

## Thermal Treatment of Salt-Loaded Zeolite

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### 1. Introduction

For disposal in a geological repository, 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 waste form containing chloride salt, two of the more important criteria are known to be leach resistance and waste form durability [1].

US Argonne National Laboratory (ANL) developed a ceramic waste form (CWF) fabrication technology for LiCl-KCl eutectic salt from ANL Experimental Breeder Reactor-II (EBR-II)[2]. The CWF, which was made by first 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 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 showed 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).

However, the waste form fabrication process for waste LiCl salt is somewhat different in mixing temperature from that for LiCl-KCl eutectic salt at US ANL. The former is mixed at 920 K, whereas, the later mixing is accomplished at 730 K. Such difference in mixing temperature results in the different major phase of SLZ, that is, zeolite Li-A from LiCl salt, and unchanged zeolite A from LiCl-KCl eutectic salt. This unchanged phase of zeolite A during an immobilization step is transformed to sodalite, which was known to be very high leach-resistant, in the step of encapsulating with borosilicate glass.

In this work, we tried to investigate the transformation of major phase of SLZ, from zeolite Li-A to Na<sub>8</sub>Cl<sub>2</sub>-Sod using zeolite only sodalite, by a quantitative analysis with a software for X-ray diffractometer during the thermal treatment under 1170 K.

### 2. Experimental

#### 2.1 Sample Preparation

The SLZ samples were prepared by mixing of LiCl salt and zeolite A with a mixing ratio of LiCl to zeolite,  $r = 15$ ,

10, 4.5, 1, 0.5, 0.4, 0.25, and 0.1, which was shown in Fig. 1. The more detailed description is showed in our previous works [3].

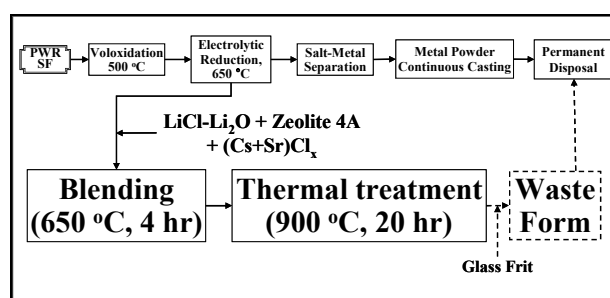


Figure 1. The schematic diagram of waste salt treatment process involving the SLZ sample preparation

#### 2.2 Analysis

The crystalline structures of SLZ sample and the thermal treated sample were quantitatively analyzed by a TOPAS software for Bruker D8 advance X-ray diffractometer.

### 3. Results and Discussion

#### 3.1 Crystal Structure of SLZ Sample and thermal treated sample

During the salt occluding in zeolite 4A (Na<sub>12</sub>Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>), the zeolite 4A 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 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 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 Li<sub>8</sub>Cl<sub>2</sub>-Sod appeared. At the very low mixing ratio,  $r=0.1$ , which was the same ratio as that of the SLZ for LiCl-KCl eutectic salt at US ANL, the stable and very high leach-resistant crystal phase, Na<sub>8</sub>Cl<sub>2</sub>-Sod (Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>) 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 (NaAlSiO<sub>4</sub>), which is known as poor leach resistant.

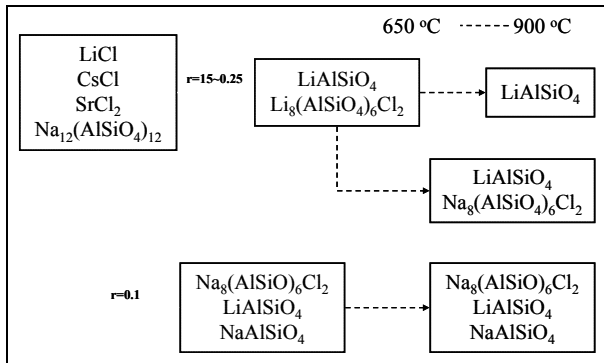


Figure 2. The transformation of SLZ sample after the thermal treatment at 1170 K

After thermal treatment at 1170 K for more than 4 h, the SLZ sample was transformed to new SLZ sample with the major phase of Na<sub>8</sub>Cl<sub>2</sub>-Sod (about 82%), and some minor phases such as about 15% nepheline and 3% Li-A.

US ANL showed that an addition of glass frit in encapsulating step was necessary to fabricate the CWF with a major crystal structure of Na<sub>8</sub>Cl<sub>2</sub>-Sod.[4]. Such addition of glass frit gave better consolidation of waste salt, however, which rather brings increase in waste volume 4 times as much as its original waste generation.

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% Na<sub>8</sub>Cl<sub>2</sub>-Sod. before the thermal treatment to one with about 58% Na<sub>8</sub>Cl<sub>2</sub>-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.

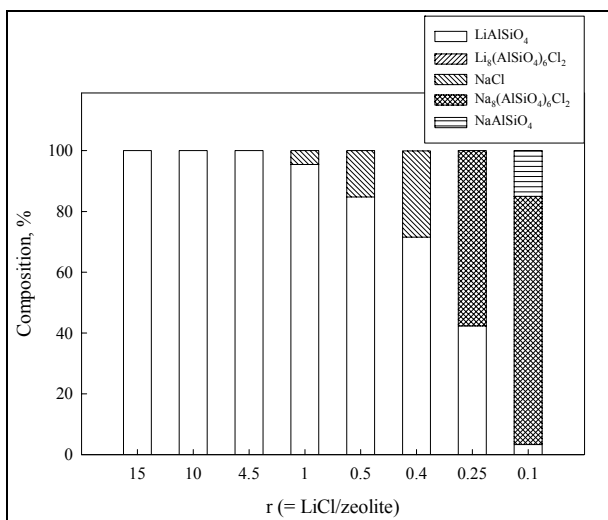


Figure 3. The crystal phase compositions of SLZ sample after thermal treatment at 1170 K.

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