Evaluation of In-Situ Tritium Transport Parameters for Type 316 Stainless Steel during Irradiation

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Motivation and Scope

► TMIST-2 Experiment
  - Measured in-reactor steady state tritium permeation through Type 316 stainless steel as a function of tritium partial pressure and temperature
  - Tritium permeation irradiation enhancement of ~3X was observed relative to ex-reactor data and accepted literature values

► Transient Analysis of TMIST-2 Data
  - Sought to elucidate insight into the mechanism for the observed permeation enhancement
  - Three independent, but related, methods were used to analyze the TMIST-2 transient data
TMIST-2 In-Reactor Tritium Permeation Experiment

- Irradiated for five cycles (257.5 EFPD at 18 MW\(_t\)) to a dose of 1.63 dpa-304SS
- Test conditions included tritium partial pressures of 0.1, 5, and 50 Pa; temperatures of 292 and 330° C
- Experiment designed by PNNL, capsules fabricated at PNNL, test train fabricated at INL
TMIST-2 In-Reactor Tritium Permeation Experiment

- Four independent active temperature-controlled capsules separated by bulkheads welded to outer pressure tube
- One test specimen per capsule with active permeating length of 10 cm
- Two thermocouples per capsule
  - Two junctions on centerline
  - Two junctions outside temperature control gas gap
- Gas lines and thermocouples brazed at bulkheads to separate capsule gas volumes
- Test specimens welded to bulkheads with areas outside active length held at much lower temperature and coated with Al to minimize extraneous permeation
TMIST-2 In-Reactor Tritium Permeation Experiment

- Copper sweep gas outlet lines used to minimize tritium loss between capsule and ion chambers/bubblers
- Tritium partial pressure and specimen temperature changed independently in stepwise fashion during irradiation
- All combinations of temperature and pressure tested at least twice at difference fluence
TMIST-2 In-Reactor Tritium Permeation Experiment

- Ion chambers used to establish steady-state (typically 6-8 days)
- Steady-state permeation rate quantified by repeated liquid scintillation counts of tritium captured in bubblers
In- vs. Ex-Reactor Permeation Behavior

- Ex-reactor permeation measurements
  - $> 100 \text{ Pa} \rightarrow \text{Diffusion-limited} \rightarrow P^{0.5}$
  - $< 100 \text{ Pa} \rightarrow \text{Surface-limited} \rightarrow P^1$

- Experiment designed to measure in-reactor steady-state permeation rate and pressure dependence to elucidate key performance phenomena

  - Direct dissociative chemisorption
    - Associated with diffusion-limited permeation
    - Disrupted ex-reactor by:
      - Surface impurities at low pressure
      - Oxide films

  - Radiation-enhanced dissociation
    - Radiolysis of $T_2$ in gas phase
    - Physical or chemical changes in surface in-reactor
Results of In-Situ Permeation Measurements

- Weak temperature dependence over specified range
- $P^{0.5}$ dependence observed
  - Suggests diffusion-limited permeation over specified pressure range
Results of In-Situ Permeation Measurements

- $P^{0.5}$ dependence permits extrapolation of ex-reactor correlation
- No transition from diffusion- to surface-limited behavior < 100 Pa
- Indicates in-reactor enhancement in permeability of ~3X

Permeability, Diffusivity, and Solubility

Permeating flux \( J \) is dependent on diffusivity \( D \) and solubility \( S \)

\[
J = -D \frac{dc}{dx} = -D \frac{c_L - c_H}{L} = D \frac{c_H}{L}
\]

\[
K = \frac{[H_{(m)}]}{[H_{2(v)}]}^{1/2} = \frac{c_H}{P^{1/2}} \Rightarrow c_H = K P^{1/2} = S P^{1/2}
\]

\[
\therefore J = \frac{DSP^{1/2}}{L}
\]

Permeability, \( \Phi \)

\[
\Phi = DS
\]

Is the \( \sim 3X \) radiation enhancement in permeability \( (\Phi) \) due to enhanced \( D \), \( S \), or both?

Sweep gas
Analytical Approach

- Attempt to extract diffusivity data by analyzing ion chamber transient data
  - Test steps exhibiting increase in flux only
  - Still evaluating methodologies for analyzing steps with decrease in flux
  - Assume slab geometry due to favorable aspect ratio per Kishimoto (1985)
Considerations and Assumptions

- In-reactor specimens located >15 m from ion chambers
  - Transport time
    - Quantified by time lag measured in ion chambers positioned at supply-side inlet and outlet (≤3 hr)
    - Transport time considered negligible relative to time needed to reach steady-state (≥144 hr)
  - Isotopic exchange
    - Possibly significant due to large surface area of tubing walls between test specimens and ion chambers
    - Tubing swamped with protium between test steps to minimize tritium cross-talk between permeation measurements

- Surface processes
  - Measured $P^{0.5}$ dependence indicates that surface decomposition and recombination are fast relative to bulk diffusion
Analysis Methods

- Time-lag analyses (Frisch 1957)
  - Integrate flux transient to obtain plot of quantity vs. time
  - Fit linear portion of curve
  - Locate t-axis intercept and calculate $D$
  - Use measured permeability and estimated $D$ to calculate $S$

$$t = \frac{L^2}{6D}$$
Analysis Methods

Rise-Time Analysis (Parker 1961)

- Used for measuring thermal diffusivity via the flash method
- Plot normalized flux ($V$) vs. $\omega$
- Solve for $D$ using half-height ($V=0.5$) and intercept methods

$$D = \frac{1.38L^2}{\pi^2 t^{1/2}}$$

$$D = \frac{0.48L^2}{\pi^2 t_x}$$
Preliminary Results

- Exponential Analysis (Pasternak et al. 1970)
  - Plot normalized flux versus function of time
  - Obtain best-fit $D$ to approximate experimental data

\[ X^2 = \frac{L^2}{4Dt} \]

\[ \frac{\Delta F}{\Delta F_\infty} = \left( \frac{4}{\sqrt{\pi}} \right) X \exp\left(-X^2\right) \]
Preliminary Interpretation of Results

- Initial estimates of $D$ based on rise-time, time-lag, and permeating membrane model:
  - Reasonable agreement between methods ($\sim 3.5 \times 10^{-9} \text{ cm}^2/\text{s}$)
  - Lower ($\sim 100X$) than accepted ex-reactor values ($\sim 1 \times 10^{-7} \text{ cm}^2/\text{s}$)
    - No physical reason to expect in-reactor reduction in $D$
    - Would require solubility enhancement $>100X$ to account for enhanced, in-reactor permeability
    - Non-physical result suggests possible distortion in response curve due to isotopic exchange

Steady-state permeation rate

Begin collecting tritium in bubblers for LSC measurement to establish permeability
Summary and Conclusions

- In-reactor permeability observed to be enhanced by ~3X relative to ex-reactor permeability
- $P^{0.5}$ pressure dependence observed at low pressure (e.g. $<100\text{Pa}$) in-reactor
  - Consistent with diffusion-limited permeation
- Preliminary analyses of transient ion chamber data reveals non-physical results
  - Possible time-lag from isotopic exchange on tubing walls between test specimen and ion chamber

Next steps

- Some estimate of ion exchange time lag may be possible from comparison of ion chamber data on inlet and outlet sides (recent work by Longhurst)
- Any correction for isotopic exchange time lag will be a large fraction of measured time constant, resulting in significant uncertainty