Tritium Desorption from Stainless Steel Surfaces at Variable Temperatures

Ryan Shea

Fairport High School

LLE Advisor: Dr. Walter Shmayda

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Abstract

      An experiment has been performed to measure the effect of temperature on the outgassing rate of tritium from stainless steel. The removal of water, and more importantly tritium, is an important issue when conducting D-T fusion experiments. Tritium can contaminate equipment and metal components of a nuclear fusion test chamber. The removal of tritium from these devices is important because it allows facility personnel to work with these devices safely. Using a helium gas stream and a glass exposure chamber insulated inside a ceramic oven, the effect of temperature on the rate of tritium desorption was measured to find the optimal temperature for the removal of tritium and water. The helium gas stream flowed through the exposure chamber at a rate of 100 ml/min to remove surface contamination from a stainless steel coupon inside the chamber. The tritium in the gas stream was transferred to a liquid solution, which was counted in a liquid scintillation counter to determine the amount of activity removed at the different temperatures. The data shows that the removal of tritium is affected by three variables: the rate of tritium diffusion to the surface from the bulk, the rate of tritium desorption from the surface, and the rate of tritium removal by the gas stream.

Introduction

      The increasing need to find an alternative fuel source has led to a similar increase in the amount of research performed to study and analyze nuclear fusion reactions. Deuterium

and tritium, (DT), are the primary source of fuel for nuclear fusion reactions. Tritium is a heavy isotope of hydrogen containing one proton and two neutrons. It is radioactive and can contaminate devices used to monitor the nuclear fusion reactions. This can lead to problems if the tritium migrates from the surface of the device into the bulk. If the bulk of an object is contaminated, simply removing tritium from the surface will fail to completely decontaminate the device because surface contamination will occur again as tritium migrates back out of the bulk. Similar problems are experienced with water contamination in industries requiring moisture-free plumbing or apparatus. Increasing purity requirements in the semiconductor industry have called for a removal of moisture from all pure gas streams. Water desorption from the inner surfaces of metal process lines can contaminate a pure gas passing through the plumbing with low levels of water vapor. This can lead to a loss of yield and lifetime in large-scale devices.

The removal of tritium and water from an object is affected by many factors. Humidity has been shown to increase the rate of removal of tritium from contaminated devices. To further understand the process by which tritium is removed from a device the effect of temperature on the rate of removal has been studied. The desorption process depends on the three main factors shown in *Figure 1*: the rate of tritium diffusion from the bulk into the surface oxide, the tritium diffusion rate through the oxide layer, and the rate of tritium removal from the surface of the air-oxide interface. Tritium diffuses from the metal bulk through the oxide layer to the surface where it desorbs into the gas stream. Each step has a distinct rate. For simplicity the three separate processes have been treated

as one process in this report. Modeling of the separate processes involved in tritium

desorption from stainless steel has been performed by Karin Hsieh[1]. She considers the

factors affecting tritium desorption from the surface and diffusion from the bulk and

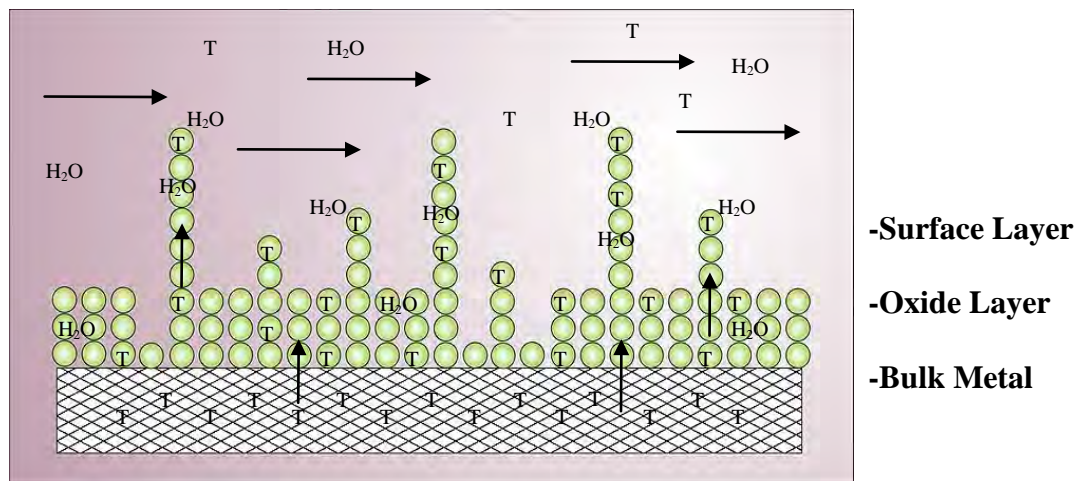through the oxide layer in her models of the tritium desorption rate.

-Surface Layer

-Oxide Layer

-Bulk Metal

Figure 1: Structure of a surface showing the bulk metal, the oxide layer, and the air-oxide

interface. Tritium diffuses from the bulk metal through the oxide layer to the

surface layer where it desorbs into the gas stream.

Experimental Setup

The experiment is illustrated in *Figure 2*. Helium flows from a high-pressure tank through

a regulator where the helium pressure is reduced to about 20 psi and into a purifier to

remove any traces of moisture and organic contamination in the helium. The helium flow

rate is set at 100 ml/min with a mass flow meter. The water vapor content in the helium is

measured with a dew point sensor, to ensure the stream is dry before it is introduced into

the exposure chamber. The exposure chamber is a 43.2 cm long quartz tube situated inside

a ceramic oven that is used to control the temperature of the tube. A thermocouple located

inside the tube sends information on the temperature back to a laptop computer where it is

recorded by a data acquisition program. The quartz tube contains one of the small tritiated

stainless steel samples, dubbed coupons due to their rectangular shape. The coupon is

pushed about 23 cm into the oven, which is then closed up to prevent any leakage of

radioactivity. The helium purge transfers tritium from the coupon surface to 100 ml of

liquid scintillation cocktail. It takes approximately 47 seconds for a slug of helium to flow

from the oven to the liquid scintillation cocktail (LSC). The collection efficiency of the

LSC approaches 100%. The activity of the tritiated LSC is monitored continuously by

sampling the LSC in a liquid scintillation counter. This device counts the number of

photons emitted by the LSC when the tritium decays into helium-3 by releasing electrons

into the cocktail. The electrons cause the LSC to fluoresce. This measurement technique

provides a very accurate count of the total radioactivity in the LSC and consequently a

good measure of how much tritium has been removed from the stainless steel coupon. The

sample of solution is returned to the vessel containing the LSC and remixed.   The activity

of the LSC increases with time as the trial progresses. The LSC sample takes about 77

seconds to complete the circuit. A program that works with the liquid scintillation counter

collects the raw data, provides a running average and converts the count per minute to

activity in microcuries per unit volume.

The data collected from each run by the data acquisition program is transferred into

a Microsoft Excel file. To help to calibrate the software and the oven, three test trials were run on low activity coupons. After the initial test coupons, four stainless steel coupons were used and labeled stainless steel coupon # 1 through 4. All of these coupons were desorbed between 439 and 454 days after the tritium exposure.
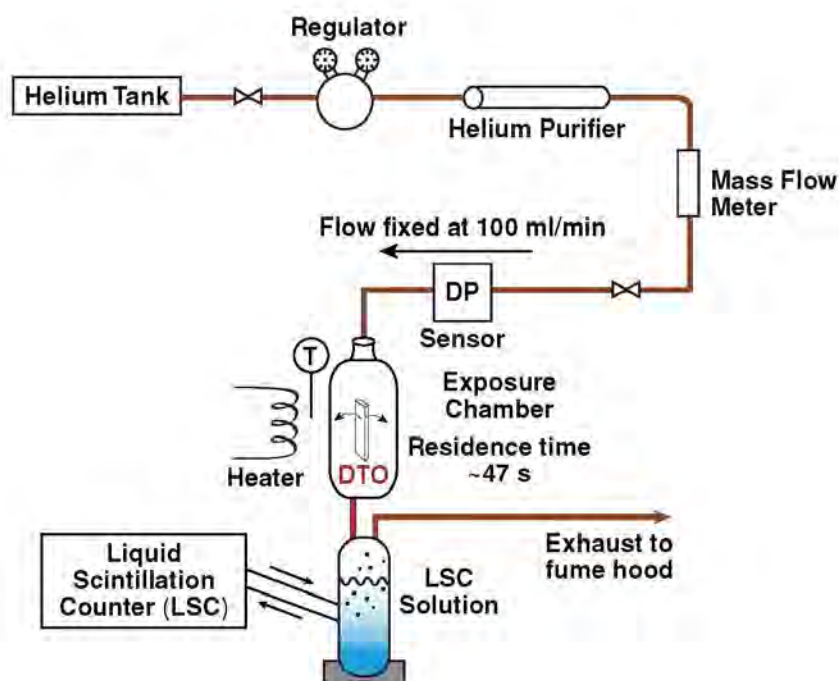

Figure 2: The experimental arrangement.

Results and Interpretation

Twenty-three experiments were performed by exposing four coupons to different temperature combinations to determine the effect of temperature on the rate of tritium removal from stainless steel. The first stainless steel coupon was baked at four consecutive

temperatures: 75°C, 150°C, 200°C, and 250°C to determine if a progressive increase in temperature will cause a progressive release of activity from the contaminated sample. As show by *Figure 3* the amount of activity collected for each trial did increase with increasing temperature. Starting with the 250°C run and for every subsequent run, the oven was kept at room temperature for 1 hour at the start of the experiment before the temperature was ramped up to the final dwell temperature. This was done to ensure that any surface contamination from the previous experiment was removed before the effect of the new temperature was monitored.

Figure 3: Evolution with time of temperature (the dashed lines) and activity (the solid lines) for the four runs of stainless steel coupon #1.

This was done to clearly demarcate the starting point of the temperature ramp and to ensure that a stable reference activity for the LSC was established for each run. The temperature oscillations observed in *Figure 3* were caused primarily by limitations in the program controlling the oven's ramp rate and dwell temperature. A comparison of runs three and four shows clearly that an increase in temperature causes an increase in the amount of tritium desorbed from a contaminated sample; however, the data does not indicate between which temperatures the greatest increase in tritium removal will occur.

Curves such as those shown in *Figure 3* do not show fully how successful each trial was in increasing the rate of tritium removal by the helium gas stream. It is more useful to plot the outgassing rate in microcuries per unit surface area per unit time against time. The conversion from activity to outgassing rate is obtained by using the following equation.

$$Outgas\ rate = \frac{d(Activity)}{dt} * \frac{1000}{60*22.24} \quad \frac{\mu Ci}{min*cm^2} \qquad (1)$$

The 1000 converts millicuries to microcuries, the 60 is used to convert seconds to minutes, and 22.24 cm^2 is the surface area of the metal coupon. Plots of outgassing rate against time are shown in *Figure 4*. This figure gives a much better measurement of how effectively tritium was outgassed from the contaminated coupon at each temperature.
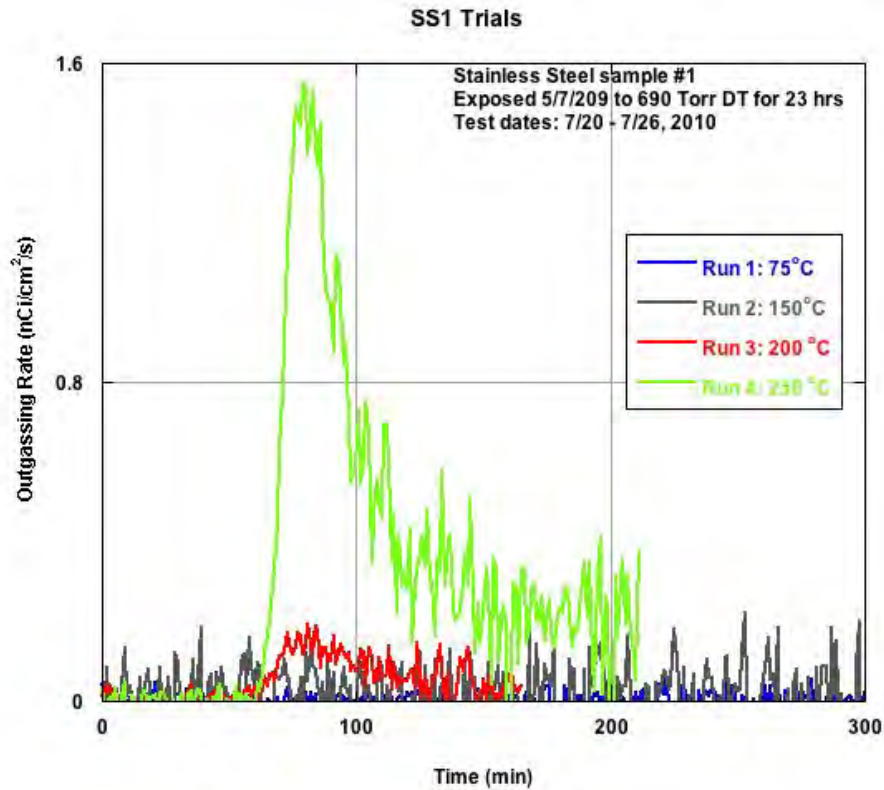
Figure 4: The outgassing rate against time for the four runs of stainless steel coupon #1.

In graphs such as *Figure 4*, a strong peak indicates that a large amount of tritium has been successfully removed from the coupon surface. Here the 75°C and 150°C runs both have very flat curves indicating much smaller outgassing rates compared to the higher temperature trials. The 200°C run has a small but noticeable peak around the 80 minute mark. This indicates that for this run outgassing of tritium was greatest at the 80th minute of the experiment. It also indicates us that using 200°C to desorb tritium was moderately successful in increasing the rate of outgassing from the contaminated coupon. A stronger peak is found for the 250°C run, approaching 1.6 nCi/cm^2/s near the 80th minute of the

trial. The 250°C run increased the outgassing rate of tritium by a factor of about 3.5

relative to the 200°C run as shown in *Figure 5*. Figure 5 provides the same data as *Figure*

4 but on an expanded scale around the time of interest, 80 min. Also noticeable is the fact

that the coupon continued to outgas tritium at relatively high rates during the 250°C run,

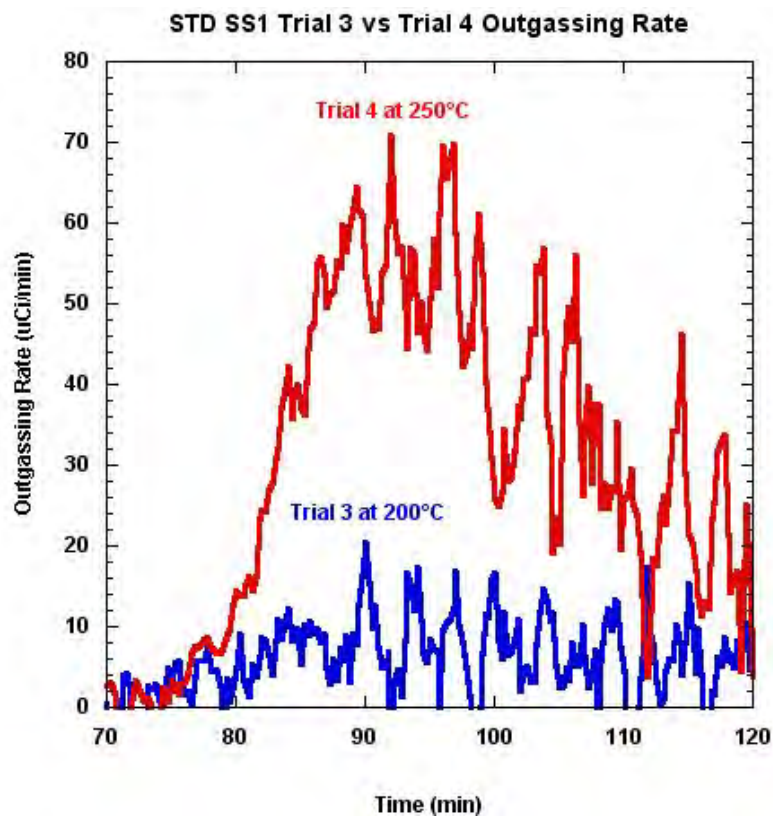confirming that a higher temperature is key when trying to remove tritium from a

contaminated metal.

Figure 5- Outgassing rate at the 200°C and 250°C runs for stainless steel coupon #1,

around the time of peak outgassing.

An important aspect of the experiment was to determine the total amount of radioactivity removed from each coupon. *Figure 6* shows the percentage of the total radioactivity that was removed during each run at each dwell temperature as well as the total amount of activity removed. It is clear from *Figure 6* that the 250°C run removed the largest amount of tritium by far from the coupon, with nearly 75% of the total tritium removed. It is also important to note that at 75°C, less than 1.5% of the total tritium is removed from the coupon.

Figure 6: Percent of the activity removed at different dwell temperatures for the four runs of stainless steel coupon #1.

To further confirm the effect of temperature on the outgassing rate of tritium from a contaminated sample, a second stainless steel coupon was subjected to a sequence of 6 bake outs at progressively higher temperature. *Figure* 7 plots the temperature (the dashed lines) and activity (the solid lines) against time for these runs. As before, each trial was held at room temperature for an hour before being ramped to the final dwell temperature. These experiments re-affirm that tritium desorption increases with increasing temperature.
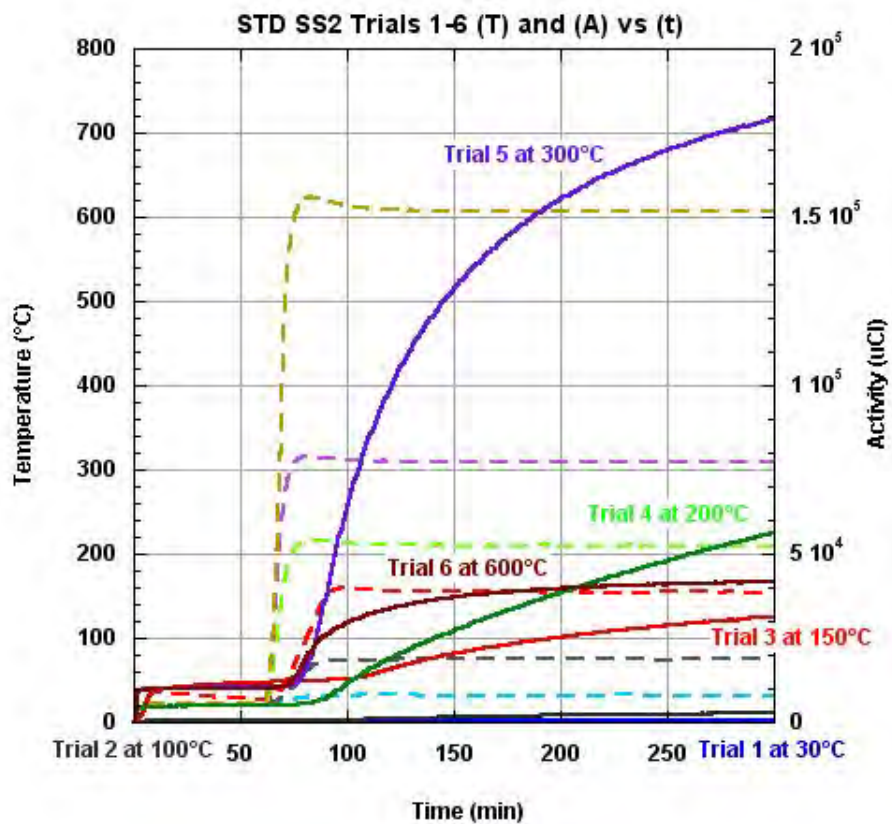

Figure 7: Evolution with time of temperature (dashed) and activity (solid) for the six sequential bake outs of stainless steel coupon #2.

Figure 7 demonstrates that increasing the bake out temperature from 100°C to

150°C increases the total activity released by a factor greater than 10. However, increasing the bake out temperature by an additional 50°C, from 150°C to 200°C, increases the total activity collected only by a factor of about 1.8. This suggests that increasing the bake out temperature above 100°C is important in increasing the total amount of tritium released from a contaminated coupon.

Figure 7 has two additional interesting aspects that should be noted. First, each trial started with a 60-minute dwell time at room temperature before ramping to the final dwell temperature within about 5 minutes. Yet on each run the activity didn't start to show this ramp until 20 minutes later, nearly 80 minutes into the run. Several modifications to the experiment were tried to reduce this response time; however, it proved impossible to reduce the response time below 75 minutes. The lag was attributed to the delayed in transferring heat from the oven to the coupon. Second, the activity collected during the 600°C bake out stagnated at 40 millicuries about 150 minutes into the run. Clearly the majority of the activity was removed from the bulk and oxide layer during the previous bake out at 300°C and suggests that it is not necessary to bake out metal at temperatures as high as 600°C. The evolution of the outgassing rates against time for these bake outs is plotted in *Figure 8*. It is noteworthy that the steady state outgassing (after the initial peak) also increases with increasing temperature, clearly demonstrated by the 200°C and 300°C runs, to suggest that the higher diffusivity of tritium leaving the metal is contributing to the outgassing rate.

The curves once again show an increase of over a factor of 10 between the outgassing rates at 100°C and 150°C. It is also important to note that the increase from 200°C to 300°C increases the outgassing rate by a factor of nearly 6.5 which can be seen clearly in *Figure 9*.
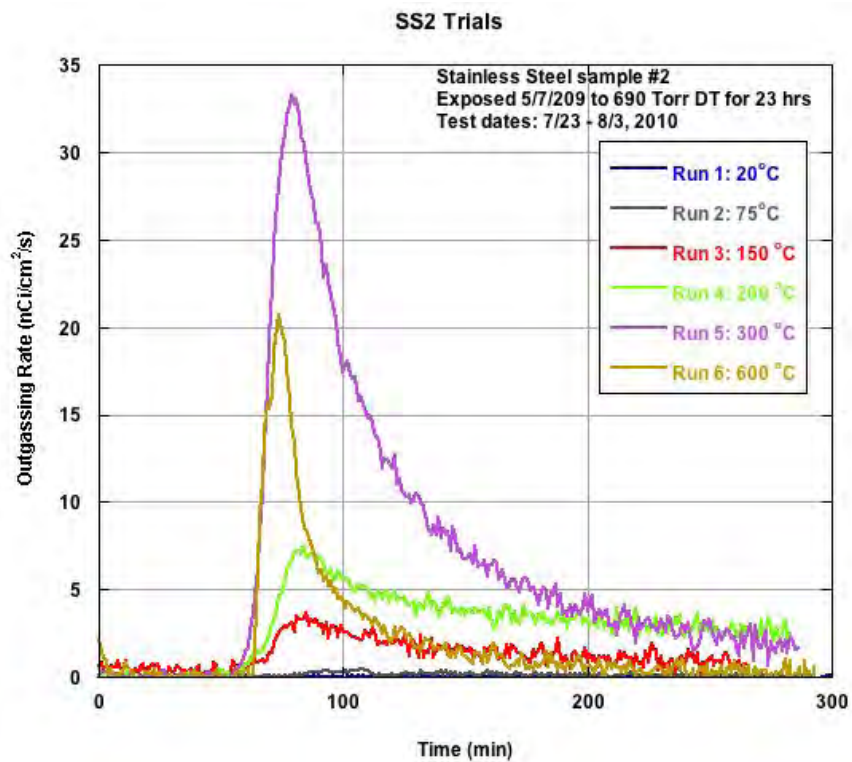

Figure 8- Outgassing rate against time for the six runs of stainless steel coupon #2.

Figure 9 zooms in on some of the data given in *Figure 8* to show how increasing the bake out temperature shifts the peak outgassing rate towards earlier times. The 150°C curve peaks around 115 minutes, the 200°C curve peaks at about 95 minutes and the 300°C curve

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peaks at about 80 minutes. The coupon temperature exceeds 100°C at earlier times as the bake out temperature increases from 150°C to 300°C and so surface desorption starts earlier.
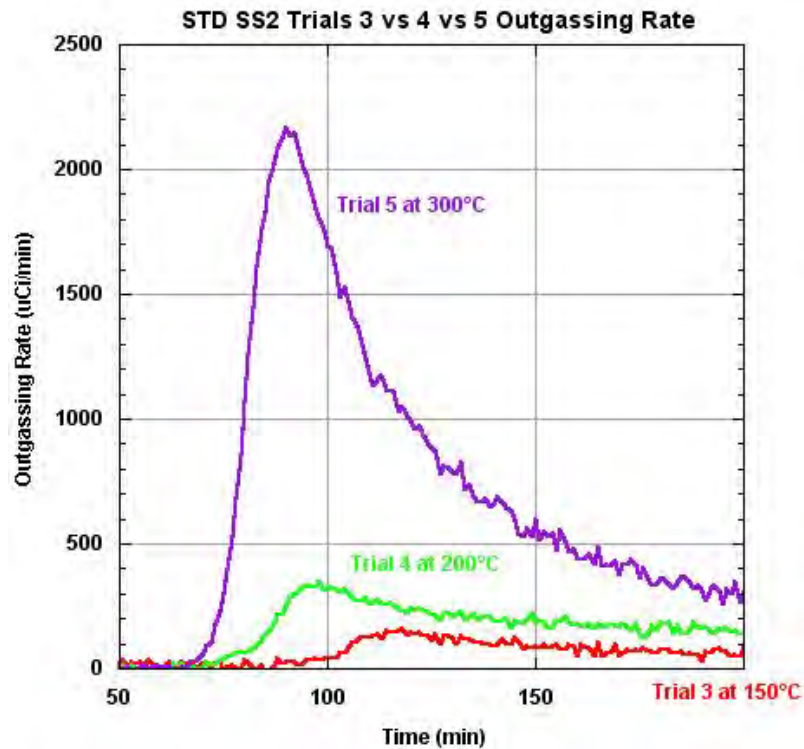

Figure 9- Peak outgassing rates for the 150°C, 200°C, and 300°C runs of stainless steel coupon #2, around the time of peak outgassing.

The percentage of the total activity removed in these runs was plotted for the different dwell temperatures in *Figure 10*. Tritium release increases noticeably once the bake out temperature exceeds 100°C. Furthermore, *Figure 10* also shows that the 300°C

run removed about 49% of the total tritium inventory whereas the 200°C bake out only removed 18% of the inventory. By comparison, the 100°C bake out only reduced the tritium inventory by about 2%. Baking out at or around 300°C is an effective and rapid way of reducing the bulk of the tritium inventory from stainless steel.
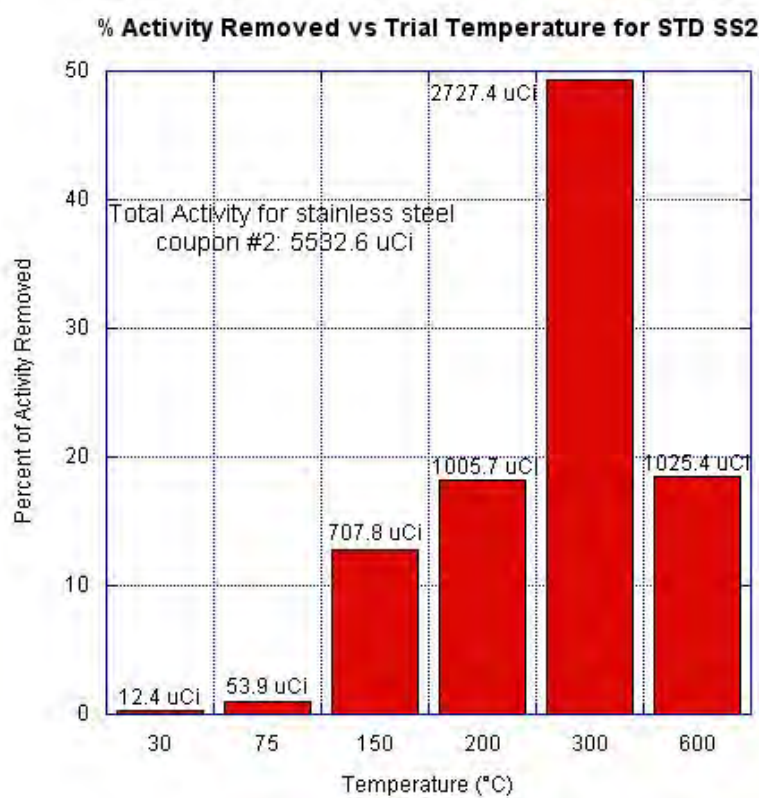

Figure 10: Percent of activity removed at different dwell temperatures for the six runs of stainless steel coupon #2.

A third stainless steel coupon was subjected to seven bake outs with a focus on

lower bake out temperatures. As shown in *Figure 11,* one trial was run at 30°C to get a

base-line activity curve and outgassing rate. Subsequently, the bake out temperature was

increased to 50°C and then incremented by 50°C in each successive run until the 200°C

run. The sequence was completed with runs at 300°C and 600°C. As in the previous

coupon most of the tritium inventory was depleted by the 300°C run. Residual tritium was

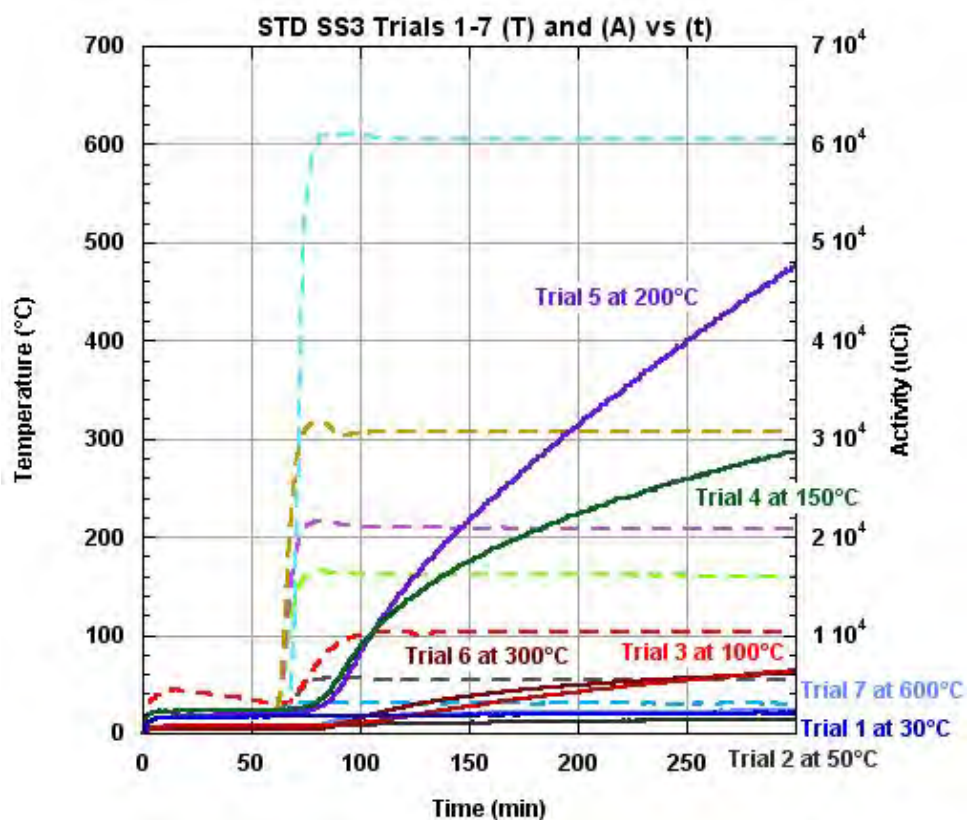released in both the 300°C and 600°C runs.

Figure 11- Temperature and activity evolution with time for the seven experimental trials of

stainless steel coupon #3.

Figure 11 shows a six-fold increase in the total activity removed when the bake out temperature is increased from 100°C to 150°C while an additional 50°C increase from 150°C to 200°C increases the total activity released by less than a factor of two. Tritium is bound to the surface and in the near surface as water. Bake out temperatures just above 100°C allow this tritium to boil off. However, the diffusion rate through the oxide and in the bulk metal is very low. Tritium in the lower oxide layers is not sufficiently mobile to reach the air-oxide interface. Consequently, increasing the temperature to 200°C has a less dramatic effect on the tritium release rate. Below 100°C tritium release is sluggish and only possible by the mostly weakly bound water molecules.

The plots of outgassing rate against time shown in *Figure 12* were obtained by differentiating the curves of *Figure 11* with respect to time. These curves highlight the difference in outgassing rate. When the bake out temperature is below 100°C, a discernable outgassing peak does not exist; when the temperature exceeds 100°C, the outgassing curve exhibits a peak approximately 20 to 40 min after the bake out begins. These curves are peaked because above 100°C there is a sudden and rapid release of surface-bound water followed by a slower, temperature-dependent diffusion-controlled transmission of tritium from the metal and the oxide to the surface where it is released to the purge gas. The diffusion of tritium from the metal bulk increases with increasing bake out temperature.
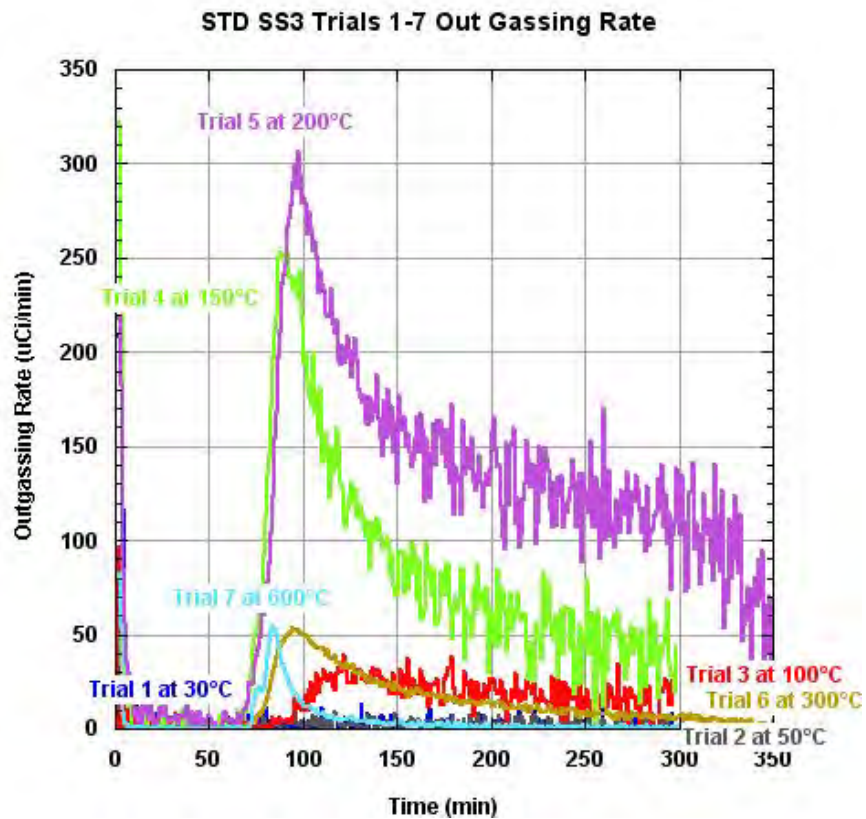
Figure 12- Outgassing rate against time for the seven experimental trials of stainless steel

coupon #3.

Inspection of *Figure 12* supports the discussion in the previous paragraph. The

outgassing rate at times long after the peak is sensitive to the bake out temperature. At

100°C and 150°C the outgassing rates at 250 min are small because the tritium that can

participate in the outgassing must be close to the air-oxide. Tritium located at greater

depths cannot reach the surface. At 150°C, the outgassing rate at 250 min is lower than for

the 200°C case for the same reason. However, at 600°C the diffusion rates are rapid compared to the rates at 300°C and the outgassing rate at long times decays towards zero much more rapidly. All the tritium is removed from the bulk more quickly at 600°C.
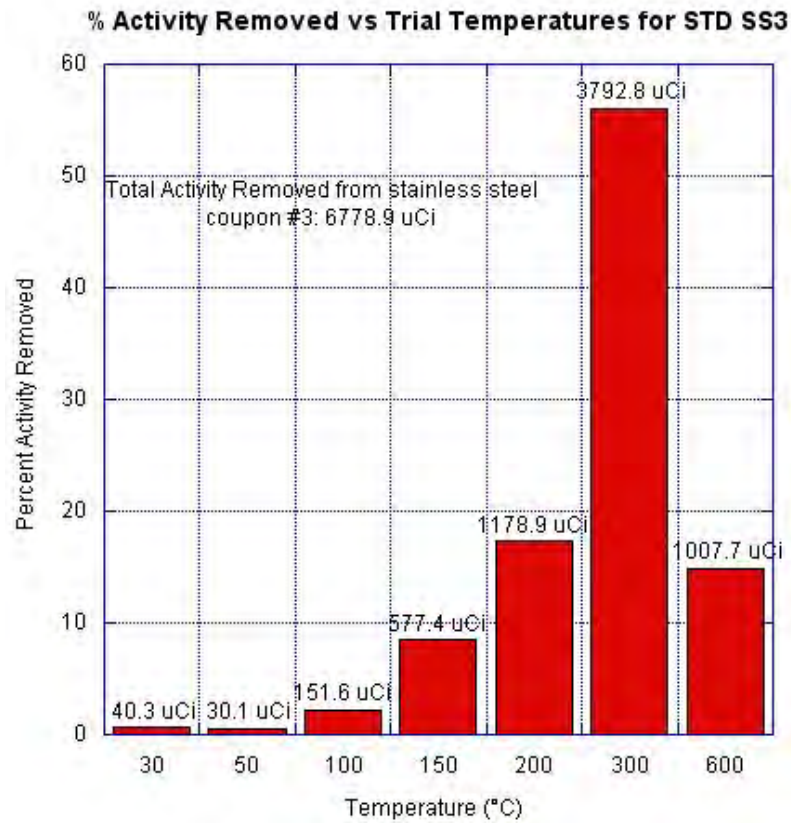

Figure 13- Percent activity removed at different dwell temperatures for the seven runs of stainless steel coupon #3.

The percentage of activity removed from the third stainless steel coupon for the seven runs was plotted against the bake out temperature in *Figure 13*. Almost 55% of the

total activity was removed in the 300°C run. This value seems high when compared to the activity curve in *Figure 11* and suggests there was an error in the data collection during the run or in the measurement of the total activity collected. The two measurements are based on independent measurement techniques. However, if the measurement of the total activity collected is erroneous, the error cannot exceed approximately 0.5 mCi because each sample is know to contain a total of 6.3 mCi. It is noteworthy that below 100°C the total amount of activity released is very small and consistent with the understanding that the tritium originates from the region close to the air-oxide interface.

   To understand more clearly the effects of just exceeding 100°C and to ensure that lowering the temperature in a sequential run does not have an unexpected effect on the outgassing rate, a fourth stainless steel coupon was baked out six times at temperatures close to 100°C. The data is shown in *Figure 14*. The temperature for each run was ramped up to the final dwell temperature after one hour, similar to the previous two coupons. *Figure 14* shows that at temperatures below 100°C, the activity slopes are flat (not peaked) and low. The outgassing rates are small. At temperatures above 100°C, the activity curves have much larger slopes and exhibit an initial peak when they are differentiated. The 50°C run has high activity because the liquid scintillation cocktail was not changed after the baseline run. The starting activity in the 85°C run was much higher than in the 125 °C case because the surface tritium was replenished by tritium diffusing from the bulk metal into the oxide layer and up to the air-oxide interface during the 125°C run. The activity in *Figure 14* is given in counts per minute instead of disintegrations per minute due to a slight

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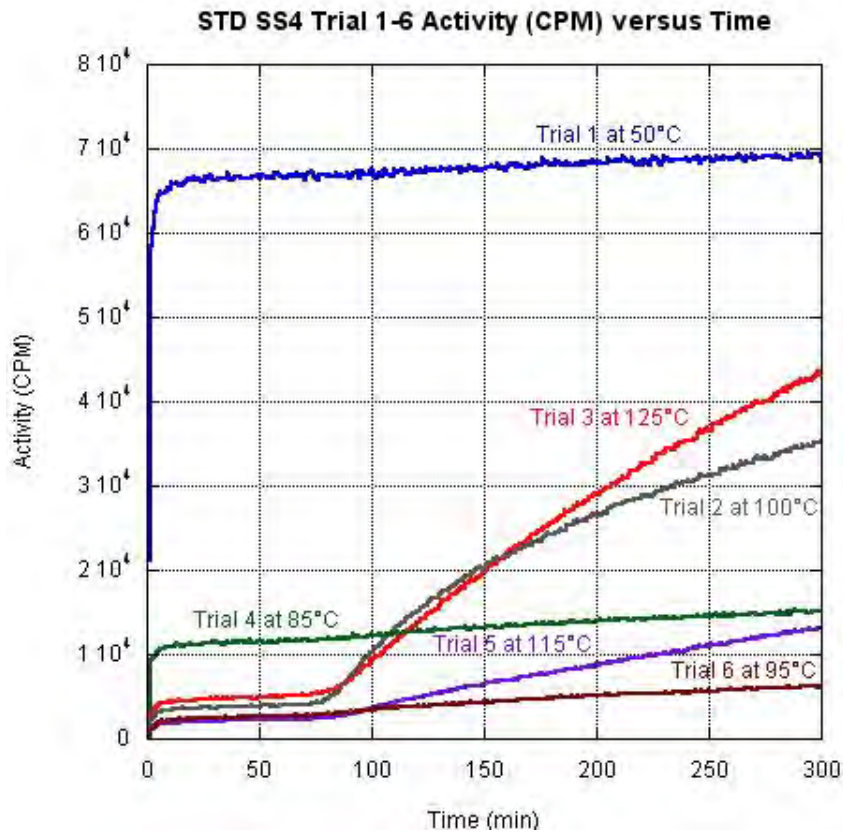glitch with the data acquisition program.

Figure 14- Activity in counts per minute against time for the six runs of stainless steel coupon #4.

Figure 15 provides the outgassing rates plotted against time for the activity curves shown in *Figure 14*. The outgassing rate decreases from run 2 to 3 even though the temperature increases. This suggests there are two processes at work: desorption from the surface and diffusion through the oxide layer. The latter process is slower and

consequently the tritium inventory in the oxide near the oxide air interface is depleted. The

tritium contribution for the bulk metal is probably not a factor because the diffusion

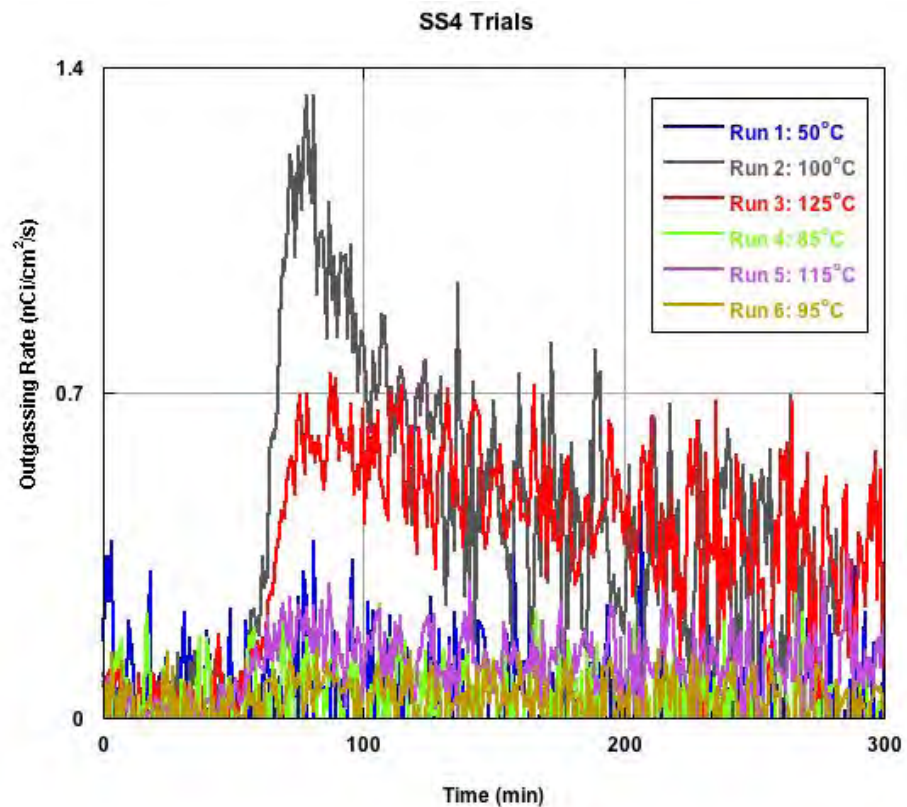coefficient is small at these temperatures.

F*igure 15 Outgassing rate against time for the six experimental trials of stainless steel*

coupon #4

Figure 15 also exhibits the expected peak in the outgassing rate when the bake out

temperature exceeds 100°C and then decreases to a negligible value once the tritium is

removed from the outermost layers. Note that the 115°C run also has a low outgassing rate

and further strengthens the suggestion that the 100°C and 125°C runs depleted the tritium inventory in the coupon's oxide layers close to the air-oxide interface.
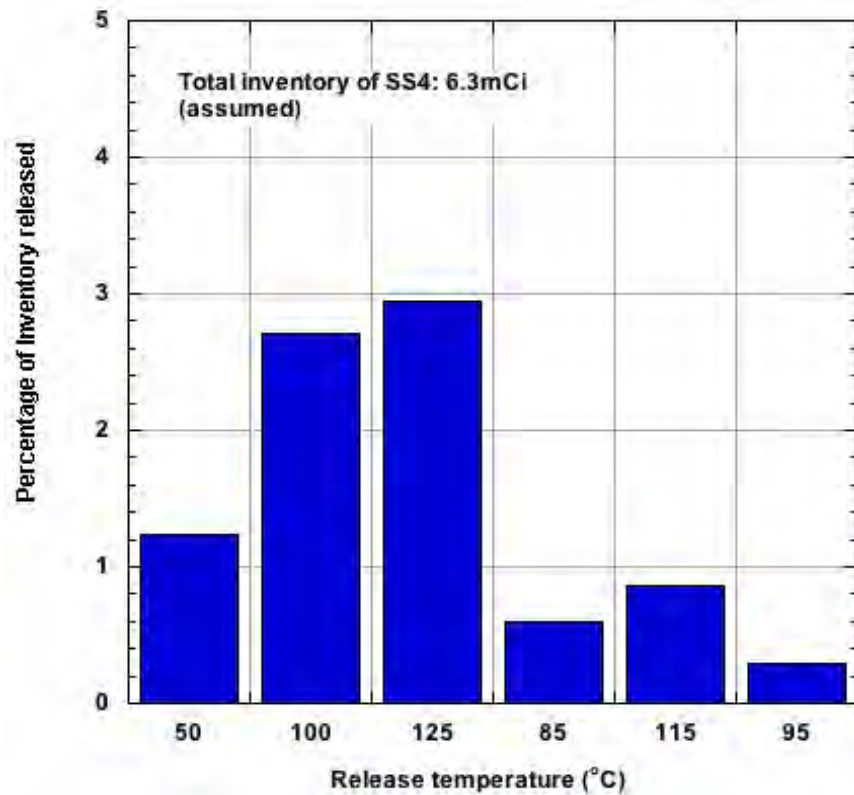

Figure 16: Percent activity removed at different dwell temperatures for the six runs of stainless steel coupon #4.

The percentages of activity removed at the different bake out temperatures are provided in *Figure 16*. Only 8.5% of the total tritium inventory was removed during these runs. Since tritium from the bulk is unlikely to contribute to the amount removed, it can be concluded that the oxide layer contains about 10% of the total tritium inventory; the

remainder of the tritium resides in the metal bulk and in the oxide layers closest to the

metal bulk. Increasing the desorption temperature slightly above 100°C is effective at

reducing the oxide-bound tritium inventory but not at depleting the total tritium inventory.

Even though there is an increase in the amount of tritium removed at 115°C relative to the

85°C run, the increase does not approach the levels of the 100°C and 125°C runs, further

supporting the contention that a significant fraction of the oxide-bound tritium had been

removed but that the innermost layers of tritium and tritium incorporated in the metal had

not been able to diffuse through the oxide layer and desorb from the surface.

Conclusion

An experiment has been performed to understand the effects of different dwell

temperatures on the desorption rate of tritium from a contaminated stainless steel coupon.

It has been shown that an increase in bake out temperature results in an increase in the

desorption rate of tritium from the metal sample. Approximately 10% of the tritium resides

near the surface under the present exposure conditions. The bake out temperature needs to

exceed 100°C if the intention is to deplete the near-surface tritium inventory and to reduce

outgassing from the metal once it is cooled to room temperature. The bake out temperature

needs to exceed 300°C if the intention is to deplete the tritium inventory in the metal bulk.

Bake out temperatures above 300°C accelerate the depletion of the tritium inventory in the

bulk.

References

1. K. Hsieh, LLE Summer High School Research Program, 2010

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