Phosphorus Research Bulletin Vol. 22 (2008) pp. 54-60

REACTION OF Ca-DEFICIENT HYDROXYAPATITE WITH HEAVY METAL IONS ALONG WITH METAL SUBSTITUTION

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Keywords: Hydroxyapatite, Heavy metal, Cationic substitution

Abstract: Reaction of Ca-deficient hydroxyapatite, HAP-400, with heavy metals, Pb (II), Fe (III), Fe (II), Cu (II), Cd (II), Cr (II), Co (II), Ni (II), and Zn (II) was investigated at 25˚C for 4 h in water, compared with stoichiometric hydroxyapatite HAP-300. From heavy metal consumption and [Ca]/[Metal], which is defined by molar ratio of eluted Ca and consumed heavy metal, the reactions of HAP-400 with the heavy metals except for Pb (II) and Fe (III) proceed via metal-adsorptive substitution mechanism. In the reactions of HAP-400 with Pb (II) and Fe (III), the metals were completely consumed with equivalent elution of Ca, but these reactions proceeded by no simple substitution mechanism to afford Pb (II)- and Fe (III)-bearing HAP-400 with specific structures, namely HAP-400-Pb and HAP-400-Fe. By XRD and FT-IR microspectroscopy, it was found that HAP-400-Pb is constituted of both newly formed lead apatite crystal and the original apatite crystal, and that HAP-400-Fe is constituted of much amorphous $FePO_4$ phase around the original apatic phase. Therefore, it was concluded that the reactions of HAP-400 with Pb (II) and Fe (III) proceed by the following mechanism: erosion of the apatic structure and formation of a brand-new structure containing metal. This mechanism can be named apatite-erosive substitution mechanism.

(Received March 24, 2008; Accepted May 14, 2008)

INTRODUCTION

Stoichiometric hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, has substitution ability with cations such as sodium[1, 2] and heavy metal[3-9] ions as well as anions such as sulfonate[1, 2] and halogen[10, 11] ions. It is supposed that Ca-deficient hydroxyapatite,[12] denoted as $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, exhibits ion substitution ability different from stoichiometric hydroxyapatite since Ca-deficient apatite has a crystal structure with many Ca-deficient sites. Ca-deficient apatite is expected to be applied to a removal agent for heavy metals. We have reported a possible application of Ca-deficient hydroxyapatite HAP-400 as an efficient removal agent for Pb^{2+} in water. The removal proceeds by elution of Ca and formation of lead apatite.[13] However, reactivity of HAP-400 with the other heavy metals has not been reported so far. Therefore, we investigated reaction of HAP-400 with heavy metals, Fe (III), Fe (II), Cu (II), Cd (II), Cr (III), Co (II), Ni (II), and Zn (II), together with Pb (II), and elucidated the reaction mechanisms.

MATERIALS AND METHODS

Stoichiometric hydroxyapatite, HAP-300 (Ca/P = 1.68; containing 2.5 wt% CO_3.), and Ca-deficient hydroxyapatite, HAP-400 (Ca/P = 1.38), were supplied from Taihei Chemical Industrial Co., Ltd. Heavy metal salts, $Pb(NO_3)_2$, $FeCl_3$, $Fe(NO_3)_3$, $FeCl_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Cr(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$, and distilled water (HPLC grade) were purchased from Wako Pure Chemical Industries, Ltd. All materials were used without further purification.

Reaction of the hydroxyapatites with heavy metals were carried out as follows: To 0.50 g of hydroxyapatite (HAP-300 or HAP-400) in an eggplant-shaped flask (200 mL) was added 100 mL of aqueous heavy metal solution (25 mM) and a stirrer bar. The mixture was shaken at 25˚C for 4 h in a concussive water incubator, M-100^N (TAITEC Co., Ltd., Saitama, Japan), and centrifuged at 3000 rpm with a centrifuge, Model B (Shimadzu Co., Kyoto, Japan) to recover supernatant solution and reacted apatite. The supernatant was analyzed with an inductively coupled plasma atomic emission spectrometer (ICP), SPS3100 (Seiko Instruments Inc.) to estimate concentrations of charged metal and eluted Ca. Among the reacted apatites, the hydroxyapatites (HAP-400 and HAP-300) reacted with Pb (II) and Fe (III) were washed with distilled water three times and dried at 150˚C overnight in a

drying oven, DZ-54 (Yamato Scientific Co., Ltd., Tokyo, Japan) to obtain the corresponding metal-bearing hydroxyapatites, HAP-400-Pb, HAP-400-Fe, HAP-300-Pb, and HAP-300-Pb.

In order to elucidate structures of apatites, an X-ray diffractometer (XRD), M18XCE (Bruker AXS GmbH, Karlsruhe, Germany) was used under the following condition: target, Cr; voltage, 30 kV; current, 100 mA. In addition, a Fourier transform infrared (FT-IR) spectrometer, System 2000 FT-IR equipped with AutoIMAGE System (Perkin-Elmer Co., Wellesley, MA, USA) was used in a microscopic reflection method.

Specific surface areas of apatites were clarified by using a high speed gas sorption analyzer, N10-12 (Yuasa Ionics Inc., Osaka, Japan), in BET method.

Elemental analysis of apatites was carried out by using the ICP instrument after the apatic samples were dissolved with 10% nitric acid.

RESULTS AND DISCUSSION

1) Reaction of apatites with heavy metals.

Hydroxyapatites, HAP-300 and HAP-400, were allowed to react with heavy metals, Pb (II), Fe (III), Fe (II), Cu (II), Cd (II), Cr (II), Co (II), Ni (II), and Zn (II). TABLE 1 shows the result, consumption (%) of charged metal and molar ratio of eluted Ca versus consumed metal, [Ca]/[Metal] (mol/mol). Attractive to metal consumption, Pb (II) and Fe (III) completely reacted with HAP-400 (No. 1-3). HAP-300 also indicated complete consumption of Fe (III), but indicated less reactivity to Pb (II) than HAP-400, as reported previously.[13] Difference between counter ions, Cl^- and NO_3^-, did not affected the Fe (III) consumptions (No. 2 and 3). The reaction of Cr (III) with both the apatites indicated high consumption more than 70% (No. 7). However, the other heavy metals, Fe (II), Cu (II), Cd (II), Co (II), Ni (II), and Zn (II), indicated low consumptions less than 30% (No. 4-6, 8-10). It was attractive that different valency between Fe (II) and Fe (III) significantly affected reactivity of both the apatites, in which Fe (III) was much more reactive (No. 2 and 4).

In the molar ratios, [Ca]/[Metal], the value for Pb (II) was near 1.0, and that for Fe (III) was around 1.5, in both the apatites. The former value implies that 1 : 1 substitution between Ca and Pb (II) occurred via the apatites, and the latter implies that 3 : 2 substitution of Ca to Fe (III) occurred. These estimations are interpreted as balanced substitution of cationic quantities between eluted Ca^{2+} and the charged metal (Pb^{2+} or Fe^{3+}). It is considered that these reactions proceeded stoichiometrically. The similar stoichiometric reactions were observed in the reactions of Cu(II), Cd (II), Ni (II), and Zn (II) with HAP-300. Elution of Ca rather than consumption of heavy metal was promoted in the reactions of Cr (III) and Co (II) with HAP-300 as well as the reaction of Cu (II) with HAP-400. Inversely, consumption of heavy metal rather than elution of Ca was promoted in the reaction of Fe (II) with HAP-300 as well as the reactions of Fe (II), Cd (II), Cr (III), Co (II), Ni (II), and Zn (II) with HAP-400. In this case, the apatites exhibited an adsorption property rather than substitution. Therefore, it was found that the

TABLE 1 Metal consumption and molar ratio [Ca]/[Metal] in substitution reaction of hydroxyapatite with heavy metal ion.

No.	Salt	Charged metal	Ion radius[a] (nm)	Metal consumption (%)[b]		[Ca]/[Metal][c]	
				HAP-400	HAP-300	HAP-400	HAP-300
1	$Pb(NO_3)_2$	Pb(II)	0.133	100	24	0.93	0.95
2	$FeCl_3$	Fe(III)	0.069	100	100	1.46	1.64
3	$Fe(NO_3)_3$	Fe(III)	0.069	100	100	1.48	1.60
4	$FeCl_2$	Fe(II)	0.075	29	25	0.27	0.73
5	$Cu(NO_3)_2$	Cu(II)	0.087	6	16	1.60	1.12
6	$Cd(NO_3)_2$	Cd(II)	0.109	15	14	0.46	1.00
7	$Cr(NO_3)_3$	Cr(III)	0.076	92	72	0.28	1.82
8	$Co(NO_3)_2$	Co(II)	0.079	29	4	0.12	1.98
9	$Ni(NO_3)_2$	Ni(II)	0.083	9	6	0.18	0.98
10	$Zn(NO_3)_2$	Zn(II)	0.088	22	15	0.57	1.09

[a] based on low spin states (reference 18 and 19). [b] determined by ICP. [c] [Ca] = eluted Ca (mol), [Metal] = consumed metal (mol).

TABLE 2 pH of metal solutions before and after reaction of heavy metals with HAP-400 or HAP-300.

No.	Salt	pH before reaction[a]	pH after reaction[b]	
			HAP-400	HAP-300
1	$Pb(NO_3)_2$	4.75	5.49	4.78
2	$FeCl_3$	2.45	4.32	5.88
3	$Fe(NO_3)_2$	2.25	5.14	5.82
4	$FeCl_2$	3.67	2.62	2.72
5	$Cu(NO_3)_2$	4.75	4.18	4.46
6	$Cd(NO_3)_2$	5.64	4.43	6.20
7	$Cr(NO_3)_3$	3.11	2.98	3.44
8	$Co(NO_3)_2$	5.60	5.59	6.44
9	$Ni(NO_3)_2$	5.78	4.82	5.60
10	$Zn(NO_3)_2$	5.79	2.62	5.74

[a] 25 mM. [b] metal solution, 100 mL; HAP, 0.5 g; 25℃; 4 h.

present reaction is dependent on combination of apatite and heavy metal.

The stoichiometric hydroxyapatite, HAP-300, which has a normal crystal structure, possibly affords the number of lattice vacancies equal to that of eluted Ca by the reaction. This makes the stoichiometric metal substitution feasible. On the other hand, Ca-deficient hydroxyapatite, HAP-400, bearing lattice vacancies by nature, induces much adsorption of heavy metals and a little elution of Ca. This is possibly regarded as an essential reaction pattern of HAP-400. The difference in reactivity between HAP-300 and HAP-400 was also recognized from the result of change in pH before and after the reactions, as shown in TABLE 2. In HAP-300, except for the case of $FeCl_2$ (No. 4), all the pH values increased after reaction. In HAP-400, except for the cases of $Pb(NO_3)_2$, $FeCl_3$, and $Fe(NO_3)_3$ (No. 1-3), all the pH values were decreased (No. 4-10). These phenomena imply that the reaction of HAP-300 affords more amounts of Ca elution, compared with HAP-400. TABLE 1 actually reveals the reactions of HAP-400 resulted in less amount of Ca elution. The reaction of Fe (III) with HAP-400 or HAP-300 is probably induced by solubilization of apatite, or much elution of Ca^{2+} and PO_4^{3-}. However, overviewing the present reactions, reactivity of the apatites is not necessarily dependent on pH values of the original metal solutions. Especially, HAP-400 indicated higher reactivity to Pb (II) than that to Cu (II), though pH of Pb (II) solution is coincident with that of Cu (II) solution. Therefore, Ca-deficient hydroxyapatite, HAP-400 features specific reactivity. In addition, the reactions of HAP-400 with Pb (II) and Fe (III) possibly proceed by a specific mechanism unlike the cases of the other metals.

2) Pb (II)- and Fe (III)-bearing hydroxyapatites

In order to elucidate the efficient reactivity of HAP-400 to Pb (II) and Fe (III), Pb(II)- and Fe(III)-bearing hydroxyapatites (HAP-300 and HAP-400), HAP-300-Pb, HAP-300-Fe, HAP-400-Pb, and HAP-400-Fe, were recovered after the reactions, and analyzed by XRD, as shown in FIGURE 1 and 2.

Compared with the XRD patterns of the original hydroxyapatites, HAP-300 and HAP-400 (FIGURE 1a and 2a), those of Pb(II)-bearing hydroxyapatites, HAP-300-Pb and HAP-400-Pb (FIGURE 1b and 2 b), exhibited the peaks for lead apatite $Pb_{10}(PO_4)_6(OH)_2$, which are denoted by asterisks in the FIGURES. TABLE 3 indicates inclusion of Ca and Pb and descent of specific surface area in HAP-300-Pb and HAP-400-Pb. However, the peaks of HAP-400-Pb seem sharper than those of HAP-300-Pb. As reported previously,[13] the reaction mechanisms for Pb are different between the cases of HAP-300 and HAP-400. The former involves only substitution of Ca^{2+} with Pb^{2+}, followed by formation of lead apatite on the surface of HAP-300. The latter involves elution of Ca^{2+} and PO_4^{3-}, followed by precipitation of newly formed lead apatite crystals at other locations of the original HAP-400 crystals. The new crystal formation has been actually observed by SEM in the previous paper.[13] This is the reason for the efficient reactivity of HAP-400 with Pb (II) as well as the sharper XRD peaks of HAP-400-Pb.

FIGURE 1c and 2c, which are concerned with Fe (III)-bearing hydroxyapatites, reveal disruption of apatic structure, or transformation into amorphous

state.[14] Suzuki et al.[6] reported that stoichiometric hydroxyapatite is subjected to attack of Fe^{3+} to the apatic lattice to produce amorphous $FePO_4 \cdot mH_2O$ (m=1~9), which indicates no degradability in acidic solution even at pH 3 or below. This report at least supports that the present HAP-300-Fe has $FePO_4$ structure. HAP-400-Fe resembles HAP-300-Fe in formula of Ca, P, and Fe as well as specific surface area. The surface areas of HAP-400-Fe and HAP-300-Fe were much lower than those of the

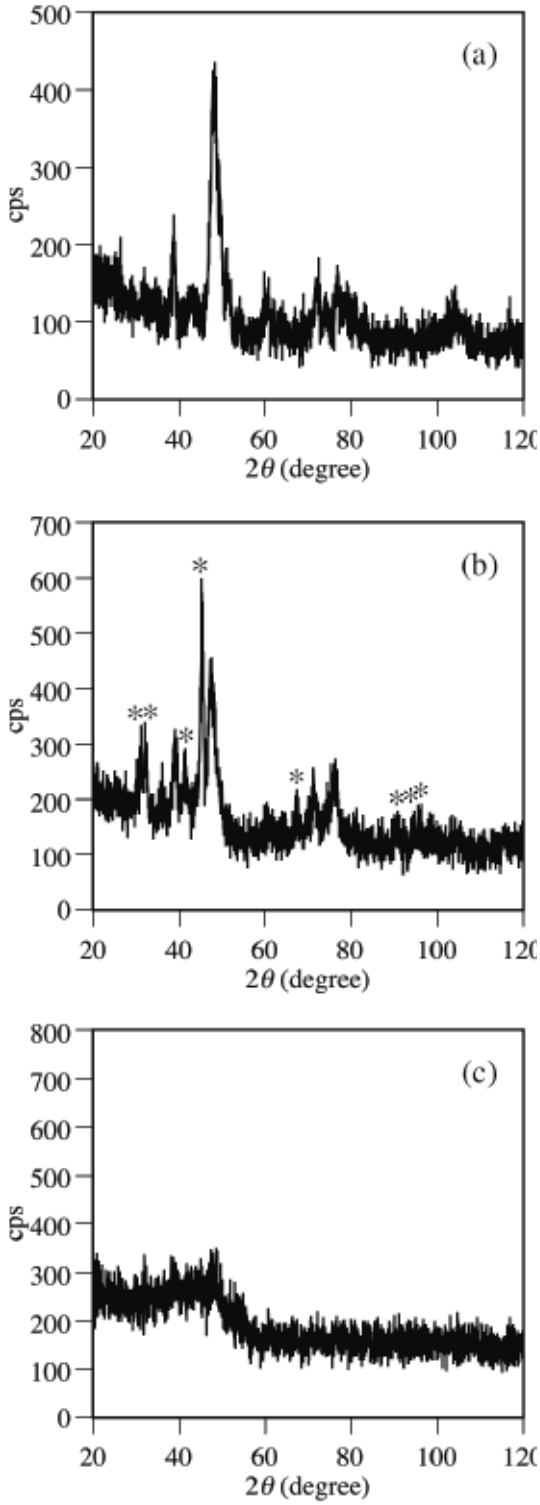


FIGURE 1 XRD patterns of HAP-300 (a), HAP-300-Pb (b), and HAP-300-Fe (c). The peaks with asterisks are assigned to lead apatite.

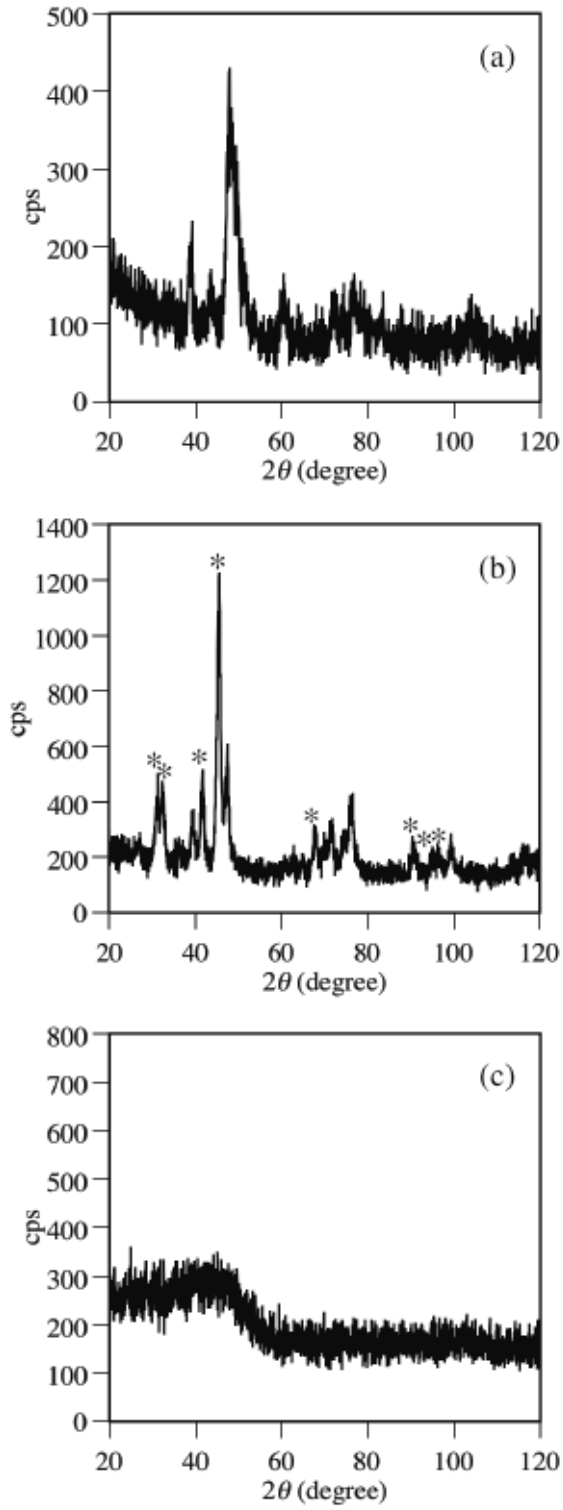


FIGURE 2 XRD patterns of HAP-400 (a), HAP-400-Pb (b), and HAP-400-Fe (c). The peaks with asterisks are assigned to lead apatite.

corresponding original hydroxyapatites (TABLE 3). Therefore, not only HAP-300-Fe but also HAP-400-Fe possibly has hydrated amorphous $FePO_4$ structure.

As additional data on the structures of HAP-400-Pb and HAP-400-Fe, FT-IR micro-spectroscopic spectra are shown in FIGURE 3.

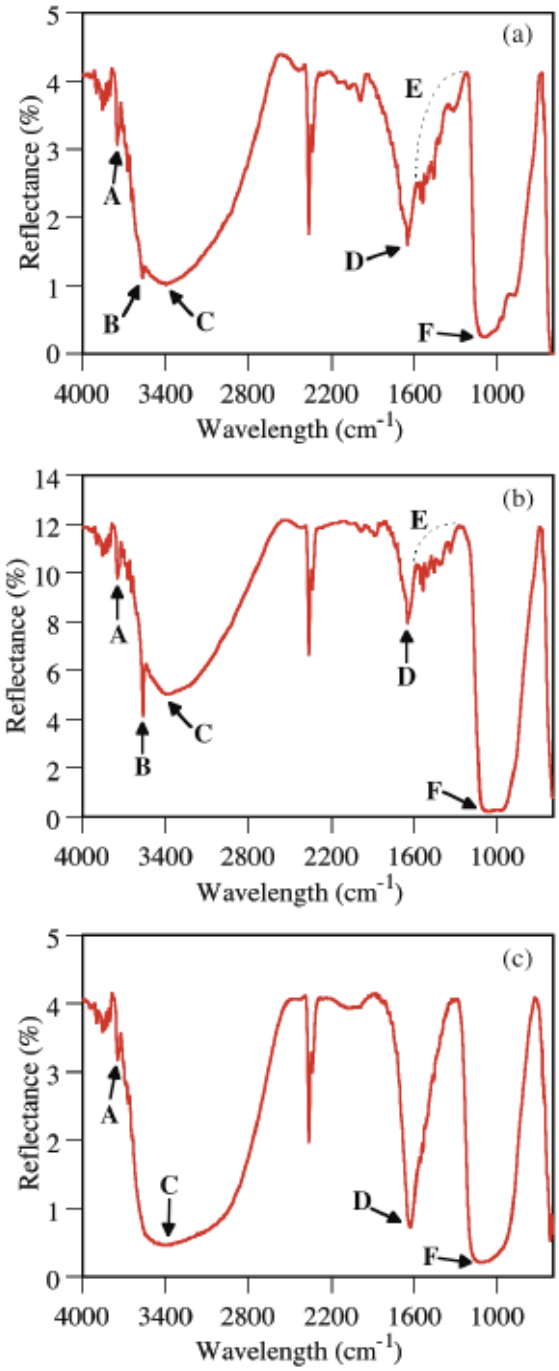


FIGURE 3 FT-IR microspectroscopic spectra of HAP-400 (a), HAP-400-Pb (b), and HAP-400-Fe (c). **A**, surface ν(OH); **B**, internal ν(OH); **C**, adsorbed H_2O ν(OH); **D**, adsorbed H_2O δ(OH); **E**, carbonate ν(CO_3); **F**, phosphate ν(PO_4).

Similarly to HAP-400, HAP-400-Pb indicated bands for surface and internal OH, adsorbed H_2O (OH), and PO_4. Especially in the internal OH band, HAP-400-Pb indicated a sharp and strong absorbance, which are attributed to existing of OH from the newly formed lead apatite crystals. On the other hand, no band for internal OH was observed in HAP-400-Fe, but broaden bands for adsorbed H_2O (OH) and PO_4 was observed. Thereby, it was reconfirmed that HAP-400-Fe is constituted of disrupted apatic structure and amorphous hydrated $FePO_4$.

TABLE 3 Properties of Pb(II)- and Fe(III)-substituted hydroxyapatites.

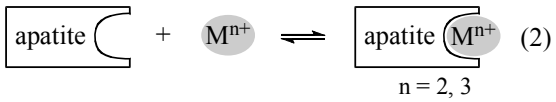
Apatites	Specific surface area (m^2/g)[a]	Elemental Analysis (wt%)[b]			
		Ca	P	Pb	Fe
HAP-400	37	32.44	18.12	-	-
HAP-400-Pb	23	8.41	5.83	56.19	-
HAP-400-Fe	15	4.39	17.76	-	28.51
HAP-300	81	37.19	17.08	-	-
HAP-300-Pb	69	24.24	7.80	27.09	-
HAP-300-Fe	17	6.27	15.80	-	28.15

[a] determined by BET method.
[b] determined by ICP.

3) Reaction mechanism

In comparison of ionization tendency (standard oxidative-reductive potential)[15] of metals employed in the present study, Ca has the highest tendency. The present reaction begins by Ca elution from hydroxyapatite, followed by incorporation of metal ion. From TABLE 3, the formula of Ca-deficient hydroxyapatite HAP-400 is denoted as $Ca_{8.3}(HPO_4)_{1.7}(PO_4)_{4.3}(OH)_{0.3}$. Although HAP-400 could be ionized with equilibrium in water (Eq. 1), the ionization hardly occurs (-log K_{sp} = 85.1 at 25°C).[16, 17] However, in case of existence of a heavy metal, the equilibrium must be shifted to the right side, or elution of Ca to produce the corresponding deficient sites. Since the radii of heavy metal ions except for Pb^{2+} are smaller than that of Ca^{2+} (TABLE 1),[18, 19] the charged metal ion can be incorporated into deficient sites produced by Ca elution (Eq. 2). In the case of HAP-400, which has many Ca-deficient sites by nature, the metal incorporation occurs regardless of elution of Ca. This mechanism is dented as metal-adsorptive substitution mechanism, applying to the following metals: Fe (II), Cd (II), Cr (III), Co (II), Ni (II), and Zn (II). Although elution of Ca rather than consumption of Cu (II) was observed, Cu (II) might indeed belong to the similar mechanism: The equilibrium of Eq. 2 might be shifted to the left side (desorption), and ionization of HAP-400 in Eq. 1 might be accelerated.

$$Ca_{8.3}(HPO_4)_{1.7}(PO_4)_{4.3}(OH)_{0.3} \rightleftharpoons 8.3Ca^{2+} + 1.7HPO_4^{2-} + 4.3PO_4^{3-} + 0.3OH^- \quad (1)$$



In the reaction of Pb (II) with HAP-400, the incorporation according to Eq. (2) possibly becomes a little difficult, since the radius of Pb^{2+} larger than Ca^{2+} (TABLE 1). Thereby elution of Ca, or ionization of HAP-400, is accelerated. Eventually, lead apatite with needle crystal is newly produced by Eq. 3, in which the equilibrium must be almost shifted to the right side, or lead apatite formation. However, judging from the case of the reaction of HAP-300 with Pb (II), there is still a little possibility that the reaction of HAP-400 with Pb (II) proceeds by Eq.2.[13]

$$10Pb^{2+} + 6PO_4^{3-} + 2OH^- \rightleftharpoons Pb_{10}(PO_4)_6(OH)_2 \quad (3)$$

In the reaction of Fe (III), the structural disruptions are due to H^+ formed by hydrolysis of Fe^{3+} with equilibrium by Eq. 4. The H^+ significantly accelerates the ionization of apatites via Eq. 1 and formation of hydrated $FePO_4$ by Eq. 5. Actually, the pH of $FeCl_3$ aqueous solution was 2.45 (strong acid), and that of the solution after the reaction of Fe (III) with the apatites was 4.32 (TABLE 2). FIGURE 4 indicates both no existence of Fe^{3+} after the reactions and proportional rise of Ca elution to initial concentration under the condition that the initial concentration is 25 mM or below. FIGURE 5 shows XRD patterns of Fe (III)-bearing HAP-400 samples obtained by the reactions of HAP-400 with lower initial concentrations, 5.0 mM (0.2 equiv.) and 12.5 mM (0.5 equiv.), of Fe (III) solutions at 25˚C for 4h. In comparison of FIGURE 5 with FIGURE 2 (a and c), it is obvious that the apatic structural disruption is dependent on initial Fe(III) concentration of the reaction. Moreover, in FIGURE 4, under the initial Fe (III) concentration more than 25 mM, each elution of Ca reached a

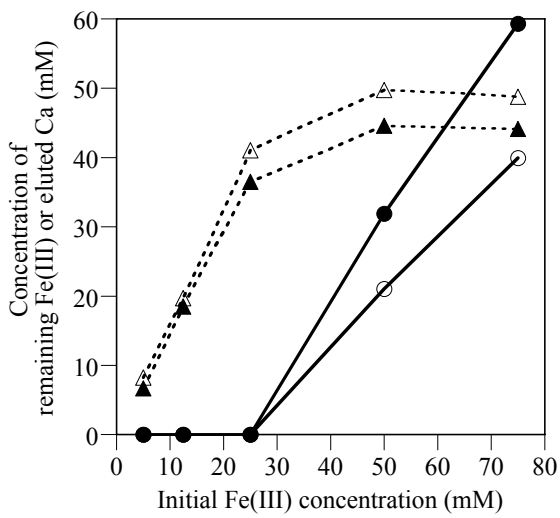


FIGURE 4 Effect of initial Fe(III) concentration to consumption of Fe(III) and elution of Ca in the reactions of HAP-300 and HAP-400 with $FeCl_3$ aqueous solution. The marks J (for HAP-400) and E (for HAP-300) on the solid lines express remaining Fe(III). The marks H (for HAP-400) and C (HAP-300) on the dotted lines express eluted Ca.

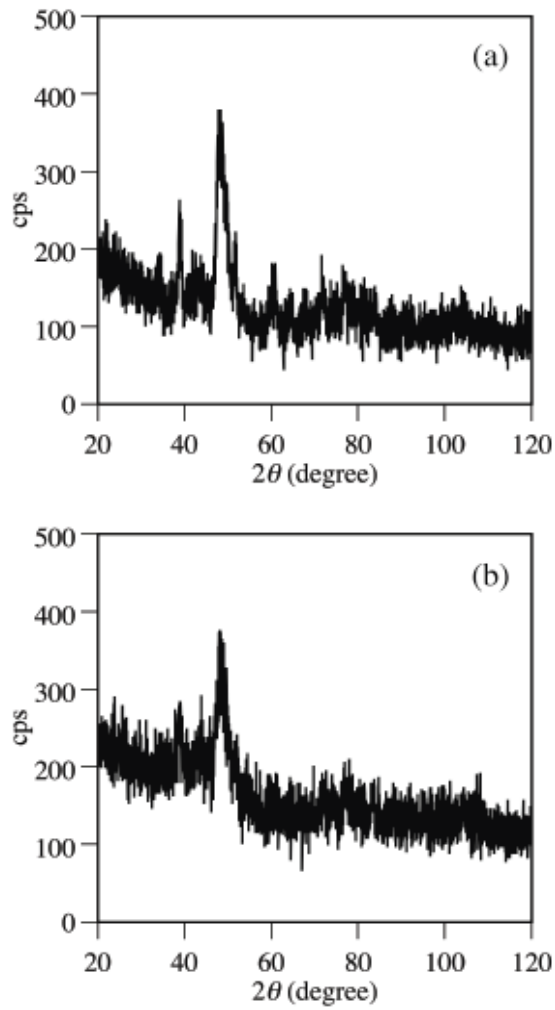


FIGURE 5 XRD patterns of Fe(III)-substituted HAP-400 samples obtained by reaction of HAP-400 with lower initial concentrations of Fe(III) at 25˚C for 4 h. (a) $[Fe^{3+}]_{inital}$ = 5.0 mM (0.2 equiv.); (b) $[Fe^{3+}]_{inital}$ = 12.5 mM (0.5 equiv.).

constant peak. Therefore, the reaction as shown in Eq. 5 should be considered irreversible. The mechanism expressed by Eq. 5 is applied to the reaction of Fe (III) with both HAP-300 and HAP-400.

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ \quad (4)$$

$$Fe^{3+} + PO_4^{3-} + 2OH^- + 2H^+ + nH_2O \longrightarrow FePO_4 \bullet mH_2O \quad (5)$$

In the reaction of Pb (II) and Fe (III) with Ca-deficient hydroxyapatite, HAP-400, Pb^{2+} and Fe^{3+} are erosive against the apatic structure along with elution of Ca^{2+}, PO_4^{3-}, and OH^- to afford newly formed metal-bearing salts, lead apatite[13] and iron phosphate, respectively. Especially in the case of Fe (III), the apatic structural erosion is crucial since HAP-400-Fe had no distinctive apatic structure (FIGURE 2c). Therefore, the reaction mechanism for the heavy metals, Pb (II) and Fe (III), are defined as apatite-erosive substitution mechanism.

CONCLUSION

The reaction of Ca-deficient hydroxyapatite, HAP-400, with heavy metals proceeds via the two mechanisms: One is metal-adsorptive substitution mechanism, and the other is apatite-erosive substitution mechanism. Seemingly stoichiometric hydroxyapatite, HAP-300, with heavy metals proceeds via the similar mechanisms, but it elutes more Ca ions than HAP-400 in the present reactions. From viewpoint of usage as a removal agent for heavy metal ions in water, it is concluded that HAP-400 will be more useful than HAP-300 because of the lower elution of Ca or the complete removal of some metals.

ACKNOWLEDGMENT

We would like to express great appreciation for using the instrument XRD, M18XCE (Bruker AXS GmbH, Karlsruhe, Germany) at Nara Prefectural Institute of Industrial Technology in Japan.

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