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Hydrogen Isotope Exchange Properties of Porous Solids Containing Hydrogen

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Porous solids such as activated alumina, silica and molecular sieves generally contain significant amounts of hydrogen atoms in the form of H_2O or OH even at high temperature and low humidity environment. A significant amount of this hydrogen is available for reversible isotopic exchange. This exchange reaction is slow under normal conditions and does not render itself to practical applications. But if the exchange kinetics is improved this reaction has the potential to be used for tritium removal from gas streams or for hydrogen isotopic separation.

The use of catalysts to improve the exchange kinetics between hydrogen isotope in the gas phase and that in the solid phase was investigated. Granules of alumina, silica and molecular sieve were coated with platinum or palladium as the catalyst. The granules were packed in a 2-cm diameter column for isotope exchange tests. Gas streams containing different concentrations of deuterium in nitrogen or argon were fed through the protium saturated column. Isotope concentration in column effluent was monitored to generate isotope break-through curves. The curves were analyzed to produce information on the kinetics and capacity of the material. The results showed that all materials tested provided some extent of isotope exchange but some were superior both in kinetics and capacity. This paper will present the test results.

L INTRODUCTION

Modern tritium processing equipment at the Savannah River Site (SRS) is enclosed inside gloveboxes to reduce tritium release to the environment. Tritium that escapes the primary containment of the equipment is confined in the glovebox nitrogen atmosphere. This atmosphere is constantly circulated through the tritium stripping system, illustrated in Figure 1, in which the

tritium is oxidized to oxide (tritiated water) and then absorbed in a dryer (molecular sieve bed). This process creates a very dry glovebox atmosphere. The difference in moisture level between the glovebox and the room causes moisture to diffuse into the glovebox atmosphere, increasing the load on the dryer (thereby decreasing the time between dryer desorption cycles). The amount of this "diffuse-in" moisture accounts for about 80% of the total moisture captured by the dryer. When one dryer becomes saturated, flow is switched to a second, identical dryer and the first is desorbed.

The desorbed water containing tritium is then reduced (cracked) using hot magnesium beds and the hydrogen isotopes are separated. The separation step uses about 90% of the isotope separation capacity of the facility. If the moisture diffusion and capture can be eliminated or significantly reduced, the requirement for water cracking and isotope separation will be greatly reduced. Furthermore, if the stripping process does not require the cracking of water, the contaminated solid waste (MgO) can be eliminated.

One way to reduce the moisture diffusion is to operate the glovebox at a moisture level closer to room humidity to reduce or eliminate the driving force for diffusion. With the present oxidation-absorption process, this is impossible, because the dryer keeps the glovebox atmosphere dry. To permit high moisture operation, a new tritium stripping process must be developed. The key is to remove low levels of tritium from the moisture containing glovebox atmosphere without removing the moisture itself. The idea is to use a solid material containing exchangeable protium as the base material. When a gas stream containing tritium and moisture is brought into contact with this material, tritium in the gas phase (elemental or oxide) exchanges with protium in the solid

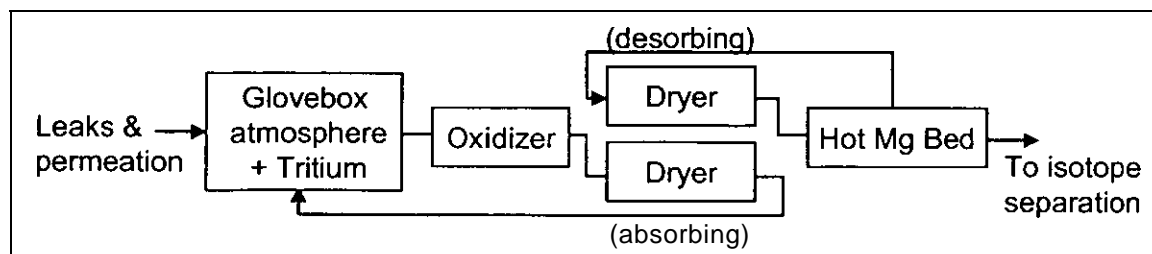


Figure 1. Schematic of Current SRS Tritium Shipper System

phases thereby removing tritium from the gas stream with no impact on the process moisture level. When the exchange material reaches equilibrium with the tritium in the process stream, it is regenerated by reverse exchange (purging with protium). The exchanged tritium is recovered with isotope separation. The exchange concept is illustrated in Figure 2, with exchangeable hydrogen represented as hydroxyl groups.

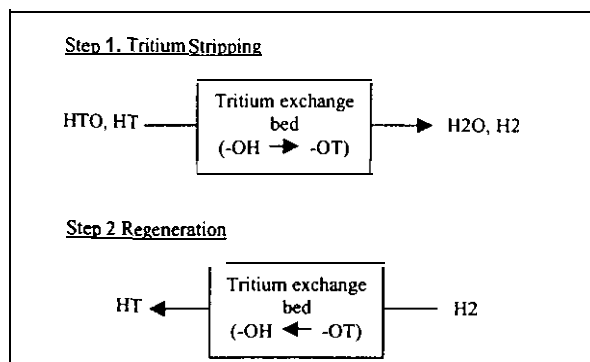


Figure 2. Isotope exchange concept to recover tritium.

II. EXPERIMENTAL

II.A. Sample Preparation

Four materials were examined in this investigation. The first was 1% Pt on alumina in the form of 1/8" spheres purchased from Engelhard. The second sample tested was 1.5% Pt on hydrogen molecular sieve, purchased from Zeolyst International (ZeolystSD02021 Platinum Catalyst). The third sample, also from Zeolyst International, was a hydrogen zeolite without Pt (CBV 780). The fourth sample tested was a nano particle alumina coated with 2% Pt from Nanophase Technologies.

In order to minimize channeling and to produce roughly similar pressure drops across the test column (1.9-cm diameter, 16-cm long), each as purchased sample was modified prior to testing. The alumina spheres from Engelhard were crushed and only 10-20 mesh particles were tested. Both samples from Zeolyst International arrived as extrudate about 6-mm long. These pieces were broken up into pieces of less than about 2 mm. The nano particle alumina from Nanophase Technologies arrived as a fine powder. The powder was mixed with water to make a paste and was dried in open air to make a cake. The dry cake was then broken up to granules between 10 and 20 mesh, soaked with a PtCl_4 solution and reduced. The reduction was performed by flowing hydrogen through the sample at 350 °C for 2 hours followed by 400 °C for 1 hour.

II.B. Experimental Apparatus

The experimental apparatus is comprised of a gas manifold, a U-shape column and an online mass spectrometer. The gas manifold consists of 1/4-inch stainless steel tubes, Nupro® valves, MKS mass flow controllers and pressure transducer. The test column is 1/4-inch diameter, 6-inch long stainless steel, and has a volume of 44 cc. The mass spectrometer is a Prisms Quadrupole Model QMS 200 M 1, Mass range 1-100 am., SEM/Faraday Detector and Gas Tight Ion source with Dual Tungsten Filaments, from Pfeiffer. A schematic is shown in Figure 3.

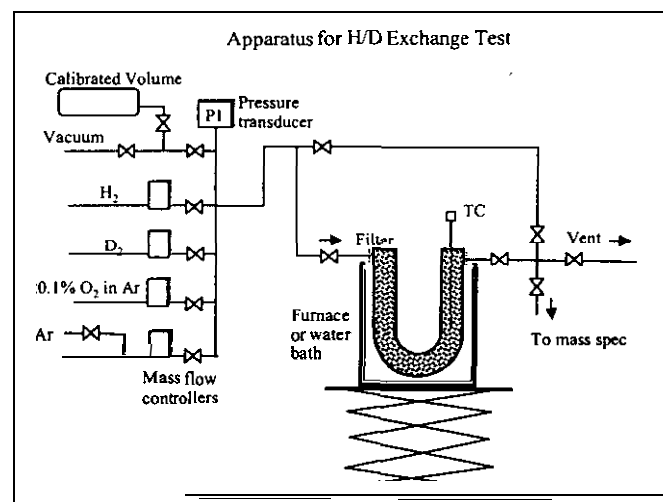


Figure 3. Schematic of hydrogen isotope exchange apparatus

II.C. Experimental procedure

Approximately 40 cubic centimeters of sample were placed in the U-shape test column for D/H exchange testing. The sample was handled in open air and was assumed to be in equilibrium with atmospheric moisture. The tests were conducted at room temperature, except for a few special tests at elevated temperatures. A test, in general, can be divided into three steps. The first step was to saturate the test material with protium by typically flowing 50 sccm via a MKS flow controller through the column. Second, the feed gas was then switched to 50 sccm deuterium. Column effluent was continuously monitored using a Pfeiffer Prisms QME spectrometer with a cycle time of 10 seconds. The deuterium displaced the protium and only protium exited the column until the breakthrough of deuterium began. Low levels of H_2O , HDO and D_2O were also present. As time increased, HD went through spike then decreased to near zero. Later, H_2 concentration decreased to near zero while D_2 increased to near 1000/.. When deuterium breakthrough was complete, the flow was switched back to protium, to

observe the reverse exchange **prope** flies. The test concluded with complete **protium** breakthrough.

II.C. Data Analysis

From the concentration versus time data, the following **can** be **calculated**: the **processing time duration**, average exit **gas composition** and the **amount of gas** exchanged when 5% and 95% of the feed isotope breaks through the **column**. The 50% and 95% are based on the total moles of **protium** in H_2 , HD, H_2O and HDO, or the total mole of **deuterium** in D_2 , HD, D_2O and HDO. A sample **performs well** if it shows a long duration of processing time before 5% of feed breaks through, a short time difference between 5 and 95% breakthrough, and a large amount of exchanged isotope. Figure 4 demonstrates a typical H₂ to D₂ exchange chromatography.

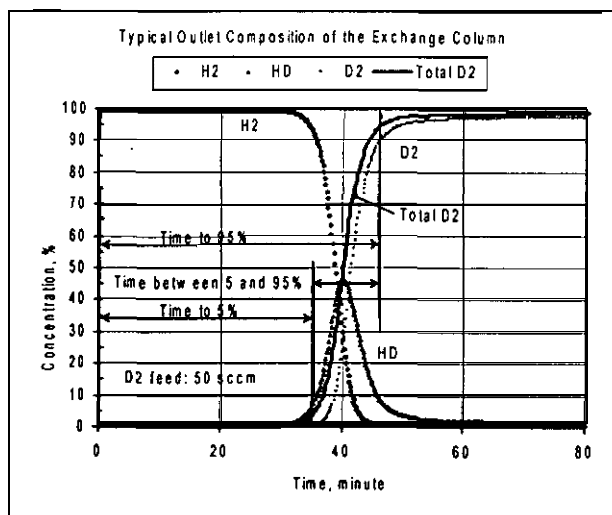


figure 4. Typical outlet composition of the exchange column and data analysis method.

111. RESULTS

III.A. 1% Pt on Alumina

The first sample tested was 1% Pt on alumina. This sample was used **as** a reference material because some exchange data had been previously **generated**.² 5% breakthrough was achieved thirty one minutes **after** the introduction of a 50 seem D₂ stream, corresponding to 2.3 moles of exchangeable hydrogen per kilogram of sample. 95% **breakthrough** occurred thirty-one minutes later, with 3.5 moles of hydrogen per kilogram of sample exchanged. During regeneration, when **protium** is fed into the column to exchange with **deuterium**, the **protium** broke through immediately and took 197 minutes to reach 95%

breakthrough. At this point the gas exchanged was 2.5 mole/kg.

Deuterium, the heavier isotope preferentially remains in the solid phase compared with the lighter **protium**. This makes this type of material **efficient** for stripping **tritium** from the gas phase. During regeneration, when **protium** or **deuterium** is used to exchange out the **tritium**, longer residence time and/or higher temperature are possible ways to improve regeneration efficiency.

III.B. 1.5% Pt on Hydrogen Molecular Sieve

The second sample tested was hydrogen molecular sieve (hydrogen zeolite) containing 1.5% Pt. A total of 7 **deuterium** exchange (D₂ exchanges H₂) and 6 **protium** exchange (H₂ exchanges D₂) tests were run on this sample.

The first test was **run** with **deuterium** feed at 50 seem, the same rate as the alumina tests earlier. The exchange data showed a very long period of no **deuterium** in the exit gas and a sharp breakthrough curve, indicating good performance. At 5% breakthrough the elapsed time was 33.4 minutes (2.85 mol/kg), versus 30.7 minutes (2.26 mol/kg) for the alumina, significant improvement in exchange capacity. The time between 5% and 95% breakthrough is 10.5 minutes **versus** 30.71 minutes for the alumina. This again is a significant improvement. At 95% breakthrough the exchanged isotope is 4.39 mol/kg, versus 3.50/kg for the alumina. The hydrogen molecular sieve showed much higher exchange capacity and exchange rate than the alumina.

The regenerative test was performed under the same circumstances as the alumina sample, 50 seem H₂. A clear but dispersed breakthrough curve was generated, indicating that the heavier **deuterium** prefers the solid phase. It took only 6.5 minutes to reach 5% breakthrough, but 103 **minutes** to 95% breakthrough. At 95% breakthrough the exchanged isotope was 3.52 mole/kg, recovering nearly all of the **deuterium**. This material showed significant improvement over the alumina in regeneration as well,

Subsequent tests under the same conditions demonstrated similar results with a decreasing trend in both capacity and kinetics. The small change might be due to the reduction of water content in the molecular sieve, since the feed gas was completely dry,

An additional test included the addition of 50 sccm **argon** to the 50 seem **deuterium** feed. The change did not seem to reduce the exchange performance, indicating favorable kinetics. The time between 5% and 95%

breakthrough was **actually reduced** from 10 to 5 minutes. More **tests are needed** to confirm this. A similar test was performed **to test** the regenerative properties. The usual flow rate **of 50 seem H₂** was reduced to 25 seem. The increased residence time was expected to reduce the amount of **protium** needed to reach the same regeneration. Time to **5% breakthrough** was 9.9 minutes compared with 6.5 minutes where **50 sccm** was the feed rate. The time to **95% breakthrough** was 175 minutes compared with 96.6 minutes. Both increases are less than 2 fold, indicating reduced rate **requires** less gas to regenerate.

Another test **used** a low concentration of **deuterium** in argon with **a small** amount of oxygen. The feed consisted of 1,48 and 1 seem of **deuterium**, argon and oxygen, respectively. The **run** continued for 185 minutes. There was no **breakthrough of deuterium** for the duration of the run. If the exchange capacity remained at 3 **mol/kg**, at 1 seem, it would **take** 21.2 hours to breakthrough. This run was not long **enough** to show the breakthrough, but it did show the presence of oxygen did not adversely affect the isotope exchange **for at least the first 3 hours**.

An additional test was performed to determine whether a higher temperature of 60 °C would improve regeneration performance. It **produced** a sharper breakthrough curve and shortened the time between 5% and 95% breakthrough by 33 minutes, from 96.6 to 63.9 minutes. **But some of this reduction** might be attributed to the reduced exchange capacity, as indicated by subsequent tests.

To test whether the decrease in sample capacity was due to moisture losses, the sample was removed from the column and exposed to open air for over a week to equalize with room moisture. **The sample** was then placed back **in the column for testing. For the deuterium** test the 5% breakthrough time was 142 minutes! This is **more** than 4 times the **first** run of this sample and close to 5 times the alumina after it went through similar exposure **to ambient moisture. The exchange** capacity at 95% breakthrough was 14 **mol/kg**. This is equivalent to 25 weight percent **of water in the** solid material. This capacity can **be preserved** if the feed stream contains moisture in the 40 or 50% relative humidity level.

III.C. Hydrogen Molecular Sieve without Pt

To illustrate the importance of platinum as a catalyst, a hydrogen molecular sieve without Pt on it was also tested. 57. breakthrough **occurred** immediately on both **the initial and regenerative** exchanges. 95% breakthrough **took 39.1 and 2.8 minutes, corresponding to 0.29 and 0.06** moles of hydrogen exchanged respectively.

III.D. 2% Pt on Nano Particle Alumina

The final series of tests were on **nano panicle** alumina with 2% Pt. **The initial exchange run with 50** seem exchange gas gave 50% and 95 % **D₂** breakthroughs at 24.0 and 31.2 minutes. These times **correspond to 1,27** and **1.41 moles of hydrogen** exchanged. The regenerative run gave 5% and 95 % **H₂** breakthroughs at 4.2 and 65.4 minutes. These times correspond to 0.2 l and 1.04 moles of **h ydrogen** exchanged.

Another test performed **on the nano** alumina included a small amount of oxygen in argon in the feed gas such that if all the added oxygen were converted to water, it would comprise 1 % of the feed. The thought was to help maintain or increase the water content in the solid, and therefore maintain or increase the exchange capacity. The results are almost exact duplicates of the initial tests, except that the **deuterium** exchange capacity actually decreased from 1.4 to 1.1 **mol/g**. The amount of added oxygen might have been too **small** to show any **effect. More tests** would be needed to study this effect.

An additional test was run with a 50/50 **mixture of protium and deuterium** containing small amounts of oxygen and argon. The rates are 24,24,0.26 and 1,03 seem, respective y. **Deuterium** was effective y removed **from** the feed mixture for 26 minutes when 5% of it broke through. The exchange capacity at 95% breakthrough was 0.78 **mol/kg**, or 80% of the exchange capacity when pure **deuterium** was used in **the** feed.

The final test on this sample was a low-flow rate (20 seem) regeneration test with small amounts of oxygen and argon in the feed (O. 13 and 0.52 **sccm**). The shape of the exchange curve is similar to the previous regenerative test at 50 seem with argon and oxygen. The exchange capacity and the amount of **protium** needed for exchange are the same. Contrary to the results from the similar test performed on the hydrogen molecular sieve, the slower flow rate (higher residence time) did not improve the performance.

IV. CONCLUSIONS

Among the 3 types of materials tested for isotope exchange application, **hydrogen** molecular sieve with 1.5% Pt catalyst was found to be the best. It **demonstrated** the best kinetics and had a capacity of up to 14 **moles per** kilogram of material. This was 4 times the capacity of activated alumina, and 10 times of that of nano alumina. Other **zeolites** such as type 4A and 5A will be tested to see if they have similar isotope exchange **properties**.

Besides favorable capacity and kinetics, as shown by the ratio of the time between 5% and 95% breakthrough to the time of 95% breakthrough, Pt coated hydrogen molecular sieve also displayed a large isotopic effect. The heavier isotope prefers the solid phase to the gas phase. This property can be applied in isotopic separation and should be further investigated.

The tests conducted in this work were screening in nature and the conclusions are preliminary. Exchange performances under various feed conditions and temperatures will be further investigated. Other variables that will need future detailed studied include response to moisture level and cycle number. The effect of a nitrogen atmosphere needs to be evaluated due to the potential complication of ammonia formation.

ACKNOWLEDGMENTS

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