Study on a minimization of LiCl waste salt generated from pyrochemical process

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1. Introduction

Pyrochemical process which is one of promising technologies enabling the recycling of Used Nuclear Fuels (UNFs) has achieved great attention due to its proliferation-resistance, low cost, and compact equipment.[1,2] Because pyrochemical process generally uses dry molten state salts as electrolytes for the recovering of U and TRU metals as valuable energy source from UNFs, the electrolyte salts are contaminated with fission products such as alkali, alkaline-earth, rare-earth, or trace amounts of TRUs during pyrochemical process. In particular, LiCl waste salt generated from electroreduction process contains highly radioactive and heat generative I/II group fission products mainly composed of Cs^{+}, Sr^{2+}, and Ba^{2+} impurities. Therefore, the fission products within the LiCl waste salt should be separated and concentrated in small volume to reduce the volume of final waste. Furthermore, it is also beneficial to reuse purified LiCl salt in the electroreduction process as an electrolyte for economic and environmental issues.

Herein, to separate fission products from waste salt generated from pyrochemical process, the waste salt treatment process has been developed. The group I/II fission products within LiCl waste salt was separated by lab-scale layer-melt crystallization recovering purified LiCl salt on cooled crystallization plate immersed in molten LiCl salt. Based on the lab-scale study, the engineering scale LiCl purification system has been constructed in PRIDE (Pyroprocessing Inactive integrated Demonstration) facility. Preliminary test for LiCl purification has been investigated with the engineering-scale LiCl purification system.

2. Materials and methods

A scheme of layer-melt crystallization is described in Fig. 1. In lab-scale study, 3kg-LiCl having impurities of CsCl, $SrCl_2$, $BaCl_2$ were melted at 700 ^{o}C in a furnace. LiCl crystals were recovered by Layer-melt crystallization,[3,4] where the purified LiCl salt is crystallized on crystallization plate that is cooled by Ar gas with a stepwise mass flow of 12.5 L/min to 1 minute and 30 L/min to 220 minutes. The temperatures of the molten salt and crystallization plate were monitored by thermocouples. In the engineering-scale study, the crystallization test was conducted with 20kg-LiCl/batch.

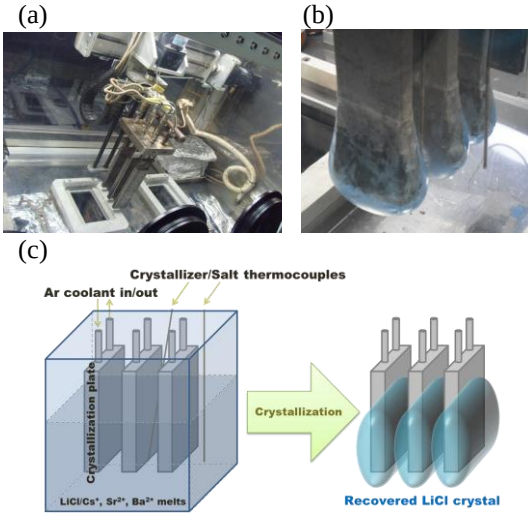

Fig. 1 (a) Lab-scale apparatus for a purification of LiCl waste salt, (b) Purified LiCl salt, and (c) Scheme of layer-melt crystallization experiment.

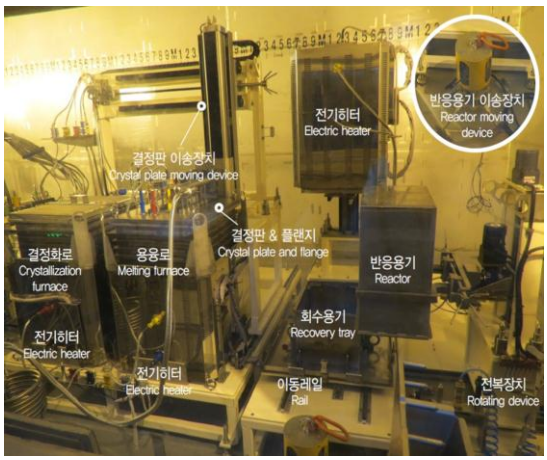

Fig. 2 Engineering-scale layer-melt crystallization equipment for the purification of LiCl waste salt.

3. Result and discussion

During the pyrochemical process, a LiCl waste salt containing alkali and alkaline-earth (Group I/II) fission products mainly composed of Cs, Sr, and Ba nuclides are generated after the electrolytic oxide reduction process. The Group I/II fission products are concentrated by a layer-melt crystallization method that uses a cold plate in a molten salt for crystallization. Purification by the layer-melt crystallization method is

efficient method because it operates even at high temperature and does not need any additional chemicals or separation columns for the separation process. Fig. 1 shows the lab-scale layer-melt crystallization system for the purification of LiCl waste salt. Under the optimized temperature and Ar flow, the LiCl crystals having around 0.03~10wt% CsCl, $SrCl_2$, and $BaCl_2$ impurities were successfully purified with the impurity separation efficiency of over 90%.

Fig. 2 shows engineering-scale layer-melt crystallization equipment for the purification of LiCl waste salt. The engineering-scale LiCl purification system capable of 20 kg-LiCl/batch has been constructed based on the result of lab-scale study that shows a high separation efficiency of over 90%. The main parts of engineering-scale LiCl waste salt purification system are described in Fig. 2. The layer crystallization system is mainly composed of crystallizer, melter, and solid detachment equipment. The LiCl waste salt is purified by following procedure. The crystallization plate is immersed in the molten LiCl salt in crystallization furnace and then LiCl crystals are formed on crystallization plate by Ar-coolant gas that is circulated by Ar circulation system. Through the crystallization process, the impurities are concentrated in a residual molten salt. The crystallizers having LiCl crystal are moved to a melting furnace, where the LiCl crystal is recovered from the crystallizers by melting. The purified LiCl salt can be obtained through a solid detachment process, where the metal crucible having LiCl solid salt is rotated and the outer wall of reactor is heated to separate LiCl salt from reactor. The purification procedures has been tested and confirmed with 20 kg pure LiCl salt. The evaluation for the efficiency of the engineering-scale LiCl waste salt purification system is now under investigation.

4. Conclusion

The LiCl waste salt generated from pyrochemical process has been successfully purified by layer-melt crystallization method with the high separation efficiency of over 90% under the existence of impurities of around 0.03~10wt% CsCl, $SrCl_2$, and $BaCl_2$ impurities. Based on the lab-scale study, the process of layer-melt crystallization has been scaled up to the engineering-scale which is capable of 20 kg-LiCl/batch. The operation procedures has been tested and confirmed by 20 kg pure LiCl salt. The evaluation for the efficiency of the engineering-scale LiCl waste salt purification system is now under investigation.

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