

# Low temperature hydrogen transport using a palladium/copper membrane

P. A. LESSING, H. C. WOOD, L. D. ZUCK

Idaho National Engineering and Environmental Laboratory, P.O. Box 1625,  
Idaho Falls, Idaho 83415, USA

E-mail: pal2@inel.gov

Results are presented from low temperature hydrogen permeation experiments using a palladium/copper membrane. Inlet pressure was varied from 5 psig to 180 psig, while temperature was varied from 25°C to 275°C. The palladium/copper membranes exhibited flow stability problems at low temperatures and pressures when using ultra high purity hydrogen. A preconditioning step of high temperatures and inlet pressures of pure hydrogen was necessary to stimulate any substantial permeate flows. After pre-conditioning, results showed zero hydrogen flow when using 3–4% hydrogen mixed with helium or argon. It is thought that the inert gas atoms were adsorbed into the membrane surface and thus blocked the hydrogen atom dissolution. When using pure hydrogen at low to moderate temperatures and low pressures, no measurable permeate flow was observed. Also, zero permeate flow was observed at relatively high temperatures (e.g., 150°C) and a low inlet pressure (5 psig). The cause of the zero permeate flow, when using pure hydrogen, was attributed to interface control of the permeation process. Interface control could be due to: (a) insufficient energy to split the hydrogen molecule into hydrogen atoms, or (b) a reversible phase change from beta to alpha of crystals at the near surface. © 2003 Kluwer Academic Publishers

## 1. Background

This article covers experimental results of an investigation to determine the low temperature hydrogen permeation of a palladium/copper membrane [1]. A potential application might be for a membrane to sustain a flux of hydrogen such that it could relieve the gas pressure from a spent nuclear fuel canister. The gas relief would ensure a canister would not exceed a specified pressure during dry storage.

Gas pressure is generated during storage of spent nuclear fuel. The pressure arises from water reacting with metals (e.g., uranium) to form hydrogen and also from various radiolysis reactions that create gases. The radiolysis reactions include decomposition of water to form hydrogen and oxygen [2]. The hydrogen gas could be removed by use of a hydrogen-permeable membrane that only allows passage of hydrogen [3].

The permeation flux of hydrogen at steady state is driven by the concentration gradient across the membrane and is obtained by integration of Fick's law:

$$\text{Flux} = J = (D/\ell)(C_1 - C_2) \quad (1)$$

Here,  $C$  is the hydrogen concentration in the metal layers immediately adjacent to the surface,  $D$  = the diffusion coefficient, and  $\ell$  = the membrane thickness.

Assuming the rate-limiting step is often the diffusion step (generally true at higher temperatures), Sievert's

law can be derived as [4]:

$$J = (D\kappa/\ell K_s)(p_1^{0.5} - p_2^{0.5}) \quad (2)$$

where,  $C = \kappa n$ ,  $n$  = atomic ratio of  $H/Pd$ ,  $\kappa$  = hydrogen concentration at  $n = 1$  ( $\text{mol}/\text{m}^3$ ),  $K_s$  = Sievert's constant = equilibrium constant for hydrogen dissolution,  $p_1$  = partial pressure of hydrogen on high pressure side of membrane, and  $p_2$  = partial pressure of hydrogen on low pressure side of membrane.

Sievert's constant,  $K_s = p^{0.5}/n$ , is effectively equivalent to Henry's law and, therefore, is only strictly applicable at low pressures. The permeation flux depends on both the equilibrium solubility of hydrogen and its rate of diffusion within the palladium membrane. Temperature greatly affects the extent of solubility and the rate of diffusion (increased diffusion coefficient) as can be seen in Equations 3 and 4:

$$K_s = (1/n_s)\exp[(\Delta H_H^0/RT) - (\Delta S_H^0/R)] \quad (3)$$

where  $\Delta H_H^0$  is the standard partial molar enthalpy of dissolution,  $\Delta S_H^0$  is the standard partial molar entropy of dissolution, and  $n_s$  is the geometrically limiting  $H/Pd$  ratio.

The diffusion coefficient ( $D$ ) is given by Equation 4.

$$D = D_0\exp[-E_D/RT] \quad (4)$$

where  $E_D$  is the activation energy for diffusion. Therefore, the permeation flux activation energy has contributions from two temperature-activated processes [ $K_s$  (solubility) and  $D$  (diffusion)].

Hydrogen permeation flux data are often reported as the so-called permeability ( $Q_{sp}$ ) that includes the thickness of the membrane and are expressed in units of  $m^3$  (STP)/m-s. The permeability is defined as:

$$Q_{sp} = J\ell v_M \quad (5)$$

where  $v_M$  is the molar volume of gaseous hydrogen under standard  $T$  and  $p$  conditions.

Substituting terms into Equation 2 yields:

$$Q_{sp} = (D\kappa v_M/K_s)(p_1^{0.5} - p_2^{0.5}) \quad (6)$$

Further substitution yields the expression for permeability (Equation 7) that clearly shows the contribution from the activation energy from solubility and diffusion:

$$Q_{sp} = Q_o(p_1^{0.5} - p_2^{0.5})\exp[-(E_D + \Delta H_H^0)/RT] \quad (7)$$

A limited amount of permeability data, diffusion coefficient data, and activation energy data are available for palladium-based membranes. There are at least three general compositional categories of palladium-based membranes: (1) pure palladium, (2) palladium/silver alloys, and (3) a palladium/copper alloy that could be considered a relatively fixed "intermediate" compound or intermetallic composition.

Each of the compositions can be found as different crystallographic types (phases), depending on the temperature. Pure palladium is found in an alpha ( $\alpha$ ) phase that is face-centered cubic (fcc) at room temperature to about 300°C and then as beta ( $\beta$ ) phase that is body-centered cubic (bcc) at higher temperatures. The alpha phase has very poor hydrogen permeability when compared to the beta phase. Alloying the palladium with silver stabilizes the high-temperature beta phase structure down to at least room temperature. Alloying with copper should also stabilize the intermetallic composition as a beta-type crystal structure.

Some literature data have been reported in units of  $ft^3/(hr\ ft^2)$ , which can be converted to units of  $m^3/(s\ m^2)$ . However, even though these data have been called "flux," the data really are  $[Jv_M]$ , because  $J$  has units of  $mole/(m^2\ s)$ .

A permeability ( $Q_{sp}$ ) value for 20–23 wt% silver alloy was reported by Knapton [5] to be about  $2.5 \times 10^{-4}\ m^3/ms$  at 350°C and 2.21 MPa (319 psi) hydrogen pressure. The Knapton permeability data for 40 wt% copper were about  $1.6 \times 10^{-4}\ m^3/ms$  at 350°C and 2.21 MPa (320.5 psi) hydrogen pressure. Information on the palladium/copper membrane was obtained from the manufacturer's web site that indicated a hydrogen flux of about 175  $ft^3/(ft^2\ hr)$  at 350°C, and 300 psig could be obtained when using hydrogen feed. Using the assumption that the data really are  $[Jv_M]$  and using a membrane thickness value of  $\ell = 25 \times 10^{-6}\ m$ , the permeability was calculated to be  $3.7 \times 10^{-7}\ m^3/ms$ .

This value is much lower than the Knapton data for palladium/copper. A need was, therefore, established for reliable low-pressure and temperature flux data.

## 2. Experimental

Each single-cell membrane had  $9.29 \times 10^{-3}\ m^2$  in surface area and was  $25 \times 10^{-6}\ m$  thick. The hydrogen flux was determined using very accurate electronic mass flow meters for the hydrogen flow through the membrane (permeate flow). The membranes were held in the approximate temperature and pressure range anticipated for representative spent nuclear fuel containers.

### 2.1. Experimental test apparatus

#### 2.1.1. Description of test apparatus

Fig. 1 shows the schematic drawing of the apparatus that was assembled for the flux and permeability tests.

Fig. 2 shows the schematic drawing of the apparatus that was assembled for the membrane endurance tests. The check valve (10) was eliminated due to concerns that the resultant backpressure (about 1.0 psi) would be enough to inhibit the hydrogen permeate flow at low inlet pressures and thus affect the results.

Fig. 3 shows a membrane assembly that is ready for testing with stainless tubing providing gas inlet and outlet paths. The inlet gas tubing is on the right. The palladium/copper membrane is contained deep within the assembly.

For the lifetime tests, gas mixtures for the high-pressure feed were used that are consistent with those generally expected for the high-pressure side of the membrane assembly during service (i.e., dilute hydrogen in helium or argon). The dilution will proportionately slow the flux of hydrogen through the membrane. However, no poisoning or oxidation effects were expected on the high-pressure side (as long as a canister is backfilled with an inert gas).

The low-pressure side of the membrane was configured to simulate an actual membrane assembly that would be exposed either to air or a one-way pressure-relief check valve. Therefore, the experimental apparatus was designed such that on the low-pressure (permeate) side there was a choice of either pure hydrogen or dilute hydrogen mixed with air. If the presence of air were to cause a drop in the flux over time, then problems could also be inferred if air might be present on the high-pressure side during service (air would be present if no inert gas was used to backfill the canister).

The first set of planned experimental tests is shown in Table I, where the pressure and temperature were to be varied with the resultant hydrogen flow rate to be measured. Selected permeate flow rate values could be converted into flux and permeability numbers. Each data point was to be measured after the hydrogen flow rate had stabilized to a steady state. To ensure steady state is reached, the data were to be measured after long times (i.e., many hours) and also after the previous data were taken at a temperature lower and after the previous data were taken at a higher temperature than the temperature under consideration. This was to be a

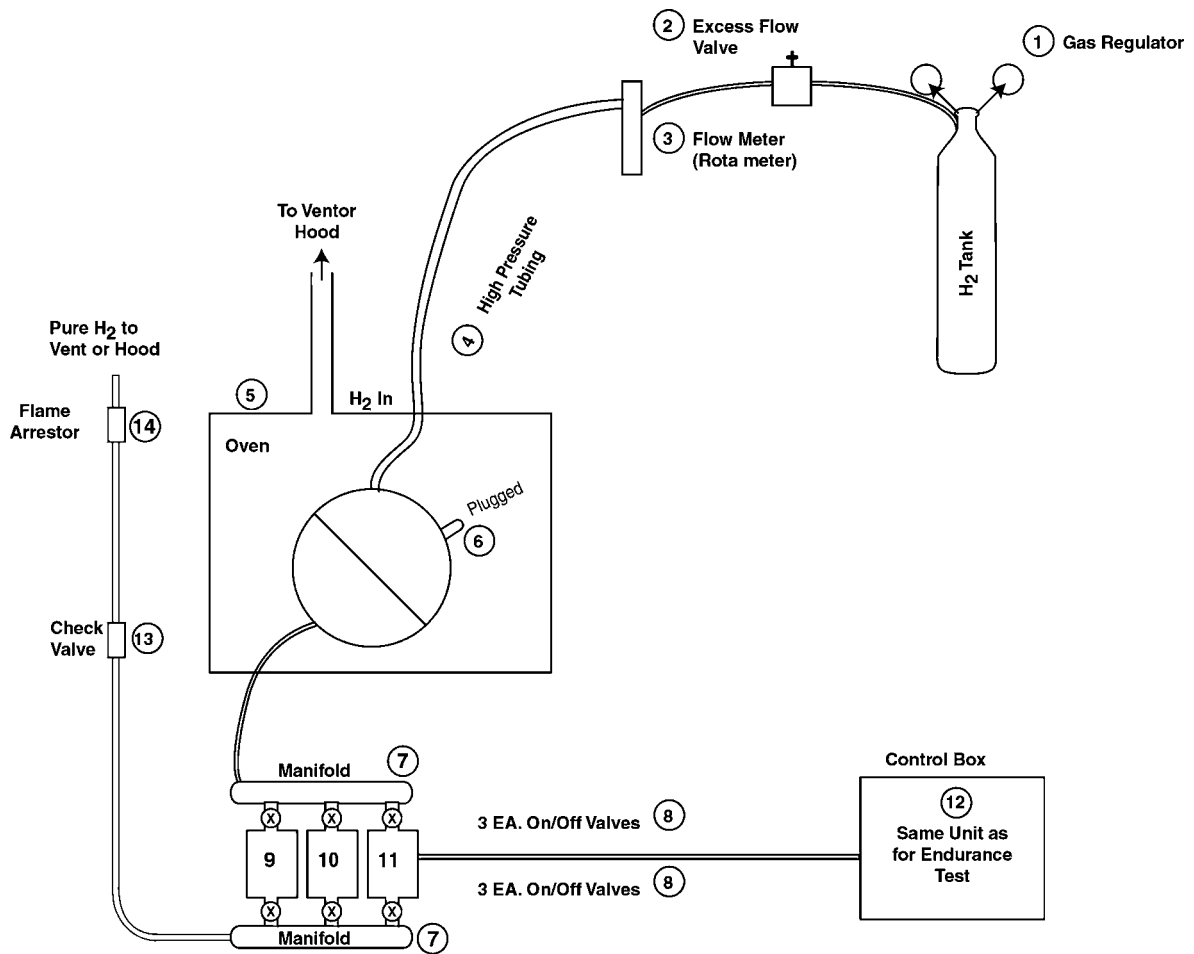


Figure 1 Schematic of flux and permeability test using pure H<sub>2</sub> gas.

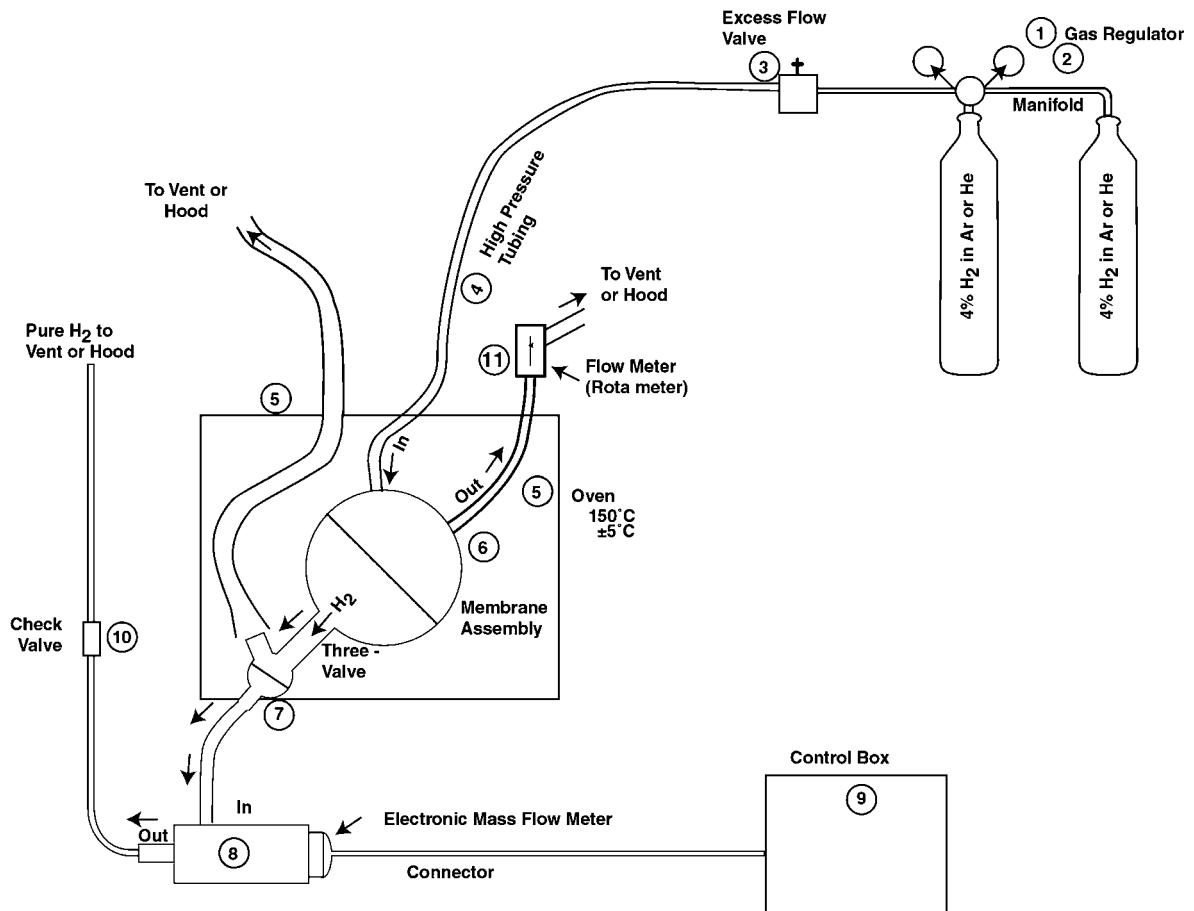


Figure 2 Schematic of long-time test using He + 4% H<sub>2</sub> gas.

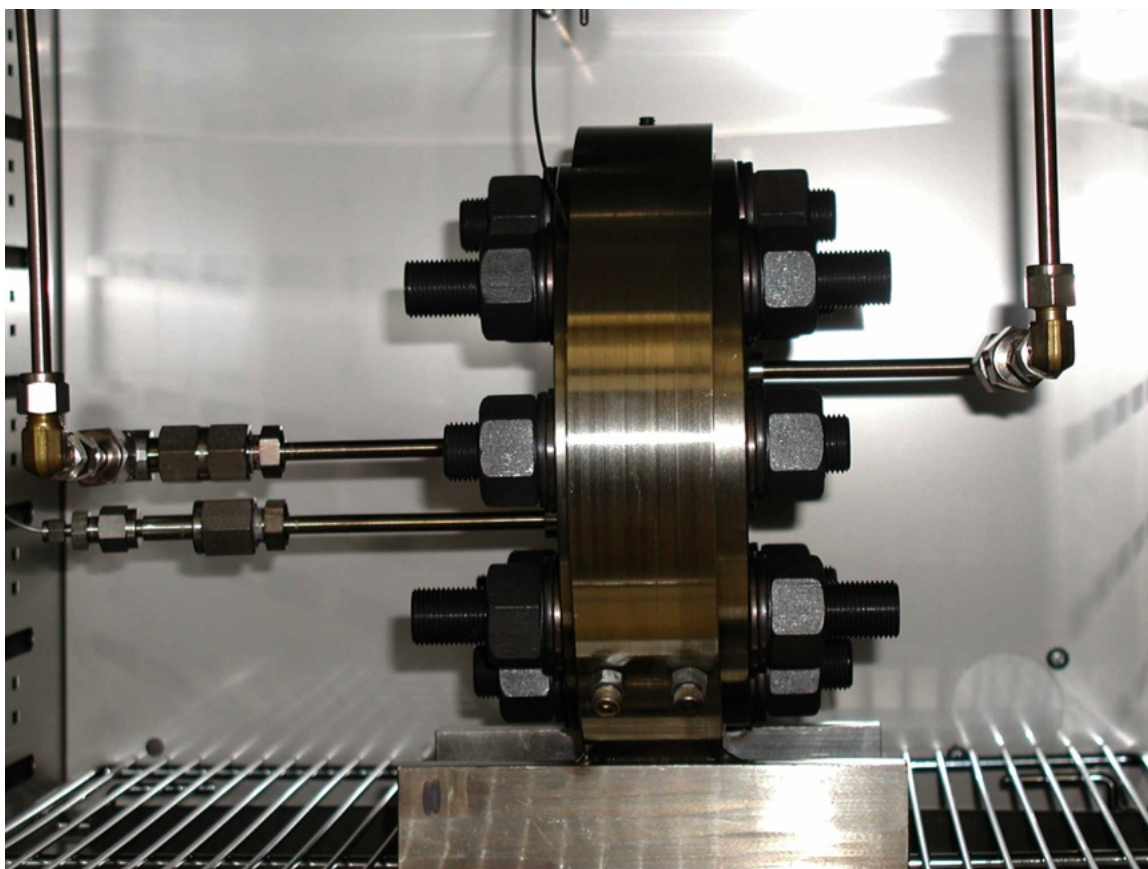


Figure 3 Membrane assembly inside test oven.

test of true equilibrium if the measured flow rate was the same when being approached from a higher and lower temperature. Therefore, 18 tests that were planned are represented by the experimental array of Table I.

Two endurance tests that were planned are shown in Table II. The temperature of 150°C was selected because it is the maximum temperature that could be expected for the membrane assembly during service and, therefore, result in the highest rate of oxidation of the membrane. The pressure of 10.0 psig was selected in order to keep gas consumption to a reasonable rate. The use of 3–4% hydrogen mixed in an inert gas was expected to reduce the flow rate of hydrogen permeate due to a reduction in the partial pressure of the hydrogen in the input gas. Therefore, a proportionately higher

amount of mixed (hydrogen plus inert) input gas flow would be needed in order to produce a desired flow of permeated hydrogen.

Hydrogen permeate flow rates were measured using the flux and permeability apparatus (Fig. 1) per the conditions of Table I. Various sensors (electronic flow meters, pressure sensors, and thermocouples) produced voltage signals that were digitized and stored on a computer using a “Lab View” program. The data were then converted to plots using an Excel program.

Special care was taken to ensure that each sensor had good electrical connection and they were providing appropriate signals into the proper channel within Lab View. Each column of data in Lab View was labeled with the name of an individual sensor. The default setting was to take data every second; however this was later changed to take data every minute.

TABLE I Planned tests to measure steady state hydrogen flux and permeability<sup>a</sup>

5 psig/25°C—L, U	5 psig/75°C—L, U	5 psig/150°C—L, U
50 psig/ 25°C—L, U	50 psig/75°C—L, U	50 psig/150°C—L, U
100 psig/25°C—L, U	100 psig/75°C—L, U	100 psig/150°C—L, U

<sup>a</sup>Input to be pure hydrogen gas.

TABLE II Planned tests to measure hydrogen flux and permeability endurance<sup>a</sup>

Reducing atmosphere on permeate side
Oxidizing atmosphere on permeate side

<sup>a</sup>Temperature = 150°C, Input pressure = 10.0 psig, Input gas = inert gas + 3–4% hydrogen, 500 hrs per test, 2 total tests.

### 3. Experimental results

A major discovery was made when hydrogen permeate flows dramatically increased after the membrane assembly was inadvertently exposed to a higher than planned inlet pressure (approximately 170 psig) while at 150°C. Conversations with the manufacturer indicated that this could be explained as alpha phase palladium/copper being converted into beta phase palladium/copper as discussed by Piper [6]. The Piper journal article documents an increase of up to two orders of magnitude in the room-temperature diffusion coefficient when alpha phase palladium/copper converts to beta phase palladium/copper (no change in alloy

TABLE III Results from pure hydrogen flux/permeability tests

Run No. (hrs)	Membrane no.	Set temperature °C (measured temperature)	Set pressure psig (measured pressure)	Permeate flow (sccm)	Previous conditions (U = upper, L = lower)
				(F= Flat, D = Decreasing, I = Increasing)	
1a (8 hr)	1	150 (152.9)	100 (104.7)	25 F	U
1a (8 hr)	2	150 (155.2)	100 (104.7)	42 D	U
1b (18 hr)	1	150 (152.9)	100 (104.8)	21.7 F	Purge
1b (18 hr)	2	150 (155.2)	100 (104.9)	16.9 D	Purge
2 (22 hr)	1	150 (153.0)	50 (48.8)	30 D	U
2 (22 hr)	2	150 (155.3)	50 (49.1)	9 F	U
3 (11 hr)	1	150 (153.1)	5 (4.2)	0 F	U
3 (11 hr)	2	150 (155.4)	5 (6.1)	0.8 D <sup>a</sup>	U
3 (19 hr)	1	150 (153.0)	5 (4.5)	0 F	U
3 (19 hr)	2	150 (155.4)	5 (5.9)	0 F	U
4 (50 hr)	1	150 (153.1)	50 (57.0)	122 I	L
4 (50 hr)	2	150 (155.3)	50 (59.3)	16 F	L
5 (35 hr)	1	150 (153.1)	100 (98.5)	325 F	L
5 (35 hr)	2	150 (155.3)	100 (110.9)	42 F	L
6 (18 hr)	1	75 (76.9)	100 (98.2)	35 F	U
6 (18 hr)	2	75 (77.4)	100 (98.4)	9 F	U
7 (16 hr)	1	75 (77.3)	50 (49.4)	12 D	U
7 (16 hr)	2	75 (77.4)	50 (49.3)	4 D	U
8 (24 hr)	1	75 (77.2)	5 (6.0)	0 F	U
8 (24 hr)	2	75 (77.4)	5 (5.6)	0.7 D <sup>a</sup>	U
9 (24 hr)	1	75 (77.2)	50 (50.5)	9.3 D	L
9 (24 hr)	2	75 (77.4)	50 (50.3)	2.4 F	L
10 (24 hr)	1	75 (77.2)	100 (99.9)	41 I	L
10 (24 hr)	2	75 (77.4)	100 (99.7)	7.6 F	L
11 (24 hr)	1	25 (36.4)	100 (101.0)	5.6 F	U
11 (24 hr)	2	25 (36.9)	100 (100.8)	1.2 F	U
12 (22 hr)	1	25 (24.8)	50 (48.5)	0 F	U
12 (22 hr)	2	25 (25.2)	50 (48.0)	0 F	U
13 (26 hr)	1	25 (24.2)	5 (7.7)	0 F	U
13 (26 hr)	2	25 (24.6)	5 (7.1)	0 F	U
14 (24 hr)	1	25 (36.4) <sup>b</sup>	50 (50.0)	1.1 F	L
14 (24 hr)	2	25 (36.9) <sup>b</sup>	50 (49.6)	0.2 F <sup>a</sup>	L
15 (24 hr)	1	25 (24.8)	100 (98.8)	2.4 F	L
15 (24 hr)	2	25 (25.1)	100 (98.5)	0.2 F <sup>a</sup>	L

<sup>a</sup>Membrane 2 flow was measured to be zero using a bubble meter when flows registered well below 1.0 sccm on its electronic flow meter.

<sup>b</sup>Room temperature, oven would not control at these low temperatures.

chemical composition). A 2.4 kcal/mole activation energy for the hydrogen diffusion was measured by Piper for the beta phase material (at low temperatures) while literature values of 5 to 6.8 kcal/mole were referenced. The temperature dependence of a diffusion coefficient  $D$  (see Equations 1 and 4) may be expressed as  $D = D_0 \exp(-E_D/RT)$ , where  $E_D$  is the activation energy for diffusion. This difference in activation energy is indicative of a different hydrogen diffusion mechanism in the beta (bcc) versus the alpha (fcc) material.

In order to precondition or normalize the crystal structure of the membranes into the beta phase, both the membranes were exposed to 275°C at 180–182 psig pure hydrogen pressure for 24 hrs. At the beginning of this bake-out, hydrogen was allowed to permeate; however, due to the large permeate flow rates, the exhaust valves were closed during the majority of the bake-out time period. The temperature excursion of the preconditioning procedure dramatically increased the throughput of pure hydrogen through both of the membranes. Permeate flow rates at the end of the heat treatment were greater than the electronic flow meters could measure (>approximately 1–2 L/min).

The experiments with pure hydrogen (Table I) were then conducted (using both membranes with a common

source of pure hydrogen), and the results are summarized in Table III. Membrane 1 and Membrane 2 were the same model and ostensibly were identical.

During Experiment 1b, it was noticed that the hydrogen permeate flow rate greatly increased when fresh hydrogen gas was purged across the inlet face of the membrane. However, this effect was temporary, and the flow rates gradually decreased with time after the initial increase. To be consistent, subsequent to Run 1a, every run began by purging fresh hydrogen gas across the inlet side of the membrane. In every run, this led to a temporary increase in the permeate flow that gradually decreased with time to the flow rate noted as the permeate flow.

Membrane 1 was initially chosen for testing with the hydrogen plus inert inlet gases. This was because it consistently showed higher permeate flow rates with pure hydrogen than did Membrane 2. The test results for permeate flows using mixed gases are shown in Table IV. Because no permeate flows could be measured using mixed hydrogen and helium (or argon), no “endurance test” experiments (see Table II) were possible.

Gas “bag” samples were taken for gas chromatography analysis to verify that the mixed gases contained the stated amount of hydrogen. Triplicate measurements

TABLE IV Test results using gas mixtures of hydrogen and inert gases

Run no. (hrs)	Membrane no.	Temperature (°C)	Pressure psig	Gas composition	Inlet flow (sccm)	Permeate flow (sccm)
16 (1.3 hr)	1	75	100	3% H <sub>2</sub> in helium	2,000	0
17 (0.7 hr)	1	75	100	3% H <sub>2</sub> in helium	4,000	0
18 (0.5 hr)	1	150	100	3% H <sub>2</sub> in helium	2,000	0
19 (0.5 hr)	1	150	100	3% H <sub>2</sub> in helium	4,000	0
20 (0.5 hr)	1	150	100	4% H <sub>2</sub> in argon	2,000	0
21 (0.5 hr)	1	150	100	4% H <sub>2</sub> in argon	4,000	0
22 (0.5 hr)	2	150	100	3% H <sub>2</sub> in helium	2,000	0
23 (0.5 hr)	2	150	100	3% H <sub>2</sub> in helium	4,000	0
24 (0.5 hr)	1	270	180	3% H <sub>2</sub> in helium	2,000	0
25 (0.5 hr)	1	270	180	4% H <sub>2</sub> in argon	2,000	0
26 (0.5)	1	270	180	Pure H <sub>2</sub>	Static	0 ; 1,500 <sup>a</sup>
27 (6 hr)	1	270	Varied	Pure H <sub>2</sub>	Static	Yes; see graph
28	2	275	180/varied	Pure H <sub>2</sub>	Static	Immediate response
29	1	275	180	4% H <sub>2</sub> in argon	4,000	0
31	2	278	180	3% H <sub>2</sub> in helium	4,000–10,000	0

<sup>a</sup>Permeate flow only resumed at end of run when pressure was dropped to below 100 psi and flow became 300–400 sccm, upon repressurizing the permeate flow exceeded 1000 sccm.

TABLE V Gas chromatography analyses of mixed gases

Sample	Labeled % H <sub>2</sub>	Measured % H <sub>2</sub>	% RSD
H <sub>2</sub> /Ar	4	4.09	
H <sub>2</sub> /Ar	4	4.16	
H <sub>2</sub> /Ar	4	4.23	1.8
H <sub>2</sub> /He	3	3.17	
H <sub>2</sub> /He	3	3.30	
H <sub>2</sub> /He	3	3.02	4.5

were conducted. Table V shows the results of the analyses.

Illustrative source graphs for the data in Tables III and IV are shown in Figs 4 through 10. The run numbers reference back to the same run numbers listed in Tables III and IV.

#### 4. Discussion of results

The greatly enhanced permeate flow after preconditioning of the membranes at high temperature and pressure (in hydrogen) is thought to be due to crystal structure conversion of all alpha crystals into beta crystals within the palladium/copper membrane. The exposure to high temperature and pressure should also increase the hydrogen solubility ( $K$ ) as indicated in Equation 2. Both effects (high diffusion through beta crystals and high solubility) are known to increase the hydrogen permeability through palladium-based membranes.

There was a large variability in hydrogen permeability of the two (supposedly equivalent) specific membranes that were tested. Membrane 1 consistently showed much higher permeate flows than Membrane 2. We do not know the reason for this behavior.

In the hydrogen flux determining runs (see results in Table III), the hydrogen permeate flows could be greatly increased by flushing fresh hydrogen across the inlet of the membranes. However, the effect was temporary and the permeate flows then decreased over a period of time to values that seemed to approach steady state. The origin of this effect is unknown. A possibility might be impurities being concentrated at the inlet side of the

membrane. However, ultra high purity hydrogen gas was used for these tests, which would tend to discount impurities as being the root cause.

The data showed that the measured flow rates cannot be classified as equilibrium values. The flow rates measured when the membrane was previously exposed to higher temperature or pressure conditions were generally significantly different than rates measured after exposure to lower temperature or pressure conditions. Thus the membranes did not return to equilibrium flow rates after excursions to another set of conditions. Amazingly, the higher rates were most often measured after exposure to lower temperature or pressure conditions. This result was unexpected. We had expected that the higher rates would be temporarily measured after exposure to higher level conditions. This is because of higher hydrogen solubility (refer to Equation 3) established at the higher temperature and pressure conditions that would be temporarily retained until diffusion removed the excess hydrogen from the crystal lattice. Because the hydrogen flow values could not be considered to be equilibrium values, it made no sense to attempt to calculate any activation energies for the permeation process.

The lack of equilibrium flow rates brings up major questions regarding the phase stability (reversibility) of the crystal structure of the membranes and if equilibrium conditions can be established at short times within the membrane. Once the membrane has been equilibrated at high temperature and pressure (to establish the beta structure and high hydrogen solubility), will the structure slowly revert to alpha structure and associated low hydrogen solubility over long times at low temperatures and pressures? In theory, the hydrogen solubility should decrease at low temperatures and pressures and, thus, be reflected in a lowered hydrogen flux. However, this effect was not found in these palladium/copper membranes. In addition, we could not use X-ray diffraction to determine if there was a reversion of the high conductivity beta phase back into the alpha phase at low temperatures and pressures because of an agreement with the manufacturer prohibiting disassembly of the membrane assemblies.

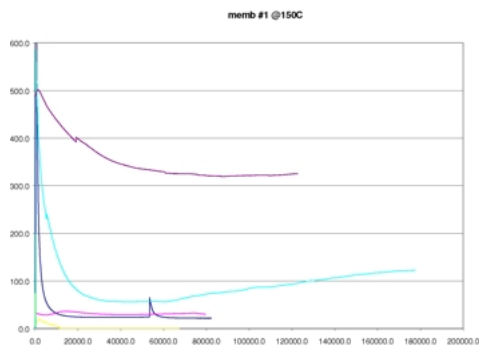


Figure 4 Permeate flows through Membrane 1 as a function of pressure at 150°C (see Table III for pressure conditions during various runs). X axis = time (seconds) Y axis = flow rate (sccm).

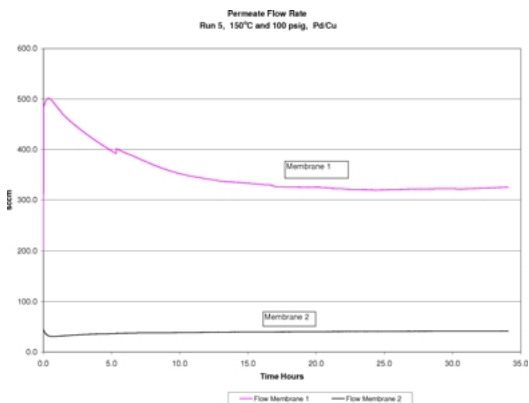


Figure 5 Permeate flow through Membrane 1 versus Membrane 2 (Run 5) at 150°C and 100 psig inlet pressure.

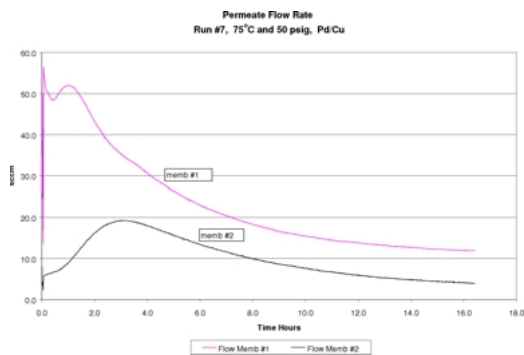


Figure 6 Permeate flow rates for Run 7, showing initial increase due to flushing with fresh hydrogen and then decrease to lower values with elapsed time. True equilibrium was not reached even after 16 hrs.

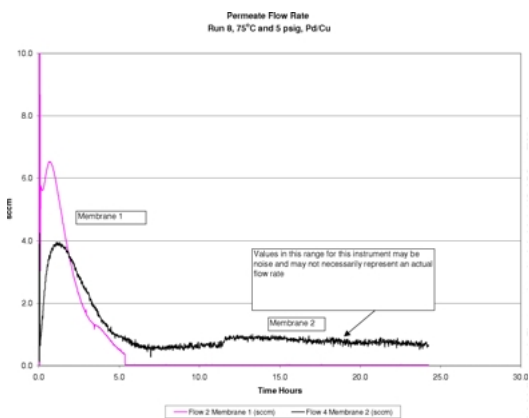


Figure 7 Run 8—initial permeate flow after flushing with new hydrogen, but then flows through Membrane 1 and Membrane 2. Both go to zero after passage of time.

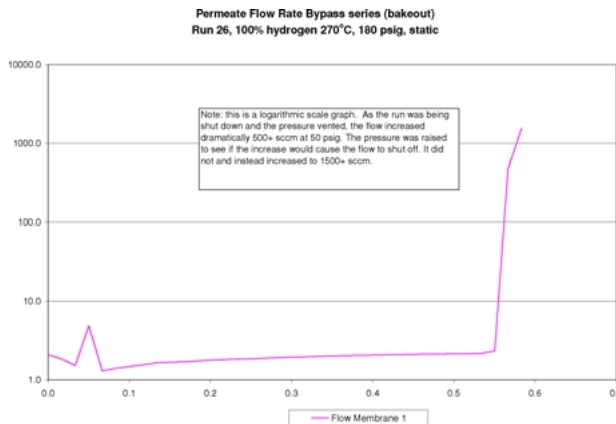


Figure 8 Permeate flow after exposure to inert gas mixture, followed by exposure to pure hydrogen. X = time (hours) and Y = flow (sccm). It took considerable elapsed time plus lowering of hydrogen pressure to stimulate permeate flow.

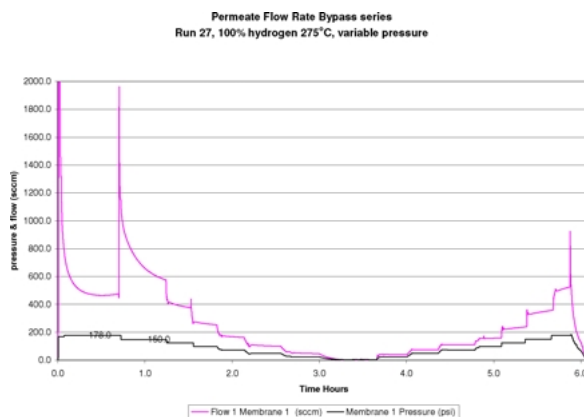


Figure 9 After Run 26 established permeate flow, Membrane 1 was responsive to a sequence of changes in the inlet pressure (at a high fixed temperature).

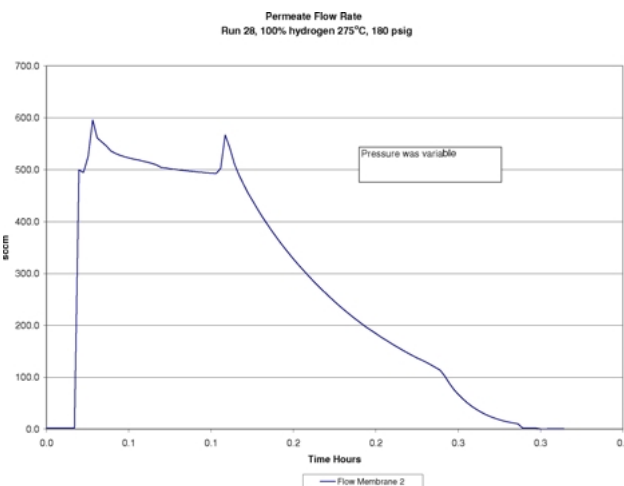


Figure 10 Membrane 2 was also responsive to inlet pressure variations at a high temperature. The pressure started at 0 psig, went through steps to a maximum of 100 psig, and then back to 0 psig.

Regarding phase reversibility, the manufacturer offered its opinion that the bulk/volume of the membrane would not revert from the beta phase to the alpha phase (even after long periods of time under low pressure and low temperature conditions). The only phase change that could possibly occur would only be in microscopic

surface layers. The manufacturer indicated that the alpha phase (basically hydrogen poor) is stable when there is no hydrogen in the membrane environment. A mixture of alpha plus beta phases can exist at room temperature if hydrogen is present. The opinion noted that once the surface of the membrane (usually 3–30 nm inward from the surface) is converted to the beta phase, it is possible to partially reverse this thin surface layer to the alpha phase. Evidently, the reversibility only extends 3 to 30 nm into the volume; the bulk of membrane should remain in the beta phase.

Experimental evidence supported the idea that there were some “interface” problems with the hydrogen permeability at low temperatures and pressures. For instance, there seems to be some sort of “step function” in the permeate flow at low temperatures and pressures. That is, the flow was zero until some defined pressure or temperature value was reached, and then the flow jumped to an easily measured value. If the process were strictly diffusion controlled, one would expect that the flow would gradually increase (or decrease) with temperature and pressure. This may or may not be associated with a possible reversion of a thin (3–30 nm) layer of the surface back to the alpha crystal phase. Interface control at low temperatures is consistent with the results of McCool and Lin [7] who concluded for very thin palladium/copper membranes that hydrogen permeation is dominated by surface reaction steps if the membrane is within the 100–200°C range.

The other interface problem is exhibited when using gas mixtures of an inert atom (either helium or argon) with the hydrogen gas. We found no experimental conditions where a permeate flow could be established when using the mixed gases. Therefore, no endurance experiments (see Table II) could be conducted. A possible explanation is that the inert gas atoms were adsorbed into surface sites of the palladium/copper membrane. The inert gas atoms then strongly interfered with the interface process of the hydrogen molecule “catalytically” splitting into hydrogen atoms that can diffuse through the membrane’s atomic lattice. Under these conditions, the assumption that Sievert’s law is applicable would be violated. The interface reaction rate, rather than the permeability process (combination of diffusion and solubility), would then govern the hydrogen flow process across the membrane. The inert gas “interface” problem might actually be related to the “interface” problem that is being exhibited at low temperatures and pressures. At the low temperatures and pressures it is possible that the reaction process that converts the hydrogen molecule into hydrogen atoms also is not happening, but for different reasons. At low temperatures and pressures, the interface reaction might not happen at all until a certain level of temperature and pressure is reached to provide sufficient energy for the splitting reaction to occur.

## 5. Conclusions

Overall, the palladium/copper membranes exhibited flow stability problems at low temperatures and

pressures when using ultra high purity hydrogen feed gas. A preconditioning step of exposing the membrane to high temperatures and inlet pressures of pure hydrogen was necessary to get any substantial permeate flows. This was attributed to an alpha to beta phase transition within the membrane. The palladium/copper membranes that were tested will not function to relieve hydrogen pressure in a spent nuclear fuel canister that is backfilled with helium gas. Experiments yielded zero hydrogen permeate flow when using inlet gases of 3% hydrogen mixed with helium or 4% hydrogen mixed with argon over a wide range of temperatures, inlet pressures, and inlet flow rates. It is thought that the inert gas atoms were adsorbed into the membrane surface and, thereby, blocked the hydrogen atom dissolution.

Using pure hydrogen at moderate temperatures and low inlet pressures (75°C and 5 psig), no measurable permeate flow was observed. At relatively high temperatures (e.g., 150°C) and a low inlet pressure (5 psig), zero permeate flow was observed. Also, zero permeate flows were observed at room temperature combined with pressures less than 50 psig. The likely cause of zero flows was attributed to interface control of the permeation process, due to: (a) insufficient energy to split the hydrogen molecule into hydrogen atoms, or (b) a reversible phase change from beta to alpha crystals at the near surface (3–30 nm) of the membrane at low temperatures and pressures.

Also, at low temperatures equilibrium flow rate values generally were not thought to be achieved because flow rates differed significantly depending on the temperature and pressure that the membrane had been exposed to immediately prior to the new measurement condition.

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