Pergamon

Cement and Concrete Research 32 (2002) 153–157

CEMENT AND CONCRETE RESEARCH

Influence of magnesia surface on the setting time of magnesia–phosphate cement

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Received 27 March 2001; accepted 30 July 2001

Abstract

The following paper presents the influence of magnesia reactivity in magnesia–phosphate cement. When water is added to cement, monoammonium dihydrogen phosphate ($NH_4H_2PO_4$ or MAP) goes in solution till saturation while magnesia (MgO) is wetted and starts to dissociate. This dissociation only depends on MgO surface, except when magnesium carbonate is present. In this case, it accelerates the dissolution process, independently of the surface state. For magnesia, the higher the amount of surface defect sites, the higher the MgO wetting. Wetting and nucleation are promoted by a large interface between MgO and MAP, because adsorption probabilities are more important. Therefore, grinding a powder allows a better reactivity. On the contrary, calcination, in a first step, enhances the surface state and then reduces MgO reactivity due to the melting of grains, which reduces the total developed surface. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Magnesia–phosphate cement; Adsorption; Grinding; Reaction; Surface defects

1. Introduction

The mixing of a powdered magnesia (MgO) with a solution of monoammonium dihydrogen phosphate ($NH_4H_2PO_4$ or MAP) leads to the formation of magnesium and ammonium phosphate crystals. The main product of hydration is struvite ($MgNH_4PO_4{\cdot}6H_2O$) [1,2].

The wetting of MgO surfaces is easier when structural defects (edges and corners) are present on the surface [3]. Wetting is therefore strongly dependent of the MgO surface state. The dissociation of MgO into Mg^{2+} ions needs the adsorption onto the surface of two supplementary molecules of water [4]. It is promoted by the solution acidity and the presence of ammonium ions [5].

Mg^{2+} ions react with six molecules of water to form $Mg(H_2O)_6^{2+}$ compounds. These compounds replace water molecules in the wetting process of magnesia. Their size avoids the adsorption of new molecules of water onto the MgO surface. $Mg(H_2O)_6^{2+}$ 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 [5].

The setting time of magnesia–phosphate cement is thus dependent on the kinetics of MgO dissociation. As MAP is introduced in excess in the mixture, this kinetics is directly bound to the MgO surface state. The high exothermicity of this reaction accelerates the kinetics and the initial set is generally identical to the final set. The MgO control (grain size, surface state, reactivity,...) is therefore essential to allow a good placing of the material. Furthermore, slow setting leads to better strength development [6]. These complexes do not react via the "through solution" mechanism, as demonstrated by Soudée and Péra [5].

2. Experimental

2.1. Properties of MgO samples

Six samples of magnesia were studied (Samples M1 to M6). Samples M1 and M2 were ground to get particles smaller than 50 μm. Samples M3 to M6 were investigated as received. Their physical properties were measured. The results are given in Table 1.

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PII: S0008-8846(01)00647-0

Table 1
Physical properties of MgO samples

Sample	BET surface area		Specific gravity
	m^2/g	m^2/cm^3	
M1	0.67	2.34	3.5
M2	0.78	2.73	3.5
M3	1.05	3.78	3.6
M4	11.09	38.08	3.2
M5	10.86	35.84	3.3
M6	49.43	163.12	3.3

Table 2
Impurities detected in MgO samples

Sample	Silicates	Carbonates	Sulfates
M1	x	–	–
M2	x	–	–
M3	–	–	–
M4	x	x	–
M5	x	x	x
M6	x	x	x

All these samples were obtained from the calcination of magnesium carbonate. Samples M1 and M3 were "dead-burned," which means calcined above 1300 °C. All samples were also investigated for their mineralogy by means of Fourier-transform infrared spectrometry and X-ray diffraction (XRD). Some impurities were detected and the results obtained are shown in Table 2.

As seen in Table 2, M3 was the purest magnesia, while M5 and M6 contained the largest amounts of impurities. Magnesium carbonate was still present in Samples M4 and M6, which means that the calcination of these products was not sufficient to get total decarbonation.

From the particle size distribution, it is possible to define a theoretical specific surface area, assuming that MgO are perfect spheres (Fig. 1). The ratio between the BET surface area and the theoretical surface area is called the deformation ratio. The higher the disorder of MgO surface, the higher is the deformation ratio. The results obtained are presented in Table 3. From Table 3, M4 and M6 appear to be the most disordered samples.

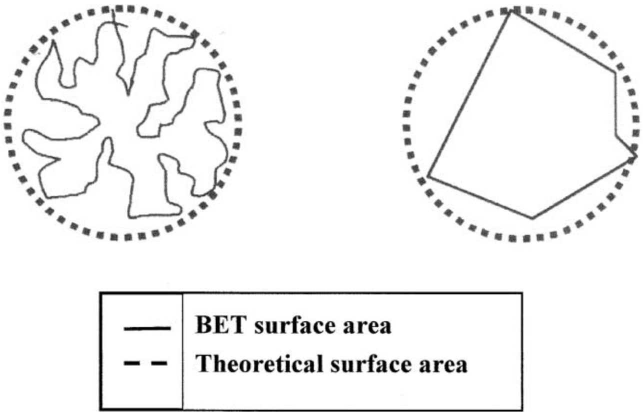

Fig. 1. Theoretical and BET surface areas.

Table 3
Theoretical surface area and deformation ratio

Sample	Theoretical surface area (m^2/cm^3)	Deformation ratio
M1	0.82	2.85
M2	1.02	2.68
M3	0.20	18.90
M4	0.89	42.79
M5	1.24	28.90
M6	2.55	63.97

Table 4
Setting times of magnesia–phosphate mortars

Magnesia	M1	M2	M3	M4	M5	M6
Setting time (min)	17.0	9.5	11.5	0.9	0.9	*

* Too rapid to be measured.

2.2. Measurements

The surface of MgO was examined by scanning electron microscopy (Hitachi S800-High resolution). The setting time of cement was measured on a mortar composed of 20 g MgO, 20 g MAP, 40 g quartz, and 22 g water, at 20 °C.

The influence of grinding and calcination was also studied on some samples.

3. Results and discussion

3.1. Comparison of the different samples

The setting times observed on Samples M1 to M6 are shown in Table 4.

The use of Samples M1 to M3 leads to setting times equal or higher than 10 min, while M4 to M6 give very quick setting. These results confirm the assumption that setting time is strongly linked to the deformation ratio and,

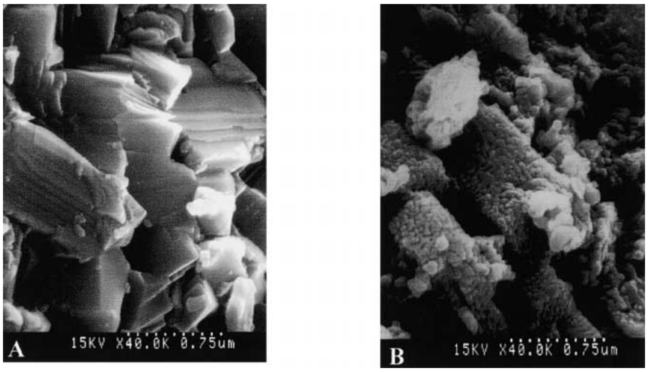

Fig. 2. Surface state of M2 (A) and M4 (B).

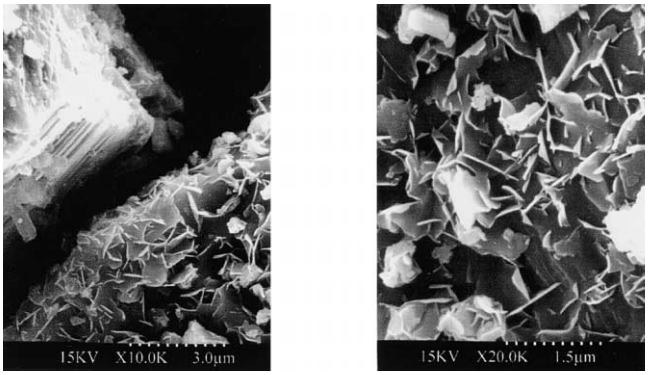

Fig. 3. Surface state of M3.

consequently, to the surface state of MgO. The rapid setting observed with Samples M4 to M6 is due to the calcination process. Total dissociation of magnesium carbonate is obtained above 1000 °C. Over 1100 °C, the MgO structure is increased and, at 1200 °C, a superstructure is obtained which, due to a surface migration of MgO molecules, tries to limit its defects [7]. The surface state of M2 and M4 is compared in Fig. 2.

The M4 surface contains much more corners and steps than M2. This disordered surface is confirmed by a higher deformation ratio value (42.79 instead of 2.68). M4 wetting is therefore quicker, and leads to higher reactivity.

Despite a relatively long setting time, M3 presents a higher deformation ratio than M1 and M2. M3 grains are coarser but some grains are covered by platy crystals (Fig. 3). These platy structures increase the BET surface area and, consequently, the deformation ratio.

The high reactivity of M6 is due to the combination of very high fineness (theoretical surface area: 2.55 m^2/cm^3) and important degree of disorder (deformation ratio: 63.97). The M6 surface is presented in Fig. 4.

Carbonates are still present in Samples M4 to M6, but at different contents. The greatest amount of magnesium carbonate determined by XRD was found in Sample M5. As the dissolution of magnesium carbonate is quicker than that of magnesia, this explains why M5 presents the same setting time as M4, despite a lower BET surface area. The high reactivity of M4 is due to a disordered surface with a high deformation ratio, while that of M5 is caused by the presence of magnesium carbonate.

Table 5
Comparison between M2 and M7

Sample	Grinding	BET surface area (m^2/cm^3)	Theoretical surface area (m^2/cm^3)	Deformation ratio	Setting time (min)
M2	Manual	2.73	1.02	2.68	9.5
M7	Knife mill	7.66	0.90	8.51	9.5

3.2. Influence of the type of grinding

M2 was obtained by grinding manually the raw magnesia with a pestle to get particles less than 50 µm. In a second series of tests, the raw magnesia was ground in a knife mill, and Sample M7 was obtained. The differences between Samples M2 and M7 are shown in Table 5.

The mechanical grinding increases the BET surface area. Fig. 5 shows the particle size distribution of Samples M2 and M7, from which the theoretical surface area was calculated. It is observed that the main peak is obtained at 45 µm for M2, while it is 35 µm for M7. The amount of particles smaller than 4 µm is higher in M2 than in M7, which contributes to a higher theoretical surface area.

Figs. 6 and 7 show the surfaces of Samples M2 and M7. M2 presents a relatively smooth surface while flat and thin crystallites appear on the M7 surface. The difference between the deformation ratios of M2 and M7 is due to these crystallites.

Nevertheless, the setting time of M2 and M7 is the same, as shown in Table 5. The presence of surface defects in M7 does not reduce the setting time. This type of defects enhances the wetting of magnesia, but it seems that crystals nucleation can only occur on thicker surfaces. With M2, the

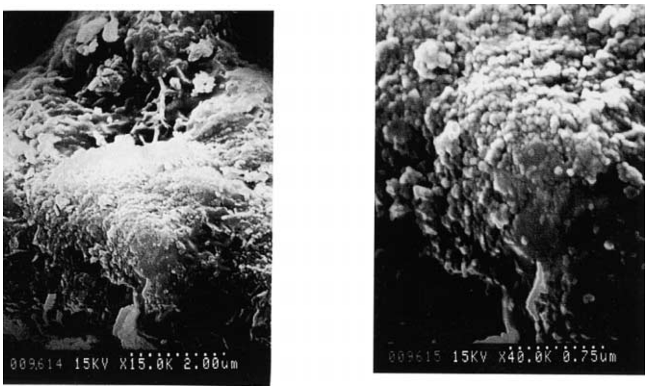

Fig. 4. Surface state of M6.

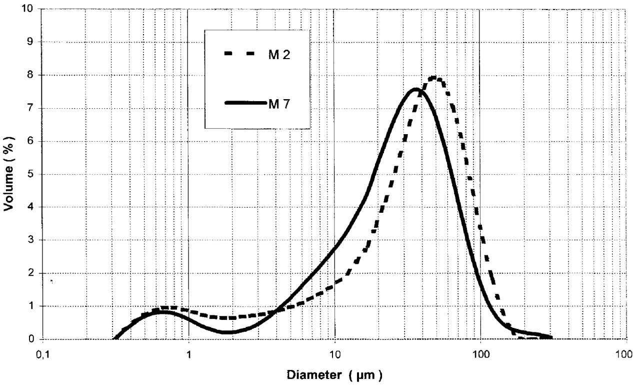

Fig. 5. Particle size distribution of M2 and M7.

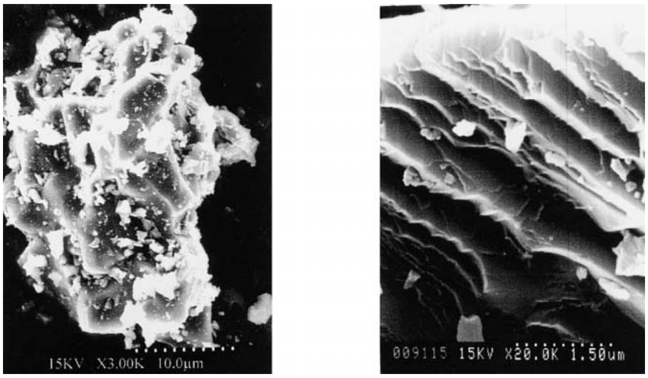

Fig. 6. Surface of M2.

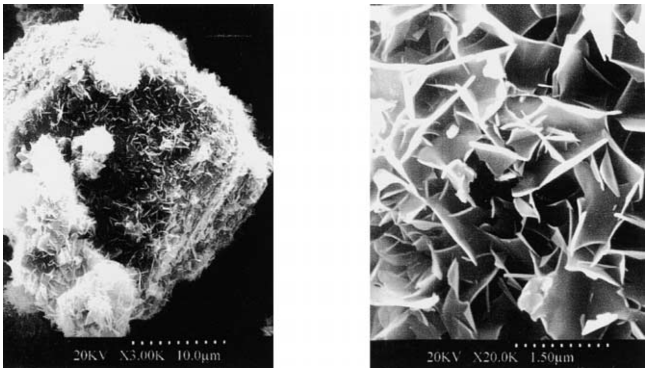

Fig. 7. Surface of M7.

dissolution is lower but the reactivity is increased by a higher theoretical surface area.

3.3. *Influence of calcination on magnesia reactivity*

Magnesia M4 was calcined at 1250 and 1500 °C, and then manually ground to get particles smaller than 80 µm. Fig. 8 presents the particle size distribution of these samples.

At 1250 °C, the quantity of fine particles is slightly increased and the peak related to coarser particles shifts from 160 to 70 µm. At 1500 °C, fine particles disappear: smaller particles melt and coarser particles are therefore obtained. These results are shown in Table 6.

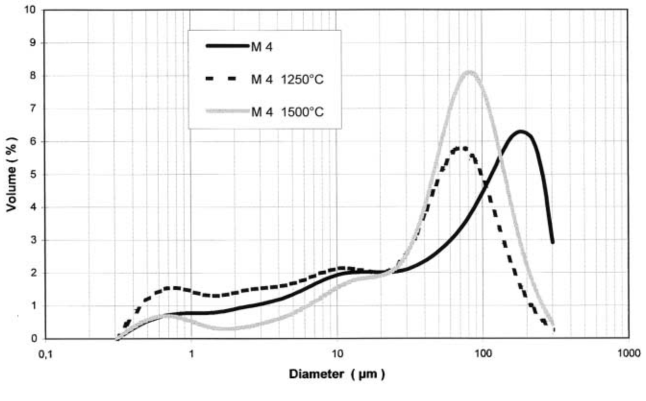

Fig. 8. Influence of calcination on the particle size distribution.

Table 6
Influence of calcination on the physical properties of magnesia

Magnesia	BET surface area (m^2/g)	Theoretical surface area (m^2/g)	Deformation ratio	Setting time (min)
M4	11.90	0.89	13.37	1
M4 (1250 °C)	3.23	1.57	2.06	2
M4 (1500 °C)	0.91	0.72	1.26	9

The calcination at 1250 °C leads to an important reorganization of the surface: the deformation ratio drops from 13.37 to 2.06. The theoretical surface area is increased by the presence of higher amount of fine particles. The setting time is delayed because of the reorganization of the surface, which limits the wetting of magnesia, as described by Ahmed et al. [7].

At 1500 °C, the theoretical surface area decreases due to the agglomeration and smaller particles sinter together. The deformation ratio also decreases and therefore, the setting time is delayed up to 9 min. As shown in Fig. 9, the surface is perfectly reorganized.

Fig. 10 also points out the agglomeration of particles at 1500 °C.

Fig. 9. Surface state of M4: before calcination (A); after calcination at 1500 °C (B).

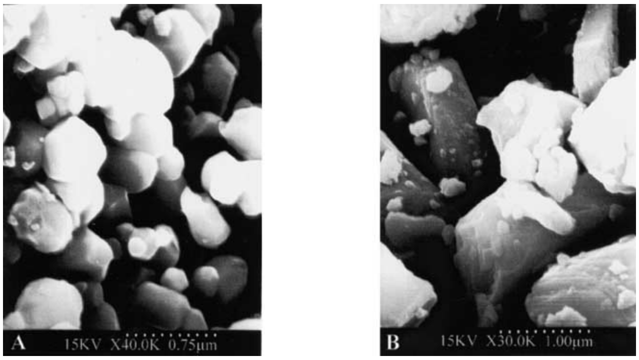

Fig. 10. Calcination of M4: 1250 °C (A); 1500 °C (B).

4. Conclusions

In magnesia–phosphate cement, the reactivity of magnesia depends upon the rate at which Mg^{2+} ions goes into solution. Indeed, the probability of substituting water molecules by $Mg(H_2O)_n{}^{2+}$ complexes during the wetting of MgO is linked to the Mg^{2+} concentration. This is the reason why the presence of magnesium carbonate as impurity in magnesia increases its reactivity, because the dissociation of magnesium carbonate is quicker than that of magnesia.

The dissociation of MgO needs a preliminary wetting. The surface state of magnesia therefore plays an important role on its reactivity. The higher the disorder of the surface, the quicker is the wetting. The total surface developed by magnesia also increases the reactivity.

Calcination of magnesia limits its reactivity. In the range of 500–1000 °C, magnesium carbonate is progressively transformed into magnesia. Between 1000 and 1250 °C, a reorganization of the surface occurs and limits the defect sites. Wetting is thus slowed down, and the reactivity of magnesia decreases. Above 1250 °C, particles melt and agglomerate. The theoretical surface area as well as the reactivity of magnesia decreases.

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