Treatment of molten salt wastes by phosphate precipitation: removal of fission product elements after pyrochemical reprocessing of spent nuclear fuels in chloride melts

Vladimir A. Volkovich [a,1], Trevor R. Griffiths [b,*], Robert C. Thied [c]

[a] *Centre for Radiochemistry Research, Department of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK*
[b] *School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*
[c] *Research and Technology, British Nuclear Fuels plc (BNFL), Sellafield, Seascale, Cumbria CA20 1PG, UK*

Abstract

The removal of fission product elements from molten salt wastes arising from pyrochemical reprocessing of spent nuclear fuels has been investigated. The experiments were conducted in LiCl–KCl eutectic at 550 °C and NaCl–KCl equimolar mixture at 750 °C. The behavior of the following individual elements was investigated: Cs, Mg, Sr, Ba, lanthanides (La to Dy), Zr, Cr, Mo, Mn, Re (to simulate Tc), Fe, Ru, Ni, Cd, Bi and Te. Lithium and sodium phosphates were used as precipitants. The efficiency of the process and the composition of the solid phases formed depend on the melt composition. The distribution coefficients of these elements between chloride melts and precipitates were determined. Some volatile chlorides were produced and rhenium metal was formed by disproportionation. Lithium-free melts favor formation of double phosphates. Some experiments in melts containing several added fission product elements were also conducted to study possible co-precipitation reactions. Rare earth elements and zirconium can be removed from both the systems studied, but alkaline earth metal fission product elements (Sr and Ba) form precipitates only in NaCl–KCl based melts. Essentially the reverse behavior was found with magnesium. Some metals form oxide rather than phosphate precipitates and the behavior of certain elements is solvent dependent. Caesium cannot be removed completely from chloride melts by a phosphate precipitation technique.

1. Introduction

At present commercial scale reprocessing of spent nuclear fuels is carried out using solvent extraction (Purex process). Wastes arising from reprocessing consist of fission product elements and some residual uranium and transuranium elements, and an indication of the quantities produced, derived from [1], are illustrated in Fig. 1. One possible alternative to existing extraction technology is pyrochemical reprocessing of spent nuclear fuels using high-temperature molten salts. There

* Corresponding author. Tel.: +44-113 343 6406; fax: +44-113 343 6565.

E-mail address: trevorg@chemistry.leeds.ac.uk (T.R. Griffiths).

[1] Present Address: Department of Rare Metals, Physical-Engineering Faculty, Ural State Technical University-UPI, 19 Mira ul., Ekaterinburg 620002, Russian Federation.

Fig. 1. Wastes arising from typical Light Water Reactor fuel irradiated to 40 000 MWd/tonne. Elements present shadowed in grey. Numbers represent amount in milligram per kilogram of uranium. Data from [1].

are currently two technological pyrochemical processes in existence, one employing NaCl–KCl melts (RIAR process, Russia) and the other using LiCl–KCl melts (ANL process, USA). After the spent fuel (either ceramic oxide or metallic) is dissolved in the melt and uranium, plutonium and the heavier actinides are removed, the melt needs to be cleansed from the remaining fission elements and corrosion products, before it can be reused. Precipitation of fission product elements as phosphates offers a possible solution. Most of the inorganic phosphates are insoluble in chloride melts and thus these precipitates can easily be separated from liquid melts. Separating wastes in phosphate form is also very convenient for future vitrification, since they form very stable non-leachable glasses, and phosphates themselves are very stable in highly radioactive environments.

Precipitation of phosphates from molten salts has been previously reported for NaCl, KCl and NaCl–KCl based melts. The elements studied included uranium [2,3], plutonium [4,5], americium and curium [6], and several lanthanides [3]. Sodium or potassium orthophosphates were employed as precipitants. For trivalent actinides and lanthanides the reactions resulted in the formation of double phosphates of composition $M_3Me_2(PO_4)_3$, $M = Na$ or K, $Me = Ce$, Pr, Nd, Sm, Eu, Gd, Pu, Am or Cm. In the case of uranium, formation of $NaUO_2PO_4$ and $NaU_2(PO_4)_3$ was reported in U(VI) and U(IV) containing melts, respectively. There is no information, however, on the precipitation of fission product elements. The solubilities of the double phosphates formed by alkali or alkaline-earth metals and lanthanides or Group 4 metals (Ti, Zr, Hf) in molten NaCl and KCl have also been measured [7–9] and found to be small ($\approx 10^{-5}$ M). It has also been reported that alkali and alkaline earth metal fission products (Rb, Cs, Sr and Ba) can be removed from molten salts by ion exchange using double alkali metal–transition metal phosphates [10–12]. It appears that phosphate precipitation in the low temperature LiCl–KCl system has not been previously

investigated. There is therefore the potential for possible specific effects due to lithium.

In the present work we have studied the reactions of alkali metal phosphates with chloride melts containing the elements found during the reprocessing of spent nuclear fuels. These include Cs, Mg, Sr, Ba, lanthanides (La to Dy), Zr, Cr, Mo, Mn, Re (to simulate Tc), Fe, Ru, Ni, Cd, Bi and Te. Co-precipitation reactions in melts containing two or three elements (chosen from Sr, Ba, Ce and Zr) were also investigated, because they are among the most abundant in spent fuels (Fig. 1).

2. Experimental

Experiments were conducted in a vertical tube furnace (Severn Science SSL Model TF428), capable of reaching 1200 °C and having a middle constant temperature zone covering approximately 20 cm. The furnace was maintained by an Omega CN76000 microprocessor-based temperature/process controller.

The reactions of a variety of metal chlorides, MCl_n, where $n = 1–5$, with lithium phosphate in molten LiCl–KCl eutectic (41.5 mol% KCl, mp 361 °C) were investigated at 550 °C. Anhydrous metal chlorides were premixed with approximately 10 g of the solid eutectic in an alumina crucible. The mixing was carried out in a dry box. The metal chlorides (MCl_n) used were CsCl, $MgCl_2$, $SrCl_2$, $BaCl_2$, $LnCl_3$ (Ln = La to Dy), $ZrCl_4$, $CrCl_3$, $MoCl_3$, $MoCl_5$, $MnCl_2$, $ReCl_5$, $FeCl_2$, $FeCl_3$, $RuCl_3$, $NiCl_2$, $CdCl_2$, $BiCl_3$ and $TeCl_4$. The crucible containing a reaction mixture was then transferred into a silica reaction cell positioned in a furnace thermostatted at the desired temperature. This cell, containing lithium phosphate precursor, as solid discs, in a sidearm, was evacuated and kept under vacuum for 20–30 min until the salts were molten. The cell was then filled with dry argon and the phosphate introduced into the melt. Due to the very low melting and boiling points of some chlorides (for example, tellurium tetrachloride), lithium phosphate, as powder, was premixed with a LiCl–

$KCl + TeCl_4$ mixture before placing the crucible into the furnace. A similar approach was applied to the systems containing $MoCl_3$ and $BiCl_3$. In spite of this precaution, during the initial heating some of the added MCl_n sublimed, particularly when $M = Te$. In experiments involving zirconium(IV), molybdenum(III and V), rhenium(V), iron(III), and ruthenium(III) chlorides, some sublimation (sometimes quite considerable) was also observed, especially during the initial melting before the addition of phosphate.

The experiments in the sodium chloride–potassium chloride equimolar mixture (min mp 658 °C) were conducted in a similar manner at 750 °C. Selected anhydrous metal chlorides were premixed with $\approx$10 g of NaCl–KCl mixture and the calculated amount of solid anhydrous sodium *ortho*-phosphate (so that the initial mole ratio of phosphate to the metal of interest was around 5) was either premixed with the solid salts or added into the melt.

After completing the experiment, the cell was opened and the crucible rapidly lifted out and transferred into a desiccator, where its contents quickly solidified on cooling. The resulting pebble-shaped product in the crucible was treated with water or dilute hydrochloric acid solution to dissolve all soluble salts. The precipitate was filtered off, washed with distilled water and dried at $\approx$120 °C. The filtrate was collected and used for the determination of the residual concentration of added elements. The precipitate was analysed chemically and by X-ray powder diffraction (Phillips PW1710 diffractometer, Ni-filtered Cu_{K_α} radiation). The results of XRD analysis are given in the Appendix A either as ASTM card indices for identified phases or positions and intensities of the peaks for currently unidentified phases.

3. Results and discussion

3.1. Caesium

Caesium was the only alkali metal investigated here. Caesium phosphate is soluble in water and therefore caesium was not expected to form an insoluble precipitate (although we had previously found that lithium phosphate is quite insoluble in molten chlorides, and that sodium phosphate is only moderately soluble [13]). The primary objective here was to study the reaction of Li_3PO_4 with LiCl–KCl–CsCl melt, and of Na_3PO_4 with NaCl–KCl–CsCl melt, and if possible to characterize the phases formed when the melt is quenched.

When Li_3PO_4 was added to the LiCl–KCl melt containing CsCl ($PO_4^{3-}:Cs^+$ mole ratio 3.55), the reaction resulted in the formation of a complicated mixture of products and an insoluble white precipitate was observed at the end of the experiment. Since alkali metal phosphates are soluble in water (lithium only

sparingly), the precipitate formed could not be separated from the melt by washing. The quenched melt was therefore ground to powder, and X-ray diffraction (XRD) patterns recorded. Only four phases were identified in the mixture, viz. LiCl, KCl, Li_3PO_4 and Cs_3PO_4. No remaining CsCl was found. This shows that the reaction between lithium phosphate and caesium chloride leads to the essentially complete formation of caesium phosphate. Upon addition of Na_3PO_4 to the NaCl–KCl melt containing CsCl ($PO_4^{3-}:Cs^+$ mole ratio 3.07), the reaction again formed a mixture of products. Several phases were identified in the quenched mixture using XRD: NaCl, $K_{0.8}Na_{0.2}Cl$, Cs_3PO_4, K_3PO_4 and CsCl. None of the following were detected: Na_3PO_4, $K_{0.6}Na_{0.4}Cl$, $K_{0.4}Na_{0.6}Cl$ and $K_{0.2}Na_{0.8}Cl$. The reaction occurring here therefore results in the formation of alkali metal phosphates with the largest available cations (K and Cs).

$$K^+ + Cs^+ + 2Na_3PO_4 \rightarrow K_3PO_4 + Cs_3PO_4 + 6Na^+ \tag{1}$$
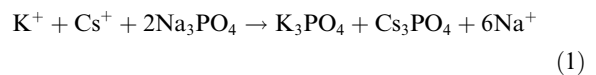
The reaction, however, did not proceed to completion and some CsCl was still present after 3 h.

Caesium therefore is likely to remain in the melt (at least partially) during the phosphate precipitation treatment in both LiCl–KCl and NaCl–KCl systems. Caesium can be removed from chloride melts by ion exchange [10–12] and this operation can be carried out after the bulk of fission products is removed from the melt. Work is currently in progress on testing various double phosphate salts and related compounds as possible ion exchange materials for caesium removal.

3.2. Magnesium, strontium and barium

First, we consider the reactions in high temperature NaCl–KCl-based melts. In strontium and barium-containing melts the corresponding crystalline double phosphates, $NaMPO_4$ ($M = Sr$, Ba), separated out, Table 1. Over 90% of barium and essentially all the strontium were converted into insoluble phosphates. The behavior of magnesium was rather different. XRD analysis did not reveal the presence of any phases in the white precipitate obtained from the magnesium-containing melt. This indicates that the precipitate was either X-ray amorphous or very finely crystalline. If the precipitate was amorphous it is possible that (at least partially) it was formed when the melt was treated with water due to the reaction of magnesium chloride with the water-soluble sodium phosphate.

When the reactions of magnesium, strontium and barium chlorides with lithium orthophosphate, in LiCl–KCl eutectic, were studied, the results obtained were considerably different from those in NaCl–KCl-based melts, Table 1.

Table 1
Precipitation of alkaline earth metal phosphates from molten salts

M	NaCl–KCl–MCl_2 + Na_3PO_4, 750 °C			LiCl–KCl–MCl_2 + Li_3PO_4, 550 °C		
	PO_4^{3-}:M^{2+} mole ratio	Solid phase composition[a] and conc. of M in ppt (wt%)	η[b]	PO_4^{3-}:M^{2+} mole ratio	Solid phase composition[a] and conc. of M in ppt (wt%)	η[b]
Mg	5.01	–[c] (9.7)	1.00	4.24	Li_3PO_4, $LiMgPO_4$, $Mg_3(PO_4)_2$ (3.5)	0.97
Sr	4.85	$NaSrPO_4$ (45.3)	0.99	4.21	Li_3PO_4[c] (5.4)	0.25
Ba	4.89	$NaBaPO_4$ (51.1)	0.93	5.02	Li_3PO_4[c] (5.4)	0.21

[a] Phases identified from X-ray powder diffraction analysis.
[b] $\eta = M_S/(M_S + M_L)$, distribution of M between solid (precipitate) and liquid (melt) phases.
[c] See text.

The individual phosphate phases, $LiMgPO_4$ and $Mg_3(PO_4)_2$, were precipitated from LiCl–KCl–$MgCl_2$ melt and the distribution coefficient was close to unity, indicating that nearly all the Mg(II) ions were converted into insoluble phosphates. For the systems containing Sr and Ba, the X-ray powder diffraction analysis of the phosphate precipitates showed the presence only of lithium phosphate. Chemical analysis of the precipitates, however, showed that they contained up to 5 wt% of the elements investigated: such concentrations are sufficient for X-ray powder diffraction analysis to detect the presence of the corresponding phase. To explain this we note that the exact chemical state of the trace ions in the Li_3PO_4-based phosphate precipitates is not fully clear. The very small radius of the Li cation makes it very unlikely that solid lithium phosphate acted as a cation exchange medium for Sr, Ba, etc. Most probably the ions of these elements are occluded or otherwise trapped into the bulk of Li_3PO_4, and thus do not exist in an individual phase.

Therefore, although the alkaline earth fission products, Sr and Ba, can be removed from NaCl–KCl based melts by precipitating them as phosphates, ion exchange might have to be used in LiCl–KCl melts.

3.3. Lanthanides

Addition of lithium phosphate to LiCl–KCl–$LnCl_3$ melts (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy) resulted in the formation of normal lanthanide phosphates, $LnPO_4$, Table 2. The major difference between the lanthanides was in the structure of the phosphates: lighter lanthanides (La to Tb) produced monoclinic or monazite type phases, and only Dy formed tetragonal or xenotime type phase. Previously we had found, using in situ electronic spectroscopy, that it takes between 3 and 4 h to complete the reaction [14]. Keeping the phosphate-to-lanthanide mole ratio around five enables essentially complete precipitation of the lanthanides.

When the experiments were conducted in NaCl–KCl based melts, using Na_3PO_4 as precipitant, the products obtained were different. The reaction led mainly to precipitation of double sodium-lanthanide phosphates, in agreement with Kryukova et al. [3]. The XRD pat-

Table 2
Precipitation of lanthanide phosphates from molten salts

Ln	NaCl–KCl–$LnCl_3$ + Na_3PO_4, 750 °C			LiCl–KCl–$LnCl_3$ + Li_3PO_4, 550 °C		
	PO_4^{3-}:Ln^{3+} mole ratio	Solid phase composition[a] and conc. of Ln in ppt (wt%)	η[b]	PO_4^{3-}:Ln^{3+} mole ratio	Solid phase composition[a] and conc. of Ln in ppt (wt%)	η[b]
La	4.98	$Na_3La(PO_4)_2$, $LaPO_4$ (40.9)	1.00	4.97	$LaPO_4$ (mon), Li_3PO_4 (44.2)	1.00
Ce	5.03	$Na_3Ce_2(PO_4)_3$ (44.6)	1.00	4.97	$CePO_4$ (mon) (60.2)	1.00
Pr	4.96	$Na_3Pr(PO_4)_2$, $PrPO_4$ (56.5)	1.00	5.06	$PrPO_4$ (mon), Li_3PO_4 (38.4)	1.00
Nd	5.09	$Na_3Nd_2(PO_4)_3$ (55.0)	1.00	4.98	$NdPO_4$ (mon), Li_3PO_4 (39.2)	1.00
Sm	5.13	$Na_3Sm(PO_4)_2$, $SmPO_4$ (48.6)	1.00	5.00	$SmPO_4$ (mon), Li_3PO_4 (38.3)	1.00
Eu	5.18	$Na_3Eu(PO_4)_2$, $EuPO_4$ (43.6)	1.00	4.98	$EuPO_4$ (mon), Li_3PO_4 (53.2)	1.00
Gd	4.98	β-$Na_3Gd(PO_4)_2$ (44.2)	1.00	5.07	$GdPO_4$ (mon), Li_3PO_4 (44.1)	1.00
Tb	5.02	β-$Na_3Tb(PO_4)_2$, $TbPO_4$ (44.1)	1.00	4.96	$TbPO_4$ (tetr), Li_3PO_4 (35.1)	1.00
Dy	5.21	β-$Na_3Dy(PO_4)_2$ (48.4)	1.00	5.07	$DyPO_4$ (tetr), Li_3PO_4 (37.6)	1.00

[a] Phases identified from X-ray powder diffraction analysis, mon – monoclinic, tetr – tetragonal phases.
[b] $\eta = M_S/(M_S + M_L)$, distribution of M between solid (precipitate) and liquid (melt) phases.

terns of these phosphates are shown in Fig. 2. We can thus conclude that the presence of large amounts of lithium in LiCl–KCl based melts (a system not been previously investigated) suppresses the formation of double lanthanide phosphate phases due to the low solubility of lithium phosphate.

Complete removal of lanthanide fission products from chloride melts, both LiCl–KCl and NaCl–KCl-based, arising from pyrochemical reprocessing of spent nuclear fuels is therefore potentially possible. When LiCl–KCl based melts are employed, the bulk of phosphate waste precipitated can be reduced due to precipitation of normal rather than double phosphates.

3.4. Zirconium, chromium, molybdenum, manganese, rhenium, iron, ruthenium, nickel, cadmium, tellurium and bismuth

The results obtained for this range of elements are summarized in Table 3. The experiments, conducted in LiCl–KCl melts, showed that not all of the elements investigated formed individual well-defined phosphate phases. Alternatively, if such phases were formed, their concentration in the precipitate was very small and thus below the detectable limit of X-ray powder diffraction analysis. Consequently, the majority of the systems investigated by X-ray powder diffraction analysis revealed the presence of only Li_3PO_4 in the final precipitates.

Individual phosphate phases were precipitated from $LiCl–KCl–MCl_n$ melts when MCl_n was $ZrCl_4$ or $CrCl_3$. Zirconium formed $KZr_2(PO_4)_3$ double phosphate, similar in composition to those reported for titanium, zirconium and hafnium [8]. Chromium was precipitated as normal phosphate, $CrPO_4$. The distribution coefficients
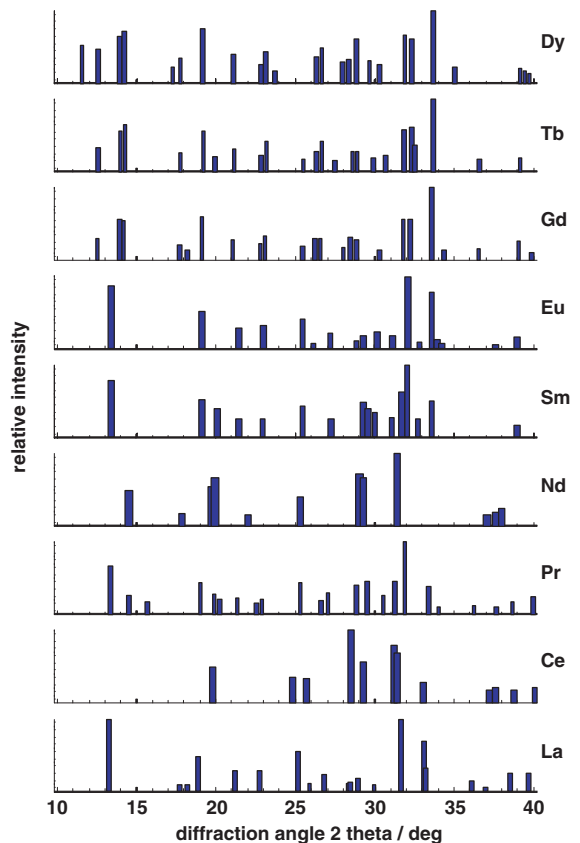

Fig. 2. XRD patterns of lanthanide phosphates precipitated from $NaCl–KCl–LnCl_3$ melt using Na_3PO_4, 750 °C. For composition description see Table 2.

Table 3
Precipitation of fission product elements from molten salts

M	NaCl–KCl–MCl$_n$ + Na$_3$PO$_4$, 750 °C			LiCl–KCl–MCl$_n$ + Li$_3$PO$_4$, 550 °C		
	PO$_4^{3-}$:M^{n+} mole ratio	Solid phase composition[a] and conc. of M in ppt (wt%)	η[b]	PO$_4^{3-}$:M^{n+} mole ratio	Solid phase composition[a] and conc. of M in ppt (wt%)	η[b]
Bi(III)	5.14	No ppt. (0)	0	5.05	BiPO$_4$, Li$_3$PO$_4$ (35.0)	1.0
Cd(II)	5.06	Cd–I (21.0)	1.00	4.90	Li$_3$PO$_4$ (0)	0
Cr(III)	5.61	Cr$_2$O$_3$ (33.1)	0.80	4.55	CrPO$_4$, Li$_3$PO$_4$ (3.1)	0.99
Fe(II)	4.90	Fe$_2$O$_3$ [Hem], γ-Fe$_2$O$_3$ (44.6)	0.95	5.02	Li$_3$PO$_4$ (4.1)	0.47
Fe(III)				4.96	Li$_3$PO$_4$ (5.3)	0.65
Mn(II)				4.89	Li$_3$PO$_4$ (1.1)	0.12
Mo(III)	4.99	Mo, MoO$_2$ (36.6)	0.61	5.05	Li$_3$PO$_4$ (2.6)	0.67
Mo(V)				5.11	Mo–I, Li$_3$PO$_4$ (3.2)	0.41
Ni(II)				4.72	Li$_3$PO$_4$ (1.7)	0.17
Re(V)	5.01	Re, ReO$_2$, Re–I (33.4)	0.35	5.25	Re, Li$_3$PO$_4$ (5.8)	0.43
Ru(III)	5.17	Ru, RuO$_x$	1.00			
Te(IV)				5.07	Li$_3$PO$_4$ (12.8)	0.94
Zr(IV)	5.08	Na$_2$Zr(PO$_4$)$_2$, ZrO$_2$, Zr–I (21.0)	0.83	5.07	KZr$_2$(PO$_4$)$_3$, Li$_3$PO$_4$ (12.1)	1.00

[a] Phases identified from X-ray powder diffraction analysis. For explanation of phases marked M–I see text. Hem – hematite phase.
[b] $\eta = M_S/(M_S + M_L)$, distribution of M between solid (precipitate) and liquid (melt) phases.

for zirconium and chromium were above 0.9, indicating that more than 90% of M^{n+} ions were converted into insoluble phosphates.

The melts containing Re(V) and Mo(V) also formed individual phases, in addition to that of Li_3PO_4 in phosphate precipitates. Metallic rhenium was found in the precipitate formed in the $LiCl–KCl–ReCl_5–Li_3PO_4$ system, but this could be due to thermal decomposition of rhenium pentachloride and the subsequent disproportionation of the rhenium trichloride so formed, viz.,

$$ReCl_5 \rightarrow ReCl_3 + Cl_2 \quad (2)$$

$$5ReCl_3 \rightarrow 3ReCl_5 + 2Re \quad (3)$$

In the precipitate formed in the molybdenum pentachloride-containing system some black phase was detected (referred to as Mo–I in Table 3). XRD peaks, identified with certainty, relate closely to those of molybdenum dioxide, MoO_2.

Chemical analysis has shown that no cadmium was present in the corresponding phosphate precipitate and the X-ray powder diffraction confirmed that the precipitate consisted entirely of lithium *ortho*-phosphate.

For the remaining systems containing Mo(III), Mn, Fe(II and III), Ru, Ni, and Te the X-ray powder diffraction analysis of the phosphate precipitates also showed the presence only of lithium phosphate even though chemical analysis revealed the presence of these elements in the precipitates. Probable trapping or occlusion reasons for this have been discussed above for strontium and barium. The distribution coefficients, η, for all the elements studied were below 0.7, and normally less than 0.5, with the exception of tellurium, where $\eta_{(Te)}$ was 0.94. This value is probably unrealistic due to the very high volatility of tellurium tetrachloride (bp 380 °C), because the tellurium not included in the precipitate has evaporated from the melt during the experiment (3 h at 550 °C).

When the above experiments were repeated in NaCl–KCl based melts at 750 °C they produced somewhat different results. Surprisingly, there was incomplete precipitation of zirconium. Apart from the double sodium–zirconium *ortho*-phosphate, $Na_2Zr(PO_4)_2$, and very small amounts of zirconium dioxide, ZrO_2, an additional, at present unidentified, phase was formed. This phase is marked as Zr–I in Table 3, and its XRD pattern does not correspond to those of zirconium normal phosphates or zirconium–alkali metal double phosphates.

Some other melts also yielded oxide phases in the precipitates. Green chromium(III) oxide and brown iron(III) oxide were formed in melts containing added $CrCl_3$ and $FeCl_2$, respectively. In the melts containing added rhenium(V) and molybdenum(III) chlorides the corresponding dioxides were precipitated, together with metallic rhenium and molybdenum. An additional phase

(marked Re–I) was also precipitated from the NaCl–KCl–ReCl$_5$ melt but the nature of this phase could not be identified from powder XRD analysis. A metallic phase was also precipitated from the melt containing added ruthenium trichloride together with ruthenium oxide.

The behavior of cadmium and bismuth in NaCl–KCl-based systems was entirely opposite to that in LiCl–KCl-based melts. No precipitate was formed in the NaCl–KCl–BiCl$_3$ melt upon the addition of Na_3PO_4 and after 3 h there was only a yellow clear melt in the crucible. In contrast, the complete precipitation of cadmium was observed, although the nature of the precipitate obtained (marked Cd–I phase, Table 3) could not be determined. The XRD pattern of the white Cd–I phase does not correspond to those of known cadmium phosphates.

Kryukova et al. [15] have reported that fusing a mixture of $RuCl_3–Na_3PO_4–NaCl$ at 810 °C, using a phosphate-to-ruthenium mole ratio of two, resulted in the formation of $Na_3Ru(PO_4)_2$. The XRD pattern of the ruthenium precipitate obtained here by adding Na_3PO_4 to $RuCl_3–NaCl–KCl$ melt did not correspond to that of $Na_3Ru(PO_4)_2$ [15] and the reaction resulted mainly in the formation of ruthenium oxides.

3.5. Precipitation of phosphates from the melts containing several fission product elements

The alkaline earth elements (strontium and barium) could not be effectively removed by phosphate precipitation from LiCl–KCl based melts. A series of experiments was performed to assess the possibility of co-precipitation of strontium and barium with cerium or zirconium. All experiments were conducted at 550 °C and the mole ratio of phosphate-to-total added metals was kept around five.

The first series of experiments was conducted in melts containing added MCl_2 (M = Sr or Ba) and $CeCl_3$. Both lithium and sodium phosphates were tried as precipitants. XRD analysis of the precipitates formed showed that in all cases the solids consisted of monoclinic cerium phosphate, $CePO_4$, and lithium phosphate. Concentrations of strontium or barium were low and no phases associated with Sr or Ba were detected by XRD analysis. After approximately three hours no cerium remained in the melt but Sr and Ba distribution coefficients were low, 0.03–0.01 for strontium and 0.02–0.04 for barium. No double phosphates were detected and the formation of double sodium–strontium or sodium–barium phosphates observed previously in NaCl–KCl-based melts was therefore due to the solvent effect. A considerable excess of the soluble phosphate would appear to be necessary for the formation of these compounds, but in LiCl–KCl-based melts all the excess phosphate ions are removed as the only sparingly soluble Li_3PO_4, a situation similar to the formation of single and double lanthanide phosphates in these melts.

Next, the experiments were repeated in LiCl–KCl–MCl_2–$ZrCl_4$ melts (M = Sr or Ba) using Li_3PO_4. The solid phases identified using XRD analysis were $Me_2Zr(PO_4)_2$, Me = Li/K, and Li_3PO_4. As with the cerium-containing melts, all the zirconium was removed in the solid phase and the distribution coefficients for Sr and Ba were 0.03 and 0.09, respectively.

Finally, experiments were performed in LiCl–KCl–MCl_2–$CeCl_3$–$ZrCl_4$ melts, again using Li_3PO_4 as precipitant. As before, all the cerium and zirconium were precipitated as $CePO_4$ and $Me_2Zr(PO_4)_2$, Me = Li/K, but over 90% of added Sr or Ba remained in the melt.

4. Summary

The behavior of solutions of a variety of metal chlorides was studied in LiCl–KCl eutectic at 550 °C in the presence of added solid Li_3PO_4 and in NaCl–KCl melts at 750 °C in the presence of Na_3PO_4. The cations investigated were Cs(I), Mg(II), Sr(II), Ba(II), Zr(IV), Cr(III), Mo(III and V), Mn(II), Re(V), Fe(II and III), Ru(III), Ni(II), Cd(II), Bi(III), Te(IV) and lanthanides (La to Dy). The distribution coefficients of most of these elements between chloride melts and precipitates were determined.

In LiCl–KCl-based melts the majority of the above elements did not form individual phosphate phases: instead, their ions were trapped or occluded in solid Li_3PO_4. Only the lanthanides, together with Mg, Zr and Cr, formed normal or double phosphates. No cadmium was converted into a solid phase.

In the NaCl–KCl-based melts a range of metallic, oxide and phosphate phases was produced. The melt could be cleaned completely of lanthanides, strontium, barium, iron, ruthenium and cadmium. No precipitate was formed in the bismuth-containing melt.

Caesium cannot be removed completely from chloride melts by a phosphate precipitation technique. Addition of Li_3PO_4 into a LiCl–KCl–CsCl melt leads upon quenching to the conversion of caesium into Cs_3PO_4. However, addition of Na_3PO_4 into a NaCl–KCl–CsCl melt, and subsequent quenching of the melt, gave only partial conversion of caesium into Cs_3PO_4.

The reactions of lithium and sodium *ortho*-phosphates with the LiCl–KCl-based melts containing two or three elements representing major fission products (strontium, barium, cerium, zirconium) were investigated at 550 °C, under static conditions, and the distribution of the elements between the melts and the solid precipitates was determined. The chloride melts can be fully purified from cerium and zirconium, which are converted into insoluble monoclinic $CePO_4$ and $M_2Zr(PO_4)_2$, M = alkali metal, by adding lithium phosphate. Neither barium nor strontium co-precipitate with cerium or zirconium phosphates and they do not form double phosphates, $NaMPO_4$ (M = Sr, Ba), in LiCl–KCl-based melts, even when sodium phosphate is used as precipitant. The formation of these double phosphates in NaCl–KCl-based melts is therefore effected by the solvent.

Phosphate precipitation thus has the potential for removing certain fission product elements from molten salt solutions arising from pyrochemical reprocessing of spent nuclear fuels. Lanthanides and some transition metals (e.g., zirconium) can be removed completely from both commercially proposed systems, LiCl–KCl and NaCl–KCl based melts. The behavior of some metals is solvent dependent: cadmium can be precipitated in NaCl–KCl melt and bismuth from LiCl–KCl melt, but not vice versa. Strontium and barium, the alkaline earth fission products, can only be removed from NaCl–KCl melts, whereas the reverse is the case for magnesium.

Appendix A. Supplementary XRD data

A.1. XRD data for various phases identified in the present study

Known phases (ASTM card indices are in brackets). Rare earth phosphates, $CePO_4$ [mon] (26–355); $PrPO_4$ [mon] (26–929); $NdPO_4$ [mon] (25–1065); $SmPO_4$ [mon] (26–949); $EuPO_4$ [mon] (25–1055); $GdPO_4$ [mon] (26–660); $DyPO_4$ [tetr] (26–593); monoclinic $LaPO_4$ and $TbPO_4$ are isostructural with other monoclinic $LnPO_4$ (Ln = Ce–Gd). Other phosphates, Li_3PO_4 (15–760); K_3PO_4 (20–921); Cs_3PO_4 (26–1097); $LiMgPO_4$ (18–735); $NaSrPO_4$ (14–269); $NaBaPO_4$ (14–204); $Mg_3(PO_4)_2$ (25–1373); $KZr_2(PO_4)_3$ (25–1206); $Na_2Zr(PO_4)_2$ (24–1178); $CrPO_4$ (9–384); $BiPO_4$ (15–766). Oxides and metals, ZrO_2 (13–307); Cr_2O_3 (6–504); MoO_2 (5–452); ReO_2 (17–600); Fe_2O_3 [Hem] (24–72); γ-Fe_2O_3 (4–755); Re (5–702); Mo (4–809); Ru (6–663). Chlorides, NaCl (5–628); $K_{0.8}Na_{0.2}Cl$ (26–921); CsCl (5–607).

Most characteristic peaks of currently unidentified phases. Zr–I: 2.63_x, 2.67_8, 8.61_7, 2.89_6, 2.65_5, 3.68_5. Re–I: 5.21_x, 1.73_5, 2.50_4, 2.01_3, 1.70_3, 1.80_2. Ru–I: 3.22_x, 2.58_x, 1.70_4, 1.71_3. Cd–I: 2.63_x, 4.30_7, 1.52_4, 2.78_3, 2.15_2.

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