TRITIUM CONTROL and CAPTURE in SALT-COOLED FISSION AND FUSION REACTORS: EXPERIENCES, MODELS, and BENCHMARKING

Workshop Proceedings

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ABSTRACT

The Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking was held on October 27-28, 2015 in Salt Lake City. The workshop objectives were to bring together researchers involved in experiments, modeling and benchmarking for tritium control at ~700°C in liquid salts and related systems to (1) exchange information and enable the future exchange of information, (2) initiate an effort for benchmarking of experiments and models, and (3) encourage cooperation between different groups working on the same challenges.

The workshop was organized by 5 organizations with common interests in tritium in salt systems at high temperatures: the Department of Nuclear Science and Engineering (NSE) at the Massachusetts Institute of Technology (MIT), the Nuclear Reactor Laboratory (NRL) at MIT, the Plasma Fusion Center (PFC) at MIT, the University of Wisconsin at Madison (UW) and the Chinese Academy of Science (CAS).

These diverse organizations have a common interest because three advanced power systems use liquid salt coolants that generate tritium and thus face common challenges. The Fluoride-salt-cooled High-temperature Reactor (FHR) uses the same graphite-matrix coated-particle fuel as high-temperature gas-cooled reactors and fluoride salt coolants. Molten salt reactors (MSRs) dissolve the fuel in a fluoride or chloride salt with release of fission product tritium to the salt. In both systems, the base-line salts contain $^7\text{Li}$. Isotopically separated lithium is used to minimize tritium production. The Chinese Academy of Science plans to start operation of a 10-MWt FHR and a 2-MWt MSR by 2020. High-magnetic field fusion machines proposed to use lithium enriched in $^6\text{Li}$ to maximize tritium generation—the fuel for a fusion machine. Advances in superconductors that enable higher power densities may require the use of lithium salts as coolants.

This proceedings summarize results from that workshop including descriptions of the power systems that use high-temperature salts, the common chemistry and tritium challenges, ongoing work removing tritium using carbon, other technologies for tritium control, and other tritium capabilities in the U.S. The appendixes include the workshop agenda, participants, and presentations from the workshop.
ACKNOWLEDGEMENTS

We would like to thank the Chinese Academy of Science, Idaho National Laboratory, Oak Ridge National Laboratory, and the U.S. Department of Energy for their assistance and support.
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1. INTRODUCTION

The Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking was held on October 27-28, 2015 in Salt Lake City. The workshop objectives were to bring together researchers involved in experiments, modeling and benchmarking for tritium control at ~700°C in liquid salts and related systems to:

- Exchange information and enable the future exchange of information
- Initiate an effort for benchmarking of experiments and models
- Encourage cooperation between different groups working on the same challenges.

The workshop was organized by five organizations with common interests in tritium control in salt systems at high temperatures:

- Department of Nuclear Science and Engineering (NSE) at the Massachusetts Institute of Technology (MIT)
- Nuclear Reactor Laboratory (NRL) at MIT
- Plasma Fusion Center (PFC) at MIT
- University of Wisconsin at Madison (UW)
- Chinese Academy of Science (CAS).

These diverse organizations have a common interest because three advanced power systems use liquid salt coolants that generate tritium and thus the need to avoid tritium (a health hazard) from escaping to the environment. The Fluoride-salt-cooled High-temperature Reactor (FHR) uses the same graphite-matrix coated-particle fuel as high-temperature gas-cooled reactors and fluoride salt coolants. Molten salt reactors (MSRs) dissolve the fuel in a fluoride or chloride salt with release of fission product tritium to the salt. In both systems, the base-line salts contain \(^7\text{Li}\). Isotopically separated lithium is used to minimize tritium production. The Chinese Academy of Science plans to start operation of a 10-MWt FHR and a 2-MWt MSR by 2020.

The third power system are advanced fusion machines with liquid-salt coolants. In fusion machines tritium is produced and used as a fuel. There are the dual requirements of (1) avoiding release of tritium to the environment and (2) efficient recovery of tritium as the fuel. The tritium inventories are several orders of magnitude larger than in fission machines. High-magnetic field fusion machines proposed to use lithium enriched in \(^6\text{Li}\) to maximize
tritium generation. Recent advances in superconductors that enable higher power densities may require the use of lithium salts as coolants.

We summarize results from that workshop including descriptions of the power systems that use high-temperature salts (Section II), the common chemistry and tritium challenges (Section III), ongoing work removing tritium using carbon (Section IV), other technologies for tritium control (Section V), and major tritium capabilities in the U.S. (Section VI). Table 1 lists the talks by general area. The workshop was organized so half the time was reserved for discussions

Appendix A contains the workshop agenda. Appendix B contains the list of participants and Appendix C are the presentations from the workshop.

Table 1: Workshop Talks by Subject Area

**Fission and Fusion Reactor Systems with Salt Cooling and Tritium Challenges**

- C. Forsberg (MIT NSE): Fluoride-Salt-Cooled High-Temperature Reactor (FHR)
- B. Sorbom (MIT PSFC): Liquid Immersion Blankets for Fusion Power Plants
- W. Liu (CAS): Thorium Molten Salt Reactor (TMSR) Project in China
- M. Laufer (UCB): Tritium and Chemistry Management for the Mark-1 PB-FHR

**Tritium Generation, Corrosion Chemistry and Modeling**

- J. Stempien (INL) Tritium Transport and Corrosion Modeling in the Fluoride Salt-Cooled High-Temperature Reactor
- T. Chrobak (UW): FLiBe Electrochemistry and Materials Corrosion Research at UW

**Tritium Control and Carbon**

- C. Contescu and T. Burchell (ORNL): Hydrogen – Carbon Interactions: A Brief Literature Survey
- T. Burchell and C. Contescu (ORNL): AGR Fuel Compact Development Program
- H. Wu (UW): Experimental Work on Tritium Transport Analysis in Flibe-Graphite system
- S. Lam (MIT NSE): Tritium Control Using Carbon Outside the Core
- H. Wu (UW) Effect of Hydrogen on Tritium Control in Molten Salt System
- D. Carpenter (MIT NRL) Planned FHR IRP-2 Tritium Experiments at the MIT NRL

**Tritium Control with Other Technologies**

- W. Liu (CAS): Tritium-Control Technologies for TMSR System in CAS (gas sparging)
- F. (UNM): Research on Techniques for Tritium Sequestration and Removal at UNM
- B. Wallace (UNM): Investigation of Tritium Control and Release Mitigation Options in Double-Wall Twisted-Tube Heat Exchangers (DT-HXRs)
- P. Humrickhouse (INL): Tritium Permeation Control and Extraction – Perspectives from Fusion System Studies
X. Sun (OSU): Tritium Management in FHRs: Ongoing and Planned Activities in Integrated Research Project Led by Georgia Tech

*Tritium Control Experience*

G. Stack (SRNL): An Overview of SRNL Tritium Activities
M. Shimada (INL): Overview of Tritium and Molten Salt FLiBe research at Safety and Tritium Applied Research (STAR) facility
D. Carpenter (MIT NRL): Experience with Tritium Evolution During Irradiation of MSRE Flibe in the MITR
D. Senor (PNNL): Irradiation Testing in Support of the Tritium Production Enterprise
2. SALT-COOLED FISSION AND FUSION POWER SYSTEMS

There is a rapidly growing interest in fission and fusion systems that use salt coolants that is driven by (1) separate developments in FHRs, MSRs, and fusion and (2) advances in gas turbines that can couple to salt-cooled reactor systems. Workshop presentations (Forsberg, Sorbom, Liu and Laufer) and discussions summarized the multiple basis for interest in developing these technologies.

2.1. Salt-Cooled Power Systems

2.1.1. Fluoride-salt-cooled High-temperature Reactors (FHRs)

The FHR uses salt coolant and the graphite-matrix coated-particle fuel developed for High-Temperature Gas-cooled Reactors (HTGRs). Advances in the fuel are enabling the development of the FHR. Because this reactor uses a proven fuel and a clean salt coolant, it is the near-term commercialization option for a salt-cooled reactor. Three different fuel designs are proposed by different groups (Fig. 1).

- **Pebble bed.** The pebble-bed FHR\(^1\) uses 3-cm diameter graphite pebbles with embedded coated-particle fuel—the same basic fuel that was used in the German HTGRs and will be used in the Chinese HTGRs that are under construction. The pebbles are 3-cm rather than the traditional 6-cm diameters used in HTGRs to increase surface area per unit volume of the core to allow higher power densities. The pebble-bed FHR design is the most developed. The Chinese Academy of Sciences plans to complete a 10 MWt pebble-bed FHR test reactor by 2020. Like pebble-bed HTGRs, this design allows online refueling. It is the near-term option.

- **Plate fuel.** Oak Ridge National Laboratory\(^2\) is developing a plate fuel where the hexagonal fuel assembly is similar in shape to a sodium-cooled reactor fuel assembly. The fuel plates are made of a carbon composite with the coated-particle fuel on the plate surfaces. It is a “traditional” type fuel assembly with a refueling strategy similar to a sodium fast reactor—another low-pressure reactor.

- **Fuel Inside Radial Moderator (FIRM).**\(^3\) This FHR core design is somewhat similar to the operating British Advanced Gas-Cooled Reactors (AGRs) except for use of salt coolant, higher power densities and the details of the fuel design. The AGRs are graphite-moderated carbon-dioxide-cooled high-temperature reactors with exit gas temperatures of 650°C. The AGR fuel consists of UO\(_2\) pellets in stainless steel pins with an assembly consisting of a circular array of pins inside an annular graphite shell. Fourteen AGRs have been operating for several decades. The FHR FIRM assembly replaces the AGR fuel assembly with a graphite cylinder containing liquid-salt cooling channels and fuel channels filled with coated-particle fuel in carbon-matrix pellets—a cylindrical variant of the prismatic fuel blocks used in some HTGRs. FIRM assemblies would be refueled using the same refueling strategies used by the AGR, pulling assemblies straight up through the vessel cover. AGRs refuel on-line at about 650°C, similar to FHR operating temperatures.
The base-line coolant is a lithium-beryllium-fluoride salt known as flibe ($^{7}$Li$_2$BeF$_4$). The characteristics of the flibe as well as other potential salts are listed in Table 2. The primary coolant system is a closed loop that operates at atmospheric pressure with nominal core coolant inlet and outlet temperatures of 600°C and 700°C respectively.

There are proposals for FHRs using advanced fuels including pin-type fuels with SiC clad. These are longer term options that do not change the need for tritium control strategies.

<table>
<thead>
<tr>
<th>Coolant</th>
<th>$T_{\text{melt}}$ (°C)</th>
<th>$T_{\text{boil}}$ (°C)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$\rho C_p$ (kJ/m$^3$ °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.7$^7$LiF-33.3BeF$_2$</td>
<td>459</td>
<td>1430</td>
<td>1940</td>
<td>4670</td>
</tr>
<tr>
<td>59.5 NaF-40.5 ZrF$_4$</td>
<td>500</td>
<td>1290</td>
<td>3140</td>
<td>3670</td>
</tr>
<tr>
<td>26 $^7$LiF-37 NaF-37 ZrF$_4$</td>
<td>436</td>
<td>2790</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>51 $^7$LiF-49 ZrF$_4$</td>
<td>509</td>
<td>3090</td>
<td>3750</td>
<td></td>
</tr>
<tr>
<td>Water (7.5 MPa)</td>
<td>0</td>
<td>290</td>
<td>732</td>
<td>4040</td>
</tr>
</tbody>
</table>

$^1$Compositions in mole percent. Salt properties at 700°C and 1 atmosphere. Pressurized water data shown at 290°C for comparison.
2.1.2. Molten Salt Reactors (MSRs)

Molten salt reactors were first developed as part of the nuclear aircraft propulsion program in the 1950s and then as a thermal-neutron-spectrum breeder reactor using the thorium fuel cycle in the 1960s. The Molten Salt Reactor Experiment (MSRE), an 8-MWt reactor (Fig. 2), successfully demonstrated the technology in the late 1960s. This reactor used flibe ($\text{Li}_2\text{BeF}_4$) salt with fuel and fission products dissolved in the salt. The reactor used bare graphite as the neutron moderator. The program was cancelled in the early 1970s when the United States decided to focus its breeder reactor program on sodium-cooled fast reactors (SFRs). In the last decade\textsuperscript{4, 5} there has been a renewed interest in MSR for several reasons.

![Fig. 2. Molten Salt Reactor Experiment](image)

- **Fuel cycle versatility.** MSRs can operate on a variety of fuel cycles including thorium breeder fuel cycles and various cycles that destroy actinides. This capability has been increased by recent work to develop fast spectrum MSRs.
- **Advancing technology.** Many of the technology challenges of the 1960s have been reduced or eliminated thanks to advances in other fields. Better high-temperature carbon forms can provide better materials for reactor internals. The development of high-temperature additive manufacturing enables fabrication of complex components including control rods, distillation columns, and other items out of molybdenum and other salt-compatible high-temperature materials. Advanced carbon and metal absorbers may enable efficient removal of noble metal fission products from the molten salt. Unless removed, these fission-
product metals plate out on heat exchanger surfaces, are a major source of short-term decay heat, and cause multiple challenges. Last, advances in metallurgy may enable development of alloys that allow higher temperature operations.

- **Safety.** MSRs enable alternative safety strategies relative to solid fuel reactors including the options of (1) dumping the liquid fuel to critically-safe passively cooled tanks under any accident scenario and (2) potentially the option to minimize the inventory of longer lived fission products such as cesium in the reactor that may dominate the accident source term and the potential for land contamination. The second option is enabled by the advancing separation technologies enabled by new materials and material fabrication methods as noted above, for components such as distillation columns.

The Chinese Academy of Science plans to build a small 2-MWt MSR by 2020 with an emphasis on the thorium fuel cycle for fuel sustainability. Several large western companies (Terrapower, Hatch) are examining MSRs as are many smaller companies.

### 2.1.3. High Magnetic-Field Fusion Reactors

Advances in magnetic fusion may drive fusion systems to use liquid salt coolants. The size of magnetic fusion devices for any given fusion power level is determined by the maximum feasible magnetic field with the size proportional to one over the magnetic field to the fourth power. Practical fusion machines require superconducting wire or tape to generate the magnetic fields to minimize electrical consumption by the magnets. However, standard superconductors lose their superconducting properties in high magnetic fields. In the last five years, methods have been developed to manufacture a new superconductor: Rare-Earth Barium Copper Oxide (REBCO). This new superconductor enables magnetic fields at the coil over 22 Tesla—more than twice the capability of older superconductors. It eliminates magnetic field strength as the primary design constraint in magnetic confinement fusion devices with the new limit being magnetic field induced stress in the coils. The REBCO is in the form of a steel tape that enables addressing the high stresses.
REBCO superconductors may enable doubling the practical peak magnetic field in a fusion machine and thus reduce the volume of fusion systems by an order of magnitude. The radius of a 500 MW plasma fusion system would be about 3 meters—the size of several magnetic fusion devices already built. Figure 3 shows JET (an existing fusion experimental device in the United Kingdom) and the proposed high magnetic field fusion system based on REBCO superconductors. It is potentially a revolution in fusion.

Increasing fusion power density by an order of magnitude improves long-term economic viability. However, it imposes major changes in fusion blanket design because of the much higher power densities. Historically proposed blankets have been solid lithium-containing materials for production of tritium fuel ($^6\text{Li} + n \rightarrow^3\text{H} + ^4\text{He}$). The higher power densities will likely require changing to a liquid blanket containing lithium—most likely flibe ($66.7\%\text{LiF}-33.3\%\text{BeF}_2$) for several reasons. A liquid blanket is needed for highly efficient neutron shielding with such high plasma fusion power densities. Fusion generates about 17 MeV per fusion of tritium and deuterium—most of this energy is in the form of 14 MeV neutrons that deposit their energy as heat in the liquid. The heat transfer challenges in solid fusion blankets become very difficult at these very high power densities. The coolant choices are (1) fluoride coolant salts—most likely flibe or (2) a liquid metal coolant containing lithium (lithium, lead-lithium, etc.). A low-electrical-conducting liquid salt rather than liquid lithium or a lead-lithium eutectic is preferred to ease magneto hydrodynamic issues such as coolant pumping and plasma control because the magnetic fields produced by external coils more rapidly penetrate through the blanket. These factors may drive magnetic fusion to liquid salt cooling.
2.2. Nuclear Air Brayton Combined Cycles (NACC)

Salt coolants were originally developed for the Aircraft Nuclear Propulsion Program in the 1950s with the goal of coupling a nuclear reactor to aircraft jet engines. They can transfer heat from the reactor to the power cycle at between 600 and 700°C. Recent advances in utility natural-gas combined-cycle technologies now enable coupling these reactors to a Nuclear Air-Brayton Combined Cycle (NACC) or potentially a Nuclear Helium Combined Cycle (NHCC). NACC can provide base-load electricity with additional variable peak electricity produced by using auxiliary natural gas, biofuels, hydrogen, or stored heat to (1) increase nuclear plant net revenue by 50 to 100% relative to base-load nuclear plants and (2) enable a low-carbon nuclear renewable electricity system. These developments create large incentives to develop salt-cooled reactors.

During base-load operation of a NACC, atmospheric air is filtered, the air is compressed, heat is added from the reactor through a coiled-tube heat exchanger (CTHX), the hot compressed air goes through turbines to produce electricity, the warm air exiting the gas turbine goes through a heat recovery steam generator to generate steam that is used to produce added electricity, and the air is exhausted to the stack. This power cycle is similar to that used in natural gas combined-cycle plants. If coupled to a salt-cooled reactor delivering heat between 600 and 700°C, heat-to-electricity efficiency is 42%. This specific example uses a modified General Electric 7FB gas turbine.

An economic analysis was done on the performance of an FHR with NACC in California and Texas using natural gas to produce peak electricity. These states have deregulated electricity markets. The peaking capability increased the plant yearly revenue by about 50% after subtracting the cost of the natural gas compared to a base-load nuclear plant. Because NACC is more efficient than a stand-alone natural-gas combined cycle plant in...
converting natural gas to electricity (uses less natural gas), its electricity production costs for peak electricity are less than a stand-alone natural gas plant; thus, it earns large profits when electricity prices are set by natural gas plants.

The addition of wind and solar in some electricity grids has resulted in significant hours per year with very low electricity prices—near zero at times of high wind or solar input. In such utility systems it is proposed that a Firebrick Resistance-Heated Energy Storage (FIRES) system replace the use of natural gas for providing heat to produce peak electricity. FIRES consists of high-temperature firebrick heated to high temperatures with electricity at times of low or negative electric prices. The firebrick, insulation systems, and most other storage system components are similar to high-temperature industrial recuperators. For peak electricity production, the compressed air after nuclear heating is sent through the firebrick to raise its temperature before going to the turbine. The round-trip storage efficiency from electricity to heat to electricity is ~66%, based on ~100% efficiency in resistance electric conversion of electricity to hot firebrick and 66% efficiency in conversion of incremental heat to electricity within NACC. FIRES enables the reactor to operate at base-load at all times while the station buys electricity from the grid at times of low prices to charge FIRES and sells electricity at times of high prices.
3. SALT CHEMISTRY AND TRITIUM GENERATION

Table 3 summarizes some of the differences and similarities in salt coolant requirements among the different reactor concepts. Carbon in the system can have a large impact on system behavior because carbon can absorb tritium and other impurities in the salt and has other chemical impacts.

Table 3. Salt Characteristics of Different Systems

<table>
<thead>
<tr>
<th>Property</th>
<th>FHR</th>
<th>MSR</th>
<th>Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>Fluoride</td>
<td>Fluoride or Chloride (fast spectrum only)</td>
<td>Fluoride (Flibe)</td>
</tr>
<tr>
<td>Impurities</td>
<td>Corrosion impurities and possible fission product impurities</td>
<td>High concentrations of fission products and actinides</td>
<td>Corrosion impurities</td>
</tr>
<tr>
<td>Use lithium salts</td>
<td>Optional</td>
<td>Depends upon goals</td>
<td>Required</td>
</tr>
<tr>
<td>Tritium production</td>
<td>Small ((^7)Li in Coolant)</td>
<td>Small ((^7)Li in Coolant)</td>
<td>High ((^6)Li in Coolant)</td>
</tr>
<tr>
<td>Tritium value</td>
<td>Waste</td>
<td>Waste</td>
<td>Fuel</td>
</tr>
<tr>
<td>Carbon in system</td>
<td>Yes</td>
<td>Depends upon option</td>
<td>No</td>
</tr>
<tr>
<td>Redox control</td>
<td>Ce(^{4+}/Ce^{3+}), other</td>
<td>U(^{3+}/U^{4+})</td>
<td>Ce(^{4+}/Ce^{3+}, Be, other)</td>
</tr>
</tbody>
</table>

The choice of salt depends upon neutronic and thermal-hydraulic considerations. Most proposed salts contain lithium because of its ability to lower the melting points of these salts to a few hundred degrees C. Flibe (Li\(_2\)BeF\(_4\)) has the best overall properties and is the choice in most proposed designs of FHRs and MSRs. For the FHR and MSR, one wants low neutron absorption cross sections with minimum tritium production. If a lithium salt is used, isotopically-separated \(^7\)Li must be used to minimize neutron absorption and tritium production. There are other salt choices for the FHR and MSR with all of the options involve complex tradeoffs. For fusion one wants to maximize tritium production (the fuel) and thus \(^6\)Li is required to maximize tritium production. For fusion systems, flibe is clearly the preferred salt coolant because it maximizes tritium production.

Under neutron irradiation these salts generate tritium by multiple pathways.

\[
\begin{align*}
\text{LiF} + \text{n} & \rightarrow \text{He} + \text{HF} \\
\text{LiF} + \text{n} & \rightarrow \text{He} + \text{HF} + \text{n'} \\
\text{F} + \text{n} & \rightarrow \text{O} + \text{H} \\
\text{BeF}_2 + \text{n} & \rightarrow \text{He} + \text{He} + 2\text{F} \\
\text{He} & \rightarrow \text{Li} + e^+ + \nu_e \quad (t_{1/2} = 0.8\text{sec})
\end{align*}
\]

Lithium-7 has a very small neutron cross section and \(^6\)Li has a large neutron cross section that maximizes tritium generation rates. With \(^7\)Li salts, the residual \(^4\)Li will partly burn out but will not go to zero if the salt also contains beryllium. Neutron reactions with beryllium will generate \(^6\)Li that is converted into tritium.

The nuclear reactions have important chemical implications. With appropriate materials of construction, clean salts have extremely low corrosion rates. This was demonstrated in the Molten Salt Reactor Experiment, an 8-MWt test reactor built and operated in the late 1960s. The secondary loop used flibe with very low corrosion rates. However, in a reactor LiF is converted to \(^3\)HF—hydrogen fluoride. Hydrogen fluoride is corrosive. Corrosion in
salt-cooled reactors (fission or fusion) is directly tied to the production of tritium. *Tritium control and corrosion control can’t be separated.*

If $^3$HF is allowed to corrode metals of construction, tritium in its molecular form will be released. To avoid corrosion redox control agents can be added to the coolant that result in converting $^3$HF to $^3$H$_2$. The redox potential determines the relative amounts $^3$HF versus $^3$H$_2$. While the $^3$HF can’t escape the system, the $^3$H$_2$ diffuses through hot metals such as heat exchangers to the environment. Maintenance of long term system integrity by assuring low corrosion rates implies converting $^3$HF to $^3$H$_2$, but $^3$H$_2$ can escape the system requiring methods for removal of $^3$H$_2$ and methods for slowing escape of $^3$H$_2$ from the system. A partial pressure of $^1$H$_2$ in the cover gas will lead to isotopic exchange with $^3$HF, producing $^3$H-$^1$H, thus affecting the tritium transport rates. At the same time, introduction of $^1$H$_2$ in the cover gas may also shift the redox potential of the salt, thus affecting corrosion control.$^{14,15,16}$

Tritium generation rates depend not only upon the salt selection and whether the reactor is a FHR, MSR, or fusion machine but also on the specific design features. This is most evident in the design of FHRs where there are large variations in the fraction of the core that is salt with a significantly higher salt fraction in a pebble-bed reactor than one with a FIRM core design. For one design of pebble-bed FHR, it was estimated$^{17}$ that ~0.03% of the tritium produced could be allowed to escape in order to stay below the tritium emission rates of the current fleet$^{18}$ of pressurized water reactors (2.2 Ci/GWe/d), or 810 Ci/GWe/y.

Stempien has built a model$^{19}$ for FHRs that accounts for tritium production, corrosion, transport that can predict behavior and calculate the impact of different methods to limit tritium loses or capture tritium. The model has been validated with the limited experimental data that is available. More experimental data is required to validate results. The model features are shown in Figure 5.

![Figure 5. TRIDENT: Tritium Diffusion Evolution and Transport](image)
TRIDENT has been used to model an FHR with a carbon bed for tritium removal as $^3\text{H}_2$. The model results are shown for one case in Table 4. In this case the carbon bed is designed to enable sufficient tritium removal to limit tritium releases to acceptable levels.

Table 4. TRIDENT Output for FHR with Tritium Carbon Absorber Bed

<table>
<thead>
<tr>
<th>Temperatures*</th>
<th>Coolant Freezing</th>
<th>459°C (FliBe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Core Outlet</td>
<td>700°C</td>
<td></td>
</tr>
<tr>
<td>ATWS</td>
<td>&lt;800°C</td>
<td></td>
</tr>
<tr>
<td>Coolant Boiling</td>
<td>1400°C (FliBe)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressures (primary loop)</th>
<th>$p_{T_2}$ Unmitigated</th>
<th>3.3-20 Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{T_2}$ with Graphite Capture</td>
<td><strong>0.03-0.08 Pa</strong> (Peak release 7.5 Ci/GW/d)</td>
<td></td>
</tr>
<tr>
<td>$p_{T_F}$ Unmitigated</td>
<td>0.03-0.075 Pa</td>
<td></td>
</tr>
<tr>
<td>$p_{T_F}$ with Graphite Capture</td>
<td><strong>0.0027-0.0045 Pa</strong> (Peak release 7.5 Ci/GW/d)</td>
<td></td>
</tr>
</tbody>
</table>

There are several observations from such modeling. The allowable tritium gas pressure in the primary system with metallic heat exchangers is on the order of magnitude of 0.05 Pa. If the tritium gas pressure is greater than this, the concentration gradients of tritium through hot heat exchangers may allow tritium to escape during operations in excess of releases from LWRs. The same limit would apply to a MSR or a fusion machine. The difference with a fusion machine is that the starting concentration of tritium in the salt is three orders of magnitude larger than in an FHR, and tritium is recovered from the salt for subsequent use as fuel. The calculated partial pressure of $^3\text{HF}$ is also given but HF can’t diffuse through hot metal. Graphite absorbs both $^3\text{H}_2$ and $^3\text{HF}$.

The requirements in Table 4 for allowable levels of tritium in the salt are strongly dependent upon permeation rates of tritium through hot heat exchanges to the environment. If high-performance coatings are incorporated into the heat exchangers to slow migration of tritium, much higher concentrations of tritium can remain in the salt. Consequently there is a tradeoff between high-efficiency removal of tritium from the salt and highly effective barriers to slow tritium transport through the heat exchangers. The CAS has a major effort to measure and develop better tritium barriers. The INL STAR facility for the fusion program has also had a major effort in measuring permeation rates through various materials.
4. TRITIUM CONTROL AND CARBON

The largest fraction of the workshop was devoted to carbon and tritium in salt-cooled systems. Carbon absorbs tritium and is chemically compatible with high-temperature salts. It is important in these systems in three different contexts.

4.1. Carbon in Reactor Cores

The FHR fuel is made of carbon and thermal spectrum MSRs use bare graphite. Tritium holdup in the carbon is significant. In the pebble-bed FHR with on-line refueling, there is the potential to use the pebbles as the main tritium capture system. In a pebble-bed reactor the pebbles circulate through the core typically once a month. There is the option of heating pebbles as they are circulated out of the core to remove the tritium before recirculating the pebbles back to the reactor core. This is not viable for other fuel forms because the carbon capability to pick up tritium will saturate due to the longer times between refuelings.

Tritium on carbon components is important in one other context. If carbon components in the nuclear system pick up a large inventory of tritium over time, this inventory could be partly released in a reactor over-temperature transient event. The equilibrium quantities of tritium in the core depend upon the average tritium levels in the coolant. The reactor core tritium inventories can be minimized by maintaining low levels of tritium in the coolant because there is an equilibrium between these tritium reservoirs.

Tritium uptake on carbon depends not only upon the carbon form but also on radiation damage in the graphite and potentially radiation flux levels. The MIT activities are primarily associated with experimental activities to understand these behaviors in 700°C salt in the MIT reactor. UW activities are investigating absorption onto previously-irradiated fuel matrix graphite.

4.2. Out-of-Core Tritium Removal with Carbon

Initial modeling indicated that a carbon bed out-of-core should be able to remove tritium from the clean salt in FHRs. The TRIDENT modeling used the limited tritium absorption data available on nuclear grade graphite for this analysis. However, non-nuclear-grade carbon forms have surface areas per unit of mass up to 1000 times larger than nuclear grade graphite—and potentially hydrogen sorption capacities a 1000 times larger. Nuclear grade graphite undergoes very high-temperature processing to produce a graphite with dimensional stability under high neutron radiation—a requirement that does not exist for any carbon absorber outside the reactor core. An out-of-core carbon bed can have the carbon and the bed optimized for tritium removal. This suggests the potential for relatively small carbon beds to efficiently remove tritium to very low concentrations. MIT (Lam) is investigating this option.

In the design of the MSRE great efforts were undertaken to avoid uptake of xenon and krypton in the graphite moderator because they are neutron absorbers. However, some uptake of xenon and krypton was observed. It is believed that these inert gases diffused into void spaces that do not fill with salt because of liquid surface tension. It is unknown at this time whether efficient carbon absorbers could be developed for MSRs to simultaneously remove tritium, krypton, and xenon—or potentially removal of the fission-product noble metals from the salt. Fission product noble metals that are generated in situ migrate to liquid-gas and liquid-solid surfaces because of the very low solubility in salts. Metals can be plated onto carbon. What is unknown is whether a practical system can be developed and what type of surface treatment of carbon may be required for noble metal fission products. That
will require good methods to generate noble metals in salts or a MSR test loop to test different carbon absorbers for noble metals.

4.3. Carbon and Corrosion

The presence of carbon in a salt system alters corrosion rates. Experiments at MIT and Wisconsin are underway to understand the various mechanisms and testing different materials with and without carbon in the system.
5. OTHER OPTIONS FOR TRITIUM REMOVAL FROM SALT

5.1. Gas Sparging

Tritium can be removed from high-temperature salt using gas sparging where an inert gas such as helium or argon is mixed with the liquid salt and tritium in different forms preferentially transfers to the gas phase and then to the off-gas system. The Chinese Academy of Science (CAS) has an ongoing experimental program to develop such a system is initially using water analogs to be followed by testing in salt systems. The CAS plans to complete by 2020 a 10 MWt FHR and a 2 MWt MSR. In a MSR, the off-gas system must remove tritium but also remove much larger quantities of fission product xenon and krypton. This creates an incentive for a common system to remove all volatile gases—a capability of a gas sparging system.

New Mexico is initiating a program using ultrasonic gas sparging. Ultrasonics can potentially create smaller gas bubbles with higher surface area and thus more efficient mass transfer of tritium to the inert gas phase. While ultrasonic gas dispersion has been used in a variety of systems, it has not been applied to very high temperature systems.

There is the option of using a spray tower or equivalent where the salt is in droplets or flowing over a high-surface area media and the purge gas is the continuous media—reverse of gas sparging. It is an option originally examined by LLNL for fusion machines. The complication with this strategy is the larger size of equipment when the purge gas is the continuous phase.

This option may be attractive for one class of advanced MSR designs that is being developed by Hatch of Canada where the liquid salt flows downward through the reactor core through constrictions to critically-safe passively-cooled dump tanks under the reactor core—a type of spray tower. The liquid salt is pumped from these tanks through the heat exchangers back to the reactor core. Any failure, including loss-of-power, results in the salt draining to a safe configuration. This configuration may allow tritium, xenon, and krypton removal options not available with other designs. The salt can be dispersed as droplets or flow over a metal mesh—both providing a high surface area for the liquid salt to allow the dissolved gases to diffuse over short distances from the liquid salt phase into the gas phase.

If a high-surface-area metal mesh is used, one would expect the noble metals to plate out on the surface of the mesh—addressing another salt cleanup challenge of MSRs. Alternatively the metal mesh could be salt pool at the bottom of the system for criticality control and noble metal plate out.

5.2. Permeators

Tritium can be removed by metallic permeators. Permeators are tubes designed for high rates of hydrogen transfer through the tube where salt would be on one side of the tube and a vacuum or hydrogen getter would be on the other side of the tube to provide a large hydrogen gradient to maximize hydrogen transport. Permeators are used in the laboratory and some process operations for tritium separation and isotopic separation of different hydrogen isotopes. Investigations are underway at Ohio State for tritium separation in salt-cooled systems using permeators.

5.3. Double-Wall Heat Exchangers

Double wall heat exchangers are used in the chemical industry where there are two fluids where violent reactions would occur if there was a tube failure. They have also been developed for sodium-cooled fast reactors for sodium water heat exchangers. Such heat exchangers can be used to block tritium transport by three mechanisms:
(1) vacuum between the tubes to capture tritium, (2) solid hydrogen getter between the tubes to sorb the tritium or
(3) flowing fluid such as lithium that acts as a getter. The disadvantages of double wall heat exchangers is cost and
added temperature drop across the heat exchanger. Oak Ridge National Laboratory, The Ohio State University and
the University of New Mexico are investigating this option for liquid salt systems.
6. TRITIUM CONTROL EXPERIENCE

There is a massive experience base in tritium separations and control from national security, heavy water reactor, high-temperature gas-cooled reactor, fusion, and research programs. This experience provides the basis for research going forward and provides many of the required research tools. It also provides proven methods to handle tritium once captured for disposal as a waste or recycle as a fuel (fusion).

In the United States there are three organizations with much of this experience. Savannah River National Laboratory has the national security tritium handling facilities. Pacific Northwest National Laboratory has been responsible for targets to produce tritium in the Watts Bar Nuclear Power Plant. Last, Idaho National Laboratory\(^{20}\) has facilities that conduct research on tritium for the fusion community. Oak Ridge National Laboratory has the expertise in carbon and done much of the work on hydrogen absorption on carbon. MIT laboratories using the MIT reactor are investigating tritium behavior in 700°C salt under neutron irradiation with the University of Wisconsin conducting similar work in a laboratory environment (no irradiation).
7. CONCLUSIONS

A confluence of events in three power technologies (FHR, MSR, and Fusion) in the last several years has created the need for control and removal of tritium from high-temperature coolant salts. While there is massive experience in tritium capture and control under many different environments, that experience has not been in 700°C salt where the tritium is in the forms of $^3$H$_2$ and $^3$HF at partial pressures of fractions of a Pa. A first workshop has been held as a starting point for a larger international cooperative effort to develop the required technologies for tritium control. A basic understanding of requirements and options has been developed but there is a large need for experimental data to develop models and engineered systems. The appendices include the agenda, the list of participants, and the presentations.
8. REFERENCES


12. C. Forsbeg, Strategies for a Low-Carbon Electricity Grid With Full Use of Nuclear, Wind and Solar Capacity to Minimize Total Costs, MIT-ANP-162, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, August 2015.


Appendix A:

Workshop Agenda
Final Agenda

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking

Salt Lake City; October 27-28, 2015
DoubleTree by Hilton Hotel Salt Lake City Airport, Salt Creek Ballroom

The objectives of the workshop are to bring together researchers involved in experiments, modeling and benchmarking for tritium control at ~700°C in liquid salts and related system to (1) exchange information and enable future exchange of information, (2) initiate an effort for benchmarking of experiments and models, and (3) encourage cooperation between different groups working on the same challenges. The workshop includes tritium sorption behavior in carbon because (1) fluoride-salt-cooled high-temperature reactors (FHRs) and some types of molten-salt reactors (MSRs) have carbon matrix fuels and/or carbon moderators and (2) several carbon forms are leading candidates to remove tritium from high-temperature salts.

The workshop goals are information exchange between the participants to enable future cooperation. The agenda will be modified based input from participants. Abstracts, papers, and presentations will be posted on the website (http://tcw15.mit.edu).

Tuesday: October 27

7:30 – 8:30 Continental Breakfast – Stillwater Poolside Atrium

8:30 – 10:00 Session 1. Welcome, Introductions, and Workshop Goals (MIT, CAS, Wisconsin)

Welcome

Introductions

Workshop Goals

Brief summaries of different programs (U.S., China, Europe, etc.)

Charles Forsberg (MIT NSE)

Xiaodong Sun (OSU)

10:00 – 10:30 Break

10:30 – 12:00 Session 2. Environment for Tritium Control

This session will include descriptions of (1) the different tritium-generating energy systems that use high temperature (~700°C) salts, (2) the environments in which the tritium is generated, and
(3) constraints on tritium removal. The goal is to define the challenges—common challenges and unique challenges with tritium capture and control associated with each technology.

*Fluoride-salt-cooled High-temperature Reactors* (Tritium environment: clean salt, carbon in system, possibility of small quantities of fission products, tritium is waste or useful product, redox control strategy?)

*Fusion ARC concept* (Tritium environment: clean salt, no carbon in system, high-efficiency recovery of tritium because tritium is the fuel, very high tritium levels, redox control?)

*Molten salt reactor (MSR)* (Tritium environment: salt with fission products and actinides, carbon may or may not be in the system, redox controlled by U+3/U+4, tritium is waste or useful product)

This session will also include discussions on tritium generation rates, required recovery rates, and various limits (Goals) that differ for various technologies.

Charles Forsberg (MIT NSE) “Fluoride-salt-cooled High-Temperature Reactors”

Brandon Sorbom (MIT PSFC) “The Fusion ARC Concept”

Cristian Contescu and Tim Burchell (ORNL) “Hydrogen – Carbon Interactions”

Tim Burchell and Cristian Contescu (ORNL) “AGR Fuel Compact Development Program”

12:00 – 1:30 Lunch – *Stillwater Poolside Atrium*

Wei Liu (CAS) “TMSR Project in China”

Michael Laufer (UCB) “Tritium and Chemistry Management for the Mark-1 PB-FHR”

1:30 – 3:00 Session 3. Tritium handling experience

Greg Staack (SRNL) “An Overview of SRNL Tritium Activities”

Masashi Shimada (INL) “Overview of Tritium and molten salt FLiBe research at Safety and Tritium Applied Research (STAR) facility”

David Carpenter (MIT NRL) “Experience with Tritium Evolution During Irradiation of MSRE Flibe in the MITR”

3:00 – 3:30 Break

3:30 – 4:30 Session 4. Characteristics of salt, corrosion, and redox on tritium control challenge

Chemistry determines tritium chemical form ($^3$H$_2$ or $^3$HF or $^3$HCl) and thus transport of tritium to the environment, tritium holdup in the system, and tritium control options. Tritium control tightly coupled to corrosion control in most but not all cases. Options for redox control and implications of those options on tritium control and capture to be discussed. (Example, if hydrogen used as part of redox control or salt cleanup, may have significant to remove with tritium)
Thomas Chrobak (UW) “FLiBe Electrochemistry and Materials Corrosion Research at UW-Madison”

Huali Wu (UW) “Effect of hydrogen on tritium control”

Wednesday October 28

7:30 – 8:30  Continental Breakfast – Stillwater Poolside Atrium

8:30 – 9:30  Session 5. Tritium and Carbon

Carbon is a large sink for tritium and a potential capture method for tritium in multiple chemical forms. What is known and not known

Huali Wu (UW) “Experimental work on tritium transport analysis in Flibe-Graphite system”

Stephen Lam (MIT NSE) “Tritium Control Using Carbon Outside the Core”

9:30 – 10:00  Break

10:00 – 12:00  Session 6. Tritium Capture

Systems for tritium capture at high temperatures in salts from salts, the gas space above, and related environments.

Paul Humrickhouse (INL) “Tritium Permeation Control and Extraction – Perspectives from Fusion System Studies”

Wei Liu (CAS) “Tritium-Control Technologies for TMSR System in CAS”

Floren Rubio (UNM) “Research on Techniques for Tritium Sequestration and Removal at UNM”

12:00 – 1:00  Lunch – Stillwater Poolside Atrium

1:00 – 2:30  Session 7. System models of tritium transport


David Senor (PNNL) “Irradiation Testing in Support of the Tritium Production Enterprise”

2:30 – 3:00  Break
3:00 – 5:00  **Session 8. Closeout and path forward**

- **David Carpenter** (MIT NRL) “Planned FHR IRP-2 Tritium Experiments”
- **Bryan Wallace** (UNM) “Investigation of Tritium Control and Release Mitigation Options in Double-Wall Twisted-Tube Heat Exchangers (DT-HXRs)”
- **Charles Forsberg** (MIT NSE)

**Thursday October 29**

- 7:30 – 8:30  Continental Breakfast – *Stillwater Poolside Atrium*
- 8:30 – 10:00  *Side Meetings as Appropriate*
- 10:00 – 10:30  Break
- 10:30 – 12:00  *Side Meetings as Appropriate*
Appendix B:

Workshop Participants
# List of Participants

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<th>Organization</th>
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<tr>
<td>Tim Flaspoehler</td>
<td>Georgia Tech</td>
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<tr>
<td>Carl Stoots</td>
<td>Idaho National Laboratory</td>
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<tr>
<td>John Stempien</td>
<td>Idaho National Laboratory</td>
</tr>
<tr>
<td>Masashi Shimada</td>
<td>Idaho National Laboratory</td>
</tr>
<tr>
<td>Paul Humrickhouse</td>
<td>Idaho National Laboratory</td>
</tr>
<tr>
<td>David Carpenter</td>
<td>Massachusetts Institute of Technology, Nuclear Reactor Laboratory</td>
</tr>
<tr>
<td>Guiqiu Zheng</td>
<td>Massachusetts Institute of Technology, Nuclear Reactor Laboratory</td>
</tr>
<tr>
<td>Charles Forsberg</td>
<td>Massachusetts Institute of Technology, Nuclear Science &amp; Engineering</td>
</tr>
<tr>
<td>Stephen Lam</td>
<td>Massachusetts Institute of Technology, Nuclear Science &amp; Engineering</td>
</tr>
<tr>
<td>Brandon Sorbom</td>
<td>Massachusetts Institute of Technology, Plasma Science &amp; Fusion Center</td>
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<tr>
<td>Cristian Contescu</td>
<td>Oak Ridge National Laboratory</td>
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<tr>
<td>Nicholas Brown</td>
<td>Oak Ridge National Laboratory</td>
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<tr>
<td>Tim Burchell</td>
<td>Oak Ridge National Laboratory</td>
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<tr>
<td>Xiaodong Sun</td>
<td>Ohio State University</td>
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<tr>
<td>David Senor</td>
<td>Pacific Northwest National Laboratory</td>
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<tr>
<td>Wei Liu</td>
<td>Shanghai Institute of Applied Physics</td>
</tr>
<tr>
<td>Greg Staack</td>
<td>Savannah River National Laboratory</td>
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<tr>
<td>Michael Laufer</td>
<td>University of California Berkeley</td>
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<tr>
<td>Bryan Wallace</td>
<td>University of New Mexico</td>
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<td>Floren Rubio</td>
<td>University of New Mexico</td>
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<tr>
<td>Guoping Cao</td>
<td>University of Wisconsin Madison</td>
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<tr>
<td>Huali Wu</td>
<td>University of Wisconsin Madison</td>
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<tr>
<td>Jee-Hoon Kim</td>
<td>University of Wisconsin Madison</td>
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<tr>
<td>Raluca Scarlat</td>
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<td>Thomas Chrobak</td>
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<td>Nisarg Patel</td>
<td>University of Wisconsin Madison</td>
</tr>
<tr>
<td>Yasir Arafat</td>
<td>Westinghouse</td>
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Workshop Presentations
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TRITIUM WORKSHOP GOALS

Charles Forsberg

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77 Massachusetts Ave; Bld. 42-207a; Cambridge, MA 02139; Tel: (617) 324-4010;
Email: cforsber@mit.edu; http://web.mit.edu/nse/people/research/forsberg.html

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors:
Experiments, Models, and Benchmarking
Salt Lake City
October 27, 2015

Three Technologies Depending Upon Liquid Salt Coolants & Control of Tritium
Fluoride-salt-cooled High Temperature Reactors: Solid Fuel & Clean Salt

Enabled by Advances In Gas-cooled High-Graphite-Matrix Coated Particle Fuel

High-Magnetic Field Fusion

Copper, $B = 3.5$ T

$P_{\text{fusion}} \sim 10$ MW

$\times B^4$

$P_{\text{fusion}} \sim 500$ MW

JET: $R \sim 3$ m
Operated in United Kingdom

Proposed: ARC: $R \sim 3.2$ m

Enabled by REBCO Superconductors that Enable Doubling Magnetic Fields
Molten Salt Reactor
Fuel Dissolved in Salt

Many Options

Enabled By Multiple Technologies and Interest In Alternative Breeder Reactors and Fuel Cycles

Common and Different Salt Challenges for FHR, MSR, and Fusion

<table>
<thead>
<tr>
<th>Property</th>
<th>FHR</th>
<th>MSR</th>
<th>Fusion</th>
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<tr>
<td>Salt</td>
<td>Fluoride</td>
<td>Fluoride or Chloride (fast spectrum only)</td>
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<tr>
<td>Impurities</td>
<td>Corrosion and possible fission product impurities</td>
<td>High concentrations of fission products and actinides</td>
<td>Corrosion impurities</td>
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<tr>
<td>Use lithium salts</td>
<td>Optional</td>
<td>Depends upon goals</td>
<td>Required</td>
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<tr>
<td>Tritium production</td>
<td>Small (7Li in Coolant)</td>
<td>Small (7Li in Coolant)</td>
<td>Very High (6Li in Coolant)</td>
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<td>Tritium value</td>
<td>Waste</td>
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<tr>
<td>Carbon in system</td>
<td>Yes</td>
<td>Depends upon option</td>
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<td>Redox control</td>
<td>Ce^{2+}/Ce^{3+}, other</td>
<td>U^{3+}/U^{4+}</td>
<td>Ce^{2+}/Ce^{3+}, Be, other</td>
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</table>
Common Technology Challenges for FHR, Fusion, and MSR

Common Challenges

- Power Cycles
- Thermohydraulics
- Mechanical Equipment
- Instrumentation
- Lithium Isotopic Separation ($^6$Li or $^7$Li)
- Tritium Generation
- Corrosion Control
- Tritium Control
Common Technology Challenges for FHR, Fusion, and MSR

Unique Capability of All Salt-Cooled Fission and Fusion Systems to Couple to Air or Helium Brayton Cycles

Salt Coolants Were Developed for the Aircraft Nuclear Propulsion Program
Salt Coolants Designed to Couple Reactors to Jet Engines

It Has Taken 50 Years for Utility Gas Turbine Technology to Mature Sufficiently to Enable Coupling with an FHR

Coupling Reactors to Gas Turbines is Transformational
Advances in natural gas combined cycles enable coupling reactors to gas turbines.

Gas-turbine technology not viable 15 years ago.

Only salt-cooled reactors (fission & fusion) couple efficiently to nuclear air-brayton combined cycles (NACC).

Commercial gas-turbine exit air compressor temperatures are between 400 and 500°C; thus, must deliver all heat above these temperatures.
Coupling Salt Fission and Fusion Reactors Using NACC Enables Base-Load Nuclear with Variable Electricity to the Grid

Stored Heat, Natural Gas, or Hydrogen

Base-Load Reactor Gas Turbine Variable Electricity

Boosts Revenue by 50 to 100% Relative to Base-load Nuclear Power Plants

Power Cycle Choices May Impact Tritium Control Strategies

- Can trap tritium in some power cycles because cold side of power cycle prevents tritium releases
  - Supercritical carbon dioxide
  - Helium Bryaton cycles
- Tritium major challenge if enters some power cycles
  - Steam cycles
  - Air-Brayton power cycles
Common Technology Challenges for FHR, Fusion, and MSR

The Coupled Challenges of Tritium Generation, Corrosion and Tritium Control

Tritium Generation, Corrosion and Control Are Coupled

Neutrons + \(^{7}\text{Li}/^{6}\text{Li}/\text{Be}\) →\(^{3}\text{HF}\)

\(^{3}\text{HF} + \text{Metal} \rightarrow \text{Corrosion} + ^{3}\text{H}_2\)

Can’t Separate Tritium Generation, Corrosion and Control
Workshop Goals

- Exchange information and enable future exchange of information
- Initiate an effort for benchmarking of experiments and models
- Encourage cooperation between different groups working on the same challenges

Common Challenges for Multiple Power Systems
Tritium Management in FHRs
Ongoing and Planned Activities in Integrated Research Project
Led by Georgia Tech

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking

Timothy Flaspoehler and Bojan Petrovic
Georgia Tech

Xiao Wu, Sheng Zhang, Richard Christensen, and Xiaodong Sun
The Ohio State University

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Salt Lake City, UT
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Outline

• Tritium Source Generation
  – Planned for Georgia Tech

• Design, Testing, Demonstration, and Modeling of Heat Exchangers for FHRs
  – Ongoing at Ohio State University
  – Heat Exchanger Design
  – Tritium Permeation Barrier Coating

• Tritium Control/Mitigation Strategy for FHRs
  – Redox Control Facility
  – Tritium Removal Facility
  – Planned Experiments
Tritium Source Generation

- **INTRODUCTION**
- **Georgia Tech: Timothy Flaspoehler**
  - Advisor (Bojan Petrovic)
- **Use neutron transport to calculate accurate tritium source in FHR**
  - Full-core
  - Time-dependent
- **Funding doesn’t start till 2nd fiscal year**

<table>
<thead>
<tr>
<th>Pathway</th>
<th>MT #</th>
<th>Scale6.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ternary Fission</td>
<td>18 (x%yield)</td>
<td>YES</td>
</tr>
<tr>
<td>$^6$Li (n, α) $^3$H or</td>
<td>107</td>
<td>NO</td>
</tr>
<tr>
<td>$^6$Li (n, t) $^4$He</td>
<td>105</td>
<td>YES</td>
</tr>
<tr>
<td>$^7$Li (n, nα) $^3$H or</td>
<td>22 / 105</td>
<td>NO / NO</td>
</tr>
<tr>
<td>$^7$Li (n, nt) $^4$He or</td>
<td>33</td>
<td>NO</td>
</tr>
<tr>
<td>$^7$Li (n, Xr)</td>
<td></td>
<td>*YES</td>
</tr>
<tr>
<td>$^{10}$B (n, 2α) $^3$H or</td>
<td>108</td>
<td>NO</td>
</tr>
<tr>
<td>$^{10}$B (n, 12α)</td>
<td>113</td>
<td>YES</td>
</tr>
<tr>
<td>$^{10}$B (n, α) $^7$Li (n, nα) $^3$H</td>
<td>107 &amp; 22</td>
<td>YES &amp; NO</td>
</tr>
</tbody>
</table>

PREVIOUS WORK

- **BACKGROUND: VHTR / NGNP goal to provide heat source for industrial applications**
  - Also without NRC licensing secondary side
  - Tritium leakage to secondary must be below EPA limits
- **RESULTS: Calculated different pathways in full-core model**
  - Used MAVRIC shielding sequence
  - Globally converged MC tallies in reflector

Tritium production from $^4$He impurities in coolant
Tritium Source Generation

PREVIOUS WORK

- RESULTS: Possible underestimate of tritium source in VHTR from impurities in graphite reflector

Table 3.1.1 Comparison of tritium generation rates in VHTR estimated in [3.1.1] and [3.1.2]

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Activity (Bq/y)</th>
<th>Production (t/s)</th>
<th>Activity (Bq/y)</th>
<th>Production (t/s)</th>
<th>Ratio (C/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ternary Fission</td>
<td>1.03E+14 (62.0%)</td>
<td>1.83E+15</td>
<td>1.03E+14 (29.8%)</td>
<td>1.83E+15</td>
<td>1.00</td>
</tr>
<tr>
<td>From $^3$He</td>
<td>2.98E+13 (18.0%)</td>
<td>5.30E+14</td>
<td>1.43E+13 (4.1%)</td>
<td>2.53E+14</td>
<td>0.48</td>
</tr>
<tr>
<td>From $^6$Li</td>
<td>2.32E+13 (14.0%)</td>
<td>4.12E+14</td>
<td>1.78E+14 (51.6%)</td>
<td>3.16E+15</td>
<td>7.67</td>
</tr>
<tr>
<td>Core Graphite</td>
<td>3.31E+12 (2.0%)</td>
<td>5.89E+13</td>
<td>5.45E+13 (15.8%)</td>
<td>9.68E+14</td>
<td>2.74</td>
</tr>
<tr>
<td>Core Matrix</td>
<td>1.66E+13 (10.0%)</td>
<td>2.94E+14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflector</td>
<td>3.32E+12 (2.6%)</td>
<td>5.88E+13</td>
<td>1.23E+14 (35.8%)</td>
<td>2.19E+15</td>
<td>37.24</td>
</tr>
<tr>
<td>From $^{10}$B</td>
<td>1.49E+13 (9.0%)</td>
<td>2.65E+14</td>
<td>5.00E+13 (14.5%)</td>
<td>8.89E+14</td>
<td>3.36</td>
</tr>
<tr>
<td>Control Rod</td>
<td>1.16E+13 (7.0%)</td>
<td>2.06E+14</td>
<td>4.35E+13 (12.6%)</td>
<td>7.74E+14</td>
<td>3.75</td>
</tr>
<tr>
<td>Absorber</td>
<td>1.66E+12 (1.0%)</td>
<td>2.94E+13</td>
<td>4.51E+12 (1.3%)</td>
<td>8.02E+13</td>
<td>2.72</td>
</tr>
<tr>
<td>Reflector</td>
<td>1.66E+12 (1.0%)</td>
<td>2.94E+13</td>
<td>2.00E+12 (6.6%)</td>
<td>3.56E+13</td>
<td>1.21</td>
</tr>
<tr>
<td>Total</td>
<td>1.71E+14</td>
<td>3.03E+15</td>
<td>3.45E+14 (100.0%)</td>
<td>6.13E+15</td>
<td>2.02</td>
</tr>
<tr>
<td>Total (Bq/y/MWt)</td>
<td>2.84E+11</td>
<td></td>
<td>7.88+11</td>
<td></td>
<td>2.77</td>
</tr>
</tbody>
</table>

Design, Testing, Demonstration, and Modeling of HXs for FHRs

- Design of Heat Exchangers (IHX, SHX, DHX, and NDHX) for AHTR, considering Tritium Management and Heat Transfer Effectiveness
  - Goal: To reduce tritium diffusion into the secondary (cold) side while maintaining heat transfer rate

- Double-wall Heat Exchangers
  - Fluted tube heat exchanger
  - Printed circuit heat exchanger

- Tritium Permeation Barrier
  - Located between the outer tube and the inner tube walls
  - Fluoride salt (FLiNaK/FLiBe)
  - Sweep gas
  - Tritium getter
Heat Exchanger Design

- Ongoing Activity for NDHX in DRACS: 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)
    - Sweep gas: Pressurized helium
    - Tritium: Trapped in the gap and taken away by sweep gas
  - Option 2: Double-wall NDHX with tritium getter in the annulus
    - Gap/annulus filled with a tritium getter (yttrium) to sequester tritium

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>

Thickness [μm] | Al₂O₃ | Cr₂O₃-SiO₂ | ZrO₂ | MSZAC | W |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03-1.4</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50-100</td>
<td>10</td>
</tr>
<tr>
<td>100-10⁴</td>
<td>292</td>
<td>50</td>
<td>3-4</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

References
- Levchuk (2004); Yang (2011); Forcey (1991); Forcey (1989)
- Nakamichi (2007)
- Nakamura (2010)
- Nakamura (2010)
- Moir (1984)
Low Tritium Permeability Metal

Tritium Permeation Barrier Coating (Cont’d)

- Tritium Permeation Reduction Factor (PRF) of candidate coatings

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

- \( \text{Al}_2\text{O}_3 \) Coating Methods
  - Hot-dip aluminization
  - 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
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**
  - FLiNaK/FLiBe could be used as the barrier in intermediate heat exchanger (IHX)
  - Tritium permeation barrier used as the outer wall coating in necessary areas

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Schematic of Tritium Mitigation/Control System for FHRs

* :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
Results from COMSOL

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

[Graph showing distribution of pressure drop and facility volume]

Computational Simulation Using COMSOL

- Plot of Salt Flow Streamlines
  - Main streamlines are splitted each time as they meet the next row of tubes

- Plot of H₂ Concentration Distribution in the Molten Salt
  - Transport coefficients of H₂ instead of T₂ in FLiBe used due to the lack of data
  - H₂ concentration decreases quickly along the salt flow path
**Code Calculation Using MATLAB**

- Overall Mass Transfer Coefficient $k_o$

$$\left(\frac{1}{k_oH_s}\right)^{\frac{1}{6}} = \left(\frac{1}{k_xH_s}\right)^{\frac{1}{6}} + \frac{t_w}{K_w} \left( \frac{p_{l,0.5}^{0.5} - p_{2,0.5}^{0.5}}{p_{l,0.5}^{0.5} - p_{0.5}^{0.5}} \right) \ln \left( \frac{p_{l,0.5}^{0.5} - p_{2,0.5}^{0.5}}{p_{l,0.5}^{0.5} - p_{0.5}^{0.5}} \right)^{\frac{1}{6}}$$

- 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>2</td>
<td>Schmidt number</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>3</td>
<td>Sherwood number</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>4</td>
<td>Peclet number</td>
<td>Peclet number</td>
</tr>
<tr>
<td>5</td>
<td>Grashof number</td>
<td>Grashof number</td>
</tr>
<tr>
<td>6</td>
<td>Stanton number</td>
<td>Stanton number</td>
</tr>
</tbody>
</table>

Sherwood number is calculated using the correlations for Nusselt number: heat transfer coefficient $h$ replaced with mass transfer coefficient $k_x$ and thermal conductivity $k$ replaced with diffusivity $D_{AB}$

The concept of heat transfer resistance is applied to mass transfer using corresponding parameters

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**Facility Design Comparisons**

<table>
<thead>
<tr>
<th>Mass flow rate of molten salt [kg/s]</th>
<th>Dimension Set A</th>
<th>Dimension Set B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tritium inlet concentration [mol/m³]</td>
<td>1.8 x 10⁻⁶</td>
<td>1.8 x 10⁻⁶</td>
</tr>
<tr>
<td>Tritium outlet concentration [mol/m³]</td>
<td>1.62 x 10⁻⁶</td>
<td>1.62 x 10⁻⁶</td>
</tr>
<tr>
<td>Tritium removal rate [mol/s]</td>
<td>1.8 x 10⁻⁷</td>
<td>1.8 x 10⁻⁷</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 x 10⁴</td>
<td>5.82 x 10⁴</td>
</tr>
<tr>
<td>Molten salt inlet flow area [m²]</td>
<td>5.54 (2.35 x 2.35)</td>
<td>5.54 (2.35 x 2.35)</td>
</tr>
<tr>
<td>Total mass transfer area [m²]</td>
<td>9.85 x 10³</td>
<td>1.02 x 10⁴</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
Contact Information

- **Georgia Tech:**
  - Timothy Flaspoehler
  - Email: timothy.flaspoehler@gatech.edu
  - Bojan Petrovic
  - Email: bojan.petrovic@gatech.edu

- **Ohio State University**
  - Xiaodong Sun
  - Email: sun.200@osu.edu
FLUORIDE-SALT-COOLED HIGH-TEMPERATURE REACTORS (FHR)

Implications for Tritium Management

Charles Forsberg

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Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models, and Benchmarking
Salt Lake City
October 27, 2015

FHR Combines Existing Technologies

**Fuel:** High-Temperature Coated-Particle Fuel Developed for High-Temperature Gas-Cooled Reactors (HTGRs)

**Coolant:** High-Temperature, Low-Pressure Liquid-Salt Coolant developed for the 1950s Aircraft Nuclear Propulsion Program

**Power Cycle:** Salt Cooling Creates New Options including Brayton Power Cycles
The FHR is a Family of Reactors

- Designs from 50 to 3000 MWt
- Different fuel geometries
- Different high-temperature salts
- Different power cycles

The Fuel

Advances in Carbon-Matrix Coated-Particle Fuel are the Enabling Technology for the FHR
FHR Uses Graphite-Matrix Coated-Particle Fuel

Same Fuel as High-Temperature Gas-Cooled Reactors in Several Different Geometric Forms

Many Fuel Options
Graphite-Matrix Coated-Particle Fuels

- Pebble Bed: Base-Case: Current technology
- Plate Fuel: Existing materials, New Design
- Fuel in Radial Moderator: Variant of HTGR Prismatic Block Fuel
Pebble-Bed FHR Reactor Built on Helium-Cooled Pebble-Bed Reactor Technology

- Most developed design and the near term option
- Similar to helium-cooled pebble bed reactors
  - FHR power density 4 to 10 times higher because liquids are better coolants than gases
  - On-line refueling (but pebbles float in salt so pebbles out top)

Plate-Fuel FHR Built Upon Sodium Fast Reactor Plant Designs

- Hexagonal fuel assembly
- Plant designs similar to sodium fast reactors (low pressure, high-temperature coolant)
- “New” fuel
  - Coated-particle fuel
  - Carbon composite plates
FIRM FHR Built upon British Advanced Gas-Cooled High-Temperature Reactor (AGR)

14 AGRs Operating (2-Reactor Plants)
Graphite Moderated, Carbon-Dioxide-Cooled, Metal-Clad Pin Fuel

- Refueling Floor
- Graphite Core
- Boiler
- Pre-Stress Concrete Reactor Vessel

Small Fuel Assemblies Held Together by Tie Rod

Use AGR Core, External Fuel Geometry and Refueling Designs

Fuel Inside Radial Moderator (FIRM) Assembly Design

- Surround fuel and coolant channels with solid graphite region
  - 54 fuel channels
  - 24 coolant channels
  - Central hole for handling and materials irradiations
- Introduces spatial resonance self-shielding:
  - Enhances resonance escape probability
  - Significantly increases fuel burnup

Fuel Design is Variant of Ft. St. Vrain Gas-Cooled High-Temperature Reactor Fuel
Similar FHR and AGR FIRM Fuel Geometry → Similar Core Designs

- Similar refueling (AGR 650°C versus 700°C peak FHR coolant temperatures)
- Similar in-core graphite inspection / maintenance
- Similar instrumentation
- Similar control rod systems
- 50-year AGR operational experience base to build upon

But FHR is Low-Pressure with Liquid Cooling so Much Smaller Machine

Advanced Fuel Option: Work at General Atomics and Elsewhere May Enable FHR Pin-Type Fuel Assemblies

- Lower fuel fabrication costs
- Lower enrichments with higher fuel loading
- Longer fuel cycle and higher burnup (less waste)
- Work in progress—being developed as part of LWR accident tolerant fuel program
The Salt Coolant

For Most Proposed FHRs The Base Case Salt is $^7\text{Li}_2\text{BeF}_4$ (Flibe)
There Are Alternative Coolant Salts

<table>
<thead>
<tr>
<th>Coolant</th>
<th>$T_{\text{melt}}$ (°C)</th>
<th>$T_{\text{boil}}$ (°C)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$\rho C_p$ (kJ/m$^3$ °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7\text{Li}_2\text{BeF}_4$ (Flibe)</td>
<td>459</td>
<td>1430</td>
<td>1940</td>
<td>4670</td>
</tr>
<tr>
<td>59.5 NaF-40.5 ZrF$_4$</td>
<td>500</td>
<td>1290</td>
<td>3140</td>
<td>3670</td>
</tr>
<tr>
<td>26 $^7\text{LiF}$-37 NaF-37 ZrF$_4$</td>
<td>436</td>
<td>2790</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>51$^7\text{LiF}$-49 ZrF$_4$</td>
<td>509</td>
<td>3090</td>
<td>3750</td>
<td></td>
</tr>
<tr>
<td>Water (7.5 MPa)</td>
<td>0</td>
<td>290</td>
<td>732</td>
<td>4040</td>
</tr>
</tbody>
</table>

Salt compositions are shown in mole percent. Salt properties at 700°C and 1 atm. Sodium-zirconium fluoride salt conductivity is estimated—not measured. Pressurized water data are shown at 290°C for comparison.
Liquid-Salt Coolant Properties Can Reduce Equipment Size and Thus Costs
(Determine Pipe, Valve, and Heat Exchanger Sizes)

Number of 1-m-diam. Pipes Needed to Transport 1000 MW(t) with 100°C Rise in Coolant Temp.

Baseline salt: Flibe: $^7\text{Li}_2\text{BeF}_4$

<table>
<thead>
<tr>
<th></th>
<th>Water (PWR)</th>
<th>Sodium (LMR)</th>
<th>Helium</th>
<th>Liquid Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>15.5</td>
<td>0.69</td>
<td>7.07</td>
<td><strong>0.69</strong></td>
</tr>
<tr>
<td>Outlet Temp (°C)</td>
<td>320</td>
<td>540</td>
<td>1000</td>
<td><strong>To 1000</strong></td>
</tr>
<tr>
<td>Coolant Velocity (m/s)</td>
<td>6</td>
<td>6</td>
<td>75</td>
<td><strong>6</strong></td>
</tr>
</tbody>
</table>

The Power Cycle
Power Cycle Options with 700°C Salt

NACC or NHCC
Nuclear Air or Nuclear Helium Brayton Combined Cycle based on natural-gas plants

Power Cycle Choices May Impact Tritium Control Strategies

- Can trap tritium in some power cycles because cold side of power cycle prevents tritium releases
  - Supercritical carbon dioxide
  - Helium Brayton cycles
- Tritium major challenge if enters some power cycles
  - Steam cycles
  - Air-Brayton power cycles
The FHR Tritium Challenge

Reactor environment
- Clean fluoride salt coolant containing Lithium-7
- Tritium generation varies by order of magnitude depending upon FHR design
- Carbon-based fuel that absorbs tritium and impacts chemistry
- Potential for small quantities of fission products from leaking fuels

Tritium challenge
- FHRs produce tritium significantly above levels requiring controls
- Tritium absorbed in graphite fuel in significant quantities
  - Possibility in pebble bed to capture tritium on pebbles and recycle pebbles with tritium removal during recycle for tritium control
  - Must consider off-normal events where tritium inventory in fuel may be released if increased core temperatures

Tritium is a waste—can recover for use but not a requirement
**Questions**

**Tritium Environment Below-Previous Slide**

- **Reactor environment**
  - Clean fluoride salt coolant containing Lithium-7
  - Inventory varies by order of magnitude depending upon design
  - Carbon-based fuel
  - Potential for small quantities of fission products from leaking fuels

- **Tritium challenge**
  - FHRs produce tritium significantly above levels requiring controls
  - Tritium absorbed in graphite fuel in significant quantities
    - Possibility in pebble bed to recycle pebbles with tritium removal during recycle for tritium control
    - Must consider off-normal events where tritium inventory in fuel may be released if increased core temperatures

- **Tritium is a waste—can recover for use but not a requirements**

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**Biography: Charles Forsberg**

Dr. Charles Forsberg is the Director and principle investigator of the High-Temperature Salt-Cooled Reactor Project and University Lead for the Idaho National Laboratory Institute for Nuclear Energy and Science (INESS) Nuclear Hybrid Energy Systems program. He is one of several co-principle investigators for the Concentrated Solar Power on Demand (CSPonD) project. He earlier was the Executive Director of the MIT Nuclear Fuel Cycle Study. Before joining MIT, he was a Corporate Fellow at Oak Ridge National Laboratory. He is a Fellow of the American Nuclear Society, a Fellow of the American Association for the Advancement of Science, and recipient of the 2005 Robert E. Wilson Award from the American Institute of Chemical Engineers for outstanding chemical engineering contributions to nuclear energy, including his work in hydrogen production and nuclear-renewable energy futures. He received the American Nuclear Society special award for innovative nuclear reactor design on salt-cooled reactors and the 2014 Seaborg Award. Dr. Forsberg earned his bachelor's degree in chemical engineering from the University of Minnesota and his doctorate in Nuclear Engineering from MIT. He has been awarded 11 patents and has published over 200 papers.
Many Teams Working on the FHR

- MIT, UCB, UW, and UNM
- Georgia Tech
- University of California, Berkeley
- University of Wisconsin, Madison
- University of New Mexico
- National Laboratories: ORNL, INL, etc.
- Chinese Academy of Science (2020 FHR test reactor)
- Vendors

<table>
<thead>
<tr>
<th>Organization</th>
<th>PI</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIT</td>
<td>Charles Forsberg</td>
<td>Market case</td>
</tr>
<tr>
<td></td>
<td>Project Leader</td>
<td>Severe Accidents</td>
</tr>
<tr>
<td></td>
<td>Lin-wen Hu</td>
<td>Irradiation experiments</td>
</tr>
<tr>
<td>University of California, Berkeley</td>
<td>Per F. Peterson</td>
<td>Thermal-hydraulics, safety</td>
</tr>
<tr>
<td></td>
<td>Massimiliano Fratoni</td>
<td>Neutronics</td>
</tr>
<tr>
<td>University of Wisconsin, Madison</td>
<td>Kumar Sridharan</td>
<td>Materials</td>
</tr>
<tr>
<td>University of New Mexico</td>
<td>Edward Blandford</td>
<td>Thermal-hydraulics, safety</td>
</tr>
</tbody>
</table>

The Idea of a Fluoride-salt-cooled High-temperature Reactor (FHR) dates to 2002

- No FHR has been built
- Compelling reasons must exist to develop a new reactor type
  - Commercial: Improve economics
  - Government: Meet national goals
  - Public: Safety against major accidents

 Massachusetts Institute of Technology
Liquid immersion blankets for fusion power plants

Brandon Nils Sorbom

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors, October 27, 2015

Thank you to all who contributed to ARC!

Co-Authors

• Justin Ball, Timothy Palmer, Franco Mangiarotti, Jennifer Sierchio, Paul Bonoli, Cale Kasten, Derek Sutherland, Harold Barnard, Christian Haakonsen, Jon Goh, Choongki Sung, and Dennis Whyte

Collaborators

• Leslie Bromberg, Charles Forsberg, Martin Greenwald, Zach Hartwig, Amanda Hubbard, Brian LaBombard, Bruce Lipschultz, Earl Marmar, Joseph Minervini, Geoff Olynyk, Michael Short, Pete Stahle, Makoto Takayasu, and Stephen Wolfe
Outline

- What functions do a fusion blanket have to perform?
- Traditional blankets vs. the liquid blanket
- How well do liquid blankets perform?
Fusion blanket systems must perform three main roles—two are different than for fission!

A blanket must:

1) Extract the energy from the fusion reactions in a useable form (same as fission)

2) Breed enough tritium to fuel the reactor

3) Shield the TF coils from high-energy neutrons

Blanket is used to extract useable energy from nuclear reactions
Energy extraction blanket requirements

- Should have favorable thermal-hydraulic properties
  - Low density and viscosity (easy to pump)
  - High heat capacity (efficient at removing heat)
  - High temperature operation (higher Carnot efficiency)
- Want something that looks like water, but at a higher temperature
- Only major difference from fission is that MHD effects in fluid become important (more on this later)

The blanket must breed fuel (tritium) for the reactor

https://www.euro-fusion.org/glossary/tritium-breeding/
Tritium breeding requirements

- 500 MWth ARC reactor consumes ~67 g of T per day
- Must provide a tritium breeding ratio (TBR) greater than 1, i.e. you get more tritium out of the blanket than you put into the reactor

\[ TBR = \frac{\text{Tritium Bred}}{\text{Tritium Consumed}} \]

- We use the ARIES criteria\(^1\) to have TBR > 1.1 to account for deficiencies in nuclear data and uncertainties in exact reactor geometry
- Lithium is by far the best material to breed tritium, so blanket must have lithium in some form
- As a bonus, the blanket could have a neutron-multiplying isotope (such as beryllium) to increase the number of low-energy neutrons to interact with Li-6

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Magnet Shielding Requirements

- All practical reactor designs utilize superconducting coils
- Critical current capability of superconductor degrades after a certain amount of damage from high-energy (> 0.1 MeV) neutrons
- REBCO high-temperature superconductors have not been tested to failure, but Nb$_3$Sn starts degrading around a neutron fluence of $3 \times 10^{18}$ neutrons/cm$^2$ for high energy neutrons

Outline

- What functions do a fusion blanket have to perform?
- Traditional blankets vs. the liquid blanket
- How well do liquid blankets perform?
“Traditional” blankets utilize a large amount of solid material

ARIES-I Blanket

Japanese Tritium Breeding Module for ITER

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Solid blankets are complicated

https://www.iter.org/newsline/-/2207
Sector maintenance is not ideal

The ARC reactor is a high-field conceptual pilot plant design

<table>
<thead>
<tr>
<th>Key Design Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion Power</td>
<td>525 MW</td>
</tr>
<tr>
<td>Total Thermal Power</td>
<td>708 MW</td>
</tr>
<tr>
<td>Net Electric Power</td>
<td>190 MW</td>
</tr>
<tr>
<td>Plasma/Electric Gain</td>
<td>13/3</td>
</tr>
<tr>
<td>Major Radius</td>
<td>3.3 m</td>
</tr>
<tr>
<td>Minor Radius</td>
<td>1.1 m</td>
</tr>
<tr>
<td>Toroidal Magnetic Field</td>
<td>9.2 T</td>
</tr>
<tr>
<td>Plasma Current</td>
<td>7.8 MA</td>
</tr>
<tr>
<td>Average Temperature</td>
<td>13.9 keV</td>
</tr>
<tr>
<td>Average Density</td>
<td>1.75 x10²⁰ m⁻³</td>
</tr>
<tr>
<td>Tritium Breeding Ratio</td>
<td>1.10</td>
</tr>
</tbody>
</table>
What makes ARC different from other reactor designs?

- ARC is compact and has a high magnetic field through the use of high-temperature superconductors
- ARC’s magnets are demountable (no sector maintenance)
- ARC has an all liquid, molten salt blanket

Liquid immersion blanket fully surrounds the vacuum vessel

Liquid blanket not required for vertical maintenance scheme, but simplifies things considerably
Outline

- What functions do a fusion blanket have to perform?
- Traditional blankets vs. the liquid blanket
- How well do liquid blankets perform?

Many liquid blanket candidates have been investigated by the fission community

- For fusion, tritium breeding sets first requirement—the liquid must have some element that can breed tritium
- As mentioned before, lithium is only practical tritium breeding material, so whatever liquid is chosen must contain lithium
- An (incomplete) list of liquid blanket materials
  - LiF-BeF₂ (FLiBe)
  - LiF-NaF-KF (FLiNaK)
  - Kf-ZrF₄
  - Kcl-MgCl₂
  - NaNO₃-NaNO₂-KNO₃
  - NaF-ZrF₄
  - PbLi
  - Liquid lithium
How does a liquid blanket stack up? – Thermohydraulics

- FLiBe and FLiNaK have the closest heat transfer properties to water
- All liquid blankets look roughly as easy to pump as water…but what about MHD?

<table>
<thead>
<tr>
<th>Property</th>
<th>FLiBe</th>
<th>FLiNaK</th>
<th>Liquid Li</th>
<th>PbLi</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (K)</td>
<td>732</td>
<td>727</td>
<td>453</td>
<td>507</td>
<td>273</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1940</td>
<td>2020</td>
<td>475</td>
<td>8940</td>
<td>1000</td>
</tr>
<tr>
<td>Specific Heat (kJ/kg K)</td>
<td>2.4</td>
<td>1.93</td>
<td>4.15</td>
<td>0.19</td>
<td>4.2</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m K)</td>
<td>1</td>
<td>0.88</td>
<td>57.7</td>
<td>19.5</td>
<td>0.58</td>
</tr>
<tr>
<td>Viscosity (mPa s)</td>
<td>6</td>
<td>4.11</td>
<td>0.280</td>
<td>0.89</td>
<td>1</td>
</tr>
<tr>
<td>Reynolds Number normalized to water</td>
<td>0.32</td>
<td>0.49</td>
<td>1.7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Prandtl Number normalized to water</td>
<td>2.4</td>
<td>1.26</td>
<td>0.002</td>
<td>0.001</td>
<td>1</td>
</tr>
</tbody>
</table>

1. Assumed characteristic length of 1m and flow velocity of 0.2 m/s

MHD effects on liquid metals lead to large pumping power requirement but molten salts are less affected

- We have a liquid moving through an extremely high magnetic field—if the liquid is conductive, this leads to MHD effects!
- Simple flow through a conducting pipe, transverse to a magnetic field leads to the relationship:

\[ P_p \propto \sigma_f B^2 \]

- Actual pumping power required is highly dependent on geometry and magnetic field structure, but calculations\(^2\) for simple cooling systems indicate that pumping power for liquid Li is ~10% of the thermal power of fusion device
- FLiBe and FLiNaK are both orders of magnitude less conductive and would have very small MHD effects

<table>
<thead>
<tr>
<th>Property</th>
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<th>FLiNaK</th>
<th>Liquid Li</th>
<th>PbLi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity, (\sigma_f) (S/m)</td>
<td>241</td>
<td>230</td>
<td>2.3x10^6</td>
<td>7.0x10^7</td>
</tr>
</tbody>
</table>

COMSOL turbulent flow simulation suggests minimal inlet velocity required to exhaust neutron heating

- FLiBe used as molten salt for COMSOL simulation, temperature-dependent properties (e.g. specific heat, thermal conductivity) manually input from literature
- MHD effects considered negligible for FLiBe and are not modeled
- Heating inputs are modeled as conduction through vacuum vessel from plasma heating and volumetric neutron heating assessed using MCNP
- Goal for ARC outlet temperature is approximately 900 K

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How does a liquid blanket stack up? – Tritium Breeding

- Unlike fission, we actually want to breed as much tritium as possible!
- For this assessment, I have used a simple MCNP model of the ARC reactor to compare our four candidates
- Neutron source is a four-volume approximation based on fusion plasma profiles, with most neutron production coming from core (also note that core shifted out due to plasma effects)
- Structural material in model is Inconel 617, a nickel-based alloy
- Vacuum vessel has internal cooling channel to model first wall cooling scheme
Natural abundance Li liquid blankets struggle to breed enough tritium

- Liquid lithium is the only blanket material which achieves TBR > 1.1
- Possible to boost breeding capacity by changing isotopic lithium fractions

Lithium must be enriched to provide adequate tritium breeding

- Li-6 has an enormously higher breeding cross section than Li-7, extending down to thermal energies
- Natural abundance is 7.5% Li-6 and 92.5% Li-7
- Enriching blanket with Li-6 will increase tritium breeding performance
Enriching to 90% Li-6 significantly improves breeding performance

- Enriching to 90% Li-6 allows FLiBe and PbLi to be used as tritium breeders
- Blanket thickness has much less of an effect on breeding for enriched blankets (this will be important later...)

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How does a liquid blanket stack up? – TF Shielding

- Also highly dependent on material and geometry
- Use same MCNP model as for tritium breeding calculations
- “Worst case” scenario considered by assessing neutron flux at inner midplane, where space is most limited
- TF lifetime calculated by assuming ARC power (525 MW) and using conservative neutron fluence limit from Nb₃Sn
Liquid blankets are abysmal neutron shields

- Would require a lot of blanket to effectively shield TF, even with the best candidate material
- This requires us to use a secondary shielding material
- Hydrides work well (this was the solution for ARC)

TF Lifetime vs. Blanket Thickness
Solid shields on inboard side improve lifetime tremendously

- Solution to TF lifetime problem in ARC was to replace inboard blanket volume with TiH$_2$ shielding (represented in orange)
- For ARC, replacing 50 cm of 70 cm blanket with hydride shielding raised TF lifetime to 10 FPY (up from 0.4 FPY for pure FLiBe)
- Since most tritium breeding was found to occur within the first 30-40 cm of blanket, TBR was largely unaffected (1.095 from 1.110)

Other observations about liquid blankets...

- Less high-Z solid material in blanket means less activated waste and liquid is constantly circulating so less overall neutron exposure to blanket
- Exothermic nuclear reactions in blanket can have a large effect on power balance (ARC blanket reactions contribute ~100 MW on top of the 500 MW of fusion power)
Are we happy or sad about using liquid blankets in fusion?

- Energy conversion? – Happy, liquid blankets have favorable thermohydraulic properties
- Tritium breeding? – Happy, achieve TBR > 1.1
- Shielding? – Mostly happy, can supplement liquid blanket with additional shielding material
- Conclusion: Liquid immersion blankets are an attractive concept, worth pursuing in fusion reactor designs.

References


2. Iter.org, http://www.iter.org/album/media/7%20-%20technical#2044


An all-liquid FLiBe blanket provides magnet shielding, tritium breeding, and is a working fluid

- Molten salt use in reactors is well-studied within fission community
- Fluorine Lithium Beryllium (FLiBe) molten salt has similar thermohydraulic properties to water—but at higher temperature (and operating window)

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>Melting Point (K)</td>
<td>732</td>
<td>273</td>
</tr>
<tr>
<td>Boiling Point (K)</td>
<td>1703</td>
<td>373</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1940</td>
<td>1000</td>
</tr>
<tr>
<td>Specific Heat (kJ/kg K)</td>
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</tr>
</tbody>
</table>
Double-walled Vacuum Vessel

Vacuum vessel has a cooling channel, with higher velocity FLiBe used as coolant
3% increase in R improves coil lifetime by a factor of 5

- Reactor lifetime limited by neutron fluence to superconducting coils
- ARC was optimized to provide the most compact reactor, so ~10 full-power year operation is acceptable
- Scaling up reactor size a small amount would allow for much longer lifetime, appropriate for a commercial power plant

ARC Inboard Radial Build

0cm 50cm 70cm 135cm 192cm 212cm 220cm 223cm 330cm

Composite Plug TF Coils Neutron Shielding Bulk Blanket Plasma Scrape - o Layer
Central Solenoid Vacuum Gaps Thermal Shielding Blanket Tank Vacuum Vessel
Neutronics simulations indicate range of possible first wall choices

- Tritium breeding ratio (TBR) must be above 1 to breed enough fuel to run reactor
- First wall material and thickness has a large effect on TBR
- ARC will allow multiple vacuum vessel/first wall configurations to be tested without building an entirely new device

Tritium Recovery System

- Full analysis beyond the scope of this conceptual design
- Through a literature search, found recent Japanese studies on T extraction from FLiBe using “counter-current extraction tower”
- Basic concept:
  - Saturate FLiBe with Be to maintain TF concentration in FLiBe
  - Pass saturated FLiBe down through series of filters with He pumped up in opposite direction
  - TF diffuses in He, and T2 is pumped out with He and separated
  - According to study, achieves T recovery > 99.9%

1.) S. Fukada, A design for recovery of tritium from FLibe loop in FFHR-2 (2007)
TBR Uncertainty in Cross Sections for MCNP Calculation

• UCLA study found 2-6% uncertainty in TBR for various materials based on uncertainties in nuclear databases

• Closest material combination to ours (FLiBe/He/FS/Be) had TBR predicted overestimate of ~4.3%

• Total uncertainty subtracted from our TBR still gives a TBR of 1.07

1.) Uncertainties in Prediction of Tritium Breeding in Candidate Blanket Designs Due to Present Uncertainties in Nuclear Data Base, M.Z. Youssef et al, (1986)

MCNP Validations

• Simple fluence validation – changed all cells to vacuum and made sure that all source neutrons accounted for

• TBR validated using simple toroidal model and comparing to UW results
Mainstream fusion community has accepted toroidal magnetic confinement as best candidate for fusion energy

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$

- Wrap linear device around into a donut (torus)
- Add a central solenoid to inductively drive current in the plasma and give field lines a helical twist—now you have a tokamak!
Fusion research is a serious, multinational effort, specifically tokamak research

ARC is significantly smaller than ITER with the same fusion power

- Both machines produce ~ 500 MW of fusion power
- Engineering drawings are same scale
The DT reaction is most favorable for a fusion reactor

- Fusion reactions which release energy are possible for many light nuclei
- The most promising reaction is the reaction between deuterium and tritium (abbreviated DT), two isotopes of hydrogen
- The sun uses pure hydrogen fusion (really inefficient but the sun is big enough)

Nuclei must overcome Coulomb repulsion in order to fuse

- Potential energy between two charged particles is given by:

\[ U = \frac{1}{4\pi \varepsilon_0} \frac{Q_1 Q_2}{r} \]
This requires particles to be moving really, really fast!

- Potential energy between two charged particles is given by:
  \[
  U = \frac{1}{4\pi \varepsilon_0} \frac{Q_1 Q_2}{r}
  \]

- As particles get close enough to fuse, potential energy “barrier” increases
  - Particles need to move fast → i.e. need high energy → i.e. need high heat
  - For D-T, minimum energy for fusion is 10 keV, roughly 100 million Kelvin*

* or Celsius, it doesn't really matter at this high of a temperature...

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Temperatures required for fusion necessitates confinement of plasma

- Matter at thermonuclear fusion temperatures only exists in a plasma state

- Plasma is the “fourth” state of matter where electrons are ripped off of nuclei and gas becomes ionized

- So how do you confine a superheated, charged gas?
Hydrogen retention mechanisms

- **Molecular H2 physisorption on porous carbons**
  - Significant at cryogenic temperatures
  - Decreases with increase of temperature
  - Well documented from prior work on H2 storage

- **Atomic H chemisorption**
  - Lower saturation capacity
  - Not as much investigated as physisorption
  - Temperature dependence may be sensitive to structural factors and state of the surface

- **Molecular H2 trapping / solubility**
  - Mixed mechanism (molecular diffusion / chemisorption)
  - Sensitive to structural factors, irradiation

Theory and modeling

- DFT calculations:
  - Dissociative chemisorption of H2 on armchair sites requires high activation energy
  - Dissociative chemisorption on zig-zag sites is easier (no activation)
  - H atom chemisorption on basal planes requires pocking of a C atom from its planar position and requires activation energy
  - The crucial step is H2 dissociation which is energetically demanding


H retention on graphite

- Retention and diffusion of H2 on isotropic graphite from Toyo Tanso
  - At 1000 C and 1 bar, H2 uptake leads to loading of up 20-600 ppm (based on pressure drop)
  - Diffusion and trapping in the graphite structure
  - Two types of trapping sites proposed (based on thermodesorption data)
  - Enhanced trapping on defective and irradiated graphite

Trapping sites in graphite

- Two types of trapping sites
  - Dangling bonds at crystallite edges (2.6 eV)
  - Interstitial sites inside crystallites (4.4 eV)
  - The prevalence of each type of sites varies with irradiation fluence


- Thermodesorption of H2 trapped in isotropic graphite is similar to that from graphite mechanically milled in a hydrogen atmosphere

Orimo, J Appl Phys 90 (2001) 1545

- The nature of trapping sites in graphite is still debated


Deuterium in graphite

- D2 thermodesorption from isotropic graphite exposed to D2 at various temperatures
  - Solubility is proportional with $P^{1/2}$
  - Three main desorption peaks
  - Evidence of various trapping sites
  - Very small CD4 desorption was found

Tritium in graphite and PyC

- Diffusion and solubility in PyC
  - $^3\text{H}_2$ diffusion in PyC is much lower than in metals, and activation energy is high, suggesting chemical bonding
  - $^2\text{H}_2$ solubility in PyC suggests a dissociative mechanism (varies with $P^{1/2}$)
  - PyC suggested as an effective barrier for T implantation in fusion reactors

  Causey, Carbon 17 (1949) 323

- Retention of D+ and T+ ions in POCO graphite
  - Plasma exposure to 100 eV ions below 500 K causes fast saturation
  - Between 500-1000 K diffusion along pore surfaces occurs deep in the sample
  - Above 1000 K the isotopes penetrate graphite and decorate high energy traps


Thermal release of tritium

- Thermal release of $^3\text{H}_2$ from irradiated graphite
  - $^3\text{H}_2$ is released as HT, and also as HTO (if oxidation occurred)
  - The release temperature increases with the increase of neutron fluence received by graphite


- Thermal release of $^3\text{H}_2$ implanted in fine grain isotropic graphite
  - Detrapping o implanted T starts at ~ 600 K, reaches maximum rate at 1100-1400 K, and is 95% completed at 1600 K
  - On single type of trapping sites was observed
  - High T retention up to high temperature suggests that graphite will retain T inventory after exposure to energetic T ions

Factors affecting H trapping

- Hydrogen trapping in neutron irradiated graphite
  - Neutron irradiation creates high energy trapping sites
  - H atoms diffusivity is 1-2 orders of magnitude lower after irradiation at only 0.047 dpa
  - Irradiation and subsequent annealing of graphite changes substantially the absorption rates


- Hydrogen retention in graphite irradiated at high temperature
  - Irradiation causes damage in graphite structure
  - H retention is significantly reduced at high temperature


Hydrogen thermodesorption

- Thermodesorption spectroscopy from H-implanted graphite
  - Thermodesorption spectroscopy can be used to characterize the energy strength of trapping sites


- Modeling H2 thermodesorption from H+ implanted graphite
  - Study showed the effect of graphite porosity and crystallite size on the number and types of trapping sites

Liu, Nucl Instruments Methods Phys Rev B 269 (2011) 431
Other works

• Modeling of reactive-diffusive transport of hydrogen after ion implantation
  – Release and retention of H in porous graphite depends on the graphite internal structure and on the energy and flux of incident ion beam
  

• Hydrogen isotopes permeations through carbon materials
  – Measurements of gas pressure driven permeation of isotopes
  

Perspectives

• Physisorption on high surface area, porous carbons is far more efficient than chemisorption on graphite
  – Requires cryogenic temperatures
  – Can be used in conjunction with a sweep gas (He) to separate T2 from T2/He mixtures

• Retention by carbon elements in contact with the molten salt (pebbles) will be difficult to control given the irradiation effects on carbon

• Salt corrosion effects on carbon (pebbles) will change the hydrogen retention properties
AGR FUEL COMPACT DEVELOPMENT

OVERVIEW OF PRESENTATION

• BACKGROUND
  – FUNCTION OF COMPACT
  – METHODS OF MANUFACTURE
  – ATTAINABLE FUEL PARTICLE VOLUME FRACTIONS
  – NEUTRON IRRADIATION DIMENSIONAL STABILITY

• RECOMMENDED APPROACH
  – METHOD & MATERIALS
THE GAS TURBINE-MODULAR HELIUM REACTOR (GT-MHR) UTILIZES CERAMIC COATED PARTICLE FUEL

FUEL PARTICLES ARE FORMED INTO 12.5 mm DIAMETER FUEL STICKS AND INSERTED INTO GRAPHITE FUEL BLOCKS.

Actual-size approx. 0.63 inches dia.
THE PEBBLE BED REACTOR UTILIZES CERAMIC COATED PARTICLE FUEL

THE TRISO FUEL PARTICLES ARE COMBINED INTO A CARBON FUEL BALL (PEBBLE) 6 cm IN DIAMETER

FUEL COMPACT: FUNCTION & TERMINOLOGY

- Renders fuel particles into handleable form (i.e., compact or fuel pebble)
- Compact comprises of fuel particles, matrix and graphite shim
- Matrix consists of filler (coke or graphite) and binder (pitch or resin)
- The matrix binds together the fuel particles and protects them from mechanical damage by failing preferentially so as to avoid damage to the fuel particle coatings
- Addition of graphite filler to the binder increases the thermal conductivity of the fuel compact, and increases dimensional stability during heat-treatment and neutron irradiation
- AGR compact is 12.5 mm dia & 49.3 mm len, and has a fuel particle volume fraction in the range 22-33.6%
AGRFUEL COMPACT DEVELOPMENT

FUEL COMPACT METHODS OF MANUFACTURE

DRAGON PROJECT ADMIX METHOD

- HIGH CHAR YIELD RESIN (PHENOL FORMALDEHYDE) SOLVATED WITH ALCOHOL
- GRAPHITIZED PETROLEUM COKE (< 50 MICRON SIZE)
- PRODUCE A RESIN COATED GRANULATED POWDER (88% FILLER)
- SIEVED, BLENDED AND MIXED WITH COATED FUEL PARTICLES
- WARM MOLDED TO FORM AND CURE BINDER, & EJECTED FROM MOLD
- CARBONIZED @ 900°C & HEAT TREATED TO 1800°C
- ATTAINABLE FUEL PARTICLE VOLUME FRACTIONS TYPICALLY < 25%
PEACH BOTTOM PROCESS (GENERAL ATOMICS)

- THERMOPLASTIC (PITCH) BINDER
- SYNTHETIC GRAPHITE FILLER (90% OF MATRIX)
- FUEL AND MATRIX COMPONENTS MIXED AND THEN GRANULATED INTO 3-9 mm PELLETS
- GRANULIZATION AVOIDS SEGREGATION OF THE HEAVIER FUEL PARTICLES & LIGHTER MATRIX COMPONENTS
- ATTAINABLE FUEL PARTICLE VOLUME FRACTION 25-35%

OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

PARTICLE OVERCOATING PROCESS

- THERMOSETTING RESIN (PHENOLIC) BINDER
- MATRIX FILLER CONSISTS OF NATURAL FLAKE AND SYNTHETIC GRAPHITE OR GRAPHITIZED PET. COKE
- RESINATED POWDER MATRIX MIX FORMED THE “A3” MATRIX (WITH 80 wt% GRAPHITE FILLER)
- MATRIX MIX FED INTO ROTATING DRUM WITH FUEL PARTICLES AND SOLVENT (METHANOL) TO “OVERCOAT” THE FUEL PARTICLE
- COMPACTS ARE WARM MOLDED TO CURE RESIN
- FINAL HEAT TREATMENT 1800-1950°C
- ATTAINABLE FUEL PARTICLE VOLUME FRACTION 5-50%
GENERAL ATOMICS MATRIX INJECTION PROCESS

- THERMOPLASTIC (PITCH) BINDER
- NATURAL GRAPHITE FILLER (~28 % OF MATRIX)
- CLOSE PACKED BED OF FUEL PARTICLES
- MATRIX HEATED ABOVE ITS SOFTENING POINT AND “INJECTED” INTO PARTICLE BED.
- COMPACT COOLED, EJECTED AND PACKED IN ALUMINA TO SUPPORT COMPACT DURING CARBONIZATION WHEN PITCH SOFTENS PRIOR TO PYROLYSIS
- ATTAINABLE FUEL PARTICLE VOLUME FRACTION < 60%

SUMMARY OF THE FUEL PARTICLE VOLUME FRACTIONS ATTAINED FROM THE VARIOUS COMPACTING PROCESSES

<table>
<thead>
<tr>
<th>FUEL COMPACTING PROCESS</th>
<th>FUEL PARTICLE VOLUME FRACTION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMIX (DRAGON REACTOR)</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>ADMIX/AGGLOMERATE (PBR)</td>
<td>25-35</td>
</tr>
<tr>
<td>PARTICLE OVERCOATING (DRAGON, AVR, THTR, HTTR, HTR-10)</td>
<td>5-50</td>
</tr>
<tr>
<td>PITCH INJECTION (FSV)</td>
<td>&lt; 60</td>
</tr>
</tbody>
</table>

AGR COMPACT FUEL PARTICLE VOL. FRACTION TARGET IS 22-33.6%
NEUTRON IRRADIATION DIMENSIONAL STABILITY OF COMPACTS

• THE FUEL COMPACT MATRIX MATERIAL SUSTAINS A SIGNIFICANT AMOUNT OF NEUTRON INDUCED DISPLACEMENT DAMAGE
• IRRADIATION BEHAVIOR OF CARBONS & GRAPHITES MARKEDLY AFFECETED BY THE DEGREE OF CRYSTALINITY OF THE MATERIAL
• AGR COMPACTS WILL HAVE A HIGH MATRIX CONTENT SO THE IRRADIATION BEHAVIOR OF THE MATRIX IS CRITICAL
• IT HAS BEEN ARGUED THAT PITCH PRECURSERS ARE MORE SUITED FOR BINDERS SINCE FOR A GIVEN FINAL HTT THEY ARE MORE CRYSTALINE THAN RESIN CHARS, ALTHOUGH PITCH IS A MAJOR SOURCE OF CHEMICAL CONTAMINATION
• LOADING THE THERMOSETTING RESIN (GLASSY CARBON) WITH A LARGE FRACTION OF HIGHLY GRAPHITIC FILLER MARKEDLY IMPROVES THE MATRIX IRRADIATION BEHAVIOR, REDUCES THERMAL SHRINKAGE ON PYROLYSIS, AND INCREASES MATRIX THERMAL CONDUCTIVITY

AGR FUEL COMPACT DEVELOPMENT

RECOMMENDED APPROACH
THE FOLLOWING FACTORS MUST BE
CONSIDERED IN RECOMMENDING AN APPROACH

1. A thermosetting resin binder has been selected for the production of AGR fuel compacts.
2. The required fuel particle volume fraction for the AGR compacts is very modest (22-33.6%) and is within the attainable range of the admix/agglomerate, the overcoating, or injection processes.
3. The most stable matrix is one with a large fraction of graphite filler.
4. Highly filled (>40 vol.%) pitch or resin matrix materials cannot be injected into packed particle beds.
5. Injectable low graphite filler content thermosetting resin binder formulations with additions of low char yield (fugitive) resin (e.g., polystyrene) were developed, but were never adopted for the manufacture of large quantities of fuel compacts.
6. The overcoating method with resin binder was used for the manufacture of fuel compacts for the Dragon and HTTR, and for fuel pebbles for the AVR, THTR and HTR-10.

AGR FUEL COMPACT
DEVELOPMENT

BASED UPON THE FORGOING DISCUSSION IT IS RECOMMENDED THAT THE PARTICLE OVERCOATING PROCESS BE ADOPTED AS THE REFERENCE METHOD FOR THE FABRICATION OF AGR FUEL COMPACTS
Outline

1. Project Overview

2. Research Progress
1. Project Overview

- January, 2011, Chinese Academy of Sciences (CAS) initiated the “Thorium Molten Salt Reactor Nuclear Energy System” (TMSR) project.

- August, 2013, TMSR has been chose as one of the National-Energy Major R&D projects of Chinese National Energy Administration (CNEA)

- 2014, Shanghai Local Government plans to start a major new-Energy project to support the TMSR project, including the manufacture of the special materials, devices, building & utilities.

2. The Aims of TMSR Project

- The Aims of TMSR Project is to develop Th-Energy, Non-electric application of Nuclear Energy based on Liquid-Fuel TMSR and Solid-Fuel TMSR during coming 20-30 years.

  - Liquid-Fuel TMSR (TMSR-LF) --- MSRs
  - Solid-Fuel TMSR (TMSR-SF1) --- FHRs

  **TMSR-SF**: Optimized for high-temperature based hybrid nuclear energy application (Non-electric application).

  **TMSR-LF**: Optimized for utilization of Thorium.
TMSR Road Map

Thorium Energy
- 2015: Initiation
- 2025: Demonstration
- 2035: Promotion
- Th-U Nucl. Data Fuel Cycle Tech
- Demonstration of Open Cycle
- Application of Open Cycle
- Verification of Closed Cycle
- Demonstration of Closed Cycle

High Temperature H₂ Production
- 2020: Proof of Principle
- 2025: Integration of Techniques Commercial Demonstration
- Industrial Scale Applications
- Mastery of Molten Salt / Loop / Air-Cooling Technologies
- Application in Arid Regions

Water-free Cooling

Small Modular Design
- R&D on Key Techniques
- Demonstration of Modular Technology
- Application of Small Modular Reactor

TMSR-SF
- 2017: CAS
- 2018: TMSR-SF Commercialization
- 2022: TMSR-SF Commercialization
- 2024: TMSR-SF Commercialization
- 2035: TMSR-SF Commercialization

TMSR-LF
- 2017: CAS
- 2022: TMSR-LF Commercialization
- 2035: TMSR-LF Commercialization

Milestones

CAS: Chinese Academy of Sciences

TMSR Goal

Long-term goals
- 100MW TMSR-SF2 Demonstration
- 10MW TMSR-LF2 Experiment

Near-term Goal
- 10MW TMSR-SF1 Experiment
- 2MW TMSR-LF1 Experiment
- TMSR Simulator (TMSR-SF0)

2015–2017
- 2018–2020
- 2021–2025
TMSR Near-term Goal

Phase-I (~2017)
- Completion of TMSR-SF simulator.
- Start to construct 10MW TMSR-SF test Reactor (TMSR-SF1), 2MW TMSR-LF test Reactor (TMSR-LF1) & Pyro-Process Facility (PDF).
- Build up full capability of non-radioactive laboratories in Jiading.

Phase II (~2020)
- Completion of the TMSR-SF1, TMSR-LF1 and PDF,
- Completion of the engineering design of 100MW TMSR-SF demonstration reactor (TMSR-SF2).
- Build up R&D abilities for future TMSR development, including the TMSR Nuclear Park in DaFeng

Outline

1. Project Overview
2. Research Progress
4 Prototype Systems and 7 key technologies

Master the key technologies of tritium control in the molten salt reactor such as tritium extraction with bubbling, tritium separation, tritium monitoring and so on.

Key technology: Tritium control

- (1) Tritium Behavior
  Chemical forms of Tritium in TMSR
  Interaction between tritium with either of coolant or metal.

- (2) Tritium Extraction
  Extraction of tritium from the molten salt

- (3) Tritium Separation
  Separation of tritium from other gaseous mixture

- (4) Tritium Storage
  Tritium storage with alloys after the recovery of tritium in TMSR

- (5) Tritium Sampling
  Sampling tritium with different chemical forms

- (6) Tritium Monitoring
TMSR International Cooperation

- Th Utilization, Reactor Tech.
- Material, Molten Salt Tech.
- Pyro-process
- Nuclear Safety Standards

Organizational Overview
The Chinese Academy of Sciences (CAS) and U.S. Department of Energy (DOE)
Nuclear Energy Cooperation Memorandum of Understanding (MOU)

MOU Executive Committee Co-Chairs
China – Mianheng Jiang (CAS)
U.S. – Pete Lyons (DOE)

Future
- Russian
- EU
- Korea
- Japan

Collaboration with USA

FHR technology
Pyro-process

FHR (solid fuel)
Safety Standards
ANSI/ANS-20.1

High-tem. Materail
Standars (ASME )

CAS-DOE MOU on
Nuclear Energy

America Society

US Industry

US DOE Lab

US University
Cooperation Workshop for R&D of Pyro-process Technology will be held in SINAP, 14-15, May, 2015. Stephen Kung, DOE; K. Michael Goff, INL & Mark A. Williamson, ANL will attend the workshop.

Started to discuss the CRADA on Pyro-process between TMSR and INL & ANL.

Thanks for Your Attention
Tritium and Chemistry Management for the Mark-1 PB-FHR

Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models, and Benchmarking
Salt Lake City
October 27, 2015

Michael Laufer
U.C. Berkeley

Mk1 PB-FHR flow schematic
The recent UC Berkeley Mk1 PB-FHR design effort had 4 goals

- Demonstrate a plausible, self-consistent Nuclear Air Combined Cycle (NACC) system design
  - Believable predictions for base-load and peaking power levels using an industry-standard design code (Thermoflex)
    » 2 archival articles now published in the ASME Journal of Engineering for Gas Turbines and Power
  - Self-consistent approach to heat air directly with primary coolant

- Provide detailed design for decay heat management systems
  - Provide basis for establishing CIET experiment test matrix
  - Enable TH code validation and benchmarking exercises

The Mk1 PB-FHR design had 4 goals (con’t)

- Develop a credible, detailed annular FHR pebble core design
  - Inner and outer graphite reflector including assembly method
  - Pebble injection and defueling
  - Coolant flow distribution and pressure loss calculations
  - Provide basis for future FHR code benchmarking
  - Neutronics/depletion/control-rod worth calculations are documented in A.T. Cisneros doctoral dissertation

- Identify additional systems and develop notional reactor building arrangement
  - “Black-box” level of design for many of these systems
  - Includes beryllium and tritium management, and chemistry control strategies
Nominal Mk1 PB-FHR Design Parameters

- Annular pebble bed core with center reflector (600/700° C Core Inlet/Outlet)
- Reactor vessel 3.5-m OD, 12.0-m high
- Power level: 236 MWth, 100 MWe (base load), 242 MWe (peak w/ gas co-fire)
- Power conversion: GE 7FB gas turbine w/ 3-pressure HRSG
- Air heaters: Two 3.5-m OD, 10.0-m high CTAHs, direct heating
- Tritium control and recovery
  - Recovery: Absorption in fuel and blanket pebbles and additional graphite media
  - Control: Diffusion barrier coating on air side of CTAHs

Equilibrium Tritium Production
~0.07 g (670 Ci) per EFPD
99.9% Target Recovery Rate

Mk1 pebble injection feeds pebbles to the bottom of the core at a controlled rate

Mk1 blanket and fuel pebbles are expected to provide an important sink for tritium
The Mk1 heat transport system delivers heated salt to the two CTAHs

Mk1 CTAHs have 36 annular sub-bundles
Tapered Mk1 CTAH tube to tube-sheet joints allow use of alumina-forming coating

Tensile test results from April 17, 2014

Mk1 CTAH hot leg stand pipes allow the use of an annular filter cartridge.

- 100% of hot salt flow can be treated before it enters the CTAH tubes
- Solid filter media can be used to remove tritium if absorption in fuel and blanket pebbles is not sufficient
Cold spray coating provides a scalable method to apply tritium diffusion barriers to tubes

- Cold spray coating uses a supersonic jet to deposit particles onto surfaces
  - Process performed at ambient pressure, so can be used for mass production of coated tubes and other primary coolant boundary external surfaces
  - Alumina forming compounds can be applied as well as other diffusion barriers

- Many possible alumina forming compounds are possible
  - Ti$_2$AlC ceramic has been demonstrated by UW Madison
  - Many ductile coating materials are also candidates
    » Kanthal (Al$_2$O$_3$ forming alloy)
    » 316SS or Alloy N alloyed with a few percent aluminum
    » Many others

Mk1 Cold Traps and Drain Tanks aid coolant chemistry control

- Cold trap filters oxides and other contaminants that precipitate at low temperature
- Cold trap also provides location to continuously contact salt with reducing agent (if used)
- Drain tank allows CTAHs to be drained for inspection/maintenance
- Drain tank provides volume to perform bulk salt clean up (e.g., HF/H$_2$ sparging) if needed during shutdown and maintenance.
An Overview of SRNL Tritium Activities

Greg Staack
Hydrogen Processing Group

Workshop on Tritium Control and Capture
October 27-28, 2015
Savannah River Site - Production Years

- Began operation in 1953
- Produce and recover nuclear materials
  - Tritium
  - U, Pu
  - Cf, Np, Cm, Am,…
- Facilities
  - Heavy water extraction plant
  - Nuclear fuel and target fabrication facility
  - Five reactors
  - Two chemical separations plants
  - Naval Fuels
  - Waste management facilities
  - Tritium

SRS produced about 36 metric tons of plutonium from 1953-1988
Savannah River Tritium Enterprise Mission

Fill Tritium Reservoirs in support of the Nation's Nuclear Stockpile
- Extract new tritium from TPBARs irradiated in TVA reactors
- Recycle gas from returned bottles
  - Receive
  - Unload
  - Reprocess
- Minimize environmental impact
- Provide a SAFE working environment
- One objective of the SRNL Hydrogen Processing Group is to provide technical support to the Facilities

Overview – Tritium Processing Research and Development Focus Areas

- **Impurity Removal**
  - Hydrogen Separation from Impurities
  - He-3 cleanup
- **Storage (Metal Hydride Beds / Tanks)**
  - Materials options based on temperature/pressure/purity requirements
  - In-bed calorimetry
- **Hydrogen Isotope Separation**
  - Thermal Cycling Absorption Process (TCAP)
- **Secondary Confinement**
- **Tritiated Water Processing / Detritiation Systems**
  - Glovebox Atmosphere Detritiation (Stripper Systems)
  - Tritium Recovery from water (Z-Bed Recovery)
  - Detritiation of process effluent gases (TPS)
- **Pumping (Evacuation/Circulation)**
- **Tritium Effects on materials**

SRNL R&D provided current metal hydride-based Tritium Processes. Current research efforts are underway to improve efficiency, decrease operation costs, and to modularize processes.
Tritium Processing at SRS – The Largest MH Based Facility in the World

Impurity Removal by Bulk Separation

Flow-Through Bed/Primary Separator

Diffuser/Permeator (Pd-Ag Membrane)
Tritium Storage: La-Ni-Al Metal Hydride for “He-3 Free” Gas Delivery

LANA properties change with tritium aging.
- Formation of “heel”
- Decreased plateau pressure
- Eventual loss of plateau
- Eventual weeping of He-3

Limited life components
He-3 recovery from retired beds is being pursued.

Three Generations of Metal Hydride Storage Bed Development

Thermal Cycling Absorption Process - TCAP

- “Heart” of the Tritium Facilities
- 4th generation of isotope separation at SRS
  - Thermal Diffusion (1955-1986)
  - Fractional Absorption (1964-1968)
  - Cryogenic Distillation (1967-2004)
- Uses Pd/k to separate hydrogen isotopes
  - Recover tritium (T₂)
  - Stack protium (H₂)
- Hot and cold N₂ for thermal swing
- Feed, product, and raffinate gases stored on LANA beds

Original plant TCAP (1994)

TCAP has advantages of being simple, compact, with low tritium inventory, and no pumps compared to traditional cryogenic or batch distillation

**Advances in Hydrogen Isotope Separation Technology**

TCAP (Thermal Cycling Absorption Process) advanced from “Pd/k – passive Plug Flow Reverser” to “Pd/k – Active Inverse Column”

**Results:** Increased throughput and improved product purity

Thermal Cycling with Hot and Cold N₂ to Electric Heating and once through LN₂ Cooling

**Results:** Decreased cycle time

---

**Glovebox Confinement Systems with Tritium Stripping**

**Glovebox/Secondary Confinement vs Fresh Air Hoods**

- Legacy facilities used once through fresh air hoods – allowed product to escape
- In order to stem releases, closed loop glovebox system employed (RTF & TEF)
- Equipped with a secondary stripper for high activity
- Emissions were reduced from 100’s kCi/year average (60’s – 80’s) to 10’s of kCi/year average now
- Closed glovebox cleanup loop requires processing of byproducts – impact not fully realized during the early days of RTF (mid 90’s)
H-Area New Manufacturing – Tritiated Waste Gas Processing

Tritium Process Impurity Removal

Molecular Sieve
- Large temperature swings
- May require upstream catalyst (e.g. water processing)
- Typically desorbed to regenerate bed, transferring impurities to a different process stream (Z-Bed Recovery or He-3 cleanup)

Non-Evaporative Getters
- Selected to “getter” various species, with or without decomposition
- Usually at elevated temperatures
- St909 crack methane, absorb carbon (not regenerated)
- St198 absorb tritium (regenerated)
Tritium Effects on Materials –Hydrides & Polymers

Hydrides:
- Pd based operations – (TCAP) long service life with clean gas
- LANA operations – limited service life due to He-3 formation
- Getters – depend on service conditions

Polymers - a necessary compromise:
- Sometimes unavoidable in tritium systems (seals, lubrication, packing, etc.)
- Polyethylene can release hydrogen, methane and other hydrocarbons
- PTFE (Teflon®) can react to form TF
- EPDM and Vespel™ polyimide – OK

Gas release from tritium aged LANA.75

Tritium aged samples of UHMW-PE, PTFE, and Vespel

Tritium Effects on Materials –Steels & Coatings

Hydrogen embrittlement of containment materials exacerbated by decay to He-3:
- Use Austenitic SS
- Do not use Ferritic, Martensitic, or Precipitation Hardened SS
- Cleanliness and Surface Coatings Are Important

Permeation Barriers – must maintain integrity with temperature fluctuations:
- Tritium wetted face
  - Additional protection for equipment
  - Manufacturing challenges
  - Must be inert to process stream
- Glovebox face
  - Reduces stripper load
  - Easier to deposit

Intergranular Cracking - characteristic of hydrogen embrittlement

We put science to work.
Application of 60+ Years of Tritium Experience to Other Areas

Current Endeavors:
- He-3 recovery from process materials
- Medical isotope production
- Fusion Support
  - ITER
  - LLE

Potential Endeavors:
- Water detritiation
- Betavoltaics
- Electron Capture Detectors
- Analytical capabilities
- T₂ Recovery from breeder materials

SRNL Support for SHINE

SHINE Medical Technologies, Inc. in Monona, WI
- Producer of medical isotopes, primarily Mo-99
- Currently no domestic producers
- NRU in Canada, the only North American producer and single largest producer in the world, is scheduled for shutdown in 2018
- Production technique favorable from a nonproliferation standpoint

SRNL leading design process for tritium system including:
- Accelerator interface
- Impurity removal
- Isotope separation
- Hydrogen storage and delivery
- Shutdown/startup protocols

*Image from SHINE Medical Technologies™ website
SRNL Support for ITER

– US ITER Project Office
  SRNL/SRNS is the Design Authority/Design Agent for the Tokamak Exhaust Processing System which is one of 16 Procurement Packages within the ITER Fuel Cycle

– ITER International Organization Direct Support
  – Tritium Analytical System Conceptual Design
  – Highly Tritiated Water processing development and design verification
  – Tritium Process Control System Conceptual Design
  – Tritium Accountability and Tracking Program Development (MC&A)
  – Tritium Storage and Delivery System Hydride Storage Bed Design Support

SRNL Support for LLE

Laboratory for Laser Energetics in Rochester, NY

– NNSA Funded for Stockpile Stewardship
– “established in 1970 as a center for the investigation of the interaction of intense radiation with matter”
– Direct drive inertial confinement fusion
– ~1mm DT “ice” target placed within 10 μm of target

SRNL involvement

– Fabricated micro -TCAP for batch isotope separation
– Provided technical guidance for startup
– Improved test results through better gas control of gas mixtures
Summary

- Tritium Processing is a complex chemical process – containment, separations, unexpected reactions, materials compatibility, and accountability.
- Tritium Processing R&D at SRNL is ongoing to ensure that both:
  - the needs of the Savannah River Tritium Enterprise are met, AND
  - the continuously evolving requirements of tomorrow’s fusion machines are met.

Thank You
Radiochemistry of Tritium and Impurities (1/2) *

- **Self-radiolysis of T\(_2\)**

  \[ T_2 \rightarrow T_2^+ + \text{others} \]
  \[ T_2^+ + T_2 \rightarrow T_3^+ + T \]
  \[ T_3^+ + e^- \rightarrow 3T \]

- **Self-radiolysis of T\(_2\)O (liquid T\(_2\)O is self heating)**

  - \( \beta \)-radiation causes the formation of T\(_2\)O\(^+\) ions, T\(_3\)O\(^+\) ions, T\(^-\) radicals, OT\(^-\) radicals, and T\(_2\)O\(_2\) via consecutive chemical reactions
    - *Due to the primary self-radiolysis products of T\(_2\)O it is highly corrosive*

  - Gas phase above T\(_2\)O becomes pressurized
    - *Radiochemical equilibrium above T\(_2\)O at 159 kPa (~1200 torr)*
    - Rate of gas production balanced by rate of (radiochemical) recombination

* Giuglia, Fusion Reactor Fuel Cycle INSTN Lecture, February 6, 2009
Radiochemistry of Tritium and Impurities (2/2) *

• Reaction of T₂ with oxygen, nitrogen and air
  
  \[ 2T_2 + O_2 \rightarrow 2T_2O \]
  \[ 3T_2 + N_2 \rightarrow 2NT_3 \]
  \[ T_2 + \text{air} \rightarrow T_2O + T_2O_2 + NO + NO_2 \]
  \[ CO_x + T_2 \rightarrow CT_4 + T_2O \]
  as well as other heavier hydrocarbons

  – Reaction products are subject to (self-) radiolysis
  – Radiochemical equilibrium composition depends on tritium concentration (ratio of T/\(\Sigma\)H) and presence of metal catalysts (especially precious metals such as Pt, Pd)

• Reaction of T₂ with methane
  – If deuterium is present 15 different labeled methanes appear in gas phase
  \[ T_2 + CH_4 \rightarrow CH_T + CH_2T_2 + CHT_3 + CT_4 \]

* Glugla, Fusion Reactor Fuel Cycle INSTN Lecture, February 6, 2009

Tritium Effects on Polymeric Materials

Polymers are a necessary compromise:
• Can’t always avoid their use in tritium systems
• Needed for seals, lubrication, packing, etc.

SRNL and others have found that:
• When polymers are exposed to ionizing radiation (for example gamma rays, alpha particles, or beta particles from tritium decay), highly reactive “free radical” groups form when the energy of the ionizing photon or particle is absorbed *
• Polyethylene is known to emit hydrogen, methane and other hydrocarbon gases upon exposure to ionizing radiation *
• Tritium can react with PTFE (Teflon ®) to form \(^3\)HF (TF) *
• Crosslinked polymers contain sulfur which can be released in sulfur byproducts due to tritium decay – catalyst and permeation membrane poison

* Effects of Tritium Exposure on UHMW-PE, PTFE, and Vespel® (U) – Clark and Shanahan – May 2006
Tritium Fuel Cycle Technologies – Pumping (evacuation)

Evaluation of pumping technologies is necessary to move tritium-containing gases without the addition of impurities (from tritium exposure) – all metal construction is desired.

Candidate Technologies

- Normetex scroll pump and Metal Bellows pump
  - Normetex pumps unavailable
  - Alternate pump testing needed
- “Booster” pump to move gases
- High vacuum pumps (turbomolecular drag pumps)

Edwards nxDS15i Dry Scroll Pump

Overview of Tritium and molten salt FLiBe research at Safety and Tritium Applied Research (STAR) facility
Outline

1. Motivation and overview of STAR research

2. Molten salt research at STAR during JUPITER-II project (April 2001 – March 2007)

3. Present capabilities

Idaho National Laboratory (INL) and fusion safety

• INL overview:
  - Geographically, the largest lab in 10 multi-program US national laboratories
  - 52 reactors were designed and built in Idaho
  - The world’s first usable electricity from nuclear energy generated in EBR-I in 1951
  - The nation’s lead laboratory for nuclear energy research and development

• Advanced Test Reactor (ATR)
  - Light water moderated/cooled with Be neutron reflector
  - Max: 250 MWth and Four Leaf Clover” design
  - Materials and fuels testing, isotope production (e.g. 60Co)

• Safety and Tritium Applied Research (STAR) Facility
  - Fusion safety and tritium research
STAR facility at Advanced Test Reactor Complex

Comparison of site size:
- INL
  - 890 sq. mile
- Rhode Island
  - 1214 sq. mile (0.73)
- Boston
  - 89.6 sq. mile (9.9)

NOTE: the number in the () is the ratio of the INL site to each site.

STAR facility is
- Supported by DOE SC Office of Fusion Energy Sciences

- Restricted to a facility total tritium inventory of less than 1.6 gram (15,390 Ci), to remain below DOE Hazard Category 3 threshold
  ➔ less than Hazard Category 3 Nuclear Facility
  - Current tritium inventory is ~ 0.35 gram (~3500 Ci)

- Specializes in:
  - Tritium (fusion fuel)
  - Activated materials (neutron-irradiated tungsten)
  - Advanced coolant (FLiBe, PbLi, He)
  - Toxic material (Be)

-Containment strategy for hazardous materials:
  - Ventilated enclosures and Laboratory hood for handling tritium
  - Gloveboxes for handling beryllium, Flibe etc..
Motivation of STAR research

- Investigate tritium related and non-tritium related experimental fusion safety research

1. **Tritium related fusion safety**
   - In-vessel tritium source term
     - Tritium retention in fusion materials
   - Ex-vessel tritium release term
     - Tritium permeation in fusion materials

2. **Non-tritium related fusion safety**
   - Dust explosivity
     - Beryllium dust
   - Steam reactivity

3. **Tritium related fission safety**
   - Tritium removal in molten salt?

---

Tritium retention studies
for fusion PFC development in Tritium Plasma Experiment

**Unique capabilities**

- Designed to measure tritium behavior (e.g. retention and permeation) in activated materials with tritium plasma (e.g. tritium/deuterium ratio ~ (0.01-0.1) at divertor relevant ion flux condition
- Capable of testing neutron-irradiated (< 1 mSv/hr @ 30cm) specimens (W, RAFM steels, etc.)
- TPE is contained within double enclosure (PermaCon Box and Glovebox)
Tritium absorption and permeation studies for fusion blanket development

- Designed to measure tritium transport properties (e.g. diffusivity, solubility, and permeability) in activated materials at realistic fusion sweep gas conditions (e.g. low tritium <10 Pa & hydrogen partial pressures < 1000 Pa, moderate < 700 C)
- Capable of testing liquid or ceramic breeder materials (e.g. PbLi, Li$_2$TiO$_3$, etc.) and disc shaped metal specimens (W, RAFM steels, etc.)

Unique capabilities

- Sub atmospheric absorption (< 0.1 MPa) up to 950 C
- Utilize three calibrated capacitance manometers (0.002, 1.3, 133 kPa)
- Capable of testing liquid or ceramic breeder materials (e.g. PbLi, Li$_2$ZrO$_3$, KO functional materials etc.) and PFC/structural material (W, RAFM steels, etc.)
- Capable of testing neutron-irradiated materials

Hydrogen/deuterium absorption studies for fusion blanket development

- This static gas absorption system studies deuterium gas absorption in materials. It is located inside Laboratory fume hood for hydrogen safety.
- Unique capabilities
  - Sub atmospheric absorption (< 0.1 MPa) up to 950 C
  - Utilize three calibrated capacitance manometers (0.002, 1.3, 133 kPa)
  - Capable of testing liquid or ceramic breeder materials (e.g. PbLi, Li$_2$ZrO$_3$, KO functional materials etc.) and PFC/structural material (W, RAFM steels, etc.)
  - Capable of testing neutron-irradiated materials
Explosive dust evaluation for fusion vacuum vessel safety in ExCEED

- Developed for evaluating explosivity of mobilized beryllium dust for ITER VV safety (particularly in the presence of hydrogen generated by beryllium-steam reactions)

- **Unique capabilities**
  - One-of-a-kind dust explosion chamber for toxic and hazardous dusts
  - A 20 Kühner liter sphere, a standard device for dust explosion testing
  - A typical measurement test series varies the dust concentration to identify the maximum pressure and maximum rate of pressure rise and the concentration at which these occur

- Future work may include combined hydrogen/dust explosions for fusion safety

Outline

1. Motivation and overview of STAR research

2. Molten salt research at STAR during JUPITER-II project (April 2001 – March 2007)

3. Present capabilities
Overview of JUPITER-II program (Apr. 2001 – Mar. 2007)

• JUPITER-II
  – Japan-USA Program of Irradiation/Integration Test for Fusion Research –II
  – Six years (2001-2006) under the collaboration implemented between MEXT (Ministry of Education, Culture, Sports, Science and Technology) and US DOE

• Task 1: Self-cooled liquid blanket

• Task 1-1: FLiBe system

  (Task 1-1-A) FLiBe Handling/Tritium Chemistry
  – Experimental work with FLiBe at STAR, INL for self-cooled liquid blanket of a fusion reactor.
  – Maintaining Flibe under a reducing atmosphere is a key issue to transform TF to T2 with a faster reaction rate compared with the residence time in blanket.
  – The purpose of the task is to clarify whether or not the Redox control of Flibe can be achieved with Be through the following reaction.
    • Be + 2 TF \( \rightarrow \) BeF$_2$ + T$_2$

  (Task 1-1-B) FLiBe Thermofluid Flow Simulation
  – Simulation work at U. of Kyoto and UCLA

Reference:
M.Shimada | FHR & Tritium WS | Salt Lake City, UT | October 27, 2015

JUPITER-II (2001-2006)
Task 1-1-A: FLiBe Chemistry Control, Corrosion, and Tritium Behavior

• Molten salt handling and purification
  – Developed Material Handling Protocol with Safety Emphasis
  – Proved Effectiveness of Hydro-fluorination Purification
  – Demonstrated Capabilities for Impurity Quantification
  – Experimental procedure:
    • BeF$_2$ and LiF powders were dried and weighted to the mole ratio of 2:1
    • Melted with helium gas purge first, and then with gas mixture of He, H$_2$, HF at 520°C to reduce inherent oxides
    • The salt was transferred to another vessel through filtered through 60 μm metal mesh frit

Table 1 Impurities in ingredients and final salt

<table>
<thead>
<tr>
<th></th>
<th>O (ppm)</th>
<th>C (ppm)</th>
<th>N (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>Cr (ppm)</th>
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<tbody>
<tr>
<td>BeF$_2$</td>
<td>5700</td>
<td>&lt;20</td>
<td>58</td>
<td>295</td>
<td>20</td>
<td>18</td>
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<tr>
<td>LiF</td>
<td>60</td>
<td>&lt;2</td>
<td>78</td>
<td>100</td>
<td>30</td>
<td>4</td>
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<tr>
<td>FLiBe</td>
<td>560</td>
<td>10</td>
<td>32</td>
<td>260</td>
<td>15</td>
<td>16</td>
</tr>
</tbody>
</table>
JUPITER-II (2001-2006)
Task 1-1-A: FLiBe Chemistry Control, Corrosion, and Tritium Behavior

- **Mobilization studies**
  - Developed and Validated Transpiration System for Vapor Pressure Measurement of Molten Salts
  - Measured FLiBe Vapor Pressure at Low-temperature range Relevant to Fusion Blanket Designs
  - **Experimental procedure:**
    - Mobilization test was performed with Ar, air, and moist air in inert gas glove box.
    - (Ar test) conducted at 500, 600, 700, and 800°C with 25 sccm Ar flow
    - (Air test) conducted at 500, 600, 700, and 800°C with 25 and 50 sccm air flow
    - (Moist air test) conducted at 600, 700, and 800°C with 25 and 50 sccm moist air flow
    - Both Ni and glassy carbon crucibles were used

![Fig. 1. Transpiration test setup.](image1)

![Fig. 2. Total pressure over FLiBe.](image2)

![Fig. 3. BeF₂ pressure in various environments.](image3)

JUPITER-II (2001-2006)
Task 1-1-A: FLiBe Chemistry Control, Corrosion, and Tritium Behavior

- **Redox control**
  - Demonstrated active control of the fluorine potential in FLiBe/Nickel systems using metallic Be
  - Proved the inhibition of FLiBe corrosion of Reduced Activation Ferritic Steel in static conditions
  - **Experimental procedure:**
    - The purpose of the task is to clarify whether or not the Redox control of Flibe can be achieved with Be through the Be + 2 TF → BeF₂ + T₂ reaction
    - HF was bubbled with He and H₂ through FLiBe with various concentration of dissolved Be (cylindrical Be rod, 0.76 cm OD and 3 cm long).
    - Ni crucible and Ni tubes were used and all the wet surface was Ni coated

![Fig. 5. Reactor for measuring redox.](image4)

![Fig. 6. HF concentration measured by QMS on the outlet of the REDOX experiment for several Be immersion times.](image5)
JUPITER-II (2001-2006)
Task 1-1-A: FLiBe Chemistry Control, Corrosion, and Tritium Behavior

- D$_2$ and T$_2$ permeation
  - Measured transport properties (diffusivity and solubility) of D$_2$ and T$_2$ in FLiBe between 550 and 700°C
  - Investigated the effect of FLiBe Redox condition on T$_2$ transport
  - **Experimental procedure:**
    - (D$_2$ test) was conducted in a cylindrically symmetric dual probe permeation pot
      - Ni crucible and Ni tubes are used
      - at 600 and 650°C at 9.0x10$^4$ Pa in Ni Probe 1
    - (T$_2$ test) was conducted in a permeation pot with 2mm thick Ni membrane
      - at 550, 600, 700 and 800°C with 1 and 20 sccm (0.1 ppm-10 vol.% T$_2$/Ar)
    - Measured with QMS and GC

Outline

1. Motivation and overview of STAR research

2. Molten salt research at STAR during JUPITER-II project (April 2001 – March 2007)

3. Present capabilities
**Tritium Gas Absorption Permeation experiment**

**Unique capabilities**

- Designed to measure transport properties (e.g. diffusivity, solubility, and permeability) of tritium at realistic blanket conditions (e.g. low tritium partial pressure < 1000 Pa) for disc geometry sample
- Capable of testing liquid breeder material (e.g. PbLi and FLiBe) and disc shaped metal
- Uniform temperature (+/- 10 C) within the test section utilizing 12” tube furnace

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**Schematic of tritium gas permeation system**

**T GAP design is based on the FLiBe permeation pot**
**Test section for Lead Lithium Eutectic (LLE)**

- Photo of Test section for lead lithium eutectic

- This test section for FLiBe can be fabricated based on LLE drawing with FLiBe compatible material (e.g. nickel) on all wet surface

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**Experimental procedure (Fe/LLE)**

- t < 0:
  - Primary/Secondary was purged with 1 % H₂/He 100/200 sccm, p₁=10⁵ Pa
  - Bake out at 600 C with for 2 hours to remove oxide
  - Test section was kept at uniform temperature (+/- 10 C) for 1 hour at t<0.
  - Traps in the α-Fe were saturated by hydrogen.
- At t=0,
  - Tritium (0.001, 0.15, 2.4 Pa T₂/He) were introduced in the primary.
- t >0 :
  - Fast breakthrough time was obtained (within a minutes) and tritium equilibrates within 30 minutes
**TMAP configuration for (1 mm) \( \alpha \)-Fe**

- **Experiment configuration**

  - TMAP for \( \alpha \)-Fe
    - 1D geometry
    - 4 enclosure species (\( H_2 \), \( T_2 \), HT, He)
    - 2 diffusion species (\( H \), \( T \))
    - 3 segments
    - 10 enclosures

**TMAP configuration for (1 mm) \( \alpha \)-Fe + (6mm) LLE**

- **Experiment configuration**

  - TMAP for \( \alpha \)-Fe + LLE
    - 1D geometry
    - 3 enclosure species (\( H_2 \), \( T_2 \), HT, He)
    - 2 diffusion species (\( H \), \( T \))
    - 4 segments
    - 10 enclosures
**Tritium retention in HFIR neutron-irradiated tungsten**

**US-Japan TITAN program (2007-2013):**
- Low-temperature (<100 °C) low-dose (0.025 & 0.3 dpa) HFIR neutron-irradiated tungsten
- Tritium was trapped in bulk (>10 μm), and retention increases at high temp. (500 °C)
- Measurement of microstructural evolution and characterization of radiation defects and defect annealing before/after plasma exposure is required to reveal trapping mechanism.

**US-Japan PHENIX program (2013-2018):**
- High-temperature (500, 800, & 1200°C) medium-dose (0.3 & 1.5 dpa) HFIR neutron-irradiated tungsten RB* irradiation with Gd thermal neutron shield
- Positron annihilation spectroscopy (PAS) at ORNL and INL will characterize radiation defects and before/after plasma exposure to reveal defect annealing mechanism.
- Nuclear reaction analysis, thermal desorption spectroscopy, and PAS is used to determine tritium migration depth and trap density for tritium retention assessment.

**History of HFIR irradiation in tungsten:**

Thermal desorption spectroscopy (TDS)

- Both TPE and NIMIIX study retention.
- To investigate retention,
  \[ R = \frac{\Phi_{\text{out}}}{\Phi_{\text{in}}} \]
- Heat samples up to 1100°C
  - Vacuum infrared tube furnace
  - Linear ramp rate
  - 6 calibrated leaks (x3 He and x3 D2)
- Analyze residual gases
  - Two quadrupole mass spectrometers
  - High resolution QMS can distinguish:
    - D2: 4.0282 amu
    - He: 4.0026 amu
Summary

• STAR at INL is DOE less than Hazard Category 3 Nuclear Facility for both fission and fusion safety R&D.
  – Maximum tritium inventory allowed 1.6 gram (15,390 Ci)
  – Capable of handling tritium, beryllium, FLiBe, and activated material
• FLiBe was extensively studied at the STAR facility during JUPITER-II program (2001-2006)
• STAR still operates 2x inert (Ar) gas gloveboxes for FLiBe use
• TGAP is capable of studying tritium permeation and absorption in FLiBe.
  – Design is based on the tritium permeation pot of FLiBe
• TPE, NIMIIX and SGAS can be used to investigate deuterium (tritium at TPE) retention in irradiated graphite for FHR.
• STAR can help develop tritium control and capture in FLiBe to enhance technical readiness level of FHR technology
Tritium Migration Analysis Program (TMAP)

- The TMAP calculates the time-dependent response of a system of solid structures or walls (may be a composite layer), and a related gas filled enclosures or rooms by including
  - Movement of gaseous species through structures surfaces, governed by dissociation/recombination, or by solution law such as Sieverts’ or Henry’s Laws
  - Movement in the structure by Fick’s-law of bulk diffusion with the possibility of specie trapping in material defects
  - Thermal response of structures to applied heat or boundary temperatures
  - Chemical reactions within the enclosures
- User specified convective flow between enclosures
- Equations governing these phenomenon are non-linear and a Newton solver is used to converge the equation set each time-step

TMAP Capabilities (cont.)

- TMAP does not treat plasma surface physics, such as sputter or sputtered material re-deposition. TMAP’s basic equations are:

\[
\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_m}{\partial x} \right) + S_m - \sum_{i=1}^{K} \frac{\partial C_i}{\partial t}
\]

\[
\frac{\partial C_i}{\partial t} = \alpha_t f_i C_m - \alpha_r C_i
\]

Surface

- \( J_{m} \) – Net specie surface flux (m\(^2\)-s\(^{-1}\))
- \( K_{d} \) – Molecular dissociation coefficient (m\(^2\)-s\(^{-1}\))
- \( K_{r} \) – Atom recombination coefficient (m\(^2\)-s\(^{-1}\))
- \( K_{s} \) – Sievert’s solubility coefficient (m\(^2\)-s\(^{-1}\))

Bulk

- \( C_{m} \) – Mobile specie concentration (m\(^{-3}\))
- \( D \) – Specie diffusion coefficient (m\(^2\)-s\(^{-1}\))
- \( K \) – Number of traps (-)
- \( C_{i} \) – Trapped specie concentration (m\(^{-3}\))
- \( \alpha_r \) – Release rate coefficient (s\(^{-1}\))
- \( \alpha_t \) – Trapping rate coefficient (s\(^{-1}\))
- \( f_i \) – Probability of landing in a trap site (-)
- \( \lambda \) – jump distance or lattice constant (m)
- \( \lambda_c \) – Trap site concentration (m\(^{-3}\))
- \( N \) – Bulk material atom density (m\(^{-3}\))
- \( \nu_o \) – Debye frequency (s\(^{-1}\))
- \( E_t \) – Trap energy (eV)

\[
\alpha_t = \frac{D}{K} \quad f_i = \frac{c_i^o - C_i}{N} \quad \alpha_r = \nu_o \exp \left( -\frac{E_t}{kT} \right)
\]
**Input parameter for TMAP modeling**

- To apply TMAP to experimental data, property data for H diffusivity, solubility, and surface recombination/dissociation coefficients in α-Fe are required.
- Physical data of tritium partial pressure and sample temperatures are also required.
- Mass transport property data used for H permeation in α-Fe are:
  - H diffusivity in alpha-iron \([m^2/s]\)
    \[ y=4.43e-8*\exp(-638.7/\text{temp}) \]
  - H solubility in alpha-iron \([1/(m^3 \text{ Pa}^{0.5})]\)
    \[ y=4.2e23*\exp(-2922.6/\text{temp}) \]
  - H/T recombination coefficient in alpha-iron \([m^4/s]\)
    \[ y=4.6e24/\text{temp}*\exp(+4365.9/\text{temp}) \]
  - H/T dissociation coefficient in alpha-iron \([m^4/s]\)
    \[ K_d = K_r \cdot K_s^2 \]

- Mass transport property data used for H permeation in PbLi from Okitsu\(^5\)

- Adjusted T diffusivity and T solubility to fit exp. data as two fitting parameters

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Experience with Tritium Evolution During Irradiation of MSRE Flibe in the MITR

David Carpenter
Group Leader, Reactor Experiments

10/27/15

Outline

- MITR Introduction
- Tritium Experiments in the MITR
  - Goals
  - Limitations
- Tritium and Other Gas Release Measurements
  - FS-1
  - FS-2
- PIE Progress

- Please interrupt
MIT Research Reactor (MITR)

- Part of independent Nuclear Reactor Laboratory
- Built on the MIT campus in 1958, upgraded in 1976
- 6 MW$_{th}$ - the 2nd largest university reactor in U.S.
- Light water-cooled, heavy water-reflected
- Operates 24/7, up to 10-week cycles

MITR Core

- 24 HEU rhomboidal elements with UAI$_x$ plate-type fuel
- 50°C outlet, atmospheric pressure
- 3 dedicated in-core experimental positions
FHR IRP Irradiation Goals

➢ To test the interactions between the flibe and potential FHR fuel and structural materials
➢ To compare material test results with parallel test at University of Wisconsin (no irradiation)
➢ To measure tritium production and partitioning among components
➢ To evaluate the experimental components and methods for future FHR-related tests—the starting point that ultimately leads to larger experiments in HFIR and ATR

Initial Flibe Irradiations

➢ Study effect of different fluoride redox potentials on salt corrosion and tritium release
➢ Tritium and salt interaction with fuel compact graphite
➢ Cracking performance of TRISO particles
➢ 300 hours

➢ First in-core irradiation of MSRE flibe in 60 years
➢ Primary goal to identify potential safety and design issues for future experiments
➢ 1000 hours
➢ 700°C
Irradiation Design Progress

- Test conditions:
  - 700°C
  - Double encapsulation (Ni, Ti)
  - He cover gas, He/Ne control gas
  - 5.5MW reactor power

- FS-2 modifications:
  - Independent irradiation facility
  - 2.7x more salt volume
  - Two fluoride potentials
  - New C/C, graphite, and TRISO particles
  - Improved gas flow and exhaust

FS-1 Loading

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Container Material Combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Two Hastelloy-N samples</td>
</tr>
<tr>
<td>B</td>
<td>Two 316 Stainless Steel samples</td>
</tr>
<tr>
<td>C</td>
<td>Three types of SiC samples:</td>
</tr>
<tr>
<td></td>
<td>R&amp;H CVD SiC</td>
</tr>
<tr>
<td></td>
<td>SiC/SiC Tyranno-SA3 CVI SiC composites</td>
</tr>
<tr>
<td></td>
<td>SiC/SiC Hi-Nicalon type-S CVI SiC composite</td>
</tr>
<tr>
<td>D</td>
<td>300 surrogate TRISO particles</td>
</tr>
<tr>
<td>E</td>
<td>Two Hastelloy-N samples in nickel-lined hole</td>
</tr>
<tr>
<td>F</td>
<td>Two 316 Stainless Steel samples in 316SS-lined hole</td>
</tr>
</tbody>
</table>
FS-1 Capsule Assembly

Graphite sample holder filled with samples and flibe

Flibe Loading

<table>
<thead>
<tr>
<th>Graphite Chamber</th>
<th>Flibe Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>21.3</td>
</tr>
<tr>
<td>B</td>
<td>21.2</td>
</tr>
<tr>
<td>C</td>
<td>21.2</td>
</tr>
<tr>
<td>D</td>
<td>21.2</td>
</tr>
<tr>
<td>E</td>
<td>18.2</td>
</tr>
<tr>
<td>F</td>
<td>18.1</td>
</tr>
</tbody>
</table>

Capsule sealed with TCs and gas sampling lines

Samples in FS-1 are all identical to UW corrosion tests

FS-1 Capsule Irradiation

- The FS-1 capsule runs inside the MITR In-Core Sample Assembly (ICSA) thimble
  - The ICSA is an instrumented inert gas irradiation facility in a central core position
- Separate gas flow in capsule and thimble
- Thermocouples in graphite for temperature measurement

<table>
<thead>
<tr>
<th></th>
<th>Fast flux (n/cm²·sec) (E &gt; 0.1 MeV)</th>
<th>Total neutron flux (n/cm²·sec)</th>
<th>Fast flux/Total flux ratio, %</th>
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<tbody>
<tr>
<td>FS-1</td>
<td>1.06×10¹⁴</td>
<td>1.38×10¹⁴</td>
<td>76.8</td>
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<tr>
<td>Flibe compartments (5.5 MW)</td>
<td>6.95×10¹³</td>
<td>4.04×10¹⁴</td>
<td>17.2</td>
</tr>
<tr>
<td>2009 PB-AHTR*</td>
<td>6.18×10¹³</td>
<td>3.64×10¹⁴</td>
<td>17.0</td>
</tr>
<tr>
<td>2011 AHTR*</td>
<td>6.18×10¹³</td>
<td>3.64×10¹⁴</td>
<td>17.0</td>
</tr>
</tbody>
</table>

**FS-1 Irradiation History**

- Slow, stepped startup with fine control through melting
- Experimented operated at 700±3°C for 1000 hours

**ICSA Irradiation Facility**
**Tritium Measurements**

- First irradiations attempted combination of real-time and integrated measurements
  - Dual compensated ion chambers used to measure real-time tritium activity
  - Six-pass water bubbler system with catalytic furnace to capture tritium in water for later liquid scintillation counting (LSC)
- This system should allow separate collection of soluble (TF, HTO, T₂O) and non-soluble (HT, T₂) species
- Bubbling with LSC has been is highly repeatable with good capture efficiency, and allows differentiation of H-3, C-14 activity
  - Released activity below range of ion chamber sensitivity/background rejection

**FS-1 Initial Findings – Tritium Activity**

- Tritium counts integrated over 24-48 hour intervals
- Tritium collected during startup was ~10% of predicted production
- Subsequently, collected less than 1% of production
- Capsule and thimble tritium levels similar
FS-1 Initial Findings - Solubility

- Tritium collected in initial impingers expected to be only water-soluble form,
- Post-catalyzing furnace the previously non-soluble species will be captured
- Only non-soluble species (T$_2$) should be released through diffusion
- Additional tests are required to identify species to explain apparent contradiction

FS-2 Loading

- Added C/C and matrix graphite, removed Hastelloy
- Redox potentials straddle the historical MSRE potential (-665 to -707 kJ/mol F$_2$)

<table>
<thead>
<tr>
<th>Graphite Holder</th>
<th>Compartment</th>
<th>Material</th>
<th>Flibe F$_2$ Potential (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>A</td>
<td>Graphites</td>
<td>-632</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>SiC/SiC, TRISO</td>
<td>-632</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>SiC/SiC, TRISO</td>
<td>-711</td>
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<tr>
<td>Lower</td>
<td>A</td>
<td>C/C</td>
<td>-632</td>
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<tr>
<td></td>
<td>B</td>
<td>SS316</td>
<td>-632</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>SS316</td>
<td>-711</td>
</tr>
</tbody>
</table>
**FS-2 Loading**

![Images of various materials and components]

**Legend:**
- **White** – Aluminum dummy element
- **Blue** – Titanium thimble
- **Orange** – Nickel capsule
- **Yellow** – Internal nickel parts
- **Gray** – Graphite sample/flibe holder

**FS-2 In-Core Facility Design**

![Graphite cross-section diagram]

**Legend:**
- **White** – Aluminum dummy element
- **Blue** – Titanium thimble
- **Orange** – Nickel capsule
- **Yellow** – Internal nickel parts
- **Gray** – Graphite sample/flibe holder

**FS-2 Position (A-1)**
FS-2 Irradiation History

- First startup did not reach the flibe melting point
  - Reduction in power to 50kW for maintenance (~50°C)
- Eventual startup to 700°C was uneventful
- Unrelated reactor SCRAM at 300hrs, restart attempt
- After several days of troubleshooting, performed short test to 3MW, then removed experiment

Tritium Release vs. Source Term

- Capsule and thimble gas tritium levels similar
  - Easy diffusion through capsule
- Majority of tritium is immediately soluble in water
  - Additional catalyzing had small effect
- Tritium release rate increases during temperature changes
- Tritium release during normal operation (5.5MW, 700°C) is same order of magnitude as FS-1 (<1% of generation)
Short Half-Life Detection

- In FS-1, problem of short-lived activation products in capsule exhaust
  - Added special gas system for FS-2

- In FS-2, highest N-16 and O-19 release when flibe was solid
  - Produced by F-19 neutron activation

- Almost no detectable release at full reactor power, 700°C

Bromine Release

- Bromine was detected in tritium collection system
  - Only from capsule gas
  - Here contrasted with Ar-41, an expected He impurity

- Highest Br levels when at low power – flibe is solid

- Not detected at full power, 700°C
FS-2 Gaseous Release Test

- Following the SCRAM, conducted a test to 3 MW to allow additional sampling
  - Added glass, paper, and charcoal filters prior to tritium capture bubblers
  - Activation products only seen from capsule

- Molybdenum release and capture on filters highest from 0-2MW (<200°C)
- W and Mo captured on glass and paper filters effectively, not on charcoal
- Br not captured on filters, minimal tritium capture on filters

- Experiment removed from reactor following the test

Post-Irradiation Examination

- FS-1 and FS-2 irradiation capsules extracted from in-core facility and transferred to Hot Box and Hot Cell, respectively
- Pressurized with helium to prevent moisture uptake
- Exterior condition of titanium pressure vessel and the nickel/Inconel capsule is excellent
Specimen Extraction

- All specimens have been removed from the FS-1 capsule and cleaned of flibe
  - Furnace operated in dry helium glove box to prevent HF generation and contain tritium
- Cleaning involved melting and collection of flibe ~500°C, followed by soaking in water at ambient conditions until weight decrease arrested
- Did not see evolution of other activation products or substantial tritium release during salt melting

Initial PIE – Corrosion & Cracking

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight change (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316ss in graphite</td>
<td>-2.2 -2.0 -1.8 -1.6 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2</td>
</tr>
<tr>
<td>316ss in 316ss</td>
<td>-2.2 -2.0 -1.8 -1.6 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2</td>
</tr>
<tr>
<td>Hastelloy N in graphite</td>
<td>-2.2 -2.0 -1.8 -1.6 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2</td>
</tr>
<tr>
<td>Hastelloy N in nickel</td>
<td>-2.2 -2.0 -1.8 -1.6 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2</td>
</tr>
</tbody>
</table>

SS316 irradiated in lined (left) and unlined (right) chambers

Surrogate TRISO particle with OPyC damage
FLiBe Electrochemistry and Materials Corrosion Research at UW-Madison

Thomas Chrobak, Karl Britsch, Dr. Guoping Cao, Dr. Kumar Sridharan, Dr. Mark Anderson
Tritium Workshop, Salt Lake City, UT
10/27/2015
Outline

• Introduction to LiF-BeF$_2$ (FLiBe)
  – Fluoride Salt Chemistry
  – Molten Salt Corrosion

• Electrochemistry Studies on Fluoride Salts
  – FLiBe Redox Measurements

• Static Corrosion Test
  – Experimental design and materials

• FLiBe Natural Circulation Flow Loop
  – Flow-assisted corrosion testing in FLiBe convection loop

Research Questions to be answered

• Will a 0.3V difference in the redox potential of FLiBe salt cause a significant increase in corrosion behavior?
  – (-1.71V) As-purified vs. (-1.41V) Be-reduced

• Does the presence of graphite in the salt facilitate corrosion?
  – Liner vs. without liner

• What is the effect of flow on corrosion?

• Is there a significant difference in corrosion behavior of samples in the cold or hot leg of a natural circulation flow loop?

• What is the compatibility of new selected materials?
More Research Questions for Consideration

• What is the optimum amount of Be that should be added to FLiBe?
  – Balance between over and under-reduction → smallest quantity possible sequentially added

<table>
<thead>
<tr>
<th>Stoichiometric</th>
<th>vs.</th>
<th>Excess</th>
</tr>
</thead>
</table>

• Does the over-abundance of Be metal in the salt cause enhanced corrosion to carbon-containing parts?
  – Possible formation of a BeC passivation layer that can keep salt redox low while protecting C from further corrosion?
  – Increased wetting of glassy carbon crucible following Be reduction
    • Convex surface before reduction vs. concave surface after reduction.

Why Use FLiBe as Liquid Salt Coolant?

• Higher outlet temperatures lead to:
  • More valuable process heat applications
  • Greater cycle efficiencies

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>300</td>
<td>15</td>
<td>0.55</td>
<td>3970</td>
<td>8.8×10⁻⁵</td>
</tr>
<tr>
<td>Helium</td>
<td>850</td>
<td>7.5</td>
<td>0.29</td>
<td>20.9</td>
<td>4.2×10⁻⁵</td>
</tr>
<tr>
<td>Sodium</td>
<td>550</td>
<td>Atmospheric</td>
<td>62</td>
<td>1008</td>
<td>2.3×10⁻⁴</td>
</tr>
<tr>
<td>Lead</td>
<td>550</td>
<td>Atmospheric</td>
<td>18.25</td>
<td>1499</td>
<td>1.67×10⁻³</td>
</tr>
<tr>
<td>FLiBe</td>
<td>650</td>
<td>Atmospheric</td>
<td>1.0</td>
<td>4683</td>
<td>5.6×10⁻³</td>
</tr>
</tbody>
</table>

• No ideal heat transfer fluid exists
• Molten fluoride salts offers a good compromise of properties
Properties of FLiBe meet most requirements for FHR Salt

• Molten Salt Primary Coolant Requirements
  ✓ Exhibit chemical stability at T > 800 °C
  ✓ Stable in an intense radiation field
  ✓ Consist of low thermal cross section elements
  ✓ Melt at useful temperature (<500 °C) without being volatile
  ✓ Compatible with high-temperature alloys and graphite

• LiF-BeF$_2$ – FLiBe as primary coolant
  + Atmospheric pressure operation
  + Good heat transfer properties
  + Neutron transparent
  + Wealth of MSRE experience
  - Tritium production from $^6$Li
  - Beryllium toxicity
  - Corrosive without chemistry control or proper materials

<table>
<thead>
<tr>
<th>Isotope</th>
<th>F</th>
<th>Be</th>
<th>Li-7</th>
<th>B-11</th>
<th>Zr</th>
<th>Rb</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Cross Section</td>
<td>0.009</td>
<td>0.010</td>
<td>0.033</td>
<td>0.05</td>
<td>0.18</td>
<td>0.37</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Overall Corrosion Process

• Impurity-driven corrosion dominates initial phase
• Thermodynamically-driven leads to continuous corrosion

Possible Corrosion Solutions
• Minimize thermal gradients?
• Use high Ni, low Cr Alloys?
  ➢ Implement chemistry control of salt with redox potential measurement to maintain high salt quality
**Thermodynamically Driven Corrosion**

- Non-favorable reactions slowly occurring
- Assisted by a temperature gradient and mass flow

\[ BeF_2 + Cr \leftrightarrow Be + CrF_2 \]

\[ K_{eq} = \frac{[Be][CrF_2]}{[BeF_2][Cr]} \]

\[ K_{eq} = 8.66 \times 10^{-13} \]

at 700 °C

\[ K_{eq} = 2.76 \times 10^{-14} \]

at 600 °C

**Impurity Driven Corrosion**

- Thermodynamically favorable reactions due to unstable impurities
- Occurs quickly in initial corrosion stages

**Metal Fluoride Impurity Reactions**

\[ M_{alloy}(s) + M_{imp}F_x(d) \rightarrow M_{alloy}F_y(d) + M_{imp}(s) \]

**Moisture Impurity Reactions**

\[ \frac{x}{2}H_2O + M_{salt}F_x \rightarrow M_{salt}O_x + \frac{x}{2}HF \]

\[ xH_2O + M_{salt}F_x \rightarrow M_{salt}(OH)_x + xHF \]

\[ M_{alloy}(s) + xHF \rightarrow M_{alloy}F_x(d) + H_2 \]
Fluoride Salt Corrosion Mechanisms

- Salt constituents are more stable than metal fluorides
- Almost no corrosion expected from pure FLiBe
- How can we ensure purity of FLiBe? \( \rightarrow \) Redox potential

**Free Energies of Salt Fluorides and Corrosion Products**

- 0.17 MoF\(_6\)
- 0.5 NiF\(_2\)
- 0.5 FeF\(_2\)
- 0.5 CrF\(_6\)
- 0.5 BeF\(_2\)
- LiF

**Corrosion Products** (less stable)

**Salt Constituents** (more stable)

Experimental facilities for electrochemical testing of FLiBe

- HP 3616A Power Supply
- Ar glovebox. O\(_2\) and Moisture <1 ppm
- Radiant heater, PID used to maintain 500±0.5°C
Dynamic reference probe design for compact redox potential testing of FLiBe

- O-Ring
- BN Spacer
- Glassy Carbon Anode
- Mo Cathode
- Mo Indicator
- Mo TC well
- K-Type TC

Dynamic Reference Electrode Measurements

- Combination of Dynamic and Static Techniques

First Phase
- Beryllium is plated from the salt onto an electrode (1)

Second Phase
- Voltage is cut, beryllium allowed to redissolve back into the salt
- Be|BeF$_2$ reference voltage is formed from dissolution reaction (2)
- As plated products deplete, voltage relaxes back to zero (3)

(Afonichkin, 2009)
Redox Probe Measurement Process

Phase I: Plating

Phase II: Voltage Measurement

Plateau voltage of Be dissolution indicates redox potential of FLiBe

Procedure:
- Start after plating time + 1 second
- (current point – moving average) < \( V_c \)?
  - If true, move on to next point, update average
- Points collected and averaged until end point exceeds a set cutoff voltage, \( V_c \).

Blue: Original data
Red: Plateau data points
Green: Average of red points
-Used as Redox Voltage
Redox potential testing of purified, unreduced UW-made FLiBe

- 24 Measurements total, average of -1.708V with standard deviation of 6.2 mV
- Average standard deviation within each batch of 3.11 mV
- All batches will be mixed together prior to crucible loading

Production, purification and reduction of UW-made FLiBe

- HF/H₂ → H₂ → Filtration
- UW FLibe
- Beryllium and Filtration 650°C
- Beryllium Reduced

As-received BeF₂ + As-received LiF
Video of FLiBe being poured from vessel into tray in glovebox

Glovebox inventory of FLiBe for all future experiments

Four nickel crucibles are fully filled and stored in jars.

Approximately 250 g of granulated salt was separated for one crucible in corrosion test.

Total of 2.2 kg of UW-made FLiBe currently stored in glass jars in Ar glovebox.
Next static corrosion experiment will test multiple variables

• Metrics to test against corrosion:
  – Redox potential effect
    • HF/H₂ Purified salt (redox potential = -1.71V)
    • Beryllium Reduced salt (redox potential = -1.41V)
  – Effect of carbon from IG-110 graphite crucible
    • Corrosion test with or without liner for 316 SS
  – New materials testing in FLiBe
    • GA SiC-SiC
    • Mo-Hf-C alloy
    • Zr/C-W Cermet

Experimental Design of Static Corrosion Experiment in FLiBe

<table>
<thead>
<tr>
<th>Crucible 1: -1.7V UW FLiBe</th>
<th>Crucible 2: -1.4V UW FLiBe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole 1: SiC → 3x SiC-SiC samples, 1x bulk SiC sample</td>
<td></td>
</tr>
<tr>
<td>Hole 2: Nuclear Graphite → 3x matrix graphite samples, 1x IG-110 sample</td>
<td></td>
</tr>
<tr>
<td>Hole 3: No liner. Mo-Hf-C → 3x Mo-Hf-C alloy samples with Mo wire suspension*</td>
<td></td>
</tr>
<tr>
<td>Hole 4: No liner. W-Zr-C → 3x W-Zr-C Cermet samples with W wire suspension*</td>
<td></td>
</tr>
<tr>
<td>Hole 5: No liner. 316 SS → 3x 316 samples with SS wire suspension*</td>
<td></td>
</tr>
<tr>
<td>Hole 6: With 316 SS liner. 316 SS → 3x 316 samples with SS wire suspension*</td>
<td></td>
</tr>
</tbody>
</table>

*Avoid dissimilar materials in contact in FLiBe wherever possible
Immediate Future Work

- Flow-assisted corrosion in natural circulation FLiBe loop
  - Corrosion samples in hot and cold legs of loop
  - Thermo-physical properties of FLiBe can be measured
  - Surge tank on top of loop for in-situ salt measurements and chemical control

FLiBe Natural Convection Loop 1/2

- FLiBe natural convection loop to be built
  - Incorporate Be-addition, redox measurement, and corrosion tests.
  - Use ports in surge tank for:
    1. Sacrificial Be rod with bellow
    2. 3-electrode redox probe
    3. Port-hole
    4. Anything else?
• 1” OD Stainless Steel tubing
  – Composition matching important
• Two double ball valves to support in-loop corrosion tests.

Thank you for your attention!

Questions?
The Effect of Hydrogen on Tritium Control in Molten Salt System

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University of Wisconsin Madison

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HEATandMASS.ep.wisc.edu

Tritium Chemical Form with He/H₂ Sparging
1. Would it be useful in the FHR system to sparge with He/H₂, for tritium control?
2. How does the diffusion coefficient differ between TF and HT? Is it important to differentiate between the two?
1. Would the fuel element be H$_2$ treated to remove oxides before introducing in the salt?
Mechanism of Tritium Release From Flibe

Many H₂ molecules exist in the system. Large release rate mainly HT.

A few H₂ molecules exist in the system, and the F⁻ potential in the system is high. Small release rate mainly TF.

A few H₂ molecules exist in the system, and the F⁻ potential in the system is low. Medium release rate mainly HT.
Workshop on Tritium Control and Capture in Salt Cooled Fission and Fusion Reactors

Salt Lake City
10.27.2015 & 10.28.2015

Experimental Work on Hydrogen Transport Analysis in Flibe-Graphite System

Huali Wu, Nisarg, Patel, Jee-hoon kim, Jayeesh Bakshi
Nuclear Engineering
University of Wisconsin Madison

huali@wisc.edu
HEATandMASS.ep.wisc.edu
Research Topic 1: Matrix Graphite Characterization

Goal:
1) To study matrix graphite microstructures—density, porosity, pore distribution, specific surface area, graphitization, etc;
2) To understand the difference between matrix graphite and nuclear graphite

<table>
<thead>
<tr>
<th>Graphite Characterization</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Apparent Density</td>
</tr>
<tr>
<td></td>
<td>Gas Pycnometer</td>
</tr>
<tr>
<td>Porosity</td>
<td>Numerical Calculation</td>
</tr>
<tr>
<td></td>
<td>BET(Nitrogen)</td>
</tr>
<tr>
<td></td>
<td>Matlab Image Analysis</td>
</tr>
<tr>
<td>Pore Distribution</td>
<td>Mercury Porosimetry</td>
</tr>
<tr>
<td>Surface Area</td>
<td>BET(Nitrogen)</td>
</tr>
<tr>
<td>Graphitization ($d_{002}$)</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>In-plane Crystalline Size</td>
<td>Raman</td>
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<tr>
<td>Other Techniques</td>
<td>SEM</td>
</tr>
<tr>
<td></td>
<td>Optical Microscopy</td>
</tr>
</tbody>
</table>

Research Topic 2: Static Salt Infiltration into Graphite

Goal:
1) to investigate salt infiltration process in graphite
2) to understand how graphite salt interaction will affect Fluoride-salt purity

Experimental Setup

Vertical Furnace
Graphite Crucible
Sample Holder
Pressure Release Hole

Sample (1200 grit polished & DI water ultrasonic cleaned)
NG: 0.0915g
MG: 0.0477g
Research Topic 3: Contact Angle Measurement - Jayee

Goal: 1) to investigate whether surface interaction between graphite and flibe will affect flibe intrusion in graphite

Experimental Setup

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Length (inches)</th>
<th>Width (inches)</th>
<th>Resistance (Ω)</th>
<th>Resistivity (Ω inch)</th>
<th>Resistivity (Ω meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.297</td>
<td>1.3082</td>
<td>0.4</td>
<td>0.4328</td>
<td>1.099 × 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.541</td>
<td>1.374 × 10^{-2}</td>
</tr>
</tbody>
</table>

Resistance Analysis

Research Topic 4: Hydrogen-Graphite Experiment (Constant Volume Method)

Goal: 1) to study hydrogen isotope transport phenomena in matrix graphite 2) to help to study hydrogen behavior in flibe-graphite system in the future (saturation-limited or diffusion-rate-limited)

Constant Volume Method
Questions to be Answered

- **Graphite Characterization:**
  - Q1: What physical properties are important for characterizing tritium transport?
  - Q2: The effect of hydrogen baking & oxidization of graphite?

- **Flibe Intrusion Experiment**
  - Q1: Will salt have significant intrusion for modern graphite?
  - Q2: Any other post experiment measurements is recommended?

- **Hydrogen-Graphite Experiment**
  - Q1: Hydrogen leak problem through the whole system?
  - Q2: Total hydrogen and hydrogen depth profile measurement?
  - Q3: How neutron irradiation will affect hydrogen transport in graphite?

- **Modeling:**
  - Q1: Appropriate software for pebble, core, system level simulation?

**SEM Image of A3**
Optical Microscopy Visual Image

A3 Matrix Graphite

IG-110 Nuclear Graphite

Pore Size Distribution of A3

Pore Size Distribution of IG-110
COMSOL is used for hydrogen transport simulation on pebble scale and also can be used for core scale, as shown in the Fig.1.

Q1: Other modeling software for pebble, core, system scale?
Tritium Control Using Carbon Outside of Core

Stephen T Lam
Charles Forsberg
Ron Ballinger

Tritium Overview

Generation
- Thermal neutron transmutation of Li-6
  \[ ^6\text{LiF} + n \rightarrow ^4\text{He} + ^3\text{HF} \]
- Initially 0.005 wt. % Li-6 in Flibe consumed but is continually produced by Be-9 transmutation:
  \[ ^{7}\text{BeF}_2 + n \rightarrow ^4\text{He} + ^6\text{He} + 2\text{F} \]
  \[ ^6\text{He} \rightarrow ^3\text{Li} + e^+ + \overline{\nu}_e \quad \left( t_{1/2} = 0.8\text{sec} \right) \]

Concerns
- Corrosion: TF oxidizes chromium in stainless steel
  \[ 2\text{TF}_{(d)} + \text{Cr}_{(s)} \rightarrow \text{CrF}_2_{(d)} + \text{T}_2_{(g)} \]
- Release: T_2 diffuses through piping and escapes to environment
- Uncertainty: Lack of industrial experience with FHR
Regulatory Tritium Limits

Limit: Concentration limits in Effluent
Target: ALARA. Similar magnitude to existing commercial reactors

<table>
<thead>
<tr>
<th>Regulation</th>
<th>Annual Radiation Dose (mrem)</th>
<th>Effluent Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mSv)</td>
<td>Air (μCi/ml)</td>
</tr>
<tr>
<td>Limit</td>
<td>10 CFR 20.1301(a)</td>
<td>100</td>
</tr>
<tr>
<td>Table 2 of Appendix B to 10 CFR 20</td>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>Standard</td>
<td>10 CFR 20.1301(e)</td>
<td>25</td>
</tr>
<tr>
<td>ALARA</td>
<td>Appendix 1 to 10 CFR 50</td>
<td>20</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>EPA standard</td>
<td>3</td>
</tr>
</tbody>
</table>

\(\text{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}
\(\text{CFR = Code of Federal Regulations}


Tritium Modeling in FHR

**Figure 1:** TRIDENT Model Overview

**TRIDENT**

Tritium Diffusion EvolutioN and Transport

Time dependent tritium in FHR model developed at MIT*:  
- Tritium generation in core  
- TF and T\(_2\) Speciation (Redox)  
- In-core graphite Up-take  
- Corrosion consumption & generation  
- Diffusion in coolant, vessels, heat exchangers, reflectors  
- Mitigation mechanisms  
- Tritium release to environment

**Tritium Production Rates**

**Estimated Base Case FHR Without Mitigation**

<table>
<thead>
<tr>
<th>Reactor Type</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><strong>Beginning of Life: 11,000</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Equilibrium: 2,900</strong></td>
</tr>
</tbody>
</table>


---

**Mechanisms and Release Rates**

**Tritium Capture Evaluation**

- Without mitigation, release to environment peak at **2410 Ci/EFPD**
- Three mitigation mechanisms were evaluated in TRIDENT

1. **Stripping Column**
   - 10 stage counter current column with 20,000 L/hr STP stripping gas
   - Release rate with column: **436 Ci/EFPD**

2. **Permeation Window**
   - Shell with permeation tubes (Nickel) with 2x heat exchanger area
   - Release rate with window: **800 Ci/EFPD**

3. **Carbon Absorber Bed**
   - 1.2(R)x3.85(H)m bed nuclear grade graphite ISO-88 with 1 regen/30 days
   - Release rate with bed: **7.5 Ci/EFPD ↔ Similar to a PWR**

**Simplified Tritium Removal Analysis**

Carbon Absorber Bed

Concept
- Counter-current pebble bed absorber for coolant from core
- Continuous on-line regeneration
- Example: High temperature tritium de-gassing

Specifications
- Bed size and flow rate (% of total primary molten salt flow)
- Operating temperatures
- Absorbent partial pressures
- Carbon type and area

Graphite Bed Location

Location
- Primary system before heat exchanger
- Full or partial flow

Current Modelling
- 1-D tritium diffusion through molten salt
- Graphite capacity limited
- Graphite ISO-88 (Nuclear grade)
Choice of Absorbent

Considerations
- Non-nuclear grade (outside of core)
- Performance under operating conditions
- Long-term behavior in FHR

Carbon Properties
- Absorption rate
- Desorption rate
- Hydrogen Capacity:
  - BET Surface Area
  - ~1 vs. 3000 m²/g (nuclear graphite vs. activated carbon)


H₂ Uptake Completion Time

Figure 6. Fractional completion for hydrogen uptake at 298 K on AX-21 (×), Maxsorb (○), CNT (□), templated carbon (+), and graphene (△) at ~6 MPa end pressure.


Figure 7. Adsorption fraction at 298 K on graphene (A) and AX-21 carbon (B) during each pressure ramp step at final pressures of: ~2 MPa (○), 6.2 MPa (△), and 7.9 MPa (□).
**H₂ Capacity vs. Temperature**

![Graph showing H₂ Capacity vs. Temperature](image)

Specific capacity of Papyex graphite under deuterium gas only at 0.66 Pa.

**Engineering implications:** Column size, percent flow, regeneration

---

**FHR Conditions**

<table>
<thead>
<tr>
<th>Temperatures*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant Freezing</td>
</tr>
<tr>
<td>Operating Core Outlet</td>
</tr>
<tr>
<td>ATWS</td>
</tr>
<tr>
<td>Coolant Boiling</td>
</tr>
</tbody>
</table>

**Pressures (primary loop) *TRIDENT Simulation**

| pₜ₂ Unmitigated              | 3.3-20 Pa |
| pₜ₂ with Graphite Capture    | 0.03-0.08 Pa (Peak release 7.5 Ci/GW/d) |
| pₜ₆ Unmitigated              | 0.03-0.075 Pa |
| pₜ₆ with Graphite Capture    | 0.0027-0.0045 Pa (Peak release 7.5 Ci/GW/d) |

**Challenge:** Low pressure and high temperature data

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Next Steps

1. Design and construct experiment for testing performance of different carbons in FHR conditions
   • Vacuum chamber
   • Temperature and pressure controls, etc.

2. Data collection to understand hydrogen uptake mechanics
   • Absorption-Desorption kinetics (trapping, diffusion, etc.)
   • Behavior in high temperature exposure, cycling

3. Modeling and technology qualification
   • Use new data to reduce model uncertainty
   • Improve predictive capability

Questions
In-Core Graphite

(Left) Mk1 pebble core geometry showing fuel pebble (green) and graphite reflector pebble (yellow) regions

(Above) A PB-FHR pebble fuel element

Replaceable Mk1 center graphite reflector

Gas Stripping Column

Schematic of a PB-FHR with multi-stage counter current gas stripper and charcoal bed


Permeation Window

- 1-D diffusion through Ni Tubes
- 20,000 m² surface area
- 27,360 permeation tubes
- Permeation tubes OD: 0.00635

Schematic of a PB-FHR Permeation Window and Activated Charcoal bed for gas recovery

Hydrogen Solubility

Hydrogen solubility of different carbons at 1000 °C and 101 kPa


Hydrogen Absorption Rates


Absorption Rate vs. Temperature

- Increasing absorption rate with increasing temperature

Hydrogen absorption rate in (a.) IG-110U, (b.) IG-430U, and (c.) ISO-880U.

Solubility vs. Temperature

- Decreasing solubility with increasing temperature
Tritium Retention vs. Irradiation

Hydrogen retention in ISO-880U and IG-430U. Irradiation was to 0.047 dpa.

- Increased retention from irradiation


Tritium Trapping vs. Irradiation

Tritium Trap Concentration (atom ppm) for H-451 and N3M

Hydrogen Diffusion vs. Irradiation

Hydrogen Diffusion with Neutron Flux at 1273K and 10 kPa


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)
  - $\text{Li}_2\text{SiO}_4$ or $\text{Li}_2\text{TiO}_3$ ceramic breeder
  - Be or Be$_{12}$Ti (lower chemical reactivity) neutron multiplier
- Liquid breeders
  - Li liquid metal
  - PbLi eutectic (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 TBMs in ITER) or PbLi breeders (EU, Indian TBMs)
- 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

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\(^1\)

---

\(^1\)H. Feuerstein, *Fusion Technology* (14th SOFT), 1986, p. 646

---

**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
**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

---


**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

<table>
<thead>
<tr>
<th>Test No.</th>
<th>L (l h⁻¹)</th>
<th>G (Nm³ min⁻¹)</th>
<th>Pₚ₃0k (Pa)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70-90</td>
<td>100</td>
<td>1200-1250</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>50-50</td>
<td>100</td>
<td>450-475</td>
<td>23-25</td>
</tr>
<tr>
<td>5</td>
<td>30-50</td>
<td>100</td>
<td>220-230</td>
<td>23-25</td>
</tr>
</tbody>
</table>

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 (Nm³ Min⁻¹)</th>
<th>Pₚ₃0k (Pa)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>80-105</td>
<td>500</td>
<td>1200-1400</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>

HCLL DEMO (14 inventory re-circulations per day) requires at least 80% efficiency even with permeation barriers (with ~100x reduction factor)

Larger scale tests, optimization planned at TRIEX loop (ENEA) but no results as of yet

---

**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 (!)

- 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?

---


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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: \( \eta = 1 - \exp\left(-\frac{r^2}{1+\zeta}\right) \)
- \( \zeta \) and \( \tau \) are dimensionless numbers that indicate the relative importance of three transport phenomena

\[ \zeta = \frac{\Phi_s}{K_rK_f \ln(r_o/r_i)} \] \( r_i \) - inner diameter of tubes  
\( r_o \) - outer diameter of tubes  
\( L \) - length of tubes  
\( v \) - PbLi velocity  
\( K_r \) - PbLi solubility  
\( K_f \) - mass transport coefficient  
\( \Phi_s \) - permeability of solid tube

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 \( K_f \)
- 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 \( K_r \)
- \( \tau \) is a ratio of axial to radial transport times:
  \[ \tau = \frac{L/v}{(r_i/2K_f)} \]
- 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 \( K_f \)...
**Mass Transport Correlations**

- $K_T$ is defined by the Sherwood number: $Sh = dK_T / D_f$
- Sherwood number correlations have the form $Sh = \beta Re^a Sc^b$
- For PbLi at 470-700 °C, $10 < Sc < 150$ ($Sc = \mu / \rho D_f$)
- 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></td>
<td>Colburn 1933</td>
<td>Heat transfer analogy</td>
</tr>
<tr>
<td>0.023</td>
<td>0.83</td>
<td>0.44</td>
<td>$2000 &lt; Re &lt; 35000$</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, cinaminic acid, and beta-naphthol in water</td>
</tr>
<tr>
<td>0.0163</td>
<td>0.83</td>
<td>0.44</td>
<td>$Sc \approx 0.6$</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 hydroxymethylcellulose solutions</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):

$$\eta \geq 0.7 \quad d \geq 0.01 m \quad \dot{m} = \rho N \pi r_i^2 v = 26000 \text{ kg/s} \quad \Delta P = \frac{f L \rho v^2}{d} \leq 1 \text{ MPa}$$
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>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>
<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>11.15</td>
<td>7.65</td>
<td>5.7</td>
<td></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>4.85</td>
<td>1.27</td>
<td>0.45</td>
<td>1681</td>
<td>425</td>
<td>148</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>η (high solubility)</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>
<td></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 Al$_2$O$_3$, Cr$_2$O$_3$, Er$_2$O$_3$
• These have achieved permeation reduction factors as high as 10,000 in the laboratory
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.

<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:

\[
W = \frac{K_s \times \sqrt{P}}{J_D}
\]


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
Tritium- Control Technologies for TMSR in CAS

Wei LIU, Zhimin DAI, Hongjie XU
Center for TMSR, CAS
2015-10-28

Outline

I. Background

II. Roadmap of Tritium-control technologies for TMSR in CAS

III. Performances at the tritium-control technologies for TMSR in CAS

IV. Summary
I. Background

1. Tritium production in TMSR (FLiBe as primary coolant, $^7$Li abundance: 99.99%)

![Diagram of the reactor core and cover gas](image)

- Main Gaseous radioactive Nuclides
  1. T (HT, $T_2$, TF)
  2. Inert gas (Kr, Xe)

2. Distribution of Tritium in TMSR

<table>
<thead>
<tr>
<th>Position</th>
<th>%</th>
<th>Bq/a*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>20 (Cited from MSRE)</td>
<td>5.5E14</td>
</tr>
<tr>
<td>Graphite</td>
<td>MSRE</td>
<td></td>
</tr>
<tr>
<td>Mezzanine</td>
<td>5.8</td>
<td>1.6E14</td>
</tr>
<tr>
<td>1st Loop</td>
<td>57.5</td>
<td>1.6E15</td>
</tr>
<tr>
<td>2nd Loop</td>
<td>16.6</td>
<td>4.6E14</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>2.8E15</td>
</tr>
</tbody>
</table>

* 10MW_th, $^7$Li99.99%, 300-days run (the calculation result)

Emission limit of tritium in 3000MW nuclear power station in China: 1.5E13 Bq/a (LWR), 4.5E14 Bq/a (HLR)

Does tritium transport into the cover gas completely? What is the chemical form of tritium?

Tritium removal: necessary and difficult
3. Considerations of Tritium control for TMSR

Remove tritium in the first loop as much as possible
Prevent tritium permeation into the second loop as much as possible

**Gas extraction system**
- In the by-pass stream
- The pump in the first loop
- Both storage and emission tanks in the first loop
- Both storage and emission tanks in the second loop

**Cover gas system**

**PM and Oil mist removal**

**Off-gas system**
- Activated carbon bed for 90-days residence time
- Ar, H₂, T, Kr-85

**Tritium removal**
- Ar, Kr-85
- Ar recycle

**Tritium barrier**

**Outside of the heat exchanger**

---

**Tritium removal**

Combination of **tritium-storage alloys** and **tritium-oxidation** with the **on-line tritium monitoring**

**Monitoring (A)**
- Ar, H₂, Kr (⁸⁵Kr), T (T₂, HT), others

**Tritium-storage alloys**
- Ar, Kr (⁸⁵Kr), others

**Monitoring (B)**

**Tritium-oxidation (Copper oxide)**
- Ar, Kr (⁸⁵Kr), T< 10⁴Bq/L

**Monitoring (C)**
- Ar recycle
Outline

I. Background

II. Roadmap of Tritium-control technologies for TMSR in CAS

III. Performances at the tritium-control technologies for TMSR in CAS

IV. Summary

II. The Roadmap of Tritium-control technologies for TMSR in CAS

(1) Tritium Behavior
   Chemical forms of Tritium in TMSR; Interaction between tritium with either of coolant or metal.

(2) Tritium Extraction
   Extraction of tritium from the molten salt

(3) Tritium Separation
   Separation of tritium from other gaseous mixture

(4) Tritium Storage
   Tritium storage with alloys after the recovery of tritium in TMSR

(5) Tritium Sampling
   Sampling tritium with different chemical forms

(6) Tritium Monitoring
Outline

I. Background

II. Roadmap of Tritium-control technologies for TMSR in CAS

III. Performances at the tritium-control technologies for TMSR in CAS

IV. Summary

1. Tritium behavior

Interaction of hydrogen isotopes with either of high-temperature molten salt or structural materials

- Test apparatus for diffusion of hydrogen isotopes in high-temperature molten salt

- Test apparatus for permeation of hydrogen isotopes in structural materials
Diffusion of Hydrogen isotopes ($\text{H}_2$, $\text{D}_2$) in high-temperature FLiNaK

Little difference of diffusion coefficient between Deuterium and hydrogen in FLiNaK

Much more solubility of deuterium than hydrogen in FLiNaK at 500-700°C

Permeability of hydrogen isotopes in Hastelloy N (left) and GH 3535 (right) alloy

$D_{\text{FLiNaK-D}} = 4.86 \times 10^{-3} \exp(-61.38 \times 10^3/R_g T)$ [m$^2$/s]
2. Tritium Extraction

Set up gas extraction system in water test loop and the separation efficiency was qualitatively analyzed.

Bubble generator

- 1 hole
- 2 holes
- 4 holes

Little effect of number of holes on the bubble size distribution at the flow rate greater than 15 m$^3$/h,

Gas separator

<table>
<thead>
<tr>
<th>Pressure Type</th>
<th>Pressure Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative Press</td>
<td>0.009 MPa</td>
</tr>
<tr>
<td>Balance</td>
<td>0.012 MPa</td>
</tr>
<tr>
<td>Positive Press</td>
<td>0.030 MPa</td>
</tr>
</tbody>
</table>

Separation efficiency of separator relating with the outlet pressure.
3. **Tritium Separation**

Successful separating xenon, krypton and hydrogen from helium environment using cryogenic technology for tritium separation

Kr、Xe <1PPb and H₂<0.1PPM after two-step frozen

Labview interface

(In-site monitoring 9-way temperature and 4-way pressure pressures as well as data acquisition)

![Labview Interface](image1.png)

4. **Tritium Storage**

Complete research platform for tritium storage using alloy

Testing system for selecting tritium-storage material

(Low pressure)  (High Pressure)

![Testing System](image2.png)

Pressure range：0.1Pa-50KPa  Pressure range：20KPa-10MPa

Testing system of tritium-reservoir performance

Tritium reservoir

![Tritium Reservoir](image3.png)

Gas distribution Detection

Control

tritium-reservoir performance Control
5. Tritium Sampling

Tritium transport in environment

Sampling tritium (HTO, HT, CH₃T, OBT): Necessary

Successful development of OBT-oxidation collection and tritium sampler

Sampling HTO, HT and CH₃T simultaneously:
Collecting efficiency >95%
6. Tritium Monitoring

- **Off-line Measurement**
  Tritium measurement platform (Detected limit of HTO < 0.5Bq/L)
  - Sampling
  - Pretreatment
  - Measurement
    - OBT collection
    - Tritium sampler
    - Distillation
    - Electrolytic enrichment
    - LSC

- **Online monitoring**
  On line monitoring of HTO, HT and Kr, Xe, simultaneously:
  - HT, HTO: 1-10^7 μCi/m^3
  - Kr and Xe: 1-10^6 μCi/m^3

---

Other studies

**Tritium barrier**

Selection of tritium barrier

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Base Metal</th>
<th>PRF**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>SS316, MANET, TIZM, Ni, Hastelloy-X</td>
<td>10 to &gt;10,000</td>
</tr>
<tr>
<td>TiC, TiN, TiO₂</td>
<td>SS316, MANET, TIZM, 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>

*permeation reduction factor
Experimental results of tritium barrier

Fabrication for tritium barrier by pack cementation

Measurement of FRF of tritium barrier

Outline

I. Background

II. Roadmap of Tritium-control technologies for TMSR in CAS

III. Performances at the tritium-control technologies for TMSR in CAS

IV. Summary
IV. Summary

1. Several test platforms for tritium control have been set up in CAS
2. Sampling and monitoring technologies have been mastered in CAS
3. Several experiments are conducting in CAS, those consist of interaction of hydrogen isotope with graphite, gas extraction in high-temperature molten salt loop
4. The chemical form of tritium in both irradiation high-temperature molten salt and graphite will be determined along with the cooperation between SINAP and MIT
Research on Techniques for Tritium Sequestration and Removal at UNM

Floren Rubio
Cole Mueller and Edward D. Blandford
University of New Mexico

Leonard J. Bond
Iowa State University
Center for Nondestructive Evaluation

Tritium Workshop
Salt Lake City, UT
October 28th, 2015

Objectives

• Previous and concurrent work on inert gas sparging
• Introduction to ultrasonics
  – Theory
  – Current industrial uses
• Inert gas sparging enhancement for salt fueled and salt cooled reactors
Sparging History in the MSR

• In the past, ORNL had investigated the use of inert gas sparging for the MSR project.

Focus of Sonomechanically Enhanced Sparging Research at UNM

• Use ultrasonic effects to increase the efficiency of inert gas sparging
  – Rectified diffusion to increase mass transfer of dissolved gasses into sparging bubbles.
  – Cavitation to reduce size of injected bubbles as well as take advantage of the degassing behavior.
  – Use water and dissolved oxygen as surrogates for molten salts and dissolved tritium.
Ultrasonic Theory

• Ultrasonic basics for process streams.
  – Sonomechanical effects
  – Sonochemical effects
• Industrial examples (non-exhaustive)
  – Metal melt degassing
  – Biological cell disruptors
  – Chemical catalysts

Sonomechanical Effects

• Rayleigh Plesset Equation
  \( R \dot{R} + \frac{3R^2}{2} = \frac{1}{\rho} \left[ \left( p_0 + 2\pi \frac{\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^n \right] + p_0 - \frac{2\pi}{R} - \frac{2\pi\dot{R}}{R} - p_0 - p_0(t) \)
  – Determines the cavitation thresholds and bubble dynamics.
  – Determines resonance frequency and size.
• Distinct regions of behavior
  – Rectified Diffusion
  – Stable Cavitation
  – Transient Cavitation
• Radiative Forces

- Near-Horn Streaming Zone Far Field
Sonochemical Effects

- Uses high intensity ultrasonics to increase chemical activity by adding energy to the chemical system by cavitation.
  - Cavitation applies localized high temperatures (~5000 K) and pressures (~10MPa).
- General categories of processes:
  - Homogenous sonochemistry of liquids
  - Heterogenous sonochemistry of liquid-liquid systems
  - Heterogenous sonochemistry of liquid-solid systems
  - Sonocatalysis

Initial Rectified Diffusion Studies

Experimental setup to capture the behavior of sparging bubbles in an ultrasonics field. The goal is to oscillate sparging bubbles in the rectified diffusion regime.

Visualizations of sparging bubbles flowing into an ultrasonic field. Bubbles were observed oscillating at around the predicted diameter.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonic Field</td>
</tr>
<tr>
<td>Intensity</td>
</tr>
</tbody>
</table>
Small Scale Test Loop

Ultrasonic Horn

Gas Removal

Cyclone Separator

Heat Exchanger

Inert Gas Injection

CW in

CW out

Test Section

DO Sensor

Small Scale Loop Test Section

Experimental Conditions

<table>
<thead>
<tr>
<th>Sonic Field</th>
<th>20 kHz, Pulsing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
<td>~0.085 W/cm²</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.25 GPM</td>
</tr>
<tr>
<td>Initial DO</td>
<td>8.0 mg/L</td>
</tr>
<tr>
<td>Final DO</td>
<td>3.0 mg/L</td>
</tr>
</tbody>
</table>
Preliminary Experimental Results for Small Scale Test Loop

Experimental Conditions

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<tr>
<td>Final DO</td>
<td>3.0 mg/L</td>
</tr>
</tbody>
</table>

Results:

20% reduction in Degassing time.

Bubbles tend to avoid near field and oscillate in anti nodes and coalesce into bubbles of the resonant size for 20 kHz.

Acoustic Reflector and Cavitation Studies

![Diagram of experimental setup with DO Sensor, Cyclone Separator, CW out, Ultrasonic Horn, CW in, and Heat Exchanger.]
Preliminary Cavitation Results

Narrow Channel Test Section

Experimental Conditions

<table>
<thead>
<tr>
<th>Sonic Field</th>
<th>20 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
<td>275 W/cm² continuous</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.25 GPM</td>
</tr>
<tr>
<td>Initial DO</td>
<td>8.0 mg/L</td>
</tr>
<tr>
<td>Final DO</td>
<td>3.0 mg/L</td>
</tr>
</tbody>
</table>

Bubbles no longer avoid near field and can start breaking up into smaller bubbles.

DO Results with Reflector and Cavitation

Result:

~70% reduction in time for the same DO reduction.

Experimental Conditions

<table>
<thead>
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<th>20 kHz</th>
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<tr>
<td>Intensity</td>
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</tr>
<tr>
<td>Final DO</td>
<td>3.0 mg/L</td>
</tr>
</tbody>
</table>
Next Steps

- Different cell geometries
  - Ring Transducers
  - Indirect Sonication
- Scale up considerations

Challenges

- Materials challenges
  - Erosion
  - Salt Compatibility
  - Activation
- High Temperatures
- High Radiation Doses
Conclusion

• Discussed the ultrasonic theory
• Ultrasonics has the potential of enhancing a known method of tritium removal for fluoride salt applications.
• Discussed some next steps and future challenges of ultrasonics with molten salts

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

John D. Stempien, PhD

Content Based on Doctoral Thesis Defense

Workshop on Tritium Control
Salt Lake City, Utah

October 28, 2015

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:
   - \(2\text{TF}(d) + \text{Cr}(s) \rightarrow \text{CrF}_2(d) + T_2(g)\)
   - Corrosion reaction consumes TF, generates \(T_2\)

2. Radiological:
   - \(T_2\) 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!

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></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><strong>FHR</strong></td>
<td><strong>11,000 (peak production rate calculated here)</strong></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

\[ \begin{align*}
\text{Neutron Transmutation Generates Tritium in Flibe} \\
^6\text{LiF} + n & \rightarrow \text{He} + (\text{TF}) \\
^7\text{LiF} + n & \rightarrow \text{He} + (\text{TF}) + n' \\
\text{BeF}_2 + n & \rightarrow ^4\text{He} + ^6\text{He} + 2F^- \\
^6\text{He} & \rightarrow ^6\text{Li} + e^+ + \bar{\nu}_e \quad (t_{1/2} = 0.8 \text{ sec}) \\
\end{align*} \]

\[ ^6\text{Li} = 0.005 \text{ wt\%} \]
\[ ^7\text{Li} = 99.995 \text{ wt\%} \]

<table>
<thead>
<tr>
<th>Cross section (b)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma^T_{\text{Li-6}} )</td>
<td>148</td>
</tr>
<tr>
<td>( \sigma^T_{\text{Be-9}} )</td>
<td>3.63\times10^{-3}</td>
</tr>
<tr>
<td>( \sigma^T_{\text{Li-7}} )</td>
<td>1.00\times10^{-3}</td>
</tr>
</tbody>
</table>
Basic Elements of TRIDENT: Effect of Redox on Corrosion and Tritium Behavior
Coolant Chemical Redox Potential Required as a Point of Reference for Modeling

Redox Potential Dictates Relative Amounts of T₂ and TF

\[ \frac{P_{T_F}^2}{P_{T_2}} = \exp\left(\frac{\Delta G_{p} - 2\Delta G_{\text{ref}}}{2RT}\right) \]

MSRE Reference
\[ \Delta G_{p} = -700.5 \text{ kJ/mol} \]

Increasing Corrosivity
Redox Potential Determines Extent of Corrosion

- For Type 316L SS in flibe at 650 °C

\[
\log [Cr_{\text{corrode}}] = K_{eq} + \log [Cr_{\text{oxid}}] + \log \left( \frac{P_{\text{T}}^{2}}{P_{\text{TF}}^{2}} \right)
\]

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

TRIDENT – TRItium Diffusion EvolutioN and Transport
TRIDENT – Selected Input/Output

• Reactor Parameters
  – Thermal power
  – Coolant inlet/outlet temperature
  – Number of coolant loops
  – Core dimensions
  – One group flux

• Fuel parameters
  – Refueling rate
  – Pebble size

• Heat exchanger parameters
  – Tube diameter
  – Number of tubes
  – Total surface area

• Tritium distribution:
  – Coolant
  – HX tube walls
  – Graphite
  – Power cycle

• Tritium release rate

• Corrosion rates

• Options
  – Redox potential
  – Performance of tritium mitigation systems

TRIDENT – Materials Property Inputs

<table>
<thead>
<tr>
<th>Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Redox Potential (specified as fluorine potential or ratio)</td>
</tr>
<tr>
<td>Flibe specific heat</td>
</tr>
<tr>
<td>Flibe density</td>
</tr>
<tr>
<td>Flibe viscosity</td>
</tr>
<tr>
<td>Henry’s law constant for T2 in flibe</td>
</tr>
<tr>
<td>Henry’s law constant for TF in flibe</td>
</tr>
<tr>
<td>Diffusion coefficient for T2 in flibe</td>
</tr>
<tr>
<td>Diffusion coefficient for TF in flibe</td>
</tr>
<tr>
<td>Diffusion coefficient for Cr2+ in flibe</td>
</tr>
<tr>
<td>Initial dissolved Cr concentration in the salt</td>
</tr>
<tr>
<td>Sieverts law constant for T2 in 316 SS</td>
</tr>
<tr>
<td>Diffusivity of T2 in 316 SS</td>
</tr>
<tr>
<td>Baseline permeation reduction factor</td>
</tr>
<tr>
<td>Cr grain boundary diffusion coefficient in 316 SS</td>
</tr>
<tr>
<td>316L SS elemental composition</td>
</tr>
<tr>
<td>316L SS density</td>
</tr>
<tr>
<td>316L SS lattice parameter</td>
</tr>
<tr>
<td>316L SS grain diameter</td>
</tr>
<tr>
<td>316 L grain boundary width</td>
</tr>
<tr>
<td>Graphite capacity for tritium</td>
</tr>
<tr>
<td>Graphite (IG-110) density</td>
</tr>
<tr>
<td>Nuclear cross sections relevant to tritium production in flibe</td>
</tr>
</tbody>
</table>
Results of TRIDENT Simulations of Baseline 236 MWt Mk1 PB-FHR

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

$T_{in} = 600 \, ^{\circ}\text{C}$

Tritium Release Rate (Ci/EFPD) to Power Cycle

- Initial buildup as tritium production balances absorption on graphite and escape to power cycle.
- Graphite begins to saturate with tritium.
- Pseudo steady state. Variation due to reduction in tritium production rate as initial Li-6 is consumed.
- Graphite saturation based on partial pressure of $T_2$ & TF and effects of online refueling.
FHR Release Rate Without Tritium Capture is High

- FHR tritium release rate with no engineered tritium mitigation systems:
  
  \~ 2500 Ci/EFPD for 236 MWt PB-FHR (10600 Ci/GWD)

- HWR tritium release rate:
  
  20 Ci/GWD

- LWR tritium release rate:
  
  \(< 1 \text{ 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
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

Counter-current Gas Stripping Schematic
Release Rate with Gas Stripping < 500 Ci/EFPD

- 10 stripping stages
- 50% of primary coolant flow (total flow: 498 kg/s, 250 L/s)
- $2 \times 10^4$ L/hr stripping gas flow rate (5.6 L/s)

![Graph showing Tritium Release Rate with and without stripping](image)

Mitigating Tritium Release: Graphite Capture

- Reactor Vessel
- Bed of graphite spheres
- Heat Exchanger
- To power cycle
Release Rate with Capture on Graphite with Online Replacement < 10 Ci/EFPD

- Pebbles replacement rate same as core pebble refueling rate (1/30th per day)
- Total bed graphite surface area: 1945 m²
- Friction pressure drop: 0.50 atm

![Graph showing tritium release rate](image)

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

![Graph showing tritium release rate with variable PRF](image)
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

### Tritium Transport with Tungsten Heat Exchanger

![Tritium Transport Graph](image)

### Variation in Tritium PRODUCTION RATE with Li-7 Enrichment

![Tritium Production Graph](image)
Variation in Tritium RELEASE RATE with Li-7 Enrichment

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

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

Conclusions on Tritium and Corrosion
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

john.stempien@inl.gov
Irradiation Testing in Support of the Tritium Production Enterprise

DJ SENOR
Pacific Northwest National Laboratory
NUEN 481/681, Texas A&M University

PNNL Roles in the Tritium Program

- TPBAR Design Authority
- TPBAR and lead use rod design and analysis
- WBN1 coolant tritium analysis and operations support
- TPBAR component development and testing
- TPBAR component procurement and assembly support
- Tritium extraction development and support
- Basic and applied research and development
  - Post-irradiation examination (PIE)
  - Ex-reactor testing
  - In-reactor testing (design, fabrication, PIE)
  - TPBAR performance model development
Tritium Production Enterprise: Background

- Tritium is required for US nuclear weapons stockpile
- Tritium has a 12.3 year half-life and must be replenished
- 1988: DOE ceased production of tritium at SRS
- 1988-1992: The US considered the use of dedicated reactors for tritium production
  - Heavy water reactors (HWRs)
  - High temperature gas-cooled reactors (HTGRs)
  - Light water reactors (LWRs)
- 1995-1998: The US considered dual-use facilities
  - Commercial LWRs
  - Accelerators
- 1995: PNNL selected by DOE to be Design Authority for Commercial Light Water Reactor irradiation demonstration

- 1995 – 1997: Lead Test Assembly (32 Tritium-Producing Burnable Absorber Rods, TPBARs) designed and built at PNNL for irradiation in TVA Watts Bar Nuclear Unit 1
- 1999: Post-irradiation examination of LTA
- 2000: The current Commercial Light Water Reactor tritium program was selected by DOE over accelerators for production
- 2001 – 2003: Design and manufacturing scale-up for production TPBARs
- 2003: First production core (240 TPBARs) irradiated at WBN1
- 2005 – 2008: TPBAR design modifications
- 2008: Modified TPBARs (Mark 9.2) first irradiated at WBN1
Tritium Target Current Technology

- TPBARs replace burnable absorber rods normally used in Westinghouse PWRs (WABAs)
  - WABA reaction:
    - $^{10}\text{B} + {\text{n}}_{\text{th}} \rightarrow ^{4}\text{He} + ^{7}\text{Li}$
  - TPBAR reaction:
    - $^{6}\text{Li} + {\text{n}}_{\text{th}} \rightarrow ^{3}\text{H} + ^{4}\text{He}$

- Reactivity worth of TPBARs is slightly greater than WABAs
- Because TPBARs provide reactivity hold-down, they are considered a safety-related component by the NRC
  - All irradiation testing work governed by QA requirements in 10 CFR 50, Appendix B so results can be applied to TPBAR modeling and design

TPBAR Irradiation Performance

- In 2004, during the first production cycle at WBN1, it was determined that TPBAR tritium permeation was higher than predicted by performance models
  - Predicted $\approx 0.5 \text{ Ci/TPBAR/cycle}$
  - Actual $\approx 4 \text{ Ci/TPBAR/cycle}$
- Even 4 Ci/TPBAR/cycle represents only about 0.04% of the tritium produced
- TVA limited the number of TPBARs that could be irradiated because of current license limits on tritium release
- Subsequent irradiations have continued, but quantities are limited to <704 TPBARs/cycle
- An irradiation testing program was implemented in 2006 to provide a scientific basis for improving performance models and providing systematic, long-term TPBAR design evolution
Irradiation Testing Program Objectives

- Overall goal is risk reduction through fundamental understanding of TPBAR performance
  - Accurately explain and predict existing permeation performance
  - Provide confidence in performance predictions to support
    - Operating condition changes
    - Supplier changes
    - Manufacturing process changes
  - Provide basis for evolutionary design changes
- The testing program was tailored to address these objectives in support of the tritium production mission

Irradiation Testing Program

- Cladding Permeation
  - TMIST-2
  - 2006-2012
- Getter Performance
  - TMED-4
  - 2008-2010
- Pellet Performance
  - TMIST-3
  - 2009-2019
- Advanced Pellet Mfg
  - TMED-3
  - 2008-2011
- Liner Oxidation
  - TMIST-1
  - TMED-1
  - 2006-2010
Motivation

- **TMIST-1/TMED-1**
  - TPBAR liners are responsible for reducing T_2O released by pellets so that T_2 can be captured by getters
  - Nascent tritium uptake in liners is beneficial
  - In-reactor oxidation rates of liner materials at low water partial pressure needed for improved TPBAR performance modeling
  - Materials with higher oxidation rates may be needed to improve TPBAR performance

- **TMIST-2**
  - Hydrogen isotope permeation through stainless steel is enhanced by irradiation (Irradiation Enhancement Factor, IEF)
  - Ex-reactor permeation may have different rate-controlling mechanism than in-reactor permeation at very low pressures (i.e. surface decomposition versus diffusion)
  - In-situ measurements support TPBAR performance modeling

Objectives

- **TMIST-1/TMED-1**
  - Quantify temperature and pressure dependence of in-reactor oxidation for liner materials
  - Quantify nascent fraction of hydrogen isotopes deposited in test specimens during oxidation
  - Evaluate irradiation performance of advanced liner materials

- **TMIST-2**
  - Quantify irradiation enhancement factor
  - Determine temperature/pressure dependence of tritium permeation through stainless steel
  - Estimate permeation contribution from triton recoil resulting from He-3 conversion
Test Specimens and Conditions
TMIST-1/TMED-1

- **Test Specimens**
  - Zircaloy-4 (radial and uniform texture)
  - Zircaloy-2
  - Surface-Modified Zircaloy-4 with four different OD Ni plating thicknesses
    - 2.5, 5, 7.5, and 10 μm
  - Seamless tubing
    - 5.3 mm OD x 0.1 mm wall x 25 mm long

- **Irradiation Conditions**
  - Temperatures of 330 and 370°C
  - He carrier gas at ~1 atm and 30 sccm
  - D₂O partial pressures of 300 and 1000 Pa
  - Irradiated for ~138 effective days at temperature (peak fast fluence, E>0.1 MeV, ~2 x 10²¹ n/cm²)
Capsule Design
TMIST-1/TMED-1

- Four specimens per capsule
- Four capsules with individual temperature control gas
  - Each specimen had unique gas gap dimensions within capsule
- Active temperature control using Type K thermocouples and He-Ne mixture in gas gap
- Fixturing to center specimens in capsule, minimize axial temperature gradients, and accommodate adjacent specimen degradation

Post-Exposure Specimen Condition

**Ex-Reactor Exposure**
- Zircaloy-4 – Fully Intact
  - 330°C, 300 Pa
- SM-10 – Some Distortion and Cracking
  - 330°C, 1000 Pa

**In-Reactor Exposure**
- Zircaloy-4 – Fully Intact
  - 330°C, 300 Pa
- SM-10 – Partially Consumed
  - 330°C, 1000 Pa

Because of SM specimen degradation, mass measurements were only useful for the Zircaloy samples
Experiment Performance
TMIST-1/TMED-1

- No significant depletion of D$_2$O at either supply pressure
- D$_2$O leak observed during second ATR cycle in 1000 Pa/370°C capsule
  - Leak mitigated by differential pressure control in temperature control gas
  - Post-irradiation neutron radiography revealed a tear in the bellows as the cause of the leak
- Capsule temperature setpoints maintained to within ±5°C
- Four thermocouples failed during irradiation (one per capsule)
  - Temperature control maintained with redundant thermocouples

Results
TMIST-1/TMED-1

- Mass Gain - Zircaloy
  - Increased with temperature both ex-reactor and in-reactor
  - No obvious dependence on D$_2$O partial pressure
  - Irradiation enhancement by a factor of ~2-3X at both temperatures for Zircaloy specimens
- Fourier Transform Infrared Spectroscopy
  - FTIR oxide thickness measurements unreliable due to fine structure patterns in the diffraction spectra
  - FTIR data showed uniform oxidation along sample length on both inner and outer surfaces
Results
TMIST-1/TMED-1

Oxide Thickness - Zircaloy
- Measured via optical and scanning electron microscopy
- Mass gain measurements used to compare measured and calculated oxide thickness assuming uniform growth of tetragonal zirconia
- In Zr-base alloys, a transition from dense tetragonal to porous tetragonal + monoclinic oxides occurs around 2 μm
  - Care must be taken when comparing pre- and post-transition oxides

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Results
TMIST-1/TMED-1

Oxide Thickness – Surface Modified
- Little irradiation enhancement is evident with thicker SM layers
- Thicker SM layers were very prone to spalling
- Dependence on both temperature and pressure
- Inner surface of SM samples exhibited significantly more oxidation than Zry-4 specimens, indicating heat treatment affected corrosion resistance of substrate
- Large radial cracks observed in SM samples extending into substrate
- Prevalence of cracks higher for thicker SM samples
- SM layers thicker than 2.5 μm are probably not desirable due to extent of oxidation and deleterious impact on Zircaloy substrate

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Results
TMIST-1/TMED-1

- Nascent Hydrogen Uptake - Zircaloy
  - Ex-reactor results appear insensitive to temperature and pressure
  - Temperature and pressure dependence of in-reactor results is unclear
  - Hydrogen uptake can be significantly enhanced by irradiation (1-4X)

- Nascent hydrogen Uptake – Surface Modified
  - Significantly more uptake than Zircaloy samples at same conditions
    - 2,000-30,000 ppm D
  - Irradiation enhancement of uptake (1-6X) is greater than irradiation enhancement in oxide thickness
  - Temperature and pressure trends are inconsistent
  - No significant dependence in D₂ uptake on SM layer thickness
  - Thicker SM layers had higher H₂ uptake (up to 10% of D₂ uptake)

- Hydride Morphology
  - Appears to be similar for in-reactor and ex-reactor exposure
  - Irradiation does not seem to affect hydride morphology
  - Hydride morphology dictated by Zircaloy texture
    - Hydrides form parallel to basal planes
Test Specimen and Conditions

**TMIST-2**

- **Test Specimen**
  - 316 stainless steel
  - 0.85 cm ID x 0.97 cm OD

- **Irradiation Conditions**
  - Temperatures of 292 and 330°C
  - He carrier gas at ~1 atm and 30 sccm
  - Tritium partial pressures of 0.1, 5, and 50 Pa, premixed in carrier gas cylinders
  - Irradiated for ~200 effective days (peak fast fluence, E>0.1 MeV, est. ~3 \times 10^{21} \text{n/cm}^2)
  - Temperature and pressure set points changed online after obtaining satisfactory permeation measurements on each experiment step
  - At least two separate measurements at each combination of temperature and pressure to evaluate possible fluence effects

---

Permeation Measurement System

**TMIST-2**

- **Tritium Permeation Measurements**
  - Real-time indication of tritium permeation rate provided by ion chambers
  - Used to determine when permeation reached steady-state (usually several days)
  - Quantitative tritium permeation results determined from periodic scintillation counter measurements of DI water bubbler vials
    - At least two collections of at least 24 hr each time a temperature/pressure combination was tested
    - Two banks of three vials each to differentiate between T_2O/HTO and T_2/HT
Results

TMIST-2

- In-reactor permeation rates through TPBAR cladding measured for the first time
- Permeation data show definite irradiation enhancement relative to ex-reactor behavior
  - Mechanism unclear
  - Currently evaluating microstructural evolution of TPBAR cladding during irradiation
- New TPBAR permeation model developed to address irradiation effect

TMIST-2 Data Showing Enhanced (~3X) In-Reactor Tritium Permeation Rate Through Uncoated Stainless Steel

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Rate-Limiting Permeation Mechanisms

- Ex-reactor permeation measurements
  - > 100 Pa → Diffusion-limited → p^{0.5}
  - < 100 Pa → Surface-limited → p^{1}
- In-reactor permeation mechanism uncertain
  - Direct dissociative chemisorption
    - Molecules adsorb and readily dissociate upon contact
    - Disrupted ex-reactor at low pressure by surface impurities or oxide films
  - Radiation-enhanced dissociation
    - Radiolysis of T_{2} in gas phase
    - Physical or chemical changes in surface in-reactor

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Results
TMIST-2

- Pressure dependence of $p^{0.5}$ observed
  - Suggests tritium permeation is rate-limited by diffusion, not surface decomposition ($p^1$)
- Temperature dependence consistent with diffusion
  - Scatter prevents determination of statistically significant trends in apparent activation energy
  - Nominal activation energies ~100 kJ/mol, consistent with diffusion-limited mechanism
  - Trend for increased permeation with temperature observed within the scatter, as expected

Microscopy
- After irradiation, grain boundaries are not as well defined
- TEM necessary to evaluate extent of irradiation damage

Auger Electron Spectroscopy
- After irradiation, the inner surface of the specimen appears to be enriched in carbon and depleted in oxygen
  - Reducing atmosphere during test
  - Source of carbon?
Results

TMIST-2

▶ Low-level $^3$He Assay

- Sample outer surface area below active region sputter-coated with Al to inhibit permeation
- $^3$He measurements made within and below active (hot) sample region
- $^3$He acts as a tracer for tritium
- Higher concentration of $^3$He in cold, sputter-coated region suggests slower tritium permeation

![Graph showing $^3$He measurements vs. distance from sample bottom](image)

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Results

TMIST-2

▶ Utilized source gas mixture of $^4$He + 1% $^3$He

- Calculations determined the conversion rate of He-3 to tritium
  - Used average neutron energy spectra for ATR
- Triton recoil distance large relative to inner diameter (2.6 vs. 0.85 cm)
- Implantation depth in stainless steel is ~ 2 μm
- Less than 4.1% (2σ confidence) of the tritium resulting from He-3 conversion permeated through the test specimen

![Diagram showing neutron and triton interactions](image)

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Data from the Testing Program Has Improved TPBAR Performance Predictions

- TROD performance prediction code models updated with data from TMIST-1, TMED-1, TMIST-2, and TMED-4
- Discrepancy between predicted and observed permeation decreased by ~30%
- Time dependence still not correctly modeled
  - Will be improved by TMIST-3 data

Pellet Performance Irradiation Experiment TMIST-3

- Data from TMIST-3 will
  - Explain time dependence of pellet tritium release and its relationship to TPBAR permeation
  - Evaluate the speciation of tritium release as a function of burnup, burnup rate, and time \((T_2O \text{ versus } T_2)\)
  - Define relationships between pellet burnup, burnup rate, and tritium release to help define an acceptable TPBAR operational envelope
  - Improve fundamental understanding of pellet microstructure and its effects on performance
  - Provide a better definition of the pellet burnup limit
  - Determine whether modifications to the pellets could improve TPBAR performance
    - Increased tritium retention
    - Increased TPBAR void volume
Test Specimens
TMIST-3

- Test specimens
  - Standard TPBAR LiAlO$_2$ pellets
    - 2 μm grain size
    - 97-98% TD
    - 1 mm wall thickness
  - Large grain LiAlO$_2$ pellets
    - 10 μm grain size
  - Porous LiAlO$_2$ pellets
    - Small pores (~90% TD)
    - Large pores (~85% TD)
  - Thin-wall LiAlO$_2$ pellets
    - 0.76 mm wall
  - Cermet pellets
    - LiAlO$_2$ particles in Zr matrix
    - Four ceramic particle loadings from 10-40 v/o

Capsule Design
TMIST-3

- Two test trains
  - TMIST-3A – Irradiate for ~1.5 yr
  - TMIST-3B – Irradiate for ~2.5 yr
- Two capsule types in each test train (41 total)
  - Flow-through – 15 total
  - Closed – 26 total
- All capsules have active He-Ne temperature control gas
  - One capsule designed to operate over a wide temperature range to evaluate temperature effects
- Flow-through capsules have He sweep gas to remove tritium for ex-reactor sampling
- 106 total leads for both test trains
Capsule Design

**TMIST-3**

- **Flow-through capsules**
  - Used for time, burnup, burnup rate, and temperature dependent tritium release measurements
  - Tritium released from pellets is carried to ex-reactor measurement system for analysis
  - Total tritium measurement only

- **Closed capsules**
  - Used for speciation measurements and pellet integrity/retention tests
  - Tritium released from pellets as T\(_2\) and T\(_2\)O is spatially segregated and gettered in-situ
  - Speciation data inferred from post-irradiation examination tritium assays
Outline

Post-Irradiation Examination for FS-1/2
- Thermal tritium release
- Imaging
- Other methods

IRP-2 Experiments
- Tritium uptake in graphite
- Tritium and activation product release
- Tritium diffusion from salt through metals
- Ongoing PIE

Suggestions, Lessons Learned?

Planned Post-Irradiation Tritium Tests

- Thermal release measurement of tritium uptake
  - Components of FS-1 and FS-2 will be progressively heated to above their irradiation temperatures to examine the tritium release
  - Important to have real-time and LSC measurement

- New methods for tritium measurement are being examined:
  - Graphite powdering and/or digestion followed by LSC
  - Pyrolysis followed by LSC
  - Proton or deuterium ion beam irradiation and gamma or fast neutron detection
  - Beta-plate imaging (concentration and gradients)
Upcoming MITR FHR Irradiations

- Designing new experimental facilities based on lessons learned from the first two flibe irradiations
  - Control of salt condensates to prevent accumulation in gas lines
  - Off-gas holdup for short half-life decay (N\textsuperscript{16} and O\textsuperscript{19})
  - Avoiding <200°C radiolysis (fluorinated compound production)

- Collaboration with Chinese Academy of Sciences on irradiation of new graphite and SiC materials in flibe

- Three types of experiments planned for IRP-2
  - Release of tritium and activation product gasses from flibe
  - Tritium uptake on graphite
  - Tritium diffusion through metals

(1) Tritium and Activation Product Release

- Initial MITR irradiations highlighted (1) the effects of unmitigated activation and radiolysis product release, and (2) variability of that release with the salt temperature

- This test is dependent on simulating the FHR core environment because the proper neutron spectrum, neutron and gamma flux, and temperature is needed

- Planning new dedicated salt irradiation facility
  - Minimize tritium sinks
  - Maximize possible flibe volume
  - Variable cover gas (sparging?) with optional H injection up- and downstream
  - Improved “fast sampling”
  - Freedom to vary reactor power / temperature (electrical secondary heating)
(2) Tritium Uptake in Graphite

- The capture of tritium via adsorption onto or diffusion into graphite has the potential to be the primary method of tritium inventory management during FHR operation.
  - Tritium uptake into graphite observed during initial irradiations, but was not primary focus

- Options for uptake facility
  - In-core, most representative environment but most limiting for size, controls, sampling
  - Independent facility using tritiated flibe generated in the MITR, gives flexibility

- Variables to investigate
  - Saturation
  - Temperature and thermal gradients
  - Radiation damage to materials, radiolysis, *in situ* generation
  - Salt chemistry, cover gas mixture
  - Material preparation (graphite types, surface preparation, etc.)

(3) Tritium Diffusion Through Metals

- Tritium transport out of the primary system is a critical phenomenon to understand and reliably control
  - Important to enable coupling to once-through gas turbine (i.e. salt-air heat exchangers)

- Work is underway (UNM) investigating double-walled heat exchangers

- Out-of-reactor facility with tritiated flibe to measure tritium transport from salt through metal surfaces
  - Primary piping
  - Heat exchangers
  - DRACS components

- Need to consider test matrix
  - Flow or static
  - Salt chemistry and temperature
  - Thermal gradients
  - Barrier coatings
  - Sweep gasses and secondary side media (air, helium, water, salt)
Additional analysis on IRP-1 specimens continues – wealth of data is available

- Weight, dimensions, spectroscopy, optical microscopy, and profilometry completed
- Analysis of cracking in TRISO particles linked to combination of irradiation and salt freeze-thaw cycles

**Post-Irradiation Examination**

![Graph showing weight change (mg/cm²) for different materials]

*Accelerated corrosion of metals in-reactor compared to UW autoclave tests.*

**Irradiated Microstructure Analysis**

- Have begun x-ray diffraction analysis of irradiated specimens
  - SiC has lower activity, good for initial measurements
  - Hastelloy N and stainless steel specimens planned
  - Probing changes in phases, swelling

- SEM/EDS starting soon
  - Identify microstructural features such as grain size, layer formation
  - Map depletion/infiltration of elements
  - Important for SiC/SiC and C/C fiber composites with matrix porosity, fiber-matrix interfaces

- Tritium thermal extraction
  - Have custom-designed furnace for tritium desorption from solids with re-capture for counting
  - Also capable of running out-of-pile tritium exposures at high temperature.
Investigation of Tritium Control and Release Mitigation Options in Double-Wall Twisted-Tube Heat Exchangers (DT-HXRs)

Bryan Wallace
Joel Hughes and Edward D. Blandford
University of New Mexico

Tritium Workshop
October 2016
Salt Lake City, Utah
Double-Wall Twisted-Tube Heat Exchangers

Double-wall twisted-tube heat exchangers are being investigated as an option for the removal of heat from molten salt coolant.

- Double-wall tubing ideal for prevention of fluids mixing
- Twisted-tubes provide increased heat transfer between mediums

Tritium Control in DT-HXRs

We will be investigating multiple methods for the control of tritium permeation throughout the DT-HXR system.

<table>
<thead>
<tr>
<th>Intermediate Fluids</th>
<th>Surface Coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>Carbides</td>
</tr>
<tr>
<td>He/O</td>
<td>Aluminides</td>
</tr>
<tr>
<td>Li</td>
<td>Titanium Ceramics</td>
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<tr>
<td></td>
<td>Tungsten</td>
</tr>
<tr>
<td></td>
<td>Yttrium (for Gettering)</td>
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</tbody>
</table>
Current Status of DOWTHERM Heat Transfer Loop

- Project start October 1, 2015
- Currently constructing experimental loop
- Low pressure heat exchangers purchased and fabricated
- Low pressure testing to begin in 2016

Project Scope

- Scoping simulation and trade-off studies for intermediate fluids considering tritium recovery
- Low pressure testing with DT-HXR
- Work on optimizing high pressure heat exchanger design
- High pressure testing coupled to S-CO$_2$ loop at SNL
- Data reduction, validation, and inspection techniques
Questions?