

## Conditioning of Waste LiCl Salt from Pyrochemical Process Using Zeolite A

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### ABSTRACT

The electrolytic (LiCl-Li<sub>2</sub>O) reduction process (Advanced spent fuel Conditioning Process; ACP) and the electro-refining process, which are being developed by the Korea Atomic Energy Research Institute (KAERI), are to generate two types of molten salt wastes such as a LiCl salt and a LiCl-KCl eutectic salt, respectively. These waste salts must meet certain criteria for a disposal. A conditioning process composed of an immobilization and then a thermal treatment, for LiCl salt waste from the ACP has been developed using zeolite A. The immobilization of molten LiCl salt waste was conducted in a blender by mixing it with zeolite A at 923 K, producing a salt-loaded zeolite (SLZ). During the immobilization, the zeolite A was transformed to zeolite Li-A [Li<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>80</sub>], with some minor phases such as a Li-type sodalite [Li<sub>8</sub>Cl<sub>2</sub>-Sod; Li<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>] and Nepheline for some zeolite-rich condition. In order to obtain a final ceramic waste form with Na-type sodalite [Na<sub>8</sub>Cl<sub>2</sub>-Sod; Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>], the very highly leach-resistant crystal phase, the SLZ with  $r$  (=LiCl/zeolite) < 0.3 should be treated in a high temperature furnace above 1173 K, which was independent from an addition of glass frit during a mixing.

### INTRODUCTION

Molten waste LiCl salt with 3wt%-Li<sub>2</sub>O, which is generated from the ACP, contains some fission products such as alkali metal, alkaline-earth, and rare-earth, mainly as chloride forms. The typical nuclides, cesium (Cs) and strontium (Sr) accumulate within the waste salt because the reduction potentials of CsCl and SrCl<sub>2</sub> are higher than those of LiCl. The waste salt, mainly a chloride form, is water-soluble, and alkali chlorides are known to be readily radiolyzed to yield interstitial halogens and metal colloids. For a disposal in a geological repository, this waste salt must meet certain acceptance criteria, whose two more important ones would be a leach resistance and a durability for a waste form containing a chloride salt even though it has not been regulated up to now in Korea.

A conditioning process for a LiCl-KCl eutectic salt from US Argonne National Laboratory (ANL) Experimental Breeder Reactor-II, which is composed of occluding salt in zeolite A at about 730 K and then encapsulating the zeolite in a borosilicate binder glass by a hot isostatic press (HIP) method or pressureless consolidation (PC) method, has been developed by US ANL [1]. The final waste form containing a waste salt is a ceramic waste form (CWF) with a phase composition of about 70% sodalite, 25% binder glass, and 5% of the inclusion phases (halite, nepheline, and various oxides and silicates). US ANL showed that the chemical durability and leach resistance of the CWF were higher than those of the glass waste form for a high level waste from an aqueous process, by a 7-day product consistency test (PCT) [2], and the crystal phase of the sodalite in the CWF was a Na-type sodalite [Na<sub>8</sub>Cl<sub>2</sub>-Sod; Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>] [3].

The melting point of LiCl salt is about 885 K, higher than that of LiCl-KCl eutectic salt (634 K), which means that the blending of the LiCl salt with zeolite was accomplished at 923 K, different from that of the LiCl-KCl eutectic salt (770 K) at US ANL. Such a difference in the blending temperature had an effect on the crystal phase of zeolite A, resulting in a SLZ with a major phase of zeolite Li-A [Li<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>80</sub>] [4], which was a different result from that of US ANL [5]. Therefore, the conditioning of waste LiCl salt by using zeolite A, especially the crystal characteristics by focusing on a transformation according to the temperature and/or mixing ratio of the LiCl salt to zeolite was investigated in this work.

## EXPERIMENTAL

The SLZ samples were prepared by an ion-exchange and a blending; for the mixing ratio of LiCl to zeolite,  $r = 15, 10, \text{ and } 4.5$ , in a batch ion-exchange vessel, and for  $r = 2, 1, 0.5, 0.25, 0.1$ , in a V-type blender. A simulated molten LiCl salt was prepared by heating the commercial LiCl powder (Aldrich, 99+%), with CsCl (Aldrich, 99.9%), SrCl<sub>2</sub> (Aldrich, 99.9%), BaCl<sub>2</sub> (Aldrich, 99.9%) and Li<sub>2</sub>O (Aldrich, 97%). The initial concentrations of Cs, Sr, Ba and Li<sub>2</sub>O were maintained at 4.19, 1.60, 3.27 and 3.00 wt%, respectively. In this study, the bead-type zeolite 4A (8 - 12 mesh) was used. A more detailed procedure is described in our previous work [4].

The elements such as Na, Li, Cs, Sr and Ba for the SLZ sample and leachate were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer, Optima 4300). The chloride concentration was measured for only the leachate by an ion chromatography (IC, Dionex DX-100). The surface area was measured by the BET measurement (Micrometrics ASAP 2400 USA). The SLZ samples were examined by using an X-ray diffractometer (XRD, Philips, X'pert MPD) to characterize the crystalline structure, and to identify the phases and the compositions.

The optimum condition to produce a CWF with a major crystal phase of Na<sub>8</sub>Cl<sub>2</sub>-Sod was determined as follows: The SLZ samples were prepared according to different mixing ratios ( $r$ ) of LiCl salt to zeolite A. Each SLZ sample's crystal phase was analyzed by XRD, and then the free chloride content [6] was also measured by using Eq. 1.

$$\text{Free Chloride Conc.} = 100\% \times \frac{x \frac{\mu\text{g Cl}^-}{\text{mL H}_2\text{O}} V_{\text{H}_2\text{O}} \frac{\text{g Cl}^-}{10^6 \mu\text{g Cl}^-}}{m_{\text{sample}} (\text{g})} \quad (\text{Eq. 1})$$

The chemical durability of the SLZ sample was measured by a 7-day PCT test, and calculated by using Eq. 2.

$$\text{NR}(i) = \frac{(C_i - B_i)}{f_s(i) \cdot m_s \cdot (SA_s / V_s)} \quad (\text{Eq. 2})$$

where the NR( $i$ ) is the normalized release of the element  $i$  from the sample  $s$ ,  $C_i$  is the concentration of the element  $i$  in the leachate from the sample  $s$ ,  $B_i$  is the concentration of element  $i$  in the leachate from a blank,  $f_s(i)$  is the average mass fraction of the element  $i$  in the sample,  $m_s$  is the original mass of sample  $s$ ,  $SA_s$  is the surface area per unit mass of sample  $s$ , and  $V_s$  is the initial volume of the leachant in the test vessel containing sample  $s$ . The crystal phase of a final waste form was measured by using a thermal-treated SLZ sample, which was only treated above 1173 K without an addition of glass frit, thus, an un-encapsulated waste form.

## RESULTS AND DISCUSSION

### *Crystal Phase Changes*

The conditioning of molten waste salt can be divided into two sequential steps, an occlusion of waste salt in a zeolite cage and an encapsulation of salt-occluded zeolite. An occlusion can be accomplished easily by just mixing of the molten waste with zeolite, no matter what mixing ratio or mixing method is used. During this occlusion step, the cationic form of fission products, such as the Cs-, Sr- and Ba-ions, are exchanged with the Na-ions of zeolite, and fixed on to the zeolite site. Thus, in view of the radionuclide such as Cs, Sr, etc., these heat-generation nuclides are immobilized on and/or within a medium, zeolite. At the same time, some chlorides are occluded within the crystal cages of zeolite, resulting in a formation of a salt-loaded zeolite (SLZ). US ANL showed that the ion-exchange and/or a salt-loading took place but that the zeolite A maintained its original crystal phase during the occlusion of the LiCl-KCl eutectic salt in zeolite A at 773 K [5]. However, the crystal phase of our SLZ, prepared by mixing the molten LiCl salt with zeolite A at 920 K, was transformed into zeolite Li-A [Li<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>80</sub>] despite the mixing ratio of LiCl to zeolite.

The detailed crystal phase changes during an attempt to establish an optimum condition to produce the CWF with a major phase of Na<sub>8</sub>Cl<sub>2</sub>-Sod could be characterized through a SLZ sample preparation and XRD spectroscopy, which

is as follows. During an ion-exchange or a blending of the LiCl salt with zeolite 4A [ $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ], the zeolite A was transformed to zeolite Li-A, 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 [ $\text{NaCl}$ ] according to the mixing ratio. And such a transformation started very quickly, from a half hour after placing the zeolite in contact with the molten LiCl salt. As the mixing ratio,  $r$  ( $=\text{LiCl}/\text{zeolite}$ ) decreased to below 0.5, halite and  $\text{Li}_8\text{Cl}_2\text{-Sod}$  appeared. At a very low mixing ratio,  $r=0.1$ , the stable and very high leach-resistant crystal phase,  $\text{Na}_8\text{Cl}_2\text{-Sod}$  was found as a major phase in the SLZ sample. This SLZ sample, however, also had some minor phases such as about 30% Li-A, 11% halite, and 20% nepheline [ $\text{NaAlSiO}_4$ ], which is known as a poor leach resistant.

After a thermal treatment above 1173 K, the same temperature as an encapsulation with a glass frit, the SLZ sample was transformed into a salt-occluded zeolite with a major phase of  $\text{Na}_8\text{Cl}_2\text{-Sod}$  (about 82%), and some minor phases such as about 15% nepheline and 3% Li-A. The SLZ sample with  $r=0.25$ , which did not contain any nepheline phase, was transformed from a crystal structure with about 44% Li-A, 41% halite, and 15%  $\text{Na}_8\text{Cl}_2\text{-Sod}$  before the thermal treatment to one with about 58%  $\text{Na}_8\text{Cl}_2\text{-Sod}$  and 42% Li-A. Therefore, the optimum mixing condition, for containing less than 5% nepheline and Li-A, seems to lie between 0.25 and 0.1. US ANL also showed that an encapsulation with glass frit at such a high temperature created CWF with a major crystal structure of  $\text{Na}_8\text{Cl}_2\text{-Sod}$  [5]. Such an addition of glass frit provided a better consolidation of the waste salt, however, it brought about a significant increase in the waste volume. Crystal phase changes according to the mixing ratio and operating temperature are summarized and shown in Fig. 1.

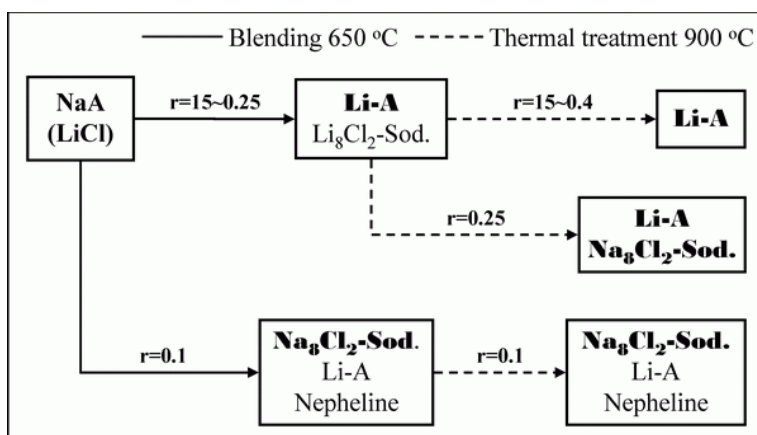


Fig. 1. Crystal phase changes during an immobilization of waste LiCl salt (bold character means major phase)

### Conditioning of the Waste LiCl Salt

A free chloride (or free salt) is the salt that is not occluded within zeolite cages, and it exists between crystals or on the surface of a crystal. Especially, the SLZ samples prepared by an ion-exchange contained some free chloride, almost up to 25 wt%. However, the SLZ sample prepared by a blending, namely the mixing ratio  $r < 1.0$  did not need to have its free salt chloride content checked, and the optimum mixing ratio to produce a high leach-resistant CWF lay below 1.0.

The normalized release rates (NR) of Cs and Sr from the SLZ sample, calculated from the results of a 7-day PCT, are shown in Table I. The SLZ samples prepared by an ion-exchange, with  $r = 15, 10,$  and  $4.5$ , were made by a collection of an occluded LiCl salt within zeolite A from the ion-exchange vessel and then a washing by demineralized water. During this water-washing step, Cs and Sr, as well as free chloride and hardened LiCl on the SLZ, were removed from the surface of the SLZ. Thus, the NRs for the SLZ samples of  $r = 15, 10,$  and  $4.5$  were lower than those of the other SLZ samples by a blending, which were not washed before a PCT.

Table I. Normalized Release rates of Cs and Sr for SLZ Samples

r (=LiCl/zeolite)	NR, g/m <sup>2</sup>	
	Cs	Sr
15	0.00434	0.00080
10	0.06883	0.00042
4.5	0.01648	0.00062
1.0	0.05494	0.27633
0.5	0.08250	0.40579
0.25	0.07168	0.07698

The normalized release rates of Sr, NR(Sr), for the blended SLZ samples with  $r = 1.0, 0.5$  and  $0.25$ , were significantly higher than those of the ion-exchanged SLZ samples with  $r = 15, 10$  and  $4.5$ . These results indicate that the  $\text{Sr}^+$ -ion hardly exchanged with the  $\text{Na}^+$ -ion, thus almost all the Sr existed on the surface of the SLZ without an ion-exchange or occlusion within the zeolite cages. The not-occluded Sr of the ion-exchanged SLZ sample was washed out before a PCT, whereas the not-occluded Sr of the blended SLZ sample was almost totally releases during a PCT. Since Cs has a higher release than the higher valence fission products such as barium, strontium, cerium, etc., and high chloride losses correlated with the high total mass losses, the most important criterion for the waste form containing a waste salt has been generally an immobilization of the fission products, especially Cs, and chloride [7]. However, our results show that Sr is a more important nuclide than Cs, because the value of NR(Sr) is five times as much as that of NR(Cs).

The optimum condition was decided based on the production of CWF with a major crystal phase of  $\text{Na}_8\text{Cl}_2\text{-Sod.}$ , which was only analyzed by XRD spectroscopy. The schematic diagram of the conditioning procedure, involving the spent oxide fuel reduction process, is shown in Fig. 2 Waste LiCl salt with 3wt%  $\text{-Li}_2\text{O}$  is generated from the electrolytic process. This LiCl- $\text{Li}_2\text{O}$  salt, which contained some heat-generation fission products such as Cs, Sr and Ba, was blended in a V-type blender at 923 K for 20 h, resulting in the production of SLZ. And then, the SLZ was encapsulated with glass frit above 1173 K for 4 h, to fabricate a final waste form. During the waste form fabrication, the crystal phase of SLZ is transformed into  $\text{Na}_8\text{Cl}_2\text{-Sod.}$

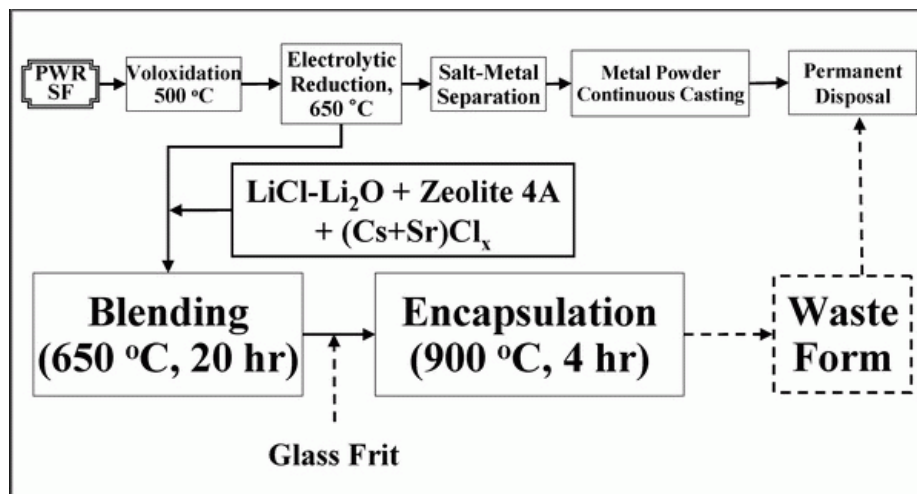


Fig. 2. The schematic diagram of waste LiCl salt conditioning procedure

## CONCLUSION

The characterization of the crystal phase for salt-loaded zeolite, which was prepared by blending the waste LiCl salt from KAERI's electrolytic reduction process with zeolite A, showed that a ceramic waste form with a  $\text{Na}_8\text{Cl}_2\text{-Sod}$  crystal structure could be formed under the limited condition of a mixing ratio of  $r (= \text{LiCl/zeolite}) < 0.25$  and a thermal treatment above 1173 K.

## ACKNOWLEDGMENTS

This work was funded by the National Mid- and Long-term Atomic Energy R&D Program supported by the Ministry of Science and Technology of Korea.

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