Tritium Transport and Corrosion Modeling in the Fluoride Salt-Cooled High-Temperature Reactor

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Content Based on Doctoral Thesis Defense

Workshop on Tritium Control
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Presentation Outline

I. Tritium poses two problems

II. These problems are coupled

III. The TRIDENT model captures these dependencies

IV. Major elements of the TRIDENT model

V. Results of FHR simulations and comparison of tritium mitigation methods
Tritium Poses Two Problems

1. Corrosion - preferential attack of Cr in alloys by TF:
   - \(2\text{TF}_\text{(d)} + \text{Cr}_\text{(s)} \rightarrow \text{CrF}_2\text{(d)} + \text{T}_2\text{(g)}\)
   - Corrosion reaction consumes TF, generates \(\text{T}_2\)

2. Radiological:
   - \(\text{T}_2\) fast diffusion through metal
   - \(T_{1/2} = 12.3\) yr
   - \(\beta = 5.9\) keV

- Must control corrosion and manage tritium escape from system
- Modeling/simulation to help evaluate tritium control options
Tritium Behavior Couples to Coolant Chemistry and Corrosion Rates

• Knowing corrosion rates is important for long-term operation:
  – Rates are sensitive to coolant impurities
  – Corrosion couples to tritium behavior!

Fluoride Salt MODERATE in Fe and Ni

Fluoride Salt HIGH in HF

Images of Inconel from ORNL-2349
FHR Produces More Tritium than Other Fission Reactors

- Tritium behavior must be characterized to build licensing case:
  - Need to know release rates
  - Need to know distribution throughout reactor

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Tritium Production Rates [Ci/GWd]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BWR*</td>
<td>12.3</td>
</tr>
<tr>
<td>PWR*</td>
<td>13.9</td>
</tr>
<tr>
<td>HTGR*</td>
<td>18.5</td>
</tr>
<tr>
<td>FBR*</td>
<td>24.9</td>
</tr>
<tr>
<td>HWR*</td>
<td>1176</td>
</tr>
<tr>
<td>FHR</td>
<td>11,000 (peak production rate calculated here)</td>
</tr>
</tbody>
</table>

TRIDENT (TRItium Diffusion EvolutioN and Transport) Was Developed to Link FHR Tritium Behavior to Coolant Chemistry
Basic Elements of TRIDENT:
Tritium Generation in Flibe Coolant
Neutron Transmutation Generates Tritium in Flibe

$^6\text{LiF} + n \rightarrow \text{He} + \text{TF}$

$^7\text{LiF} + n \rightarrow \text{He} + \text{TF} + n'$

$\text{BeF}_2 + n \rightarrow ^4\text{He} + ^6\text{He} + 2F^-$

$^6\text{He} \rightarrow ^6\text{Li} + e^+ + \bar{\nu}_e \quad (t_{1/2} = 0.8 \text{ sec})$

$^6\text{Li} = 0.005 \text{ wt}\%$

$^7\text{Li} = 99.995 \text{ wt}\%$

<table>
<thead>
<tr>
<th>One-group Cross section (b)</th>
<th>$\sigma^{T}_{\text{Li-6}}$</th>
<th>148</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma^{\alpha}_{\text{Be-9}}$</td>
<td>3.63x10^{-3}</td>
<td></td>
</tr>
<tr>
<td>$\sigma^{T}_{\text{Li-7}}$</td>
<td>1.00x10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>
FHR Tritium Production Rate is Not Constant

\[ \dot{T}(t) = \phi \sigma_{Li-7}^T N_{Li-7} + \phi \sigma_{Li-6}^T \left( \frac{V_{core}}{V_{loop}} \phi \sigma_{Li-6}^{abs} \right) \left( N_{Li-6}^o e^{-\frac{V_{core}}{V_{loop}} \phi \sigma_{Li-6}^{abs} t} + \frac{\phi \sigma_{Be-9}^\alpha N_{Be-9}}{\phi \sigma_{Li-6}^{abs}} \left( 1 - e^{-\frac{V_{core}}{V_{loop}} \phi \sigma_{Li-6}^{abs} t} \right) \right) \]

- T production from Li-7
- T production from Li-6
- T production from Li-6 from Be-9
Basic Elements of TRIDENT: Effect of Redox on Corrosion and Tritium Behavior
Coolant Chemical Redox Potential Required as a Point of Reference for Modeling

Free Energy of Formation (kJ/mol fluorine atom) vs Temperature (°C)

- FHR Must Operate Here
- Structural Metals
- Flibe Coolant

Calculated MSRE Equivalent Redox Potential

Trends for:
- LiF
- BeF2
- CrF2
- FeF2
- NiF2
- HF
- 100:1 ratio of UF4:UF3
Redox Potential Dictates Relative Amounts of $T_2$ and TF

\[
\frac{P_{TF}^2}{P_{T2}} = \exp \left( \frac{\Delta G_{F2} - 2\Delta G^o_{TF}}{2RT} \right)^2
\]

Increasing Corrosivity

$\Delta G_{F2} = -700.5$ kJ/mol

Coolant Redox Potential (kJ/mol $F_2$)

Ratio $[P_{TF}]^2/[P_{T2}]$

MSRE Reference
Redox Potential Determines Extent of Corrosion

- For Type 316L SS in flibe at 650 °C

\[
\log \left[ Cr_{\text{coolant}} \right] = K_{eq} + \log \left[ Cr_{\text{metal}} \right] + \log \left( \frac{P_{TF}^2}{P_{T2}} \right)
\]
TRIDENT Tritium Diffusion and Corrosion Models Were Benchmarked Against Experiments

• Tritium diffusion in Nickel/Flibe and Nickel/Flinak systems

• Corrosion and corrosion product mass transfer in flibe containing dissolved UF₃/UF₄
Modeling Tritium Behavior in the FHR: TRIDENT Code Description
<table>
<thead>
<tr>
<th>Reactor Parameters</th>
<th>Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal power</td>
<td>Baseline Redox Potential (specified as fluorine potential or ratio)</td>
</tr>
<tr>
<td>Coolant inlet/outlet temperature</td>
<td>Flibe specific heat</td>
</tr>
<tr>
<td>Number of coolant loops</td>
<td>Flibe density</td>
</tr>
<tr>
<td>Core dimensions</td>
<td>Flibe viscosity</td>
</tr>
<tr>
<td>One group flux</td>
<td>Henry’s law constant for T₂ in flibe</td>
</tr>
<tr>
<td>Fuel parameters</td>
<td>Henry’s law constant for TF in flibe</td>
</tr>
<tr>
<td>Refueling rate</td>
<td>Diffusion coefficient for T₂ in flibe</td>
</tr>
<tr>
<td>Pebble size</td>
<td>Diffusion coefficient for TF in flibe</td>
</tr>
<tr>
<td>Heat exchanger parameters</td>
<td>Diffusion coefficient for Cr²⁺ in flibe</td>
</tr>
<tr>
<td>Tube diameter</td>
<td>Initial dissolved Cr concentration in the salt</td>
</tr>
<tr>
<td>Number of tubes</td>
<td>Sieverts law constant for T₂ in 316 SS</td>
</tr>
<tr>
<td>Total surface area</td>
<td>Diffusivity of T₂ in 316 SS</td>
</tr>
<tr>
<td>Tritium release rate</td>
<td>Baseline permeation reduction factor</td>
</tr>
<tr>
<td>Corrosion rates</td>
<td>Cr grain boundary diffusion coefficient in 316 SS</td>
</tr>
<tr>
<td>Tritium distribution:</td>
<td>316L SS elemental composition</td>
</tr>
<tr>
<td>Coolant</td>
<td>316L SS density</td>
</tr>
<tr>
<td>HX tube walls</td>
<td>316L SS lattice parameter</td>
</tr>
<tr>
<td>Graphite</td>
<td>316L SS grain diameter</td>
</tr>
<tr>
<td>Power cycle</td>
<td>316 L grain boundary width</td>
</tr>
<tr>
<td>Power cycle</td>
<td>Graphite capacity for tritium</td>
</tr>
<tr>
<td>Nuclear cross sections relevant to tritium production in flibe</td>
<td>Graphite (IG-110) density</td>
</tr>
</tbody>
</table>
Results of TRIDENT Simulations of Baseline 236 MWt Mk1 PB-FHR

\[ T_{\text{out}} = 700 \, ^\circ\text{C} \]

\[ T_{\text{in}} = 600 \, ^\circ\text{C} \]
Tritium Release Rate (Ci/EFPD) to Power Cycle

Pseudo steady state. Variation due to reduction in tritium production rate as initial Li-6 is consumed.

Graphite saturation based on partial pressure of T2 & TF and effects of online refueling.

Graphite begins to saturate with tritium.

Initial buildup as tritium production balances absorption on graphite and escape to power cycle.
Cr Coolant Concentration (ppm)

Rate of corrosion equal to rate of deposition
Net Weight Change After 200 EFPD Due to Cr Mass Transfer

- **Net Weight Change (mg/cm²)**
  - **Temperature Profile**

  - **Location Within Loop**: Core, Hot Leg, Heat Exchanger, Cold Leg

  - **Temperature (°C)**
    - 0 to 700
  - **Net Weight Change After 200 EFPD Due to Cr Mass Transfer**
FHR Release Rate Without Tritium Capture is High

• FHR tritium release rate with no engineered tritium mitigation systems:

  ~ 2500 Ci/EPFD for 236 MWt PB-FHR (10600 Ci/GWD)

• HWR tritium release rate:

  20 Ci/GWD

• LWR tritium release rate:

  < 1 Ci/GWD
TRIDENT Simulations of Proposed Tritium Mitigation Methods

- Permeation windows
- Counter-current gas stripping
- Capture on graphite outside of core
- Oxide layer on air-facing side of heat exchanger
- Tungsten heat exchanger
- Increased Li-7 enrichment in flibe
Permeation Window

- Make a structure with a high surface area
- Construct the structure out of a metal with high hydrogen permeability

<table>
<thead>
<tr>
<th></th>
<th>Permeability (mol H₂/m-s-MPa⁰.⁵) at 873 K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 SS</td>
<td>5.5 x 10⁻⁸</td>
<td>Tanabe, 1984</td>
</tr>
<tr>
<td>Ni</td>
<td>3.7 x 10⁻⁷</td>
<td>Tanabe, 1984</td>
</tr>
<tr>
<td>Pd</td>
<td>2.5 x 10⁻⁵</td>
<td>Steward, 1983</td>
</tr>
</tbody>
</table>
Permeation Window Schematic

Permeator

Activated Charcoal Bed

Sweep Gas Flow

Reactor Vessel

Heat Exchanger

To power cycle
Release Rate with Permeation Window < 800 Ci/EFPD

- Ni permeation window, salt on one side, sweep gas on other side
- Permeator surface area = HX and 2 times HX
- 100% of coolant flow

![Graph showing release rate with permeation window](graph.png)
Counter-current Gas Stripping Schematic

- Reactor Vessel
- Heat Exchanger
- Activated Charcoal Bed
- Stripping Gas Flow
- Gas Stripping Column

To power cycle
Release Rate with Gas Stripping < 500 Ci/EFPD

- 10 stripping stages
- 50% of primary coolant flow (total flow: 498 kg/s, 250 L/s)
- 2x10^4 L/hr stripping gas flow rate (5.6 L/s)
Mitigating Tritium Release: Graphite Capture

![Diagram showing a reactor vessel, heat exchanger, and bed of graphite spheres to mitigate tritium release.]

- Reactor Vessel
- Bed of graphite spheres
- Heat Exchanger
- To power cycle
- Pebbles replacement rate same as core pebble refueling rate (1/30\textsuperscript{th} per day)
- Total bed graphite surface area: 1945 m\textsuperscript{2}
- Friction pressure drop: 0.50 atm

Release Rate with Capture on Graphite with Online Replacement < 10 Ci/EFPD

- **Tritium Release Rate (Ci/EFPD)**
- **EFPD**

\[\text{Without packed bed of graphite}\]
\[\text{With packed bed of graphite}\]
Release Rate with Variable PRF

- Baseline assumes permeation reduction factor (PRF) of 10 for 316 SS
- Increasing PRF causes a pile-up of tritium in the HX tube wall
- Increased PRF delays, but does not reduce tritium release
Tungsten is stable in flibe
- W has low hydrogen solubility: $1.4 \times 10^{-3}$ mol H$_2$/m$^3$-MPa$^{0.5}$ compared to 62.9 for 316
- Could be applied as flibe facing coating on stainless steel (apply Ni between W and SS)
- Also would protect Cr from selective oxidation
Variation in Tritium PRODUCTION RATE with Li-7 Enrichment
Variation in Tritium RELEASE RATE with Li-7 Enrichment

Size of graphite bed reduced by factor of 4
Analysis of tritium behavior at above-normal temperatures in the FHR for Beyond Design Basis Accidents (BDBA)
Tritium Desorption at High Temperatures Simulated with TRIDENT

- System allowed to reach steady state
- Coolant inlet and outlet temperatures increased by 300 °C and maintained for 15 days
- Normal operation resumed after 15 days at high temperature
Conclusions and Future Work
TRIDENT Provides FHR System Modeling Capabilities

• TRItium Diffusion EvolutioN and Transport (TRIDENT)
  – Corrosion and tritium behavior coupled
  – Predicted tritium distribution/release in FHR systems
  – Predicted/Compared effectiveness of tritium capture systems
Conclusions on Tritium and Corrosion

Simulations show:

• Corrosion rate with controlled redox: 0.08 mg/cm² per EFPY

• Tritium release rates without engineered solutions: 2500 Ci/d

• Proposed New Solutions:
  – Sorption on bed of graphite release rates < 10 Ci/EFPD
  – Increase Li-7 enrichment to 99.999 wt%
  – Use of W permeation barrier
Selected Future Work

• Wide option space for tritium control, need to optimize capture systems

• Explore use of graphite specifically engineered for tritium capture (outside of core)

• May include radiation effects on graphite for tritium absorption

• Tritium/Protium isotopic exchange reactions if H₂ deliberately added to system

• Add detail to corrosion model: currently 1D grain boundaries, in reality grain boundaries are 3D networks

• Highlights need for experimental work:
  – Tritium transport in flowing salt contacting metal membranes and graphite
  – Tritium uptake and desorption kinetics on graphite in salt at low partial pressures and relevant temperatures
Thank You

Questions
Comments

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