

## Treatment of Waste Salt from the Advanced spent fuel Conditioning Process (I) - Characterization of Zeolite A in Molten LiCl Salt -

Jeong-Guk Kim, Jae-Hee Lee, Jae-Hyung Yoo, and Joon-Hyung Kim  
Nuclear Chemical Engineering Research Dept., Atomic Energy Research Institute  
jungkim@kaeri.re.kr

### 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. These waste salts must meet some criteria for disposal. A conditioning process for LiCl salt waste from ACP has been developed using zeolite A.

This treatment process of waste salt using zeolite A was first developed by US ANL (Argonne National Laboratory) for LiCl-KCl eutectic salt waste from an electro-refining process of EBR (Experimental Breeder Reactor)-II spent fuel [1]. This process has been developed recently, and a ceramic waste form (CWF) is produced in demonstration-scale V-mixer (50 kg/batch). However, ANL process is different from KAERI treatment process in waste salt, the former is LiCl-KCl eutectic salt and the latter is LiCl salt. Because of melting point, the immobilization of eutectic salt is carried out at about 770 K, whereas LiCl salt at around 920 K. Such difference has an effect on properties of immobilization media, zeolite A. Here, zeolite A in high-temperature (923 K) molten LiCl salt was characterized by XRD, Ion-exchange, etc., and evaluated if a promising media or not.

### 2. Ceramic Waste Form

#### 2.1 ANL Process

The CWF is produced in a batch process by mixing and blending the LiCl-KCl eutectic salt, periodically removed from the electro-refiner, with zeolite 4A at 770 K to occlude the waste-loaded salt within the cages of the zeolite crystal lattice. Such treatment makes the active fission products (alkalis, alkaline earths, and rare earths) and transuranic elements of the electrolyte. Originally salt-loaded zeolite (SLZ) was mixed with a borosilicate glass and consolidated at high temperature (1120 to 1170 K) and pressure (100 to 170 MPa) in a hot isostatic press (HIP) to make the final waste form. But, the CWF is now fabricated by pressureless consolidation (PC) method, which is putting the glass-mixed SOZ in a kiln with 1120 K for about 4 h at 1 atm. pressure of argon gas. US ANL reported recently that PC CWF showed superior properties in a view of disposal than HIP CWF [2].

### 3. Experimental

#### 3.1 Apparatus

SLZ was prepared by two different methods, batch ion exchange for LiCl/zeolite = 15, 10, 4.5, and direct blending for LiCl/zeolite = 2, 1, 0.5, 0.25. The schematic diagram of a batch ion exchanger was shown in Fig. 1. A detailed description was showed in reference [3].

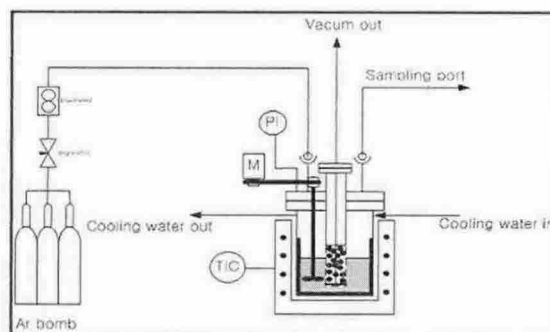


Figure 1. A schematic diagram of a batch ion exchanger.

#### 3.2 Chemicals

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 SrCl<sub>2</sub> (Aldrich, 99.9%) powders in an Ar glove box, and then heating under Ar gas flow. Two types of zeolite A, 4A and 5A (Aldrich, Molecular Sieves), with three different forms, powder (+325 mesh), pellet (1.4 mm), and bead (8-12 mesh) were used. All zeolites were dehydrated before use by heating with a purge of highly-pure nitrogen gas (99.999+%), and stored in an Ar glove box.

#### 3.3 Sample Preparation

For the mixing ratios of LiCl to zeolite,  $r = 15, 10, 4.5$ , the SLZ samples were prepared in a batch ion exchanger. And, for  $r = 2, 1, 0.5, 0.25$ , a direct blender was used to prepare the SLZ samples. A detailed procedure was showed in reference [3].

#### 3.4 Ion Exchange

The ion exchange between zeolite and molten LiCl salt was performed in the batch-type ion exchanger. The

rod with a basket filled with the bead- or pellet-type zeolite was let down for the zeolite to be submerged into the molten LiCl salt of 923 K. For the case of powder-type zeolite was pre-mixed with LiCl powder before placing a reaction vessel in the reactor. The ion-exchanged zeolite was washed free of residual salt on the zeolite surface, and dried at 383 K.

### 3.5 Analysis

The compositions of the sampled salt, such as Na, Ca, Li, Cs, Sr, were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer, Optima 4300). The compositions of the salt-occluded zeolite, such as Na, Si, Al, Ca, Cl, were analyzed by an electron probe X-ray micro-analyzer (EPMA, CAMECA, SX-50). The crystalline structure was analyzed by an X-ray diffractometer (XRD, Philips, X'pert MPD).

## 4. Results and Discussion

### 4.1 Transformation of Zeolite Crystal

The XRD patterns of the ion-exchanged zeolite sample of the bead type zeolite 4A-molten LiCl salt system at 923 K showed a transformation of zeolite crystal from zeolite 4A ( $\text{Na}_{12}\text{Al}_2\text{Si}_{12}\text{O}_{48}$ ) to a major phase of zeolite Li-A ( $\text{Li}_2\text{Al}_2\text{Si}_{12}\text{O}_{80}$ ) for all the mixing ratios. When the mixing ratio was 15 and 10, another minor phase of sodalite ( $\text{Li}_8(\text{AlSiO}_4)_6\text{Cl}_2$ ) was also found. These results are somewhat different from those of the LiCl-KCl eutectic salt - zeolite A system by US ANL. ANL's salt-loaded zeolite sample, which were prepared by blending and ion-exchange at 775 K or 825 K, maintained their original crystal phase, zeolite A, even in the final ceramic waste form which was prepared by the HIP of a mixture of the salt-loaded zeolite with a glass binder at 170 MPa and 900 K [2].

### 4.2 Ion Exchange between Zeolite and Molten LiCl salt

A plot of the Na concentration in the molten LiCl salt during a batch ion-exchange between the molten LiCl salt and the zeolite 4A for  $r=15$  is shown in Fig. 2. The Na concentration reaches a maximum within 1 h, and then decreases slightly. Cs and Sr uptakes in the molten LiCl salt during the batch ion-exchange with the bead type zeolite 4A reach a steady state very quickly, within

1 h of contact, and are maintained constant. These results indicate that the removal of radionuclide by an ion-exchange of zeolite is actually effective only when the concentration of the fission product, here Cs, is high enough, and zeolite maintains its ion-exchange capability even at 923 K. The ion-exchange of the zeolite at a high temperature has to be studied to understand the detailed mechanism.

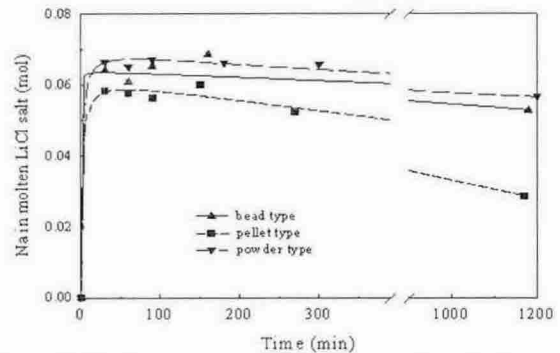


Figure 2. Na-ion uptakes versus contact time in the zeolite A-molten LiCl salt system.

## 5. Conclusion

To develop a treatment process of the waste salt from the ACP using zeolite A, the behavior of zeolite A in molten LiCl salt with CsCl and SrCl<sub>2</sub> at 923 K has been investigated. A batch ion exchange experiment with CsCl and SrCl<sub>2</sub> at 923 K shows that an ion-exchange between the Na<sup>+</sup>-ion in the zeolite A and the Li<sup>+</sup>-, Cs<sup>+</sup>-, and Sr<sup>2+</sup>- ions in the molten salt is very quick. When the zeolite A is contacted with molten LiCl salt, the crystal structure is transformed to zeolite Li-A (major phase), and/or sodalite (minor phase) at a high LiCl/zeolite ratio

## REFERENCES

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- [2] M.A. Lewis, M.C. Hash, A.S. Hebden, and W.L. Ebert, "Tests with Ceramic Waste Form Materials Made by Pressureless Consolidation," ANL-02/10, Argonne National Laboratory (2002).
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