Distribution of Tritium in the Near Surface of 316 Stainless Steel

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Tritium Focus Group Meeting
Oak Ridge, TN
15–17 May 2018

- Tritium concentration ($\mu$Ci/cm$^3$)
- Distance into the metal ($\mu$m)
- Bulk solubility range
- Storage times: 33 days, 35 days, 40 days, 49 days, 68 days, 82 days, 83 days, 90 days, 233 days
- $\text{ZnCl}_2$ washes: 1.8 days, 1.9 days, 3 days, 2 days, 2 days
- Acid etches: 1.8 days, 1.9 days, 3 days, 2 days, 2 days
The near surface of stainless steel retains high concentrations of tritium

- Tritium concentration profiles were measured using a combination of a ZnCl₂ wash, followed by acid etching
  - separation of tritium in adsorbed water and bulk steel
  - etching resolution ~10 nm
- Tritium concentrations in the near surface (<10 μm) do not change significantly between 33 and 233 days of storage
  - suggests very slow diffusion
- Migration to the surface is observed when the surface is depleted of tritium by acid etching
Tritium binds to stainless-steel surfaces as tritiated water.

Liquid-like layers (physisorbed) are affected by changing relative humidity.

Ice-like layers (chemisorbed) are affected by changing temperature.

Hydroxyl layer

Metal oxide

Metal lattice

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

Solubility at 25°C and 1 atm ≈ 1.9 mol/m³
The surface water layer of adsorbed water also controls tritium egress.

- Remove adsorbed tritium by:
  - surfactant
  - chemical
  - plasma
  - heat
  - etc.

\[
\text{Solubility ratio} = \frac{S_{\text{surf}}}{S_{\text{bulk}}} = \frac{c_{\text{surf}}^{eq}}{c_{\text{bulk}}^{eq}}
\]
An aqueous ZnCl₂ solution is expected to displace all adsorbed water

- Tanaka et al.* measured hydroxyl concentrations using ZnCl₂ + NH₄Cl
- This method removes all hydrogen atoms from the surface but does not etch into the metal
- Measure liberated tritium using liquid scintillation counting

ZnCl₂ solution liberates adsorbed tritium.**

Diluted aqua regia used to dissolve stainless steel

- Aqua regia is a 3:1 mixture of HCl and HNO₃
  - two dilutions used
  - lower acid concentrations reduce etch rate
- Solid iron is oxidized to form iron(II) or iron(III) chlorides
- After etching, solutions brought to pH ~ 0 to measure using liquid scintillation counting
  - pH > 1 to 2 results in precipitation of iron hydroxide

Increasing etch time and/or acid concentration
Large surface concentrations indicate tritium retention in adsorbed water and metal oxide layers

Concentration profiles do not significantly change between 33 and 233 days of storage.

- Samples stored in individual storage pods under dry helium
  - dew point < −70°C
- Suggests presence of trap sites and/or slow diffusion

![Tritium concentration vs. distance into the metal](chart)

- ZnCl₂ washes

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Calculations suggest room temperature diffusion is very slow.

- Lowered diffusivity by a factor of $8 \times 10^5$ relative to the survey.
- Increased solubility by $5\times$ relative to survey.

\[
D = 3 \times 10^{-16} \text{ cm}^2/\text{s} \\
S = 2 \times 10^5 \mu\text{Ci/cm}^3 \ (6.9 \text{ mol/m}^3)
\]
Etching experiments show tritium migration to the surface

- Several etching series were performed
  - sample stored in air
  - ZnCl₂ wash post storage
  - short etch series

- ZnCl₂ washes after storage removed a large quantity of tritium
Summary/Conclusions

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Preloading the samples with H$_2$ or D$_2$ does not change the steady-state tritium concentration profiles

- Several samples preloaded with H$_2$ or D$_2$
  - 24 h, 1 atm, 25°C
- Similar concentration profiles observed
- Trapping not observed OR traps not filled in preloading