Water Desorption from Metallic Surfaces at Room Temperature

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Abstract

Water adsorption and desorption is a major issue in industries that handle ultra-pure gases. For example, in the semiconductor industry, water desorption into pure gas streams can contaminate the entire stream and reduce the yield and lifetime of large-scale integrated devices. An experiment has been performed to understand the process by which water adsorbs and desorbs from metallic surfaces so as to help prevent moisture contamination. Tritium, which is a radioactive isotope of hydrogen, was used in this experiment as a tracer to label water molecules attached to metals and monitor the rate at which desorption occurs. Tritium is an ideal tracer because, as an isotope of hydrogen, it can replace hydrogen in water (H_2O) to form tritiated water (HTO). In this experiment, copper with HTO bound to its surface was exposed to a helium carrier with varying amounts of humidity and the rate of exchange between the carrier-borne H_2O and the surface-bound HTO was measured as a function of carrier humidity. Two processes control the rate of exchange: the arrival rate of water vapor to the surface when the metal is first exposed to the humidity and the rate of tritium diffusion from the metal when the upper oxide layers are tritium deficient in the later phase.

Introduction

Water molecules often attach to surfaces through a process named adsorption and similarly detach from a surface by desorption. As more water molecules attach, monolayers or multiple layers of water molecules are formed on the surface. The first

layer that adsorbs to the surface dissociates from H_2O into an H and an OH. The succeeding layers of H_2O bond to the hydrogen ends of the first layer (see Fig. 1).

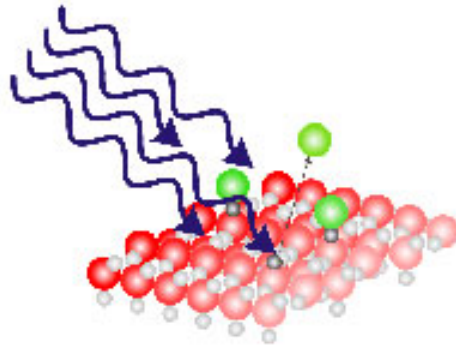

Fig. 1: A representation of the process of adsorption and desorption. The red and gray spheres are the adsorbed H_2O molecules while the green are H_2O molecules desorbing.

The water molecules that bond to the surface can be entrained into gases that are near the surface. In certain controlled settings, this is an issue because the water can contaminate pure gases. One of these settings is gas streams in industry.[1,2,3] Due to the process of adsorption and desorption, pure gas streams are likely to become contaminated if water is present on the surface of pipes and equipment present in the gas stream. The process of water adsorption and desorption is a prominent concern in contamination control throughout industry settings.

The objective is to understand water adsorption and desorption so as to help prevent moisture contamination.[4,5] In this process, tritium, an isotope of hydrogen that

contains one proton and two neutrons, is used as a diagnostic. There are two main reasons for the use of tritium in this experiment: (1) Because it is an isotope, it can interact with water and form tritiated water; and (2) Tritium is sensitive and can be identified if 1 in 10^{12} of particles in a system is a triton.

Experimental Setup

The purpose of the experiment being performed is to try and understand the process by which adsorption and desorption occur. To understand this, a basic replica was made of the process that industries use when transporting gases.

The experiment as shown in Figure 2 is started with a source of compressed helium from a tank that is sent through a helium purifier. The helium is then divided into two streams, both of which are controlled separately by mass flow meters. One of these streams remains dry, while the other is run through a water-filled humidifier (B0), thereby humidifying one stream. The combined flow rate of the two streams is limited to 100 ml/min by the operator; however, each stream has the potential to reach a flow rate of up to 200 ml/min. The streams then combine and pass through a dew point sensor used to measure the overall humidity of the stream. The sensor is connected to a small, digital readout that displays the dew point in degrees Celsius. Next, the helium passes through an exposure chamber containing a tritiated copper coupon. The water in the helium stream adsorbs onto the coupon's surface and a hydrogen exchanges with the tritium to form tritiated water, HTO or T_2O. These are two forms of water in which tritium has become part of the molecule. Then, the HTO or T_2O desorbs and the stream

continues into a bubbler containing 100 ml of liquid scintillation cocktail solution (LSC, B1). The helium stream deposits the majority of tritium that was "carried" into this bubbler.

Two small diameter hoses run between this bubbler and a Beta-RAM, a liquid scintillation counter that actively measures radioactivity in counts per minute/ml (CPM/ml). After this, the helium stream continues on to a bubbler (B2) filled with 100 ml of water where the remnants of the tritium are deposited. Dew point measurements were recorded manually throughout the runs through the use of the digital dew point sensor display.
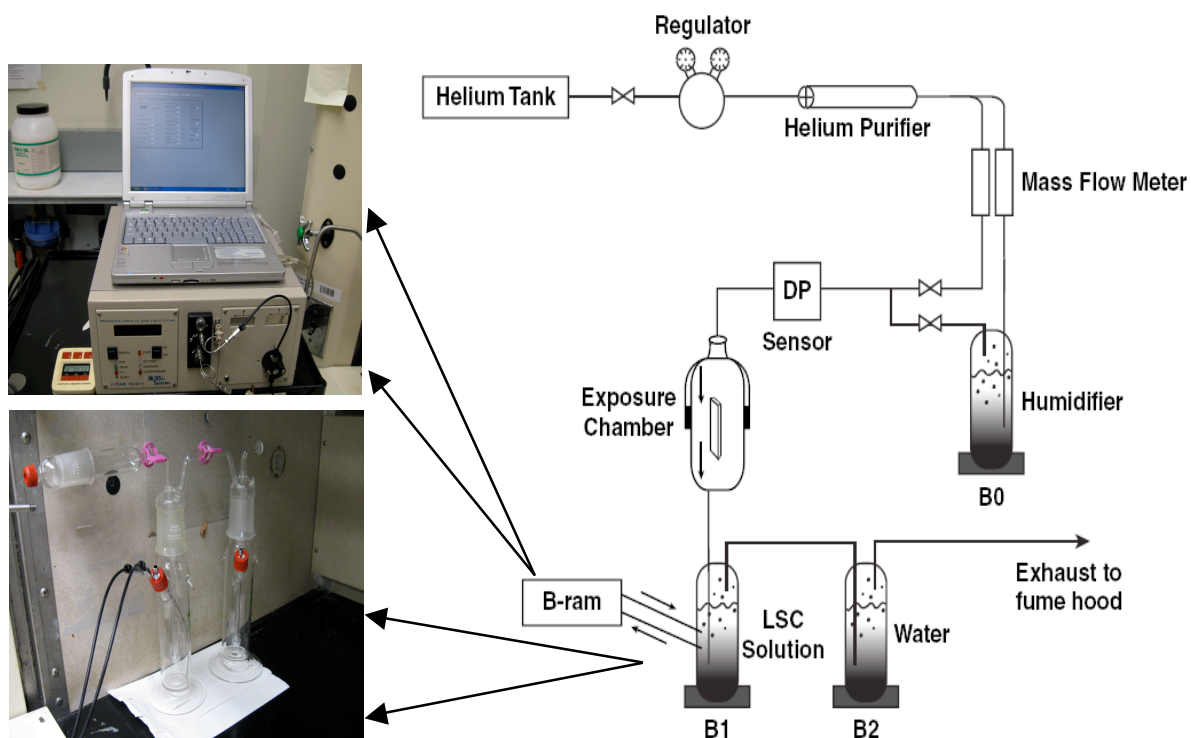

Fig. 2: Experimental system setup. Data was collected by way of the Beta-RAM software from the B1 bubbler

Data Processing

For the duration of the experiments, the system was constantly monitored by data acquisition software. The data acquisition software was a Beta-RAM system that was connected to a Beta-RAM program and a Microsoft Excel file. The Beta-RAM program recorded data in Excel after each minute of runtime. The data that was recorded automatically included the run number, the date, time, and the activity in CPM/ml. Data was taken from individual runs and compiled to reveal the entire data from an experiment. Concluding each run, a graph plotting the activity in the B1 bubbler against time was made in the Excel program. The system was also manually monitored before, during, and after the experiments. At the start and before concluding an experiment, the dew point was recorded, along with the time, date, and experimental information such as percent humidity or amount of HTO. In addition, when running pure water throughout the system, absent of tritium, the mass of the B0 humidifier was measured. This was done to understand the amount of water passing through the system and the loss in mass of water in the humidifier in relation to experiment duration and humidity of water within the carrier stream. This mass of water was then compared to the mass of water ($\dot{m} = \frac{dm}{dt}$) calculated to travel through the system during an experiment with the equation:

$$\dot{m} = \frac{P_V \, F_{carrier}}{R \, T_S} * \frac{M_W}{\rho} \qquad (1)$$

where P_V is the water vapor pressure, $F_{carrier}$ is the flow rate of the purge stream

(liters/min), R is the universal gas constant, T_s is the temperature of the gas, M_w is the molecular mass of water, and ρ is the density of water (g/ml). In addition to monitoring the system, one-milliliter samples were collected after each run and measured in a liquid scintillation counter to calculate the final activity in each bubbler. The samples were counted for activity in counts per minute. This was done to calculate the amount of tritium removed from the coupon and therefore estimate the approximate amount of water adsorbing onto and desorbing from the coupon.

HTO Experiments

Various experiments were performed in order to achieve a greater understanding of how the system operates, more specifically system response times and Beta-RAM operation. Three experiments were run where the humidifier bubbler was deliberately contaminated with HTO. The first experimental run used 10 milliliters of HTO added to the humidifier, the next 20 ml, and the last 40 ml. The Beta-RAM system monitored the approximate activity of the LSC bubbler in counts per minute (CPM). The data was then graphed comparing the activity in CPM/ml and the time in minutes (see Fig. 3). The graph revealed three slopes, one for each amount of HTO added, that show the relationship between the concentration of HTO and activity against time. Figure 3 also shows a transition time between the slopes for each addition of HTO to the humidifier. Because the activity data for the graph was taken from the LSC bubbler, and activity started out in the humidifier, a certain amount of time was required for the activity to transfer through the system. As a result, there is a transition between slopes as the

activity is gradually increasing until it reaches a steady rate. This transition time is also the system response time, or the approximate amount of time it takes for the Beta-RAM system to respond to the change in activity. The results of these experiments showed that the approximate response time of the system was around 2 minutes. In addition, the normalization of these three slopes was found. The normalization N can be found with the equation
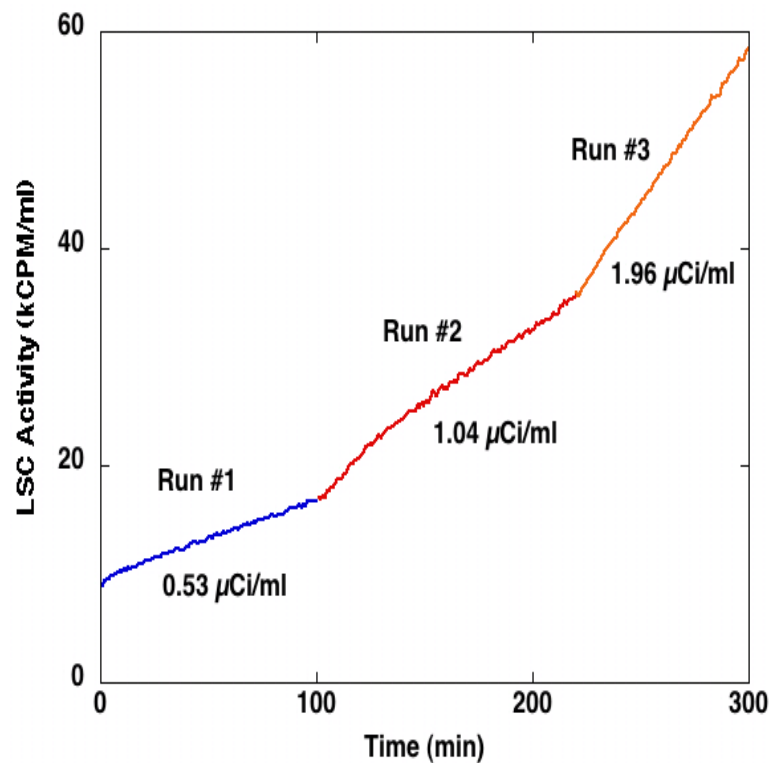
$$N = B / A \tag{2}$$

Fig. 3: *Tritiated water runs prior to coupon experiments. The graph compares the activity (CPM/ml) versus time (minutes) of the 3 different tests: 10 ml of HTO, 20 ml, and 40 ml.*

where B is the LSC solution's activity measured during a run and A is the concentration

of tritium (µCi/ml) in the humidifier. After all the activities were normalized and then graphed as shown in Figure 4, the slopes were calculated and found to be the same for the 3 runs using 10 ml, 20 ml, and 40 ml of HTO in 100ml of water, respectively. The normalization is used to show that the flow rate of water through the system was constant as the activity within bubbler B0 was changed after each run. This slope represents the amount of water traveling through the system.
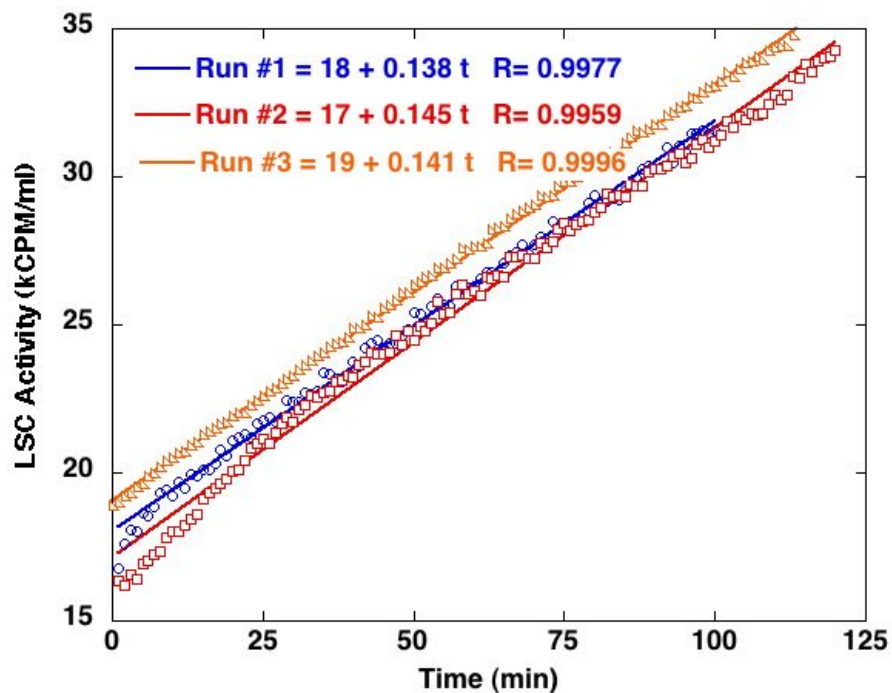

Fig. 4: Normalized data that reveals a constant flow of H_2O through the system during the tritiated water experiments.

Equation 3 can be used to calculate the activity increase in the LSC cocktail ($\dot{A} = \dfrac{dA}{dt}$)

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$$\dot{A} = A * \dot{m}\, V \qquad (3)$$

where A is the activity in the B0 bubbler, $\dot{m}$ is given by equation (1), and V is the volume of liquid scintillator in the collector. By dividing $\dot{A}$ by A for each experiment, the relation becomes independent of activity and reveals that the rate of water transfer in each run is identical.

$$\frac{\dot{A}}{A} = \dot{m} * V \qquad (4)$$

The slopes of each curve in Figure 4 are identical as predicted by equation 4 and equal to approximately 0.17 ml/min when the flow rate is 100% wet.

The amount of water traveling through the system from the humidifier to the collector can also be calculated using the equations:

$$\dot{n} = \frac{P * \dot{V}}{R\,T} \qquad (5)$$

and

$$ml\ of\, H_2O\Big/ \text{min} = \dot{n}\, M_w \qquad (6)$$

where $\dot{n}$ is the number of moles of water per unit time, P is the water vapor pressure, $\dot{V}$ is the volumetric flow rate of the carrier, t is time, R is the universal gas constant, T is the carrier temperature, and M_W is the molecular mass of water. This equation estimates that the amount of water traveling from the humidifier to the collector during

an experiment will be approximately 0.2 ml/min, a value close to that obtained in the experimental runs. This shows that the ideal gas law given by Eqn. 5 can be used to accurately predict water transport in the carrier.

Copper Coupon Experiments

Following the tritiated water experiments, experiments were performed with copper coupons that had been previously exposed to tritium. Several runs have been performed on two separate coupons. After compiling data collected from runs on the first coupon, several aspects of the system were understood. The first was the repeatability of the system. The system was first run dry at 100 ml/min of helium with a relative humidity of around 0.01%, yielding the blue curve in Fig 5, which graphs activity against time. After this run was concluded, another run was performed where one stream was humidified at a flow rate of 10 ml/min, while the other stream remained dry but moved at a flow rate of 90 ml/min. This run had an approximate relative humidity of 2%. Subsequently, another dry run was performed. By alternating from a dry run to a humidified run and then back to a dry run, the plots in Fig. 5 of the first and third runs, which were dry, reveal consistency after HTO had contaminated the system during the second run. The system was additionally run at a relative humidity of approximately 3%, revealing a similar data plot as the first humidified run. Before a third humidified run with a relative humidity of 11% was performed, the system was run dry for two runs to clear out any remaining HTO. The data that was graphed in Fig. 5 revealed that the dry run had a certain initial slope. When the humidity increased from a relative humidity of

0.013% to 2%, the initial slope of the curve increased, and when the humidity returned to 0.013%, the initial slope of the curve returned to its previous value for times below 100 min.
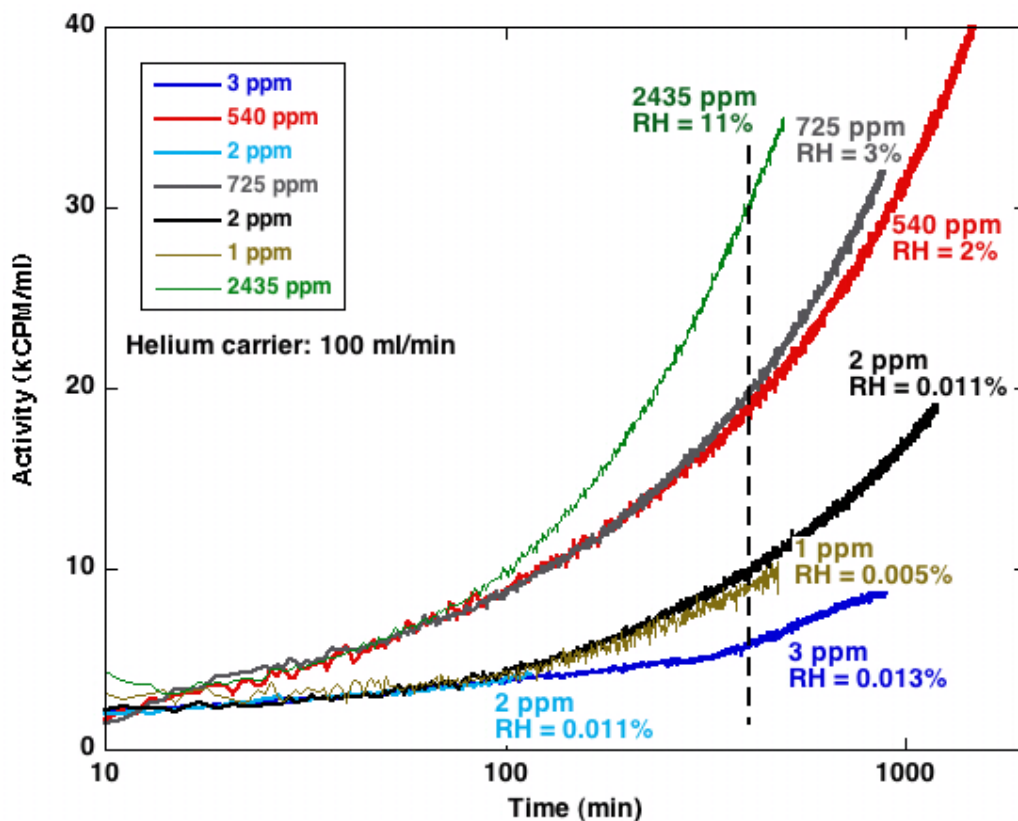

Fig. 5: Results from the first tritiated copper coupon experiments. The graphs compare the activity (CPM/ml) versus time (minutes) of 7 different tests with varying humidity in the helium stream.

A second observation was that as the relative humidity of the carrier increased, the amount of tritium desorption from the copper surface increased.

Another set of experiments was performed using a second coupon in which the

humidity of the runs was consistently increased from the first run to the last. In addition, the system was run dry at the beginning of each run for one hour to demonstrate that there is an immediate change in activity released from the coupon when the humidity is changed from dry to a specific humidity. The accumulation of activity in the collector is shown in Fig. 6 for each run. An expanded version of Fig. 6 is provided in Fig. 7 for times close to the point when humidity is introduced.
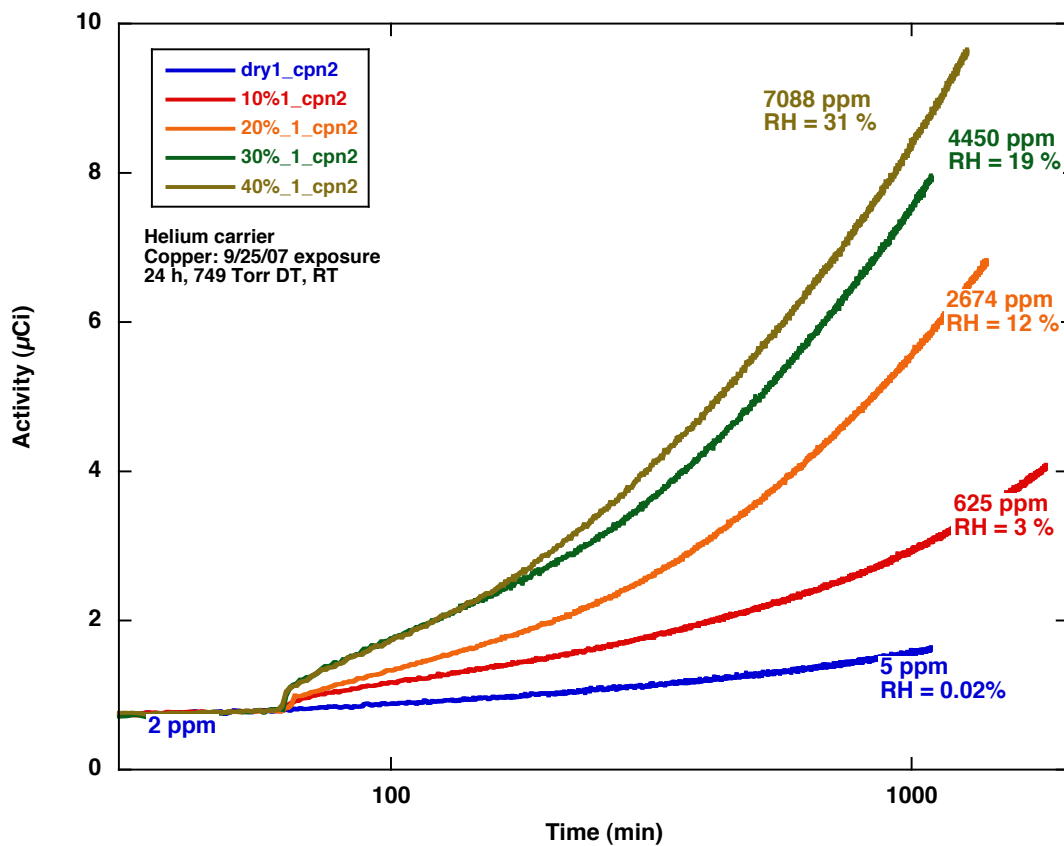

Fig. 6: Results from the second tritiated copper coupon experiments. The graphs compare the activity (CPM/ml) versus time (minutes) of 5 different tests with increasing amounts of humidity in the helium

Two more observations were made from these results. The first was that as the relative humidity increased, the initial rate of tritium desorption increased as shown in Table 1.

Relative humidity in carrier (%)	Initial tritium desorption rate (nCi/min)
0.02	1.4
3	3.9
12	6.7
19	11.0
31	11.0

Table 1: Initial tritium desorption rates from a copper coupon as a function of the relative humidity of the carrier
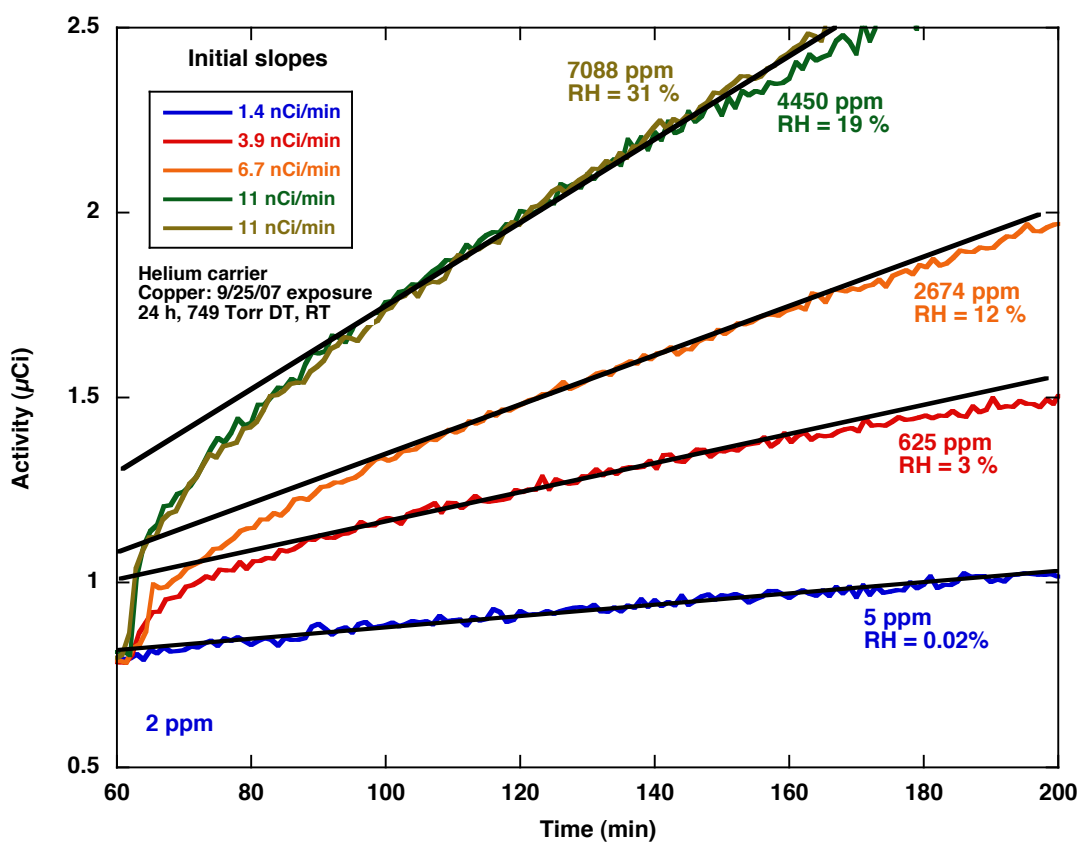

Fig. 7: Enlargement of Fig. 6 near the point in time when the carrier is humidified.

The second observation was that as the relative humidity increased, the initial desorption rate appears to reach a limit as seen in Table 1 and Figure 7. For each of the runs with a relative humidity between 19% and 31%, the slope of the curves remained around an average of 11.0 µCi/min. Inspection of the data in Fig.7 shows that the curves begin to fall beneath the linear extrapolation with increasing time because the water layers on the surface of the metal are being depleted of tritium.

Tritium Removal Limits

There appear to be two different limits for tritium desorption. The first can be understood because, as the humidified helium stream passes over the copper coupon, there is a certain amount of tritium that can be removed from the top monolayers of water on the surface of the copper coupon (see Fig. 8). As this amount of tritium is depleted, the second limit of tritium desorption can be seen. This limit is the process by which tritium molecules that are in solution in the copper migrate through the water layers to the surface of the coupon as illustrated in Fig. 8. This was demonstrated from the result that, as the water vapor pressure in the experiment was increased, the slope of the activity in the first bubbler against time appeared to reach a limit.
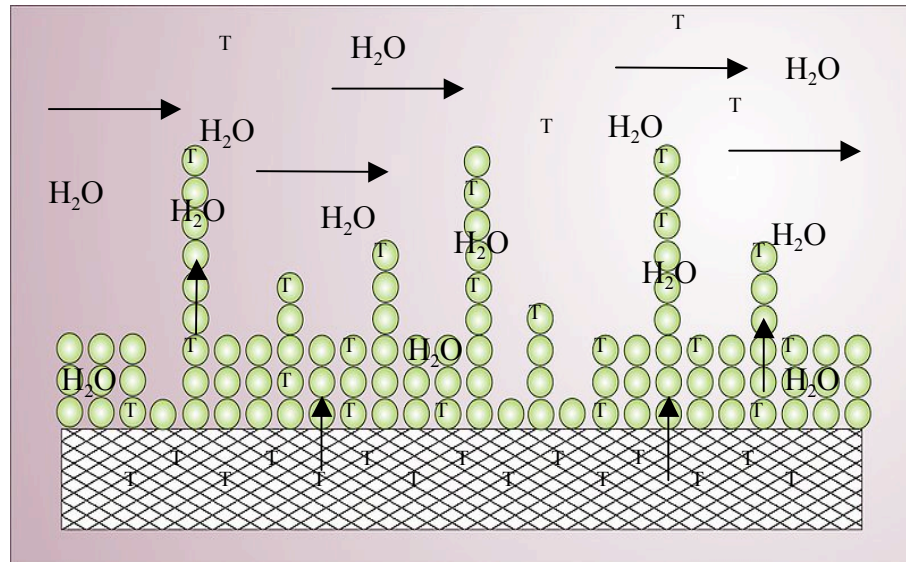
Fig. 8: Image depicting the process that occurs as a humidified helium stream passes over a tritiated copper coupon. It also shows the two limits to the process of adsorption and desorption.

Conclusion

Experiments have been performed to study and understand the processes by which water desorbs from copper. Tritium, which is a radioactive isotope of hydrogen, was used as a tracer to label water molecules attached to copper and monitor the rate at which desorption occurs. It was concluded that the rate of tritiated water (HTO) desorption from a copper surface increases with an increasing water vapor pressure. Therefore, the more humidified an environment is, the greater the desorption that will occur. Through these experiments, it was also found that the rate at which HTO desorbs approaches a limiting value. Additional experiments would provide more data to substantiate these conclusions.

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