A new method for the stabilisation/solidification of radioactive waste salt (LiCl, LiCl-KCl) from a pyrochemical process

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Abstract

The metal chloride waste generated from the pyrochemical process to recover uranium and TRUs has been considered a problematic waste due to high volatility and low compatibility with conventional silicate glass. Our research group has suggested the dechlorination approach for the management of this kind of waste using a synthetic composite, SAP (SiO_2-Al_2O_3-P_2O_5). In this study, the de-chlorination behaviour of chloride waste was investigated using SAPs. By using one matrix, the volatile chloride waste could be stabilised and solidified to a durable waste form. The method suggested in this study can provide a chance to minimise the waste volume for the final disposal of salt wastes from a pyrochemical process.

Introduction

A pyrochemical process to recover uranium and TRUs consists of a series of electrolytic processes using metal salts such as alkali metal chlorides. During the process, uranium and TRU elements are recovered in a metallic form and a series of fission products are left in the electrolyte. This radioactive waste is one of the problematic wastes not to directly apply to the conventional vitrification process due to high volatility and low compatibility with silicate glass.

The glass-bonded sodalite has been suggested as one of the ceramisation methods to immobilise volatile metal chlorides into sodalite structure [1-3]. As another example for a use of Cl-immobilised mineral, Metcalfe and Donald suggested a method to immobilise $CaCl_2$ waste into $Ca_5(PO_4)_3Cl$ [4]. Also, vitrification using a specific glass has been reported by Lavrinovich *et al.* [4-5]. Different from these direct immobilisation methods using sodalite or phosphate-based glass, some dechlorinations to remove the intrinsic limitation due to the Cl-induced disadvantages have been investigated by other countries. Leturcq *et al.* suggested a wet conversion using a KOH solution, where the Cl was recovered as $AlCl_3$ in an aqueous media to immobilise it into wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$); fission products were converted into hydroxides, and then vitrified by a conventional process [6]. Donze and his co-workers also studied the thermal conversion of metal chlorides into a phosphate glass using $NH_4H_2PO_4$ as a phosphate source, where NH_4Cl or HCl were generated by two reaction routes [7].

Our research group studied the chemical conversion of metal chlorides into manageable products at a high temperature using inorganic composite that consists of SiO_2, Al_2O_3, and P_2O_5. This study presents the dechlorination behaviour of LiCl and LiCl-KCl salt and the characteristics of the unique waste forms. This method can provide some information on the approach to the immobilisation of waste salt.

Experiment

The inorganic composite for de-chlorination was synthesised by a conventional 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 sources of Si, Al and P, respectively. All reagents were dissolved in $EtOH/H_2O$ and the mixture was placed in an electric oven at 55~70^{0}C after being tightly sealed. After gelling/aging for 3 days, the transparent hydrogels were dried at 110^{0}C for 2 days and then thermally treated at 600^{0}C for 2 hrs. The prepared inorganic composite was used as a stabiliser for waste salt. For the enhancement of reactivity or consolidation, $FeCl_3 \cdot 6H_2O$ or H_3BO_3 as a source of Fe_2O_3 or B_2O_3 was added to the SiO_2-Al_2O_3-P_2O_5 (SAP) composite during the synthetic procedure. For target wastes, chemical reagents of LiCl, CsCl and $SrCl_2$ (99% purity, Junsei, Japan) were used as surrogates of the radioactive molten salt waste in this study; a simulated LiCl waste composed of 90 wt% LiCl, 6.8wt % CsCl and 3.2 wt% $SrCl_2$, and a simulated LiCl-KCl waste, 40.5 wt% LiCl, 49.5 wt% KCl, 5 wt% CsCl and 5 wt% $SrCl_2$. The salt powder was thoroughly mixed using mortar in an argon atmosphere, and then it was dried at 300^{0}C in an electric oven for the removal of residual moisture of salt. This dried salt was used in a series of experiments. The experiments were performed using an electric furnace. For dechlorination reaction, the oxygen glass with a flow rate, ~5L/min, was injected into the furnace, where the alumina crucible was used to easily detach reaction products. The consolidation tests were conducted in an inert atmosphere using a graphite mold or crucible.

Results and discussion

Figure 1: XRD patterns of a series of reaction products with different salt system at 650°C

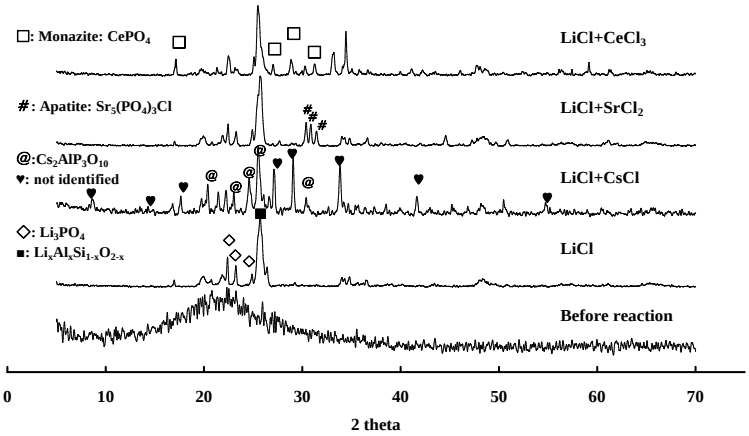


Figure 1 indicates the XRD patterns of the reaction products for each metal chloride, LiCl, CsCl, $SrCl_2$ and $CeCl_3$. The reaction ratio was set to LiCl/MCl=4 on a mol base and Salt/SAP=0.7 on a weight base. The reaction products are metal-aluminosilicate, metal-aluminophosphate and metal phosphate as expected in Figure 1. These reactions are simply expressed as follows:

- $LiCl+SAP \rightarrow Li_3PO_4 + Li_xAl_xSi_{1-x}O_{2-x} + Cl_2$;
- $LiCl+CsCl +SAP \rightarrow Li_3PO_4+Cs_2AlP_3O_{10}+$ (Li, Cs)-alumniosilicate$+Cl_2$;
- $LiCl+SrCl_2+SAP \rightarrow Li_3PO_4+Li_xAl_xSi_{1-x}O_{2-x} + Sr_5(PO_4)_3Cl+Cl_2$;
- $LiCl+CeCl_3 +SAP \rightarrow Li_3PO_4+Li_xAl_xSi_{1-x}O_{2-x} + CePO_4+Cl_2$, under the oxidative condition.

Figure 2: XRD patterns of reaction products for LiCl-KCl waste salt at different temperatures

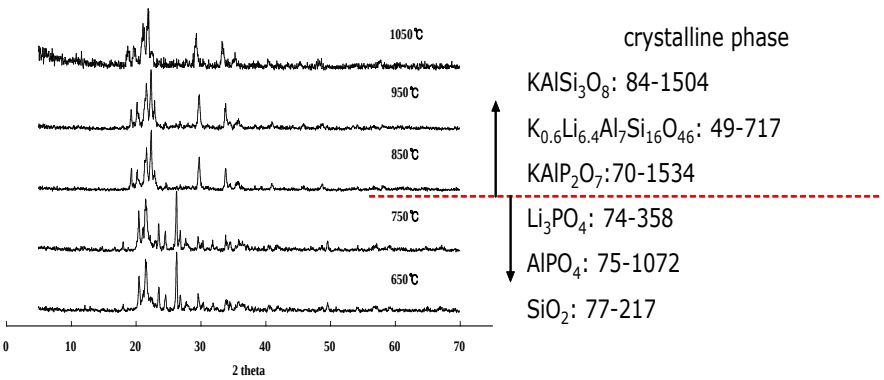
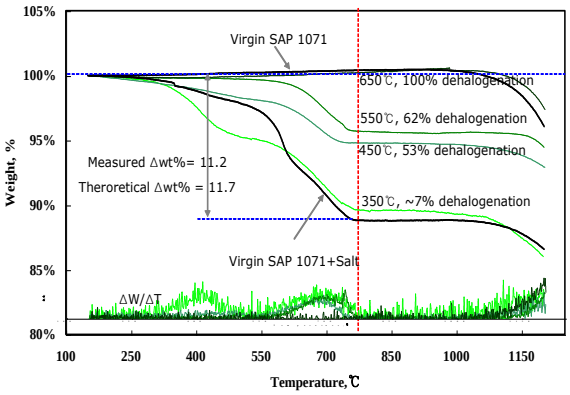


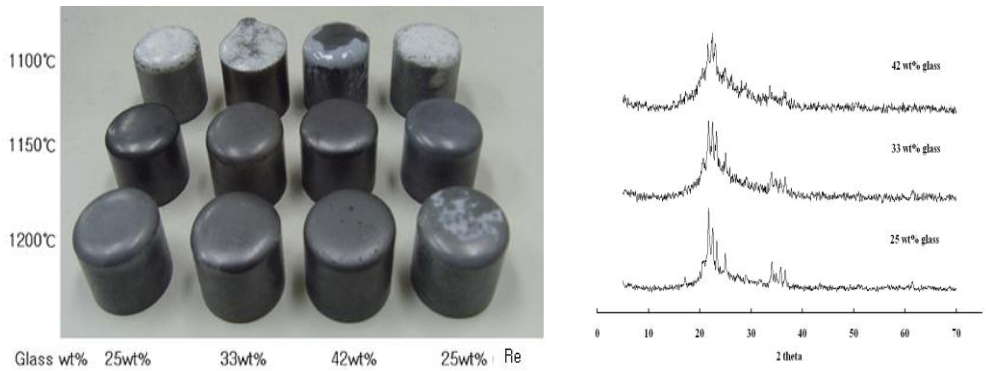
Figure 2 shows the XRD patterns of the reaction product with temperatures under a condition of SAP/LiCl-KCl = 3 in weight. Below 750°C, the main crystalline phases Li_3PO_4, $AlPO_4$ and SiO_2 but the crystalline phase was changed to metal aluminosilicates and metal alumino-phosphates. This result indicated that potassium also reacted with SAP to produce K-related compounds as lithium chloride did. It is well known, such reaction products are thermally stable and relatively less soluble in water. As these products have low volatility, they can be treated at high temperatures.

Figure 3: TGA curves of reaction product obtained at different temperatures for LiCl-KCl



Considering the oxidation of metal halide by dechlorination, 1 gram of simulated waste salt was changed to about 0.53 gram of product after reaction (4g mixture=3g SAP + 1 g salt, 3.53 g product). Therefore, the theoretical weight loss is about 11.7%. As shown in Figure 3, the weight loss of the mixture before the reaction was about 11.2%. It is noted that the weight change rate with temperatures (ΔW/ΔT) indicated two peaks at about 400 and 700^{0}C and they could be defined as reaction temperatures. From the XRD analysis, the residual peak of metal chloride was assigned to KCl. Considering the melting point of simulated salt (~360^{0}C), the weight loss below 550^{0}C would be attributed to the oxidation of mainly LiCl. As LiCl disappeared in LiCl-KCl salt, the melting point of salt increases and the reaction range would move to higher temperatures.

Figure 4: Photograph and XRD patterns of solidified products prepared by different mixing ratios of glass

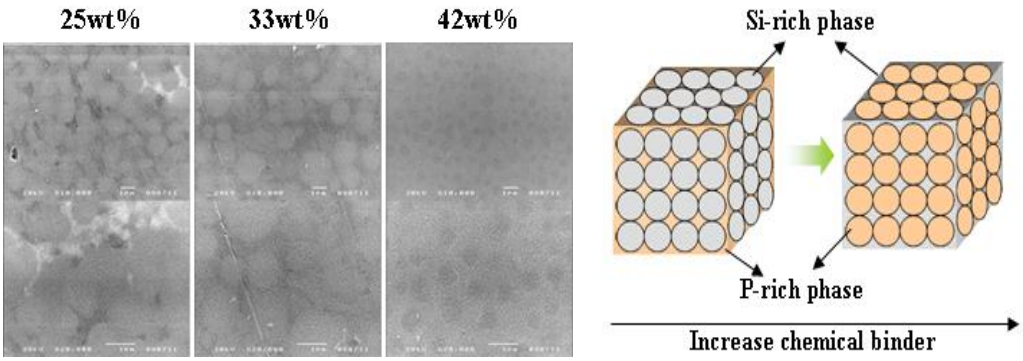


(a) Photograph of solidified products

(b) XRD patterns of each solidified product

Figure 4 shows the photograph and XRD patterns of solidified products prepared by mixing at different ratios of glass at different temperatures. Using a borosilicate glass, a series of monolithic waste form was successfully fabricated; the density was about 2.4 g/cm^3 and there was no bulk separation. In the waste forms, the residual crystalline phases were SiO_2 and Li_3PO_4 but the peaks were not great.

Figure 5: Morphology of waste forms with different mixing ratios of glass



(a) SEM image (b) Conceptual morphology of wasteform

To the naked eye, the waste form has high uniformity and is very densified; no bubble or bulk separations. However, in µm scale, there was phase separation, as shown in Figure 5(a). The waste form has domain-matrix structure, where the domain or matrix component depends on the glass wt%. If the reaction product is spherical and closed packed, the void fraction or the required volume of glass as binder would be about 33~34%. For this reason, we changed the glass wt% from 25 to 42 wt%. From the elemental analysis of each phase, it could be found that, below 33 wt% of glass, the component of the domain consists mainly of silicon while that of the matrix is mainly phosphorous; the waste form consists of a Si-rich phase and a P-rich phase. This trend was changed by increasing the glass wt%. Above 33 wt% of glass, the waste form has a P-rich domain-Si-rich matrix. As shown in Figure 5, the domain size was about 1~2 µm and the component of domain depends on the glass wt%. Also, the domain consists of a sub-domain with 20~30 nm size, where the domain-matrix structure is maintained. This unique morphology would affect chemical durability.

Figure 6: Micro-structure of virgin SAP, reacted SAP and consolidated form by FE-SEM

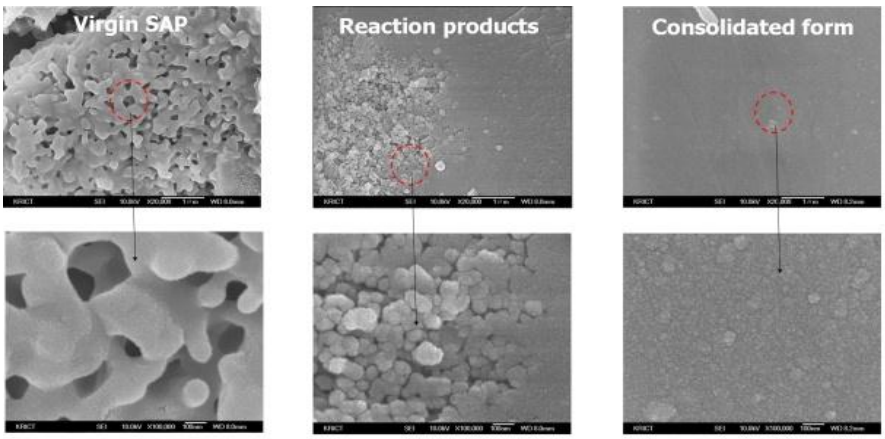


Figure 6 shows the microstructure of virgin SAP, products and the consolidated form in 100 nm scale. Virgin SAP consists of agglomerates of about 10 nm particles and it has about the same size of pore. After reaction, the pore disappeared but the grain with 100 nm size maintained. The materials after reaction were more densified. After consolidation, some of 100 nm particles were seen dimly. It should be noted that the unit grain of waste form is about 10 nm grain or particles. The products were really well-interacted with a given glass.

Figure 7: Normalised mass loss (g/m²) range of each element in the waste form fabricated by SAP for LiCl-KCl salt (tested by PCT-A method)

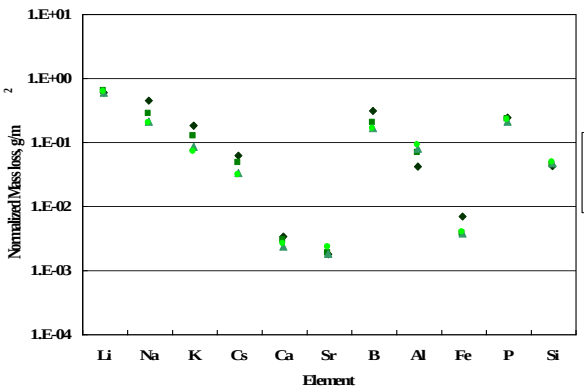


Figure 7 presents the normalised mass loss (g/m²) for 12 samples by PCT-A method, where the mass loss decreased with the processing temperature but there was little difference with the mixing ratio or glass composition. From these leaching tests, the mass loss range of each element could be obtained; 10^{-1}~10^{-2}g/m² for alkali metal, about 10^{-3}g/m² for alkali earth metal and 10^{-1}~10^{-2}g/m² for main component of waste form. It should be noted that for Cs and Sr, the mass loss was about 10^{-3}g/m². As shown in Table 1, some physical properties of waste forms are similar to other radioactive borosilicate glassy waste forms.

Table 1: Some physical properties of waste form

Physical properity	Measured value
Density (ρ)	2.35~2.4 g/cm³
Thermal Conductivity (k)	1.1~1.4 W/mK
Thermal Capacity (Cp)	0.96~1.07 J/gK
Glass Transition Temperature (Tg)	753~800 K (480~527°C)
Thermal expansion coefficient (TEC)	~3.0E-6 K^{-1}
Micro-hardness	486 ± 14.9 Hv (4.76 Gpa± 0.15)

Conclusion

This study presents a new approach for the immobilisation of radioactive LiCl or LiCl-KCl waste salt and describes the dechlorination behaviour, the morphology of waste form and chemical durability by PCT-A method. Using an inorganic composite, SAP (SiO_2-Al_2O_3-P_2O_5), the volatile metal chloride waste was stabilised and successfully solidified to a monolithic waste form composed of silicate and phosphate compounds. In conclusion, this method can provide a chance to reduce the final volume for disposal and to maintain the total amount of Cl used in a pyrochemical process.

References

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