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FUSION-RELEVANT TRITIUM INTERACTIONS WITH SS316L STAINLESS STEEL

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Abstract

Austenitic stainless steel AISI 316L is an important material for nuclear fusion reactor components, including walls, tubing, and tritium fuel cycle systems, due to its corrosion resistance, temperature stability, and weldability. However, its susceptibility to hydrogen diffusion and embrittlement at elevated temperatures poses significant challenges for safety and fuel economy in fusion reactors. This study investigates the interactions of AISI 316L with a mixture of tritiated hydrogen gas (HT) and helium at elevated temperatures, focusing on tritium oxidation, permeation, and desorption behaviours. Static and dynamic permeation experiments have been conducted using 316L foils exposed to a He+0.1% H_2/HT at temperatures ranging from ambient to 400°C. Results revealed that the conversion of HT to HTO is temperature-dependent, reaching full conversion around 300°C. Temperature dependency of HTO production showed that dynamic flow conditions shift HTO formation to lower temperatures compared to static conditions, which may suggest a surface-activated process facilitated by flow. Thermal desorption experiments were performed on tritium-loaded 316L samples. Desorbed tritium was collected in water bubblers and analysed using liquid scintillation counting revealing retention at temperatures larger than 800°C. The study also explored the impact of oxide formation on tritium permeation. These findings underscore the importance of surface chemistry and microstructure in governing tritium transport and oxidation in 316L, providing insights for the design and operation of fusion reactor components.

1. INTRODUCTION

Austenitic stainless steel is central to the design and operation of nuclear fusion reactor components, since it is the structural material for walls, tubing in tritium fuel cycle and its processing systems [1]. Due to the high mobility of hydrogen, the transport of radioactive hydrogen isotope tritium raises questions about safety and the fuel economy in reactors[2]. Interactions of interest for stainless steel include those with tritiated hydrogen gas at elevated temperatures, additionally, effects of helium are also important since it is a decay product of tritium as well as commonly used inert gas.

There are many types of stainless steel with unique composition and properties. The main categories of stainless steel are based on their microstructure which is determined by element composition in the alloy. Main categories of SS are austenitic, ferritic and martensitic stainless steels. Austenitic SS is composed of 16-26% chromium, 6-22% nickel, up to 2% of manganese and small amounts of other elements[3]. S316L is the preferred austenitic steel alloy in fusion related context - e.g., ITER specifies 316L(N)-IG for its vacuum vessel—illustrating how central 316L-class steels are to primary containment in fusion hardware[4]. AISI 316L is preferred due to its low carbon and molybdenum enhanced corrosion, temperature resistance and improved weldability for leak-proof system building. Chemical composition of SS 316L is provided in table 1.

TABLE 1. CHEMICAL COMPOSITION OF AISI 316L [5]

Element	Cr	Ni	Mo	Mn	Si	Cu	N	C	P	S	Fe
wt. %	17,00-19,00	13,00-15,00	2,25-3,00	2,00	0,75	0,5	0,1	0,03	0,025	0,01	Balance

Although AISI 316L is widely used for various gas containment including tritium, it remains susceptible to hydrogen diffusion and, under elevated temperatures – embrittlement, making evaluation of these effects essential for designing safety-critical systems. Diffusion is the process of the penetrant molecules (hydrogen) movement within the mass of the material due to concentration gradient. Permeation describes the overall mass transport of the gas or liquid penetrant through the material. Permeation occurs in combination with the two physical processes: diffusion and dissolution – the process of initially filling up the material with hydrogen [6]. Once the hydrogen atoms enter the material, they are either captured by the defect sinks (e.g., vacancy clusters, interfaces, and voids) or diffuse within the crystals or via another fast diffusion pathways [7]. When hydrogen is trapped at

saturable traps the pressure dependence of diffusivity and deviations from Arrhenius behaviour at low temperatures and/or small thicknesses can be acquired. This can be explained by two phenomena:

— dissociation and recombination processes at the surfaces are rate limiting in comparison to bulk diffusion
— diffusion through surface barriers like oxide layers with much lower diffusivity than the bulk material is rate limiting[6]

For low partial pressures of hydrogen, dissociation is deemed to be the limiting step making surface conditions highly impactful on diffusion results.

For desorption to take place both diffusion and detrapping should be considered as simultaneous processes. Hydrogen desorption from the austenitic steels occurs primarily through diffusion after detrapping and the diffusion rate is lower than the detrapping rate[9].

Main factors influencing materials structure are its production phase as well as conditions in which it is utilized. Hydrogen as well as oxygen and other impurities can be trapped within the material during the production phase. For hydrogen, the main source is water [10]. Due to the manufacturing process of austenite steels some concentrations of oxygen will inevitably be trapped within the material matrix. Hot pressing or rolling which tends to retain less oxygen than forging and casting can still create inclusions that can be trapped with various desorption energies. These inclusions can influence materials toughness and potentially impact its ability to corrode or even react. Oxygen concentrations up to 190 ppm can be found in 316L steel [11].

Surface catalysis of H_2 and O_2 on various classes of metals is a well know attribute, although such an attribute has not been described for stainless steel. The first stage of the reaction is oxygen activation; therefore, it is also interesting for oxide formation studies, which can impact permeation as well as other properties [12]. Some oxide formation is reported to happen during hydrogen permeation testing of stainless steel at elevated temperatures, noticeable by change of colour of the sample after experiment. The high-temperature permeation test results showed that the hydrogen isotopes permeability exhibited a decreasing trend for the oxidized stainless steels compared with the unoxidized samples, and the efficiency of hydrogen isotopes permeation varied in the range of 10-1000 times. By analysing the microstructure and combining it with the research on tritium permeation barrier coatings, it was suggested that the degree of permeability reduction may be related to the compactness of the formed oxide films [13]. A study has revealed that, due to oxide formation on the surface, air baked samples show slightly lower outgassing compared to in-situ bake out, for the same heat treatment parameters [14].

In this study these interactions with AISI 316 L samples are investigated, by conducting diffusion experiments by loading SS316L samples with helium and tritiated hydrogen gas mixture, followed by analysis of thermally desorbed tritium and tracking of tritium oxidation into tritiated water.

2. EXPERIMENTAL

2.1. Assessment of tritium oxidation and permeation through SS 316 L

Stainless steel AISI 316 L foil (*GoodFellow Inc*, thickness 0,025 mm) sample was inserted in a permeation system with sample being fixed between two stainless steel flanges. Permeation system consists of two stainless steel loops: tritium loop (filled with tritium containing gas) and permeation loop (containing gas measured for permeated tritium) (see Figure 1), with a testing sample stationed in between (d=3.7 cm, active area 11,6 cm^2); permeation system is placed into a furnace. Two types of permeation experiments were carried out – static and dynamic in order to assess the impact of flow on the tritium permeation and oxidation.

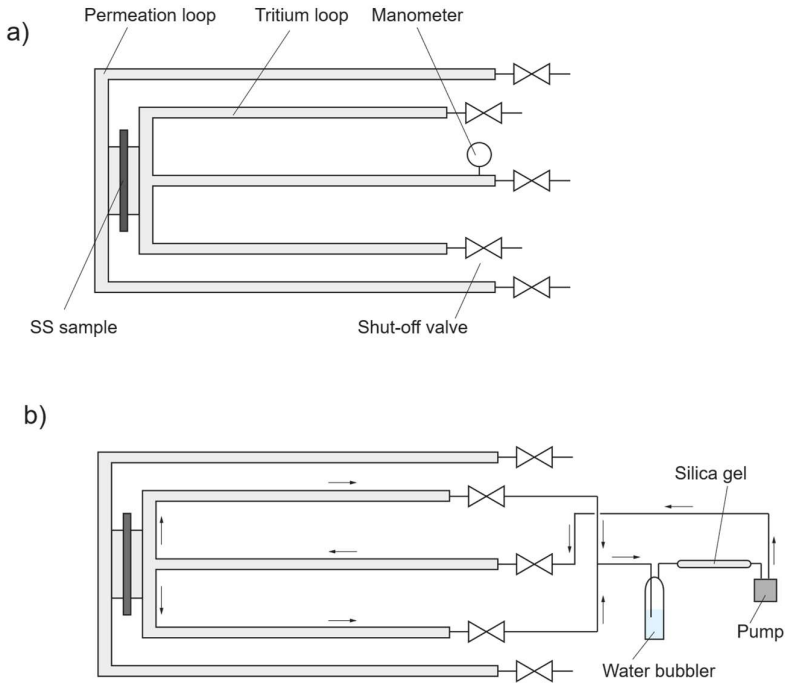

FIG. 1. Permeation system setup in a) static regime; b) dynamic regime

2.1.1. Static permeation experiment

Prior to exposure, permeation loop of the system was purged with synthetic air and hermetically sealed. The tritium loop was then filled with a helium gas mixture containing 0,1% H_2/HT (1 GBq m^{-3}, *TRITEC*), pressurized to 60 mbar relative to ambient pressure and sealed. Permeation system was heated for prescribed durations at set temperatures from room up to 400 °C.

For quantification, the loops were opened and purged with synthetic air for the permeation loop and helium for the tritium loop *(flow rate 10L/h)*. Loops were purged through a water bubbler to collect the HTO fraction. After the bubbler, gas is lead through a silica gel column to remove residual H_2O/HTO vapor before entering a tritium monitor (*TEM 2100A* equipped with a gas flow proportional detector *DDH 32*) to detect tritium in HT form. Ar+10% CH_4 was used as the counting gas with flow rate of 30L/h and proportion 3:1 to measuring gasses (Synthetic air, He). Tritium in HTO form was measured with liquid scintillation counting (*PerkinElmer TriCarb 2910*) by taking aliquot from water bubbler and mixing with a scintillation cocktail *PerkinElmer "Ultima Gold"*.

2.1.2. Dynamic permeation experiment

In a dynamic permeation experiment tritium loop was connected to a water bubbler for formed HTO collection, a silica gel column for gas drying flowing through a pump (*CS Micropumps, R404-STEP*) for continuous flow (see Figure 1b). Tritium loop was first rinsed with pure helium (purity 5.0) and afterwards filled with helium gas mixture containing 0,1% H_2/HT. After the purging tritium loop is sealed and pump was turned on at a flow rate of 0,5 L/h. Permeation loop was purged with synthetic air and sealed; permeation loop remained static. The system was heated for various times at different temperatures. After the experiment, tritium was quantified by the same procedure as described previously for static experiment.

2.2. SS 316 L loading followed by desorbed tritium measurements

Before sample loading with tritium, stainless steel samples were pretreated with hydrogen. Stainless steel samples were placed into a quartz tube housed within a tube furnace. One end of the tube was connected to both hydrogen (purity 5.0) and helium containing 0,1% H_2/HT gas cylinder via a three-way valve, while the other end was

connected to a water bubbler. The system was purged with hydrogen for 15 minutes (flow ~15 L/h) and both ends of the tube were closed. System was heated up to 350°C at 20°C/min and held at constant temperature for 20 h.

After the hydrogen pretreatment, without opening the system and while still at elevated temperature, three-way valve was switched to introduce He + 0,1% H_2/HT gas mixture. The tube was purged for 15 minutes with ~15 L/h gas flow, then sealed and heated to 450°C for 4 h. Afterwards, sample was extracted from the tube and immediately put up for desorption experiments.

2.2.1. Thermal desorption

The tritium-loaded SS316L sample was placed in a ceramic vessel within a tube furnace. Inlet of the vessel was supplied with synthetic air, and the outlet was connected to a water bubbler for HTO capture. The sample was heated from ambient to 1000 °C at 5 °C min^{-1} under a constant synthetic-air flow of 10 L h^{-1}. The bubbler was replaced at 200 °C intervals to collect desorbed HTO fractions. HTO activity in each bubbler was quantified by liquid scintillation counting.

2.2.2. Room temperature desorption experiments

(a) Desorption in water:
Test tubes with 15 mL deionised water for the experiment were prepared. Immediately after loading, the SS sample was immersed in the first test tube, and the timing started. After selected amount of time the specimen was removed and transferred sequentially to the next tube, thereby collecting time-resolved HTO desorption fractions. Following each run, an aliquot from every tube was analysed by liquid scintillation counting to determine the HTO desorbed as a function of time. After 8h specimens were placed in 100 mL glass bottles fitted with a gas inlet and outlet on the cap: the bottle contained 50 mL of deionized water (50 mL headspace). The bottle was stored for 20 days and at defined intervals, tritium in the air above water and in the aqueous phase was quantified.

(b) Desorption in air:
After loading the SS specimen was transferred to a room temperature quartz tube whose inlet was supplied with synthetic air at 3 L/h flow and whose outlet was connected to a water bubbler for desorbed HTO capture. After the sample was inserted into a tube, timing was immediately started. 1 mL aliquots were withdrawn from the bubbler. The collection schedule mirrored the water-desorption experiment. After completion all collected water samples were analysed by liquid scintillation counting. After 8h specimens were placed in 100 mL glass bottles fitted with a gas inlet and outlet on the cap. The bottle was stored for 20 days and at defined intervals, tritium in the air above water and in the aqueous phase was quantified.

For headspace measurements, the bottle inlet was connected to a synthetic air supply (5 L/h) and the outlet to a 50 mL water bubbler. Each bottle was purged for 10 min; desorbed tritium (as HTO) was captured in the bubbler and quantified by liquid scintillation counting (LSC). For the specimen stored in water, 1 mL aliquots of the bottle water were also withdrawn and analysed by LSC to determine desorbed HTO. After each sampling, the inlet and outlet were resealed and the bottles returned to storage until the next time point.

3. RESULTS AND DISCUSSION

3.1. Assessment of tritium oxidation and permeation through SS 316 L

Permeation experiments were performed in both dynamic and static regimes over a selection of temperatures. Activities in the tritium and permeation loops were quantified to determine HT and HTO fractions. In nearly all cases, the permeation loop activity was at or below the limits of quantification—8 Bq for HTO (liquid scintillation) and 73 Bq for HT (tritium monitor) - precluding reliable determination of diffusion coefficients and permeation processes. Nonetheless, the experiments provided an insight into oxidation chemistry – an increase of HT conversion into HTO by increasing temperature and its dependence on flow regime.

3.1.3. Impact of flow to HT/HTO fraction results

Permeation experiments were conducted at temperatures ranging from 50 to 400 °C in both static and dynamic regimes (see FIG 2). Results of both regimes show an increase in water production by increasing the experimental temperature. The process seems to initiate at temperatures higher than 100°C. Total HT transformation into HTO can be noted at 400°C. For the assessment of flows impact on HT/HTO fraction results HTO production temperature dependency was approximated using a following sigmoid function:

$$HTO\ production = \frac{100}{(1 + e^{(-k(t-t_{ox}))})}$$

where t – temperature, °C, k and t_{ox} are empirical constants optimized using least squares method.

The function was chosen due to tritium introduced believed to be the limiting constituent in the HTO production reaction. Thus, temperature dependency scatter would eventually reach a constant value – 100% of HT transformed into HTO. Values of empirical constants acquired by approximation are summarized in Table 2. Such sigmoidal dependence might be an indication of catalytic nature of the reaction.

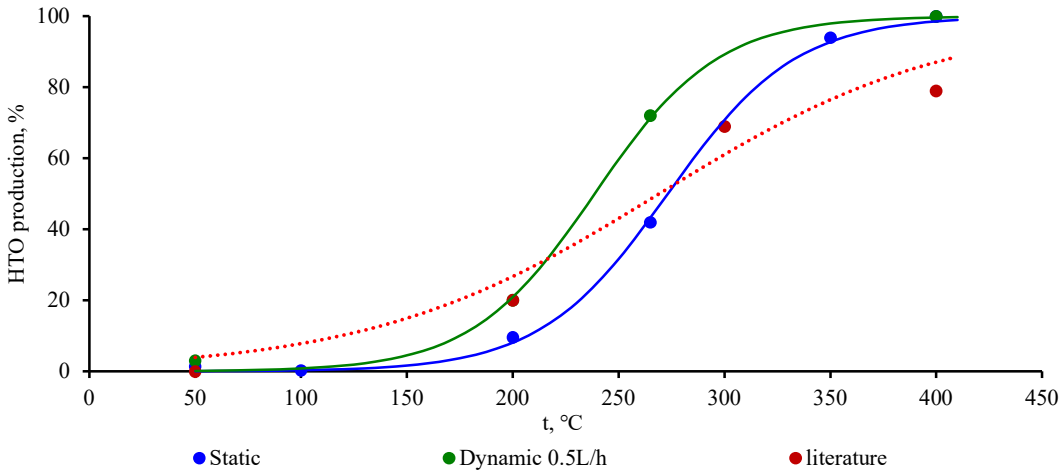

FIG. 2. HTO fraction temperature dependency approximation including literature data [15]

TABLE 2. EMPIRICAL CONSTANTS ACQUIRED BY APPROXIMATION

	Dynamic	Static	Literature [15]
k	0.034	0.033	0.018
t_{ox}	239	273	269

Dynamic experiments show higher HTO production at lower temperatures and reach a steady state around 300°C, indicating that flow has an impact on HTO production in this experimental setup. Such results may imply that the reaction is surface activated, and the flow introduced in the dynamic regime facilitates HTO production due to active product transfer away from the surface. If true, increase of flow rate may increase HTO even more. Additional experiments are necessary to confirm this.

Results were compared with those found in literature, which shows results similar to those of static experiments for t_{ox} – temperature (literature results were also performed in a static regime), at which oxidation occurs. k governs the rate of oxidation – smaller k values give a wider peak with larger deviation. Difference in k values may be explained by multiple factors – total amount of tritium introduced within the system, different surface areas in the two experiments (sample surface in this experiment is about 2x larger than the one used in [15]). This deviation may also be influenced by the chosen experiment length in the literature which is 8h. Our experiments show that a plateau is reached sometime between 4 and 20h, 8h lays somewhere in between but additional experiments are needed to confirm if it is sufficient.

To further illustrate the temperature at which the process occurred, sigmoid equation was derived to get a probability density function (PDF) rather than a cumulative one:

$$y = \frac{e^{-k_1(t-k_2)}}{(1+e^{-k_1(t-k_2)})^2}$$

Resulting distributions can be found in Figure 3.

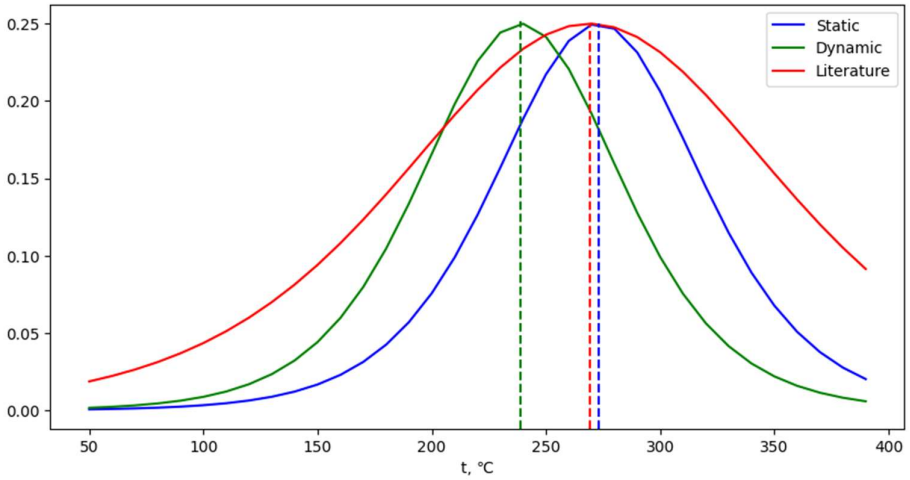

FIG. 5. HTO fraction temperature dependency approximation including literature data [15] (PDF)

Based on the temperature range at which the process takes place, the relevant reactions based on SS316L composition may be:

$NiO + H_2 \rightarrow Ni + H_2O$ (200-400°C)
$MnO_2 + H_2 \rightarrow MnO + H_2O$ (170-800°C)
Surface catalysed $H_2 + O_2 \rightarrow H_2O$

Rate at which the reaction occurs gives indications that surface catalysed HTO production may be the favourable one, but additional experiments are necessary for confirmation.

3.2. Assessment of tritium desorption for loaded AISI 316L

Since loading is done at 450°C most of the desorbed tritium is expected to be in oxidised form of HTO instead of HT that's why desorbed tritium is collected in water bubblers and measured with liquid scintillation.

3.2.1. Thermal desorption

Thermal desorption was done for both loaded AISI 316L samples with hydrogen pretreatment. Desorbed tritium was collected in fractions not continuously measured, therefore only amount of tritium in temperature ranges are available. Data is presented in Figure 6.

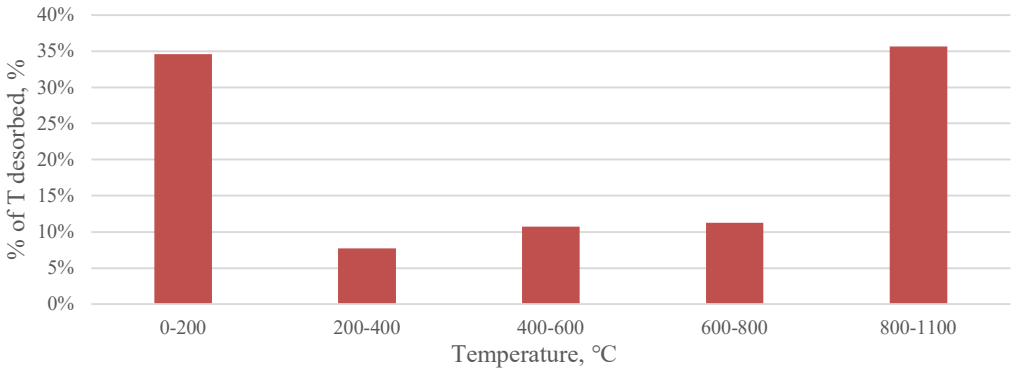

FIG. 6. Tritium quantity desorbed in temperature range fractions

Results show a large fraction of tritium being released both at temperatures below 200°C as well as temperatures above 800°C - around the threshold for prolonged use. Hot working of SS316L is performed in temperatures ranging from 900 up to 1200°C, while water quenching or rapid cooling for corrosion resistance is done at 1038°C and might have an influence on tritium desorption temperature. Role of hydrogen pre-treatment must also be further investigated as indications of hydrogen pre-treatment facilitating tritium diffusion have previously been reported.

3.2.2. Tritium room temperature desorption experiments

For room temperature desorption experiments desorbed tritium (as HTO) in air and water media was collected in water, and cumulative activity was reported as specific activity Bq/mL. The results are compiled in Figure 7.

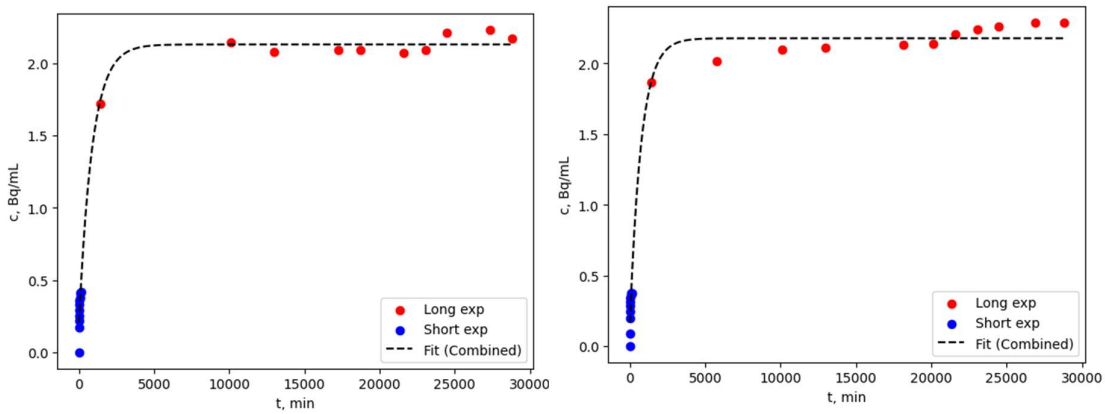

FIG. 7. Cumulative tritium activity over time for desorption in air and water media

By comparing total desorbed tritium activity for sample stored in air or water (sum of the tritium in water and air above it) media, no distinct difference between them can be seen. Both medias reach about the same level of tritium concentration (2Bq/mL) and similar diffusion coefficient of $2 \cdot 10^{-11}$ cm^2/s although additional experiments in the region of interest for out-diffusion ranging from 1 to 3 days must be further investigated. It must be noted that these values are acquired for oxidized SS316L samples with hydrogen pre-treatment not those of pristine specimens.

4. CONCLUSIONS

Valuable insights in tritium interactions with SS316L have been obtained with the most notable ones being the tracking of HTO production by increase in temperature, as well as the discovery of a tritium trapping site at temperatures larger than 800°C as well as out-diffusion coefficient of HTO from oxidized SS316L. The results

presented here may be used in modelling to assess tritium accounting as well as needed safety requirements where SS316L stainless steel and tritium are present.

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