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Practical-Scale Tests of Cryogenic Molecular Sieve for Separating Low-Concentration Hydrogen Isotopes from Helium

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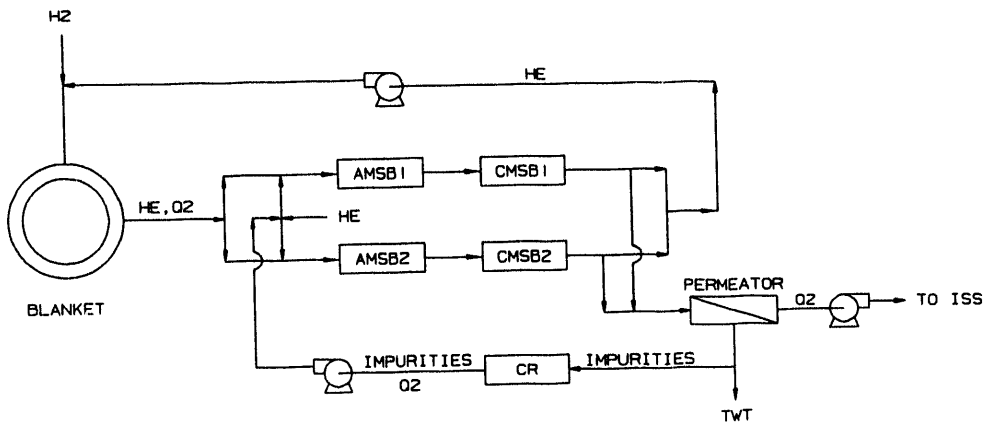
Abstract

Earlier bench-scale work at the Tritium Systems Test Assembly (TSTA) at Los Alamos National Laboratory examined a number of adsorbents for their suitability for separating low-concentration hydrogen (no tritium) from helium. One of the effective adsorbents was Linde 5A molecular sieve. Recently, experiments including tritium were conducted using practical-scale adsorbers. These tests used existing cryogenic molecular sieve beds (CMSB's) which each contain about 1.6 kg of Linde 5A molecular sieve. They are part of the TSTA integrated tritium processing system. Gas was fed to each CMSB at about 13 SLPM with a nominal composition of 99% He, 0.98% H_2 and 0.02% HT. In all cases, for an extended period of time, the beds allowed no detectable (via Raman spectroscopy) hydrogen isotopes to escape in the bed effluent. Thereafter, the hydrogen isotopes appeared in the bed exit with a relatively sharp breakthrough curve. This work concludes that cryogenic molecular sieve adsorption is an practical and effective means of separating low-concentration hydrogen isotopes from a helium carrier.

Introduction

There are a number of cases in fusion fuel processing where low-concentration hydrogen isotopes need to be separated from helium. Usually the helium is a purge gas used to move hydrogen isotopes from one location to another. One of the most notable applications is associated with removing tritium from a solid ceramic breeder. For some designs which have been considered, helium with about 1% protium is purged through the ceramic. The protium exchanges with tritium which has been bred in the solid. The resulting gas composed of helium (~99%), protium (~1%) and tritium (~0.01%) flows out of the blanket and, for further processing, requires separation of the hydrogen isotopes and the helium.

Earlier bench-scale work [1] at the Tritium Systems Test Assembly (TSTA) at Los Alamos National Laboratory examined a number of adsorbents for their suitability for separating low-concentration hydrogen (no tritium) from helium. One of the effective adsorbents was Linde 5A molecular sieve. Practical-scale, tritium-compatible beds packed with this adsorbent already exist at TSTA. They have now been used to separate



Legend

AMSB	Ambient Molecular Sieve Bed
CMSB	Cryogenic Molecular Sieve Bed
CR	Catalytic Reactor
ISS	Isotope Separation System
TWT	Tritium Waste Treatment

Figure 1 Breeding Blanket Processing System Proposed for Ceramic Lithium Blanket Processing

low-concentration hydrogen isotopes (Q_2) from He. The purpose of this paper is to report results from these experiments.

Ceramic Breeding Blanket Processing

Figure 1 shows a system which could be used for processing a ceramic lithium breeding blanket. H_2 is added to He so that about 1% H_2 in He is swept through the blanket. The protium exchanges with tritium held in the blanket material so that the blanket exhaust is composed of He and a mixture of H_2 and HT. This stream may also contain some impurities, so the first processing step is an ambient temperature molecular sieve bed (AMSB) where impurities such as water are collected. Next is a cryogenic temperature molecular sieve bed (CMSB) where the remaining impurities and the hydrogen isotopes are collected. Exiting the CMSB is relatively pure He which is recycled back to the blanket.

When the CMSB is saturated with Q_2 it is taken off line for regeneration and its companion bed can be put into service. A CMSB is regenerated by warming. The Q_2 desorbs and is sent to a Pd/Ag permeator. The permeate from this device is ultrapure Q_2 which can be sent directly to the isotope separation system (ISS). The retentate or "bleed" stream is sent to a shift catalyst bed where reactions such as steam reforming and water gas shift can be used to move hydrogen isotopes from impurities such as CQ_4 and Q_2O to the form of Q_2. This stream of Q_2 and impurities is recycled back through the regenerating CMSB train and over the permeator again. This circulation is continued until all of the Q_2 has desorbed from the CMSB and all of the Q has been recovered from the

impurities. The remaining tritium-free impurities are exhausted to the tritium waste treatment (TWT) system.

Experimental

Within the various subsystems at TSTA exist all of the components necessary to demonstrate the process shown in figure 1. The Fuel CleanUp (FCU) system includes cryogenic molecular sieve beds (CMSB's) which each contain about 1.6 kg of Linde 5A molecular sieve. In the place of AMSB's shown on figure 1, the FCU uses cold traps (freezers). A Pd/Ag permeator existed in the Japan Fuel CleanUp (JFCU) system. TSTA also has an isotope separation system comprised of four cryogenic distillation columns. All of the components are of ITER-relevant size. Tubing interconnects these components so they can be tested as an integrated system.

The actual setup used for this experiment is shown in figure 2. The flows in lines 2 and 5 were controlled at 12.6 and 0.15 SLPM, respectively. The combination of these two flows were fed to one of the two liquid nitrogen-cooled CMSB's. Thus, the bed feed (line 1) flowrate was 12.75 SLPM with a nominal composition (before breakthrough) of 99% He, 0.98% H_2 and 0.02% HT. The gas exiting the CMSB (line 2) was recycled back to the CMSB feed using a metal bellows pump. A mixture of 2% HT in H_2 (line 5) was added to this recycle stream to maintain the desired bed feed composition. The gas composition at both the feed and exit of the CMSB's was monitored alternately using on-line Raman spectroscopy.

After hydrogen isotopes appeared in the CMSB exit, the Q_2 makeup (line 5) was turned

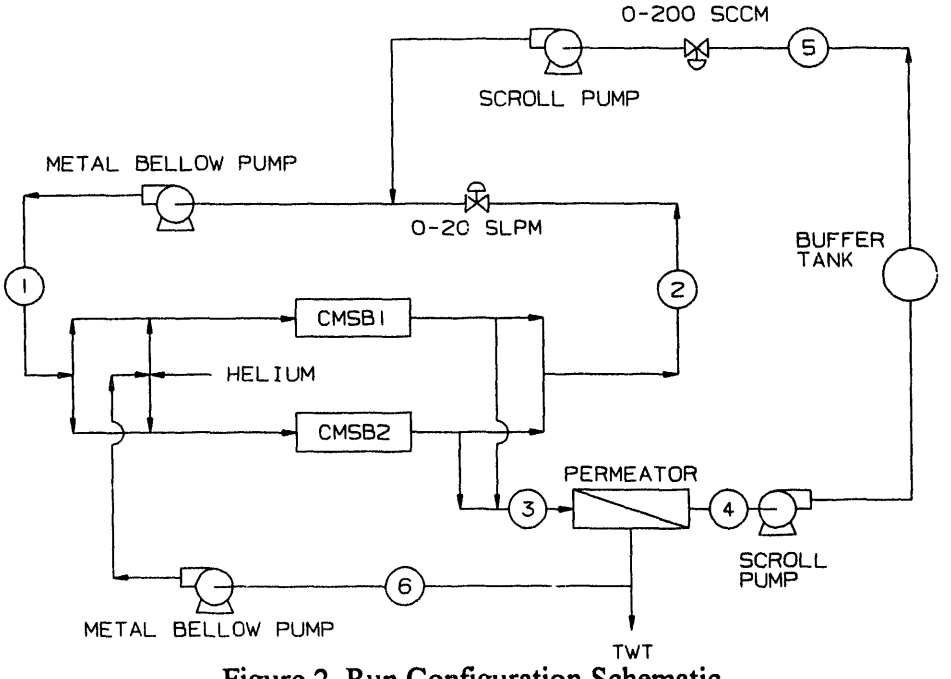


Figure 2 Run Configuration Schematic

off. Circulation was continued until a steady state circulation loop composition was achieved. The equilibrium pressure and composition was recorded to compare to previously determined isotherm values.

After equilibrium data was recorded, the CMSB was warmed and the desorbed gas was sent to line 3 and was processed with the Pd/Ag permeator. The ultrapure Q_2 permeate (line 4) was stored in a buffer volume. The retentate or bleed (line 6) was recirculated back to the CMSB feed. Eventually almost all of the Q_2 was removed from the circulation gas.

Results and Discussion

Three bed loading/regeneration cycles were completed during this campaign. Each cycle took one working day to complete.

For the first test cycle, CMSB1 was loaded. However, due to time limitations, this bed loading was not done in a steady manner. Rather, the Q_2 mixture was rapidly added to the line 1-2 circulation loop. The results from this experiment were not meaningful for "breakthrough" information, but were only valuable for equilibrium information.

On the following two days, CMSB2 and CMSB1 were loaded in a controlled manner. The line 1-2 circulation loop was first filled with He and a flowrate of about 13 SLPM (standard liters per minute) was maintained. To this loop, 0.15 SLPM of the Q_2 mixture was added. Thus, the actual CMSB feed was about 1.15% Q_2. For both of these tests, gas analysis showed no detectable Q_2 (about 100 ppm) at the CMSB exit for an extended period of time, i.e. more than four hours. Thereafter, the Q_2 at the bed exit was observed to rise rather rapidly and continued to rise until the Q_2 makeup was stopped. Then, the composition leveled off at a steady state value.

Table 1 summarizes the equilibrium or isotherm information that can be drawn from these experiments. Using the equilibrium H_2 composition and total pressure, the H_2 partial pressure could be determined and the result is recorded. Using pressure-volume-temperature measurements, the total amount of H_2 added during a run was calculated and is listed. This value was divided by the approximate weight of sieve in each CMSB to determine the equilibrium bed loading and this result is given in Table 1.

For comparison purposes, the Langmuir isotherm equation determined for Linde 5A sieve in [1] was used to calculate the bed loading that should be expected. These values are much larger than the ones determined from the practical-scale beds. However, this is not entirely unexpected. The beds used in this work have been in place and in tritium service for about eight years. There is uncertainty regarding the amount of sieve originally loaded into these beds and even more uncertainty after years of service. These larger beds were not designed for high temperature regeneration and residual material such as water on the beds would reduce their capacity. Thus, it is not surprising that the fresh, well regenerated

sieve used in [1] would have a higher capacity. Due to these uncertainties regarding the state of the practical-scale CMSB's, no definitive conclusions should be drawn from these data.

Table 1 Equilibrium Results Summary

Run	Bed	H_2 Conc. (%)	HT Conc. (%)	T_2 Conc. (%)	Total Pres. (torr)	H_2 Partial Pres. (torr)	H_2 Adsorbed (Std. L)	Bed Loading (this work) (Std. L H_2/gm Sieve)	Bed Loading Extrapolated from [1]
1	CMSB1	1.82	0.055	ND	1159	21.1	56.3	35.2	51.7
2	CMSB1	1.68	0.030	ND	821	13.8	44.5	27.8	45.8
3	CMSB2	2.56	0.069	ND	672	17.2	45.7	28.6	49.0

Note: ND means None Detectable

Breakthrough curves for the second CMSB1 loading (run 2) and the CMSB2 loading (run 3) are shown on figures 3 and 4, respectively. Shown are the total H_2 composition at the bed exit and the bed exit pressure as a function of time after initiation of Q_2 addition. Also available from Raman analysis and shown on figures 3 and 4 are the fractions of H_2 in the "odd" and "even" spin states. An examination of the first part of the breakthrough curves reveals that the "even" H_2 breaks through first. Intermittently, analysis was also performed for HT and T_2, but these values were just at or below the Raman limits of detection.

As shown on figures 3 and 4, runs were conducted at different total pressures. This was by design so that the beds were exposed to different Q_2 partial pressures. Prior to breakthrough, the pressure for run 2 increased from about 645 to 660, while the corresponding values for run 3 were about 450 to 465 torr. The feed composition was the same for both runs, so the partial pressure difference between the runs was simply proportional to the total pressure. At a higher partial pressure, beds should load with more Q_2 and breakthrough should be delayed. Indeed this was observed as the lower pressure run 3 (figure 4) broke through after about 176 minutes, while the higher pressure run 2 (figure 3) broke through after about 280 minutes.

The single most remarkable result from these experiments is the relatively long time during which there is no detectable H_2 at the bed exit. A consideration in adsorber design is the "length of unused bed". This is a measure of the amount of unloaded adsorbent remaining when the adsorbate appears at the bed exit. It is apparent that for this work the length of unused bed is relatively short.

Further scrutiny of figures 3 and 4 discloses that the breakthrough curves have two distinct slopes. The first and more rapid rise has the shape that would be expected for a "once-through" experiment where the bed exhaust is not recycled back to the feed. However, this experiment does recycle the exhaust back to the feed. As breakthrough progresses, the recycled gas contains increasing amounts of Q_2 that combines with the constant flow of Q_2 makeup. The result is that the Q_2 composition or partial pressure in the bed feed increases. This, in turn, increases the equilibrium loading that the CMSB

adsorbs. The second, less steep slope on figures 3 and 4 is indicative of this regime where the entire length of the bed is being loaded to higher adsorbed compositions.

Apparent on figures 3 and 4 are two distinct slopes for the total system pressure curves. The first, less steep increase, coincides with the period before H_2 appears at the CMSB exit. This increase is interpreted to be due to additional helium filling the loop as it is being displaced from the CMSB by Q_2. After breakthrough, the total pressure increases more rapidly since the Q_2 makeup is no longer all being adsorbed. When the Q_2 injection is turned off, there is a brief equilibration period before the pressure reaches a steady state value.

The pressures used to determine the equilibrium data reported in Table 1 are not shown on figures 3 and 4. Following the period of data collection shown on those figures, the circulation flowrate was decreased substantially so that pressure drops throughout the loop were minimal. Otherwise, a significant pressure drop would exist across the CMSB and a bed loading would vary along the length of the bed. The equilibrium pressures and compositions were measured after equilibration at the reduced flowrate.

During run 2 there is a gap in the H_2 data between 200 and 260 minutes. At that time the Raman spectrometer was tuned to observe the HT concentration. There was none detectable. This indicates that HT did not breakthrough before H_2. Indeed, this is the expected result based on chromatography experiments which indicate that the order of elution for hydrogen isotopes is H_2, HD, HT, D_2, DT and T_2.

Conclusions

The most remarkable conclusion from this work is the relatively long period of time during which no Q_2 was observed at the exit from the CMSB during its loading. This indicates that, even at low partial pressures (10-20 torr), liquid nitrogen-cooled, Linde 5A molecular sieve has considerable affinity and capacity for Q_2. It is, therefore, concluded that this material is appropriate for separating low concentration Q_2 from He such as might be encountered when processing the effluent from a ceramic Li breeding blanket. This confirms that the process shown in figure 1 is a workable solution for this application. There was nothing unexpected encountered in this work due to the presence of tritium compared to previous non-tritium experiments. No quantitative conclusions can be drawn from this work regarding equilibrium loading values for the adsorbent tested, but the numbers calculated are qualitatively in agreement with earlier experiments which were better suited for making these measurements.

References

[1] Willms, R. S., "Cryogenic Adsorption of Low-Concentration Hydrogen on Charcoal, 5A Molecular Sieve, UOP S-115, ZSM-5 and Wessalith DAY", Presented at the 15th IEEE Symposium on Fusion Engineering, Hyannis, Massachusetts, October 11-15, 1993.

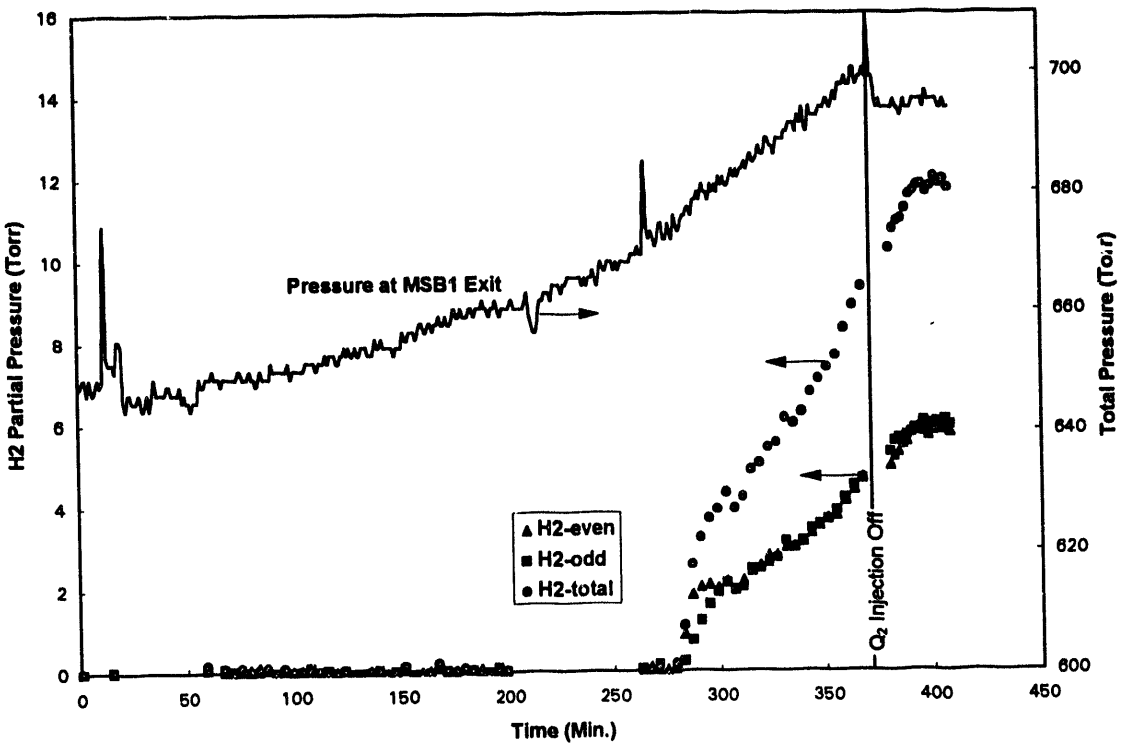


Figure 3 Breakthrough Curve for Second CMSB1 Loading (Run 2)

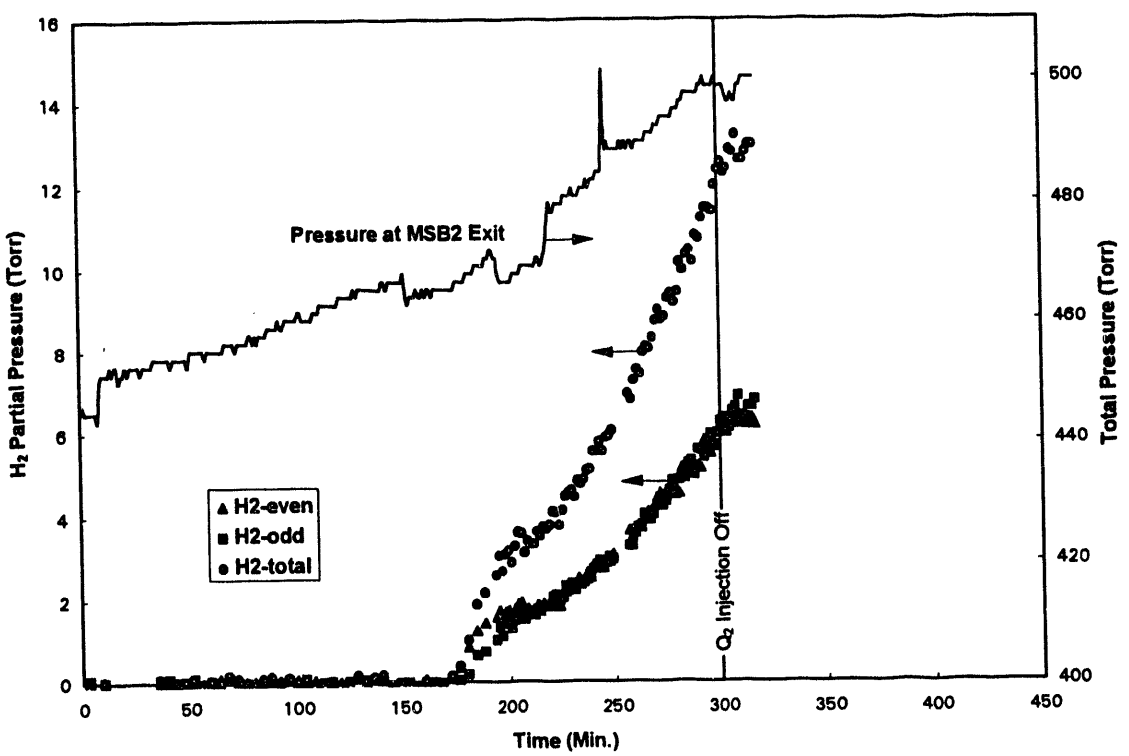


Figure 4 Breakthrough Curve for CMSB2 Loading (Run 3)

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