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Factors influencing properties of phosphate cement-based binder for rapid repair of concrete[1]

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Abstract

Phosphate cement-based binders were prepared by mixing MgO powder (M) with $NH_4H_2PO_4$ powder (P) and borax powder (B). Effects of various factors including the amount of retarder B, P/M ratio, fineness of M, and addition of fly ash and environment temperature on setting time and mechanical properties of magnesium phosphate cement-based binder (MPB) were investigated. Results showed that the setting time and early strength of MPB were mainly controlled by the amount of B, the fineness of M, and temperature, but that these factors had little influence on the final strength of the binder. It is interesting that MPB sets and hardens within 1 h, even at -10°C. A setting and hardening mechanism on MPB is proposed.

Keywords: Phosphate cement; Magnesium; Repair of concrete; Setting time; Strength

The proper selection of materials for a repair program is normally more involved and more important than selection for new construction. Moreover, the compatibility of repair materials with the original concrete, especially their coefficient of thermal expansion and modulus of elasticity, is very important for a successful repair.

The damage of airport runways, highway pavements, key municipal roads, and other concrete structures causes serious problems and costs millions of dollars to repair. Part of the problem comes from the fact that the repair work interrupts the service of structures for a long time if traditional cementing materials are used. Using special, very rapid-setting materials can shorten this delay. However, such a material also has to have high early strength and bond strength to old concrete, long enough setting time, and good compatibility with old concrete.

Sarkar reviewed the research works on phosphate cement-based binders for concrete repair [1]. Sugama and Kukacka [2,3] have studied the magnesia-diammonium phosphate/ammonium polyphosphate-water systems and discussed the kinetics and mechanism of reactions, microstructure, strength, nature of hydrates, and the retarding mechanism of borax. The first systematic research on commercial magnesium-phosphate cement was reported by Abdelrazig et al. [4]. Popovis et al. [5] studied both commercially available magnesium-phosphate and magnesium/aluminium-phosphate systems in detail. Abdelrazig et al. [6,7] studied the strength, porosity, hydration products, and morphology in magnesia-mono-ammonium phosphate-water systems. Seehra et al. [8] investigated the characteristics, durability, and field application of this special cement. However, many others are either recorded in patents or kept as trade secrets, and therefore few details about making these binders are known.

1. Experimental

1.1. Materials

MgO powder, calcined at >1500°C and having a specific surface of $1260 \sim 3500$ cm^2/g, was made in the laboratory. Its specific gravity is approximately 3.475, and the content of MgO is 94%. Laboratory reagent grade mono-ammonium phosphate ($NH_4H_2PO_4$) and borax ($Na_2B_4O_7 \cdot 10H_2O$), and potable water were used. A fly ash of class I according to the Chinese standard JGJ 28-86 was used, with a specific surface of approximately 7500 cm^2/g. MPB was prepared by mixing MgO and $NH_4H_2PO_4$ powder with and without borax and fly ash; then it could be used like ordinary portland cement. The procedure of making MPB paste was the same as that of making cement paste.

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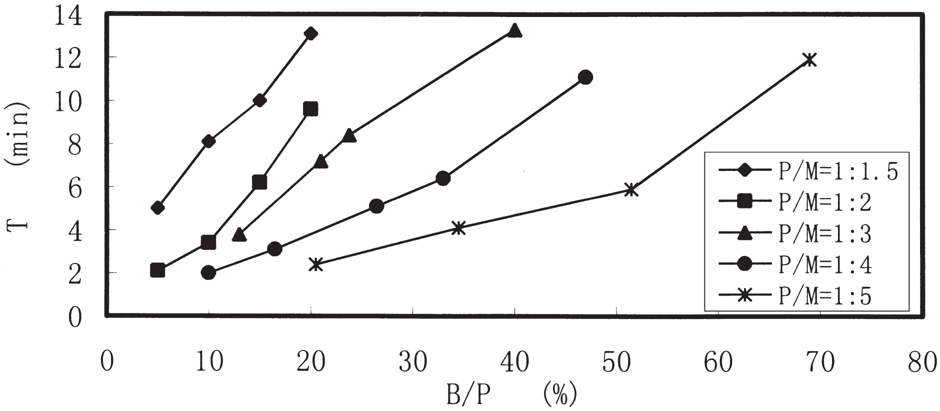

Fig. 1. Relationship of B/P and setting time.

1.2. Test methods

Setting time of MPB paste was measured with the Vicat apparatus and the needle (Wuxi Construction Machine Factory, Jiangshu, P.R.C.). Due to a very rapid setting rate, it was measured once per 15 s near the initial setting and once per 30 s near the final setting. Since the time between the initial and final setting was very short (several minutes), only the initial setting time was presented in this paper.

The compressive strength of MPB paste was measured with the common method. Specimens of the size 2 × 2 × 2 cm were used. Bond strength of MPB paste with old concrete was indirectly measured with the flexural strength. The old concrete with the size of 4 × 4 × 16 cm is a mixture of portland cement, water, quartz sand, and marble aggregate (with the size of 5 ~ 10 mm) in proportions of 1:0.50:1.58:2.66 by weight. Concrete specimens were broken in the middle before testing; then these two parts of the specimen were bonded together with the prepared MPB paste, and the surplus paste was squeezed and cleared out by hand.

All the above specimens were demoulded within 1 h after casting and air-cured at 20 ± 5°C until testing. The bond strength is the value of measured flexural strength when the broken place is at the bond interface, and is larger than the measured strength when the broken place is not at the bond interface.

2. Results and discussion

2.1. Setting time of MPB

2.1.1. Retarder and P/M ratio

In order to get long enough setting time (the initial time), a retarder has to be added to the MPB mixture, due to very rapid setting. Borax was selected as the retarder of MPB after many tests. From Fig. 1 and Fig. 2 it can be seen that the setting time (T) is lengthened with the increase in the content of B for various P/M ratios. However, when B/P is taken as the abscissa, for the same B/P ratio, the T values of MPB of various P/M ratios are different and largely scattered; i.e., they have little relativity with B/P.

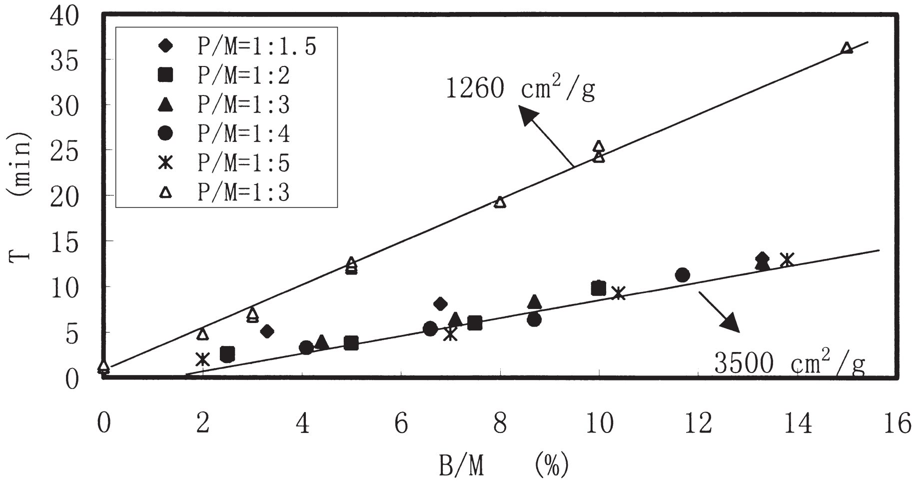

Fig. 2. Relationship of B/M and setting time.

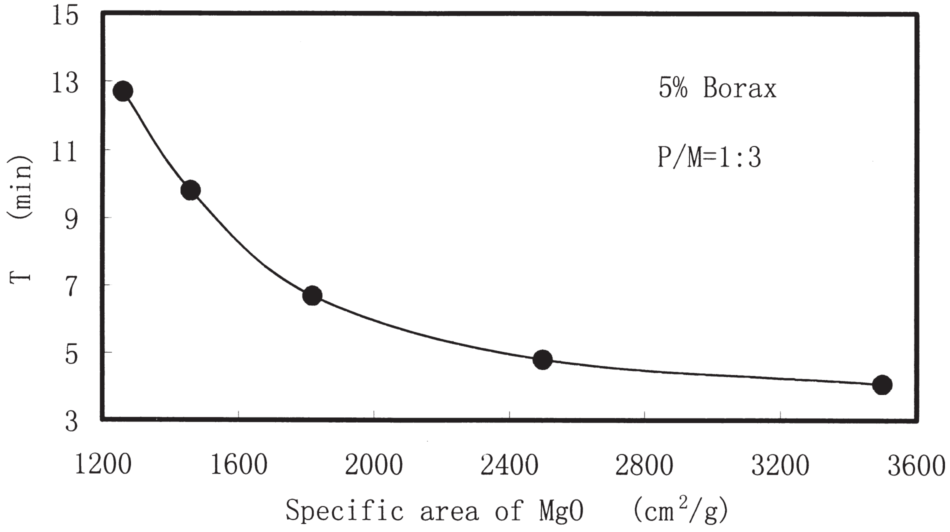

Fig. 3. Effect of the fineness of MgO on setting time of MPB.

Fig. 2 shows that the relativity between T and B/M is very high; i.e., for the same B/M value, the T values of MPB of various P/M ratios are similar and therefore the addition of B mainly depends on the amount of MgO.

From the above results it can be concluded that the retarding action of B is directed toward MgO and is not related to P, and therefore B/M is taken as the controlling factor of the setting time of MPB. Fig. 2 shows that the setting time of MPB is controlled from several minutes to >1 h by adjusting the addition of B, which meets the demands of various engineering applications.

2.1.2. Fineness of MgO

The fineness of MgO is expressed with Blaine specific surface. Fig. 3 shows that the setting time of MPB is significantly shortened with the increase in the specific surface of MgO for the same proportion (B about 5%). When the specific surface is above 3000 cm^2/g, the setting of MPB is too rapid to cast. Fig. 2 shows that the addition of B increases with the specific surface of MgO in order to keep the same setting time; i.e., the retarding action of B is more effective for the coarser MgO.

As with other materials, the larger the fineness is, the higher the activity of reaction is. Consequently, the larger the specific surface of MgO is, the quicker the setting and the formation of hydrates are. Moreover, for the same addition of B, the content of retarder per specific surface of MgO decreases with the increase in the specific surface; therefore the setting of MPB is quicker. In this paper, the specific surface of MgO is 1260 cm^2/g if there is no special explanation.

2.1.3. Temperature

Generally, the rate of reaction increases with temperature. Fig. 4 clearly shows that the setting time obviously shortens with the increase in temperature. However, MPB is

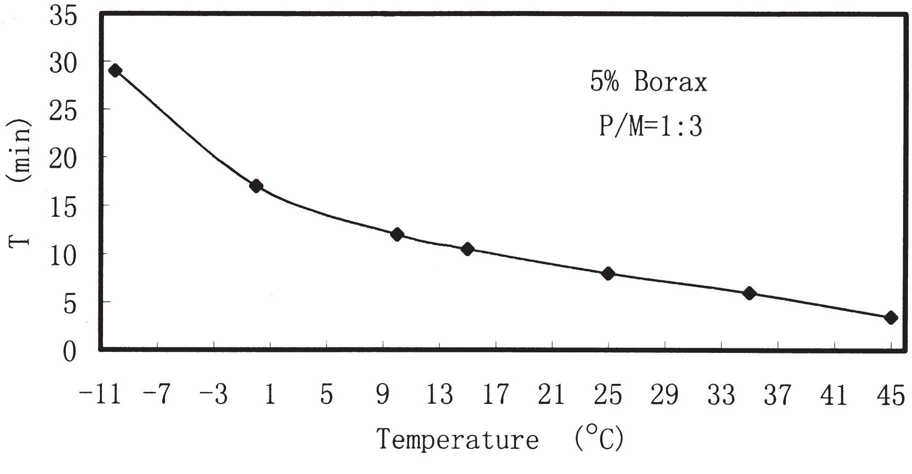

Fig. 4. Effect of temperature on setting time of MPB.

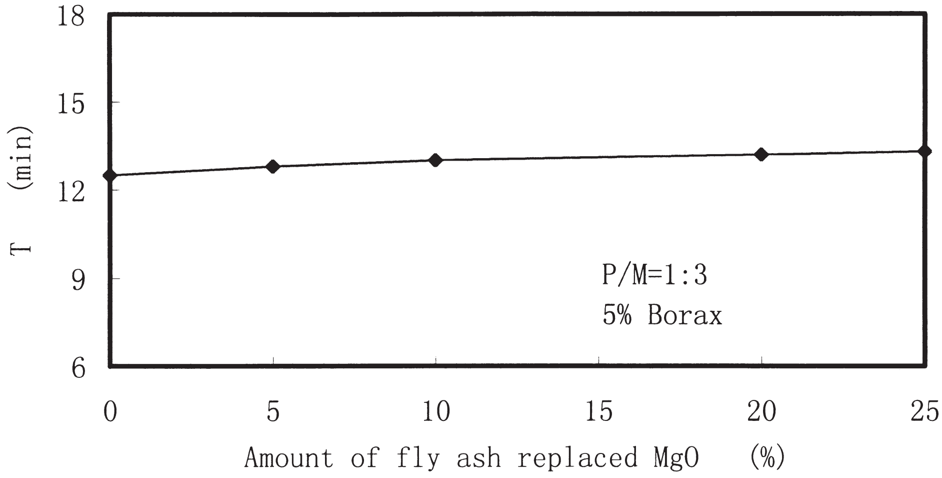

Fig. 5. Effect of fly ash on setting time of MPB.

set and hardened within 1 h even though the temperature is −10°C. MPB is very suitable for application to the low-temperature repair because it doesn't need heat-curing or use of antifreezing admixture.

2.1.4. Fly ash

Because the color of MPB is brownish yellow and is obviously different from that of portland cement, fly ash is added into MPB to get a color similar to that of portland cement. The setting time shortens a little with the increase in the amount of fly ash (see Fig. 5). In other words, for various service environments and engineering demands, the proper setting time can be determined by adjusting the content of retarder B and the fineness of MgO.

2.2. Compressive strength of MPB

2.2.1. P/M ratio

From Table 1 it can be clearly seen that the compressive strength of MPB increases with the decrease in P/M ratio or the increase in the content of MgO. The strength is maximum when P/M ratio is 1/4 ~ 1/5.

The amount of hydrates decreases with the amount of $NH_4H_2PO_4$ and, therefore, the strength of MPB will theoretically decrease. On the contrary, why does the strength of MPB increase with the decrease in the amount of P? From the proportions of MPB it can be calculated that MPB paste consists mainly of unhydrated grains of MgO and phosphate hydrates, and the strength of grain of MgO is much higher than that of phosphate hydrates. Therefore, the lesser the amount of P, the higher the strength of MPB paste, as long as the amount of phosphate hydrates is high enough to surround grains of MgO thoroughly.

2.2.2. Retarder

For various mix proportions of MPB, the early strength (before one day) significantly decreases with the increase in the amount of retarder B, but the strength after seven days is not obviously different (see Table 2). The strength at 1 h is too low to be measured when the amount of B is ⩾10%. However, the workability of MPB is significantly improved with the increase in amount of B.

2.2.3. Fineness of MgO

Effects of the fineness of MgO on the strength of MPB are shown in Table 3. The larger the specific surface of MgO, the quicker the development of the early strength of MPB, but the difference of the strength by the fineness of MgO is small after three days (i.e., the fineness of MgO has little influence on the final strength of MPB). However, from the viewpoint of controlling of setting time and cost of materials, the application of the coarser MgO powder has more benefits.

Table 1
Effect of P/M ratio on compressive strength of MPB paste

	Compressive strength, (MPa)								
P:M ratio*	1 h	3 h	1 day	3 days	7 days	28 days	65 days	90 days	180 days
1:2	8.8	30.8	35.5	49.0	52.2	60.0	—	—	—
1:3	9.8	34.0	69.5	73.4	75.5	77.5	77.8	78.1	78.9
1:4	11.5	41.5	72.0	76.7	80.2	88.0	86.8	90.1	89.8
1:5	14.3	43.9	74.4	80.8	83.4	94.1	92.2	93.4	92.8
1:6	15.5	37.0	69.5	70.7	78.8	85.8	—	—	—

* W/C, 0.10; B, 5%.

Table 2
Effect of the amount of retarder B on compressive strength of MPB paste

Mix proportions*		Compressive strength (MPa)								
P:M	B (%)	1 h	3 h	1 day	3 days	7 days	28 days	65 days	90 days	180 days
1:3	3	22.2	43.0	70.2	74.7	76.3	78.2	—	—	—
	5	9.8	38.0	69.5	73.4	75.5	77.5	77.8	78.1	78.9
	10	—	12.5	55.2	63.2	71.2	73.1	74.1	75.8	77.1
1:4	3	29.0	45.2	78.5	86.7	88.3	94.6	—	—	—
	5	11.5	41.5	72.0	76.7	80.2	88.0	86.8	90.1	89.8
	10	—	11.0	55.6	72.8	74.1	86.6	—	—	—
	15	—	6.2	66.9	72.2	75.6	87.4	85.1	—	—

* W/C, 0.10.

Table 3
Effect of the fineness of MgO on compressive strength of MPB paste

		Compressive strength (MPa)					
P:M ratio*	Fineness (cm^2/g)	1 h	3 h	1 day	3 days	7 days	28 days
1:3	3500	36.5	54.2	74.6	76.2	77.1	78.4
1:3	1260	9.8	38.0	69.5	73.4	75.5	77.5

* W/C, 0.10; B, 5%.

Table 4
Effect of W/C on compressive strength of MPB paste

	Compressive strength (MPa)					
W/C*	1 h	3 h	1 day	3 days	7 days	28 days
0.09	8.5	38.2	70.5	80.4	78.2	84.2
0.10	9.8	38.0	69.5	73.4	75.5	77.5
0.11	8.2	33.1	70.0	71.8	72.7	73.8
0.12	8.5	29.5	55.9	70.8	71.9	74.8

* P:M ratio, 1:3; B, 5%.

2.2.4. w/c

Table 4 shows that the strength of MPB paste decreases slightly with the increase in w/c. However, the effect of w/c on the workability of paste is obvious.

2.2.5. Fly ash

The utilization of fly ash is first to adjust the color and reduce the cost of MPB, but fly ash also has many technological benefits as shown in Table 5. The one-hour strength decreases, but after one day increases with the amount of fly ash. Moreover, the addition of fly ash significantly improves the workability of MPB; i.e., this type of fly ash has some water-reduction effect that mainly depends on the dense and rolling effects of the finer grains of fly ash.

From the above results of compressive strength of MPB paste, it can be seen that for all cases, the strength development within one day is very quick, but that after seven days is very slow. Further, the early strength (before one day) of MPB mainly depends on the amount of retarder B, the fineness of MgO powder, and the environment temperature, but the final strength is mainly controlled by the P/M and w/c ratios. By adjusting the fineness of MgO and the proportion of MPB, one-hour strength of approximately 40 MPa can be achieved. The typical curves of strength development of MPB paste are presented in Fig. 6.

2.3. Bond strength of MPB to old concrete

The bond strength to old concrete is one of the most important parameters of a repaired material. The results of the bond strength of MPB to old concrete in various conditions

Table 5
Effect of the amount of fly ash on compressive strength of MPB paste

Mix proportions*			Compressive strength (MPa)					
P	M	F	1 h	3 h	1 day	3 days	7 days	28 days
40	120	0	39.5	68.2	74.8	76.1	77.0	78.1
40	114	6	37.0	67.0	74.1	74.3	78.6	79.2
40	108	12	34.6	63.0	74.5	75.3	76.0	80.1
40	102	18	29.5	53.4	70.1	75.2	76.5	77.6

* W/C. 0.10; B, 4.4%; fineness of M, 3500 cm^2/g.

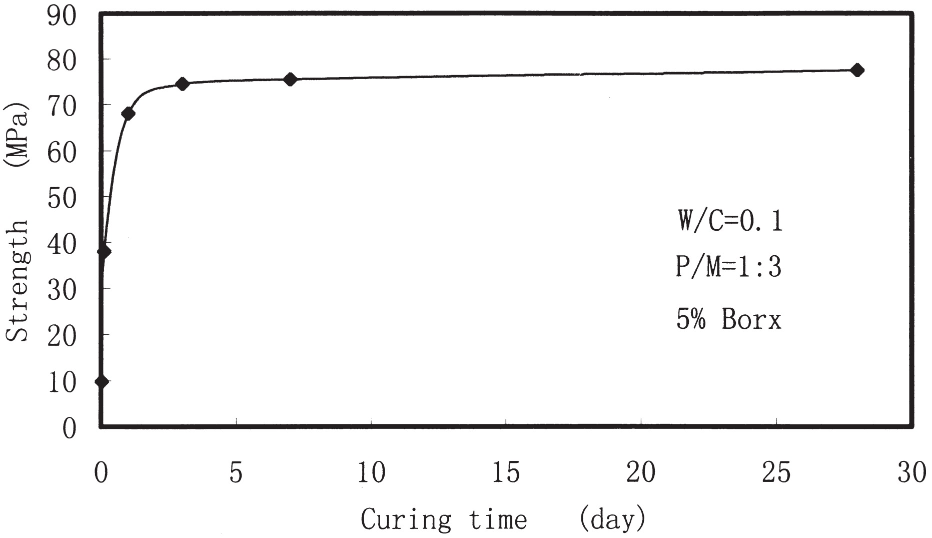

Fig. 6. Development of strength of MPB paste cured in air.

are given in Table 6. As with compressive strength, retarder B has great influence on the early bond strength (before one day) to old concrete, but little influence on the final bond strength. The bond strength to old concrete increases with the specific surface of MgO, especially the early bond strength (before one day).

2.4. Set and hardened mechanism of MPB

2.4.1. XRD analysis

The results of XRD analysis are presented in Fig. 7. From Fig. 7 it can be seen that the peaks of $NH_4H_2PO_4$ (3.09, 5.36, 2.0, 3.75Å) disappear within 1 h after casting and many hydrates are formed, but the amount and types of hydrates have not obviously increased. Main hydrates are of four types: struvite [$NH_4MgPO_4 \cdot 6H_2O$ (4.26, 2.92, 5.6, 5.91, 5.38 Å)], bobierrite [$Mg_3(PO_4)_2 \cdot 4H_2O$ (4.14, 2.65 Å)], dittmarite [$NH_4MgPO_4 \cdot H_2O$ (2.69, 2.92, 2.97 Å)], and hannayite [$(NH_4)_2Mg_3(HPO_4)_4 \cdot 8H_2O$ (3.29, 3.46 Å)] in the order of the amount of hydrates. However, the amount of unhydrated MgO (2.10, 2.43, 2.32 Å) is most dominant in either early or late hydration.

2.4.2. Analysis of set and hardened mechanism

The hydration reaction of MPB is basically an acid-alkali neutralizing and exothermal reaction through solution. Many researchers concluded that the hydrates of MPB were struvite and bobierrite, and other intermediate hydrates [9], as our results concluded. The main reactions are as follows:

$$MgO + NH_4H_2PO_4 + H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O$$

$$MgO + NH_4H_2PO_4 + H_2O \rightarrow Mg_3(PO_4)_2 \cdot 4H_2O$$

From the above reactions and proportions of MPB, it can be calculated that the amount of MgO is much greater than the amount required for these reactions, and much unhydrated MgO exists in the hardened paste of MPB, which is proved by XRD analysis (see Fig. 7). According to the above results, the hydrated mechanism of MPB is proposed as follows:

- The anions and cations of retarder B and phosphate P are quickly dissolved in water, after mixing water is added into the MPB mixture.
- $B_4O_7^{2-}$ ions are first absorbed on the surface of MgO grains, then a layer of magnesium borate compounds is formed around the magnesia grains that hinders the contact of NH_4^+ and $H_2PO_4^-$with MgO grains and therefore gets the retarding effect.
- Some amorphous hydrated gels of phosphate hydrates are initially formed around magnesia grains when NH_4^+ and $H_2PO_4^-$ ions successively diffuse through the film of magnesium borates to reach the surface of

Table 6
Effect of the fineness of M and the amount of B on bond strength of MPB to old concrete

			Bond strength (MPa)				
Fineness (cm^2/g)	B (%)*	W/C	3 h	10 h	1 day	3 days	7 days
1260	5	0.10	5.52	7.11	7.20	8.1†	8.2†
1260	10	0.10	3.70	6.40	7.15	8.05	7.1†
2500	5	0.10	6.0	8.1	8.6†	9.0†	8.7†

* W/C, 0.10; † place of break is not bond interface.

MgO and Mg^{2+} diffuses through the film into solution. With time, many phosphate hydrates are formed and slowly crystallize. Then the films of magnesium borates are destroyed by phosphate hydrates due to volume expansion, and therefore many NH_4^+ and $H_2PO_4^-$ ions can contact Mg^{2+} and a great amount of phosphate hydrates are quickly formed, which makes MPB paste set.

- With time, phosphate hydrates continually increase and accrete out of magnesia grains, and finally all

M---MgO
P---$NH_4H_2PO_4$
S---$NH_4MgPO_4 \cdot 6H_2O$
B---$Mg_3(PO_4)_2 \cdot 4H_2O$
D---$NH_4MgPO_4 \cdot H_2O$
H---$(NH_4)_2Mg_3(HPO_4)_4 \cdot 8H_2O$

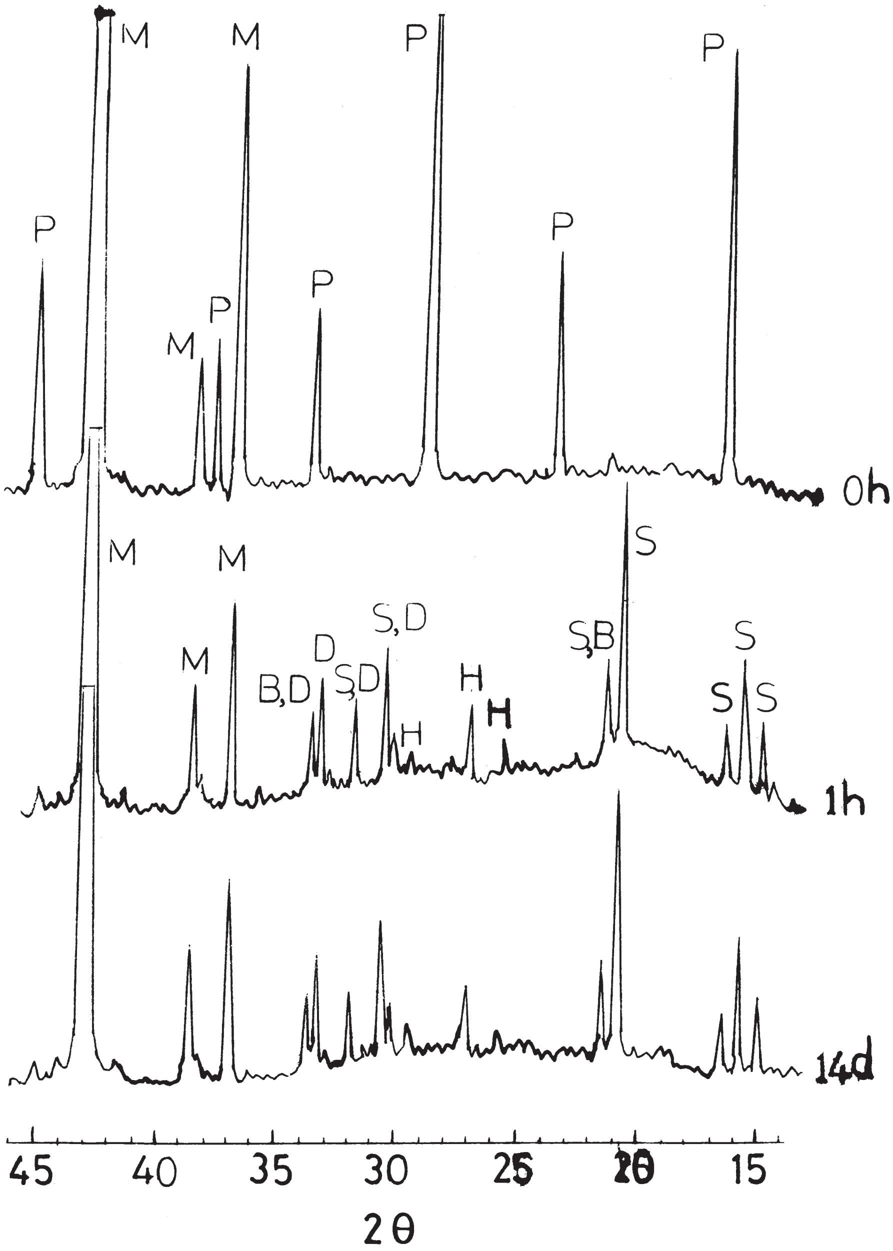

Fig. 7. Results of XRD analysis of MPB at different curing times.

magnesia grains are surrounded by phosphate hydrates and interlock together into a whole that makes MPB paste harden.

3. Summary

The setting time of MPB is mainly controlled by the amount of retarder B, the fineness of MgO, and temperature, which can be easily adjusted from several minutes to one hour. MPB paste can be set and hardened within one hour even at $-10°C$ due to its high hydrated heat.

The early strength (before one day) mainly depends on the amount of retarder B and the fineness of MgO, but they have little influence on the final strength. By adjusting the fineness of MgO and the proportion of MPB, high one-hour compressive strength of about 40 MPa, three-hour bond strength of 5.5 MPa, and seven-hour compressive and bond strength of >70 MPa and >8.0 MPa, respectively, are achieved.

The maximum strength of MPB paste is achieved when the P/M ratio is in the range of $1/4 \sim 1/5$. The specific surface of MgO need to be only 1260 cm^2/g, much less than that of portland cement, because the reaction of hydration of MPB is very rapid.

The retarding effect of borax directs toward MgO and is not related to $NH_4H_2PO_4$. For the same fineness of MgO, the setting time of different proportions is similar when B/M ratio is constant.

Addition of fly ash adjusts the color of MPB paste to the same as that of portland cement paste and obviously improves the workability of MPB paste, but has little influence on the setting time. In contrast, the addition of fly ash reduces one-hour strength, but enhances the final strength.

The amount and types of hydrates of MPB paste do not significantly change after one hour. Main hydrates of MPB paste are of four types: struvite $NH_4MgPO_4 \cdot 6H_2O$, bobierrite $Mg_3(PO_4)_2 \cdot 4H_2O$, dittmarite $NH_4MgPO_4 \cdot H_2O$, and hannayite $(NH_4)_2Mg_3(HPO_4)_4 \cdot 8H_2O$ (in the order of amount of hydrate). Moreover, a large amount of unhydrated MgO is in MPB paste.

In conclusion, MPB materials have many good properties, such as rapid hardening but long enough setting time to cast, high early strength, good bond, and compatibility with old concrete. Therefore, MPB is very suitable for repairing highway pavements, airport runways, bridge decks, key municipal roads, and other concrete structures rapidly, especially in low-temperature conditions.

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