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Validation of Hydrogen Exchange Methodology on Molecular Sieves for Tritium Removal from Contaminated Water

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INTRODUCTION

Tritium contaminated water is a critical issue for nuclear power reactors as well as research facilities and those working to reduce cold-war era waste. An example includes leakage of tritium into the ground water at Vermont Yankee Nuclear Power Station. It was discovered in recent years that the tritium level in a ground water monitor well reached 293,000 pCi/liter vs. NRC's required level to report of 30,000 pCi/liter. Renewal of the license to continue operations is in question. [1,2] In addition, planned tritium plants for ITER (International Fusion Energy) and IFE (Inertial Fusion Energy) will be required to process huge volumes of tritium contaminated water, some of it highly tritiated water (~50% T). [3] The Savannah River Site (SRS) Tritium Facility processes about 200,000 liters/year of gaseous hydrogen isotopes originated from captured contaminated water. The method discussed later in this manuscript may be beneficial in processing the tritium contaminated water found at these and other sites.

SRS Tritiated Water Process

Molecular sieves (MS) have been used extensively to dry both tritiated and non-tritiated gas streams. The process currently used at SRS for removing the tritiated water vapor from the non-catalyzed molecular sieve beds involves heating the bed and passing the desorbed gas through hot magnesium beds to "crack" the water vapor and convert it to hydrogen isotopes in gaseous form (Equation 1, shown below). The hydrogen isotopes can easily be processed by a hydrogen isotope separation process, such as the Thermal Cycling Absorption Process (TCAP). One significant drawback of this process is that the magnesium bed is consumed by this process and must be disposed as waste. This results in significant annual operating and disposal expenses.

$\text{Mg (solid, hot)} + \text{DTO (vapor)} \rightarrow \text{MgO (solid)} + \text{DT(gas)} + D_2\text{(gas)} + T_2\text{(gas)}$ (Eqn. 1)

Capture and Exchange Method

A novel method has been demonstrated by Savannah River National Laboratory (SRNL) to remove the tritium from heavy water. This process is based on previous studies [4-6] that have shown that the hydrogen in the water trapped on molecular sieves is available for isotopic exchange, which would reduce tritium activity in the subsequent water recovery. Water containing two or more hydrogen isotopes can be transferred to or trapped directly on a platinum-coated molecular sieve (Pt/MS) bed or transferred to the Pt-MS bed. This could lead to the development of reusable tritiated water storage beds that could be processed to remove the tritium without the use of the magnesium beds.

Under ambient conditions H_2 will exchange with D_2 in D_2O adsorbed on Pt-catalyzed molecular sieves, leaving H_2O adsorbed on the molecular sieves. This process, termed the Capture and Exchange Method, is shown in Figure 1. The platinum-catalyzed molecular sieve (Pt/MS) bed then undergoes a two-step process, isotopic exchange and regeneration. The tritium in the bed can be recovered via purging (swamping) with another hydrogen isotope (H or D). As mentioned previously, the capture and exchange method can be used for the removal of tritium from contaminated water. Thermodynamically, oxygen favors the heavier hydrogen isotope; so much more of the lighter isotope is needed to free the heavier isotope from the molecular sieve bed. Enough purge gas can reduce the concentration of the retained heavier isotope to ppm levels while retaining essentially all of the water on the bed. Following isotopic exchange, the Pt/MS bed is regenerated, which typically is accomplished by heating the bed and flowing an inert gas through the bed to remove the adsorbed water.

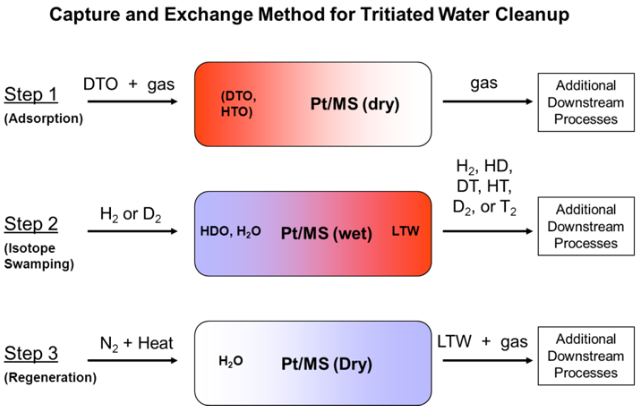
Capture and Exchange Method for Tritiated Water Cleanup

Fig. 1. Schematic of Capture and Exchange Method

DESCRIPTION OF THE ACTUAL WORK

The overall goal of this project was to evaluate the hydrogen isotope exchange performance of a previously identified molecular sieve material. This is accomplished using two techniques of Pt catalysis loading. In addition the percentage of Pt was varied to find the optimal catalyst conditions. A molecular sieve sample was chosen (based on literature research) which exhibits good hydrogen isotope exchange activity, high water adsorption capacity with minimum tritium retention, and good thermostability.

Several-catalyzed molecular sieves were prepared using two different methods, a Pt deposition method and a Pt ion exchange method. Samples of Pt-MS were prepared with 0.5%, 1.0%, 1.5%, and 2.0% Pt catalyst by weight. A total of seven samples have been analyzed to determine the hydrogen isotope exchange efficiency of the various materials. The only sample that was not analyzed was the Pt-MS sample prepared with 0.5% using the ion exchange method. Each of the 7 samples were loaded into the test cell, baked and dried under a nitrogen purge at 350°C, loaded with 15% D_2O by weight, and then exchanged with protium.

During the hydrogen isotope exchange process, the amount of deuterium in the exhaust stream was measured using a micro gas chromatograph and a residual gas analyzer. The use of a micro gas chromatograph allowed for detection of deuterium to the ppm level. This is a significant accomplishment compared to the original scoping studies where the amount of deuterium in the exhaust was only measurable down to 1% (using an RGA) and it was not possible to get an accurate measurement of the concentration of D_2 in the gas phase.

RESULTS

Figure 2 shows the combined graph for the four molecular sieve samples that were catalyzed using the Pt deposition method. The curve associated with the 1.0% Pt-MS sample has a very small increase in the D_2 concentration. The molecular sieve sample with 1.5% Pt had the largest initial spike in the D_2 concentration, and also had the longest plateau region. All four of the samples exhibit a plateau at 2.3% D_2 in the exhaust stream. The fact that the samples with the 0.5% and 1.0% Pt deposited on the molecular sieves did not exhibit a significant D_2 spike can possibly be attributed to an incomplete D_2O loading on the molecular sieves.

Figure 3 shows a combined graph for the three molecular sieve samples that were prepared using the ion exchange method. It is interesting to note that the height of the initial spike decreases with increasing amount of Pt catalyst. In addition, all of the samples plateau at ~2.3% D_2 in the exhaust stream. The D_2 concentration for the Pt-MS sample with 2.0% Pt begins to decrease gradually after roughly 64 L of H_2 exchange gas. The Pt-MS sample that was catalyzed with 1.5% Pt decreases after ~74 L of H_2 exchange gas flowed through the system. After ~76 L of H_2 exchange gas has flowed through the Pt-MS sample with 1.0% Pt, the D_2 concentration begins to gradually decrease.

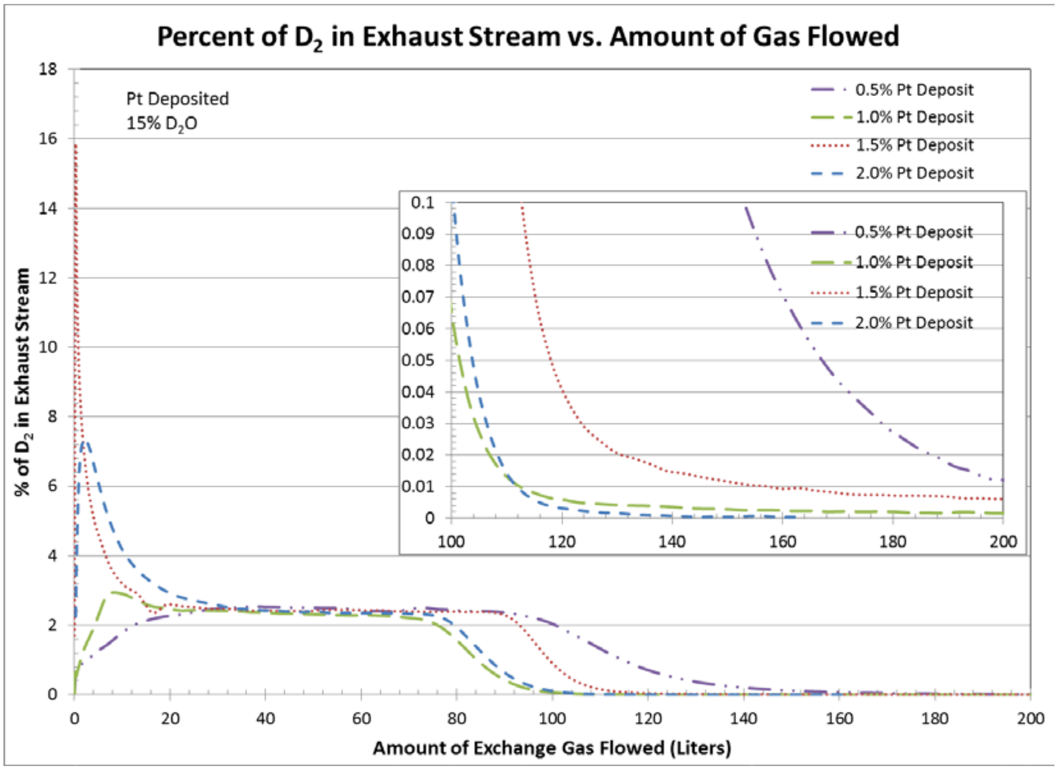

Fig. 2. Percent of D_2 in the exhaust stream vs. the amount of gas flowed for Pt-MS catalyzed using the Pt deposition method.

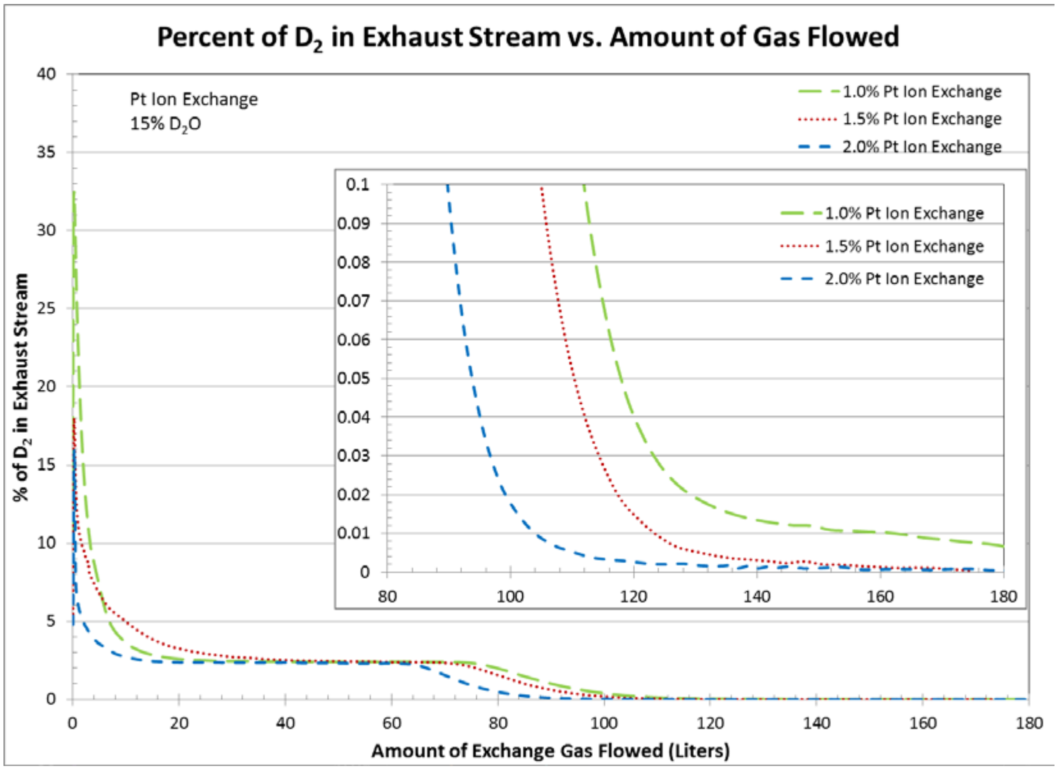

Fig. 3.Percent of D_2 in the exhaust stream vs. the amount of gas flowed for Pt-MS catalyzed using the ion exchange method.

A summary of the hydrogen isotope exchange performance for the six Pt-catalyzed molecular sieve samples is shown in Table I. The criteria used in the evaluation to determine the optimal Pt-MS material for the hydrogen isotope exchange included the amount of H_2 exchange gas needed to reduce the D_2 concentration below 1000 ppm, the concentration of the D_2 in the exhaust stream after 100 L of exchange gas, and finally the concentration of D_2 in the exhaust stream after 150 L of H_2 exchange gas.

TABLE I. Summary of Hydrogen Isotope Exchange Performance

Sample	**Amount of H_2 Exchange gas to get below 1000 ppm D_2**	**Concentration of D_2 after 100 L of H_2 exchange gas**	**Concentration of D_2 after 150 L of H_2 exchange gas**
1.0% Pt Deposit	97 L	699 ppm	28 ppm
1.5% Pt Deposit	110 L	8993 ppm	113 ppm
2.0% Pt Deposit	100 L	912 ppm	5 ppm
1.0% Pt Ion Exchange	112 L	3709 ppm	108 ppm
1.5% Pt Ion Exchange Trial #1	121 L	5180 ppm	n/a
1.5% Pt Ion Exchange Trial #2	106 L	1945 ppm	19 ppm
2.0% Pt Ion Exchange	89 L	155 ppm	10 ppm

The molecular sieve sample that exhibited the best overall performance based on the above criteria was the Pt-MS sample that was catalyzed with 2.0% Pt using the ion exchange method. This sample needed 89 L of H_2 exchange gas to reduce the D_2 concentration in the exhaust stream to less than 1000 ppm. This is nearly 10 L less than the other samples. In addition, the D_2 concentration in the exhaust stream was 155 ppm after 100 L of H_2 exchange gas had been flowed through the system. This represents a hydrogen exchange efficiency of roughly 6 times the next best sample.

The sample that was catalyzed with 1.0% Pt using the Pt deposition method was the second best sample based on the amount of exchange gas that was needed to reduce the D_2 concentration to below 1000 ppm. Considering the fact that the initial D_2 spike for this particular sample was relatively small, this sample may not actually be the most efficient at exchanging the hydrogen isotopes. It is possible that the D_2O loading was less than the desired 15% for this particular sample.

SUMMARY

The results presented have shown the viability of using the capture and exchange method to remove large amounts of tritium from contaminated water. A total of eight Pt-catalyzed molecular sieve samples were prepared using the Pt-deposition and Pt-ion exchange methods and seven were subsequently analyzed to determine the hydrogen isotope exchange efficiency of the materials.

Based on the criteria for the evaluation of the molecular sieve materials, the sample that was catalyzed with 2.0% Pt using the ion exchange method had the highest hydrogen isotope exchange efficiency. Additional testing may be necessary using this particular material.

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