

IMMOBILISATION OF MOLTEN LiCl WASTE USING ZEOLITE A

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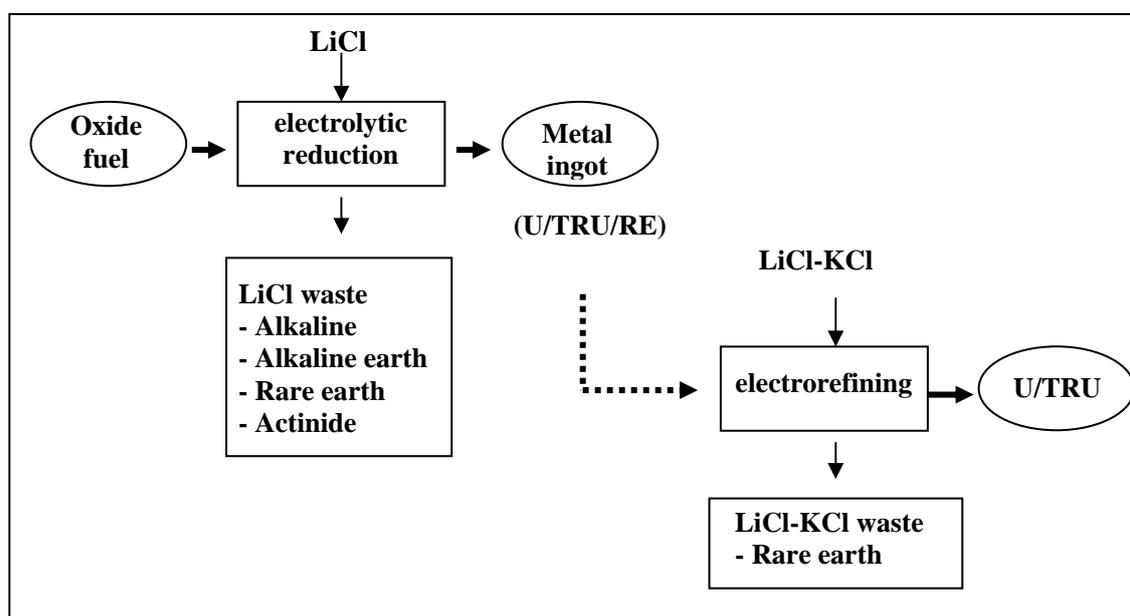
Abstract

The oxide fuel reduction process, based on an electrochemical method as well as the long-lived radioactive nuclides partitioning process based on pyroprocessing, which are being developed at the Korea Atomic Energy Research Institute (KAERI), are to generate molten salt wastes such as a LiCl salt and a LiCl-KCl eutectic salt, respectively. The treatment process of waste LiCl salt, consisting of an incorporation of the salts into zeolite 4A and then a hot pressing with a glass frit to form a salt-loaded waste form, is being studied now. Free chloride content, chemical durability by a 7-day PCT, equivalents of the elements loaded within the salt-zeolite have been compared for the SLZ samples with different mixing ratios of the LiCl salt to zeolite 4A, resulting in an optimum mixing ratio of LiCl to zeolite, $r = 1.0$, which must be confirmed by the long-term behavior of a vitrified waste form.

Introduction

The Korean R&D projects related to the proliferation-resistant back-end fuel cycle, mainly composed of an electrolytic reduction of spent fuel and an electrorefining, as shown in Figure 1, have been developed since 1997. From these processes, two types of waste salts, a LiCl salt from the oxide reduction process and a LiCl-KCl eutectic salt from the electrorefining process for a long-lived radioactive nuclides partitioning, are generated. These waste salts are water-soluble, and are known to be readily radiolyzed to yield interstitial halogens and metal colloids. As the first step to develop a proper method to reduce the waste generation and cost, the optimum immobilization condition using zeolite 4A was investigated.

Figure 1. A concept of the pyrochemical process for the oxide spent fuel in Korea



The fabrication of a ceramic waste form, which was made by a blending of the LiCl-KCl eutectic waste salt with zeolite 4A to occlude the waste-loaded salt within the cages of zeolite and then a mixing with a borosilicate glass frit followed by a consolidation at a pressureless condition, has been recently developed by US Argonne National Laboratory (ANL) [1]. Here ANL showed that zeolite 4A was a good immobilization matrix for waste salt, and did not transform in a zeolite crystal during a blending with the waste salt at 770 K. Such a transformation from zeolite 4A to sodalite happened during the pressureless consolidation (PC), that is, just by putting a glass-mixed salt-loaded zeolite (SLZ) in a kiln at 1120 K for 4 h at 1 atmosphere of argon gas [2].

However, zeolite 4A changed its crystal to that of Li-A when mixed with a molten LiCl at 920 K, as shown in our previous work [3]. This transformation of zeolite 4A into zeolite Li-A or sodalite brings about a need of a characterization of the SLZ to develop a proper mixing ratio of LiCl to zeolite 4A. Thus, some SLZ samples were prepared with different mixing ratios, and then their properties were characterized such as the free chloride content, product consistency test (PCT), phase transition at a high-temperature condition, etc.

Experimental

SLZ sample preparation

For the mixing ratio of LiCl to zeolite, $r = 15, 10, \text{ and } 4.5$, the SLZ samples were prepared in a batch ion-exchange vessel. And, for $r = 2, 1, 0.5, \text{ and } 0.25$, a direct blender was used. A simulated molten LiCl salt was prepared by heating the commercial LiCl powder (Aldrich, 99+%), with CsCl (Aldrich, 99.9%) and SrCl₂ (Aldrich, 99.9%) as two major fission products. The initial concentrations of Cs and Sr were maintained at 4.43 and 1.68 wt%, respectively. In this study, the bead-type zeolite 4A (8 - 12 mesh) were mainly used because of an easy handling. A more detailed procedure is described in our previous work [3].

Free chloride content

A free chloride (or free salt) is the salt that is not occluded within zeolite cages, and exists between crystals or on the surface of a crystal. Especially, the SLZ sample, prepared by an ion-exchange with a pellet- or bead-type zeolite 4A, contained some free chloride, almost up to 25 wt%. Up to now, a standard method to determine the free chloride content has not been defined. US ANL adopted the amount of Cl-ion in a residual solution that was filtered after an immersion of 1 g SLZ in 50 ml demineralized water for 1 min as a 'free salt' [4]. The free chloride content of SLZ in this study was determined by using Equation 1 for only the SLZ samples prepared by blending.

Equation 1

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

Product consistency test (PCT)

The product consistency test (PCT) is an evaluation method of a chemical durability. The PCT-7 day was conducted in accordance with ASTM C1285-94 [5], with the exceptions of using a non-crushed material. 30 mL of demineralized water was used for 3 g of the bead-type SLZ sample. The concentrations of Cs and Sr were measured to calculate the normalized release rate, NR, as shown in Equation 2.

Equation 2

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

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 surface area was measured by BET measurement (Micrometrics ASAP 2400 USA).

Analyses

The elements such as Na, Li, Cs, and Sr for the SLZ sample and leachate were analyzed by a inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer, Optima 4300). These elements were also analyzed by an electron probe X-ray micro-analyzer (EPMA, CAMECA, SX-50). 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, etc.

Results and Discussion

As mentioned above, the free chloride contents of the SLZ samples prepared by an ion-exchange, with $r = 15, 10,$ and $4.5,$ were more than 20 wt%. Thus, the free chloride content was measured for the SLZ samples prepared by blending, with $r = 1.0$ and $0.25,$ as shown in Table 1. The free chloride contents were affected by the mixing ratio, and also might have a certain relation to an addition of alkaline or alkali metal nuclides. When the Cs^+ -ion, which was known to be a more fast and strongly exchanged cation with Na^+ -ion in zeolite [6], is ion-exchanged, it might stand in the path of the water into the zeolite cage.

Table 1. Free chloride content of SLZ sample ($r = 1.0$ and 0.25)

Salt r	LiCl only		LiCl + Cs		LiCl + Sr		LiCl + Cs, Sr	
	1.0	0.25	1.0	0.25	1.0	0.25	1.0	0.25
Free salt content (wt%)	16.3	10.2	11.0	6.2	11.6	8.6	9.6	2.8

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 2. The SLZ samples prepared by an ion-exchange, with $r = 15, 10,$ and $4.5,$ were made by a collection of the solidified LiCl salt with zeolite 4A 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 we did not wash before PCT

Table 2. Normalized release rates of Cs and Sr for SLZ samples

r (=LiCl/zeolite)	NR, g/m ²	
	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 , which were significantly higher than those of the ion-exchanged SLZ samples with $r = 15, 10$ and 4.5 . These results indicate that Sr⁺-ion hardly exchanged with 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 PCT, whereas the not-occluded Sr of the blended SLZ sample was almost totally releases during PCT.

The values of NR(Cs) in this study, $0.55 - 0.83 \text{ g/m}^2$, were just two or three times that of the ceramic waste form, which was made by the following steps at US ANL: preparing the LiCl-KCl eutectic waste salt, drying the powder-type zeolite with a nominal size of $-120 +325$ mesh, blending the zeolite and salt in a rotating dual-cone vessel at 500°C for about 20 h, mixing the glass and SLZ, and a pressureless consolidation at about 900°C for 8 h. Even if we performed a 7-day PCT with an un-crushed SLZ sample, where as ANL did with a crushed sample of the ceramic waste form, the effect of a vitrification for the alkali metal and alkaline earth fission products, such as Cs or Sr, was not significant. These fission products may not be dissolved in the glass binder in a final waste form [1], but they remain as an adsorbed or an ion-exchanged form on the surface of zeolite.

Since Cs has a higher release than the higher valence fission products such as barium, strontium, cerium, lanthanum, and yttrium, and high chloride losses correlated with the high total mass losses, the most important criterion for the waste form containing 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(Sr).

The equivalents of the elements loaded within the SLZ per unit cell according to the LiCl/zeolite 4A ratio, calculated from the ICP analyses for the SLZ samples prepared by a blending ($r = 1.0, 0.5$, and 0.25), are shown in Table 3. The two most important fission products, Cs and Sr, were more occluded within the SLZ sample with $r = 1.0$ than the other two SLZ samples. The SLZ sample with $r = 1.0$, however, released lots of Cl-ions. Therefore, our future work will be concerned with an immobilization of chloride during solidification and an improvement of the chemical durability of the final waste form for longer times. Also, this result needs to be confirmed by a long-term test.

Conclusion

To develop an optimum immobilization condition for molten LiCl waste from the KAERI's electrolytic reduction process of spent fuel using zeolite 4A, we prepared some SLZ samples with different mixing ratios of LiCl salt to zeolite, and then compared the characteristics such as free chloride content, chemical durability by 7-day PCT, equivalents of the elements loaded within the salt-zeolite, etc. These comparisons resulted in an optimum mixing ratio of LiCl to zeolite, $r = 1.0$, which must be confirmed by the long-term behavior of a vitrified waste form.

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Table 3. The equivalents of constituents loaded with the blended SLZ samples per unit cell

	Elements	$r = 1.0$	$r = 0.5$	$r = 0.25$
Total	Li	42.76	26.12	11.02
	Na	3.96	11.97	3.22
	Cs	0.48	0.37	0.12
	Sr	0.60	0.39	0.23
	Cl	NA*	NA	NA
Not occluded	Li	9.23	2.97	0.08
	Na	1.72	4.25	1.71
	Cs	0.11	0.06	0.03
	Sr	0.14	0.09	0.02
	Cl	9.13	7.31	2.01
Occluded within SLZ	Li	33.53	23.16	10.94
	Na	2.25	7.72	1.51
	CS	0.37	0.31	0.09
	Sr	0.46	0.30	0.22
	Cl	NA	NA	NA

* NA: not analyzed

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