
Dependence of Tritium Release on Temperature and Water Vapor from Stainless Steel

Introduction

Tritium has applications in the pharmaceutical industry as a radioactive tracer, in the radioluminescent industry as a scintillant driver, and in nuclear fusion as a fuel. When metal surfaces are exposed to tritium gas, compounds absorbed on the metal surfaces (such as water and volatile organic species) chemically react with the tritons. Subsequently, the contaminated surfaces desorb tritiated water and volatile organics. Contact with these surfaces can pose a health hazard to workers. Additionally, desorption of tritiated species from the surfaces constitutes a respirable dose.

Understanding the mechanisms associated with hydrogen adsorption on metal surfaces and its subsequent transport into the bulk can reduce the susceptibility of surfaces becoming contaminated and can lead to improved decontamination techniques. More generally, tritium can be used as a sensitive tracer to study surface chemistry and hydrogen transport. Elemental tritium readily converts into tritiated water on metallic surfaces.^{1,2} Desorption of water from inner surfaces of process lines containing ultrapure gas streams can compromise the reliability of semiconductor chips. Additionally, reactive gases used to fabricate large-scale integrated chips combine with this water to form acids or submicron-sized particles that degrade interconnects on the chips to reduce their lifespan and reliability.³⁻⁵

This article compares the effectiveness of heat and moisture to desorb gases from metal surfaces using tritium as a tracer. In the first series of experiments, temperatures up to 600°C were used to measure the desorption spectrum from stainless-steel samples under dry purge conditions. The second series of experiments compared tritium release at a fixed humidity of 8760 ppm in the carrier while varying the metal temperature from 100°C to 130°C. The final set of measurements investigated the impact of varying humidity while holding the sample at a fixed temperature of 100°C.

Experimental Procedure

These experiments used 316 stainless-steel samples that were 5 cm long × 1.8 cm wide × 0.3 cm thick. The samples

were exposed to 690 Torr of DT gas, 40% T/D ratio, for 23 h at room temperature and stored under vacuum at room temperature until retrieved for the desorption studies, after which they were stored under helium. The experiments were conducted 440 days after exposure. The samples were exposed briefly to air during the transfer from storage to the desorption facility.

The desorption facility, described in detail in Ref. 6, comprises a 100-cm³, heated quartz tube that holds the sample, a set of two gas spargers to extract water-soluble gases from the helium purge stream, and an on-line liquid scintillation counter to measure the activity collected in the spargers in real time. The performance of the spargers has been discussed in detail in Ref. 7. Tritium that desorbs from metal surfaces is predominantly found in water-soluble species.⁷

Each sample was heated by convection in a uniform heating zone within the quartz furnace. A thermocouple attached to the sample provided a direct measurement of the sample temperature. The humidity of the helium purge stream was adjusted by blending a purge steam that bubbled through a humidifier with a bypass stream. The humidity was measured on-line and indirectly from the rate of water loss from the humidifier.

The on-line liquid scintillation counter tracked the activity increase in the first sparger, containing 100 ml of liquid scintillation fluid, as the desorption progressed. This signal provided a measure of the tritium inventory contained in the sample. The differential of this signal provided the tritium outgassing rate as a function of time as the desorption proceeded. The overall system response time was of the order of 2 min.

Results

1. Thermally Driven Outgassing into a Dry Stream

To investigate the effect of temperature on the outgassing rate, each sample was subjected to six sequential bake-outs at progressively higher temperatures in a dry helium purge. Each trial started by holding the sample at room temperature for 1 h to establish a background outgassing rate. The temperature was ramped to the dwell temperature and held at that temperature

for roughly an additional 3 h. The sample attained the dwell temperature within 5 min of starting the temperature ramp. After each run, the sample was allowed to cool to room temperature. The same sample was used for all of the runs in this series. Runs were conducted in order of increasing temperature.

The activity collected in the first sparger for these runs is shown in Fig. 140.25. The background levels observed in the first hour have been arbitrarily set to zero. Activity is observed to increase in the first sparger ~5 min after the initiation of the temperature ramp. A total of 5.5 mCi of tritium was recovered from this sample. This tritium inventory is representative of all the samples exposed to 690 Torr of 40% T/D gas during the campaign. The percentage recovered after each sequential run is listed in the inset of Fig. 140.25. The majority of the tritium was released from the surface when the bake-out temperature was of the order of 300°C. This finding is consistent with previous studies.⁶

The outgassing rates were computed by differentiating the table inset shown in Fig. 140.25. The outgassing rate for each run is plotted in Fig. 140.26. The outgassing rate increases rapidly with increasing temperature, even in the absence of humidity. A 120-fold increase in the outgassing rate is observed when the bake-out temperature increases from 75°C to 300°C.

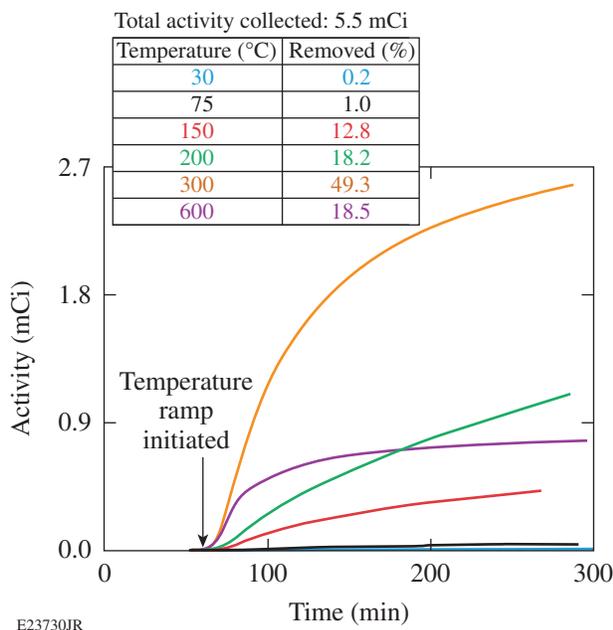


Figure 140.25 The cumulative quantity of tritium released from a stainless-steel sample for sequential bake-outs at progressively higher temperatures in a purge stream containing 4 ppm of water vapor.

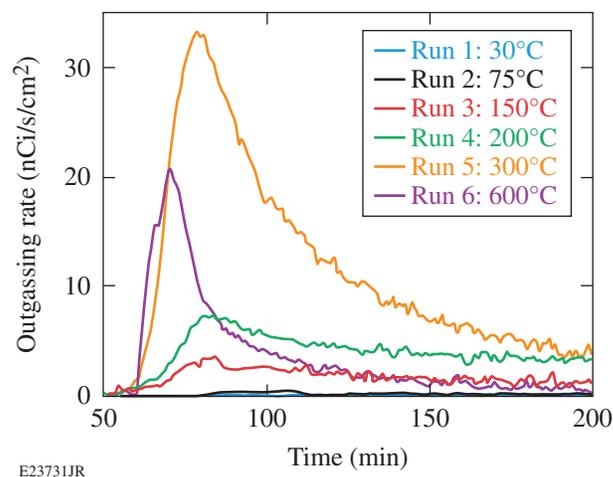


Figure 140.26 The outgassing rates of tritium from a stainless-steel sample for sequential bake-outs at progressively higher temperatures in a 4-ppm purge stream.

The exception to this trend is Run 6, conducted at 600°C. The lower outgassing rate in that case suggests that the tritium inventory within the sample has been depleted.

2. Humidity-Stimulated Outgassing from 30°C Metal

The effect of humidity on the outgassing rate was measured by purging a fresh sample with helium containing two sequentially increasing amounts of moisture—1120 ppm and 6740 ppm of water vapor in the carrier. Each run was initially purged with the helium stream containing 4 ppm of water vapor for 2 h to establish a baseline outgassing rate. The outgassing rate for each of the three runs is provided in Fig. 140.27.

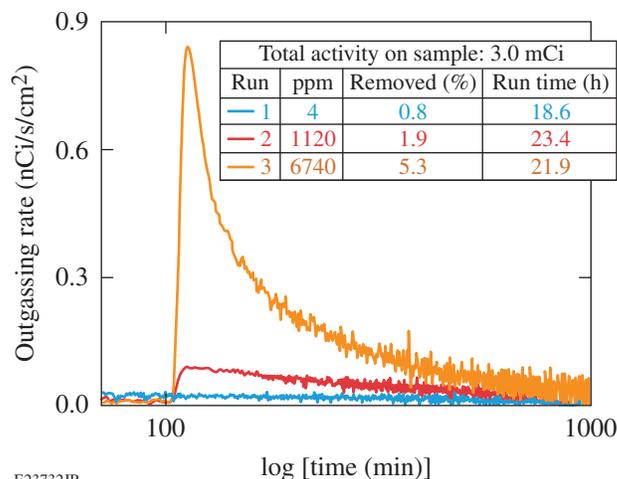


Figure 140.27 The outgassing rates of tritium from a stainless-steel sample at 30°C exposed to increased moisture content in the purge stream.

An inspection of Fig. 140.27 provides two conclusions: (1) the peak outgassing rate increases with increasing humidity and (2) increasing the water content in the purge stream sixfold from 1120 ppm to 6740 ppm increases the peak outgassing rate tenfold from 0.084 to 0.84 nCi/cm²/s. In both humid runs, the outgassing rate approaches the low-humidity outgassing rate, even though the residual tritium inventory on the sample remains high. Only 2% of the tritium is removed from the sample when it is exposed to 1120 ppm of moisture in helium, and an additional 5.3% is removed when the water content is increased to 6740 ppm. Diffusion of tritons from the near surface to the surface of the stainless steel or from the inner oxide layers appears to limit the rate of tritium outgassing at room temperature. It is noteworthy that ~8% of the tritium inventory resides in and can be removed from the near surface with humidity. Finally, humidity-stimulated peak outgassing rates are seen to be at least one order of magnitude lower than thermally driven peak outgassing rates. For example, a peak outgassing rate of 34 nCi/cm²/s was attained at 300°C compared to 0.84 nCi/cm²/s achieved with 6740 ppm of water vapor.

Figure 140.28 further demonstrates that the rate-limiting step in humidity-stimulated outgassing is triton diffusion to the surface. A second stainless-steel sample was decontaminated

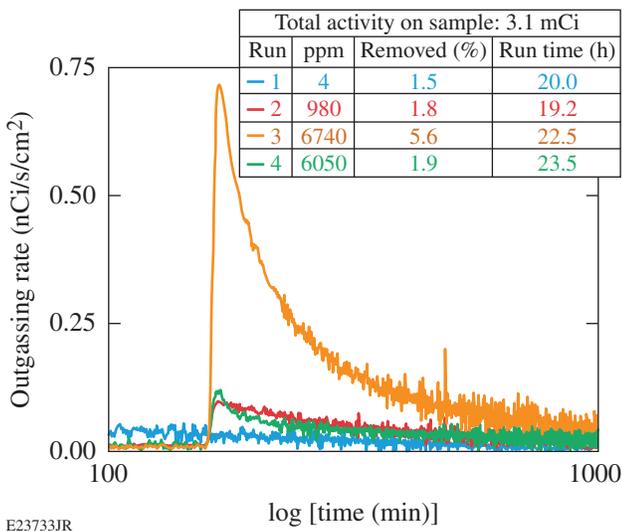


Figure 140.28
The humidity-stimulated outgassing rates of tritium from a second stainless-steel sample at 30°C.

using a similar purge protocol to that described above. In this case, however, a second high-humidity run (Run 4) was added to the protocol.

Overall, the outgassing behavior of the second stainless-steel sample is very similar to that observed for the first sample. The quantities of tritium removed from the two samples are also similar. However, repeating a second run with high humidity 2 h after the first high-humidity run did not recover the original enhanced outgassing rate. The outgassing rate is only slightly higher than that observed at the end of the first high-humidity run. Tritons were not available at the sample surface for exchange with water vapor, even though ~90% of the tritium inventory remains in the sample.

3. Humidity-Stimulated Outgassing from Warm Metals

The relative contribution of humidity to the outgassing rate from warm metal surfaces was measured by subjecting a fresh sample to four sequential bake-outs at progressively higher temperatures in a wet purge stream. The humidity was fixed at 8760 ppm of water vapor in the carrier. The bake-out temperatures increased from 100°C to 130°C in 10°C steps. The outgassing rates for the four runs, provided in Fig. 140.29, were arbitrarily set to zero at the start of each run for the comparison.

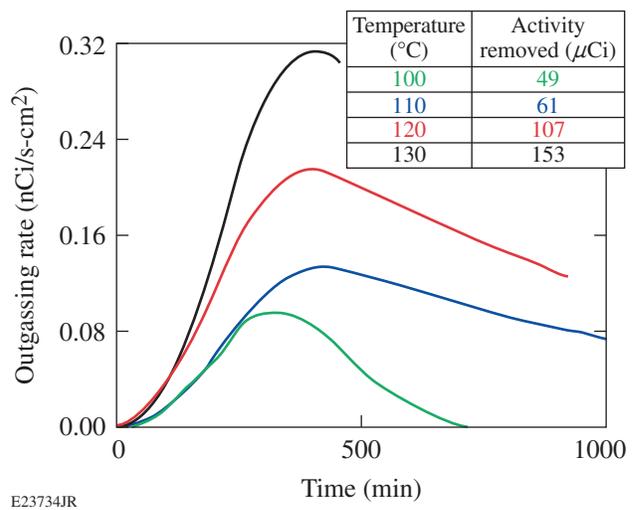


Figure 140.29
Outgassing rates for stainless steel heated from 100°C to 130°C in 10°C steps into a helium purge stream containing 8760 ppm of water vapor.

Three observations can be drawn from Fig. 140.29: (1) the quantity of tritium extracted from the sample increases with metal temperature as expected; (2) the peak outgassing rate increases with temperature; and (3) the rate of change in the outgassing rate also increases with temperature. With the exception of the 100°C run, the outgassing rate appears to decline more rapidly with time after the peak as the sample temperature increases, suggesting that the inventory of tritons that can participate in the desorption process is finite. Increasing the sample temperature appears to involve tritons deeper in the subsurface but this reservoir is depleted more rapidly.

In a second experiment set up to investigate humidity-stimulated desorption from warm stainless steel, the temperature was fixed at 100°C and the humidity changed from 4 ppm to 1000 ppm. The stainless-steel sample was purged with a dry (4 ppm of water vapor) helium stream at room temperature to establish the baseline outgassing rate. After 30 min, the sample temperature was raised to and held at 100°C. Five hours later, the humidity of the purge stream was increased from 10 ppm of water to 1000 ppm. The outgassing curves are provided in Fig. 140.30.

Figure 140.30 shows that outgassing rates for the two cases evolved in a similar manner, first increasing to a peak and then decreasing toward a steady-state outgassing rate after a long

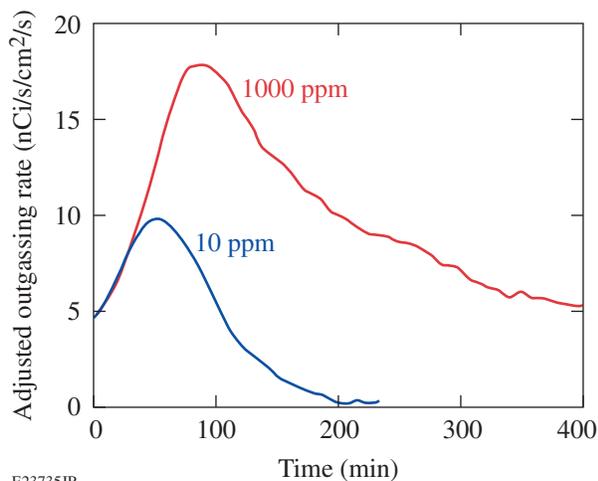


Figure 140.30
The temporal evolution of the outgassing rate variation from stainless steel held at 100°C and exposed to a purge stream containing 10 ppm and then 1000 ppm of water vapor.

time. The profiles are more reminiscent of thermal desorption than humidity-stimulated desorption. Increasing the humidity increased the tritium removal rate. Tritium desorption from stainless steel held at 100°C depends on the water-vapor flux to the surface or on the isotherm for water adsorption on stainless steel.

4. Discussion

The tritium-concentration profile's dependence on distance was calculated using the Crank–Nicolson equation.⁸ This approach relies on flux balances across a grid spanning the metal depth and uses a finite-difference solution to the diffusion equation. The calculation determines where the tritium is located during the loading phase and how that profile evolves during the storage of the stainless-steel samples. Three major assumptions were used in this calculation:

- The concentration of tritium at the surface was constant during loading.
- No tritium was lost during the storage period.
- The oxide and metal bulk concentrations at the oxide–metal interface were related by the ratio of their respective solubilities:

$$C_{\text{oxide}} = \frac{S_{\text{oxide}}}{S_{\text{bulk}}} * C_{\text{bulk}} \quad (1)$$

While the metal bulk solubility is a known value, the oxide solubility was determined by varying its value until the calculated total activity in the sample agreed with the measured value. The difference between calculation and experiment was minimized with the Minuit routine contained in the ROOT data analysis package from CERN. The resulting oxide solubility is 6000 ± 200 times greater than the metal bulk solubility.

To calculate the amount of tritium that participates in each experiment, the penetration depth must be known. As tritium diffuses from the bulk to the surface, the tritium concentration profile in the metal will develop into an error function. The concentration at the oxide–metal interface will be low compared to the concentration deep in the bulk. The distance (z) that a triton can diffuse from the bulk into the oxide layer at a given temperature depends on time (t) according to Eq. (2):

$$z = \sqrt{4 * D(T) * t} \quad (2)$$

where D is the diffusivity of the triton in stainless steel at temperature T . The tritium diffusivity in stainless steel^{9,10} at 130°C is 9.9×10^{-10} cm²/s. Tritons in the bulk metal located 109 μ m beyond the oxide–metal interface cannot contribute to the desorption flux over the course of a 500-min experiment. The diffusivity decreases to 5.4×10^{-12} cm²/s at 30°C and the tritons penetration depth drops to 8 μ m.

Integrating the tritium concentration profile over the penetration depth yields the calculated amount of tritium that can contribute during an experiment. Using a depth of 8 μ m, which corresponds to the data in Fig. 140.27, the calculated activity that can contribute is 281 μ Ci. This value compares with 243 μ Ci of tritium collected during the three runs shown in Fig. 140.27.

5. Conclusions

Baking out stainless steel at or above 300°C is an effective method of reducing the tritium inventory in stainless steel. Humidity-stimulated peak outgassing rates are seen to be at least one order of magnitude lower than thermally driven peak outgassing rates.

The quantity of tritium removed increases with humidity. A sixfold increase in moisture content in the purge stream generates at least a tenfold improvement in the peak outgassing rate.

Calculations show more activity is present than is actually removed during each experiment, suggesting that the bulk diffusivity limits tritium removal.

ACKNOWLEDGMENT

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