Tritium permeation control and extraction—perspectives from fusion systems studies

Paul W. Humrickhouse

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors
Salt Lake City, Utah
October 28, 2015
Outline

• Tritium in fission and fusion reactors: similarities and differences
• Overview of breeding concepts for fusion
• Tritium management in fusion
• Concepts for tritium extraction from liquids
• Permeation barriers
• Permeation scaling with pressure
• Conclusions and recommendations for future research
Tritium generation in fission and fusion reactors

- Tritium generation in salt-cooled fission reactors is large relative to other fission reactors, but several orders of magnitude less than fusion.

<table>
<thead>
<tr>
<th></th>
<th>PWR(^1)</th>
<th>CANDU(^1)</th>
<th>Gas-cooled reactor(^1)</th>
<th>Molten salt reactor(^1)</th>
<th>ITER</th>
<th>FNSF</th>
<th>DEMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>T generated (kg/y)</td>
<td>0.000075</td>
<td>0.1</td>
<td>0.002</td>
<td>0.09</td>
<td>0.0042</td>
<td>1 - 10</td>
<td>100 - 167</td>
</tr>
</tbody>
</table>

- Fusion consumes ~55 kg of tritium per GW-year of fusion power, and must necessarily breed this amount from lithium.
- Tritium is very mobile and will permeate through solids at high temperature; losses must be limited to < 20 Ci/day (very roughly 1 g/yr).
- A fusion reactor must recover and separate bred tritium for re-use as fuel; in a fission reactor is it a waste product.
- Strategies for tritium permeation control and extraction investigated for fusion should apply to salt-cooled fission reactors.

\(^{1}\)H. Schmutz, INL/EXT-12-26758, 2012
Tritium breeding materials in fusion

- Tritium is bred via neutron interactions with materials enriched in lithium-6

- Solid breeders (beds with ~1 mm diameter pebbles)
  - $\text{Li}_4\text{SiO}_4$ or $\text{Li}_2\text{TiO}_3$ ceramic breeder
  - Be or $\text{Be}_{12}\text{Ti}$ (lower chemical reactivity) neutron multiplier

- Liquid breeders
  - Li liquid metal
  - PbLi eutectic ($\text{Pb}$ is a multiplier; less chemically reactive than Li)
  - FLiBe (requires additional Be multiplier)

- Current research is focused on solid ceramic (European, Japanese, Korean, Chinese, and Indian TBM in ITER) or PbLi breeders (EU, Indian TBM) or PbLi breeders

- The US does not have a TBM program, but our reference design is based on a PbLi breeder
**PbLi breeder concepts**

- **Structural material:** reduced activation ferritic-martensitic (RAFM) steel
  - Limited to 550 °C operation, maybe lower (~480 °C) due to PbLi corrosion

- **Helium-cooled lead-lithium (HCLL)**
  - EU ITER TBM design and DEMO concept
  - PbLi breeder flows very slowly and serves no cooling function
  - High tritium partial pressure; permeation barriers required
  - Cooling is provided entirely by separate helium channels

- **Dual-coolant lead-lithium (DCLL)**
  - US TBM conceptual design (not pursued) and DEMO concept
  - Higher PbLi flow rates
    - Low tritium partial pressures *if extraction system is highly efficient*
    - ~50% of power extracted from PbLi, ~50% from separate helium coolant
  - SiC flow channel inserts for thermal (potential PbLi temp ~700 °C), and electrical (mitigate MHD forces) insulation, and corrosion barrier
Tritium solubility in PbLi, FLiBe, and metals


Tritium control in fusion

- Both PbLi and FLiBe have low tritium solubilities - this results in a higher tritium partial pressure and tends to drive permeation losses through solid structures

- Extraction concepts therefore attempt to do the following:
  - Provide a medium (purge gas, getter, etc.) where tritium will preferentially accumulate, relative to structural materials
  - Maximize the contact area of the breeder/coolant with this medium
  - Minimize the transport distance through the breeder/coolant to reach this medium
  - Maximize the residence time in the extraction system (i.e. reduce the flow rate)

- These same ideas for PbLi should be applicable to FLiBe or other molten salts (chemistry may complicate things somewhat)

- Additionally, one can apply permeation barriers (e.g. in the form of coatings) to structural materials - probably necessary for fusion, not for fission
Tritium extraction concepts

- Immersed getters
- Liquid getter/cold trap
- Release to purge gas or vacuum
  - Bubblers, spray/droplets, extraction columns
- Vacuum permeator
Immersed Getters

• Getters such as U, Zr(Co), Pd, Ti, etc. are commonly used to remove tritium from gases (Example: a 60g U bed can hold 2g tritium)

• Immersed getters (V, Nb, Ta) have been proposed in the past to remove tritium from PbLi

• Principle demonstrated at small scale with V in PbLi, though not to saturation\(^1\)

• Issues:
  – Integrity of material (getter beds for gases are reduced to fines and require ceramic filters)
  – Lifetime of beds under cyclic loading (e.g. daily)
  – Deleterious effects of impurities including oxygen

\(^1\)H. Feuerstein, *Fusion Technology (14\(^{th}\) SOFT)*, 1986, p. 646
Liquid metal getter with cold trap

• Concept investigated at KIT in the 1980s
  – Intermediate NaK loop proposed, which acts as a tritium getter
  – NaK cooled so as to precipitate solid hydrides
  – Tritium removed from solid hydrides by vacuum pumping

• Might also take the form of a thin film between concentric HX tubes
  – Processing rate required for fusion may imply large heat loss
  – Salt-cooled fission reactors may require only infrequent batch processing and have minimal impact on HX performance
  – Li suitable for fission reactors where subsequent extraction is unnecessary
    • High saturated concentration
    • Less chemically reactive than Na/NaK
Droplets in vacuum

- Concept: spray coolant as small droplets into a purge gas or vacuum
- Small droplets provide high surface area and small transport distance
- “Vacuum Disengager” proposed for HYLIFE-II IFE design study\(^1\)
- Analytical solution and numerical models suggested 99.9% efficiency; no experiments performed
- Now under investigation for PbLi (as “Vacuum Sieve Tray”)\(^2\)
- Different analytical solution and numerical models suggest 70% efficiency achievable
- Measured extraction was lower than predicted by 10x, but models depend on (uncertain) solubility and diffusivity


\(^2\)F. Okino, *FED* 87 (2012) 1014-1018
Compact Mass Extractor

- Gas/Liquid Contactor – planned for HCLL (TBM and DEMO)
- Structured packing disperses PbLi flow and creates a large interfacial area between PbLi and gas
- ≤30% efficiency for single column as tested in MELODIE loop\(^1\)
- HCLL DEMO (14 inventory re-circulations per day) requires at least 80% efficiency\(^2\) even with permeation barriers (with ~100x reduction factor)
- Larger scale tests, optimization planned at TRIEX loop (ENEA) but no results as of yet

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**Extraction tests in a non-immersed hydraulic configuration (\(T = 673\) K)**

<table>
<thead>
<tr>
<th>Test No.</th>
<th>(L) (l h(^{-1}))</th>
<th>(G) (Nm(^3) min(^{-1}))</th>
<th>(P_{H,IE}) (Pa)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70–90</td>
<td>100</td>
<td>1200–1350</td>
<td>20–22</td>
</tr>
<tr>
<td>2</td>
<td>30–50</td>
<td>100</td>
<td>1000–1100</td>
<td>29–31</td>
</tr>
<tr>
<td>3</td>
<td>30–50</td>
<td>500</td>
<td>975–1000</td>
<td>29–31</td>
</tr>
<tr>
<td>4</td>
<td>30–50</td>
<td>100</td>
<td>450–475</td>
<td>23–25</td>
</tr>
<tr>
<td>5</td>
<td>50–50</td>
<td>100</td>
<td>220–230</td>
<td>23–25</td>
</tr>
</tbody>
</table>

**Extraction tests in an immersed hydraulic configuration (\(T = 673\) K)**

<table>
<thead>
<tr>
<th>Test No.</th>
<th>(L) (l h(^{-1}))</th>
<th>(G) (Nm(^3) Min(^{-1}))</th>
<th>(P_{H,IE}) (Pa)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>80–105</td>
<td>500</td>
<td>1300–1400</td>
<td>10–12</td>
</tr>
<tr>
<td>7</td>
<td>80–105</td>
<td>1000</td>
<td>1200</td>
<td>9–11</td>
</tr>
<tr>
<td>8</td>
<td>50–65</td>
<td>1000</td>
<td>1150–1200</td>
<td>&gt; 14</td>
</tr>
</tbody>
</table>

\(^1\)N. Alpy et al. *FED 49-50* (2000) 775-780

Vacuum permeator

• For a PbLi-cooled (e.g. DCLL) or salt-cooled fission or fusion reactor, higher flow rates must be processed
  – Simple scaling from most efficient MELODIE tests indicates that for a DCLL blanket (~470 inventory re-circulations/day), 240,000 extraction columns would be required\(^1\) (!)

• DCLL flow rates are much higher (~470 inventory re-circulations/day required)

• Similar performance in a much smaller device is potentially achievable with a vacuum permeator

• Concept: a shell-and-tube mass exchanger with tritium-laden primary, vacuum secondary, and high-permeability, thin-walled tubes

• Required efficiency depends on the reactor design (losses), but:
  – What is achievable?
  – How does it scale?

\(^1\)B. Merrill, 2005/06/15 ARIES meeting
Permeator extraction efficiency

- Transport processes in a permeator tube:
  - Advection in PbLi in the axial direction
  - Convective mass transport in PbLi in the radial direction
  - Permeation (Diffusion) through solid in the radial direction

- Can be solved analytically:
  \[ \eta = 1 - \exp\left( -\frac{\tau \zeta}{1 + \zeta} \right) \]

- \( \zeta \) and \( \tau \) are dimensionless numbers that indicate the relative importance of three transport phenomena

\[ \zeta = \frac{\Phi_s}{K_T K_i r_i \ln(r_o/r_i)} \]
\[ \tau = \frac{2 K_T L}{v r_i} \]

- \( r_i \): inner diameter of tubes
- \( r_o \): outer diameter of tubes
- \( L \): length of tubes
- \( v \): PbLi velocity
- \( K_i \): PbLi solubility
- \( K_T \): mass transport coefficient
- \( \Phi_s \): permeability of solid tube

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1. P. Humrickhouse *Fusion Science and Technology* 68 (2015) 295-302
Significance of $\zeta$ and $\tau$

- $\zeta$ indicates whether radial transport is limited by mass transport in PbLi, or by permeation through the solid tube wall.
- When $\zeta \ll 1$: Diffusion in the solid is limiting; there is no dependence on the PbLi transport property $K_T$.
- When $\zeta \gg 1$: Mass transport in the PbLi is limiting; there is no dependence on the solid transport properties $\Phi_s, r_o$ or PbLi solubility $K_l$.

$\tau$ is a ratio of axial to radial transport times:

$$\tau = \frac{(L/v)}{(r_i/2K_T)}$$

- When $\tau \gg 1$, tritium is swept through the length of the permeator tube before it has a chance to migrate radially.
- Need to evaluate $K_T$…
Mass Transport Correlations

- $K_T$ is defined by the Sherwood number: $\text{Sh} = dK_T / D_l$
- Sherwood number correlations have the form $\text{Sh} = \beta \text{Re}^a \text{Sc}^b$
- For PbLi at 470-700 °C, 10 < Sc < 150 ($\text{Sc} = \mu / \rho D_l$)
- The correlations below are remarkably consistent with each other, and with the heat transfer analogy- this approach is valid
- The choice of correlation is not a significant source of uncertainty in this analysis relative to other parameters

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>a</th>
<th>b</th>
<th>Range</th>
<th>Reference</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023</td>
<td>4/5</td>
<td>1/3</td>
<td>2000 &lt; Re &lt; 35000</td>
<td>Colburn 1933</td>
<td>Heat transfer analogy</td>
</tr>
<tr>
<td></td>
<td>0.6 &lt; Sc &lt; 2.5</td>
<td></td>
<td></td>
<td>Gilliland and Sherwood 1934</td>
<td>Vaporization of nine different liquids in air</td>
</tr>
<tr>
<td>0.0328</td>
<td>0.77</td>
<td>0.33</td>
<td>3000 &lt; Re &lt; 40000</td>
<td>Johnstone and Pigford 1942</td>
<td>Distillation of five different substances in a wetted-wall column</td>
</tr>
<tr>
<td>0.023</td>
<td>0.83</td>
<td>1/3</td>
<td>2000 &lt; Re &lt; 70000</td>
<td>Linton and Sherwood 1950</td>
<td>Solution of benzoic acid, cinnamic acid, and beta-naphthol in water</td>
</tr>
<tr>
<td></td>
<td>1000 &lt; Sc &lt; 2260</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0163</td>
<td>0.83</td>
<td>0.44</td>
<td>Sc ~ 0.6</td>
<td>Kafesjian et al. 1961</td>
<td>Vaporization of water in a wetted-wall tower</td>
</tr>
<tr>
<td>0.0096</td>
<td>0.913</td>
<td>0.346</td>
<td>10000 &lt; Re &lt; 100000</td>
<td>Harriott and Hamilton 1965</td>
<td>Benzoic acid in glycerin-water, and hydroxymethycellulose solutions</td>
</tr>
<tr>
<td></td>
<td>430 &lt; Sc &lt; 10000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Permeator Optimization

• Regardless of the transport regime, permeator efficiency is always increased by:
  – Increasing the temperature, $T$
  – Increasing the tube length, $L$
  – Decreasing the permeator velocity, $v$ (e.g. by increasing the number of permeator tubes)
  – Decreasing the tube diameter, $d$

• Using the analytical solution, we can optimize the design (minimize the total volume)

• The following slide does so for different materials and temperatures, subject to the following constraints (from ARIES-CS):

\[
\begin{align*}
\eta & \geq 0.7 \\
d & \geq 0.01 \text{ m} \\
m & = \rho N \pi r_i^2 v = 26000 \text{ kg/s} \\
\Delta p & = f \frac{L \rho v^2}{d \, 2} \leq 1 \text{ MPa}
\end{align*}
\]
## Tube material comparison

<table>
<thead>
<tr>
<th></th>
<th>B&amp;W PWR steam generator</th>
<th>RAFM 470 °C</th>
<th>RAFM 470 °C</th>
<th>RAFM 470 °C</th>
<th>Vanadium 400 °C</th>
<th>Vanadium 500 °C</th>
<th>Vanadium 600 °C</th>
<th>Vanadium 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>η (low solubility)</td>
<td></td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Tubes (#)</td>
<td>15,000</td>
<td>343,521</td>
<td>68,704</td>
<td>19,432</td>
<td>13,347</td>
<td>10,136</td>
<td>8,274</td>
<td>7,095</td>
</tr>
<tr>
<td>Tube length (m)</td>
<td>20.7</td>
<td>8.54</td>
<td>16.61</td>
<td>37.3</td>
<td>18.25</td>
<td>11.15</td>
<td>7.65</td>
<td>5.7</td>
</tr>
<tr>
<td>v (m/s)</td>
<td>0.1</td>
<td>0.5</td>
<td>1.77</td>
<td>2.55</td>
<td>3.4</td>
<td>4.22</td>
<td>4.98</td>
<td></td>
</tr>
<tr>
<td>Total volume (m³)</td>
<td>61.8</td>
<td>278.7</td>
<td>108.42</td>
<td>69.0</td>
<td>23.15</td>
<td>10.74</td>
<td>6.01</td>
<td>3.84</td>
</tr>
<tr>
<td>ζ</td>
<td></td>
<td>4.85</td>
<td>1.27</td>
<td>0.45</td>
<td>1681</td>
<td>425</td>
<td>148</td>
<td>65</td>
</tr>
<tr>
<td>η (high solubility)</td>
<td></td>
<td>0.10</td>
<td>0.04</td>
<td>0.03</td>
<td>0.47</td>
<td>0.36</td>
<td>0.29</td>
<td>0.23</td>
</tr>
</tbody>
</table>

• There is a significant size/cost advantage to high-permeability materials
Group 5 Metals - oxidation

- Group 5 metals have very high tritium permeabilities and from that standpoint are promising tube materials.
- They are compatible with PbLi, but the oxygen partial pressure on the vacuum side must be kept below $10^{-10}$ Pa to prevent oxidation\(^1\).
- Application of a Pd coating can prevent this, and commercial hydrogen purifiers based on this concept are available.
- They have a very narrow range of operation around 400 °C.
  - At lower temperatures, hydrides form and embrittle the structure.
  - At higher temperatures, Pd and substrate diffuse together, reducing (irreversibly) the tritium permeability.

\(^1\)R. Kurtz, 2005 ITER TBM meeting

Potential solutions

- Inter-diffusion of Pd and substrate can be prevented by an intermediate layer that separates them
  - Such composites are being actively investigated in the hydrogen energy research community
  - These are typically ceramics with some porosity so as not to prevent tritium permeation
    - Al$_2$O$_3$, Nb$_2$C, HfN, YSZ, etc. mentioned in literature
- Alloys?
  - V-Ni, Pd-Cu, V-Ti, V-Cu, others mentioned in literature
- Other coatings- Pd is necessary for separation from other gases, but we only need to prevent oxidation
**Permeation Barriers**

- Even under relatively optimistic assumptions for the extraction system, fusion systems studies usually find a permeation reduction factor (PRF) of 10-1000 on structures is necessary to meet release limits.
- Many barriers have been investigated experimentally, such as low-permeability metals (e.g. aluminum) or ceramics such as $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$, $\text{Er}_2\text{O}_3$.
- These have achieved permeation reduction factors as high as 10,000 in the laboratory.

Levchuck et al.  
*JNM 328* (2004) 103

Al$_2$O$_3$ deposition by CVD - Jürgen Konys
Permeation Barriers in a Radiation Environment

- While permeation reduction factors up to 10,000 have been measured in the laboratory, reactor tests on the same materials have not achieved this.

Irradiation testing of tritium/hydrogen barriers

<table>
<thead>
<tr>
<th>Test</th>
<th>Tritium source</th>
<th>Tritium sink</th>
<th>Reactor</th>
<th>Barrier system</th>
<th>Temperature (°C)</th>
<th>Effective PRF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBRETTO-2</td>
<td>Pb-17Li</td>
<td>He + H₂</td>
<td>HFR</td>
<td>Alum/316L</td>
<td>275–440</td>
<td>&lt;80</td>
<td>[41, 42]</td>
</tr>
<tr>
<td>LIBRETTO-3</td>
<td>Pb-17Li</td>
<td>He + H₂</td>
<td>HFR</td>
<td>316L/TiC</td>
<td>280–450</td>
<td>3</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al₂O₃/316L</td>
<td>280–450</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>316L/alum/Al₂O₃</td>
<td>280–450</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>TREXMAN</td>
<td>Pb-17Li</td>
<td>He + H₂</td>
<td>YAYOI</td>
<td>Cr₂O₃/SS316</td>
<td>600</td>
<td>10</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SS316/Cr₂O₃</td>
<td>600</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Loop-1</td>
<td>LiAlO₂</td>
<td>H₂O</td>
<td>ATR</td>
<td>Alum/SS316/alum</td>
<td>318</td>
<td>150</td>
<td>[44]</td>
</tr>
<tr>
<td>WC-1</td>
<td>LiAlO₂</td>
<td>H₂O</td>
<td>ATR</td>
<td>Alum/SS316/alum</td>
<td>&lt;330</td>
<td>150</td>
<td>[45]</td>
</tr>
</tbody>
</table>

- This reduction may result from damage (e.g. cracking) of the barrier, an increase in defects, or some other effect under irradiation.
Permeation scaling with pressure

- Permeation usually scales with the square root of partial pressure, implying that it is limited by diffusion through the solid.
- Low pressures or surface changes can result in surface-limiting and a change to linear dependence on partial pressure.
- Systems designed to achieve low tritium partial pressures need to investigate this experimentally.
  - Dimensionless number governs transition:
    \[ W = \frac{K_A x \sqrt{P}}{K_S D} \]

W ~ 1


Conclusions

• A number of tritium capture/extraction concepts have been proposed for fusion over the last several decades

• Some of these have been investigated experimentally, but none on the scale (size, tritium inventory) or under the conditions (radiation, high temperatures, long times) necessary for fusion

• Because of the low solubility of tritium in both PbLi and molten salts (including FLiBe), extraction techniques developed for PbLi are likely applicable to salt-cooled fusion and fission reactors as well

• Tritium generation will be orders of magnitude lower in fission reactors, for which tritium is a much more manageable problem
  – Tritium must be captured, but not necessarily separated/purified
  – Extraction systems may only need to process a fraction of the coolant on each pass
  – Permeation barriers may be unnecessary; for fusion it will be difficult to keep losses sufficiently low without them