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# Partitioning of Tritium Between Surface and Bulk of 316 Stainless Steel at Room Temperature

## Introduction

The interaction of tritium with the native oxides on the surface of stainless steel is the first step toward adsorption and absorption of tritium into the bulk stainless-steel lattice. Understanding this fundamental interaction is necessary for the development of surfaces that minimize tritium absorption and tritium permeation through piping materials in nuclear reactors. Much work has been done to measure the distribution of tritium within stainless-steel samples<sup>1–7</sup> and to test the influence of different surface modifications on the absorption and permeation of tritium through stainless steel.<sup>8–15</sup> Several conclusions can already be drawn from this body of work. Firstly, the surface comprising <15 nm and near surface comprising <0.1- $\mu\text{m}$  layers of tritium-loaded stainless-steel samples contain relatively large fractions of the total tritium inventory.<sup>4</sup> These large surface concentrations are likely caused by tritium dissolved within the ubiquitous adsorbed water layers on stainless-steel surfaces.<sup>16–19</sup> Secondly, the relatively large surface concentrations are strongly influenced by the condition of the metal surface.<sup>19</sup> Finally, modifying the metal surface can significantly alter the permeation<sup>8,9,12,14</sup> and absorption<sup>13,15</sup> of tritium into the substrate metal, an effect likely caused by a local equilibrium established between the tritium concentrations in the adsorbed water layers and the bulk metal lattice.<sup>20</sup>

In this article we present new data about the tritium partition between the adsorbed water layers and the bulk metal lattice. This distribution was measured using two different techniques: a low-temperature pulsed plasma<sup>20</sup> and an aqueous  $\text{ZnCl}_2$  method adapted from Tanaka *et al.*<sup>21</sup> Both methods remove surface-adsorbed tritium. Thermal desorption was also used to measure tritium dissolved in the bulk metal lattice. The pulsed-plasma and  $\text{ZnCl}_2$  methods allow for the removal of the adsorbed water layers without etching into the substrate metal lattice. The pulsed-plasma method accomplishes this by bombarding the surface with energetic ions. The  $\text{ZnCl}_2$  method removes the adsorbed water layers by binding the  $\text{ZnCl}_2$  complex to the oxygen atoms in the hydroxyl layer. This hydroxyl layer is directly bound to the underlying native metal oxide that forms naturally on exposure to ambient air. By binding

the  $\text{ZnCl}_2$  complex to the surface, the multilayer structure of adsorbed water is expected to be liberated into solution, along with any tritium contained therein. Both surface removal techniques allow for the measurement of tritium adsorbed solely within the adsorbed water layers and at a finer resolution than has been reported to date.

## Experimental Setups and Procedures

Samples of  $5.1 \times 1.9 \times 0.3\text{-cm}^3$  dimensions were cut from a common plate of 316 stainless steel. The total geometric surface area of each sample was  $23.5\text{ cm}^2$ . A surface layer of  $\sim 0.86\text{-mm}$  depth was machined away to eliminate any surface inclusions produced in the manufacturing process and to expose the base metal lattice. The machining process produces surface striations along the machining path's axis, which adds to the overall surface roughness as discussed elsewhere.<sup>15</sup>

Two surface treatments were used to probe the relationship between surface finish and tritium uptake compared to unmodified surfaces. Samples that did not receive any pretreatments served as benchmarks and were labeled "as received." Ten as-received samples were baked for 2 h in dry helium at  $200^\circ\text{C}$  in a dry box to remove physisorbed water from the surface. These samples were labeled "as-received (baked)." Another subset of as-received samples was mechanically polished using  $3\ \mu\text{m}$  of MetaDi Mono Suspension diamond paste with a low-nap cloth wheel, followed by a final polish with  $0.3\ \mu\text{m}$  of  $\alpha$ -alumina provided by a commercial vendor. These samples were labeled as "polished." The surface roughness of the samples was measured with a Zygo NEXview interferometer. The average surface roughness for an as-received sample was  $0.27 \pm 0.06\ \mu\text{m}$ . Polished samples showed an average surface roughness of  $0.02 \pm 0.01\ \mu\text{m}$ .

All samples were placed in an ultrasonic bath and subjected to three washes: first with acetone to degrease the surfaces, then with isopropyl alcohol, and finally with de-ionized water to remove any chemical residue. The samples were then transferred to a glove box and stored under dry helium at a dew point of  $-65^\circ\text{C}$ . After drying in the glove box, the samples

were loaded with tritium by exposure to a 1-atm mixture of DT gas with an isotopic ratio comprising 70% tritium and 30% deuterium. The tritium partial pressure was 0.54 atm. The samples were soaked in the DT gas mixture for 24 h at room temperature. Under these exposure conditions the diffusivity of tritium through stainless steel is  $3.76 \times 10^{-16} \text{ m}^2/\text{s}$  at room temperature<sup>20</sup> and the tritium concentration within the bulk is not expected to be at equilibrium. After this loading, each sample was placed in an individual pod of a storage rack and sealed under dry helium to provide leak-tight storage. The storage racks were placed in a transfer box filled with a dry nitrogen atmosphere in order to minimize air exposure during the transfer from the storage rack to the experimental setup. All samples were stored in the racks until retrieved for an experiment.

The samples were subjected to one of three treatments: thermal desorption, plasma irradiation, or  $\text{ZnCl}_2$  washes. In the first treatment, a sample was subjected to temperature-programmed thermal desorption (TPD) to release and measure the total quantity of tritium retained by the metal sample. Tritium release was measured by scintillation counting of the activity collected with bubblers using a Perkin Elmer Tri-Carb 2910 TR liquid scintillation counter. In the second treatment, a sample was exposed to a room-temperature Tonks–Langmuir pulsed, radio-frequency–driven plasma to release and measure the quantity of tritium bound on and in the near surface. Tritium release was measured with an in-line ionization chamber. The pulse duration was 2 s followed by a 20-min dwell between each pulse. After the pulsed-plasma treatment, the sample was placed in the thermal desorption setup to measure the residual tritium in the bulk of the metal. Both of these techniques are described in detail elsewhere;<sup>20,22</sup> however, some improvements have been recently installed. The carrier gas used in the TPD procedure has been upgraded to ultrahigh-purity argon, and a load-lock system is used to transfer samples from storage into the pulsed-plasma chamber to minimize exposing samples to air during the transfer.

In the third treatment, samples were washed in an aqueous  $\text{ZnCl}_2$  solution to remove adsorbed tritium following a method adapted from Tanaka *et al.*<sup>21</sup> In this case, a sample was removed from storage under argon and soaked in a beaker containing 25 mL of 4-M ammonium chloride, 12.5 mL of 0.4-M  $\text{ZnCl}_2$ , and 12.5 mL of de-ionized water with the pH adjusted to 7 using concentrated ammonium hydroxide. The solution was stirred for 5 min. Afterward, the sample was removed, dried with filter paper, and placed in the thermal desorption setup to measure the residual tritium in the bulk of the metal. The activity of

the tritium removed by the  $\text{ZnCl}_2$  mixture and by the drying filter paper was measured using liquid scintillation counting to give the total quantity of surface tritium removed in the wash.

## Results and Discussion

To determine the tritium removal efficiencies of the pulsed-plasma and  $\text{ZnCl}_2$  methods, a series of six samples were treated with each method. Following the pulsed-plasma or the  $\text{ZnCl}_2$  treatment, each sample was heated to 700°C in the thermal desorption facility in order to measure the residual tritium in the sample bulk. Surface activities collected from the two sample sets are shown in Figs. 153.38–153.40. The first set of measurements focused on determining the total tritium inventory and its fractionation between surface and bulk. Samples were subjected to either thermal desorption or the  $\text{ZnCl}_2$  treatment followed by thermal desorption. In the second set of measurements, the efficacy of removing surface tritium by pulsed plasma or by  $\text{ZnCl}_2$  washes was compared. Samples were washed in the  $\text{ZnCl}_2$  solution or exposed to the pulsed plasma and then heated in the thermal desorption facility. Figures 153.38–153.40 compare the quantities of tritium removed from the surface and from the bulk for the as-received, as-received (baked), and the polished cases.

The data collected using the first series of samples are shown in Figs. 153.38 and 153.39. These data were collected

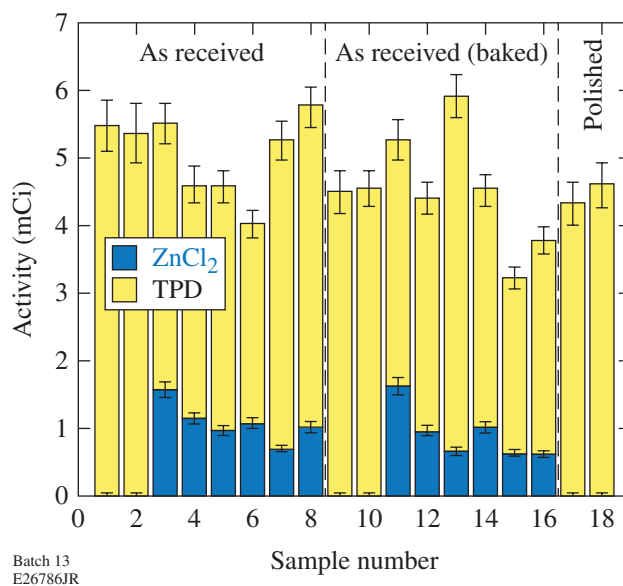


Figure 153.38 The total tritium inventory for as-received, as-received (baked), and polished stainless-steel samples. Tritium fractionation between the surface and bulk for as-received and as-received (baked) samples was determined using the  $\text{ZnCl}_2$  treatment method. TPD: temperature-programmed desorption.

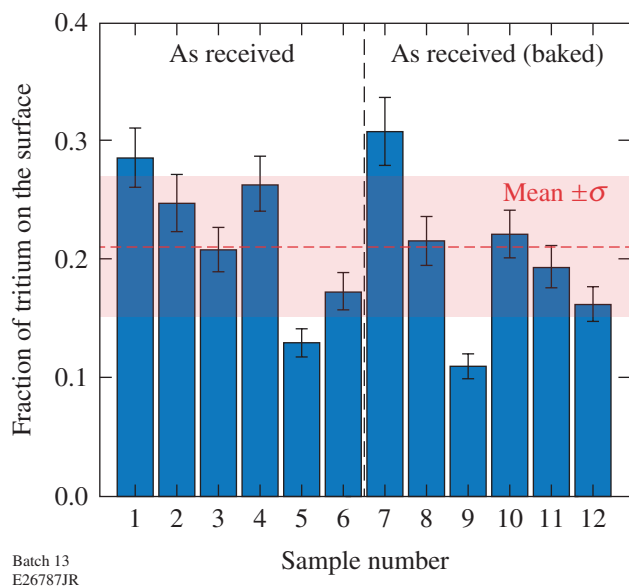


Figure 153.39

The relative fraction of the total tritium inventory residing on the surface of as-received and as-received (baked) stainless-steel samples. The horizontal dashed line provides the mean fraction without differentiating between the two treatments. The shaded band illustrates one standard deviation about the mean.

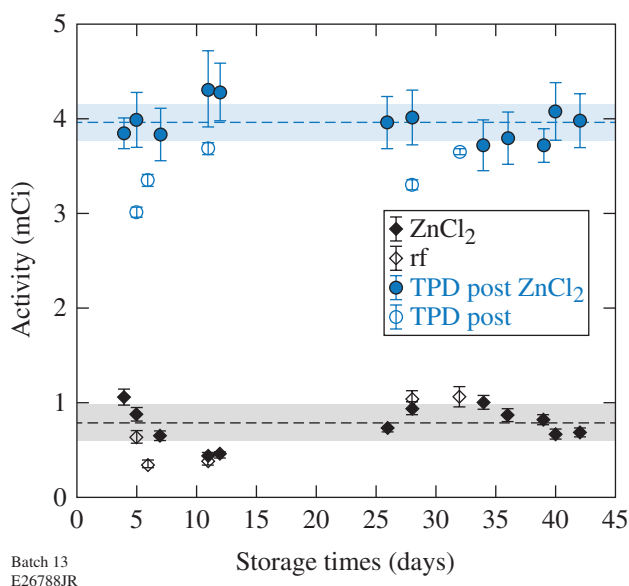


Figure 153.40

Change in the surface and bulk activities in stainless steel over 42 days of storage. Surface activity was measured using  $\text{ZnCl}_2$  or pulsed plasma. Bulk activity was measured using thermal desorption. Samples subjected to pulsed plasma + thermal desorption are shown as open symbols. Samples subjected to  $\text{ZnCl}_2$  + thermal desorption are shown as solid symbols. The mean surface activity is  $0.8 \pm 0.2$  mCi; the mean bulk activity is  $4.0 \pm 0.2$  mCi. The shaded bands illustrate one standard deviation about the mean. rf: radio frequency.

using a set of as-received samples, a set of as-received (baked) samples, and a set of mechanically polished samples. In this series, each sample was subjected to either thermal desorption alone or the combined procedure of a  $\text{ZnCl}_2$  treatment followed by thermal desorption. The data in each plot are grouped by sample pretreatment, with the as-received sample on the left followed by the as-received (baked) samples in the center panel followed by the mechanically polished samples on the right. Figure 153.38 shows the total tritium inventory deduced for each sample. For cases where the  $\text{ZnCl}_2$  surface treatment was applied, Fig. 153.38 also provides an estimate of the surface-to-bulk fractionation.

Comparing the data from samples subjected to thermal desorption only, both mechanically polished and baked samples contain similar quantities of tritium, of the order of 4.5 mCi; however, both sample sets have absorbed  $\sim 18\%$  less tritium than the untreated as-received samples. The similarity between the total tritium inventories in mechanically polished and as-received (baked) samples suggests that surface roughness alone does not determine the total quantity of absorbed tritium, even though, after polishing, the roughness decreased tenfold. The results of the combined  $\text{ZnCl}_2$  and thermal-desorption methods do not show a clear trend with sample baking.

Figure 153.39 shows the fraction of the total tritium inventory removed from the as-received and as-received (baked) samples using the  $\text{ZnCl}_2$  treatment method. These fractions were calculated using the absolute activities provided in Fig. 153.38. Each fraction was calculated by dividing the measured quantity removed by the  $\text{ZnCl}_2$  solution by sum of the quantities removed by the  $\text{ZnCl}_2$  solution and the subsequent thermal desorption. The mean fraction of tritium on the surface and one standard deviation about the mean are also shown in Fig. 153.39.

The data in Fig. 153.39 show that the  $\text{ZnCl}_2$  solution is capable of removing  $21 \pm 6\%$  of the total tritium inventory. This fraction of surface tritium removed is similar to that observed by acid etching.<sup>4</sup> However, given the fact that  $\text{ZnCl}_2$  undercuts hydroxyls from the stainless-steel surfaces and releases all surface-bound water,<sup>21</sup> the present results suggest that the tritium removed by the  $\text{ZnCl}_2$  solution resided solely in the adsorbed water layers. Approximately 21% of the total tritium inventory is retained on the surface of stainless steel.

The tritium occupancy in the water adsorbed on the metal surface can be estimated from first-principles calculations as follows: Water bonded to hydroxyls above the metal oxide

forms a water “ice” layer.<sup>16</sup> The lattice parameter for that ice is 0.448 nm (Ref. 23). Assuming that the water layers above the metal oxide comprise a single hydroxyl layer, one ice layer, and zero to two adsorbed water layers, depending on the ambient relative humidity conditions,<sup>24</sup> then the areal density of protons present on the metal surface will range from  $1.77 \times 10^{15}$  to  $3.76 \times 10^{15}$  protons/cm<sup>2</sup>. The surface area of the samples used in this experiment was 23.5 cm<sup>2</sup>. Adjusting the area by using a roughness factor of 2.4 for smooth 300 series stainless steel,<sup>25</sup> the total number of protons on the sample surface and consequently the number of sites available for tritons to replace protons will range from 1.0 to  $2.1 \times 10^{17}$  sites. On average,  $1.0 \pm 0.3$  mCi or equivalently  $2.08 \times 10^{16}$  tritons were collected from the water layers adsorbed on the stainless-steel samples listed in Fig. 153.38. The triton surface occupancy dependence on the number of adsorbed water layers is provided in Table 153.VIII and is seen to range from 11% to 25% of the available sites, depending on the actual relative humidity of the environment. Only the hydroxyl and ice layers are expected to be present on the samples used in this study since the experimental procedure minimized air exposure during the loading and storage cycles.

Table 153.VIII: Dependence of tritium occupancy in surface water layers on the number of adsorbed water layers.

Number of adsorbed water layers	0	1	2
Number of available sites for tritons ( $10^{16}$ )	8.4	14.1	19.7
Tritium occupancy in the surface layers (%)	25	15	11

The potential change in the distribution between surface-bound tritium and tritium residing in bulk steel was monitored over 42 days using a second series of samples. During this 42-day interval, the samples were kept under argon at room temperature. These measurements used only as-received samples that were subjected first to either ZnCl<sub>2</sub> or the pulsed-plasma treatments, followed by thermal desorption to determine the residual tritium. Figure 153.40 shows the dependence of the partition of tritium between the surface and bulk on time. The dashed lines in the figure are the mean surface and bulk activities:  $0.8 \pm 0.2$  mCi and  $4.0 \pm 0.2$  mCi, respectively. The shaded bands represent one standard deviation width centered about their respective mean.

The quantities of tritium removed by pulsed-plasma and ZnCl<sub>2</sub> washes are similar within experimental error. The

pulsed-plasma method removes adsorbed tritium by low-energy argon-ion bombardment of the surface with a negligible contribution of tritium from the underlying substrate metal.<sup>20</sup> The ZnCl<sub>2</sub> method removes the hydroxyl layer bonded to the metal oxide layer and liberates all water layers between the hydroxyl layer and the uppermost surface by replacing the hydroxyl layer with a zinc complex. Concurrence between these two independent surface-stripping methods reinforces the assumption that the released tritium originated from adsorbed surface water and hydroxyls. The adsorbed water layers contain  $16 \pm 4\%$  of the total tritium inventory present in these samples. Measurements from the set of samples discussed in Fig. 153.39 showed that the adsorbed water layer contained  $21 \pm 6\%$ . The measurements from both data sets are equal within the experimental errors.

While the pulsed-plasma and ZnCl<sub>2</sub> methods extracted similar quantities of presumably surface-adsorbed tritium, the subsequent thermal desorption measurements performed on samples exposed to the pulsed plasma showed systematically less residual tritium presumably removed from bulk of the samples. The consistently lower tritium quantities obtained from thermal desorption are likely due to unaccounted losses occurring during the transfer of the samples from the plasma chamber to the thermal desorption oven. These low-yield samples were exposed to laboratory air for longer periods than after the ZnCl<sub>2</sub> treatment. For this reason, the means calculated in Fig. 153.40 do not include the pulsed-plasma radio-frequency (rf) data.

Figure 153.40 also shows that there is no measurable redistribution of tritium between the surface and bulk over the 42-day storage period. While it is reasonable to assume that Fickian diffusion is taking place within the metal bulk, it is clear that a significant number of surface-bound tritons are not entering the metal lattice, even though the tritium concentration on the surface is significantly larger than that in the bulk of the metal. It is evident, however, that the rate of tritium migration from the surface into the metal lattice at room temperature is very slow and does not depend on lattice diffusivity of tritium in bulk stainless steel. Acid etching is needed to determine the concentration profiles in the bulk and the influence of storage time on these profiles.

The total amount of tritium collected from the bulk of 316 stainless steel suggests that tritium retention at defect sites within the metal lattice dominate lattice solubility. For the loading conditions presented here and using solubility and

diffusivity frequency factors and activation energies for tritium in 316 stainless steel compiled for higher temperatures<sup>20</sup> and extrapolated to room temperature, the samples are expected to contain ~0.5 mCi after a 24-h room-temperature exposure to tritium if the semi-infinite diffusion equation applies. However, the data shown in Figs. 153.38 and 153.40 demonstrate that 3 to 4 mCi are present. Defect sites, grain boundaries, vacancies, etc., increase the effective solubility of the metal about eightfold above that predicted by measurements at the higher temperatures.

### Conclusions

The partition of tritium between the near surface and the bulk for 316 stainless-steel samples has been measured after exposure to tritium gas at room temperature. Pulsed-plasma exposures and a ZnCl<sub>2</sub> wash surface treatment were used to remove tritium present in the water layers of the surface. Thermal desorption provided a good measure of the residual tritium in the bulk metal lattice. Several conclusions were made based on the data:

- The ZnCl<sub>2</sub> wash treatment and pulsed-plasma exposures provide independent techniques to release and measure the quantity of tritium within the adsorbed water layers. Both methods extract similar amounts of tritium from the adsorbed surface water layers.
- The quantity of surface-adsorbed tritium accounts for 17% to 20% of the total inventory absorbed by a stainless-steel sample after a 24-h exposure to DT gas at room temperature. This result agrees with published data<sup>4</sup> obtained by acid etching.
- Redistribution of tritium between the surface and the bulk of stainless steel, if it occurs, is very slow. Tritium does not appear to migrate into the metal bulk at a rate defined by lattice diffusivity.

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### REFERENCES

1. A. Perevezentsev *et al.*, *Fusion Sci. Technol.* **41**, 746 (2002).
2. Y. Torikai *et al.*, *J. Nucl. Mater.* **329–333**, 1624 (2004).
3. Y. Torikai *et al.*, *Fusion Sci. Technol.* **48**, 177 (2005).
4. R.-D. Penzhorn *et al.*, *J. Nucl. Mater.* **353**, 66 (2006).
5. Y. Torikai *et al.*, *J. Nucl. Mater.* **363–365**, 462 (2007).
6. S. Naoe *et al.*, *Fusion Sci. Technol.* **54**, 515 (2008).
7. R.-D. Penzhorn *et al.*, *Fusion Sci. Technol.* **64**, 45 (2013).
8. P. Weinhold *et al.*, *J. Nucl. Mater.* **93–94**, 866 (1980).
9. W. T. Shmayda, F. Waelbroeck, J. Winter, P. Wienhold, T. Banno, and N. P. Kherani, *Fusion Technol.* **8**, 2285 (1985).
10. T. Hirabayashi, M. Saeki, and E. Tachikawa, *J. Nucl. Mater.* **127**, 187 (1985).
11. N. M. Masaki, T. Hirabayashi, and M. Saeki, *Fusion Technol.* **15**, 1337 (1989).
12. K. Isobe *et al.*, *Fusion Sci. Technol.* **54**, 553 (2008).
13. Y. Ozeki *et al.*, *Fusion Sci. Technol.* **60**, 1499 (2011).
14. Q. Li *et al.*, *Int. J. Hydrog. Energy* **40**, 6459 (2015).
15. C. Fagan, M. Sharpe, W. T. Shmayda, and W. U. Schröder, *Fusion Sci. Technol.* **71**, 275 (2017).
16. P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).
17. T. Ohmi *et al.*, *Rev. Sci. Instrum.* **64**, 2683 (1993).
18. T. Shiraishi, S. Odoi, and M. Nishikawa, *J. Nucl. Sci. Technol.* **34**, 687 (1997).
19. M. Nishikawa *et al.*, *J. Nucl. Mater.* **227**, 99 (2000).
20. M. Sharpe, W. T. Shmayda, and W. U. Schröder, *Fusion Sci. Technol.* **70**, 97 (2016).
21. Y. Tanaka *et al.*, *Mater. Trans.* **49**, 805 (2008).
22. W. T. Shmayda, M. Sharpe, A. M. Boyce, R. Shea, B. Petroski, and W. U. Schröder, *Fusion Sci. Technol.* **68**, 766 (2015).
23. K. Röttger *et al.*, *Acta. Cryst.* **B68**, 91 (2012).
24. R. Schwartz, *Metrologia* **31**, 117 (1994).
25. M. Troy and J. P. Wightman, *J. Vac. Sci. Technol.* **8**, 515 (1971).