
Development and Demonstration of an *In-Situ* Tritium Scavenger

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ABSTRACT:

In gas-cooled and salt-cooled advanced reactors, tritium (^3H) is produced by neutron transmutation of lithium-6, beryllium-9, or helium-3, when they are present in the primary coolant circuit. Tritium is a low-energy beta emitter, and it has a half-life of 12 years. At high temperature, tritium has high diffusivity through metals and metal alloys, so it readily diffuses through the high surface area metal heat exchangers, as well as through piping and vessel walls and, eventually, is released to the environment. Thus, an effective method of controlling tritium emissions to the atmosphere and diffusion to downstream fluid streams needs to be developed and demonstrated. This need is particularly pertinent for high temperature reactors that may couple to open-air Brayton cycles, such as molten salt reactors (MSR) and fluoride salt-cooled reactors (FHR) [1]. Tritium management is also particularly pertinent for nuclear process heat applications of high and very high temperature reactors, such as the FHR, because tritium would diffuse downstream, potentially contaminating the chemical or mineral products that are being produced using nuclear heat.

The objective of this project is to use an inherent feature of salt- and gas-cooled reactors towards the capture and removal of tritium from the primary coolant system: the presence of the graphite moderator. Graphite is expected to have high affinity for hydrogen and all of its isotopes, and some evidence of its tritium absorption effectiveness was observed in the MSRE reactor, at ORNL in the 1970s [2]. The fuel elements of HTGR and FHR reactors consist of a graphite matrix that encases fuel particles; so the fuel inherently provides removable graphite of high surface area. The objectives of the proposed project are to:

1. Characterize tritium transport in liquid fluoride salts (nominally 2FLi-BeF_2 , “flibe”) and graphite
2. Demonstrate the in-situ effectiveness of tritium absorption by the graphite fuel elements
3. Develop a design for a graphite bed tritium filter that can integrate with salt-to-air heat exchangers.

The kinetics of entry of the isotopes of hydrogen into graphite will be studied using transient electrochemical techniques [3] and electrochemical impedance spectroscopy [4]. In particular, double step potentiostatic polarization will be used to first inject hydrogen into the substrate by stepping the potential in the negative direction to cause proton reduction at the surface. Some of the resulting hydrogen atoms will recombine to form hydrogen gas, but a large fraction of the hydrogen atoms will penetrate into the lattice where they will diffuse away from the interface. During the diffusion time, some of the hydrogen will become trapped in the lattice. Some of these traps are “reversible,” in that the hydrogen can be recovered by reverse polarization, with the reversible traps commonly being non-hydride forming impurities or dislocations, while other hydrogen atoms become “irreversibly trapped” and cannot be recovered by reverse polarization. Irreversible traps are commonly voids, within which the hydrogen atoms recombine to form molecular hydrogen that cannot diffuse through the lattice, or the hydrogen

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atoms react with hydride-forming impurities (e.g., Si, Ti, Zr, Mg, and so forth), which do not dissociate once formed. After some time (an important experimental variable), the potential is stepped in the positive direction to oxidize the absorbed hydrogen at the interface as it reaches the surface by diffusion and as it is released from the reversible traps. The resulting transient in the current allows determination of the diffusivity of hydrogen in graphite and liquid salt and the fraction of the total hydrogen that is reversibly and irreversibly trapped in the lattice. Solution of the diffusion equations for this method has been reported by Pound, et.al. [11] and the method has been successfully demonstrated for the entry and trapping of hydrogen in metal alloys in contact with aqueous environments, but to our knowledge, this method has not been applied to salt or graphite systems.

An alternative, and perhaps superior, method involves the use of electrochemical impedance spectroscopy (EIS) [4], of which Macdonald is recognized as being a pioneer. In this method, an alternating voltage is applied to the graphite specimen at either the open circuit potential or at a negative potential at which hydrogen is being injected into the lattice. The alternating voltage generates a sinusoidal concentration wave of hydrogen atoms at the surface that extends into the substrate, with an amplitude that is attenuated with distance. As the frequency is lowered, the wave penetrates further into the substrate, thereby interrogating the lattice at increasing depth. The resulting current is sensitive to the diffusion and reversible/irreversible trapping of hydrogen. This methodology has been demonstrated by Macdonald for the study of defect structures of passive films that form on metal surfaces. EIS has not been applied to salt or graphite systems.

These electrochemical techniques will then be extendable to measurement of diffusion coefficients of other isotopes in fluoride salts and graphite, such as corrosion products, activation products, or fission products, which is of tremendous value for the reactor and reprocessing molten salt communities. The electrochemical techniques will be complemented by hydrogen isotope imaging techniques, from which we will extract tritium diffusion coefficients in fluoride salts and graphite, and mass transfer convection coefficients from the liquid salts to the graphite elements. This will provide confirmatory data for the validity of the transport properties obtained by electrochemical methods.

A major goal of the proposed research is the development of an equilibrium “install and forget” reference electrode that will allow high precision electrochemical measurements to be made in flibe. This is an essential requirement of the proposed electrochemical work. We also propose to develop electrodes that will sense the activity of H^+ (and D^+ and T^+) in flibe, which is information that is needed for the successful implication of the DPS and EIS methods for characterizing the entry and transport of hydrogen isotopes in graphite. Finally, we propose using a zero resistance ammeter to characterize galvanic coupling between graphite and metal alloys, which, in turn, provides the driving force (overpotential) for the reduction of protons on the graphite surface.

The successful accomplishment of this work will result in unprecedented tools being available for characterizing tritium transport and more broadly radioisotope transport in flibe. This tool also has direct applicability to the study of corrosivity and chemistry control approaches in flibe systems.

Using the transport data and the mechanistic understanding of tritium transport obtained, we will assess if the FHR graphite fuel elements can be a sufficiently effective in-situ tritium sink. We will also develop a design of a graphite bed tritium filtration system for the coolant, to be integrated with the salt-to-air heat exchangers, or as stand-alone equipment upstream of the salt-to-air heat exchangers in FHR and MSR.

References: [1] R. O. Scarlat et al. Design and licensing strategies for the fluoride-salt-cooled, high-temperature reactor (FHR) technology. *Progress in Nuclear Energy*. 2014. [2] L.E. McNeese, “Semi-annual Progress Report for Period Ending August 31, 1974,” Oak Ridge National Laboratory, ORNL-5011, pg. 30, 1974. [3] D. D. Macdonald, “Transient Techniques in Electrochemistry”, Plenum Press, NY, 1977. [4] D. D. Macdonald and M.C.H. McKubre. “Impedance Measurements in Electrochemical Systems”. Chapter 2 in *Modern Aspects of Electrochemistry*. 14, 61(1982).