Hydraulic Properties of the Tricalcium Phosphate-Dicalcium Phosphate Mixture

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第三リン酸カルシウム-第二リン酸カルシウム系混合物の水和凝結特性

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A new combination of α - $\text{Ca}_3(\text{PO}_4)_2$ (TCP) and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD), each of which alone had a low or no hydraulicity, was proposed and investigated on its hydraulic properties. This combination showed a high hydraulicity probably due to the complementarity that the hydrolysis of TCP to octacalcium phosphate (OCP) was accelerated by the coexistence of DCPD and vice versa. Setting times were 9-30 min and reaction products were OCP only in the range of 1.20 to 1.47 in the mixing molar ratio Ca/P. Hardened bodies soaked in 0.9% NaCl solution at 37°C for 1 day had a porosity of $49 \pm 3\%$ and a wet compressive strength of 14-19 MPa, in comparison with $52 \pm 4\%$ and 6-11 MPa for a $\text{Ca}_4(\text{PO}_4)_3\text{O}$ -DCPD combination and $66 \pm 2\%$ and ca. 2 MPa for a DCPD- CaCO_3 combination.

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1. Introduction

Since the finding of the hydraulicity of tricalcium phosphate (TCP; $\text{Ca}_3(\text{PO}_4)_2$),¹⁾ the system $\text{CaO-P}_2\text{O}_5$ has become of interest as a new compositional series of cementitious materials, particularly in the field of bio-restorative materials. Until now, mixed-component hydraulic materials such as tetracalcium phosphate (TeCP; $\text{Ca}_4(\text{PO}_4)_2\text{O}$)-brushite (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$),^{2),3)} TeCP-TCP⁴⁾, and DCPD- CaCO_3 ⁵⁾ combinations have been also developed. These hydraulic materials can be also solidified by using acidic aqueous solutions.^{3),6)-7)}

In this work, a TCP-DCPD combination was newly proposed and investigated with expectations for the hydrolysis to octacalcium phosphate (OCP; $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) and the resulting hardening. The formation of OCP is conceivable stoichiometrically and from the fact that the solubility isotherms of TCP and DCPD as a function of pH have an intersection called a singular point which lies above the isotherm for OCP.^{2),8)}

2. Experimental

TCP with the high temperature form α was prepared by heating the stoichiometric mixture of reagent grade DCPD and CaCO_3 at 1250°C,

subsequently air-quenched and ground to pass through a 150 mesh sieve. The TCP and DCPD were mixed using an agate mortar at Ca/P molar ratios between 1.00 and 1.50. Changes in pH of suspensions of 1.0 g of powder sample in 50 ml of H_2O were followed continuously with stirring at 37°C. Reaction products were identified by X-ray diffraction and IR spectroscopy. Setting runs were carried out at 37°C for pastes with a powder/ H_2O mixing ratio of 1.6 ± 0.1 by weight. Setting time was measured according to JIS T 6604 using a Bicat needle. Hardened bodies (10mm in diameter and 10-20mm in height) were soaked in a physiological salt solution (0.9wt% NaCl) at physiological temperature (37°C), and then examined with respect to wet strength, porosity and SEM microstructure. For comparison, various hydraulic materials were also provided using TCP, TeCP, DCPD and its anhydride (DCPA) and CaCO_3 .

3. Results and discussion

Figure 1 shows pH changes in the suspension state of TCP-DCPD- H_2O mixtures with different Ca/P mixing ratios. Reaction products from TCP-DCPD mixtures were only OCP. Both TCP alone and DCPD alone showed no detectable hydrolysis change in H_2O under conditions

Fig. 1. Changes in pH of suspensions of TCP-DCPD mixtures at 37°C with time (Powder/H₂O=1g/50ml). TCP/DCPD mixing ratios are expressed by Ca/P molar ratio.

used here. So, the pH drops observed in the systems DCPD-H₂O (Ca/P=1.00) and TCP-H₂O (Ca/P=1.50) were inferred to be almost due to the dissolutions of DCPD and TCP. When TCP added to the system DCPD-H₂O, the pH of the suspension was kept higher, which was advantageous for the hydrolysis of DCPD to OCP or hydroxyapatite (HAp).⁹⁾ This effect was similar to that of the addition of CaCO₃ to the system DCPD-H₂O for spontaneous hydrolysis of DCPD to carbonated apatite.⁵⁾ On the contrary, the hydrolysis of TCP to OCP was accelerated by a pH lowering effect of DCPD added to the system TCP-H₂O. Such a complementarity was a feature of this combination. Consequently, TCP and DCPD could be hydrolysed without any intentional pH adjustment, which means that the combination has a potentiality of hardening. The formation of OCP would follow, for instance,

and as an overall reaction,

Under these consideration, hardening runs were carried out and as a result, a high hydraulicity of this combination, each of which had a low (TCP) or no hydraulicity (DCPD), was ascertained.

Table 1 lists a setting time and related data for a TCP-DCPD mixture with data for other combinations of calcium phosphates. The TCP-DCPD mixture, as far as setting time is concerned, could be applicable to dental restora-

Table 1. Setting times and related data at 37°C for hydraulic calcium phosphates combinations.

Hydraulic mixture ^{a)}		Ca/P (mol ratio)	Setting time (min)	Conversion (%) ^{b)} and product ^{c)}
Component A	B			
α -TCP	DCPD	1.33	9-10	80, OCP
	DCPA	1.33	-100	
β -TCP	DCPD	1.33	100-120	
	DCPD	1.67	5-7	60, HAp
TeCP	DCPA	1.67	-9	
	α -TCP	1.67	-130	20 ⁺ , HAp
DCPD	CaCO ₃	1.67	60-120	100, CO ₃ Ap

a) α -TCP (TCP in the text): α -Ca₃(PO₄)₂,

β -TCP: β -Ca₃(PO₄)₂, DCPD: CaHPO₄·2H₂O,

DCPA: CaHPO₄, TeCP: Ca₄(PO₄)₂O.

b) Estimation by X-ray diffraction of component

A, 1 day after soaking in 0.9% NaCl solution.

c) OCP: Ca₅H₂(PO₄)₆·5H₂O, HAp: Hydroxyapatite,
CO₃Ap: Carbonated HAp.

tion as well as the TeCP-DCPD mixture.³⁾ Setting times became longer with departing from around Ca/P=1.33 corresponding to the ratio of OCP as shown in Fig. 2. Reaction products were only OCP at TCP/DCPD mixing ratios ranging from 1.20 to 1.47 in Ca/P ratio.

Figure 3 shows changes in wet strength of hardened bodies prepared from TCP-DCPD (Ca/P=1.33), TeCP-DCPD (Ca/P=1.67) and DCPD-CaCO₃ (Ca/P=1.67) combinations. Although the TeCP-DCPD was best in initial strength, since about 1 day after the soaking the TCP-DCPD gave the most improved strengths. This improvement occurred probably with increases in degree of the reaction and the resulting entanglement of the product, i.e., OCP. Porosities after 1 day were 49±3% for TCP-DCPD, 52±4% for TeCP-DCPD and 66±2% for DCPD-CaCO₃. According to SEM observations (Fig. 4), the TCP-DCPD produced hardened bodies having a homogeneous texture compared

Fig. 2. A relationship between setting time and TCP/DCPD mixing ratio expressed by Ca/P molar ratio (37°C, powder/H₂O=1.6±0.1).

Fig. 3. Effect of soaking in 0.9% NaCl solution at 37°C on wet compressive (σ_c) and wet diametral tensile (σ_d) strengths of hardened bodies prepared from each paste of TCP-DCPD with Ca/P=1.33 (●), TeCP-DCPD with Ca/P=1.67 (▲) and DCPD-CaCO₃ with Ca/P=1.67 (■) combinations. $\sigma_d = 2P / \pi Dt$ (P : load, D : sample diameter, t : sample height)

with the other two. This homogeneity might cause comparatively high strengths. The hardenings of these combinations were considered to be due to the formation and entanglement of OCP or HAp microcrystals.

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References

- 1) H. Monma and T. Kanazawa, *Yogyo-Kyokai-Shi*, 84, 209-13 (1976).
- 2) W. E. Brown and L. C. Chow, U. S. Pat. 4518430 (1985).
- 3) Y. Doi, Y. Takezawa, S. Shibata, N. Wakamatsu, H. Kamemizu, T. Goto, M. Iijima, Y. Moriwaki, K. Uno, F. Kubo and Y. Haeuchi, *Shika Zairyo Kikai*, 6, 53-58 (1987).
- 4) S. Takagi, T. Oku, K. Shigeru and T. Shishikura, Abstr. of 1987 Ann. Meet. of The Ceram. Soc. Japan, 931-32 (1987).
- 5) H. Monma, *Yogyo-Kyokai-Shi*, 95, 146-47 (1987).
- 6) H. Nakajima, H. Monma and H. Hashimoto, *Gypsum & Lime*, No. 210, 43-48 (1987).
- 7) F. Sugihara, M. Yamada, S. Akamatsu, S. Shimada,

Fig. 4. SEM photographs of hardened bodies (A: from TCP-DCPD with Ca/P=1.33, B: from TeCP-DCPD with Ca/P=1.67 and C: from DCPD-CaCO₃ with Ca/P=1.67) 1 day after soaking in 0.9% NaCl solution at 37°C.

Bars: 10 μ m.

- K. Toyooka, I. Kishida, Y. Mandai and H. Oonishi, *Seitai Zairyo*, 4, 199-206 (1986).
- 8) B. O. Fowler and S. Kuroda, *Calcif. Tissue Int.*, 38, 197-208 (1986).
- 9) H. Monma and T. Kamiya, *J. Mater. Sci.*, 22, 4247-50 (1987).