Tritium Transport in Fluoride-Salt Cooled High Temperature Reactors (FHR)

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Outline

1. Overview of FHR technology
2. Tritium management in the FHR
3. Tritium transport in the salt-graphite system
4. Future work
FHRs: Solid Fuel, Salt Cooled Reactors

Liquid fluoride salt coolants
- Excellent heat transfer
- Transparent, clean fluoride salt
- Boiling point ~1400°C
- Reacts very slowly in air
- No energy source to pressurize containment

But high freezing temperature (459°C)
And industrial safety required for Be

Coated particle fuel (TRISO Fuel)

FHRs have uniquely large fuel thermal margin

[Graph showing failure fraction vs. fuel temperature]
Nuclear Air-Brayton Combined Cycle (NACC)

Fluoride Salt Coolants Were Developed for the Aircraft Nuclear Propulsion Program

Conventional combined cycle gas plants achieve efficiencies of 50-60%

http://www.industcards.com/cc-usa-in-mi.htm
Nuclear Air-Brayton Combined Cycle (NACC)

Modified GE 7FA Turbine for Co-fired NACC

Base-load power: 42% efficiency (100 MWe)

Gas co-firing: 66% efficiency (242 MWe)
FHR Physical Plant Arrangement
Coiled Tube Air Heaters (CTAHs)

GE 7FA Turbine
Hot Air Leg
Cold Air Leg

CTAH
Salt Pumps
Hot Salt Well
Hot Salt Leg
Cold Salt Leg
PB-FHR Core

P.V. Gilli et al., “Radial Flow Heat Exchanger,”
U.S. Patent Number 3712370, Filing date:
PB-FHR Mark 1 Core Design

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Tritium Source Term

- The main sources of tritium production are Li-6 and Li-7

\[ ^1_0 n + ^6_3 Li \rightarrow ^3_1 H + ^4_2 He \quad ^7_3 Li + ^1_0 n \rightarrow ^4_2 He + ^1_0 n + ^3_1 H \]

- Natural Li isotopic composition: 7.5% \(^{6}\text{Li} \) – 92.5% \(^{7}\text{Li} \)
- Target \(^{6}\text{Li} \) start-up concentration: 60 ppm \(^{6}\text{Li} \)
- Steady state \(^{6}\text{Li} \) concentration: 8 ppm \(^{6}\text{Li} \)

- Lithium-6 is continuously created:

\[ ^1_0 n + ^9_4 \text{Be} \rightarrow ^6_2 \text{He} + ^4_2 \text{He} \quad ^6_2 \text{He} \rightarrow ^3_3 \text{Li} + ^0_{-1} e \]

- Natural Be isotopic composition: 100% \(^{9}\text{Be} \)

Cross Sections for \((n,\alpha)\) Reactions
Tritium Source Term

![Estimated Tritium Production Rate in the Mk1 PB-FHR Core](image)

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Tritium Production Rate (Ci/EFPY)</th>
<th>Tritium Production Rate (g/year per GWe)</th>
<th>Tritium Production Rate (Ci/year per GWe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-FHR</td>
<td>176</td>
<td>176</td>
<td>1.7 x 10^6</td>
</tr>
<tr>
<td>PWR (average)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.73 x 10^3</td>
</tr>
<tr>
<td>CANDU (Darlington)</td>
<td>576</td>
<td>576</td>
<td>8.0 x 10^6</td>
</tr>
<tr>
<td>PBMR</td>
<td>512</td>
<td>512</td>
<td>4.9 x 10^6</td>
</tr>
<tr>
<td>MSR</td>
<td>92</td>
<td>92</td>
<td>0.65 x 10^6</td>
</tr>
</tbody>
</table>

2. Ohashi, Hirofumi and Sherman, Steven R. Tritium Movement and Accumulation in the NGNP System Interface and Hydrogen Plant. s.l. : Idaho National Laboratory, 2007. INL/EXT-07-12746
FHR Tritium Emission Target

(Based on tritium production at steady state flibe isotopic composition, per GWe)

- FHR production: \((1.7) \times 10^6\) Ci/yr (176 g/yr)
- If 100% released to air: \(10^{-5}\) Ci/kg air (0.5x10^{-7} NRC limit)
  - Reduce by a factor of 200
- PWR emissions: \((0.7) \times 10^3\) Ci/yr (0.075 g/yr)
  - Reduce by a factor of 2000

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Table 1. Regulatory constraints on tritium in the United States.

<table>
<thead>
<tr>
<th>Regulation</th>
<th>Annual Radiation Dose (mrem)</th>
<th>Effluent Concentration</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Air ((\mu Ci/ml))</td>
<td>Water ((\mu Ci/ml))</td>
</tr>
<tr>
<td>Limit</td>
<td></td>
<td>100</td>
<td>1 \times 10^7</td>
<td>37</td>
</tr>
<tr>
<td>10 CFR 20.1301(a)1</td>
<td></td>
<td></td>
<td>3.7 \times 10^3</td>
<td>1 \times 10^3</td>
</tr>
<tr>
<td>10 CFR 20.1301(e)</td>
<td>50</td>
<td>0.5</td>
<td>(5 \times 10^8)^a</td>
<td>(1.85 \times 10^8)^a</td>
</tr>
<tr>
<td>ALARA</td>
<td>Appendix I to 10 CFR 50</td>
<td>15</td>
<td>(3 \times 10^8)^a</td>
<td>(1.11 \times 10^8)^a</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>EPA standard</td>
<td>4</td>
<td>-</td>
<td>(6 \times 10^5)^a</td>
</tr>
</tbody>
</table>

\(a\): Calculated by assuming the linear relationship between the annual dose of 50 mrem and the values in Table 2 of Appendix B of 10 CFR 20.

ALARA — as low as reasonably achievable
CFR = Code of Federal Regulations
EPA = U.S. Environmental Protection Agency

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Ohashi, Hirofumi and Sherman, Steven R. Tritium Movement and Accumulation in the NGNP System Interface and Hydrogen Plant. s.l. : Idaho National Laboratory, 2007. INL/EXT-07-12746
Tritium Sinks and Sources

Absorption in the fuel elements (via mass convection from the bulk salt to the fuel surface, and subsequent transport and trapping within the fuel element)

Chemistry will Determine $[T_2]/[TF]$
Alternative Tritium Sinks

- Fuel elements (pebbles: 100 days to full BU)
- Reflector pebbles
- Graphite particle absorber: annular cartridges of ~2.0-mm carbon spheres
- Gas sparging
- Double-wall heat exchangers
- Membrane separation system
# Tritium Permeation Barriers for CTAH tubes

<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>

## Barriers to release through CTAH

- 4x lower mass convection coefficient than the pebble bed
- Aluminum Oxide Tritium permeation barrier: Kanthal AF or Alkrothal 14; ~0.1 mm
- Ensure low tritium concentration in the flibe at CTAH inlet: $10^{-12}$ to $10^{-23}$ wt fraction ($10^{-5}$ to $10^{-17}$ g/m³)

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SINAP Gas Sparging Studies

Experimental results of gas extraction (Bubble generator + Gas separator) for separating the gas from water environment

Average bubble diameter: 0.55 mm
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Tritium Transport Scales of Interest

Core

Fuel Element

Temperature

Flow

Generation

Concentration

$c_{\text{out}}$

$c_{\text{in}}$

$c_{\text{max}}$

$c_{\text{bulk}}$

$\Delta c_{\text{salt}}$

$\Delta c_{\text{surface}}$

$\Delta c_{\text{pebble}}$

$c_{\text{surface}}$

$c_{\text{interior}}$
Table I. Perfect Sink Calculation Input and Outputs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt Average Temperature</td>
<td>923.15</td>
<td>K</td>
<td>Carbon Molecular Weight</td>
<td>12</td>
<td>g/mol</td>
</tr>
<tr>
<td>Reynolds Number</td>
<td>500</td>
<td>-</td>
<td>Tritium Molecular Weight</td>
<td>3</td>
<td>g/mol</td>
</tr>
<tr>
<td>Diffusivity (Tritium in FLiBe)</td>
<td>3.90E-09</td>
<td>m²/s</td>
<td>Graphite Density</td>
<td>1.70E+06</td>
<td>g/m³</td>
</tr>
<tr>
<td>Pebble Diameter</td>
<td>0.03</td>
<td>m</td>
<td>Pebble Life</td>
<td>1.4</td>
<td>yr</td>
</tr>
<tr>
<td>Salt Viscosity</td>
<td>6.78E-03</td>
<td>kg/(m*s)</td>
<td>FLiBe Volume</td>
<td>46.82</td>
<td>m³</td>
</tr>
<tr>
<td>Salt Density</td>
<td>1.96E+03</td>
<td>kg/m³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt Kinematic Viscosity</td>
<td>3.45E-06</td>
<td>m²/s</td>
<td>Mass Transfer Coefficient</td>
<td>5.74E-05</td>
<td>m/s</td>
</tr>
<tr>
<td>Schmidt Number (v/D)</td>
<td>885.25</td>
<td>-</td>
<td>Bulk Salt Concentration Steady State</td>
<td>2.38E-06</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Steady State Production Rate</td>
<td>2.66E-07</td>
<td>mol/s</td>
<td>Bulk Salt Concentration Startup</td>
<td>1.15E-05</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Startup Production Rate</td>
<td>1.28E-06</td>
<td>mol/s</td>
<td>Graphite Saturation Steady State</td>
<td>0.27</td>
<td>µg T/g C</td>
</tr>
<tr>
<td>Pebble Surface Area</td>
<td>1945.27</td>
<td>m²</td>
<td>Graphite Saturation Startup</td>
<td>1.28</td>
<td>µg T/g C</td>
</tr>
</tbody>
</table>

Table I. Summary of Tritium Saturation in Graphite

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope Pressure [Pa]</td>
<td>133 - 101325</td>
<td>2500 - 90000</td>
<td>10000</td>
<td>0.14</td>
<td>MSRE Salt</td>
</tr>
<tr>
<td>Saturation [ppm]</td>
<td>10 - 70</td>
<td>50 - 220</td>
<td>80</td>
<td>1 - 14</td>
<td>0.1 - 20</td>
</tr>
</tbody>
</table>
Background Information: MSRE

- ORNL-4865: Graphite stringers (CGB) from MSRE were analyzed for tritium with depth profiling. Contains information on FP distributions and transport.

- ORNL-5011: Small graphite samples were exposed to $T_2$ gas and analyzed.

- Briggs (1972): Measured and calculated distributions of tritium in the MSRE.

- Does this data lend itself to useful benchmark exercises?

- If so, what assumptions about the MSRE and its operations limit application to FHR?
What data is relevant?

- 750 C for 6.5 hr in P_T2 = 0.14 Pa on 1 cm^3 specimens.
- POCO AXF-5Q graphite taken as the example (non-oxidized).

Figure 1. COMSOL Model of Strehlow Data

Transport Mechanisms in Graphite

Quentin Deslot and Michael Young

Graphite structure and mechanism for tritium diffusion and trapping in graphite, from Atsumi

- In Graphite, a complex mechanism:
  - Both TF and T2 can diffuse
  - Diffusion: 3 Paths
  - Solubility: Chemisorption on several Traps

\[ \text{C•} + \text{T} \downarrow \text{gas} \rightarrow \text{C–T} \]
Modeling of MSRE Depth Profile

Trapping Model

\[
\frac{dC}{dt} = D \cdot \frac{\partial^2 C}{\partial x^2} - g \cdot C + b \cdot M
\]

\[
\frac{dM}{dt} = g \cdot C - b \cdot M
\]
Matrix Graphite and Nuclear Graphite

### Table I. Composition of Matrix graphite Material [23]

<table>
<thead>
<tr>
<th>Matrix</th>
<th>A3-3</th>
<th>A3-3 (1950)</th>
<th>A3-27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural flake graphite</td>
<td>72 wt%</td>
<td>72 wt%</td>
<td>71.2 wt%</td>
</tr>
<tr>
<td>Graphitized petroleum coke</td>
<td>18 wt%</td>
<td>18 wt%</td>
<td>17.8 wt%</td>
</tr>
<tr>
<td>Non-graphitized binder</td>
<td>10 wt%</td>
<td>10 wt%</td>
<td>11.0 wt%</td>
</tr>
<tr>
<td>Final heat treatment (°C)</td>
<td>1800</td>
<td>1950</td>
<td>1950</td>
</tr>
</tbody>
</table>

### Table I. Difference between Nuclear Graphite and Matrix graphite

<table>
<thead>
<tr>
<th>Name</th>
<th>Nuclear Graphite</th>
<th>Matrix graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Material</td>
<td>Coke grain Petroleum /coal tar pitch</td>
<td>Graphite grain Un-graphitized binder</td>
</tr>
<tr>
<td>Heat Treatment Temperature (K)</td>
<td>&gt;2973</td>
<td>&lt;2273</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.68</td>
<td>1.764</td>
</tr>
<tr>
<td>Particle Size(μm)</td>
<td>20</td>
<td>11.3</td>
</tr>
<tr>
<td>Open Porosity (vol %)</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Closed Porosity (vol %)</td>
<td>7</td>
<td>25</td>
</tr>
</tbody>
</table>

1. Property data for nuclear graphite is based on virgin graphite block from EDF UNGG Reactor [33].
2. Property data for Matrix graphite is based on A3-27 Matrix graphite manufactured by Germany [23].
Irradiation Effects

Figure 1. Granular Diffusion Coefficients with Graphite Damage [12]

Figure 2. Hydrogen Retention with Graphite Damage [21]
MITR FHR Irradiations

- Two in-core irradiations completed: 300 and 1000 hours at 700°C
  - Double-encapsulation with nickel inner vessel, graphite liner, titanium cold-wall
  - 100-300g of MSRE secondary flibe
  - Nuclear heating with ±3°C temperature control (He/Ne)
  - Separate gas flows in each containment, tritium collected

➢ Future irradiations for IRP-2
  - Tritium uptake from flibe into irradiated graphite (reflector, fuel matrix, etc.)
  - Transport and release of gaseous tritium and activation products (from flibe and corrosion)
  - Tritium diffusion from salt through metals (heat exchangers)
  - Incorporate electrical heating for temperature control independent of reactor power
Proposed Work

- **Goals:**
  - How much tritium will be retained in an FHR fuel pebble?
  - How long will it take for the pebble to reach equilibrium tritium concentration?

- **Studies:**
  - What is the mechanism of tritium transport and trapping in matrix graphite?
  - What data from nuclear graphite is relevant?
  - What data from higher temperature is relevant?
  - Characterize irradiation effects
  - What is the effect of salt intrusion?
  - What are the desorption characteristics – important for fuel handing

- **Ongoing Experiments**
  1. Salt intrusion experiment
  2. Contact angle measurements
  3. Hydrogen absorption experiment
  4. Electrochemical impedance spectroscopy – 2015 NEUP Grant
Electrochemical Techniques in Flibe
Francesco Carotti

Jenkins et al. 1968

Used by: Dr. Straka et al. at UJV (Czech Republic)

Problems:
• Never used for more than 80hrs
• Reaction of Ni2+ ions with boron nitrite (important at low concentrations)
• LaF3 difficult to machine? Expensive? Fragile?
Flibe Intrusion in Graphite
Nisarg Patel and Huali Wu

GDMS Results

Matrix Graphite Characterization

Electron Microprobes Results
Flibe Intrusion in Graphite
Nisarg Patel and Huali Wu

Electron Microprobe Results

Matrix Graphite Characterization

F vs depth

F ppmwt
-1000.000
0.000
1000.000
2000.000
3000.000
4000.000
Depth in microns

-0.25
0.25
0.75
1.25
1.75
2.25
2.75
3.25
F ppmwt [ppm wt]

-1000.000
0.000
1000.000
Micrometers

Electron Microprobe Results

Matrix Graphite Characterization
Proposed Work

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