Adsorbed Water Layers Influence Tritium Migration into/out of Stainless-Steel 316

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Adsorbed water layers influence tritium migration in stainless steel 316 at ambient temperatures (25°C)

- A multi-layer structure exists on stainless-steel surfaces
  - mixed metal oxide (Fe₂O₃/Cr₂O₃)
  - hydroxide
  - adsorbed water
- Tritium contained within the adsorbed water layers can explain reported large surface concentrations
- ZnCl₂ solution effectively removes adsorbed tritium
- Quantitative Tritium Migration Model (QTRIMM) successfully describes
  - the amount of adsorbed tritium remaining after a storage period
  - chronic release during storage
Large tritium concentrations are observed on stainless-steel surfaces

Chronic release depletes tritium in the near surface

Tritium binds to stainless steel surfaces as tritiated water.

Adsorbed water layers contain a large number of potential tritium binding sites

\[ 10^6 \frac{\text{mol} \, H}{m^3} \]

Solubility @ 25°C & 1 atm ≈ 0.2 – 5 mol/m³

Adsorbed water layers have sufficient volume and site density to describe observed surface concentrations

- Numerous studies report surface concentrations for air exposed samples
- Assuming all tritium is contained within adsorbed water layers

\[ N_{ML} = \frac{[T]_{surf} \cdot V_{surf}}{\lambda \cdot \chi_T \cdot SA \cdot \rho_{surf}} \]

- \([T]_{surf}\) = surface concentration
- \(V_{surf}\) = volume of surface
- \(SA\) = surface area
- \(\lambda\) = tritium decay constant
- \(\chi_T\) = mole fraction of tritium in the loading gas
- \(\rho_{surf} = 10^{15} \text{ H}_2\text{O molecules/cm}^2\)


5% relative humidity
Published XPS data confirms the presence of hydroxyls and adsorbed layers on stainless steel 316

Depth profiles measured by Tardio et al. show adsorbed water and hydroxyls bound to the native metal-oxide.

- Depth profiles were measured using secondary ion mass spectroscopy (SIMS)
  - 0.4 nm (1 ML) adsorbed water layer
  - 1 nm (3 ML) hydroxyl layer
  - Mixed Fe$^{3+}$ and Cr$^{3+}$ metal oxide layers beneath hydroxyl layers

Assume two rapid equilibration processes control tritium migration into the metal lattice.
Equilibrium #1: Assume rapid isotope exchange

From Equilibrium #1
\[ A_{\text{surf}} \propto P_T \times Q \]

Equilibrium #1
\[ \frac{P_T}{P_{\text{total}}} \propto \chi_{\text{surf}} \]

Q = quantity of adsorbed water
\[ P_T = \text{tritium partial pressure} \]
\[ \chi_{\text{surf}} = \text{tritium mole fraction on the surface} \]
Equilibrium #2: Assume rapid migration across water/metal interface

**Equilibrium #1**
\[
\frac{P_T}{P_{\text{total}}} \propto \chi_{\text{surf}}
\]

**From Equilibrium #1**
\[
A_{\text{surf}} \propto P_T \cdot Q
\]

**Equilibrium #2**
Solubility ratio
\[
\frac{S_{\text{surf}}}{S_{\text{bulk}}} = \frac{c_{\text{surf}}^{\text{eq}}}{c_{\text{bulk}}^{\text{eq}}}
\]

Q = quantity of adsorbed water
\[P_T\] = tritium partial pressure
\[\chi_{\text{surf}}\] = tritium mole fraction on the surface
\[S_{\text{surf}}\] = tritium surface solubility
\[S_{\text{bulk}}\] = tritium solubility in the metal lattice
\[c_{\text{i}}^{\text{eq}}\] = equilibrium concentration in region "i"
The surface layer of adsorbed water also controls tritium egress during surface cleaning.

Variable parameters:
- Quantity of adsorbed water (Q)
- Removal rate (v)

Remove adsorbed tritium by:
- Surfactant
- Chemical
- Plasma
- Heat
- etc.

Increased cleaning

Solubility ratio
\[
\frac{S_{\text{surf}}}{S_{\text{bulk}}} = \frac{c_{\text{surf}}^{\text{eq}}}{c_{\text{bulk}}^{\text{eq}}}
\]
Total tritium inventories were measured using linear thermal desorption

\[ \langle x \rangle \approx \sqrt{4Dt} \approx 0.5 \text{ cm} \]

Expect all tritium to be removed during thermal desorption.

*HTO = tritiated water
An aqueous ZnCl$_2$ solution expected to displace all adsorbed water

- Tanaka *et al.* measured hydroxyl concentrations using ZnCl$_2$+NH$_4$Cl
- Method removes all hydrogen atoms from the surface
  - Does not etch into the metal
- Measure liberated tritium using liquid scintillation counting

Expect ZnCl$_2$ solution to liberate all adsorbed tritium

ZnCl₂ treatments suggest adsorbed water and hydroxyl layers contain ~20% of the total tritium inventory.

- Adsorbed water and hydroxyls were removed using ZnCl₂ solution*
- The remaining tritium was removed using thermal desorption

Chronic release measured using thermal desorption and ZnCl₂ treatments

- Samples loaded & stored under the same conditions
  - Stored in separate containers
- Residual bulk tritium measured using thermal desorption
- Residual surface tritium measured using ZnCl₂ treatments
  - 26 ± 7 MBq (0.7 mCi) remain after ~90 days
Measured chronic release described using the model

release rate = −\nu * c_{surf}
\nu = 1.2 \times 10^{-7} /\text{sec}
c_{surf} = \text{surface concentration}
\langle \text{rate} \rangle \approx 0.30 \% /\text{day}^*

Solubility and quantity of adsorbed water (Q) also adjusted while fitting data
• solubility increased by a factor of 2.2†
• Q = 57 \, \mu \text{mol} \, \text{H}_2\text{O}/\text{m}^2 \, (3.4 \, \text{ML} \, \text{H}_2\text{O})

†M. Sharpe et al., Fusion Sci. Tech. 70, 97 (2016)
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Native metal oxide layers have little effect on tritium migration through the near surface of SS316 at 25°C.

\[
D = 1.3 \times 10^{-16} \text{ m}^2/\text{sec} \quad (1)
\]

\[
D = 3.5 \times 10^{-16} \text{ m}^2/\text{sec} \quad (2)
\]

*Shown references are not included in median value

(3) M. Sharpe et al., Fusion Sci. Tech. 70, 97 (2016).
Plasma-induced ion sputtering can measure tritium migration to the surface

- Samples exposed to a series of 2-s plasma pulses
- Base pressure $\approx 10^{-4}$ Torr
  - trace water in the vacuum system redeposits on the metal surface within 10 s

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Adsorbed water layer</th>
<th>Bulk metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
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<tr>
<td>HTO</td>
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</table>

*rf = radio frequency
QTRIMM can be used to describe the migration of tritium in the near surface region of stainless steel

- Samples were exposed to sequential, short plasma exposures
  - 20-min dwell periods allow for tritium migration
- Removal from surface alone results in exponential dependence
- Diffusion-limited migration to the surface describes the measured data

M. Sharpe et al., Fusion Sci. Tech. 70, 97 (2016)