Characteristics of dechlorination for LiCl salt by the surface temperature-controlled reactor

In Hak Cho[a*], Hwan-Seo Park[b], Soo Na Ahn[b], Hee-Chul Eun[b], In-Tae Kim[b], Yong-Jun Cho[b],
[A]*Fine Chemical Engineering and Applied Chemistry, Chungnam National University, 99 Daehak-ro, Yuseong-Gu, Daejeon, 305-764*
[b]*Advanced Fuel Cycle Department, Korea Atomic Energy Research, Institute, 150 Deokjin-Dong, Yuseong-Gu, Daejeon, 305-353*
[*]*Corresponding author: choinhak@kaeri.re.kr*

1. Introduction

Molten salt waste is generated from a pyrochemical process to separate reusable U and TRU elements from a spent nuclear fuel. The spent lithium chloride waste is highly soluble in water and contains volatile radioactive elements such as Cs. However, these wastes are difficult to directly immobilize into durable matrix such as glass or ceramic wasteform for final disposal [1]. ANL(Argonne National Laboratory) suggested the conversion of metal chloride into a sodalite for the immobilization of a chloride waste, glass-bonded sodalite, which was fabricated at about 915 ℃ after mixing the salt-loaded zeolite and borosilicate glass powder. Although this wasteform shows high leach-resistance, the waste volume greatly increases [2]. The previous study was to treat metal chloride wastes by using SAP(SiO_2-Al_2O_3-P_2O_5) materials [3]. By using this method, the final waste volume reduced and leach-resistance was good. In this study, characteristics of dechlorination reaction of LiCl with an inorganic composite, SAP, was investigated by using a specific surface temperature-controlled reactor.

2. Methods and Results

The composite, SAP(SiO_2-Al_2O_3-P_2O_5), was prepared by a sol-gel process. Tetraethyl orthosilicate (TEOS, Aldrich, 98%) and aluminium chlorided ($AlCl_3 \cdot 6H_2O$, Junsei, 98%) and phosphoric acid (H_3PO_4, Junsei, 85%) were used as sources of Si, Al, and P, respectively. The molar ratio of Si/Al/P was 1/1/1.25. All reagents were dissolved in EtOH/H_2O and the mixture was placed in an electric oven at 50-70 ℃ after being tightly sealed. After a gelling/aging for 3 days, the transparent hydrogels were dried at 110 ℃ for 2 days and then thermally treated at 650 ℃ for 2 h. Final products (SAP) after pulverizing to about 100 µm were used as a stabilizer for treating the salt wastes. LiCl, CsCl, and $SrCl_2$ with a composition of 90, 6.8, 3.2 wt% respectively, were used to simulate the waste salt. The metal chloride/SAP mixing ratio was 1/2, and the reaction time was 30-50 h, the surface temperature of reactor was changed in 500~700℃.

Fig. 1 shows a schematic of experimental apparatus of the surface temperature-controlled reactor. Two heaters, which are the upper and downer part, are used to control the surface temperature. As shown as Fig. 1, the red bars indicate the surface reaction area. Fig. 2(a) shows the effect of surface temperature on the reaction. Slightly below melting point (580℃), the reaction rate continuously decreased while the dechlorination maintained in about 400min slightly above melting point (630℃). It could be indicated that a molten state of LiCl is more favorable in dechlorination reaction and the reactor with screw-impeller was well operated under the solid-liquid system. When the temperature was changed from 580℃ to 680℃, a rapid increase of reaction rate was observed. It showed that the dechlorination is very sensitive to temperature and the reactor had good performance on the target reaction. Fig. 2(b) shows the result of dechlorination under the stepwise increase of reaction temperature, 500~700℃. Similar to Fig. 2(a), the reaction had three distinctive reaction regions. Below melting point of LiCl, the reaction gradually decreased and it would converge to a reaction yield. However, the reaction above the melting point of LiCl lasted for hundreds of minute, and then, it was terminated. When the reaction yield approached to about 80%, the reaction rate was not greatly changed with temperature and continuously decreased as it did below the melting point of LiCl. From these results, it would note that the reaction in the screw-impeller reactor had three reaction steps, a heating of mixture, stable reaction and a tailed reaction. At a sufficient heat or temperature, the time of heating of mixture is very short and the mixture entered into the stable reaction step. But, at an insufficient heat or temperature, the mixture goes into the tailed reaction step instead of the stable reaction step. Consequently, the reaction gradually terminated at a given temperature. Therefore, for higher reaction rate of dechlorination, the reaction temperature requires above the melting point of LiCl under the condition that the mixture is sufficiently pre-heated. Fig. 3 shows the reaction products by the surface-controlled reactor. The upper XRD patterns were assigned to the unreacted LiCl where the reaction yield was about 60%. The lower XRD patterns are assigned to lithium phosphate, lithium aluminosilicate and aluminium phosphate, where the product was obtained by stepwise reaction at 500~700℃, and the unreacted LiCl was not detected. This means that the dechlorination reaction was successfully performed by the surface temperature controlled reactor.

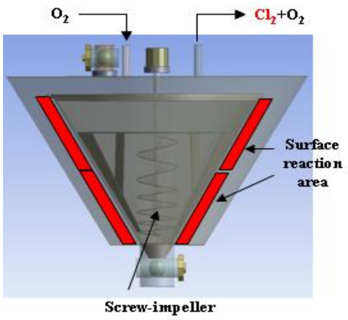
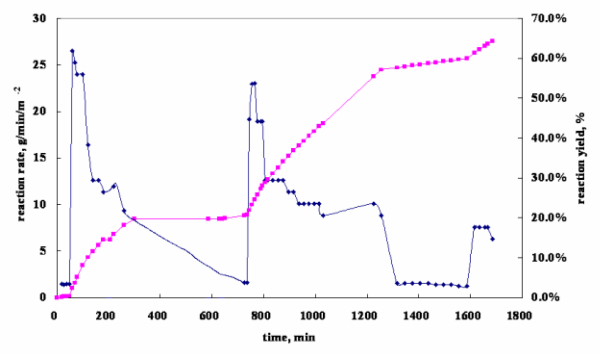


Fig. 1. A schematic of experimental apparatus of the surface temperature-controlled reactor



a) Results of dichloride for metal chloride by using SAP at 580-680 ℃

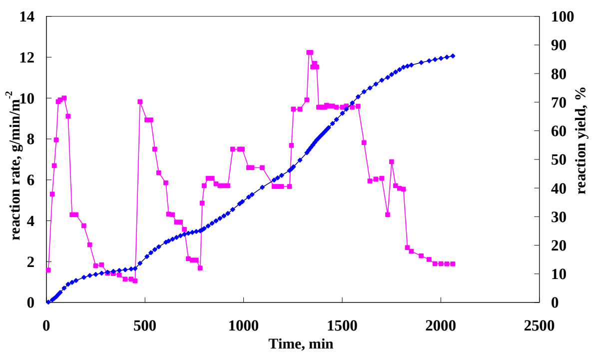


Fig. 2. b) Results of dichloride for metal chloride by using SAP at 500-700 ℃

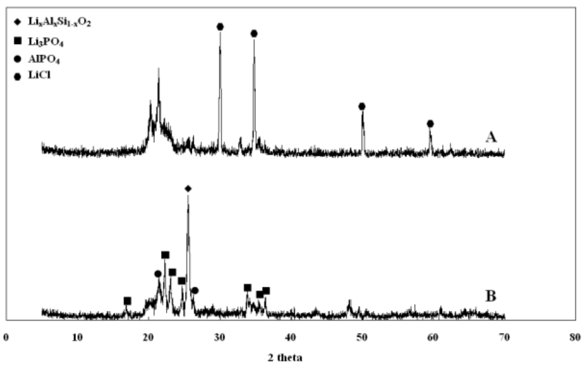


Fig. 3. XRD patterns of before reaction and after reaction with metal chloride

4. Conclusions

The surface temperature-controlled reaction was designed to avoid the agglomeration of powder in the solid-liquid system. When the inner temperature of reactor is above the melting point of salt, a mass of dough with LiCl and SAP powder would be formed and this deteriorate the reaction process and equipments. In this study, only the surface temperature was controlled and the reaction was successfully proceeded without equipment trouble or agglomeration. From these experiments, the basic design of reactor could be considered to be proper and effective.

REFERENCES

[1] I. E. Donald, B. L. Metcalef, R. N. J. Taylor, The immobilization of high level radioactive waste using ceramic and glasses, Journal of Material Science, 32, 5851, 1997.

[2] Lamgregts. M, Frank. S. M, Characterization of cesium containing glass-bonded ceramic waste forms, Microporous Meseporous Mater, 64, 1-9, 2003.

[3] H. S. Park, I. T. Kim, Y. Z. Cho, H. C. Eun, H. S. Lee, Stabilization/Solidification of radioactive salt waste by using $xSiO_2$-yAl_2O_3-zP_2O_5 (SAP) material at molten salt state, Environment Science & Technology, 42, 9357, 2008.