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Flibe-Tritium Research for Fission or Fusion Reactors at Kyushu University

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There is increasing interest in using ionic molten-salt Flibe not only as self-cooled tritium(T)-breeding material in a fusion reactor blanket but also as fuel solvent of molten-salt fission reactors. Application of Flibe to T-breeding fluid for a stellarator-type fusion reactor operated at a high magnetic field brings large simplification of its blanket structure, allowing continuous operation under high-beta plasma conditions. Using mixed Flibe-ThF_4+UF_4 fuel in molten salt fission reactors permits stable long-term operation without fuel exchange. When Flibe or Flinak is irradiated by neutrons, however, acid and corrosive TF is generated, and some T permeates through structural walls. In order to solve these problems, chemical conditions of Flibe are changed using the redox-control reaction, $Be+2TF=BeF_2+T_2$. In addition, permeation of hydrogen isotopes is lowered by enhancing T recovery rates. Part of Flibe-tritium researches are performed at Idaho National Laboratory (INL) under the Japan-US collaboration work of JUPITER-II. Our own contributions to the topics are shortly introduced in this paper.

Keywords: Flibe, tritium, fusion reactor, molten salt fission reactor, permeation

1. Introduction

Flibe is a stable mixed molten salt composed of $2LiF+BeF_2$ in molar ratio (2:1) with melting point of 459ºC. Flinak (LiF+NaF+KF) is also a stable molten salt with 0.465:0.115:0.42 in molar ratio and a similar m.p. of 454ºC. The Flibe and Flinak ionic salts are planned to be used not only for a tritium(T)-breeding blanket in fusion reactors such as FFHR-2 at National Institute for Fusion Sciences (NIFS) in Japan [11,13,15,17] but also as fuel solvent in small molten salt fission reactors such as FUJI [21]. The former is intensively investigated under the direction of Prof. Sagara of NIFS [11,13,15,17]. Flibe is chemically and physically stable even at high temperature. Its low electric conductivity makes more suitable when utilizing in stellarator-type fusion reactors, which can be operated under conditions of a high beta magnetic field. Flibe can achieve the T self-sufficient condition of tritium breeding ratio *TBR*>1 [20], which is required for a fusion blanket. Flinak also gives a higher *TBR* value with use of Be [21].

Since Flibe heated to above m.p. can dissolve ThF_4 and UF_4 in any composition, it is used as fuel solvent in molten salt fission reactors. ^{232}Th is a fertile material which can be converted into fissile ^{233}U by a sequence of neutron-absorption reactions and the two beta decays, *i.e.* $^{232}Th + n \rightarrow {}^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U$. The earliest molten salt reactor was set up in Oak Ridge National Laboratory (ORNL) in the 1960's. China is recently interested in its application to fuel solvent for the Thorium Molten Salt Reactor (TMSR), because of their large possible reserves and less generation of radioactive waste. TMSR can be operated for extended time without fuel discharge. The experimental fission reactor will be constructed in Shanghai Institute of Applied Physics, China Academy of Engineering Physics (SINAP, CAEP) in the near future. In this context, a

Fig. 1 Photos of solid Flibe at room temperature and transparent molten salt when its melts

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collaboration work on tritium release and measurement in the TMSR was recently initiated between researchers of SINAP, CAEP and our Kyushu University.

Generally, molten ionic salts of Flibe and Flinak are stable even under air at high-temperature. They become transparent when they are melted as shown in Fig. 1. When Flibe or Flinak is used for fusion or fission reactors under a high-intensity neutron flux or high-temperature conditions, various advantages and disadvantages are observed. The advantages of Flibe or Flinak can be summarized as follows: (i) comparatively low reactivity with O_2 or H_2O, (ii) low electric conductivity, (iii) low T solubility, and (iv) easy T recovery. On the other hand, the disadvantages when using Flibe or Flinak are (i) generation of chemically reactive TF under neutron irradiation, (ii) comparatively high viscosity (8.6 mPa・s at 600ºC of Flibe compared with 1.0 mPa・s at 20ºC of H_2O), which leads to high pumping power, (iii) the experimental increase of viscosity with increase of BeF_2 content, and (iv) high T permeability through some metals.

Many experiments have been carried out under the Japan-US collaboration work called JUPITER-II in 2001-2006 and our contributions within the frame of the domestic collaboration have continued since then. Part of the tritium research was performed in the Safety and Tritium Applied Research (STAR) facility of Idaho National Laboratory (INL). Many achievements are summarized in the references of the present paper [1-18]. Our T-related experimental or design-based research on applications of the molten salts Flibe and Flinak to fusion or fission reactors is briefly introduced in the present paper. The introduction is mainly devoted to our own studies due to the limit of paper length.

2. Redox Control

When mixed molten salt of Flibe or Flinak is exposed to neutron flux in fission or fusion reactors, tritium fluoride (TF) is generated by the reaction of LiF with neutrons as follows:

$^{6}LiF + n = TF + {}^{4}He$

$^{7}LiF + n = TF + {}^{4}He + n'$

The reaction cross-section of ^{6}Li with thermal neutrons is very large. On the other hand, that with ^{7}Li is small and has the threshold energy of 2.47 MeV. Therefore, enrichment of ^{6}Li is often necessary to achieve high *TBR*, when applied in a fusion reactor blanket. Since the reaction product TF is a strong acid, it corrodes metallic walls. Consequently, TF is converted into molecular T_2 or HT, which is chemically compatible with metallic walls and the fluorine is allowed to react with metallic Be. The reduction/oxidation (redox) control reaction in the liquid phase of Be (dissolved in Flibe) + 2TF (HF) ⟶ $BeF_2 + T_2$ (H_2) is used for the purpose. The experimental results are summarized in Fig. 2. It is assumed in the calculation that the Be dissolution rate is constant, the above reaction is second-order in HF concentration and contributions of the reverse reaction are negligibly small. As seen in the figure, close agreement is obtained between experiment and calculation regardless of the HF concentration and the Be dissolution concentration. A reaction rate constant is obtained from fitting between experimental results and calculations as shown in Fig. 2.

Since the solubility of T_2 generated by the reaction in Flibe is very low, T easily permeates through structural materials of fusion or fission reactors. Therefore, highly efficient procedures for T recovery from the Flibe flow in fission or fusion reactors and an effective T permeation protection are necessary in order to operate safely fusion or

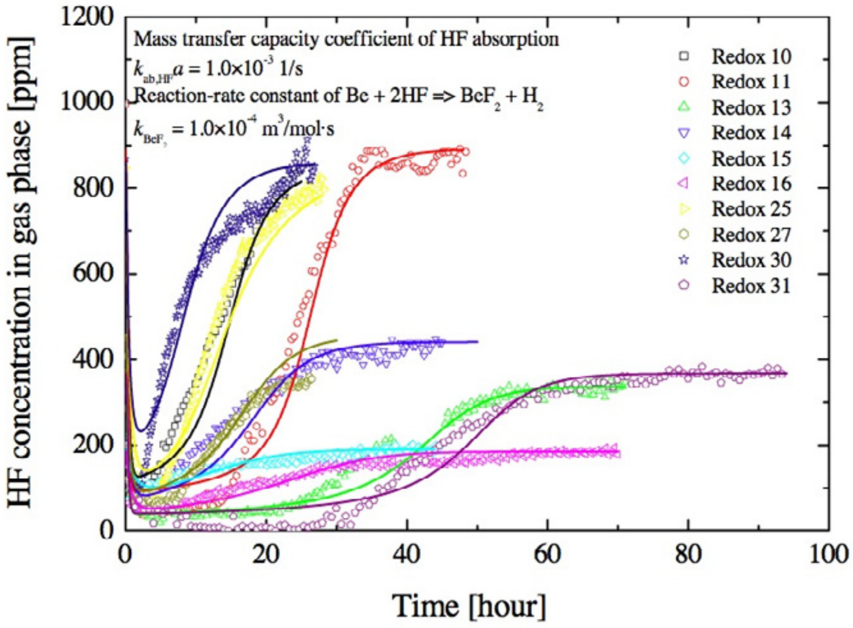

Fig. 2 Comparison between experiment and calculation of reaction of $2HF+Be \rightarrow BeF_2+H_2$ in liquid Flibe

fission reactors. Our previous work on T recovery and permeation through Flibe covers the following five topics, (i) diffusivity and solubility of hydrogen isotopes in Flibe or Flinak, (ii) Flibe purification and redox control by Be, (iii) chemical analysis of T in Flibe, (iv) design of equipment to recover T from Flibe, (v) design of Flibe blanket, *etc*. Many of these results are described in the references [1-18]. In the next section we focus on the solubility and permeability of hydrogen isotopes in Flibe or Flinak.

3. Solubility and Permeability of H Isotopes in Flibe or Flinak

Fusion or fission communities are much interested in two liquid breeders Flibe and Flinak, and many of their various properties have been investigated experimentally. Solubility and permeability of H isotopes in Flibe or Flinak molten salts are very important factors for the design of fusion reactors and to estimate the T-breeding performance. Solubility is related to the T inventory and permeability to T leakage through boundaries. Fig. 3 correlates solubility constants for various gases in Flibe and Flinak. Dissolution of gases in Flibe or Flinak follows Henry's law described by $c_k = K_{H,k} p_k$, where c_k and p_k are the concentration of gas k dissolved in the molten salt and the partial pressure of gas k, respectively. $K_{H,k}$ (k=H_2, He, Ar, Xe) is the Henry constant of gas k. These gases are dissolved in atomic or molecular form in Flibe and Flinak, and the major force acting between molten salt and dissolved inert gas is surface tension. Therefore, the solubility constant $K_{H,k}$ is given by the following equation regardless of Flibe and Flinak:

$$K_{H,k} = \exp\left(-\frac{E_0 + 4\pi N_A r_{b,k}{}^2\gamma}{R_g T}\right) \qquad (1),$$

where $r_{b,k}$ is the atomic or molecular radius of the gaseous species k, N_A the Avogadro number, R_g the gas law constant, T temperature and γ the surface tension of Flibe or Flinak. Although E_0 is a constant for inert gases, in case of H_2 another attractive force between this molecule and the molten salt plays a role. Therefore the solubility of H_2 shows different tendency from that of inert gases (see Fig. 3).

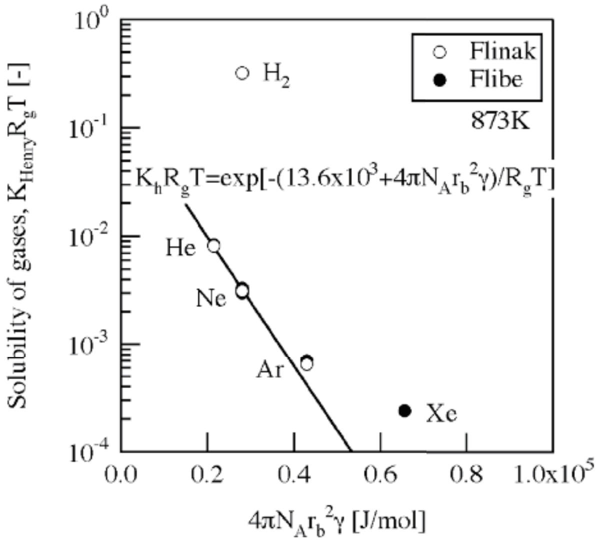

Fig. 3 Solubilities of H_2, He, Ar, Xe in Flibe or Flinak

The product of diffusivity D_{H2} and solubility $K_{H,H2}$ is equal to the permeability when no retardation on material-gas interface occurs. The steady-state H_2 permeation rate denoted by j_{H2} is proportional to the partial pressure difference between the upstream and downstream sides denoted by $p_{H2,up}$ and $p_{H2,down}$, respectively, and is expressed as follows:

$$j_{H_2} = \frac{K_{H,H_2} D_{H_2}}{\delta}\left(p_{H_2,up} - p_{H_2,down}\right) \qquad (2),$$

where δ is the thickness of the molten salt layer and D_{H2} is the diffusivity of H_2 in Flibe or Flinak.

4. Recovery of Tritium from Flibe or Flinak

The equilibrium partial pressure of T dissolved in Flibe or Flinak and vapor pressure of Flibe are shown in Fig. 4 together with other liquid blanket candidates. As seen there, the T equilibrium pressure over Flibe is the highest, being about 10^5 Pa for 1ppm T dissolved in Flibe. Therefore, simple He gas purge is promising to recover T in Flibe if direct contact between gas and liquid is possible. If direct contact is unsuitable, the problem is avoided by means of a

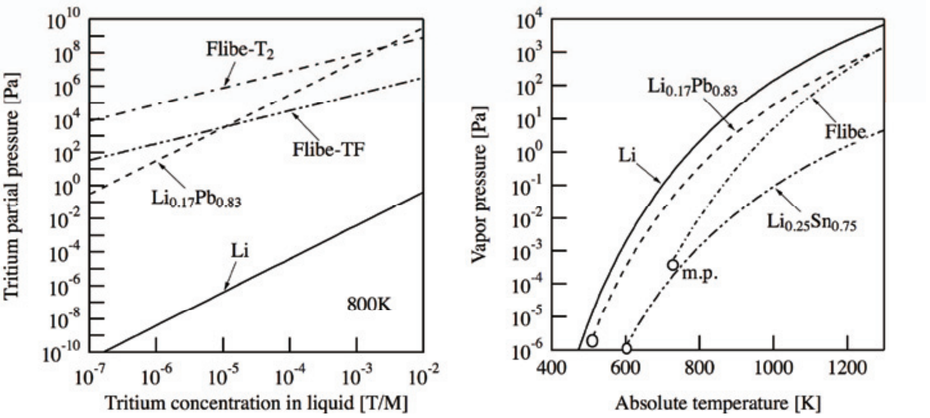

Fig. 4 Comparison of T equilibrium pressure and vapor pressure among Li, $Li_{17}Pb_{83}$ and Flibe

permeation window. If the redox control is not successful, the chemical form of tritium remains to be TF. The equilibrium pressure of TF is, however, about 1/200 of T_2. Therefore the efficiency of gas purge is reduced.

Fig. 5 shows a schematic view of a He-Flibe counter-current extraction tower. Tritium dissolved in Flibe at the tower inlet diffuses from the Flibe bulk to the Flibe-He interface. When it arrives at the surfaces, T desorbs to the He side. Then T_2 gas diffuses through the He-side boundary layer. T_2 in He is purged out to the gas outlet. In order to keep good contact between He and Flibe, inert metal packing is placed inside of the tower. Rashig ring, Dixon ring or equivalents can be used as usually packed in commercial gas-liquid extraction towers such as distillation process. Analytical study on T recovery from Flibe using the counter-current tower is being performed in Japan and China, but no experimental result has been presented.

Here, we compare Li chemical activity in the liquid blanket candidates among Li, Flibe, $Li_{17}Pb_{83}$ and $Li_{25}Sn_{75}$ eutectic alloys. Li has the highest vapor pressure among them. Since the chemical activity of Li is high, its use in fusion reactors may be limited for safety reasons even though its *TBR* is the largest among the four candidates. The vapor pressure of $Li_{17}Pb_{83}$ is lower than that of Li. The chemical activity of Li in the $Li_{17}Pb_{83}$ eutectic alloy decreases with increasing temperature as one can see when comparing the difference in vapor pressure between Li and $Li_{17}Pb_{83}$, which slightly spreads with increasing temperature. Judging from the viewpoint of vapor pressure, Flibe and $Li_{25}Sn_{75}$ are the lower group. The chemical activity of Li is low. Since the vapor pressure of Flibe is about 10^{-2} Pa at 800 K, its vaporization is negligibly small even when its accidental release happens (see Fig. 4). Therefore, Flibe is the safest materials among the four candidates. $Li_{25}Sn_{75}$ cannot constitute any blanket design of *TBR*>1.

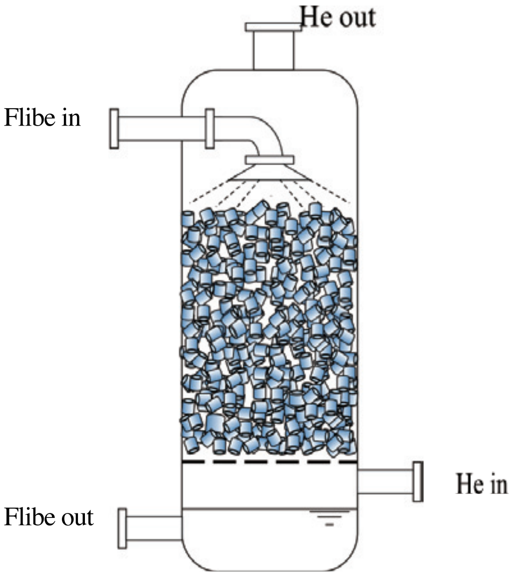

Fig. 5 Overview of He-Flibe counter-current extraction tower

5. Thorium as Fertile Material for Molten Salt Reactor

When a Flibe molten salt mixed with UF_4 and TF_4 is used as fuel of a molten salt fission reactor, the largest disadvantage is the strong gamma ray originated from ^{232}U or its daughter nuclei ^{208}Tl. The gamma ray energy from ^{208}Tl is 2.8MeV. Therefore, the designed molten salt reactor should be buried under the ground in order to decrease non-necessary exposure to gamma rays (see Fig. 6). The figure shows an example for the molten salt reactor cited in the reference [19]. One generation path of ^{232}U from ^{232}Th fuel is considered to be $^{232}Th(n,2n)^{231}Th$, $^{231}Th \rightarrow ^{231}Pa$, $^{231}Pa(n,\gamma)^{232}Pa$, and finally $^{232}Pa \rightarrow ^{232}U$. The first (n,2n) reaction occurs only with fast neutrons. The threshold energy is 6.5MeV. Therefore, neutron slow-down using a resonable moderator is effective in order to decrease the generation of ^{232}U. Another path for the generation of ^{231}Th is the neutron capture reaction of ^{230}Th. This isotope is present as a natural impurity in ^{232}Th. ^{230}Th is a daughter

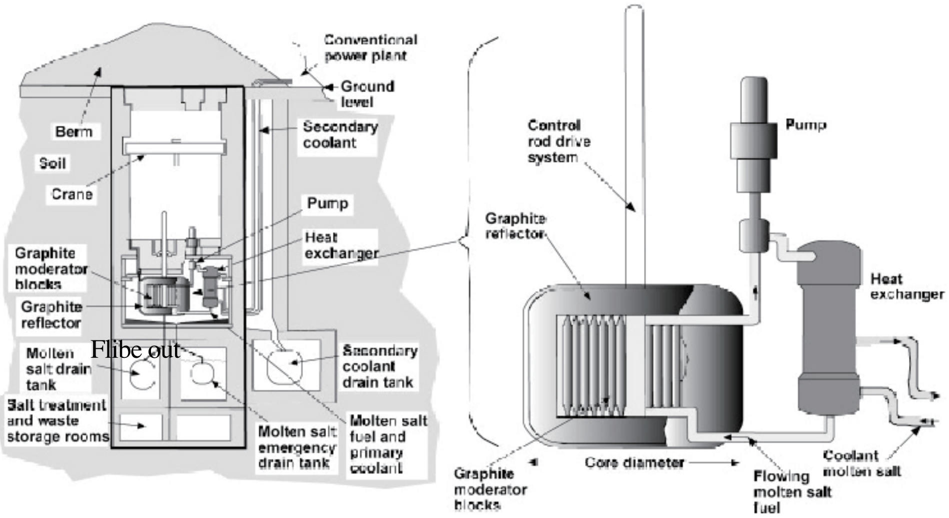

Fig. 6 Conceptual design of underground molten salt fission reactor. Figure is cited from the address [19].

product of the alfa decay of ^{238}U. When ^{231}Th is generated, as described above, the same path works to generate ^{208}Tl. Therefore, it is effective to separate natural U from natural Th (almost 100% ^{232}Th) beforehand in order to minimize the generation of high intensity gamma ray. The chemical separation between U and Th will be performed by a solvent extraction technique using Tributyl phosphate (TBP) as solvent.

6. Conclusions

Applications of molten salt Flibe or Flinak to fusion or fission reactors and our previous research on these topics were presented. Since Flibe and Flinak show not only proper T breeding ability for fusion reactors but also less reactivity with O_2 or H_2O regardless of slightly larger viscosity than other breeding materials, they can be used as a blanket fluid of a FFHR-2 fusion reactor. The advantages of molten salts were discussed here. On the other hand, corrosive TF acid is generated when exposed to neutrons. In order to solve this problem, the Be redox control reaction was shown to be effective. Since the solubility of T_2 (H_2) is comparatively small, although it is larger than that of inert gases, the T_2 recovery is readily carried out with a He-Flibe counter-current extraction tower. When Flibe mixed with fertile Th is exposed to neutrons, strong gamma rays are emitted from the Th fuel. The problem of strong gamma radiation is mitigated by placing the whole Th fission reactor under the ground. Impurity removal in natural Th can decrease the strong gamma ray originated from ^{208}Tl.

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