

# Detritiation of type 316 stainless steel by treatment with liquids at ambient temperature

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## Abstract

The detritiation efficiency of type 316 stainless steel (SS316) using liquids reagents (distilled deionized water, concentrated aqueous ammonia or a diluted hydrochloric acid/nitric acid mixture) was investigated at ambient temperature by means of liquid scintillation counting (LSC) and  $\beta$ -ray-induced X-ray spectrometry (BIXS). After a fast initial removal of tritium trapped on the outermost surface of SS316 with a rate in the order water < ammonia < acid mixture a slow chronic liberation of tritium into all three liquids sets in. First results indicate that chronic release occurs with a rate of approx. 0.2% per day. The long-term release was found to be largely independent from the kind of liquid agent into which the metal is submerged and from the initial loading of the SS316 specimen. From a practical point of view, the release rate of tritium into liquids is too slow for conditioning applications. Complementary evidence for the occurrence of a chronic liberation of tritium from SS316 into air at ambient temperature was obtained from tritium depth profiling of aged specimens by acid etching.

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## 1. Introduction

The detritiation of stainless steel is a topic of considerable economical implications within the frame of the worldwide ongoing development of fusion energy, because much tritiated stainless steel waste will be generated during the operation of large fusion machines. One type of stainless steel currently used for the manufacture of components installed in experimental fusion devices like JET (Joint Euro-

pean Torus) is type 316 (SS316) [1]. This steel is particularly common in the tritium plant required for fuel handling, storage, purification, and supply. There is thus an urgent need for the development of reliable technologies for the conditioning of tritium-contaminated SS316-waste having a variety of configurations and sizes, different degrees of contamination and, depending upon its application and previous history in the machine, a variety of surface and/or bulk trace element compositions.

From a practical point of view, gentle techniques designed to accomplish a rapid removal of a considerable fraction of the incorporated tritium, must preferably be developed. The aim is to rapidly

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achieve high DFs (decontamination factor = initial activity/final activity) compatible with the current margins established for the low level waste (LLW) category. This goal is of importance not only from an ecological point of view, but also indispensable out of economical considerations.

While in recent years the thermal deactivation of tritium-contaminated stainless steel in the presence of different sweep gases such as air [2], gas mixtures containing hydrogen, moisture, ammonia or ozone [2–6], by heating with an open flame [2] have received considerable attention, comparatively little is known on the mechanism and degree of decontamination achievable when contaminated materials are subjected to treatment with liquid reagents [7]. To gain a more thorough understanding of this topic, a systematic study on the detritiation efficiency of SS316 submerged in different reactive liquids at ambient temperature was performed. The reagents compared were (1) pure deionized water, (2) concentrated aqueous ammonia, and (3) a water–diluted HCl/HNO<sub>3</sub> acid mixture.

## 2. Experimental

### 2.1. Loading of specimens with tritium

All experiments were carried out with specimens of type SS316 stainless steel obtained from Nilaco, Japan. Its chemical composition is given by the manufacturer as 16–18% Cr, 10–14% Ni, 2–3% Mo, <2% Mn, and <1% Si (the balance percent being Fe). All examined specimens were machined in the own workshop, their dimensions approximating very closely 15 × 15 × 0.5 mm. The good reproducibility of these dimensions was verified by weight determinations, i.e. the average density of a large number of SS 316 stainless steel specimens was found to be (7.6178 ± 0.0757) g/cm<sup>3</sup>, when the dimensions given above were assumed.

As a rule 10 SS316 specimens were loaded with tritium in a single run. Prior to loading, the specimens were cleaned repeatedly with water in an ultrasonic bath and degreased in a second ultrasonic bath containing acetone. After drying, the ten specimens were separated from each other with a small amount of quartz wool, introduced into an UHV-tight quartz tube and degassed by evacuation at ambient temperature for several days until a vacuum of <10<sup>-5</sup> Pa was attained. Subsequently the specimens were heated at 400 K for several days after which the temperature was further raised in 50 K steps up to a final temperature of 673 K, while uninterruptedly pumping until a vacuum < 10<sup>-6</sup> Pa was reached. All in all the vacuum annealing treatment at elevated temperatures lasted for six or seven days. The objective of the treatment was to remove all weakly adsorbed water from the surface of the specimens. ZrNiH<sub>x</sub>T<sub>z</sub> was used as tritium source. To liberate the hydrogen–tritium mixture the getter was heated up to 923 K. At this temperature, the partial pressure of water is more than two orders of magnitude less than that of hydrogen [8]. More details on the loading apparatus can be found in a previous publication [3].

Immediately following the pretreatment, all 10 specimens were loaded simultaneously under the conditions summarized in Table 1, using a hydrogen/tritium mixture containing 32% tritium. Depending upon the selected loading parameters, the tritium inventories in the specimens covered a broad range of tritium contents, i.e. 0.5–13 MBq.

### 2.2. Determination of the tritium content and profile via full etching with acids

Numerous SS316 specimens of series H, F or Π (arbitrary designations) were subjected to a full etching treatment with the objective of (1) determining their total tritium content and (2) resolving their

Table 1  
Loading conditions of SS316 specimens with a gaseous hydrogen/tritium mixture (32% tritium)

| Arbitrary specimen designation | Loading date     | Loading conditions (pressure/time/temperature) | Actual average total tritium inventory <sup>a</sup> (MBq) |
|--------------------------------|------------------|--|---|
| Π                              | 27 November 2002 | 0.141 kPa, 8 h, 473 K                          | 0.490 ± 0.117 (4)   |
| H                              | 18 April 2002    | 1 kPa, 3 h, 523 K                              | 12.85 ± 0.67 (5)  |
| F                              | 2 April 2001     | 1.17 kPa, 3 h, 523 K                           | 5.18 <sup>b</sup> (1)                                     |

<sup>a</sup> Number of tritium measurements yielding the average value is given in parenthesis. The inventories were determined either by full etching or by thermal release.

<sup>b</sup> Tritium loading determined by etching on 3rd March 2003 plus that evolved into liquid water. The tritium loading of specimen F determined on 2nd April 2001 was 14 (MBq).

tritium depth profile. The dates at which the various specimens were loaded are given in Table 1. Tritium inventories of specimens loaded simultaneously were determined either by full etching or by a thermal release technique based on a conventional flow system described in a former paper [3]. The results from both techniques were found to agree well. While series H and F specimens were respectively charged with tritium approx. eight months and two years before treatment with a liquid reagent, series II specimens were loaded approximately three weeks before initiation of the leaching runs.

For full etching, each single tritium-loaded specimen was submerged successively into one of 24 small flasks containing a solution consisting of a 1 ml concentrated acid mixture (HCl:HNO<sub>3</sub> = 3:1) diluted in 1 ml deionized water. The flasks were regularly shaken to assure homogeneous contact between the specimen and the etching solution. After an appropriate period of exposure to the etching solution, the specimen was removed from the acid and rinsed repeatedly from both sides with altogether 8 ml deionized water. The rinsed water was dropped into the flask containing the etching solution to collect quantitatively all etched tritium and further dilute the acid. Finally, the tritium in each flask was quantified by conventional LSC using a type LB-5 instrument purchased from ALOCA, Japan.

At the end of the etching procedure the specimen was completely dissolved. The thickness of the surface layer removed in each singular etching step was calculated from the known dimensions of the specimen and the determined weight loss. Etched specimens showed flat and bright surfaces; visual inspection gave no indication of pit corrosion or non-homogeneous material removal.

### 2.3. Determination of the tritium release into liquid reagents

To determine the tritium release into liquid reagents, single tritium-loaded SS316 specimens of series H, II or F, having rather different tritium contents and storage history (see Table 1), were each placed in a closed flask containing either 10 ml deionized water, or 10 ml concentrated aqueous ammonia, or a 1 ml HCl:HNO<sub>3</sub> = 3:1 acid mixture diluted in 9 ml water to reduce the etching rate. The evolution of tritium into the water was obtained from 0.05 ml aliquots taken periodically from the flasks over accumulated periods ranging from min-

utes up to several months. For tritium analysis 15 ml of LSC cocktail were added to the aliquots and the resulting solution counted by LSC.

## 3. Results and discussion

### 3.1. Tritium content and depth profile

Typical etching results obtained with a single freshly loaded SS316 specimen of series II are presented in Table 2 and plotted as cross sectional profile in Fig. 1. In agreement with a loading mechanism based on thermal diffusion, the concentration of tritium in the SS316 specimen decreases continuously with progressing depth towards the middle of the specimen, reaching a minimum at this point. The minimum reflects the fact that under the employed loading conditions (see Table 1) the tritium level in the bulk was below the equilibrium solubility concentration, i.e.  $(1.0\text{--}2.8) \times 10^2$  MBq/cm<sup>3</sup> (at 473 K and 0.14 kPa HT with 32% T content) [9,10]. As apparent from the data in Table 2, the highest specific concentration of tritium, i.e. 25.8 GBq/cm<sup>3</sup>, was observed at the outermost surface of the specimen at depths of less than 0.02 μm, suggesting another mechanism of tritium retention at this depth level (most probably an oxide

Table 2  
Etching of specimen II-12

| Depth (μm) | Accumulated etched depth (μm) | Total tritium released from each etching step (Bq) | Tritium concentration in the etched layer (MBq/cm <sup>3</sup> ) |
|------------|-------------------------------|--|--|
| 0.0118     | 0.0118                        | 68 500   | 25 800   |
| 0.0677     | 0.0795                        | 10 800   | 710  |
| 0.109      | 0.188                         | 6060   | 247  |
| 0.265      | 0.453                         | 5740   | 96.3   |
| 0.283      | 0.736                         | 5940   | 93.4   |
| 0.433      | 1.17                          | 5930   | 61.0   |
| 0.665      | 1.83                          | 8740   | 58.4   |
| 0.730      | 2.56                          | 7240   | 44.1   |
| 2.95       | 5.52                          | 10 600   | 16.0   |
| 3.66       | 9.18                          | 5670   | 6.88   |
| 3.91       | 13.1                          | 6180   | 7.02   |
| 7.93       | 21.0                          | 17 700   | 9.93   |
| 10.7       | 31.8                          | 26 800   | 11.1   |
| 14.5       | 46.2                          | 33 000   | 10.1   |
| 22.8       | 69.0                          | 38 300   | 7.47   |
| 38.7       | 108                           | 39 300   | 4.51   |
| 23.1       | 131                           | 12 800   | 2.46   |
| 42.8       | 174                           | 14 200   | 1.37   |
| 32.7       | 206                           | 4740   | 0.64   |
| 44.0       | 250                           | 5210   | 0.53   |

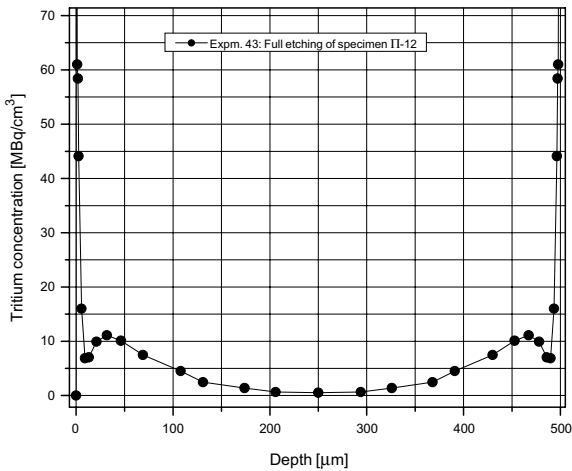


Fig. 1. Tritium depth profile across a SS316 series II specimen (to improve the resolution the highest tritium concentrations on the outermost surface of the specimen are not shown). The tritium concentrations are those in the respective etched layers.

layer). The concentration profile of tritium, which at least initially decreases very rapidly with progressing depth, shows a second smaller maximum at a depth of approx. 30  $\mu\text{m}$  (see Fig. 1). This maximum results from a progressive depletion at room temperature of tritium trapped immediately below the surface zone. It is possibly due to cracks in the oxide layer or an inter-granular diffusion through the oxide layer enhanced by isotopic exchange with ambient moisture taking place with tritium that has reached the surface.<sup>1</sup> This process must be faster than tritium regrowth from the bulk [10]. The sum of all partial tritium determinations by etching delivers the total tritium content in the specimen. For specimen II-12 it was found to be 0.334 MBq (Table 2). The depth profile in tritium concentration agrees well – even in details – with a profile published by Austin and Elleman [11]. They incorporated tritium into stainless steel by thermal anneal of a LiF surface blanket previously irradiated with neutrons and obtained a depth profile by electropolishing in an acid mixture. The relative topmost tritium concentration reported in Ref. [11] is much lower than that found in this work. This is not surprising considering that in the first etch they

<sup>1</sup> The partial pressure of moisture, which is known to enhance the liberation of the comparatively small fraction of the total tritium present on the surface, has no discernable influence on the rate of thermal release of tritium from the bulk of stainless steel [6].

removed a total of 1  $\mu\text{m}$  from the surface (compared to 0.01  $\mu\text{m}$  in this work) and the concentration drop of tritium at the top surface is extremely steep (see Table 2).

Except for the particularly high specific concentration of tritium on the outermost surface, the etching cross sectional depth profile of a series H stainless steel specimen (see Fig. 2, where the maximum tritium concentration on the surface, i.e. 15 GBq/cm<sup>3</sup>, was omitted for resolution reasons) is completely different from that of a series II (see Fig. 1). The depth profile of an H-series specimen, which was stored under a hood at ambient conditions for approx. eight months, provides evidence that during extended storage a significant fraction of the tritium trapped in the metal escaped the solid matrix into ambient air. This is inferred from the maximum in tritium concentration at the center of the specimen as opposed to the minimum in freshly charged specimens. In accordance with expectations, the maximum of specimen H-IX and the minimum of specimen II-12, i.e. 400 and 0.5 MBq/cm<sup>3</sup>, respectively, reflect the initial concentrations in these specimens, i.e. 12.85 and 0.40 MBq, respectively, and the used loading conditions (see Table 1).

Analogous to the depth profile of specimen H-IX depicted in Fig. 2, the depth profile of specimen F-III (see Fig. 3), stored over a period of almost two years under a hood and then submerged into water for nearly three months, also showed a maximum at its center, but, on account of the longer aging period, much less pronounced than that of specimen H-IX. In addition, because of an expedient isotopic

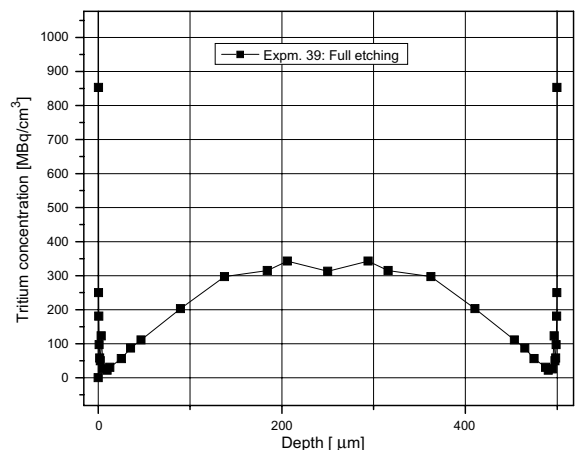


Fig. 2. Tritium depth profile across specimen H-IX (the highest tritium concentrations on the topmost surface, i.e. 15 GBq/cm<sup>3</sup>, is not shown).

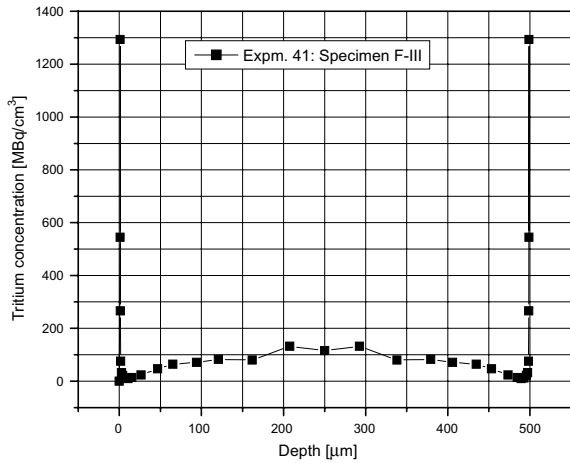


Fig. 3. Full etching of F-III specimen after being submerged into deionized water for several months (the highest concentration of tritium on the topmost surface, i.e. 1.3 GBq/cm<sup>3</sup>, is included).

exchange with liquid water and insufficient time allocation for regrowth, the tritium concentration on the surface of specimen F-III (1.3 GBq/cm<sup>3</sup>) was lower by about an order of magnitude than that on specimen H-IX (15 GBq/cm<sup>3</sup>), which was not previously subjected to interaction with any liquid reagent (the initial tritium inventory in both specimens differed only by a factor of approx. 2).

These observations clearly indicate that tritium captured in stainless steel specimens outgasses chronically. Further evidence for a chronic release is provided by the loading data of specimen F (see Table 1). This specimen lost more than 60% of its original tritium during a storage period of 630 days, which yields a daily release fraction of 0.2% (assuming a constant chronic release over the time period under consideration). Interestingly, Surette and McElroy [12] have reported a chronic tritium loss from degreased stainless steel (it was not specified whether of type SS316 or SS304) stored under open air for a period totaling one year of 0.17% per day.

### 3.2. Tritium release into liquid reagents

Several publications [12–14] have dealt with the slow liberation of tritium into ambient air from stainless steel previously exposed to tritium at room temperature, but no quantitative or semi-quantitative evaluation of such ‘chronic’ release into liquids at low temperature has so far been reported, especially for specimens loaded at elevated temperatures.

#### 3.2.1. Tritium release into water

The tritium releases from specimens of series H (H-VI), Π (Π-14), and series F (F-III) into liquid water are plotted in Figs. 4–6. The initial tritium inventory was obtained from the sum of the amount of tritium removed during the respective release experiment and the tritium content remaining in the specimen after completion of the corresponding leaching study (determined either by full etching or thermal release). These results constitute strong experimental evidence for the occurrence of a slow chronic release of tritium from tritium-loaded SS316 specimens into liquid water at ambient

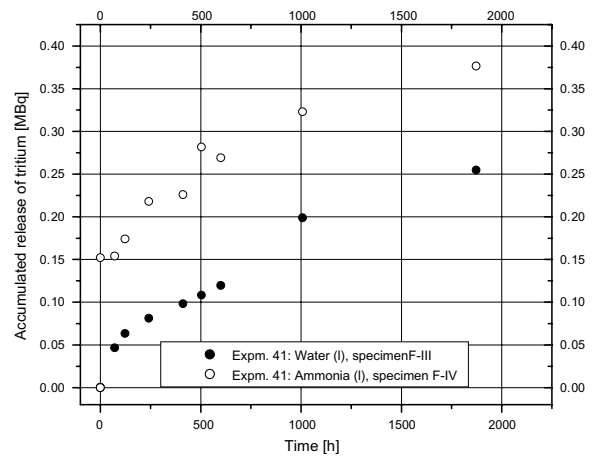


Fig. 4. Release of tritium into liquid water (●) and aqueous ammonia (○) at ambient temperature from a SS316 specimen exposed to tritium about eight months before these measurements.

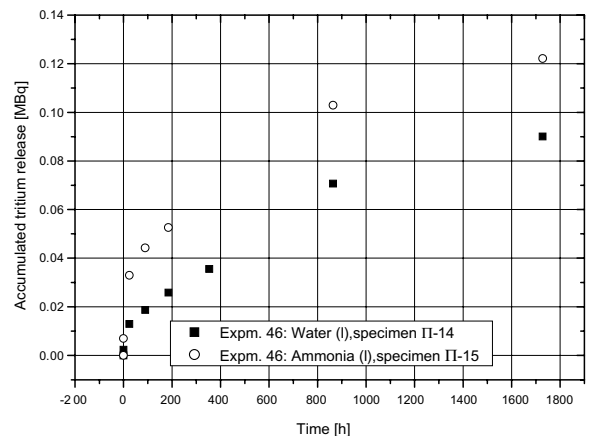


Fig. 5. Release of tritium from a freshly loaded SS316 specimen into liquid water (●) and liquid ammonia (○) at room temperature.

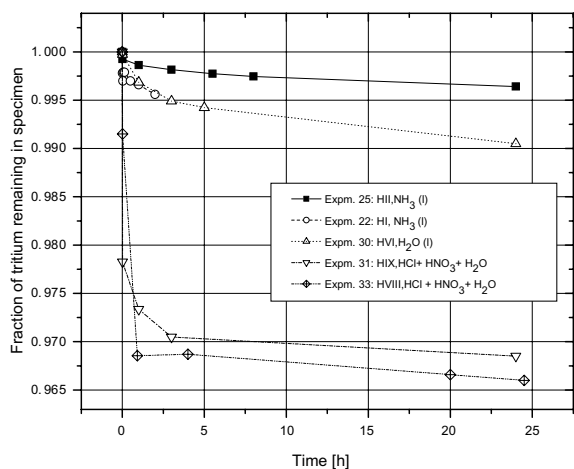


Fig. 6. Comparison between the tritium release rates from SS316 into liquid water, liquid ammonia or a liquid mixture of acids at ambient temperature using specimens of series H.

temperature. Since tritium is also liberated chronically into ambient air with a rate of similar order of magnitude, it appears that the migration of tritium from the bulk to the surface and/or a recombination-kinetics of Q or OQ (Q = H, T) groups are rate-determining (see Section 3) [15].

### 3.2.2. Tritium release into concentrated aqueous ammonia

Figs. 4–6 summarize tritium release data from specimens of series H (H-I and H-II), from one specimen of series II (II-15) and one of series F (F-IV) into concentrated aqueous ammonia. The LSC analyses reveal that about 0.44%, i.e. 0.057 MBq, of the total tritium immobilized in specimen H-I was released into ammonia fairly rapidly, i.e. after 2 h of submersion at ambient temperature. This is grossly in line with tritium surface measurements of specimen H-I taken before and after exposure to aqueous ammonia using the BIXS technique [3,16]. While the BIXS-spectra before and after exposure to ammonia showed the same peaks, the intensity of the characteristic Ar(K $\alpha$ )-rays induced by  $\beta$ -rays diminished by about 9%, suggesting that roughly this amount of surface tritium was released into ammonia during the time period in question. On the basis of the BIXS result the tritium activity in a surface volume element of a series H specimen having a thickness of 1  $\mu$ m can be estimated to be of the order of 0.87 MBq. Nine percent of this activity amounts to about 0.08 MBq, which is of the same order of magnitude as that obtained from leaching/LSC, i.e. 0.05 MBq. Thus only 0.45% of the

total activity and only 9% of that present on the top-most surface were released.

The results plotted in Figs. 4–6 substantiate the conclusion that at ambient temperature a slow persistent release of tritium from tritium-loaded SS316 takes place into strong liquid reagents, the rate of release into aqueous ammonia being comparable to that into water.

In a single run, the thermal release rate of tritium at 573 K from specimen H-X was compared with that from a similar one (H-II) previously exposed for 24 h to aqueous ammonia. Fig. 7 shows that such a pre-exposure has no measurable impact on the release rate of tritium when argon is used as carrier gas. However, further experiments are needed to verify whether this treatment has indeed no influence on the stainless steel surface or the characteristics of the ammonia-exposed specimen are quickly restored to the original ones after a brief contact with air.

### 3.2.3. Tritium release into a diluted HCl/HNO<sub>3</sub> solution

The release of tritium from two SS316 specimens of series H (H-VIII and H-IX) into an acid mixture was also investigated (see Fig. 6). In one case, i.e. specimen H-VIII, the actual weight loss of the specimen (initial weight 0.86629 g) caused by corrosive reaction with the reagent was determined to be 0.278 mg following an integral exposure of 24.5 h. The removed layer was calculated to have a thickness of 0.0802  $\mu$ m and the liberated tritium to correspond to a fraction of only 2.9% of the total tritium

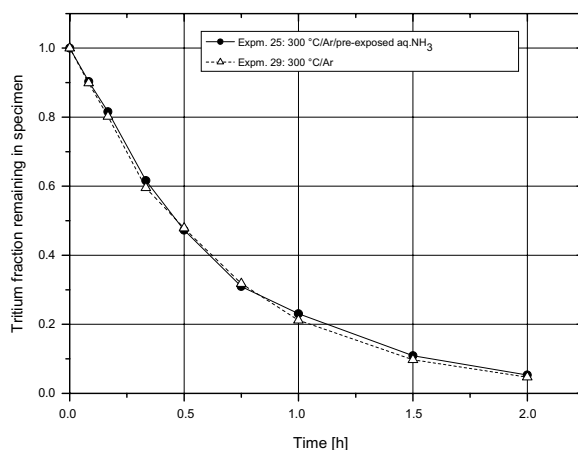


Fig. 7. Effect of pre-exposure to aqueous ammonia on the thermal release rate of tritium from a tritium-loaded SS316 specimen.

initially present in the sample. The treatment thus only pertained the tritium on the surface.

### 3.2.4. Comparison of the detritiation effectiveness of different liquid reagents

As Fig. 6 illustrates, already an exposure of a few hours provides first evidence for a chronic release of tritium into all three investigated liquid reagents from SS316 specimens loaded thermally with tritium. The only difference between water, ammonia and the diluted mixture of acids is that the latter induces a more rapid initial release. Still preliminary observations indicate that the efficiency in removing outermost tritium increases in the order water < ammonia < mixture of acids. The stronger effect of the acid mixture is attributed to a chemical reaction with the oxide surface layer protecting the specimens [17]. The initial release rate of tritium from specimens containing  $(13.0 \pm 0.3)$  MBq of tritium into all three examined liquids was estimated to be  $(3.7 \pm 1.3) \times 10^{-4}$  (MBq/h cm<sup>2</sup>).

From the runs performed over very extended periods of time with SS316 specimens of series F (F-III and F-IV) using water and aqueous ammonia as leaching agents (see Fig. 4) it is seen that the release rates slowly but progressively decrease. After 1872 h exposure time about 4.9% and 7.3% of the tritium was liberated into water and ammonia, respectively. As apparent, only ammonia induces a rapid initial liberation of tritium. Thereafter the release rates into water and into ammonia are similar. This is consistent with the conclusion given above that the chronic release rate is primarily governed by bulk diffusion and not much influenced by the type of leaching reagent.

Additional long-term experiments performed with water and ammonia using freshly loaded SS316 specimens of series II (II-14 and II-15, see Fig. 5) instead of aged ones substantiate these findings, i.e. (1) ammonia is slightly more effective than water concerning the initial tritium release and (2) the long-term release rate is practically the same irrespective of whether the specimen is submerged

into water or ammonia. As with aged specimens, the long-term release rate shows a tendency to level off with time. Moreover, the rate of tritium migration through the metal/liquid interface does not appear to correlate with the tritium loading level of the specimen. As shown in Table 3, under analogous experimental conditions a much higher percentage of tritium was liberated from specimens of low loading (series II) than from those of high loading (series F) (both having equal dimension). As the release rate is determined by the transition from the solid to the liquid phase, this can be attributed to the much higher relative surface/bulk ratio of tritium in specimens of low loading in comparison to those having a high one.

### 3.3. Mechanism of tritium release

Gaseous tritium, incorporated on and into SS316 at ambient or higher temperature, is predominantly desorbed as tritiated water [2,12,17]. This is explained by the existence on the metal surface as well as in the inter-granular bulk zone of an oxide (probably Cr<sub>2</sub>O<sub>3</sub>) with its associated OH (OT) and O groups [16,18,19]. Desorbed water can conceivably be formed from a reaction between adjacent adsorbed OH/OT groups, via oxidation reactions taking place during desorption of hydrogen in the presence of air [12], and/or from a combination between OH (or OT) groups with dissolved atomic H (or T) [20]. The release of tritium present in the bulk of SS316 into liquid reagents probably takes place via migration to the surface followed by a direct solid/liquid interaction. This ambient temperature migration may be enhanced by  $\beta$ -radiation emitted by tritium.

An accumulation of tritium at the topmost layers is evident from the etching depth profiles depicted in Figs. 1–3 and data given in Table 2. This trapping can be explained by diffusion through a thin surface oxide layer and/or retention in dislocations arising from rolling of the metal sheets during the manufacturing process. One consequence of this trapping is

Table 3  
Comparison of the chronic release rates of tritium from SS316 stored under water or ammonia

| Expm. | Specimen | Initial activity (MBq) | Duration of storage (h) | Reagent | Released activity (MBq) | Overall fraction lost (%) |
|-------|----------|------------------------|-------------------------|---------|-------------------------|---------------------------|
| 41    | F-III    | 5.18                   | 1872                    | Ammonia | 0.377                   | 7.3                       |
|       | F-IV     | 5.18                   | 1872                    | Water   | 0.255                   | 4.9                       |
| 46    | II-14    | 0.407                  | 1728                    | Ammonia | 0.090                   | 22.1                      |
|       | II-15    | 0.407                  | 1728                    | Water   | 0.122                   | 30.0                      |

a retarded release of tritium. In polar liquid media, such as the ones examined in this study, only surface bound tritium will readily undergo isotopic exchange diminishing the surface concentration of tritium. The long-term release from the bulk and that from the subsurface are governed by a much slower transport mechanism.

From the literature it is known that the water surface coverage of SS316 is of the order of  $10^{15}$  molecules/cm<sup>2</sup> [16,21]. Because all specimens were long in contact with ambient air before undergoing etching, a concentration of this order should prevail. Under this presumption it is seen that the amount of tritium released from the first contact of the specimen with water (or acid or ammonia), i.e.  $<10^5$  Bq (see for instance Table 2), is lower than what can be calculated from the above given maximum coverage, i.e.  $5 \times 10^6$  Bq (taken into account that only 32% of the hydrogen is tritium). This is an indication that in spite of the high specific tritium concentration found by etching on the topmost surface of the SS specimens, much of the tritium on the outermost metal surface has already been lost to the ambient via isotopic exchange with atmospheric moisture. This holds both for old and freshly loaded specimens, i.e. H-IX, II-12 and II-21. Hence, the rate of regrowth of tritium at the surface of stainless steel is lower than the rate of isotopic exchange with ambient moisture.

On the basis of the known permeation coefficients for hydrogen in stainless steel the uptake of tritium by this metal will be very slow at room temperature [22,23]. Hirabayashi and Saeki [17], on the other hand, have shown that during an exposure over 35 days to 13.3 kPa tritium at 293 K this gas penetrates into the bulk of SS316 up to a depth of 50  $\mu$ m with a diffusion constant of  $6.4 \times 10^{-17}$  m<sup>2</sup>/s. Results from this work indicate that, a slow desorption of tritium from stainless steel takes place at ambient temperature. The extent to which (i) cracks in the oxide layer, or (ii) inter-granular diffusion through the oxide layer or (iii) the  $\beta$ -radiation emitted by tritium make contributions to such a process still needs to be clarified. Chemical modifications of the topmost surface during pretreatment of the stainless steel before or during loading could also play a role [24].

A comparison of the chronic release rates of tritium into liquids (Table 3) with those into air, which were quantified by Surette and McElroy [12], would predict a tritium liberation of 52% for specimens of series II and of 49% for specimens of series F after storage periods under air of 1728 and 1872 h,

respectively. These values are appreciably higher than those given in Table 3. Considering, however, that the specimens of Surette and McElroy were exposed to tritium only at ambient temperature, a faster chronic evolution of tritium is not surprising.

### 3.4. Implications for waste conditioning

Tritium-contaminated stainless steel could conceivably be conditioned by treatment with reactive liquid reagents. If water is used, the resulting radioactive secondary waste could be processed together with other waste streams in a water detritiation system of the type currently proposed for ITER [25]. In the case of SS316 exposed to tritium at 298 K a simple treatment with water can bring about a significant DF of the order of 9 [7,17]. The effectiveness of this treatment relies on the fact that during exposure to tritium at ambient temperature this gas does not penetrate deeper into the bulk than a few 10  $\mu$ m. According to Ref. [7] almost complete removal of all tritium sorbed at ambient temperature can be accomplished in a two-step procedure: dipping first into diluted HCl and then treating with a CuSO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub> solution to enhance inter-granular corrosion. The drawback of this approach is that the resulting tritium-contaminated liquid will be of rather complex chemical composition and correspondingly problematical in terms of waste disposal.

In the case of SS316 components previously exposed to tritium at elevated temperatures, a submersion into water (or any other liquid reagent) will only lead to a small DF. To further increase this DF, unacceptably long exposure times are required. For this type of components the approach is therefore of practical application.

To attain high DF's with stainless steel previously exposed to tritium at elevated temperatures a surface layer having a thickness of the order of that penetrated by the tritium, i.e. several hundred  $\mu$ m, must be removed (see Figs. 1–3). This can only be accomplished with a strong acid mixture or other more drastic treatment like mechanical abrasion.

## 4. Conclusions

A slow chronic liberation of tritium incorporated into stainless steel sets in at ambient temperature into reactive liquids with a rate comparable to that observed into air. Evidence for the occurrence of such chronic release was obtained not only from long-term release experiments, but also from depth



profiling by acid etching. The latter technique documents the release from the perspective of the metallic matrix.

It is shown that a simple deactivation of SS316 charged thermally with tritium using reactive liquid agents (concentrated ammonia, water, or a diluted nitric–hydrochloric acid mixture) does not constitute a promising approach, because at ambient temperature only a small fraction of the tritium is removed quickly. The chronic release of tritium predominating subsequently is associated with exceedingly long time constants, making this type of conditioning unattractive from a practical point of view.

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