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# TRITIUM PRODUCTION AND PERMEATION IN HIGH-TEMPERATURE REACTOR SYSTEMS

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## ABSTRACT

Tritium $({}^3_1H)$ is a radioactive isotope of hydrogen 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 ${}^7Li$. Also in fusion, the concept of breeding tritium during the fusion reaction is of significance for the future needs of a large-scale fusion power plant. Tritium is of special interest among the fission products created in next-generation nuclear reactors such as gas cooled reactors and molten salt reactors, because of the large quantities produced when compared with conventional light-water reactors (LWR) and the higher temperatures of operation for these systems enhances permeation. To prevent the tritium contamination of proposed reactor buildings and surrounding sites, this paper examines the root causes and potential solutions for mitigation of permeation 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 along with mitigation strategies for tritium permeation.

## INTRODUCTION

Hydrogen is the most common element in the universe, representing about three-quarters of the measurable mass. It is very light, often just 1 proton weighing approximately 1 atomic mass unit (amu), usually in the form of $H_2$, and diffuses readily through most media, especially at elevated temperatures. It is also highly reactive, reducing other compounds such as atmospheric oxygen:

$$H_2(\mathrm{g}) + \frac{1}{2}O_2(\mathrm{g}) \rightarrow H_2O(l)\,;\ \Delta H^0 = -285\,\frac{kJ}{mol} \tag{1}$$

The large negative value for the standard enthalpy of formation, $\Delta H^0$ indicates that the reaction is very exothermic, so the reverse reaction takes a significant amount of energy to complete.

Tritium $({}^3_1H)$ is a radioactive isotope of hydrogen with a nucleus composed of 1 proton and 2 neutrons. Tritium $({}^3_1H)$ is the heaviest and only radioactive isotope of hydrogen with a physical half-life at 12.3 years, in nature it is a result of cosmic ray interactions in the atmosphere. As discussed in National Council on Radiation Protection and Measurements (NCRP), "*When tritium atoms are formed by cosmic radiation, they initially have high kinetic energy. The most probable initial reaction for tritium at pressures below atmospheric is a three body collision with oxygen to form the stable compound* $T_2O$*. Subsequent reactions of the* $T_2O$ *would be expected to yield tritiated water (HTO), but not HT (similar to hydrogen gas), in the atmosphere. Repeated photochemical decomposition of* $T_2O$ *and reactions with ozone are necessary to account for the relative abundance of HT and HTO.*" The tritium concentration in atmospheric hydrogen is stable. The vapor, HTO, is formed readily and is the most commonly encountered form of tritium in the environment. Gaseous tritium ($T_2$) at room temperature tends to form HT by isotopic exchange reaction with gaseous hydrogen if present. The nuclide, ${}^3$H decays to form ${}^3$He by emission of beta particle with a maximum energy of 18.6 keV and an average energy of 5.7 keV [1].

Tritium is formed in nuclear reactors by ternary fission events (rare emissions of three nuclides rather than two during fission) and neutron absorption (and subsequent decay) of predecessor radionuclides, particularly ${}^6Li$ and ${}^7Li$ and by activation of light elements such as Boron (${}^{10}B$), which is used for reactivity control in Pressurized Water Reactors (PWRs).

Tritium follows closely the reactions of ordinary hydrogen, but the relatively large mass differences make isotopic effects easily discernible. The properties of the oxides of the three hydrogen isotopes are listed in Table 1[2].

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**TABLE 1. THERMODYNAMIC PROPERTIES OF THE OXIDES OF THE HYDROGEN ISOTOPES [2].**

| Property | HTO | $H_2O$ | $D_2O$ | $T_2O$ |
|---|---|---|---|---|
| Boiling Point ($^oC$) | 100.76 | 100 | 101.42 | 101.51 |
| Triple Point Temperature ($^oC$) | 2.25 | 0.01 | 3.82 | 4.49 |
| Triple Point Pressure (mm Hg) | 4.73 | 4.58 | 5.02 | 4.87 |
| Heat of vaporization @ boiling point (kcal $mole^{-1}$) | 9.91 | 9.72 | 9.9 | 10.1 |

## TRITIUM PRODUCTION IN NUCLEAR REACTORS

Tritium is produced by thermal or fast neutron reactions with various light elements found in the nuclear reactors.

Tritium is of special interest among the fission products created in next-generation nuclear power plants mainly because of its mobility. Substantial amounts of experimental data suggest that hydrogen permeates readily in metals at elevated temperatures, and some data may be found suggesting that tritium behaves similarly in these high-temperature applications [3]. The anticipated difficulty in containing tritium justifies special care in system design, as it is considered a biohazard and thus has health and safety concern. A sound understanding of tritium's generation pathways, as well as its properties and possible ways to prevent its escape are necessary to establish a confinement strategy for advanced reactor designs. In the following sections, different reactor types are discussed along with different reactions for tritium formation.

### Light Water Reactors

As indicated in NCRP, the annual rate of production of the fission product tritium by a 1000 $MW_e$ LWR is in the range of 15,000 to 25,000 Ci (this estimates takes into account the production and fissioning of Pu, which has a tritium yield twice that of U). Zirconium, which is used as a cladding alloy, combines with tritium to form zirconium hydride (tritide), which also results in retention of tritium in stable form. Thus, tritium is released only through defects in the zirconium alloy clad, which are very infrequent. Prior to 1971, control rods of boron carbide encased in stainless steel were used in BWRs, which led to production of an additional 10,000 Ci of tritium annually [4] and the tritium formed in the fuel readily diffused through the stainless steel cladding. Since 1971, gadolinium oxide, which does not produce tritium, has been incorporated in BWR fuel to control excess reactivity. In PWRs, the control rods are made of an alloy of silver, indium, and cadmium, which does not generate/produce tritium. However, to control excess reactivity, boric acid is used that generates 700 Ci of tritium per year from a 1000 $MW_e$ PWR [1]. Table 2 shows the reported release rates for tritium for LWRs with zirconium alloy clad fuel. Equation 2 is most important in PWRs for tritium generation.

$$ {}^{10}_{5}B + n \rightarrow 2\,{}^{4}_{2}He + {}^{3}_{1}H + 0.324\ MeV;\ \sigma_{\text{th}} = 12\ \text{mb} \tag{2}$$

**TABLE 2. REPORTED TRITIUM RELEASE RATES (1972–74) FOR LWRS WITH ZIRCONIUM ALLOY-CLAD FUEL [1].**

| Reactor Parameters | BWR | PWR |
|---|---|---|
| Number of reactors | 9 | 9 |
| Total Power (MW) | 17,000 | 20,000 |
| Total nuclear thermal output ( full power $MW_t$ years) | 36,000 | 22,000 |
| Tritium released (all reactors, 3 years) | | |
| Gaseous (Ci) | 210 | 240 |
| Liquid (Ci) | 490 | 5500 |
| Total (Ci) | 700 | 5800 |
| Specific release rate ratio, (Ci $MWt^{-1}y^{-1}$) | 0.02 | 0.26 |
| Average release per $GW_e$ (Ci $y^{-1}$) | 63 | 830 |

### Heavy Water Reactors

The use of heavy water as a moderator in Canada Deuterium Uranium (CANDU) reactors permits fission of natural uranium oxide fuel, but results in the production of tritium by neutron activation of the deuterium to a degree far in excess of that produced in the fuel [5]. The anticipated levels of tritium in the heavy water after several years of operation exceed 5 Ci per liter. Equation 3 illustrates the primary reaction in CANDU reactors for tritium generation.

$$ {}^{2}_{1}H + n \rightarrow {}^{3}_{1}H + \gamma + 6.26\ MeV;\ \sigma_{\text{th}} = 550\ \mu\text{b} \tag{3}$$

### Advanced Reactors

Advanced reactors, such as high-temperature gas cooled reactors (HTGR), will operate at higher temperatures with higher fuel burnup, and potentially will have a more efficient power production cycle. In HTGRs, the primary coolant is helium; the tritium generated will exist in elemental form rather than water. 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, the primary mechanism for tritium formation is via activation of impurities (such as $^6$Li and boron) in the bulk graphite moderator and through ternary fission, as shown in Table 3. These neutron events may produce tritium, as shown in Equation 4. This equation illustrates one possible nuclear reaction producing tritium, though there are many possible pathways for tritium generation:

$$ {}^{12}_{6}C + n \rightarrow {}^{4}_{2}He + {}^{3}_{1}H + {}^{6}_{3}Li + 23.4\ MeV. \tag{4}$$

In any system where hydrogen diffusion is of interest, concentration gradients act as a driving force for movement within the system. Yook et al. [6] provided tritium production rates on a thermal reactor basis. Table 3 shows estimated tritium production for a pebble-type gas-cooled reactor for 2,250 MW(t).

**TABLE 3. SOURCES AND RATES OF PRODUCTION IN A 2,250 MW(T) HTGR [6].**

| Source | Production Rate (Ci/day) |
|---|---|
| Ternary Fission | 40 |
| $^{3}He$(n,p)$^{3}H$ | 3 |
| $^{6}Li$(n,α)$^{3}H$ | 2 |
| $^{10}B$(n,α α)$^{3}H$ | 3 |
| Total | 48 |

Preliminary efforts at modeling tritium permeation [6] suggest that gas-cooled reactors will be within regulatory limits because of the relatively low production rates shown above.

The tritium production in gas cooled reactors is much less than in molten salt reactors (MSRs). The primary system of a typical MSR uses molten salt with fuel material dissolved directly in the circulating salt. Current concept such as the advanced high temperature reactor (AHTR) and fluoride salt cooled high temperature reactor (FHR) use molten salt in combination with solid, stationary fuel. However, much of the MSR-related experience is directly relevant to the AHTR and FHR because of the primary loop reference salt for AHTR and FHR is $Li_2BeF_4$, which is referred to as "FLiBe," was also used as the primary coolant for MSRs. Equations 5–8 characterize tritium formation in MSRs:

$$^{6}_{3}Li + n \rightarrow {}^{4}_{2}He + {}^{3}_{1}H + 4.8\ MeV;\ \sigma_{\mathrm{th}} = 940\ \mathrm{b} \tag{5}$$

$$^{7}_{3}Li + n + 2.47\ MeV \rightarrow {}^{4}_{2}He + {}^{3}_{1}H + n;\ \sigma_{\mathrm{avg}} = 20\ \mathrm{mb} \tag{6}$$

$$^{7}_{3}Li + n + 3.35\ MeV \rightarrow {}^{5}_{2}He + {}^{3}_{1}H;\ \sigma_{\mathrm{avg}} = 20\ \mathrm{mb} \tag{7}$$

$$^{19}_{9}F + n + 7.56\ MeV \rightarrow {}^{17}_{8}O + {}^{3}_{1}H;\ \sigma_{\mathrm{avg}} = 30\ \mu\mathrm{b} \tag{8}$$

In the above reactions (Equations 2–8), the parameter $\sigma_x$ represents the absorption cross section for the parent nuclide in barns (b) and the subscript refers to the energy of the incident neutron, where *th* refers to thermal with neutron energies ≈0.02 eV, and *avg*, refers to average neutron energies. Larger numbers indicate a 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 $\sigma_{\mathrm{th}235U}$=587b). However, heavy water molecules and $^{7}Li$ subjected to long periods of neutron bombardment (for example, 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 total number of neutronic collisions with parent nuclides. Table 4 shows estimated tritium formation rates for four reactor types: MSR, CANDU (heavy water reactor), HTGR, and PWR.

**TABLE 4. SOURCES AND RATES OF PRODUCTION OF TRITIUM 1000 MW(E) REACTOR [7,8,9].**

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

Tritium formation rates (as HT or $T_2$) from $^{7}Li$ in molten salt reactors can be compared to rates of HTO formation in CANDU reactors. Lithium neutron absorption has been emphasized in the literature, without discussion of the other components likely to produce tritium in a molten salt reactor. Table 5 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 the continued emphasis on Lithium ($^{6}Li$ and $^{7}Li$) absorption.

**TABLE 5. SOURCES AND RATES OF PRODUCTION OF TRITIUM IN A 1000 MW(E) (2250 MW(T)) MSBR[8].**

| | Production Rate (Ci/day) |
|---|---|
| $^{6}Li$(n,α)$^{3}H$ | 1210 |
| $^{7}Li$(n,α n)$^{3}H$ | 1170 |
| Ternary Fission | 31 |
| $^{19}F$(n,$^{17}O$)$^{3}H$ | 9 |
| Total | 2420 |

Tritium, like hydrogen, can diffuse through metals at high temperatures and therefore, various schemes for trapping the tritium to reduce release from the primary circuit appear necessary and are discussed later in the paper.

## TRITIUM PERMEATION

FLiBe has been emphasized for use as the AHTR primary coolant, mainly because of its higher heat-transfer performance and lower neutron absorption cross section. But, a particular concern is the production of tritium gas (mainly because of lithium in the salt), which could permeate through the Intermediate Heat Exchanger (IHX) to the process application, as shown in Figure 1. Testing of diffusion of tritium surrogates across prototypical subassemblies will provide data for extrapolation to the larger assemblies [10].

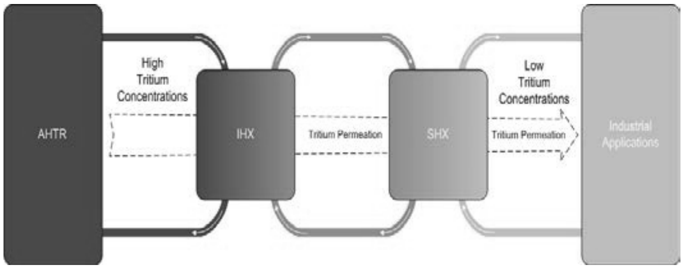

**FIGURE 1. TRITIUM PERMEATION PATHWAY IN THE HEAT TRANSPORT LOOP.**

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, small molecular size and high vapor pressure [11,12]. 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 [13] because of its roles in chemical manufacturing, petroleum refining, and nuclear engineering. Classical diffusion theory predicts that in most cases diffusivity (and hence, permeability) for two particles with different masses could be corrected according to Equation 9, known as the "isotope effect":

$$D_2 = D_1 * \sqrt{\frac{m_1}{m_2}} \tag{9}$$

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 [15,16]. Tritium migration in FLiBe is dependent on the partial pressure of hydrogen (or HT) in the blanket gas (Argon or Helium), 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 [11,17]

The permeation of tritium through FLiBe is thought to be limited by the rate of transport of $T^+$ ions through the molten salt [18] since diffusion (transport) through the salt is independent of hydrogen activity or partial pressure [17]. At 873 K (600°C) the overall mass transfer coefficient in static FLiBe was measured by Suzuki et al. [17] to be between $7.5 \times 10^{-6}$ and $1.1 \times 10^{-5}$ ($m\ s^{-1}$) for two selected rates of purge gas bubbling.

### Tritium Permeation through Containment Metal.

The permeability of hydrogen or tritium in metallic alloys depends on alloy composition and microstructure. Permeability data for one metal may not represent another alloy very well [3,14]. Future work on tritium permeability should include verification of permeability data for each alloy of interest to better define permeability of required alloys.

Hydrogen permeates though metal relatively easily compared to other gases, especially at high temperatures [3]. 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 as structural materials in gas cooled reactors because they are rated for high-temperature applications and resist thermal fatigue [19,20].

Structural material candidates for AHTRs 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 [3,18] and low chromium composition, which enhances 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[21]. However, oxidized coatings are prone to reduction by fluoride salts, especially at elevated temperatures, which may induce unacceptable rates of corrosion if the oxide is not replenished. Surface defects in oxide coatings still remain a problem. Table 6 shows the permeabilities of hydrogen in selected high temperature alloys.

**Table 6. Permeabilities of Hydrogen in Selected Alloys[21].**

| Alloy | Temp (°C) | Permeation Rate at 1 torr, metal thickness 1 mm ($cm^3$ $H_2$ (STP)/cm.sec.$atm^{1/2}$) | Pressure Range (torr) |
|---|---|---|---|
| Hastelloy N | 605 | $(2.7\pm0.2) \times 10^{-3}$ | $4\times10^{-3}$ to 750 |
| Incoloy 800H | 649 | $(1.6\pm0.2) \times 10^{-3}$ | 1 to 750 |
| Incoloy 800H with Oxidation | 649 | $(4.7\pm0.4) \times 10^{-6}$ | 10 to 750 |

## MITIGATION/CONTROL STRATEGIES

In advanced reactors such as AHTR and HTGR, tritium is transported by diffusion and convection through the carrier salt or gas, pipes or containment vessels, and heat exchangers. Since CANDU reactor technology is relatively mature, one might wonder why further developments in mitigation strategies are required before an AHTR is built. Though CANDU has higher 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 [22]. 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 including [8]:

- 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 literature. The goal of all mitigation strategies is to transport tritium consistently to some controlled removal process [23], 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.

## 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 large number of studies on $H_2$ is because it is comparatively easier to work with and theoretical similarity of diatomic hydrogen gas to HT.

In general, hydrogen diffuses in pure metals by occupying interstitial spaces. Permeation rate is dependent on the partial pressure of hydrogen (tritium) and the system temperature [13]. At the temperatures of interest for high-temperature MSRs, permeation occurs relatively easily in pure metals. Since metal oxides are partially resistant to hydrogen permeation [23], 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 pipes 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 [21]. Tungsten, in particular, forms bonds with silicon atoms that reduce hydrogen permeation by 1 to 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 [21]. This method is expensive; 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.

## Inert Gas Sparging

Gas sparging is a relatively old technology for tritium management (though it does lead to some neutronic/reactivity concerns that should also be considered, if performed in the reactor vessel); 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 [18]. Subsequent to diffusion into the bulk gas, tritium may be removed from the gas [23]; a palladium membrane has been suggested for this application [24]. Other removal strategies have also been evaluated, including thermal diffusion and cryogenic distillation [24].

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 [23], 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 [25]. 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.

## 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 [11]. 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:

$$2H^- \rightarrow H_2 + 2e^- \qquad (10)$$

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 (compared to the deposition of metals and pyrolyzed hydrocarbons in the MSRE [26]).

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 a 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.

## Heat Exchanger Geometric Considerations

At elevated temperatures, with relatively good solubility of hydrogen in steam, the steam generator becomes the component of primary concern for tritium transport in a power generating MSR and AHTR. Reducing the area exposed to contact with one or both thermal fluids could help reduce the rate of migration of tritium in the system, but also does lead to reduction in the effectiveness of heat transfer, thus it is a tradeoff. This is an area of ongoing research [27, 28] and could be applied to first-of-a-kind prototype of an AHTR to gain experience in order to come up with a design of an optimized heat exchanger.

Other alternative could be utilizing a duplex type heat exchanger with flowing liquid lithium in between duplex tubes [29]. As lithium has very high solubility for tritium and might be able to absorb it all up, as it permeates through from the primary system. Also SiC could potentially be utilized ( as the construction material for the secondary side heat exchanger as it has very low permeability to tritium, but there still exists some fabrication issues which needs further development.

## MODELING COMPARISON OF HYDROGEN AND TRITIUM PERMEATION IN SELECTED ALLOYS

To estimate the tritium permeation rates for the alloys of interest in advanced reactors, a model is presented here that may be used to compare alloy types at different temperatures. For further details refer to Schmutz et.al [10].

Atlas et al. [23] 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 $7.8603 \times 10^{15}$ tritium per second. Assuming forced convection and rapid mixing, the tritium content in each subsequent loop can be modeled by:

$$m_1(t) = m_p + m_1(t-1) - S * j_{12}(t) \tag{11}$$

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

$$m_3(t) = m_3(t-1) - S * j_{23}(t) \tag{13}$$

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. Assuming $H_2$ is present in the system then the sample flux is calculated by:

$$j_{12} = \frac{D(\sqrt{P_1} - \sqrt{P_2})}{l} \tag{14}$$

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 walls, 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:

$$D = A * \exp\left({}^{-E_a}/_{RT}\right) \tag{15}$$

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

Depending on the salt being used in the secondary coolant the solubility of hydrogen in the salt can be determined. As a result, the partial pressure can be determined by [23]:

$$P_i = \frac{m_i}{V_i * Sol} \tag{16}$$

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 $i$. Table 7 and 8 shows the parameters for the Arrhenius equation for solubility and permeability.

**TABLE 7. ARRHENIUS PARAMETERS FOR SOLUBILITY.**

| Salt | A (mol m$^{-3}$Pa$^{-1}$) | E$_a$ (J/mol) | Reference |
|---|---|---|---|
| FLiBe | $7.892 \times 10^{-2}$ | $35.4 \times 10^3$ | 23 |
| FLiNaK | $3.98 \times 10^{-7}$ | $34.4 \times 10^3$ | 18 |

**TABLE 8. ARRHENIUS PARAMETERS FOR PERMEABILITY.**

| Alloy | A (m$^3$(STP)m$^{-1}$s$^{-1}$Pa$^{-0.5}$) | E$_a$ (J/mol) | Temperature Range (°C) | Gas ID | Reference |
|---|---|---|---|---|---|
| Incoloy 800H | $1.13 \times 10^{-7}$ | 90430 | 650–950 | H | 3 |
| Incoloy 800H | $8.17 \times 10^{-9}$ | 67410 | 350–750 | T | 3 |
| Inconel 617 | $1.69 \times 10^{-7}$ | 89180 | 650–950 | H | 3 |
| Hastelloy N | $2.59 \times 10^{-8}$ | 77990 | ≈650 | H | 23 |

No removal strategy is modeled in this code. Various alloys are used as inputs and the time until the loop becomes saturated is determined and all tritium generated begins to permeate through the loop. This will establish a residence time (break through time) for each alloy, during which tritium may be removed by any of the methods mentioned above. Hence, a long residence time represents a longer period (though it is very small when compared with the operating life of the reactor) during which tritium may be removed and is preferred.

While data for the metals of interest and coolants (such as FLiBe and FLiNaK) were found for this study, data on the solubility of hydrogen in KF-$ZrF_4$ could not be found. Both FLiNaK and KF-$ZrF_4$ are potential candidates for secondary salts mainly because of their heat transfer and transport characteristics [28]. Future work should include an analysis featuring this secondary salt.

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.

## RESULTS AND DISCUSSION

Any salt could be used in the secondary system, 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. A comparison of the permeation rate through the system for each alloy of interest is shown in Figure 2. Arrhenius parameters were used for FLiBe in the primary loop and FLiNaK in the secondary loop.

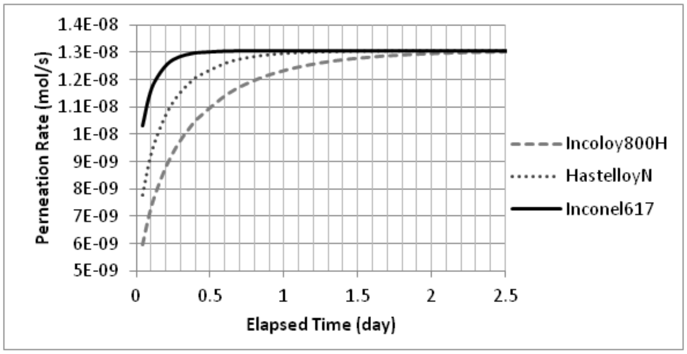

**FIGURE 2. SELECTED ALLOYS' PERMEATION RATE AT 550°C.**

All Ni alloys under consideration eventually allow hydrogen to permeate through after 2 days, which suggests that the advance reactor designs need tritium mitigation strategies. Increasing the temperature by 50°C from 550°C (shown in Figure 2) to 600°C (shown in Figure 3) accelerates convergence of permeation rates for the metals. Irrespective of increase in temperature, the permeation time is very short when compared to reactor cycle length.

At higher temperatures, the permeation rates become virtually indistinguishable from one another by the time 0.25 day or less has 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.

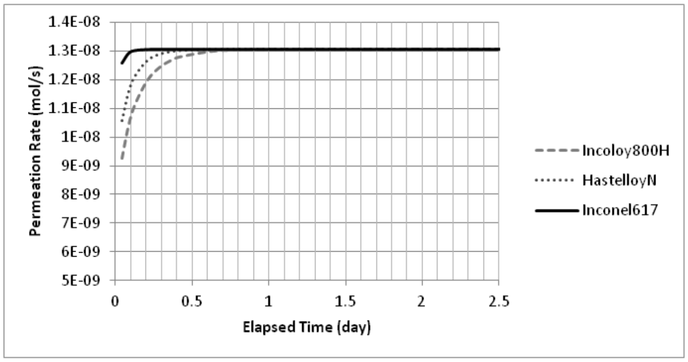

**FIGURE 3. SELECTED ALLOYS' PERMEATION RATE AT 600°C.**

To understand similarities and differences in the permeation of hydrogen and tritium, a comparison study was carried out, as shown in Figure 4. Unfortunately, data for tritium and hydrogen permeation is only available for Incoloy 800H, and large uncertainties in the Arrhenius form of the permeability compound leads to the difficulty of comparison.

The key to mitigate tritium permeation is to apply the mitigation strategies discussed earlier in the primary and secondary loop such that negligible amount (i.e. below regulatory requirement) of tritium is present at the power production or process application side.

The large degree of overlap should also emphasize the difficulty of distinguishing tritium permeation rates from hydrogen permeation rates (difference in rate being very small) in Incoloy 800H, as shown in Figure 4 and 5.

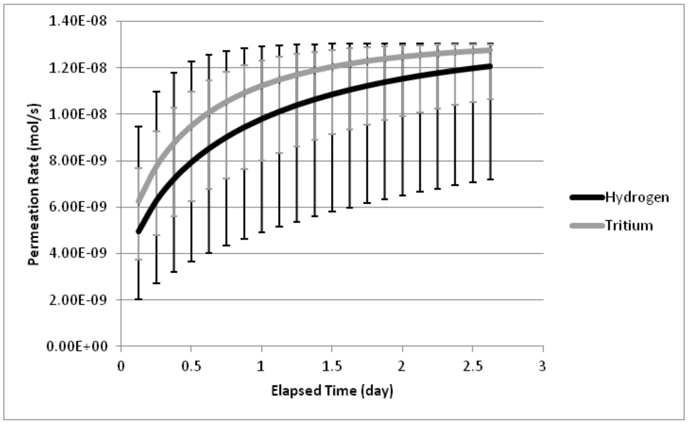

**FIGURE 4. PERMEATION IN INCOLOY 800H AT 450°C.**

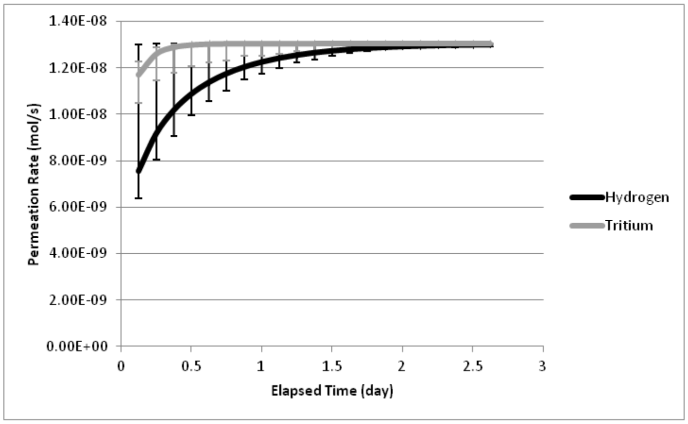

FIGURE 5. PERMEATION IN INCOLOY 800H AT 550°C.

## CONCLUSIONS

Studies of several commercial LWRs by NCRP have shown that the average annual release to the environment by a $1GW_e$ reactor was about 60Ci $y^{-1}$ for BWR, and 830 Ci $y^{-1}$ for PWR.

For advanced reactors the tritium is formed in somewhat large quantities in AHTRs when compared with HTGRs, where lithium 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. Capture/ removal methods of tritium from advanced reactors have not yet been established, but must be addressed before the plants are licensed or commercialized.

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

A model predicting transport of tritium through a system was also presented for Incoloy 800H, Hastelloy N, and Inconel617, the alloys of current interest for advanced reactors. Irrespective of differences in structural composition of the materials at higher temperature (>600°C) permeation rates were very similar for all candidate alloys, thus enforcing tritium mitigation strategy even further for AHTR development.

## FUTURE WORK

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

- Determination of parameters for Arrhenius solubilities of hydrogen in other molten salts of interest (e.g., KF-$ZrF_4$)
- Determination of parameters for Arrhenius permeabilities of tritium in other potential structural metals (e.g., Hastelloy N and Inconel 617).

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, and considering reactivity concerns in the core
- Refinement of the geometric configuration of the intermediate heat exchangers, minimizing tritium flux
- Material with high solubility to avoid significant partial pressures, which drives permeation.

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