Evaluation of Hydrogen Isotope Exchange Methodology on Adsorbents for Tritium Removal

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The Savannah River National Laboratory has demonstrated a potential process that can be used to remove tritium from tritiated water using Pt-catalyzed molecular sieves. The process is an elemental isotope exchange process in which H_2 (when flowed through the molecular sieves) will exchange with the adsorbed water, D_2O, leaving H_2O adsorbed on the molecular sieves. Various formulations of catalyzed molecular sieve material were prepared using two different techniques, Pt-implantation and Pt-ion exchange. This technology has been demonstrated for a protium (H) and deuterium (D) system, but can also be used for the removal of tritium from contaminated water (T_2O, HTO, and DTO) using D_2 (or H_2).

I. INTRODUCTION

Tritium contaminated water is a critical issue for nuclear power reactors, particularly when ground water is contaminated by leakage. A case on hand is Vermont Yankee Nuclear PowerStation. It was discovered in recent years that the tritium level in a ground water monitor well reached 1.084×10^4 Bq/liter (293,000 pCi/liter) vs. the US Nuclear Regulatory Commission's (NRC) required reporting level of 1.110×10^3 Bq/liter (30,000 pCi/liter).[1,2] Planned tritium plants, such as those for the ITER and LIFE (Laser Inertial Fusion Engine) fusion programs, will be required to process huge volumes of tritium contaminated water.[3]

The process used at the Savannah River Site to remove the tritiated water from non-catalyzed molecular sieve beds currently involves heating the bed and passing the desorbed gas through a hot magnesium bed, which converts the water vapor into MgO and hydrogen (H_2, D_2, or T_2). When the Mg is completely consumed, the Mg bed is removed from the process and disposed of as low level radioactive waste.

Other processes in use or being developed for use to detritiate water include water distillation,[4] catalytic liquid or vapor phase exchange, and combined electrolysis and catalytic exchange.[5] Molecular sieves (zeolites) have been used extensively to dry both tritiated and non-tritiated gas streams. It has been shown in the literature that the hydrogen in the water trapped on a molecular sieve is available for isotopic exchange,[6,7] which would reduce the tritium activity in the subsequent water recovery.

This paper presents the results of the evaluation of an elemental isotope exchange process, referred to as the Capture and Exchange Method. In this process, highly tritiated water (HTW or T_2O) is adsorbed directly on a Pt-catalyzed molecular sieve bed. The Pt/MS bed undergoes a two-step process for removal of the tritium, isotopic exchange and regeneration. The tritium in the bed can be recovered via purging (swamping) with another hydrogen isotope (H or D). Thermodynamically, molecular sieves favor the heavier isotope so an excess of the lighter isotope is necessary to free the heavier isotope from the molecular sieve bed. The use of sufficient purge gas reduces the concentration of the retained heavier isotope to ppm levels while retaining essentially all of the water on the bed. The resultant gas stream (DT, H_2, and T_2) is sent downstream for further processing. Following the isotope exchange, the Pt/MS bed is be regenerated which is typically accomplished by heating the bed and flowing inert gas through the bed to remove the water. The schematic of the capture and exchange method is shown in Figure 1. The results reported here were obtained using hydrogen and deuterated water and additional testing is with tritiated water and deuterium is planned.

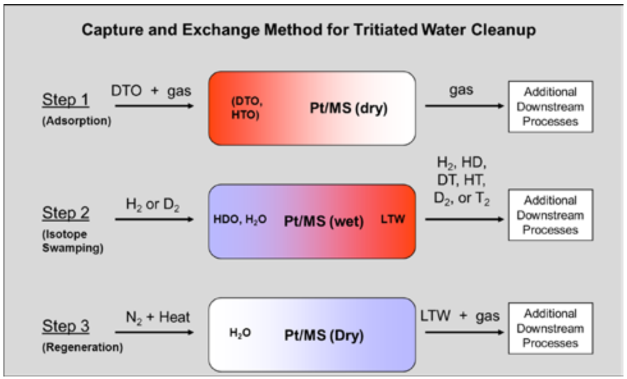

Figure 1: Capture and Exchange Method for Processing Tritiated Water.

The isotope exchange process discussed here is expected to be more efficient than alternative processes, including the current Mg bed technology, and it is a very feasible method for handling HTW. In addition, the capture and exchange method results in the generation of less radioactive waste, resulting in reduced operating costs.

II. EXPERIMENTAL SUMMARY

The development of the capture and exchange process includes the selection of a viable material based on the desired criteria, a material preparation phase, and a material testing phase to determine the hydrogen isotope exchange efficiency.

II.A. Material Selection

Identification of the adsorbent substrate for the catalyzed isotopic exchange process is based on key selection criteria. The material selection criteria for the isotopic exchange column includes high activity for D and T exchange between the water and diatomic gas molecules without drying during the regeneration process, high adsorption capacity, minimal tritium retention, and good thermostability to ensure process life.

II.A.1. Potential Adsorbent Materials to be Considered for the Catalyzed Isotopic Exchange Process

A-type (i.e. 3A, 4A and 5A) and Faujasite (e.g. 13X) molecular sieves are commonly used in radioactive processes. Their alumina-silicate structure is resistant to radiation even in porous form, and is thermally stable which allows these materials to be regenerated for many cycles without significant loss in the adsorption capacity. A-type zeolites have the same framework structure but are formed with different cations. X- and Y- type zeolites share the same Faujasite framework structure, with the SiO_2/Al_2O_3 ratio less than 3 for X-type molecular sieves and greater than 3 for Y-type molecular sieves

II.A.2. Moisture Adsorption Capacity of zeolites

A- and X- type zeolites can adsorb 20 kg moisture per 100 kg zeolite with very low moisture vapor pressure, e.g., < 13.33 Pa (0.1 torr), at ambient temperature.[8] The isotherm curve is very steep for the quantity of moisture adsorbed versus pressure. This is an important feature for the isotope exchange process to minimize drying the bed with the purge/exchange gas. Silica gel and zeolites with high SiO_2/Al_2O_3 ratio tend to have less steep slopes in the moisture adsorption isotherm at low vapor pressure[9-11]. These silica-rich materials are expected to have less tritium retention, however, will lose adsorbed moisture during purging with a dry gas. Removing moisture from zeolite not only reduces isotope exchange capacity, but also results in faster tritium breakthrough, which is an undesirable side effect.

II.A.3 Tritium Retention of Zeolites

Even though most of the adsorbed tritium can be removed by heating to temperatures just below the onset of the structural degradation, molecular sieve beds are typically regenerated for decontamination at lower operating temperatures in a tritium plant. A study that evaluated the tritium retention of 5A zeolite during regeneration using dry air at 320°C, for 2 hours at ambient pressure found that the bed retained about 8% of adsorbed tritiated water, and it was retained during repeated drying using dry air.[12] This portion of irreversibly adsorbed tritium is likely chemically bound tritium, such as hydroxyl groups on the molecular sieve surface. However, this retained tritiated water was mostly removed (Decontamination Factor = 69) when treated with humid air, indicating isotopic exchange activity.

Pure zeolite materials are fine powders of micron size (μm) crystals that are made into various shapes for practical applications. A commercial zeolite product typically contains 70-80% zeolite with the remainder as support and binder material (alumina, clay, etc.) to form pellets, beads or extrudates. A study of mordenite zeolite with and without support showed that the material with the support retained significantly more tritium (up to 1200 times) after regeneration using dry gas at 450°C under vacuum for 48 hours.[13] The irreversible portion of moisture, or surface hydroxyl groups, may be mostly on γ-alumina or silica alumina support while the zeolite powder itself has little or no tritium retention. The recent advances in the catalyst industry for silica bound zeolites are of much interest to this process since it may eliminate entirely the hydroxyl groups from the traditional alumina binder, therefore could reduce the tritium retention to negligible quantities. The measurement of the residual tritium using the finished zeolite product is important to determine the tritium retention properties.

II.A.4 Thermostability of zeolites

The zeolite thermostability is determined by the temperatures at which structural degradation is first observed after 16 hours in dry air: 800°C for 3A, 660°C for 4A, 540°C for 5A, and 710°C for 13X.[14] On the other hand, many zeolites undergo structural degradation in steam at much lower temperatures than those observed in dry air. For example, 13X loses 60% of its structure after treatment in 100% steam for 8 hours at 300°C. During the regeneration process that uses a slow heating rate with a dry purging gas, only dry zeolite is exposed to high temperatures. Therefore, the thermostability of the selected zeolite materials should not be a concern with typical regeneration conditions at 250 - 350°C. As a general rule, zeolites with a higher SiO_2/Al_2O_3 ratio (e.g. Y, ZSM-5, silicalite, etc.) normally have greater thermostability.

II.A.5. Summary of Material Selection

Based on the comparison of the key selection criteria, it was determined that the preferred material that exhibits desired hydrogen isotope exchange properties is a Pt-catalyzed Y-type zeolite.

II.B. Summary of Experimental Testing

The experimental testing consists of two separate activities. The first activity is the preparation of the Pt-catalyzed molecular sieve materials and the second activity is the testing of the prepared materials.

II.B.1. Material Preparation

The Pt-catalyzed molecular sieve materials were prepared using two different methods. The first method was a Pt-implantation method where the Pt was deposited directly on the surface of the molecular sieves (commercially available Y-type zeolite). In the second method, the Pt was ion exchanged with the hydrogen ions in the molecular sieve framework and becomes part of the structure of the molecular sieve. Various formulations (at 1.0% and 1.5% Pt loading) using the two methods were prepared and subsequently tested for hydrogen isotope exchange properties.

II.B.2.Material Testing

The second phase of this project was to determine the hydrogen isotope exchange efficiency of the manufactured Pt-catalyzed molecular sieve materials. The Pt-catalyzed molecular sieve materials were loaded in the experimental test cells and subsequently dried to remove any residual moisture adsorbed on the molecular sieves. The molecular sieves were dried under an argon purge (2 L/minute) at 400°C for 24 hours. The experimental test cells were ¾" stainless steel tubing, 0.1524 m (6 inches) long, with #12 VCR fittings on both ends of the test cell. The test cells were loaded with approximately 20 g of Pt-MS material for each test. Once dried, the Pt-catalyzed molecular sieve material was loaded with D_2O. Protium, H_2, was flowed through the test cell under ambient conditions where the H_2 exchanges with the D_2 in the D_2O leaving H_2O adsorbed on the molecular sieves. During the hydrogen isotope exchange process, the H_2 flow rate was 4.167×10^{-7} m^3/s (25 standard cubic centimeters per minute). Residual gas analysis was used to verify the hydrogen isotope exchange and determine the efficiency.

III. RESULTS

All four of the Pt-catalyzed molecular sieve samples (1.0% and 1.5% Pt deposited on the surface of the molecular sieves and 1.0% and 1.5% Pt ion exchanged) showed clear evidence of hydrogen isotope exchange activity. The results of the isotope exchange testing are shown in Figure 2 and Figure 3. In each of the experimental tests, the hydrogen (protium) exchanges with the deuterium in the D_2O adsorbed on the molecular sieves (15% by wt). In the figures below, there are increases in the mass spectrometer signals for masses 3 and 4 (HD and D_2, respectively) and a marked decrease in mass 2 (H_2). As the H_2 gas is flowed through the Pt-catalyzed molecular sieves, the mass 4 signal decreases over time indicating the exchange of D_2 with H_2 in the adsorbed D_2O. Mass spectrometer data was recorded using an Inficon Transpector 2 and Pfeiffer Prisma mass spectrometers.

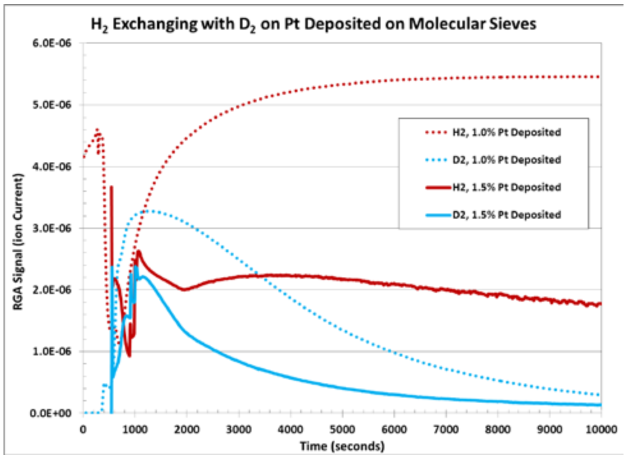

Figure 2: Plots of H_2 and D_2 mass spectrometer signal as H_2 exchanges with D_2 using two compositions of Pt deposited on Molecular Sieve.

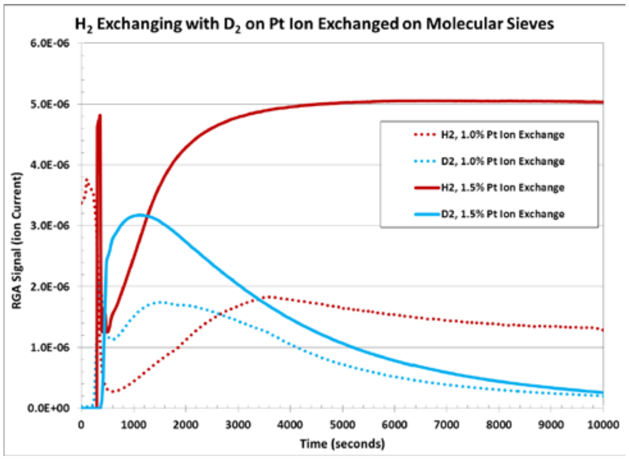

Figure 3: Plots of H_2 and D_2 mass spectrometer signal as H_2 exchanges with D_2 using two compositions of Pt ion exchanged in the Molecular Sieves.

Figure 4 shows the amount of D remaining on the molecular sieves relative to the amount of H_2 that was flowed through the system. This plot shows that regardless of the catalyst level or the method of preparing the catalyzed molecular sieves, the amount of exchange gas needed to reduce the D_2 content below the detection limit is nearly the same. This indicates that the current instrumentation is not sensitive enough to adequately determine the performance difference between the Pt-catalyzed samples. Additional testing is needed (and planned), utilizing methods to increase the sensitivity of the D_2 detection.

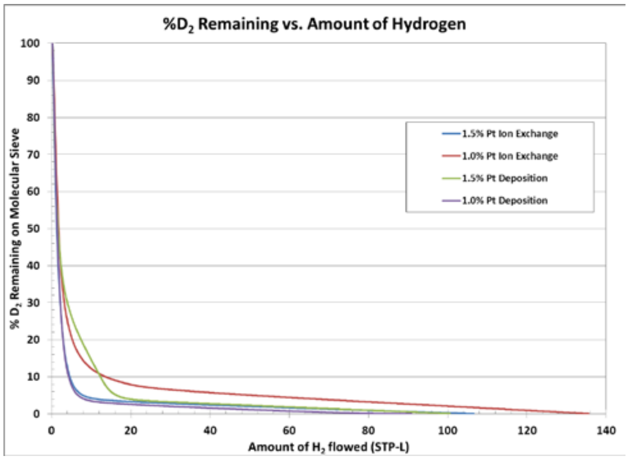

Figure 4: Plot of the amount of D remaining on the molecular sieves relative to the amount of H_2 that was flowed through the system.

IV. CONCLUSIONS

In this project, two methods for Pt-catalyzing the molecular sieve material were successfully developed and experimentally verified. The first method involves depositing the Pt on the surface of the molecular sieves and the second method is an ion exchange method in which the Pt ions are exchanged with the hydrogen ions in the molecular sieve thus becoming part of the structure. The Pt-catalyzed molecular sieves show hydrogen isotope exchange activity for the four samples tested. The molecular sieve samples with the 1.5% Pt exhibited the most efficient hydrogen isotope exchange, based on the length of time for the mass 4 signal to decrease.

Future testing will focus on increasing the sensitivity of the instrumentation for detecting the D_2. This will allow for the determination of the hydrogen isotope exchange performance of each of the materials.

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