Effects of carbonate inclusion on fluoride ion removal by hydroxyapatite: A discussion from the viewpoint of hydroxyapatite dissolution

Sota TERASAKA, Masanobu KAMITAKAHARA,† Taishi YOKOI‡ and Hideaki MATSUBARA

Graduate School of Environmental Studies, Tohoku University, 6–6–20 Aoba, Aramaki, Aoba-ku, Sendai 980–8579, Japan

Hydroxyapatite (HA) can be used for removing F⁻. Materials containing HA for removing F⁻ can be obtained from biological wastes, and these HA might contain carbonate ions. The dissolution behavior of HA should affect the F⁻ removal as fluorapatite (FA) formation at HA surface by the dissolution of HA and subsequent precipitation of FA results in the removal of F⁻. In this study, we examined the relationship between the dissolution and F⁻ removal rates of carbonated HA (CHA). CHA samples with different carbonate contents were prepared by a hydrothermal process. The dissolution and F⁻ removal rates were investigated by immersing the samples in pH 5 and 7 buffer solutions in the absence and presence of F⁻, respectively. The dissolution and F⁻ removal rates were increased with an increase of carbonate-ion content in the samples. Dissolution and F⁻ removal rates at pH 5 were larger than that at pH 7. The pseudo-second order kinetic model provides a good fit for the F⁻ removal process. An increase in the kinetic constant of dissolution decreases the kinetic constant of the F⁻ removal process for samples with high carbonate contents at pH 5.

©2016 The Ceramic Society of Japan. All rights reserved.

Key-words: Hydroxyapatite, Carbonate ion, Fluoride ion, Dissolution

1. Introduction

Water is essential for our lives and it is important to maintain the quality of drinking water without the presence of harmful matters. Fluoride ion (F⁻) is one of the contaminants to be removed since ingestion of water with high F⁻ concentrations can cause dental and skeletal disorders. Although the World Health Organization (WHO) has recommended F⁻ levels of less than 1.5 mg·dm⁻³ in drinking water, water in many areas around the world exceeds this level. Hence, a relatively inexpensive material for removing F⁻ from water should be prepared. Hydroxyapatite (HA) can be used for removing F⁻ effectively from water to achieve F⁻ levels of less than 1.5 mg·dm⁻³. Materials containing HA can be synthesized from biological waste materials such as bones, seashells, coral, and egg-shells. HA has a composition of Ca₁₀(PO₄)₆(OH)₂ and it can form solid solutions with various ions. HA derived from biological waste materials might contain 2–8 mass % of carbonate ions (carbonated HA; CHA). However, effects of carbonate inclusion on the F⁻ removal ability of HA have not been previously investigated. Hence, it is important to study the effects of CO₃²⁻ present in HA on the removal of F⁻ in order to fabricate effective F⁻ removal materials.

Three different mechanisms have been reported for the removal of F⁻, namely, surface adsorption, substitution in the HA crystal lattice, and dissolution of HA and precipitation of fluorapatite (FA). FA is formed when OH⁻ ions in HA are substituted with F⁻ ions. Sternitzke et al. reported that the removal of F⁻ occurs via the formation of FA at the HA surface, resulting in the formation of FA layer of few nanometers in thickness on the surface of HA. Considering the report on the formation of FA layer with thicknesses larger than 1, c-lattice constant values of HA, the mechanism of “dissolution of HA and precipitation of FA” is considered to be the dominant factor in the removal of F⁻. According to this mechanism, mainly the dissolution rate of HA contributes to the F⁻ removal process. The dissolution rate of CHA was found to be larger than that of pure HA under physiological conditions by several researchers. Moreover, the dissolution rate of CHA increases with a decrease in the pH of the solution. In the present study, we focus on the effect of CO₃²⁻ inclusion on dissolution and F⁻ removal rates of HA under different pH conditions. CHA particles were synthesized by a hydrothermal process to investigate their dissolution and F⁻ removal rates. F⁻ removal rates of samples are discussed with respect to their dissolution rate.

2. Experimental

2.1 Preparation of CHA samples

CHA particles were prepared according to a previously reported hydrothermal method, since this synthesis method produces HA particles with high crystallinities and small size distributions. A solution containing (NH₄)₂HPO₄ and NH₄HCO₃ was prepared by dissolving (NH₄)₂HPO₄ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and NH₄HCO₃ (Sigma-Aldrich, Co., LLC, St. Louis, MO, USA) in distilled water. The concentration of (NH₄)₂HPO₄ was 0.30 mol·dm⁻³, and two different concentrations of NH₄HCO₃ were used (0.30 and 1.2 mol·dm⁻³). The pH of the solution was adjusted to 10 by the addition of NH₃ solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan). 0.50 mol·dm⁻³ of Ca(NO₃)₂ solution was prepared by dissolving

DOI: http://dx.doi.org/10.2109/jcersj2.16186
Ca(NO\textsubscript{3})\textsubscript{2}-4H\textsubscript{2}O (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in distilled water, and the pH of the Ca(NO\textsubscript{3})\textsubscript{2} solution was adjusted to 10 by adding the NH\textsubscript{3} solution. Then, 20 cm\textsuperscript{3} of Ca(NO\textsubscript{3})\textsubscript{2} solution was added to 20 cm\textsuperscript{3} of the solution containing (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} and NH\textsubscript{4}HCO\textsubscript{3} at 30°C. White precipitates were immediately formed on mixing. The pH of the resultant slurry was adjusted to 10 by adding the NH\textsubscript{3} solution. 40 cm\textsuperscript{3} of the resultant slurry was transferred into a Teflon\textsuperscript{TM}-lined autoclave and was heated at 200°C for 24 h. After 24 h, the precipitate was collected by centrifugation, washed with water, and dried at 90°C. The samples were ground by a mortar after drying. Samples synthesized with 0.30 and 1.2 mol dm\textsuperscript{-3} NH\textsubscript{4}HCO\textsubscript{3} solutions are named as HA\textsubscript{C1} and HA\textsubscript{C4}, respectively. HA\textsubscript{C0} was prepared without adding NH\textsubscript{4}HCO\textsubscript{3} during the synthesis in order to compare it with HA\textsubscript{C1} and HA\textsubscript{C4}, keeping all other synthesis conditions the same.

Crystalline phases of the samples were characterized by X-ray diffraction (XRD, RINT2200VL; Rigaku, Tokyo, Japan) using Cu K\textalpha radiation. Fourier transform infrared spectroscopy (FTIR, FT/IR-6200; JASCO, Tokyo, Japan) was employed for the chemical structure analysis of the samples in the form using the KBr pellet method. Morphology of the samples was examined using scanning transmission electron microscopy (STEM, SU8000; Hitachi, Tokyo, Japan). Samples were dispersed in ethanol and the suspension was dropped on a micro-grid (NP-SU8000; Hitachi, Tokyo, Japan). Samples were dispersed in KBr pellet method. Morphology of the samples was examined using scanning transmission electron microscopy (STEM, SU8000; Hitachi, Tokyo, Japan). Samples were dispersed in ethanol and the suspension was dropped on a micro-grid (NP-SU8000; Hitachi, Tokyo, Japan). Samples were dispersed in ethanol and the suspension was dropped on a micro-grid (NP-SU8000; Hitachi, Tokyo, Japan). Samples were dispersed in ethanol and the suspension was dropped on a micro-grid (NP-SU8000; Hitachi, Tokyo, Japan).

2.2 Dissolution test

The dissolution rate of the samples was evaluated as follows. An acetate buffer solution with a pH of 5 and a 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) buffer solution with a pH of 7 were used for the dissolution test. The acetate buffer solution was prepared by mixing 0.10 mol dm\textsuperscript{-3} acetic acid and 0.10 mol dm\textsuperscript{-3} sodium acetate solutions. HEPES buffer solution was prepared by mixing 0.10 mol dm\textsuperscript{-3} HEPES and 0.10 mol dm\textsuperscript{-3} sodium hydroxide solutions. Acetic acid, sodium acetate trihydrate, and sodium hydroxide were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. HEPES was purchased from Dojindo Laboratories, Ltd., Kumamoto, Japan. Samples with a surface area of 5 m\textsuperscript{2} were immersed in 15 cm\textsuperscript{3} of acetate or HEPES buffer solutions. The mixture was shaken at 125 rpm at 30°C. After 15, 60, 360, and 720 min of shaking, the supernatant solution was collected by centrifugation. The pH of the solution was measured using a pH electrode (9631-39-6439) were observed in the XRD pattern of all the samples. FTIR spectra of the samples are shown in Fig. 2. The absorption peaks observed at 570, 600, 960, 1050, and 1100 cm\textsuperscript{-1} in Fig. 2(a) could be assigned to phosphate ions (PO\textsubscript{4}\textsuperscript{3-}) in HA and

2.3 F\textsuperscript{-} removal test

The abilities of the samples in removing F\textsuperscript{-} were evaluated. 20 mg dm\textsuperscript{-3} F\textsuperscript{-} solutions with pH values of 5 or 7 were prepared by dissolving NaF (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in acetate buffer (pH 5) and HEPES buffer (pH 7). Experimental conditions used for the F\textsuperscript{-} removal test were similar to that of the dissolution test. Samples with a surface area of 5 m\textsuperscript{2} were immersed in 15 cm\textsuperscript{3} of the F\textsuperscript{-} solution. This solution was shaken at 125 rpm at 30°C. After 15, 60, 360 and 720 min, the supernatant solution was obtained by centrifugation. The pH of the solution was measured as mentioned in section 2.2. Then, 3.0 cm\textsuperscript{3} of total ionic strength adjustment buffer (TISAB\textsuperscript{20}) was added to 13 cm\textsuperscript{3} of supernatant liquid, and F\textsuperscript{-} concentration in the solution was measured by an F\textsuperscript{-} selective electrode (6561-10C, Horiba, Ltd., Kyoto, Japan). The dissolution tests were repeated for three times for each sample. Potassium chloride was purchased from Nacalai Tesque, Inc., Kyoto, Japan.

3. Results

3.1 Characterization of the samples

Figure 1 shows the XRD patterns of the samples. Only diffraction peaks corresponding to HA (PDF#89-6439) were observed in the XRD pattern of all the samples. FTIR spectra of the samples are shown in Fig. 2. The absorption peaks observed at 570, 600, 960, 1050, and 1100 cm\textsuperscript{-1} in Fig. 2(a) could be assigned to phosphate ions (PO\textsubscript{4}\textsuperscript{3-}) in HA and

![Fig. 1. XRD patterns of the samples.](image-url)

![Fig. 2. FTIR spectra of the samples: (a) from 2000 to 400 cm\textsuperscript{-1}, and (b) magnified spectra in the range of 900 to 850 cm\textsuperscript{-1}.](image-url)
Table 1. Content of carbonate ions calculated from the element analysis and the specific surface area of the samples

| Sample  | Content of CO$_3^{2-}$ calculated from element analysis/mass % | Specific surface area /m$^2$·g$^{-1}$ |
|---------|---------------------------------------------------------------|-------------------------------------|
| HA.C0   | 1.9                                                            | 50                                  |
| HA.C1   | 4.6                                                            | 52                                  |
| HA.C4   | 5.0                                                            | 62                                  |

the absorption peak corresponding to hydroxide ions (OH$^-$) in HA is observed at 630 cm$^{-1}$ for all samples. Intensity of the peak at 630 cm$^{-1}$ is found to decrease with an increase in the concentration of carbonate ions added during the synthesis. Absorption peaks corresponding to CO$_3^{2-}$ in HA are observed at 873, 880, 1410, and 1450 cm$^{-1}$ for HA.C1 and HA.C4 samples. On the other hand, these peaks of CO$_3^{2-}$ are found to be very weak in the absorption spectra of HA.C0. This result indicates that CO$_3^{2-}$ contents in HA.C1 and HA.C4 samples are higher than that of HA.C0. Magnified FTIR spectra in the range of 850 to 900 cm$^{-1}$ are shown in Fig. 2(b). Absorption peaks at 873 cm$^{-1}$ indicate B-type CHA in which PO$_4^{3-}$ in HA are substituted with CO$_3^{2-}$, and the absorption peaks at 880 cm$^{-1}$ indicate A-type CHA in which OH$^-$ ions are substituted with CO$_3^{2-}$. Absorption peaks were observed at 873 and 880 cm$^{-1}$ for HA.C1 and HA.C4, indicating that both the samples were of AB-type CHA.

STEM images of the sample surfaces are shown in Fig. 3. Particles in HA.C0 exhibit a seed-like morphology, whereas seed-like and spherical particles were present in HA.C1. HA.C4 mostly consists of spherical particles. Spherical particles in HA.C1 and HA.C4 are found to be smaller than the seed-like particles in HA.C0. Morphology of the particles changes from seed-like to spherical with an increase in the concentration of NH$_4$HCO$_3$ added during the synthesis.

Table 1 shows the content of carbonate present in the sample and the specific surface area of the samples. The content of carbonate ions in HA.C0, HA.C1, and HA.C4 are found to be 1.9, 4.6, and 5.0 mass %, respectively. Carbonate content in the samples increases with an increase in the concentration of CO$_3^{2-}$ added during the synthesis. The specific surface areas of the samples determined by the N$_2$-BET method are found to be in the order of HA.C0 < HA.C1 < HA.C4. The specific surface area increased with an increase in the concentration of the NH$_4$HCO$_3$ solution added during the synthesis.

3.2 Dissolution test

Figure 4 indicates the changes in Ca$^{2+}$ concentration in each solution during the dissolution test. The error bar corresponds to the standard deviation of the measured values. Ca$^{2+}$ concentration increases with time in all the solutions. The pH of the solution remained the same throughout the dissolution test (data is not shown). The increase in the Ca$^{2+}$ concentration can be attributed to dissolution of the samples in the solution. Increase in Ca$^{2+}$ concentration in the pH 5 buffer solution is found to be larger than that in the pH 7 buffer. In addition, the increase in Ca$^{2+}$ concentration in the case of samples synthesized in the presence of NH$_4$HCO$_3$ is found to be larger than that of the samples synthesized without using NH$_4$HCO$_3$.

3.3 F$^-$ removal test

Figure 5 indicates the changes in F$^-$ concentrations during the F$^-$ removal test. The error bar corresponds to the standard deviation of the measured values. A decrease in the concentration of F$^-$ with time is observed in all cases. The pH of the solutions remained almost constant during the F$^-$ removal test (data is not shown). Decrease in the concentration of F$^-$ in the solutions could be attributed to the increase of the amount of F$^-$ removed by the HA samples. The amount of F$^-$ removed by the samples in the pH 5 buffer solutions is found to be larger than that by the samples immersed in the pH 7 buffer solutions. In acidic conditions, higher amounts of F$^-$ were removed by HA.C1 and HA.C4 compared to HA.C0. However, similar amounts F$^-$ were removed by the three samples in neutral pH conditions.

4. Discussion

AB-type CHA particles were prepared by adding NH$_4$HCO$_3$ ions during the synthesis. Although the concentration of NH$_4$HCO$_3$ in the starting solution was increased from 0.30 to 1.2 mol·dm$^{-3}$,
the content of carbonate ions in the product increased only from 4.6 to 5.0 mass%. This could be attributed to the substitution limit under current synthesis conditions. The size of the particles in HA.C1 becomes smaller on the addition of carbonate ions (as compared to HA.C0) and the particle morphology changes from seed-like to spherical. A similar tendency has been reported previously.25),27) We assume that dissolution of HA occurs via a diffusion-controlled process and the surface area of the sample remains intact during the dissolution test. Noyes-Whitney model32) was applied for describing the dissolution process (Fig. 4), which could be represented as:

\[
\frac{dC_{(Ca)}}{dt} = k_{e(Ca)}(C_{S(Ca)} - C_{(Ca)}).
\] (2)

Equation (2) can be rearranged as follows:

\[
C_{(Ca)} = C_{S(Ca)}(1 - e^{-k_{e(Ca)}t}),
\] (3)

where \(C_{(Ca)}\) (mg·dm\(^{-3}\)) is the concentration of \(Ca^{2+}\) at time \(t\) (min), \(k_{e(Ca)}\) (min\(^{-1}\)) is the dissolution kinetic constant, and \(C_{S(Ca)}\) (mg·dm\(^{-3}\)) is the concentration of \(Ca^{2+}\) at equilibrium. Figure 6 shows the kinetic data that was fitted with the Noyes-Whitney model. \(C_{S(Ca)}\) and \(k_{e(Ca)}\) values obtained from the Noyes-Whitney fit (Fig. 6) are shown in Table 2. The initial dissolution rate of \(Ca^{2+}\) \((t = 0)\), \(v_0(Ca)\) (\(\mu\)mol·m\(^{-2}\)·min\(^{-1}\)), calculated from Eq. (2), is also given in Table 2.

In order to investigate the mechanism of \(F^-\) removal by HA, a pseudo-second order kinetic model was considered.1),7),33),34)

The pseudo-second order kinetic model can be expressed as:

\[
\frac{dF(t)}{dt} = k_{e(F)}(q_{e(F)} - q(t)).
\] (4)

The Eq. (4) can be rearranged as follows:

\[
\frac{t}{q(t)} = \frac{t}{q_{e(F)}} + \frac{1}{k_{e(F)}q_{e(F)}}.
\] (5)

The pseudo-second order kinetic model

![Fig. 5. Changes in \(F^-\) concentration during the \(F^-\) removal test.](image)

![Fig. 6. Plot for the dissolution rate model. \(t\) is time, \(C_{(Ca)}\) is concentration of \(Ca^{2+}\), \(C_{S(Ca)}\) is equilibrium concentration of \(Ca^{2+}\), and \(k_{e(Ca)}\) is dissolution kinetic constant.](image)

**Table 2.** Kinetic parameters calculated from the dissolution rate model

| Sample        | \(C_{S(Ca)}\) \((\text{mg·dm}^{-3})\) | \(k_{e(Ca)}\) \((\text{min}^{-1})\) | \(v_0(Ca)\) \((\text{\(\mu\)mol·m}^{-2}\cdot\text{min}^{-1})\) |
|---------------|------------------|------------------|------------------|
| HA.C0 (pH 5) | 135              | 0.118            | 1.2              |
| HA.C1 (pH 5) | 175              | 0.128            | 1.7              |
| HA.C4 (pH 5) | 198              | 0.138            | 2.1              |
| HA.C0 (pH 7) | 8.62             | 0.0980           | 0.063            |
| HA.C1 (pH 7) | 13.9             | 0.109            | 0.11             |
| HA.C4 (pH 7) | 21.3             | 0.115            | 0.18             |

![Fig. 7. Plot for the pseudo-second order reaction rate. \(t\) is time, \(q_{e(F)}\) is removal amount of \(F^-,\) \(q(t)\) is equilibrium removal amount of \(F^-,\) and \(k_{e(F)}\) is kinetic constant of pseudo-second order kinetic model.](image)
Table 3. Kinetic parameters calculated from the pseudo-second order kinetic model

| Sample     | \( q_0(F) /\text{mg·m}^{-2} \) | \( k_{(F)} /\text{min}^{-1} \) | \( v_{(F)} /\text{µmol·m}^{-2}·\text{min}^{-1} \) |
|------------|-------------------------------|-------------------------------|-----------------------------------------------|
| HA.C0 (pH 5) | 0.050                         | 5.2                           | 0.69                                          |
| HA.C1 (pH 5) | 0.058                         | 2.0                           | 0.35                                          |
| HA.C4 (pH 5) | 0.056                         | 1.9                           | 0.32                                          |
| HA.C0 (pH 7) | 0.038                         | 4.9                           | 0.38                                          |
| HA.C1 (pH 7) | 0.039                         | 4.6                           | 0.36                                          |
| HA.C4 (pH 7) | 0.041                         | 4.8                           | 0.42                                          |

Fig. 8. Relationship between the amount of \( F^- \) removed at equilibrium \( (q_{(F)}%) \) and equilibrium concentration of \( Ca^{2+} (C_{Ca}) \).

Fig. 9. Relationship between the kinetic constants of removal of \( F^- \) \( (k_{(F)}) \) and dissolution \( (k_{(Ca)}) \).

Fig. 10. Relationship between the initial rate of removal of \( F^- \) \( (v_{(F)}%) \) and dissolution \( Ca^{2+} (v_{(Ca)}) \).

has been applied in the case of chemical adsorption.\(^{35} \) Calculated values of \( q_{(F)} \) and \( k_{(F)} \) from the plots of \( t \) versus \( t_0(F_0) \) \(^{-1} \) \((\text{Fig. 7}) \) are shown in Table 3. The initial \( F^- \) removal rate \( (t = 0), v_{(F)}(\text{µmol·m}^{-2}·\text{min}^{-1}) \), calculated from Eq. (4) is also given in Table 3.

We examined the relationship between the kinetic parameters of \( F^- \) removal by HA and the dissolution of HA. Figure 8 illustrates the relationship between the amount of \( F^- \) removed at equilibrium \( (q_{(F)}%) \) and the concentration of \( Ca^{2+} (C_{Ca}) \). The \( q_{(F)} \) value increases with an increase in \( C_{Ca} \). We assume that the \( F^- \) removal capacity increases with an increase in the solubility of HA since high solubility can cause a large amount of \( Ca^{2+} \) and \( PO_4^{3-} \) to be used in the formation of FA.

Figure 9 illustrates the relationship between the kinetic constant of \( F^- \) removal process \( (k_{(F)}) \) and that of the dissolution process \( (k_{(Ca)}) \). The kinetic constant, \( k_{(F)} \), does not vary much in the pH 7 buffer solutions, whereas it decreases with an increase in \( k_{(Ca)} \) in the pH 5 buffer solution. However, the \( F^- \) removal and dissolution rates depend not only on the kinetic constants but also on the equilibrium concentrations. Therefore, the initial rate of \( F^- \) removal \( (v_{(F)}%) \) and that of dissolution \( (v_{(Ca)}) \) were calculated assuming time, \( t = 0 \). Figure 10 illustrates the relationship between \( v_{(F)} \) and \( v_{(Ca)} \). The value of \( v_{(F)} \) increases with an increase in \( v_{(Ca)} \) values in pH 7 buffer solutions, while \( v_{(F)} \) decreases with an increase in \( v_{(Ca)} \) in pH 5 buffer solutions. The initial rate of \( F^- \) removal increases with an increase in the initial dissolution rate at low dissolution rate values, but it decreases with an increase in the initial dissolution rate at high dissolution rate values.

As the solubility product of FA \([Ksp = 10^{-120.0}]\), which is given as the ion product of the \( Ca_{10}(PO_4)_6F_2 \) is smaller than that of HA \([Ksp = 10^{-316.8}]\), which is given as the ion product of the \( Ca_{10}(PO_4)_6(OH)_2 \),\(^{36} \) the concentration of \( F^- \) in the \( F^- \) removal test is found to be much higher than that of \( OH^- \). The equilibrium condition is assumed to achieve when FA or \( F^- \)-substituted HA covers the HA surface. Assuming that all of the \( F^- \) ions removed are used in the formation of homogeneous FA layer on the surface of HA.C1 particles at pH 5, the thickness of the FA layer can be calculated to be about 0.6 nm, which is lower than the \( a, c \)-lattice constant of FA. This implies that the monolayer formation of FA does not occur and \( F^- \) only partially substitute \( OH^- \). The dissolution kinetic constants for HA.C1 and HA.C4 at pH 5 are found to be larger compared with the other conditions; however, their kinetic constants in the \( F^- \) removal process are found to be smaller (Fig. 9). This indicates that the formation of \( F^- \)-substituted HA reaches the equilibrium more slowly at high dissolution kinetic constant values compared to that at low dissolution kinetic constant values. More information can be obtained from Fig. 10. When the initial dissolution rate is relatively low [HA.C0 (pH 5), HA.C0 (pH 7), HA.C1 (pH 7) and HA.C4 (pH 7)], the rate of supply of \( Ca^{2+} \) and phosphate ions \( (PO_4^{3-}) \) into the solution increases with an increase in the initial dissolution rate of HA. Thus, the rate of \( F^- \)-substituted HA formation also increases with an increase in the dissolution rate of HA. On the other hand, when the initial dissolution rate is high as...
in the case of HA.C1 and HA.C4 at pH 5, the surface area of HA on which the F⁻-substituted HA can be formed decreases by the dissolution of HA. F⁻-substituted HA formation and the F⁻-substituted HA nucleation sites are restricted due to the dissolution of HA.

We expected that the particle size should have been changed when "dissolution of HA and precipitation of FA" occurred. HA.C1 particles after the F⁻ test (pH 5, 720 min) were observed by STEM, and the sizes of the long and short axes of the HA.C1 particles were measured from the STEM images. The sizes of the long and short axes of the HA.C1 particles before the F⁻ removal test were 47 ± 15 and 30 ± 7 nm, respectively, and those of the HA.C1 particles after the F⁻ removal test were 50 ± 19 and 31 ± 7 nm, respectively. The tendency that the size of the CHA particles slightly increased after the F⁻ removal test was observed. It is considered that the size of the CHA particles increased after the F⁻ removal test because HA was dissolved and F⁻-substituted HA was formed on the other HA particles or another site on the same HA particle. The changes in particle sizes would support the mechanism of "dissolution of HA and precipitation of FA" in the removal of F⁻ by HA.

We have discussed the process of F⁻ removal by CHA samples with different carbonate contents in relation to their dissolution rate. However, two other mechanisms, namely, surface adsorption⁹ and substitution in the HA crystal lattice⁴⁰ have been previously reported and it is difficult to exclude these mechanisms using the data obtained from this study. The inclusion of carbonate ions might also affect these mechanisms, and more research needs to be carried out to examine the mechanism of F⁻ removal by HA.

5. Conclusion

AB-type CHA particles were synthesized by a hydrothermal process. The dissolution and the amount of F⁻ removed by the CHA samples were larger than that of the non-carbonated HA samples. The dissolution and the amount of F⁻ removed from pH 5 buffer solutions were larger than those at pH 7. The pseudo-second order kinetic model provides a good fit for the F⁻ removal process. The increase in the kinetic constant of dissolution decreases the kinetic constant of F⁻ removal for CHA samples with high carbonate contents in the pH 5 buffer solution.

Acknowledgement

We are grateful for the experimental support of Prof. M. Kawashita and Ms. Y. Nakano of Tohoku University.

References

1) C. S. Sundaram, N. Viswanathan and S. Meenakshi, J. Hazard. Mater., 155, 206–215 (2008).
2) V. Badillo-Almaraz, J. Armando Flores, H. Arriola, F. López and L. Ruiz-Ramírez, J. Radioanal. Nucl. Chem., 271, 741–744 (2007).
3) L. E. L. Hammari, A. Laghzizil, P. Barboux, K. Lahlil and A. Saouabi, J. Hazard. Mater., 114, 41–44 (2004).
4) M. Jiménez-Reyes and M. Solache-Rios, J. Hazard. Mater., 180, 297–302 (2010).
5) J. Favell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell and Y. Magara, “Fluoride in Drinking-water”, IWA, London (2006).
6) N. A. Medellin-Castillo, R. Leyva-Ramos, R. Ocampo-Perez, R. F. García de la Cruz, A. Aragon-Piña, J. M. Martínez-Rosales, R. M. Guerrero-Coronado and L. Fuentes-Rubio, Ind. Eng. Chem. Res., 46, 9205–9212 (2007).
7) S. Gao, R. Sun, Z. Wei, H. Zhao, H. Li and F. Hu, J. Fluor. Chem., 130, 550–556 (2009).
8) I. Abe, S. Iwasaki, T. Tokimoto, N. Kawasaki, T. Nakamura and S. Tanada, J. Colloid Interface Sci., 275, 35–39 (2004).
9) V. Stermitzke, R. Kaegi, J. N. Audinot, E. Lewin, J. G. Hering and C. A. Johnson, Environ. Sci. Technol., 46, 802–809 (2012).
10) S. Terasaka, M. Kamitakahara, T. Yokoi and K. Ioku, J. Ceram. Soc. Japan, 122, 995–999 (2014).
11) R. Leyva-Ramos, J. Rivera-Utrilla, N. A. Medellin-Castillo and M. Sanchez-Polo, Chem. Eng. J., 158, 458–467 (2010).
12) J. Christoffersen, M. R. Christoffersen, R. Larsen and I. J. Möller, Water Res., 25, 227–229 (1991).
13) M. S. Islam, D. Ueno, T. Someya and K. Inoue, Environ. Control Biol., 50, 81–89 (2012).
14) A. F. Lemos, J. H. G. Rocha, S. S. F. Quaresma, S. Kannan, F. N. Oktar, S. Agathopoulos and J. M. F. Ferreira, J. Eur. Ceram. Soc., 26, 3639–3646 (2006).
15) S. Terasaka, M. Kamitakahara, T. Yokoi and H. Matsubara, Mater. Trans., 56, 1509–1512 (2015).
16) D. M. Roy and S. K. Linnehan, Nature, 247, 220–222 (1974).
17) F. Habib, S. Alam, N. Irfan and W. Iqbal, J. Chem. Soc. Pak., 34, 584–588 (2012).
18) A. Krajewski, M. Mazzocchi, P. L. Buldini, A. Ravaglioli, A. Tinti, P. Taddéi and C. Fagnano, J. Mol. Struct., 744, 221–228 (2005).
19) À. Bengtsson, A. Shchukarev, P. Persson and S. Sjöberg, Langmuir, 25, 2355–2362 (2009).
20) H. G. McCann, J. Biol. Chem., 201, 247–259 (1953).
21) J. Lin, S. Raghavan and D. W. Fuerstenau, Colloids Surf., 3, 357–370 (1981).
22) J. C. Elliott, “Structure and chemistry of the apatites and other calcium orthophosphates. Studies in organic chemistry”, Elsevier, Amsterdam (1994).
23) M. T. Fulmer, I. C. Ison, C. R. Hankemayer, B. R. Constantz and I. Ross, Biomaterials, 23, 751–755 (2002).
24) Y. Doi, T. Shibuon, T. Morikawi, T. Kajimoto and Y. Iwayama, J. Biomed. Mater. Res., 39, 603–610 (1998).
25) F. Ren, Y. Leng, Y. Ding and K. Wang, CrystEngComm, 15, 2137–2146 (2013).
26) S. P. Parthiban, I. Y. Kim, K. Kikuta and C. Ohtsuki, J. Ceram. Soc. Japan, 119, 947–953 (2011).
27) C. C. Kee, H. Ismail and A. F. M. Noor, J. Mater. Sci. Technol., 29, 761–764 (2013).
28) M. Frant and J. M. Ross, Jr., Anal. Chem., 40, 1169–1171 (1968).
29) R. N. Panda, M. F. Hsieh, R. J. Chung and T. S. Chin, J. Phys. Chem. Solids, 64, 193–199 (2003).
30) S. Koutsopoulos, J. Biomed. Mater. Res., 62, 600–612 (2002).
31) D. P. Minh, N. D. Tran, A. Nziouhou and P. Sharrock, Mater. Res. Bull., 51, 236–243 (2014).
32) A. Dokoumetzidis and P. Macheras, Int. J. Pharm., 321, 1–11 (2006).
33) S. Gao, J. Cui and Z. Wei, J. Fluor. Chem., 130, 1035–1041 (2009).
34) G. E. J. Peine, M. K. Ghosh, Y. J. Ng, T. B. Issa, S. Anand and P. Singh, J. Hazard. Mater., 185, 29–37 (2011).
35) Y. Lei, J. J. Guan, W. Chen, Q. F. Ke, C. Q. Zhang and Y. P. Guo, RSC Advances, 5, 25462–25470 (2015).
36) S. V. Dorozhkin, J. Mater. Sci., 42, 1061–1095 (2007).