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Mechanism of setting reaction in magnesia-phosphate cements

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Abstract

This paper tries to explain the setting mechanism of magnesia-phosphate cements obtained by mixing equal qualities of magnesia (MgO) and monoammonium dihydrogen phosphate ($NH_4H_2PO_4$) or MAP. As soon as mixing water is added to the mixture, the MAP goes into solution till saturation while magnesia starts to be wetted. The drop in pH observed during this period leads to the dissociation of magnesia through an acid-base reaction. The kinetics of this reaction depends upon the MgO surface structure. Mg^{2+} ions present in solution are complexed into Mg $(H_2O)_6^{2+}$ and can substitute to molecules of water and be adsorbed on the MgO surface. These complexes remain attached to the surface and recover it progressively. Ions PO_4^{3-} and NH_4^+ and $Mg(H_2O)_6^{2+}$ complexes can come close to the surface and develop a struvite network, owing to hydrogen bonds. This explanation results from analyses of solutions, X-ray diffractometry, and scanning electron microscopy.

Keywords: Hydration; Microstructure; Chemically bonded ceramics; MgO

1. Introduction

Chemically bonded ceramics (CBCs) can be processed at low temperatures [1,2]. Magnesia-phosphate cements (MPC) belong to these CBCs and develop strength rapidly. They are attractive for applications such as rapid-repair materials for deteriorated bridge decks, highways, and airport runways, and solidification and stabilization of radioactive waste, because fabrication can be achieved at room temperature or slightly elevated temperatures to minimize processing concerns [3–7].

MPCs involve an acid-base reaction between MgO and some compounds containing ammonium and phosphate ions, like phosphoric acid, monoammonium dihydrogen phosphate ($NH_4H_2PO_4$ or MAP), or diammonium phosphate [$(NH_4)_2HPO_4$ or DAP]. A number of mechanisms have been proposed during the last several decades to describe interactions between MgO and $NH_4H_2PO_4$ [8]. The proposed reaction products are:

A: $Mg_3(PO_4)_2$ xH_2O, where $x = 0$ and 4, and $Mg_2(HPO_4)_2$, [9];
B: $NH_4MgPO_4 \cdot 6H_2O$ (major) and $Mg_3(PO_4)_2 \cdot 4H_2O$ (minor), [10–11];
C: $Mg(NH_4)H_2(PO_4)_2 4H_2O$ and $NH_4MgPO_4 \cdot xH_2O$, where $x = 4$ and 6 [12]; and
D: a gel-like bond and coprecipitation complex products [13].

In coordinating their findings with cited literature, Allan and Asgar [11] proposed the $NH_4MgPO_4 \cdot 6H_2O$ (struvite) as the reaction product and surmised that the $Mg_3(PO_4)_2 \cdot 4H_2O$ should form, but this has not been experimentally identified. Connaway-Wagner et al. [14] have detected struvite as the sole phosphate reaction product according to X-ray powder diffraction and P magic angle spinning nuclear magnetic resonance, while Suguma and Kukacka [15] also detected $Mg_3(PO_4)_2 \cdot 4H_2O$ and $Mg(OH)_2$. This observation was disputed by Abdelrazig and Sharp [16].

The mechanism of setting remains imperfectly explained. Some authors consider that it is a through-solution process including the dissolution of MAP and a part of MgO [8,17–19]. Ions in solution form hydrates that gather around a nucleation point [19]. Neiman and Sarma [8] observed the presence of an amorphous phase within the first hours, surrounding excess MgO and the filler. Colloidal hydrated particles form around the nuclei of struvite ($NH_4MgPO_4 \cdot 6H_2O$). These particles then initiate a setting phenomenon through a gel-like interaction. This initial reaction takes place in an aqueous medium involving several molecules of $NH_4H_2PO_4$ with an equivalent number of MgO molecules in solution, giving rise to a multimolecular

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framework of $NH_4MgPO_4 \cdot 6H_2O$, which is schematically represented as $(NH_4MgPO_4 \cdot 6H_2O)_n$. With a low value of n, such as n = 3, it forms a ring of –O–P–O–Mg–O–P– chain, and the ring is surrounded by hydrogen-rich species, such as H_2O and $NH_4^+ \cdot H_2O$ groups. These groups form hydrogen bonds with excess water, $NH_4H_2PO_4$, and other $(NH_4MgPO_4 \cdot 6H_2O)_n$ structures, resulting in colloidal-type particles. These particles then coagulate around excess MgO and filler SiO_2 particles, thus initiating the setting reaction. At longer times, Neiman and Sarma [8] observed a crystalline reaction product, which was mostly struvite, in agreement with the observations of Abdelrazig et al. [17,19]. Sarkar [20] proposed another mechanism: an insoluble diffusion barrier coating is formed around MgO grains, consisting of polyphosphate units cross-linked with Mg^{2+} ions and coinciding with the onset of setting. With time, this gel slowly crystallizes into an interlocking microstructure of struvite, contributing significantly to the onset of hardening and stiffening of the cement paste.

In a recent study [21], Hall and Stevens have shown by X-ray diffraction that the major reaction product was struvite. Evidence was also found to suggest the presence of an amorphous or poorly crystalline phase with a lower degree of hydration in mortars prepared with water contents less than 8%.

The development of catalysis and physics of thin layers has focused several investigations on the dissolution mechanisms of MgO [22]. It has been found that the dissolution kinetics of MgO depends on a number of intrinsic and extrinsic factors such as the extent of dissolution, pH, surface structure, surface hydration, species in solution, and impurity and dopant concentrations.

Based on some of these findings, this paper aims to propose a new hypothetical mechanism for the setting of magnesia-phosphate cement.

2. Methods

2.1. Materials

Two commercially available varieties of dead-burned magnesia (MgO) were used for our investigations. They were obtained by calcining magnesium hydroxy-carbonate $[Mg_5(OH)_2(CO_3)_4]$ at 1,500°C (m_1) and 1,100°C (m_2), respectively. The physical properties of these products are shown in Table 1. The theoretical specific surface area of each magnesia was computed from the particle size distribution, assuming that each grain was a perfect sphere.

Table 1
Physical properties of MgO

Reference	BET specific surface area (m^2/g)	Theoretical specific surface area (m^2/g)	Particle size distribution (μM)		
			<300	<10	D_{50}
m_1	0.34	0.12	100%	7%	66
m_2	11.9	0.28	100%	23%	63

For the acidic component, reagent grade MAP was used. Fine siliceous sand (S) was also used for preparation of mortars. The mixture proportions of mortars were: MgO:$NH_4H_2PO_4$:S = 1:1:2. A liquid:solid ratio of 1:4 was employed. The mixture was poured into cylinders (∅ = 45 mm; height = 25 mm) for the setting time measurements. The mortar started to set when the Vicat's needle encountered some difficulty in penetrating the mortar; this needle was not equipped with the usual 700-g mass. The final set was measured as for normal Portland cement. This process allowed a distinction between the initiation of setting and the end of setting, which cannot be done applying the usual process due to a very short setting time.

2.2. Test methods

The interface tension between magnesia and an aqueous solution was assessed by measuring the wetting angle (θ) obtained when a drop of this solution reached magnesia. There was no wetting when θ = 0°, and wetting was perfect when θ = 180°. The angle was measured using a binocular lens (Olympus France, Runcis, France).

Ionic chromatography analyses were carried out using a DIONEX DX 1000 chromatograph (Dionex, Jouyen Josas, France), on solutions containing either magnesia and water or magnesia, MAP, and water. The identification of hydrates was done by means of X-ray diffraction and the MgO surfaces were observed using a scanning electron microscope (HITACHI S8000-high resolution (Hitachi Elexience, Verrieres le Buisson, France).

3. Results and discussion

3.1. Dissolution of MAP and MgO

The MAP dissolves rapidly to achieve saturation according to Eqs. (1), (2), (3), and the fractions of PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ ions are given by Eqs. (4) and (5):

$$NH_4H_2PO_4 \rightarrow NH_4^+ + PO_4^{3-} + 2H^+ \quad (1)$$

$$NH_4H_2PO_4 \rightarrow NH_4^+ + HPO_4^{2-} + H^+ \quad (2)$$

$$NH_4H_2PO_4 \rightarrow NH_4^+ + H_2PO_4^- \quad (3)$$

$$[H_2PO_4^-]/[H_2PO_4^-][H^+] = c^{te} \quad (4)$$

$$[H_2PO_4^{2-}]/[PO_4^{3-}][H^+] = c^{te} \quad (5)$$

Fig. 1 shows the variation of pH with time for mortar prepared with magnesia m_1. Within the first minute, the MAP dissolution leads to a pH drop. The proportions of ions PO_4^{3-}, $H_2PO_4^-$, and HPO_4^{2-} are given by Eqs. (4) and (5). If MAP is introduced in excess, the remaining solid phase can only dissolve if either hydrates are formed, consuming phosphate and ammonium ions, or if the temperature increases, thus enhancing the solubility.

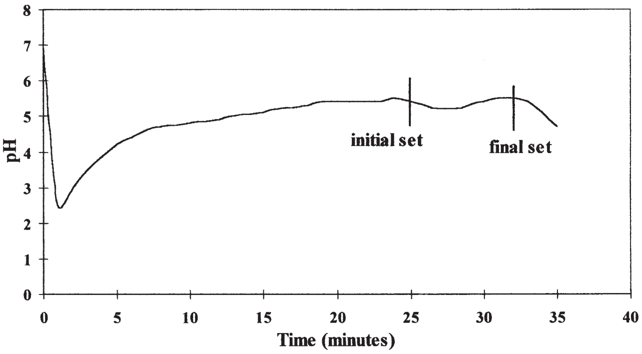

Fig. 1. Variation of pH with time. Mortar containing m_1.

Magnesia is slightly soluble in water and its dissociation occurs according to Eqs. (6), (7), and (8):

$$MgO + H_2O \rightarrow MgOH^{+} + OH^{-} \quad (6)$$

$$MgOH^{+} + 2H_2O \rightarrow Mg(OH)_2 + H_3O^{+} \quad (7)$$

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^{-} \quad (8)$$

MgO surfaces must therefore successively adsorb one molecule of water, then two more, which allows the dissociation of $Mg(OH)_2$, leading to one Mg^{2+} and two OH^- ions [20]. The presence of these OH^- ions explains the pH increase observed in Fig. 1. When the pH increases, MgO starts to dissolve.

The wetting angles and setting times of each magnesia (m_1 or m_2) are reported in Table 2. From Table 2, it appears that wetting of m_2 was better than that of m_1. This is due to a difference in their surface structure, as shown in Fig. 2. Magnesia m_1 exhibits crystalline structure well, while m_2 presents a lot of surface defects. This is also confirmed by the ratio between the Brunauer, Emmett and Teller (BET) specific surface area and the theoretical value presented in Table 1: This ratio is 2.8 for m_1 and 42.5 for m_2. This ratio represents the degree of deformation of a grain compared with a perfect sphere. The higher this ratio, the higher the degree of disorder in the solid. Magnesia m_2 is therefore more disordered than m_1. This is due to the temperature of calcination at which m_2 was prepared. Ahmed et al. [23] have shown that at temperatures greater than 1,100°C, a reconstruction of MgO surface occurred, limiting the amount of defects. Scamehorn et al. [24] have pointed out that the adsorption of water on MgO surface is highly dependent on the type of defects present on the surface: it is more difficult on a clean and smooth surface, which explains the best wetting of m_2. Ionic chromatography measurements (Fig. 3) show that the quantity of dissolved Mg^{2+} ions was more important for m_2 than for m_1. From these results, it seems that the higher the wetting, the higher the dissolution of magnesia, which leads to a shorter setting time: 1 min for m_2 and 22 min for m_1.

The results presented in Fig. 4 point out that the dissolution of magnesia also depends upon the quantity of MAP present in the solution. The higher the MAP concentration, the higher the magnesia dissociation. Therefore, when the pH becomes acidic due to the introduction of MAP, magnesia dissolves, yielding two OH^- ions and brings back the pH to a neutral value. The lower the pH, the higher the dissolution. Therefore, the dissociation of magnesia is an acid-base

Table 2
Properties of m_1 and m_2

Reference	Wetting angle (°)	Setting time (min)
m_1	30	22
m_2	140	1

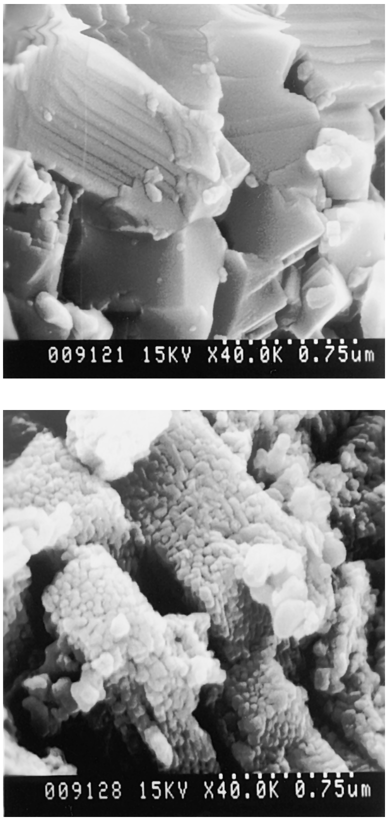

Fig. 2. Surface structure of m_1 and m_2.

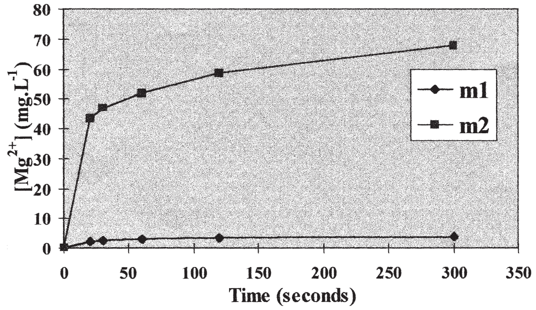

Fig. 3. Dissolution of m_1 and m_2.

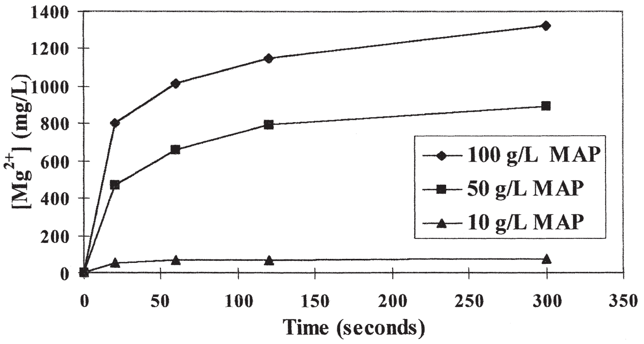

Fig. 4. Dissolution of magnesia m_1 as a function of MAP concentration.

reaction; more specially, the magnesia surface is basic with structural defects and the solvent is acidic.

Fig. 5 shows the wetting angle of a drop of water and a drop of 100 g/L MAP solution on magnesia m_1 surface. This angle is about the same in each case.

As presented in Table 3, although the wetting angle is the same, the quantity of dissolved Mg^{2+} ions is much more important in MAP solution than in water. Furthermore, despite a higher wetting (140° instead of 30°), the dissociation of magnesia are two distinct phenomena. To be dissolved magnesia needs an initial wetting but, as shown by Heidberg et al. [25], wetting can remain undissociative.

3.2. Crystals growth

Gonzalez-Munoz et al. [26] have shown that the production of struvite could be achieved with the physical presence of bacteria. From this study, it seems that struvite crystallization is achieved in two ways. First, the metabolic activity of the bacteria, with NH_4^+ release and the consequent pH increase. Second, the cellular membrane fraction resulting from autolysis induces the nucleation process. Struvite crystallizes in both liquid and solid media.

To verify such an assumption, we carried out two series of setting tests: in the first one, the mixing water was deionized; in the second one, the mixing water was tap water having stagnated for several days to allow the development of bacteria. In each case, the setting time was the same and X-ray diffraction analyses show that struvite was the main hydrate to be formed. The presence of bacteria does not affect the production of struvite, and it seems that in magnesia-phosphate cements, the development of hydrates occurs without nucleation. To confirm this missing nucleation, the following solution was prepared: 50 g $MgSO_4 \cdot 7H_2O$ and 24 g $NH_4H_2PO_4$ were dissolved in 150 g water. The solution was then filtered and after 1 h, no germination was observed. The introduction of magnesia m_1 led to the occurrence of crystals within 20 min. With m_2, these crystals appeared within 1 min and were identified by X-ray diffraction as struvite. These results confirm the rapid setting of magnesia-phosphate cements, which seems due to a reaction involving magnesia surface.

Recent studies [22] have shown that the dissociation of

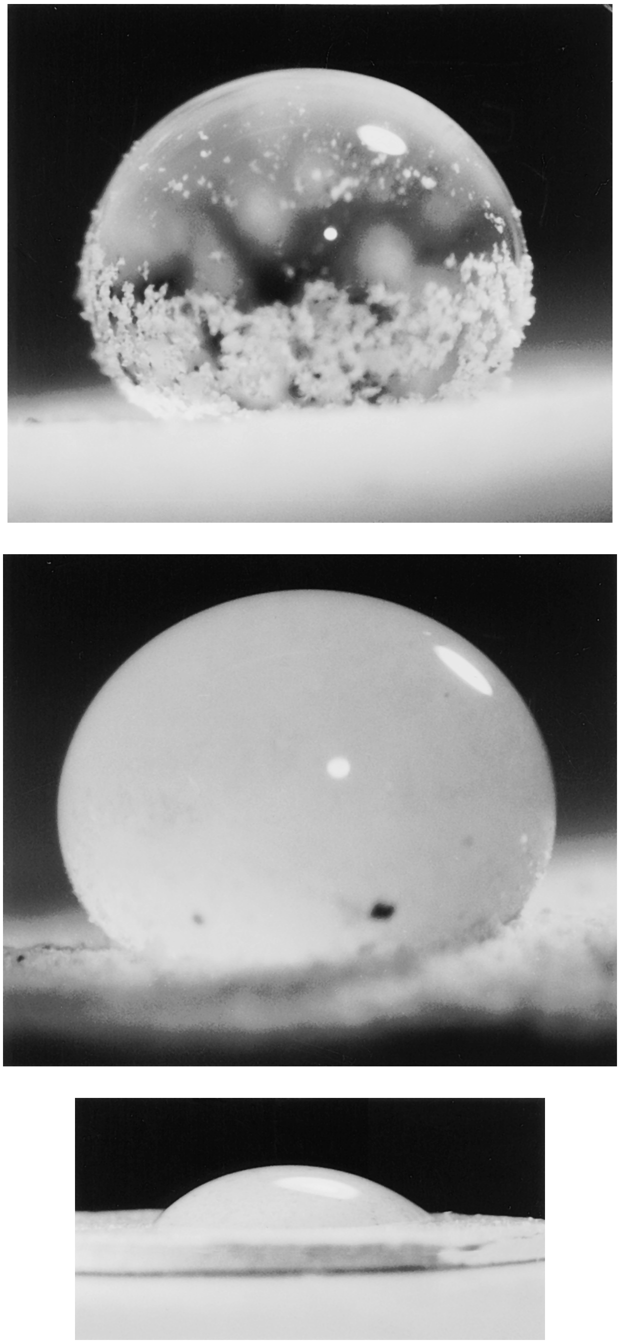

Fig. 5. Wetting angles of m_1 and m_2 with different solutions: (top) m_1 and water; (middle) m_1 and MAP solution; (bottom) m_2 and water.

Table 3
Wetting angle and dissolved Mg^{2+} ions

Magnesia	Solvent	Wetting angle (°)	Mg^{2+} ions within 1 min
m_1	Water	30	2.9 mg/L
m_1	100 g/L MAP solution	30	1,014.6 mg/L
m_2	Water	140	51.7 mg/L

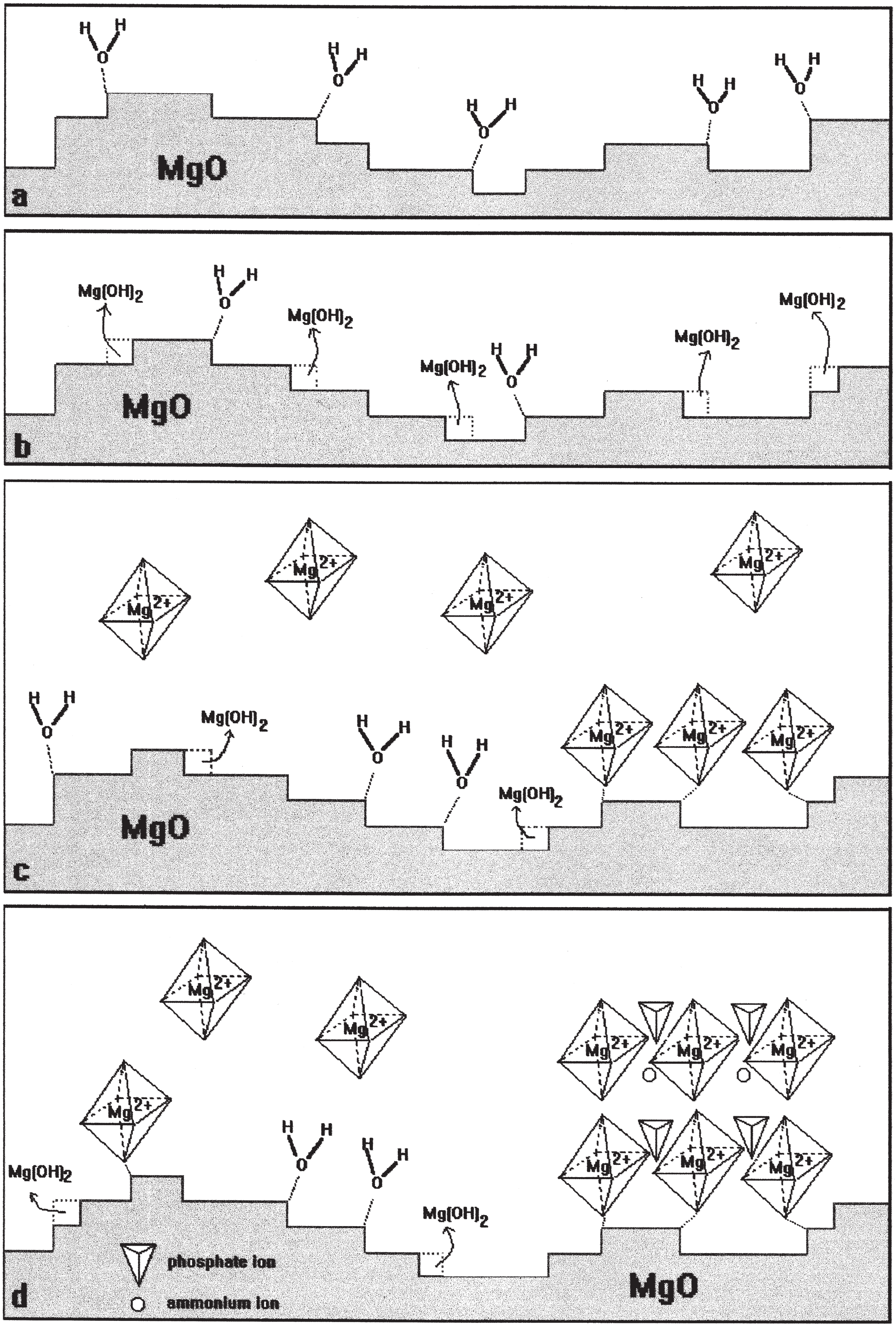

Fig. 6. Dissolution of MgO and development of crystals.

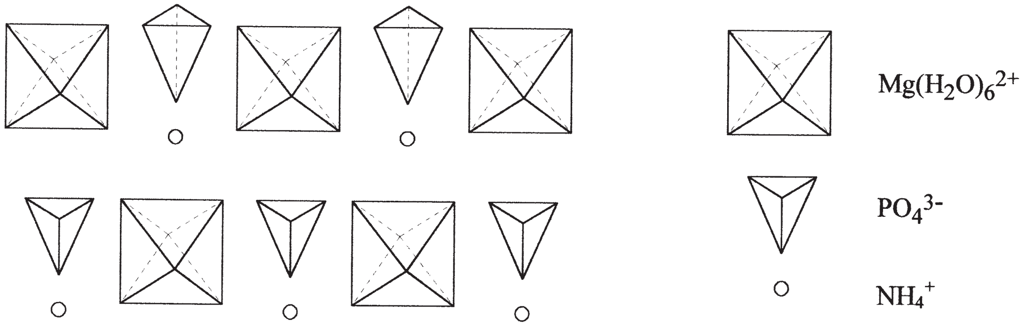

Fig. 7. Structure of struvite.

magnesia needed the successive adsorption of one molecule of water, then two more, which allowed an $Mg(OH)_2$ compound to leave the structure and immediately decompose into one Mg^{2+} ion and two OH^- ions (Figs. 6a and b). Once in solution, Mg^{2+} ions form an $Mg(H_2O)_n^{2+}$ complex, and generally n = 6 [27]. During the wetting of magnesia surface, it is possible that an Mg $(H_2O)_6^{2+}$ octahedron substitutes to one molecule of water. The two supplementary molecules of water needed for the achievement of MgO dissociation therefore cannot approach to the surface. The $Mg(H_2O)_6^{2+}$ remains hooked to the surface. Several adsorbed complexes can thus present sites for crystallization, as shown in Fig. 6b.

The structure of struvite presented in Fig. 7 consists of PO_4^{3-} tetrahedra, $Mg(H_2O)_6^{2+}$ octahedra, and NH_4^+ groups, held together by hydrogen bonds [28].

Fig. 8. Development of struvite crystals.

The MgO surface, partially covered by Mg $(H_2O)_6^{2+}$ complexes, ions PO_4^{3-}, and NH_4^+ present in solution, can come close together and, owing to hydrogen bonds, generate a struvite network (Fig. 6d).

The crystals grow around magnesia grains and connect, coating filler grains and developing a cementitious matrix (Fig. 8). The reaction stops when the magnesia grains are entirely covered by hydrates and can no longer dissolve. The reaction can also stop when one of the two reactants (MAP or water) is missing.

4. Conclusions

When a magnesia-phosphate cement is mixed with water, an exothermic reaction occurs, leading to a hardened product within a few minutes. The dissolution of magnesia is an acid-base reaction between basic surfaces of MgO and the acid MAP solution generated by the instantaneous dissolution of MAP in water. The setting time depends on the structure of MgO surface. The more disordered the surface, the more basic it is, and therefore the kinetics of wetting is high. The dissociation depends on both this wetting and the MAP concentration of the solution.

Struvite crystals do not appear after a nucleation process induced by a high degree of saturation. Crystallization starts when $Mg(H_2O)_6^{2+}$ complexes substitute to molecules of water during the wetting of MgO surfaces. Opposite to molecules of water that lead to the dissociation of magnesia, $Mg(H_2O)_6^{2+}$ complexes remain attached to the surface and progressively cover it. PO_4^{3-} and NH_4^+ ions and $Mg(H_2O)_6^{2+}$ complexes can therefore develop a struvite network, from the surface, owing to hydrogen bonds.

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