

SIMPLIFIED ANALYSIS OF A "PLUG-FLOW" PALLADIUM PERMEATOR

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Introduction

Palladium's exclusive permeability for hydrogen isotopes is ideally suited for separating hydrogen isotopes from other components. Thus, as a unit operation, palladium-silver permeators are expected to find wide application in fusion fuel (deuterium and tritium) processing.

The ideal geometry for separating hydrogen isotopes (Q_2) from other components (hereafter referred to as inert) is shown in figure 1. The feed which contains both Q_2 and inert flows into an annular space. The outer wall of the annulus is Pd-Ag and the inner wall is a stainless steel capillary tube. The Q_2 permeates through the Pd-Ag and is pumped away by a vacuum pump. The inert and whatever Q_2 remains at the end of the Pd-Ag tube is carried away by the capillary tube positioned in the center of the Pd-Ag tube.

This configuration is considered ideal largely because of the fact that tritium is being handled. Commercial Pd-Ag based hydrogen purifiers usually operate with feed pressures of 10-20 atmospheres and the permeate is exhausted at ambient pressure. However, due to the hazards of working with tritium, it is preferable for fusion fuel processing applications to work with maximum pressures not far above ambient, so the permeation driving force is provided by evacuating the permeate side rather than pressurizing the feed. Given this constraint, the geometry shown in figure 1 maximizes the partial pressure driving force by 1) allowing for maximal conductance on the permeate side which is needed for effective evacuation, 2) introducing the feed into an annular space which results in an ability to maintain the feed pressure down the length of the tube (with minimal pressure drop due to viscous losses), and 3) using a "plug flow" pattern. Further, using this annular design maximizes the permeation area to volume ratio which allows for maximal permeation of

hydrogen isotopes. It is this type of permeator, which is commercially available, that is considered in this paper.

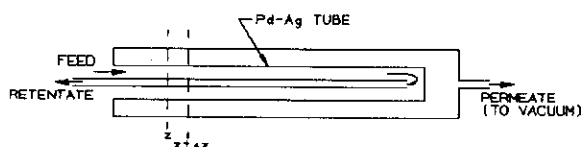


Figure 1 Ideal Geometry for Pd-Ag Permeator

Description of the Pseudo-Single Isotope Treatment

In the following discussion only the case of a single permeating component in an inert carrier is considered. This simplifies the equations and makes the underlying principles easier to understand. The results obviously apply directly to permeators which only handle one hydrogen isotope, but usually for the multi-component case the equations are also the ones needed for design purposes. Since feed concentrations may vary considerably, design must consider the worst case. Often this means that if all isotopes will be encountered then the pure tritium (the isotope with the lowest permeability) physical properties should be used. This will add a margin of safety to the design. The fact that these equations apply only to this single or pseudo-single component case is designated by a subscript "Q" in the equations. Consideration of equations which include multi-component effects will be given in future publications.

Equations For A Plug-Flow Permeator

Consider a control volume on figure 1 bounded by planes at axial positions z and $z+\Delta z$. It is assumed that there are no axial concentration gradients due to diffusion and that the control volume is well mixed so that there are no radial concentration gradients. At steady state, flow into the

volume across plane z must either leave the volume by permeating through the tube wall or flowing out across plane $z+\Delta z$. Thus:

$$F_{Q(z)} = F_{Q(z+\Delta z)} + G_{Q(z+\Delta z/2)} \quad (1)$$

where F_Q is the flowrate of hydrogen isotopes in the axial direction and G_Q is the permeation rate through the Pd-Ag tube. For cylindrical geometry the permeation rate is given by:

$$G_Q = \frac{2\pi\Delta z n_i K_Q}{\ln(r^p/r^r)} (\sqrt{p_Q^r} - \sqrt{p_Q^p}) \quad (2)$$

where n_i is the number of permeator tubes; K_Q is the permeability; r^p and r^r are the outside and inside radius of the Pd-Ag tube, respectively; and p_Q^r and p_Q^p are the hydrogen isotope partial pressures on the retentate and permeate sides, respectively. Substituting (2) into (1):

$$F_{Q(z)} = F_{Q(z+\Delta z)} + \frac{2\pi\Delta z n_i K_Q}{\ln(r^p/r^r)} (\sqrt{p_Q^r} - \sqrt{p_Q^p})_{(z+\Delta z/2)} \quad (3)$$

Rearranging and letting Δz become infinitesimally small:

$$\frac{dF_Q}{dz} = \frac{-2\pi n_i K_Q}{\ln(r^p/r^r)} (\sqrt{p_Q^r} - \sqrt{p_Q^p}) \quad (4)$$

p_Q^r can be calculated in terms of flows and the total pressure at any position z by:

$$p_Q^r = \frac{F_Q}{F_Q + F_{inert}} P_{tot} \quad (5)$$

where F_{inert} is the flowrate of inert gas and P_{tot} is the total pressure of the retentate. F_{inert} is constant and for a properly sized permeator. P_{tot} will also be constant (no viscous pressure drop in the annulus). p_Q^p will usually be constant and have a small value. This small value will be negligible at the beginning of the permeator, but as p_Q^r becomes small, p_Q^p will define the lower limit to which F_Q will decrease.

It is convenient to collect constants in (4) and define:

$$B_Q = \frac{2\pi n_i K_Q}{\ln(r^p/r^r)} \quad (6)$$

Then, using (5) and (6), equation (4) can be rewritten as:

$$\frac{dF_Q}{dz} = -B_Q \left(\sqrt{\frac{P_{tot} F_Q}{F_Q + F_{inert}}} - \sqrt{p_Q^p} \right) \quad (7)$$

It is straight forward to integrate this equation numerically using any standard technique such as Runge-Kutta. Other properties of interest may be calculated at each position z by using (5) to calculate the partial pressure and G_Q may get determined by the difference in F_Q between adjacent integration steps (or by applying equation (2), but that would be redundant).

A limiting case of interest for equation (7) is when p_Q^p is set to zero. If the shell of the permeator is well evacuated, this assumption is fairly accurate and, for design purposes, the effect on calculating the useful length of the permeator (the point at which F_Q reaches a minimum) will be negligible. Then (7) becomes:

$$\frac{dF_Q}{dz} = -B_Q \sqrt{\frac{P_{tot} F_Q}{F_Q + F_{inert}}} \quad (8)$$

The analytical solution of (8) is:

$$\sqrt{F_{Q,b}^2 + F_{inert} F_{Q,b}} - \sqrt{F_{Q,a}^2 + F_{inert} F_{Q,a}} + F_{inert} \ln \left(\frac{\sqrt{F_{Q,b}} + \sqrt{F_{Q,b} + F_{inert}}}{\sqrt{F_{Q,a}} + \sqrt{F_{Q,a} + F_{inert}}} \right) = -B_Q \sqrt{P_{tot}} (z_b - z_a) \quad (9)$$

limited by $z_b \leq z_c$, where z_c corresponds to $F_{Q,b} = 0$

where subscript "a" and "b" refer to two points of interest in the permeator. For instance, if the conditions at the entrance (point "a") are known, then the conditions at any other position (point "b") can be determined. The limiting condition, $z_b \leq z_c$, must be imposed to avoid the square root of negative numbers.

Table 1: Typical Experimental Results (Run #1)

Temperature: 400 C, Ar: 7%, H₂: 46.5%, D₂: 46.5%, Permeate Pressure: 4 mbar

Flow (SLPM)			Pressure (mbar)		Concentration			K _Q (Calculated)
Feed	Permeate	Retentate	Feed	Retentate	Retentate Ar (%)	Retentate H/D	Permeate H/D	$\left(\frac{\text{SLPM}}{\text{m}\sqrt{\text{atm}}} \right)$
1.28	1.17	0.091	1005	994	98.5	1.21	1.01	-
1.84	1.70	0.139	1003	979	98.8	1.03	1.00	-
2.01	1.85	0.151	1003	973	98.8	1.08	0.99	-
2.43	2.24	0.184	999	959	98.7	1.14	0.99	-
2.92	2.70	0.221	998	948	98.6	1.09	1.00	-
3.21	2.97	0.230	1004	956	98.8	0.98	1.04	-
3.56	3.29	0.262	1002	943	98.7	1.02	1.00	-
3.75	3.46	0.278	1001	936	98.7	1.10	1.00	-
4.10	3.78	0.303	1001	929	98.7	1.03	1.00	-
4.34	4.01	0.321	1002	926	98.7	0.99	1.03	-
4.53	4.19	0.336	999	916	98.8	0.85	0.99	-
4.78	4.42	0.352	1000	912	98.4	0.72	0.98	-
4.95	4.56	0.368	1003	910	98.1	0.58	0.99	-
5.30	4.98	0.392	1003	904	94.3	0.41	1.01	-
5.69	5.21	0.467	1001	878	87.2	0.32	1.17	-
5.81	5.29	0.528	1001	867	78.9	0.25	1.19	0.00510
5.92	5.34	0.570	1000	854	74.3	0.27	1.02	0.00514
5.97	5.35	0.580	1001	847	69.6	0.29	1.03	0.00513
6.03	5.40	0.625	1003	840	60.1	0.32	1.02	0.00507
6.20	5.44	0.768	1001	796	49.0	0.35	1.03	0.00504
6.27	5.50	0.772	1003	790	50.8	0.36	1.03	0.00512
6.57	5.70	0.882	1002	767	47.5	0.36	1.20	0.00528
6.96	5.83	1.155	1003	695	37.4	0.42	1.11	0.00533
7.50	5.93	1.600	1001	538	29.7	0.50	1.15	0.00538
8.04	5.98	2.060	1002	249	24.3	0.56	1.19	0.00541

Experimental Work and Results

Experiments have been performed using a commercially available permeator supplied by Rosemount GmbH. The permeator has 22 tubes which have an inner and outer diameter of 0.0031 and 0.0033 m, respectively, and a length of 0.53 m. The total permeation surface area of this permeator is 0.12 m². The geometry of the tubes have capillaries down their center and have flow patterns as shown in figure 1.

An experiment consisted of preparing a mixture of Ar, H₂ and D₂ in a large tank. This was fed using a flow controller to the permeator at a set pressure (1 atm) while maintaining the permeator temperature at 400 C. The permeate side was held at a fixed pressure (between 4 and 10 mbar) with a vacuum pump. After exiting the permeator, both the permeate and retentate were returned to the large tank.

After selecting a feed flowrate, setting the permeate pressure and waiting for steady-state to be achieved, various measurements were made. These included the permeate and retentate flowrates; the feed and retentate pressures; the Ar concentration in the retentate; and the H/D ratios in the retentate and permeate. Typical results (for run #1) are shown in Table 1.

Discussion

A plot of the permeate and retentate flowrates *versus* the total inlet flowrate for run #1 is given in figure 2. Up to an inlet flowrate of about 5.5 SLPM, essentially all of the hydrogen isotopes permeate. Thus, in this "presaturated" regime, feed gas is simply segregated into all Q₂ going to the permeate and all inert going to the retentate. This explains the linear shape of both curves up to 5.5 SLPM.

As flowrate is increased further, the Q₂ "breaks through"

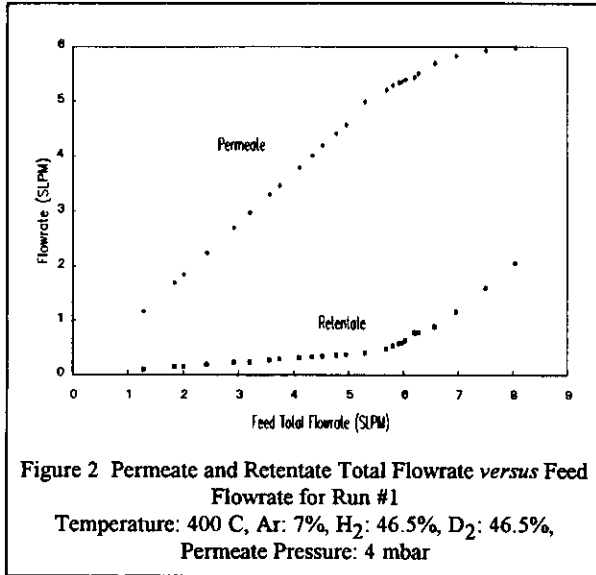


Figure 2 Permeate and Retentate Total Flowrate versus Feed Flowrate for Run #1
 Temperature: 400 C, Ar: 7%, H₂: 46.5%, D₂: 46.5%,
 Permeate Pressure: 4 mbar

the permeator and exhausts in the retentate as well as in the permeate. At these higher flowrates the permeator can be considered "saturated" meaning that all permeator area is being utilized for permeation. The last 2 or three points on figure 2 (7 - 8 SLPM) can be considered to be in this fully "saturated" region.

In this saturated region equation (9) can be used to analyze the data. Prior to break through, the physical length of the permeator is greater than z_c and thus, use of equation (9) is not meaningful. After break through,

equation (9) is meaningful, and all terms in equations (9) and (6) are known except for the effective permeability, K_Q. This calculation is straightforward and has been done. The results for run #1 are given in the last column of Table 1. In this case, the only calculations which are consequential are those with flowrates above 7 SLPM where the permeability is determined to be about 0.0054 SLPM/m/√atm.

There were a total of 16 runs performed and each was analyzed as just described. The experimental conditions used for each of these runs are summarized in Table 2. The last column gives the results of the permeability calculations. For three of the runs (2, 3 and 7) the permeability could not be determined since the flowrate was not increased beyond the "break through" point. The average of the remaining 13 permeability calculations is 0.0058 SLPM/m/√atm with values ranging between 0.0051 and 0.0066. This compares favorably with permeabilities for H₂ and D₂ reported by Yoshida, *et al.* (1) which were 0.0059 and 0.0035 SLPM/m/√atm, respectively.

These permeability calculations are summarized graphically on figure 3. The permeability calculated from each run is plotted versus the hydrogen fraction of the Q₂ in the permeator feed. The apparent positive slope of this data is consistent with the understanding that pure H₂ has a higher permeability than pure D₂.

Future Work

This analysis was not intended to rigorously determine hydrogen isotope permeabilities in Pd-Ag, but only to verify that the mathematical treatment developed here is proper. Future single isotope experiments may be performed for this purpose. The values reported here are for a pseudo-single isotope or an "effective permeability".

Table 2 Summary of all Runs

Run #	P _{tot} (mbar)	P _Q ^p (mbar)	Ar (%)	H ₂ (%)	D ₂ (%)	K _Q (SLPM/m/√atm)
1	1000	4	7	46.5	46.5	0.0054
2	1000	10	7	46.5	46.5	?
3	1000	3	7	46.5	46.5	?
4	1000	4	7	62	31	0.0051
5	1000	10	7	69.75	23.25	0.0053
6	1000	4	7	69.75	23.25	0.0054
7	1000	3	7	69.75	23.25	?
8	1000	10	0	50	50	0.0056
9	1000	7	0	50	50	0.0057
10	1000	4	0	50	50	0.0057
11	1000	5	93	7	0	0.0060
12	1000	10	0	66.67	33.33	0.0060
13	1000	7	0	66.67	33.33	0.0061
14	1000	4	0	66.67	33.33	0.0065
15	1000	10	0	83.33	16.67	0.0065
16	1000	4	0	83.33	16.67	0.0066

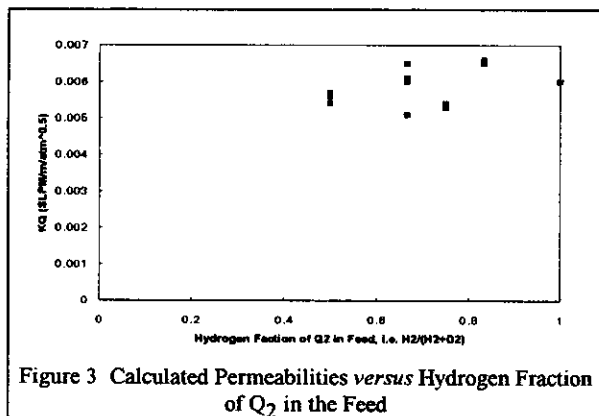


Figure 3 Calculated Permeabilities versus Hydrogen Fraction of Q₂ in the Feed

It is also intended to analyze this and future data using a multi-component treatment

Conclusions

A pseudo-single isotope description of an ideal geometry permeator has been presented. This analysis has been verified by comparison with experimental data. Calculated effective permeabilities (mixed H₂ and D₂) ranged between 0.0051 and 0.0066 SLPM/m/ $\sqrt{\text{atm}}$. The scatter in the results are believed to be due to both variations in the isotopic mixtures used and normal experimental uncertainties. The results compare favorably with other results found in the literature. The straightforward method of permeator analysis presented here is recommended as an effective means of quickly evaluating, understanding and predicting a permeator's performance. It offers great utility, as well, for permeator design.

References

1. Yoshida, H., S. Konishi and Y. Naruse, Preliminary Design of a Fusion Reactor Fuel Cleanup System by the Palladium-Alloy Membrane Method, *Nuc. Tech./Fusion*, 3 (1983) 471-484.