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Reaction rate of beryllium with fluorine ion for Flibe redox control

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Abstract

An experimental effort to apply Flibe (a mixed molten salt of $2LiF + BeF_2$) to a self-cooled liquid blanket of a fusion reactor was carried out under a Japan–US collaboration called JUPITER-II. Maintaining Flibe under a reducing atmosphere is a key issue to transform TF to T_2 with a faster reaction rate compared with the residence time in blanket. One of the tasks was to clarify whether or not the redox control of Flibe can be achieved with Be. The dissolution rate of a Be rod and the reaction rate of $Be + 2HF = BeF_2 + H_2$ in Flibe were experimentally determined. Sufficiently fast rates of the Be dissolution and the reduction reaction of HF to H_2 were clarified by our redox control experiment. Close agreement was obtained between experiments and our simplified complete-mixing model. In particular, the reaction between Be and a F^- ion immediately after their contact was found to be limited by diffusion of the F^- ion.

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1. Introduction

As a promising advanced liquid blanket material, Flibe (a mixed molten salt of $2LiF + BeF_2$) has several advantages: low reactivity with oxygen and water even at 600 °C and lower electric conductivity. Consequently, it has a lower magneto-hydrodynamic (MHD) effect than other liquid blanket materials such as Li and Li–Pb eutectic alloy. Therefore, Flibe was adopted into a Japanese conceptual design of force-free helical reactor, FFHR-2 [1,2]. Previously, some physical or chemical properties were determined in the molten salt fission reactor experiment at ORNL [3], and afterwards tritium release from irradiated Flibe was measured by Japanese researchers [4,5]. However, the chemical behavior of tritium in Flibe was not clarified sufficiently. The largest problem to overcome in a

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Nomenclature

A_{Be}	surface area of Be rod, m^2
A_g	surface area of He bubble and Flibe overlayer, m^2
c	total molar concentration of Flibe or gas phase, mol/m^3
K_{Henry}	Henry's solubility constant of H_2 or HF in Flibe, mol/m^3 Pa
k_{abs}	absorption rate constant of H_2 or HF, m/s
$k_{dis,Be}$	dissolution rate constant of Be, (Be/Li_2BeF_4)/s
k_{BeF_2}	reaction rate constant of BeF_2 formation, mol/m^3 s
m_{TF-T_2}	transformation rate from HF to H_2, mol/m^3 s
R_g	gas law constant, m^3 Pa/K mol
T	temperature, K
t	time, s
V	volume of Flibe or gas phase, m^3
W	molar flow rate of gas, mol/s
x	molar fraction of HF or Be in molten Flibe, –
y_{HF}	HF molar fraction in gas phase, –

self-cooled Flibe blanket is to control the generation of TF. This is because TF is not only very corrosive to structural materials but also the reduced product T_2 is permeable through the materials. Previously, it was proved that the corrosion rate of 316 stainless-steel was reduced to a negligible level by the addition of Be to Flibe [6]. However, quantitative evaluation has not been performed on the Be dissolution rate and the reduction reaction between Be and F^- ions. In order to control the redox (reduction–oxidation) condition of Flibe, dissolution of Be and transformation of TF (or HF) to T_2 (or H_2) is being investigated at INL as one of the most important tasks of a Japan–US joint study program called JUPITER-II [7–12]. Metallic Be was considered one of the most promising redox control agents through the reaction of $Be + 2TF = BeF_2 + T_2$. When the redox reaction is successfully controlled by metallic Be, the tritium chemical form in Flibe will be T_2. Then, tritium permeation through structural materials becomes crucial because of its low solubility and, therefore, its high equilibrium pressure. In order to reduce the tritium permeation, the condition of the extremely low T_2 concentration should be realized and, therefore, high tritium recovery is demanded in the Flibe self-cooled system [13]. Tritium leak rate is estimated to be large, unless the tritium concentration dissolved in Flibe is extremely low and a proper coating material is developed to suppress tritium permeation. Consequently, the transformation of TF to T_2 by redox control demands not only the high tritium recovery but also the control of T_2 permeation down to an acceptable rate. Unfortunately, there was no information on the TF concentration dependence of the above redox control reaction and the rate and amount of Be dissolution before starting our study. In the present paper, several reaction rate constants on the redox control by Be are quantitatively determined in our collaboration experiment of JUPITER-II.

2. Experimental results of redox control by Be

2.1. Experimental conditions

An experimental apparatus to investigate the Be redox control of Flibe was already shown in previous papers [8,9]. A powder mixture of 540 g of BeF_2 and 2LiF was melted in a Ni crucible. After purification of Flibe by various $HF + H_2 + He$ mixtures for a sufficient time, a mixture of HF (0 or 500–2000 ppm) + H_2 (the H_2/HF ratio of 10, 20 or ∞) in He was introduced into the molten Flibe with a constant flow rate of 110–130 cm^3(NTP)/min at 530 °C. The compositions of Li, Be, F and other metallic impurities in the mixed molten salt were determined by an ICP-mass-spectrometer after sampling a small piece of Flibe. After immersing a Be rod 5.1 mm in diameter with 5.0 cm^2 of exposed surface area in Flibe during a specified period from 5 to 60 min, variations of the effluent HF and H_2 concentrations with time were determined by an auto-titrator and a quadrupole mass-spectrometer. The dissolution or absorption rates of Be, HF and H_2 and the reaction rate between Be and F^- ions dissolved in Flibe were determined based on comparison between experimental HF and H_2 effluent curves and numerical simulation curves.

2.2. H_2 and HF absorption rate into Flibe

Fig. 1 shows typical effluent curves of H_2 or HF when constant concentrations of H_2 or HF were bubbled through the molten Flibe. All the notations in the figure are listed in Nomenclature. A fast response for H_2 and a delayed one for HF were observed in their respective H_2 and HF curves. The differences in response are due to the rates and amounts of absorption of H_2 and HF into the Flibe. The lines in the figure were expressed in terms of respective linear absorption rate constants, $k_{\mathrm{abs,H_2}}A_{\mathrm{g}}$ and $k_{\mathrm{abs,HF}}A_{\mathrm{g}}$ and saturated concentrations of H_2 and HF dissolved in Flibe, $x_{\mathrm{H_2,sat}}$ and $x_{\mathrm{HF,sat}}$. In addition, A_{g} is the surface area that includes bubble surfaces and the overlayer of Flibe.

When the solubilities of H_2 and HF are low and Flibe–gas interaction is expected to be small, their solubilities should obey Henry's law. Previous solubility data also supported Henry's law [14,15]. It was considered that the solubilities of H_2 and HF in Flibe obey Henry's law also in the present experiment. Their values were determined as follows: $K_{\mathrm{Henry,H_2}} = 1.24 \times 10^{-3}\ \mathrm{mol\ H_2/m^3\ Pa}$ and $k_{\mathrm{abs,}}\ H_2A_{\mathrm{g}} = 1 \times 10^{-5}\ \mathrm{m^3/s}$ for H_2 absorption, and $K_{\mathrm{Henry,HF}} = 6.61 \times 10^{-2}\ \mathrm{mol\ HF/m^3\ Pa}$ and $k_{\mathrm{abs,\ HF}}A_{\mathrm{g}} = 1 \times 10^{-7}\ \mathrm{m^3/s}$ for HF absorption. The $K_{\mathrm{Henry,H_2}}$ value determined here agreed with our data determined by the D_2 permeability through Flibe [10–12]. However, the fact of $K_{\mathrm{Henry,H_2}}$ being consistent with our D_2 permeability data does not mean that hydrogen isotopes always exist as a bi-molecular form in Flibe. The values of $K_{\mathrm{Henry,H_2}}$ and $K_{\mathrm{Henry,HF}}$ were about ten times higher than data published in ORNL previously [14,15]. This may be because the chemical form of hydrogen atoms in Flibe is strongly related to the redox control condition as will be shown below.

2.3. Be dissolution rate into Flibe

A proper Be dissolution rate (not too fast or too slow) is a key for the redox control. Fig. 2 shows the molar fraction of Be dissolved in Flibe, x_{Be}, determined from HF effluent curves as a function of the Be immersion period, t_{Be}. Although the Be concentration in Flibe was measured directly by ICP-mass spectrometry, the difference in concentration between a small amount of dissolved Be and the major component of BeF_2 composing Flibe was too small to distinguish the Be dissolution rate. The value of x_{Be} on the vertical axis was determined from the equivalent amount of reacted HF in that introduced into the pot by $HF + H_2 + He$ gas bubbling.

As seen in the figure, the dissolution rate was correlated to a linear equation, and its rate constant was $k_{\mathrm{dis,Be}}A_{\mathrm{Be}} = 8.9 \times 10^{-8}$ $(\mathrm{Be/Li_2BeF_4})$/s. The saturated concentration of Be, $x_{\mathrm{Be,sat}}$, was estimated as 2.7×10^{-4} in molar ratio of $\mathrm{Be/Li_2BeF_4}$ without a galvanic-coupling effect between Ni and Be [7]. When the galvanic-coupling effect was present, $x_{\mathrm{Be,sat}}$ became around 6×10^{-3}. The value of $x_{\mathrm{Be,sat}}$ was such that the use of Be as a neutron multiplier

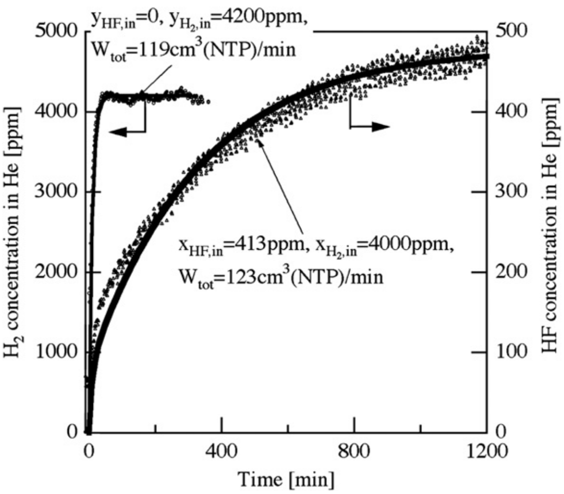

Fig. 1. H_2 or HF concentration curve after gas introduction into Flibe.

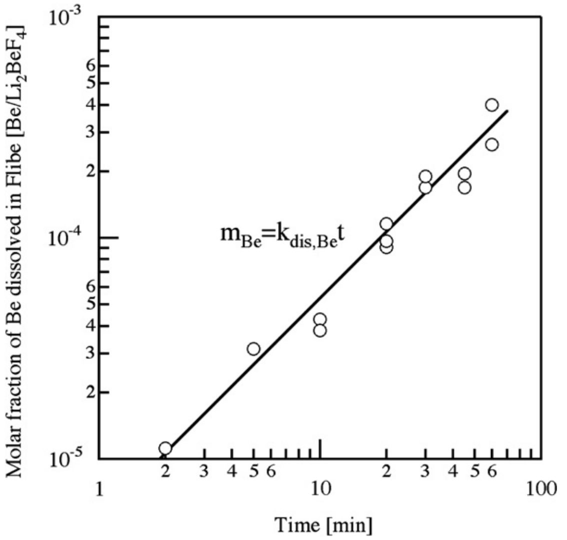

Fig. 2. Be dissolution amount as a function of immersion time.

as well as a redox control agent in Flibe flowing through a self-cooled blanket is feasible. The line in the figure was calculated from the linear dissolution model. The linearity in the wide-range means that Be dissolution reached a steady-state rate immediately after the Be immersion.

2.4. Reaction rate between Be and HF dissolved in Flibe

Fig. 3 shows typical results of the HF effluent curves as a function of time after the Be rod was immersed in Flibe at $t = 0$. Conditions for three different runs are as follows: $y_{\mathrm{HF,in}} = 915$ ppm and $t_{\mathrm{Be}} = 45$ min for Run 11, $y_{\mathrm{HF,in}} = 436$ ppm and $t_{\mathrm{Be}} = 10$ min for Run 14 and $y_{\mathrm{HF,in}} = 192$ ppm and $t_{\mathrm{Be}} = 5$ min for Run 16. The total flow rate was 120 cm^3(NTP)/min throughout the three runs. Before starting each experiment, a H_2/HF gas mixture with He balance was continuously bubbled through the Flibe crucible. When the Be rod was immersed into Flibe during a specified time of t_{Be}, the outlet HF concentration dropped drastically. It should be noted that the Be dissolution is deeply related with the galvanic-coupling effect between Be and Ni. When the Be rod was electrically isolated from others, no redox control could be achieved. In other words, it is probable that Be was dissolved in Flibe as an ion. After a large time delay, the outlet HF concentration gradually returned to the original inlet HF concentration. The measured HF concentrations for the various values of the Be immersion time and the inlet HF concentration were reproduced with good agreement by calculations (dashed lines) using a complete-mixing model described in the next section. Close agreement in the HF effluent curves was obtained between experiment and calculation.

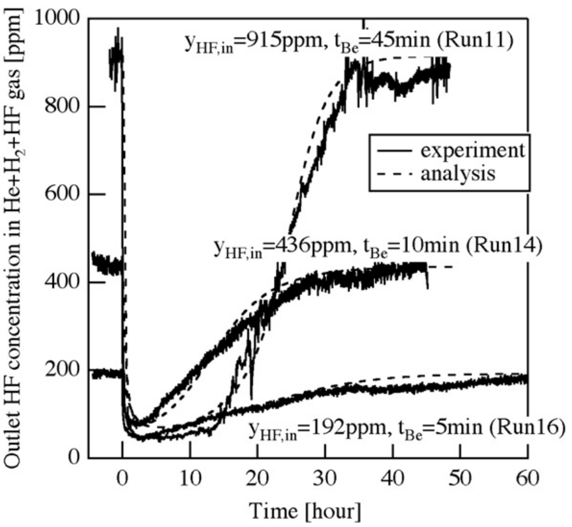

Fig. 3. Comparison between experiment and calculation for Flibe redox control.

3. Analysis of reaction between Be and HF dissolved in Flibe

3.1. Overall reaction rate equation

We focused on the overall material balance of Be and HF dissolved in Flibe and HF in He bubbled through a Ni crucible. Calculation was carried out under the assumption of a complete-mixing model, where the HF concentrations in the gas phase and molten Flibe, y_{HF} and x_{HF}, and the Be concentration dissolved in Flibe, x_{Be}, are uniform because of sufficient bubbling rates. Then, variations of y_{HF}, x_{HF} and x_{Be} with time are expressed as follows:

$$V_g c_g \frac{dy_{\mathrm{HF}}}{dt} = W(y_{\mathrm{HF,in}} - y_{\mathrm{HF}}) - k_{\mathrm{abs,HF}} A_g c_g (y_{\mathrm{HF}} - K_{\mathrm{Henry,HF}} R_g T x_{\mathrm{HF}}), \quad (1)$$

$$V_{\mathrm{Flibe}} c_{\mathrm{Flibe}} \frac{dx_{\mathrm{HF}}}{dt} = k_{\mathrm{abs,HF}} A_g c_g (y_{\mathrm{HF}} - K_{\mathrm{Henry,HF}} R_g T x_{\mathrm{HF}}) - 2V_{\mathrm{Flibe}} m_{\mathrm{HF}\to\mathrm{H_2}}, \quad (2)$$

$$V_{\mathrm{Flibe}} c_{\mathrm{Flibe}} \frac{dx_{\mathrm{Be}}}{dt} = V_{\mathrm{Flibe}} c_{\mathrm{Flibe}} k_{\mathrm{dis,Be}} A_{\mathrm{Be}} - V_{\mathrm{Flibe}} m_{\mathrm{HF}\to\mathrm{H_2}}. \quad (3)$$

All the notations in the equations are listed in Nomenclature. The transformation rate of HF to H_2, $m_{\mathrm{HF-H_2}}$, in Eqs. (2) and (3) was expressed in terms of the apparent reaction rate constants, $k_{\mathrm{BeF_2}}$ and $k_{\mathrm{MF_2}}$, as follows:

$$m_{\mathrm{HF}\to\mathrm{H_2}} = k_{\mathrm{BeF_2}}(x_{\mathrm{Be}} x_{\mathrm{HF}}^2 - K_{\mathrm{Be-BeF_2}} x_{\mathrm{BeF_2}} x_{\mathrm{H_2}}) + \sum_i k_{\mathrm{MF_2}}(x_{\mathrm{M}} x_{\mathrm{HF}}^2 - K_{\mathrm{M-MF_2}} x_{\mathrm{MF_2}} x_{\mathrm{H_2}}). \quad (4)$$

Here, $K_{\mathrm{M-MF_2}}$ is the thermodynamic equilibrium constant of the following reaction:

$$\mathrm{MF_2 + T_2 = M + 2TF}. \quad (5)$$

Since BeF_2 is very stable thermodynamically, the reverse reaction in the first term on the right-hand side of Eq. (4) can be ignored. The second term in Eq. (4)

is an impurity effect and will be discussed in the next section. The word ‘apparent’ means that $k_{\mathrm{BeF_2}}$ can depend on x_{Be} and x_{HF}. Based on the comparison in the HF and Be concentrations between the experiment and simulation, $k_{\mathrm{BeF_2}}$ was found to be independent of x_{Be}. On the other hand, two cases of the dependence of $k_{\mathrm{BeF_2}}$ on x_{HF} were investigated as follows; (i) $k_{\mathrm{BeF_2}}$ is independent of x_{HF} (i.e., the second-order reaction rate on x_{HF}) and (ii) $k_{\mathrm{BeF_2}}$ is in reverse proportion to x_{HF} (i.e., the first-order reaction rate on x_{HF}). After simulating HF curves under a wide-range of experimental conditions, the case (ii) assuming the first-order reaction rate gave better fitting. Consequently, Eq. (4) was reduced to the following simplified equation in terms of a modified reaction rate constant, $k^*_{\mathrm{BeF_2}}$, that includes the contribution of impurity metals

$$m_{\mathrm{HF}\to\mathrm{H_2}} = k^*_{\mathrm{BeF_2}} x_{\mathrm{Be}} x_{\mathrm{HF}}. \tag{6}$$

The $k^*_{\mathrm{BeF_2}}$ value determined from the comparison between experiment and calculation was $1.5 \times 10^6\ \mathrm{mol/m^3\ s}$. The deviation between experiment and calculation defined as $\{(y_{\mathrm{HF}})_{\mathrm{exp}} - (y_{\mathrm{HF}})_{\mathrm{cal}}\}/(y_{\mathrm{HF,in}})_{\mathrm{exp}}$ was within 10% for the three runs.

Lines in Fig. 4 in the logarithmic scale as well as Fig. 3 in the linear scale are calculated by Eqs. (1), (2), (3) and (6) under the assumption of the first-order reaction rate. Good agreement was obtained between the experiment and calculation. Therefore, it was found that the present results can provide the quantitative prediction of the redox control of Flibe by Be in a Flibe blanket. However, there seemed to be appreciable difference between experiment and calculation immediately after or during the Be immersion that will be discussed in Section 4.

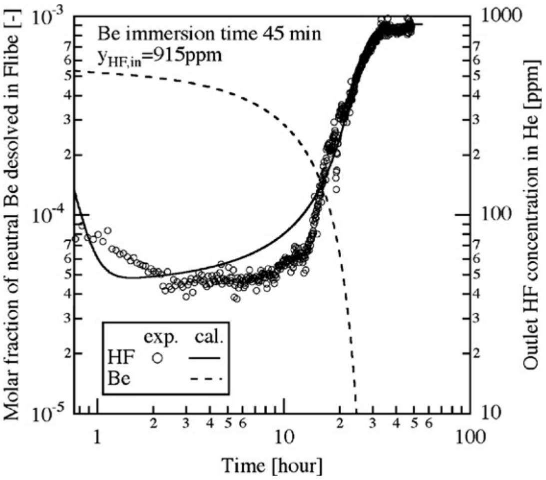

Fig. 4. Typical variations of HF and Be concentrations in Flibe.

3.2. Impurity effect on redox control

Effects of metallic impurities included in Flibe are inevitable. Impurities in molten Flibe after HF purification were detected by the ICP-mass spectrometry and were Cr 12 ppm, Fe 100 ppm, Mn 3 ppm and Ni 6 ppm. The compositions were near to the impurity level of Flibe used in ORNL previously (Fe 21 ppm, Ni 8 ppm, Cr 61 ppm and S 3 ppm) [15]. If Flibe contacts Reduced Activation Ferritic/Martensitic Steel, Fe, Cr, W and so on are possibly included as impurities in the future self-cooled Flibe blanket. Judging from the Gibbs free-energy change of Eq. (5), Fe was considered the most critical impurity for the redox control. Even if Be particles can change TF (or HF) to T_2 (or H_2), there is a possibility that Fe can affect the TF concentration in the blanket through the second term in Eq. (3). We should mention that the $k_{\mathrm{BeF_2}}$ value determined here includes contributions of metallic impurities, mainly Fe.

4. Discussion of redox control by Be rod in fusion blanket

Below we address the redox control by Be immediately after or during Be making contact with the molten Flibe. This condition can simulate the circumstance of flowing Flibe that contacts a Be redox controller in a Flibe self-cooled blanket. We do not always assume that the Be neutron multiplier is placed in a position making contact with a Flibe coolant directly. Fig. 5 shows variations of the HF concentration in the gas phase with time immediately after or during the Be immersion into Flibe. Drastic change of the HF concentration was observed regardless of different HF concentrations and immersion periods. Several things were noticed from the figure: (i) the decrease in y_{HF} continued for a certain time even when Be was withdrawn from the Flibe, (ii) the initial HF decrease rate was correlated to the relation of $y_{\mathrm{HF}}/y_{\mathrm{HF,in}} = kt^{-n}$ regardless of different conditions of $y_{\mathrm{HF,in}}$ and t_{Be}, and (iii) since the residence time of supplied gas was less than 0.1 h, variations of y_{HF} with time were independent of the residence time. Consequently, the behavior should be explained based on the concentration changes of HF and Be dissolved in Flibe immediately after contacting the Be rod. The Be concentra-

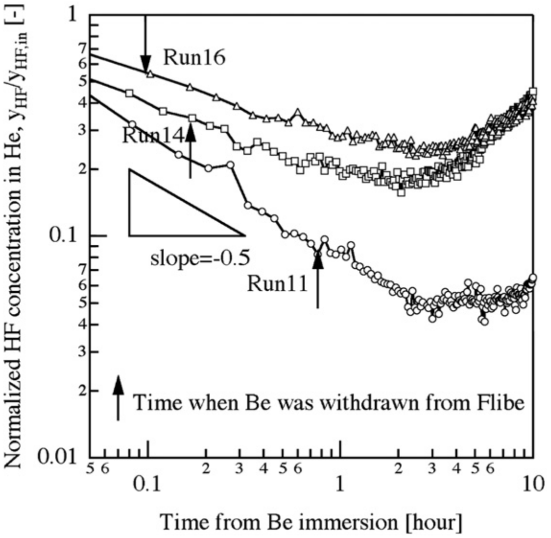

Fig. 5. Initial behavior of HF concentration.

tion was almost constant immediately after the Be withdrawal as seen in the dashed line of Fig. 4. The experimental results showed that the value of index n in the relation of $y_{HF}/y_{HF,in}$ was around 0.5. This implies that the reaction of Be and HF is controlled by diffusion of the F^- ions in the Flibe molten salt.

Since the partial pressure of TF generated in a self-cooled fusion blanket to maintain a steady-state fusion power of 1 GW [16,17] is around 10 Pa, the condition is near Run 16. Therefore, m_{TF-T_2} will be expressed by the first-order reaction of x_{TF} even in actual blanket conditions. Consequently, the expected rate of the TF to T_2 transformation is so fast that the x_{TF} value is kept low. Then, the transformation ratio of T_2/TF at the blanket outlet is expected to be high. The present study proved that the redox control by Be can be achieved even under the TF concentration expected in the FFHR-2 Flibe blanket.

It is important to estimate how the physical property of Flibe, such as viscosity, changes with the addition of Be. The consumption rate of LiF in a Flibe blanket for tritium production to maintain a steady-state fusion power of 1 GW is 64 mol/day. Therefore, an additional 32 mol/day of Be is necessary for the redox control. In summary, LiF of 96 mol/day should be added to maintain the same blanket composition during the steady-state operation of a fusion reactor. The amount is not large compared with the total Flibe volume of the whole blanket that is estimated to be the order of mmol. However, the constant addition of Be for redox control as well as the Li consumption for tritium generation brings the increase of Flibe viscosity. An increase in the 6% BeF_2 concentration ($2LiF + 1.1BeF_2$) results in an increase in Flibe viscosity from 0.008 Pa s to 0.01 Pa s at 600 °C. Therefore, the proper adjustment of Flibe components is necessary to operate the Flibe blanket in the long range.

5. Conclusions

The redox control of Flibe by Be was successfully proved experimentally, and the prompt transformation of HF to H_2 was completed in the Flibe crucible. With the use of the HF solubility ($K_{Henry,HF} = 6.61 \times 10^2$ mol HF/m^3 Pa), the HF absorption rate constant ($k_{abs,HF}A_g = 1 \times 10^{-7}$ m^3/s), and the Be dissolution rate constant ($k_{dis,Be} = 8.9 \times 10^{-8}$ (Be/Li_2BeF_4)/s) determined experimentally, the transformation rate of HF to H_2 in molten Flibe under the assumption of the complete-mixing model could well simulate experimental HF curves. The modified first-order rate constant for $Be + 2HF = BeF_2 + H_2$ was 1.5×10^6 mol/m^3 s. In particular, since the decreasing rate of the HF concentration was correlated to $y_{HF}/y_{HF,in} = kt^{-0.5}$ during and immediately after the Be immersion, the rate-determining step of the redox control reaction was diffusion of F^- ions in Flibe. The expected rate of the TF to T_2 transformation in a Flibe self-cooled blanket system became sufficiently fast to keep the TF concentration low. As a result, a high transformation ratio of T_2/TF at the blanket outlet is expected in a FFHR-2 when Be is used for the redox control agent material.

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