Isotopic Exchange Over a Platinized Molecular Sieve

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Abstract

Tritium is a radioactive isotope of hydrogen used at LLE as a fusion fuel. The release of tritium to the workspace and to the environment must be controlled and minimized. The classical method of removing tritium from air relies on oxidizing elemental tritium to form tritated water (HTO) followed by capture of the HTO on a molecular sieve drier. This work investigated the ability of platinized molecular sieve (Pt/MS) loaded with either light (H_2O) or heavy (D_2O) water to capture tritium. Deuterium was used as a surrogate for tritium in all the experiments. Hot copper/zinc beds were used to make heavy and light water to preload the Pt/MS bed. Either H_2 or D_2 gas was purged through the water-loaded Pt/MS bed while the composition of the Pt/MS bed effluent bed was monitored. The results showed that D_2 displaces H_2 from H_2O that is present in the Pt/MS bed with high efficiency. H_2 can also displace D_2 from the D_2O present in the Pt/MS bed but this process is less efficient.

1. Introduction

Tritium is an isotope of hydrogen that is used in many experiments at the Laboratory for Laser Energetics (LLE). However, since tritium is a low-energy beta emitter, its consumption via inhalation and its absorption through skin or through water can result in radiological doses that approach state-imposed limits for people consistently exposed to it (1). Additionally, low-level releases to the environment can accumulate and contaminate the environs of LLE. The typical process used at LLE to contain tritium is a method known as "burn and dry" (2). This strategy oxidizes elemental tritium turning it into tritated water, which is then captured on a molecular sieve drier. This method requires the presence of oxygen and leads to the production of large quantities of low-activity water that need to be disposed of.

To enhance the capture of tritium in air without generating large amounts of low-level waste, we pursued an alternative concept. Prior experiments that were focused on testing metals determined that platinum was most effective at exchanging hydrogen out of the hydroxyl group (3). We decided to use the specific platinum molecular sieve Pt/4A MS because Heung and Staack found that Pt/4A MS had the best capacity and kinetics (4). The goal of this research was to further optimize the efficiency of Pt/4A MS. Parameters that affect the isotopic exchange efficiency are temperature, flow rate and the mass of isotope used to displace the isotope absorbed on the Pt/MS. In the experiments we conducted, the Pt/MS bed was preloaded with H_2O or D_2O and the isotopic exchange capabilities were measured by flowing D_2 or H_2 over the bed at conditions using various temperatures and flow rates.
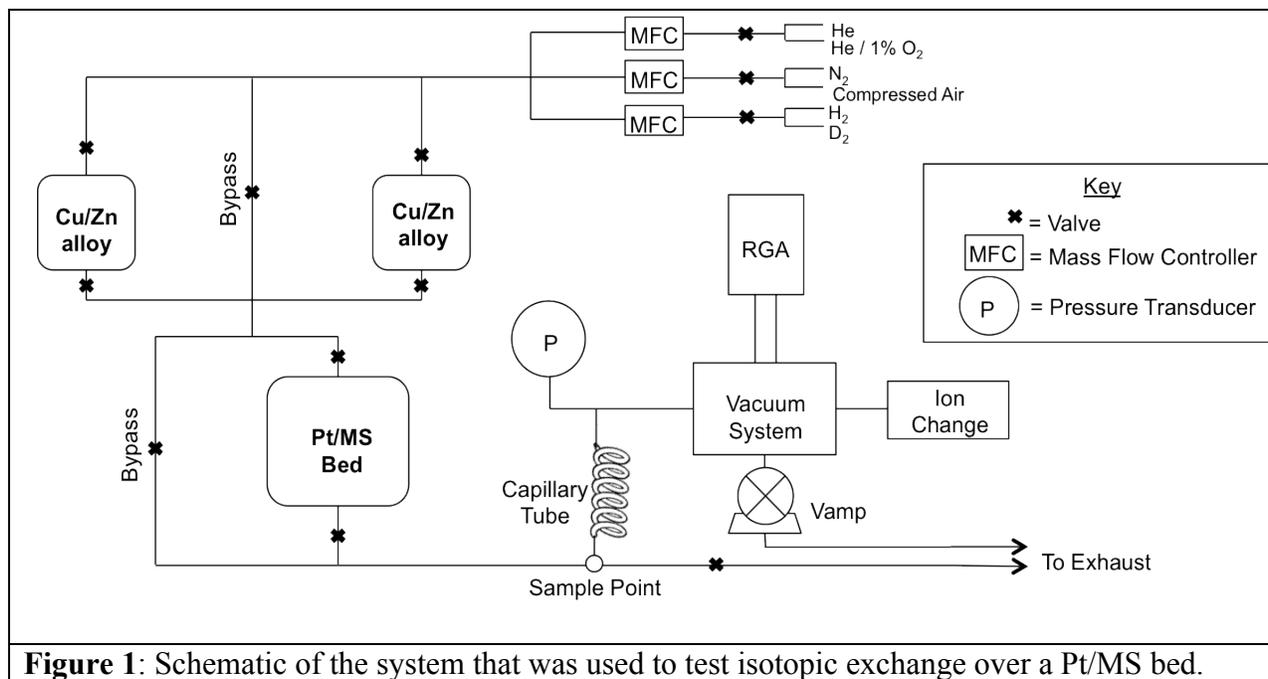
Figure 1: Schematic of the system that was used to test isotopic exchange over a Pt/MS bed.

2. Experimental Layout

A system was designed to test the ability of a Pt/MS bed to conduct isotopic exchange between isotopes of hydrogen. As displayed in Fig. 1, the system comprises multiple gas tanks or

lines (He, He/1% O_2, N_2, compressed air, D_2 and H_2), two Cu/Zn alloy beds, the Pt/MS bed and a residual gas analyzer (RGA) to measure effluent from the beds. Gas is purged into the system from the tanks at specific flow rates controlled by mass flow controllers (MFC). The gases can then be directed using valves into the Cu/Zn alloy beds in order to make H_2O or D_2O or go through the bypass. The H_2O or D_2O can then be loaded onto the Pt/MS bed, preparing it for the test. Various combinations of gases at differing flow rates can then be purged into the Pt/MS bed allowing for isotopic exchange to occur. The effluent from the Pt/MS bed can then be measured by extracting the mixture of gases at the sampling point and sending them to the RGA. The RGA system includes capillary tubing, a pressure transducer, a vacuum system, an ion cage and an amplifier. The RGA is connected to a computer that allows the partial pressures of the gases in the effluent during experimentation to be tracked and recorded. The Cu/Zn alloy beds and Pt/MS bed are kept at elevated temperatures using band heaters that are monitored with thermocouples. Sections of the system are wrapped in electric heating tape to stop the volatile gases such as water from condensing inside the tubing.

3. Experimental Procedure

The process to test whether isotopic exchange over a Pt/MS bed is viable starts with preloading the Pt/MS bed with either H_2O or D_2O. Once the bed is filled with light or heavy water, combinations of gases are flowed into the bed. For example, to test the ability of D_2 to displace H_2O, D_2 was flowed into the preloaded Pt/MS bed at different flow rates with another gas such as N_2 acting as a carrier gas. The influence of temperature on the isotopic exchange rate was investigated by varying the temperature of the Pt/MS bed. The experiments were repeated with H_2 gas flowed into a D_2O-preloaded Pt/MS bed. The RGA was used to measure partial pressures of the effluent of the bed in order to measure what gas was being pushed out of the bed

and what gas remained inside the bed. Since partial pressure data depend on several parameters, the flow rate was calculated using Eqn. (1),

$$Flow\ Rate = \frac{Partial\ Pressure}{Calibration\ Partial\ Pressure} \times Calibration\ Flow\ Rate\ From\ MFC \qquad (1)$$

where the calibration quantities were obtained prior to each run as described in Sec. 4. The isotopic exchange occurring inside the Pt/MS bed is presented as flow rate data [mL/min] versus time or quantity of gas flowed into the Pt/MS bed.

4. Calibration

Before the main experimentation could be conducted, preliminary calibration data was recorded. Gathering calibration data simply means recording the partial pressure readings the RGA produces at specific flow rates for individual gases. Valves leading into the Cu/Zn alloy beds and the Pt/MS bed were shut and the gas was sent through the bypasses directly to the sampling point. Gas was released into the system at a specific flow rate (measured by the MFC) until the partial pressure reading from the RGA leveled out. This partial pressure and the flow rate were then recorded. This enabled partial pressures collected by the RGA during experimentation to be converted into flow rate data using Eqn. (1), even when gases were being trapped inside the Pt/MS bed.

5. Results

The experimentation was based around three variables: flow rate, temperature of the Pt/MS bed and the difference of the abilities of H_2 and D_2 in isotopic exchange. Fig. 2 shows a side-by-side comparison of the gases leaving the Pt/MS bed filled with light water as a function of time as D_2 flows over the Pt/MS bed at two different flow rates. In this figure the temperature of the Pt/MS is fixed at $20^{\circ}C$ and the nitrogen carrier is set to 200 ml/min. The deuterium flow

rate through the bypass is set to 50 ml/min and 100 ml/min in the upper and lower panels, respectively. At time approximately 15 min, when the D_2 flow is diverted from the bypass to the bed, the composition of the downstream hydrogen changes from pure D_2 to ~ 82% H_2 and ~10% HD. Evidently at least 92% of the incoming D_2 displaces H_2 from the water bound to the MS to form an H_2 effluent. This exchange process continues for about 60 min with a D_2 flow rate of 50 ml/min before D_2 appears downstream. Increasing the flow rate from 50 to 100 ml/min improves the isotopic exchange to 92% H_2 and decreases the production of the mixed isotope, HD, to 6%. The D_2 purge gas appears in the effluent about 30 min after the purge is diverted into the bed.

Figure 2: Flow rates as a function of time of H_2, HD and D_2 leaving a Pt/MS bed preloaded with H_2O, for two different flow rates of D_2 injected into the bed [50 ml/min (top), 100 ml/min (bottom)].
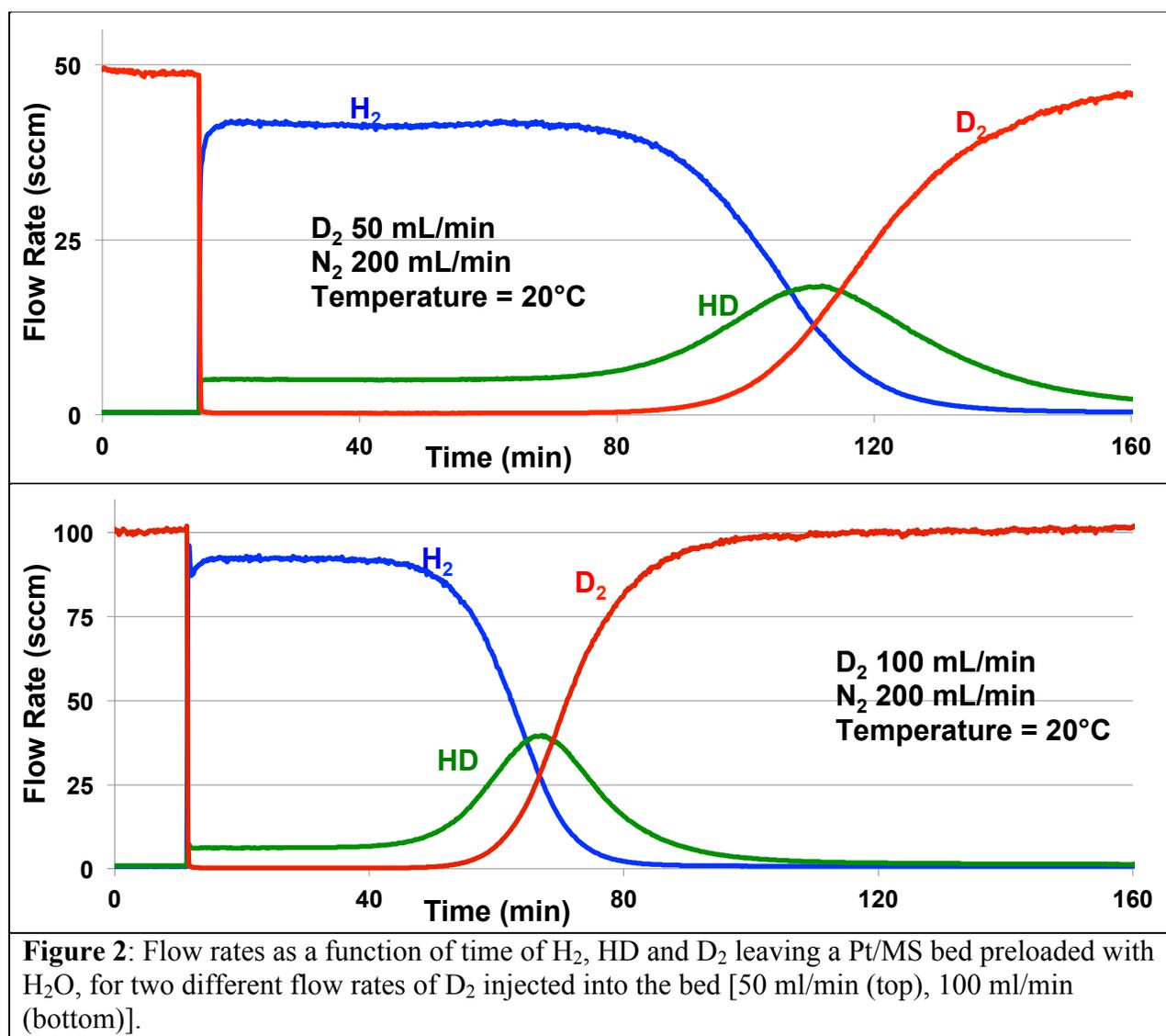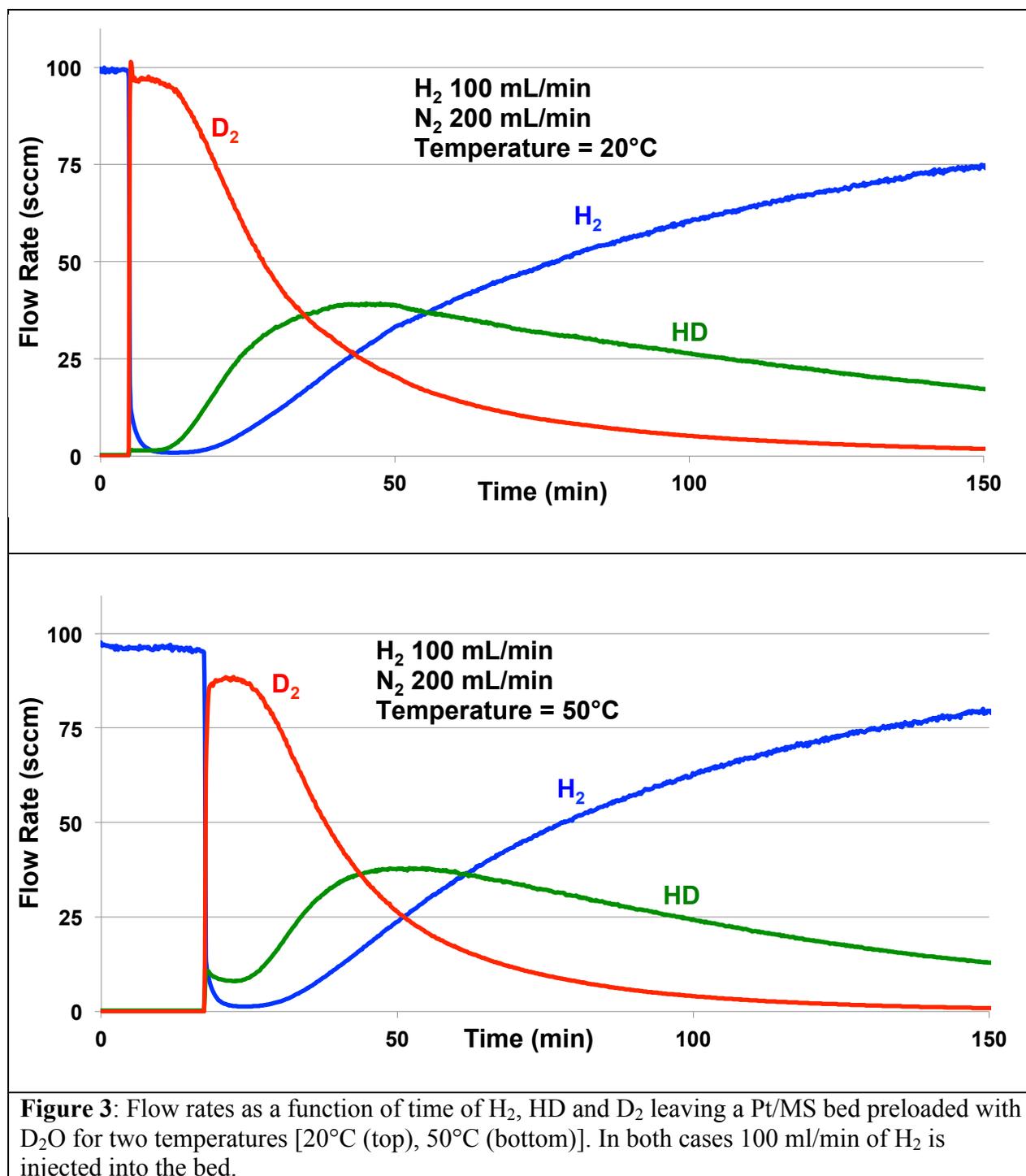
Fig. 3 shows the effect of displacing D_2 bound to a Pt/MS bed preloaded with D_2O when H_2 is flowed through the bed. In this case the H_2 flow rate is fixed at 100 ml/min, the N_2 carrier flow rate remains fixed at 200 ml/min and the temperature of the Pt/MS bed is set to $20^{\circ}C$ in the upper panel and to $50^{\circ}C$ in the lower panel. As in the previous case Fig. 3 shows the evolution of the hydrogen composition with time. When the hydrogen stream is directed into the bed around the 20-minute mark H_2 is observed to disappear from the bed effluent with a concomitant increase in D_2 and HD. This figure shows that while it is possible to displace the heavier isotope with the lighter one, the high displacement effectiveness lasts about 10 minutes. Increasing the bed temperature from 20°C to $50^{\circ}C$ degrades the isotopic exchange effectiveness by encouraging the formation of HD. A comparison of Figs. 2 and 3 shows that the heavier isotope is more efficient at displacing the lighter isotope for a significantly longer time.

Figure 3: Flow rates as a function of time of H_2, HD and D_2 leaving a Pt/MS bed preloaded with D_2O for two temperatures [20°C (top), 50°C (bottom)]. In both cases 100 ml/min of H_2 is injected into the bed.

The displacement efficiency, defined as the percentage of the injected gas that is captured

in the Pt/MS bed, is quantified in Fig. 4, which is obtained by integrating data shown in Figs. 2

and 3 with respect to time. Fig. 4 compares the displacement efficiency using either D_2 or H_2 as

the injected gas, as a function of the amount of injected gas passed through the bed, for the same flow rate and bed temperature. The figure shows that 92% of the D_2 entering the bed is used to displace bound hydrogen. This displacement efficiency continues until approximately 4 liters of gas have been injected into the bed. In contrast, the effectiveness of hydrogen at displacing deuterium drops to 50% after just 2 liters of hydrogen have been injected into the bed. Clearly, the heavier isotope can displace the lighter isotope more efficiently.

Fig. 5 provides the dependence of displacement efficiency of isotopic exchange on injected volume at various deuterium flow rates. It is evident that increasing the flow rate through the bed improves the exchange rate. However, a point will be reached where higher flow rates will cause laminar flow to deteriorate into a turbulent flow. This could counteract the increase in efficiency and may cause the system to become less efficient. This point of conversion can be predicted by the Reynolds number, which is directly related to areal velocity or flow rate and is <10 in our system. Mixing may be important, so it might be that a higher Reynolds number and therefore a certain degree of turbulence could be desirable since this would allow for more surface area for the exchange to occur. The impact of increasing the Reynolds number on the efficiency of the system may warrant more experimentation.
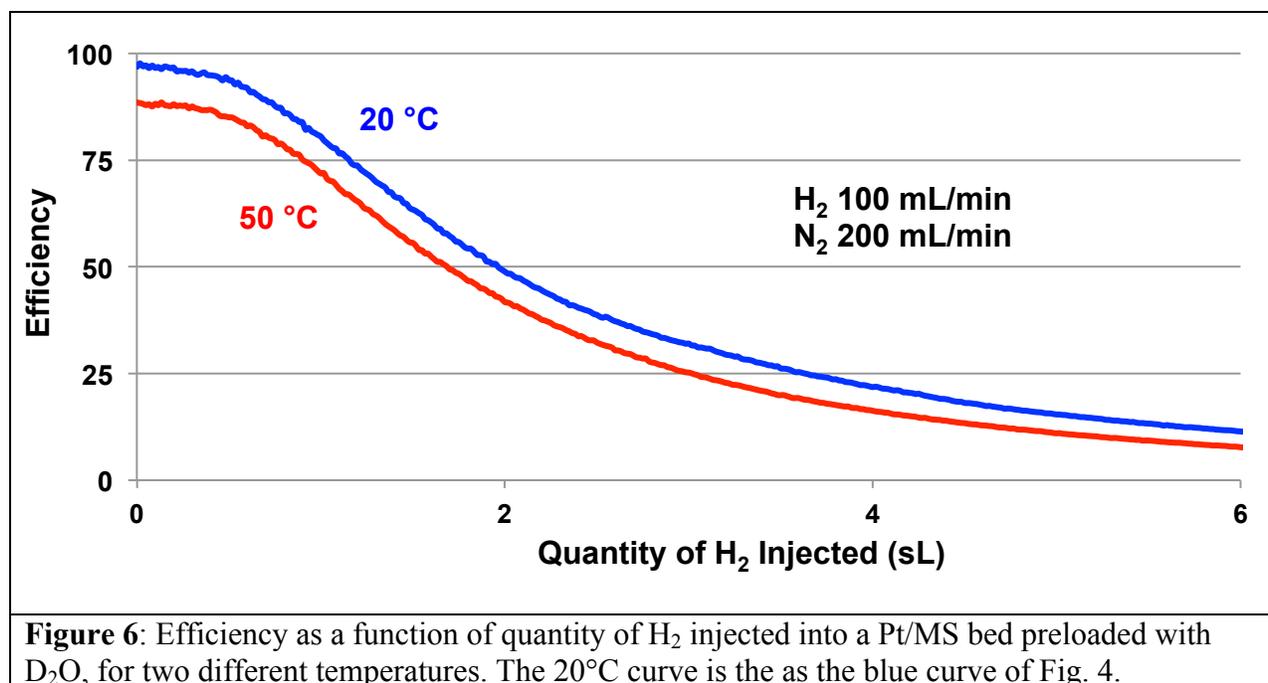
Fig. 6 plots the displacement efficiency with which H_2 is captured in a Pt/MS bed preloaded with D_2O as a function of injected volume for two temperatures. A higher temperature results in a lower efficiency. Similar behavior has been observed when using deuterium as the injected gas.
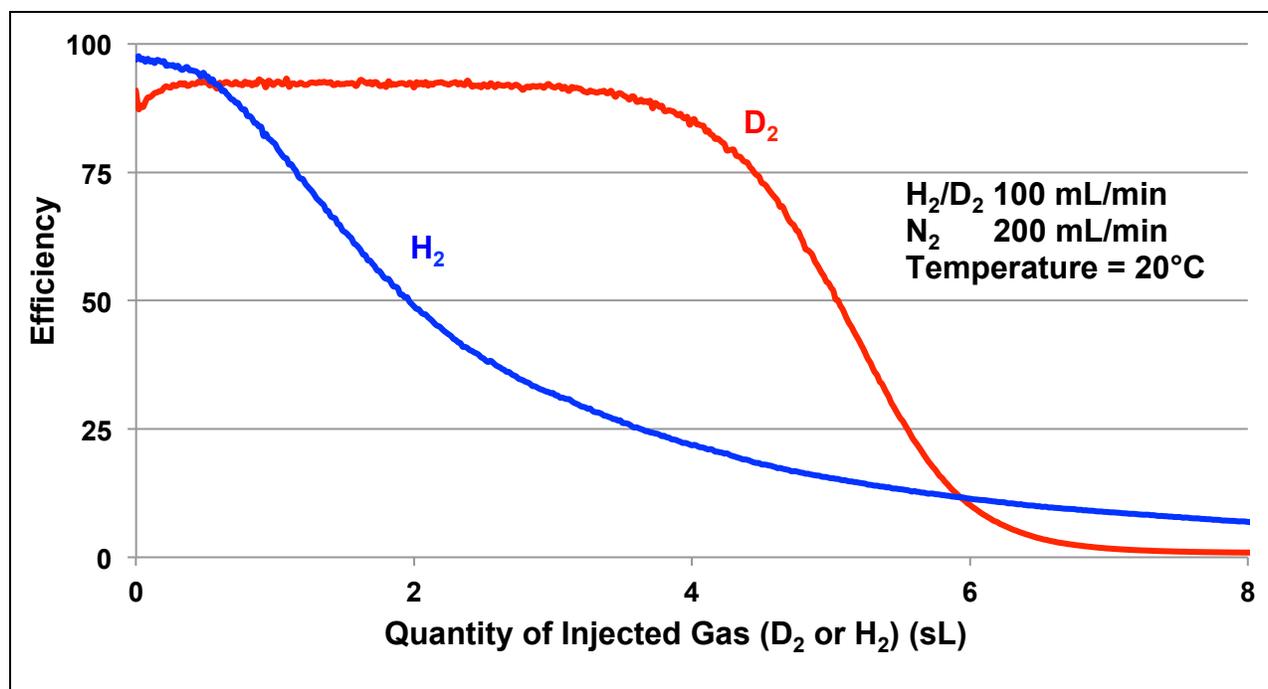
Figure 4: Red curve: displacement efficiency with which injected D_2 is captured in a Pt/MS bed preloaded with H_2O, as a function of the quantity of injected D_2. Blue curve: same for injected H_2 and a bed preloaded with D_2O.
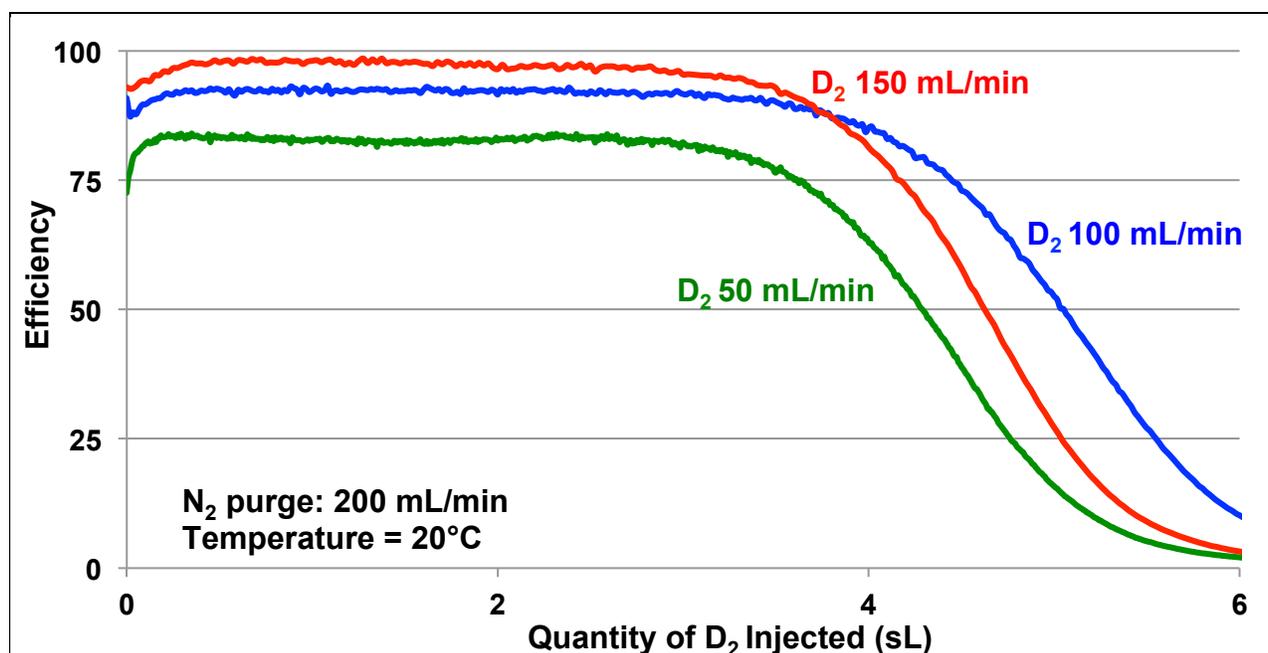
Figure 5: Displacement efficiency of D_2 in a Pt/MS bed preloaded with H_2O as a function of the quantity of injected D_2, for three D_2 flow rates. The curve for 100 ml/min matches the red curve of Fig. 4 (note the different horizontal scale).

Figure 6: Efficiency as a function of quantity of H_2 injected into a Pt/MS bed preloaded with D_2O, for two different temperatures. The 20°C curve is the as the blue curve of Fig. 4.

7. Conclusions

Our experiments afford several conclusions:

1) The heavier isotope of hydrogen is more efficient at displacing bound hydrogen with respect to isotopic exchange inside the Pt/MS bed. Noting that we used deuterium as a surrogate for tritium, it seems likely that tritium would perform in a similar manner.

2) Injecting the gas into the Pt/MS bed at higher flow rates increases the displacement efficiency. Because of this, a system that would implement this technology for tritium mitigation should be designed to withstand high flow rates to optimize efficiency.

3) Isotopic exchange is more efficient at lower temperatures.

A limitation of our study is the relatively small scale on which these pilot experiments were conducted. Large full-scale tritium mitigation systems, which will require Pt/MS beds with far larger capacity, would potentially react differently to the parameter variations tested here. For example, the Reynolds number must be kept low to ensure that the flow through a scaled-up

Pt/MS bed remains laminar. This can be accomplished by decreasing the mean velocity of the gas through the bed as the diameter increases or by simply keeping the diameter constant and increasing the length of the bed. An alternative solution could be to maintain single small beds but assemble them into a parallel mitigation system. The translation of this work to large-scale systems could provide an effective and feasible solution to the problem of tritium containment.

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9. References

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