

# A study on Immobilization of Waste Chloride Salt Using Zeolite Only

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## 1. Introduction

The oxide fuel reduction process based on the electrochemical method (Advanced spent fuel Conditioning Process; ACP) and the long-lived radioactive nuclides partitioning process based on 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 LiCl salt and LiCl-KCl eutectic salt, respectively. Actually the constituents of waste salt are water-soluble. And, alkali halides are known to be readily radiolyzed to yield interstitial halogens and metal colloids. For disposal in a geological repository, the 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].

These waste salts must meet some criteria for disposal. A conditioning process for LiCl salt waste from ACP has been developed using zeolite A, since zeolite is known to be stable at a high temperature. During the preparation of immobilized product using zeolite, the original immobilized matrix, zeolite A, was transformed to various zeolite crystal structures such as Li-A,  $\text{Li}_8\text{Cl}_2$ -Sodalite ( $\text{Li}_8\text{Cl}_2$ -Sod),  $\text{Na}_8\text{Cl}_2$ -Sodalite ( $\text{Na}_8\text{Cl}_2$ -Sod), and Nepheline. Among those transformed 4 crystal structures, Nepheline has the lowest leach resistance. Therefore, to make a good immobilized product, the transformation to Nepheline must be minimized.

US ANL has adapted the addition of glass frit to make a final waste form, with a major crystal structure of  $\text{Na}_8\text{Cl}_2$ -Sod, for treatment of LiCl-KCl eutectic waste salt from the electro-refining process [2]. Such addition, however, finally results in increase of the amount of total radioactive waste.

In this work, we tried to find a condition to give a good immobilized product with crystal structure of  $\text{Na}_8\text{Cl}_2$ -Sod using zeolite only, thus finally results in minimization of waste volume.

## 2. Experimental

### 2.1 Sample Preparation

For the mixing ratios of LiCl to zeolite,  $r = 15, 10, 4.5$ , the salt-loaded zeolite (SLZ) samples were prepared in a batch ion exchanger. And, for  $r = 1, 0.5, 0.4, 0.25, 0.1$  a

direct blender was used. A detailed procedure was showed in reference [3].

To make the final immobilized products, with structure of  $\text{Na}_8\text{Cl}_2$ -Sod, the SLZ samples were thermally treated at about 1170 K for 4 hrs.

### 2.2 Chemicals and Analyses

A molten LiCl salt was prepared by heating the commercial LiCl powder (Aldrich, 99+%) to 923 K for 0.5 h. Here only two major nuclide elements, Cesium (Cs) and Strontium (Sr), were considered. The simulated waste salt was prepared by the physical mixing of LiCl, CsCl (Aldrich, 99.9%), and  $\text{SrCl}_2$  (Aldrich, 99.9%) powders in an Ar glove box, and then heating under Ar gas flow. Bead-type zeolite A, (NaA or 4A form, Aldrich, Molecular Sieves), with a size of 8-12 mesh, was dehydrated before use by heating with a purge of highly-pure nitrogen gas (99.999+%), and stored in an Ar glove box.

The compositions of the sampled salt, such as Na, Ca, Li, Cs, Sr, were determined by a inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer, Optima 4300). The crystalline structure was analyzed by an X-ray diffractometer (XRD, Philips, X'pert MPD).

## 3. Results and Discussion

### 3.1 Crystal Structure of SLZ Sample

Our previous works [4] showed that zeolite 4A ( $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ) was transformed to a major phase of zeolite Li-A ( $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_{80}$ ) for all the mixing ratios. And such transformation seemed to be started very early, from a half hour after contacting the zeolite with molten LiCl salt. When the mixing ratio was 15 and 10, another minor phase,  $\text{Li}_8\text{Cl}_2$ -Sod, was also found. The formation of  $\text{Li}_8\text{Cl}_2$ -Sod reduces as the mixing ratio decreases.  $\text{Na}_8\text{Cl}_2$ -Sod phase was formed in the SLZ sample with a ration of 0.1.

US ANL [5] showed that the waste form with a major crystal structure of  $\text{Na}_8\text{Cl}_2$ -Sod had a good leach resistance. To fabricate such high integrated waste form, the blending followed by mixing with glass frit in 1120 – 1170 K was necessary. This result was accomplished for the LiCl-KCl eutectic waste salt, with its low melting

point of 634 K. However, this method rather brings increase in waste volume 4 times as much as its original waste generation.

### 3.2 Crystal Structure of Immobilized Product

Through only thermal treatment at 1170 K for 4 hrs, the minor phase of SLZ sample above the mixing ratio,  $r=0.4$ ,  $\text{Li}_8\text{Cl}_2\text{-Sod.}$ , was disappeared, and the major phase only, Li-A, remained, as shown Table 1. For  $r=0.25$ , a new crystal phase,  $\text{Na}_8\text{Cl}_2\text{-Sod.}$ , was appeared instead of  $\text{Li}_8\text{Cl}_2\text{-Sod.}$  For  $r=0.1$ , its original crystal phase, consisted of two major phases of  $\text{Na}_8\text{Cl}_2\text{-Sod.}$  and Li-A, and a minor phase of Nepheline, was transformed to a major phase of  $\text{Na}_8\text{Cl}_2\text{-Sod.}$  and two minor phases of Li-A and Nepheline, as shown in Fig. 1.

Table 1. Crystal phases of SLZ sample and immobilized product by XRD patterns.

r(=LiCl/zeolite)		SLZ sample	Immobilized product
15	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
10	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
4.5	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
1.0	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
0.5	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
0.4	major	Li-A	Li-A
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
0.25	major	Li-A	Li-A $\text{Na}_8\text{Cl}_2\text{-Sod.}$
	minor	$\text{Li}_8\text{Cl}_2\text{-Sod.}$	
0.1	major	$\text{Na}_8\text{Cl}_2\text{-Sod.}$ Li-A	$\text{Na}_8\text{Cl}_2\text{-Sod.}$ Li-A Nepheline
	minor	Nepheline	

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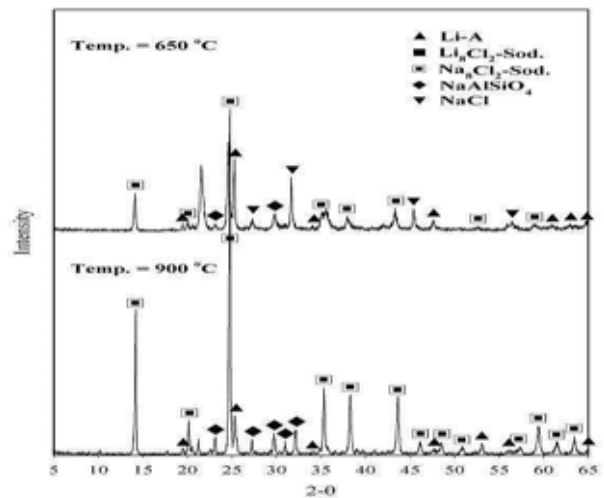


Figure 1. XRD patterns of the SLZ sample (above) and immobilized product (below) for mixing ratio,  $r=0.1$ .