immobilization of LiCl-KCl waste by an inorganic composite composing of silicate and phosphate compounds

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1. Introduction

Pyrochemical process as a dry method to recover uranium and transuranic elements consists of a series of electrolytic processes, where metal chlorides are used as electrolytes and would be released as radioactive waste containing small content of fission products. These kinds of wastes are problematic wastes not to be applicable directly to a conventional solidification process due to their physicochemical properties such as volatility and low compatibility with silicate glass. For LiCl-KCl waste generated from the electrometallurgical process to treat spent metal fuel, Argonne National Laboratory has been developed "Glass-bonded sodalite" as a wasteform [1]. Different from this method immobilizing Cl, our research group adapted the dechlorination approach to remove the Cl-induced problem, where SiO_2-Al_2O_3-P_2O_5 (SAP) was used for dechlorination of LiCl-KCl. By this method, LiCl-KCl waste was stabilized and solidified to a durable wasteform. In this study, morphology of wasteform was investigated by a SAP.

2. Methods and Results

The inorganic material, SiO_2-Al_2O_3-P_2O_5(**SAP**), was prepared by a sol-gel process. Tetraethyl orthosilicate (TEOS, Aldrich, 98%), aluminum chlorides ($AlCl_3 \cdot 6H_2O$, Junsei, 98%) and phosphoric acid (H_3PO_4, Junsei, 85%) were used as precursors of Si, Al and P, respectively. The molar ratio of Si/Al/P was adjusted to 1/0.75/1. The SAP was mixed with simulated salt waste (90wt%LiCl-KCl, 5wt% CsCl and 5wt% $SrCl_2$) with a mixing ratio, SAP/salt=3, and the mixture was reacted at 350~650°C for 10~24hrs. As a chemical binder, AlFe3 glass (3.23wt%Li_2O, 6.46wt% Na_2O, 7.53wt% CaO, 7.00wt% B_2O_3, 10.77wt%Al_2O_3 and 58.15wt% SiO_2) was mixed with reaction product at 25~40wt% mixing ratios and the mixture was heat-treated to form consolidate products at 950~1150°C.

Figure 1 shows the XRD patterns of products at different temperature. At the reaction temperature, 650°C, the main crystalline phases were assigned to Li3PO4, AlPO4 and SiO2. After the reaction at 650°C, the product was heat-treated from 750°C to 1050°C. The main crystalline phase was changed and it was assigned to $KAlP_2O_7$, $K_{0.6}Li_{6.4}Al_7Si_{16}O_{46}$ and $KAlSi_3O8$ above 750°C. It should be noted that the Li or K-related compounds were survived at an elevated temperature. Fig. 2 showed the XRD patterns of the consolidated forms heat-treated at 950~1150°C, where the consolidated form were fabricated with AlFe3 glass at 25~40wt% mixing ratio. At 950°C, one of SiO2 crystalline, tridymite , was detected but they are formed to be amorphous at other temperatures. This means that the reaction products effectively reacted with a given glass or dissolved in the glass matrix.

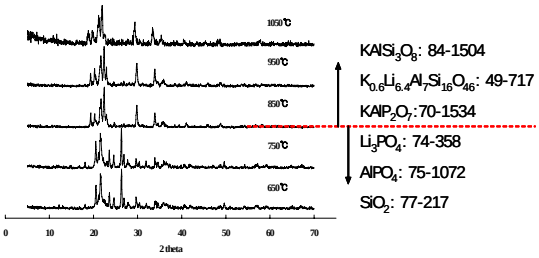
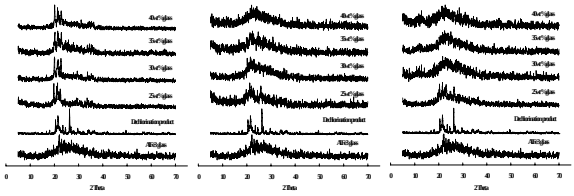


Fig. 1 XRD patterns of reaction products heat-treated at different temperature.



(a) 950°C (b) 1050°C (c) 1150°C

Fig. 2. XRD patterns of consolidated form fabricated at different temperature.

Fig 3 showed the SEM image and element mapping image of a series of consolidated form. In the hundreds μm scale, the phase in consolidated form did not have distinctive bulk separation. For higher resolution, FE-SEM images were indicated in Fig. 4. The virgin SAP was found to be formed as agglomeration of 100nm particles composing of 10nm unit particle.

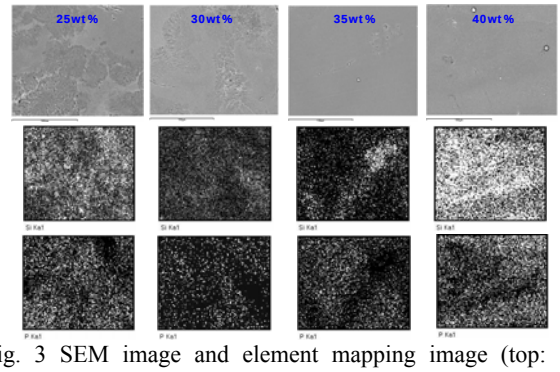


Fig. 3 SEM image and element mapping image (top: Si, bottom: P)

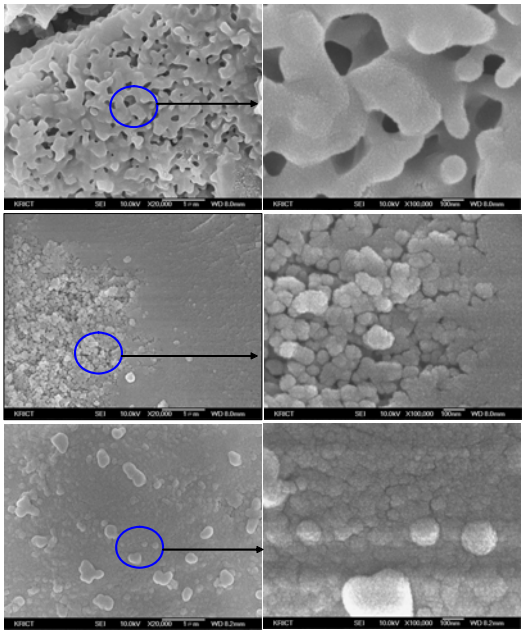


Fig. 4. FE-SEM image of virgin SAP(top), product(mid) and consolidated form(bottom) with 25wt% mixing ratio of glass.

The virgin SAP had lots of pore in the matrix but the pore disappeared after reaction. Also, the morphology of consolidated form was not great changed, compared with reaction products. There would be two possible interactions between a given glass and reaction products. Aluminosilicates in the product would be chemically interacted with a melted glass at a given temperature, where melted glass or its resultant phase would be soaked into the 100nm particles. At this moment, the Si-rich phase (melted amorphous phase) physically interacted with phosphates in the product and it would separate into very small phase with P-related compounds. From these reasons, the consolidated form became amorphous and the micro-structure was not great changed.

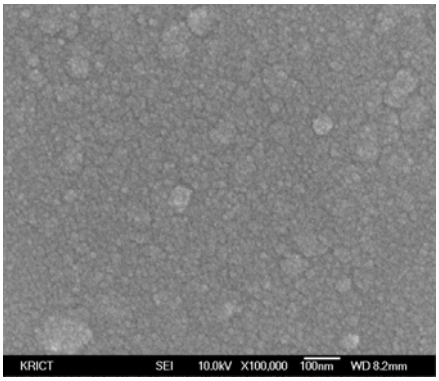


Fig. 5 FE-SEM image of consolidated form with 35wt% mixing ratio of glass

Fig. 5 indicated one of proof that the melted glass or Si-rich phase took the 100nm particles agglomerated with 10nm unit particles to pieces at higher mixing ratio of glass. From these results, the conceptual consolidation process was roughly described as follows.

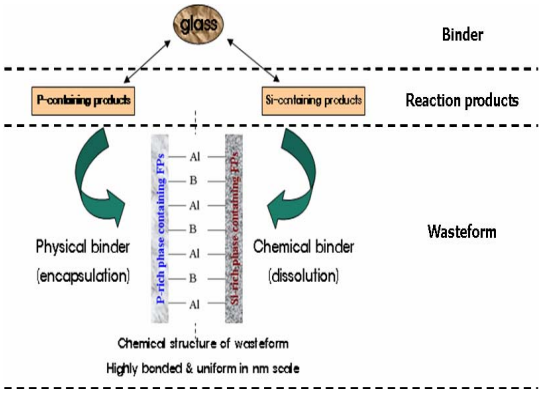


Fig. 6 Description on conceptual consolidation process

The reaction products by SAP have two kinds of compounds, Si-containing and P-containing phase. If silica-based glass is used as a chemical binder, the kind of interaction is "chemical reaction (dissolution)" for Si-containing and "physical interaction encapsulation) for P-containing phase. From these phenomena, the consolidated form has Si-rich phase and P-rich phase, where two phases are uniformly distributed in several tens of nm scale. The grain size in the matrix would depends on the Si or P conent of the consolidated form.

3. Conclusions

A stabilization/solidification of LiCl-KCl waste for disposal has been developed by using a synthetic composite. In this study, the consolidation phenomena of reaction products composing of Si- and P-related compounds during heat-treatment was described by XRD, SEM and FE-SEM measurement. Unique interactions between a chemical binder and product generated a unique consolidated form that consists of Si-rich phase and P-rich phase. Some physical and chemical properties of this wasteform are under investigation.

REFERENCES

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