12. M. U. Haddad, D. W. Fowler, and D. R. Paul. Factors Affecting Curing and Strength of Polymer Concrete. *ACI Journal*, Sept.–Oct. 1983, pp. 396–401.
13. P. S. Romano and H. Buttrick. *Evaluation of Bridge Patching Materials (Polymer Concrete)*. Report R-30-0, Massachusetts Department of Transportation, Boston, June 1981.
14. R. Johnson. *Resins and Non-Portland Cements for Construction in the Cold*. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 80–35, Hanover, N.H., Sept. 1980.
15. G. P. Beer, D. W. Fowler, A. H. Meyer, and D. R. Paul. *Laboratory Tests on Selected Rapid-Setting Repair Materials*. Report No. CTR 3-9-82-311-2, BER, University of Texas, Austin, Feb. 1984.
16. A. M. Pailleri and J. J. Serrano. Concrete Reinforced with Metal Fibre-Thermal Treatment by Means of Electric Conductivity. IRRD-106169, *Bulletin of the Central Laboratory of Bridges and Highways, Paris, France*, March 1977, p. 149.

Publication of this paper sponsored by Committee on Mechanical Properties of Concrete.

Early Age Properties of Magnesium Phosphate-Based Cements Under Various Temperature Conditions

SANDOR POPOVICS AND N. RAJENDRAN

Presented in this paper are the effects of temperature on the early age properties of two rapid-hardening magnesium phosphate-based cements and their combinations, as follows: *(a)* magnesium phosphate cement for cold and regular weather use; *(b)* magnesium phosphate cement for hot weather use; *(c)* a 50-50 blend of magnesium phosphate cement and magnesium phosphate cement for hot weather use; and *(d)* magnesium phosphate cement with the addition of borax. A combination of both mechanical (setting and compressive strength) and physicochemical (X-ray diffraction; optical microscopy and infrared spectroscopy) tests was performed. Overall, 35 mixes were made, cured under various temperature conditions, and tested. The strengths were determined at the ages of 1, 3, and 24 hr. Freeze-thaw experiment was left for future work. The tests revealed that all the above cements develop almost 2,000 psi (14 MPa) compressive strength within an hour regardless of various curing conditions; the 28 days' strengths are more than 4,500 psi (31 MPa); and the 90 days' strengths are more than 6,500 psi (45 MPa) under normal curing conditions. Thus, their applicability for rapid road repair and other concrete repair works seems promising. Further, the MPH cement appears to have the best mechanical properties among them all under the majority of weather conditions.

S. Popovics, Department of Civil Engineering, Drexel University, Philadelphia, Pa. 19104. N. Rajendran, New Jersey Department of Transportation, 600 Cramer Building, Route 38, Mt. Holly, N.J. 08060.

Rapid hardening cements have an important application in the repair of concrete structures. Especially, their high early strengths could solve many emergency repair works such as pot holes, concrete pavements, airport runways, wall patching, bridge decks, and other concrete structures. The investigation focused on

1. Conducting laboratory experiments to determine the strength effects of various curing conditions on these cements; and
2. Using physicochemical methods such as X-ray diffraction, optical microscopy, and infrared spectroscopy to obtain the basic nature of rapid-hardening magnesium phosphate base cements.

This paper is the continuation of an earlier publication on rapid-hardening cements for repair of concrete *(1)*. The investigation on later age properties will be presented in the next paper.

SUMMARY OF AN EARLIER INVESTIGATION

The main goal of earlier research with the same materials was to identify or modify an existing inorganic cementing material that would be suitable for emergency repair of damaged airport

runways under war conditions. The following objectives were set for this research: the selected cements should have *(a)* at least 2,000 psi compressive strength at the age of 1 hr, *(b)* adequate flexural strength, *(c)* a long enough setting time, *(d)* good bond strength, *(e)* good volume stability, *(f)* good durability, and *(g)* wear resistance under almost all weather conditions.

Based on the reported field experience and laboratory data, the following four promising commercially available cements were selected for further investigation, keeping the above objectives in mind:

1. Magnesium phosphate-based cements with both hot and cold weather formulas;
2. Their combinations (i.e., 50-50 blend and borax addition);
3. Aluminum phosphate cement; and
4. Jet cement.

Both mechanical (compressive strength 1 hr, 3 hr, and 24 hr; flow, and setting time) and physicochemical tests (optical microscopy, pH measurements, X-ray diffraction, scanning electron microscopy, and infrared spectroscopy) were performed. These screening tests revealed that the magnesium phosphate-based cements and their modification appeared to be most promising among the cements tested.

MATERIALS

The magnesium phosphate cements investigated are commercially available under the brand name of SET 45 and come in two formulas to cover all weather conditions. One is the cold formula, the magnesium phosphate cement (MPC) recommended for use in cold and regular weather temperatures; the other is the hot formula, the magnesium phosphate cement recommended for hot weather conditions (MPH), used because of its slower hydration. Both formulas are granular materials consisting of a powdery cementitious material and sand in the proportion of 1 to 4 by weight *(1)*. According to the manufacturer, MPH also contains boric acid. Among the other tested cements are a 50-50 blend of cold and hot formulas (MPCH); cold formula with a 0.34 percent borax addition (MPCB1); and cold formula with a 0.7 percent borax addition (MPCB2).

Many additives and admixtures were tried with magnesium phosphate (MP) cements to plasticize the mixtures, and to retard the setting, or both. None were effective with MP cements except for borax and ammonium polyphosphate solution. Only borax was used in these experiments.

MECHANICAL TESTS AND RESULTS

The mechanical testing concentrated on the effects of temperature on the setting time and compressive strength development of mortars at the ages of 1, 3, and 24 hr. Overall, 35 mixes were made, cured under various temperature conditions, and tested. These conditions were the following (Table 1):

1. High curing temperature with or without precooling the components representing hot weather construction;
2. Low curing temperature with or without preheating or precooling the components representing cold weather construction; and
3. Normal curing temperature but in a humid environment.

Nine 3- × 6-in. (76- × 152-mm) cylinders were cast from each mix. Mortar of flowing consistency, that is of flow of approximately 150 percent as determined by ASTM C230-80, was used for all mixes.

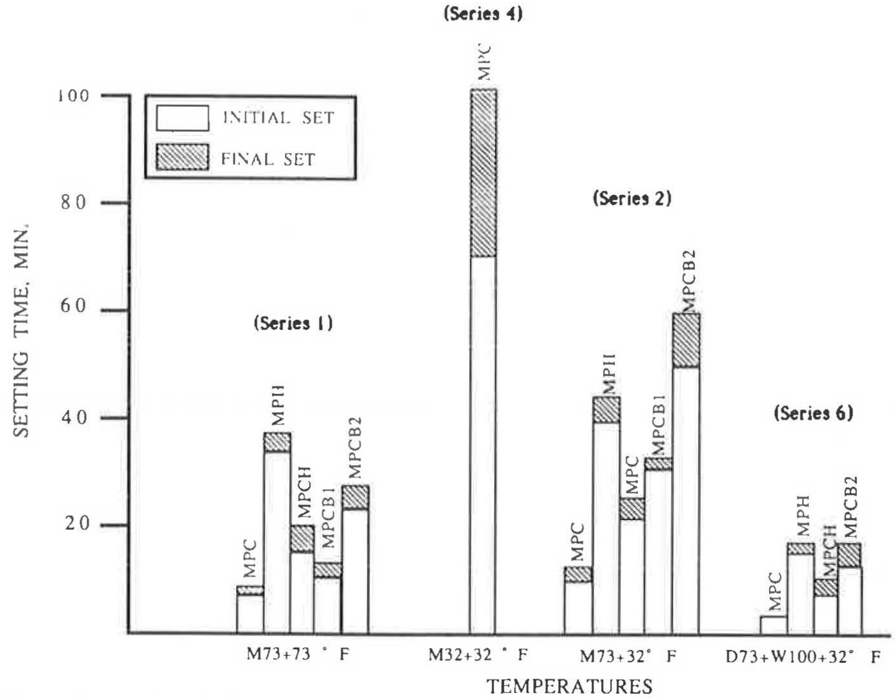
Fresh Mortar

The mixer used was a 3-speed bench model of approximately $^1/_6$-ft^3 capacity with a stainless steel bowl and planetary action. It complies with ASTM C305. The mixing procedure used for all batches was as follows: The mixing water was poured into the bowl and the premixed dry components were added to the water. These were mixed together first for 30 sec at low speed then for 90 sec at medium speed. When borax was used it was premixed with the dry mixture. Immediately after mixing, the time of setting test (ASTM C191-77) was performed using

TABLE 1 TEMPERATURE DETAILS OF MAGNESIUM PHOSPHATE MIX SERIES

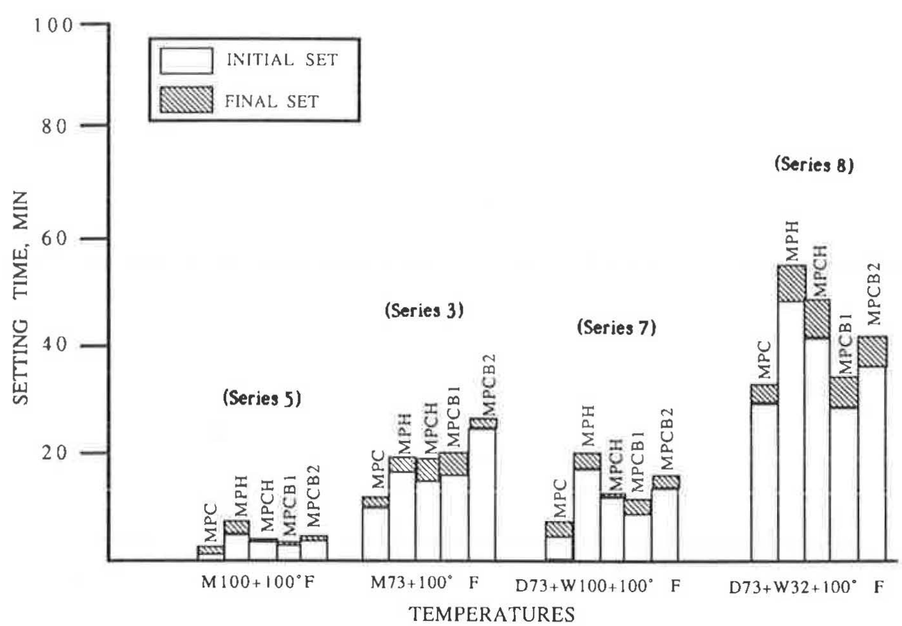
Mix Series Number	Temperature, °F[a]				Number of Mixes in Each Series
	MP Dry Mixture	Water	Mixing Bowl	Air Curing at 50% RH	
1	73	73	73	73	5
2	73	73	73	32	5
3	73	73	73	100	5
4	32	32	32	32	1
5	100	100	100	100	5
6	73	100	73	32	4
7	73	100	73	100	5
8	73	32	73	100	5

NOTE: °C = (°F − 32)/1.8.
[a]Temperature fluctuation ± 2°F.



Note: The numbers indicate temperatures. M = fresh concrete after mixing, D = dry formula, and W = mixing water.

FIGURE 1 Setting times under cold-curing conditions compared to cure at 73°F.



Note: The numbers indicate temperatures. M = fresh concrete after mixing, D = dry formula, and W = mixing water.

FIGURE 2 Setting times under hot-curing conditions.

Vicat apparatus and the needle. The results are presented in Figures 1 and 2 as well as in Tables 2 through 8.

Temperature development during setting was also measured in the MPC and MPH mortars. The starting temperature of the mortar and the ambient temperatures were close to 73°F (23°C). The thermometer was embedded in the center of uninsulated 3- × 6-in. (76- × 152-mm) cylindrical specimens. The purpose was: *(a)* to correlate the heat development with setting time, and *(b)* to determine the maximum temperature that a small amount of MP mortar could reach with time. The results are presented in Figure 3.

TABLE 2 FIRST SERIES: SETTING AND COMPRESSIVE STRENGTH OF MAGNESIUM PHOSPHATE MORTARS MIXED AND CURED AT 73°F

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	7 min 30 sec	9 min 30 sec	2,580	2,810	2,920
MPH	10	–	34 min 30 sec	37 min 15 sec	2,930	3,000	3,100
MPCH	11	–	16 min	20 min	2,840	3,080	3,220
MPCB1	10.5	0.34	11 min 30 sec	13 min 30 sec	3,150	3,160	3,840
MPCB2	10.5	0.70	24 min	27 min	1,920	2,140	2,850

NOTE: Consistency of the fresh mortars was flowing (ASTM C230-80). All the specimens were air cured at ambient temperature of 73°F. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.

TABLE 3 SECOND AND FOURTH SERIES: PROPERTIES OF MAGNESIUM PHOSPHATE MORTARS AIR CURED AT 32°F I

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	10 min	12 min	2,700	2,800	2,840
MPH	10	–	40 min	44 min	2,690	3,690	3,850
MPCH	11	–	21 min	25 min	2,240	2,660	2,670
MPCB1	10.5	0.34	31 min	33 min	2,020	2,860	2,990
MPCB2	10.5	0.70	45 min	50 min	710[b]	1,130	2,990
MPC (Fourth Series)	12	–	1 hr 10 min	1 hr 45 min	–[c]	2,090	3,200

NOTE: The dry mixture and mixing water had ambient temperature except for Mix MPC where the components were precooled at 32°F. Consistency of the fresh mortars was flowing. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.
[b]Since the specimens were too weak for 1-hr test, this value was obtained at 2 hr.
[c]The specimens were too weak for the 1-hr test.

TABLE 4 THIRD SERIES: PROPERTIES OF MP MORTARS AIR CURED AT 100°F I

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	10 min	11 min	2,370	2,530	2,740
MPH	10	–	17 min 30 sec	19 min	3,240	3,600	4,120
MPCH	11	–	16 min 15 sec	19 min	2,600	2,860	3,340
MPCB1	10.5	0.34	17 min 30 sec	20 min 15 sec	2,250	2,460	2,910
MPCB2	10.5	0.70	24 min 30 sec	26 min 30 sec	2,300	2,820	3,190

NOTE: The MP dry mixture and mixing water had ambient temperature of 73°F. Consistency of the fresh mortars was flowing. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.

Hardened Mortar

Altogether a series of eight strength tests were performed at different temperatures of dry mixtures, mixing water, and curing conditions (Table 1). The five formulas tested were described earlier in the Materials section of this paper.

Disposable waxed cardboard cylindrical molds of 3- × 6-in. (76- × 152-mm) size were used. All specimens were prepared according to ASTM C192-81. The mixing and casting were done within 5 min at ambient temperature 73.4°F ± 3°F (23°C ± 1.7°C) and 50 percent relative humidity (RH). The specimens were then cured at three different temperatures (Table 1) to

TABLE 5 FIFTH SERIES: PROPERTIES OF MAGNESIUM PHOSPHATE MORTARS AIR CURED AT 100°F II

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	13	–	1 min	1 min 10 sec	–[b]	–[b]	–[b]
MPH	12	–	4 min	6 min	2,390	2,660	2,520
MPCH	13	–	3 min	3 min 30 sec	1,820	1,910	1,900
MPCB1	13	0.34	2 min	2 min 30 sec	1,840	2,000	2,270
MPCB2	13	0.70	3 min	3 min 30 sec	2,420	2,520	2,560

NOTE: The dry mixture, water and mixing bowl were preheated at 100°F. Consistency of the fresh mortars was flowing. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.
[b]Cylinders could not be cast because of rapid setting.

TABLE 6 SIXTH SERIES: PROPERTIES OF MAGNESIUM PHOSPHATE MORTARS AIR CURED AT 32°F II

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	3 min	3 min	1,820	1,910	2,120
MPH	10	–	16 min	18 min	3,470	3,770	4,050
MPCH	11	–	7 min 30 sec	10 min	3,150	3,060	3,290
MPCB2	10.5	0.70	12 min 10 sec	16 min 45 sec	3,070	3,240	3,610

NOTE: The mixtures had room temperature and the mixing water 100°F. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.

TABLE 7 SEVENTH SERIES: PROPERTIES OF MAGNESIUM PHOSPHATE MORTARS AIR CURED AT 100°F III

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	5 min 14 sec	6 min 25 sec	3,160	3,460	3,870
MPH	10	–	18 min	20 min	3,090	3,250	4,190
MPCH	11	–	11 min 5 sec	12 min 55 sec	2,230	2,280	2,480
MPCB1	10.5	0.34	9 min 20 sec	11 min 48 sec	2,490	2,460	2,760
MPCB2	10.5	0.70	13 min 47 sec	15 min 12 sec	1,920	1,990	2,420

NOTE: The dry mixtures had ambient temperature and the mixing water 100°F. Consistency of the fresh mortars was flowing. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.

simulate different weather conditions. Cylinders were capped according to ASTM C617-83 and tested for compressive strength at the ages of 1, 3, and 24 hr at ambient temperature.

The series of eight strength tests were conducted as follows:

First Series: all five mixtures were mixed, placed, and air cured at ambient laboratory temperature until break. The results are presented in Table 2 and Figure 4.

Second Series: the dry mixture, mixing bowl, and water were at ambient temperature and the specimens were air cured at 32°F (0°C) in a cooled environmental chamber until break (Table 3 and Figure 4).

Third Series: similar to the second series, except that the specimens were air cured at 100°F (38°C) in an oven immediately after mixing until break (Table 4 and Figure 5).

Fourth Series: only one mix was made. The dry mixture,

TABLE 8 EIGHTH SERIES: PROPERTIES OF MAGNESIUM PHOSPHATE MORTARS AIR CURED AT 100°F IV

Mix Designation	Water[a]	Admixture Borax[a]	Setting Time		Compressive Strength (psi) by Time (hr)		
			Initial	Final	1	3	24
MPC	11	–	28 min 50 sec	33 min 44 sec	1,570	1,900	2,130
MPH	10	–	49 min 52 sec	55 min 25 sec	–[b]	2,230	2,800
MPCH	11	–	43 min 44 sec	49 min 55 sec	–[b]	1,650	2,360
MPCB1	10.5	0.34	29 min 50 sec	34 min 5 sec	1,960	2,100	2,750
MPCB2	10.5	0.70	38 min 12 sec	42 min 54 sec	–[b]	2,060	2,460

NOTE: The dry mixtures had ambient temperature and the mixing water 32°F. Consistency of the fresh mortars was flowing. 145 psi = 1 MPa; t°F = (t°C ÷ 0.55) + 32.
[a]Percent by weight of the dry mixture.
[b]The specimens were too weak for the 1-hr test.

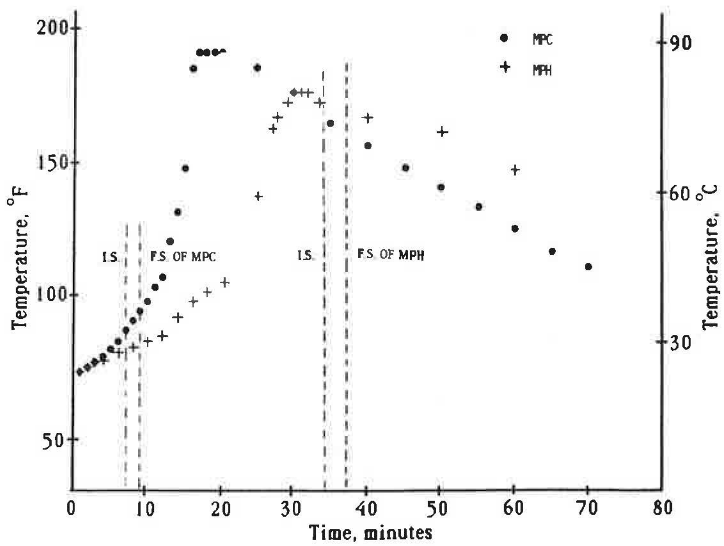


FIGURE 3 Temperatures of MP mortars during setting at ambient temperature and 50 percent relative humidity.

water, and mixing bowl were precooled at 32°F (0°C), and the specimens were air cured at 32°F (0°C) until break (Table 3 and Figure 4).

Fifth Series: the dry mixture, water, and bowl were preheated at 100°F (38°C) and the specimens were air cured at 100°F (38°C) until break (Table 5 and Figure 5).

Sixth and Seventh Series: the dry mixture and bowl were at ambient temperature (73°F) and the water was at 100°F (38°C). Specimens in the sixth series were air cured at 32°F (0°C) (Table 6), and in the seventh series were air cured at 100°F (38°C) until break (Table 7 and Figure 5).

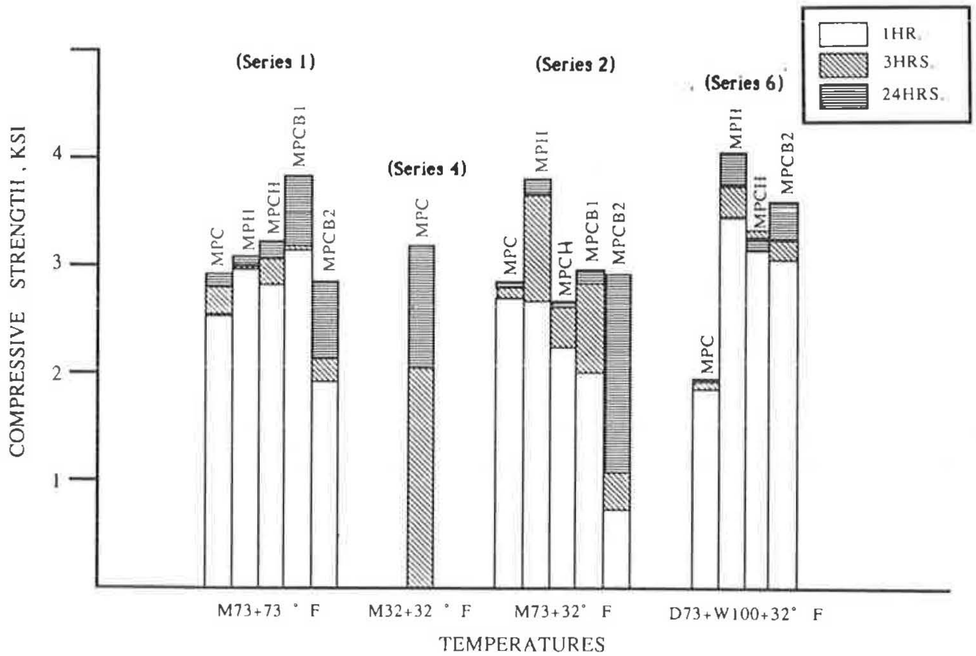
Eighth Series: the dry mixture was at the ambient temperature, water was at 32°F (0°C), and the specimens were air cured at 100°F (39°C) until break (Table 8 and Figure 5).

ANALYSIS AND DISCUSSION OF MECHANICAL TEST RESULTS

Flow

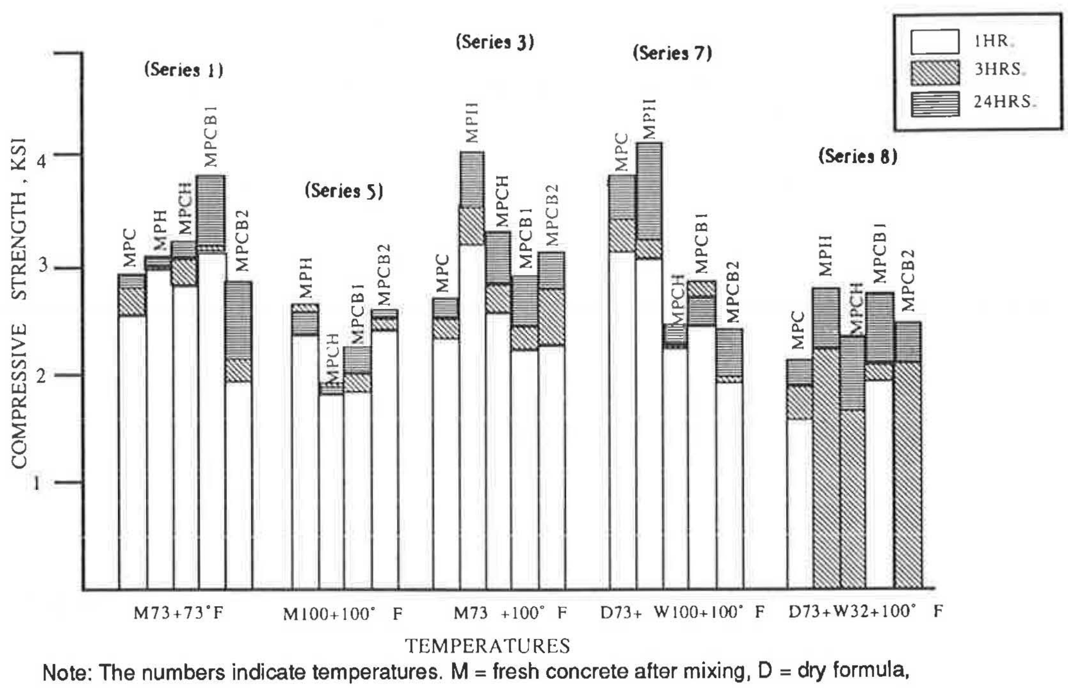
For all mix series, mortars of flowing consistency (i.e., 150-percent flow) were used. Not only does flowing consistency lengthen the setting time, but it also speeds up the construction by the simplification of the repair technique.

It can be seen from Table 2 that the water required to achieve 150-percent flow for MPH mortar is less than that for the MPC mortar under identical conditions. This is attributed to the presence of boric acid in the MPH mixture. A similar liquifying trend was observed when a small quantity of borax was added



Note: The numbers indicate temperatures. M = fresh concrete after mixing, D = dry formula, and W = mixing water.

FIGURE 4 Compressive strengths under cold curing conditions as compared to cure at 73°F.



Note: The numbers indicate temperatures. M = fresh concrete after mixing, D = dry formula, and W = mixing water.

FIGURE 5 Compressive strengths under hot curing conditions as compared to cure at 73°F.

to the MPC mixture. Consequently, it is not surprising that the water quantities required to achieve flowing consistency for the MPC mixture blended with MPH mixture, as well as for the MPC mixture blended with borax, are higher than that for the hot mixture. The same trend was also observed for all mix series regardless of the temperature of the dry mixture, water, and curing conditions.

Setting Time

The initial and final setting times for MP mortars are shown in Figures 1 and 2 as well as in Tables 2 through 8. These setting times are much shorter than those of the standard portland cements (2, p. 370). It can be seen from Table 2 that the initial and final setting times of the MPC mortar in the first series are

less than 10 min at room temperature (73°F). MPH mortar has longer setting times with even less water content than the MPC mortar. Further, the 50-50 blend of MPC and MPH as well as MPC mixture with borax have in-between setting times. The delay in setting times in the MPH is due to the coarser MgO phase and the presence of borax. The retarding effect of borax was also observed in the MPC mixture blended with borax. An increase in borax addition increases the set retardation as reflected in the MPCB2 mixture.

Temperature Development During Setting

During the setting process all cements emit heat as the hydration is an exothermic process. The faster the setting, the faster the heat development. Thus the MPC develops hydration heat more rapidly and reaches the higher temperature than MPH (Figure 3).

The fact that the setting times of the MPC mixture precede the peak temperature, whereas those of MPH follow it, is probably due to the set-retarding effect of boric acid present in MPH.

Compressive Strength

First Series

It can be seen from Figure 4 that compressive strengths greater than 2,000 psi were achieved with almost all mixes within an hour. The MPH mortar achieved 90–95 percent of its 24-hr compressive strength within an hour, the other MP mortars showing less percentage gains. It can be seen from Table 2 that high strengths were also exhibited by MPCB1. If the results of MPCB1 are compared to those of MPCB2, it appears that the higher percent of borax can decisively increase the delay in setting time and reduce the early compressive strength at ambient temperature curing. Note also that the standard compressive strength of a structural concrete with Type III cement of plastic consistency is around 1,500 (10.3) to 2,000 (13.8) psi (MPa) at the age of 24 hr.

Other Series

For most combinations of temperatures of ingredients and curing conditions, MPH mortar exhibits higher early (1-, 3-, and 24-hr) strengths than the other mortars (Figures 4 and 5).

Almost all MP mortars, regardless of different combinations of temperatures, surpassed 2,000 psi compressive strength at the age of 1 hr. Among these, the MPH mortar provided the highest strengths.

PHYSICOCHEMICAL EXAMINATIONS

Physicochemical tests were performed parallel to the mechanical tests. The following tests were applied: X-ray diffraction, optical microscopy, and infrared spectroscopy (IR). The hydration processes of MP cements at 73°F (23°C) temperature were described in earlier research *(1)*. In this paper the effects of higher and lower-than-normal temperatures on the hydration process are discussed. Essentially, the same mixtures were used in the physicochemical examinations that were subjected to mechanical testing, mentioned previously.

Specimen Preparation

The material that passed sieve No. 200 was used in the physicochemical experiments. This is referred to as MP cement and called MP paste when mixed with water.

In order to keep the process of hydration in MP pastes similar to that in MP mortars, the water-cement ratios were kept the same in the two mixtures instead of the water-to-solid ratio. For MP mortars, water-to-solid ratio of 0.105 by weight corresponds to water-cement ratio of 0. 525 by weight in paste. Therefore, this water-cement ratio was kept the same while working with MP pastes.

The cements for these pastes were obtained from the five formulas described earlier in the Materials section. The quantities of 1.75 and 3.5 percent of borax are expressed in terms of the cementitious phase of MP. When they are expressed as total solids, the corresponding quantities are 0.35 percent and 0.70 percent, respectively.

X-Ray Diffraction

The X-ray diffractometer was used with a CA-7 diffraction tube. Copper K_α radiation was applied, and all the patterns were run at the same settings of the diffractometer.

A general feature of all five MP mixtures cured at 100°F (38°C) is that the two main hydration products are similar to those observed at curing at 73°F (23°C); these are: ammonium magnesium phosphate hexahydrate ($NH_4MgPO_4.6H_2O$) and ammonium magnesium phosphate monohydrate ($NH_4MgPO_4.H_2O$) *(1)*. These are referred to as hexahydrate and monohydrate, or hexa and mono, respectively. In all the mixtures the monohydrate was present in larger quantities at high curing temperature.

In addition to the similarities, there are also certain differences between the hydration process at normal and that at 100°F (38°C) curing temperature. For instance, the mono-hexa ratio slowly decreases with curing time at normal temperature, but it increases at high temperature. Another difference revealed by the comparison of Figures 6 and 7 is that a characteristic diffraction peak of the hexahydrate at $2\theta = 32.5°$ (d = 2.67Å is either totally missing or reduced in the X-ray patterns of the three fastest hydrating cements (MPC cured at 100°F) out of the tested five MP cements when cured at elevated temperature. A possible explanation for this phenomenon is irregularity in the crystal growth at the high rate of hydration. This explanation is supported by the observation that MPH mortar with its slower rate of hydration develops higher strengths than the comparable, but faster, MPC mortar.

The same five mixtures were tested at 32°F (0°C) curing temperature as at the high temperature. The general characteristic of these hydrated pastes is that the X-ray diffraction patterns of all five mixtures are practically identical at various ages after low-temperature curing showing only hexahydrate as the main crystalline product. The hydration characteristics of

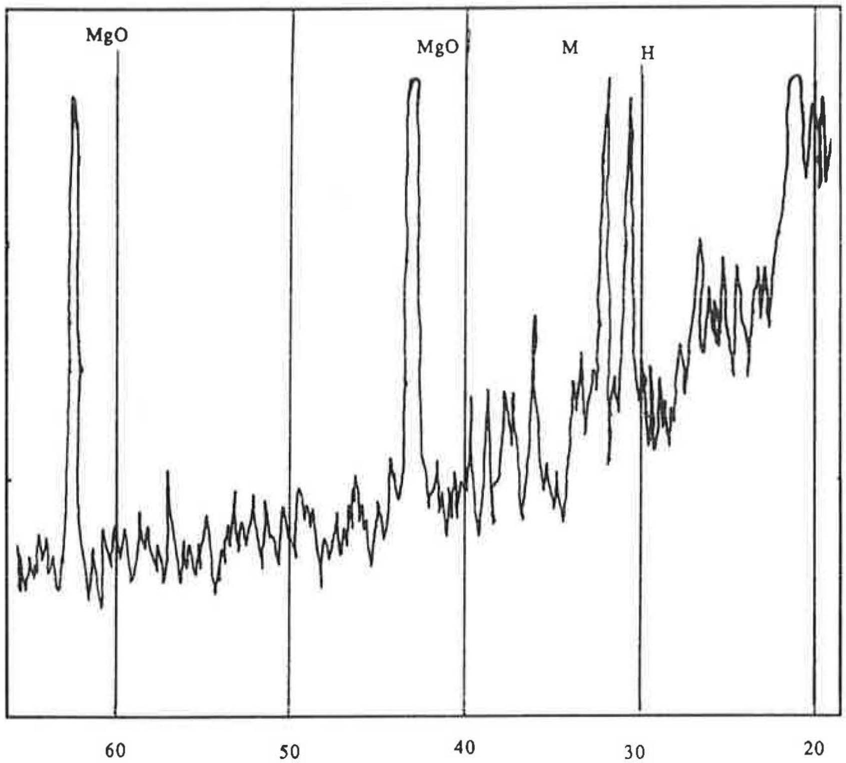


FIGURE 6 X-ray diffraction pattern of MPC paste mixed and cured at 100°F (38°C) at 1 hr.

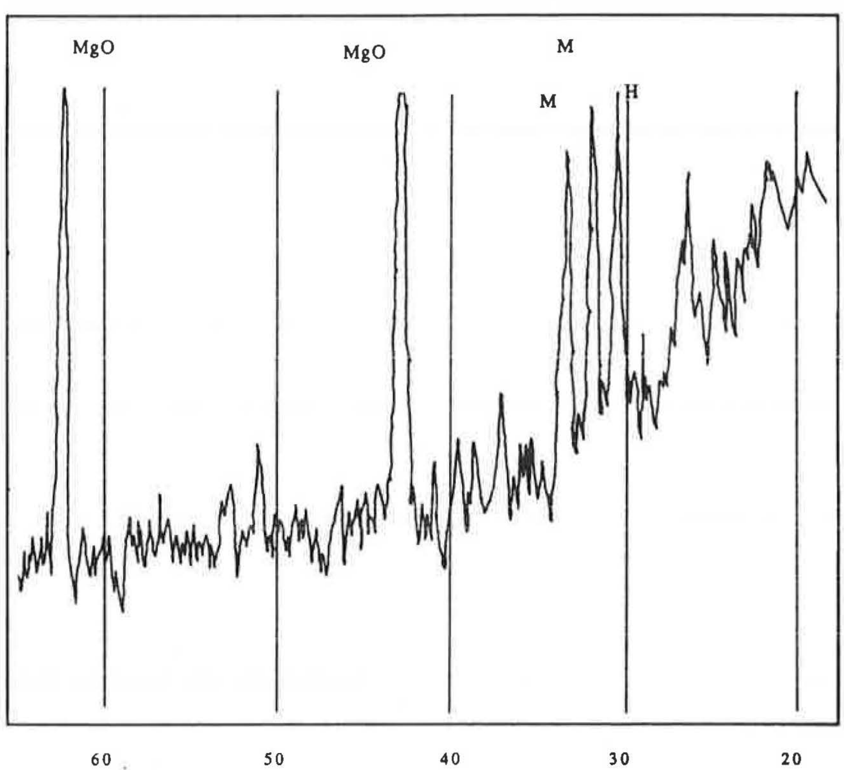


FIGURE 7 X-ray diffraction pattern of MPH paste mixed and cured at 100°F (38°C) at 1 hr.

TABLE 9 HYDRATION CHARACTERISTICS OF MAGNESIUM PHOSPHATE CEMENT PASTES

			Curing Temperature 77°F Wet			
Characteristics	30°F	77°F Dry	Short Period	Long Period	100°F	200°F
Unhydrated MgO	Present	Present	Present	Absent	Present	Absent
Monohydrate	Absent	Present	Present	Absent	Present	Absent
Hexahydrate	Present	Present	Present	Absent	Present	Absent
Mono/Hexa	<<1	>1	>1	N/A	>1	N/A
Degree of Hydration	Low	Medium	Medium	High	High	High

NOTE: N/A = not applicable.

TABLE 10 HYDRATION CHARACTERISTICS OF MAGNESIUM PHOSPHATE CEMENT (for hot weather use)

		Curing Temperature		
Characteristics	30°F	77°F	100°F	100°F
Unhydrated MgO	Present	Present	Present	Present
Monohydrate	Absent	Present	Present	Present
Hexahydrate	Present	Present	Present	Absent
Mono/Hexa	<<1	<1 decreases with time	>1 increases with time	N/A
Degree of Hydration	Low	Medium	High	High

NOTE: N/A = not applicable.

MP pastes under various curing temperatures are given in Tables 9 and 10.

Infrared (IR) Spectroscopy

An Infracord spectrophotometer was used. The IR patterns of 73°F (23°C) curing are characterized by a single band at approximately 1000 cm^{-1}, which is in most cases asymmetrical having a shoulder. The band was assigned to the hexahydrate, and the shoulder to the monohydrate *(1)*. In IR spectra at 100°F (38°C) the shoulder develops into a band of approximately the same intensity as the band assigned to hexahydrate (Figure 8). This means that the amount of monohydrate increases at 100°F (38°C), the finding already established from the X-ray patterns.

Optical Microscopic Examinations

Pastes were prepared from the material passing sieve No. 200 and examined under the optical microscope immediately after mixing. The magnification used was 45X. When water is added to MP cements, the liquid gets thicker within a matter of minutes and finally crystallizes, forming a bond between the undissolved particles consisting most probably of the magnesium oxide.

The size of magnesium oxide particles in MPC paste is much smaller than the size of magnesium oxide particles in MPH paste. This difference may contribute to faster hardening of MPC mortars.

COMPARISON OF THE TESTED MATERIALS

1. MPH mortar requires the least amount of mixing water to achieve flowing consistency, that is approximately 150 percent flow measured, according to ASTM C230-80. The water required for MPC blended with borax is less than that for MPC mortar but greater than that for MPH mortar (Table 2).
2. The MPC mixture has the shortest setting times. The initial and final setting times are shorter than 10 min. The setting times become much shorter at elevated temperatures, but the ranking order from the longest to the shortest times remains the same. Typically, the MPH mixture has the longest setting, even at elevated temperatures (Figures 1 and 2).
3. Parallel to the setting times, MPH mortar develops less heat than MPC mortar (Figure 3).
4. Almost all MP mortars, regardless of the different curing conditions, surpass 2,000 psi compressive strength at the age of 1 hr. Among these, the MPH mortar usually exhibits the highest strengths (Figures 4 and 5).
5. Borax addition can decisively increase the setting times and reduce the early strengths (Table 2).
6. The MPH formula contains coarser MgO particles than the MPC formula and a small addition of boric acid.
7. Based on the setting time and early compressive strengths at different combinations of temperatures, the MP mixtures were ranked and presented in Table 11. Rank 1 represents the highest and 3 the lowest rank for construction purposes. For instance, the MPCB1 mixture exhibits the highest strength at room temperature. Nevertheless, it does not receive the top rating because its setting time is too short, less than 15 min.
8. The mono-hexa ratio and the quality of the crystalline phase of the hydration product depend on the rate of hydration. The monohydrate is the main crystalline product when the hydration is rapid; that is, its amount increases with the fineness of MgO phase and with temperature. Conversely, the amount of hexahydrate decreases with decreases in the same parameters. The quality of hexahydrate crystals is also affected by temperature because they may grow irregularly when the hydration rate is high (high temperature curing).
9. The MPH paste and blends of MPC and MPH do not suffer any large chemical changes during curing. Thus, they are considered more stable than MPC pastes.

Comparison of the Effects of Curing Temperature

As far as the effects of temperature are concerned, it appears that the temperature of the fresh mortar has a greater influence

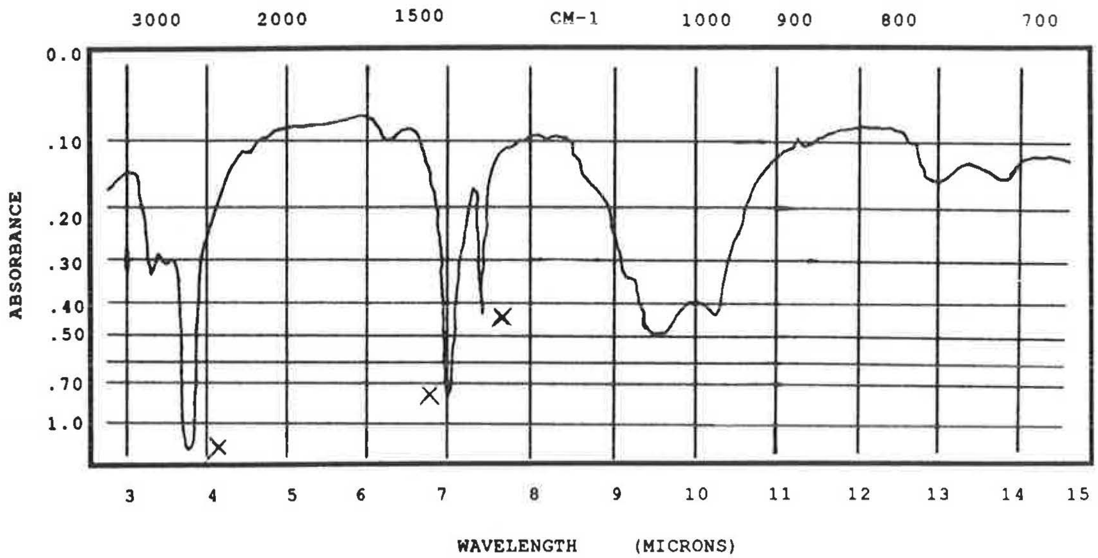


FIGURE 8 IR spectrum of MPC paste mixed and cured at 100°F (38°C) at 3 days.

TABLE 11 RANKING OF MAGNESIUM PHOSPHATE MIXTURES

Mix Series	Temperature of Ingredients and Curing	Ranking	Remarks
1	Simulation of normal weather conditions: Ingredients, mixing bowl and curing had room temperature of 73°F (23°C).	1. MPH 2. MPCB1 3. MPCH	
2	Simulation of winter conditions I: Ingredients and mixing bowl had room temperature, but the specimens were cured at 32°F.	1. MPH 2. MPCB1 3. MPCH	
3	Simulation of summer conditions I: Ingredients and mixing bowl had room temperature, but the specimens were cured at 100°F.	1. MPH 2. MPCB2 3. MPCH	
4	Simulation of winter conditions II: Ingredients, mixing bowl were precooled at 32°F, and the specimens were air cured at 32°F.	1. MPC	Early strengths are low. The use of ingredients of room temperature is recommended. (See Mix Series 2)
5	Simulation of summer conditions II: Ingredients, mixing bowl were preheated, and the specimens were air cured at 100°F.	1. MPH 2. MPCB2 3. MPCB1	The setting time is too short. The use of ingredients of room temperature or cooled water is recommended. (See Mix Series 3 and 8)
6	Simulation of winter conditions III: Dry mixture and mixing bowl had room temperature, and water had 100°F, but the specimens were cured at 32°F.	1. MPH 2. MPCB1 3. MPCH	
7	Simulation of summer conditions III: Ingredients and mixing bowl had room temperature and water had 100°F, but the specimens were cured at 100°F.	1. MPH 2. MPCB1 3. MPCH	
8	Simulation of summer conditions IV: Ingredients and mixing bowl had room temperature, and water had 32°F, but the specimens were cured at 100°F.	1. MPH 2. MPCB1 3. MPC	

NOTE: Rank 1 is the best.

on the 1-hr strength than the curing temperature. For instance, lowering of the curing temperature from 73°F (23°C) to 32°F (0°C), or raising it to 100°F (38°C) hardly affected the strengths when the temperature of the fresh mortar was 73°F (23°C) (Figures 4 and 5). In contradistinction, when the temperature of the fresh concrete was 32°F (0°C), cold curing produced practically zero compressive strengths at 1 hr, although the strengths increased considerably by 3, and especially by 24 hr. Also, fresh mortar of 100°F (39°C) produced relatively low strengths, sometimes even strength retrogression at the age of 24 hr under hot curing (Table 5 and Figure 5). Similar observations can be made about the measured setting times.

The meaning of this for the practicing engineer is that when these rapid hardening materials are used under extreme temperature conditions, the mortar components, that is the dry mixture as well as the mixing water, should be protected from the temperature extremes. If the temperature of the fresh mortar is not much lower than 73°F (23°C) in cold weather, or not much higher than that in hot weather, the construction engineer should not have much trouble either with the setting times or with the strengths of most of these mortars.

CONCLUSIONS

Almost all MP mortars surpassed 2,000 psi compressive strength at the age of 1 hr despite differences in curing conditions. The test results of the mechanical and physicochemical examinations revealed that the MPH mortar appears to have the best mechanical properties under the applied temperature conditions, except winter condition II in Table 11. The physicochemical investigation showed that the hydration products of the MP cements are influenced by the curing temperature. For instance, of two main hydration products identified in the hardened MP cements, monohydrate is the main product under high temperature curing (e.g., when the hydration is rapid), and hexahydrate is the main product under low temperature curing (e.g., when the hydration is slower). It was also found that the hexahydrate crystals may grow irregularly when the hydration rate is high, thus reducing the strength. In addition, the temperature of the mortar at casting seems to have greater influence on the rate of hydration of MP cements than the temperature of the subsequent curing. Therefore, the use of mortar at 73°F is recommended under all weather conditions.

ACKNOWLEDGMENTS

The research reported, sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, is gratefully acknowledged. The U.S. government is authorized to reproduce and distribute reprints for governmental purposes, notwithstanding any copyright notation thereon. Thanks are also due to M. Penko for performing the physicochemical tests.

REFERENCES

1. S. Popovics, N. Rajendran, and M. Penko. Rapid Hardening Cements for Repair of Concrete (in preparation). *ACI Journal*, 1987.
2. S. Popovics. *Concrete-Making Materials*. Hemisphere Publishing Corp., Washington, D.C., 1979.

Publication of this paper sponsored by Committee on Mechanical Properties of Concrete.