



Technical Note

Employing high-temperature gas flux in a residual salt separation technique for pyroprocessing

Sung-Wook Kim^{*}, Dong Hyeon Heo, Hyun Woo Kang, Sun-Seok Hong, Sang-Kwon Lee, Min Ku Jeon, Jin-Mok Hur, Eun-Young Choi

Korea Atomic Energy Research Institute, Republic of Korea

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ABSTRACT

Residual salt separation is an essential step in pyroprocessing because its reaction products, as prepared by electrochemical unit processes, contain frozen residual electrolyte species, which are generally composed of alkali-metal chloride salts (e.g., LiCl, KCl). In this study, a simple technique that utilizes high-temperature gas flux as a driving force to melt and push out the residual salt in the reaction products was developed. This technique is simple as it only requires the use of a heating gun in combination with a gas injection system. Consequently, $\text{LiNO}_3\text{-ZrO}_2$ and LiCl-ZrO_2 mixtures were successfully separated by the high-temperature gas injection (separation efficiency > 93%), thereby demonstrating the viability of this simple technique for residual salt separation.

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1. Introduction

Pyroprocessing is a high-temperature electrochemistry-based technology that is implemented to manage used nuclear fuels [1,2]. Its electrochemical unit processes use molten salt electrolytes, such as LiCl and LiCl–KCl, as reaction media [1–3]. Thus, reaction products recovered after the unit processes must contain the residual salt compounds in a frozen state [4–7]. These residual salts should be separated from the reaction products to ensure product quality and prevent their side reactions in subsequent processes.

A vacuum distillation technique has been developed to separate the residual salts; with this technique, the salt phases are evaporated at an elevated temperature (~1400 °C) in a vacuum environment [4–7]. Such distillators are very complex, as they require a heating/cooling system and vacuum components [4–7]. More specifically, because heating and cooling of the distillators is time expensive, it consumes a significant portion of the required time of operation. For instance, more than 24 h is required for the full operation of the distillator developed at Argonne National

Laboratory, although the actual distillation time is only 1–2 h [4]. In addition, the high-temperature operation may reduce the product quality because of the side reactions occurring at the distillation temperature (e.g., oxidation of U, U–Fe alloy formation) [8,9].

Recently, we developed the residual salt separation techniques for the recovery of electrochemical reaction products via liquid-solid separation [10,11]. One way is to hold the reaction product basket simply above the liquid-phase salt inside the reactor after the electrochemical reaction is done to drain the residual salt inside the basket [10]. This technique requires an undesirably long drain time (~24 h) for the separation [10]. Another way is the liquid-solid separation using centrifugal force as driving force [11]. This technique showed high separation efficiency (>99%), but it requires complex equipment to apply the centrifugal force (e.g., rotation motor, power transmission), which may induce difficulty in remote-operation and maintenance of the device [11].

In this technical note, a simple technique that uses a heating gun is proposed as a potential residual salt separation technique. This study is mainly focused on the separation behavior of LiCl salt (electrolyte of oxide reduction) to show its feasibility for the post treatment of the oxide reduction products. Application of this technique is expected to expand to LiCl–KCl salt (electrolyte of electrorefining) according to its lower melting point (~350 °C at eutectic composition) than that of LiCl (~610 °C). High-temperature gas flux is injected into the reaction product/salt mixture to change

^{*} Corresponding author. Nuclear Fuel Cycle Process Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea.

E-mail address: swkim818@kaeri.re.kr (S.-W. Kim).

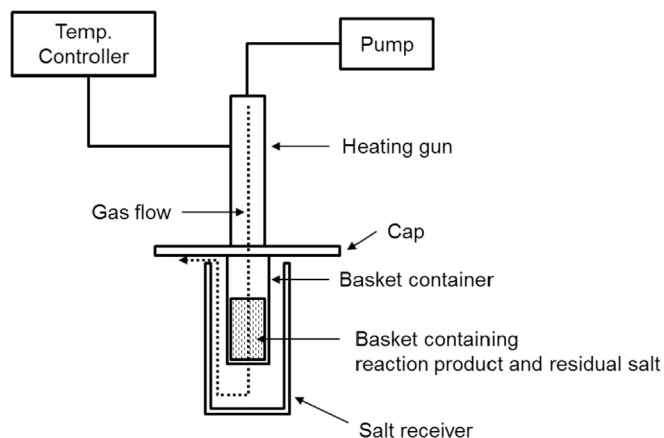


Fig. 1. Configuration of the integrated residual salt separation system using a heating-gun.

Table 1
Summary of experimental condition.

| Salt | LiNO ₃ | LiCl |
|----------------------------|-------------------|---------|
| Melting point (°C) | 255 | 610 |
| Operation Temperature (°C) | 350 | 750/850 |
| Ambient | Air | Air/Ar |

the state of the residual salt to a liquid state. Then, momentum transfer is carried out as the gas flux pushes the liquid salt out of the reaction product. Hence, the operation temperature could be lowered to the vacuum distillation temperature (gas-solid separation), because the liquid-solid separation is conducted in this system. Furthermore, the proposed technique does not require the employment of any extra equipment other than the heating gun. It is expected that the entire process can be completed in a relatively short period of time because no pre-heating is needed, and the

process has a high cooling rate, which is made possible by the low operation temperature, localized heating area, and the continuous injection of room-temperature gas through the gun during the cooling sequence.

2. Experimental methods

LiNO₃ (99%, Samchun Chemical, South Korea) and LiCl (99%, Alfa Aesar, USA) were chosen as the salt phases. ZrO₂ balls (Y₂O₃-stabilized, diameter = 5 mm, Hankook Ceratec, South Korea) were used as the surrogate material for the solid-state reaction products since the actual reaction products (e.g., U) are radioactive. Fig. 1 presents the schematic configuration of the residual salt separation system suggested in this study. Ten ZrO₂ balls were loaded into a stainless-steel basket (diameter = 12.5 mm, height = 21 mm) with punched holes (diameter = 2 mm) that acted as passages for the liquefied salt phase removal. The ZrO₂ loading basket was subsequently immersed into molten LiNO₃ (~300 °C) or LiCl (~650 °C) to prepare the ZrO₂-salt mixture. Then, the basket was placed inside a basket container, which was equipped with a heating gun (SEN Air Heater, Inflight Industrial, Japan). The assembled equipment was placed on a salt receiver, which was subjected to room-temperature conditions with no heat insulation. The heating gun was covered with ceramic fibers (Cerakwool, KCC, South Korea) for heat insulation, and a programmable controller (UP35A, Yokogawa, Japan) was used to adjust the output power of the heating gun. Gas flux was supplied into the heating gun by using an air pump (capacity = 30 L min⁻¹, APN-240N series, Iwaki, Japan). Calculated linear velocity of the gas flow is approximately 4 m s⁻¹ (inner diameter of the heating gun = 12.5 mm) and, however, it may be varied depending on temperature and pressure. The experiment was conducted in an air environment, and inside an Ar-filled glove box. Table 1 summarized the experimental conditions for the salt-phase removal. The weight before and after the experiment was measured by an electric balance (resolution = 0.01 g, FX-2000i, A&D Company Ltd., Japan).

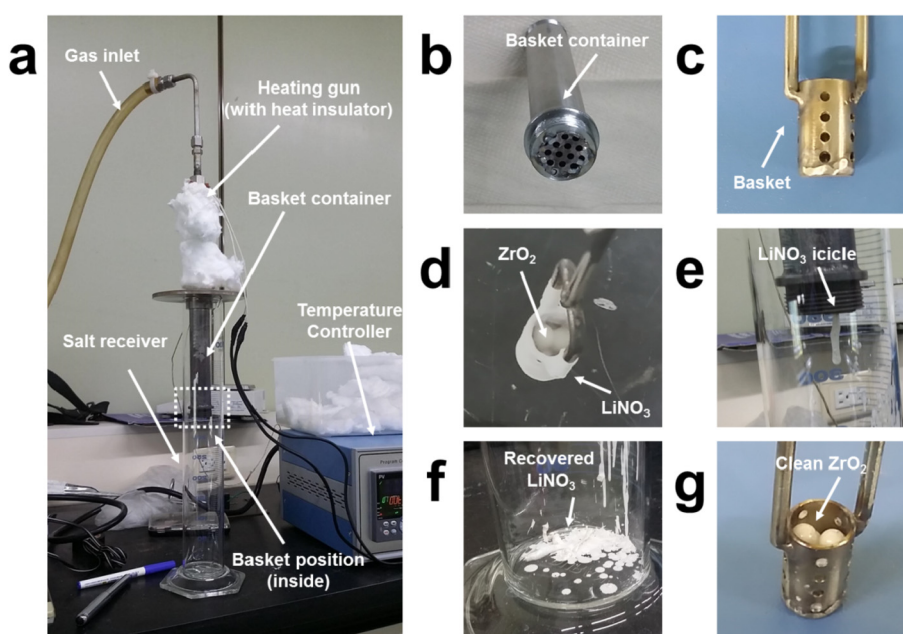


Fig. 2. LiNO₃-ZrO₂ separation experiment: (a) configuration, (b) basket container, (c) basket, (d) LiNO₃-ZrO₂ mixture-containing basket, (e) LiNO₃ icicle formation during the injection, (f) recovered LiNO₃ in the salt receiver after the injection, and (g) recovered ZrO₂-containing basket after the injection with a clean surface.

3. Results and discussion

This study was aimed to simulate the physical liquid-solid separation characteristics of the pyroprocessing products containing the residual salt compounds. To minimize unexpected side reactions during the high-temperature separation process, chemically stable surrogate (ZrO_2) was chosen. ZrO_2 compounds are widely used as ceramic components for the development of the pyroprocessing equipment because of their chemical stabilities against the chloride-based molten salts [12–14]. It was reported that the Y_2O_3 -stabilized ZrO_2 , which is the identical compound to the ZrO_2 balls used in the experiment, is stable in the LiCl molten salt except evolution of a polymorph phase [12]. The stability of the Y_2O_3 -stabilized ZrO_2 in the $LiNO_3$ molten salt was also investigated [15]. In this respect, only the physical process between the salt phases and the ZrO_2 balls was expected in this study.

A preliminary test was performed with low-melting-point $LiNO_3$ (melting point = 255 °C) and ZrO_2 in ambient air. Fig. 2a shows a photograph of the $LiNO_3$ – ZrO_2 separation system, which includes the heating gun. The bottom of the basket container was designed to include a punched plate to enable separation of the liquefied salt phases (Fig. 2b). The ZrO_2 balls were loaded into the basket (Fig. 2c), which was then dipped into the molten $LiNO_3$ to make the mixture (Fig. 2d). The gas temperature of the heating gun was maintained at 350 °C with the air injection. During the injection of high-temperature air, drops of the molten $LiNO_3$ fell down onto the salt receiver, whereas some of the molten $LiNO_3$ was observed to form icicles, which are eventually break off once they reach a certain size (Fig. 2e and f). Since the heated gas flow is the only heat source, the temperature of the salt receiver remained below the melting point of $LiNO_3$; thus, the $LiNO_3$ that dropped down onto the salt receiver tended to be consolidated into a bulk solid (Fig. 2f), instead of forming a powder; this is the primary recovery form for the vacuum distillation [5]. Moreover, this form is beneficial for handling the recovered salt for subsequent processing. Fig. 2g shows the clean surface of the ZrO_2 balls following the injection, indicating that the frozen $LiNO_3$ in the basket was successfully removed. Approximately 93% of $LiNO_3$ was separated out of the basket following the high-temperature gas injection (loading amount: 1.67 g; separated amount: 1.55 g), demonstrating the feasibility of this simple technique.

Prior to the LiCl– ZrO_2 separation test, a LiCl recovery test with no ZrO_2 was carried out in an open-air environment to determine whether this technique is feasible under ambient air conditions at the high operation temperature (melting point of LiCl = 610 °C). Crushed LiCl ingots (Fig. 3a) were installed inside the basket container. Although the same equipment used in the $LiNO_3$ – ZrO_2 experiment (Fig. 2a) was used in the LiCl recovery test, LiCl was not properly collected after the air injection at 750 °C, as is shown in Fig. 3b and c. Moreover, the liquefied LiCl tended to form small icicles at the bottom of the basket container (Fig. 3b), and only a few LiCl crystals were recovered in the salt container (Fig. 3c). This implies that the temperature drop across the bottom of the basket container is critical for the recovery of the liquefied LiCl. Thus, the structure of the basket container was changed to shorten the length from the heating gun outlet, and a pipe was connected to the bottom of the basket container (Fig. 3d and e). The basket container and the pipe were covered with the heat-insulating ceramic fibers, as is shown in Fig. 3f, to minimize heat loss and thus maintain an appropriate temperature around the LiCl ingot. With this modification, the LiCl ingot was successfully removed from the container after the air injection at 750 °C (Fig. 3g), with the residual LiCl determined to be negligible (Fig. 3h). Note that the recovered LiCl was dark brown in color (Fig. 3g) owing to the oxidation of the stainless-steel parts that occurred as a result of being exposed to

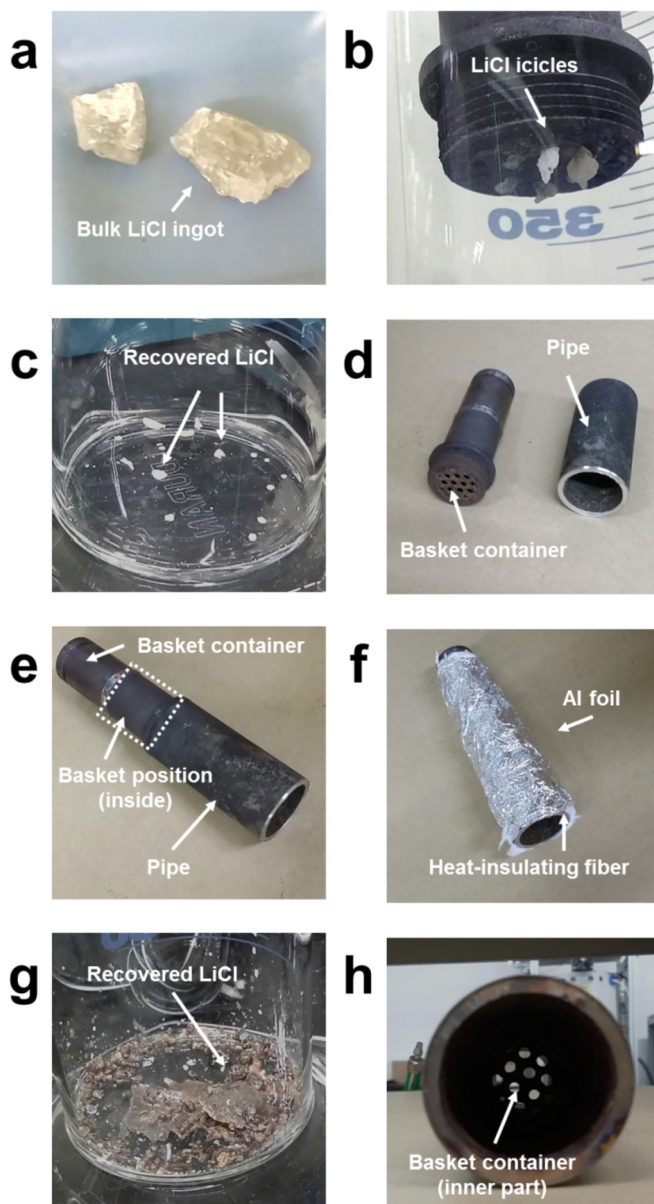


Fig. 3. LiCl recovery experiment and equipment modification: (a) bulk LiCl ingot, (b) LiCl icicle residue after the injection (before the modification), (c) recovered LiCl after the injection (before the modification), (d) modified basket container with the pipe, (e) assembled basket container with the pipe, (f) insulator-covered basket container with the pipe, (g) recovered LiCl after the injection (after the modification), and (h) inner area of the basket container after the injection (after the modification).

the surrounding air. Consequently, the LiCl separation, which requires high-temperature operation, is not preferred in the air environment owing to the oxidation of the equipment.

The salt separation experiment for the LiCl– ZrO_2 mixture was conducted by using the modified system. The experiment was performed inside an Ar-filled glove box to prevent the oxidation of the equipment. Fig. 4a shows the basket containing the LiCl– ZrO_2 mixture. After the mixture was placed inside the basket container shown in Fig. 4b, the LiCl– ZrO_2 separation experiment was performed at 750 °C. No LiCl was recovered after the Ar injection, but small icicles had formed at the bottom of the basket container (Fig. 4c). This indicates that the frozen LiCl melting and separation processes were anomalous at this temperature. This is due to the low specific heat of Ar ($\sim 20.79 \text{ J mol}^{-1} \text{ K}^{-1}$) as compared to that of

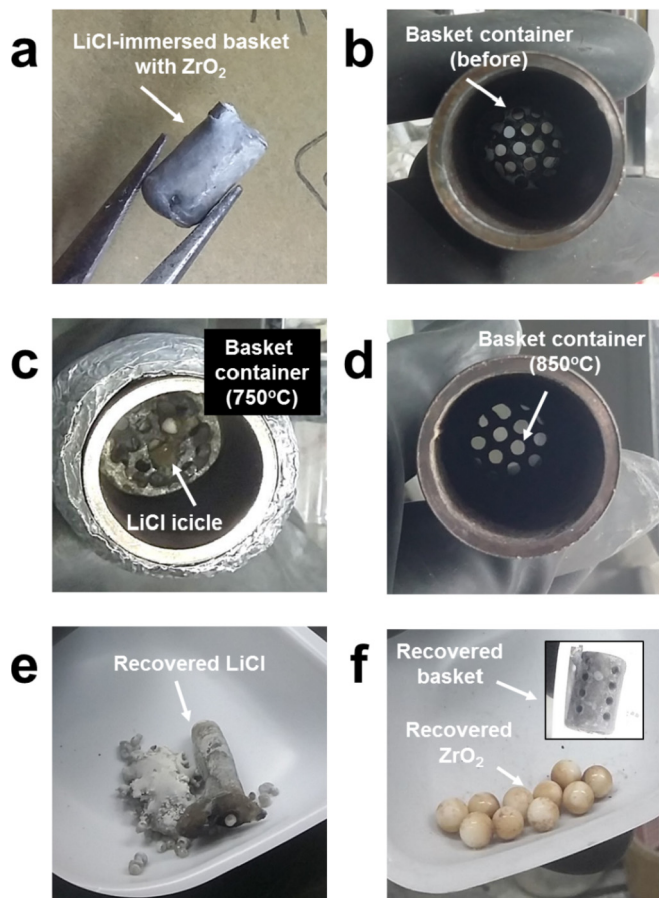


Fig. 4. LiCl–ZrO₂ separation experiment: (a) LiCl–ZrO₂ mixture-containing basket, (b–d) the basket container (b) before and (c–d) after the injection at (c) 750 and (d) 850 °C; (e) the recovered LiCl after the injection at 850 °C, (f) the recovered ZrO₂ balls after injection at 850 °C (inset: recovered basket).

air ($\sim 29.19 \text{ J mol}^{-1} \text{ K}^{-1}$), which consequently resulted in poor heat transfer. To overcome this problem, the heating gun temperature was increased to 850 °C in the Ar environment. Under this higher temperature condition, the frozen LiCl was removed from the basket so that it could be recovered in the salt receiver, as is shown in Fig. 4d and e. Subsequently, no noticeable LiCl residue was found to have remained inside the basket container (Fig. 4d) and the recovered LiCl had white-grey color because of the reduced oxidation of the equipment in the Ar-filled glove box. The ZrO₂ balls were removed from the basket with ease as a result of the residual salt separation (Fig. 4f), thus leaving an empty basket (inset of Fig. 4f). Consequently, 2.99 g of the 3.18 g of LiCl loaded into the basket was recovered; this corresponds to a recovery efficiency of 94%.

The process time of the LiCl–ZrO₂ separation test is given in Table 2, with comparison to the distillation experiment done by our group [8]. The distillation was carried out using $\sim 6 \text{ g}$ of the oxide reduction products which contain $\sim 1 \text{ g}$ of the residual salt at a 850–950 °C [8]. Total operation time was less than 5 h for the heating

gun technique. On the other hand, the distillation technique required more time. The cooling time is not given in Ref. 8 but, in general, overnight cooling was needed due to the heat insulation of the furnace system. Such fast operation is beneficial to minimize the salt-related side reactions, especially for the oxide reduction products (metal phases), which can be re-converted back to the original oxide phases (e.g., $\text{U} + 2\text{Li}_2\text{O} = \text{UO}_2 + 4\text{Li}$) even at 650 °C in the LiCl–Li₂O molten salt at the prolonged immersion time [16]. Relatively poor heat conduction by the gas flux would be concerned in large-scale systems with respect to the liquid–solid separation time and adopting the high-power heating gun is needed to ensure sufficient heat generation (by heater) and fast heat conduction (by flux).

Although this preliminary study shows the promising results on the residual salt separation, the separation efficiency need to be further improved (>99%) to suppress the side effects of the residual salt in the subsequent processes. Indeed, nearly 100% of the separation efficiency with more than 98% of the recovery efficiency was achieved through the vacuum distillation of the LiCl salt [5]. This becomes more important when considering the ZrO₂ balls with clean and smooth surface were used in this study. The actual pyroprocessing products have complicated morphologies. For instance, oxide reduction products have porous structures and U dendrites are obtained after electrorefining [3,6]. It is considered that the separation efficiency would be reduced when the actual reaction products are used as some of the salt can be trapped inside small spaces (e.g., pores) in the actual products. In this respect, further research effort should be made to increase the efficiency using the actual reaction products. Even though the efficiency cannot meet the requirement, this heating gun technique can be applied as a former step of the residual salt distillation to reduce the process load. Salt-related side reactions occurring during the high-temperature distillation, such as oxidation of metal products of oxide reduction [8], are expected to be minimized with this pre-treatment.

4. Conclusions

In this study, conceptual experiments were performed by implementing a simple residual salt separation technique that uses the high-temperature gas flux to properly treat the reaction products of pyroprocessing electrochemical processes. Consequently, LiNO₃–ZrO₂ and LiCl–ZrO₂ mixtures were successfully separated by using high-temperature gas injection. This simple technique has several advantages over the conventional vacuum distillation technique, particularly with respect to equipment complexity, operation temperature, operation time, and operation convenience. To build upon the results presented here, a scale-up study ($\sim \text{kg}$ scale) should be performed to achieve a higher separation efficiency (>99%) at a lower operation temperature (<700 °C) to enable applicability to actual pyroprocessing.

Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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Table 2

Comparison of operation time of the residual salt separation techniques.

| | Heating (h) | Separation (h) | Cooling (h) |
|--------------------------------|-------------|----------------|-------------|
| High-temperature gas injection | ~ 0.2 | ~ 2 | ~ 2 |
| Distillation [8] | ~ 5 | ~ 2 | Overnight |

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