Dechlorination of LiCl-KCl waste by using an inorganic composite (SAP 1071) and fabrication of wasteforms

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1. Introduction

Pyrochemical process to recover U and TRU indispensably generates radioactive waste salt which contains a series of fission products left in the electrolyte during the electrolytic process of spent nuclear fuel. The waste are consist of mainly metal chlorides and it is not applicable to a conventional solidification process due to its physicochemical properties such as its volatility and low comparability with silicate glass [1]. In this study, by using an inorganic composite, SAP 1071, stabilization/solidification of waste salt was investigated.

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, a series of glass with different compositions (Table 1) was used to consolidate the reaction products.

Table 1. The glass composition used in this study

	Al-Fe	Al-Fe1	Al-Fe2	Al-Fe3	Al-Fe4
Al_2O_3	11.54	9.95	10.36	10.77	9.03
B_2O_3	5.77	6.47	6.73	7.00	11.74
CaO	15.38	10.95	9.32	7.53	2.71
Fe_2O_3	11.54	9.95	8.33	6.82	9.03
Li_2O		2.99	3.11	3.23	2.71
Na_2O	5.77	5.97	6.22	6.46	6.05
SiO_2	50.00	53.73	55.94	58.18	58.72
Softening Point, ℃	697	661.98	667.76	673.5	682.6
Working Point, ℃	946	902.70	917.17	931.9	940.4
Melting Point, ℃	1,269	1207.69	1231.01	1,254.4	1,236.0

Figure 1 shows the results of thermo gravimetric analysis of each product at different temperature for 10hrs. After dechlorination between LiCl-KCl waste and SAP 1071, the residual weight is theoretically about 88.3wt%. The measured is about 88.8wt%. As the increase of the reaction temperature, the dechlorination rate increased from about 7% at 350°C to 100% at 650°C. As shown in the figure 1, there was two distinctive weight loss steps, 400°C range and 700°C range.

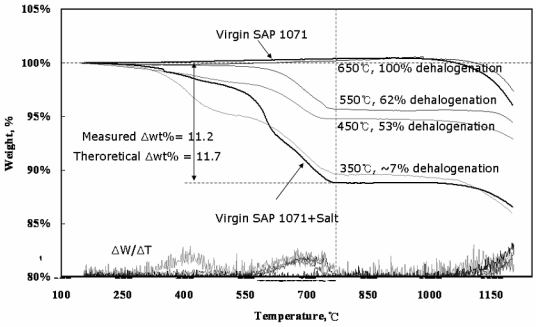


Figure 1. TGA curves of each sample after dechlorination reaction at different temperature.

Figure 2 indicated the reaction rate of mixture under sequential increase of reaction temperature. At this experiment, the reaction time at each step was 10 hrs. The reaction rate is very similar to TGA analysis results.

Up to 550°C, the reaction rate was about 65t% at maximum and the reaction was complete at 650°C. At low reaction temperature, LiCl in LiCl-KCl would be preferentially reacted and it would make the melting temperature of the unreacted waste salt increased. This is why the reaction rate is about 65%. Below the reaction temperature, 650°C, the reaction rate approaches the maximum value. This trend also could be confirmed by the TGA analysis, two weight loss steps.

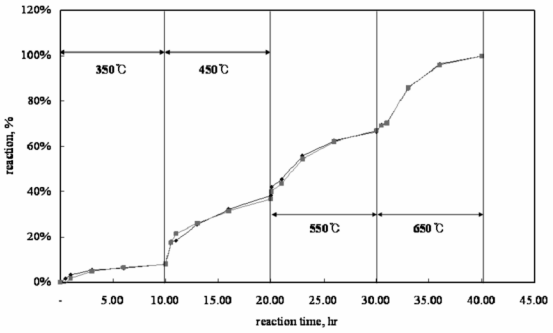


Figure 2. Dechlorination rate of mixture at sequential increase of reaction temperature.

The reaction products could be consolidated with different mixing ratio of a series of glasses at 950~1150°C. Figure 3 shows the consolidated products at 1050°C for 4hrs. As shown in the photographs, all the samples did not show the bulk phase separation and they appeared like very uniform. However, the inner phase has some porosity that makes the density and rigidity of wasteform decreased. Under given conditions, AlFe3 glass showed relatively higher densified feature (lower porosity) than other products. It is noted that increase of consolidation temperature above 1050°C would not provide a great change in the monolithic phase.

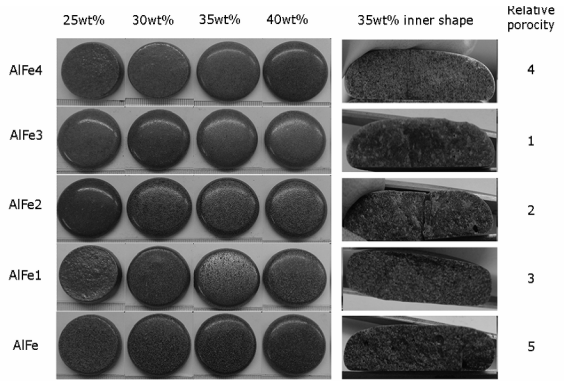


Figure 3. Photographs of consolidated products with different glasses at 1050°C for 4hrs

Table 2 shows the weight change fraction before and after consolidation. As shown in the table, the change were not depends on the temperature, glass content and glass composition. Considering the error range in measuring the weight, the weight change was not great and there would be little possibility of vaporization of volatile compounds.

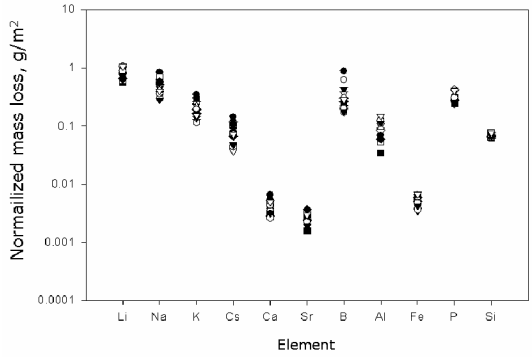
Table 2 indicated the weight change before and after consolidation step at different temperatures.

Temp'	Glass wt%	AlFe	AlFe1	AlFe2	AlFe3	AlFe4
950℃	25wt%	0.002	0.002	0.005	0.004	-
	30wt%	0.001	0.001	0.001	0.003	-
	35wt%	0.005	0.000	0.002	0.001	-
	40wt%	0.001	0.001	0.003	0.002	-
1050℃	25wt%	-	0.007	0.002	0.003	-
	30wt%	-	0.005	0.002	0.005	-
	35wt%	-	0.002	0.000	0.006	-
	40wt%	-	0.002	0.001	0.003	-
1150℃	25wt%	-	0.001	-	0.007	0.004
	30wt%	0.004	0.001	0.005	0.002	0.002
	35wt%	0.003	0.000	0.003	0.004	0.003
	40wt%	0.002	0.006	0.001	0.001	0.002

Figure 4 shows the results of PCT-A test for 16samples prepared at 1050°C. The normalized mass loss was about 10^{-1}~10^{-2} g/m^2 for alkali metals, 10^{-3} g/m^2 for alkali earth metals and 10^{-1}~10^{-3} g/m^2 for main element of consolidated products. Leach-resistance of main radionuclides, Cs and Sr, was very reasonable and comparable other radioactive wasteform.

3. Conclusions

In this study, a stabilization/solidification of LiCl-KCl waste for disposal was described by using a synthetic composite. Dechlorination method can provide the chance to control the volatile radionuclides or compounds during the fabrication of wasteform. In order to prepare a monolithic wasteform without porosity, compatibility test between the glass composition and reaction products at a consolidation temperature should be studied. Morphology and physiochemical properties of wasteform for LiCl-KCl waste are being investigated



REFERENCES

[1] B.L. Metcalfe, I.W. Donald, Candidate Wasteform for the Immobilization of Chlorides-Containing Radioactive Waste, Journal of Non-Crystalline Solids, Vol.348, p.225, 2004.