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Hydration behavior of calcium phosphates is analogous to hydration behavior of calcium silicates

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Abstract

Similarities between the hydration of calcium silicates and calcium phosphates are discussed. Calcium silicate hydration forms C-S-H, while calcium phosphate hydration forms hydroxyapatite (HAp). Both are compounds of variable composition, both incorporate water, and both exhibit high surface areas. Although both are weakly crystalline, HAp is so because of small crystallite size. Calcium phosphates and calcium silicates both undergo pozzolanic reactions and Hadley grains form in both systems. The origin of Hadley-like grains and the mechanisms limiting the rate of hydration in the calcium phosphate system are described. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Calcium silicates and calcium phosphates can both develop desirable physical properties as a result of undergoing hydration reactions. Calcium silicates are familiar as constitutents of Portland cement, whereas calcium phosphates are the mineral constitutents of hard tissues and form an important class of phosphors. While the applications for these compounds are vastly different, there are significant similarities between them. The purpose of this paper is twofold: (1) to compare the characteristics of calcium silicates and calcium phosphates and (2) to describe the mechanisms of hydrolysis of calcium phosphates, as a basis for developing insight to the hydration of calcium silicates.

2. Overview

2.1. Hydration of $3CaO \cdot SiO_2$ vs. $4CaO \cdot P_2O_5$ (formation of hydrated compounds and calcium hydroxide)

The hydration of tricalcium silicate is shown in Eq. (1):

$$3CaO \cdot SiO_2 + {\sim}5.3H_2O \Rightarrow {\sim}1.7CaO \cdot SiO_2 \cdot 4H_2O + {\sim}1.3Ca(OH)_2 \quad (1)$$

The uncertainty in the precise composition of calcium silicate hydrate (C-S-H) necessitates the use of approximate compositions but it is well accepted that the Ca/Si ratio of C-S-H in equilibrium with $Ca(OH)_2$ is near 1.7 [1].

Equivocation is not required when expressing the compositions of the calcium phosphate that forms when tetracalcium phosphate (TetCP) hydrates, as shown in Eq. (2):

$$3[4CaO \cdot P_2O_5] + 3H_2O \Rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2Ca(OH)_2 \quad (2)$$

In this instance the reaction products are stoichiometric hydroxyapatite (HAp) and calcium hydroxide (CH) [2].

The latter reaction has been suggested as a means to fill root canals in teeth [3]. The high pH associated with the formation of CH is not considered problematic because it is desirable to destroy any bacterial colonies that may be present.

Although C_3S hydration is regarded as rapid for applications in civil engineering, that of TetCP is regarded as slow for dental applications. Regardless of the differences in the chemistries, both reactions are limited by the accretion of hydration products in the vicinities of the anhydrous particle surfaces. Thus, in both instances the liquid and solid reactants become physically separated from one another and subsequent reactions become diffusionally controlled.

However, these reactions only illustrate one composition of the C-S-H or HAp that may form. It is well recognized that C-S-H can exist over a range of compositions that extend from 0.833 (Ca/Si = 5/6) to 2.0 or more [4]. HAp also exists over a compositional range. In this instance the Ca/P

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ratio varies from ~1.4 to 1.84. $Ca_{10}(PO_4)_6(OH)_2$ has a Ca/P ratio of 1.67 and is likely to be the terminal composition formed at low temperature. In the apatite structure Ca coordinates with PO_4 tetrahedra in such a way that OH columns occur. When the Ca/P ratio is 1.84 $Ca_{11}(PO_4)_6O_2$, each pair of protons in these columns is replaced by a Ca [5]. The composition of HAp formed when the Ca/P ratio is 1.5 is $Ca_9HPO_4(PO_4)_5OH$. Although it has been reported that an apatite of composition $Ca_8(HPO_4)_2(PO_4)_4$ (Ca/P = 1.33) can form [6], this appears not to have been confirmed.

2.2. Pozzolanic-type reactions

The pozzolanic reaction that occurs in the calcium silicate system is typically expressed as that shown in Eq. (3):

$$xCa(OH)_2 + SiO_2 + nH_2O \Rightarrow xCaO \cdot SiO_2 \cdot nH_2O, \quad \text{where } 0.833 \leq x \leq \sim 1.7. \tag{3}$$

where SiO_2 represents some source of reactive silica, such as in fly ash, natural pozzolans, or silica fume.

The analog of the pozzolanic reaction in the calcium phosphate system cannot be expressed in terms of a single equation. Table 1 lists the various calcium phosphate compounds in order of increasing basicity. Viewing HAp as a salt formed by an acid-base reaction, there are a number of combinations of calcium phosphates that can undergo a pozzolanic reaction. In analogy with the pozzolanic reaction forming C-S-H, combinations of solids more acidic and more basic than the product must react. TetCP is the only calcium phosphate more basic than HAp and is the source of the $Ca(OH)_2$. A variety of acidic calcium phosphates could be used as the SiO_2 analog. Among these the following have been studied in some detail (7) [see Eq. (4)]:

$$2CaHPO_4(\cdot 2H_2O) + 2Ca_4(PO_4)_2O \Rightarrow Ca_{10}(PO_4)_6(OH)_2(+2H_2O) \tag{4}$$

If in strict analogy with the pozzolanic reaction in cements, TetCP hydrates to form HAp and CH according to Eq. (2), then reacts as shown in Eq. (5):

$$6CaHPO_4(\cdot 2H_2O) + 4Ca(OH)_2 \Rightarrow Ca_{10}(PO_4)_6(OH)_2(+nH_2O) \tag{5}$$

where n = 5 or 18. However, as will be discussed, the hydrolysis reactions of TetCP and the acidic calcium phosphates are coupled and solid CH does not form. Thus, from a mechanistic standpoint it is useful to express these reactions by using Eq. (4) or, where calcium-deficient HAp forms, according to Eq. (6):

$$6CaHPO_4(\cdot 2H_2O) + 3Ca_4(PO_4)_2O \Rightarrow 2Ca_9(HPO_4)(PO_4)_5OH(+nH_2O) \tag{6}$$

where n = 1 or 13.

Another example of an analog of the pozzolanic reaction is the formation of calcium-deficient HAp using monocalcium phosphate monohydrate [8], as shown in Eq. (7):

$$2Ca(H_2PO_4)_2 \cdot H_2O + 4Ca_4(PO_4)_2O \Rightarrow 2Ca_9(HPO_4)(PO_4)_5OH + 2H_2O \tag{7}$$

However, in this instance, the reaction does proceed in two steps. In the first step, monocalcium phosphate monohydrate reacts with TetCP to rapidly form $CaHPO_4 \cdot 2H_2O$. This, in turn, reacts with the remaining TetCP to form HAp. In addition to the pozzolanic reaction, the calcium phosphate system offers a reaction in which single-phase HAp forms from a single solid precursor, as depicted in Eq. (8):

$$3\alpha Ca_3(PO_4)_2 + H_2O \Rightarrow Ca_9(HPO_4)(PO_4)_5OH \tag{8}$$

In analogy with calcium silicate hydrates, the surface areas of HAp formed by these reactions are typically high. For example, the specific surface area of calcium deficient HAp formed according to Eq. (6) is approximately 135–180 m^2/g [9]. However, high surface area is conferred to HAp by small crystallite size and not as a result of formation of an amorphous or poorly crystalline solid.

2.3. Mechanisms of HAp formation

One method that has been applied to illustrate the mechanism by which HAp forms by dissolution-precipitation reactions is the solubility diagram. Solubility diagrams plot the variations in the molar solubilities of the relevant compounds as a function of pH. Variation in solubility is typically expressed in terms of the concentration of one of the ions that are common to all the relevant compounds. For calcium phosphates, it is common to plot the solubility diagram using the calcium concentrations (or activities) as a function of pH. Although phosphate could be used, analysis is complicated by the variability in phosphate speciation. A solubility diagram for selected calcium phosphates is shown in Fig. 1 for a pH range from about 4 to about 9 [after ref.

Table 1
Calcium Orthophosphates

Formula	Name	Ca/P Ratio
$2Ca(H_2PO_4)_2 \cdot H_2O$	Monocalcium Phosphate Monohydrate (MCPM)	0.5
$2Ca(H_2PO_4)_2$	Monocalcium Phosphate (MCP)	0.5
$CaHPO_4 \cdot 2H_2O$	Dicalcium Phosphate Dihydrate (DCPD)	1.0
$CaHPO_4$	Dicalcium Phosphate (DCP)	1.0
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	Octacalcium Phosphate (OCP)	1.33
α–, β-$Ca_3(PO_4)_2$	Tricalcium Phosphate (TCP)	1.5
~$Ca_9(PO_4)_6 \cdot 3H_2O$	Amorphous Calcium Phosphate (ACP)	1.5
~$2Ca_9(HPO_4)(PO_4)_5OH$, $Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite (HAp)	~1.5-1.67
$Ca_4(PO_4)_2O(4CaO \cdot P_2O_5)$	Tetracalcium Phosphate (TetCP)	2.0

10]. Solubility isotherms are shown for HAp, $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, and for $Ca_4(PO_4)_2O$. The stable calcium phosphate is that which has the lowest solubility at a given pH. Thus, a stable calcium phosphate will also have the lowest calcium concentration. The stable calcium phosphate over the range of pH above about 4.2 is HAp. HAp and $CaHPO_4$ have equivalent stabilities at pH 4.2, indicating these to be the equilibrium assemblages of phases at this pH. This occurs when the solution is mutually and simultaneously saturated with respect to these two solids.

Although only two of the calcium phosphates represented on the diagram are stable, a variety of other solubility behavior can be represented. For example, although $CaHPO_4 \cdot 2H_2O$ has a true solubility, it is not a stable compound at the conditions represented. However, $CaHPO_4 \cdot 2H_2O$ exists in metastable equilibrium with HAp at a pH near 4.6. This equilibrium condition is metastable in that the solubility isotherm for HAp at this pH occurs at a lower Ca ion concentration (or activity).

$Ca_4(PO_4)_2O$ lacks a true solubility and, as a consequence, cannot be regarded as existing in equilibrium in aqueous solution with any other calcium phosphate. In spite of this, the mechanistic consequences of dissolution of $Ca_4(PO_4)_2O$ with $CaHPO_4(\cdot 2H_2O)$ can be explored. To do so requires the assumption that $Ca_4(PO_4)_2O$ dissolution attains a steady state rate that depends on pH. For example, the cohydrolysis of a particulate mixture of $Ca_4(PO_4)_2O$ and $CaHPO_4$ will tend to result in the solution attaining a condition at a pH near approximately 7.8, where a pseudo-metastable equilibrium exists. However, the solubility isotherm for HAp occurs at a significantly lower Ca ion concentration. Thus, the dissolution of $Ca_4(PO_4)_2O$ and $CaHPO_4$ results in a solution that is supersaturated with respect to HAp. This supersaturation provides the driving force for HAp formation. Significant in this analysis is the use of the concept of equilibria in the exploration of the behavior of a compound ($Ca_4(PO_4)_2O$), which, in analogy with C_3S, lacks a true solubility.

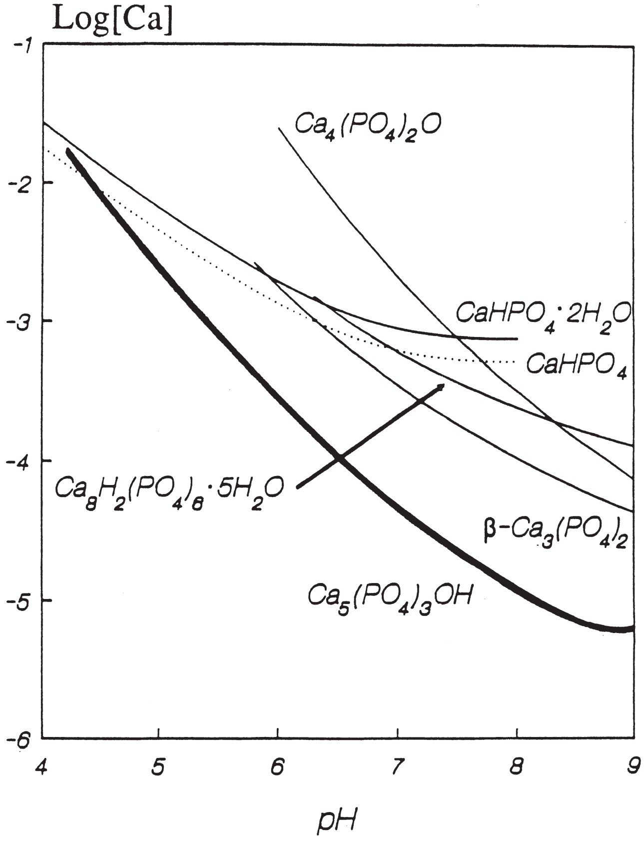

Fig. 1. The solubility diagram for selected calcium phosphates (after [10]). Reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, Ohio 43086-6136. Copyright 1987 by The American Ceramic Society. All rights reserved.

Fig. 2 shows the variation in pH with time when particulate $CaHPO_4$ and $Ca_4(PO_4)_2O$ are mixed in mole ratios varying from 1:2 to 1:1 and then hydrolyzed in water [11]. If the pH was about 7.8, the dissolution rates of these solids would support the establishment of the metastable condition described above. Alternatively, as shown in Fig. 2, the attainment of a steady state pH significantly above this value is suggestive that the dissolution of the acidic reactant is rate-limiting. Companion microstructural observation revealed the presence of Hadley-like grains. In some instances empty shells were observed; in others a small grain of HAp was observed to have formed within the shell.

Although the solubility diagram is an extremely useful representational tool, it is inadequate to illustrate the mechanistic path taken in HAp and Hadley-like grain formation for two reasons. First, the solubility diagram does not represent the compositional variability of HAp. When the solubility diagram is viewed in terms of its ability to represent equilibria between solid and liquid phase, it can be regarded as a sort of phase diagram. The solubility diagram for the calcium phosphate system can be regarded as a ternary CaO-P_2O_5-H_2O system at constant temperature and pressure. Thus, invariance occurs when two solids coexist in equilibrium with the solution. Second, the solubility diagram does not illustrate the aspects important in hydration (i.e., mechanistic paths associated with dissolution cannot be readily followed).

As a consequence of these limitations, the ternary CaO-P_2O_5-H_2O diagram was determined. The concepts used in the construction of this diagram were initially developed when the room temperature phase behavior of C-S-H was determined by establishing the CaO-SiO_2-H_2O diagram [4]. Although the CaO-SiO_2-H_2O system contains only a single ternary intermediate compound of variable composition (C-S-H), its construction is complicated by the range of solubility exhibited by the hydrous silica. Because of this, a method was developed that involved the representation of molar solubilities by plotting their n^{th} roots [4,12,13]. This method was also employed in constructing the CaO-P_2O_5-H_2O diagram [14] which is represented schematically in Fig. 3. The compositional points for $CaHPO_4(\cdot 2H_2O)$ are shown. The

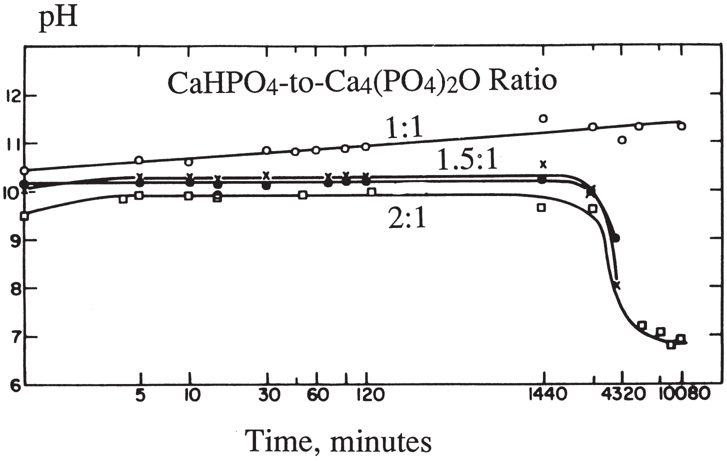

Fig. 2. Variation in pH with time when HAp forms according to Eq. 4 (after [11]). Reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, Ohio 43086-6136. Copyright 1991 by The American Ceramic Society. All rights reserved.

range of compositions for HAp are shown. The solubility isotherms for HAp and $CaHPO_4$ are shown and the invariant points involving HAp and $CaHPO_4$ and HAp and CH can be observed. Interpretation of the diagram in Fig. 3 establishes the bases for the kinetics of HAp formation and for the microstructures of the HAp observed.

If a crystallite of $CaHPO_4$ is placed in water, Ca and phosphate will enter solution in a molar ratio of 1:1. As $CaHPO_4$ dissolution continues, this solution becomes saturated with respect to HAp. However, because the solution remains undersaturated with respect to $CaHPO_4$, it continues to dissolve. As a consequence, critical supersaturation with respect to HAp occurs, resulting in HAp precipitation. Because of HAp precipitation, the Ca/P ratio of the solution decreases to less than 1. As these processes of $CaHPO_4$ dissolution and HAp precipitation continue, the invariant point between them is reached; a solution saturated with respect to $CaHPO_4$ is achieved; and further $CaHPO_4$ dissolution ceases. Because $CaHPO_4(\cdot 2H_2O)$ dissolution does not result in a saturated solution without the formation of a second solid phase, their dissolution is incongruent. These phenomena explain why the dissolution of the acidic reactant is rate limiting and the origin of the Hadley-type grains form. Applying the concept of local equilibrium, the formation of HAp will occur regardless of the presence of TetCP. HAp will nucleate and grow at the locations where the degree of

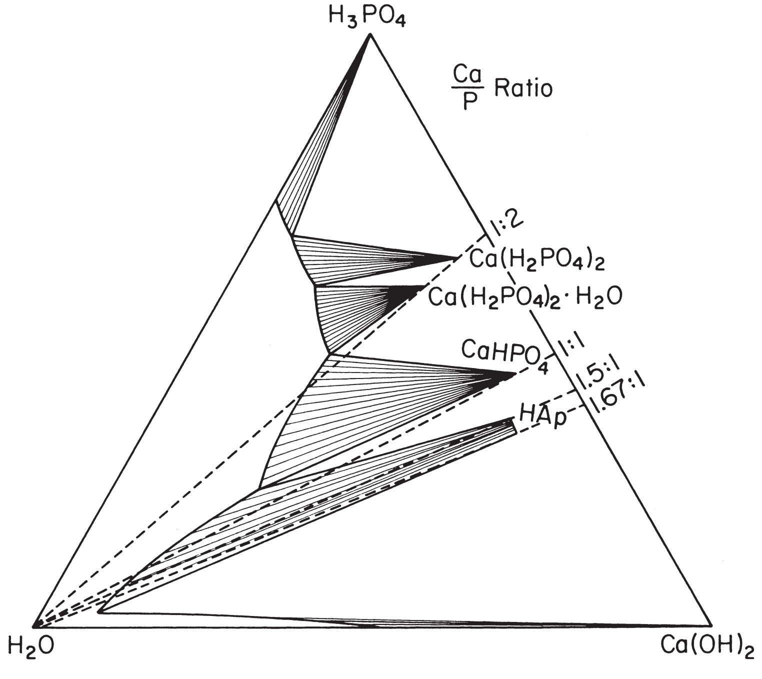

Fig. 3. The CaO-P_2O_5-H_2O ternary diagram (after [14]). Reprinted with permission of The American Ceramic Society, Post Office Box 6136, Westerville, Ohio 43086-6136. Copyright 1987 by The American Ceramic Society. All rights reserved.

supersaturation is the highest, namely, at the $CaHPO_4$ surfaces. Thus, as hydration proceeds, the $CaHPO_4$ surfaces become covered with HAp. This results in their progressive isolation from solution and an elevated pH as the $Ca_4(PO_4)_2O$ continues to dissolve. Coverage of $CaHPO_4$ by HAp also results in the formation of the shell-like morphological features reminiscent of Hadely grains. Thus, both the kinetics of hydration and the microstructural development in the formation of HAp by a cementlike reaction can be related to the phase diagram.

3. Conclusions

The formation of HAp and C-S-H exhibit similar hydration behavior in a variety of ways. Both HAp and C-S-H are compounds of variable composition. Both HAp and C-S-H tend to form at or near the surfaces of the anhydrous precursors and, in doing so, affect subsequent rates of hydration. Although HAp is more crystalline, both C-S-H and HAp tend to exhibit high surface areas. Alternatively, these compounds show significant nanostructural differences. HAp contains isolated phosphate tetrahedra while the silica tetrahedra in C-S-H form more extended structures. In spite of these differences, the phenomena driving dissolution/precipitation reactions common to cements appear to influence both kinetics and microstructural development in ways that transcend composition.

Acknowledgments

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