Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 10-11, 2007

Leaching Behavior of Solidified Products Containing Molten Salt Waste

Intae Kim, Hwanseo Park, Hwanyoung Kim and Joonhyung Kim.
Korea Atomic Energy Research Institute
nitkim@kaeri.re.kr

1. Introduction

There has been recently much interest on the immobilization of molten salt wastes generated from the pyroprocess to recover/separate uranium, transuranic or rare earth elements from nuclear spent fuel. This waste is difficult to be applied to the conventional vitrification due to the high volatility of chloride compounds and the compatibility with silicate glasses. Glass-bonded sodalite ($Na_6M_2Al_6Si_6O_{24}Cl_2$, ***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℃, lower than the melting temperature of many borosilicate glasses (~1150℃).

In previous study, our research group suggested an alternative method using gel-route pretreatment for removing Cl-induced disadvantage such as volatility, low disposal efficiency by limitation on the immobilization matrix and etc. In Si-P-Al gel-forming system, metal chlorides are converted into metal aluminosilicate, metal aluminophosphate and metal phosphate; the vaporization of Cs is quite low upto 1150℃. With this thermal stability, the gel product were solidified by mixing with a glass powder as an arbitrary choice and its leached fraction of Cs and Sr under a PCT-A test condition were 0.72% and 0.012%, respectively [6].

Although previous study showed the "stabilization" of metal chlorides via newly developed method, solidification conditions such as thermal condition, glass composition, mixing ratio of glass, waste loading and etc., were not investigated. This is related to leaching resistance that is one of major factors in the assessment of wasteform. In this study, a series of solidified products prepared at different conditions were evaluated on the leach-resistance by ISO dynamic leaching test method. Also, the result was compared with leach-resistance of glass-bonded zeolite wasteform. These results can give reliability on the wasteform prepared via GRSS method for final disposal.

2. Experimental

The material system was designed with sodium silicate (**Si**) as a gelling agent, phosphoric acid (**P**) as a catalyst/stabilizer, aluminum nitrate (**Al**) as a property promoter and H_2O as a solvent. LiCl, CsCl and $SrCl_2$ (99% purity, Merck) with a composition of 90wt%, 6.8wt% and 3.2 wt%, respectively, were used to simulate the waste salt. The gel-forming compositions were Si/P/Al=0.4/0.4/0.2 and 0.35/0.35/0.3 with different waste loadings. Each material was dissolved in deionized water at room temperature and mixed with strongly stirring for 5 min to obtain clear solution. The mixture was poured into a plastic bottle and placed into electric furnace after tightly sealed. Gelation was carried out at 70℃ for 7 days, and the products were dried at 110℃ for 2~3 days. The gel products were mixed with glass powder with a mixing ratio of 43(gel product):57(glass) by weight. The glass composition was 7.74wt% Na_2O, 1.60wt% CaO, 22.84wt% B_2O_3, 8.84wt% Al_2O_3 and 58.98wt% SiO_2. This powder mixture was heat-treated at 1100℃ for 2 hrs without pressing. Glass-bonded zeolite (**GBZ**) was prepared by a procedure given elsewhere [3].

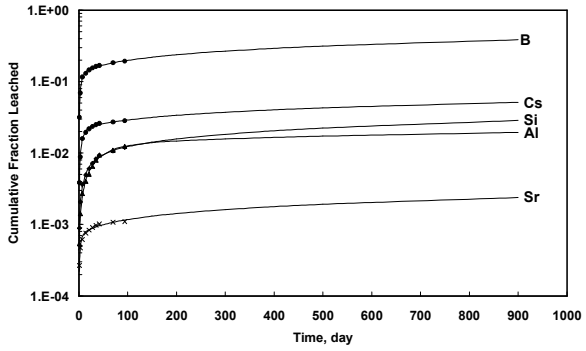
The ISO method as a leaching test was performed to 100day and CFL (Cumulative Fraction Leached) at 900day was predicted by a semi-empirical equation.

3. Result

Generally, it is well accepted that leaching of an element from a solid phase is a result made by complex mechanism combined with dissolution-precipitation, diffusion, sorption-desorption, etc. The leaching mechanism of the components from glassy waste form can be classified into wash-off, diffusion, and dissolution at the interface. The following time-dependent terms describing important rate-limiting leaching mechanisms were used to calculate the cumulative fraction leached and then to figure out the leaching behavior of materials as a function of time [7].

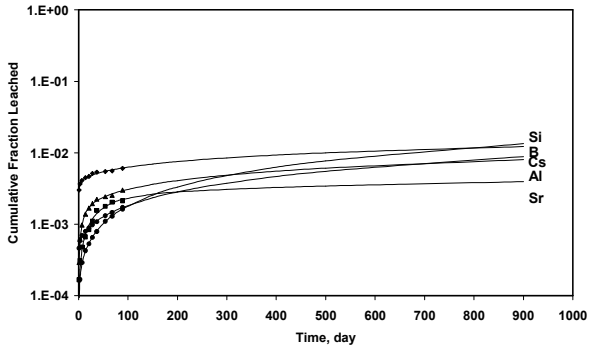
$$CFL= k_1[1-\exp(-k_2t)]+k_3t0.5+k_4t \quad (1)$$

Each term in equation (1) describes about wash-off, leaching by diffusion and matrix dissolution. The results of leaching test and predicted results are plotted in figure 1. From the results, the solidified product (**SP**) by GRSS is more leach-resistant than glass-bonded zeolite by ANL method. For Cs, CFL of GBZ was ten times higher than that of SP while those of Sr were little difference. For SP, leaching of Al, B and Sr are controlled by diffusion but Cs and Si are leached by dissolution as the test time increases. For GBZ, the dominant leaching mechanism of all components is diffusion-controlled. This is probably caused by the function of binder. Glass used in ANL method might be functioned as only physical binder but in GRSS method it acts as a chemical binder. The chemical binder can dissolve radionuclides in unstable phase into matrix.



	Al	B	Si	Sr	Cs
k1	1.07E-02	1.05E-01	4.26E-03	5.70E-04	1.79E-02
k2	2.40E-02	2.47E-01	4.63E-02	3.32E-01	1.65E-01
k3	2.91E-04	9.34E-03	8.10E-04	6.03E-05	1.12E-03
k4	1.69E-14	3.28E-12	2.63E-13	1.16E-13	7.79E-13
R2	0.9998	0.9924	0.9997	0.9998	0.9998

(a) glass-bonded zeolite wasteform



	Al	B	Si	Sr	Cs
k1	7.58E-04	3.33E-03	9.95E-05	1.87E-03	4.22E-04
k2	9.35E-02	1.65E+00	4.67E-01	2.04E-02	1.39E+04
k3	2.28E-04	2.97E-04	3.38E-05	6.94E-05	7.11E-05
k4	4.69E-07	1.70E-13	1.37E-05	3.64E-15	6.99E-06
R2	0.9965	0.9809	0.9990	0.9838	0.9968

(b) Solidified product prepared by GRSS method

Figure 1. CFL (Cumulative Fraction Leached) with time

4. Conclusion

This study investigated the leaching behavior of solidified product containing molten salt wastes and compared with glass-bonded zeolite wasteform. The predicted CFL shows that dominant leaching mechanism of Cs is dissolution-controlled. From the results, it can be concluded that GRSS method as an immobilization technology on the molten salt waste is more useful than ANL method using zeolite. More researches on chemical durability are proceeded.

REFERENCES

[1] D. Lexa, L. Leibowitz, J. Kropf, On the reactive occlusion of the (uranium trichloride + lithium chloride + potassium chloride) eutectic salt in zeolite 4A. *J. Nucl. Mater*. Vol. 279, pp. 57-64, 2000.

[2] M. Lambregts, S.M. Frank, Characterization of cesium containing glass-bonded ceramic waste forms. *Microporous. Mesoporous. Mater*., Vol. 64, pp.1-9, 2003

[3] W.L. Ebert, M.A. Lewis, S.G. Johnson, The precision of product consistency tests conducted with a glass-bonded ceramic waste form. *J. Nucl. Mater.*, Vol. 305, pp. 37-51, 2002

[4] L.R. Morss, M.A. Lewis, M.K. Lichmann, D. Lexa, Cerium, uranium, and plutonium behavior in glass-bonded sodalite, a ceramic nuclear waste form. *J. Alloy. Compd*., Vol. 303-304, pp. 42-48, 2000.

[5] M.K. Lichmann, D.T. Reed, A.J. Kropf, S.B. Aase, M.A. Lewis, EXAFS/XANES studies of plutonium-loaded sodalite/glass waste forms. *J. Nucl. Mater.*, Vol. 297, pp. 303-312, 2001.

[6] H.S. Park, I.T. Kim, H.Y. Kim, S.K. Ryu, J.H. Kim, Stabilization/Solidification of Radioactive Salt Waste via Gel-Route Pretreatment, *Environ. Sci. Tech*. Vol**.** 41, pp. 1345-1351, 2006