Immobilization of Aqueous Heavy Metal Cations with Phosphates and Sulfates

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The dissolution–precipitation mechanism has been suggested for the immobilization of aqueous lead cation with calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; CaHAp). Here Na_2HPO_4, K_2HPO_4, $MgHPO_4$ and $CaHPO_4$ were employed for CaHAp. These hydrogenphosphates could favorably remove Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} from aqueous solution for 0.5 h at 293 K. The removability of those hydrogenphosphates was evidently greater than that of CaHAp and seemed to be dependent on solubility of those hydrogenphosphates and the hydration enthalpy of those heavy metal cations. The structures of phosphates recovered after immobilization of Pb^{2+}, Cd^{2+}, and Co^{2+} were strongly influenced by the pH in the aqueous solution, while the structures after immobilization of Cu^{2+} for 0.5 and 12 h were amorphous compound and $Cu_2(PO_4)(OH)$, respectively. The employment of solid state ^{31}P MAS NMR and XRD revealed that the amorphous compound was also $Cu_2(PO_4)(OH)$. The removability found with those hydrogenphosphates was also observed in the immobilization of Pb^{2+} with $MgSO_4$ and $CaSO_4$.

Chemical immobilization of waste materials has the potential to reduce the leachability of heavy metals in the waste. The principal purpose during immobilization is to produce new mineral compounds with reduced solubilities and enhanced geochemical stability in a leaching environment. One immobilization agent of recent interest, particularly for Pb^{2+}, is $PO_4{}^{3-}$. Phosphate-containing minerals have been considered as sources of $PO_4{}^{3-}$. To immobilize Pb^{2+} from waste solutions and soils, the dissolution of the less stable mineral [e.g., calcium hydroxyapatite (CaHAp), $Ca_{10}(PO_4)_6(OH)_2$] followed by subsequent precipitation of the more stable metal phosphate [lead hydroxyapatite (PbHAp), $Pb_{10}(PO_4)_6(OH)_2$] has been extensively investigated.[1–7] Several groups suggested the following dissolution–precipitation mechanism for the immobilization of Pb^{2+} from aqueous solution.[2–4,6]

(1) Dissolution process:

$$\begin{aligned} &Ca_{10}(PO_4)_6(OH)_2\ \text{(solid)} + 14H^+\ \text{(aq)} \\ &\quad \Leftrightarrow 10Ca^{2+}\ \text{(aq)} + 6H_2PO_4{}^-\ \text{(aq)} + 2H_2O \end{aligned} \tag{1}$$

(2) Precipitation process:

$$\begin{aligned} &10Pb^{2+}\ \text{(aq)} + 6H_2PO4^-\ \text{(aq)} + 2H_2O \\ &\quad \Leftrightarrow Pb_{10}(PO_4)_6(OH)_2\ \text{(solid)} + 14H^+\ \text{(aq)} \end{aligned} \tag{2}$$

This mechanism suggests that phosphates may be employed for CaHAp. They can dissolve more easily than CaHAp into aqueous solution, followed by the formation of $H_2PO_4{}^-$. Indeed β-$Ca_3(PO_4)_2$, $CaHPO_4\cdot 2H_2O$ and $Ca(H_2PO_4)_2\cdot H_2O$ could favorably immobilize aqueous Pb^{2+} while $CaHPO_4\cdot 2H_2O$ could additionally immobilize aqueous Cd^{2+}, Co^{2+} and Cu^{2+},[8,9] indicating that the employment of hydrogenphosphates for the immobilization of aqueous heavy metal cations is attractive. In the present study, properties of Na_2HPO_4, K_2HPO_4, $MgHPO_4$ and $CaHPO_4$ for the immobilization of aqueous heavy metal cations such as Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} have been investigated. Furthermore $MgSO_4$ and $CaSO_4$ have been also employed for the immobilization of aqueous Pb^{2+}, since the employment of these sulfates seems to be possible in the dissolution–precipitation mechanism.

Experimental

All chemicals were purchased from Wako Pure Chemicals, Osaka, Japan and used as supplied. Standard solutions for inductively coupled plasma (ICP) measurement were obtained from Kanto Kagaku, Tokyo, Japan. Each aqueous solution (100 mL), to which a known quantity of Pb^{2+}, Cd^{2+}, Co^{2+} or Cu^{2+} as nitrate or acetate had been added, was stirred at 120 rpm in a constant temperature bath at 293 K for 20 min. The initial solution pH was adjusted by the addition of HNO_3 when needed. Then a known quantity of $Na_2HPO_4\cdot 7H_2O$, K_2HPO_4, $MgHPO_4\cdot 3H_2O$, $CaHPO_4\cdot 2H_2O$, $MgSO_4$ or $CaSO_4\cdot 2H_2O$ was added to the solution. After the specified period, the solution was removed by filtration, and either the supernatant or the filtrate, the latter dissolved in HNO_3 solution, was analyzed by ICP (Shimadzu ICPS-5000). The solution pH was measured with a pH meter (Horiba M-11). Powder X-ray diffraction (XRD) patterns of filtrates dried at 353 K overnight were recorded with Rigaku RINT2500X using monochromatized Cu Kα radiation at 40 kV and 100 mA. Solid state ^{31}P magic-angle spinning nuclear magnetic resonance (MAS NMR) of the solid samples was obtained with a Bruker AVANCE DSX300wbs, with an external reference of $NH_4H_2PO_4$ at 1.00 ppm at room temperature and a spinning rate of 7 kHz.

Results and Discussion

Immobilization with Na_2HPO_4. In order to examine the possibility for the immobilization of aqueous heavy metals with

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Table 1. Initial Solution Concentration and Removability after the Immobilization of Aqueous Heavy Metal Cations with 2.32 mmol of K_2HPO_4, $MgHPO_4 \cdot 3H_2O$ or $CaHPO_4 \cdot 2H_2O$ at 293 K

Hydrogenphosphate	Immobilization Time/h	Solution concentration (mmol/100 mL)			
		Pb^{2+}	Cd^{2+}	Co^{2+}	Cu^{2+}
$Na_2HPO_4 \cdot 7H_2O$	0	2.49	2.73	2.31	2.33
	0.5	(100%)	(83.1%)	(81.4%)	(73.4%)
K_2HPO_4	0	2.49	2.52	2.43	2.20
	0.5	(99.6%)	(79.4%)	(74.9%)	(68.6%)
$MgHPO_4 \cdot 3H_2O$	0	2.49	2.44	2.36	2.30
	0.5	(99.6%)	(34.8%)	(18.2%)	(39.6%)
	6.0	(100%)	(67.6%)	(47.9%)	(70.0%)
$CaHPO_4 \cdot 2H_2O$	0	2.63	2.57	2.09	2.41
	0.5	(100%)	(11.3%)	(9.1%)	(13.3%)
	5.0	(100%)	(82.9%)	(50.2%)	(45.2%)

Values in parenthesis: removability from the aqueous solution.

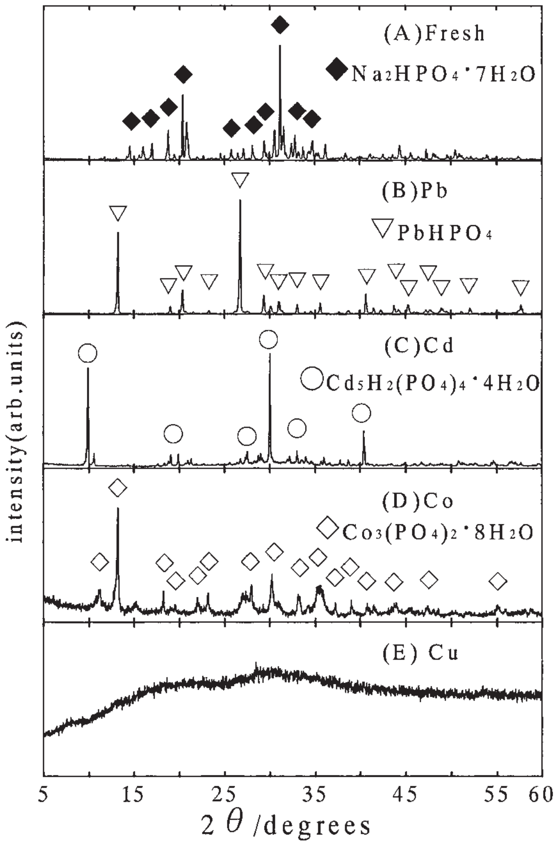

Fig. 1. XRD patterns of fresh $Na_2HPO_4 \cdot 7H_2O$ (A) and the solids recovered after the immobilization of Pb^{2+} (B), Cd^{2+} (C), Co^{2+} (D) and Cu^{2+} (E) for 0.5 h.

hydrogenphosphates, we employed $Na_2HPO_4 \cdot 7H_2O$ (3.1 mmol) for the removal of Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} (2.49, 2.73, 2.31 and 2.33 mmol/100 mL, respectively, supplied as nitrate). After 0.5 h, 100, 83.1, 81.4 and 73.4% of Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+}, respectively, were removed from the corresponding aqueous solutions (Table 1). It is worthwhile to mention that 2.3 mmol $CaHPO_4 \cdot 2H_2O$ could remove 100, 11.3, 9.1 and 13.3% of Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+}, respectively, for 0.5 h (Table 1), indicating that Na_2HPO_4 is one of the attractive reagents for the immobilization of those aqueous heavy metal cations. XRD patterns of solid recovered after 0.5 h immobilization showed that Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} were immobilized onto $Na_2HPO_4 \cdot 7H_2O$ (JCPDS 10-0191) as $PbHPO_4$ (JCPDS 29-0773), $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ (JCPDS 23-0091), $Co_3(PO_4)_2 \cdot 8H_2O$ (JCPDS 33-0432) and an amorphous compound, respectively (Fig. 1). The solid recovered after the immobilization of those four heavy metal cations was identified as a dissimilar type of phosphate, while the shift of solution pH during the immobilization from 0 to 0.5 h of Pb^{2+} (4.2 to 2.9), Cd^{2+} (5.1 to 3.1), Co^{2+} (5.4 to 4.2) and Cu^{2+} (4.1 to 3.5) was also dependent on those four cations. Since a specific type of phosphate anion, $H_2PO_4^-$ and HPO_4^{2-} is mainly formed in the aqueous solution under acidic and neutral conditions, respectively,[10] the effects of solution pH on the type of solid recovered after the immobilization are of interest. When initial solution pH for the immobilization of Co^{2+}, which was supplied as nitrate or acetate, with Na_2HPO_4 was adjusted at 5.4, 4.9, and 3.0 or 6.4 and 4.4, respectively, XRD patterns of the solids recovered after immobilization for 0.5 h under the above-described conditions except pH revealed that $Co_3(PO_4)_2 \cdot 8H_2O$ and $CoHPO_4 \cdot 1.5H_2O$ (JCPDS 22-0222) were formed at pH values from 6.8 and 5.4 and at those from 4.9 to 3.9, respectively. Therefore the contribution of the effect of pH is evident for the crystalline phase of the solids recovered after immobilization. When initial solution pH for the immobilization of Co^{2+}, which was supplied as nitrate, with Na_2HPO_4 was adjusted at 5.4, 4.9, and 3.0, the removabilities of Co^{2+} were 81.3, 82.6 and 78.5%, respectively, indicating that immobilization of Co^{2+} was not dependent on pH under the present conditions. The removabilities of 92.0 and 57.0% were observed when initial solution pH for the immobilization of Co^{2+} (which was supplied as acetate but not nitrate) with the hydrogenphosphate was adjusted at 6.8 and 4.4, indicating that acetate and nitrate may exert dissimilar influences on the immobilization. As mentioned, Pb^{2+} could be completely removed from the aqueous solution while certain amounts of Cd^{2+}, Co^{2+} and Cu^{2+} were still present in the solutions after the immobilization under the conditions described above. Unfortunately the extension of the immobilization time from 0.5 to 2 h afforded the essentially identical removability for Cd^{2+}, Co^{2+} and Cu^{2+}, indicating that the formation of insoluble phosphate including those cations over the surface of Na_2HPO_4 resulted in the obstruction of the solution of Na_2HPO_4. However

Table 2. Crystalline Phase of the Solids Recovered after the Immobilization of Aqueous Pb^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+} with K_2HPO_4 for 0.5 h, $MgHPO_4$ for 6.0 h, and $CaHPO_4$ for 5.0 h and the Shift of the Solution pH during the Immobilization

Hydrogenphosphate	Crystalline phase			
	Pb^{2+}	Cd^{2+}	Co^{2+}	Cu^{2+}
K_2HPO_4	$PbHPO_4$ (4.2 to 3.1)	$Cd_5H_2(PO_4)_4 \cdot 4H_2O$ (5.1 to 3.6)	$CoHPO_4 \cdot 1.5H_2O$ (4.9 to 4.3)	amorphous (4.3 to 3.0)
$MgHPO_4 \cdot 3H_2O$	$Pb_{10}(PO_4)_6(OH)_2$ (4.1 to 2.3)	amorphous (5.0 to 3.9)	$Co_3(PO_4)_2 \cdot 8H_2O$ (5.2 to 5.4)	amorphous (4.1 to 3.6)
$CaHPO_4 \cdot 2H_2O$	$PbHPO_4$ (3.9 to 3.5)	$Cd_5H_2(PO_4)_4 \cdot 4H_2O$ (4.9 to 3.8)	$Co_3(PO_4)_2 \cdot 8H_2O$ (4.7 to 4.7)	amorphous (4.2 to 3.6)

Values in parenthesis: the solution pH during the immobilization.

97.9, 100 and 100% of Cd^{2+}, Co^{2+} and Cu^{2+}, respectively, were immobilized for 5 h with $Na_2HPO_4 \cdot 7H_2O$ (3.1 mmol) from the aqueous solution upon the adjustment of their initial concentrations to be 1.4, 1.5 and 1.5 mmol/100 mL, respectively. Such similarity means that the immobilization could be completed when the surface of $Na_2HPO_4 \cdot 7H_2O$ was not completely covered with insoluble phosphates including Cd^{2+}, Co^{2+} and Cu^{2+}.

Immobilization with K_2HPO_4, $MgHPO_4$ and $CaHPO_4$. To provide further information on immobilization of those heavy metal cations from the aqueous solution with other hydrogenphosphates, we emploed K_2HPO_4, $MgHPO_4$ and $CaHPO_4$ for Na_2HPO_4. Table 1 describes the results of the immobilization of aqueous Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} with those hydrogen phosphates. The immobilization with K_2HPO_4 proceeded favorably within 0.5 h, as observed with $Na_2HPO_4 \cdot 7H_2O$, and the removability increased in the order $Cu^{2+} < Co^{2+} < Cd^{2+} < Pb^{2+}$. However, the short immobilization time of 0.5 h was not sufficient with $MgHPO_4 \cdot 3H_2O$ and $CaHPO_4 \cdot 2H_2O$ and the corresponding results from the immobilization for 0.5 h with those alkali metal hydrogenphosphates were observed after the immobilization of 6 h and 5 h, respectively. Therefore, the longer immobilization time may be favorable to the diffusion of the component ions formed from those alkaline-earth hydrogenphosphates, resulting in the enhancement of the removability. Based on this dissolution–precipitation mechanism, facile dissolution of those hydrogenphosphates is desirable for the effective immobilization. Since the solubilities of $Na_2HPO_4 \cdot 7H_2O$ (185 at 313 K)[11] and K_2HPO_4 (150 at room temperature)[11] are evidently greater than those of $MgHPO_4 \cdot 3H_2O$ (slightly dissolved)[11] and $CaHPO_4 \cdot 2H_2O$ (0.017 at 298 K),[11] the immobilization with those alkali metal hydrogenphosphates proceeds more favorably than that with those alkaline earth metal hydrogenphosphates. The removability with $CaHPO_4 \cdot 2H_2O$ increased in the order $Cu^{2+} < Co^{2+} < Cd^{2+} < Pb^{2+}$, as observed with $Na_2HPO_4 \cdot 7H_2O$ and K_2HPO_4, while the order was $Co^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$ with $MgHPO_4 \cdot 3H_2O$. Such results indicate that Pb^{2+} and Cd^{2+} may be immobilized more easily that Co^{2+} and Cu^{2+}, except for the immobilization of Cu^{2+} with the magnesium salt. In the immobilization of aqueous heavy metal cations with CaHAp ($Ca_{10}(PO_4)_6(OH)_2$), it has been already reported that heavy metal cations, which possess similar ionic radius lengths to that of Ca^{2+} (0.114–0.126 nm)[12] could be favorably removed from the aqueous solution, based on the investigation of the rate but not of the equilibrium. However, except for the immobilization of Cu^{2+} with $MgHPO_4 \cdot 3H_2O$, the removability similarly increased in the order Cu^{2+} (0.087 nm)[12] < Co^{2+} (0.079–0.089 nm)[12] < Cd^{2+} (0.092–0.109 nm)[12] < Pb^{2+} (0.133–0.143 nm)[12] although the hydrogenphosphates, which consisted of alkali metal or alkaline earth metal cations with dissimilar ionic radii, were employed in the present study (Na^+: 0.113–0.116 nm, K^+: 0.152–0.165 nm and Mg^{2+}: 0.071–0.086 nm).[12] It seems to be of interest to note that the order of hydration enthalpy in aqueous solution of those heavy metal cations (Cu^{2+} (−2100 kJ/mol)[13] < Co^{2+} (−1996 kJ/mol)[13] < Cd^{2+} (−1807 kJ/mol)[13] < Pb^{2+} (−1481 kJ/mol))[13] is identical to that of the removability of those cations. So it may be reasonable that the removability of Cu^{2+} and Co^{2+} is rather suppressed by the formation of the corresponding stable hydrate. Table 2 describes the crystalline phase of the solids recovered after the immobilization of heavy metal cations with K_2HPO_4, $MgHPO_4$ and $CaHPO_4$, which was determined with XRD, and the shift of solution pH during the immobilization for 0.5, 6 and 5 h, respectively. The analysis with XRD of the samples recovered from the immobilization of Pb^{2+}, Cd^{2+}, and Co^{2+} with those hydrogenphosphates showed that $Pb_{10}(PO_4)_6(OH)_2$ (JCPDS 8-0259), $Cd_5H_2(PO_4)_4 \cdot 4H_2O$, and $CoHPO_4 \cdot 1.5H_2O$ (JCPDS 22-0222) were formed at rather acidic final pH while the formation of $PbHPO_4$, amorphous Cd-compound, and $Co_3(PO_4)_2 \cdot 8H_2O$ occurred at rather natural final pH value. Again it is evident that the crystalline phase of the solids recovered from the immobilization is influenced by the solution pH, as observed in the immobilization with Na_2HPO_4. Unfortunately no information on the crystalline phase of the solid recovered from the immobilization of Cu^{2+} with those hydrogenphosphates was obtained with XRD, probably due to the low crystallinity of the solid. In order to enhance the crystallinity of the amorphous Cu-compound, we kept the solid used for the immobilization of Cu^{2+} with K_2HPO_4 for 0.5 h (under the conditions employed in obtaining the results shown in Tables 1 and 2) in the solution without stirring for 12 h. The formation of $Cu_2(PO_4)(OH)$ (JCPDS 36-0404) was confirmed with XRD of the solid recovered after 12 h. Solid state ^{31}P MAS NMR of those solids recovered after 0.5 and 12 h showed essentially identical patterns, indicating that the amorphous Cu-compound obtained from the immobilization of Cu^{2+} with K_2HPO_4 for 0.5 h may be also $Cu_2(PO_4)(OH)$ with a low crystallinity (Fig. 2). It should be noted that ^{31}P MAS NMR signal extensively shifted from 3.7

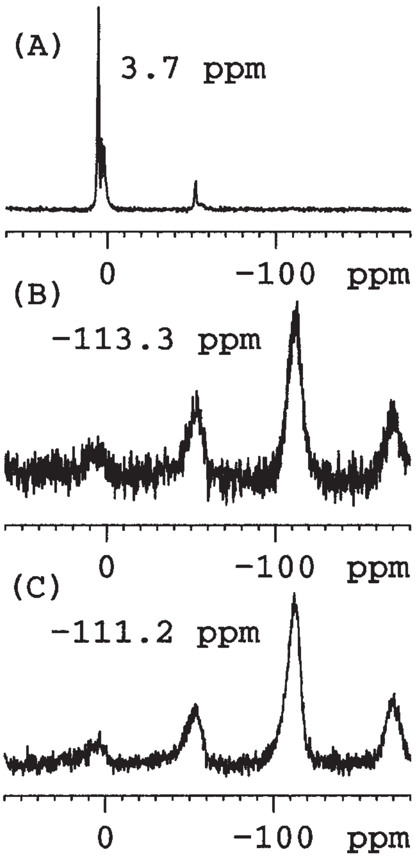

Fig. 2. ^{31}P MAS NMR of fresh K_2HPO_4 (A) and the solids recovered after the immobilization of Cu^{2+} for 0.5 (B) and 12 h (C).

ppm to higher magnetic field of ca. −110 ppm and the broadening of the signals was evident after the immobilization. The coupling constants of phosphorus to Cu nuclei, $^1J(^{63}Cu, ^{31}P)$ and $^1J(^{65}Cu, ^{31}P)$, are greater than 1000 Hz and evidently greater that those of phosphorus to alkali nuclei (less than 100 Hz),[14] resulting in the observation of the broadening of the peak. Furthermore, the ^{31}P chemical shift range of pentavalent tetracoordinate phosphorous extends essentially between +150 and −100 ppm.[14] Therefore the ^{31}P MAS NMR of the sample after the immobilization with Cu^{2+} may reveal the formation of a Cu-compound with weak magnetic properties.

Immobilization of Pb^{2+} with $MgSO_4$ and $CaSO_4$. Based on dissolution–precipitation mechanism, that is, the solution of an immobilization reagent to form aqueous reactive anions followed by the reaction between the anions and aqueous heavy metal cations to form insoluble compounds, the employment of other compounds rather than phosphate is possible. Since waste solutions from car-batteries carried in used vehicles, in which Pb^{2+} and $SO_4{}^{2-}$ are present, are regarded as questionable, as suggested by the Japan Association of City Mayors in 2001, the combination of sulfate as an immobilization reagent and aqueous Pb^{2+} seems to be attractive. Therefore $MgSO_4$ (solubility = 26 at 273 K)[11] and $CaSO_4 \cdot 2H_2O$ (0.26 at 293 K)[11] were employed for hydrogenphosphates in the immobilization of aqueous Pb^{2+}. When 2.32 mmol of $MgSO_4$ and $CaSO_4 \cdot 2H_2O$ was employed for the immobilization of Pb^{2+} (2.40 mmol/100 mL) for 0.5 h, 96.3% and 83.8%, respectively, of Pb^{2+} were removed from the solution; XRD showed that Pb^{2+} was immobilized onto the recovered solid as $PbSO_4$ (JCPDS 36-1461).

In the present study, various immobilization reagents, which were selected in regard to the dissolution–precipitation mechanism for the immobilization of Pb^{2+} with calcium hydroxyapatite, were employed for the removal of heavy metal cations from the aqueous solution. Since excellent immobilization of aqueous heavy metal cations was observed with the employment of those reagents, it should be possible to develop the immobilization reagents based on the mechanism.

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