

Treatment of Waste Salt from the Advanced spent fuel Conditioning Process (II) - Optimum Immobilization Condition -

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1. Introduction

Since zeolite is known to be stable at a high temperature, it has been reported as a promising immobilization matrix for waste salt. The crystal structure of dehydrated zeolite A breaks down above 1060 K, resulting in the formation of an amorphous solid and re-crystallization to beta-Cristobalite [1]. This structural degradation depends on the existence of chlorides. When contacted to HCl, zeolite 4A is not stable even at 473 K.

The optimum consolidation condition for LiCl salt waste from the oxide fuel reduction process based on the electrochemical method (Advanced spent fuel Conditioning Process; ACP) has been studied using zeolite A since 2001. 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.

In this work, we prepared some samples with different mixing ratios of LiCl salt to zeolite A, and then compared some characteristics such as thermal stability, salt occlusion, free chloride content, leach resistance, mixing effect, etc.

2. Results and Discussion

2.1 Thermal Stability

Salt-loaded zeolite (SLZ) samples were tested by thermogravimetry (TG). Zeolite is generally one of very hygroscopic materials, and especially zeolite 4A is widely used as an absorber. However, if zeolite occluded salt, it is not an absorber any more. During the TG test up to 920 K, the maximum weight reduction of SLZ sample, contained even hygroscopic water, was less than 5 %, which means the SLZ hardly absorbs water even room storage condition.

2.2 Salt Occlusion

US ANL reported that zeolite A could occlude about 11 Cl-ions per unit cell. However, zeolite 4A can easily transform into Sodalite, one of natural zeolite, under high temperature condition with salt. If zeolite 4A transformed to Sodalite, a Cl-occlusion ability of Sodalite within internal cages would reduce to one third

of that for zeolite 4A [2]. A more compact sodalite structure than that of zeolite 4A does not have alpha cages, and all of the chlorides, as well as the cations, must reside in the beta cages, which has a pore diameter, 0.25 nm. Because unit cell contents of zeolite A and sodalite are different each other, a comparison for the amounts of Cl-ions per unit cell is not easy. The amounts of Cl-ions per unit cell, calculated relatively on the basis of the same amount of alumina, were a maximum of 3.8 for the SLZ sample.

2.3 Free Chloride Content

Free chloride is the salt that is not occluded within zeolite cages, and exists between crystals or on the surface of crystal. Especially, the pellet-type SLZ samples prepared by ion exchange contain lots of free chloride, up to 25 wt%. A standard method to determine the free chloride content does not exist up to now. US ANL adopted the amount of Cl-ion in residual solution that filtered after immersion of 1 g SLZ in 50 ml demineralized water for 1 min [3]. The free chloride content of SLZ in this study was determined for the SLZ samples prepared by blending, as of Eq. (1), showed in Table 1.

$$\text{Free Chloride Conc.} = 100\% \times \frac{x \cdot \frac{\mu\text{g Cl}^-}{\text{mL H}_2\text{O}} \cdot V_{\text{H}_2\text{O}} \cdot \frac{\text{g Cl}^-}{10^6 \mu\text{g Cl}^-}}{m_{\text{sample}} (\text{g})} \quad (1)$$

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

r (=salt/zeo l.)	LiCl only	LiCl + Cs	LiCl + Sr	LiCl+Cs
	1.0	1.0	1.0	1.0
0.25	0.25	0.25	0.25	0.25
Free salt content	16.3	11.0	11.6	9.6
	10.2	6.2	8.6	2.8

2.4 Leach Resistance

The leach resistance of SLZ samples was evaluated by PCT-7 day test [4], whose results, calculated in normalized release rate (NRR) for Cs and Sr, are showed in Tab. 2. Since PCT test was performed after removal of free chloride for the fist three SLZ samples, their NRR values were somewhat lower than those of the other samples.

Table 2. Normalized release rates of Cs and Sr

r of SLZ	NRR, g/cm ² day	
	Cs	Sr
15	6.2	1.1
10	98.3	0.6
4.5	23.5	0.9
1.0	78.5	394.8
0.5	117.9	579.7
0.25	102.4	110.0

2.5 Optimum Immobilization Condition

The equivalents of nuclide elements loaded within zeolite per unit cell according to mixing ratio of LiCl to zeolite 4A, calculated from an ICP analysis for the SLZ samples prepared by blending ($r = 1.0, 0.5, \text{ and } 0.25$), were showed in Tab. 3. As shown in this table, the SLZ sample of $r=1.0$ occluded more Cs- and Sr-ions than others. And, this sample also showed a good leach resistance, as described in above section.

Table 3. The equivalents of constituents loaded within zeolite per unit cell ($r = 1.0, 0.5, 0.25$)

	element	$r = 1.0$	$r = 0.5$	$r = 0.25$
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
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
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

Actually the long-term behavior of final waste form is more important in a view of disposal. Therefore, this result needs confirmation by the long-term characterization such as a leach or a durability test of solidified waste form.

5. Conclusion

To develop an optimum immobilization condition for molten LiCl waste from ACP using zeolite A, we prepared some SLZ samples with different mixing ratios of LiCl salt to zeolite A, and then compared the characteristics such as thermal stability, salt occlusion, free chloride content, leach resistance, mixing effect, etc. These comparisons bring an optimum mixing ratio of LiCl to zeolite, $r = 1.0$, which result needs to be confirmed by the long-term behavior solidified waste form

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