



Evaporation behavior of lithium, potassium, uranium and rare earth chlorides in pyroprocessing



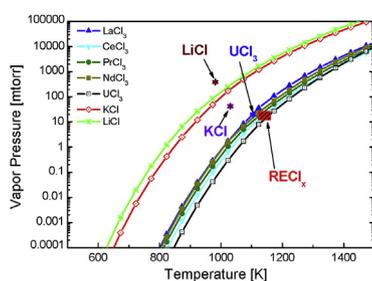
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HIGHLIGHTS

- The evaporation temperature of Li, K, U and rare earth (RE) chlorides was evaluated under vacuum.
- $\text{LiCl} < \text{KCl} < \text{UCl}_3 < \text{RE-Cl}$ was evaporated in order during the cathode process.
- Contamination of uranium products by the back-reaction of RE chloride was negligible.

GRAPHICAL ABSTRACT



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ABSTRACT

The evaporation behaviors of Li, K, U, and rare earth (RE) chlorides were examined for the cathode process in pyroprocessing. The evaporation temperatures of the chlorides were evaluated in vacuum by measuring the weight decrease. In addition, an evaporation test up to 1473 K of the cathode process using a surrogate mixture of uranium and chlorides was conducted. It was found that LiCl evaporated more readily than the other chlorides. The weight of LiCl was rapidly decreased at temperatures above 981 K, while that of KCl was decreased above 1035 K, indicating the evaporation. UCl_3 evaporated at temperatures above 1103 K. RE chlorides showed a similar evaporation behavior, evaporating first at 1158 K then rapidly evaporating at temperatures above 1230 K. Thus, the order of evaporation with increasing temperature was found to be $\text{LiCl} < \text{KCl} < \text{UCl}_3 < \text{RE chlorides}$, with different RE chlorides evaporating at similar temperature. The surrogate test confirmed the observed evaporation trend of the chlorides during the cathode process, and revealed that the contamination of uranium remains by the back-reaction of RE chlorides is negligible.

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1. Introduction

Electrorefining is one of the most important pyroprocessing techniques for the recovery of useful elements from spent fuel [1,2]. In the electrorefining process, spent fuel dissolves into a molten LiCl-KCl eutectic salt by electrolysis, and uranium is selectively

deposited onto the cathode surface. The uranium deposits collected from the cathode contain about 30 wt% of chlorides, and thus the uranium deposits must be purified and consolidated into an ingot by a cathode process [3–6].

The composition of the adhered chlorides to the uranium dendrites obtained after electrorefining is complicated. In order to achieve high current efficiency for uranium recovery, small amounts of UCl_3 (between 3 and 9 wt%) is added to the LiCl-KCl salt as an ionic conductor [7]. Various rare earth (RE) metals, such as Ce, Pr, Nd, La, etc., also dissolve into the molten salt in their chloride

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form during the process, because spent fuel generally contains RE metals as fission products [8]. These complicated salts adhere to the uranium dendrites after the electrorefining process, and are thus present during the cathode process.

The Korea Atomic Energy Research Institute (KAERI) has split the cathode process into two separate processes, i.e., salt distillation and ingot casting, to improve the efficiency and productivity of uranium recovery [9,10]. The chloride impurities are removed from uranium dendrites by salt distillation in vacuum at temperatures above 1073 K, and are recovered for reuse in electrorefining [11]. Following salt distillation, the nearly pure uranium dendrites (>99%) are consolidated into an ingot.

It is well known that pure materials have different vapor pressures at certain temperatures. Thus, materials with higher vapor pressure are readily removed at higher temperatures. Since the adhered chlorides have a much higher vapor pressure than pure uranium, the salts can be selectively removed, leaving behind pure uranium dendrites [11,12]. This is the general concept of the salt-distillation system used in pyroprocessing. Thus, it is important to study the evaporation behavior of chlorides adhered to the uranium dendrites in order to understand and optimize the salt-distillation system. Park et al. has previously characterized the evaporation behavior of LiCl-KCl eutectic salts. It is reported that LiCl and KCl were evaporated in vacuum at temperatures ranging from 873 to 973 K¹². However, research on the evaporation of U and RE chlorides is still insufficient. The evaporation behavior of UCl₃ is important not only to remove it from the uranium dendrites completely, but also to recover the UCl₃ for reuse. The evaporation behaviors of RE chlorides need to be studied for the complete purification of uranium and to examine the possibility of RE contamination of the uranium products by the metal-salt back reaction as follows:



Thus, the objective of this study is to examine the evaporation behavior of Li, K, U, and RE chlorides during the cathode process in pyroprocessing. In addition to LiCl, KCl, and UCl₃, we determined the content of CeCl₃, PrCl₃, NdCl₃, and LaCl₃ as representative of RE chlorides based on the established material flow in pyroprocessing [8,13]. We characterized the evaporation temperature of these chlorides in vacuum by measuring the weight decrease. The experimental results were then compared to those of thermodynamic calculations. Additionally, we prepared a mixture of uranium and Li, K, U, and RE chlorides to simulate the cathode process. The so-called surrogate mixture was heated up to 1473 K under vacuum in order to study the purification and consolidation of uranium using a well-defined system. We analyzed the composition of the product obtained after the test and the distillation behavior of the chlorides was discussed in detail based on the results.

2. Experimental

2.1. Experimental apparatus

Fig. 1 shows a schematic of the experimental apparatus used for the evaporation test. The apparatus was composed of a glove box system, a 2-zone tube furnace, an internal vacuum tube, an evacuation system, a load-cell, a salt condenser, and a control unit. The glove box was filled with Ar gas, and an atmosphere containing less than 20 ppm of O₂ and less than 5 ppm of H₂O was maintained during the test. The 2-zone tube furnace (165 mm Φ × 700 mm H) was designed to heat up the internal vacuum tube to 1473 K. The top zone was maintained at a higher temperature than the bottom zone to create a temperature gradient in the vacuum tube from top

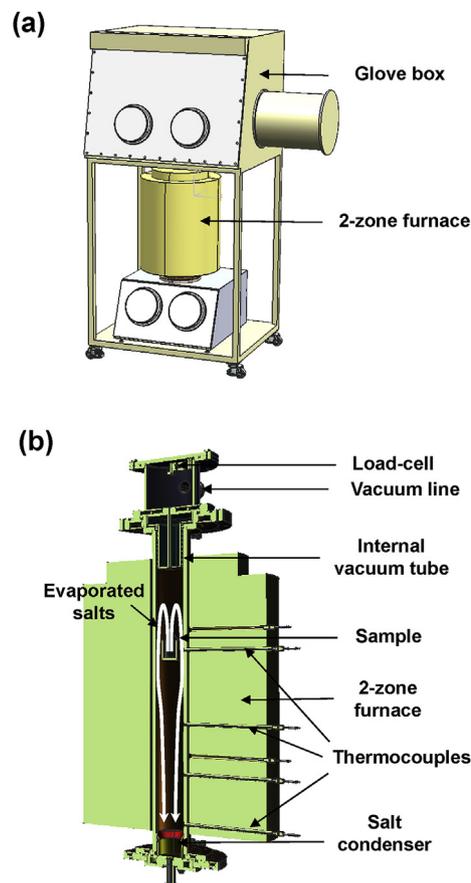


Fig. 1. A schematics of the (a) experimental apparatus and (b) cross-section of 2 zone furnace for evaporation test.

to bottom. The temperature gradient ensured salt vapor flow into the salt condenser. Before the test, the internal vacuum tube was evacuated by a rotary pump. Inconel 625 alloy was the material used for the internal vacuum tube due to its excellent strength at high temperatures. The load-cell was installed at the top flange of the internal vacuum tube to measure the weight change of the sample. The furnace temperature was controlled by a programmable control unit.

2.2. Sample preparation

RE chloride (CeCl₃, PrCl₃, NdCl₃, and LaCl₃) powders (Alfa Aesar, A Johnson Matthey Company) were used for the evaporation test. The purity of the RE chloride powders was greater than 99.9%. UCl₃ was synthesized in the laboratory by the chemical reaction between U and CdCl₂:



Detailed procedures for UCl₃ preparation can be found in the literature [14,15]. Subsequently, UCl₃ was dissolved in LiCl-KCl salt. The obtained LiCl-KCl-UCl₃ salt was directly used for the evaporation test, as the UCl₃ was difficult to separate from the LiCl-KCl salt mixture. The concentration of UCl₃ was estimated to be 20–25 wt%, because the concentration differed a little depending on the point of sampling.

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