

TRITIUM LOSS IN MOLTEN FLIBE SYSTEMS^a

Glen R. Longhurst
Idaho National Engineering and
Environmental Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-3860, USA
208-526-9950, Fax 208-526-2930
gxl@inel.gov

Robert A. Anderl
Idaho National Engineering and
Environmental Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-7113, USA
208-533-4153, Fax 208-533-4207
gxl@inel.gov

R. Scott Willms
Los Alamos National Laboratory,
MS C-348
Los Alamos, NM 87545, USA
505-667-5802, Fax 505-665-4148
rsw@lanl.gov

ABSTRACT

An emerging issue relative to beryllium technology in fusion involves tritium interactions with molten beryllium-bearing salts. Innovative designs for fusion reactors, both magnetic and inertially confined, feature the molten salt mixture $2\text{LiF}\cdot\text{BeF}_2$, commonly called Flibe, as a tritium breeder and coolant. Tritium is bred in the Flibe as neutrons from the plasma are absorbed by Li atoms, which then transmute to tritium and helium. Transmutation of tritium from Be also occurs. Among the issues to be resolved for such coolant systems is the potential loss of tritium from the Flibe coolant to the walls of the system, particularly through heat exchanger tubes, and from there into secondary coolants or working fluids and the environment. Effectively removing tritium from Flibe in clean-up units is also important.

In quiescent or low Reynolds number flow, tritium movement through Flibe is governed by diffusion. For Flibe in turbulent flow, as in heat exchanger tubes, transport is by turbulent mixing, and the same flow conditions and structural design features that maximize heat transfer to the heat exchanger walls will enhance the transport of tritium to those same surfaces. Analyses have been performed to estimate the fractional loss of tritium through heat exchanger tubes and release rates from Flibe droplets in vacuum disengagers in molten Flibe systems. The calculations suggest unacceptably large losses of tritium through heat exchanger tubes. The gravity of the implications of these estimates calls for experimental verification to determine if tritium losses through molten Flibe heat exchangers or other Flibe systems can really be so high and whether vacuum disengagers will really work. There is also a need for better information on evolution of tritium from Flibe droplets in a vacuum.

Several experiments are presently being planned to address these issues and are discussed. These include experiments to induce tritium in Flibe using spontaneous fission neutrons, experiments in flowing loops to evaluate tritium losses through heat exchanger walls, and exploration of schemes for tritium extraction from molten Flibe.

I. INTRODUCTION

The molten salt mixture $2\text{LiF}\cdot\text{BeF}_2$, commonly referred to as Flibe, is under consideration for use in fusion reactors. In magnetic fusion energy (MFE) reactor designs, the Flibe has been considered as a renewable surface for interfacing with the plasma in high plasma-flux regions and as a tritium-breeding coolant. In inertial fusion energy (IFE) designs, it has been considered as a shielding medium from both neutrons and the hydrodynamic blast of IFE targets. In this report, we consider issues associated with tritium production in and release from Flibe in fusion reactor systems and experiments planned to examine those issues. These issues include chemical and radiological concerns as well as those associated with operational and environmental hazards.

II. FLIBE APPLICATIONS

The use of molten Flibe as a coolant for fusion reactors has several engineering and safety advantages. Flibe serves as a high temperature heat transfer fluid that achieves high thermal efficiencies, acts as a good radiation shield, and has modest to good fluid flow properties.¹

Flibe is used at high temperature, but low pressure. Any ex-vessel cracks in the coolant piping are expected to produce small leaks, due to the low coolant pressure.

^a Work performed for U.S. Department of Energy, Office of Science, under DOE Idaho Operations Office Contract DE-AC07-94ID13223.

Only a low frequency pipe rupture event (i.e., less than 10^4 /year) should lead to a large coolant spill.

One of the early applications of Flibe in fusion reactor designs was in HYLIFE-II.² In that IFE design, Flibe is circulated at the rate of about $60 \text{ m}^3/\text{s}$ through a set of fixed and oscillating jets and serves to shield the first wall from the blast and neutrons as well as to breed tritium. Two banks of movable jets, oscillating sinusoidally but 180° out of phase with each other, provide a moving cavity into which a target pellet can be fired (as from a rifle) and ignited by either laser or heavy ion beam drivers. The stationary jets complete the coverage for the shielding function.

Since then, Flibe has been considered as a coolant and as a plasma-facing material by the Advanced Liquid Plasma Surface (ALPS) and Advanced Power Extraction (APEX) projects within the U.S. DOE Office of Fusion Energy Sciences, and for the Force Free Helical Reactor (FFHR).³ Studies are presently underway to develop

methods of getting molten Flibe to conform to the desired shapes in dynamic flow situations and to investigate tritium breeding and extraction, chemical compatibility, and other issues relevant to the application of Flibe in advanced magnetic fusion designs.⁴⁻⁷

TRITIUM PRODUCTION AND LOSS

The HYLIFE-II inertial fusion design concept using Flibe was investigated for activation. Principal radioisotopes created from neutron activation of pure Flibe are ^{10}Be , ^3H , and ^{18}F .⁸ The dominant activation product is ^{18}F .^{8,9} During a spill, gaseous tritium, in the form of TF or HT, may be released.

One of the inducements for Flibe in fusion reactors is its inherent ability to produce the fusion fuel tritium from the reaction of fusion neutrons with the lithium in the Flibe. Beryllium will also generate tritium by neutron transmutations. Figure 1 shows the activation and decay schemes associated with tritium production in Flibe.¹⁰

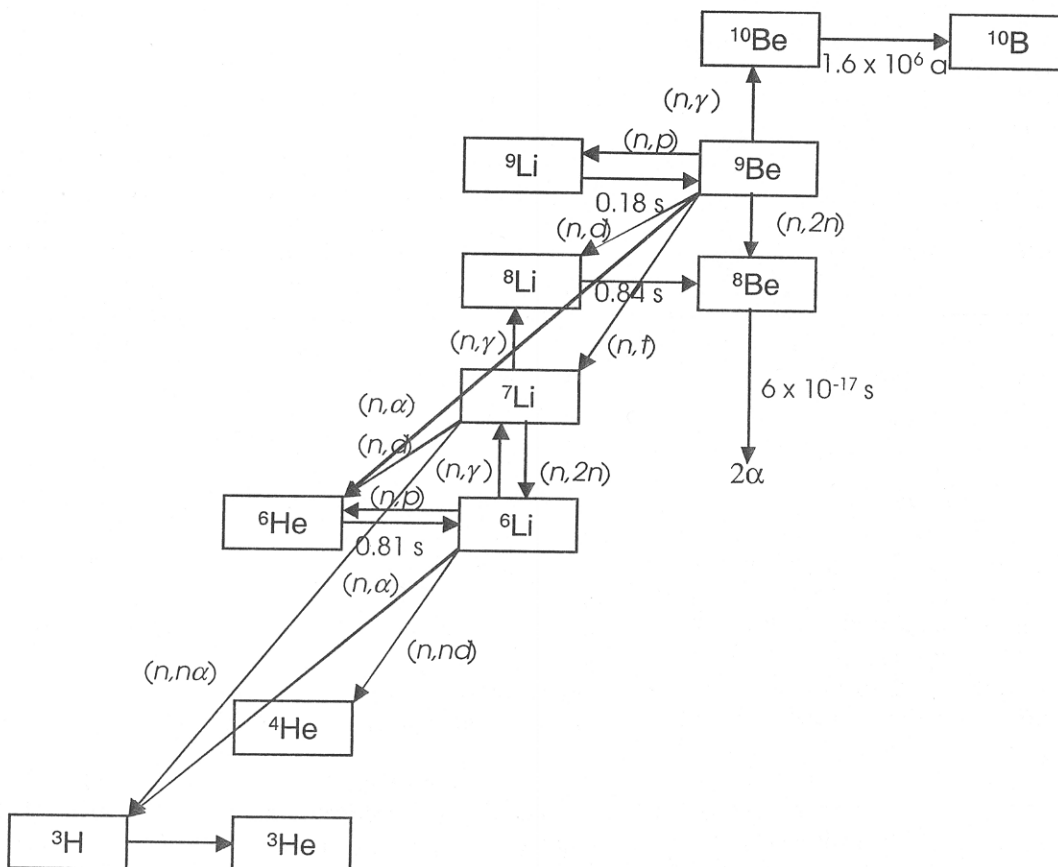


Figure 1. Activation and decay paths for lithium and beryllium in Flibe.

An important concern regarding tritium produced in Flibe is its propagation to other parts of a fusion system. Solubility of hydrogen isotopes in Flibe is very low.¹¹ That means that even a small concentration of tritium produced in the Flibe by neutron transmutations will have a very high chemical potential and will readily exit the Flibe by whatever means are available. A particular concern in this regard is its ability to pass through the walls of heat exchanger tubes or other structures and enter the atmosphere or a secondary coolant stream. Transport of tritium in Flibe flowing in heat transfer systems is largely by convection. Therefore, the same design configurations that will be used to maximize heat transfer from the Flibe will also maximize the transport of tritium.¹² During an accidental spill, gaseous tritium in the form of TF or HT may be released from the Flibe as well.

A second concern for Flibe is the ability to remove tritium from the Flibe at the locations desired in the Flibe loop and in a time sufficiently short to be practical. For the HYLIFE II design, the method chosen for tritium removal was a vacuum disengager in which tiny droplets are created and allowed to fall through a vacuum.¹² During the fall, tritium evolves from the droplets by diffusion. Key design considerations then were associated with the time required to remove the desired amount of tritium, the droplet size, and vacuum pumping requirements.

III. ANALYSIS

Two analytical investigations were performed in an attempt to evaluate the significance of these issues in the context of the HYLIFE II design study. They are reviewed here, but the reader is invited to review the detailed reports for a full description of the methods and results.

A. Loss in Tubes

The first analysis explored the rate at which tritium produced in Flibe may permeate through heat exchanger tubes.^{13,14} Flibe was assumed to pass through a long 316 stainless steel tube of fixed diameter. The flow was assumed to be turbulent and well developed over the entire length of the tube. Under those circumstances, transport of energy, momentum, and dissolved hydrogen molecules is governed by turbulent diffusion. Hence, energy density (represented by temperature), momentum density (velocity), and tritium concentration were assumed to have similar profiles in the radial direction.¹⁵ For simplicity it was assumed that tritium was the only hydrogen species present. The tube was assumed to be in a counter-flow heat exchanger such that the bulk temperature of the Flibe varied linearly over the length of the tube, and the wall

temperature was taken to be lower than the local Flibe bulk temperature by a constant increment, ΔT .

At the tube wall, tritium diffuses in the boundary layer with assumed diffusivity[16]

$$D \left(\frac{\text{m}^2}{\text{s}} \right) = 2.137 \times 10^{-6} \exp \left(- \frac{0.462 \text{eV}}{kT} \right) \quad (1)$$

where k is Boltzmann's constant and T is temperature. At the wall surface, the concentration of tritium in the Flibe was assumed to equate to an equivalent gas pressure or chemical potential through Henry's law according to¹¹

$$S \left(\frac{\text{atom}}{\text{m}^3 \text{Pa}} \right) = 2.58 \times 10^{17} \exp \left(- \frac{0.457 \text{eV}}{kT} \right) \quad (2)$$

That equivalent pressure, in turn, implied uptake in stainless steel through a Sieverts' law solubility[17]

$$S \left(\frac{\text{atom}}{\text{m}^3 \text{Pa}^{1/2}} \right) = 5.14 \times 10^{23} \exp \left(- \frac{0.144 \text{eV}}{kT} \right) \quad (3)$$

involving a recombination rate-limited surface exchange process.¹⁸ It was not known whether molecules would form at the interface and then dissociate to enter the tube walls or whether the tritium would go in directly. It was optimistically assumed that T_2 molecules diffused through the Flibe such that the exchange rate was second order in the Flibe tritium concentration. In reality the tritium atoms exist mainly as ions in the Flibe⁵ and HT should be considered as well, because some protium will also be present. If a Sieverts'-law solution boundary condition were assumed, or if molecular recombination followed by dissociation were not involved, loss rates of tritium from the Flibe would be faster yet. If the molecules are mostly TF, then the process would exhibit yet different results.

Tritium entering the stainless steel was then assumed to move by diffusion through the tube wall and to recombine on the outer side, again in a second-order process. Because of turbulent mixing outside the tube, the partial pressure of T_2 outside the tube was assumed to be a constant. These processes are illustrated in Figure 2.

Making use of the Reynolds-Lewis analogy,¹⁵ it was then possible to numerically calculate tritium concentration profiles over the length of the tube and the resulting permeation fraction. Figure 3 shows calculated radial concentration profiles inside the tube. The concentration has been made dimensionless by normalizing to a concentration defined in terms of the wall permeation flux

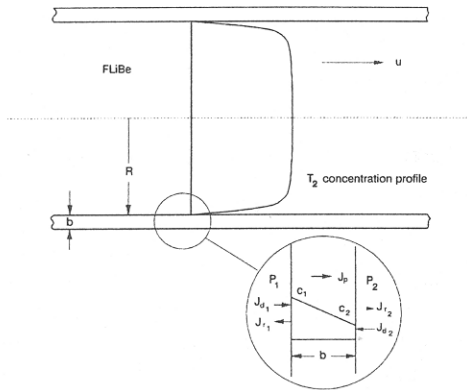


Figure 2. Relationships between various parameters considered in analysis of tritium loss through heat exchanger tube wall.

and a reference velocity given by the wall shear stress and

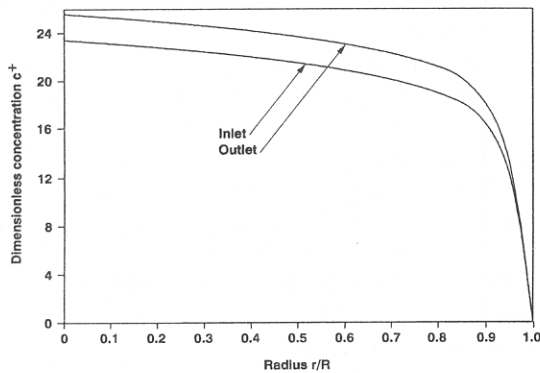


Figure 3. Normalized tritium concentrations calculated for molten Flibe flowing through a tube 2 cm in diameter and 10 m long. The actual (non-normalized) outlet concentration is only a small fraction of that at the inlet.

the Flibe density.

Figure 4 shows axial concentration profiles for various assumptions regarding the effectiveness of a dissociation/recombination barrier on the inside wall of a heat exchanger tube 2 cm in diameter and 10 m long with Flibe flowing at 1.8 m/s and an inlet temperature of 943 K. It may be seen there that a very substantial permeation barrier is needed to prevent almost the entire tritium content of the Flibe from being lost through the tube wall. Such barriers for use in Flibe systems have not yet been developed. This highlights the significance of the problem associated with tube wall loss.

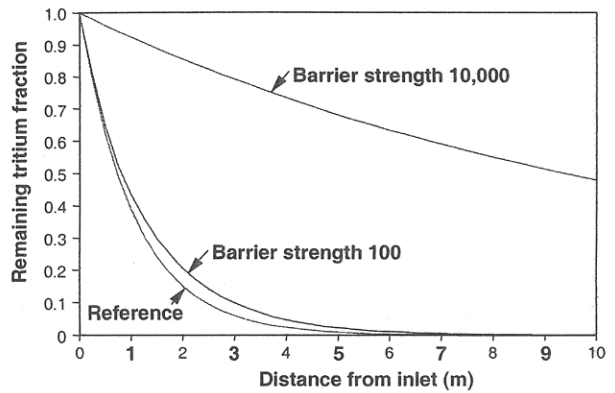


Figure 4. Axial tritium concentration profiles calculated for Flibe flowing at 1.8 m/s in a 10-m long x 2-cm diameter heat exchanger tube for various permeation barrier strengths (inhibitions to dissociation/recombination) on the inner tube wall.

B. Detritiation of Droplets

With the continual buildup of tritium in the Flibe by neutron transmutation, there is a need for a means of removing the tritium in controlled ways to prevent its dispersion through heat exchanger tubes. In the HYLIFE II design, that was accommodated using tritium disengagers, columns through which small Flibe droplets could fall under vacuum.¹⁹ The concept required tritium in the droplets to diffuse to the surface and recombine, coming off as free molecular gas that could be pumped away to separation and storage. A key issue in the design was the rate at which such tritium evolution could occur. That obviously impacted the required droplet size and the height through which the droplets would have to fall. The detailed solution for the amount of dissolved solute retained in a spherical droplet where diffusion governs is²⁰

$$\Phi = \frac{P_\infty}{P_0} + 6 \left(1 - \frac{P_\infty}{P_0} \right) \sum_{m=1}^{\infty} \exp(-\lambda_m^2 Fo) \frac{[\sin(\lambda_m) - \lambda_m \cos(\lambda_m)]^2}{[\lambda_m - \sin(\lambda_m) \cos(\lambda_m)]} \tag{4}$$

where P_∞ and P_0 are the ultimate and initial tritium concentrations, respectively, Fo is a dimensionless time or Fourier number based on diffusivity D and droplet radius r

$$Fo = \frac{tD}{r^2} \tag{5}$$

and the λ_m are solutions to the characteristic equation

$$\lambda_m \cot(\lambda_m) = 1 - Bi \tag{6}$$

Here **Bi** is a Biot number

$$Bi = \frac{hr}{D} \tag{7}$$

where **h** is the surface mass transfer coefficient for the tritium.

Time evolution histories were found for a range of Biot numbers. These are shown as functions of the dimensionless time **Fo** in Figure 5.

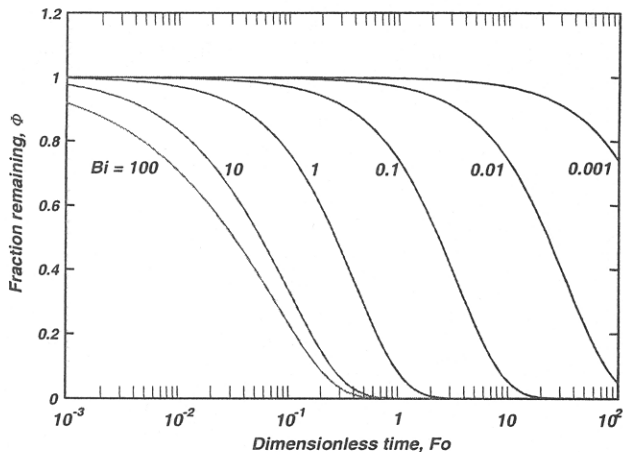


Figure 5. The fraction of tritium remaining in a droplet subject to idealized diffusion to the surface depends on the diffusivity, surface mass transfer coefficient, and droplet radius as they appear in the **Fo** and **Bi** numbers. The tritium does not come out faster at higher **Bi** numbers.

Therefore, assuming diffusion is the dominant transport mechanism of tritium in the Flibe and the surface mass transfer proceeds as presently understood, it should be possible to determine the optimum droplet diameter and vacuum residence time for effective removal of the tritium in this way.

Not included in this analysis was the extent to which internal flows within the droplets, induced by the droplet formation process, could accelerate transport of tritium from within the droplet to the droplet surface. Any assistance in bringing tritium to the droplet surface by internal circulation will only improve performance. There was some scatter in published data for the mass transfer coefficient for tritium evolution from the surface. Further, we were not sure of the chemical form of the tritium in the droplet and assumed elemental gas here.

These unknowns and uncertainties point out the need for detailed experiments to be conducted with Flibe to

evaluate key parameters involved with tritium production in and release from molten Flibe in the dynamic environments of a fusion reactor.

IV. EXPERIMENTS

Several experiments are in progress or are being considered for exploring tritium safety issues in Flibe. Many of these are concerned with the mobilization of tritium from Flibe.^{21,22} It is not clear whether there are reasonable means for getting tritium into Flibe for such experiments other than actual neutron irradiation. This is because of the complex chemistry of the various reactions involving the fluorine, beryllium, lithium, and the tritium produced. One priority in the forthcoming research should be to develop a successful tritiating procedure for Flibe.

A. Reactor Test

Suzuki and co-workers⁵ described work to determine mechanisms for the change of chemical species of tritium in Flibe. In that work, a container of molten Flibe was placed in an irradiation position of the YAYOI reactor at the University of Tokyo. Tritium was produced in the Flibe by fission neutrons, released from the Flibe as HT or TF, and swept by a mixture of helium and hydrogen in a purge gas stream to analysis stations. The TF fraction was determined by converting TF to HT on an aluminum reduction bed followed by ion chamber counting and comparing the total tritium count from that stream with the count from another ion chamber on a stream in which the TF had been absorbed by a molecular sieve bed.

They found that for H₂ concentrations in the purge gas of 1 percent or less, the rate of HT release from the Flibe was controlled by the H₂ partial pressure. At very low H₂ partial pressures (100 Pa or 1000 appm or less), the tritium coming from the Flibe was mainly as TF. For H₂ concentrations of 10 percent or more, they found release was first order in tritium concentration and that HT release rate was controlled by diffusion to the surface.

One aspect not clear in the work at YAYOI was the extent to which recombination of T⁺ ions with surface H was responsible for HT formation as opposed to formation of HT in the Flibe fluid, as they postulated, with subsequent diffusion of HT molecules through the Flibe. Likewise, it could not be determined whether TF molecules were formed in the bulk Flibe or at the surface. In light of the very low solubility for hydrogen isotopes in Flibe, the surface recombination pathway seems more likely.

It is evident from Figure 1 above that some protium will be present in the Flibe mixture from (n,p) reactions.

Some deuterium may also be present. These hydrogenic species will probably be as prevalent as will the tritium. These appear not to have been considered in the model presented, and the rates of HF and DF formation were not measured.

If there is a free Flibe surface with available hydrogenic species, then this process of flooding with protium to reduce TF release and the attendant corrosion problems will be applicable, and the rates measured will be very useful. For the HYLIFE-II vacuum disengager, where no sweep gas is present, or for flow in heat exchanger tubes, it is not clear what the release rates or species will be.

B. FLIQUIRE

One experiment presently being initiated at the Idaho National Engineering and Environmental Laboratory is the Fusion Liquid Release Experiment (FLIQUIRE). This experiment, shown schematically in Figure 6, was initiated in response to the need to understand the chemistry and mechanisms for mobilization of beryllium or fluorine compounds and activation products, including tritium, resident in molten Flibe. As discussed previously, tritium may be produced in Flibe by the reaction of a neutron with

The FLIQUIRE experiment will have many of the same features and limitations as the YAYOI experiment, but it has the benefit of not requiring installation in a fission reactor. A modification to allow tritium permeation measurements through the inner vessel wall with only a small amount of inert cover gas over the Flibe would be useful in evaluating the direct transfer of tritium from the Flibe to structures.

The FLIQUIRE experiment is presently in design. Analyses have indicated tritium production rates may be on the order of 10^{12} tritium atoms per hour from a 1.0 mg Cf-252 source acting on a 200-mL Flibe volume with a 40-cm Be reflector. Improved tritium production rates may be achieved with a ZrH_{16} moderator and a more optimal reflector configuration.

C. Tritium-Flibe Chemistry Experiments

The lack of tritium-Flibe chemistry data has prompted a proposal as part of the US-Japan fusion collaboration. Specifically this proposal is between the Japanese University Community (Monbusho) and the U.S.-DOE. The general issues that this collaboration will seek to address are:

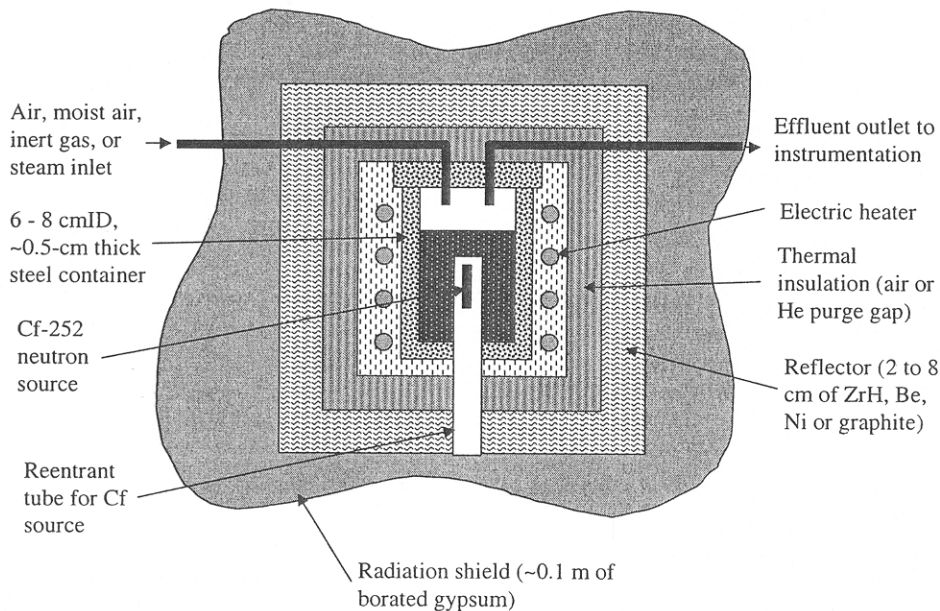


Figure 6. FLIQUIRE experiment for investigation of tritium interactions with molten Flibe.

a lithium atom, the destruction of which would effectively liberate a fluorine atom. Tritium may also be produced by interaction of a neutron with a beryllium atom, as shown in Figure 1. Other hydrogenic species will also be produced.

- Fundamental parameters
 - Equilibrium
 - Kinetics
 - Chemical reactions

- Tritium removal
 - Technology choice
 - Product characterization
- Heat Exchanger Interactions
 - T permeation
 - Permeation barrier testing
 - Corrosion
- Materials corrosion testing
- Impurity control
 - Be screen
 - Other
- Chemistry control
 - H₂ addition for TF control
 - Other addition for control and makeup
- Tritium product purification
 - Technology choice
 - Waste issues
- Coolant tritium removal
 - Characterize stream

The collaboration will begin with the construction of a number of experiments in which the Flibe is not flowing. These experiments will be designed to measure a specific physical or chemical property such as solubility and mass transfer coefficient. The results of these experiments will lead to the construction and testing of an integrated tritium-Flibe handling loop. The loop will include sections of Flibe storage and supply, tritium addition, chemical addition, tritium extraction, heat exchanger mockup, and corrosion test sections. It is also proposed to include sections for tritium purification and heat exchanger coolant characterization. Analysis points throughout the loop will facilitate characterization of the Flibe at all points in the loop. If funded, this work is expected to begin in the 2001 time frame. The experiments will be conducted in the U.S., mostly likely at Los Alamos National Laboratory.

V. CONCLUSIONS

Use of Flibe in fusion reactors offers new and interesting possibilities for coping with heat loads to walls as well as breeding tritium directly in the coolant. With those possibilities come concerns for adequate tritium management. It will be important to extract tritium from the Flibe in an efficient and controlled way at appropriate locations in the Flibe circuit and to prevent tritium from penetrating fusion reactor structures, especially coolant system structures, in other areas.

Relatively little has been done experimentally to determine the properties and parameters needed for adequate assessment of these tritium management issues. It will be important to understand thoroughly the chemistry of

tritium and other hydrogenic species in the Flibe as well as that of the fluoride ions that will be liberated by neutron transmutations. Other issues of importance are the determination of the mechanisms by which tritium moves through the Flibe and where and how it recombines to leave the Flibe.

These issues are beginning to be addressed by experiments in the U.S. and Japan. These experiments are beginning with static pool experiments. It is important to generate the tritium and other reactive species in the Flibe by neutron transmutation since uptake in other ways is difficult and will probably not give the appropriate fidelity to chemical reactions and transport processes involving those species. It is hoped that experiments will eventually evolve to dynamic loop experiments to evaluate loss of tritium through heat exchanger tubes and related issues of barrier effectiveness and detritiation mechanisms.

REFERENCES

1. R. W. Moir, "HYLIFE-II Inertial Confinement Fusion Reactor Design," *Fusion Technology*, 19 (May 1991) pp. 617-624.
2. R. W. Moir et al., "HYLIFE-II: A molten-salt inertial fusion energy power plant design—Final Report," *Fusion Technology*, 25 (1994) 5-25.
3. A. Sagara et al., "Materials design and related R&D issues for the force-free helical reactor (FFHR)," *Journal of Nuclear Materials*, 258-263 (1998) pp. 2079-2082.
4. H. Moriyama et al., "Molten salts in fusion nuclear technology," *Fusion Engineering and Design*, 39-40 (1998) pp. 627-637.
5. A. Suzuki et al., "Change of tritium species in Li₂BeF₄ molten salt breeder under neutron irradiation at elevated temperature," *Journal of Nuclear Materials*, 258-263 (1998) pp. 519-524.
6. T. Terai et al., "Compatibility of structural materials with Li₂BeF₄ molten salt breeder," *Journal of Nuclear Materials*, 258-263 (1998) pp. 513-518.
7. A. Suzuki et al., "Mechanism on Change of Tritium species in Li₂BeF₄ Molten Salt Breeder under Neutron Irradiation at Elevated Temperature," *Fusion Technology*, 34 (Nov 1988) pp.526-530.

8. M. T. Tobin, "Neutronics Analysis for HYLIFE-II," *Fusion Technology*, 19 (May 1991) pp. 763-769.
9. T. J. Dolan and G. R. Longhurst, *Safety and Environmental Issues of HYLIFE-II*, EGG-FSP-8653, Idaho National Engineering Laboratory (October 1989).
10. F. W. Walker et al., eds., *Nuclides and Isotopes*, 14th Ed., General Electric Company, San Jose, CA (1989).
11. A. P. Malilnauskas and D. M. Richardson, "The solubilities of hydrogen, deuterium and helium in molten Li_2BeF_4 ," *Industrial and Engineering Chemistry. Fundamentals*, 13 (1974) pp. 242-245.
12. G. R. Longhurst and T. J. Dolan, *HYLIFE-II Tritium Management System*, EGG-FSP-9971, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho (1993).
13. G. R. Longhurst, *Permeation of Tritium through HYLIFE-II Heat Exchanger Tubes*, EGG-FSP-8678, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho (September 1989).
14. G. R. Longhurst and T. J. Dolan, "Tritium Permeation Losses in HYLIFE-II Heat Exchanger Tubes," *Fusion Technology*, 19 (May 1991) pp. 820-825.
15. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, New York (1960) pp. 630, 384, 186.
16. J. Oishi et al., "Tritium recovery from molten LiF-BeF_2 salt," *Fusion Engineering and Design*, 8 (1989) pp. 317-321.
17. T. Tanabe et al., "Hydrogen Transport in Stainless Steels," *Journal of Nuclear Materials*, 122 & 123 (1984) pp. 1568-1572.
18. M. I. Baskes, "A Calculation of the Surface Recombination Rate Constant for Hydrogen Isotopes on Metals," *Journal of Nuclear Materials*, 92 (1980) p. 3.18
19. T. J. Dolan, G. R. Longhurst, and E. Garcia-Otero, *A Vacuum Disengager for Tritium Removal from HYLIFE-II reactor Flibe*, EGG-M-91508, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho (March 1992).
20. G. R. Longhurst, *Gas Evolution from Spheres*, EGG-FSP-9634, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho (April 1991).
21. Y. Asaoka et al., "Equilibrium Distributions of Tritium in Liquid Lithium/Molten Salt Systems," *Journal of Nuclear Materials*, 179-181 (1991) pp. 879-881.
22. J. Oishi et al., "Tritium Recovery from Molten LiF-BeF_2 Salt," *Fusion Engineering and Design*, 8 (1989) pp. 317-321.