

A Fabrication of Salt-Loaded Ceramic Waste Form

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1. Introduction

The waste salts such as molten LiCl salt from an oxide fuel reduction process and molten LiCl-KCl eutectic salt from an electro refining process must meet the acceptance criteria for a disposal in geological repository. Two of the more important criteria in waste form containing chloride salts are known to be leach resistance and waste form durability [1].

According to US Argonne National Laboratory (ANL), a ceramic waste form (CWF), which was prepared by pressureless consolidation (PC) of eutectic LiCl-KCl salt-loaded zeolite (SLZ) [2], has as a good quality as that of high level radioactive waste (HLW) glass. ANL has developed the CWF fabrication method as follows: The eutectic LiCl-KCl salt recovered from the electrorefiner is size-reduced to facilitate occlusion in zeolite by crushing and grinding under an argon atmosphere. The crushed salt is mechanically mixed with dried zeolite 4A in a V-mixer at a salt loading about 10 mass % then heated to about 723 K for 16 h to occlude salt within the zeolite cages. And the SLZ is then mixed with a borosilicate binder glass in a V-mixer (without heating) at a 3:1 mass ratio. The mixture is loaded into fill cans the processed at about 1188 K for about 72 h. As the mixture is heated above about 1123 K during the encapsulating step, the SLZ converts to the mineral sodalite, $\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$, which incorporates most of the occluded salt into its structure. The glass becomes sufficiently fluid during bonded sodalite material referred to as the CWF, which contains 8 mass % salt.

We also developed the CWR fabrication technology for a waste LiCl salt from an electrolytic reduction process (ACP; advanced spent fuel conditioning process). A melting point of the LiCl salt is higher than that of the eutectic LiCl-KCl salt, therefore, a crystalline behavior during producing CWF is somewhat different from that of ANL. Therefore, the changes of immobilization media, which had been started from zeolite A, for the fabrication of LiCl salt-loaded CWF, and some results of qualification test and analysis, are introduced in this work.

2. Procedure

2.1 Fabrication of CWF

The SLZ samples were prepared by mixing of the LiCl salt and zeolite A with a mixing ratio of LiCl to zeolite, $r = 0.3 \sim 0.1$, which was shown in Fig. 1. The more detailed description is showed in our previous works [3].



Figure 1. Salt-loaded ceramic waste form fabrication procedure

2.2 Test and Analysis

The product consistency of the CWF was tested according to a PCT (product consistency test) - 7 day [4], and a leachate was analyzed by a inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer, Optima 4300). The crystalline structures of SLZ sample, the thermal treated sample and the CWF were quantitatively analyzed by a TOPAS software for Bruker D8 advance X-ray diffractometer.

3. Results and Discussion

3.1 Crystal Structure Changes during Fabrication of CWF

During occlusion of the waste salt in zeolite 4A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$) for $r > 0.25$, the zeolite 4A was

transformed to zeolite Li-A ($\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$), with some minor phases such as $\text{Li}_8\text{Cl}_2\text{-Sod}$ ($\text{Li}_8(\text{AlSiO}_4)_6\text{Cl}_2$) and halite (NaCl). And such transformation started very fast, from a half hour after contacting the zeolite with molten LiCl salt.

For r ($=\text{LiCl}/\text{zeolite}$) < 0.25 , halite and $\text{Li}_8\text{Cl}_2\text{-Sod}$ appeared, and the stable and very high leach-resistant crystal phase, $\text{Na}_8\text{Cl}_2\text{-Sod}$ ($\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$) was found as a major phase in SLZ sample for $r=0.1$. This SLZ sample, however, also had some minor phases such as below 3% Li-A, 12% nepheline (NaAlSiO_4), which is known as poor leach resistant.

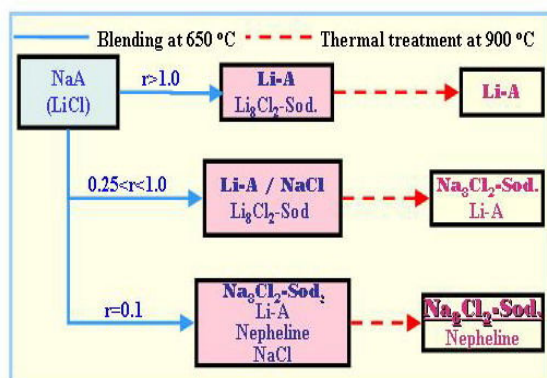


Figure 2. The transformation of SLZ sample after the thermal treatment at 1170 K

The PCT-7 day was conducted in accordance with ASTM C1285-94 [4], with the exceptions of using a non-crushed material. 50 mL of demineralized water was used for 5 g of the CWF sample. The concentrations of Cs and Sr were measured to calculate the normalized release rate (NRR), with a unit of $\text{g}/\text{m}^2\cdot\text{d}$. For the mixing ratio, $r=0.1$, the normalized release rate of Cs and Sr, $\text{NRR}(\text{Cs})$ and $\text{NRR}(\text{Sr})$, were 1.0×10^{-1} and $2.0 \times 10^{-2} \text{ g}/\text{m}^2\cdot\text{d}$, respectively. For the case of $R=0.25$, however, $\text{NRR}(\text{Cs})$ and $\text{NRR}(\text{Sr})$ were somewhat high, 1.15 and $9.2 \times 10^{-2} \text{ g}/\text{m}^2\cdot\text{d}$, respectively.

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