

## Immobilization of molten salt waste into $MZr_2(PO_4)_3$ (M=Li, Na, Cs, Sr)

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Amorphous zirconium phosphate ( $Zr(HPO_4)_2 \cdot nH_2O$ , AM-ZP) has been investigated as a material for selective removal of Cs or Sr from molten salt waste at aqueous state and its ceramic waste form. NZP ( $MZr_2P_3O_{12}$ , M=Li, Na, Cs, and Sr), was synthesized by three methods and evaluated their durability by the Product Consistency Test (PCT) method. AM-ZP has a high selectivity on Cs and Sr even in the presence of Li with high concentration. From the leaching data, the leached fractions ( $LF_\infty$ ) of each product at a given time in infinite leachate volume can be calculated by a semi-empirical equation. The  $LF_\infty$  of Li, Na, Cs and Sr on the product prepared by composition-adjusting process were 0.143, 0.078, 0.017, and 0.034, respectively. It can be concluded that AM-ZP is an effective material for selective removal of radionuclides from molten salt waste and its metal-loaded ZP can be changed into a durable waste form close to NZP structure by a composition-adjusting process.

### Introduction

In the treatment of liquid radioactive wastes,  $^{137}Cs$  and  $^{90}Sr$  are major radionuclides to be selectively removed and immobilized into durable host materials by reasonable processes. For the selective removal of radionuclides, inorganic ion exchangers as the separation agent were preferred to organic systems because the former has superior radiation stability and thermal stability. In choosing a useful ion-exchanger, it should be considered its immobilization-ability as a host matrix of radionuclides because the Cs- or Sr-loaded materials need to be changed to the monolithic waste form for the final disposal.

Group (IV) phosphates has been interested recently by their unique properties: high thermal, radiation and chemical stability, resistance to oxidation, and selectivity to certain ions and molecules.<sup>1</sup> Also, NZP (sodium zirconium phosphate) has been considered one of potential candidates as a durable host material which can immobilize various elements into its crystalline structure.<sup>2</sup> Among the phosphate ion-exchangers, amorphous zirconium phosphate or its crystalline form ( $\alpha$ -ZrP,  $Zr(HPO_4)_2 \cdot H_2O$ ) is an effective material used to remove  $^{137}Cs$  and  $^{90}Sr$  from the aqueous wastes because the metal-loaded ZrP can be easily converted into NZP structure by heating to about 1000 °C.<sup>3</sup>

Molten salt waste, which generated from electro-metallurgical process recovering uranium and transuranic elements, consists of mainly metal chlorides (90 wt% LiCl, 10 wt% CsCl/SrCl<sub>2</sub> and a minor quantity of actinide oxides in Korea)<sup>4</sup> and can not be directly applied to vitrification or ceramization for the final disposal because of their volatility and high content of alkali salts. Unlike from the ANL method using zeolite

to treat salt waste at molten phase,<sup>5–7</sup> our research group considered a new concept using ZrP in aqueous salt solution. It is desirable to use ZrP for the treatment of molten salt waste because the presence of lithium ions would not be deteriorous to Cs ion-exchange.<sup>8</sup> It has been also reported that Cs can be immobilized by a crystalline Zr phosphate with a three dimensional structure ( $CsZr_2P_3O_{12}$ ) by ion-exchanging Cs into  $\gamma$ -ZrP ( $Zr(HPO_4)_2 \cdot 2H_2O$ ) and subsequent heat-treatment at 850–1000 °C.<sup>9</sup> This method, however, indispensably generates undesirable phase of  $ZrP_2O_7$  or  $CsPO_3$ , resulting poor leach-resistance.<sup>10</sup>

The present paper reports the behavior of ion-exchange on amorphous ZrP to treat the aqueous salt solution and the durability of the product to stabilize unstable phases generated during the heat-treatment of metal-loaded ZrP for the phase change into NZP structure.

### Experimental

#### Materials

LiCl, CsCl and SrCl<sub>2</sub> (99% purity, Junsei, Japan) as surrogates of radioactive molten salt waste were used in this study. Amorphous  $Zr(HPO_4)_2 \cdot nH_2O$  (AM-ZP) were prepared by using  $ZrCl_4$  (99% purity, Showa, Japan) and  $H_3PO_4$  (85% purity, Showa, Japan). Solution A contains required amounts of metal chloride dissolved in 50 ml  $H_2O$  and Solutions B and C contain  $ZrCl_4$  and  $H_3PO_4$ , respectively. As a gelling agent and stabilizer, sodium silicate (36 wt%  $Na_2O$  and 64 wt%  $SiO_2$ , Junsei, Japan) was used. For the ion-exchange experiment, AM-ZP was synthesized by a procedure given elsewhere.<sup>11</sup> With P/Zr molar ratio of 2, Solution C was poured into Solution B. The mixture was strongly stirred for 24 hours, filtered, washed with deionized water and dried at 110 °C for 1 day. This product was used in the IEP.

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*Ion-exchange and synthesis of NZP*

(a) *Ion-exchange process (IEP)*: In order to confirm the selectivity of AM-ZP on the metal elements, equilibrium ion-exchange experiment was carried out with 1 g of AM-ZP in 100 ml of salt solution containing single component or multi-component system at 30 °C for 7 days. Also, the removal behavior of Cs in the presence of high concentration of Li was investigated in order to confirm the applicability of AM-ZP to the molten salt waste. Also, the immobilization of Cs or Sr by using AM-ZP at 30 °C was carried out with 10 g of AM-ZP in 100 ml of Solution A at 2M for 7 days for the perfect saturation. The saturated AM-ZP was washed thoroughly with deionized water and dried at 110 °C. These AM-ZPs were heat-treated at 700, 800 and 900 °C for 2 hours and their phase change into NZP structure was investigated by XRD analysis. The materials synthesized by this method were named as AM-LiZP, AM-NaZP, AM-CsZP and AM-SrZP.

(b) *Precipitation process (PP)*: This process is to synthesize NZP structure as well as to simulate the local imperfect reaction which might be indispensably generated in the ceramization of radioactive wastes. Imperfect reaction can be simulated by the use of excess amount of Zr and P to confirm that the radionuclides are completely immobilized in NZP structure. For this purpose, the batch composition of metal elements was fixed at 80% of reaction ratio (metal:Zr:P = 0.8:2:3, not 1:2:3). Mixture of Solutions A and C with required molar ratios was poured into Solution B and strongly stirred for 2 hours for obtaining a homogenized white slurry. The mixture was moved into tightly sealed plastic bottles and placed into an electric oven at 70 °C for 3 days. For slow drying, the seal was punched to make a few holes. The samples were dried at 70 °C for 3 days, and subsequently at 110 °C for 2 days. They were heat-treated at 600, 700, 800, and 900 °C for 2 hours and analyzed by XRD. The materials synthesized by this method were named as PP-LiZP, PP-NaZP, PP-CsZP and PP-SrZP.

(c) *Composition-adjusting precipitation/gelation process (CPGP)*: In order to use the  $Zr(HPO_4)_2 \cdot nH_2O$  as an ion-exchanger and a host material for radionuclides, it is necessary to stabilize the unstable phase and to make the structure of heat-treated materials close to NZP ones. This was carried out by the addition of sodium silicate to the precipitation process (PP). The amount of sodium silicate was determined by considering the amount of metal element in the reaction. Its experimental procedure is the same as the PP procedure, except that sodium silicate solution was poured into the white slurry mixture before the placement into the electric oven and the final mixture was additionally stirred strongly for 1 hour. These materials synthesized by CPGP were named as GP-LiZP, GP-NaZP, GP-CsZP and GP-SrZP.

*Product consistency test (PCT)*

The durability test was carried out by the PCT method. The heat-treated products (900 °C) of each procedure were chosen as test samples. The products were pulverized and fractioned with metal sieve in size of 75–150  $\mu m$ . The leachate/sample ratio (ml/g) was changed from 100 to 1000. The leaching test was conducted at 90 °C for 7 days and the leached solution was analyzed by ICP-MS and AAS.

**Result and discussion***Selective removal of radionuclide by AM-ZP*

It was noticed that there exists Li as a competitive cation in high concentration in molten salt waste. It is important to confirm whether Cs as a volatile radionuclide could be preferentially immobilized into AM-ZP or not. This was evaluated by equilibrium ion-exchange experiments. Figure 1 shows the ion-exchange isotherm of the elements at 30 °C. The ion-exchange capacity of each cation ( $Q_{max}$ ) was obtained by fitting the data with the Langmuir model:

$$Q = Q_{max} \cdot b \cdot C_{eq} / (1 + b \cdot C_{eq})$$

where  $Q$  is the amount of ion-exchanged metal ions per gram of AM-ZP (meq/g),  $C_{eq}$  is the equilibrium concentration of the metal ions in solution (mol/l),  $Q_{max}$  is the monolayer capacity (or maximum capacity) and  $b$  is a parameter of the Langmuir isotherm. The Langmuir model was fitted with the experimental data. The ( $Q_{max}$ ) values of Li, Na, Cs and Sr were 0.41, 0.59, 1.07, 0.67 meq/g, respectively. For Cs, the ion-exchange capacity of amorphous  $Zr(HPO_4)_2 \cdot nH_2O$  was about 1 meq/g. Figure 2 shows the removal efficiency of the cations under equimolar concentrations. The  $x$ -coordinates express the ratio ( $R$ ) of the amount of Cs in the solution to the maximum capacity of Cs. In the given range of  $R$ , the AM-ZP shows much higher removal of Cs than those of other cations and the order of removal was the same as the capacity for each element. It is noticed that the removal of Sr and Na rapidly decreased above  $R=0.25$ , where the total amount of metal cations in the solution is equal to the capacity of Cs. Li was slightly removed in the given conditions. The increase of  $R$ , which means the increase of the excess amount of metal cations in the solution compared to the capacity of AM-ZP, shows mainly the removal of Cs. The selectivity ( $\alpha$ ) of Cs on the competitive ions can be expressed as:

$$\alpha = \frac{\text{Amount of Cs sorbed on AM - ZP}}{\text{Amount of competitive ions sorbed on AM - ZP}}$$

As shown in Fig. 3,  $\alpha_{Li}$  has much higher value than that of Na or Sr, suggesting that AM-ZP is possible to apply to a waste solution with the presence of Li at high concentration. With increasing  $R$ ,  $\alpha_{Li}$  sharply decreased below  $R=0.25$  and slowly changed above  $R=0.5$ , while  $\alpha_{Na}$  or  $\alpha_{Sr}$  rapidly increased to about  $R=1.0$ , and then decreased. This trend of the selectivity of Cs suggested that the selective immobilization of Cs or Sr into AM-ZP from molten salt solution is possible. This can be confirmed with experiments with real Li/Cs molar ratio

of 50, in molten salt waste. Figure 4 shows the results of the equilibrium experiments with changing the mass of AM-ZP at the same Li/Cs ratio. The removal efficiency of Cs approached to 95% at the mass/volume = 9 g/100 ml and the removal of Cs was not affected by the existence of Li with high concentration. From the results described above, the AM-ZP could be applied to the selective removal of Cs in molten salt waste and this can give the resistance of Cs to the volatilization at high temperature.

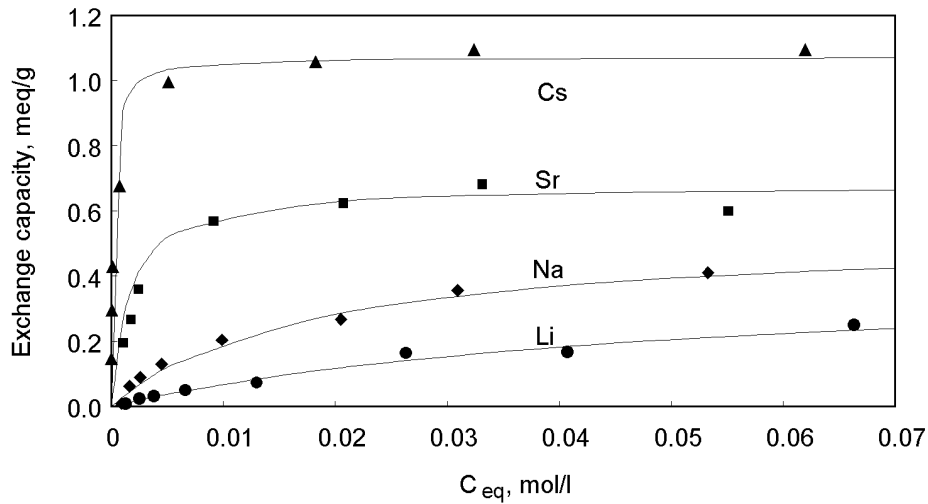


Fig. 1. Ion-exchange isotherm of amorphous zirconium phosphate for Li, Na, Cs, and Sr at 30 °C

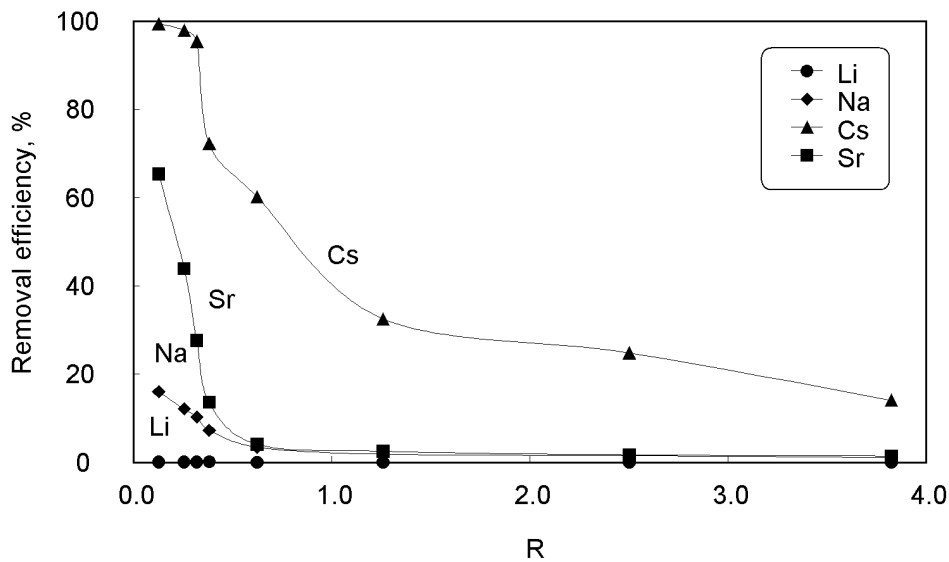


Fig. 2. Removal efficiency of amorphous zirconium phosphate of Li, Na, Cs and Sr in equimolar multi-component system at 30 °C,  $R = (\text{amount of Cs in solution})/(\text{maximum capacity of amorphous zirconium phosphate})$

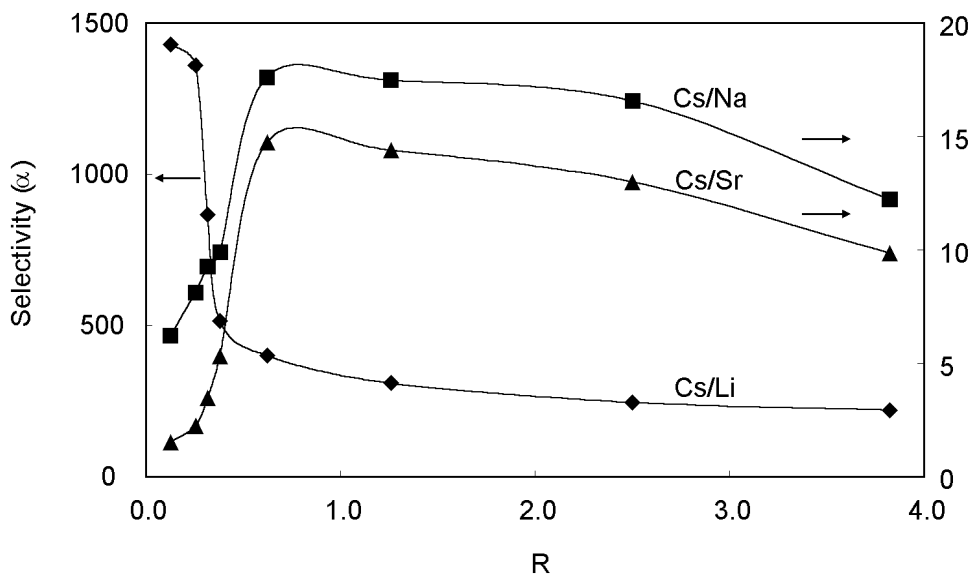


Fig. 3. Selectivity of Cs on Li, Na and Sr in equimolar multi-component system at 30 °C

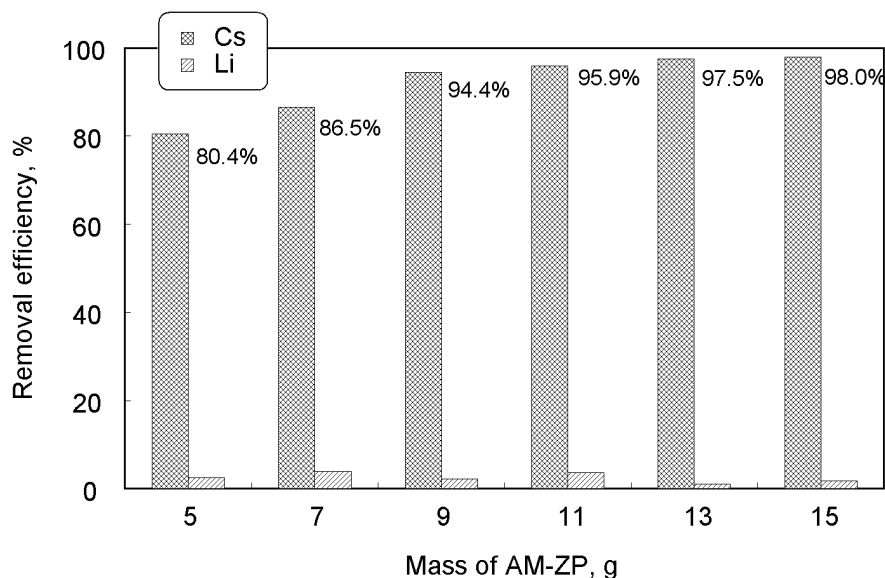


Fig. 4. Removal efficiency of Cs and Li with various mass of amorphous zirconium phosphate at  $LiCl/CsCl = 50$  and  $LiCl = 2M$  (mol/l)

*Development of NZP structure by each procedure*

Our concern on the treatment of radioactive molten salt was whether the radionuclides could be stabilized into a durable material, generating little secondary radioactive waste due to the volatilization and controlling the unstable phase due to imperfect reaction. The results of ion-exchange experiments indicated that Cs interacted with AM-ZP. Followed by this experiment, it was confirmed that the NZP phase could be developed from metal-loaded AM-ZP by heat-treatment. Because of the low content of Cs or Sr in

molten salt waste, it is difficult to assign the phase change of Cs-loaded AM-ZP or Sr-loaded AM-ZP processed with a waste of real composition. The IEP method to synthesize NZP structure can be considered to verify the structural change of metal-loaded AM-ZP into NZP phase. Figure 5 shows the XRD patterns of no metal-loaded AM-ZP heat-treated at different temperature. The AM-ZP with layered two dimensional structure was changed into  $ZrP_2O_7$  above 600 °C, in contrary to  $HZr_2(PO_4)_3$  with three dimensional structure. However, the AM-ZP saturated with each element at high concentration contained metal zirconium

phosphate [MZP:  $NaZr_2(PO_4)_3$ ,  $CsZr_2(PO_4)_3$ ,  $SrZr_4(PO_4)_6$ ] with three dimensional structure as well as  $ZrP_2O_7$  after the heat-treatment, as shown in Fig. 6. In Li-loaded AM-ZP, a layered structure of  $Li_2Zr(PO_4)_2$ , was formed under the same condition. Metal-loaded AM-ZP was easily converted into durable NZP phase by heat treatment but this procedure can generate undesirable  $ZrP_2O_7$  phase by dehydration of  $Zr(HPO_4)_2$ .  $ZrP_2O_7$  would be hydrolyzed into  $Zr^{4+}$  and polyphosphate ions, decreasing the pH of the aqueous environment.

As shown in Fig. 6, the synthesized products by the PP method contained NZP phase and  $ZrP_2O_7$  after heat-treatment at 900 °C. The PP method was intended to simulate the imperfect reaction of NZP under non-equivalent reaction ratio which could be processed always at heterogeneous precipitation reaction system in  $\mu m$  scale. From the XRD analysis, the product of imperfect reaction was  $ZrP_2O_7$ . This means that this phase could be inevitably generated and should be considered as a primary phase to be controlled to accomplish the structure close to NZP ones. Other

undesirable phases that might exist in the product could not be detected by XRD analysis. Also, it is noticed that an undesirable phase with layered two dimensional structure,  $Li_2Zr(PO_4)_2$ , was not formed by the PP procedure. In the PP process, AM-ZP at the initial step of the precipitation reaction would be formed and the subsequent ion-exchange be proceeded. At the ion-exchange step, the difference between IEP and PP method would be the localization of metal in AM-ZP. In the case of IEP procedure, the uptake of metal takes place in the bulk phase separation from the solution and the metal cations diffuse to the surface of AM-ZP. However, in the PP procedure, AM-ZP is formed under the existence of metal cations and this makes the diffusion-distance of metal be short and no bulk separation occurs. Therefore, the localization of metal in AM-ZP is lower in the PP method than in the IEP method. This is why a layered structure was not formed in the PP method. These results indicated that in the treatment of molten salt waste by NZP ceramic waste form, the undesirable phases can be controlled, but  $ZrP_2O_7$  is not avoidable.

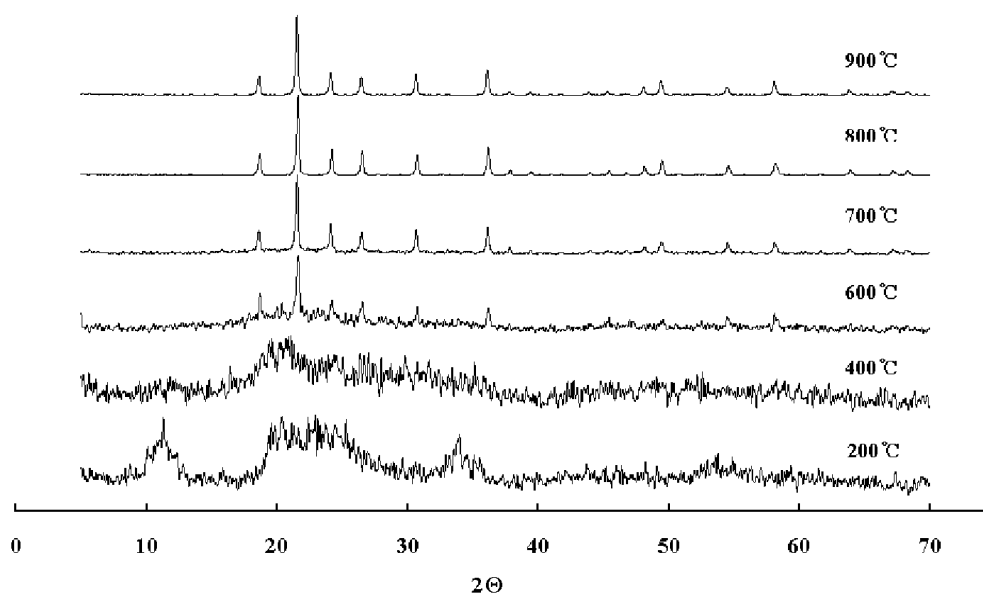
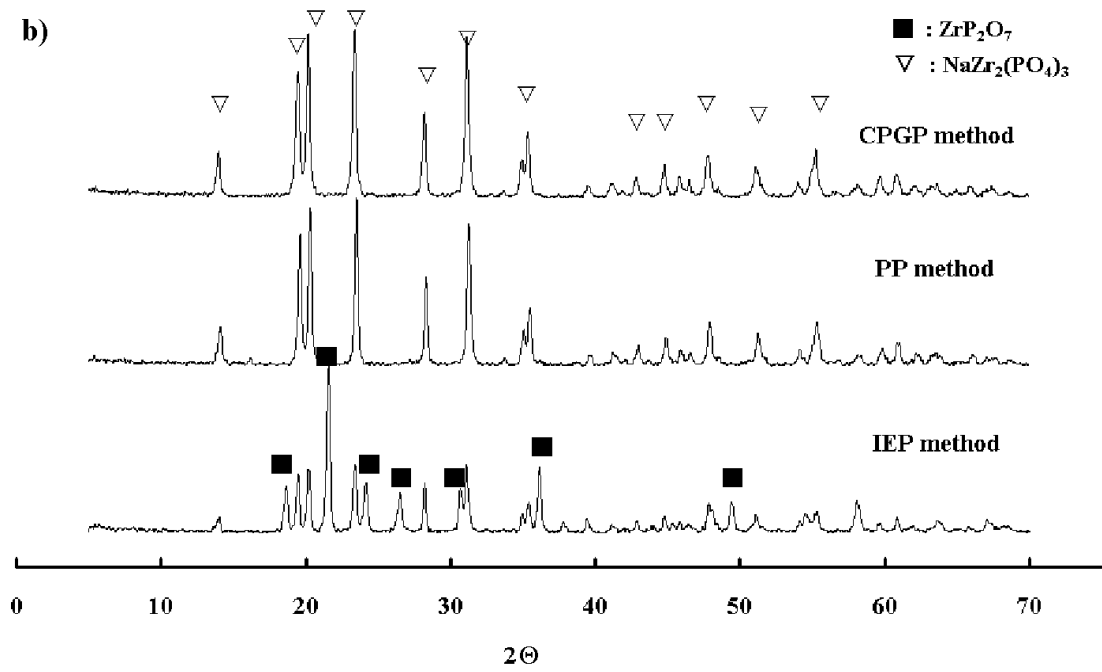
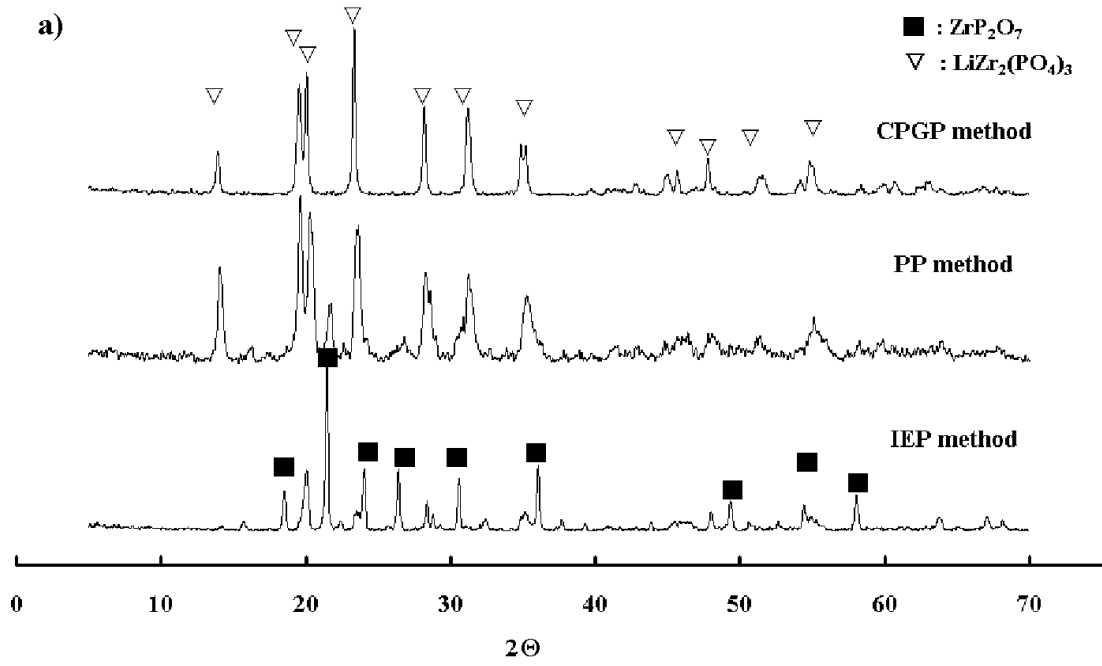


Fig. 5. XRD patterns of no metal-loaded amorphous zirconium phosphate heat-treated at different temperatures for 2 hours



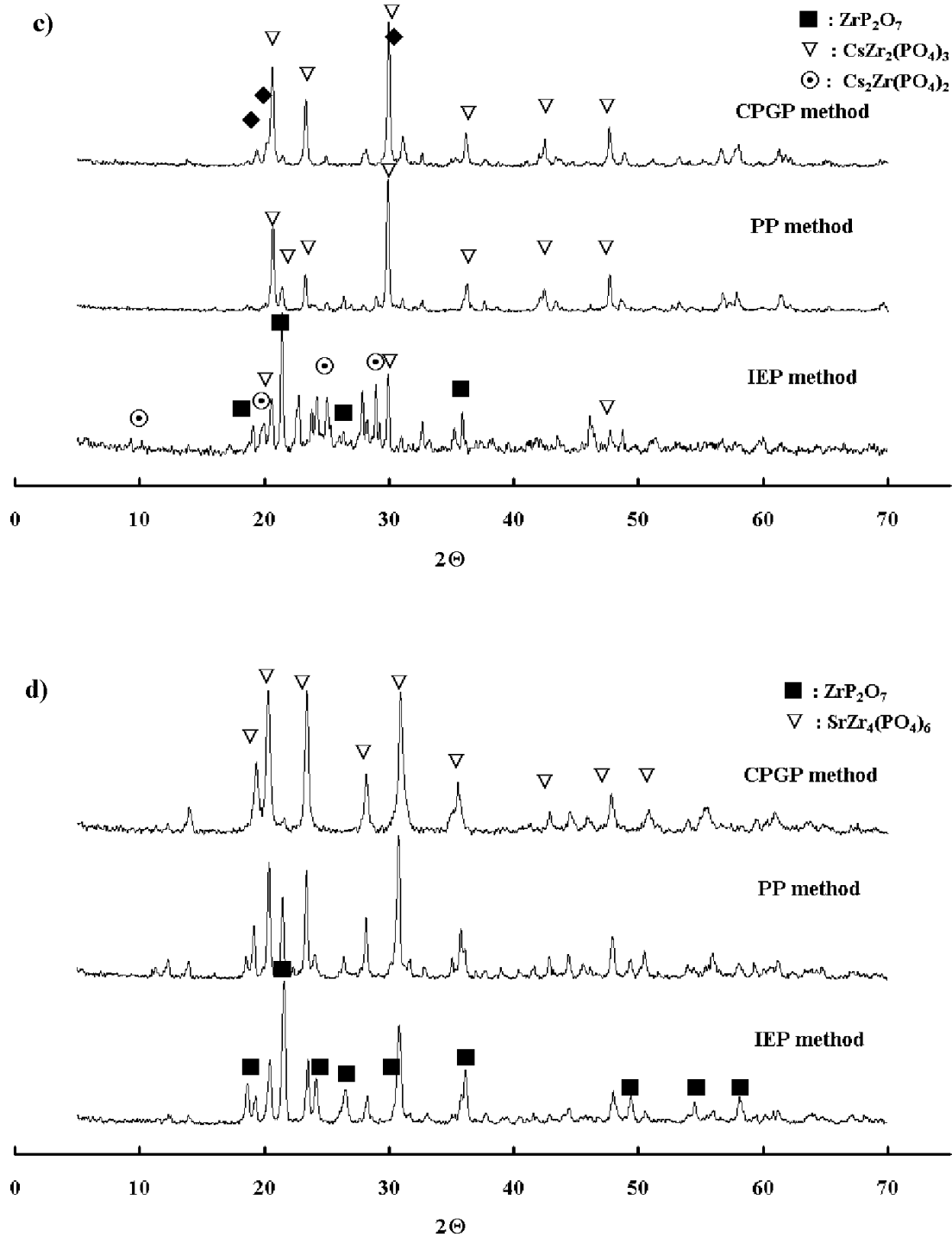


Fig. 6. XRD patterns of the products synthesized by various methods after heat-treatment at 900 °C; (a) Li, (b) Na, (c) Cs, (d) Sr

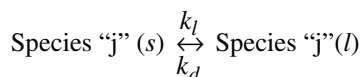
The ceramization of waste requires an excess amount of material to embrace radionuclides. In NZP ceramic waste form, this can generate an undesirable phase described above. The selectivity of Cs on the AM-ZP enables us to solve this problem. For the perfect

conversion of Cs into NZP structure, non-equivalent reaction ratio is required and the product contains an undesirable phase caused by the insufficient amount of metal. CPGP method can solve this problem. All the products synthesized by CPGP method are formed as

only NZP structure without ZrP<sub>2</sub>O<sub>7</sub> or layered structure after the heat-treatment above 900 °C. The addition of sodium silicate solution gives rise to two positive effects: (a) adjusting the required amount of metal in NZP structure and (b) gelation of the reaction system. The selectivity of AM-ZP makes Cs sorbed, Na would supplement the amount of metal required to the NZP structure rather than act as a competitive ion. This way Cs is perfectly immobilized into the NZP structure. As shown in Fig. 6c, GP-CsZP contains mainly CsZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub> and NaZr<sub>2</sub>P<sub>2</sub>O<sub>12</sub> as a minor phase.

*Evaluation of the durability by Product Consistency Test (PCT)*

In addition to the undesirable phase, other phases that might not detected by XRD analysis would affect the durability of the ceramic waste form. Depending on the synthesis methods, its crystallinity might be changed. The leaching procedure of a sample is affected by various known, not exactly defined physico-chemical interactions: diffusion, dissolution-precipitation, sorption-desorption, etc. Generally, the leachate/sample ratio in PCT method is very high compared to the solubility of durable materials and the chemical modification at the surface of the sample could take place with the change of equilibrium concentration. PESCATORE et al.<sup>12</sup> suggested a complex leaching model describing surface phenomena based on the kinetics of exchanges of species between the surface of solid (s) and the aqueous solution (l):



where  $k_l$  and  $k_d$  are phenomenological rate constants describing the kinetics of all elementary processes: releasing or attaching species from or onto the surface,

respectively. In a short time, the cumulative fraction leached can be expressed by:

$$F(t)=k_l(1-\exp[-(k_l+\beta k_d)t]) \tag{1}$$

where the constant  $\beta$  is related to the ratio of solid surface area to aqueous solution volume. Introducing the overall distribution constant  $K$ , Eq. (1) can be reduced to:

$$\begin{aligned} K &= f(1/V) \\ K &= -m/V+n \end{aligned} \tag{2}$$

$$K = k_l/k_d \approx \text{leached fraction}/(1-\text{leached fraction})$$

where  $m$  and  $n$  are constants. When the volume of leachate is close to infinite,  $K_\infty=n$ , where the concentration gradient and mass transfer rate is maximum. The parameter,  $m$ , is related to the surface area of the solid sample and indicate the stability of the product. With these values, the products prepared by the three methods can be evaluated. Using the experimental data, Fig. 7 was obtained as  $K$  versus  $V$  and each  $K_\infty$ ,  $m$  and  $LF_\infty$  is indicated in Table 1.

The value of  $K_\infty$  of AM-LiZP, AM-NaZP and AM-CsZP products slightly changed with  $V$  and are very high. This could be attributed to the unstable phase in these products. The  $K_\infty$  of the products synthesized by PP or CPGP methods are relatively lower than that by IEP method and well fitted with Eq. (2). The value  $m$  of each product shows the stability of NZP for each metal, where lower  $m$  means higher stability. CsZP and SrZP had lower  $m$  than LiZP and NaZP. From these  $m$  and  $n$ , it could be concluded that the product by CPGP method has lower amount of unstable fraction than those by other methods and shows the highest durability. It was noticed that the leached fraction of Sr changed little regardless of the synthesis methods. Alkaline earth elements can react with phosphate to produce stable products and this is why the leached fraction of Sr is low even in the product by the IEP method.

Table 1. Comparison on the overall distribution constant ( $K_\infty$ ) and leached fraction ( $LF_\infty$ ) at a given time in infinite leachate volume

Element	$K_\infty (=n)$			$m$			$LF_\infty$		
	IEP	PP	CPGP	IEP	PP	CPGP	IEP	PP	CPGP
Li	2.266	0.305	0.167	–	9.79	11.81	0.694	0.234	0.143
Na	0.396	0.161	0.084	–	6.23	3.72	0.284	0.139	0.078
Cs	0.360	0.036	0.017	–	1.24	0.67	0.265	0.035	0.017
Sr	0.036	0.050	0.035	–	2.38	1.96	0.035	0.048	0.034



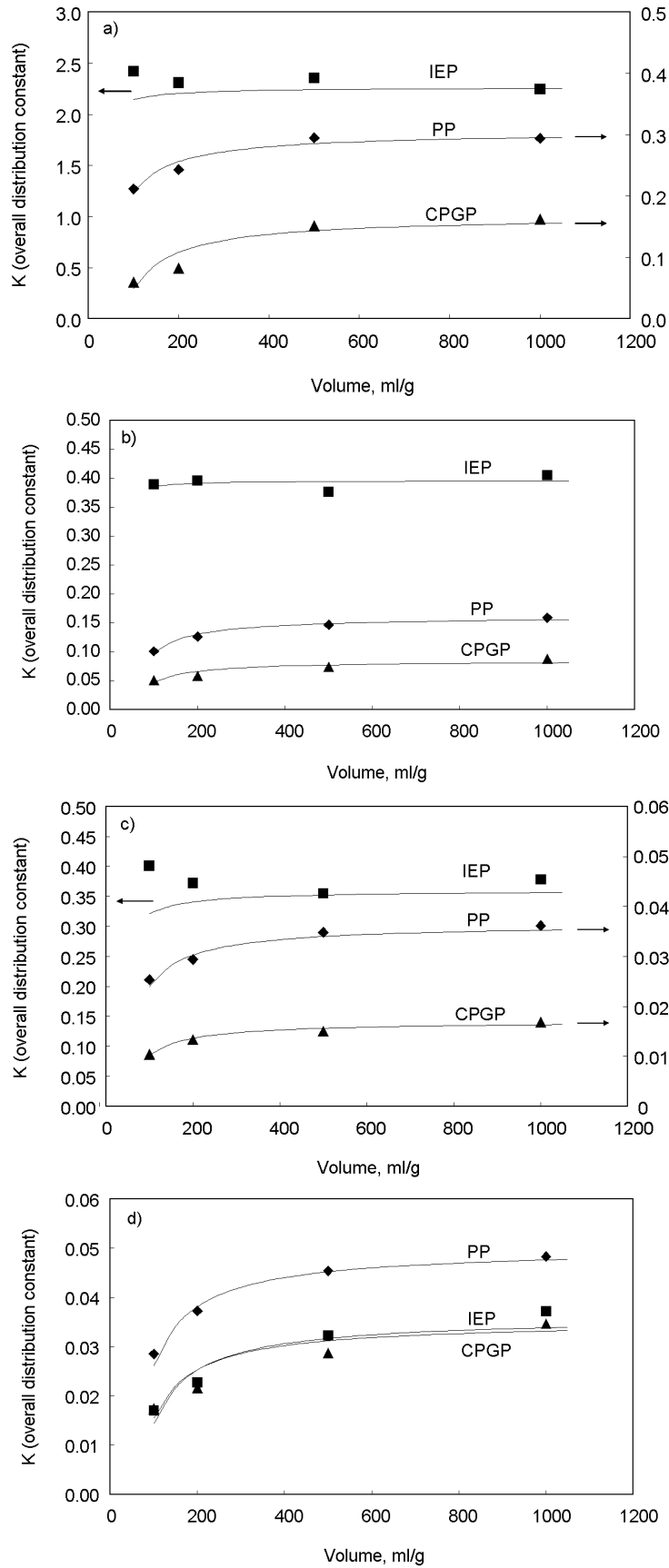


Fig. 7. Leaching behavior of the product prepared by various methods; (a) Li, (b) Na, (c) Cs, (d) Sr

### Conclusions

From the results of the equilibrium ion-exchange experiments, the amorphous ZrP can selectively remove Cs or Sr in the presence of a competitive ion of high concentration and could be applied to the molten salt waste for the recovery of LiCl. However, the metal-loaded ZrP after heat-treatment was not perfectly converted into NZP structure and contained high content of unstable phases ( $LF_\infty = 0.265$  for Cs). Using sodium silicate solution for the stabilization of the unstable phase makes the product close to the NZP structure and  $LF_\infty$  lower than ten times. Amorphous ZrP is a useful material for the selective removal of Cs or Sr from molten salt solution and can be changed into a durable host material of radionuclides by the composition-adjusting process.

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