Tritium Formation and Mitigation in High Temperature Reactors

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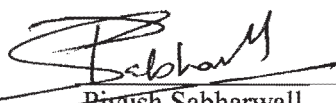
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ABSTRACT

Tritium is a radiologically active isotope of hydrogen. It is formed in nuclear reactors by neutron absorption and ternary fission events and can subsequently escape into the environment. In order to prevent the tritium contamination of proposed reactor buildings and surrounding sites, this paper examines the root causes and potential solutions for the production of this radionuclide, including materials selection and inert gas sparging. A model is presented that can be used to predict permeation rates of hydrogen through metallic alloys at temperatures from 450–750°C. Results of the diffusion model are presented for one steady-state value of tritium production in the reactor.

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Tritium Formation and Mitigation in High Temperature Reactors

1.   INTRODUCTION

Hydrogen is the most common element in the universe, representing about three-quarters of the measurable mass. It is very light, often just one proton weighing approximately one atomic mass unit (amu) and propagates readily through most media, especially at elevated temperatures. It is also highly reactive, reducing other compounds such as atmospheric oxygen:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \; ; \; \Delta H^0 = -285 \frac{kJ}{mol} \tag{1}$$

The large negative value for the standard enthalpy of formation, ΔH^0 indicates that the reaction is very exothermic, so the reverse reaction takes a significant amount of energy to complete, and elemental hydrogen (diatomic form) is rarely observed in nature.

Tritium ($_1^3H$) is a radioactive isotope of hydrogen with a nucleus composed of one proton and two neutrons. It is formed by ternary fission events (rare emissions of three nuclides rather than two during a fission) and neutron absorption (and subsequent decay) of predecessor radionuclides, particularly ^6Li and ^7Li.[1] It is used in low-temperature chemical lighting applications, such as exit signs, guns sights, and wristwatches; however, its permeability has not been extensively investigated in high temperature systems (>450°C), possibly because of the costs of mitigating the thermal and radiological hazards present when working with tritium at these temperatures.

Tritium is of special interest among the fission products created in next-generation nuclear power plants because of the large quantities produced. Substantial amounts of experimental data suggest that hydrogen propagates readily in metals at elevated temperatures, and some data may be found suggesting that tritium behaves similarly in these high temperature applications.[2] The anticipated difficulty in containing tritium justifies special care in system design. A sound understanding of tritium's generation pathways, as well as its properties and possible ways to prevent its escape are an integral part of any containment plan for advanced high temperature reactors (AHTRs).

2.   TRITIUM FORMATION

In general, tritium is formed in the fission event that follows neutron absorption by parent nuclides. Differing reactor types form tritium in different ways and in different amounts: in a pressurized water reactor (PWR), tritium is formed by neutron absorption by the boric acid (neutron poison) in the water; in a CANDU heavy water reactor, tritium (as DTO – heavy tritiated water) is produced from neutron absorption by deuterium in the heavy water.[1,3] Equation 2 illustrates the primary reaction in CANDU reactors, Equation 3 is most important in PWRs, and Equations 4–7 characterize tritium formation in molten salt reactors (MSRs):

$$_1^2H + n \rightarrow {}_1^3H + \gamma + 6.26 \; MeV; \sigma_{th} = 550 \; \mu b \tag{2}$$

$$_5^{10}B + n \rightarrow 2_2^4He + {}_1^3H + 0.324 \; MeV; \sigma_{th} = 12 \; mb \tag{3}$$

$$_3^6Li + n \rightarrow {}_2^4He + {}_1^3H + 4.8 \; MeV; \sigma_{th} = 940 \; b \tag{4}$$

$$_3^7Li + n + 2.47 \; MeV \rightarrow {}_2^4He + {}_1^3H + n; \sigma_{avg} = 20 \; mb \tag{5}$$

$$_3^7Li + n + 3.35 \; MeV \rightarrow {}_1^5H + {}_1^3H; \sigma_{avg} = 20 \; mb \tag{6}$$

$$_9^{19}F + n + 7.56 \; MeV \rightarrow {}_8^{17}O + {}_1^3H; \sigma_{avg} = 30 \; \mu b \tag{7}$$

In the above reactions, the parameter σ_x represents the absorption cross section for the parent nuclide in barns (b) and the subscript refers to the energy of the incident neutron, whether *th*, thermal (neutron energies ≈0.02 eV), or *avg*, average. Larger numbers indicate greater probability of neutron absorption.

Inspection reveals that the absorption cross-sections are, in most cases, quite small compared to the values for primary fuel (for example, ^{235}U has a cross section of $\sigma_{th\,235U}$=587 b). However, heavy water molecules and ^7Li ions subjected to long periods of neutron bombardment (as a moderator in a CANDU or as coolant in an MSR) generate a substantial amount of tritium at steady-state[4] because of the large number of neutronic collisions with parent nuclides per unit time. Table 1 shows estimated tritium formation rates for four reactor types: MSR, CANDU heavy water reactor, high temperature gas-cooled reactor (HTGR), and PWR.

Table 1. Sources and rates of production
of tritium 1000 MW(e) reactor.[4,5,6]

Reactor Type	Tritium Formation Rate (Ci/day)
MSR	2400
CANDU	2700
HTGR	50
PWR	2

3. TRITIUM IN THE ENVIRONMENT

Once tritium is generated in the primary coolant (e.g., molten salt or helium coolants), it begins to advect through the coolant and high temperature metals used for containment and heat exchangers.[8] This is of particular concern because hydrogen's high permeability at elevated temperature (which is theoretically similar to that of tritium) results in unacceptably high rates of discharge to the environment.[1]

Once discharged to the environment, tritium transmutes into helium with a half-life of 12.3 years according to Equation 8:[1,4]

$$^{3}_{1}H \rightarrow \beta^- + \bar{\nu} + {^{3}_{2}He}.$$ (8)

Beta particles generated in this way form an internal hazard,[2] i.e., they can be blocked by skin if emitted externally,[1] but if taken into the body, internal emissions can damage cells or genetic material. For this reason, creation of compounds such as HTO (tritiated water) or HT (tritium-substituted diatomic hydrogen gas) is of particular concern, since they enable absorption through skin or ingestion.[8,10] Allowable levels of tritium are regulated by both the U.S. Nuclear Regulatory Commission (NRC) and Environmental Protection Agency (EPA). These agencies recommend maximum total intake levels of 1.3 mrem/yr from HTO in drinking water (or 20,000 pCi/L),[1,7,11] which are thought to be well below acceptable hazard levels for the public.[11]

3.1 Tritium Detection

Although the system will be specified to limit the amount of tritium discharged into the environment, some tritium will inevitably escape from the system. The risk of released tritium depends on its form when released[11,2]—HTO is ingestible and absorbable through skin while HT is inhalable or ingestible only. It is therefore important to measure tritiated water concentrations at the same time as HT emissions in plant areas[12] to ensure worker safety. HTO may be measured with tuned lasers[12] to detect isotope concentration by detection of photons emitted because of the selective absorption of laser radiation in liquid or vaporized HTO. HT is a permanent (noncondensible) gas, and gross leakage should be measured using quadruple mass spectrometers, which measure charge-to-mass ratio. One serious disadvantage of measuring charge-to-mass ratio is the inability to distinguish between HT and ^{4}He. If helium gas is used

as the sweep gas or as a coolant, however, detection of either HT or ^{4}He will indicate a problem requiring immediate attention. For this reason quadrupole spectrometers remain attractive for this application because of their suitability for long-term operation with little need for recalibration and maintenance.[13]

Tritium is chemically identical to hydrogen and reacts very exothermically to form tritiated water (HTO) so it is almost always found in this form after release to the atmosphere. Because it is chemically identical to ordinary water,[11] separation would require inefficient isotope enrichment technologies that can only process small amounts of chemical at a time[9,14]; thus, what would likely be cost prohibitive makes tritium cleanup infeasible in most cases and reinforces the importance of tritium capture within the primary or secondary coolant loop.

4. HIGH TEMPERATURE REACTOR TYPES

The strategic goal of the Next Generation Reactor Program[15] is to broaden the environmental and economic benefits of nuclear energy in the U.S. economy by producing sustainable power to meet growing energy demands and demonstrating the reactor's applicability to market sectors not being served by light water reactors. There are two types of reactors under consideration for this program, which generate significant amounts of tritium: high-temperature MSRs; fluoride salt cooled high temperature reactors (FHRs such as AHTR), and HTGRs such as the very high temperature gas-cooled reactor (VHTR).

5. TRITIUM FORMATION IN HIGH-TEMPERATURE MOLTEN SALT (FLIBE) REACTORS

In a lithium-containing MSR, the primary tritium-producing reactions[1,5] are:

$$^6_3Li + n \rightarrow \, ^4_2He + \, ^3_1H + 4.8 \, MeV; \; \sigma_{th} = 940 \text{ b} \tag{9}$$

$$^7_3Li + n + 2.47 \, MeV \rightarrow \, ^4_2He + \, ^3_1H + n; \; \sigma_{avg} = 20 \text{ mb} \tag{10}$$

$$^7_3Li + n + 3.35 \, MeV \rightarrow \, ^5_1H + \, ^3_1H; \; \sigma_{avg} = 20 \text{ mb} \tag{11}$$

Neutron absorption by ^6Li is characterized by a large absorption cross-section, meaning that thermal neutrons are more likely to be absorbed by ^6Li in a collision than a collision with ^{235}U.[9] Though the small amount of natural ^6Li is consumed in this process, it is replenished by neutron absorption in beryllium (Equation 12), thus maintaining an equilibrium concentration ^6Li.[4]

Tritium formation rates (as HT or T_2) from ^7Li in molten salt reactors can be compared to rates of HTO formation in CANDU reactors. Though ^7Li and ^2H have small absorption cross sections, a large number of neutron events produce a relatively large amount of tritium.[1,9] ^7Li has an absorption cross section that varies widely with incident neutron energy, making it difficult to compare directly to other absorption cross sections; however, it is always several orders of magnitude smaller than the cross section for ^6Li[1,16,17] so a single average value is reported.

So far we have emphasized lithium neutron absorption without discussion of the other components likely to produce tritium in a molten salt reactor. Table 2 shows very low relative rates of formation for ternary events and neutron absorption by ^{19}F in a molten salt breeder reactor scaled by Briggs to 1000 MW(e) (2,250 MW(t)), justifying our continued emphasis on ^6Li and ^7Li absorption.

Table 2. Sources and rates of production of tritium in a 1000 MW(e) (2250 MW(t)) MSBR.[5]

	Production Rate (Ci/day)
$^6Li(n,\alpha)^3H$	1210
$^7Li(n,\alpha \, n)^3H$	1170
Ternary Fission	31

$^{19}F(n, ^{17}O)^3H$	9
Total	2420

5.1 Coolant Salt Composition

Since it is common to separate ^6Li from ^7Li using staged mercury solvent extraction,[14] one may wonder why ^7Li isn't used exclusively because of its lower cross section or replaced with another cation, entirely, side-stepping the problem of neutron absorption. There are two reasons that totally pure ^7Li is not used. First, lithium mixtures in salts for nuclear applications are already 99.99+% ^7Li,[4,5,18] which implies that further separation will be impractical because of limitations in isotope separation technology and prohibitive costs. Furthermore, ^6Li can be generated in situ when lithium fluoride-beryllium fluoride (FLiBe) coolant salt is circulated in a neutron-rich environment (e.g., in the core). It is produced by the following reaction:[5,9]

$$^9_5Be + n \rightarrow {}^4_2He + {}^6_3Li + 2.91 \; MeV; \;\; \sigma_{avg} = 36 \text{ mb}. \tag{12}$$
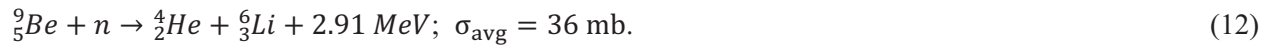
This reaction supplies about half of the ^6Li consumed in tritium formation, while the remainder comes from replacement coolant introduced to replenish depleted or degraded FLiBe.[1,5]

If the FliBe coolant were to be replaced with some other primary coolant salt, other candidate salts would have to meet the same strict requirements, including thermal stability at high temperature, stability in a neutron rich environment, and suitable thermolytic properties.[18,19] Primary salt mixtures must also be compatible with the uranium, plutonium and thorium salts that act as fuel, and which may be dissolved in the primary salt (as in a fuel salt); alternatively these could leak into the primary salt if the fuel is physically separated from the salt (as in a pebble bed or prismatic type FHR). Secondary coolants also need to be specified for thermal properties; however compatibility with fluorinated fissile isotopes (such as UF_4 or PuF_4) is necessary only in the event of catastrophic failures that lead to mixing of the primary and secondary coolants.

Most other potential cations or polyatomic ions with low neutron capture cross sections that could potentially replace lithium and beryllium are either unstable at high temperature or high-melting binary salts. Likewise, other low-neutron absorbing anions (such as ^{37}Cl) fail on other criteria, leaving lithium, beryllium, and fluorine as the only components currently thought suitable for the fuel salt.[20,21] Chosen for neutron stability and favorable thermal properties, one mixture fraction for LiF and BeF_2 must be selected to balance the other demands on the primary coolant. The particular composition for the FLiBe primary salt is chosen to optimize the conflicting demands for a relatively low melting point to minimize inlet reactor temperatures and low viscosity to minimize pumping costs.[20,22]

6. TRITIUM FORMATION IN HTGRs

All nuclear-grade graphite produces tritium via ternary fission reactions, which though is small compared to tritium production from lithium ions in MSRs, and must still be accounted for.[4] HTGRs are usually designed as either prismatic block or pebble bed types, and are normally designed with helium as a primary coolant. Regardless of type, as long as the primary coolant does not contain lithium, the primary mechanism for tritium formation is neutron absorbance in the bulk moderator graphite with minor ^6Li impurities in it. These neutron events may produce tritium as in Equation 3 or Equation 13, which then advects into the primary coolant.[5] Equation 13 illustrates one possible ternary fission producing tritium, though there are many possible pathways for tritium generation:

$$^{12}_6C + n \rightarrow {}^4_2He + {}^3_1H + {}^6_3Li + 23.4 \; MeV. \tag{13}$$

In any system where hydrogen diffusion is of interest, concentration gradients act as a driving force for movement within the system. As with an MSR, higher partial pressures (a measure of concentration) of tritium will cause diffusion into all secondary lines, including the power loop fluid. If the system

operates on an open Brayton cycle, tritium that permeates into this power fluid is released directly to the atmosphere; however, even if a closed cycle is used, tritium may still permeate through the containment system into the environment.

Yook et al.[23] provided tritium production rates on a thermal reactor basis. Table 3 shows estimated tritium production for a pebble-type gas-cooled reactor scaled to 2,250 MW(t) for comparison to production rates shown in Table 2 above.

Table 3. Sources and rates of production in a 2,250 MW(t) HTGR.

	Production Rate (Ci/day)
Ternary Fission	40
$^3He(\text{n,p})^3H$	3
$^6Li(\text{n,}\alpha)^3H$	2
$^{10}B(\text{n,}\alpha\ \alpha)^3H$	3
Total	48

Preliminary efforts at modeling tritium permeation[23] suggest that gas-cooled reactors will be within regulatory limits $(2.7 \times 10^{-5}$ Ci/g $H_2)$[24] because of the relatively low production values shown above. As a result, the rest of this analysis focuses on tritium production and permeation in MSRs (AHTR).

7.   TRITIUM PERMEATION

Once generated in FLiBe or graphite, tritium transmission depends on the molecular form it assumes, with HT being the most difficult to contain because of its low solubility and high vapor pressure.[8,25] For this reason, tritium management should focus on containment of the gaseous HT form.

The permeability of diatomic hydrogen has been of interest for many years[26] because of its roles in chemicals manufacturing, petroleum refining, and nuclear engineering. Classical diffusion theory predicts that diffusivity (and hence, permeability) for two particles with different masses could be corrected according to Equation 14, known as the "isotope effect":

$$D_2 = D_1 * \sqrt{\frac{m_1}{m_2}}. \tag{14}$$

In the case of tritium permeability, hydrogen permeabilities should be corrected by a factor of $\sqrt{1/3}$. Some studies have corroborated this effect within the bounds of experimental error for deuterium,[27-29] but this has not yet been well established for tritium. Unfortunately, another complication arises as the permeability of hydrogen or tritium in metallic alloys depend on differences in alloy composition and microstructure, and permeability data for one metal may not represent another alloy very well.[2,30] In particular, some alloys may induce an inverse isotope effect where the diffusion rates of a heavier isotope exceed that of hydrogen in the same alloy because of quantum or other effects.[31,32] Future work on tritium permeability should include data generation and statistical verification of permeability data for each alloy of interest to better predict rates of transmission.

7.1   Tritium Permeation in Coolant Salts

Tritium migration in FLiBe is dependent on the partial pressure of hydrogen (or HT) in the blanket gas, since this affects the chemical form of the tritium produced. Higher partial pressures result in greater HT formation, while lower partial pressures favor formation of the corrosive but less permeable TF.[8,33]

The permeation of tritium through FLiBe is thought to be limited by the rate of transport of T^+ ions through the molten salt,[34] since diffusion through the salt is independent of hydrogen activity or partial

pressure.[33] At 873 K (600°C) the overall mass transfer coefficient was measured by Suzuki et al.[33] to be between $7.5*10^{-6}$ and $1.1*10^{-5}$ (m s^{-1}) for two selected rates of purge gas bubbling.

7.2 Tritium Permeation Containment Metal

Hydrogen permeates though metal relatively easily compared to other gases, especially at high temperatures.[2] HTGRs require structural metals stable at elevated temperatures with good resistance to creep fatigue from cyclical heating and cooling. Incoloy 800H and Inconel 617 are good candidates for materials of construction in gas cooled reactors because they are rated for high temperature applications and resist thermal fatigue.[35,36]

Structural materials candidates for MSRs must meet the same thermal requirements as materials for HTGRs, but must also resist corrosion by fluoride salts. Hastelloy N and Incoloy 800H are good candidates for these reactors because of nickel alloys' resistance to deformation at high temperatures[2,34] and low chromium nickel alloys' superior resistance to corrosion in pure fluoride salts.

Permeability of hydrogen through metals with an oxide coat on their surfaces has been verified to be lower (usually by 1–3 orders of magnitude) than that of unoxidized metals.[37] However, oxidized coatings are prone to reduction by fluoride salts, especially at elevated temperatures, which may induce unacceptable rates of corrosion if replenished.

Table 4. Permeabilities of hydrogen in selected alloys.[37]

Alloy	Temp (°C)	Permeation Rate at 1 torr, metal thickness 1 mm (cm^3 (STP) hr^{-1} cm^{-2})	Pressure Range (torr)
Hastelloy N	605	(2.7 ± 0.2)x10^{-3}	4x10^{-3} to 750
Incoloy 800H	649	(1.6 ± 0.2)x10^{-3}	1 to 750
Incoloy 800H with Oxidation	649	(4.7 ± 0.4)x10^{-6}	10 to 750

8. MITIGATION

Once formed, tritium is transported by diffusion through the carrier salt, pipes or containment vessels, and heat exchangers.[1] Since CANDU reactor technology is relatively mature, one might wonder why further development in mitigation strategies are required before an AHTR can be built. Though CANDU have similar rates of tritium generation, the molecular form of that tritium is different, appearing as DTO rather than HT. DTO does not permeate through metals very well, and mitigation in these systems focuses on leak prevention and detection and renewing the heavy water,[3] while mitigation in molten salt reactors must contain the more volatile HT, requiring different strategies for mitigation and containment.

Focusing on diffusion through the salt and pipe walls, Briggs proposed a number of possible mitigation strategies for HT (or T_2) in his 1971 work,[5] including:

- Use of materials with reduced permeability to hydrogen/tritium
- Inert gas sparging, including bubbling in the primary salt and side-stream contacting
- Additional coolant lines between the primary line and the energy transporting (steam) line
- Adding hydrides to the primary salt to increase the solubility of tritium
- Chemical removal of hydrogen from the salt and/or sparging gas to enhance recovery.

Some of these concepts have been examined in multiple studies, while others have not yet received much attention in peer reviewed journals. An additional mitigation strategy for tritium suggested by Sabharwall[15] is consideration of the geometric properties of the heat exchangers (heat transfer area, plate thickness, etc.).

The goal of all mitigation strategies is to consistently transport tritium to some controlled removal process,[1] thus avoiding pollution and cleanup problems. The goal need not necessarily be to eliminate tritium diffusion or permeation at some specific stage in the system; a combination of strategies may be used to better achieve the overall goal, rather than a focus on one particular part of the process.

8.1 Materials Resistant to Permeation

Perhaps the most studied contribution to tritium containment has been the characterization and development of materials resistant to hydrogen permeation. One possible reason for the comparatively large number of studies on tritium permeability is the theoretical similarity of diatomic hydrogen gas to HT and the interest in hydrogen permeability through a variety of alloys in many industries.[26]

In general, hydrogen diffuses in pure metals by occupying interstitial spaces. Permeation rate is dependent on partial pressure of hydrogen (tritium) and system temperature.[26] At the temperatures of interest for a high-temperature MSRs, permeation occurs relatively easily in pure metals. Since metal oxides are partially resistant to hydrogen permeation,[1] it has been suggested that oxidizing system piping prior to run-time may help reduce the rate of hydrogen loss into the atmosphere. In practice, the molten salt can reduce oxidized pipe at elevated temperatures inducing high rates of corrosion; this method may have limited application unless some oxidized form of the metal is layered within the pipe, out of contact with the reducing salt.

Experimentation has revealed that some metals in complex with silicon are especially resistant to hydrogen permeation.[37] Tungsten, in particular, forms bonds with silicon atoms that reduce hydrogen permeation by 1-2 orders of magnitude and may merit further investigation as a diffusion-reducing coating, though there is some concern that this compound may diffuse into the base metal over time, reducing its effectiveness.[37] This method is expensive, so unless significant cost reductions are achieved, it may only be practical for very high-transfer process components such as the primary heat exchanger and the steam generator.

8.2 Inert Gas Sparging

Gas sparging is a relatively old technology for tritium management: the molten salt experiment at Oak Ridge National Laboratory and all subsequent reactor experiments have implemented some form of this mitigation strategy. In general, a helium or argon gas is used to cover the reactive salt to prevent corrosion at the salt-gas interface on the metal of construction. This gas may pick up some of the tritium in the salt through diffusion; the amount that diffuses depends on the form of tritium (TF is more effectively removed).[34] Subsequent to diffusion into the bulk gas, tritium may be removed from the gas;[1] a palladium membrane has been suggested for this application.[10] Other removal strategies have also been evaluated, including thermal diffusion and cryogenic distillation.[10]

Unfortunately, because of rates of diffusion at the salt-inert gas interface, this system must have a total transfer area comparable to that of the heat exchanger to be effective,[1] which may be infeasible because of limitations of bubble volume in the salt and reactor complex size considerations. Thus, refinement of the gaseous purge strategy and supplemental methods of mitigation are desirable.

Some work has been done on ultrasonic degassing in the molten salt to improve the diffusion of hydrogen into the gaseous purge.[18] This method uses ultrasound to release dissolved tritium from the salt before it can diffuse through heat exchanger walls into secondary or steam cycle lines, however it is not yet mature.

8.3 Additional Coolant Lines

Most modern designs for heat conduction from the reactor core include two salt lines and a power cycle fluid such as steam. The primary fuel salt and a secondary coolant line conduct heat to the steam generation system, which subsequently work on a turbine to produce grid power.

Including additional lines may help to further reduce the tritium transported to the steam generator, since tritium must diffuse through all metallic boundaries and intermediate salts. In this manner the timeframe for diffusion into inert gas lines can be extended. The major disadvantage with this method is a substantial increase in capital and operating costs for piping, instrumentation, salt, and inert gas components as well as the potential for thermal efficiency losses inherent in enlarging any system.

8.4   Chemical Removal and Metal Hydrides

In theory, adding metal hydrides to the coolant salt may increase its potential as a solvent for hydrogen absorption, increasing tritium's residence time in the salt and reducing its tendency to permeate through heat exchangers.[5] Though this process has not been formally investigated, the addition of this kind of compound may prove difficult because of the hydride ion's tendency to react according to

$$2H^- \rightarrow H_2 + 2e^-. \tag{15}$$

In a conductive solution (such as molten salt), conveyance of the resulting electrons is greatly facilitated, and this reaction could be expected to proceed relatively rapidly. Furthermore, the hydride ions reducing tendency may serve to form water from metallic oxides, greatly enhancing the corrosivity of the salt and depositing a metal film in the system as oxidized metals are reduced. This could possibly alter the flow characteristics in the core if deposition occurs on the graphite moderator, or valve sticking/plugging could occur if these deposits are found inside a valve (compare to the deposition of metals and pyrolyzed hydrocarbons in the MSRE[38]).

Chemical removal (preferential absorption and reaction in another substance) may prove difficult because of the incompatibility of molten salts with most types of materials. If some type of reusable solvent with good tritium transport properties is discovered that does not negatively impact molten salt's good thermal properties or increase corrosion losses by dilution (or some other means), this substance could become more important than any other mitigation strategy in terms of cost-effectiveness. Unfortunately no good candidates for this role are currently known, and accidental discovery seems the most likely development pathway for such a compound.

8.5   Heat Exchanger Geometric Considerations

Elevated temperatures, high surface area, and the relatively good solubility of hydrogen in steam make the steam generator the component of primary concern for tritium transport in a power generating MSR.[1,21] Reducing the area exposed to contact with one or both thermal fluids could help reduce the rate of migration of tritium in the system. This is an area of ongoing research,[15] but the maturity of heat exchanger technology suggests that currently available technologies may be implemented in MSR prototypes to simplify the overall design and reduce first-of-a-kind startup problems, thus other mitigation strategies may be more heavily emphasized in a prototype AHTR.

9.   MODELING COMPARISON OF HYDROGEN AND TRITIUM PERMEATION IN SELECTED ALLOYS

In order to estimate the tritium emission rates for the alloys of interest in MSRs and gas-cooled reactors, a model is presented here that may be used to compare alloy types at different temperatures.

Atlas et al.[1] presented a simplified model for tritium transport through a primary and secondary loop into a power cycle loop, many elements of which are duplicated as follows: a 900 MW(t) reactor running at steady-state was assumed to have a constant production rate of 7.8603×10^{15} tritium per second. Assuming forced convection and rapid mixing, the tritium content in each subsequent loop can be modeled by:

$$m_1(t) = m_p + m_1(t-1) - S * j_{12}(t) \tag{16}$$

$$m_2(t) = m_2(t-1) - S * \left(j_{12}(t) - j_{23}(t) \right) \tag{17}$$

$$m_3(t) = m_3(t-1) - S * j_{23}(t) \tag{18}$$

where m_p is the steady-state source term, m_1 is the amount of tritium in the primary salt loop, m_2 is the amount in the secondary loop, and m_3 is the amount in the tertiary (power cycle) loop; S is the surface area of the primary and intermediate heat exchangers; and j_{12} and j_{23} are tritium fluxes for the primary and secondary heat exchangers respectively.

The flux parameters are assumed to be in the diffusion-limited regime (proportional to the square root of pressure). Thus a sample flux may be calculated by

$$j_{12} = \frac{D\left(\sqrt{P_1} - \sqrt{P_2}\right)}{l} \tag{19}$$

where D is the permeability of hydrogen in the alloy, P_1 and P_2 are the partial pressures of hydrogen on each side of the heat exchanger, and l is the thickness of the alloy, assumed to be 2.0 mm for all cases. Permeability of hydrogen in metallic alloys may be modeled using a modified Arrhenius equation such as

$$D = A * \exp\left(-E_a / RT\right) \tag{20}$$

where D is the permeability of hydrogen in the metal of interest, A is a pre-exponential factor, and E_a is a pseudo-activation energy parameter. This form can be used to predict the effect of temperature on the permeability.

Partial pressures of hydrogen in each salt are predicted using solubility of hydrogen in the alloy as

$$P_i = \frac{m_i}{V_i * Sol} \tag{21}$$

where P_i is the partial pressure of hydrogen in loop i, V_i is the volume of coolant in loop i, and Sol is the solubility of hydrogen in the Arrhenius form for loop i. Parameters for the Arrhenius equations for permeability and solubility are listed in Tables 5 and 6.

No removal strategy is modeled in this code. Various alloys are used as inputs and the time until the loop becomes saturated and all tritium generated begins to permeate through the loop is shown. This will establish a residence time for each alloy, during which tritium may be removed by any of the methods mentioned above. Hence, a long residence time (the time to steady-state) represents a longer period during which tritium may be removed and is preferred.

While data for the metals of interest and FLiBe were found for this study, data on the solubility of hydrogen in KF-ZrF$_4$ could not be found. Future work should include an analysis featuring this secondary salt, since it has been chosen for use as a secondary coolant in the AHTR.[39]

Table 5. Arrhenius parameters for permeability.

Alloy	A (m^3(STP)m^{-1}s^{-1}Pa$^{-0.5}$)	E$_a$ (J/mol)	Temperature Range ($^\circ$C)	Gas ID	Reference
Incoloy 800H	1.13×10^{-7}	90430	650-950	H	2
Incoloy 800H	8.17×10^{-9}	67410	350-750	T	2
Inconel 617	1.69×10^{-7}	89180	650-950	H	2
Hastelloy N	2.59×10^{-8}	77990	≈650	H	1

Table 6. Arrhenius parameters for solubility.

Salt	A (mol m^{-3}Pa^{-1})	E$_a$ (J/mol)	Reference
FLiBe	7.892×10^{-2}	35.4×10^3	1
FLiNaK	3.98×10^{-7}	-34.4×10^3	34

These parameters are computed for several temperatures up to those anticipated for the near-term advanced concept reactors (750°C). Permeability of hydrogen and tritium are also compared for multiple temperatures in Incoloy 800H.

10. RESULTS AND DISCUSSION

The code was written and executed within the Visual Basic Advanced compiler for Microsoft Excel© as shown in Appendix A. One disadvantage of this iterative time step approach is that it becomes mathematically possible to obtain negative (reverse) fluxes through the heat exchangers, if the flux through the first heat exchanger exceeds the source term (if the partial pressure in the secondary loop becomes greater than the partial pressure in the primary loop), causing run-time errors.

This may happen if the time step is too large, or because of poorly modeled behavior in the coolant salt due to its Arrhenius form. The code uses a nested loop to avoid issues with excessively large time steps, but recalculates previous values when iterating to the specified elapsed time; i.e. it is computationally expensive. Figure 1 shows the solubility of hydrogen using the Arrhenius parameters shown in Table 6. Here, as the partial pressures from the solubilities diverge at increasing temperatures, the driving force for permeation increases exponentially, and the model destabilizes at large time steps. So, as temperature increases, the time step must be decreased to compensate, requiring longer run times.
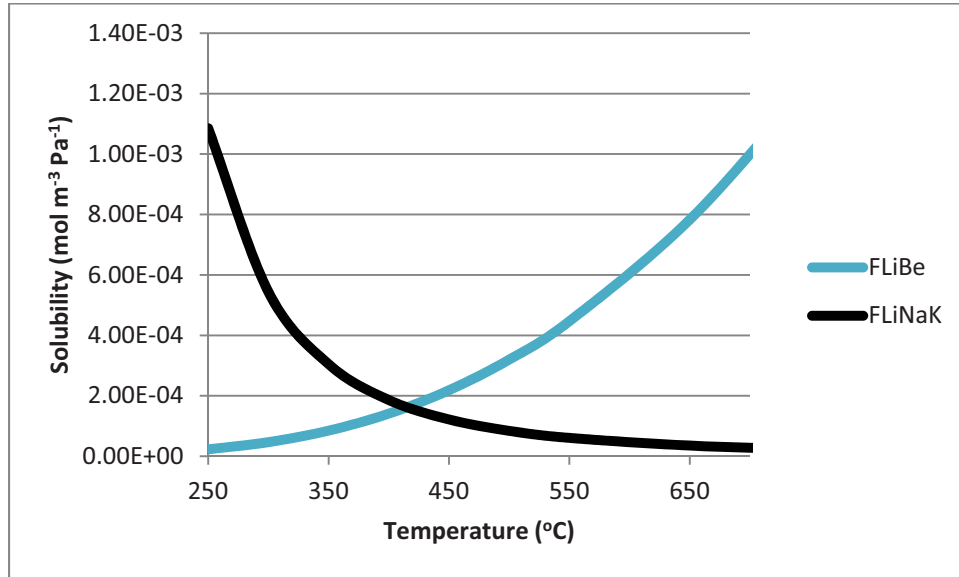
Figure 1. Solubility of hydrogen in coolant salts.

Any salt could be used in the secondary line, provided that solubility data is put into the correct form for the model and verified to ensure that the partial pressure in the secondary loop does not exceed that of the primary loop. In particular, solubility parameters for $KF\text{-}ZrF_4$ should be obtained in order to model tritium transport in AHTR, however as data for $KF\text{-}ZrF_4$ was unavailable, Arrhenius parameters were used for FLiBe in the primary loop and FLiNaK in the secondary loop.

A comparison of the permeation rate through the system for each alloy of interest is shown in Figure 2.

Figure 2. Selected alloys' permeation rate at 550°C.

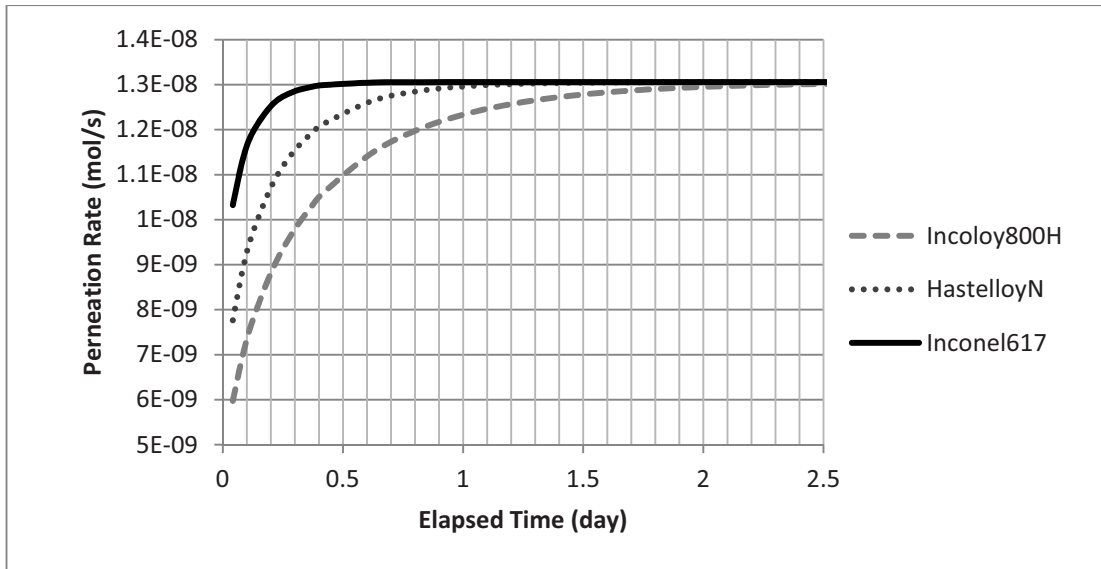Since no tritium is removed in this model, all alloys eventually allow hydrogen to permeate at its steady-state value of production, however metals that approach this value more slowly offer better resistance to hydrogen permeation and should be preferred. This is because better resistance to permeation implies that tritium will diffuse more readily into the purge gas than the containment metal, enhancing tritium removal.

Inspection reveals that Incoloy 800H approaches the steady-state production value most slowly at moderate temperatures up to 550°C, however, at moderately high temperatures (greater than 600°C) this comparative advantage is rapidly lost. In other words, the total time of transient tritium permeation behavior (representing the tritium residence time in the salt) converges to a smaller value for all candidate metals at high temperatures. This occurs because all metals offer less resistance to diffusion at elevated temperature. Figures 2 and 3 illustrates this trend: increasing the temperature by 50°C from 550°C (shown in Figure 2) to 600°C (shown in Figure 3) causes the permeation rates for the metals to converge by the time approximately 0.5 day (half a day) have passed. At higher temperatures, the permeation rates become virtually indistinguishable from one another by the time 0.25 day or less have passed. This suggests irrespective of differences in structural material (Incoloy 800H, Hastelloy N and Inconel 617) of consideration, at higher temperature (>600°C) permeation rates will be similar for all candidate alloys.
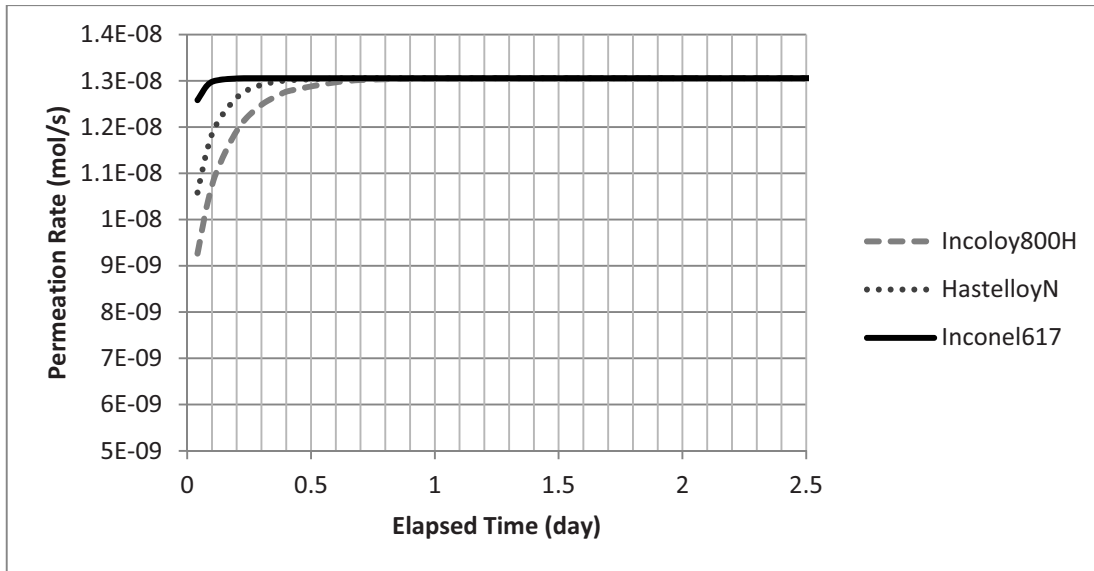
11

Figure 3. Selected alloys' permeation rate at 600°C.

In order to understand similarities and differences in permeation of hydrogen and tritium, comparative study was carried out. Unfortunately, data for tritium and hydrogen permeation comparison is only available for Incoloy 800H and large uncertainties in the Arrhenius form of the permeability compound the difficulty of comparison.

Clearly the transient permeation rate for each species is heavily dependent on the choice of Arrhenius parameters, however if no move is made toward mitigation, all cases will eventually reach the steady-state condition where all tritium formed in the core is eventually released to the system. The key to maximizing the amount of tritium removal is the selection of materials that delay this steady-state condition as long as possible (have the slowest diffusion parameters), allowing tritium to be removed from the system before it permeates into the coupled power system or process application. For this reason it is important to establish Arrhenius parameters for each material as accurately as possible. Parameters for a variety of low to moderate pressures and moderate to high temperatures are shown in Table 7. In order to directly compare these parameters, it is assumed that permeability is independent of these variables. In other words, it is assumed that extrapolation of the Arrhenius equation to all temperatures and partial pressures of interest is appropriate.

Table 7. Literature values of permeability and activation energy for hydrogen permeation in selected alloys.[2]

K0 $(cm^3 \, H_2 \, (STP) \, cm^{-1} \, s^{-1} \, atm^{-0.5})$	Q (Kcal/mol)	Temp Range (C)	Pressure Range atm
Incoloy 800, Hydrogen Permeability			
7.39×10^{-2}	17.7	600-950	5×10^{-4}-0.5
1.76×10^{-2}	15.3	700-950	1-5
7.58×10^{-2}	16.8	760-960	1
4.03×10^{-1}	20.6	600-1050	1-10
4.02×10^{-2}	15.5	450-950	5-10
5.90×10^{-2}	15.5	450-950	5-10
6.02×10^{-2}	16.6	500-1000	0.1-1
2.44×10^{-3}	13.1	300-600	0.13-08

9.24x10⁻²	18.0	750-950	<40
Incoloy800, Tritium Permeability			
2.60x10⁻²	16.1	350-750	2 ppm ³H, 1 atm H₂
1.50x10⁻³	13.5	750-950	1x10-4
Inconel 617, Hydrogen Permeability			
2.28x10⁻¹	18.9	600-1050	1-10
1.39x10⁻¹	19.8	750-950	<40

Without direct access to the data from which the Arrhenius parameters were derived, two strategies were used to show the uncertainties in permeation rate: tritium, which has only two reported sets of Arrhenius permeabilities, is shown using the minimum and maximum permeability of the two parameter sets as well as an intermediate value calculated from the other two parameters. This intermediate value, an arithmetic mean, $\overline{E_a}$, was calculated from the two E_a parameters. Hydrogen permeabilities have more data points, so parameter sets were chosen as close to the median, first quartile, and third quartile permeabilities as possible to represent the likely range of permeabilities.

Figures 4 and 5 shows that the prediction band for tritium is highly sensitive to temperature, and the range of likely permeation rates for tritium decrease sharply with increased temperature while the prediction band for hydrogen permeation remains large. These figures should not be used as evidence that high nickel alloys induce an inverse isotope effect or any other such claim. Though the high temperature permeation rates may appear to be significantly different, the differences may be an artifact of the way in which the uncertainty is calculated, since the severe limits on available data for tritium permeability give it an artificially low uncertainty.

The large degree of overlap should also emphasize the difficulty of distinguishing tritium permeation rates from hydrogen permeation rates. Collection of sufficient data to show significant statistical difference is necessary before a conclusion on the similarity or difference of permeation rates can be given with a reasonable degree of confidence. Nevertheless, as temperatures rise, the time required to reach steady-state decreases and permeation rates converge, regardless of the potential differences between tritium and hydrogen permeabilities in Incoloy 800H.
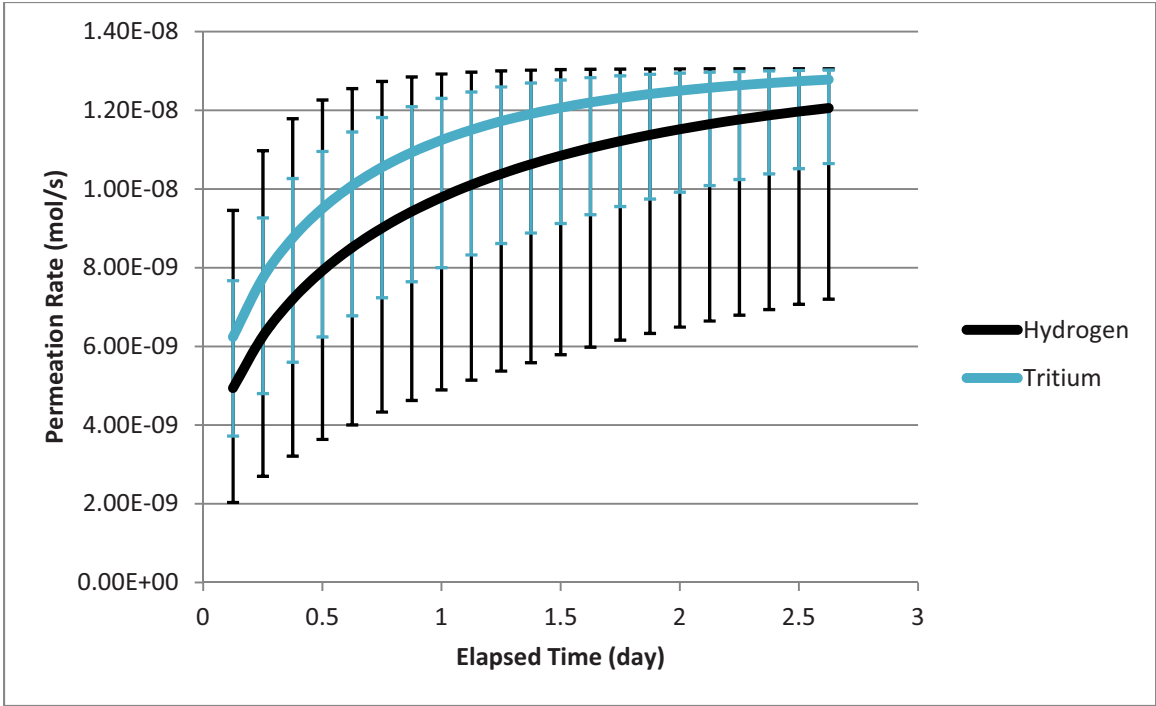
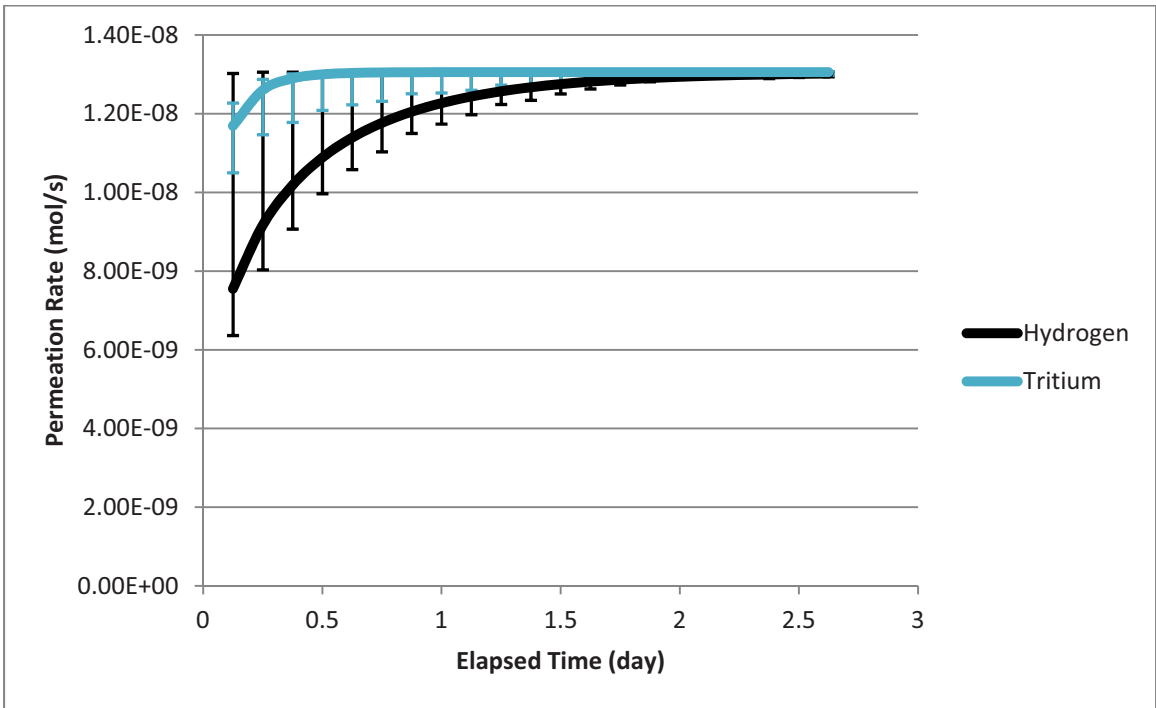Figure 4. Permeation in Incoloy 800H at 450°C.

Figure 5. Permeation in Incoloy 800H at 550°C.

11. CONCLUSIONS

Tritium is formed in somewhat large quantities in MSRs,[1] where lithium ions in the salt may absorb neutrons from the fission reaction. Tritium may then diffuse through the salt mixture, pipe walls, and heat

exchanger walls into the steam generator and could possibly escape from the system with the steam or in the industrial process application. As a radioactive isotope of hydrogen, tritium forms a hazardous gas or liquid if released into the atmosphere, so emissions should be avoided.

Strategies for mitigation were discussed, including advanced materials for the piping and heat exchangers, inert gas sparging, additional coolant lines, and metal hydride addition or chemical removal.

A model predicting transport of tritium through a system was also presented, with results for Incoloy 800H, Hastelloy N, and Inconel 617, the alloys of current interest for MSRs (such as FHRs/AHTR) and gas-cooled reactors with no tritium removal from the system to show the time until saturation. This model illustrates the limitations of alloy selection as a means of mitigating tritium release, since at moderate to high temperatures (450 to 650°C) the difference in hydrogen's ability to permeate through all alloys becomes negligible.

12. FUTURE WORK

Further refinement of the Arrhenius models should help accurately predict system properties. This should include:

- Validation of parameters for Arrhenius solubilities of hydrogen in FLiBe and FLiNaK

- Determination of parameters for Arrhenius solubilities of hydrogen in other molten salts of interest (e.g. KF-ZrF$_4$)

- Validation of parameters for Arrhenius permeabilities of tritium in Incoloy 800H

- Determination of parameters for Arrhenius permeabilities of tritium in other potential structural metals (e.g. Hastelloy N and Inconel 617)

Validation of existing parameters is important because of the logarithmic form of the linearized Arrhenius equation. The natural logarithm introduces large uncertainties in the pre-exponential factor and the pseudo activation energy parameter. Large data sets are required for rigorous analysis leading to higher confidence in the permeability prediction equations.

Analysis of statistical data regarding the relative permeabilities of hydrogen and tritium is desirable, since very few studies characterize the potential differences between hydrogen permeabilities, which are relatively easy to study, and tritium permeabilities, which require containment systems.

Further exploration of the mitigation strategies with the most potential for near-term development could also be pursued, including:

- Additional development of permeation-resistant coatings, including W-Si and various carbides

- Ultrasonic degassing to facilitate removal of tritium, reducing required total bubble volume for gas sparging

- Refinement of the geometric configuration of the intermediate heat exchangers, minimizing tritium flux

- Discovery of reusable solvents for direct tritium removal from molten salt.

13. REFERENCES

1. Atlas, M., Brickner, N., Chen, W. & Tsai, D., *Tritium Management Approach for FHRs Using Supercritical Steam, Open-Air Brayton, and Closed Gas Brayton Power Cycles*. UCTBTH-12-0006 (2012).

2. Calderoni, P. & Ebner, M. A., *Hydrogen Permeability of Incoloy 800H, Inconel 617 and Haynes 230 Alloys*. INL/EXT-10-19387 (2010).

3. Park, Tae-Keun; Kim, Seon-Ki. "Tritium: its generation and pathways to the environment at CANDU 6 generating stations." *Nuclear Engineering and Design*, 163, 405-411 (1996).

4. Ingersoll, D. T. et al., *Status of Preconceptual Design of the Asvanced High-Temperature Reactor (AHTR)*. ORNL/TM-2004/104 (2004).

5. Briggs, R. B., "Tritium in Molten Salt Reactors." *Reactor Technology*, 14 (4), 335-342 (1971).

6. Canadian Nuclear Safety Commission, Evaluation of Facilities Handling Tritium. INFO-0796, Available at http://nuclearsafety.gc.ca/eng/readingroom/healthstudies/tritium/Evaluation_of_ facilities_handling_tritium_info-0796_e.pdf.

7. Nuclear Regulatory Commission, "Frequently Asked Questions About Liquid Radioactive Releases," Available at http://www/nrc/gov/reading-rm/doc-collections/cfr/part020/part020-appb.html.

8. Suzuki, A., Terai, T. & Tanaka, S., "Tritium Release Behavior from Li2BeF4 Molten Salt by Permeation Through Structural Materials." *Fusion Engineering and Design*, 51-52, 863-868 (2000).

9. Shultis, J. K. & Faw, R. E., *Fundamentals of Nuclear Science and Engineering*, CRC Press, Boca Raton, 2008.

10. Shapiro, M. D. & Reed, C. M., *Removal of Tritium from the Molten Salt Breeder Reactor Fuel*. ORNL-MIT-117 (1970).

11. Nuclear Regulatory Commission, "Backgrounder on Tritium, Radiation Protection Limits, and Drinking Water Standards," Available at http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/tritium-radiation-fs.html.

12. Cherrier, P. P. & Reid, J., "High-Sensitivity Detection of Tritiated Water Vapour Using Tunable Diode Lasers." *Nuclear Instruments and Methods in Physics Research*, 257, 412-416 (1987).

13. Miller, P. E. & Denton, B. M., "The Quadrupole Mass Filter: Basic Operating Concepts." *Journal of Chemical Education*, 617-622 (1986).

14. Ragheb, M., *Isotopic Separation and Enrichment. Nuclear, Plasma and Radiation Science: Inventing the Future* (2012).

15. Sabharwall, P., Kim, E. S., McKellar, M., Anderson, N. & Patterson, M., *Process Heat Exchanger Options for the Advanced High Temperature Reactor*. INL/EXT-11-21584 (2011).

16. Smith, D. L., Meadows, J. W., Bretscher, M. M. & Cox, S. A., *Cross-Section Measurement for the 7Li(n,n't)4He Reaction at 14.74 MeV*. ANL/NDM-87: (Argonne National Lab, Argonne, 1984).

17. Oak Ridge National Laboratory, "Nuclear Cross Sections for Technology," *Proceedings of the International Conference on Nuclear Cross Sections for Technology (U.S. Department of Commerce National Bureau of Standards, Oak Ridge, 1979)*.

18. Holcomb, D. E., Cetiner, S. M., Flanagan, G. F., Peretz, F. J. & Yoder, G. L. . J., *An Analysis of Testing Requirements for Fluoride Salt-Cooled High Temperature Reactor Components*. ORNL/TM-2009/297, Oak Ridge National Laboratory, 2009.

19. Sabharwall, P. et al., *Molten Salts for High Temperature Reactors: University of Wisconsin Molten Salt Corrosion and FLow Loop Experiments-Issues Identified and Path Forward*. INL/EXT-10-18090 (2010).

20. Oak Ridge National Laboratory, *The Development Status of Molten Salt Breeder Reactors*. ORNL-4812, U.S. Department of Commerce, Springfield, 1972.

21. Sohal, M. S. et al., *Conceptual Design of Forced Convection Molten Salt Heat Transfer Testing Loop*. INL/EXT-10-19908 (2010).

22. Wang, Z. & Dai-Kai-Sze, *FLiBe: What Do We Know?* DKS/APEX-ALPS/NM/7-98/1 (Albuquerque, 1998).

23. Yook, D., Lee, K. J., Lee, Y. & Hong, D., *Estimation of the Tritium Behavior in the Pebble Type Gas Cooled Reactor for Hydrogen Production*. *Journal of Nuclear Science and Technology*, 43 (12), 1522-1529 (2006).

24. IAEA, *International Basic Safety Standards for Protection against Ionizing Radiation and the Safety of Radiation Sources*. Safety series (1996), Vol. 115.

25. Terai, T., Suzuki, A. & Tanaka, S., "Tritium Release from Li2BeF4 Molten Salt Breeder Under Neutron Irradiation at Elevated Temperature." *Fusion Technology*, 39, 768-772 (2001).

26. Wipf, W., "Solubility and Diffusion of Hydrogen in Pure Metals and Alloys." *Physica Scripta T94*, 43-51 (2000).

27. Ali-Khan, I.; Dietz, K. J.; Waelbroeck, F. G.; Wienhold, P., "The Rate of Hydrogen Release out of Clean Metallic Surfaces." *Journal of Nuclear Materials*, 76-77, 337-343 (1978).

28. Kizu, K.; Pisarev, A.; Tanabe, T., "Co-permeation of Deuterium and Hydrogen through Pd." *Journal of Nuclear Materials*, 289, 291-302 (2001).

29. Shiraishi, T.; Nishikawa, M.; Fukumatsu, T., "Permeation of Multi-component Hydrogen Isotopes through Nickel." *Journal of Nuclear Materials*, 254, 205-214 (1998).

30. Takeda, T., Iwatsuki, J. & Inagaki, Y., "Permeability of Hydrogen and Deuterium of Hastelloy XR." *Journal of Nuclear Materials* 326, 47-58 (2004).

31. Baer, R.; Zeiri, Y.; Kosloff, R., "Quantum diffusion of hydrogen and deuterium on nickel (100)." *Surface Science*, 411, 783-788 (1998).

32. Mak, C. H.; Brand, J. L.; Koehler, B. G.; George, S. M., "Isotope Effect in the Surface Diffusion of Hydrogen and Deuterium on Ru(001)." *Surface Science*, 188, 312-320 (1987).

33. Suzuki, A., Terai, T. & Tanaka, S., "In-Situ HT Release Behavior from Molten Li2BeF4 Salt." *Fusion Engineering and Design*, 39-40, 781-785 (1998).

34. Fukada, S. & Morisaki, A., "Hydrogen Permeability Through a Mixed Molten Salt of LiF, NaF and KF (Flinak) as a Heat-Transfer Fluid." *Journal of Nuclear Materials*, 358, 235-242 (2006).

35. Totemeier, T. C. & Tian, H., "Creep-Fatigue Environment Interactions in Inconel 617." *Materials Science and Engineering*, A (468-470), 81-87 (2006).

36. Ren, W. & Swimdeman, R., "A Review of Aging Effects in Alloy 617 for Gen IV Nuclear Reactor Applications," *PVP2006-ICPVT-11 2006 ASME Pressure Vessels and Piping Division Conference, Vancouver, BC, Canada, 2006* (unpublished).

37. Strehlow, R. A. & Savage, H. C., "The Permeation of Hydrogen Isotopes Through Structural Metals at Low Pressures and Through Metals with Oxide Film Barriers." *Nuclear Technology* 22, 127-137 (1974).

38. Thoma, R. A. *Chemical Aspects of MSRE Operations*. ORNL-4658. Oak Ridge National Laboratory. 1971.

39. Sabharwal, P. et al., Feasibility Study of Secondary Heat Exchanger Concepts for the Advanced High Temperature Reactor. INL/EXT-11-23076 (Idaho Falls, 2011).

Appendix A

Visual Basic Model Code

Appendix A
Visual Basic Model Code

```vb
Option Explicit
'********************************************************************
Function tritiumTransport(temperature As Double, elapsedTime As
    Integer, alloyType As String, Optional areaHX As Double, Optional
    IncTperm As Boolean) As Double
'********************************************************************
'This function calculates the number of moles transported through a
    'primary and secondary salt loop into a working loop (ie a steam
    'power loop). Naturally, this function is highly sensitive to the
    'assumed heat exchanger area, so this has been included as an
    'optional argument. Also note that this function is intended to
    'populate a table, as with cols 'for each temperature and rows for
    'each time (hours unless modified)

'Allowable temperatures are in Kelvin (K) up to 1023, after which the
    'model destabilizes
'Allowable alloyTypes are HastelloyN, Incoloy800H, and Inconel 617
'Allowable areaHXs are in m2 note that this assumes all heat
    'exchangers are equally sized


'********************************************************************
'Constants
Const Rg As Double = 8.314                  'J/molK ideal gas constant
Const Na As Double = 6.022e+23              'Avogadro's number

'********************************************************************
'Alloy Properties
Const E_incoloy800H As Double = 90430       'activation energy
    'Arrhenius form of permeability J/mol
Const A_incoloy800H As Double = 1.13e-07    'pre-exponential factor
        'Arrhenius form of permeability
        'm3(STP)/(m.s.Pa^0.5)

Const E_hastelloyN As Double = 77990#       'activation energy
    Arrhenius form of permeability J/mol
Const A_hastelloyN As Double = 2.59e-08     'pre-exponential factor
    'Arrhenius form of permeability
    'm3(STP)/(m.s.Pa^0.5)

Const E_Inconel617 As Double = 89180        'activation energy
    Arrhenius form of permeability J/mol
Const A_Inconel617 As Double = 1.69e-07     'pre-exponential factor
        'Arrhenius form of permeability
        'm3(STP)/(m.s.Pa^0.5)
```

```
'******************************************************************
'Salt Properties
Const E_flibe As Double = 35403#            'activation energy
    Arrhenius form solubility J/mol
Const A_flibe As Double = 0.07892           'pre-exponential factor
    'Arrhenius form solubility
    'mol.m-3.Pa-1


Const E_flinak As Double = -34400#          'activation energy
    Arrhenius form solubility J/mol
Const A_flinak As Double = 3.98e-07         'pre-exponential factor
      'Arrhenius form solubility
      'mol.m-3.Pa-1


'We could add the properties for a secondary loop of NaF-ZrF4 here if
    'desired


'******************************************************************
'Transfer Properties
Const priVol As Double = 15                 'm3 primary coolant volume
Const secVol As Double = 4                  'm3 secondary coolant
    'volume
Const PRF As Double = 1                     'permeation reduction
    'factor. Basically just a knob to fiddle with when speculating
    'about how reducing the permeation would affect the system. 1
    'indicates no 'reduction


Const charThickness As Double = 0.002       'm. characteristic
    'thickness of the alloy


'******************************************************************
'Source term (given in Atlas, et al, "Tritum Management Approach for
    'FHR's Using 'Supercritical Steam, Open-Air Brayton, and Closed
    'Gas Brayton Power Cycles". UCBTH-12-006. May 2012


Const tritiumSource As Double = 7.86403e+15 / Na
    'moles per second gen at steady state


'******************************************************************
'Check to see if user has entered some heat exchanger data
'Boolean check to see whether the variable in the argument has been
    'Initialized. In this case, an uninitialized varible (0) indicates
    'that <user> has left this field blank.


If areaHX = 0 Then
    areaHX = 1200

                                            'm2 Default HX area for
    'heat exchangers. Taken from UCBTH-12-006
```

```
End If


'*****************************************************************
'Initialize the appropriate case. User has entered the correct string
     'or an error 'message will appear.

Dim Ea As Double                          'Generic Arrhenius
     'diffusion activation energy
Dim Aa As Double                          'Generic Arrhenius
     'diffusion pre-exponential factor

Select Case alloyType
    Case "HastelloyN"
            Ea = E_hastelloyN
            Aa = A_hastelloyN
    Case "Incoloy800H"
            'Check to see whether the special case of tritium data is
    'pertinent (vs the usual H data)
            If IncTperm = True Then        'Boolean Check: is this
    'var initialized?
                Ea = 67410
                Aa = 8.17e-09
            Else
            Ea = E_incoloy800H
            Aa = A_incoloy800H
            End If
    Case "Inconel617"
            Ea = E_Inconel617
            Aa = A_Inconel617
    Case Else
            MsgBox ("Error: alloyType is not supported. Allowable
    types are case sensitive and include HastelloyN, Incoloy800H, and
    Inconel617.")
    End Select

'*****************************************************************
'Calculate the Hydrogen permeability of the chosen alloy at input
     'temperature T
Dim Kx As Double
Kx = Aa * Exp(-Ea / (Rg * temperature))    'permeability mol.m-1.s-
     '1.Pa-0.5

'*****************************************************************
'Calculate the solubility of Hydrogen in the primary and secondary
     'lines
Dim solPrimary As Double
Dim solSecondary As Double
```

```vba
solPrimary = A_flibe * Exp(-E_flibe / (Rg * temperature))
'mol.m-3.Pa-1

solSecondary = A_flinak * Exp(-E_flinak / (Rg * temperature))
'mol.m-3.Pa-1


'*********************************************************************
'Tritium in loop array declarations
Dim TprimaryLoop() As Double
Dim TsecondaryLoop() As Double
Dim TsteamLoop() As Double

'These are dynamic arrays, resize them for the elapsedTime
ReDim TprimaryLoop(0 To elapsedTime + 1)
ReDim TsecondaryLoop(0 To elapsedTime + 1)
ReDim TsteamLoop(0 To elapsedTime + 1)

'Declare some constants for use in the loop
Dim molP1 As Double
    molP1 = solPrimary * priVol
Dim molP2 As Double
    molP2 = solSecondary * secVol
Dim permT As Double
    permT = Kx / (PRF * charThickness)

'Declare variables to be used in loop
Dim source As Double
Dim Tcounter1 As Double
Dim Tcounter2 As Double
Dim TcounterSteam As Double
'The counter variables are used to make the arrays easier to write

Dim partPprimary As Double
Dim partPsecondary As Double
Dim hxFlux1 As Double
Dim hxFlux2 As Double

'Begin the loop
Dim scounter As Double
Dim hourcounter As Double
Dim sTimestep As Double

sTimestep = 1 / 20                           'In seconds. This is used
    'to correct instabilities from rounding errors with large pressure
    'driving forces

For hourcounter = 0 To elapsedTime
    'an interior loop must be used for stability
    For scounter = 0 To 3600 / sTimestep
```

```
        source = tritiumSource * sTimestep
        'This is mol/s * sec i.e. it is a number of moles to be
            'transported
        partPprimary = Tcounter1 / molP1
        partPsecondary = Tcounter2 / molP2

        hxFlux1 = (Sqr(partPprimary) - Sqr(partPsecondary)) * permT
        hxFlux2 = Sqr(partPsecondary) * permT

        Tcounter1 = Tcounter1 + source - (sTimestep * areaHX *
            hxFlux1)
        Tcounter2 = Tcounter2 + sTimestep * areaHX * (hxFlux1 -
            hxFlux2)
        TcounterSteam = TcounterSteam + sTimestep * areaHX * hxFlux2
    Next
    TprimaryLoop(hourcounter) = Tcounter1
    TsecondaryLoop(hourcounter) = Tcounter2
    TsteamLoop(hourcounter) = TcounterSteam

Next

'Output the last element of the desired array to the cell
tritiumTransport = hxFlux2 * areaHX

End Function
```