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HE^3 OUTGASSING FROM FOUR WORKING PALLADIUM AND URANIUM BEDS*

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Abstract

The He^3 output from two palladium and two uranium beds storing T_2 and D-T was studied as a function of time. Three of the beds were started new and watched for a year; the fourth bed was twelve years old. All four were beds used in routine tritium handling. Initial stoichiometries were $PdT_{0.3}$ and $UT_{0.7}$ so that both operated at similar 1 to 130 kPa pressures. The He^3 from palladium ranged from the 0.002 mol% lower level of sensitivity to 0.01% for Pd/T_2 at one year of age. The U/T system showed 0.1% He^3 at 4 to 62 days and 0.1 to 10% at longer times, with the first cuts being high in He^3. The palladium bed with 95 to 97% pure T_2 enriches the output to as high as a 97 to 99%.

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For gettering and storing tritium both uranium and palladium beds are useful. With the advent of fusion research, the need to provide tritium with as little He^3 in it as possible, has become important. It is possible to pass the tritium through a palladium membrane at 870 to 970 K and achieve high purity,[1] but a separate storage bed is still needed. Actually, the beds themselves may be used to clean the tritium. Grilly used uranium for his famous tritium vapor pressure measurement,[2] and Haag and Hermann noted similar results for palladium.[3] The problem with uranium tritide is that the He^3 begins to outgas at about 300 days with almost all of it coming forth at 1000 days.[4] This outgassing of older uranium tritide means that some He^3 will be present in tritium released from the bed. We shall here show limited data indicating that even less He^3 comes from palladium beds.

Two palladium beds and two uranium beds were sampled for this report. Three were begun fresh and one was measured only after twelve years. Two used pure tritium and two used D-T. All four were working beds, which means their loads went up and down and that no special care was given to their treatment.

The palladium beds were run at starting hydrogen atom-to-metal ratio's of 0.22 to 0.49, so that $PdT_{0.3}$ was the average initial stoichiometry. The uranium beds were run at ratios of 0.60 - 0.73 so that $UT_{0.7}$ was the average. The temperatures and pressures are shown in Table 1 for the beds containing pure tritium. The variability comes from the varying stoichiometry in different runs. The palladium data fits well to the literature vapor pressure of $PdT_{0.3}$ of[5]

$$P(kPa) = 5.65 \times 10^6 \exp(-4000/T) \quad (1)$$

The Table 1 uranium pressures are 2-3 times lower than the values obtained by interpolation from the literature for $UT_{0.7}$ of[6]

$$\ln P(kPa) \simeq -\frac{9400}{T} + 18.67. \quad (2)$$

The difference could be caused by the improper placement of the temperature sensor. However, Table 1 plus Eqs. 1 and 2 show that our beds are basically performing the way they are supposed to. For our stoichiometries, the pressures are about the same, but the uranium bed requires a temperature higher by 300 K.

The palladium beds sit inside stainless steel cans 0.10 m long by 0.025 m inner diameter, with an internal volume of about 50 $\mu(m^3)$. Tubes enter at the top and bottom with stainless steel frits to keep the palladium inside. The palladium powder comes with a surface area of 7140 m^2/kg with 50% of the particles being 3μm or less in size.[7] The largest initially acknowledged contaminant is 0.74 wt% oxygen. The palladium powder is pressed to a density of 3000 kg/m^3. The frits are also pressed in and the end caps welded in place. Metal wrap-around heaters of 300-400 W are used. Cooling is carried out with liquid nitrogen, either by dunking the unit or passing the coolant through coils around the can.

The uranium beds are U-shaped tubes about 0.3 m long and 0.15 m wide. The tube inner diameter is 13.7 mm. The uranium (enriched in 238) comes in 5 mm cubes.[8] To remove oxides, the uranium is washed for 5 minutes in 35%

nitric acid and is then rinsed in water and alcohol. It is poured into the U-shaped tube to a density of 1000 kg/m^3. When hydrided, the powder will swell by a factor of four. The uranium is held in place by stainless steel wool and frits because it will break into sub-μm sized particles when hydrided. The end caps with valves are welded into place. Glass tape heaters of 300-400 W are used. Because of the U-shape, the total gas path length is about 0.7 m in the uranium, as compared with 0.1 m in the palladium bed.

It is interesting to compare the two types of beds. Each is roughly 0.35 m by 0.17 m by 0.05 m in size, including all valves and pipes. The Pd bed contains 1.45 mols of metal and the U-bed 0.5 mol metal. The Pd goes to 0.3 atom of hydrogen per Pd atom and the U to 0.7 atom. The result is 0.44 at% hydrogen on the Pd and 0.35% at% on the U. Because of the higher density as the hydride, the palladium bed holds 25% more hydrogen than does the uranium bed of the same overall size, at least with the geometry we are using.

The palladium is activated by first passing dry air through at 470 to 520 K for four hours to remove organics. After pumping out, 2.5 mols of deuterium is passed through at 520 K to reduce the palladium oxide. The bed is then pumped out overnight to 10^{-4} Pa. The uranium is activated by first heating to 670 K overnight in a vacuum. The uranium is then reacted with deuterium at 420 K and the gas is desorbed at 570 K. This is done three times, whereupon the metal cubes have been changed into a power with a surface area of 600 to 1000 m^2/kg.

We have periodically sampled our beds by heating to remove aliquots of the hydrogen, each of which is analyzed for He^3. Typical aliquots were: 0-0.5%, 0.5-1, 1-5, 5-10, 10-15, 15-20, and 20-30 or 40%.

The He^3 analysis is performed by gettering the hydrogen with a titanium sublimation pump (TSP) and then measuring the residual He^3 with a Varian CH5 magnetic sector mass spectrometer. A current of 44 A is run through the TSP filament for 100 s to lay down a fresh layer of titanium. A gas sample of 0.003 m^3 at 0.1 Pa is pumped by the TSP. By P-V-T, the residual He^3 may be measured to 100 ppm. The mass spectrometer is run at 79.1 eV in order to ionize the helium and obtain a high-efficiency signal of 1300 counts per 10^{-4} Pa. Base-line noise limits the sensitivity for He^3 detection to 20 ppm - an improvement of five over P-V-T. In order to obtain this value, the gas samples should be run the same day as they are taken off the traps, so that the amount of He^3 formed in waiting for the analysis is small. The amount of He^3 formed in tritium is 0.00128 mol%/hour. An example of a good data point is: measured 0.0061 mol%; corrected to time zero 0.003%. The correction after only a few hours is substantial, and the time of the experiment also helps to set our estimated 20 ppm lower limit of accuracy.

The He^3 data is shown in Fig. 1 for four beds. The x-axis is the total percent of T_2 or D-T gas off the bed at the time of measurement. The y-axis is the mol% He^3 found in the T_2 of D-T gas. Two sets of results fall below the 0.002% lower limit of sensitivity: the Pd/T_2 results from 26-113 days since birth and the single Pd/D-T measurement 343 days after birth. The data at 209 and 491 days is for the Pd/T_2 bed, and it shows that some He^3 is now coming off. The 4-62 day and 313 day uranium data is for the trap with only pure T_2, whereas the 12-year-old trap has seen all manner of D-T in its history. It must be admitted that the U/T_2 has never been stripped, whereas the Pd/T_2 bed was stripped twice, ie. heated to 470 K (no higher, or

sintering will occur) and then pumped out to 10^{-4} Pa. The cleaning of the Pd bed is the result of greater continuous use.

The results of Fig. 1 show that the two uranium beds indeed omit one to two orders of magnitude more He^3 than do the two palladium beds, under the working conditions of these systems.

An interesting feature of the palladium bed is its ability to enrich pure tritium, a feature that was not observed in the uranium beds. The idea of using a palladium column for concentrating tritium was presented thirty years ago by Chadwick.[9] We here obtain similar benefits from the palladium bed. The data are shown in Table 2 for the Pd/T_2 bed already considered. If 95 to 98 mol% T_2 was put on the bed, the first 40-50 % off was all higher in tritium, with the best being seen in the early cuts: 95% is converted to 97% and 98 to 99%. When 99% T_2 is introduced, there is no further improvement, probably because of the hydrogen and deuterium impurities present from earlier runs.

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8. The uranium is from Y-12, Oak Ridge National Laboratory, Oak Ridge, TN.
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Table 1. Comparison of temperatures and pressures for the palladium and uranium traps containing pure tritium. The initial T/Pd ratios are 0.22 to 0.49 for Pd and 0.60 to 0.73 for U.

% T_2 off	Temp. (K)		Pressure (kPa)	
	Pd	U	Pd	U
0.5	255-273	518-598	1.2-2.3	1.2-1.7
1-1.5	267-279	538-617	2.4-4.3	2.5-3.3
5-6	304-325	588-659	12-24	12-17
9-11	316-335	623-678	17-36	24-34
20-22	333-364	637-722	39-85	50-69
30-45	357-380	670-733	58-127	107-111

Table 2. Maximum enrichment of tritium from the Pd/T_2 bed. For 95 to 98% T_2 in, enrichment occurs in the first 40 to 50% of the gas taken off.

	Initial Mol T			Final Mol T			
	T	D	H	T	D	H	Aliquot
Pd/T2 Bed	95.4	3.5	1.1	97.3	2.1	0.6	6-15%
	95.4	3.5	1.1	97.5	2.2	0.3	1-5%
	98.2	0.8	1.0	98.9	0.7	0.4	6-10%
	98.2	0.8	1.0	99.2	0.5	0.3	1-10%
	99.5	0.3	0.2	99.4	0.4	0.2	1-16%

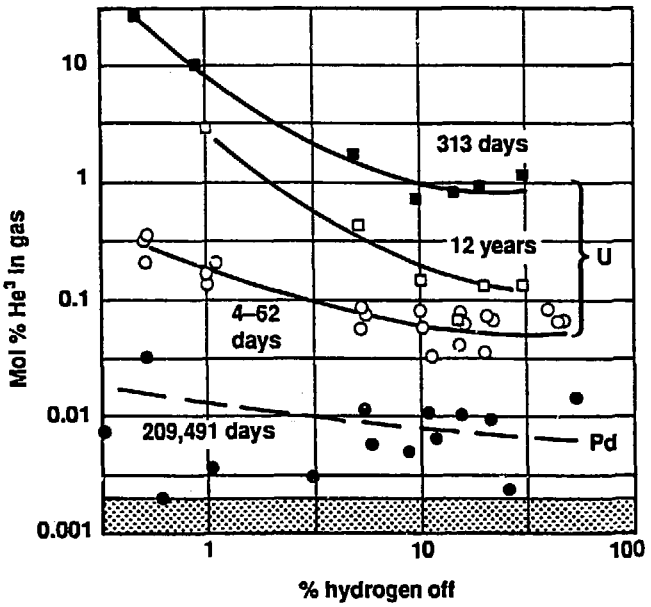

Fig. 1. Comparison of He^3 in T_2 and D-T gas removed from two Pd and two U traps. The 26-113 day Pd T_2 and the 343 day Pd/D-T data all fell below the 0.002% lower level of sensitivity.