Tritium Management in FHRs

Workshop on Molten Salt Reactor Technologies — Commemorating the 50th Anniversary of the Startup of the MSRE

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Work Supported by DOE Nuclear Energy University Programs

10/16/2015
Outline

• Background
• Tritium Transport Theory
• Transport Coefficients of H₂/T₂ in Materials
• Tritium Control/Mitigation Strategy for FHRs
  – Redox Control Facility
  – Tritium Removal Facility
  – Heat Exchanger Design
  – Tritium Permeation Barrier Coating
  – Planned Experiments
Background: Tritium Issue in FHRs

- **Tritium Production is an important safety issue in FHRs**
  - Only radionuclide with the potential for significant release under normal operating conditions without fuel failure
  - Large generation rate

- **Tritium Source in FHRs: Ternary fission and neutron activation of $^{6}\text{Li, }^{7}\text{Li, }^{9}\text{Be, }^{19}\text{F}$**
  - $^{3}\text{Li} + n \rightarrow ^{2}\text{He} + ^{1}\text{H}$
  - $^{3}\text{Li} + n \rightarrow ^{4}\text{He} + ^{1}\text{H} + n$
  - $^{3}\text{Li} + n \rightarrow ^{5}\text{He} + ^{1}\text{H}$
  - $^{4}\text{Be} + n \rightarrow ^{2}\text{He} + ^{6}\text{Li}$
  - $^{9}\text{F} + n \rightarrow ^{17}\text{O} + ^{1}\text{H}$

- **Tritium Production Rate**
  - AHTR (2400 MWth): Estimated at 5000 Ci/day at startup
  - 500 Ci/day at steady-state operation
  - PWR (1000 MWe): 1.9 Ci/day
Background: Tritium Issue in FHRs (Cont’d)

- **Generated Tritium can:**
  - Be trapped by the carbonaceous materials in the primary loop
  - Escape through the primary coolant surface into the cover gas
  - Permeate through the reactor vessel, piping and heat exchanger tubing
    - High-temperature salt
    - Large surface area

- **Ongoing Integrated Research Projects on FHRs**
  - MIT-led: Investigating tritium removal by carbon absorption and providing fundamental data to validate tritium models
  - GT-led: Improving accuracy of tritium generation rate calculation and investigating approaches to contain tritium in heat exchangers

- **Goals**
  - To develop a tritium management/control strategy for FHRs
  - To decrease the tritium release rate of FHRs
  - To collect the tritium extracted from the primary loop
• Diffusion – Fick’s Law \[ \vec{J} = -D \nabla c \]

• Dissolution
  – Non-metal: Henry’s Law: \[ p = Kc \]
  – Metal: Sievert’s Law: \[ p^{0.5} = Kc \]

• Species Conservation Equation
\[
\frac{\partial c}{\partial t} + \nabla \cdot (\vec{u}c) = \nabla \cdot (D \nabla c) + \dot{R}
\]
• **Diffusivity, Solubility, and Permeability**
  
  – Diffusivity $D$ – [m$^2$/s]
  
  – Solubility $K$
    
    ▪ [mol/m$^3$Pa] for liquid solvent
    ▪ [mol/m$^3$Pa$^{0.5}$] for solid solvent
  
  – Permeability $P$
    
    ▪ [mol/m-s-Pa] for liquid permeable material
    ▪ [mol/m-s-Pa$^{0.5}$] for solid permeable material

  Permeability $= \text{Diffusivity} \times \text{Solubility}$

• **Diffusivities of Hydrogen Isotopes**

$$\frac{D_T}{D_H} = \sqrt[3]{\frac{M_H}{M_T}} = \frac{1}{\sqrt{3}}$$
<table>
<thead>
<tr>
<th>Material</th>
<th>Solubility</th>
<th>Diffusivity $[\text{m}^2/\text{s}]$</th>
<th>Permeability $[\text{mol/m-s-Pa}]$</th>
<th>Isotope</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLiNaK</td>
<td>$5.66\times10^{-9}$ [mol/m$^3$-Pa]</td>
<td>$8.64\times10^{-10}$</td>
<td>$4.89\times10^{-18}$ [mol/m-s-Pa]</td>
<td>H</td>
<td>Fukada (2006)</td>
</tr>
<tr>
<td>FLiBe</td>
<td>$1.04\times10^{-3}$ [mol/m$^3$-Pa]</td>
<td>$5.18\times10^{-9}$</td>
<td>$5.38\times10^{-12}$ [mol/m-s-Pa]</td>
<td>T</td>
<td>Simpson (2006)</td>
</tr>
<tr>
<td>Palladium</td>
<td>$2.09$ [mol/m$^3$Pa$^{0.5}$]</td>
<td>$1.75\times10^{-8}$</td>
<td>$3.66\times10^{-8}$ [mol/m-s-Pa$^{0.5}$]</td>
<td>H</td>
<td>Calderoni (2008)</td>
</tr>
<tr>
<td>Nickel</td>
<td>$2.47\times10^{-1}$ [mol/m$^3$-Pa$^{0.5}$]</td>
<td>$3.76\times10^{-9}$</td>
<td>$9.30\times10^{-10}$ [mol/m-s-Pa$^{0.5}$]</td>
<td>H</td>
<td>Calderoni (2008)</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>$9.28\times10^{-2}$ [mol/m$^3$-Pa$^{0.5}$]</td>
<td>$1.66\times10^{-9}$</td>
<td>$1.54\times10^{-10}$ [mol/m-s-Pa$^{0.5}$]</td>
<td>H</td>
<td>Calderoni (2008)</td>
</tr>
<tr>
<td>Air</td>
<td>$12.47$ [mol/m$^3$], 1atm</td>
<td>$6.10\times10^{-5}$</td>
<td>$7.61\times10^{-4}$ [mol/m-s], 1atm</td>
<td>H</td>
<td>Marrero (1972)</td>
</tr>
<tr>
<td>He</td>
<td>$12.47$ [mol/m$^3$], 1atm</td>
<td>$7.18\times10^{-5}$</td>
<td>$8.95\times10^{-4}$ [mol/m-s], 1atm</td>
<td>H</td>
<td>Marrero (1972)</td>
</tr>
</tbody>
</table>
Hydrogen Transport Coefficients in FLiBe

**FLiBe Diffusivity**

Temperature [K]

- Fukada, Anderl, Sagara, Nishikawa (2005) Deuterium
- Fukada, Anderl, Sagara, Nishikawa (2005) Tritium

**FLiBe Solubility**

Temperature [K]

- Malinauskas, Richardson (1974) Protium
- Fukada, Anderl, Sagara, Nishikawa (2005) Deuterium
- Malinauskas Deuterium
- Field Deuterium
Hydrogen Transport Coefficients in FLiNaK

**FLiNaK Diffusivity**

- Katsuta, Furukawa (1978) Tritium
- Fukada, Merisaki (2006) Protium

**FLiNaK Solubility**

- Terai (1986) Protium
- Fukada, Merisaki (2006) Protium
- Fukada (2012) Protium
Tritium Control/Mitigation Strategy for FHRs

- **Generation**
  - Major form of tritium in the core: TF (corrosive)

- **Redox Control**
  - Beryllium metal is used to convert TF to $T_2$: $Be + 2TF \rightarrow T_2 + BeF_2$

- **Tritium Removal Facility**
  - Goal: Removal rate similar to the production rate
  - Cross-flow plate-type $T_2$ removal facility

- **Tritium Permeation Barrier**
  - FLiBe/FLiNaK could be used as the barrier in intermediate heat exchanger (IHX)
  - Tritium permeation barrier used as the outer wall coating in necessary areas
*1. HT exists if $H_2$ is used in the purging gas
   2. Studies have shown that by adding $H_2$ in the purging gas, $T_2$ removal efficiency can be improved
Redox Control Facility

- Easy Replenishment of Redox Pellets
- Modular Design
  - Located prior to the tritium removal module
- Pellet with SS316 Core
  - Beryllium pellets with a spherical SS316 core
  - To avoid used (smaller) pellets from being carried away by the salt with meshed grids
Tritium Removal Facility

- **Cross-flow Configuration**
  - Purging gas flows in the tube bank
  - Molten salt flows in the perpendicular direction to the tube bank
  - Increase the salt flow turbulence level

- **Modular Design**
  - Located after the redox control facility
  - Flexibility for applications of different tritium removal rates

Cut view of a unit cell of the facility

Front view  Side view  Top view
• Plot of Salt Flow Streamlines
  - Main streamlines are splitted each time as they meet the next row of tubes

• Plot of $H_2$ Concentration Distribution in the Molten Salt
  - Transport coefficients of $H_2$ instead of $T_2$ in FLiBe used due to the lack of data
  - $H_2$ concentration decreases quickly along the salt flow path
Results from COMSOL

- Comparison of Tritium Removal Facility Models
- Main Variables
  - Tube size
  - Tube pitch
  - Salt inlet flow velocity

Distribution of pressure drop and facility volume

Pressure drop \([x10^3 \text{kPa}]\)

Total volume of tritium removal facility \([x10^3 \text{m}^3]\)
Code Calculation Using MATLAB

- Overall Mass Transfer Coefficient $k_o$

$$\left( \frac{1}{k_o H_s} \right)^{\frac{1}{2}} = \left( \frac{1}{k_s H_s} \right)^{\frac{1}{2}} + \left[ \frac{K_w}{t_w} \left( \frac{p_{1,in}^{0.5} - p_{2}^{0.5}}{p_{1,out}^{0.5} - p_{2,in}^{0.5}} \right) \ln \left( \frac{p_{1,in}^{0.5} - p_{2,in}^{0.5}}{p_{1,out}^{0.5} - p_{2,in}^{0.5}} \right) \right]^{\frac{1}{2}}$$

- Corresponding Dimensionless Groups of Mass and Heat Transfer

<table>
<thead>
<tr>
<th>No.</th>
<th>Mass transfer</th>
<th>Heat transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reynolds number</td>
<td>Reynolds number</td>
</tr>
<tr>
<td></td>
<td>$Rc = \frac{\rho v D}{\mu}$</td>
<td>$Rc = \frac{\rho v D}{\mu}$</td>
</tr>
<tr>
<td>2</td>
<td>Schmidt number</td>
<td>Prandtl number</td>
</tr>
<tr>
<td></td>
<td>$Sc = \frac{\mu}{\rho D_{AB}}$</td>
<td>$Pr = \frac{c_p \mu}{k} = \frac{\nu}{\alpha}$</td>
</tr>
<tr>
<td>3</td>
<td>Sherwood number</td>
<td>Nusselt number</td>
</tr>
<tr>
<td></td>
<td>$Sh = \frac{k_x D}{D_{AB}}$</td>
<td>$Nu = \frac{hD}{k}$</td>
</tr>
<tr>
<td>4</td>
<td>Peclet number</td>
<td>Peclet number</td>
</tr>
<tr>
<td></td>
<td>$Pe = Re Sc$</td>
<td>$Pe = Re Sc$</td>
</tr>
<tr>
<td></td>
<td>Grashof number</td>
<td>Grashof number</td>
</tr>
<tr>
<td>5</td>
<td>$Gr = \frac{gD^3(\Delta \rho)(\frac{\rho_v}{\rho})^2}{\mu^2}$</td>
<td>$\beta = \text{coefficient of expansion}$</td>
</tr>
<tr>
<td></td>
<td>Stanton number</td>
<td>Stanton number</td>
</tr>
<tr>
<td>6</td>
<td>$St = \frac{Sh}{Re Sc} = \frac{Sh}{Pec}$</td>
<td>$St = \frac{Nu}{Re Pr} = \frac{Sh}{Pec}$</td>
</tr>
</tbody>
</table>
Facility Design Comparisons

<table>
<thead>
<tr>
<th></th>
<th>Dimension Set A</th>
<th>Dimension Set B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow rate of molten salt [kg/s]</td>
<td>11190.8</td>
<td></td>
</tr>
<tr>
<td>Tritium inlet concentration [mol/m³]</td>
<td>$1.8 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Tritium outlet concentration [mol/m³]</td>
<td>$1.62 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Tritium removal rate [mol/s]</td>
<td>$1.8 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>Tube OD [in]</td>
<td>1.050</td>
<td>1.315</td>
</tr>
<tr>
<td>Tube ID [in]</td>
<td>0.824</td>
<td>1.049</td>
</tr>
<tr>
<td>Tube wall thickness [in]</td>
<td>0.113</td>
<td>0.133</td>
</tr>
<tr>
<td>Tube bank pitch [in]</td>
<td>1.31 (Pitch/OD = 1.25)</td>
<td>1.64 (Pitch/OD = 1.25)</td>
</tr>
<tr>
<td>Tube length [in]</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Tube number</td>
<td>49971</td>
<td>41365</td>
</tr>
<tr>
<td>Molten salt inlet frontal velocity [m/s]</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Re</td>
<td>$4.64 \times 10^4$</td>
<td>$5.82 \times 10^4$</td>
</tr>
<tr>
<td>Molten salt inlet flow area [m²]</td>
<td>5.54 (2.35 × 2.35)</td>
<td>5.54 (2.35 × 2.35)</td>
</tr>
<tr>
<td>Total mass transfer area [m²]</td>
<td>$9.85 \times 10^3$</td>
<td>$1.02 \times 10^4$</td>
</tr>
<tr>
<td>Molten salt flow length estimated [m]</td>
<td>20.61 (in the direction normal to the tube bank)</td>
<td>26.72 (in the direction normal to the tube bank)</td>
</tr>
<tr>
<td>Molten salt frictional pressure loss [kPa]</td>
<td>197</td>
<td>189</td>
</tr>
</tbody>
</table>

- Fluoride salt flow rate from the AHTR preliminary design
- Tritium inlet concentration is raised to 10 times of that equivalent to the tritium production rate in the core
• Design of Heat Exchangers (IHX, SHX, DHX, and NDHX) for AHTR, considering tritium management and heat transfer effectiveness (GT-led FHR-IRP)
  – Goal: To reduce tritium diffusion into the secondary (cold) side while maintaining heat transfer rate

• Double-wall Heat Exchanger

• Tritium Permeation Barrier
  – Located between the outer tube and the inner tube walls
  – Fluoride salt (FLiBe/FLiNaK)
  – Sweep gas
    ▪ Helium
  – Tritium getter
• Ongoing work for NDHX: Two preliminary designs being considered
  – Option 1: Double-wall NDHX with sweep gas in the annulus
    ▪ Inner tube: Allow tritium permeation
    ▪ Outer tube: Inhibit tritium permeation (with surface treatment if necessary)
    ▪ Tritium: Trapped in the gap and taken away by sweep gas
  – Option 2: Double-wall NDHX with tritium getter in the annulus
    ▪ The gap/annulus is filled with a tritium getter (yttrium)
## Tritium Permeation Barrier Coating

### Surface Treatment: Tritium Permeation Barrier

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Base Metal</th>
<th>PRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>SS316, MANET, TZM, Ni, Hastalloy-X</td>
<td>10 to &gt;10,000</td>
</tr>
<tr>
<td>TiC, TiN, TiO₂</td>
<td>SS316, MANET, TZM, Ti</td>
<td>3 to &gt;10,000</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>SS316</td>
<td>10 to 100</td>
</tr>
<tr>
<td>Si</td>
<td>Steels</td>
<td>10</td>
</tr>
<tr>
<td>BN</td>
<td>304SS</td>
<td>100</td>
</tr>
<tr>
<td>N</td>
<td>Fe</td>
<td>10 to 20</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>Steels</td>
<td>40 to 700</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thickness [µm]</th>
<th>Al₂O₃</th>
<th>Cr₂O₃-SiO₂</th>
<th>ZrO₂</th>
<th>MSZAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03-1.4</td>
<td>0.03-1.4</td>
<td>50</td>
<td>50</td>
<td>50-100</td>
</tr>
<tr>
<td>PRF</td>
<td>100-10⁴</td>
<td>292</td>
<td>50</td>
<td>3-4</td>
</tr>
</tbody>
</table>

Tritium Permeation Barrier Coating (Cont’d)

- Tritium Permeation Reduction Factor (PRF) of candidate coatings

\[ PRF = \frac{\text{Permeation flux without coating}}{\text{Permeation flux with coating}} \]

- \( \text{Al}_2\text{O}_3 \) Coating Methods
  - Hot-dip aluminazation
  - Chemical vapor deposition (CVD)
  - Sol-gel

- Potential Issues with \( \text{Al}_2\text{O}_3 \) Coating
  - Integrity is crucial to the surface coating
  - Cracks can lead to significant decrease in the PRF
Planned Experiments

- Measurement of $H_2$ Diffusivity/Solubility in FLiNaK

- Validation of Cross-flow Tritium Removal Facility

Bubbling $H_2$ into FLiNaK to obtain the initial $H_2$ concentration for the removal facility

Total amount of hydrogen in the downstream purging gas vs. time

Flux of hydrogen in the downstream purging gas vs. time
We would like to acknowledge the support provided by

- U.S. Department of Energy (DOE) Nuclear Energy University Programs (NEUP)

- Ohio Supercomputer Center (OSC)
You are Invited!

- **Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors**, October 27-28, 2015, Salt Lake City, Utah
- Hosted by the MIT Nuclear Science and Engineering Department, Nuclear Reactor Laboratory, and Plasma Science and Fusion Center, the University of Wisconsin–Madison, and the Chinese Academy of Sciences
- Bringing together different communities working on the problems of tritium management at high temperature for an exchange of information and to encourage cooperation
- For more information and to register, please see the Workshop webpage: [http://tcw15.mit.edu](http://tcw15.mit.edu)
- **No Charge** for attending the workshop and reduced hotel room rate may still be available
- Questions? Contact David Carpenter: david_c@mit.edu