

The evaporation behaviors of rare-earth-doped FLiNaK melts during low-pressure distillation

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Abstract Low pressure distillation of FLiNaK containing rare earth fluorides was carried out to investigate evaporation behaviors of FLiNaK as well as decontamination of rare earth fluorides. Evaporation rate of NdF₃–FLiNaK increased with rising temperature. Decontamination factors (DFs) of six rare earth elements were around 10³ and 10⁴ except europium due to the formation of EuF₂. A higher DF of europium up to 1.4 × 10³ was obtained upon the addition of oxidant CeF₄. A hundred-gram scale experiment on FLiNaK containing NdF₃ and EuF₃ was performed, with a recovery ratio of 94.2% and the DF of europium to 2.4 × 10³ at 900 °C.

Keywords Molten salt · Low pressure distillation · Decontamination factor · Rare earth fluoride

Introduction

Molten salt reactor (MSR), a unique liquid fuel reactor among the advanced fourth generation reactors, has received much attention from the international nuclear community

recently [1–4]. Materials such as uranium and carrier salt can be extracted from the irradiated fuel by pyroprocessing methods. A major character of molten salt reactor is the use of molten salt consisting of alkali metal (usually highly enriched ⁷Li) and alkaline earth metal fluorides as fuel carrier and coolant of the reactor. In MSRs, the abundance of ⁷Li in LiF should be higher than 99.99% to reduce the neutron loss arising from ⁶Li which has a large neutron capture cross section. Due to the very high cost for the production of ⁷LiF, it would significantly increase the economy of nuclear power if ⁷LiF could be efficiently recycled without contaminations such as fission products.

Since the vapor pressure of fluoride carrier salt is higher than that of fission products, it is possible to separate them by low pressure distillation, generally less than 10⁴ Pa at high temperature such that the carrier salt can be recycled with high purity. Low pressure distillation has a number of advantages such as simplicity, high efficiency and no by-product, for which it has been widely used in the recovery and purification of molten salt [5–14].

In the 1960s, Oak Ridge National Laboratory began to develop the techniques for low pressure distillation of molten salt, which mainly focused on the measurement and assessment of the relative volatilities for rare earth fission products. Based on the vapor pressure data of rare earth fluorides, LiF and BeF₂, Kelly [5] proposed that low pressure distillation could be used to remove the fission products effectively from the molten salt reactor experiment (MSRE) fuel salt. The experiment showed that the decontamination factor for europium was about 50 after the carrier salts were completely distilled. Hightower [6] measured the relative volatilities of a series of rare earth fluorides with respect to LiF at 1000 °C. The results revealed that the rare earth trifluorides (except EuF₃), YF₃, BaF₂, and SrF₂ whose relative volatilities were between 10⁻⁴ and 10⁻⁵ could be

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substantially removed by distillation. However, the DF of EuF_3 was lower than that of others due to its higher relative volatility of 10^{-3} . Scott [7] used a cold-finger method to measure the relative volatilities of some trivalent rare earth fluorides between 900 and 1050 °C, which showed that the average relative volatilities of fluorides with respect to LiF varied from 0.01 to 0.05. According to these volatility data, the author suggested some modifications of this technique to improve and purity of carrier salt. Cantor reported [8] the measurements made by the transpiration method where the relative volatility of LaF_3 was determined to be 1.4×10^{-3} at 1000 °C and 1.1×10^{-3} at 1028 °C, respectively.

Although there are several experimental studies on the separation efficiencies for rare earth fluorides, it's difficult to use these data for the MSR reprocessing design due to the data discrepancies. Further investigations on the distillation behavior of rare earth fluorides are necessary. Comparing with the previous reported results, our study originated to improve the decontamination factor of EuF_3 by using redox method and these results provide credible data for a hundred-gram scale distillation. In the present work, the evaporation behaviors of rare earth doped FLiNaK melts were examined by using a thermogravimetric equipment, where the influence of temperature on the evaporation rate of FLiNaK and the decontamination of various rare earth fluorides were investigated. A lower DF was obtained for EuF_3 due to the formation of EuF_2 at high temperature. Addition of CeF_4 was able to suppress the reduction of EuF_3 , thus increase the corresponding DF. Experiment on a hundred-gram scale was performed as well to verify the DF of EuF_3 and evaluate the feasibility for the purification of FLiNaK using low pressure distillation technique.

Materials and methods

Reagents and materials

FLiNaK eutectic was prepared according to the procedures described in our previous work [15]. The mole fractions of LiF, NaF and KF are 46.5, 11.5 and 42.0% respectively. The melting point of the eutectic is 454 °C and the purity was better than 99.9%.

High purity (99.99%) anhydrous rare earth fluorides (NdF_3 , GdF_3 , CeF_3 , SmF_3 , EuF_3 , LaF_3 and CeF_4) were purchased from Sigma-Aldrich, China. All other reagents were of analytical grade and used without further purification.

Experimental setup

Batch experiment was adopted in this present work. Each run contains charging salt, distillation, and sample analysis.

The thermogravimetric (TG) equipment was used to carry out the gram-scale distillation experiment, where the sample evaporated was no more than 10 g. 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 shown in Fig. 1a. The two heaters can be programmed to raise the temperature up to 1200 °C independently and the system pressure can be controlled under 10 Pa. The load cell on the top of the furnace is used to record the change of salt mass up to 8000 ± 0.01 g. In general, the evaporation area is about the same as that of the nickel crucible with an inner diameter of 30 mm. An integrated nickel sleeve assembly was used to collect the condensate, by which the recovery ratio can be derived.

A hundred-gram scale distillation experiment of FLiNaK salt was carried out using a vertical closed chamber system, shown in Fig. 1b. The temperature gradient for distillation under 10^{-3} Pa inside the chamber is maintained by three electric heaters and the bottom of the chamber below the salt collector is cooled by water. The distillation chamber (d 200 mm, h 650 mm), sample boat, and salt collector are made of stainless steel (SUS-310S).

Method

Melt preparation

The FLiNaK melt containing rare earth fluoride was prepared in a home-made electrical furnace (maximum temperature: 1000 °C) connected with an argon glove-box, the details of which have been reported elsewhere [15]. Certain amounts of pretreated rare earth fluorides (NdF_3 , EuF_3 , SmF_3 , GdF_3 , LaF_3 , CeF_3) were mixed with the FLiNaK eutectic in a nickel crucible, which was placed inside the furnace vessel. After the vessel was sealed, it was first heated to 300 °C and maintained for 2 h to remove the trace moisture. Then the temperature was raised to 730 °C, at which the mixed salt was heated for 5 h until completely melted. The prepared melt was slowly cooled down to ambient temperature.

Low pressure distillation

For thermogravimetric experiments, about 10 g samples were loaded into the nickel crucible, which was then placed in the heating zone of the evaporator. Both evaporating and condensing 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 different target evaporation temperatures. The whole heating-up process was conducted under argon atmosphere to minimize the salt evaporation. During

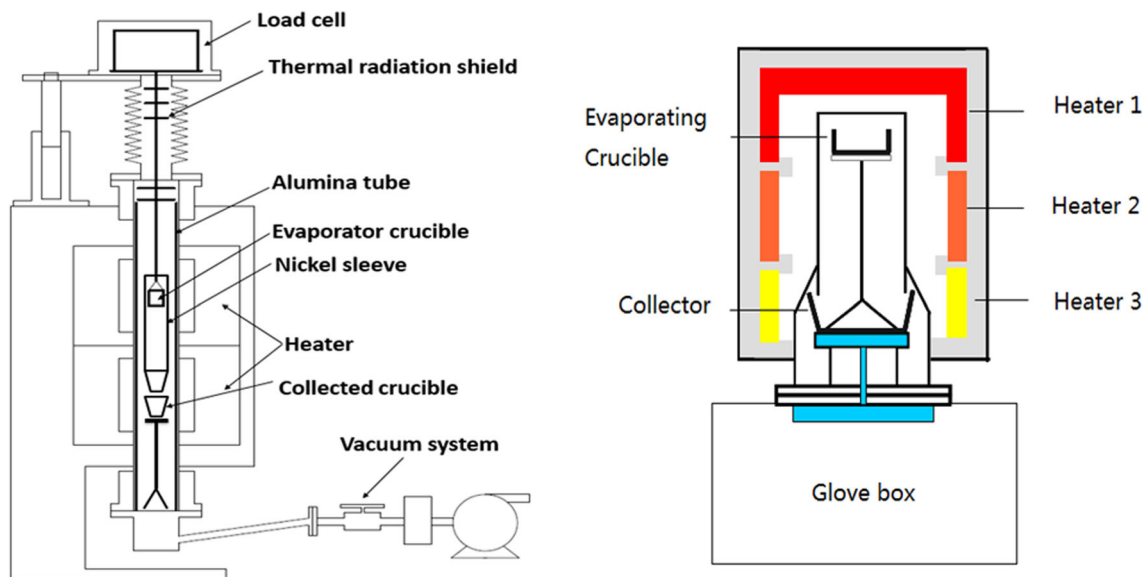


Fig. 1 **a** A schematic diagram of thermogravimetric evaporation equipment in gram-scale. **b** Closed chamber distillation system in hundred-gram scale

the evaporation process at a certain temperature, the pressure inside the evaporator was 10 Pa and the vacuum pump was on throughout the experiment. The behaviors of salt distillation were monitored by the weight loss of the load cell as a function of temperature and time.

For hundred-gram scale distillation experiment performed inside the closed chamber system, the distillation process is driven by the temperature gradient under vacuum [9]. The salt mixture (FLiNaK containing 1 wt% NdF_3 and 1 wt% EuF_3) was gradually heated at 0.01 Pa until the temperature increased to 550 °C, at which the vacuum pump was turned off and the whole distillation chamber was isolated. During the subsequent distillation process, the temperature of the upper chamber was maintained over 900 °C by heater 1, and both the middle and lower parts were maintained around 800 and 500 °C respectively by heaters 2 and 3.

Sample analysis

The concentrations of rare earth elements in the salts left in the nickel crucible and collected in the receiver were determined by induced coupled plasma atomic emission spectrometer (ICP-AES, Optima 8000, Perkin Elmer Company). About 100 mg salt samples were dissolved in 10 mL 10 M nitric acid at 190 °C for 2 h using a microwave system (CEM, USA) according to the literature [16]. The digest was then transferred to a plastic tube and diluted for ICP-AES analysis.

DF was used to evaluate the separation efficiency of rare earth from the carrier salt, which was obtained by the mass

fraction ratio of the rare earth fluoride in the eutectic salt (m_1) and condensed salt (m_2) as follows:

$$DF = m_1/m_2$$

Room temperature X-ray photoelectron spectroscopy (XPS, Shimadzu/Kratos AXIS UltraDLD, Kratos Analytical) was employed to probe the oxidation state of Eu in EuF_3 reagent and EuF_3 -FLiNaK sample melted at 800 °C using a standard monochromatic source (Al K_{α}) operated at 150 W.

Results and discussion

Dependence of evaporation rate on temperature

The thermogravimetric analysis was performed from room temperature to target evaporation temperature which ranged from 800 to 1000 °C. A typical thermogravimetric curve of 3 wt% NdF_3 -FLiNaK is shown in Fig. 2, where the evaporation was carried out at 900 °C for 40 min. On the basis of the sharp decrease during the evaporation process at 900 °C, an evaporation rate of $(4.6 \pm 0.1) \times 10^{-2} \text{ g/cm}^2 \text{ min}$ is derived by differential thermogravimetric analysis. Similar thermogravimetric curves were obtained at different evaporation temperatures, and the corresponding evaporation rates are listed in Table 1. It is obvious that the evaporation rate is correlated with the temperature, suggesting a higher distillation temperature is favored for a shorter distillation time and better purification efficiency as discussed below.

DF of rare earth fluorides

Influence of the temperature

The variation of DF for NdF_3 from 800 to 1000 °C is shown in Table 2, and the evaporation time was 40 min, where DF increases from 8.1×10^2 to 7.4×10^3 as the temperature is raised. Cantor [8] obtained the relative volatility of LaF_3 at 1000 and 1028 °C in FLiBe molten salt by using transpiration method, and the relative volatilities were 1.4×10^{-3} and 1.1×10^{-3} , respectively, which approximately correspond to DFs of 9.1×10^2 and 1.15×10^3 . It was also indicated that the DF could reach 7.4×10^3 if the temperature was further raised. Scott [7] measured the relative volatilities of seven rare earth fluorides at 900–1050 °C, which showed a decrease in relative volatility (increase in DF) with the increasing temperature for six trivalent fluorides except for the tetravalent CeF_4 . The dependence of DF on temperature from our experiments is consistent with the previous report.

As shown in Table 1, the molten salt is evaporated very rapidly at higher temperature. It is possible that the evaporation rate of molten salt increases more than that of the rare earth fluorides due to the change of the vapor pressure between them with the rising temperature. It is clear that a higher temperature is preferred not only for a faster recovery of molten salt but also for a higher purification efficiency as long as side effects such as corrosion of the distillation equipment materials could be under control. Hence, a medium distillation temperature of 900 °C was chosen for the following experiments.

Influence of rare earth species

In addition to NdF_3 , the DFs of another five rare earth fluorides were also determined in our experiments where mixed salts containing 3% (mass percentage) rare earth were used.

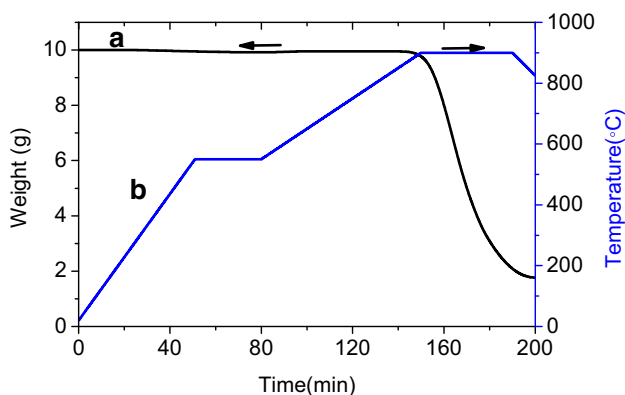


Fig. 2 Thermogravimetric curve of 3 wt% NdF_3 -FLiNaK at 900 °C. **a** Weight change curve; **b** temperature change curve

The results listed in Table 3 show that the DFs range from 10^3 to 10^4 for all the rare earth fluorides except EuF_3 . The relative volatilities of trivalent rare earth fluorides versus LiF obtained by Scott were within the range of 0.01–0.05 [7]. Such low DFs (a hundred or less) makes it less likely to recycle the carrier salt with high purity using low pressure distillation, and fractional distillation was recommended instead. However, the experimental relative volatilities reported by Hightower [6] in molten FLiBe were between 10^{-4} and 10^{-5} , about 2–3 orders of magnitude lower than those reported by Scott. Our experimental results are very close to Hightower's measurements, suggesting it is still possible to recover and purify the carrier salts that meet the requirements for reuse in molten salt reactor via low pressure distillation.

Although there are some discrepancies on the known relative volatilities due to different experimental conditions, it is certain that EuF_3 behaves differently from other trivalent rare earth fluorides during distillation, which is most likely due to the special chemical properties of europium. It is well known that the +3 oxidation state is most stable for the rare earth elements with 4f electronic shell while europium is one of the few exceptions which possess less stable +2 state. In aqueous solution, trivalent europium can be reduced to divalent state such that it can be easily separated from other rare earth species due to the large difference in chemical properties between the two oxidation states. As for the molten salt system, it has been reported that trivalent europium could be reduced to divalent state in LiCl–KCl [17] eutectic. Our recent investigations revealed the coexistence of both Eu^{3+} and Eu^{2+} in FLiNaK eutectic [18], where the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio was determined to be 4.4:10 based on XPS analysis. In the present work, small amounts of divalent europium were identified in the mechanical mixture of EuF_3 and FLiNaK as revealed by the 1124 and 1134 eV peaks observed in the XPS spectrum shown in Fig. 3a. The relative intensities of 0.78:10 for both peaks indicated the untreated EuF_3 sample is actually composed of 92.8% EuF_3 and 7.2% EuF_2 . To probe the influence of temperature on the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio, the EuF_3 -FLiNaK mixture was heated until melted, and the melt was kept at 800 °C for 5 h. An increase for the 1124 eV peak was observed for the cooled melted sample with the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio being 4.9:10 (Fig. 3b). The concentration of Eu^{2+} is about 5 times more than that before melting, suggesting divalent europium is formed from the reduction of trivalent state at high temperature.

The XPS spectra clearly demonstrate the reduction of Eu^{3+} to Eu^{2+} in FLiNaK eutectic at high temperature, which should account for the unusual low DF of EuF_3 during distillation. If such reduction could be suppressed, it would be possible to obtain a DF of EuF_3 comparable to those of other rare earth fluorides. CeF_4 is a strong oxidant which is capable of oxidizing Eu^{2+} to Eu^{3+} without

Table 1 Variation of evaporation rate of 3 wt% NdF₃-FLiNaK vs. temperature

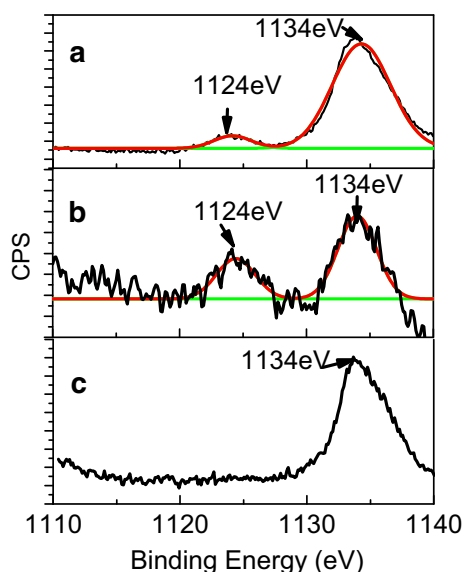
Temperature (°C)	800	850	900	950	1000
Evaporation rate (10 ⁻² g/cm ² min)	1.7 ± 0.2	3.0 ± 0.3	4.6 ± 0.1	5.3 ± 0.5	7.0 ± 0.5

Table 2 Variation of DF for NdF₃ vs. temperature (evaporation time: 40 min)

Temp (°C)	800	850	900	950	1000
DF (10 ³)	0.8 ± 0.1	1.3 ± 0.2	2.7 ± 0.4	5.8 ± 0.5	7.4 ± 0.4

Table 3 DFs of rare earth fluorides at 900 °C

Rare earth fluorides (3 wt%)	Decontamination factors	Content in condensed salt (ppm)
NdF ₃	2.9 × 10 ³	7.8
SmF ₃	2.9 × 10 ⁴	0.65
LaF ₃	2.3 × 10 ⁴	0.91
EuF ₃	2.3 × 10 ²	98
CeF ₃	6.9 × 10 ³	2.9
GdF ₃	1.4 × 10 ³	15

**Fig. 3** XPS spectra of mixed EuF₃-FLiNaK salt. **a** Mechanical mixture at room temperature; **b** melted at 800 °C for 5 h; **c** melted at 800 °C for 5 h in the presence of CeF₄

introducing contaminations into the melt. As a result, low pressure distillation experiments of EuF₃-FLiNaK molten salt at 900 °C were repeated twice with the addition of CeF₄. As expected, the DFs of EuF₃ in molten FLiNaK in the presence of CeF₄ were significantly increased to 1.4 × 10³ and 1.5 × 10³, about the same as those of other rare earth fluorides. The XPS spectrum (Fig. 3c) of the sample after distillation reveals the presence of the Eu³⁺ peak at 1134 eV while the 1124 eV peak due to Eu²⁺ completely disappears. Both distillation experiments and spectroscopic results provide solid evidence that it is Eu²⁺ that causes a low DF of EuF₃ which could however be significantly improved by adding CeF₄ into the melt.

Separation efficiency of hundred-gram scale melt

According to the experimental results obtained in the thermogravimetric equipment, a hundred grams experiment of molten FLiNaK containing 1 wt% NdF₃ and 1 wt% EuF₃ was performed in a closed chamber distillation system. To further confirm the reasonable feasibility, NdF₃ was chosen as a typical species of rare earth fluorides. About 1.5 wt% CeF₄ was added into the salt prior to the distillation conducted at 900 °C for 90 min. The recovery ratio of FLiNaK eutectic could reach 94.2% when 96.3% of carrier salts were evaporated. The DF of europium was 2.6 × 10³, almost the same as that of NdF₃ (2.4 × 10³). Both recovery ratio and purity of the condensate suggest the high capability of our closed-chamber distillation equipment in the recycle and purification of molten salts on a hundred-gram scale.

It should be noted that CeF₄ was introduced into the mixed salt as an oxidant to improve the DF of europium in the closed-chamber distillation experiments. The residual cerium in the collected salt was found to be 26.4 ppm with a DF of 3.1 × 10³. Fortunately the neutron capture cross sections of natural cerium isotopes are very small, even smaller than those of europium isotopes by several orders of magnitude. As a result, the very small amount of cerium in the collected salt after distillation would not cause a noticeable decrease of neutron economy for molten salt reactor.

Conclusion

In this paper, the evaporation behaviors of rare earth doped FLiNaK under low pressure were investigated in a thermogravimetric equipment. The evaporation rate under 5 Pa

increased from 0.017 to 0.07 g cm⁻² min⁻¹ as the temperature was raised from 800 to 1000 °C. A similar trend was observed for the DF of rare earth fluorides which were determined to be 10³ at 900 °C with the exception of EuF₃. The unusual low DF of EuF₃ arises from the formation of EuF₂ when the melt was heated to 800 °C as revealed by XPS. Addition of CeF₄ effectively suppressed the reduction of EuF₃, which in turn improve the corresponding DF to 1.4 × 10³, on the same order of magnitude of other rare earth fluorides. On the basis of the results from gram scale experiments, a hundred-gram scale experiment on FLiNaK containing 1 wt% NdF₃, 1 wt% EuF₃ and 1.5 wt% CeF₄ was performed in a closed-chamber distillation equipment at 900 °C, which gave a recovery ratio of 94.2% for the FLiNaK salt with almost equal DFs (2.4 × 10³) for both EuF₃ and NdF₃. The results from large scale experiment suggest it is feasible to efficiently recycle the FLiNaK salt with high purity by low pressure distillation technique.

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Glossary

Decontamination factor	Mass fraction ratio of analyzed element in the evaporated sample and condensed salt, abbreviated as DF
Separation efficiency of EuF ₃	Mass ratio of EuF ₃ in residual salt after distillation and EuF ₃ in the original salt
Recovery ratio	Mass ratio of collected salt and evaporated salt

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