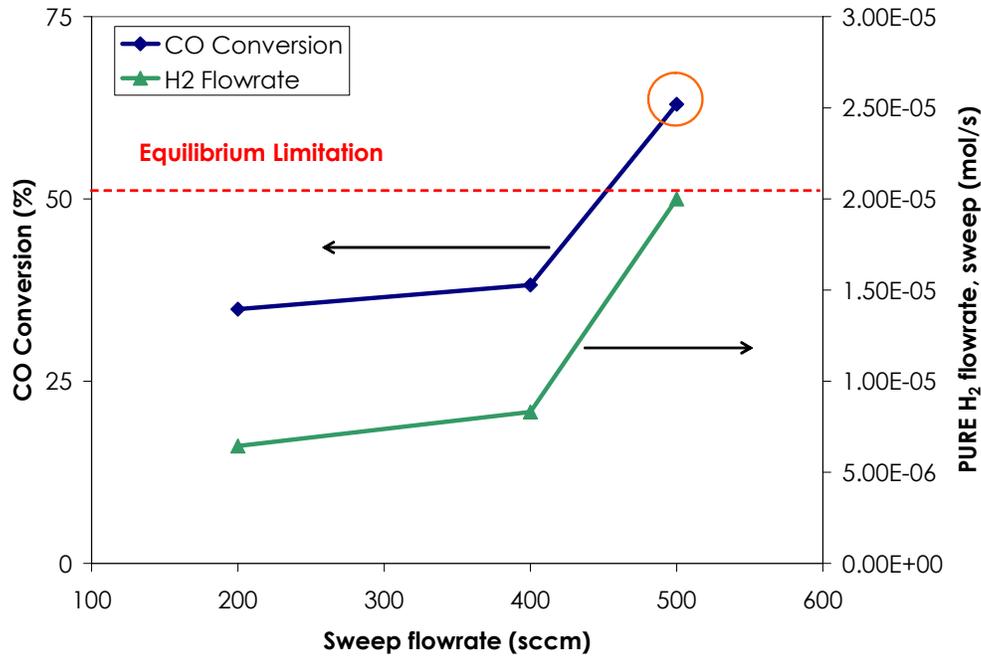


Figure 12. Performance of a Pd tubular fWGS membrane reactor at 900°C and 16 bar, stoichiometric feed of CO and H₂O, argon sweep gas at 900°C and 15 bar, “pure H₂” means only hydrogen permeated the membrane

9. Conclusions

- Pd/Cu is a promising, completely hydrogen selective membrane material that exhibits superior mechanical properties relative to Pd. The Pd/Cu permeance is less than that of pure Pd, but low temperature Pd₆₀/Cu₄₀ bcc permeance is comparable to that of Pd, as is Pd-rich fcc membrane, such as the Pd₈₀/Cu₂₀ alloy.
- Unlike Pd, the fcc phase of the Pd/Cu alloy (over the range of compositions tested) retains nearly all of its permeance in the presence of 1000 ppm H₂S, but the permeance of the bcc phase is rapidly and significantly reduced.
- Initial tests indicate that Pd/Cu is not poisoned by CO, a major constituent of the water-gas shift reaction.
- Although exposure to high temperature oxygen can roughen the Pd/Cu surface and enhance permeance, this roughening could cause the failure of the Pd/Cu, especially if ultra-thin foils are used.

- Like Pd, the Pd/Cu surface enhances the rate of the WGS reaction at elevated temperature, which would improve the performance of the WGSR membrane reactor.
- Although a Pd/Cu membrane reactor has not been evaluated at this point, initial results from a thin-walled Pd tubular reactor operating at 900°C indicate that it is possible to exceed the CO conversion of a conventional reactor while producing H₂ in the permeate without the need to introduce heterogeneous catalyst particles.
- Currently, the minimum copper content required for H₂S resistance is being evaluated. Future tests will focus on the effect of other contaminants (e.g. NH₃, HCl) on the membrane, the evaluation of ternary alloy membranes, and collaborations with researchers depositing ultra-thin Pd/Cu alloys on porous and dense substrates.
- Follow up Pd and Pd/Cu tubular membrane reactors are also being designed and assembled in an effort to conduct more extensive and longer duration tests of the WGSR assisted by membrane reactors.

10. References

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