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ATMOSPHERIC DETRITIATION SYSTEM PERFORMANCE

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ABSTRACT

An investigation of the performance of atmospheric detritiation systems and of possible ways for improving their performance was undertaken. Small-scale experiments demonstrated that system performance is strongly dependent on catalyst bed temperature. That may be helped by addition of protium to the process gas stream, but added protium at constant temperature does not increase conversion to HTO. Collection of the HTO on dry sieve with residual HTO fraction of less than one part in 10^7 was observed. Ways suggested for improvement in collection of HTO on molecular sieve beds include adding H_2O to the stream entering the molecular sieve and premoistening of the sieve with H_2O. While these improvement schemes may reduce HTO emissions they increase the amount of tritiated waste that must be handled.

INTRODUCTION

In tritium-burning fusion facilities such as the Tokamak Fusion Test Reactor (TFTR) or in future machines such as the Compact Ignition Tokamak (CIT) or the International Thermonuclear Experimental Reactor (ITER) the possibility of an accidental release of tritium to the reactor hall or in the tritium storage and handling facility will make an atmospheric detritiation system (ADS) necessary. These systems are designed to convert tritiated gases to HTO in a catalytic reactor and then collect the HTO on zeolite molecular sieve beds. In addition to cleanup of accidental spills, this technology is applicable to cleanup of glovebox atmospheres and for the routine collection or recovery of tritium produced in the blanket.

Because of a wide variation in ADS performance levels, there has been some uncertainty as to whether or not special techniques would be necessary or useful to minimize the HTO inventory in the cleanup system and/or the HTO levels in effluents from the ADS. From a safety perspective, it will be advantageous to minimize HTO levels in the effluent of the ADS and the amount of tritiated waste that must be disposed of.

Considerable variation has been reported in the detritiation factors attainable by the oxidation/water collection process. Single-pass detritiation factors from less than 10^4 to more than 10^7 have been reported.[1-4] Catalyst temperature and the residence time of the process gas stream in the catalyst appear to be principally responsible for the variation in performance.

ADS operation is a two-step process, conversion of tritiated gases to HTO and removal of HTO from the gas stream. If the HTO produced in the ADS is not removed to less than one part in 10^5, the safety hazard will actually be increased due to the greater biological effects of HTO over elemental tritium.

Three techniques for improving ADS performance have been suggested: (1) hydrogen swamping or the addition of excess protium to the process gas stream entering the ADS, (2) water swamping or adding H_2O to the stream entering the molecular sieve beds, and (3) premoistening of the molecular sieve to enhance HTO removal. These have been the subject of a joint research effort at the Tritium Systems Test Assembly (TSTA) at the Los Alamos National Laboratory. The project involved personnel from TSTA, from the Princeton Plasma Physics Laboratory (PPPL), and from the Idaho National Engineering Laboratory (INEL). In this paper we present results of those investigations. These include experimental results using the Dedicated Cleanup System (DCS) at TSTA and supporting bench-top experiments. Also, work reported by others which relates to ADS improvement schemes is discussed.

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CONVERSION OF TRITIATED GASES TO HTO

Temperature Sensitivity

The catalyzed oxidation reaction is known to be very temperature sensitive. Data of Tanaka and Kiyose[5] for the conversion factor CF (defined as the ratio of the unoxidized tritium concentration entering the catalyst bed to that leaving it) for tritium oxidation on CuO at temperatures of 473 - 673 K generally fit the functional form

$$CF = \exp[K_1 \; V/Q \; \exp(K_2 T)] \qquad [1]$$

where V is the volume of the catalyst bed, Q is the flow rate of the gas through it (V/Q is thus the residence time of the gas in the catalyst bed), T represents catalyst temperature, and the K_i are constants. The data of Gildea, Wall, and Gede[3] for hydrogen and methane oxidation on Englehard A-16648 catalyst at temperatures of 316 - 743 K also appear to fit the functional form of Eq.[1].

To investigate the temperature sensitivity for the Englehard A-16825 catalyst used in many of the systems at TSTA, the apparatus shown schematically in Figure 1 was assembled. Water siphoned between open and closed jars provided nearly constant pressure to a gas reservoir with variable volume. Closed cycle pumping of the gas from the reservoir, through the ion chamber and back to the reservoir provided mixing. The catalyst bed was 1.27-cm (1/2-in) copper tubing, wrapped with a heater tape and furnished with a temperature controller, into which 100 grams of catalyst (nominally 3-mm dia x 3-mm long pellets with a 10-cm stack height) had been placed between plugs of stainless steel wool. Upstream of the catalyst material and still in the heated zone was a 10-cm column of brass chips which served to preheat the gas stream passing through the catalyst.

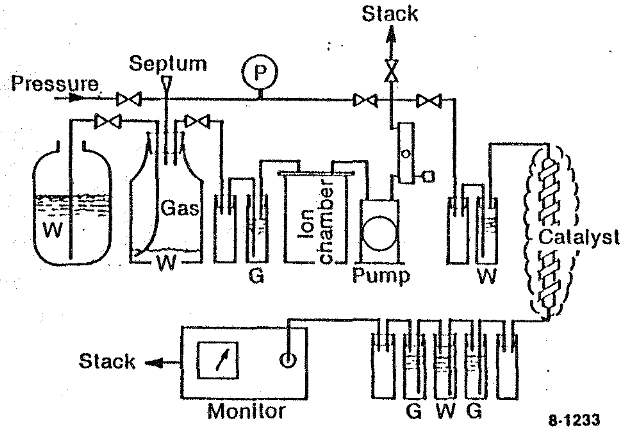

Figure 1. Apparatus used to evaluate temperature sensitivity and hydrogen swamping effects.

T_2 was injected into the reservoir using a syringe and mixed by recirculation. Gas was drawn through a glycol bubbler to dry it, through the ion chamber that monitored the T_2 activity, through the flowmeter, and then through a water bubbler before going to the catalyst. The water bubbler was intended to minimize the uptake of HTO by the catalyst substrate,[6] though this was inconsequential to the conversion measurements (they were made only on dried T_2-bearing gas). Following the catalyst bed, a series of glycol and water bubblers was used to trap HTO while passing unoxidized T_2. The glycol bubblers had a measured collection efficiency for HTO of 87%. The intermediate water bubbler ensured that effectively all of the HTO surviving the first glycol trap would be caught in the second. A standard ion-chamber type tritium monitor was used to measure residual tritium in the gas stream. The conversion factor, CF, was evaluated from the readings made using the ion chamber and the tritium monitor.

To evaluate the temperature sensitivity of the CF for this catalyst, a sequence of five tests was run with 810 - 890 MBq/m^3 (22 - 24 mCi/m^3) of T_2 in the reservoir and a flow rate of 0.42 L/min (catalyst residence time of 1.4 s). Temperature was varied between 373 and 673 K in 50 K increments by adjusting the catalyst bed temperature controller. Care was used to maintain catalyst temperature during each test within 5 K. CFs measured in these tests fit within 2% the function

$$CF = 37 \exp[2.1\text{x}10^{-8} \exp(.023 \; T)] \qquad [2]$$

This is similar to Eq.[1] but V/Q is missing (all tests had the same V/Q -- the interest was temperature sensitivity), and there is a premultiplying constant. The reason for the premultiplier (which represents the conversion rate at low temperatures) may be parital conversion taking place other than on the catalyst bed or a finite conversion rate at low temperatures. The important thing is that conversion sharply accelerates above 623 K.

Hydrogen Swamping

A means suggested for improving the fraction of tritium oxidized was hydrogen swamping, i.e., the addition of excess protium to the process gas stream. This may improve performance in two ways. First, given that tritiated molecules dissociate on the surface of the catalyst, two reactions appear to compete for the T atoms:

$$H + T <\!\!-\!\!-\!\!> HT \qquad [3]$$

$$OH + T <\!\!-\!\!-\!\!> HTO. \qquad [4]$$

It has been observed[7,8] that, at least on platinum and palladium surfaces, OH formation is apparently the rate governing step in the process of oxidizing hydrogen, or in this case conversion of tritiated gases to HTO. It was postulated that the excess protium may enhance formation of OH so that reaction [4] would be accelerated.

The second way in which excess protium may improve conversion to HTO is that the energy released from the oxidation of the additional hydrogen may raise the bed temperature. ADS designs frequently lack auxiliary heating on the catalyst beds for simplicity and cost. A prior experience at TSTA[9] showed a significant but temporary increase in the catalyst bed temperature and in the detritiation factor of the Tritiated Waste Treatment System[10] when excess protium was in the gas stream. Whether the temperature change was responsible for the improved performance or whether chemical effects prevailed was not known.

In constant temperature experiments at the Sandia Livermore Laboratory[3] and at the University of Tokyo[5] it was found that the conversion factor for catalytic oxidation of hydrogen isotopes was actually reduced by the addition of protium. That is consistent with the observation that OH formation is rate limiting and implies excess protium stimulates reaction [3] at the expense of tritium oxidation via reaction [4].

To further investigate the effect of excess hydrogen at constant temperature, tests were conducted using the apparatus shown in Figure 1 and mixtures in various ratios of tritium and protium or deuterium. T_2 injected with a syringe through the septum was mixed with air and varying quantities of protium or deuterium which had been similarly injected. Tritium activities between 0.74 and 46 GBq/m^3 (0.02 and 1.25 Ci/m^3) were measured. Protium- (deuterium-) to-tritium ratios varied over more than six orders of magnitude. Two flow rates, 0.42 and 0.14 L/min, through the catalyst gave residence times in the catalyst of 1.4 s and 4.0 s, respectively. Temperatures varied from 668 to 700 K but were constant within 5 K during each test.

Figure 2 shows the conversion factors resulting from these measurements which have been corrected for temperature departures from 673 K using Eq. [2]. There was no significant difference in the temperature corrected conversion factors seen over the entire range of H_2 to T_2 ratios tested nor between the H_2 and D_2 tests though a slight decline with higher H_2/T_2 ratios may be evident. This negative correlation is less pronounced than that observed in the other experiments referred to above,[3,5] however, the hydrogen fraction of the total gas pressure in the present tests, never exceed 0.08%, substantially less than the 1%-levels at which the conversion factors were seen to decrease markedly in the other experiments.

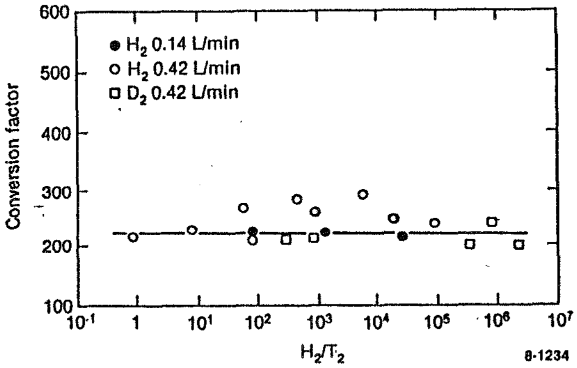

Figure 2. Conversion factors for a range of hydrogen swamping ratios normalized to 673 K.

It is apparent from these results that that completeness of tritium conversion to HTO is closely keyed to the temperature of the catalyst and not significantly to the amount of excess hydrogen present. Considering the risks of using hydrogen, it seems prudent to use auxiliary heating systems on ADS catalyst beds rather than rely on excess hydrogen for heating if ambient temperature performance is inadequate.

MOLECULAR SIEVE BED PERFORMANCE

Performance Test

The DCS at TSTA was used in a series of scoping tests to evaluate performance of the molecular sieve beds (MSBs) and suggested schemes for improving MSB operation. The DCS is a small-scale ADS adapted to experimentation involving hardware and procedure variations. Figure 3 shows the effective configuration of the DCS during these experiments.

The reservoir was a 1-m^3 exposure chamber. Reservoir tritium levels were controlled using a T_2 supply bottle with a circulation pump and ion chamber monitor located in an adjacent glovebox. In the main loop flow rates of up to 50 L/min are possible using a reciprocating compressor. The 0.7-L catalyst bed (Englehard A-16825 catalyst) was heated directly using resistance heaters and by preheated gases. Two identical molecular sieve beds (MSBs) each holding about 5.7 kg of sieve were followed by dual water bubblers to monitor HTO emissions from the MSBs. The collection efficiency of the bubblers for HTO in the gas streams was measured to be 94-99%. Exhaust was directed to the Tritiated Waste Treatment (TWT) system at TSTA without recirculation, though it could be returned to the reservoir or directly to the compressor inlet.

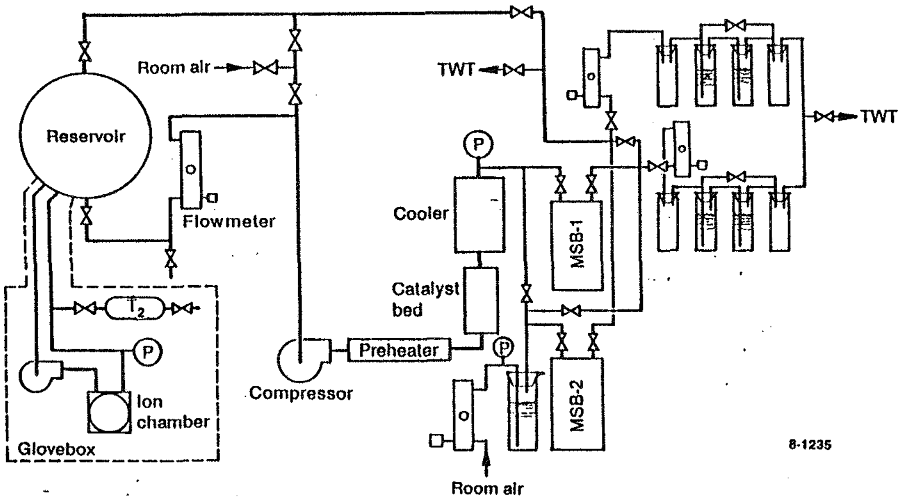

Figure 3. Effective configuration of the Dedicated Cleanup System (DCS) for tests of molecular sieve bed effectiveness and ways to improve it.

In operation, air, either from the room or from the reservoir carrying 40-80 GBq/m^3 (1-2 Ci/m^3) of T_2 (with room air replacement), was pumped through the preheater, through the catalyst bed (operated at 673 +/- 10 K with > 99.5% conversion to HTO), and through the cooling heat exchanger. The flow could then be routed through either of the MSBs or split using flow meters and flow-control valves with half going to each of the two MSBs which were followed by dual water bubblers. Water swamping of the stream to MSB-2 was possible through a water bubbler with its own flow meter and pressure gage attached upstream of the MSB-2 inlet. Depending on DCS performance, direct observation of the ability of the proposed techniques for improving HTO capture from the stream should be observable by comparing HTO trapped in the downstream bubblers for operation with one dry bed and one premoistened bed, or with one dry stream and one water-swamped stream to identical dry beds.

Several tests were conducted to evaluate the two schemes proposed for improving MSB performance, but none were very successful. Results from one will be shown here. With the bed configured as shown in Figure 3 and new, dry Union Carbide Type 4A sieve in the two identical MSBs, the DCS was operated at a flow rate of 4 L/min (2 L/min through each MSB) for approximately one hour. Gas residence times in the catalyst bed (10 s) and in the molecular sieve beds (3.7 min) were longer than in most ADS systems to accommodate bubbler operation. Initially, desiccated room air was processed for an hour. It entered through the flowmeter into the compressor. The flow was stopped at 20 minute intervals, and scintillation samples were withdrawn from the bubblers.

After what appears to be an initial transient, the collection rate of HTO from what must be a system background averaged 93 Bq/min (2.5 nCi/min) through each branch of the DCS with higher quantities coming from the MSB-2 side. The water in the bubblers was then changed to minimize the background reading, and the test was resumed at twice the flow rate and with desiccated but HT-laden air having an activity of 100 GBq/m^3 (2.7 Ci/m^3) entering the DCS from the reservoir.

The DCS was operated for another hour, again stopping at 20 minute intervals for scintillation samples to be withdrawn from the bubblers. At the end of that time, a side stream of air nearly saturated with water was added to the inlet of MSB-2. It had a flow rate of 3.9 L/min, so the total flow through MSB-2 was 7.8 L/min while that through MSB-1 remained at 3.8 L/min. Operation for another hour was conducted, again sampling at 20-minute intervals. The results of scintillation counts on the bubbler samples are shown in Figure 4.

Examination of these data indicates that the rate of HTO rise in the bubblers did not increase when the HT was added to the input stream. It actually dropped slightly, probably an effect of increasing the flowrate. That the reduction in capture rate was not due to a loss in bubbler efficiency is evidenced by the fact that > 99% of the HTO was caught in the first bubbler in each pair. The amount of HTO collected is proportional to the rate of collection in each branch. Apparently, the measurement was of HTO emanating from the DCS itself or from the sieve bed, and none of the HTO produced by the catalyst was making it through the molecular sieve.

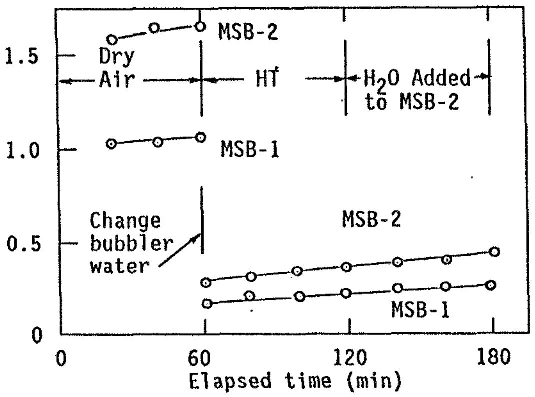

Figure 4. Results from one DCS experiment.

A second observation is that there was no statistically significant change in the HTO collection rate downstream of MSB-2 when the flow through MSB-2 was increased by adding the water-saturated side stream. If the source of HTO was the structure upstream from the sieve, prior experience suggests that the extra water in the gas stream should substantially increase the rate at which HTO was released from the surfaces of the structure. This is supports the interpretation that the HTO seen was not coming through the MSBs from the catalyst bed or structure upstream from the sieve, but rather from the structure downstream.

A final observation is that with an HT processing rate of 0.3 MBq/min (16 mCi/min) for each of the branches of the DCS, making the arbitrary assumption that a collection rate change of 10% (50 Bq/min or 1.3 nCi/min) would be visible leads to the conclusion that the HTO removal factor (input HTO/output HTO) of the MSBs under these conditions must be at least 1.2×10^7. This is quite acceptable for most ADS applications. However, the use of new zeolite and the long residence times in the MSBs means this is probably an optimistic value, as is discussed in what follows.

MSB Performance Improvement

The perceived mechanisms by which zeolites adsorb water suggest schemes for possible improvements in MSB performance. As previously noted, the addition of excess H_2O to the gas stream entering the MSB, and premoistening the sieve with H_2O have been suggested as possible improvement techniques. Attempts at evaluating both of these techniques in the present work were unsuccessful due to DCS contamination and excellent performance of the DCS sieve beds. However, other researchers have published results that give insight to the validity of these methods.

Water Swamping. The vapor pressure in a stream leaving a molecular sieve bed is related to the moisture adsorbed on the last part of the bed traversed by the gas. If that sieve is nominally dry (e.g., < 2 wt% water), the total water vapor pressure leaving the sieve will be at a low value (<.05 Pa) until breakthrough occurs. The HTO fraction in the stream leaving the bed will reflect the HTO fraction in the last sieve traversed by the gas stream. Dilution of the HTO in the input stream by adding extra H_2O would result in quicker breakthrough, but the HTO fraction in the adsorbed water, and thus in the exiting gas stream, should be lower. This effect was seen in studies by Ono et al.[11] and by Tanaka and co-workers.[12]

Water swamping appears to be influenced by isotopic effects. In breakthrough tests conducted by Tanaka et al.,[12] it was consistently observed that H_2O appeared in the outlet stream sooner and rose more abruptly than HTO over a wide range of HTO/H_2O ratios. They reported a separation factor, defined by

$$SF = \frac{(HTO/H_2O)_{adsorbed}}{(HTO/H_2O)_{gas\ phase}}, \qquad [4]$$

on 4A sieve of 1.12 +/- 0.03 for temperatures greater than 223 K and up to 1.24 below 216 K. The values greater than unity imply that HTO is bound more tightly to the sieve than is H_2O. This has a favorable effect while extracting HTO from a gas stream but suggests that the HTO fraction in the residual water on a regenerated sieve bed will be higher than that in the gas passing through it before regeneration.

Water swamping has the disadvantage that it fills the molecular sieve bed much more quickly with tritiated water. This water must be removed from the ADS and disposed of. If the process is applied to systems that would otherwise require fairly frequent regeneration, this could be problematic. The advantages may be reduced inventory and lower HTO levels in MSB effluent.

Premoistening Sieve. The second technique proposed for improving HTO collection efficiency was the preloading of the molecular sieve bed with H_2O. It has been hypothesized that the scavenging of HTO by exchanging HTO in the gas for H_2O adsorbed on the sieve may be more rapid than simple dry-bed adsorption if the sieve is premoistened. This could be particularly useful in low-residence time MSBs. In the Japanese experiments referred to[11,12] a high degree of detritiation was observed in a stream having an H_2O/HTO ratio of 10^8 and a dew point of 213 K (vapor pressure of 1 Pa) by molecular sieve material that had been premoistened to a 283-K dew point (equilibrium vapor pressure of 1.23 kPa). Hence, even though there was a net flow of moisture to the gas stream from the sieve, there was a substantial reduction in the HTO in the gas stream. They also saw a reduction of about 30% in HTO breakthrough time compared with similar tests using dry sieve. Because of detection thresholds it could not be determined whether the small fraction of HTO making it through the sieve before breakthrough was greater or less for the premoistened sieve than for the dry sieve.

Breck[13] points out that when zeolite is highly dehydrated, the cations migrate to partially block the micropores leading to the internal cages where water adsorption takes place. This tends to retard adsorption. It is evident from manufacturer's isotherm data, and it was concluded by Tanaka et al.,[12] that the adsorption mechanism changes for a critical moisture loading (about 4.5% for 4A zeolite). Tanaka et al. postulated that the mechanism changes from attachment, diffusion along micropores to internal cages, and subsequent adsorption on those internal surfaces to adsorption in coarse structural macropores at that loading. Though not demonstrable from experimental data,[12] partially preloading the sieve with water to fill the internal cages may substantially accelerate the extraction of HTO from the stream by facilitating exchange of adsorbed H_2O for gaseous HTO at a faster rate than adsorption onto dry sieve would allow. This would probably be accompanied by a reduced capacity for HTO before adsorbed HTO also exchanges and diminishes the net extraction rate. It implies a gradual breakthrough of HTO on premoistened sieve rather than the more sudden break-throughs characteristic of dry sieve.

Even if HTO removal proves to be initially faster with premoistened sieve than with a dry-bed, the frequent regeneration and remoistening (perhaps flushing) of the sieve required to keep HTO levels low in the water adsorbed on the sieve suggest that waste disposal may be problematic with this technique. HTO content in the waste would be lower, but there would be so much more of it.

CONCLUSIONS

It may be concluded that while hydrogen swamping may raise the temperature of the catalyst bed and thus increase conversion to HTO, it appears to be otherwise deleterious. Water swamping of the stream to the MSB and premoistening of the sieve with H_2O may result in lower HTO fractions in MSB effluent, though this remains to be conclusively proved. Each technique discussed will increase the amount of tritiated waste that must be disposed of and in that sense adds risk and cost to ADS operation.

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