The Hydration of α -Tricalcium Phosphate

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1. Introduction

Compositional and structural changes of slightly water-soluble calcium phosphate—*i.e.*, monetite, brushite, whitlockite, and amorphous calcium phosphate (corresponding to the composition of tricalcium phosphate hydrate)—under various solution conditions were investigated by previous researchers^{1)~4)}. These products were always apatitic compounds. The authors have found that when α -tricalcium phosphate was treated in boiling water a similar phase change occurred and the products were obtained as hardened bodies. On the other hand, β -tricalcium phosphate, α - and β -calcium pyrophosphates did not show such a phase change when these phosphates were treated in the same manner. It seemed there have been no reports on the conversion and hydraulic property of α -tricalcium phosphate. The present paper deals with the conditions for the conversion reaction of the phosphate and some properties of the product.

2. Experimental

2.1 Materials

Alpha tricalcium phosphate, α - $\text{Ca}_3(\text{PO}_4)_2$, was synthesized by heating an equimolar mixture of $\text{Ca}_2\text{P}_2\text{O}_7$ and CaCO_3 at 1100°C for 9 h and subsequent heating at 1300°C for 1 h. The phosphate sample was identified by X-ray diffraction, and ground to 200 mesh.

2.2 Hydration reaction

The hydration reactions were carried out in water with initial pH values of 8.1 and 11.4 at $60\sim 100^\circ\text{C}$ without stirring. A Pyrex flask equipped with a capillary tube of 2 mm in inner diameter was used for the reaction. The pH was adjusted with an aqueous solution of 24.0 mM $\text{Ca}(\text{OH})_2$ (pH=12.8). The solid-solution mixing was made at a room temperature, and the ratio used here was 1 to 6 in weight. Prior to the mixing, it was confirmed that the hydration reaction did not occur even if the mixture was settled down for overnight at room temperature. The solid-solution mixture placed in the flask was enough degassed at room temperature using a water jet pump, and then settled down in

order to sediment the dispersoid at the bottom of the flask. The reaction was started by dipping the flask into a water bath maintained at a given temperature. The hydration rate was estimated by both continuous reading of the liquid level depression in the capillary, corresponding to an apparent amount of water uptake during the hydration, and pH-measurement of the supernatant solution over the solid. The solution was pipetted out through a sintered glass filter and cooled to room temperature, and then the pH was measured. The residual solid was washed with water and dried in air at 100°C for 3 h. The reading and measurement were started after the thermal expansion effects of the dipped mixture and flask were removed. The time required for the removal was 5~10 minutes.

2.3 Various analytical tests

The products obtained from the hydration experiment were tested by the following analyses. Calcium was determined by standard EDTA titration, phosphorus by spectrophotometric phosphovanadomolybdate method, and water by measurement of a heating weight loss at 1300°C for 1 h. Thermogravimetric curves were obtained by weight-measuring before and after heating in steps to 800°C , and by using a Shimadzu recording microbalance RNB-50 V with a heating rate of $2^\circ\text{C}/\text{min}$. Differential thermal analysis was conducted up to 1000°C with heating rates of $2\sim 20^\circ\text{C}/\text{min}$, and the standard material being α - Al_2O_3 . X-ray powder diffraction was carried out using Cu K_α radiation. Infrared spectra were recorded by a Hitachi 285 grating spectrophotometer in the region $4000\sim 400\text{ cm}^{-1}$ using the KBr pellet method.

3. Results and discussion

3.1 Hydration process

Figure 1 shows the apparent water uptake during the hydration of α - $\text{Ca}_3(\text{PO}_4)_2$. The curves rose after induction periods whose durations varied with the reaction temperature and the initial pH, and then had a tendency to flatten out in final periods.

Fig. 1. Hydration of α -tricalcium phosphate under various solution conditions.
Initial pH: —11.4, ...8.1.
Solution temperature ($^{\circ}\text{C}$): 1, 1'=100, 2=90, 3, 3'=85, 4=80, 5=75, 6, 6'=70, 7=60.

Fig. 2. Change of pH of supernatant solution over α -tricalcium phosphate with time.
Solution temperature ($^{\circ}\text{C}$): ●, ▲=100, ■=80.

The time required for this flattening out increased with a decrease in temperature, while the water uptake rate seemed to decrease with a decrease in pH. This temperature effect reflects the fact that the hydration rate decreases with a decrease in temperature. The pH effect suggests that the supernatant pH decreases as the hydration proceeds, and a limiting pH is required for the reaction.

Figure 2 shows the typical pH drops with time. The curve shapes were essentially similar to those of the water uptake curves. The products obtained at the final stage of the reaction (Fig. 2) were found to have only apatitic structure. The final pH values seemed to reach around 5, and the reaction might be stopped at this fixed pH value. The pH drops were possibly due to reactions such as

However, the products obtained experimentally had a different composition from the stoichiometric hydroxyapatite (refer to Table 1). Then these reactions were considered to proceed slightly.

Table 1. Compositions and crystalline phases of products.

Sample No.	Treatment ^{a)} ($^{\circ}\text{C}$ -min)	Compositions (%)			Ca/P (molar ratio)	Crystalline phase ^{b)}
		CaO	P ₂ O ₅	H ₂ O		
1	100-10	52.7	43.8	3.4	1.53	Ap, αT
2	" -20	51.7	42.8	4.3	1.53	Ap, αT
3	" -30	51.8	43.1	4.6	1.52	Ap, αT
4	" -40	52.3	43.3	4.8	1.53	Ap
6	" -60	52.1	43.4	4.5	1.52	Ap
7	80-70	51.7	43.6	4.6	1.50	Ap, αT
9	" -90	52.0	43.9	4.5	1.50	Ap, αT
12	" -120	51.8	43.8	4.8	1.50	Ap

a) α -Ca₃(PO₄)₂/solution=1/6 (in weight), initial pH=11.4.

b) Ap: apatite, αT : α -Ca₃(PO₄)₂.

3.2 Some properties of products

3.2.1 Hydraulic property The products from the hydration experiment were obtained as hardened bodies. The molded specimens with 5~6 cm in length were prepared using a Pyrex tube of 14 mm in inner diameter in the same manner as the hydration experiment. Then the specimens were cut out to appropriate lengths of 0.8~2.8 cm. The molded products had bulk densities of 0.9~1.2 g/cm³, compressive strengths of 150~160 kg/cm², and tensile strengths of 20~30 kg/cm². If the strengths are further improved, the hardened materials may be applied to bioceramics or others. This problem is under study at present.

3.2.2 Composition and crystalline phase

All the hydrated products gave an X-ray pattern similar to that of apatite having ideally a Ca/P molar ratio of 1.67 as shown in Equation (1) or (2). Table 1 lists the chemical compositions and crystalline phases of products found intermediately during the hydration process at 80 and 100 $^{\circ}\text{C}$, and pH=11.4. However, the Ca/P ratios of the products were 1.50~1.53 throughout the hydration and coincided with 1.50 of the starting phosphate within an experimental error. The combined water content was estimated to be 4.5~4.8% for the products obtained finally at 80~100 $^{\circ}\text{C}$ and pH=11.4. The sufficiently hydrated products were identified to be a so-called "calcium deficient hydroxyapatite" with a Ca/P ratio near 1.50. Therefore, the formula of the products should be represented as

where $x+y \approx 2.5$, and y means a molar sum of structural water occupying Ca²⁺ or OH⁻ vacancies⁵⁾ and adsorbed water. This formula may be reasonable rather than 3 Ca₃(PO₄)₂· n H₂O, $n=x+y$. The presence of HPO₄²⁻ and OH⁻ groups was ascertained by infrared spectroscopy. The overall charge balance in the apatite lattice is apparently maintained through the uptake of one OH⁻ with one H⁺, that is, one water molecule. In other words, H₂O is introduced into α -Ca₃(PO₄)₂ by a reaction:

Fig. 3. Thermogravimetric curves of products.
—: by using electro-microbalance.
.....: by weight-measuring before and after heating.

Sample: ▲No. 1, ●No. 6, △No. 7,
○No. 12, —No. 6.

and this introduction converts α - $\text{Ca}_3(\text{PO}_4)_2$ into a calcium deficient hydroxyapatite missing one mole calcium ion. The products under the other conditions in the present study were also possibly expressed by the above formula (3). Similar many

formula have been described in the literature^{9)~11)} in order to interpret nonstoichiometric hydroxyapatites with various Ca/P ratios, a few of which are shown for Ca/P=1.50 as follows:

3.2.3 Thermogravimetric analysis

Figure 3 shows the changes in weight with heat-treatment of the products. On heating to 700°C, approximate 75% of the total water (2.5 mol/l mol apatite) lost continuously keeping the apatitic structure, and on heating to 700~800°C the remained water lost rapidly through the formation of β -tricalcium phosphate. However, the stoichiometric hydroxyapatite with a Ca/P=1.67 maintains virtually its structure up to 1200°C¹²⁾. If the deficient apatite decomposes accompanying only water removal from the structural OH^- , x in the formula (3) can be estimated to be about 1.25, and y 1.25. Then the formula was written as

Consequently, the 75%-loss up to 700°C can be accounted for by water liberation from the adsorbed and structural H_2O 's, and by dehydration of HPO_4^{2-} , and the remained 25%-loss above 700°C by OH^- .

Fig. 4. Effect of heat-treatment of product on infrared absorption spectrum.

Sample: No. 6.

Heat-treatment: a=100°C-3 h, b=200°C-2 h,
c=320°C-2 h, d=450°C-2 h,
e=650°C-2 h, f=800°C-1 h.

This interpretation could be supported also by thermal changes of the two anionic species as described in the following section (3.2.4).

3.2.4 Infrared absorption spectra An attempt was made to establish the above formula (3) by infrared spectrophotometry. The spectra are shown in Fig. 4. The presence of structural OH⁻ and HPO₄²⁻ groups in the products was suggested by the absorption bands at 625 and 3575 cm⁻¹, and 860 cm⁻¹ (P-O-H), respectively⁵³. The band at 860 cm⁻¹ disappeared gradually with heating to 200~450°C, and the gradual appearance of a broad absorption band at about 720 cm⁻¹ assigned to pyrophosphate resided in a nascent state or amorphous surroundings^{53,133}. In addition, the absorption intensities at both 3575 and 625 cm⁻¹ assigned to OH stretching and librational modes seemed to increase during the heating. These thermal changes may be interpreted by assuming the following intramolecular reactions :

where the species in brackets show constituents of the apatitic compound. The band at 720 cm⁻¹ disappeared at 650°C. Along with the appearance of a sharp band at 753 cm⁻¹, assignable to highly crystallized or tightly combined P₂O₇⁴⁻. The spectrum of the sample treated at 800°C showed β-tricalcium phosphate being a converted crystalline material formed by an intramolecular degradation such as :

3.2.5 Differential thermal analysis The DTA curves of the products had a single endothermic peak at around 790~870°C due to the decomposition of the apatite into β-tricalcium phosphate accompanying water liberation. No peak due to dehydration below 700°C indicated that the dehydration occurred gradually or continuously. A typical change of the DTA peak profile with heating rate (*h*, °C/min) is shown in Fig. 5. The dependence of the peak temperature (*T_m*) measured at the minimum point on *h*^{1/2} is shown in Fig. 6. The critical *T_m* at *h*=0 was 755°C. This value shows the true temperature for the decomposition. An apparent activation energy (*E_a*) for the decomposition reaction is given by the following equation¹⁴³ :

$$\ln(T_m^2/h) = (E_a/RT_m) + \ln(E_a/AR) \quad (12)$$

where *A* is the Arrhenius preexponential term in the expression for the reaction rate constant. *E_a* was evaluated to be 65 kcal/mol.

4. Conclusion

(1) The hydration of α-tricalcium phosphate was conducted below 100°C in water with pH values of 8.1 and 11.4. The hydration rate decreased with decreases in temperature and pH. The hydration

Fig. 5. DTA profiles and peak temperatures obtained at various heating rates.

Sample: No. 6. Heating rate (°C/min) : a=2, b=5, c=10, d=20.

Fig. 6 Relationship between peak temperature (*T_m*) and heating rate (*h*).

Sample: No. 6.

proceeded scarcely at room temperature. A limiting pH seemed to be required for the proceeding of the hydration, and the pH was estimated to be about 5.

(2) The products were obtained as hardened bodies. The sufficiently hydrated products were identified to be a calcium deficient hydroxyapatite with a Ca/P molar ratio near 1.50 and a water content of about 4.7%. This apatite contained acid phosphate ions, hydroxide ions, and water molecules.

(3) When the calcium deficient hydroxyapatite was heated to 700°C, approximate 75% of the total combined water lost continuously keeping the apatitic structure, accompanying disappearance of acid phosphate ions and appearance of pyrophosphate ions. The remained water lost rapidly at 755°C along with disappearance of hydroxide ions and endothermic

formation of β -tricalcium phosphate. An apparent activation energy for this decomposition reaction was evaluated to be 65 kcal/mol.

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α -燐酸カルシウムの水和

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α -燐酸カルシウムの水和反応が塩基性液中, 100°C 以下で生じることを見出した. 反応は温度および pH 低下とともに遅くなり, 室温および pH 約 5 以下ではほとんど進行しなかった. 水和反応生成物は硬化体として得られた. 十分に水和させた生成物は, Ca/P モル比=1.5 のカルシウム欠損水酸アパタイトであると同定された. このアパタイト中には水分子, OH⁻ および HPO₄²⁻ の H として約 4.7% の水成分が含まれていた. アパタイト

構造は 700°C までの加熱によって全含有水分の約 75% を揮発させても安定であった. このとき HPO₄²⁻ の消滅と P₂O₇⁴⁻ の生成とが確認された. 残りの水分は, OH⁻ の除去と β -燐酸カルシウムの生成とを伴って, 755°C で急激に放出された. アパタイト-燐酸カルシウム分解反応の見掛け 活性化エネルギーは 65 kcal/mol であった.

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訂 正

窯業協会誌 84 [3] 1976 の和文目次を下記のように訂正し, ここにお詫び致します.

項 目	誤	正
和文目次	マグネシア・バイクリスタルでの透光性及ばす結晶格子異方性の影響	マグネシア・バイクリスタルでの破壊挙動における粒界の影響