

Crystal Phase Changes of Zeolite in Immobilization of Waste LiCl Salt

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ABSTRACT

The electrolytic reduction process and the electrorefining process, which are being developed at the Korea Atomic Energy Research Institute (KAERI), are to generate molten waste salts such as LiCl salt and LiCl-KCl eutectic salt, respectively. Our goal in waste salt management is to minimize a total waste generation and fabricate a very low-leaching waste form such as a ceramic waste form. Zeolite has been known to one of the most desirable media to immobilize waste salt, which is water soluble and easily radiolyzed. Zeolite can be also used to the removal of fission products from the spent waste salt. Molten LiCl salt is mixed with zeolite A at 650°C to form a salt-loaded zeolite, and then thermally treated in above 900°C to become an immobilized product with crystal phase of Li_8Cl_2 -Sodalite. In this work, a crystal phase changes of immobilization medium, zeolite, during immobilization of molten LiCl salt using zeolite A is introduced.

INTRODUCTION

Molten LiCl salt with 3wt%- Li_2O , which is generated from the electrolytic reduction process, 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 potential of CsCl and SrCl_2 are higher than those of LiCl. The waste salt, mainly chloride form, is water-soluble, and alkali chlorides are known to be readily radiolyzed to yield interstitial halogens and

metal colloids. For disposal in a geological repository, this waste salt must meet the acceptance criteria. For a waste form containing chloride salt, two of the more important criteria are leach resistance and waste form durability [1].

A conditioning process for LiCl-KCl eutectic salt from US Argonne National Laboratory (ANL) Experimental Breeder Reactor-II (EBR-II), which is composed of occluding salt in zeolite A at 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 [2]. The final waste form containing waste salt is a ceramic waste form (CWF) with the phase composition of about 70% sodalite, 25% binder glass, and a 5% total of inclusion phases (halite, nepheline, and various oxides and silicates). US ANL reported that the chemical durability and leach resistance of the CWF were higher than those of glass waste form for high level waste from aqueous process, by a 7-day product consistency test (PCT) [3].

During the first step to occlude waste salt in zeolite, the cationic form of fission products, such as Cs-, Sr- and Ba-ions, are exchanged with Na-ions of zeolite, and fixed on the zeolite site. At the same time, some chlorides are occluded within the crystal cages of zeolite, resulting in formation of a salt-loaded zeolite (SLZ). The second step of conditioning is encapsulation of the SLZ with glass above 1220 K. which finally result in transformation of the SLZ into sodalite with an aperture size of just 0.22 nm.

The melting point of LiCl salt is about 885 K, which is higher than that of LiCl-KCl eutectic salt (634 K), which resulting that the blending of LiCl salt with zeolite was accomplished at 920 K, different from that of LiCl-KCl eutectic salt (770 K). Therefore, the behavior of zeolite, especially crystal characteristics focused on transformation according to temperature and/or mixing ratio of LiCl salt to zeolite was introduced in this work.

EXPERIMENTAL

The SLZ samples were prepared by ion-exchange and 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%),

SrCl₂ (Aldrich, 99.9%), BaCl₂ (Aldrich, 99.9%) and Li₂O (Aldrich, 97%). The initial concentrations of Cs, Sr, Ba and Li₂O 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) were mainly 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 a 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 SLZ samples were examined using X-ray diffractometer (XRD, Philips, X'pert MPD) to characterize the crystalline structure, identify the phases and compositions.

RESULTS AND DISCUSSION

Crystal Phase Changes

During blending of LiCl salt with zeolite 4A (Na₁₂Al₁₂Si₁₂O₄₈), the immobilization medium, zeolite 4A, was transformed to zeolite Li-A (Li₂Al₂Si₂O₈₀), with some minor phases such as Li₈Cl₂-Sod (Li₈(AlSiO₄)₆Cl₂) and halite (NaCl) according to the mixing ratio. And such transformation started very fast, from a half hour after contacting the zeolite with molten LiCl salt. As the mixing ratio, r (=LiCl/zeolite) decreased below 0.5, halite and Li₈Cl₂-Sod. appeared. At the very low mixing ratio, $r=0.1$, which was the almost same ratio as that of the SLZ for LiCl-KCl eutectic salt at US ANL, the stable and very high leach-resistant crystal phase, Na₈Cl₂-Sod (Na₈(AlSiO₄)₆Cl₂) was found as a major phase in SLZ sample. This SLZ sample, however, also had some minor phases such as about 30% Li-A, 11% halite, and 20% nepheline (NaAlSiO₄), which is known as poor leach resistant.

After thermal treatment above 1170 K, the same temperature as encapsulation with glass frit, for more than 4 h, the SLZ sample was transformed into a salt-occluded zeolite with a major phase of Na₈Cl₂-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 the crystal structure with about 44% Li-A, 41% halite, and 15% Na₈Cl₂-Sod. before the thermal treatment to one with about 58% Na₈Cl₂-Sod. and 42% Li-A. Therefore, the optimum mixing condition, containing less

both 5% nepheline and Li-A, seems to lie between 0.25 and 0.1. US ANL also showed that the thermal treatment with glass frit at such high temperature made the CWF with a major crystal structure of $\text{Na}_8\text{Cl}_2\text{-Sod.}$ [5]. Such addition of glass frit gave better consolidation of waste salt, however, which rather brings significantly increase in waste volume. Crystal phase changes according to mixing ratio and operating temperature are summarized and shown in Fig. 1.

Conditioning of Waste LiCl Salt

The schematic diagram of conditioning procedure, involving the spent oxide fuel reduction process, is shown in Fig. 2 Waste LiCl salt with 3wt%- Li_2O is generated from the electrolytic process. This LiCl- Li_2O salt, contained some heat-generation fission products such as Cs, Sr and Ba, is blended in V-type blender at 923 K for 20 h, resulting in producing SLZ. And then, the SLZ is 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 $\text{Na}_8\text{Cl}_2\text{-Sod.}$

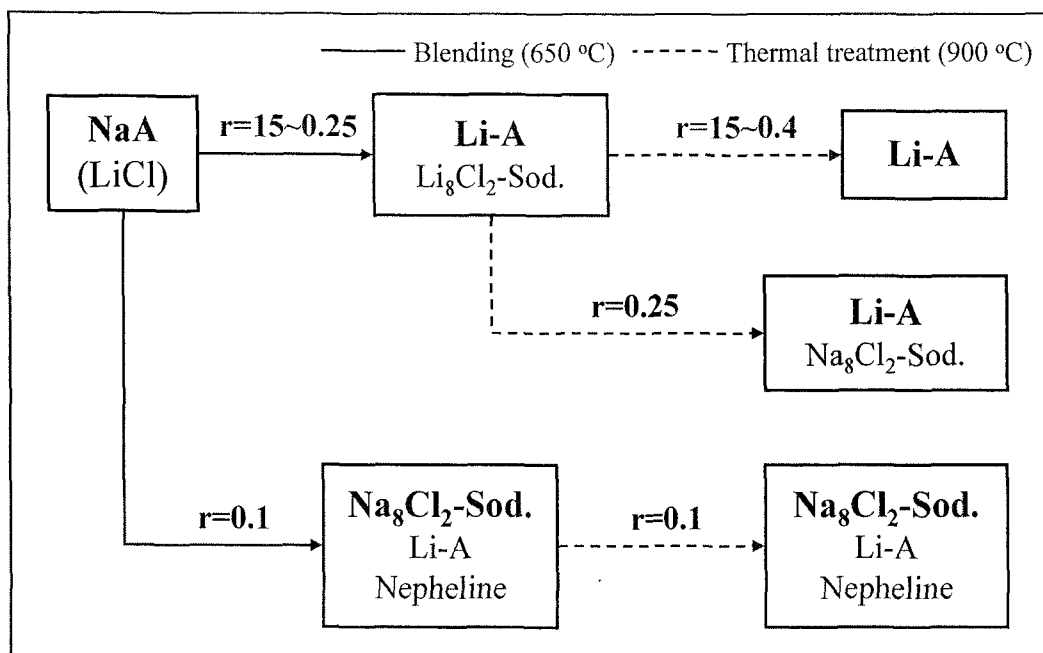


Figure 1. Crystal phase changes for immobilization of waste LiCl salt
(bold character means major phase)

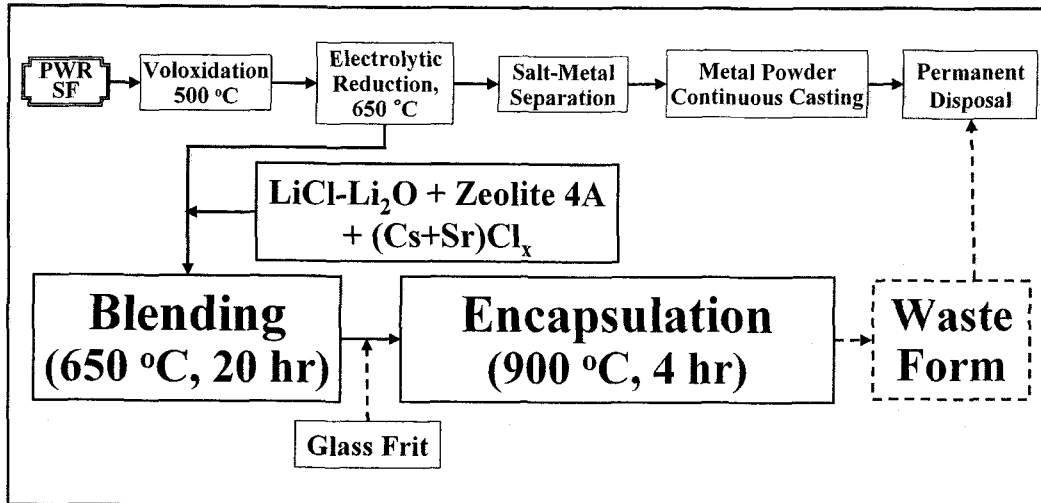


Figure 2. The schematic diagram of waste LiCl salt conditioning procedure

CONCLUSION

The characterization of crystal phase for SLZ, prepared by blending of the waste LiCl salt from KAERI's electrolytic reduction process with zeolite A, showed that a ceramic waste form with Na₈Cl₂-Sod. crystal structure could be formed in the limited conditions of mixing ratio, $r (=LiCl/zeolite) < 0.25$ and thermal treatment above 1170 K

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