

Dechlorination Reaction of Metal Chloride Wastes with Inorganic Composite ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$) at 650 °C

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1. Introduction

Pyrochemical process to recover uranium and transuranic elements from the spent nuclear fuel indispensably generates radioactive metal chlorides waste containing fission products. These wastes are difficult to solidify and stabilize by conventional method due to their volatility and low comparability with silicate glass. Our research group is under development of dechlorination method to remove Cl-induced problems. For dechlorination of metal chloride waste, an inorganic composite, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ (SAP), has been investigated as dechlorination agent. The composite reacts with metal chloride to produce aluminosilicates, aluminophosphate and orthophosphate. The products are thermally stable up to 1200°C and compatible with silicate glass. In this study, modified SAP containing Fe_2O_3 as another component was investigated to enhance the dechlorination reaction and characterize the reaction behavior of LiCl.

2. Methods and Results

The composites, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ (Modified SAP, M-SAP), were prepared by a sol-gel process. Tetraethyl orthosilicate (TEOS), aluminum chlorides (AlCl_3), phosphoric acid (H_3PO_4) and FeCl_3 were used as sources of Si, Al, P and Fe, respectively. The molar ratio of Si/Al/P was set to 1/1/1.25 (SAP 125) as a reference composite. For the modified SAPs, the molar ratio of Al in the reference composite was replaced with the Fe from 0.05 to 0.2. All reagents were dissolved in EtOH/ H_2O , and the mixture was placed in a convection oven at 50-70°C after being tightly sealed. After a gelling/aging for 3 days, the transparent hydrogels were dried at 110°C for 2 days and then thermally treated at 650°C for 3 h. A simulated waste with 90wt% LiCl, 6.8wt% CsCl and 3.2wt% SrCl_2 was prepared by mixing and grinding each reagent.

The SAP125 and M-SAPs were thoroughly mixed with a simulated waste in a glove box. The mixture was reacted at 650°C in an oxidative atmosphere. The reaction yield was calculated with the weight change data with time. The obtained products were consolidated with some borosilicate glass and phosphate glass as chemical binder. The consolidation experiments were performed at 1050°C for 4hrs. The chemical durability of final products was evaluated by the PCT-A method. The virgin SAPs and final products were

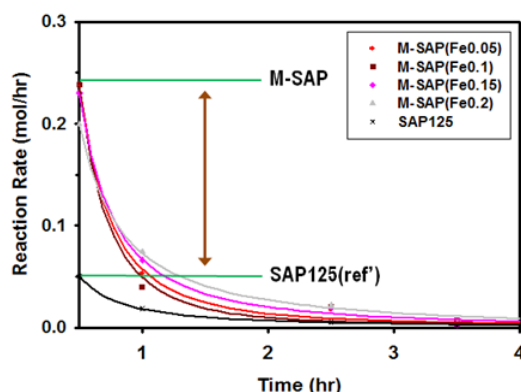


Fig.1 The reaction rate of dechlorination reaction with SAP/Salt ratio, 1.5 in weight at 650 °C.

analyzed by XRD, TGA, FT-IR and MAS-NMR measurement. Fig. 1 showed the reaction rate of a series of SAPs with time. The initial reaction rate for SAP 125 was about 0.05mol/hr while M-SAPs had about 0.2~0.25mol/hr. Also, Under the same condition, the reaction rate of a M-SAP(Fe0.1) had relatively faster than other M-SAPs but the trend on the rate with Fe content was not detected.

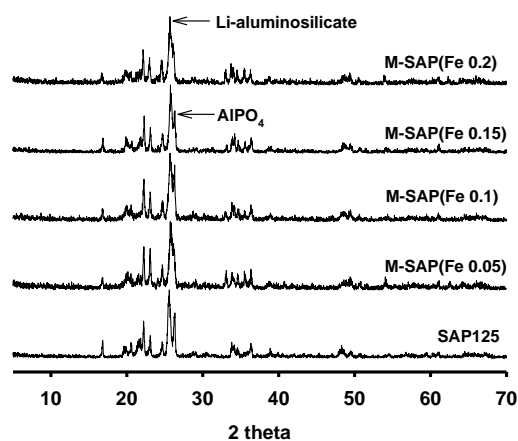


Fig. 2 The XRD patterns of products by a series of SAPs at 650 °C for 24hrs (SAP/salt=2).

Fig. 2 showed the XRD patterns of products with Fe content in SAP. The main crystalline phases were assigned to Li_3PO_4 , Li-aluminosilicate and AlPO_4 . The peak intensity of AlPO_4 for M-SAP(Fe=0.1) was higher than those for other M-SAPs. This means that the M-SAP(Fe0.1) has a higher capacity to de-chlorinate LiCl

than other M-SAPs. For this reason, the SAP/salt ratio was changed from 2 to 1.5 in weight. Fig. 3 showed the result of TGA of products with a SAP/salt ratio, 1.5. The weight loss at about 600°C is caused by the vaporization of unreacted LiCl. SAP125 and M-SAP(Fe=0.05) had about 0.5wt% weight loss at this temperature but other M-SAPs had no weight loss.

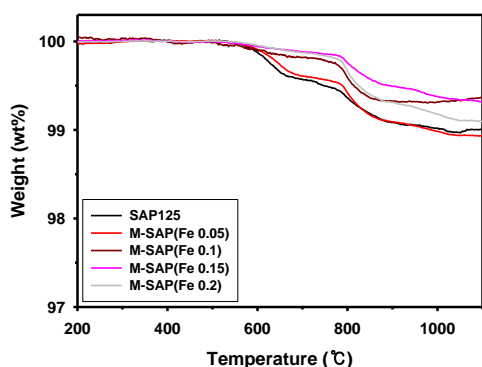
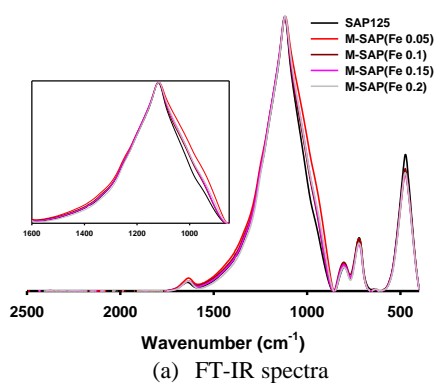
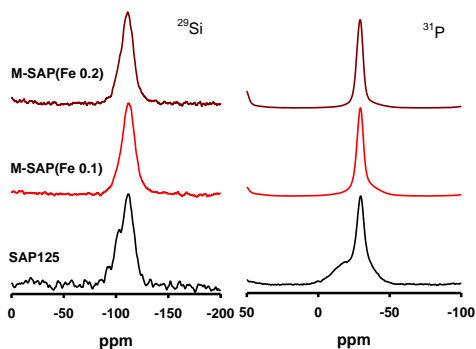


Fig. 3 Thermo gravimetric analysis of reaction products with SAP/Salt ratio = 1.5 in weight.



(a) FT-IR spectra



(b) MAS-NMR spectra (left: Si²⁹, right P³¹)
Fig. 4 Spectroscopic analysis of M-SAPs.

Fig. 4 showed the spectra of FT-IR and MAS-NMR of virgin SAPs. The XRD patterns of virgin SAPs indicated the amorphous phases, aluminosilicates and aluminophosphates, which could not be detected in XRD analysis. The FT-IR spectra indicated that some peaks in wave number were changed with Fe content. The MAS-NMR spectra also showed the change of chemical environment of Si and P with Fe content. The

spectra of Al²⁷ were not affected with Fe content. Based on the spectroscopic analysis, the addition of Fe₂O₃ increases the content of bridging oxygen in glassy phosphate of SAPs and decreases the Al number connected with Si nucleus. This phenomenon would enhance the dechlorination reaction/capacity of M-SAPs.

Fig. 4 showed the consolidated form fabricated at 1050°C for 4 hrs. The reaction products had phosphate and silicate compounds, and compatibility depends on the kind of chemical binder. As shown in Fig. 4, the bulk shape is different, depending on the type of chemical binder. SAP 125 and M-SAP with Fe=0.1~0.2 showed good shape but other products had poor shape, regardless of the type of glass.



Fig. 4 Photographs of consolidated forms prepared by using different glass.

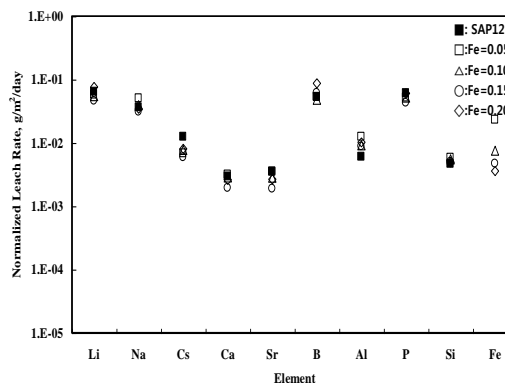


Fig. 5 Result of PCT-A test for consolidated forms

Fig. 5 indicated the result of PCT-A test for the consolidated forms with G2 glass. The leach rate of Cs and Sr was slightly lowered with Fe content in M-SAP. It was noted that the addition of Fe₂O₃ into SAP increases the leach-resistance of alkali and alkali earth elements, except Na. Also, the main unstable element P had been relatively stabilized with Fe content.

3. Conclusions

In this study, the dechlorination reaction of M-SAPs and its wasteform performance was roughly investigated. Some more information on the dechlorination reaction should be found by delicate experiments. However, the experimental results could indicate that the addition of Fe₂O₃ into the SAP is favorable in dechlorination reaction and immobilization of fission products, Cs/Sr.