

# The evaporation behaviour of ThF<sub>4</sub> mixed of FLiNaK melt during low-pressure distillation

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## ABSTRACT

Low-pressure distillation of FLiNaK melt containing 50 wt % ThF<sub>4</sub> was carried out at 910 °C and <10 Pa using thermogravimetric equipment. The weight loss curve indicated clearly two stages: a rapid distillation stage in the initial period following a very long slow stage. The analysis results showed the rapid distillation originated from the evaporation of FLiNaK, while the slow process was attributed to the evaporation of ThF<sub>4</sub> and FLiNaK complexes. Because of the co-evaporation of ThF<sub>4</sub> and FLiNaK, it seems not feasible to separate ThF<sub>4</sub> from mixture salt. Hence, FLiNaK and ThF<sub>4</sub> may be recovered simultaneously by distillation.

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## 1. Introduction

The molten salt reactor (MSR), a unique liquid fuel reactor among the advanced fourth-generation reactors, has received much attention from the international nuclear community [1]. To achieve highly efficient operation, the MSR must be close-coupled to an on-line pyrochemical separation facility to process the irradiated fuels. For this reason, MSR has promoted the development of a number of pyrochemical separation techniques, such as uranium fluorination, reductive extraction, and low-pressure distillation [2].

ORNL has suggested that low-pressure distillation may be used to recover FLiBe carrier salt containing valuable <sup>7</sup>LiF with 99.995% isotope abundance, leaving the lanthanides and alkaline-earth metal fission products in the residue for discard. After purification, the recovered FLiBe carrier salt was recycled to MSR. Based on this purpose, in the 1960s, ORNL conducted a series of studies on

the low-pressure distillation of molten salts, and a great effort was devoted to the measurement and evaluation of the relative volatilities of fission products to LiF, mainly for rare earth elements [3–5]. On the basis of these studies, an engineering scale test of the low-pressure distillation for real irradiated fuel from MSRE was completed successfully in 1968 [6]. All these tests have demonstrated that the application of low-pressure distillation is feasible for simultaneously recovering carrier salts and removing rare earth fission products adequately [7].

Thorium, a fertile nuclide, is important for the sustainable development of nuclear power. MSR is particularly suitable for the utilization of thorium resources. As early as the 1960s, Oak Ridge National Laboratory (ORNL) proposed a conceptual design of a molten-salt breeder reactor (MSBR) [8]. Recently, development plans on thorium-based molten salt reactors have become one of the hotspots in studies of the application of nuclear power [9]. Consequently, it is essential for radiochemists to ascertain the effect of ThF<sub>4</sub> in molten salt on the pyrochemical separation of irradiated fuels.

In a related study of the molten salt system involving ThF<sub>4</sub>, Smith et al. [10] collected a series of liquid-vapor equilibrium data, including relative volatilities, effective activity coefficients, and apparent partial pressures, for the major components in the LiF-

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BeF<sub>2</sub>-ThF<sub>4</sub> system over the temperature range of 900 °C–1050 °C [10]. The authors indicated that rare-earth-thorium separation could be achieved by distillation, but the temperature would have to be at least 1200 °C. To the best of our knowledge, little basic information on the relative volatilities of the molten salt system containing ThF<sub>4</sub> has been presented, and no study on the low-pressure distillation of the molten salt system containing ThF<sub>4</sub> has been reported.

In this study, the low-pressure distillation of a 50 wt % ThF<sub>4</sub>-FLiNaK molten salt mixture was investigated with the aims of observing the evaporation behavior of molten salt containing ThF<sub>4</sub>, and exploring the possibility for the recovery of carrier salts and ThF<sub>4</sub>. The reason for choosing the concentration of 50 wt % ThF<sub>4</sub> was that the molar fraction of ThF<sub>4</sub> (11.8 mol %) in this mixture was close to that (12 mol %) in a single-fluid MSBR salt, as proposed by ORNL [8].

## 2. Experiment

### 2.1. Reagents and equipment

LiF, NaF and KF with 99.99% purity were purchased from Sigma-Aldrich, China, and the oxygen content was determined to be 400 ppm. ThF<sub>4</sub> with 99.9% purity was provided by the Changchun Institute of Applied Chemistry (CAS), and the oxygen content was 4000 ppm. All other reagents were of analytical grade and were used without further purification.

Distillation experiments of the ThF<sub>4</sub>-FLiNaK eutectic salt were performed using thermogravimetric (TG) equipment. It is composed of an alumina tube (d 60 mm, h 1000 mm), a load cell, two electric heaters, an evaporator crucible, a collected crucible, a thermal radiation shield and a pump system as described previously [11].

### 2.2. Experimental method

#### 2.2.1. Preparation of melt salt

According to the mole ratio of LiF, NaF and KF (46.5–11.5–42 mol %), certain amounts of LiF, NaF and KF were weighed in a glove box filled with Ar, mixed thoroughly and loaded into a nickel crucible. The mixture was melted for 48 h at 550 °C in a furnace under an argon atmosphere to obtain the FLiNaK eutectic salt. An equivalent amount of ThF<sub>4</sub> was mixed with the FLiNaK eutectic to prepare 50 wt % ThF<sub>4</sub>-FLiNaK in a similar way. The composition and homogeneity of the mixed salt were examined by ICP-OES (Optima 8000, PerkinElmer Co. USA). The impurity of oxygen in the 50 wt % ThF<sub>4</sub>-FLiNaK salt was determined to be approximately 2000 ppm by an oxygen analyser (LECO RO-600 USA).

#### 2.2.2. Low-pressure distillation

A 20 g sample of a 50 wt % ThF<sub>4</sub>-FLiNaK molten salt was loaded in a nickel crucible and suspended under the load cell. In general, the evaporation area is about the same as that of the nickel crucible with an inner diameter of 25 mm and the surface area of 4.9 cm<sup>2</sup>. To eliminate air from the furnace, the thermogravimetric equipment underwent several cycles of evacuation and filling with argon. Evaporating zones were heated to 550 °C with a heating rate of 10 °C/min. The temperature was maintained at 550 °C for 40 min until the salt melted completely, after which it was eventually raised to 910 °C with a heating rate of 8 °C/min. The whole heating-up process was conducted under argon atmosphere to minimize the salt evaporation and the vacuum pump was shut down until 910 °C. When the temperature reaches 910 °C, the pump was turned on and the pressure was sharply decreased. Throughout the distillation process the pressure kept about 10 Pa. The weight loss was monitored by the load cell as a function of time and utilized to calculate the vaporization rate of the molten salt, if necessary. T = 0 (see Fig. 1 (a)) was the point when evaporation starts. The experiment was terminated when the weight loss no longer changed.

To investigate the process of weight loss for each component of the fluoride salt mixture in more detail, the low-pressure distillation of 20 g of 50 wt % ThF<sub>4</sub>-FLiNaK molten salt began in a similar manner. However, when the weight loss reached a required time point, the distillation was stopped, and the residual molten salt in the crucible was transferred to a glove box and ground to a powder. A small fraction of the sample was used to analyse the relative contents of Li, Na, K, and Th. After weighing, the remaining molten salt was returned to the crucible for subsequent distillation. At the next designated time, the same experimental procedures were repeated.

### 2.3. Analytical method

The concentrations of Li, Na, K, Th in the salts left in the nickel crucible were determined by ICP-OES [11,12]. Briefly, 50 mg of powdered samples was blended with 10 mL of concentrated nitric acid and 0.5 g of aluminium nitrate. The mixture was digested at 190 °C for 2 h using a microwave system. The resultant clarifying solution was transferred to a plastic tube and diluted for ICP-OES analysis. To avoid any matrix effect on the ICP-OES measurements, the standard range was prepared with the same concentration of aluminium nitrate. Each sample was analyzed for three times and the relative error of parallel samples is below 5%.

For the qualitative measurements and phase analysis of residue salt, powder X-ray diffraction (XRD) was used with CuK $\alpha$  radiation (PANalytical, DY3614, Netherlands). The diffraction patterns were obtained over a 2 $\theta$  range of 10–90° with a step size of 0.02°.

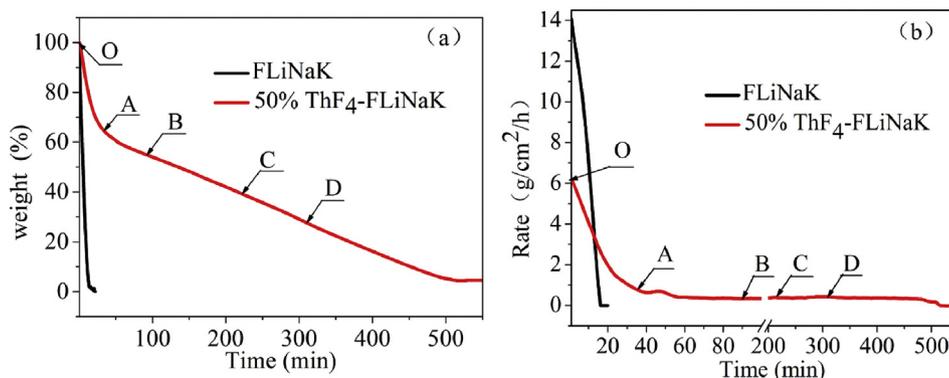


Fig. 1. wt loss (a) and distillation rate curves (b) for the 50 wt % ThF<sub>4</sub>-FLiNaK mixture and FLiNaK salt at 910 °C, 10 Pa.

### 3. Results and discussion

Low-pressure distillation of the 50 wt % ThF<sub>4</sub>–FLiNaK mixture was performed at 910 °C and <10 Pa pressure. The experiment showed that almost all of the molten salts, including thorium fluorides, were vaporized, and a nearly negligible amount of residues remained on the bottom of the crucible. The resultant thermogravimetric curve and differential distillation rate curve are shown in Fig. 1. As a comparison, low-pressure distillation of the FLiNaK carrier salt was performed under the same conditions, and the results are also given in the same figure. The difference of thermogravimetric curves and distillation rate curves between the ThF<sub>4</sub>–FLiNaK mixture and the FLiNaK carrier salt is very obvious. Complete evaporation of 20 g of ThF<sub>4</sub>–FLiNaK containing 10 g of FLiNaK needed a time of 565 min, which was more than 30 times longer than that of 10 g of the FLiNaK carrier salt. Regarding the evaporation rate curves, it was shown that the evaporation rate of FLiNaK decreased rapidly from 13.5 g/cm<sup>2</sup>/h at the beginning to zero within approximately 17 min. However, the evaporation rate of 50 wt % ThF<sub>4</sub>–FLiNaK decreased from 6.5 g/cm<sup>2</sup>/h at the beginning, passed through a short transition area, and then continued through a low speed zone for more than 400 min, where the evaporation rate decreased slightly from 0.3 g/cm<sup>2</sup>/h to 0.2 g/cm<sup>2</sup>/h. The experimental results implied an occurrence of great change in the evaporation behaviour of the carrier salt after the addition of thorium fluoride.

To better understand the reasons for the change in evaporation behaviour, we need to know the details of the weight loss process for the various components of the ThF<sub>4</sub>–FLiNaK mixture. In this experiment, the samples from the distillation residues were extracted at a number of selected points of take-off, A, B, C and D (the corresponding distillation times were approximately 35, 90, 220, and 310 min, respectively as Fig. 1) and subjected to analyze the metal elements by the ICP-OES analysis indicated that Li, Na, K and Th existed in the residue, with no nickel fluoride being observed. A set of typical experimental data on the relative concentrations of Li, Na, K and Th is listed in Table 1.

Knowing the weights of residual molten salt at the point of take-off, the weights of LiF, NaF, KF and ThF<sub>4</sub> in the residual molten salt at the points of take-off were obtained after correction for the weight loss of the residues induced by the sample analyses. The calculated results at different points of take-off are shown in Fig. 2. Knowing the weights of LiF, NaF, KF and ThF<sub>4</sub> both in the original ThF<sub>4</sub>–FLiNaK mixture and in the residual molten salt, the differences between them were used to determine the weight loss for each component at each time interval from the beginning of distillation to the corresponding points of take-off. The weight losses for each component are presented as percentages of their original weight, and these variations between points of take-off are given in Fig. 3.

Smith et al. [10] has measured liquid-vapor equilibrium data for LiF–BeF<sub>2</sub>–ThF<sub>4</sub> system by the transpiration method. On the basis of these data, the authors have obtained relative volatilities and apparent partial pressures for the major components. However, the difference in partial pressure data from the reference's values was

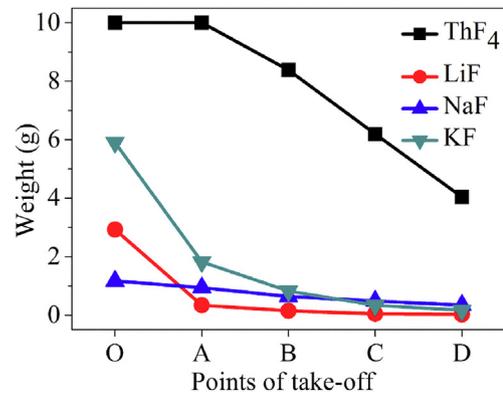


Fig. 2. Weights of composites in residual salts at various points of take-off.

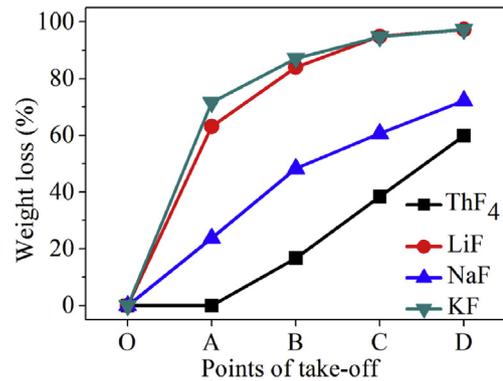


Fig. 3. Relative weight loss of various composites in residual salts at various points of take-off.

existed, probably due to the occurrence of association and complexation. Consequently the authors introduced following equation (1) and explain reasonably the difference.

$$P_A = P_A^0 \cdot X_A \cdot \gamma_A \quad (1)$$

Where  $P_A$  is the apparent partial pressure of component A,  $P_A^0$  is the vapour pressure of pure A,  $X_A$  is the mole fraction of A in solution, and  $\gamma_A$  is the activity coefficient for the component A. Meanwhile, the activity coefficient  $\gamma_A$  is related to the interaction between component A and other components in the solution. It is easy to understand that distillation rate of a molten salt depends on its apparent partial pressure. The detailed distillation behaviour and their evolution of each component in the molten salt would be explained well in terms of the vapour pressure of pure component, the variation in mole fractions, and activity coefficients in the low-pressure distillation of the 50 wt % ThF<sub>4</sub>–FLiNaK mixture.

As reported in References [13,14], the vapor pressures of LiF, NaF,

**Table 1**  
Content of Li, Na, K and Th in residual salt at various points of take-off.

Points of take-off	Element content (%)				Balance of components (%)
	Li	Na	K	Th	
O	3.94 ± 0.04	3.20 ± 0.03	19.8 ± 0.21	37.7 ± 1.1	98–102
A	1.84 ± 0.02	3.82 ± 0.05	9.08 ± 0.18	56.3 ± 2.0	99–105
B	0.98 ± 0.02	3.18 ± 0.05	5.04 ± 0.11	57.4 ± 2.0	90–96
C	0.46 ± 0.01	3.55 ± 0.09	3.01 ± 0.07	62.2 ± 2.5	91–99
D	0.33 ± 0.01	3.42 ± 0.10	2.04 ± 0.04	62.3 ± 3.2	90–97

Note: O represents the original mixture salt.

KF and ThF<sub>4</sub> are 0.47, 0.45, 5.17 and 0.0668 mm Hg at 1000 °C, respectively. Moreover, the mole fractions of KF and LiF were almost four times higher than those of NaF and ThF<sub>4</sub>. Consequently, it might be expected that the evaporation rate followed the order of KF > LiF > NaF > ThF<sub>4</sub> in the initial stage of distillation. As shown in Figs. 2 and 3, the weight loss of the molten salt mixture was mainly caused by the evaporation of KF and LiF in the initial stage, supporting the expectation mentioned above very well. Although the weight of ThF<sub>4</sub> was as high as 50% of the weight of the molten salt mixture, its mole fraction was only 11.8%, close to that of NaF. Because of its very low vapor pressure, no weight loss of ThF<sub>4</sub> was found during the initial stage. This statement was confirmed by an additional experiment in which the condensate from the distillation of the molten salt mixture was collected and analysed. Chemical analysis indicated that the relative content of ThF<sub>4</sub> was only 0.16% in the recovered condensate.

It is interesting to note the weight loss of KF and LiF. As mentioned above, the vapour pressures of KF was almost 10 times higher than that of LiF. In fact, however, the weight loss or the rate of volatilization for KF was slightly greater than that for LiF in the whole distillation process, as seen in Figs. 2 and 3. Especially results presented in Fig. 3 showed that the rate of volatilization of LiF and KF are very close at take-off C and D. The reason is based on the main idea that the weight loss or the rate of volatilization of given component in a molten salt is dependent not only on vapor pressure in its pure state, but also on mole fraction and activity coefficient. At very beginning (point O), total mole number of LiF was greater than that of KF. More importantly, as pointed below in this paper, a part of KF was combined with ThF<sub>4</sub>, leading to the decrease in mole number of free KF or activity coefficient decreased. Due to these two factors, the decreased volatilization rate of KF was very closed to the volatilization rate of LiF.

Due to the continual evaporation of large amounts of KF and LiF from the salt, their mole fractions decreased rapidly, leading to a decrease in the overall distillation rate. In contrast, the mole fractions of NaF and ThF<sub>4</sub> increased gradually. As a result, ThF<sub>4</sub> evaporation began to contribute to the weight loss of the mixed molten salt. After, the weight loss of KF and LiF reached approximately 80% and the weight loss of NaF reached approximately 50%, the distillation process arrived at the low speed evaporation zone (see Fig. 1B and C and D and Fig. 3). Meanwhile, the weight loss of the molten salt was dominated by the evaporation of ThF<sub>4</sub>. Moreover, this distillation process lasted for over 80% of the total distillation period until the end of low-pressure distillation.

It is worth noting that alkali metal fluorides always accompanied the evaporation of ThF<sub>4</sub> over the entire distillation process from beginning to end (see Figs. 2 and 3), although their vapor pressures are much higher than that of ThF<sub>4</sub>. This phenomenon may hopefully result from the change of activity coefficients in equation (1), following the form of complexes between the alkali-metal fluorides and ThF<sub>4</sub>.

Several authors have studied the complexation of the alkali-metal fluorides with ThF<sub>4</sub> in the equilibrium state of the mixed molten salt. The research techniques included analysis of the composition and crystal structure, construction of a phase diagram, thermodynamic calculations and so on. The molten salt systems studied were some binary or ternary systems, such as LiF-ThF<sub>4</sub>, NaF-ThF<sub>4</sub>, KF-ThF<sub>4</sub>, and NaF-KF-ThF<sub>4</sub> [15–20]. The formation of a number of complexes, such as NaThF<sub>5</sub>, KThF<sub>5</sub> and NaKThF<sub>6</sub>, has been identified in the melts. The knowledge obtained from these studies would be useful to better understand the low-pressure distillation of the quaternary ThF<sub>4</sub>-FLiNaK molten salt system.

Considering the possible interaction between these fluorides, more attention should be placed on mole quantities in the residual salt instead of the weight loss. The relative concentrations for these

metal elements determined by ICP-OES were transformed into their mole numbers. The mole quantities of LiF, NaF, KF and ThF<sub>4</sub> in the original molten salt (represented as point O) and the residual salts, sampled at each point of take-off, are listed in Table 2. As shown in Table 2, the mole quantity of ThF<sub>4</sub> is much lower than the total moles of LiF, NaF and KF in the original salt and the salt at point A. The formation of complexes containing Th, if any, would not obviously affect the distillation behaviour. At points B, C, and D in the low-speed evaporation zones, however, the mole quantity of ThF<sub>4</sub> becomes the largest. More importantly, this value is close to the equimultiple or sum of mole quantities of the alkali-metal fluorides, exhibiting an essential character of a complex composed of ThF<sub>4</sub> and alkali-metal fluorides.

To confirm the hypothesis on the formation of the complex, XRD technology was used to analyse the original molten salt (labelled by O; see Fig. 4) and the residual salts at points B, C and D. The resultant XRD spectra for the original molten salt mixture showed that some K<sub>7</sub>Th<sub>2</sub>F<sub>15</sub> compounds were formed via complexation of ThF<sub>4</sub> and KF, except for the simple fluorides LiF, NaF, KF. As the distillation began, the compound with the composition K<sub>7</sub>Th<sub>6</sub>F<sub>31</sub> was dominant in the XRD spectrum with the simple alkali metal fluorides replaced gradually. Following distillation, the complexes formed by ThF<sub>4</sub> with NaF and KF, K<sub>7</sub>Th<sub>6</sub>F<sub>31</sub> and Na<sub>2</sub>ThF<sub>6</sub> appeared simultaneously, while the simple alkali metal fluorides completely disappeared. Finally, the complexes formed by ThF<sub>4</sub> and NaF, Na<sub>2</sub>ThF<sub>6</sub> and NaThF<sub>5</sub>, were dominant in the XRD spectrum instead of K<sub>7</sub>Th<sub>6</sub>F<sub>31</sub>. The information obtained by XRD technology provided direct evidence for the formation of complexes between ThF<sub>4</sub> and alkali metals. Moreover, the XRD spectra also revealed the evolution of the complex species from K<sub>7</sub>Th<sub>6</sub>F<sub>31</sub> to Na<sub>2</sub>ThF<sub>6</sub> and NaThF<sub>5</sub> in the final moment of the distillation process, which was in reasonable agreement with increasing the mole ratio of NaF to KF in Table 2.

The experimental results based on the analysis of both molar quantities and XRD congruently support that alkali metal fluoride existed in the form of complexes coupled with ThF<sub>4</sub> and that the distillation was a co-evaporation process of the complexes in the low-speed distillation zone. Due to the complexation with ThF<sub>4</sub>, which has very low vapor pressure, the volatility of alkali metal fluoride was remarkably inhibited. As a result, the co-distillation process led to a form of low-speed distillation zone amounting to over 80% of the total distillation time. The weight loss in the low-speed distillation zone was controlled mainly by ThF<sub>4</sub>, which has a very large molecular quantity. Moreover, Table 2 and Fig. 4 also showed that the composition of the complexes transitioned from K<sub>7</sub>Th<sub>6</sub>F<sub>31</sub> to Na<sub>2</sub>ThF<sub>6</sub>. The transition of the composition of the complexes was responsible for the slight decrease in the evaporation rate in the low-speed distillation zone from 0.3 g/cm<sup>2</sup>/h to 0.2 g/cm<sup>2</sup>/h, as mentioned above.

Unfortunately, the co-distillation of alkali metal fluoride with ThF<sub>4</sub> means that low-pressure distillation, as a method for separation of the FLiNaK carrier salt containing high concentration of ThF<sub>4</sub>, was not feasible. As estimated from the experimental data

**Table 2**  
Content of LiF, NaF, KF and ThF<sub>4</sub> in residual salt at various points of take-off.

Points of take-off	Content (10 <sup>-3</sup> mol)			
	LiF	NaF	KF	ThF <sub>4</sub>
O	113 ± 1	27.9 ± 0.3	101.7 ± 1.1	32.5 ± 1.0
A	13.1 ± 0.1	22.4 ± 0.3	31.4 ± 0.6	32.5 ± 1.2
B	5.67 ± 0.09	15.2 ± 0.2	14.2 ± 0.3	27.2 ± 0.9
C	1.82 ± 0.04	11.6 ± 0.3	5.79 ± 0.14	20.1 ± 0.8
D	0.96 ± 0.03	8.18 ± 0.23	2.88 ± 0.06	13.1 ± 0.7

Note: Calculated value from the concentration of Li, Na, K and Th in residual salt and the weight of residual salt at various points of take-off.

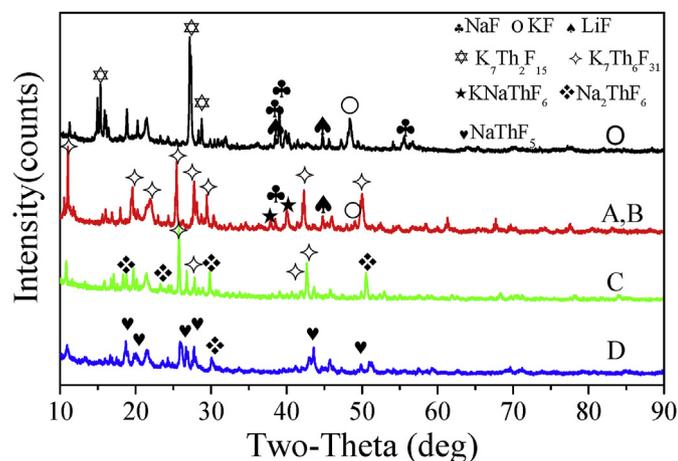


Fig. 4. XRD spectra of residual salts at various points of take-off.

obtained in this work, when 90 wt % of the FLiNaK carrier salt was recovered, over 30 wt % of ThF<sub>4</sub> was evaporated and collected in the condensate. An alternative strategy is supposed to recover FLiNaK and ThF<sub>4</sub> molten salt simultaneously by low-pressure distillation, leaving fission products in the distillation residue. However, this new draft seems not to be preferable if taking energy consumption and separation efficiency into account.

According to the requirement for processing the irradiated fuel from thorium-based molten salt reactor, ThF<sub>4</sub> and LiF should be recovered respectively, and fission products should be removed as much as possible. Unfortunately, the co-distillation of alkali metal fluoride with ThF<sub>4</sub> means that low-pressure distillation, as a method for separation of the FLiNaK carrier salt from ThF<sub>4</sub>, was not feasible. As estimated from the experimental data obtained in this work, when 90 wt % of the FLiNaK carrier salt was recovered, over 30 wt % of ThF<sub>4</sub> was also evaporated and collected in the condensate. An alternative strategy is supposed to recover FLiNaK and ThF<sub>4</sub> molten salt simultaneously by low-pressure distillation, leaving fission products in the distillation residue. However, this needs to increase the volatilization rate of ThF<sub>4</sub> by enhancement of distillation temperature. Similar conclusion also was mentioned in Ref. [10], where the low-distillation of FLiBe molten salt with ThF<sub>4</sub> was studied.

#### 4. Conclusion

The low-pressure distillation of a 50 wt % ThF<sub>4</sub>–FLiNaK molten salt mixture was studied at 900 °C and <10 Pa pressure. Conclusions are drawn as follows:

1. The molten salt mixture began with rapid distillation, followed by a long low-speed distillation zone. Compared with the distillation of the FLiNaK carrier salt without ThF<sub>4</sub>, the total distillation time for 50 wt % ThF<sub>4</sub>–FLiNaK molten salt increased by a factor of thirty, with the time of low-speed distillation being over 80% of the entire distillation.
2. The rapid distillation rate originated mainly from the evaporation of LiF and KF in the molten salt, while the evaporation of the complex formed from alkali-metal fluorides with ThF<sub>4</sub> was responsible for the low-speed distillation.
3. Because of the formation of complexes, it is not feasible to separate ThF<sub>4</sub> from alkali metal fluorides with containing high ThF<sub>4</sub> concentration salt only by low-pressure distillation. An alternative strategy is supposed to recover FLiNaK and ThF<sub>4</sub> molten salt simultaneously by low-pressure distillation, leaving

fission products in the distillation residue which needs further study.

This study provides valuable information for the treatment of molten salt containing thorium fluoride. Further study on the low-pressure distillation of a FLiBe molten salt containing ThF<sub>4</sub> is in progress in our laboratory.

#### Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jnucmat.2019.07.026>.

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