

Dechlorination and Stabilization of Molten Salt Waste by Using $x\text{SiO}_2\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{P}_2\text{O}_5$ at Melting Temperature

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1. Introduction

Molten salt waste, which is generated from the pyroprocess to separate uranium and trans-uranium elements from spent nuclear fuel, has been interested to researchers in the radioactive waste management. For its final disposal, direct immobilization into a suitable host matrix or indirect solidification by other chemical routes requires the control of chlorides and its volatility since molten salt wastes mainly consist of volatile metal chlorides. Glass-bonded sodalite ($\text{Na}_6\text{M}_2\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, I-5) suggested by Argonne National Laboratory (ANL), to the present, could be a practical solution to the immobilization of this waste, where waste form can be fabricated at about 915°C , lower than the melting temperature of many borosilicate glasses ($\sim 1150^\circ\text{C}$). A wet dechlorination to oxides or a thermal conversion into borate glass was suggested to remove Cl from salt waste (6-7) and it seemed that the preference of radionuclides for the intended chemical conversions or immobilizations described above could be hardly accomplished or failed, except the phosphate precipitation method suggested by Volkovich and his co-workers (8).

Our research group suggested a novel method to treat molten salt waste, named GRSS (Gel-Route Stabilization/Solidification) using Si-P-Al system as a gel-forming system. This showed little vaporization during high temperature process and good leach-resistance on Cs and Sr.

As another method, this study suggested a method to stabilize molten salt wastes by using $x\text{SiO}_2\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{P}_2\text{O}_5$ material. GRSS method is considered as a "reaction system" to completely convert salt waste into stable product while the inorganic material used in this study is a stabilizer for salt wastes. Using this material, this study investigated the reactivity on different metal chlorides, thermal stability, leach-resistance and etc.

2. Experimental

As a stabilizer, SAP ($x\text{SiO}_2\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{P}_2\text{O}_5$) was prepared by conventional so-gel process; the raw materials are TEOS(tetraethyl orthosilicate), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and H_3PO_4 . Al and P sources were dissolved into distilled water and mixed with TEOS in ethanol. The clear solution was poured into plastic bottle and tightly sealed after stirring for 10min. Gel was formed at 55°C in 24 hr. Aging was carried out at 75°C and 90°C for 7 days. The hydrogel was heat-treated at 600°C for 2 hrs

for the dehydration and the evaporation of solvent. Si/Al/P molar ratios are 2/1/1 and 1/1/1. The prepared SAP was mixed with metal chlorides and reacted at 650, 750 and 850 for 6 hrs in atmospheric condition. Also, simulated salt wastes containing 90wt% LiCl, 6.8wt% CsCl and 3.2wt% SrCl₂ were reacted with SAP with different weight ratios of SAP/salt. The reaction products were analyzed by XRD, and TG/DTA. Also, PCT-A leaching method was carried out to evaluate the residual Cl and leach-resistance by using ICP-AES and AAS.

3. Result

Figure 1 shows the XRD patterns of products reacted with different metal chlorides and SAP. LiCl, CsCl, SrCl₂ and CeCl₃ were converted into $\text{Li}_x\text{Al}_y\text{Si}_{1-x}\text{O}_{2-x}$, Li_3PO_4 , $\text{Cs}_2\text{AlP}_3\text{O}_{10}$, $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ and CePO_4 , regardless of given Si/P/Al molar ratios. These products are well known as stable compounds. During the conversion reaction, Cl₂ gas are generated

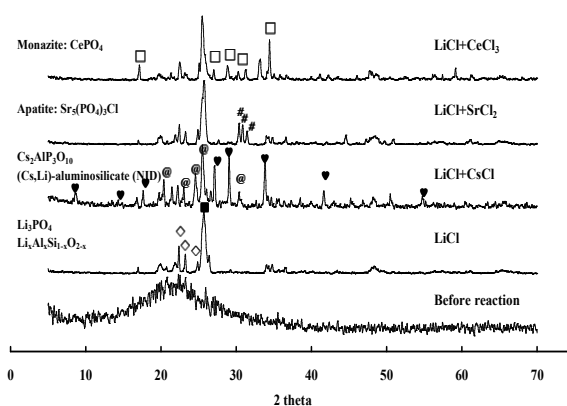
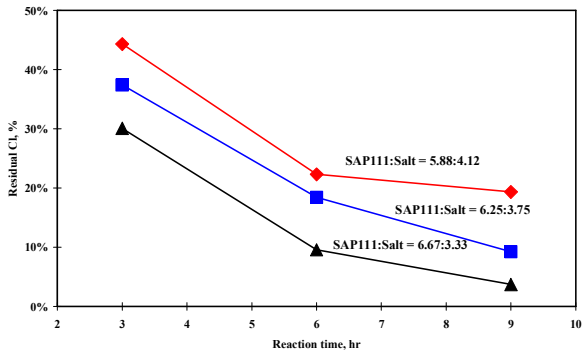


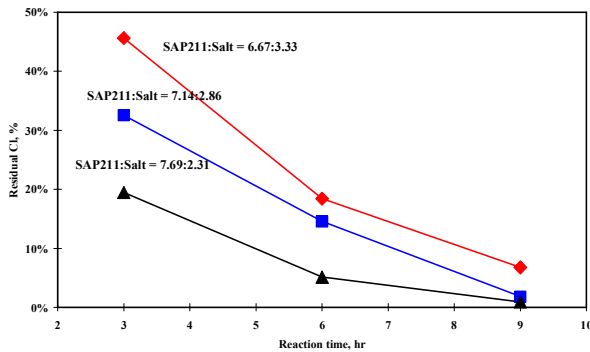
Figure 1. XRD patterns of reaction product between SAP and metal chlorides.

Figure 2 shows the residual Cl % evaluated by PCT-3day. The leached amount of Cl might be caused by residual metal chlorides or reaction products; apatite containing Cl are well known as durable material and the effect on the leached amount of Cl can be negligible. Therefore, residual Cl % can inform us the conversion rate on dechlorination. From the results, SAP with molar ratio of Si/Al/P=1/1/1 showed 80~96% conversion rate while the conversion rates of SAP with molar ratio of Si/Al/P=2/1/1 were about 93~99%. Compared with ANL method (salt/zeolite= $\sim 1/10$), this

method greatly reduce the amount of stabilizer for salt wastes (salt/SAP~1/2).



(a) Si/P/Al=1/1/1



(b) Si/P/Al=2/1/1

Figure 2. Residual Cl% with reaction time

Table 1. Leached fraction of reaction products (%)

Salt/SAP	Si/Al/P=1/1/1/			Si/Al/P=2/1/1		
	0.7	0.6	0.5	0.5	0.4	0.3
Li	2.15	2.6	2.95	1.89	2.06	2.68
Cs	1.29	0.65	0.42	0.35	0.29	0.49
Sr	0.0046	0.0033	0.0022	0.026	0.024	0.013

Table 3 shows the leached fraction evaluated by PCT-7day. At Salt/SAP=0.5, the leached fraction of Cs and Sr were about 0.42% and 0.0022, respectively.

4. Conclusion

This study suggested a new method to treat molten salt waste by using SAP ($x\text{SiO}_2\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{P}_2\text{O}_5$) material. All metal chlorides were converted into chemically durable compounds. The weight ratio of salt/SAP to treat molten salt waste in this study was about five times higher than salt/zeolite in ANL method. This method can be considered as an alternative on the stabilization of molten salt wastes

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