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Tritiated Water on Molecular Sieve without Hydrogen Production

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Abstract

Several molecular sieve beds loaded with tritiated water failed to generate hydrogen gas from tritium self-radiolysis at the expected rate. Preliminary gamma-ray irradiation experiments of 4A molecular sieve with varying amounts of oxygen in the over-gas evoke a quenching mechanism. The data suggest that the gas phase rate constant for the production of hydrogen gas is several orders of magnitude smaller than the third order rate constant for scavenging of radical fragments by oxygen. For the production of hydrogen gas, $k_{rx} = (19.6 \pm 4.5) \text{ sec}^{-1}$ under oxygen scavenging conditions.

Introduction

One of the most efficient and safest ways to handle tritiated water is to sorb the water onto a molecular sieve. Pelletized 4A molecular sieve [1] is ideally suited for drying moisture from a gas stream, and consequently was used at the Princeton Plasma Physics Laboratory (PPPL) Tokamak Fusion Test Reactor (TFTR) for the safe handling and disposing of tritiated water on Disposable Molecular Sieve Beds (DMSB). For sufficient amounts of tritium, the molecular sieve can be regenerated and the tritium recovered with high efficiency. For lesser amounts of tritium, the 4A molecular sieve is ideal for safe long-term storage.

The radiolysis of water sorbed onto molecular sieve produces hydrogen gas with an efficiency of about 0.5 molecules of hydrogen produced for every 100 eV of energy deposited in the molecular sieve [2]. The rate of gas production from self-radiolysis of tritium-contaminated water on molecular sieve has been described [3]. Self-radiolysis of water is one of the mechanisms that can increase the pressure in a sealed molecular sieve bed [4]. However, recent measurements of the over pressure on several DMSBs from PPPL reveal that the expected pressure increase is not observed. A quenching process by residual oxygen in the DMSBs has been identified as the explanation for this observation from data produced in gamma-ray irradiation of molecular sieve.

Background

The DMSBs were designed as pressure vessels because of the possibility of hydrogen gas generation from the radiolysis of tritiated water [5]. For a maximum allowed amount of tritium, the molecular sieve vessel must be able to contain the maximum calculated pressure possible from tritium decay and radiolysis. For example, for a Type B DMSB used at PPPL with a free volume of about 17 L, 925 TBq (25,000 curies) of tritium produces an added pressure of about 1.72 MPa of hydrogen gas from self-radiolysis of tritiated water in a time consistent with about 10 half-lives for tritium. Tritium half-life is 12.3 years [6]. Therefore, the Type B vessel is capable of containing 2.58 MPa (1.5 times the design pressure)[7].

Water vapor, nitrogen and oxygen gases adsorb to the surface of molecular sieves. Hydrogenous species from the TFTR exhaust gases were oxidized to water over a hot catalyst with an over-stoichiometric amount of added oxygen. Since the process stream at PPPL was nitrogen gas at a total pressure of about 0.133 MPa with low levels of water vapor and small amounts of oxygen, the DMSBs were loaded with all the water vapor and an equilibrium amount of nitrogen and oxygen during processing. When removed from the process system, the bed contained a non-uniform distribution of water and adsorbed nitrogen and oxygen gas.

Experimental

Over 30 Type B DMSBs were loaded with tritiated water during the high-powered D-T Fusion experimental program at PPPL as described. Pressure and composition measurements of the gas phase above the sieve were made prior to the regeneration process to recover tritium. The pressure was measured with a Sensotec model AP122CP300 pressure transducer, and the gas analysis was made on a Finnigan-Mat magnetic sector mass spectrometer model number 271.

Table 1. DMSB Data

Bed #	Time (Days)	Curies*	Press (Torr)	³ He (Torr)	T ₂ (gms)	$\frac{D_2O_{des}}{D_2O_{load}}$
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		Ci_0	ΔCi	Calc.	Obs.	Calc.	Obs	Exp.	Obs.	
533 ^b	122	8753	163	930	979	6	3	0.66	0.9	0.74
502 ^a	821	12,120	1439	2266	956	53	34	1.11	1.1	1.0
501	913	2789	366	1143	875	14	6	0.14	0.2	0.6
503 ^a	821	12,986	1542	2375	----	57	----	1.01	0.75	0.85
556 ^b	60	22,605	208	978	924	7	4	1.86	2.0	0.8
552 ^b	60	14,813	136	903	980	5	2	1.07	1.3	0.7
500 ^a	791	18,084	2074	2932	996	77	46	1.48	----	0.9
510 ^a	913	22,605	2963	3864	1160	109	75	1.43	1.0	0.7
519 ^a	791	22,124	2537	3417	960	94	71	1.73	1.8	0.85
515 ^a	791	21,899	2511	3390	932	93	62	1.54	2.5	0.76
518 ^a	852	20,688	2544	3424	1064	94	61	2.1	1.6	1.2
557 ^b	270	20,626	840	1640	1134	31	28	1.7	1.5	0.84
550 ^b	320	7402	356	1133	921	13	9	0.7	1.7	0.95
506 ^a	1092	9803	1517	2349	1245	56	51	0.82	0.8	0.95

^a: 4A-DG Lot#: 936393070142; ^b: 4A-DG Lot#: 936393070143 * $1Ci = 3.7 \times 10^{10} Bq$

Gamma-ray irradiation experiments were conducted in a J.L. Sheperd Model 109 irradiator. A 10 gram sample of the exact molecular sieve used in the DMSBs was placed in a reaction vessel of about 15 cm³ volume, and evacuated at 393K for several hours, and backfilled with argon. This left the oxygen content over the molecular sieve at various concentrations. Degassed water was added to the molecular sieve to achieve about a 15 weight percent loading. Samples were irradiated for one hour with an absorbed dose of about 9.22×10^5 Rad/hr (5.7×10^{19} eV_{abs}/gm). Gas analysis of the over pressure before and after irradiation was by gas chromatography.

Table 2. Gamma Ray Data

%O ₂	%H ₂	G(+H ₂)
20	0.021	0.017
2	0.024	0.017
1.1	0.15	0.11
<0.05	0.44	0.32

Results

Table 1 contains the data from fourteen DMSB analyses. The first column is the serial number of the individual DMSBs that have been analyzed. The Time column is the number of days the beds were sealed after removal from the process. Ci_0 is the initial amount of curies of tritium sorbed onto each DMSB; ΔCi is the number of curies that decayed during the time in storage because of tritium decay. The Pressure column includes the calculated partial pressure of hydrogen expected for the amount of tritium that had decayed plus 760 Torr[3], and the observed total pressure for each bed. The ^3He column includes the calculated partial pressure of helium-3 expected for the amount of tritium that had decayed, and the observed partial pressure of helium-3 for each bed. The T_2 column includes the mass of tritium expected to be recovered after subtracting the amount that had decayed from the initial amount (Ci_0) and adjusting for the fraction of water recovered; the observed amount of tritium in grams that was recovered is shown (9615 Ci per gram [6]). The last column is the ratio of the amount of water that was desorbed to the amount of water that was loaded onto each DMSB.

Table 2 shows the preliminary data from the gamma-ray irradiations. The data clearly show that for a decreasing amount of oxygen in the overpressure, an increasing amount of hydrogen is produced. G(+H₂) is the g-value for the production of hydrogen by the radiolysis of water per 100 eV of absorbed dose.

Discussion

1. Pressure

The data in Table 1 show that the calculated pressure was generally not observed. Since the bed was opened to the atmosphere prior to sealing the connections for storage, the initial pressure at the beginning of storage was 0.1013 MPa (760 Torr). Nevertheless, two beds show an observed pressure greater than that calculated. For DMSB 552, the observed pressure is from water migration causing desorption of nitrogen gas. [4] The time in storage was too short for a significant amount of hydrogen expected from tritium decay, but long enough for the migration of water and release of nitrogen gas to pressurize the bed. For DMSB 533, the initial amount of tritium was low enough that, again, there was not a significant amount of hydrogen expected from tritium radiolysis during the time in storage. The observed pressures for these two beds are understood by the water migration mechanism. The rest of the beds all show pressures much less than the calculated pressure from tritium decay alone, yet greater than 0.1013 MPa (760 Torr). These, too, can be understood by the water migration mechanism, and not by a tritium decay mechanism.

2. Gas Phase Analysis

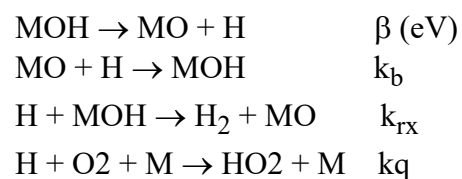
Insignificant amounts of hydrogen species were observed in the gas phase before regeneration of the DMSBs. This is consistent with the lack of a pressure increase as a function of tritium decay. Less than 0.2 mole percent total hydrogens were observed where several mole percent was calculated to have been produced. And virtually no tritium was observed. Analysis of the gas phase showed mainly nitrogen, helium-3 and argon, with small amounts of oxygen. The process stream at PPPL was nitrogen at 0.133 MPa; therefore significant amounts of nitrogen sorbed on the molecular sieve during processing. The observation of argon is reasonable since the bed connections to the process were purged with argon gas prior to line break procedures. A small amount of oxygen is observed because the bed was exposed to the laboratory atmosphere during removal from the process. Oxygen was also added to the DMSBS as a function of processing hydrogenous species to water. Based on a calculated amount of helium-3 from the amount of tritium that decayed, only some of the helium-3 was observed. The low helium-3 measurements show that tritium continued to decay during storage, and are consistent with attempts to measure helium-3 from tritium decay on molecular sieve elsewhere [8]. But the lack of hydrogen gas in these analyses is exceptional.

After DMSB regeneration, the recovered tritium and water show that tritium was present in the water sorbed onto the molecular sieve. The amount of recovered tritium was approximately the amount of tritium loaded onto the beds once decay is accounted for, and the desorbed fraction of the loaded water is taken into consideration. The assumption is that any water not desorbed would contain an equilibrium amount of tritium, thus decreasing the recoverable amount by the fraction in the last column in Table 1.

The data in Table 1 also indicate the magnitude of the errors associated with making these measurements, and set the level of uncertainty these data contain. Notwithstanding the noticeable level of uncertainty, the very low level of hydrogen observed in each DMSB data set cannot be a result of systematic or experimental error.

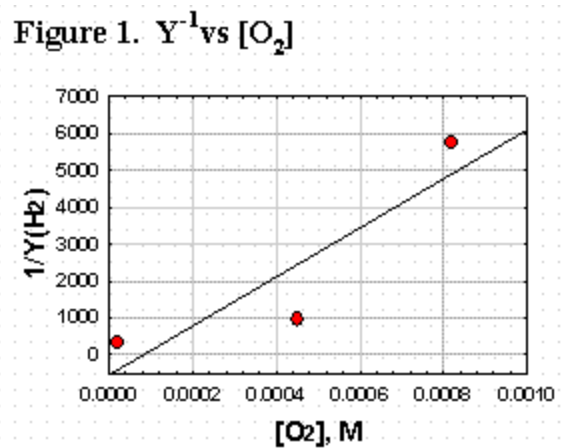
3. Oxygen Quenching Mechanism

The analysis of the over pressure in the DMSBs clearly shows that there is an extreme reduction in the production of hydrogen gas expected from self-radiolysis. The preliminary hydrogen gas production data vs oxygen on molecular sieve from the gamma-ray experiments (Table 2) allows an initial determination of the quenching kinetics assuming the following mechanism.



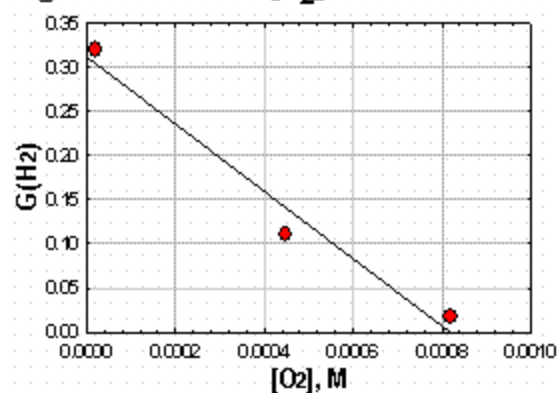
The first step is the production of hydrogen atoms from beta radiolysis of the hydroxide surface. Water on molecular sieve at less than saturation can be characterized as a hydroxide surface (weak dissociative chemisorption) rather than water molecules sorbed onto the surface [9]. The second step is the recombination of the radical with the surface, k_b . The third step is the scavenging of a hydrogen atom from the hydroxide surface to produce hydrogen gas, k_{rx} . And the last step is the scavenging of hydrogen atoms by residual oxygen causing the quenching of the production of hydrogen gas, k_q . Using the stationary state approximation for hydrogen atoms, the rate law for the production of hydrogen gas can be calculated using this mechanism. (see **4. Oxygen Quenching Rate Law** below).

Figure 1 shows a plot of the data in Table 2 using the derived rate law. From a first order regression of the data, the slope is $(6.64 \pm 1.4) \times 10^6$ and the intercept is 526. According to the derived rate law, the intercept should be greater than one; the data are obviously demonstrating their preliminary nature.



Nevertheless, using the slope and the derived ratio of the rate constants, the rate constant for the production of hydrogen gas under gamma ray irradiation and oxygen scavenging is calculated to be $k_{rx} = (19.6 \pm 4.5) \text{ sec}^{-1}$. A literature value for the rate constant for the gas phase scavenging reaction of hydrogen atoms by oxygen to form HO_2 , a third order reaction, is $k_q \approx 1.3 \times 10^8 \text{ L}^2/\text{mole}^2\text{-sec}$ [10]. An estimate of the geminate recombination rate constant, k_d , is about $1.4 \times 10^2 \text{ sec}^{-1}$ based on data collected here under oxygen scavenging conditions. These preliminary calculated rate constants show that the competition for the hydrogen atoms by oxygen greatly minimizes the production of hydrogen gas to such an extent that it becomes insignificant over the lifetime of tritium decay.

Figure 2 is a plot of the calculated G-value for the production of hydrogen gas from gamma-radiolysis of tritiated water vs $[O_2]$. In the absence of oxygen, the reported G-value is 0.3 to 0.5 molecules of hydrogen per 100 eV of absorbed energy [2]. The extrapolated zero oxygen G-value from this work is 0.31 molecules per 100 eV absorbed, in good agreement with the literature data.

Figure 2. G-value vs [O₂]

4. Oxygen Quenching Rate Law

Using the steady state approximation for hydrogen atoms,

$$\frac{d[H]}{dt} = 0 = eV_{abs} - [H](k_d + k_{rx} + k_q[O_2])$$

$$[H]_{ss} = \frac{eV_{abs}}{k_d + k_{rx} + k_q[O_2]}$$

The rate of hydrogen production is therefore,

$$\frac{d[H_2]}{dt} = k_{rx}[H]_{ss} = \frac{k_{rx}(eV_{abs})}{k_d + k_{rx} + k_q[O_2]}$$

The yield (Y) is defined as the molecules of hydrogen gas produced per eV absorbed. Therefore,

$$Y(H_2) = \frac{k_{rx}}{k_d + k_{rx} + k_q[O_2]}$$

This equation may be put in the linear form

$$\frac{1}{Y} = \frac{k_d + k_{rx}}{k_{rx}} + \frac{k_q}{k_{rx}}[O_2]$$

where the slope of the plot of Y^{-1} vs $[O_2]$ is k_q/k_{rx} , and the intercept is $(k_d + k_{rx})/k_{rx}$.

Conclusion

The failure to observe hydrogen gas in the over-pressure of several DMSBs sorbed with tritiated water prompted an investigation to understand this anomaly. An oxygen quenching mechanism was proposed to account for the lack of hydrogen gas. Oxygen was added to the DMSBs as part of the processing of hydrogenous species in the exhaust of the PPPL Tokamak. Preliminary data from gamma-ray irradiation experiments of molecular sieve with varying amounts of oxygen in the over-pressure showed that as the oxygen content was increased, the hydrogen production was decreased for similar absorbed doses. This oxygen quenching mechanism is responsible for the lack of hydrogen in the gas phase of the DMSBs.

Investigations are continuing to gather better irradiation data and verify the magnitude of the calculated rate constants. Adding oxygen, or air, to a molecular sieve bed that has the potential to produce hydrogen gas from self-radiolysis may at first glance go against safety considerations. But understanding the quenching mechanisms of oxygen in these molecular sieve beds has lead to a safer procedure to store tritiated water for long term recovery.

Acknowledgment

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References

1. Molecular Sieve Type 4A Pellets, Water Adsorption Isotherms, UOP, Molecular Sieve Department, 307 Fellowship Road, Suite 207, Mt. Laurel, NJ, 08054.
2. Mikio Nakashima and Enzo Tachikawa, "Radiolytic Gas Production from Tritiated Water Adsorbed on Molecular sieve 5A", Journal of Nuclear Science and Technology, 24, (1987) 41.
3. R. Tom Walters, "The Mechanism of Self- Radiolysis of Tritiated Water on Molecular Sieve: Gas Phase Hydrogen Isotopic Distribution", *SOFT-96*, 19th Symposium on Fusion Technology, September 16-20, 1996, Lisbon, Portugal.
4. Water migration, from saturated parts of the molecular sieve bed to dryer parts, with a concomitant release of nitrogen gas, has been shown to cause the observed 30 to 40 kPa increase in pressure in the DMSBs. R. Tom Walters and Lloyd Ciebiera, "Water migration on molecular sieve: a mechanism for pressure increase not related to tritium decay in a sealed molecular sieve bed", *in prepration*.
5. The Type A DMSB: US Patent # 5,464,988, Nov. 7, 1995. Inventors: Rich Rossmassler, Lloyd Ciebiera, Francis J. Tulipano, Sylvester Vinson, R. Tom Walters.
6. P. Clark Souers, "Hydrogen properties for fusion energy", University of California Press, Berkeley, 1986, pg. 206.
7. "Calculations on Key Parameters of Type B DMSB", EAD-4718, TD-1827, from H. Murray, February 4, 1994, Internal PPPL Document.

8. Richard V. Carlson, Richard Wilhelm and Kenju Okuno, "Studies of tritiated water absorbed on molecular sieve", private communication, Los Alamos National Laboratory, 1996.
9. V.E. Henrich and P.A. Cox, "The Surface Science of Metal Oxides", Cambridge University Press, 1994, pg. 256.
10. S.W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill Book Company, New York, 1960, page 310.