Technical Note

Residual salt separation technique using centrifugal force for pyroprocessing

Sung-Wook Kim[*], Jong Kwang Lee, Dongseok Ryu, Min Ku Jeon, Sun-Seok Hong, Dong Hyun Heo, Eun-Young Choi

Korea Atomic Energy Research Institute, South Korea

ARTICLE INFO

ABSTRACT

Pyroprocessing uses various molten salts during electrochemical unit processes. Reaction products after the electrochemical processes must contain a significant amount of residual salts to be separated. Vacuum distillation is a common method to separate the residual salts; however, its high operation temperature may cause side reactions. In this study, a simple rotation technique using centrifugal force was suggested to separate the residual salts from the reaction products at relatively low temperature compared to the distillation technique. When a reaction product container with porous wall rotates inside a vessel heated above the melting point of the residual salt, the residual salt in the liquid phase is separated through centrifugal force. It was shown that the $LiNO_3$-Al_2O_3 mixture can be separated by this technique to leave solid Al_2O_3 inside the container, with a separation efficiency of 99.4%.

1. Introduction

The accumulation of spent nuclear fuels (SNFs) is a global issue, and abatement technology for such high-level radioactive waste should be developed [1,2]. Since it was successfully demonstrated through the EBR-II (Experimental Breeder Reactor-II) project that pyroprocessing can recycle metal fuels of sodium-cooled fast reactors [3], there has been an attempt to employ pyroprocessing for the recycling of SNFs from pressurized water reactors [4,5]. Pyroprocessing is composed of various physical, chemical, and electrochemical unit processes to separate, recycle, and store the radioactive elements in the SNFs [4,5]. Among them, the electrochemical processes (e.g., electrolytic reduction, electrorefining, and electrowinning) use molten salts, such as LiCl and LiCl-KCl (normally, near eutectic composition), as electrolyte materials [4,5]. Therefore, the reaction products of these processes, which were immersed in the molten salts, must contain residual salts with them [6–8]. The residual salts should be properly removed to ensure an adequate quality of the reaction products of each electrochemical process.

Distillation (gas-solid separation) has been commonly accepted for separating the residual salts from the reaction products during pyroprocessing [6–8]. This process requires high temperature (up to 1400 °C) and low pressure (down to vacuum level) to increase the evaporation rate of the salt phases [6–8]. However, a high-temperature operation is not preferred in this system owing to a degradation of the reaction products. For instance, metal products (e.g., metallic U) after the electrolytic reduction can be partially reconverted into the original oxide phase (e.g., UO_2) with the presence of Li_2O in the residual LiCl salt during the high-temperature distillation [8]. This is critical because transferring re-oxidized phases (e.g., UO_2) to subsequent processes results in poor production yield of whole pyroprocessing as the oxide phases cannot be further treated in the electrorefining process. In addition, metallic actinides (dominantly, U) may experience eutectic melting with Fe and other elements in the metal containers (generally, made with stainless steel) of the reaction products at an elevated temperature (e.g., eutectic point of U-Fe system: ~725 °C at 34 at% of Fe) [9]. Although lowering the operation temperature is beneficial to guarantee the quality of the distillation products, it will lead to low distillation efficiency at the same time owing to a reduced vapor pressure of the salt phases, which is the key driving force of this process.

Recently, we proposed a simple liquid-solid separation technique using a heating gun with no vacuum system [10]. Injecting

* Corresponding author. Pyroprocessing Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, South Korea.
E-mail address: swkim818@kaeri.re.kr (S.-W. Kim).

heated gas with an adequate flux can melt and remove the salts on the surface of the solid products through the heat and momentum transfer of the high-temperature gas particles. The operation temperature of this technique is maintained near the melting point of the salt phase by controlling the heating gun power and gas flow rate, and thus the above mentioned problems can be avoided. However, it is questionable whether this heating gun technique can be scaled-up for a large-scale pyroprocessing system upon its requirements of significant heat and gas flux.

In this study, we investigated the liquid-solid separation process using centrifugal force to drive the liquid-phase removal from the reaction products. It was expected that the liquid-phase salt can be easily separated from the reaction product when the reaction product container is rotated at an adequate temperature (>melting point).

2. Materials and methods

Figs. 1 and 2 show a schematic design and photographs of the residual salt separation equipment, respectively. A reaction product container (120 mm L × 120 mm H × 20 mm W) is inserted into the outer vessel (ϕ207 × 232 mm H) to hang the container on the upper part of the vessel. The wall of the container has holes (diameter of 2 mm, equally spaced with distance of 4 mm) to expel the liquid phase from the container so that it can be recovered on the bottom of the outer vessel. The outer vessel is connected to a rotor to obtain a centrifugal force. The rotation speed can be adjusted using a logic-controlled servo-motor (1.5 kW) connected to the rotor through a power transmission. The outer vessel is covered with a furnace for heating to melt the salt phase. The top part of the rotor is water-cooled to protect the servo-motor, bearing, and power transmission from the heat.

Low-melting-point salt, $LiNO_3$ (255 °C), was chosen as a surrogate material of the salt phases (i.e., $LiCl$, $LiCl$-KCl) for experimental convenience. The liquid density of $LiNO_3$ is approximately 1.75 g cm^{-3}, which is comparable to that of $LiCl$ (~1.55 g cm^{-3}) and $LiCl$-KCl (~1.65 g cm^{-3}). The viscosity of $LiNO_3$ (~5.1 mPa s at 270 °C, ~3.0 mPa s at 349 °C) is higher than that of $LiCl$ (~1.4 mPa s at 647 °C) and $LiCl$-KCl (~2.2 mPa s at 500 °C) [11–13]. Thus, it is considered that the use of $LiNO_3$ is under harsher conditions than that of $LiCl$ and $LiCl$-KCl for a liquid-solid separation experiment. Al_2O_3 tubes (Haldenwanger, Germany) of 6 mm in diameter with six longitudinal holes (diameter: 1 mm) were cut into small pellets (length: 7 mm in average) for the use of a solid material instead of the radioactive SNFs.

The Al_2O_3 pellets were loaded inside the reaction product container, and molten $LiNO_3$ (99.0%, Samchun Chemical, Republic of Korea) was poured into the Al_2O_3-loading container to make an Al_2O_3-$LiNO_3$ mixture. Then, all of the equipment was assembled for the experiment. The furnace temperature was elevated to 350 °C at a heating rate of 100 °C h^{-1}. After waiting for 30 min at 350 °C, the rotor was rotated at 2000 RPM for 20 min for the separation. Cooling water was circulated during the whole experiment to prevent the heat from over-heating the mechanical parts (servo-motor, bearing, power transmission). For comparison, an additional experiment was conducted without the rotation to clarify the effects of the rotation operation. The waiting time at 350 °C was 50 min in this experiment.

3. Results and discussion

This study was mainly focused on the conceptual separation experiment of the electrolytic reduction products, composed of the metal products (mainly, pelletized form) and residual $LiCl$ (containing Li_2O), because suppressing the re-oxidation behavior is an important issue [8]. The dimension of the Al_2O_3 pellets is set comparable to that of the simulated SNF pellets (diameter: 6.2 mm, length: 7.0 mm), which were developed as feed materials for the engineering-scale electrolytic reduction system [14]. Since the macroscopic structural change of the feed materials before and after the electrolytic reduction is not that remarkable [15], it is thought that use of these Al_2O_3 pellets can simulate the salt separation behavior of the electrolytic reduction products, at least in bulk dimension (pellet-to-pellet and pellet-to-basket). The residual salt removal in the bulk dimension is meaningful for the treatment of the electrolytic reduction products because the most of the residual $LiCl$ is expected to exist in this area. For instance, assuming that the residual salt amount is 20 wt% to the electrolytic products and the porosity of the reduced pellets (metallic U) is 30%, approximately 87% of the residual salt is located in the bulk area and other are inside the pores of the pellets.

Fig. 3 shows the Al_2O_3 pellets and the Al_2O_3-loading container before and after pouring of the $LiNO_3$ salt. The loading amount of Al_2O_3 was approximately 254 g (Table 1), which is equivalent to 1228 g of metallic U estimated through a simple comparison of density of both materials (3.95 g cm^{-3} for Al_2O_3, 19.1 g cm^{-3} for
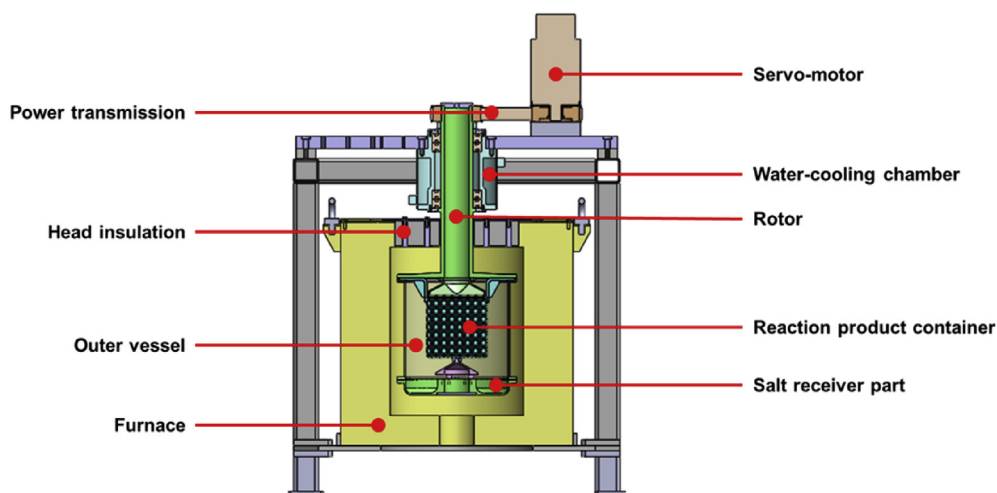

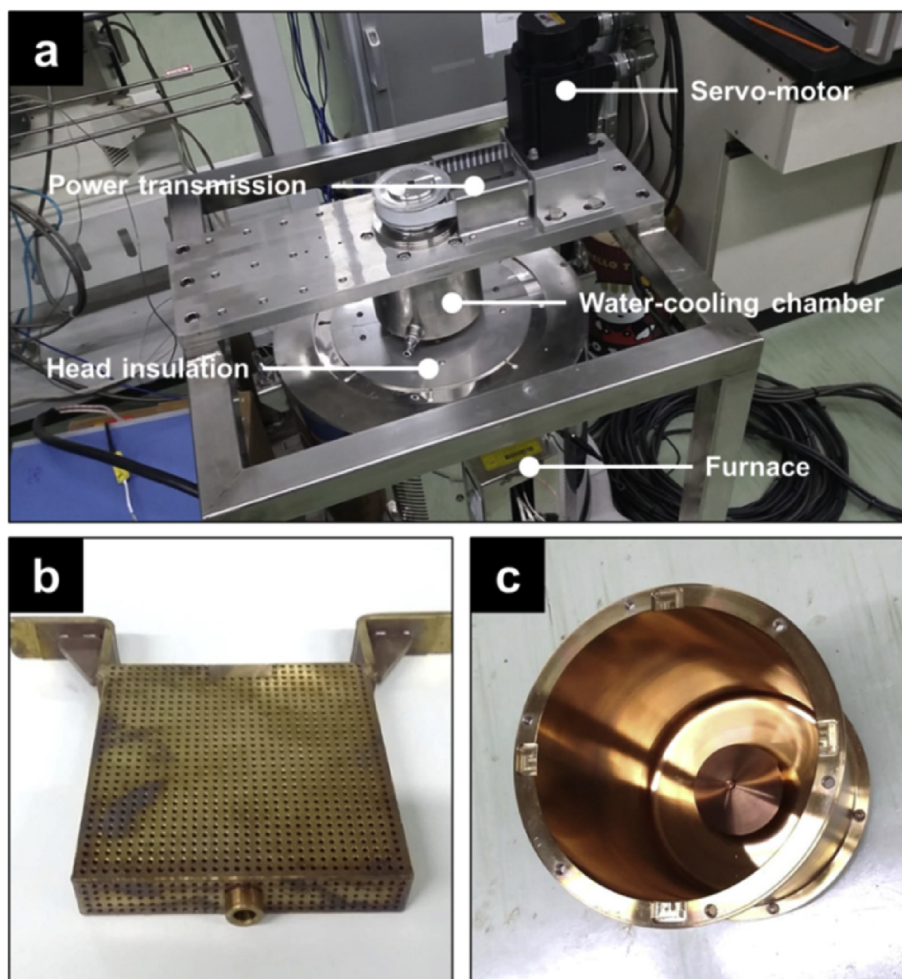Fig. 1. Schematic illustration of the residual salt separation equipment.

Fig. 2. Photographs of the residual salt separation equipment: (a) assembled structure, (b) reaction product container, and (c) outer vessel.
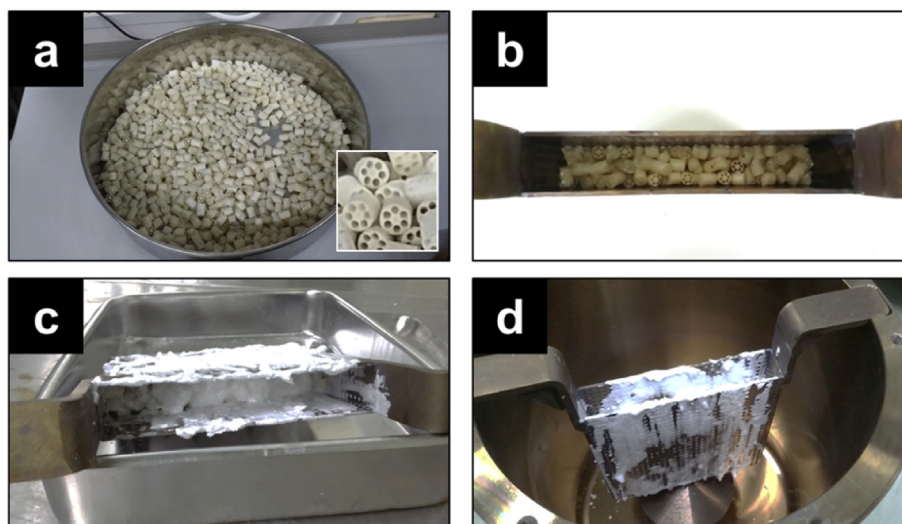

Fig. 3. Photographs of sample preparation procedure: (a) Al_2O_3 pellets, (b) Al_2O_3-loading container, (c) $LiNO_3$-poured container, and (d) $LiNO_3$-poured container placed on outer vessel.

metallic U). This scale is consistent to that of the pilot-scale electrolytic reducer under development [16].

After the rotation at 350 °C, the $LiNO_3$ salt was successfully removed from the container and it was collected at the bottom of the outer vessel, as shown in Fig. 4a and b. The Al_2O_3 pellets were easily recovered by flipping the container upside down. Only a few

Table 1
Summary of residual salt separation experiment with rotation.

Before experiment	Initial Al₂O₃ loading	253.97 g
	Initial LiNO₃ loading	208.28 g
After experiment	Recovered Al₂O₃	254.77 g
	Separated LiNO₃ from container	206.99 g
	Residual LiNO₃ inside Al₂O₃ pellets	0.80 g
	Residual LiNO₃ inside container	0.49 g
	Recovered LiNO₃ inside outer vessel	106.94 g
	LiNO₃ loss	100.05 g

pellets and a negligible amount of $LiNO_3$ remained inside the container, as shown in Fig. 4c. The remaining pellets inside the container were simply extracted by a small mechanical impact. Fig. 4d shows a magnified image of the recovered Al_2O_3 pellet. The residual $LiNO_3$ was hardly seen even inside the holes, which indicates that this simple technique is viable for the residual salt separation. Table 1 summarizes the experimental results. The residual amount of $LiNO_3$ inside the Al_2O_3 pellets and the container was calculated by measuring the weight before and after rinsing them with water. The salt separation efficiency (defined by ratio of separated $LiNO_3$ from the container to the initial $LiNO_3$ loading) from the container is approximately 99.4%, demonstrating the superiority of this technique. Only 0.4% and 0.2% of $LiNO_3$ remained in the Al_2O_3 pellets and the container, respectively. However, only half of the separated $LiNO_3$ was recovered at the bottom of the outer vessel. It is thought that thermal decomposition of $LiNO_3$ would greatly affect the salt loss. It was reported that $LiNO_3$ can be thermally decomposed around the operation temperature evolving O_2, NO, NO_2, and N_2 gases [17,18].

It should be noted that gravitation force would be another driving force of the liquid-solid separation. To clarify the effect of the centrifugal force on the separation process, an additional experiment was conducted without rotating the container. No external force except gravity was induced during this experiment. Fig. 5a shows that most of the $LiNO_3$ on the outer wall and the top of the container was removed well. However, a significant amount of $LiNO_3$ still remained inside the container as shown in Fig. 5b. Many holes in the container wall were blocked with white-colored material, $LiNO_3$. This means that a physical interaction (e.g., surface tension) between the liquid ($LiNO_3$) and the solid (Al_2O_3 and

container wall) disturbed the liquid phase from moving down. When flipping the container, only a few Al_2O_3 pellets fell down, indicating that most of the Al_2O_3 pellets were strongly combined to the container by the frozen $LiNO_3$ salt (Fig. 5c). A strong mechanical impact with a hammer was required for the recovery of the Al_2O_3 pellets out of the container. The frozen $LiNO_3$ crystals were easily seen after the recovery of the Al_2O_3 pellets, as shown in Fig. 5d. Table 2 summarizes the results of this experiment. The separation efficiency is only 76.2%. The overall results indicate that the gravity can lead to liquid-solid separation at a certain level, but additional forces such as centrifugal force must be needed for higher efficiency (>99%).

It was shown that this simple technique is promising for a residual salt separation. For the application of this technique in large-scale pyroprocessing, there are several challenges to be further investigated, as listed below:

- High temperature operation: The melting points of LiCl (~610 °C) and LiCl-KCl (~353 °C) are higher than that of $LiNO_3$ and hence a high-temperature operation is required. Under this condition, thermal damage and deformation of the equipment should be investigated. Material stabilities against chemicals such as LiCl and LiCl-KCl also need to be examined.
- Handling the actual reaction products: This study investigated the separation behavior of the residual salts from the reaction products in the pelletized form, to simulate the liquid-solid separation of the electrolytic reduction products. It was demonstrated that this technique is feasible for the residual salt separation at least in the bulk area, where the residual salt exists dominantly. The actual electrolytic reduction products, however, have micro-porous structures in the individual pellets owing to volume reduction during the de-oxidation process [15]. It is not clear at this moment whether the centrifugal force is strong enough to get rid of the residual salts inside the micro-pores. If the residual salts inside the pores are not properly removed, two-step residual salt separation would be considered. Most of the residual salts can be separated during the centrifugal step and the remaining salts can be removed at the subsequent distillation step. This two-step approach can minimize the re-oxidation behavior of the electrolytic reduction products as most of Li_2O, causing the re-oxidation of the metal products [8],
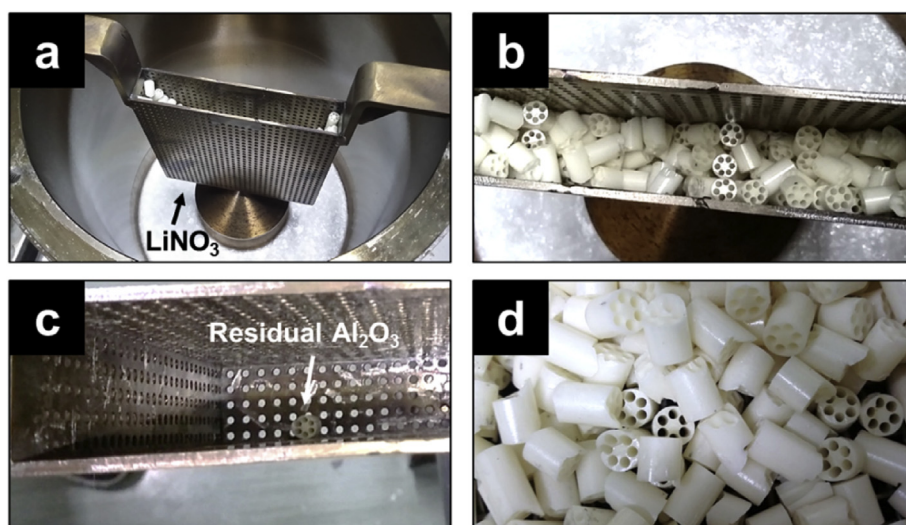

Fig. 4. Photographs of samples after residual salt separation process with rotation: (a) container and outer vessel, (b) Al_2O_3 pellets inside container, (c) inner wall of container after flipping for Al_2O_3 pellet recovery, and (d) recovered Al_2O_3 pellets.
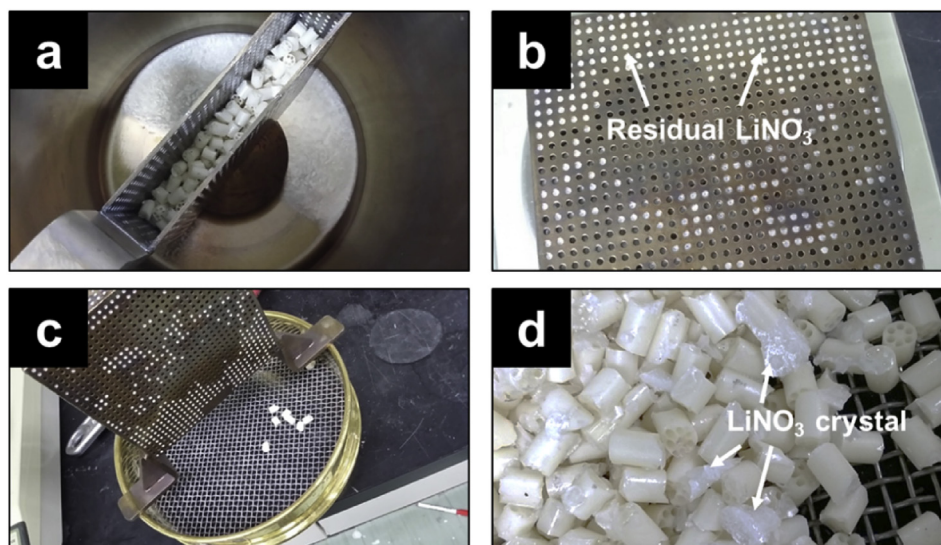
Fig. 5. Photographs of samples after residual salt separation process without rotation: (a) container and outer vessel, (b) outer wall of container, (c) flipped container, and (d) recovered Al_2O_3 pellets with $LiNO_3$ crystals.

Table 2
Summary of residual salt separation experiment without rotation.

Before experiment	Initial Al_2O_3 loading	253.96 g
	Initial $LiNO_3$ loading	242.62 g
After experiment	Separated $LiNO_3$ from container	184.94 g
	Residual $LiNO_3$ inside container	57.68 g
	Recovered $LiNO_3$ inside outer vessel	126.30 g
	$LiNO_3$ loss	58.64 g

can be removed along with the LiCl separation before the high-temperature distillation. Application of this technique to the electrorefining products would be more challenging because the electrorefining products tend to form micro-sized U dendrites with the residual salts [19—21]. The dendrites are deposited on the surface of cathode rods and thus the residual salt separator needs to be designed to handle the whole cathode assembly. Or, the dendrites can be easily recovered by using graphite and W cathodes [19,20], and then the recovered products can be loaded inside the product container for the residual salt separation. Note that the hole size of the container have to be smaller than the size of the reaction products to prevent the escape of the reaction products.

- Design reflecting remote operation procedure: A pyroprocessing facility handles high-level radioactive species, and thus remote operation without human access is required. Various remote operating tools (e.g., manipulator, gantry robot) are under consideration and the design for the process equipment needs to be fit with these tools. In addition, assembly/disassembly operation and maintenance procedures should be simplified for remote operation.

4. Conclusion

In this study, we proposed a simple centrifugal technique to separate the residual salts in the reaction products of the electrochemical unit processes in pyroprocessing. $LiNO_3$ (liquid) and Al_2O_3 (solid) were chosen as the test materials. The centrifugal force assisted the liquid-phase separation of $LiNO_3$ from the Al_2O_3-loading container to achieve a high separation efficiency of ~99.4%.

This technique can be adopted to pyroprocessing; however, further examination should be done on more realistic environments reflecting the operation temperature, test materials, and remote operation procedures.

Conflicts of interest

All authors have no conflicts of interest.

Acknowledgements

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