Phosphates behaviours in conversion of FP chlorides

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ABSTRACT

The spent electrolyte of the pyroprocessing by metal electrorefining method should be considered for recycling after removal of fission products (FP) such as, alkali metals (AL), alkaline earth metals (ALE), and/or rare earth elements (REE), to reduce the volume of high-level radioactive waste. Among the various methods suggested for this purpose is precipitation by converting FP from chlorides to phosphates. Authors have been carrying out the theoretical analysis and experiment showing the behaviours of phosphate precipitates so as to estimate the feasibility of this method. From acquired results, it was found that AL except lithium and ALE are unlikely to form phosphate precipitates. However their conversion behaviours including REE were compatible with the theoretical analysis; in the case of $LaPO_4$ as one of the REE precipitates, submicron-size particles could be observed while that of Li_3PO_4 was larger; the precipitates were apt to grow larger at higher temperature; etc.

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1. Introduction

For the reprocessing in the nuclear fuel cycle system, the aqueous method applying a liquid–liquid extraction known as Purex process is the current widespread method used in several countries. On the other hand, the pyroprocessing as non-aqueous reprocessing is regarded as a promising candidate corresponding to some of the next generation reactors [1]. There are several kinds of pyroprocessing, e.g., the fluoride volatility process by fluorination, the liquid–liquid extraction process by melts, the pyrochemical process by molten salt as medium, etc. Among them, the pyrochemical process is evaluated as a complementary concept for the fast reactor (FR) metal fuel reprocessing in FaCT (Fast Reactor Cycle Technology Development) project designated as one of the national critical technologies of Japan [2]. The pyrochemical process, however, possessing its inherent problems have yet to be solved. For example, the removal of fission products (FP) in the spent electrolyte. The treatment by the zeolite sorption method [3–5] following actinoid elements (An) recovery by reduction and extraction [6] should be further established to reduce the volume of high-level radioactive waste (HLW).

The [3LiCl(59 mol%)–2KCl(41 mol%)] eutectic medium used in the pyrochemical process by the electrorefining method will be contaminated by the accumulation of various An and FP due to prolonged electrolytic operation. The eutectic medium containing An and/or FP, regarded as a spent electrolyte at certain stage, can cause the rising of the melting point of the electrolytic bath and/or lowering the current efficiency. Some measures e.g., its replacement by a virgin medium, etc. should be taken to maintain its stable condition. The constant replacement of the electrolyte, however, could lead to the generation of enormous volume of HLW because the spent electrolyte as a waste salt is classified as HLW. In terms of environmental load reduction and economical improvement, it is desirable to have the spent electrolyte purified for recycling by removing its FP.

Besides the zeolite sorption method mainly developed at the Argonne National Laboratory in the USA, the contaminants precipitation methods by converting contaminants to insoluble compounds are undertaken by the Research Institute of Atomic Reactors [RIAR] [7] in Russia as well as a few other countries that are anticipated to reduce the total volume of HLW. In the case of the contaminants precipitation method developed by RIAR, their objective is to remove contaminants such as the MA and the rare earth elements [REE] from NaCl to 2CsCl, the medium component, before its disposal. Although RIAR has proven its conceptual validity, further investigation is required for its possible application to the spent 3LiCl–2KCl electrolyte recycle process due to differences in the chemical composition, operational temperature, etc.

In this paper, the preliminary experiment is carried out to assess the feasibility of the conversion method using phosphate as additive for the removal of various FP chlorides in 3LiCl–2KCl melt. In the experiment, typical simple salt, i.e., LiCl or CsCl as alkali metal chloride, $SrCl_2$ as alkaline earth metal chloride, or $LaCl_3$ as lanthanoid chloride, is used as phosphate conversion target and then recovery methods of FP constituents in the melt are discussed from obtained results by the thermodynamic approach.

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2. Experimental

To understand the phosphate conversion behaviours of FP chlorides, the surrogate spent electrolyte was made up by mixing 20 g of 3LiCl–2KCl eutectic (Aldrich-APL USA, 99.99% purity) and 0.05 mol of simple salt that is LiCl (Sigma–Aldrich Co., 99.995% purity), CsCl (Kojundo Chemical Laboratory Co. Ltd., Japan, 99.999% purity), $SrCl_2$ (Aldrich-APL USA, 99.99% purity) or $LaCl_3$ (Kojundo Chemical Laboratory Co. Ltd., 99.9% purity) in an alumina crucible (Nikkato Corp. Japan, 52 mm OD × 67 mmH, 99.6% purity). Then 3 or 4.5 times more of the required equivalent for conversion of additive such as Li_3PO_4 (Kojundo Chemical Laboratory Co. Ltd., 99% purity) or K_3PO_4 (Kojundo Chemical Laboratory Co. Ltd., 99% purity) which possess same metal ions as the eutectic was added on the mixture. This procedure was carried out in a glove-box under an argon gas atmosphere at ambient temperature. After preparation, the crucible was put in the electric furnace in the glove-box and heated at 793 K or 873 K for 2 h following preheating at 573 K for 1 h. During experiment, mixture was occasionally stirred with the stainless steel wire to promote reaction. The temperature in the crucible was measured by the type K (chromel–alumel) thermocouple and was appropriately controlled manually. Subsequently, the crucible was cooled spontaneously, and then it was taken out of the glove-box to recover the precipitates.
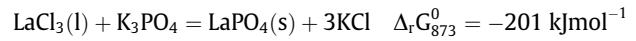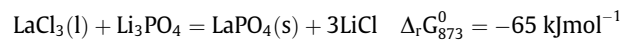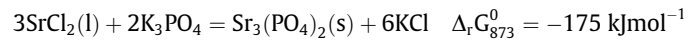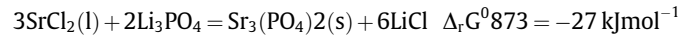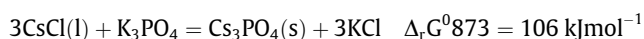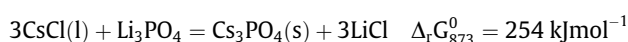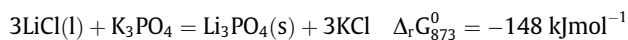
The solidified mixture was washed in 500 ml of the distilled water repeatedly for 5 times to separate the insoluble phosphate and soluble substances such as LiCl, KCl, etc. The dissolved solution with precipitate was filtrated with the suction filter using 0.2 μm pore-size membrane filter (ADVANTEC, Japan) and some constituents in supernatant water were determined by the inductive coupled plasma spectrometry (ICP-AES: Shimadzu ICPS-2000, Japan) for La, the flame atomic absorption spectrophotometer (Hitachi-Science & Technology Z-5300, Japan) for Li and the flame/graphite furnace atomic absorption spectrophotometer (Hitachi-Science & Technology Z-2000) for Cs, respectively.

The particles, which were obtained by drying the precipitate in the electric oven at 373 K for 24 h, were observed with the scanning electron microscope (SEM:JEOL Ltd., JSM-5900, Japan) and were measured their sizes and distributions with the automatic centrifugal particle analyser (Horiba CAPA300, Japan) followed by mixing for 5 min in an ultrasonic bath (Branson Ultrasonics, Bransonic B2200, USA). Their crystal structures were determined with the X-ray powder diffraction (XRD) analyzer (RIGAKU RINT-2000, Japan, X-ray source: Cu Kα).

3. Results and discussion

3.1. Thermodynamic consideration

Prior to start of experiment, the estimation for the phosphate conversion behaviours of each chloride was done by comparison with the standard reaction Gibbs function. Few thermodynamic properties of phosphates, however, were found from the literature reference. The necessary data were obtained by CALPHAD method, using existing phase diagrams [8–11], that presented enough values to assume their behaviours. In this paper, values of the standard reaction Gibbs function in kilojoules per mole of phosphate ion (PO_4^{3-})) for conversion of chlorides to phosphates at 873 K were calculated from acquired thermodynamic properties as below:

$$3LiCl(l) + K_3PO_4 = Li_3PO_4(s) + 3KCl \quad \Delta_rG^0_{873} = -148 \text{ kJmol}^{-1}$$

$$3CsCl(l) + Li_3PO_4 = Cs_3PO_4(s) + 3LiCl \quad \Delta_rG^0_{873} = 254 \text{ kJmol}^{-1}$$

$$3CsCl(l) + K_3PO_4 = Cs_3PO_4(s) + 3KCl \quad \Delta_rG^0873 = 106 \text{ kJmol}^{-1}$$

$$3SrCl_2(l) + 2Li_3PO_4 = Sr_3(PO_4)2(s) + 6LiCl \quad \Delta_rG^0873 = -27 \text{ kJmol}^{-1}$$

$$3SrCl_2(l) + 2K_3PO_4 = Sr_3(PO_4)_2(s) + 6KCl \quad \Delta_rG^0_{873} = -175 \text{ kJmol}^{-1}$$

$$LaCl_3(l) + Li_3PO_4 = LaPO_4(s) + 3LiCl \quad \Delta_rG^0_{873} = -65 \text{ kJmol}^{-1}$$

$$LaCl_3(l) + K_3PO_4 = LaPO_4(s) + 3KCl \quad \Delta_rG^0_{873} = -201 \text{ kJmol}^{-1}$$

Judging from the occurrences of exergonic or endergonic reaction, the formation reaction of Li_3PO_4, $Sr_3(PO_4)_2$ and $LaPO_4$ would proceed with appropriate alkali phosphate as additive but Cs_3PO_4 would not form under this condition. Based on these result, most possible chloride to form the phosphate would be LiCl, $LaCl_3$, and then $SrCl_2$, respectively. K_3PO_4 was also used as the additive. It would first convert LiCl, which is the main constituent of the spent electrolyte to Li_3PO_4 that would act on FP chlorides directly.

3.2. Phosphate conversion of LiCl

Even though LiCl is not the target substance to convert to phosphate, it is worth using it as one of the surrogates of FP chlorides from the following view points:

(1) as reported in the result of thermodynamic simulation, it would readily convert to phosphate;
(2) as Li_3PO_4 is a refractory substance as shown in Table 1 [12], its recovery would be possible after dissolving soluble substances into water.

Experimental result of the conversion of LiCl to phosphate by the addition of 4.5 times of required quantity of K_3PO_4, found only simple Li_3PO_4 was recovered as precipitate after filtration of dissolved sample in water based on the analytical results of crystal structure of particle with XRD (refer to Figs. 1 and 2), which agrees with the result of theoretical analysis. Their recovery ratio was approximately 34.9% at 793 K and 59.6% at 873 K, respectively,

Table 1
Physical properties of Li and K compounds related to the phosphate conversion.

Chemical formula	Molecular weight	Melting point (K)	Density (g cm^{-3})	Solubility (g/100 g H$_2$O)
LiCl	42.394	883	2.07	84.5
KCl	74.551	1044	1.988	35.5
Li_3PO_4	115.794	1478	2.46	0.027
K_3PO_4	212.266	1613	2.564	106
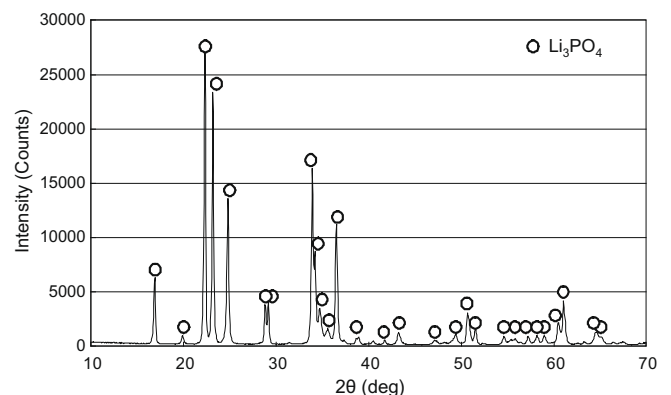
Fig. 1. Analytical result with XRD of crystal structure of precipitate formed at 793 K.
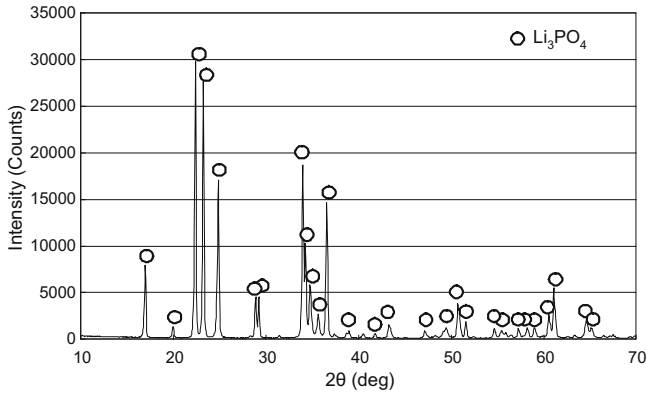
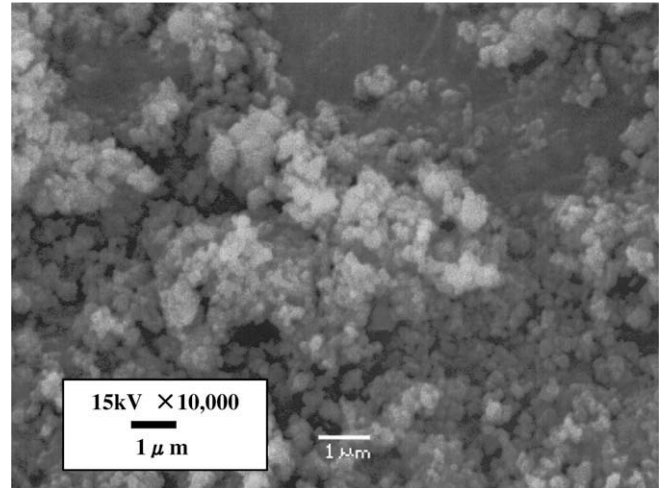Fig. 2. Analytical result with XRD of crystal structure of precipitate formed at 873 K.

Fig. 5. Particle of Li_3PO_4 formed at 793 K.

corresponding to the whole LiCl quantity in the sample which means higher recovery could be expected at higher temperature. At the same time, the particle size would grow bigger at higher temperature as shown in Figs. 3 and 4, approximately 2 μm on the average at 793 K and approximately 2.3 μm on the average at 873 K. The particle formation is shown In Figs. 5 and 6.

To measure the actual particle size, a polycarboxylic high molecular weight dispersant (Geosper K, Flowric Co. Ltd., Japan), diluted with water to 0.1 wt% was added into the sample solution containing the particle. The mean particle size after dispersing
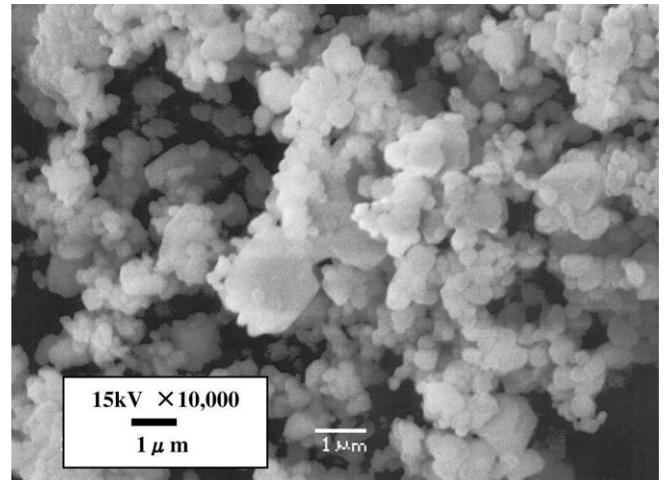

Fig. 6. Particle of Li_3PO_4 formed at 873 K.

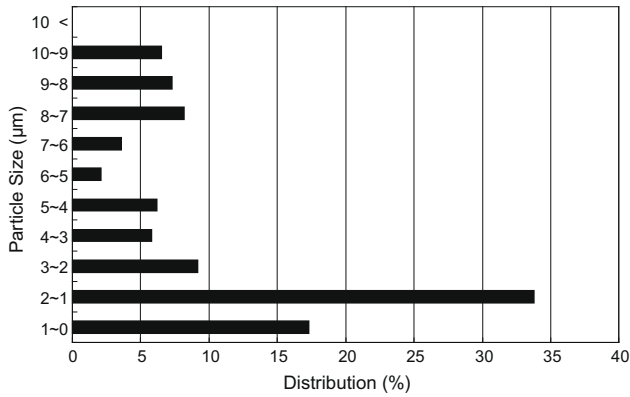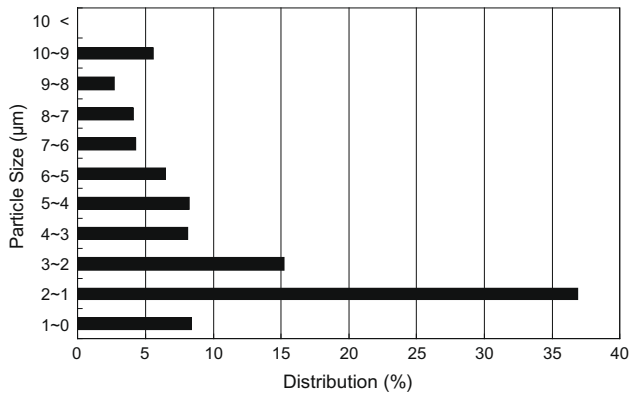became approximately 1 μm at 873 K. Fig. 7, which shows its integral distribution of Li_3PO_4 with/without adding the dispersant at 873 K, indicates that 40–50% of particle in whole after dispersing is more than 1 μm.

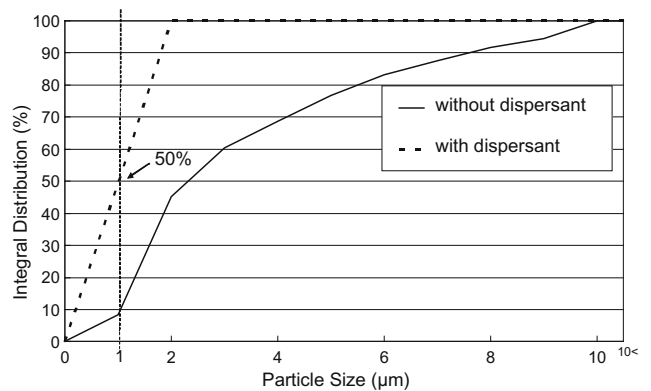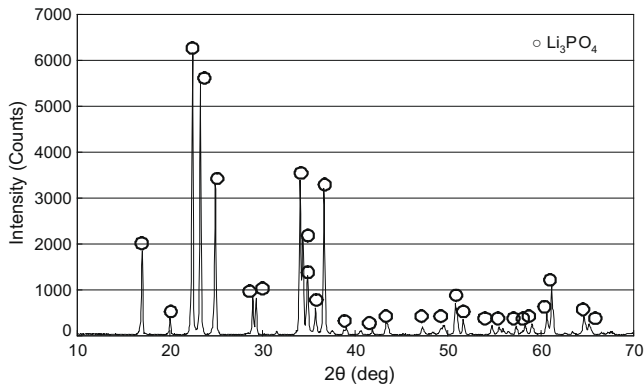Fig. 3. Particle size distribution of Li_3PO_4 formed at 793 K.

Fig. 4. Particle size distribution of Li_3PO_4 formed at 873 K.

Fig. 7. Integral distribution of Li_3PO_4 formed at 873 K.

Fig. 8. Analytical result with XRD of precipitate formed by conversion of CsCl with K_3PO_4.

Table 2
Physical properties of some FP compounds in the spent electrolyte.

| Chemical formula	Molecular weight	Melting point (K)	Density (g cm^{-3})	Solubility (g/100 g H_2O)
CsCl	168.358	918 [12]	3.988 [12]	191 [12]
SrCl$_2$	158.53	1147 [12]	3.052 [12]	54.7 [12]
LaCl$_3$	245.264	1132 [12]	3.84 [12]	95.7 [12]
Cs$_3$PO$_4$	493.69	Unknown	4.56 [13]	Unknown
Sr$_3$(PO$_4$)$_2$	452.8	1893 [14]	4.537*	0.0000111 [12]
LaPO$_4$	233.88	2550 [11]	5.067 [15]	Unknown

* Calculated value.
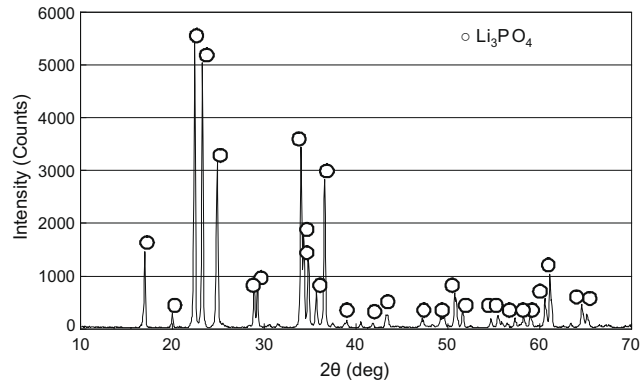
Fig. 9. Analytical result with XRD of precipitate formed by conversion of SrCl$_2$ with K_3PO_4.
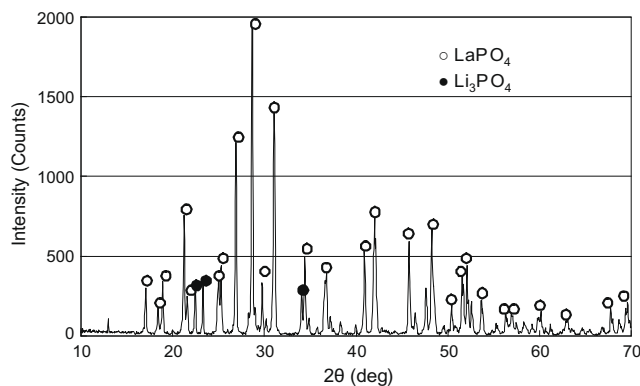
Fig. 10. Analytical result with XRD of precipitate formed by conversion of LaCl$_3$ with Li$_3$PO$_4$.

3.3. Possible formation of phosphate precipitate from CsCl, SrCl$_2$ or LaCl$_3$

The alkali metal, alkaline earth metal and lanthanoid chlorides are the main soluble FP chlorides in the medium. Among these elements, it was found that Li forms the insoluble phosphate based on
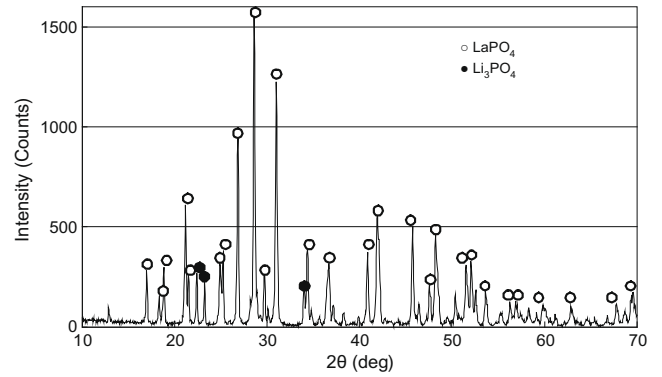
Fig. 11. Analytical result with XRD of precipitate formed by conversion of LaCl$_3$ with K_3PO_4.
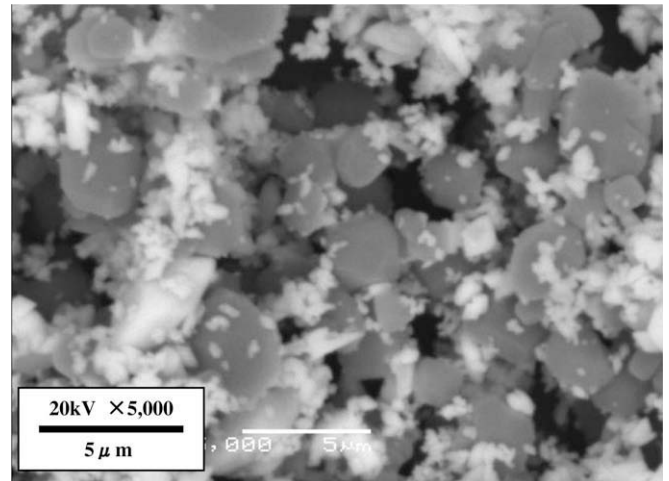
Fig. 12. Particle of LaPO$_4$ formed by the reaction with Li$_3$PO$_4$ at 873 K.
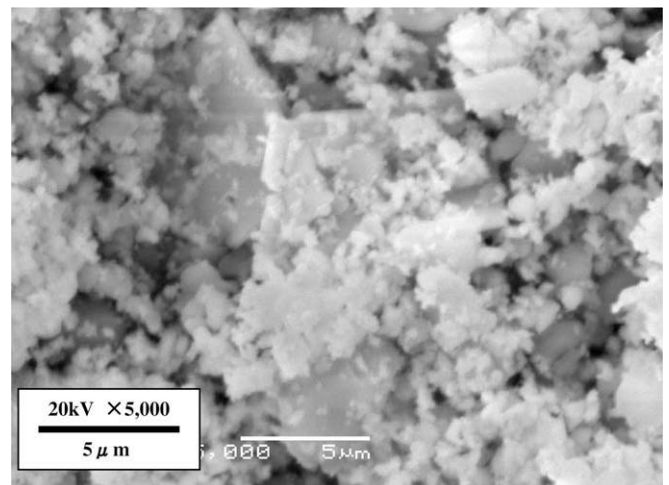
Fig. 13. Particle of LaPO$_4$ formed by the reaction with K_3PO_4 at 873 K.

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Fig. 14. Particle size distributions of LaPO$_4$ formed at 873 K.

Fig. 15. Integral distribution of LaPO$_4$ formed at 873 K.

results of theoretical and experimental analysis. Subsequently, the conversion experiment was carried out to observe the behaviours of other elements such as CsCl, SrCl$_2$ and LaCl$_3$.

In agreement with thermodynamic analysis, in the case of Cs as alkali metal, it would not form the phosphate but remain as chloride through reacting with a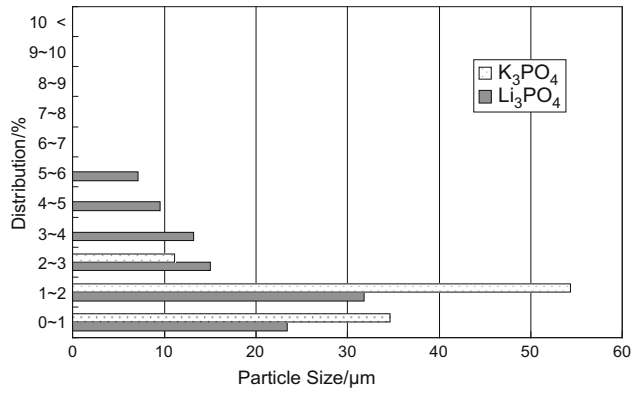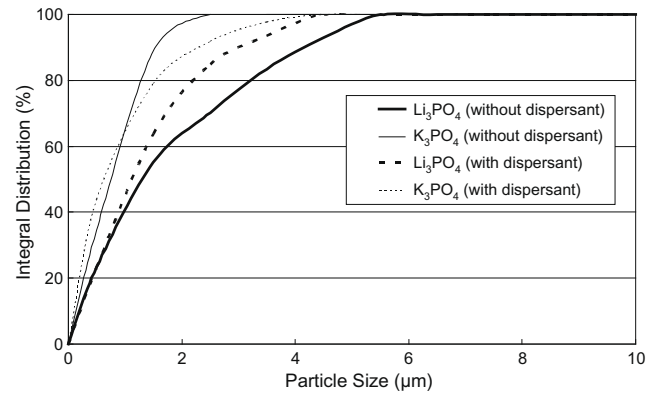dditive. This tendency is consistent with the analytical result with XRD of precipitate that was acquired by washing and drying the solidified surrogate electrolyte after experiment. From the analysis, no Cs$_3$PO$_4$ could be found but Li$_3$PO$_4$ was detected as shown in Fig. 8. If Cs$_3$PO$_4$ existed as a

Table 3
Composition of the spent electrolyte in the electrorefining method.

Group	Symbol	Atomic number	Atomic/molecular weight	m.p. (°C)	b.p. (°C)	Density (g/cm³)	Elements in S.S. (kg/d)	Elements in S.S. (mol/d)	Mole fraction	Ref.
Alkali Metals	Rb	37	85.468	39.3	688	1.53	0.009866	0.115435	7.92244E-05	[12]
	Cs	55	132.905	28.5	671	1.93	0.170134	1.280117	0.000878558	[12]
Alkaline-earth metals	Sr	38	87.62	777	1382	2.64	0.221383	2.526631	0.001734053	[12]
	Ba	4	137.327	727	1867	3.62	0.808617	5.888256	0.004041171	[12]
Rare-earth 1	Y	39	88.906	1522	3345	4.47	0.150853	1.696766	0.001164508	[12]
	Eu	63	151.964	822	1529	5.24	0.070543	0.464206	0.000318589	[12]
	Sm	62	150.36	1074	1794	7.52	0.618605	4.114157	0.002823588	[12]
Rare-earth 2	Ce	58	140.116	798	3443	6.77	1.3891	9.91393	0.006804032	[12]
	Pr	59	140.908	931	3520	6.77	0.69455	4.929104	0.003382894	[12]
	Nd	60	144.24	1021	3074	7.01	2.313205	16.0372	0.011006492	[12]
	Pm	61	(145)	–	–	–	0.043145	−0.29755	−0.00020421	[17]
Rare-earth 3	La	57	138.906	918	3464	6.15	0.683626	4.921502	0.003377677	[12]
	Gd	64	157.25	1313	3273	7.9	0.076374	0.485684	0.00033333	[12]
Transition element A	Mo	42	95.94	2622	4639	10.2	0	0	0	[12]
	Tc	43	98	2157	4265	11	0	0	0	[12]
	Ru	44	85.468	39.3	688	1.53	0	0	0	[12]
	Rh	45	102.906	1963	3695	12.4	0	0	0	[12]
	Pd	46	106.42	1554.8	2963	12	0	0	0	[12]
	Ag	47	107.868	961.78	2162	10.5	0	0	0	[12]
Typical elements	Cd	48	112.411	321.069	767	8.69	0	0	0	[12]
	Sn (white)	50	118.71	231.93	2602	7.265	0	0	0	[12]
Halogen	I	53	126.905	113.7	184.4	4.933	0.162388	1.279603	0.000878205	[12]
	Br	35	79.904	−7.2	58.8	3.1028	0.007612	0.095264	6.53804E-05	[12]
Chalcogen	Se (α)	34	78.96	221	685	4.39	0.023702	0.300172	0.000206011	[12]
	Sb	51	121.76	630.628	1587	6.68	0.013739	0.11284	7.74431E-05	[12]
	Te	52	127.6	449.51	988	6.24	0.312559	2.449522	0.001681132	[12]
Noble gases	Kr	36	83.8	−157.375 tp	−153.34	3.425	0	0	0	[12]
	Xe	54	131.29	−111.745 tp	−108.09	5.366	0	0	0	[12]
Bond Na	Na	11	22.99	97.794	882.94	0.97	3.23	140.4959	0.096423752	[12]
							Sub total	196.8087	0.13507183	[12]
Medium	LiCl–KCl	–	55.59 (ave.)	352	–	1.648	70.01	–	–	[18]
59 mol%	LiCl	–	42.394	610	1383	2.07	31.50726	–	–	[12]
41 mol%	KCl	–	74.551	771	1.988	38.50274	–	–	–	[12]
Composition	Li	3	6.941	180.5	1342	0.534	5.158558	743.201	0.510066453	[12]
	K	19	39.098	63.5	759	0.89	20.19262	516.4617	0.354452959	[12]
							Total	1457.067	0.999999663	
Fuel	Zr	40	91.224	1854	4409	6.52	0	0	0	[12]
Halogen	Cl	17	35.453	−101.5	−34.04	2.898	–	–	–	[12]

Abbreviations: t.p.: Triple point; m.p.: melting point; b.p.: boiling point; S.S.: spent salt.

constituent of precipitate, it would retain due to less dissolution after washing by water because of its lower solubility as shown in Table 2 [12–16].

In the case of Sr as alkaline earth metal, though it would be possible to form the phosphate theoretically, $Sr_3(PO_4)_2$ could not be detected in the precipitate at all with XRD as in the case of Cs (refer to Fig. 9). This phenomenon should be further investigated from viewpoints of accuracy of thermodynamic properties of $Sr_3(PO_4)_2$, e.g., the activity of Sr compounds in the melt, the validity of experimental condition, etc.

$LaCl_3$ is easier to convert to phosphate than $SrCl_2$ as stated previously. The experimental result shows that $LaPO_4$ could be observed in the precipitate with Li_3PO_4 as shown in Fig. 10 using Li_3PO_4 as the additive. In Fig. 11, K_3PO_4 was used as the additive. The two samples of washing water obtained by filtration of dissolving electrolytes following conversion by the addition of Li_3PO_4 or K_3PO_4 were analysed with the ICP-AES but La could not be detected in both of them which means the phosphate conversion ratio of La would be 100% with any additives. Figs. 12 and 13 show the particles of precipitate which were observed with SEM. From these figures, the particle size of $LaPO_4$ formed by the reaction with K_3PO_4 was relatively smaller than that of Li_3PO_4. The automatic centrifugal particle analyser was used to measure the actual particle sizes and the distribution of the $LaPO_4$. The mean particle sizes using Li_3PO_4 or K_3PO_4 as the additive are 1.84 μm and 1.28 μm, respectively. With/without using dispersant, their particle size distributions are shown in Fig. 14 and their integral distributions are shown in Fig. 15. In view of these results, the particle size of $LaPO_4$ shows a tendency to be smaller than that of Li_3PO_4 and some of them are limited to submicron-size. The formation of different particle sizes depends to certain extent, from the kind of additives used. Li_3PO_4 and K_3PO_4 should be discussed by means of the analysis of the reaction process, etc., to determine their chemical and physical properties.

3.4. Estimation of phosphate conversion behaviours of other FP chlorides

It was clarified through experiment mentioned above earlier that $LiCl$ and $LaCl_3$ could form insoluble phosphate precipitates in the molten salt but $SrCl_2$ could not. Here we will estimate the behaviours of other FP chlorides by the thermodynamic approach.

The theoretical composition of spent electrolyte was simulated by ORIGEN-2 code [17] which was developed at Oak Ridge National Laboratory for use in calculation of the nuclide composition, etc. The condition of the spent metal fuel employed for this computation is assumed that it is irradiated to 98GWd/t of burnup (average 48GWd/t, the breeding ratio of 1.2) and is stored for 4 years of cooling time. From the calculated result, its rough composition would be 34.3 t of heavy metals (details: 30.4 t of uranium, 3.8 t of plutonium, and 0.1 t of minor actinoids), 4.2 t of zirconium, 0.8 t of the bond sodium and 3.7 t of FP and its final composition after reprocessing would change as shown in Table 3 [12,18,19]. In this table, besides chemical symbols and their corresponding amount in the spent fuel, additional necessary physical properties are also presented.

Among these constituents, alkali metals, alkaline earth metals, rare earth elements, halogen, chalcogen elements, the bond sodium and medium (LiCl–KCl) are the main substances which compose the final spent electrolyte in basically chloride form and could obtain the thermodynamic properties of seven kinds of phosphates [20–28], e.g., $Ba_3(PO_4)_2$, $CePO_4$, $PrPO_4$, $NdPO_4$, $SmPO_4$, $EuPO_4$ and $GdPO_4$ by CALPHAD method. Using acquired values, the standard reaction Gibbs function in kilojoules per mole of phosphate ion (PO_4^{3-}) for conversion of chlorides to phosphates at 873 K were calculated and summarized in Table 4.

Table 4
Standard reaction Gibbs function for phosphates conversion of FP chlorides at 873 K.

Chemical formula	Chemical reaction formula	$\Delta_r G^0_{873}$ (kJ/mol PO_4^-)
$Ba_2(PO_4)_2$	$3BaCl_2 + 2Li_3PO_4$	83
	$3BaCl_2 + 2K_3PO_4$	−65
$CePO_4$	$CeCl_3 + Li_3PO_4$	−75
	$CeCl_3 + K_3PO_4$	−223
$PrPO_4$	$PrCl_3 + Li_3PO_4$	−73
	$PrCl_3 + K_3PO_4$	−221
$NdPO_4$	$NdCl_3 + Li_3PO_4$	−96.1
	$NdCl_3 + K_3PO_4$	−244
$SmPO_4$	$SmCl_3 + Li_3PO_4$	−108
	$SmCl_3 + K_3PO_4$	−256
$EuPO_4$	$EuCl_3 + Li_3PO_4$	−129
	$EuCl_3 + K_3PO_4$	−277
$GdPO_4$	$GdCl_3 + Li_3PO_4$	−132
	$GdCl_3 + K_3PO_4$	−280

In consideration of former results, those values in Table 4 are quite reliable, e.g., it is expected that $Ba_3(PO_4)_2$ would not form by the phosphate conversion, but all rare earth elements indicated in this table would convert to insoluble phosphates more readily than La.

This estimation should be elucidated by additional experiments.

4. Conclusion

The removal of FP from the spent electrolyte to recycle it as the medium is necessary in order to reduce the HLW arising from the pyroprocessing. For application of phosphate conversion method to regenerate the spent electrolyte, the behaviours of FP in the melt were estimated by the thermodynamic approach and preliminary phosphate conversion experiment using the surrogate spent electrolyte which was prepared by mixing the specific amount of simple salt such as LiCl, CsCl, $SrCl_2$ or $LaCl_3$ in 3LiCl–2KCl eutectic.

By adding Li_3PO_4 or K_3PO_4 to the melt of surrogate spent electrolyte, Li and La had been converted to phosphates and formed the precipitates, whereas Cs and Sr had not. From the observation of the particle sizes of each precipitate, it was found that size of the Li_3PO_4 particles is larger than that of $LaPO_4$ which contains the submicron-size particles.

Judging from the thermodynamic and experimental results, Li_3PO_4 as the excess additive or the reaction product by conversion of LiCl which is a constituent of the medium and lanthanoid phosphates could be removed as precipitates. However, as alkali metals and alkaline earth metals would not form precipitate, other measures should be taken for some kind of selective removal system like the use of molecular sieve, or the precipitation condition of double salts [28] such as, $M(I)M(IV)_2(PO_4)$, $M(I)_3 M(III)_2(PO_4)_3$, etc. Here, M(I) refers to Na or K, M(III) to Ce, Pr, Nd, Sm, Eu or Gd, and M(IV) to Ti,Zr, Hf, Th or U.

It is necessary to carry out further experiments not only by adding simple FP but various combination of FP into the medium as well as obtaining more data on thermodynamic properties for more complicated and accurate analysis of the real solutes.

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