Working Paper for
Materials, Activation, Tritium, and Transport (MATT) Group

TRITIUM CONTROL AND CAPTURE IN SALT-COOLED FISSION AND FUSION REACTORS: STATUS, CHALLENGES, and PATH FORWARD

Integrated Research Project Workshop
Fluoride-salt-cooled High-Temperature Reactor (FHR) Workshop
Berkeley, California
April 14-15, 2015

Discussion paper reviews why the interest in salt-cooled fission and fusion energy systems and the current status of technologies to remove tritium from 600 to 700°C salts. The primary emphasis is on tritium control but related subjects such as noble metal removal from salts (MSR) are also discussed where the same technology may be used for multiple purposes. Appreciate any review comments. Paper will be converted to a journal paper after the workshop. Please send any comments or suggestions to cforsber@mit.edu

Revision Date: 29 March 2016

TRITIUM CONTROL AND CAPTURE IN SALT-COOLED FISSION AND FUSION REACTORS: STATUS, CHALLENGES, and PATH FORWARD

Charles W. Forsberg[1], Stephen Lam[1], David M. Carpenter[2], Dennis G. Whyte[3], Raluca Scarlat[4], Cristian Contescu[5] and Liu Wei[6]

[1]Dept. of Nuclear Science and Engineering, MIT, 77 Massachusetts Ave., Cambridge, MA 02139, cforsber@mit.edu
[2]Nuclear Reactor Laboratory, MIT, 77 Massachusetts Ave., Cambridge, MA 02139
[3]Plasma Fusion Center, MIT, 77 Massachusetts Ave., Cambridge, MA 02139
[4]University of Wisconsin, Madison, WI 53706
[5]Oak Ridge National Laboratory, Oak Ridge, TN 37831
[6]SINAP, 500 Jialuo Hwy, Jiading, Shanghai, China, 201800

Three advanced power systems use liquid salt coolants that generate tritium and thus face the common challenges of containing and capturing tritium to prevent its release 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 clean fluoride salt coolants. Molten salt reactors (MSRs) dissolve the fuel in a fluoride or chloride salt with release of fission product tritium into the salt. In both systems, the base-line salts contain isotopically separated ^{7}Li 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. For high-magnetic-field fusion machines, the use lithium enriched in ^{6}Li is proposed 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 for fusion blankets and as coolants.

Recent technical advances in these three reactor classes have resulted in increased government and private interest—and the beginning of a coordinated effort to address the tritium control challenges in 700°C molten salt systems. We describe characteristics of salt-cooled fission and fusion machines, the basis for growing interest in these technologies, tritium generation in molten salts, the environment for tritium capture, models for high-temperature tritium transport in salt systems, alternative strategies for tritium control, and ongoing experimental work. Several methods to control tritium appear viable. Limited experimental data is the primary constraint for designing efficient cost-effective methods of tritium control.

I. INTRODUCTION

Recent technology advances are creating growing interests in three nuclear technologies that require high-temperature salt coolants: (1) Fluoride-salt-cooled High-Temperature Reactors (FHRs) with solid fuel and liquid salt coolants, (2) Molten Salt Reactors (MSRs) with the fuel dissolved in the salt coolant, and (3) high-magnetic-field fusion machines with immersion salt coolant blankets. In each system the coolant is a high-temperature liquid salt that produces tritium; thus, there is the common technical challenge of tritium control and capture in salt at temperatures typically between 600 and 700°C.

Two sequential workshops were held to address common challenges: (1) *Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking* [1, 2] and (2) *FHR Integrated Research Project (IRP-2) Workshop 2: Benchmarking* [3]. 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, (2) initiate an effort for benchmarking of experiments and models, and (3) encourage cooperation between different groups working on the same challenges.

This paper summarizes workshop results 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 tritium barriers (IV).

II. SALT-COOLED POWER SYSTEMS

There is a rapidly growing interest in fission and fusion systems using salt coolants [4, 5] that is driven by separate developments in (1) FHRs, MSRs, and fusion and (2) gas turbine power systems that can couple to salt-cooled reactor systems. The interest in developing these technologies is the driving force for the need to develop tritium control technologies in 700°C salt.

The choice of salt depends upon the application but in most cases the base-line coolant is a lithium-beryllium-fluoride salt known as flibe ($^7Li_2BeF_4$) because it has the best thermal hydraulic and neutronic properties. However, it does generate tritium if irradiated. There have been many studies comparing salts for specific applications [6-12]. The characteristics of the flibe as well as some of the other potential salts are listed in Table 1.

Table 1. FHR Coolant Options[1]

Coolant	T_{melt} (°C)	T_{boil} (°C)	P (kg/m^3)	ρC_p (kJ/m^3 °C)
66.7^{7}LiF-33.3BeF$_2$	**459**	**1430**	**1940**	**4670**
59.5 NaF-40.5 ZrF$_4$	500	1290	3140	3670
26 ^{7}LiF-37 NaF-37 ZrF$_4$	436		2790	3500
51 ^{7}LiF-49 ZrF$_4$	509		3090	3750
Water (7.5 MPa)	0	290	732	4040

[1] Compositions in mole percent. Salt properties at 700°C and 1 atmosphere. Pressurized water data shown at 290°C for comparison

All proposed salts are multicomponent salts to lower the melting points. 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.

II.A. Salt-Cooled Power Systems

II.A.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 the FHR 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 [13] uses 3-cm diameter graphite pebbles with embedded coated-particle fuel—the same basic fuel geometry 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 [14] 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-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).* This FHR core design [15, 16] is somewhat similar to the operating British Advanced Gas-Cooled Reactors (AGRs) except for use of a salt coolant, higher power densities and the details of the fuel design. The AGRs are graphite-moderated carbon-dioxide-cooled high-temperature reactors with gas exit 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.

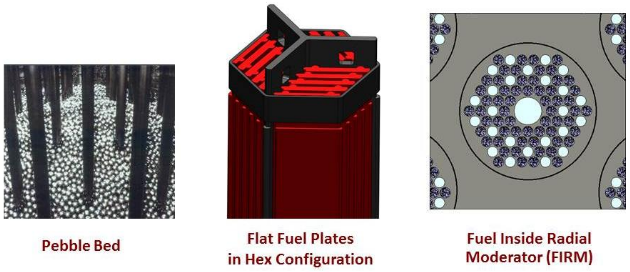

Fig. 1. Alternative FHR Fuel Designs

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.

The base-line coolant is a lithium-beryllium-fluoride salt known as flibe ($^7Li_2BeF_4$) because it has the best thermal hydraulic and neutronic properties but it has two drawbacks. Isotopically-separated ^7Li is expensive and beryllium is toxic. The other salts can be used but with neutronic or thermal hydraulic penalties. All the concepts have operating temperatures between 600 and 700°C respectively. The lower temperature is partly based on being significantly above the melting points of these salts and the higher temperature is based on existing commercially-qualified materials for primary heat exchangers. Because FHRs use liquid rather than gas coolants, their power densities are four to ten times higher than comparable gas-cooled reactors.

II.A.2. Molten Salt Reactors (MSRs)

Molten salt reactors were first developed as part of the aircraft nuclear propulsion program in the 1950s and then as thermal-neutron-spectrum breeder reactors 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 ($^7Li_2BeF_4$) 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 [17-20] there has been a renewed interest in MSRs for several reasons—partly because of changing goals and partly because of technological advances over the last several decades in other fields that have addressed some of the MSR developmental challenges.

Fig. 2. Molten Salt Reactor Experiment

- *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 longer-lasting materials for reactor internals. New materials may enable high-temperature (>1000°C) distillation to simplify removal of fission products from the liquid fuel salt. Those materials include carbon-carbon composites and high-temperature metals such as molybdenum where new high-temperature additive manufacturing technologies enable fabrication of complex components including distillation columns to enable salt purification.
- *Safety*. MSRs enable alternative safety strategies relative to solid fuel reactors including (1) dumping the liquid fuel to critically-safe passively-cooled tanks under any accident scenario and (2) potentially minimizing 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 advanced separation technologies to remove and solidify selected fission products while the reactor is on line.

Three classes of MSRs are being investigated [20] with different characteristics, but have common high-temperature salt challenges.

- *Thermal-neutron-spectrum MSRs*. These MSRs use fluoride salts with fuel dissolved in the salt and graphite in the reactor core to create a thermal neutron spectrum. The MSRE was this type of MSR. The Chinese Academy of Science (CAS) plan to build a small 2-MWt MSR by 2020 with an emphasis on the thorium fuel cycle for fuel sustainability.
- *Fast-spectrum MSRs*. These MSRs use either fluoride or chloride salts with fuel dissolved in the salt. There are no neutron moderators in the system. Examples include the European concept that uses a lithium heavy-metal fluoride salt and the Terrapower concept that uses a chloride salt.
- *Fast-spectrum Pin MSRs*. These MSRs [21] use two molten salts with reactor designs somewhat similar to sodium-cooled fast reactors. The fuel pins contain liquid chloride salts with dissolved fuel. A second clean liquid salt is used to cool the fuel assemblies. The replacement of solid fuel in the fuel pins with a liquid fuel salt (1) allows higher temperatures, (2) enables a traditional fast reactor with a large negative temperature coefficient due to expansion of the liquid fuel with temperature, (3) minimizes stresses on the cladding, and (4) provides a simplified method to recycle fuel or replace cladding.

II.A.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 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 while minimizing electrical consumption by the magnets. However, superconductors lose their superconducting properties in high magnetic fields.

In the last five years, methods have been developed to manufacture Rare-Earth Barium Copper Oxide (REBCO) superconductor tapes. This 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 with power levels of ~10 MW. 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 [22]. Figure 4 shows the high-magnetic field fusion system in more detail.

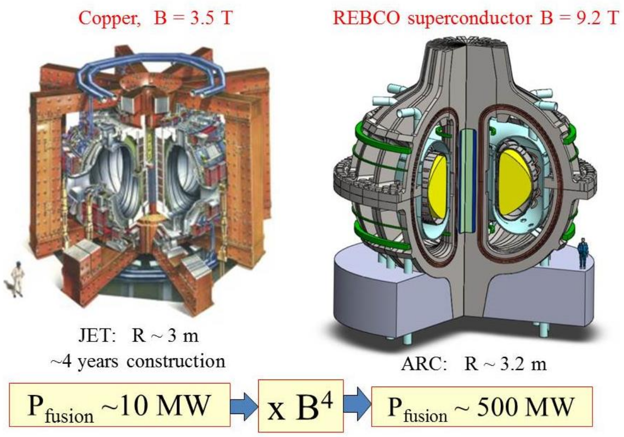

Fig. 3. Impact of Higher-Field Superconductors on the Size of Magnetic Fusion System

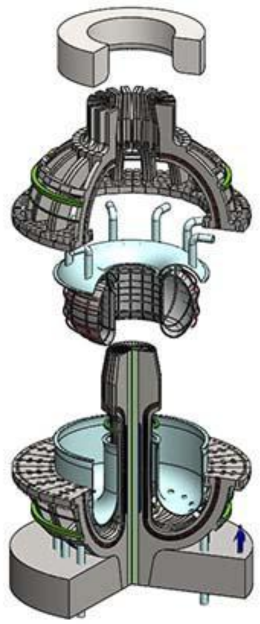

Fig. 4. ARC Concept with Salt Blanket (blue) and Demountable Superconducting REBCO Magnets

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 higher power densities. Historically proposed blankets have been solid lithium-containing materials for production of tritium fuel ($^{6}\mathrm{Li} + n \rightarrow {}^{3}\mathrm{H} + {}^{4}\mathrm{He}$). The higher power densities will likely require changing to a liquid blanket (Fig. 4) containing lithium—most likely flibe ($66.7{}^{6}\mathrm{LiF}$-$33.3\mathrm{BeF}_2$). With a liquid blanket (blue in figures) it is easier to assure effective neutron shielding (no holes or cracks) with ultra-high radiation levels. Fusion generates about 17 MeV per fusion of tritium and deuterium—most of this energy is in the form of 14 MeV neutrons. The liquid salt slows down the neutrons, captures the neutrons to produce tritium, and absorbs the heat (14 MeV) in the liquid. The heat transfer challenges in solid fusion blankets become very difficult at these very high power densities.

The liquid blanket choices are (1) 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 with the very large magnetic fields associated with these new superconductors.

II.B. 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 were chosen because they could meet the requirements of the jet engines—delivering heat to the power cycle between 600 and 700°C. Recent advances in utility natural-gas combined-cycle technologies now enable coupling these reactors to an open Nuclear Air-Brayton Combined Cycle (NACC) or closed Brayton power cycle. This enables providing 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 (Fig. 5) of a NACC [23-26], atmospheric air is filtered, the air is compressed, heat is added from the reactor through a liquid-salt coiled-tube heat exchanger (CTHX), the hot compressed air goes through a turbine to produce electricity, the air is reheated and goes through a second turbine, the warm air exiting the gas turbine goes through a heat recovery steam generator (HRSG) to generate steam that is used to produce added electricity, and the air is exhausted to the stack. 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.

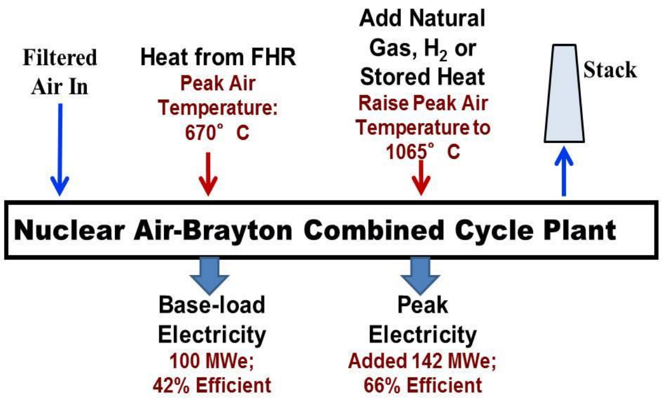

Fig. 5. Nuclear Air-Brayton Combined Cycle (NACC)

The base-load NACC temperatures, determined by heat-exchanger materials constraints, are far below maximum peak gas turbine temperatures. Thus, there is the option of adding heat (natural gas, stored heat, etc.) after the nuclear heating to further raise compressed gas temperatures before entering a power turbine—a topping cycle. The incremental heat-to-electricity efficiency depends upon the design, ranging from 66 to 70%. This is the most efficient system known to convert heat to electricity based on existing technology.

An economic analysis [27] 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 [28-30]. In such utility systems it is proposed that a Firebrick Resistance-Heated Energy Storage (FIRES) system [26] replace the use of natural gas for providing heat to produce peak electricity in the NACC power cycle. 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.

The advanced gas-turbine power cycles create large economic incentives to develop salt-cooled reactor systems using salt coolants originally developed to enable coupling a reactor to a jet engine.

III. SALT CHEMISTRY AND TRITIUM GENERATION

Table 2 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. The choice of salt depends upon neutronic and thermal-hydraulic considerations.

Table 2. Salt Characteristics of Different Systems

Property	FHR	MSR	Fusion
Salt	Fluoride	Fluoride or Chloride (fast spectrum only)	Fluoride (Flibe)
Impurities	Corrosion impurities and possible fission product impurities	High concentrations of fission products and actinides	Corrosion impurities
Use lithium salts	Optional	Depends upon goals	Required
Tritium production	Small (^{7}Li in Coolant)	Small (^{7}Li in Coolant)	High (^{6}Li in Coolant)
Tritium value	Waste	Waste	Fuel
Carbon in system	Yes	Depends upon option	No
Redox control	Ce^{+2}/Ce^{+3}, other	U^{+3}/U^{+4}	Ce^{+2}/Ce^{+3}, Be, other

Most proposed salts contain lithium because of its ability to lower the melting points of these salts to a few hundred degrees C. 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 the required salt coolant because it maximizes tritium production.

Under neutron irradiation these salts generate tritium by multiple pathways.

$$^{6}\mathrm{LiF} + n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{HF} \tag{1}$$

$$^{7}\mathrm{LiF} + n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{HF} + n' \tag{2}$$

$${}^{19}_{9}\mathrm{F} + n \rightarrow {}^{17}_{8}\mathrm{O} + {}^{3}_{1}\mathrm{H} \tag{3}$$

$${}^{9}_{4}\mathrm{BeF}_2 + n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{6}_{2}\mathrm{He} + 2\mathrm{F} \tag{4}$$

$${}^{6}_{2}\mathrm{He} \rightarrow {}^{6}_{3}\mathrm{Li} + e^{+} + \overline{\nu}_{e} \quad \left(t_{1/2} = 0.8\sec\right) \tag{5}$$

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 ^{6}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 where 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 generated. To avoid corrosion, redox control agents can be added to the coolant for 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, atomic ^{3}H from $^{3}H_2$ 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 H_2 in the cover gas may also shift the redox potential of the salt, thus affecting corrosion control [31-36].

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 in a FIRM core design. For one design of pebble-bed FHR, it was estimated [13] 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 [37] of pressurized water reactors (2.2 Ci/GWe/d), or 810 Ci/GWe/y.

Stempien [34-36] has built a model (Fig. 6) for FHRs that accounts for tritium production, corrosion, and 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.

TRIDENT has been used to model an FHR with a carbon bed for tritium removal as $^3H_2$ (the model accounts for the diffusion and removal of HF to the graphite as well). The model results are shown for one case in Table 3. In this case the carbon bed is designed to enable sufficient tritium removal to limit tritium releases to acceptable levels. TRIDENT simulates tritium production and removal with time including buildup of tritium in sinks and other transient phenomena.

Several conclusions follow 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 [37]. 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}HF is also given but HF can't diffuse through hot metal. Graphite absorbs both $^3H_2$ and ^{3}HF.

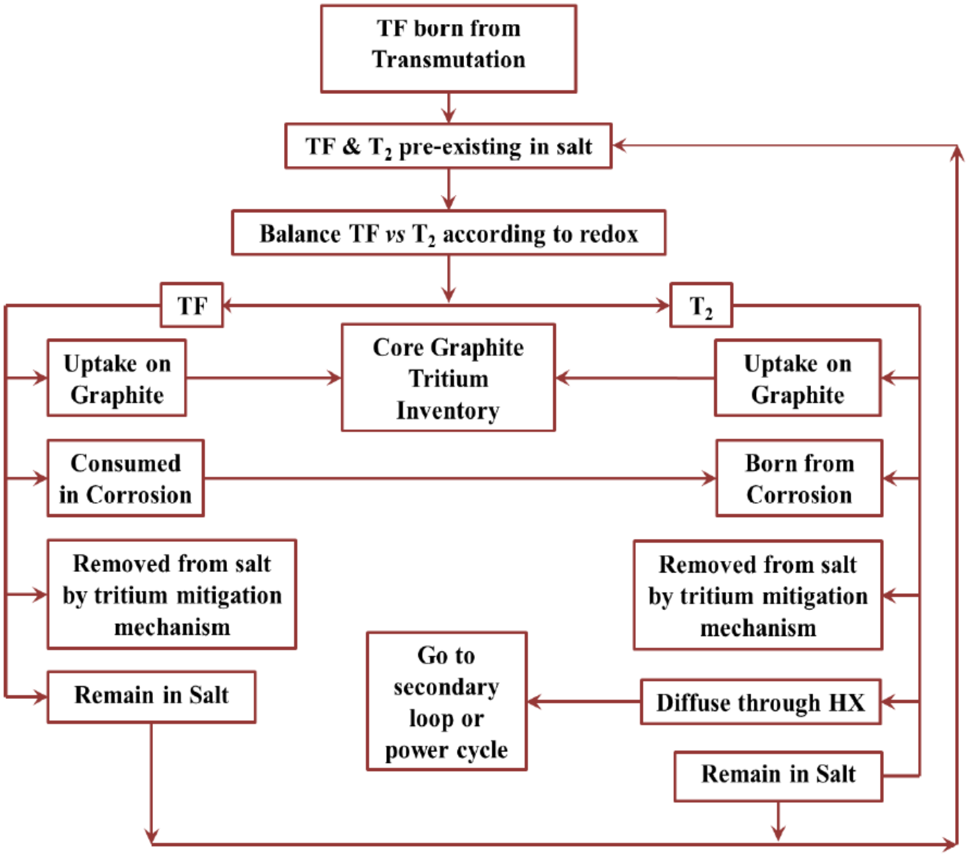

Figure 6. TRIDENT: Tritium Diffusion EvolutioN and Transport

The requirements in Table 3 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, 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. Salts dissolve oxides and most other permeation barriers and thus in most cases the barrier would have to be on the outside of the tube. The exception is tungsten that is corrosion resistant in liquid salts.

There are other incentives to minimize tritium levels in reactors. If there is a higher partial pressure of tritium, there will be more sorption of tritium on carbon and other materials in the reactor core. Under accident conditions where the temperature increases, this tritium would be desorbed.

Table 3. TRIDENT Output for FHR with Tritium Carbon Absorber Bed

Temperatures*	
Coolant Freezing	459^{o}C (FliBe)
Operating Core Outlet	700^{o}C
ATWS	$<800^{o}$C
Coolant Boiling	1400^{o}C (FliBe)
Pressures (primary loop)	
p_{T2} Unmitigated	3.3-20 Pa
p_{T2} with Graphite Capture	**0.03-0.08 Pa** (Peak release 7.5 Ci/GW/d)
p_{TF} Unmitigated	0.03-0.075 Pa
p_{TF} with Graphite Capture	**0.0027-0.0045 Pa** (Peak release 7.5 Ci/GW/d)

*TRIDENT Simulation

There may be other incentives to keep tritium levels very low in the salt coolant. There is some evidence that the permeation rate for metal heat exchangers outside the reactor below 100 Pa is surface limited and varies as the hydrogen pressure whereas above 100 Pa the permeation rate is diffusion limited and varies as the pressure to the one-half power [38]. The practical implication is that the permeation rate decreases at a faster rate as the pressure goes below 100 Pa (surface limited)—implying the potential that permeation rates may be an order of magnitude less at very low tritium pressures.

IV. TRITIUM CONTROL AND CARBON

Carbon in the form of isotropic graphite is used in FHRs and thermal-spectrum MSRs as a neutron moderator. The fuel microspheres designed for FHRs and HTGRs are dispersed in graphite matrix and packed as pebbles, compacts (FIRM assembly) or other geometries. There is a great deal of information about the behavior of graphite in nuclear reactors. In the U.S., most of the work on nuclear-grade graphite has been done at Oak Ridge National Laboratory [39, 40].

The Molten Salts Reactor Experiment at ORNL proved that graphite can physically withstand intense neutron irradiation in high temperature flibe [41] and also showed significant tritium uptake in the graphite. It also identified issues that need to be mitigated: (1) salt penetration in graphite porosity may cause local hot spots where the graphite damage may be accelerated; and (2) retention of fission products (^{135}Xe, noble metals) has an adverse effect on reactor performance by absorbing neutrons. In this context, it is important to make a clear distinction between a MSR with dissolved fuel and an FHR or fusion reactor with clean salt. In the MSR, the salt with fuel generates heat at high rates due to fission in the reactor core. If any of that salt penetrates the carbon, it brings with it the high rate of heat generation that can create a hot spot where the salt penetrates the carbon.

The solution identified by MSRE project and pursued currently by Chinese Academy of Sciences [42] is sealing graphite porosity by surface coating with an impermeable layer of pyrolytic carbon (PyC). This layer has high degree of planar orientation and substantially reduces infiltration of molten salt and gases in graphite but requires careful engineering to avoid the potential for separation because graphite and PyC have different rates of dimensional changes during irradiation [43]. The PyC coating is expected to substantially reduce the structural damage that might be caused by the known tendency of Li^{+} and F^{-} ions intercalation of between graphite layers [44]. However, such layers may also impact tritium kinetics of absorption. Such considerations indicate that tritium and carbon behavior in the reactor core may be different than tritium and carbon behavior outside the core in MSRs. Sealing of carbon surfaces in the core is probably not required for an FHR with clean non-fuel coolant salt. Tritium in carbon is important in these systems in three different contexts that have three different environments.

IV.A. Carbon in Reactor Cores

The FHR fuel contains carbon, and thermal-spectrum MSRs use graphite as the neutron moderator. Tritium holdup in the carbon may be significant, although there are order-of-magnitude uncertainties for maximum hydrogen solubility in graphite at high temperatures [45, 46]. In addition, the fuel assembly contains a graphite matrix material that the fuel particles are embedded in. This material has different characteristics than bulk graphite moderator.

In a pebble-bed FHR with on-line refueling, there is the potential to use the pebbles as the main tritium capture system. Pebbles, as being designed for gas-cooled reactors, have no protective PyC coating as might be required for carbon in a MSR core. It is known that hydrogen isotopes permeate through graphite at high temperatures, move along crystallite boundaries, and eventually become trapped as atoms at the edges sites and defects of graphite crystallites [47], This dissociative chemisorption process is easier on carbon atoms at zigzag terminal positions of graphene sheets than at armchair positions [48] and is much more difficult on defect-free basal planes [49].

The fuel pebbles enter the core, flow through the core, and exit the core with a residence time of about a month. When a pebble exits the core its burnup is measured. If the pebble is not fully burned, it is returned to the core with an average pebble flowing through the core about a dozen times before becoming spent nuclear fuel (SNF). There is the option of heating the pebbles as they are circulated out of the core to remove the tritium before sending the pebbles back to the reactor core. If all tritium were absorbed onto the fuel elements in a pebble-bed FHR, a loading of 2-10 wppm T/C would be necessary [50]. This is not viable for other fuel forms because the carbon capability to pick up tritium will saturate due to the longer times between refueling.

The matrix carbon material used in fuel pebbles [51] has lower graphitization temperature than isotropic graphite and is more sensitive to oxidation [52]. For the same reason, it is expected to be more reactive towards H (or T) atomic species that might be trapped from molten salts. After all, the fact that tritium is present as an ion (T^+) in the salt and not in molecular form (T_2) makes chemisorption more favorable. Dissociation of H_2 (T_2) is a great energy penalty for formation of new >C-H (or >C-T) bonds. In systems where H_2 occurred on catalytic sites, new >C-H bonds were formed even at room temperature [53]. However, this assumption needs further verification.

The equilibrium quantities of tritium in the core depend upon the average tritium levels in the coolant; thus, inventories can be minimized by maintaining low levels of tritium in the coolant. Tritium inventories can also impact spent nuclear fuel and graphite management [54] where there may be incentives to heat SNF before long-term storage to drive off salts and tritium

It has not been determined at FHR conditions if hydrogen absorption into graphite is kinetics-limited or solubility-limited [55]. If it is kinetics-limited, the rate-determining step can be mass convection in the salt, salt-graphite interface transport, intragraphite diffusion, or carbon-hydrogen reaction kinetics.

There is the option of adding hydrogen to the salt to dilute the tritium. If the reactor has a hundred times as much non-radioactive hydrogen added to the system as there is tritium, several things occur. Hydrogen sorption on carbon is limited; thus if everything else is held constant, the tritium inventory in the core graphite is reduced by a factor of a 100. Similarly, the allowable hydrogen release rate from the system can be increased by a factor of 100 without changing absolute tritium releases. The added hydrogen would increase the waste stream containing the tritium by a factor of 100; however, the total tritium produced is small. A further complication is that there will be some hydrogen outgassing from the carbon in the fuel—added hydrogen would make variations in hydrogen outgassing less important. In some systems it would make tritium removal easier. Added hydrogen will change the redox of the salt; that is, the relative amounts of H_2 versus HF.

In the MSRE, the carbon was reactor-grade graphite used as a neutron moderator. The requirements for tritium control were not initially understood and the tritium uptake in graphite was not fully appreciated until the MSRE core graphite was analyzed for tritium. Since then, there have been several major programs [50] to understand tritium uptake in carbon in HTGRs and other reactors with graphite cores—both for operational reactors and in terms of decommissioning reactors with graphite cores. Fusion programs have also done limited work on tritium uptake on carbon.

Tritium uptake on carbon depends upon the carbon form, radiation damage to the graphite and potentially radiation flux levels. Carbon and other materials are being irradiated [56] at MIT in 700°C flibe to understand this tritium behavior while similar experiments with irradiated and unirradiated samples are underway at Wisconsin [57].

IV.B. Out-of-Core Tritium Removal with Carbon

Initial modeling indicated that out-of-core carbon beds 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 (IG110U) for this analysis. However, porous carbon forms have surface areas per unit of mass up to 1000 times larger than carbon forms used in the cores of nuclear reactors—and potentially hydrogen sorption capacities a 1000 times larger. Equally important, in the last decade there has been a massive effort to examine carbon as a hydrogen storage system. While most of this work has been associated with hydrogen sorption on carbon at very low or near room temperature, that work [58, 59] strongly suggests how to improve hydrogen uptake at higher temperatures. Nuclear-grade graphite undergoes high-temperature processing to produce a graphite with dimensional stability under high neutron radiation—a requirement that does not exist for a 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 in all salt-cooled reactor systems—fission and fusion.

There are other factors that may favor out-of-reactor-core tritium removal. Radiation reduces hydrogen atom diffusivity in graphite by one or two orders of magnitude after relatively low levels of irradiation—slowing the kinetics of tritium capture [60].

There has also been a massive and continuing effort to understand the behavior of carbon and hydrogen in a different context at higher temperatures but below those found in salt-cooled reactors. Much of this effort is associated with high-surface-area carbons used as a support structure for catalysts for (1) hydrogenation of various organics and (2) low-temperature fuel cells. Figure 7 shows carbon with platinum nanoparticles used in some chemical reactors and low-temperature hydrogen fuel cells. These are industrial materials manufactured on a large scale with well proven industrial processes.

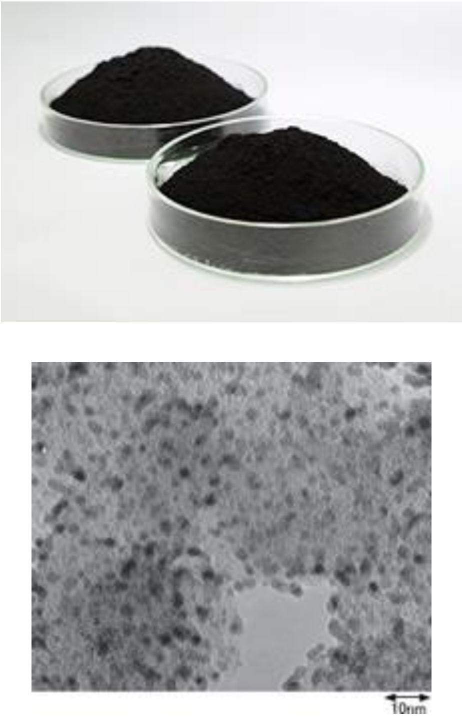

Fig. 7. Platinum on Carbon and TEM of Platinum Nanoparticles (Courtsy of Tanaka, http://pro.tanaka.co.jp/en/products/group_f/f_5.html)

This has multiple implications. First, noble-metal nanoparticles improve the kinetics of hydrogen sorption on some types of carbon [61, 62]. Whether this will be of major importance at higher temperatures is not fully known. Second, the ability to put various metals on carbon may enable a carbon bed to be used to remove metallic impurities in liquid salts.

If there are fuel failures with coated particle fuels, silver preferentially leaks out. In MSRs, large quantities of noble metal fission products are generated in the salt [63]. These noble metals plate out everywhere including on carbon surfaces but with a preference for metal surfaces. The noble metals are a major source of decay heat and result in MSR heat exchangers having extremely high radiation levels and significant decay heat even if the molten salt is drained from the heat exchangers. Noble metal fission product removal has been a significant challenge.

With an external carbon bed, there is the option to coat much of the carbon with nickel or another metal to create an ultra-high metal surface area. The expectation would be that noble metal fission products would plate out efficiently onto these surfaces. If the surfaces were a material such as nickel that is highly permeable to hydrogen, the result may be a carbon that also removes tritium. This would result in a MSR primary system with much lower levels of radioactivity when the fuel salt is drained from the system. None of these commercial carbon forms existed when the MSRE was built and thus none were examined at that time for either tritium or noble metal removal.

There is one last potential application of an external carbon bed—removal of fission product gases xenon and krypton. This is a more speculative option. In the design of the MSRE, 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 [63] in the graphite in the core. It is believed that these inert gases diffused into void spaces that do not fill with salt because of liquid surface tension. There is the option to choose carbon to maximize xenon and krypton uptake. It is unknown at this time whether efficient carbon absorbers could be developed for MSRs to simultaneously remove tritium, krypton, and xenon at reactor temperatures.

There are a limited number of other possible absorbers for tritium that are chemically compatible with high-temperature salts. These are primarily metals such as nickel. What sets carbon apart from all other materials is its extremely high surface area—the basis for its use as a support structure for catalysts.

Separate but partly coupled from the choice of absorber is the choice of absorber bed, each with different characteristics.

- *Fluidized bed*. The carbon particles are mixed with the hot salt. This is the simplest but least efficient absorber bed.
- *Fixed bed.* The carbon is fixed in a tank or cartridge and salt flows through it. Tritium initially loads on the inlet side of the bed and then progressively loads the bed over time. Two or more fixed beds are used with one bed being regenerated while the other removes tritium. This is similar to many water ion exchange cleanup systems.
- *Moving bed.* In a moving bed the carbon flows counter current to the flowing salt. This is the most complex option but with the greatest capabilities including continuous regeneration of the carbon bed and the potential to control redox potential.

The efficacy of any of these systems for tritium removal depends upon the fraction of the salt flow sent through the absorber bed and its location. If the goal is to minimize tritium in all forms in the reactor, a full-flow carbon bed between the reactor core and heat exchangers would be used. This minimizes tritium in the system.

The most capable tritium removal system is the moving bed absorber. A high-performance moving bed system is shown schematically in Fig. 8 for removal of tritium from salt.

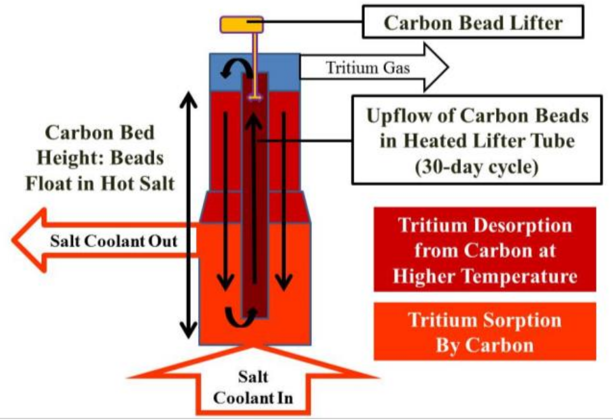

Fig. 8 Tritium Carbon Absorber Bed

Hot salt from the reactor core enters the carbon absorber bed and tritium is absorbed onto the carbon in a counter-current absorber configuration. Salt flows upward while the carbon beads flow downward in the column so the carbon with the highest tritium content contacts the salt with the highest tritium content. Fresh carbon beads with low tritium content are exposed to the salt leaving the bed with a low tritium concentration. Counter-current flow maximizes tritium removal and tritium bed loading. The carbon beads float in the salt. While the theoretical density of graphite is higher than salt, most carbon forms have lower densities.

At the bottom of the absorber bed the carbon beads enter an insulated and heated lifter tube that circulates the beads from the bottom to the top of the bed with the help of the carbon bead lifter. As the beads move upward and are heated, the tritium is desorbed and exits the reactor via the gas space above the top of the bed.

The carbon beads are returned to the absorber bed in a downcomer that is also heated. The temperature in the downcomer at the top matches the peak temperature in the lifter tube. Heating the carbon beads removes the tritium. There is the option of injecting (1) an inert gas, (2) hydrogen or (3) a mixture [H_2, HF, inert gas] into the downcomer. This stripper gas would move upward in the downcomer and also exit to the off-gas system. The use of a stripper gas, depending upon the gas composition, has several functions.

- *Tritium removal*. An inert gas will shift the equilibrium and remove added tritium from the carbon. Alternatively if a mixture of inert gas and non-radioactive H_2 is injected into the downcomer, the non-radioactive hydrogen isotopically exchanges with the residual tritium in the carbon and lowers the residual tritium content of the carbon. This non-radioactive H_2 absorbed on the carbon will then exchange with tritium from the salt in the lower absorber bed lowering the residual tritium concentration in the liquid salt leaving the carbon bed. That, in turn, lowers release of tritium by diffusion through the hot heat exchangers. The hydrogen content of the carbon leaving the downcomer is determined by the carbon temperature. Higher temperatures imply less hydrogen on the carbon beads. The penalty of injecting non-radioactive hydrogen is additional hydrogen in the tritium that must be disposed of with the tritium.
- *Redox control*. Using a mixture of H_2/HF in the stripper gas may allow the control the redox potential in the flibe. In the Molten Salt Reactor Experiment the redox potential at 650°C was maintained at -700.5 KJ/mol-F_2 to minimize corrosion. That redox potential could be maintained in the FHR [4] if the ratio of partial pressures is:

  $$P_{TF}/(P_{T2})^{0.5} = 9.2\cdot 10^{-5}$$

  This would require a reliable capability to measure salt redox potential on-line to adjust the relative amounts of hydrogen and hydrogen fluoride in the stripper gas. The H_2/HF absorbed on the carbon can be controlled by the temperature in the bottom half of the downcomer.

Once tritium, Xe, and Kr are recovered, there are many technologies for separation and storage at lower temperatures outside the reactor. Low-pressure Xe and Kr absorption, separation, and storage has been demonstrated on porous (activated) carbon materials at temperatures close to room temperature [64]. Tritium can be stored on a wide variety of materials from uranium hydride beds to carbon at low temperatures—with many more options if tritium is converted into water.

Several experimental programs are underway to measure hydrogen behavior for tritium removal to enable design of a tritium control system. MIT [65] is measuring hydrogen sorption and desorption on different nuclear and porous carbon forms at pressures near 1 Pa (FHR tritium pressure) over temperature ranges of 400 to 1100°C.

Using static and dynamic flow methods for chemisorption analysis, the adsorption capacity and relative uptake rate of hydrogen on different carbon forms will be tested. These forms include high-performance activated carbons such as Maxsorb MSC-30, which demonstrated high H_2 uptake room temperature and pressure [51], nuclear grade graphite IG-110U, fuel matrix graphite and carbon-carbon composites that are proposed for ORNL’s plate fuel. By testing different forms of carbon that could exist in the FHR system, the performance of systems-level models can be improved.

Hydrogen and deuterium surrogates will be used and results will be extrapolated to tritium using rate theory as required based on results. The hydrogen adsorbed will be determined by measuring small fluctuations in pressures of an experimental sample cell. The experiments will be conducted over FHR operating conditions of temperatures from salt freezing at 459^{o}C to transient condition at 800^{o}C and pressures of <1Pa required to minimize release relative to the unmitigated case predicted by TRIDENT [34-36]. The primary instruments that will be used include a Quantachrome Autosorb IQ-C for chemisorption and a Pfeiffer Prisma Plus for mass spectrometry during temperature programmed desorption.

In addition to the adsorption of hydrogen on different carbons, various microstructural characteristics will be determined through BET surface area analysis, pore size distribution, Raman spectroscopy, X-ray diffraction and scanning electron microscopy. By understanding the effective diffusion pathways and identifying reactive hydrogen-binding sites, carbons can be selected or designed for each application.

The University of Wisconsin [50] is characterizing tritium transport across the salt-carbon interfaces and into the carbon. Wisconsin and MIT [56] are conducting integrated tests of tritium behavior on carbon that includes irradiating various forms of carbon in 700°C salt. These programs are expected to develop the required information on carbon tritium behavior in salt to predict tritium behavior in salt-cooled reactors and design tritium removal systems. The different programs (MIT, Wisconsin, CAS, etc.) have chosen several carbon forms for testing [3].

IV.C. Carbon and Corrosion

The presence of carbon in a salt system alters corrosion rates. Experiments at MIT and Wisconsin [67] are underway to understand the various mechanisms and testing different materials with and without carbon in the system.

V. OTHER OPTIONS FOR TRITIUM REMOVAL FROM SALT

V.A. Gas Sparging

Tritium can be removed from high-temperature liquid salt using gas sparging where an inert gas such as helium or argon is mixed with the liquid salt, promoting the preferential transfer of tritium in different forms to the gas phase and then to the off-gas system. The primary requirement is a high gas-liquid surface area for efficient transport of tritium from the liquid to gas phase.

The CAS plans to complete by 2020 a 10 MWt FHR and a 2 MWt MSR. They are developing a gas sparging system [68] to remove xenon and krypton from the MSR—a system that will also remove tritium and tritium fluoride Helium will be injected into the salt with a venture type bubble generator (0.3 to 0.5 mm bubbles) and removed with a centrifugal separator. A water version of the gas-liquid separator being used to develop the technology is shown in Fig. 9. The liquid with gas bubbles flows in from the right through swirling vanes to create a rod-type gas zone in the middle, the gas is removed, and the liquid flows through recovery vanes before exiting the system.

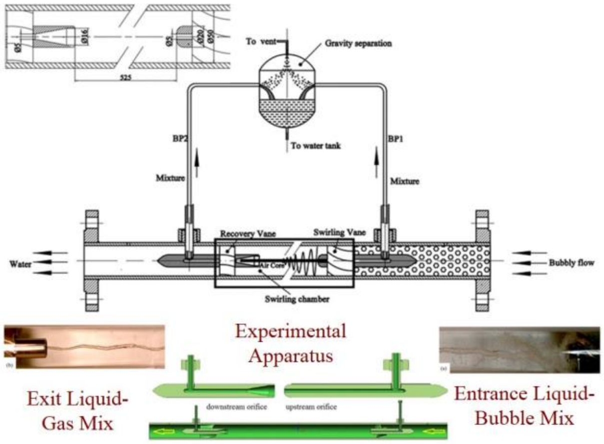

Fig. 9. Gas-Liquid Separator Design

New Mexico [69, 70] 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. The CAS and New Mexico programs are complimentary—ultrasonics improves mass transfer and the CAS system improves gas-liquid separations. 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 system where the liquid salt is in droplets or flowing over a high-surface area media such as a distillation-column mesh packing and the purge gas or vacuum is the continuous media—reverse of gas sparging. It is an option originally examined by Lawrence Livermore National Laboratory [71] for salt-cooled fusion machines where it was proposed that the droplets be sprayed into a vacuum tower. The engineering challenge is to provide an efficient pathway for the tritium gas to exit the tower.

The alternative to a vacuum is to have a purge gas flowing counter-current to the gas droplets. This option may be attractive for one class of advanced MSR designs that is being developed by Hatch of Canada [72] 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.

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 (tritium, xenon, and krypton) 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. Engineered high-surface-area packings have been developed over the last 30 years for use in distillation columns and scrubbers.

V.B. 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 The Ohio State University (OSU) [73-74] and Oak Ridge National Laboratory [75] for tritium separation in salt-cooled systems using permeators. A large part of this effort is to find ways to increase salt turbulence near the tubes to increase the rate of tritium transport from the salt to the permeator tubes. At OSU various fixed bed and permeator options [74] for tritium removal were evaluated and a preliminary design of a permeator for a tritium removal facility with a cross-flow configuration between the salt and carrier gas has been developed. Computational simulations have been performed to evaluate the mass transfer efficiency. A small-scale validation experiment of the proposed tritium permeator using hydrogen as a surrogate is being planned.

V.C. Double-Wall Heat Exchangers

Double wall heat exchangers are used in the chemical industry when 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 double wall system is both a barrier to tritium release and a collection system. The disadvantages of double wall heat exchangers are cost and added temperature drops across the heat exchangers. Oak Ridge National Laboratory [76], The Ohio State University [77], and the University of New Mexico [78, 79] are investigating this tritium control and capture option for liquid salt systems.

At OSU, a natural draft heat exchanger (NDHX) is currently being designed and optimized for the direct reactor auxiliary cooling system (DRACS). In this design, DRACS secondary fluoride salt of flows inside the inner tubes and sweep gas (helium) flows in the annuli with air flowing outside the tubes. A fraction of the heat and tritium is removed by the sweep gas and the remaining by the outside air. A MATLAB code involving heat transfer and tritium mass transfer is being developed to aid the design optimization of such an NDHX.

VI. TRITIUM BARRIERS

There is a large literature and experience base on barriers to prevent diffusion of tritium to the environment. Better barriers reduces the requirements on the tritium removal systems in that the allowable concentrations in the salt may be higher; but, it does not change the need for a tritium removal system. Without a tritium removal system the tritium concentrations continue to increase creating a larger driving force for tritium diffusion through containment barriers. In the context of salt-cooled systems, the CAS is currently measuring permeation of hydrogen through various materials of construction and alternative methods to reduce tritium diffusion in salt-cooled reactors.

The INL STAR facility for the fusion program has also had a major effort in measuring permeation rates through various materials [80].

Two specific examples types of tritium barriers were identified in terms of applicability to salt cooled reactors. Tritium production targets in pressurized water reactors (~300°C) use aluminide coatings [1] on the inside of 316SS to prevent tritium losses. This is the only industrial-scale system identified today where tritium barriers must work for long periods of time at high temperatures on an industrial process in a nuclear system with large tritium inventories. Aluminide coatings are incompatible with salts but could be used on the exterior sides of salt heat exchangers or inside double-wall heat exchangers to stop tritium. Second, tungsten can be plated onto the inside of heat exchangers as a tritium barrier [36, 81, 82]. Tungsten plating has been used for other applications. Tungsten is chemically compatible with liquid salts whereas most other tritium barriers are not chemically compatible with high temperature salts.

VII. TRITIUM CONTROL EXPERIENCE

There is a large experience base in tritium separations and control from national security, heavy water reactor, HTGR, 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). However, this experience does not include tritium capture and control in 700°C fluoride and chloride salts.

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 [78] 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 adsorption 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).

VIII. 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 $^3H_2$ and ^3HF at partial pressures of fractions of a Pa.

The current status of tritium control and capture is that limited data indicates it is feasible to maintain very low levels of tritium in a salt-cooled reactor using carbon. However, the experimental data base of tritium sorption on carbon at the required conditions is small with large uncertainties. The advances in carbon technology may enable dramatic improvements in removal of tritium and other impurities from these salts. What sets carbon apart from all other tritium removal options is its extreme surface area for potentially rapid tritium uptake and the wide variety of options. Current programs are underway to collect the experimental information needed to design tritium removal systems for salt-cooled reactor.

The status of other control technologies is somewhat behind that of capture on carbon—but experimental work is expected to provide answers in the next several years.

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 support and assistance.

LIST of ACRONYMS

CAS	Chinese Academy of Science
CTHX	Coiled Tube Heat Exchanger
Flibe	Li_2BeF_4
FHR	Fluoride-salt-cooled High-Temperature Reactor
FIRM	Fuel Inside Radial Moderator
INL	Idaho National Laboratory
MIT	Massachusetts Institute of Technology
MSR	Molten Salt Reactor
NACC	Nuclear Air-Brayton Combined Cycle
NDHX	Natural Draft Heat Exchanger
NRL	Nuclear Reactor Laboratory (MIT)
NSE	Nuclear Science and Engineering Department (MIT)
ORNL	Oak Ridge National Laboratory
OSU	The Ohio State University
PFC	Plasma Fusion Center (MIT)
PNNL	Pacific Northwest National Laboratory
REBCO	Rare Earth Barium Copper Oxide (superconductor)
SRNL	Savannah River National Laboratory
TRIDENT	Tritium Diffusion EvolutioN and Transport
UNM	University of New Mexico (Albuquerque)
UW	University of Wisconsin (Madison)

REFERENCES

1. C. FORSBERG et al., *Proceedings of the Workshop on Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors: Experiments, Models and Benchmarking*, CANES ANP- 165, Center for Advanced Nuclear Energy Systems, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Salt Lake City, Oct. 27-28, 2015.
2. C. Forsberg et. al,, "Tritium Control and Capture in Salt-Cooled Fission and Fusion Reactors", Paper 16825, Proc. of the 11th International Conference on Tritium Science & Technology (TRITIUM 2016), Charleston, South Carolina, April 17-22, 2016
3. P. F. PETERSON, FHR Integrated Research Project (IRP-2) Workshop 2: Benchmarking, Berkeley, California, April 14-15, 2016
4. J. SERP et al. "The Molten Salt Reactor (MSR) in Generation IV: Overview and Perspectives", *Progress in Nuclear Energy*, **77**, 308-319, 2014.
5. C. FORSBERG and D. WHYTE," Converging Fission and Fusion Systems Toward High-Temperature Liquid-Salt Coolants: Implications for Research and development", Proc. International Congress on Advanced Nuclear Power Plants (ICAPP 2016), San Francisco, California April 17-20, 2016.
6. R. SERRANO-LOPEZ et al., "Molten Salts Database for Energy Applications", *Chemical Engineering and Processing: Process Intensification*, September 15, 2013.
7. D. E. HOLCOMB and S. M. CETINER, *An Overview of Liquid-Fluoride-Salt Heat Transport Systems*, Oak Ridge National Laboratory, ORNL/TM-2010/156, September 2010.
8. D. F. WILLIAMS, *Additional Physical Property Measurements and Assessment of Salt Compositions Proposed for the Intermediate Heat Transfer Loop*, Oak Ridge National Laboratory, ORNL/GEN4/LTR-06-033, September 2006.
9. D. F. WILLIAMS, L. M. TOTH, and K. T. CLARNO, *Assessment of Candidate Molten Salt Coolants for the Advanced High-Temperature Reactor (AHTR)*, Oak Ridge National Laboratory, ORNL/TM-2006/12.
10. D. F. WILLIAMS, *Assessment of Candidate Molten Salt Coolants for the NGNH/NHI Heat-Transfer-Loop*, Oak Ridge National Laboratory, ORNL/TM-2006/69, June 2006.
11. B. ROMATOSKI, "Review of Fluoride Salt-Cooled High Temperature Reactor LiF-BeF2 (Flibe) Coolant Properties", *Proc. of 2014 American Nuclear Society*, June 2014.
12. R. ROMATOSKI, L. W. HU, and C. W. FORSBERG, "Uncertainty Propagation of Coolant Properties in a Fluoride Salt-Cooled High Temperature Reactor", *Proc. 2016 International Congress on Advanced Power Plants*, San Francisco, California, April 2016.
13. C. ANDREADES et al., *Technical Description of the "Mark 1" Pebble-Bed Fluoride-Salt-Cooled High-Temperature Reactor (PB-FHR) Power Plant*, UCBTH-14-002, University of California at Berkeley, September 30, 2014.
14. D. WANG, G. L. YODER, D. POINTER, and D. E. HOLCOMB, "Thermal Hydraulics Analysis of the Advanced High Temperature Reactor," *Nuclear Engineering and Design*, **294**, 73-85, August 2015.
15. J., RICHARD, *Design Optimization and Analysis of a Fluoride Salt Cooled High Temperature Test Reactor for Accelerated Fuels and Materials Testing and Nonproliferation and Safeguards Evaluations*, PhD Thesis, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, September 2015.
16. C. W. FORSBERG, J. Richard, J. Pounders, R. Kochendarfer, K. Stein, E. Shwageraus, and G. Parks, "Development of a Fluoride-Salt-Cooled High-Temperature Reactor (FHR) Using Advanced Gas-Cooled Reactor (AGR) Technology", Paper 13983, Transactions American Nuclear Society Annual Meeting, San Antonio, Texas, June 7-11, 2015.
17. Institut de Radioprotection et de Surete Nuclaire, Review of Generation IV Nuclear Energy Systems.
18. NUCLEAR ENERGY AGENCY, Organization for Economic Co-Operation and Development, *Introduction of Thorium in the Nuclear Fuel Cycle*, NEA No. 7224, 2015
19. B. BURKHARDT et. al., "Technology Assessment of an Advanced Reactor Design – A Case Study on a Molten Salt Reactor (MSR)", *2016 International Congress on the Advances in*

Nuclear Power Plants (ICAPP 2016), San Francisco, California, April 17-20, 2016.

20. OAK RIDGE NATIONAL LABORATORY, Workshop: From the MSRE to a New Emerging Class of Reactors 50 Years Later, Oak Ridge, Tennessee, October 15-16, 2016
21. I. SCOTT, “Static Fuel Molten Salt Reactors Simpler, Cheaper, and Safer” Moltex Energy, http://www.moltexenergy.com/
22. B. N. SORBOM, J. Ball, T.R. Palmer, F.J. Mangiarotti, J.M. Sierchio, P. Bonoli, C. Kasten, D.A. Sutherland, H.S. Barnard, C.B. Haakonsen, J. Goh, C. Sung, D.G. Whyte, ARC: A compact, high-field, fusion nuclear science facility and demonstration power plant with demountable magnets, *Fusion Engineering and Design*, **100**, 378-405, ISSN 0920-3796, http://dx.doi.org/10.1016/j.fusengdes.2015.07.008, November 2015.
23. C. ANDREADES, R. O. Scarlat, L. Dempsey, and P. F. Peterson, Reheating Air-Brayton Combined Cycle Power Conversion Design and Performance Under Normal Ambient Conditions”, *J. of Engineering for Gas Turbines and Power*, *136*, June 2014.
24. C. ANDREADES, L. Dempsey, and P. F. Peterson, “Reheating Air-Brayton Combined Cycle Power Conversion Off-Normal and Transient Performance”, *J. of Engineering for Gas Turbines and Power*, *136*, July 2014.
25. B. ZOHURI, P. J. McDaniel, and C. R. DeOliveira, “Advanced Nuclear Open Air-Brayton Cycles for Highly Efficient Power Conversion,” *Nuclear Technology*, **192**, 48-60, October 2015, http://dx.doi.org/10.13182/NT14-42.
26. D. C. STACK, D. Curtis, R. Ibekwe, C. Forsberg, “Conceptual Design and Market Assessment of Firebrick Resistance Heated Energy Storage (FIRES) – Avoiding Wind and Solar Electricity Price Collapse to Improve Nuclear, Wind, and Solar Economics”, *International Congress on Advanced Nuclear Power Plants (ICAPP 2016),* Paper 16622, San Francisco, California, April 17-20, 2016.
27. C. W. FORSBERG et al., *Fluoride-salt-cooled High-Temperature Reactor (FHR) Commercial Basis and Commercialization Strategy*, MIT-ANP-TR-153, Massachusetts Institute of Technology, Cambridge, MA, December 2014.
28. MASSACHUSETTS INSTITUTE OF TECHNOLOGY, *Future of Solar Energy*, 2015.
29. 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.
30. A. MILLS and R. WISER, *Changes in the Economic Value of Variable Generation at High Penetration Levels: A Pilot Case Study of California*, LBNL-5445E, June 2012
31. TERAI and TANAKA, “Tritium Release Behavior from Liquid Tritium Breeding Materials for Fusion Reactor Blanket under Neutron Irradiation,” *Progress in Nuclear Energy*, **32** (*1-2*), 97-112, 1989.
32. SUZUKI, “Tritium Release Behavior from Li_2BeF_4 Molten Salt by Permeation through Structural Materials-A, *Fusion Engineering and Design*, 2000.
33. S. T. TAKAYUKI TERAI, A. SUZUKI, “In-situ Tritium Release Behavior from Molten Salt under Neutron Irradiation”, *Fusion Technology*, **30**, 1996.
34. J. D. STEMPIEN, R. G. Ballinger, and C. W. Forsberg, “An Integrated Model of Tritium Transport and Corrosion in Fluoride Salt-Cooled High-Temperature Reactors (FHRs) – Part I: Theory and Benchmarking, *Nuclear Engineering and Design* (Submitted).
35. J. STEMPIEN, R. G. Ballinger, and C. W. Forsberg, “An Integrated Model of Tritium Transport and Corrosion in Fluoride Salt-Cooled High-Temperature Reactors (FHRs) – Part II: Simulations in FHRs”, *Nuclear Engineering and Design* (Submitted)
36. J. D. STEMPIEN, *Tritium Transport, Corrosion, and Fuel Performance Modeling in a Fluoride Salt-Cooled High-Temperature Reactor (FHR)*, PhD Thesis, Massachusetts Institute of Technology, June 2015.
37. H. T. PETERSON and D. A. Baker, “Tritium Production, Releases, and Population Doses at Nuclear Reactors,” *Fusion Technology*, **8**, 2544-2550, 1985.

38. W. G. LUSCHER et al., “In-situ Measurement of Tritium Permeation Through Stainless Steel”, *J. of Nuclear Materials*, **437**, 373-379, 2013.
39. T. D. BURCHELL, “2.10 Graphite: Properties and Characteristics”, *Comprehensive Nuclear Materials*, **2**, 285-305, 2012
40. T. D. BURCHELL, “4.10 Radiation Effects in Graphite”, *Comprehensive Nuclear Materials*, **4**, 299-324, 2012.
41. P. R. KASTEN et al., *Graphite Behavior and its Effects on MSBR Performance*, ORNL-TM-2136 (1969).
42. X. HE et al., "Protection of nuclear Graphite towards liquid fluoride salt by isotropic pyrolytic carbon coating", *Journal Nuclear Materials* **442** (2013) 306-308.
43. S. FENG, "Sealing nuclear graphite with pyrolytic carbon", *J. Nuclear Materials* **441** (449-454, 2013.
44. O. TANAIKE, M. INAGAKI, "Degradation of carbon materials by intercalation", *Carbon* **37** 1759-1769, 1999.
45. R. A. CAUSEY et al, "The retention of deuterium and tritium in POCO AXF-5Q graphite", *J. Vac, Sci, Technol*. A4 (1986) 1189-1192
46. H. ATSUMI et al, "Absorption and deosprtion of deuterium on graphite", *J. Nuclear Materials* 155-157, 241-245, 1988.
47. H. ATSUMI, "Mechanism of hdyrogen trapping and transport in carbon materials", *Physica Scripta*, T103, 77-80, 2003.
48. W. A. DINO, H2 dissociative adsorption at the zigzag edges of graphite, e-J. Surf. Sci. *Nanotech*. 2 (2004) 77-80.
49. Y. MIURA et al. “First Principles Studies for the Dissociative Adsorption of H2 on Graphene, *J. Appl. Phys*. **93,** 3395-3400, 2003
50. M. YOUNG et. al, “Characterization of Tritium Transport in the Flibe-Graphite System, for In-Situ Tritium Absorption by the Fuel Elements of the Fluoride-Salt-Cooled High-Temperature Reactor (FHR)”, *Proceedings of the International Topical Meeting on Nuclear Reactor Thermalhydraulics (NURETH-16).* Chicago, IL. Aug. 30 – Sept. 4, 2015.
51. P. J. PAPPANO et al, “A novel approach to fabricate fuel compact for the next generation nuclear plant (NGNP)” *J. Nuclear Materials*, **381**, 25-38, 2008
52. C. CONTESCU et al, Practical aspects for characterizing air oxidation of graphite, *J Nuclear Materials*, **381**, 15-24, 2008
53. C. CONTESCU, "Detection of hydrogen spillover in palladium-modified activated carbon fibers during hydrogen adsorption", *J Phys Chem* **113**, 5886-5890, 2009
54. C. W. FORSBERG and P. F. Peterson, “Spent Nuclear Fuel and Graphite Management for Salt-Cooled Reactors: Storage, Safeguards, and Repository Disposal”, *Nuclear Technology*, **191**, August 2015.
55. R. A CAUSEY, Hydrogen diffusion and solubility in pyrolytic carbon, Carbon **17**, 323-328, 1979
56. D. CARPENTER et al., “Findings of the Second Round of Fluoride Salt High Temperature Reactor Materials Irradiation Tests at the MIT Research Reactor,” *Proceedings of the 2015 International Conference on Advances in Nuclear Power Plants: ICAPP 2015*, Nice, France, May 3-6 2015
57. G. ZHENG, et. al, “The Effect of Tritium Generation on Alloys Corrosion in Molten Li_2BeF_4 (FLiBe) Salt, *Proc. TRITIUM 2016*, Charleston, South Carolina, April 17-22, 2016.
58. L. HE et. al., “Investigation of Morphology and Hydrogen Adsorption Capacity in Disordered Carbons”, *Carbon*, **80**, 82-90 (2014).
59. V. V. BHAT et al., “Atypical Hydrogen Uptake on Chemically Activated, Ultramicroporous Carbon, “ *Carbon*, **48**, 1331-1340, 2010.
60. H. ATSUMI et al, Hydrogen trapping in neutron-irrdiated graphite, *J. Nuclear Materials*, 386-388, 379-38, 2009.
61. V. V. BHAT et al., “Kinetic Effect of Pd Additions on the Hydrogen Uptake of Chemically-Activated Ultramicroporous Carbon, *Carbon*, **48**, 2361-2380, 2010.
62. V. V. Bhat et al, “The Role of Destabilization of Pallidadium Hydride in the Hydrogen Uptake of Pd-Containing Activated Carbons, *Nanotechnology*, **20**, 2009.
63. E. L. COMPERE, S. S. KIRSLIS, E. G. BOHLMANN, F. F. BLANKENSHIP and W. H. GRIMES, Fission Product Behavior in the Molten Salt Reactor Experiment, ORNL-4865, Oak Ridge National Laboratory, Oak Ridge, TN, Oct, 1975.

64. M. M. DUBININ et al, Pore structure of carbon adsorbents and the adsorbability of gases and vapors. 2. Analysis of the results of a study of krypton and xenon adsorption, Bulletin Acad. Sciences USSR, Div. Chemical Sci. **29**, 1029-1033, 1980
65. S. LAM, C. W. FORSBERG, R.G. BALLINGER, and R. SCARLAT, "Using Carbon to Remove Tritium and Other Impurities from 700°C Salt Coolants from Fission and Fusion Power," *The World Conference on Carbon, Carbon 2016*, State College, Pennsylvania, July 10-15, 2016.
66. Wang, L., Stuckert, N.R., Yang, R.T., "Unique Hydrogen Adsorption Properties on Graphene," AIChE Journal. 57, 2903-2908 (2011).
67. G. Zheng, et al. "The Effect of Tritium Generation on Alloys Corrosion in Molten Li_2BeF_4 (FLiBe) Salt", *Tritium 2016*, Charleston, SC, April 17-22, 2016.
68. J. L YIN, J. J Li, Y. F Ma, H. Li, W. Liu and D. Z Wang, Study on the Air Core Formation of a Gas–Liquid Separator, *Journal of Fluids Engineering*, **137**, 1-9, 2015
69. F. L. Rubio, E. D. Blandford, and L. Bond, "Sonoprocessing Applications in Advanced Nuclear Technologies", Ultrasonics Chemistry (Submitted to journal in December 2015)
70. F. L. Rubio, L. Bond, and E. D. Blandford, "Sonoprocessing Applications for Advanced Nuclear Technologies," Transactions 2014 American Nuclear Society Winter Meeting Anaheim, California, November 9-13, 2014.
71. R. W. Moir et al., *Helium-Cooled Molten-Salt Fusion Breeder*, Lawrence Livermore National Laboratory, UCID-20153, December 1984.
72. A. SHAW, "A Staged Approach to the Design of a Nuclear Reactor", Hatch, Inc., *Workshop: From the MSRE to a New Emerging Class of Reactors 50 Years Later*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 15-16, 2016
73. X. Wu, I. H. Kim, D. Arcilesi, X. Sun, R. Christensen, and P. Sabharwall, "Computer Simulation of Tritium Removal Facility Design," *The 10th International Topical Meeting on Nuclear Thermal Hydraulics, Operation and Safety (NUTHOS-10)*, Okinawa, Japan, NUTHOS10-1204, 2014.
74. X. Wu, D. Arcilesi, X. Sun, R. Christensen, P. Sabharwall, "Conceptual Design of Tritium Removal Facility for FHRs," *Proceedings of the 16th International Topical Meeting on Nuclear Reactor Thermal Hydraulics (NURETH-16),* August 30 – September 4, 2015, Chicago, IL., pp. 4935-4948.
75. ORNL permeator
76. ORNL double wall HX
77. F. RAHNEMA, et al. "Integrated Approach to Fluoride High Temperature Reactor Technology and Licensing Challenges (FHR-IRP)", FY 2016 Q1 Quarterly Report, January 2016.
78. J. HUGHES and E. D. Blandford, "Compact Double-wall Twisted-tube Heat Exchanger for the Fluoride salt-cooled High-temperature Reactor (FHR) and Implications for In-Service Inspection," *Transactions 2014 American Nuclear Society Winter Meeting*, Anaheim, California, November 9-13, 2014
79. F. L. RUBIO, B. Wallace, and E. D. Blandford, "Analysis of Tritium Migration and Proposed Capture/Removal Methods in Fluoride salt-cooled High-temperature Reactors (FHRs)" *11th International Conference on Tritium Science &Technology (TRITIUM-2016),* Charleston, SC USA, April 17-22, 2016 (POSTER).
80. D. A. PETTI et. al., "JUPITER-II molten salt Flibe research: An update on tritium, mobilization and redox chemistry experiments," *Fusion Engineering and Design*, **81**, 1439-1449, 2006.
81. T. J. DOLAN, G. R. LONGHURST, and E. GARCIA-OTERO, "A Vacuum Disengager for Tritium Removal from HYLIFE-II Flibe", *Fusion Technology*, 21, 1949-1954, May 1992.
82. R. W. Moir et. al., "Design of a Helium-Cooled Molten-Salt Fusion Breeder", *Fusion Technology*, 8, 465-473, July 1985.