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Evaluation and mitigation of tritium memory in detritiation dryers

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Abstract

In atmospheric detritiation, and other tritium processes, tritium is adsorbed on zeolites (molecular sieves) in the form of tritiated water. Regeneration removes almost all the physically adsorbed water, but a proportion remains permanently in the zeolite and binder structure as chemically bound water or hydroxyl groups. Exchange between adsorbed water and bound water means that tritiated water is retained in the structure after regeneration. At the end of its life, the zeolite therefore constitutes a tritiated waste. Furthermore, if an atmosphere detritiation dryer (ADD) gets highly contaminated from a tritium spill, retained tritium contaminates both the small amount of vapour leaving the bed during the next drying cycle, and the water produced in the subsequent regeneration. This report first describes experiments to measure the tritiated water retained in a 5A zeolite bed after standard regeneration treatments, and then investigates strategies to mitigate the effect: more thorough regeneration and isotope swamping or elution. The effect of zeolite aging after thermal cycling is also seen. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

1.1. Problems caused by tritium retention in ADDS

Tritium handling laboratories and fusion power plants need systems to remove tritium from room air, to limit tritium emission; and from inert gases, to clean up glove-box atmospheres. The usual approach is to oxidize the tritium using a catalyst and then adsorb the resulting tritiated water vapour in a dryer bed containing zeolite (molecular sieve). There are two or more beds for continuous operation; each bed in turn is regenerated, usually with hot gas. Such a temperature-swing adsorption process is a mature industrial technology by which gas streams can be dehumidified down to dew points as low as 193 K. If the tritium content of the air humidity is constant, the decontamination factor for tritium is the ratio of the humidities of the inlet and outlet gases. However, if a bed sees a high activity of tritium, such as that produced by a tritium release into the room, it is found that during the following adsorption cycle the decontamination factor using that bed is poorer than the ratio of inlet and outlet humidities. This 'memory effect' is caused by the retention of a fraction of the tritiated water in the zeolite, which is not removed by normal regeneration. In fact, the water vapour in the outlet gas has a specific activity (Bq/kg water) close to that of the water adsorbed during the previous cycle [1]. In extreme cases, the memory effect could require to put out of service the atmosphere detritiation system. Another reason for lowering tritium retention is to reduce the activity of the spent zeolite in radioactive waste disposal.

1.2. Interpreting tritium memory data

The separation factor between HTO and H_2O is independent of the isotopic abundance of tritium. This has been confirmed by Ono et al. [2] for measurements covering four decades of HTO concentration. It means the amount of HTO adsorbed or retained in a bed is

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proportional to the HTO/H_2O ratio in the feed. This means that experiments using trace levels of tritium can be used to predict the behaviour of an ADD at much higher tritium concentrations.

Experiments to measure the HTO and H_2O release from dryers are more difficult than one would imagine. One encounters large errors due to the effect of moisture on ionization chambers, inefficiency in bubblers and inaccurate dewpoint measurements. Confusing results have given rise to misleading interpretations, based on a number of misconceptions:

- Confusion about isotopic separation effects. These are not important in dryers. Unlike in a chromatography column, the water in a dryer is adsorbed only once, so the maximum separation effect is set by the separation factor, which is only about 1.1 for HTO/H_2O in 5A zeolite at the typical adiabatic adsorption temperature [2,3]; HTO being preferentially adsorbed. Confirmation of this assertion comes from the careful measurements of Tanaka et al. [4]: they showed that the H_2O/HTO ratio in vapour exiting a dryer was very close to that of the feed, except for a transient rise in H_2O/HTO at the 'elbow' of the breakthrough curve, with a maximum value given roughly by the separation factor. Even this small separation may be an exaggeration, for it is not clear whether the results are compensated for the separation factor in evaporation of HTO in the inlet bubbler, which would work in the same direction. Chromatographic effects could possibly multiply the separation factor in the case of inefficient adsorption of water vapour by the bed.
- Confusion about 'roll-up' of HTO by H_2O [5]. Competitive adsorption between HTO and H_2O on a 5A molecular sieve is well described by a binary Langmuir isotherm [6]. In an initially clean bed, this always leads to a solute propagation characterized by a plateau of pure light component (H_2O) higher than the feed concentration (roll-up) which separates the leading front of the light component and the rear mixed front of both components. Roll-up of the heavy component (HTO) must be stated on physical basis implying the violation of the requirement that the initial state must propagate ahead of the feed state [7]. Of course, the HTO may exchange with H_2O vapour behind the adsorption front, but this is elution, not roll-up.
- The lack of understanding of tritium retention: it was assumed that the amount of (tritiated) water retained could be simply calculated from the adsorption isotherm applied to the conditions of regeneration. However, Toci et al. [8] showed that, apart from this reversibly adsorbed water, water is also retained more strongly by chemical bonding: it does not show up on the adsorption isotherm because it is never released during normal regeneration. This irreversibly retained water becomes contaminated with tritium, due to exchange of whole molecules, hydroxyl ions, or hydrogen atoms with tritiated water in the feed. During the next adsorption cycle, the same exchange process causes tritium contamination of the product stream. The chemical binding of the water takes place at various sites both in zeolites themselves and in the binders added for making pellets. After a thorough dryer regeneration, most of the tritium retained in the adsorbent is in chemically bound water. However, the paper of Toci et al. concentrated on the limits to reducing tritium retention, and not on tritium retention in practical ADDs, where regeneration may be less complete. In this case the retention predicted by the adsorption isotherm could dominate.

1.3. Objectives

The first aim of this work is to measure the total retention of tritium in a model adsorption bed operated under realistic regeneration conditions. The study is focused on a 5A zeolite which, together with 4A and 13X zeolites, is usually employed in dehumidification processes for industrial as well as nuclear applications, and is the reference drying material in the ITER design.

The second aim is to see how varying the regeneration procedure according to three different strategies can reduce the tritium memory effect in an ADD.

The first strategy is to increase regeneration time or temperature, still using dry air.

The second strategy is to add plain water vapour to the regeneration gas. The effect of removing the tritiated water is commonly called isotope swamping, although in fact it is a combination of isotope swamping and exchange of whole water molecules i.e. elution. This idea was proposed by Dombra et al. [9] who showed by numerical simulation that it should greatly improve the detritiation factor of an air detritiation dryer. However, being unaware of the irreversible water retention, they based their calculations of water retention on adsorption isotherms, so the predictions must be over-optimistic. An attempt to measure the effect on the performance of a full-scale dryer [3] was frustrated by a confusing control test result (after which the dryer was decommissioned). Water injection during dryer regeneration was shown to elute tritiated water. But the rate could not be accurately assessed: the gas recirculated through the bed and a condenser at 283 K, and the rate of tritium removal was limited by the fraction of water removed during each recirculation, not by the elution rate.

The third strategy we examine is to remove tritium by isotope swamping using a gas mixture containing hydrogen.

In this paper 'Q_2O' means 'quantity of partially tritiated water', i.e. (H_2O + HTO), with units of kilograms, whereas 'HTO' refers to the radioactive part of the water, expressed in Bq.

2. Experimental

2.1. Apparatus

The apparatus (Fig. 1) was installed in the Low Level Tritium Laboratory (LLTL) of the Joint Research Centre-Ispra Site. The adsorbent bed consisted of a 316-stainless steel cylindrical tube (24 mm i.d. × 100 mm length) filled with 1/16″ pellets of 5A zeolite. Glass wool end-plugs prevented the gas stream carrying away zeolite particles. The bed was vertical; gas flowed downwards during adsorption and regeneration. Heating tape, wound around the bed, was capable of heating the bed at the rate of about 10 K per minute, up to a maximum of 723 K.

All pipes and valves of the apparatus were of 316 stainless steel and heated to about 343 K to avoid condensation and to reduce adsorption on the internal surfaces. Dry chromatographic-purity gases were supplied via MKS mass-flow controllers. Capacitance-type hygrometers from Michell Instruments, with Cermet sensors, and Druck capacitance pressure gauges (0–0.3 MPa) monitored the inlet and outlet of the bed. Humid air for the adsorption step was supplied by flowing dry chromatographic air through either a single bubbler containing plain water, or through an identical bubbler containing tritiated water of specific activity 4.625 GBq kg^{-3} (0.125 Ci l^{-1}).

The bed is very small compared to practical ADDs. However, the small size enables us to capture all the HTO which escapes and to measure it precisely by liquid scintillation counting. Factors which could affect scale-up of the results are channeling, dead-volumes and heat exchange between bed, walls and the surroundings. 24 mm was calculated to be the minimum diameter which can be used with 1/16″ pellets without significant effects from gas channeling along the walls. Dead volume effects were shown to be unimportant by the control test described below. Despite the small size, adsorption in the bed was nearly adiabatic, because the heating tape also functioned as a thermal insulator.

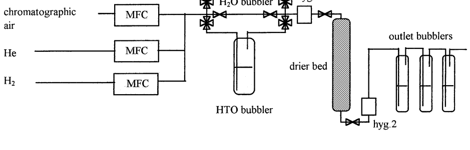

Fig. 1. Schematic representation of the experimental apparatus for evaluating performance of a detritiation dryer.

2.2. Procedures

After filling with 5A zeolite, the bed was initially activated at 623 K for 48 h, using chromatographic dry helium flowing at 2.23×10^{-2} mmol s^{-1}. Activation reduced the mass of the pellets by about 10% from 30.4×10^{-3} kg to a final weight of 27.2×10^{-3} kg.

The change in weight of the inlet bubblers indicated the amount of water passed during a step: dividing by the volume of air used, we calculated the dewpoint; it was always close to 293 K. This procedure was more accurate than using the hygrometer at the bed inlet to measure high humidities: it gave irreproducible results at high dewpoints (>about 273 K).

The hygrometers worked well at low dewpoints: the amount of water vapour breaking through the bed during adsorption steps was estimated by time-integrating the outlet water vapour content and multiplying by the air flow-rate.

The amount of tritium passed during a step was determined by combining the weight data with specific activity measurements of the bubbler water before and after the step. Specific activity was measured by scintillation counting: three samples of 0.5 ml were drawn from the bubbler water using an automatic pipette, injected in a vial with 5 ml of Packard 'Ultima gold' liquid scintillation cocktail, and counted for 10 minutes in a Tri-Carb 1900 TR counter from Packard-Canberra. The counter was calibrated regularly using quenched tritium standards.

Tritiated water vapour escaping the bed during any step was collected by bubbling the outlet stream through a triple bubbler initially containing plain water. Collection efficiency was better than 99%, for the final bubbler never contained more than 1% of the total tritium collected.

Following experience coming from ADDs installed in CANDU reactor generating stations [10], regeneration was done in the co-current mode allowing also the plant to be simpler. The regeneration gas was either dry gas (chromatographic air or He + 3 vol.% H_2, specified <1 ppm water), or chromatographic air humidified by passing through a plain water bubbler at ambient temperature. The humid air, and the helium/hydrogen mixture, served to investigate the effects of isotopic swamping on the tritium retention after regeneration. When the helium/hydrogen mixture was used, a commercial bubbler set was added to the outlet. This incorporated air injection and a catalytic oxidation furnace to convert HT to HTO for collection in the subsequent bubbler.

2.3. Description of tests.

Table 1 shows the standard operating conditions for the tests. Most tests used a regeneration temperature of 593 K. This is the characteristic temperature of the system air – water vapour – 5A zeolite, according to the definition given by Basmadjian et al. [11]: it minimizes the energy cost of heating the regeneration gas and raising the bed to the regeneration temperature.

The gas velocity should be scaled to the size of the bed in order to give a reasonable contact time. The values in Table 1 give a superficial velocity during adsorption of about 0.07 m s^{-1}. Assuming a bed porosity equal to 0.4, it results in a gas contact time in the bed of about 0.6 s; about the same in a full scale ADD [10]. Shorter contact times would extend the mass transfer region to the whole length of our bed, giving inefficient adsorption and making measurements very difficult.

The water vapour content of the air at the end of regeneration was close to or below 1% that of the inlet air during the preceding adsorption step. This means that the regeneration time corresponded to the so-called 'time to 1%' ($t_{1\%}$); again an industry standard [11]. The gas flow rate in all steps was set at the maximum value which would not cause pellet fluidization in up-flow (although we always used down-flow in the present tests, we wanted the possibility of comparing countercurrent flow in the future).

The time for the adsorption step was chosen to give about 80% bed saturation. Preliminary tests had shown that this allowed a small but measurable (milligrams) amount of water vapour to break through.

Series A tests evaluated the tritium memory of the dryer bed after a standard industrial regeneration; 593 K and passing 10 kg dry air/kg zeolite. Other operating conditions of the experimental runs are summarized in Table 1. Tritiated water is used for the first adsorption step; following a standard regeneration, the second adsorption step uses plain water. This mixes with the tritium in the memory of the bed, so that most of it is eluted during the final standard regeneration step. Thus the tritium detected in the water expelled during the final regeneration step indicates the tritium memory of the zeolite for standard regeneration conditions. In an attempt to stop interference between tests, additional regeneration steps (using dry air) were carried out at the end of each test, as described in Section 3.

Series B tests differed from series A tests firstly by adding a second regeneration step (reg2) carried out immediately after the first standard regeneration (reg1). The additional regeneration used the same physical conditions as reg1 (see Table 1), but used three different gases: either dry air, air saturated with H_2O vapour at ambient temperature, or He plus 3 vol.% of H_2. Sampling the outlet bubblers showed the tritium removal rate, confirming the efficacy of the swamping procedure. Instead of measuring the tritium retention by a second adsorption and regeneration step, the tritium was thoroughly removed in a final regeneration step (reg.F) in which air humidified with ~2% H_2O was passed for 2 h at 723 K, followed by dry air for 2 h (other conditions in Table 2).

Table 1
Standard operating conditions of experimental runs

Flow configuration	Down flow in all steps
System pressure	0.1–0.12 MPa (1–1.2 bar)
Specific activity in tritiated water inlet bubbler	4.625 GBq kg^{-1} (0.125 Ci 1^{-1})
Adsorption steps (ads1 or ads2)	
Temperature	Ambient
Inlet dew point	293 ± 1 K (about 2.3 vol.% H_2O)
Pressure drop	<2 kPa
Time	2 h
Total water vapour injected (typical)	$4–4.5 \times 10^{-3}$ kg
Air flow rate	1.29 mmol/s (1.73 Nl/min)
Tritium activity injected during ads1 (typical)	18.520 MBq (500–540 μCi)
Outlet dewpoint before breakthrough	213 K
Saturation of bed at breakthrough	~80% of total adsorption capacity
Standard Regeneration steps (reg1 or reg2)	
Temperature	593 K
Pressure drop	<7 kPa (0.07 bar)
Time	2 h
Air flow rate	1.29 mmol/s (1.73 Nl/min)
Total air used in regeneration	10 kg/kg zeolite pellets
Final outlet dewpoint	≈239 K (p_{H_2O}≈0.2 kPa)

Table 2
Summary of tests

Series A tests (evaluation of tritium memory)
2 h of adsorption from chromatographic air saturated with tritiated water (step *ads*1)
2 h of regeneration with dry chromatographic air (step *reg*1)
2 h of adsorption from chromatographic air saturated by H_2O (step *ads*2)
2 h of regeneration with dry chromatographic air (step *reg*2)

Series B tests (improved regeneration)
2 h of adsorption from air saturated by Q_2O (step *ads*1)
2 h of regeneration with dry air (step *reg*1)
2 h of regeneration with dry air or with air saturated by H_2O or with He containing 3 vol.% of H_2 (step *reg*2)
Final regeneration/cleaning: 2 h wet air + 2 h dry air at 723 K (step *reg.F*)

Series C tests (optimization)
2 h of adsorption from air saturated by Q_2O (step *ads*1)
1 or 2 h of regeneration with dry air (step *reg*1)
1 or 2 h of regeneration with dry air or with air saturated by H_2O of with He containing 3 vol.% of H_2 (step *reg*2)
2 h of adsorption with air saturated by H_2O (step *ads*2)
Final regeneration/cleaning: 2 h wet air + 2 h dry air at 723 K (step *reg.F*)

Series C tests were similar to series A tests except that there were two consecutive regeneration steps (regl + reg2) after ads1. As well as examining the effect of isotopic swamping in reg2, the times of reg1 and reg2 were varied in order to see if an useful reduction in tritium retention could be obtained without extending regeneration time or increasing the amount of regeneration gas. As in B series tests, a final regeneration step (reg.F) cleaned the bed for the following test.

3. Results and discussion

3.1. Operating a model ADD using standard conditions

During an adsorption step the outlet dewpoint fell steadily and then suddenly rose, marking the start of breakthrough. The sudden rise demonstrates that the kinetics of adsorption is fast, supporting the assumption that the air at the end of the bed is close to equilibrium with the dried sorbent until the adsorption front arrives. The slow fall of dew point is probably due to drying of the outlet pipe because the equilibrium dew point after our thorough regeneration is much lower. A full-scale ADD shows the same apparent behaviour [3], but in this case the initial decrease in dew point is due to a moisture gradient in the bed after (less complete) regeneration.

Tests A1–A3 all used the same procedure to measure tritium retention in the zeolite bed after a standard regeneration. Test A4 was a control test to find the tritium memory of the circuit apart from the zeolite. This is more important in these small-scale tests than in a full-scale ADD because of the larger ratio of surface area: zeolite volume. The zeolite pellets were removed from the bed after reg1, so that only tritium from the walls contributed to the tritium contamination of ads2 and reg2, which used the same conditions as in tests A1–A3.

Table 3 shows the mass balance for water during series A tests. The amount of water vapour breaking through during ads1 increased with successive tests, as the amount of water injected increased. More water entered in later tests because the ambient temperature increased. More water broke through during ads2 than during ads1 because the inlet H_2O bubbler was warmer.

Table 4 shows the total activity of tritiated water adsorbed by the bed during ads1 and how much came out: by breakthrough during ads1; by desorption during reg1; by contamination of the water vapour break-

Table 3
Water mass-balance during series A tests

Step	ads1			reg1	ads2			reg2
Test	Q_2O_{ads} (10^{-3} kg)	t_{br} (s/60)	Q_2O_{out} (10^{-6} kg)	d.p. (K)	H_2O_{in} (10^{-3} kg)	t_{br} (s/60)	H_2O_{out} (10^{-6} kg)	d.p. (K)
A1	3.97	103	3.31	237	4.52	92	11.6	232
A2	3.58	96	4.44	235	4.55	85	28.1	243
A3	3.95	94	15.8	239	4.47	79	57.0	241
A4	3.98	95	30.0	242	4.50 *	0 *	(all) *	234

* ads = (in–out) during an adsorption step; out = amount breaking through during an adsorption step; t_{br} = breakthrough time of water vapour during an adsorption step; d.p. = dew point of effluent gas at the end of a regeneration step. Other conditions in Table 1.

Table 4
HTO balance for runs of type A on a packed bed of a commercial 5A zeolite

Step	ads1		reg1	ads2	reg2	
Test	HTO_{ads} (MBq)	HTO_{out} (MBq)	HTO_{out} (MBq)	HTO_{out} (MBq)	HTO_{out} (MBq)	HTO retention R (%)
A1	18.74	0.0108	17.08	0.082	1.48	8.6
A2	18.82	0.0189	17.05	0.134	1.51	8.9
A3	19.17	0.0480	17.14	0.155	1.40	8.3
A4	20.41	0.0662	17.19	0.068 [a]	0.0067 [a]	0.34 [a]

ads = (in–out) during an adsorption step; out = amount breaking through during a step.

[a] after removing zeolite (control test for retention by walls etc.). Conditions as in Table 1.

through in ads2, and contamination of the water desorbed during reg2.

If we compare the Bq of tritiated water breaking through during ads1 with the total Bq injected, we see that the average tritium decontamination factor for the air is between 10^2 and 10^3.

The specific activity of the water which broke through during ads1 (dividing column 3 of Table 4 by column 4 of Table 3) was between 2.2 and 4.2 GBq kg^{-1}. Compared to 4.6 GBq kg^{-1} in the inlet water, there is an apparent isotope separation in the bed. However, the quantity of break-through water is calculated by integrating the output of a hygrometer. An error of 1–3 deg. in the measured dewpoint would account for the differences in specific activity between the runs, which all used the same procedure. Therefore, the apparent isotope separation is inside the range of the experimental error. From the literature [2], one could expect a separation factor of about 1.1 for a single adsorption.

One can estimate the specific activity of the tritiated water vapour which breaks through the bed during the plain water adsorption step ads2: one divides the Bq collected in ads2 (Table 3). by the estimated milligrams of water vapour leaving the bed during ads2 (Table 3). The result is an average of 3.8 GBq kg^{-1}, which is close to the activity of tritiated water injected in ads1: 4.6 GBq kg^{-1}. This result confirms the theory [1] that the effect of tritium memory on dryer performance can be estimated quite well by assuming that the water vapour which gets through a dryer during an adsorption step has the same specific activity as the water adsorbed in the previous adsorption step. The reason is that the small amount of water vapour which escapes the dryer has exchanged isotopically with the much larger quantity of tritiated water retained from the previous adsorption cycle, in the unsaturated region of the bed. The theory only holds for conventional regeneration with dry gas, because humidity present in the regeneration gas would tend to dilute the HTO retained in the bed. This effect would be seen when the total water content of the regeneration air is comparable or greater than the quantity of Q_2O retained in the bed. Similarly, the theory requires that the fraction of water vapour escaping the dryer during the second adsorption step is small compared to the Q_2O retained in the unsaturated part of the bed.

3.2. Evaluation of the tritium retention after standard regeneration

It is important to know the retention of tritiated water, R, defined as

$$R = \frac{\text{HTO in the zeolite pellets after regeneration}}{\text{HTO in the zeolite pellets before regeneration}} = \frac{C + D + E - F}{A + G - B} \cong \frac{C}{A},$$

where A = HTO injected in ads1 (Table 4), B = HTO broken through during ads1 (Table 4), C = HTO out during reg2 (Table 4), D = HTO still retained in bed after reg2 = $R \times C$, E = HTO broken through during ads2 (Table 3), F = HTO retained on the walls after reg1 (see below), G = HTO remaining in bed from previous test (= 0 for A1; $\cong R \times C$ for A2, A3).

F is found from the result of control test A4, where the zeolite was removed after ads1. It shows a retention by the walls of 0.34% of the tritium injected in ads1 (since the walls are heated to avoid condensation, probably most of this HTO was retained in the hygrometer elements rather than on the walls of the bed). Using the approximate formula C/A underestimated R(%) by between 0.7 and 1.

Table 4 shows that *the average HTO retention after a standard regeneration is 8.6% of the HTO loaded in the preceding adsorption step, for a bed loaded to 80% saturation. This is equivalent to 6.9% of the HTO loaded in a fully saturated bed* (because regeneration was co-current, the HTO contaminates the whole bed before leaving, so the Bq of retained Q_2O hardly depends on the degree of bed saturation). Multiplying by the adsorption capacity of 5A (18% by weight for $p_{H_2O} = 2$ kPa; $T = 298$ K) gives a retention *of 1.2% expressed as kg Q_2O/kg zeolite.*

3.3. Effect of repeated regenerations

At the end of test A1–A3, the adsorbent bed was given another two regenerations (reg3 and reg4) to see the effect of repeated regenerations of tritium retention and to reduce the amount of HTO carried over to the next test. The extra HTO recovered during these regenerations is shown in Table 5. These can be added to the HTO recovered during reg2 to see the effect on HTO retention of repeating or extending the standard regeneration. The amounts are 2–3 orders of magnitude below the HTO recovered during reg2: double regeneration reduces the % retention by only average 0.07 and triple regeneration contributes a further decrement of 0.02. Thus, for an open-loop regeneration, one expects *no significant improvement in HTO retention from doubling or tripling the standard regeneration time* ($t_{1\%}$)*, using the same dry air flow rate*.

Test A3 shows that even if one raises the regeneration temperature to 723 K (the limit of thermal stability of the zeolite) the extra HTO recovered by one or two extra regenerations only reduced the retention from 8.6% after the standard regeneration to about 8.3%. Thus, *using dry gas for an open-loop regeneration, there is little scope for reducing the HTO retention by increasing regeneration temperature beyond the characteristic temperature of the system*.

3.4. Reducing tritium retention by isotope swamping (series B results)

Before starting the series B tests, fresh 5A zeolite was loaded and activated as before. Practically all the tritium was removed in reg.F due to the high temperature and isotopic swamping, so the calculation of *R* needed fewer corrections than with A series tests.

Table 5
Q_2O removed by further regenerations after A series tests

Test	$T_{\mathrm{reg}3,4}$ (K)	reg3 HTO$_{\mathrm{out}}$ (kBq)	reg4 HTO$_{\mathrm{out}}$ (kBq)
A1	593	8.77	1.89
A2	593	16.6	4.81
A3	723	48.1	9.25

reg3,4: 2 h, dry air; out = amount breaking through during a regeneration step. See Table 1 for other conditions.

Looking at test B1 in Table 6, we see confirmation that repeating a standard dry regeneration has little effect on the HTO retention. However, test B2 shows that *using humid air (saturated at ~293 K) for reg2 enormously reduces the retention:* the combination of reg1 and reg2 in this test leaves only 0.11% of the tritium adsorbed in ads1. As the amount of tritium left in the bed at the end of reg1 was about 8% of that adsorbed, the isotopic swamping in reg2 has decontaminated the bed by a factor of about 70. The amount of H_2O used for the swamping was about the same as the mass of Q_2O loaded.

By contrast, *isotopic swamping by He + 3 vol.%* H_2 *has only a moderate effect on tritium retention*, reducing it from around 8% to 5.6% of the HTO originally adsorbed in ads1. Thus the isotopic swamping effect in this case is significant, but not very useful in terms of decontaminating the bed.

Fig. 2 shows a histogram representing the rate at which HTO leaves the bed during reg1 (dry air) of test B2, found by repeatedly taking water samples from the outlet bubblers. The curve is the smoothest one which would give the same integrated area as the histogram during each time interval. The initial rise indicates the

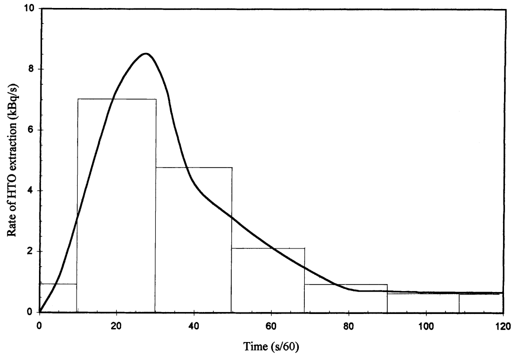

Fig. 2. Rate of HTO removal during step reg1 of test B2 (final bed temperature = 593 K, dry air flowrate = 1.29 mmol s^{-1}). Bubbler data as shown by histogram: the curve is the smoothest one which gives the same area in each histogram segment.

Table 6
Results of series B tests

Step	ads1			reg1 + reg2		reg.F	
Test	HTO$_{\mathrm{ads}}$ (MBq)	HTO$_{\mathrm{out}}$ (MBq)	Q_2O_{out} (10^{-3} kg)	Conditions	HTO$_{\mathrm{out}}$ (MBq)	HTO$_{\mathrm{out}}$ (MBq)	*R* (%)
B1	19.46	0.189	0.040	2 h dry air + 2 h dry air	17.97	1.48	7.6
B2	19.45	0.163	0.042	2 h dry air + 2 h humid air	19.56	0.022	0.11
B3	19.43	0.215	0.047	2 h dry air + 2 h He + 3% H_2	18.21	1.09	5.6

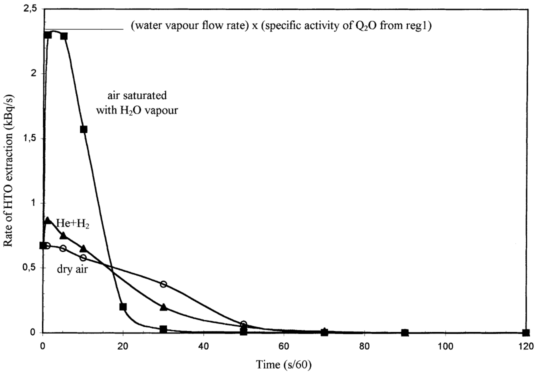

Fig. 3. Rate of HTO leaving during step reg2 of B series tests (bed temperature = 593 K, regenerating gas flowrate = 1.29 mmol s^{-1}). Curves constructed as in Fig. 2.

heating time: little HTO is released below 473 K. At the end of 2 h HTO is still leaving the bed at 8% of the maximum rate.

Fig. 3 shows the rates at which HTO leaves the bed during reg2 of tests B1, B2 and B3. The curves were produced in the same way as in Fig. 2 (the data points represent the mid-points of the horizontal segments of the histograms equivalent to that in Fig. 2). Since reg2 followed directly on reg1 while the bed was already at temperature, the starting rate is the final rate in Fig. 2.

In test B1 (dry air in reg2) the rate HTO left the bed declined steadily and reduces to very low values after about one hour of reg2. Presumably at this point (3 h altogether at 593 K with dry air) there is practically no more physically adsorbed water present: we have reached the limit of detritiation using dry air. However, the value of R in this test, 7.6%, shows that we are still a long way from eliminating tritium retention (because of the chemically bonded water still present).

In test B2 the introduction of water vapour from the start of reg2 (which followed immediately on reg1 without cooling) causes an immediate increase in HTO release rate due to isotopic swamping: the data is compatible *with the Q_2O released in the first stages having the same Bq/kg as the Q_2O retained in the bed after ads1.*

The tritium release curve from reg2 of test B3, using He + 3 vol.% H_2, is close to an exponential decay. This implies that the rate of HTO removal is proportional to the amount of HTO remaining, which is consistent with rate control by the isotope exchange process.

3.5. Trying to reduce regeneration time (series C tests)

Series C tests used the same bed as series B. Like the series A tests, series C tests are double-cycle tests: the HTO retained after a particular regeneration treatment is measured by the contamination of plain water used in a second adsorption step. The final regeneration, used to remove practically all the tritium contamination, used the same procedure as reg.F in series B tests.

Tests C1, C2 and C3 used a two-stage regeneration treatment (without allowing the bed to cool down between stages) between ads1 and ads2: in contrast to B series tests, the total regeneration time for (reg1 + reg2) = (1 h + 1 h) was made the same as the standard regeneration time. This means that both the time and the amount of gas passed were halved compared to reg1 and reg2 of the equivalent B series tests.

Test C1 used dry air for both reg1 and reg2 steps, as a control test: the tritium retention (Table 7) was in line with that found previously for a standard regeneration.

Test C2, which used humid air for reg2, showed a fourfold reduction in tritium retention compared to test C1: rather disappointing compared to the 70-fold reduction seen in test B2 compared with B1. The reason can clearly be seen from Fig. 2: after 60 min regeneration with dry air about 30% of the Q_2O from ads1 is still present. Fig. 3 shows that in B2 the H_2O front passes in less than 60 min; it did not in C2 because the 30% water left after ads1 slowed the progress of the front.

Test C3, using He + 3 vol.% H_2 in reg2, shows a significant but moderate reduction in tritium retention compared to dry air; of the same order as seen in test B3 (2 h + 2 h using the same gases). This is in line with our

Table 7
Results of series C tests 1–3

Step	ads1		reg1 + reg2	ads2		reg.F	
Test	HTO_{ads} (MBq)	Q_2O_{out} (10^{-6} kg)	Conditions	HTO_{out} (MBq)	Q_2O_{out} (10^{-6} kg)	HTO_{out} (MBq)	R (%)
C1	19.13	63	1 h dry air + 1 h dry air	0.596	248	1.53	8.0
C2	19.22	48	1 h dry air + 1 h humid air	0.411	105	0.42	2.2
C3	19.17	79	1 h dry air + 1 h He + 3%H_2	0.403	218	0.67	3.5

ads1: 2 h, $T = 298$ K, air saturated with Q_2O vapour; reg1, reg2: $T = 593$ K, ads2: 2 h, $T = 298$ K, air saturated with H_2O vapour, 4.5×10^{-3} kg of H_2O introduced; reg.F: $T = 723$ K, air saturated with H_2O vapour for 2 h + dry air for 2 h. Other conditions in Table 1.

proposition that the rate of tritium removal in He + 3 vol.% H_2 is limited by the isotope exchange rate: R does not depend so strongly on the effectiveness of reg1 because more HTO retained after reg1 also means a faster rate of tritium removal.

3.6. Reproducibility and aging (series C tests)

Table 8 shows the results of a further three series 3 tests carried out to investigate test reproducibility, to confirm the important result on water vapour swamping (test B2) and to examine the effect of material aging.

Tests C4 and C6 are identical, and share the same reg1+ reg2 combination as test B2: the results show that R cannot be measured with great precision when the retention is very low, but the values are reassuringly straddle the value of $R = 0.11\%$ in test B2.

An effect of zeolite pellet aging is seen in series B and C tests, which used the same bed. Looking at the second columns of Tables 6–8, we see a steady decrease in the amount of HTO adsorbed by the bed in ads1, even though amount injected is increasing. The total mass of Q_2O adsorbed shows the same trend (results not shown). The adsorption capacity of the bed is decreasing: it has decreased about 9% between tests B1 and C6 (actually more, if we take into account that the bed was less saturated in the earlier tests). This can be ascribed to the effects of the final regenerations (reg.F) at 723 K, conducted at the end of each B and C series tests for 2 h in humid air + 2 h in dry air: a total of 32 h at 723 K by the time of the last test. The high temperature has caused aging of the zeolite equivalent to years of operating up to 593 K. The effect is due to the partial decomposition of the zeolite into alumina and silica [8]. The good news is that the aging does not appear to make the HTO retention any worse: indeed if we compare test B1 with C5 we see that the retention (after standard regeneration for 2 + 2 h in dry air) has decreased from 7.6% to 5.2%. This is not unexpected: Toci et al. [8] showed that hydroxyl ions in the zeolite and binder structure cause tritium retention: high temperature treatment (calcining) irreversibly decomposes hydroxides to oxides.

4. Conclusions

The following conclusions may be drawn:

1. Isotopic separation effects and 'roll-up' effects are not important in ADDs, at least under the conditions used in this study. Similar conclusions were drawn from experimental results obtained on a 4A zeolite over a wide range of operating conditions [1].
2. For ADDs thoroughly regenerated (to a residual moisture loading of 1% or lower), the main problems of tritium retention lie with irreversibly retained water in the pellets. This water is not released by conventional regeneration, and does not show up on adsorption isotherms used for dryer design.
3. After standard regeneration carried out in a co-current configuration (used in many ADDs installed in CANDU reactor systems), the bed retained about **8.6%** (±0.3) of the HTO loaded in the preceding adsorption step; using:
   - – 80% bed saturation during adsorption step;
   - – a standard industrial regeneration procedure for a dryer: operating at the energy-saving 'characteristic temperature' (593 K) and passing 10 kg dry air per kg zeolite to arrive at '$t_{1\%}$' (the outlet p_{H_2O} in regeneration reaches <1% the inlet p_{H_2O} in adsorption).
4. This figure is equivalent to **6.9%** of the HTO loaded in a fully saturated bed, or **1.2%** in terms of kg Q_2O/kg zeolite.
5. Repeating the standard (dry) regeneration, or increasing the regeneration temperature to the limit of thermal stability of the zeolite (723 K) made very little difference to the amount of HTO retained.
6. Using *humidified air* in the second regeneration step reduced the measured HTO retention to 0.11% (±0.05) (the amount of water used for swamping was about the same as was loaded in the adsorption step).
7. Humid regeneration is only so effective if the bed has been thoroughly regenerated with dry air first: halving the time of the dry regeneration step resulted in a much smaller effect from humid regeneration (2.2% HTO retention).

Table 8
Results of series C tests 4–6

Step	ads1		reg1 + reg2	ads2		reg.F	
Test	HTO_{ads} (MBq)	Q_2O_{out} (10^{-3} kg)	Conditions	HTO_{out} (MBq)	Q_2O_{out} (10^{-3} kg)	HTO_{out} (MBq)	R (%)
C4	19.13	0.200	2 h dry air + 2 h humid air	0.00407	0.565	0.00352	0.04
C5	18.12	0.262	2 h dry air + 2 h dry air	0.181	0.661	0.7550	5.2
C6	17.89	0.283	2 h dry air + 2 h humid air	0.0215	0.750	0.00666	0.16

ads1: 2 h, $T = 298$ K, air saturated with Q_2O vapour, reg1, reg2: $T = 593$ K, ads2: 2 h, $T = 298$ K, air saturated with H_2O vapour, 4.5×10^{-3} kg of H_2O introduced; reg.F: $T = 723$ K, air saturated with H_2O vapour for 2 h + dry air for 2 h. Other conditions in Table 1.

8. Isotopic swamping using **He + 3 vol.% H_2** in a second standard regeneration step had only a moderate effect on tritium retention, reducing it to **5.6%** of the HTO originally adsorbed. The rate of tritium removal is limited by the isotope exchange rate.
9. During adsorption, the first water vapour which breaks through the dryer has the same specific activity (Bq/kg) as the water retained in the bed after the previous regeneration. If regeneration was co-current without isotope swamping, this is practically the same as the specific activity of the water loaded in the previous adsorption cycle. Thus *the tritium decontamination factor for an ADD can be estimated from the drying factor and this specific activity, provided the ADD has a good drying performance*. Similar results were found on a 4A zeolite [1], suggesting that, *for an efficient ADD, the tritium decontamination factor should be independent of the adsorber material and the regeneration procedure* (*without isotope swamping*).
10. The 5A pellets were artificially aged by cycling to 723 K for a total of 32 h at temperature (equivalent to years of service at 593 K). The HTO retention declined more than 30%, while adsorption capacity declined little more than 9%.

We are now measuring HTO retention in a specially prepared mordenite adsorbent material: initial results show that it is much less than for 5A zeolite [12]. Furthermore, a model is being developed to predict the effectiveness of different isotopic swamping procedures.

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