Pb²⁺-Uptake Property of Octacalcium Phosphate Cement in Solution

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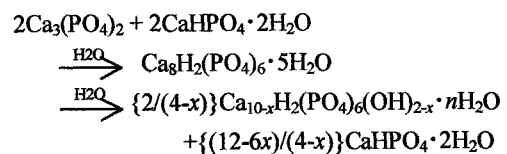Fax:81-0426-28-4626, e-mail:monma@cc.kogakuin.ac.jp

The Pb^{2+}-uptake property of octacalcium phosphate (OCP) cement was investigated at 25-75℃ in batch and flow systems. The OCP cement powder was composed of a mixture of α-$Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$. Pb^{2+}-containing solutions (adjusted to pH4) of 100-1000 ppm were prepared from $PbCl_2$ and $Pb(NO_3)_2$. In batch runs, Pb^{2+}-removal rates were markedly larger in $PbCl_2$ solutions than in $Pb(NO_3)_2$ solutions. Removal times required for [Pb^{2+}] decreasing below 0.01 ppm were markedly shorter in $PbCl_2$ solutions than in $Pb(NO_3)_2$ solutions. The co-existence of Cl^- ions with Pb^{2+} ions was very effective for the Pb^{2+}-uptake property of the cement. The uptake reaction was apparently the ion-exchange reaction $Ca^{2+} \leftrightarrow Pb^{2+}$. The Pb^{2+}-uptake property of the cement was better than that of synthetic HAp. Reaction products were $(Ca,Pb)_{10}(PO_4)_6(OH)_2$, $Pb_{10}(PO_4)_6(OH)_2$, $(Ca,Pb)_{10}(PO_4)_6(Cl,OH)_2$ or $Pb_{10}(PO_4)_6Cl_2$. Apparent activation energies for the Pb^{2+}-removal reaction were 8.2-8.5 kJ/mol in $PbCl_2$ solutions and 26-44 kJ/mol in $Pb(NO_3)_2$ solutions. In flow runs using the cement with a bed of 35 mm diameter and 1mm thick, breaking points of Pb^{2+}-effluent curves were 50 ml for 1000 ppm Pb^{2+} solution, 100 ml for 500 ppm, 230 ml for 200 ppm, and above 300 ml for 100 ppm.

Keywords: Calcium phosphate cement, Removal of lead ion, Hydroxyapatite, Lead apatite

1. INTRODUCTION

The Ca^{2+} ions of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; designated as HAp) are cation-exchangeable for various heavy metal ions in solution [1-3], and in addition the OH^- ions are also exchangeable for Cl^- ions when Cl^- ions co-existed with metal ions [1,2]. Particularly, bio-hazardous Pb^{2+} ions are of great subject. For instance, concentrations of Pb^{2+} in water-supply are regulated to be less than 10 ppb in WHO and Canada, less than 15 ppb in USA, and less than 50 ppb in Japan. In such circumstances, HAp has become of interest in the purification of industrial wastewater containing heavy metal ions. In the present work, the authors noted octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$; OCP) which resembles compositionally and structurally HAp. OCP is well-known as a thermodynamically metastable phase with respect to HAp in solution. Actually an OCP cement was used instead of synthetic OCP. The cement powder hardens with the reaction change into OCP or HAp depending on co-existing ions [4]. In other words, an effective incorporation of Pb^{2+}

into the OCP or HAp structure could be expected because that the occasion of ionic rearrangements of the cement components into OCP or HAp are concerned in the Pb^{2+}-uptake. The Pb^{2+}-uptake property of the cement were investigated by batch and flow methods. The reactions of the cement into OCP or HAp are written as follows,

$$2Ca_3(PO_4)_2 + 2CaHPO_4 \cdot 2H_2O$$
$$\xrightarrow{H2O} Ca_8H_2(PO_4)_6 \cdot 5H_2O$$
$$\xrightarrow{H2O} \{2/(4\text{-}x)\}Ca_{10\text{-}x}H_2(PO_4)_6(OH)_{2\text{-}x} \cdot nH_2O$$
$$+\{(12\text{-}6x)/(4\text{-}x)\}CaHPO_4 \cdot 2H_2O$$

where the formation of Ca-deficient HAp is assumed and stoichiometric H_2O molecules are omitted. The formation of HAp is known to be very speedy even in the presence of trace amounts of F^- ions [5].

2. EXPERIMENTAL

OCP cement powder was prepared by mixing thermally synthesized α-$Ca_3(PO_4)_2$ and reagent

$CaHPO_4 \cdot 2H_2O$ with an 1:1 molar ratio. Synthetic HAp was prepared by a conventional precipitation method [6]. Both OCP cement and HAp samples were ground to pass through a 150 mesh. The Pb^{2+}-containing solutions with 100-1000 ppm were prepared from reagent $PbCl_2$ and $Pb(NO_3)_2$. The solutions prepared were adjusted to pH4 with a dilute HCl or HNO_3 solution. In the batch experiment, suspensions of 1.0g (12.20 mmol Ca^{2+}) of the OCP cement in 400ml of 100-1000 ppm Pb^{2+}-containing solutions (0.48-4.83 mmol/dm³) were stirred at 25, 50, and 75℃, and decreases of [Pb^{2+}] in solution were followed with time by ion-chromatography. Completion times for removal of Pb^{2+} from Pb^{2+}-containing solutions were adopted to be times required for [Pb^{2+}] decreasing below 0.01 ppm.

In the flow experiment, first 0.25 g of the OCP cement was suspended in water, and the suspension was poured into a glass filter (4G) with 35 mm diameter and 50 mm depth. The resulting pasty wet bed on the filter was ca. 1 mm thick. Then 100-1000 ppm solutions of Pb^{2+} were passed through the bed at a flow rate of 10 ml/min at room temperature, and [Pb^{2+}]s in effluent fractions were analyzed by ion-chromatography.

3. RESULTS AND DISCUSSION

3.1 Pb^{2+}-removal process in the batch system

Figure 1 shows decreases of [Pb^{2+}] in solution mixed with the OCP cement. Initial Pb^{2+}-removal rates were markedly larger in $PbCl_2$ solutions of than rates in $Pb(NO_3)_2$ solutions. For instance, rapid decreases of

[Pb^{2+}] were observed for initial 5 min in $PbCl_2$ solutions in comparison with for 1 h in $Pb(NO_3)_2$ solutions. Completion times for reaching a [Pb^{2+}] level below 0.01 ppm were also markedly shorter in $PbCl_2$ solutions than in $Pb(NO_3)_2$ solutions. Table I summarized completion times. Chloride ions co-existed with Pb^{2+} ions was strongly effective for the Pb^{2+}-uptake properties of the OCP cement. Consequently completion times could be shortens by adding chloride ions and also increasing temperature. Figure 2 shows Pb^{2+}-uptake properties of the OCP cement and synthetic HAp. The Pb^{2+}-uptake performance tended to be OCP cement > Synthetic HAp.

Table 1 Pb^{2+}-removal from solutions with various initial Pb^{2+} concentrations ([Pb^{2+}]$_0$) by OCP cement. (1g-OCP cement / 400 ml Pb $^{2+}$ solution adjusted to pH4, with stirring)

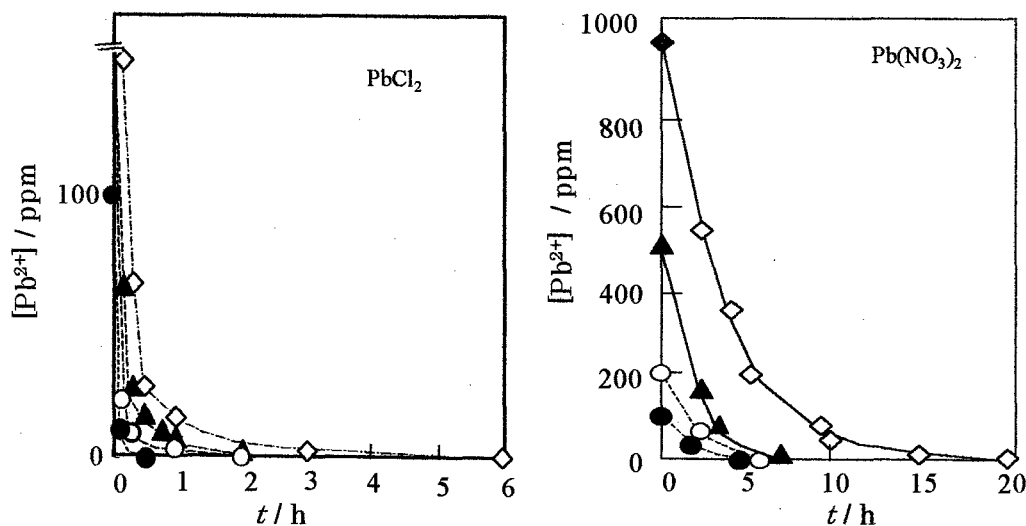| Temp. /℃	Pb solution used (pH4)	Completion time for removal of Pb^{2+} / h			
		[Pb^{2+}]$_0$ = 100ppm	[Pb^{2+}]$_0$ = 200ppm	[Pb^{2+}]$_0$ = 500ppm	[Pb^{2+}]$_0$ = 1000ppm
25	$PbCl_2$	1	2	3	6
	$Pb(NO_3)_2$	5	6	7	20
50	$PbCl_2$	0.5	1	2	4
	$Pb(NO_3)_2$	3	3	5	12
75	$PbCl_2$	0.25	0.5	1	3
	$Pb(NO_3)_2$	0.5	1	2	6

Fig. 1   Removal of Pb^{2+} from $PbCl_2$ and $Pb(NO_3)_2$ solutions by OCP cement (25℃).
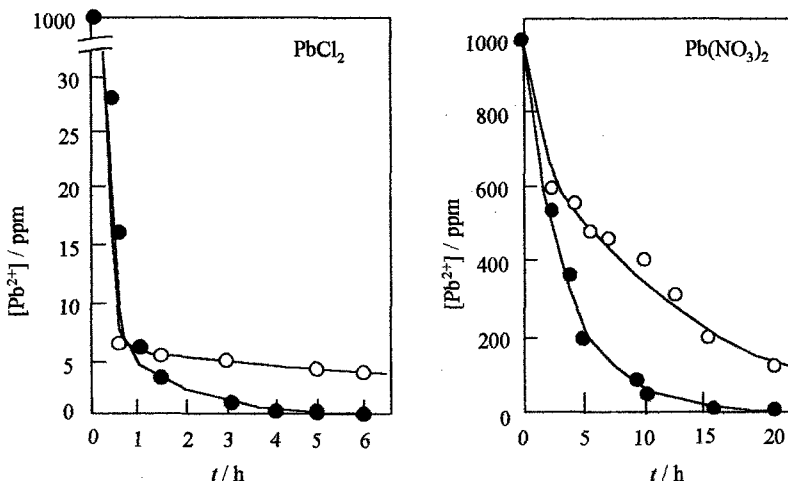Initial [Pb^{2+}]: ●100ppm, ○200ppm, ▲500ppm, ◇1000ppm

Fig. 2 Removal of Pb^{2+} from $PbCl_2$ (left) and $Pb(NO_3)_2$ (right) solutions (adjusted to pH4) at 25°C by OCP cement (●) and synthetic HAp (○)(Initial $[Pb^{2+}]$:1000 ppm)

3.2 Products in the batch system

Figure 3 shows XRD patterns of solid products after completion of Pb^{2+}-removal from Pb^{2+} solutions. Reaction products were considered to be $(Ca,Pb)_{10}$ $(PO_4)_6(OH)_2$, $Pb_{10}(PO_4)_6(OH)_2$, $(Ca,Pb)_{10}(PO_4)_6(Cl, OH)$ $_2$ and $Pb_{10}(PO_4)_6Cl_2$ depending on degrees of Pb^{2+}- and Cl^--uptake into HAp.

3.3 Pb^{2+}-removal kinetics in the batch system

Table II shows molar ratios of Pb^{2+} removed from solution to Ca^{2+} released into solution in the system of OCP cement and Pb^{2+}-containing solution. The molar ratios near 1.0 indicated apparently the ion-exchange $Ca^{2+} \leftrightarrow Pb^{2+}$. Lower ratios observed in the $PbCl_2$ solutions suggested that partially Cl^--dissolving HAp might be a little more soluble compared to pure HAp. Actually the Pb^{2+}-uptake reaction was thought to occur

through the dissolution of the OCP cement components and subsequent precipitation of apatite. The Pb^{2+}-removal curves obeyed first order kinetics good with respect to $[Pb^{2+}]$ in solution (Figures are omitted). Rate constants obtained were, for instance, 19.8 h^{-1} and 1.4 h^{-1} in 100 ppm Pb^{2+} solutions prepared from $PbCl_2$

Table II Ratio of Pb^{2+} removed to Ca^{2+} released after completion for Pb^{2+}-removal in the system of 1g-OCP cement / 400ml Pb^{2+} solution at 25°C.

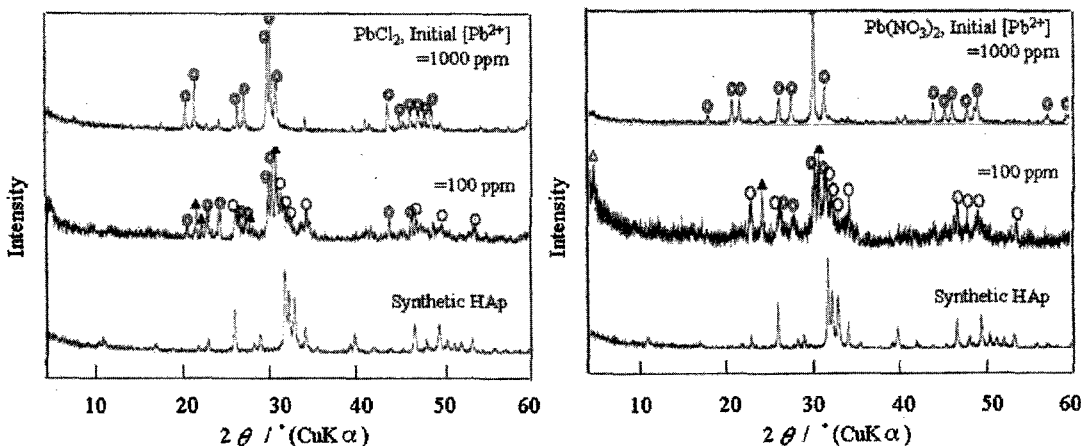|	Pb^{2+} removed / Ca^{2+} released / molar ratio			
Pb solution used (pH4)	$[Pb^{2+}]_0$ = 100ppm	$[Pb^{2+}]_0$ = 200ppm	$[Pb^{2+}]_0$ = 500ppm	$[Pb^{2+}]_0$ = 1000ppm
$PbCl_2$	0.26	0.39	0.86	0.86
$Pb(NO_3)_2$	0.96	0.97	0.94	0.97

Fig.3 XRD patterns of OCP cement products after completion of Pb^{2+}-removal from Pb^{2+} solutions at 25°C and synthetic HAp. ○:HAp, ◎:Pb^{2+}-dissolving chloroapatite, ▲ :Unreacted α -$Ca_3(PO_4)_2$
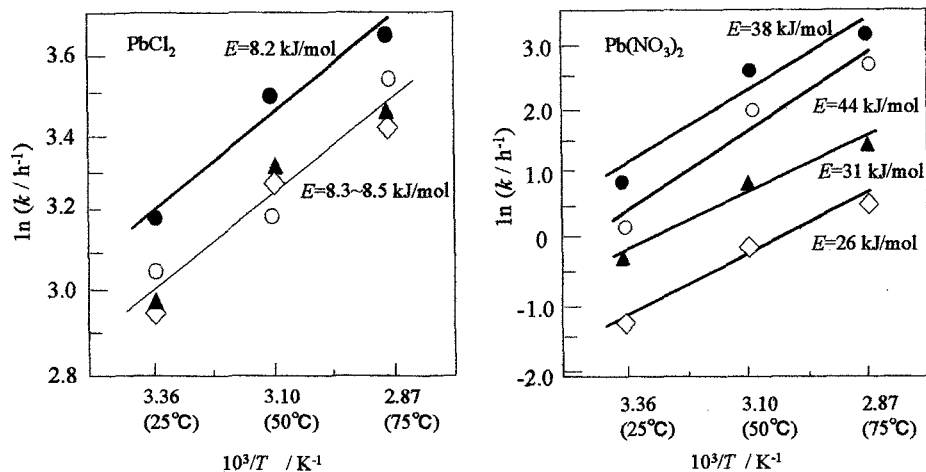
Fig. 4 Arrhenius plots of rate constants obtained by the first reaction rate equation
$(\ln[Pb^{2+}]/[Pb^{2+}]o = -kt)$ in the system OCP cement - $PbCl_2$ solutions.
Initial $[Pb^{2+}]$: ●:100ppm ○:200ppm ▲:500ppm ◇:1000ppm

and $Pb(NO_3)_2$, respectively. Figure 4 shows Arrhenius plots of rate constants vs. reciprocal temperatures. Apparent activation energies were very low, i.e., 8.2-8.5 kJ/mol in $PbCl_2$ solutions and 26-44 kJ/mol in $Pb(NO_3)_2$ solutions.

3.4 Pb^{2+}-removal in the flow system

Figure 5 shows Pb^{2+}-effluent curves in flow experiments. Breaking points were over 300 ml for flowing 100 ppm Pb^{2+} solution, 220 ml for 200 ppm, 100 ml for 500 ppm and 50 ml for 1000 ppm Pb^{2+}.
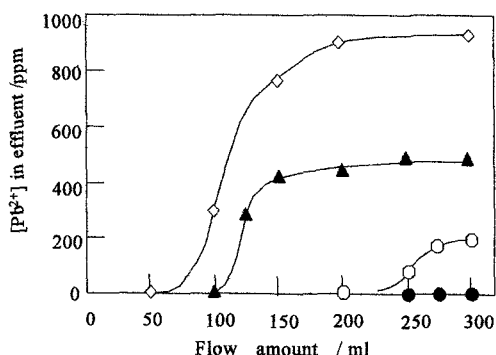

Fig. 5 Pb^{2+}-effluent curves using a bed of 35 mm diameter and 1 mm thick of OCP cement with a flow of 10 ml/min. $[Pb^{2+}]$ of flowing solution prepared from $PbCl_2$: ◇1000ppm, ▲500ppm, ○200ppm, ●100ppm

4. CONCLUSIONS

The Pb^{2+}-uptake property of octacalcium phosphate (OCP) cement was investigated at 25-75°C in 100-1000 ppm Pb^{2+} solutions adjusted to pH4. In batch runs, Pb^{2+}-removal rates were markedly larger in $PbCl_2$ solutions than in $Pb(NO_3)_2$ solutions. Removal times required for $[Pb^{2+}]$ decreasing below 0.01 ppm were

markedly shorter in $PbCl_2$ solutions than in $Pb(NO_3)_2$ solutions. The co-existence of Cl^- ions with Pb^{2+} ions was strongly effective for the Pb^{2+}-uptake properties of the cement. The uptake reaction was apparently the ion-exchange reaction $Ca^{2+} \leftrightarrow Pb^{2+}$. The Pb^{2+}-uptake property of the OCP cement was better than that of synthetic HAp. Reaction products were $(Ca,Pb)_{10}(PO_4)_6$ $(OH)_2$, $Pb_{10}(PO_4)_6(OH)_2$, $(Ca,Pb)_{10}$ $(PO_4)_6$ $(Cl,OH)_2$ or $Pb_{10}(PO_4)_6Cl_2$. Apparent activation energies for the Pb^{2+}-removal reaction were 8.2-8.5 kJ/mol in $PbCl_2$ solutions and 26-44 kJ/mol in $Pb(NO_3)_2$ solutions. In flow runs using the OCP cement with a bed of 35 mm diameter and 1mm thick, breaking points of Pb^{2+}-effluent curves were 50 ml for 1000 ppm Pb^{2+} solution, 100 ml for 500 ppm, 230 ml for 200 ppm, and above 300 ml for 100 ppm.

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