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Melt-crystallization monitoring system for the purification of 10 kg-scale LiCl salt waste

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ABSTRACT

Salt waste treatment process in the pyrochemical process is under development to separate or concentrate fission products from the LiCl salt waste and to minimize waste volume by recycling the purified LiCl salt into the electrochemical process. In particular, the Cs nuclide in the LiCl salt waste is difficult to separate by chemical method, so that melt-crystallization method has been employed and engineering-scale melt-crystallization system capable of 20 kg/batch treatment has been designed and installed at the PyRoprocess Inactive integrated Demonstration (PRIDE) facility. In this study, in order to evaluate scaled-up design of melt-crystallization process, the preliminary crystallization test was conducted with 10 kg LiCl salt waste having surrogate Cs, Sr, and Ba nuclides. In consideration of temperature gradients generated inside the crystallization vessel owing to the scale-up, melt-crystallization monitoring system was developed. Using the monitoring system, we could obtain purified LiCl crystal with uniform distribution of quantity on 6 crystallization plates and high separation efficiency of over 90% at various cooling conditions.

1. Introduction

Currently, Korea Atomic Energy Research Institute (KAERI) is developing pyrochemical process for the recycling of PWR spent nuclear fuels using electrochemical method to achieve the volume reduction of radioactive waste. Entire flow diagram of the pyrochemical process being developed at KAERI is depicted in Fig. 1 (Lee et al., 2011a,b, 2013a,b; Ko et al., 2014). Wastes generated from the decladding/voloxidation process, oxide reduction process, and electrorefining/electrowinning process are broadly classified into metal waste such as non-fuel bearing components (NFBC) and cladding hulls, filter waste from off-gas treatment process capturing gaseous fission products, and salt waste arising from the electrochemical processes after sufficient use of chloride salts as molten state electrolytes. Waste treatment processes are intended to minimize these wastes generated from a series of processes. In particular, salt waste treatment process is developed to separate fission products from the metal chloride salt and recycle the purified metal chloride salt into the electrochemical process again to reduce the salt waste.

KAERI's pyrochemical process generates two types of salt waste, one is LiCl salt waste having group I and II nuclides such as cesium and strontium from the oxide reduction process and the other one is LiCl-KCl eutectic salt waste having rare earth nuclide and trace amount of transuranic elements from the electrorefining and electrowinning process. Rare earth nuclides in the LiCl-KCl eutectic salt are planned to be separated by chemical method using oxidation using oxygen sparging (Cho et al., 2009), phosphorylation (Lee et al., 2013c; Eun et al., 2013a; Cho et al., 2013), and carbonation (Eun et al., 2015, 2016) at the molten state. Subsequently, the purified salt is obtained by distillation process (Eun et al., 2012, 2013b, 2014). However, in case of LiCl salt waste, the Cs nuclide is difficult to separate using chemical reaction owing to its chemical similarity to the Li element in the LiCl salt waste. Therefore, if a salt waste contains cesium nuclide, physical separation method should be applied to the separation process. Among a physical separation method, KAERI's waste treatment process has employed melt-crystallization method for the separation of cesium and strontium nuclide in the LiCl salt waste considering that the process would be operated at high temperature over melting temperature of LiCl salt. Our group revealed that the melt-crystallization method can separate cesium and strontium/barium nuclide from the LiCl salt waste with high efficiency using lab-scale melt-crystallization apparatus which is capable of 3 kg/batch treatment. The nuclide separation efficiency was found to be over 90% by optimization of crystallization growth rate and control of process monitoring system (Cho et al., 2010, 2011; Choi et al., 2013). Based on the results of the lab-scale melt-crystallization study, engineering-scale melt-crystallization system capable of 20 kg/

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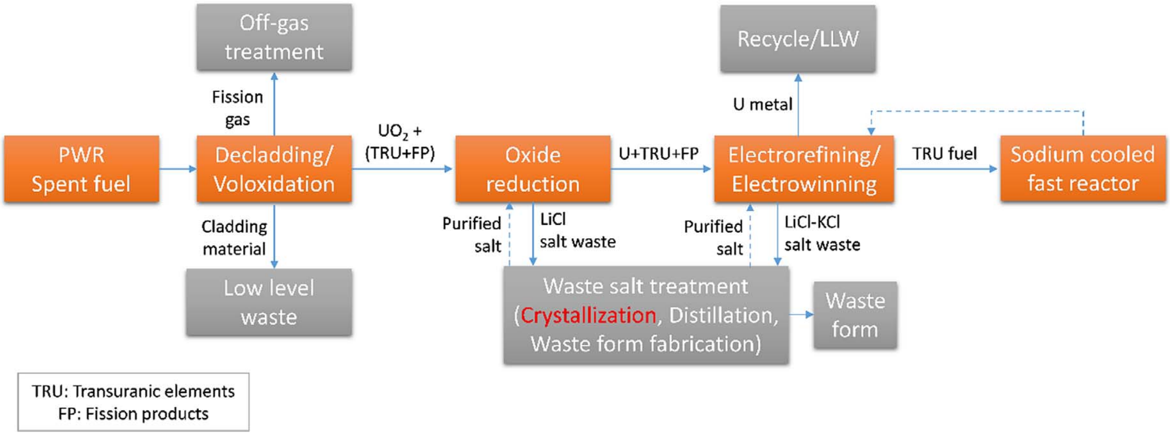

Fig. 1. Flow diagram of the pyrochemical process developed at KAERI.

batch treatment has been designed and equipped at the PyRoprocess Inactive integrated Demonstration (PRIDE) facility that is constructed for the demonstration of pyrochemical process using simulated fuel (Lee et al., 2011a,b, 2013a).

In this study, in order to evaluate scaled-up design of melt-crystallization process, the preliminary melt-crystallization test was conducted using the engineering-scale melt-crystallization system with 10 kg LiCl salt waste having surrogate group I and II nuclides under various cooling condition of crystallization plates. In consideration of temperature gradients generated inside the crystallization vessel owing to the scale-up from lab-scale (3 kg/batch) to engineering scale (20 kg/batch), melt-crystallization monitoring system was developed to prevent a formation of over-grown LiCl crystal.

2. Experimental

All chemicals were used without further purification. LiCl (anhydrous, 99% purity), CsCl (anhydrous, 99.9% purity), $SrCl_2$ (anhydrous, 99.5% purity), and $BaCl_2$ (anhydrous, 99.998% purity) were received from Alfa Aesar. Detailed crystallization tests are as follows. The initial concentration of cesium and strontium/barium nuclides are set based on the properties of LiCl waste salt generated after oxide reduction process. Surrogate 11.50 kg LiCl salt waste having 0.03 wt% CsCl (0.003 kg), 1.11 wt% $SrCl_2$ (0.128 kg) and 2.31 wt% $BaCl_2$ (0.266 kg) were charged in the crystallization vessel made of Inconel-625 material and melted at 700 °C in the crystallization furnace. Then, crystallizer having 6 crystallization plates were immersed in the molten LiCl salt waste and the LiCl crystals were recovered on the 6 crystallization plates by cooling the plates using Ar coolant gas. To determine nuclide separation efficiency of melt-crystallization system under various cooling condition, the Ar coolant gas was supplied inside the crystallization plates by Ar circulation system with a stepwise mass flow of 10 L/min to 1 min and 40 L/min to 360 min, 480 min, and 600 min for Batch-1, Batch-2, and Batch-3, respectively. Resulting cooling conditions that indicate increasing rate of Ar coolant gas were 0.083 L/min, 0.063, and 0.050 L/min for Batch-1, Batch-2, and Batch-3, respectively. Crystallization process was terminated using monitoring system measuring temperatures between crystallization plates taking into account the fact that the temperature decreases steeply when properly grown crystals hinder the thermocouple between crystallization plates. Separation efficiencies (%) were calculated by the relationship of $(C_{before} - C_{after})/C_{before} \times 100$, where C_{before} and C_{after} are nuclides concentration in the LiCl salt waste before and after crystallization process. Molten salt samples for the concentration measurement were obtained using sampling dishes and after cooled to room temperature, they are dissolved in a distilled water. Concentration of cesium nuclide was measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with a Thermo Elemental (Xseries X5) and concentrations of strontium/barium nuclides were measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with a Perkin Elmer (Optima 4300DV).

Engineering scale melt-crystallization system has been constructed in the Ar cell of the PRIDE facility, where the atmosphere of the cell is charged with Ar gas to prevent water and oxygen. As shown in Fig. 2, the system consists of a crystallization furnace, a melting furnace, a crystallizer having 6 crystallization plates, and an automated crystallizer moving device. The melting furnace is used to recover purified LiCl salt from the crystallization plates after melt-crystallization process, where the melt is obtained from the crystallization plates by heating the LiCl crystals grown on the plates after they were transferred to the melting furnace using the moving device. The crystallizer and reaction vessels are made of Inconel-625 in consideration of high operation temperature and corrosion property of molten LiCl salt. All of the operations such as furnace heating, injection of Ar coolant gas, moving of

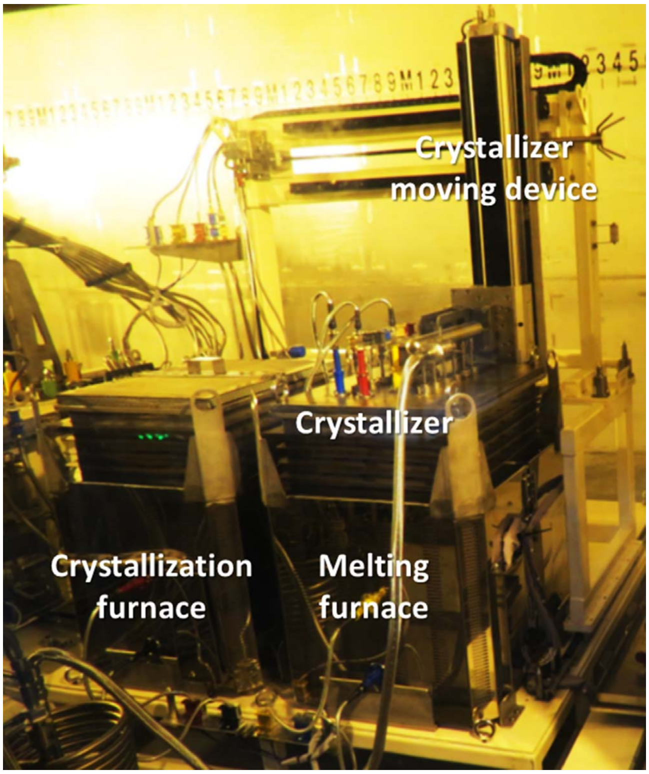

Fig. 2. Engineering scale melt-crystallization system in the PRIDE facility.