Title no. 84-M9

Rapid Hardening Cements for Repair of Concrete

by Sandor Popovics, N. Rajendran, and Michael Penko

This paper presents the results of an investigation on very rapidly hardening cements. Rapid hardening cements are those that can develop several thousand psi compressive strength within a few hours. Since these cements were developed just recently, very little laboratory and even less practical experience have been obtained with them. Therefore, this paper presents the results of a laboratory investigation on four such cements. These cements are:

1. magnesium phosphate cement for cold and regular weather use (MPC);

2. magnesium phosphate cement for hot weather use (MPH);

3. aluminum phosphate cement (MAP); and

4. regulated set cement (RS).

A combination of both mechanical and physicochemical tests were performed. Several chemical admixtures were also tried with these cements. The tests revealed that the magnesium phosphate base cements exhibit the most rapid strength development.

The presented investigation concentrates on the strength development at early ages. Other important properties of these mixtures (durability, etc.) will be presented in another paper.

Keywords: cement pastes; compressive strength; **concretes;** electron microscopes; heat of hydration; **high early strength cements;** hydration; infrared spectroscopy; magnesium; mortars (material); portland cements; **regulated set cements; repairs; setting time;** strength; x-ray diffraction.

The deterioration of highway pavements, airport runways, bridge decks, marine structures and other concrete structures poses serious problems and requires millions of dollars to renovate them. Part of the problem comes from the fact that repair interrupts the use of structures for a long time if traditional cementing materials are used. This delay can be reduced by using nontraditional, very rapidly hardening cementing material. Such a material should have special properties, such as high early strength, long enough setting time, and bond to old concrete. Therefore, an investigation was performed to identify or develop an inorganic cement that is suitable for rapid repair of concrete structures. The laboratory investigation was performed in two directions:

1. mechanical experiments to determine the technically important properties of these cements; and
2. investigation about the basic nature of rapid hardening cements with or without chemical modifications by using physicochemical methods, such as x-ray diffraction, scanning electron microscopy, and infrared spectroscopy.

Four promising commercially available rapid hardening cements were selected for this research. They are:

1. magnesium phosphate cement for cold and regular weather use (MPC);
2. magnesium phosphate cement for hot weather use (MPH);
3. aluminum phosphate cement (MAP); and
4. regulated set cement (RS).

The description of the tested materials, methods, and the obtained results are presented in the following paragraphs.

RESEARCH SIGNIFICANCE

If some of the very rapidly hardening cements are shown to be suitable for pavement and other concrete repair, the use of these materials would greatly reduce the duration of interruption of the use of the structure under repair. The investigation presented here is a step in this direction.

CEMENTING MATERIALS AND ADMIXTURES

The magnesium phosphate mixtures came in two formulas to cover all weather conditions. One is the "cold" formula, which is recommended for use in cold and regular weather temperatures (MPC); the other is the "hot" formula, for hot-weather conditions (MPH). Both formulas are granular materials consisting of a powdery cementitious material and sand in the proportion of 1:4 by weight. The cementitious materials is a blend of magnesium oxide (MgO) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) with a small amount of fly ash. These react with water rapidly producing strength and heat. The hot-weather formula also contains boric acid as a set retarder. This paper will refer to these two formulas in dry, granular state as MPC mixture and MPH mixture, respectively. When water is added to a mixture, it is called mortar instead of mix-

Received Feb. 13, 1986, and reviewed under Institute publication policies. Pertinent discussion will be published in the November-December 1987 *ACI Materials Journal* if received by Aug. 1, 1987.

Sandor Popovics, FACI, FASCE is a professor of civil engineering at Drexel University, Philadelphia, Pa. He received his PhD from Purdue University and has been engaged in teaching, research, and consulting work for the past 30 years. Dr. Popovics is the author of numerous papers and four books, including the recently published Concrete Making Materials *and* Fundamentals of Portland Cement Concrete. *He is currently a member of ACI Committees 211, Proportioning Mixtures; 222, Corrosion of Metals; 226, Fly Ash, Other Pozzolans, and Slag; 309, Consolidation; and 548, Polymers in Concrete; ASTM Committees C9-1-5, International Relations, and C9-2-1, Statistical Analysis; TRB Committee A2-E3, Mechanical Properties of Concrete; and RILEM Committee 50 FMC, Concrete Proportioning.*

N. Rajendran is an assistant engineer in the New Jersey State Department of Transportation. He received his BS in civil engineering from Madras University, India, and holds two masters degrees, one in Marine Structures from Karnataka Regional Engineering College, India, and the second in structural engineering from the South Dakota School of Mines and Technology. He served as a design engineer at Maskus Port Trust, India, and research specialist at Drexel University, Philadelphia. His research interests include sea erosion control and rapid hardening cements. He has several publications in these areas.

Michael Penko received his BSc degree in physical chemistry from the University of Ljubljana, Yugoslavia, in 1971. After that he worked as a research assistant at the Institut Boris Kidric in the Department for Structural Chemistry. There he took his MSc degree in 1976, majoring in infrared and Raman spectroscopy. He obtained his PhD in materials from Purdue University, Lafayette, Ind., in 1983. In 1984 he worked as a post-doctoral fellow in the civil engineering department at Drexel University, Pa. Presently, he is working at the Institute for Testing and Research in Materials and Structures in Ljubljana, Yugoslavia.

ture. A third term used in this paper is "cement." This is the portion of the mixture that passes a No. 200 (75 μm) sieve. The mixture of cement and water is called "paste." These terms are also applicable to other cements in this paper.

The aluminum-phosphate (MAP) mixture consists of a granular solid and a liquid compound. The solid material is a blend of the powder of magnesium oxide (MgO) with fly ash, sand, and pea gravel in the proportion of 1:1.5:4.0 by weight. The manufacturer does not specify the fly ash content. The liquid component is a 50 percent by weight water solution of $Al(H_2PO_4)_3$. The magnesium oxide reacts chemically with the liquid component producing rapid strength and heat development.

The regulated set (RS) cement, which is a chemically modified portland cement, is a yellowish powdery material with the appearance of portland cement. It does not contain any mineral aggregate. When mortar was prepared, four parts of fine aggregate were added to this cement to simulate the other cement mortars. The main difference between regulated set cement and traditional portland cement is that, in regulated set cement, the C_3A phase is replaced with a calcium haloaluminate having the formula $11CaO \cdot 7Al_2O_3 \cdot CaX_2$ ($C_{11}A_7CaX_2$). This latter is even more reactive than C_3A, and an addition of a sulfate more soluble than gypsum is needed. Calcium sulfate hemihydrate may therefore be added.

Three water reducers conforming to ASTM C 494 were used. A water-dispersible epoxy was also used.

MECHANICAL TEST METHODS AND RESULTS

The mechanical testing concentrated on the early strength developing capabilities as well as on the flow, setting times, and heat liberation during setting at room temperature.

Fresh concrete

The mixer used was a three-speed bench model of approximately ⅙ ft^3 (0.005 m^3) capacity with a stainless steel bowl and planetary action. It complies with ASTM C 305.

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 an admixture was used it was premixed with the mixing water or with the portion of it. Immediately after mixing, the flow test (ASTM C 230-80) with 25 drops, time of setting test (ASTM C 191-77), and temperature change measurements during setting were performed. The results of the temperature and pH measurements, as well as optical microscopic examinations, are not reported here because of space restriction.

A wide variety of water-reducing admixtures were added to all four cements. It was established that none of the tested plasticizers were effective with MPC and MPH cements or with the MAP cement. They were, however, effective with RS cement.

Some of the results obtained on fresh mortars are presented in Tables 1 through 5.

Hardened concrete

For the determination of compressive strength, 27 mix series were made. Nine 2-in. (50-mm) cubes were prepared from each series according to ASTM C 109. The specimens were removed from the mold 40 to 50 min after mixing and air cured at 73.4 F ± 3 F (23 C ± 1.7 C) and 50 percent relative humidity until the break. Compressive tests were run on specimens at the age of 1 hr, 3 hr, and 24 hr again according to ASTM C 109. Three specimens were tested for each age. The strength results are given in Tables 1 through 3.

In another series, 22 mixes were made according to ASTM C 192. Each mix contained 21 2 x 4-in. (50 x 100-mm) cylindrical specimens. They were stripped in 40 to 50 min after mixing and kept at room temperature and 50 percent relative humidity for 24 hours, i.e., 73.4 F ± 3 F (23 C ± 1.7 C). Then they were kept in a moist room (73F and 100 percent relative humidity) until the break. These specimens were tested at the age of 1 hr, 3 hr, 24 hr, 7 days, 28 days, and 90 days and a few tests were run at 465 days. Three specimens were tested for each age. These test results are presented in Tables 4 and 5.

ANALYSIS AND DISCUSSION OF MECHANICAL TEST RESULTS

Flow

The relationship between flow and water content for the MPC and MPH mortars is shown in Fig. 1. The flow increases with an increase in water content as expected, but the rate decreases at higher water contents for both mortars.

Table 1 — Properties of magnesium phosphate (MP) mortars

Mix designation		Water,* percent	Flow, percent	Setting time		Compressive strength, psi[†]		
				Initial	Final	1 hr	3 hr	24 hr
MPC	SC1	10.0	146	9 min 45 sec	13 min 30 sec	5640	7050	7110
	SC2	8.0	111	9 min	11 min 45 sec	6100	11060	12130
	SC3	5.5	28	6 min 30 sec	8 min 30 sec	10140	11690	11940
MPH	SH1	10.0	150	40 min	47 min	‡	1670	6540
	SH2	8.0	109	49 min	60 min	‡	1930	9080
	SH3	5.5	20	30 min 30 sec	36 min 30 sec	‡	3570	8900
50 percent MPC	SCH1	10.0	149	15 min	18 min 30 sec	3150	6350	7420
+	SCH2	8.0	102	29 min 30 sec	33 min 30 sec	‡	4710	10130
50 percent MPH	SCH3	5.5	28	18 min	20 min 15 sec	2640	8180	11810
MPC	SCB1	10.0	150	17 min	21 min	2790	5250	5920
+	SCB2	8.0	106	19 min	21 min 30 sec	1090	5040	8000
0.34 percent borax	SCB3	5.5	27	17 min 45 sec	22 min	3100	10690	11590
MPC + 2 percent Plastocrete 161R	SS4	7.0	107	13 min	16 min 30 sec	2890	3810	
MPC + 16.8 percent Nicklepoxy	SE4	3.75	150	11 min 15 sec	20 min	780	1580	2110

*Percent by weight of the dry mixture.
[†]1 psi = 0.006895 MPa.
[‡]1 hr test could not be performed because specimens were too weak to be removed from the mold.

Table 2—Properties of aluminum phosphate (MAP) mortars and concretes

Mix designation	Water + AlP liquid,* percent	Flow, percent	Setting time		Compressive strength, psi[†]		
			Initial	Final	1 hr	3 hr	24 hr
AL1[‡]	0 + 15.8	77	23 min 15 sec	26 min	430	1930	7240
AL2[‡]	0 + 16.5	93	22 min	25 min	220	720	5690
AL3[‡]	0 + 18.0	91	14 min 15 sec	19 min	330	2080	6540
AL4[‡]	0.76 + 16.5	97	13 min 30 sec	16 min 30 sec	610	3140	5410
AL5[‡]	1.52 + 16.5	111	17 min	19 min 45 sec	370	3320	5325
ALC1[§]	0 + 12.4	51	19 min	22 min	400	1830	6980
ALC2[§]	0 + 12.4	45	14 min	19 min	560	2520	6930
ALC3[§]	0.76 + 11.6	53	14 min	18 min	340	2340	3350
ALC4[§]	1.36 + 11.6	73	19 min	30 min	310	1360	4540

*Percent by weight of the dry mixture. The liquid contains 50 percent water solution of $Al(H_2PO_4)_3$.
[†]1 psi = 0.006895 MPa.
[‡]Aggregate retained on sieve #4 was removed.
[§]Gravel particles retained on sieve #4 and passing ⅜ in. were removed from the mixture provided by the manufacturer and replaced by crushed stone particles of the same size.

The figure also shows that MPH mortars produce larger flow than MPC mortars under identical conditions. This is attributed to the presence of boric acid in the MPH mixture. A similar trend was observed when a small quantity of borax was added to the MPC mixture. It is not surprising, then, that the flows for the

Table 3 — Properties of regulated cement (RS) mortars

Mix designation		Water,* percent	Flow, percent	Setting time		Compressive strength, psi†		
				Initial	Final	1 hr	3 hr	24 hr
RS cement mixture	JW1	10.0	5	6 min 30 sec	14 min	1190	2600	4420
RS cement mixture	JW2	13.6	76	12 min 45 sec	26 min	450	1560	2760
RS cement mixture +0.6 percent Mighty 150	JW3	13.0	140	24 min	41 min	210	1680	2710
RS cement mixture +0.6 percent Pozzolith 200 XR	JW4	13.0	137	73 min		‡	20	1780

*Percent by weight of the dry mixture.
†1 psi = 0.006895 MPa.
‡One-hr test could not be performed because the specimens were too weak to be removed from the mold.

MPC mixture blended with the MPH mixture, and MPC mixture blended with borax are between the flow of MPC mortar and that of the MPH mortar (Table 1).

The data from Tables 2 and 3 also show that the MPA and RS mortars exhibit less flow at the same water content than the comparable MPC and MPH mortars. Further, it was observed during mixing that the MAP mortars are stickier than the other mortars. It can also be seen from Table 2 that the 100 percent flow was achieved only once by using 18 percent liquid in MAP mixture.

Efforts were made to improve the fluidity of mortars by the use of plasticizers and superplasticizers. The obtained test results show, however, that these admixtures worked well only with the RS cement and portland cement.

Setting time

The initial and final setting times were run in accordance with ASTM C 191 using the Vicat apparatus and the needle. These setting times for MPC and MPH mortars are shown in Fig. 2. It can be seen that the initial setting times of the MPC formula are regularly less than 10 min and the time of final setting is less than 15 min at room temperature. These setting times are too short for traditional construction techniques so the manufacturer came out with another formula, the MPH mixture, which has much longer times of setting. It can also be seen that the 50-50 blend of MPC and MPH formulas, as well as cold formula with borax, have in-between setting times.

Another noticeable trend is that the setting times decrease with decreasing water content more or less in the same way as the setting time of portland cement. The setting times of the MAP concretes and MAP mortars are between those of comparable MPC and MPH mortars. The same statement is valid for mortars made with RS cement except for mixture JW 3 and 4 where plasticizing admixtures were used. Here the times of setting are very long but, unfortunately, the strengths are also low.

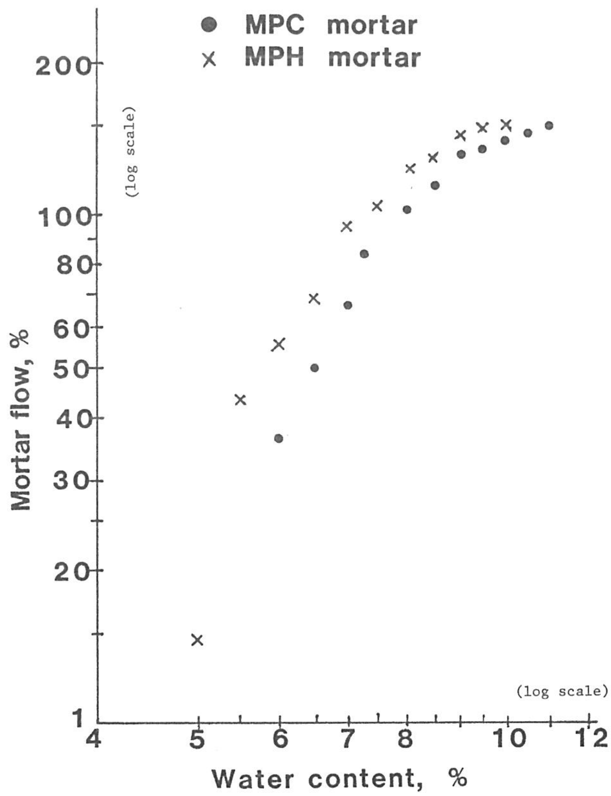

Fig. 1 — Standard flow of MP mortars as a function of water content

Considering the shortness of setting times of the mortars that have high enough one-hr strength, it is obvious that a special, simple, but rapid construction method is needed when magnesium phosphate cement mortars and concretes are used. One such method occurs when the mortar is used in a fluid state instead of the usual plastic consistency. Not only would this somewhat lengthen the setting time but it would also speed up the construction by the elimination of the need for compaction. For this reason, the work presented here has focused on mortars of fluid consis-

Table 4 — Properties of MPC mortars as a function of the water content*

Mix designation	Water,† percent	Flow, percent	Compressive strength, psi‡					
			1 hr	3 hr	1 day	7 days	28 days	90 days
ASC1	6.0	36	7320	9150	8410	8000	8260	9280
ASC2	6.5	50	7290	8700	8560	8240	7500	8550
ASC3	7.0	66	7550	8210	8770	8400	7860	8180
ASC4	7.27	84	7870	8160	8740	8340	8320	8310
ASC5	8.0	103	6240	6150	8090	7710	6580	6820
ASC6	8.5	115	5850	5620	6950	5920	5540	5730
ASC7	9.0	131	4660	5110	5600	5470	4870	6050
ASC8	9.5	134	4510	4500	4810	4630	4520	6190
ASC9	10.0	141	3910	3960	4670	4140	4160	6400
ASC10	10.5	145	2610	2800	3280	3330	3220	
ASC11	11.0	150	2490	2840	3230	3000	2940	4580

*The strength specimens were 2 x 4 in. (50 x 101 mm) cylinders.
†Percent by weight of the dry mixture.
‡1 psi = 0.006895 MPa.

Table 5 — Properties of MPH mortars as a function of the water content*

Mix designation	Water,† percent	Flow, percent	Compressive strength, psi‡						
			1 hr	3 hr	1 day	7 days	28 days	90 days	465 days
ASH1	5.0	15	§	3320	6880	7910	8210	9530	8090
ASH2	5.5	43	1460	4660	7800	8470	7640	8340	
ASH3	6.0	56	§	2390	6570	7000	7590	8130	6730
ASH4	6.5	69	§	3050	8010	8100	8820	8300	7390
ASH5	7.0	95	§	3010	7610	7460	7470	8020	7540
ASH6	7.5	103	§	3840	7090	7980	8090	8240	
ASH7	8.0	124	§	2500	5600	6400	6690	6900	
ASH8	8.5	127	§	4650	7920	7660	7770	8180	7830
ASH9	9	143	§	2360	4950	4990	5510	6370	
ASH10	9.5	148	§	2140	3920	4860	5410	6490	
ASH11	10.0	150	§	1640	3440	3820	4110	5460	5890

*The strength specimens were 2 x 4 in. (50 x 101 mm) cylinders.
†Percent by weight of the dry mixture.
‡1 psi = 0.006895 MPa.
§One hour tests could not be performed because specimens were too weak to remove from the mold.

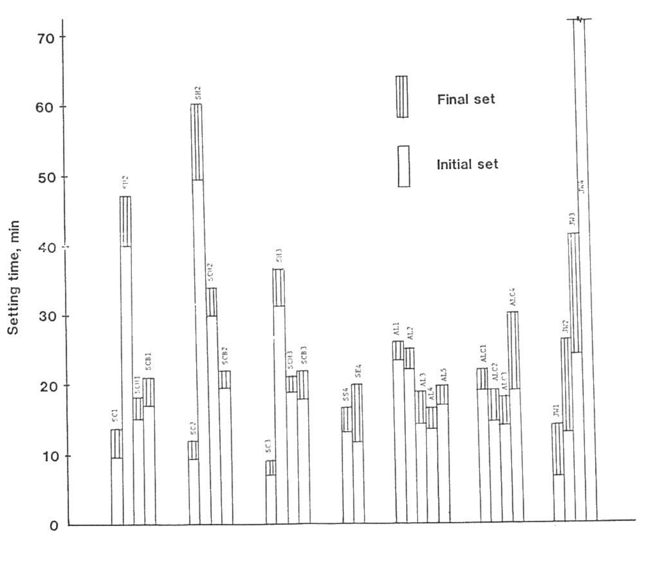

Fig. 2 — Initial and final setting times of tested mixtures

tency, that is, when the standard flow is approximately 150 percent.

Compressive strength

Compressive strength versus water content for magnesium phosphate cement mortars at 1, 3, and 24 hr is presented in Table 1. It can be seen from the table that, for all cases, the MPC mortar exhibits higher strengths than the MPH mortars up to the first 24 hr. Further, high early strength of about 10,000 psi was achieved within an hour with low water content. The general trend is that the strengths of MPC and MPH mortars decrease with an increase in water content, that is, except the strength at medium water content (8 percent) at 24 hr.

Borax blended with MPC, and MPH blended with MPC, exhibit different behavior; that is, the strength is more at high and low water contents than at medium water content at the age of 1 and 3 hr, but at the age of

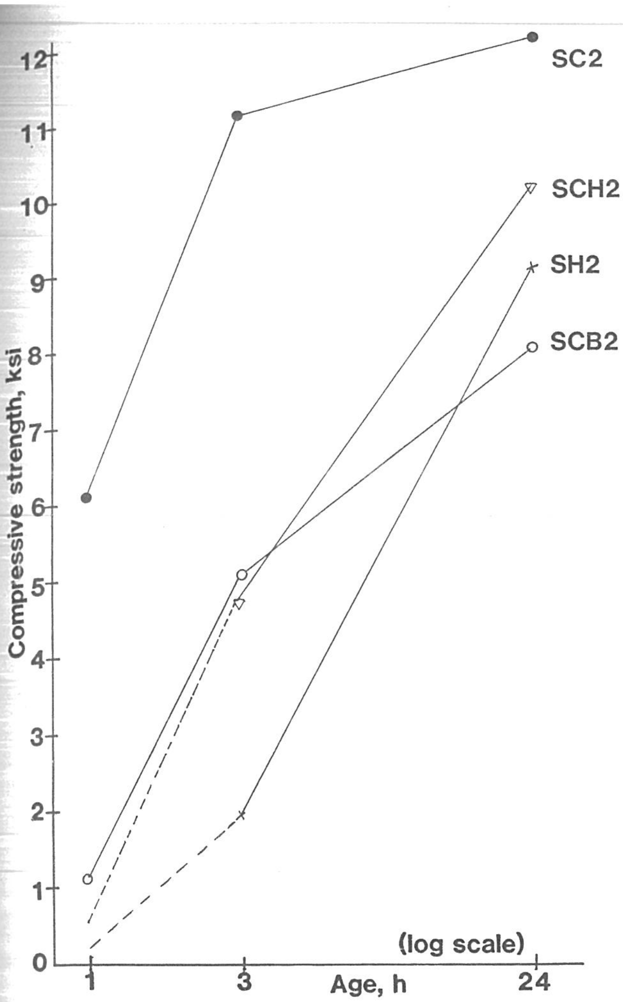

Fig. 3 — Relationship between compressive strength and early age of MP mortars with medium (8 percent) water content

24 hr the strength decreases with an increase in water content. The reason for these discrepancies is not clear at present.

In general, higher than 2000 psi strength was achieved within an hour for almost all water contents with magnesium phosphate cements.

The relationships between cube strength and early age (up to 24 hr) of MPC, MPH, and RS mortars are presented in Table 1 through 3. It is apparent that the strength increases with an increase in age for all mortars similarly to conventional portland cements, although the rate of strength development is greater. For almost all cases, the strength of MPC mortar exhibits higher early strength than the other mortars. It can be seen from Fig. 3 that there is a sudden increase in strength for MPC mortar (SC2) up to the age of 3 hr, after which there is not much appreciable rise in strength. In contrast, the strength of MPH mortar (SH2) starts increasing rapidly after the age 3 hr.

It is quite apparent that the strength of the blend of MPC with MPH formula falls between these two mortar strengths as expected. A similar phenomenon was also observed when a small quantity of borax was mixed with cold mortar.

Further, it can be seen from Tables 2 and 3 that the MAP concrete and mortar and also RS mortar produce lesser strengths at the age of one hour. The strengths start gaining only after 3 hr. However, these strengths are less than those of the MPC and MPH mortars with comparable water contents.

The relationship between cylinder strength and age of MP mortars after wet curing up to 90 days is shown in Tables 4 and 5. It can be seen that the strengths of MPC mortars increase up to 7 days, then there is a decreasing strength reduction at the age of 28 days, after which they start increasing again. No such strength reduction was observed with wet cured MPH mortars. Nevertheless, according to the manufacturer, wet curing should be considered as potentially harmful for these mixtures. The mechanism of the strength-decreasing effect of moisture, when there is any, in MP mixtures, is not known for sure. A hypothesis is that the presence of moisture helps one of the hydration products, namely, the monohydrate, recrystallize as hexahydrate, which in turn can produce strength reduction similar to the recrystallization of high-alumina cement paste under wet conditions.

PHYSICOCHEMICAL EXAMINATIONS

Parallel to the mechanical tests, physicochemical examinations were also performed. The following tests were applied for the study of composition, morphology, and hydration process: optical microscopy, pH measurements, x-ray diffraction, scanning electron microscopy (SEM), and infrared spectroscopy (IR).

X-ray diffraction

Magnesium phosphate cements and pastes — The x-ray diffractometer was used with CA-7 diffraction tube. Copper K_{α} radiation was applied and all the patterns were run at the same settings of the diffractometer.

The MPC and MPH *cements* yield rather similar x-ray patterns (Fig. 4 and 5). Both are composed of two crystalline ingredients, namely MgO and $NH_4H_2PO_4$. In the x-ray pattern of the MPH cement, an additional small peak is observed at $2\Theta = 27$ deg. This peak belongs to quartz.

Four different *pastes* were prepared with two different water-cement ratios, namely at 0.525 and 0.375 by weight. These two ratios correspond to the water-to-solid ratios 0.1 and 0.075 when the sand is not sieved out. The cements were the following:

1. MPC cement;
2. MPH cement;
3. MPC cement + 1.7 percent borax; and
4. 50 percent MPC cement + 50 percent MPH cement.

Mixing was performed in plastic vials that were sealed with a very tight lid and stored at room temperature. X-ray patterns were taken at 1 hr. As far as the hydrated MP pastes are concerned, it was seen from the x-ray patterns that there are no ammonium dihydrogen phosphate peaks present any more after 1 hr, or even

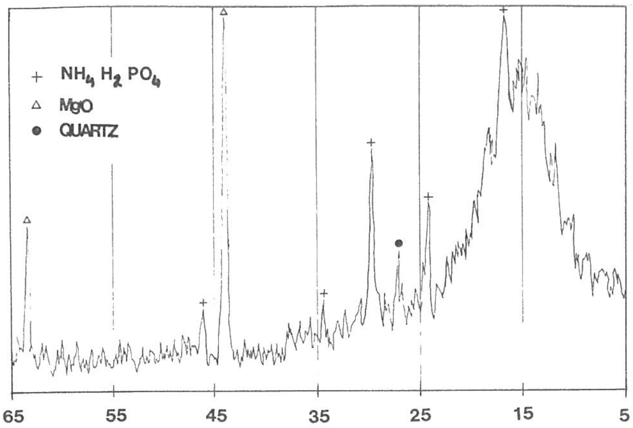

Fig. 4 — X-ray diffraction pattern of MPH cement passing sieve No. 200

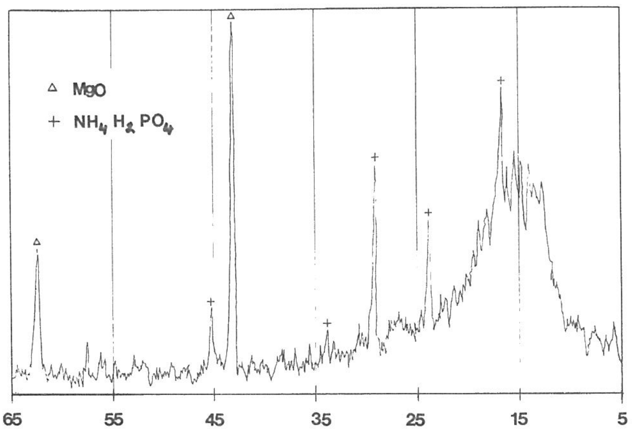

Fig. 5 — X-ray diffraction pattern of MPC cement passing sieve No. 200

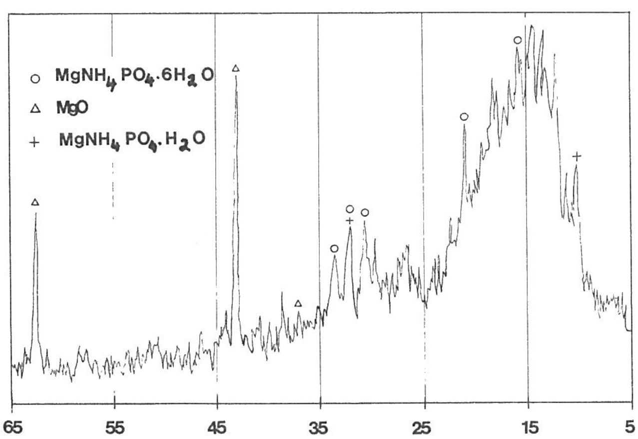

Fig. 6 — X-ray diffraction pattern of MPH paste of low water content (w/c = 0.375 by weight) at 1 hr

20 min of hydration. Instead, some new peaks have shown up. This indicates that the $NH_4H_2PO_4$ is dissolved and reacted quickly. This is true for all four examined systems at both water-cement ratios.

The two major products of this early hydration have been identified as ammonium magnesium phosphate

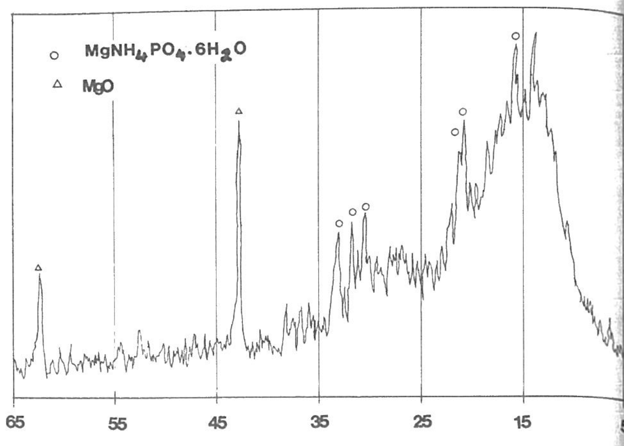

Fig. 7 — X-ray diffraction pattern of MPH paste of low water content (w/c = 0.375 by weight) at 7 days

hexahydrate ($NH_4MgPO_4 \cdot 6H_2O$) and ammonium magnesium phosphate monohydrate ($NH_4MgPO_4 \cdot H_2O$). They are referred to as hexahydrate and monohydrate, or hexa and mono, respectively.

Both hydrates can be formed at the same time during hydration but one of them is usually dominating. The following factors favor the increase of the amount of hexahydrate:

1. MPH cement;
2. High water-cement ratio;
3. Long hydration time.

Therefore, the following factors increase the amount of monohydrate:

1. MPC cement;
2. Low water-cement ratio;
3. Short hydration time.

The most important factor seems to be the choice of cement for the mono-hexa ratio. This comes as a surprise because the x-ray patterns of the two dry unhydrated MP cement formulas do not differ significantly and the chemical compositions also seem to be the same. A reasonable explanation is the smaller particle size of MgO in the two mixtures. Changes in the x-ray patterns after one or more days of hydration are slow but definite. For instance, the amount of monohydrate decreases with time and, in this case, after 7 days totally disappears (Fig. 6 and 7). The hypothesis is that monohydrate takes up some additional water with time and recrystallizes into hexahydrate.

When the two cements are mixed in a 1:1 ratio, both hydrates are formed at a low water-cement ratio and no monohydrate is observed (or just a little) at high water-cement ratio.

An addition of borax in the quantity of 1.7 percent by weight to MPC cement affects the physical properties of the mortar; nevertheless, the effect does not show up in the x-ray patterns.

MAP and RS cements — The MgO peak in the x-ray diffraction pattern of MAP cement is much less intensive than that in the magnesium phosphate cements.

X-ray pattern of RS cement is similar to the pattern of portland cement Type III. The difference appears as

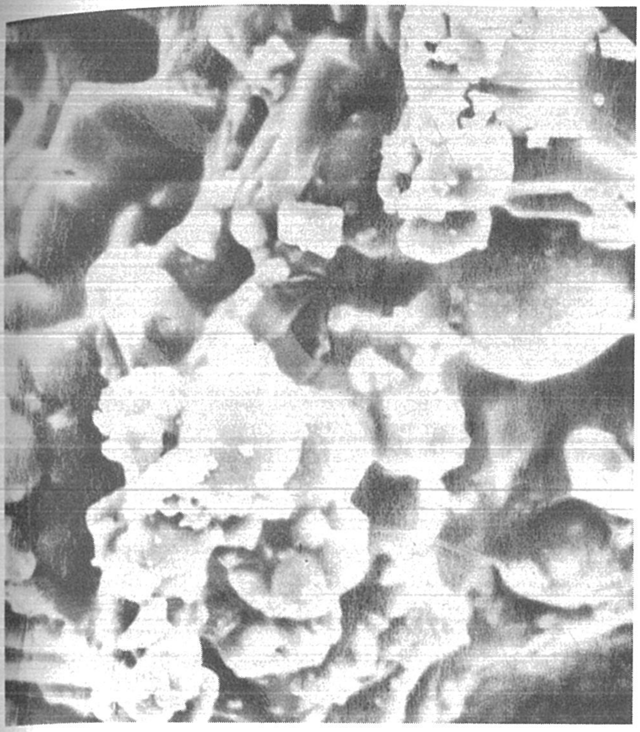

Fig. 8 — SEM picture of MPH paste of high water content (w/c = 0.525 by weight) at 3 days; magnification: 2000x

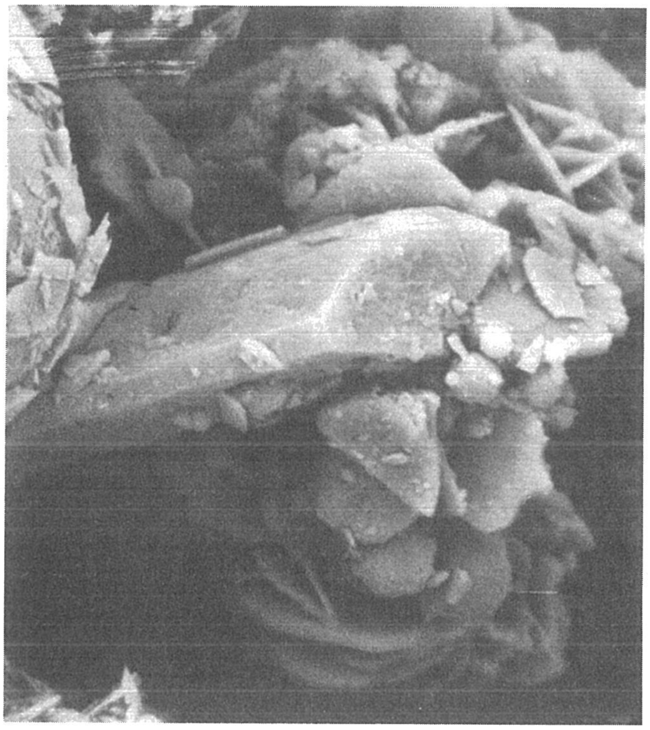

Fig. 9 — SEM picture of MPC paste of high water content (w/c = 0.525 by weight) at 3 days; magnification: 2000x

few additional diffraction peaks that belong to calcium sulfate (anhydrite) and $C_{11}A_7 \cdot CaF_2$. The latter component is not present in ordinary portland cements.

As the hydration proceeds, the diffraction peaks of anhydrite and $C_{11}A_7 \cdot CaF_2$ become weaker. Nevertheless, they are still strong after 3 hr of hydration. Even after 3 days of hydration there is still some unhydrated $C_{11}A_7CaF_2$. This explains why RS cement did not develop as high early strengths as the other cements tested.

Scanning electron microscopy (SEM)

The SEM investigation was performed with 2000 and 5000 magnifications of the following 3 day old cement pastes:

MPC cement	w/c = 0.525
MPH cement	w/c = 0.525
MPC + 1.7 percent borax	w/c = 0.525
MPC (50 percent) + MPH (50 percent)	w/c = 0.525

It was observed that the samples morphologically differ, each one having some characteristics of its own. For example, there is a noticeable decrease in crystallinity in MPH paste as compared to MPC paste (Fig. 8 and 9). In the latter, extremely well developed crystal forms are observed.

It has been established that the well-developed orthorombic single crystal (Fig. 9) is struvite ($NH_4MgPO_4 \cdot 6H_2O$).

MPH paste is of lower crystallinity. Occasional crystals are identified as $NH_4MgPO_4 \cdot 6H_20$. There are many in this paste as expected from the corresponding X-ray patterns. It is interesting to mention that they grow in a little different way than in the MPC paste.

As discussed earlier, an addition of borax to the MPC formula does not change the x-ray patterns considerably; however, it has quite an influence on the morphological structure. The same crystal types are still observed as in the sample without borax, but the crystals are one-half to one-third smaller in size . In addition, a new poorly crystallized material is formed that seems to glue the rest of the crystals together.

SEM examination of paste made of MPC (50 percent) and MPH (50 percent) reveals a combination of morphological characteristics of the two.

To show the differences in morphology between MP and portland cement, Fig. 10 shows a SEM photograph of a 1-day old portland cement Type III paste with w/c = 0.35. The magnification is 2000x. The difference in morphology is quite obvious. For instance, the chosen area shows a plethora of needle-like crystals in the portland cement paste missing in the MP pastes. These crystals are ettringite and are very characteristic for early strength portland cements rich in aluminate and gypsum.

Infrared spectroscopy (IR)

An infracord spectrophotometer was used. Hardened cement pastes were thoroughly ground with a small addition of mineral oil into a fine paste that was placed between two NaC1 plates. The plates were then pressed together to get the paste into a thin film. These specimens were tested when they were 7 days old. The same specimens were also used in x-ray diffraction ex-

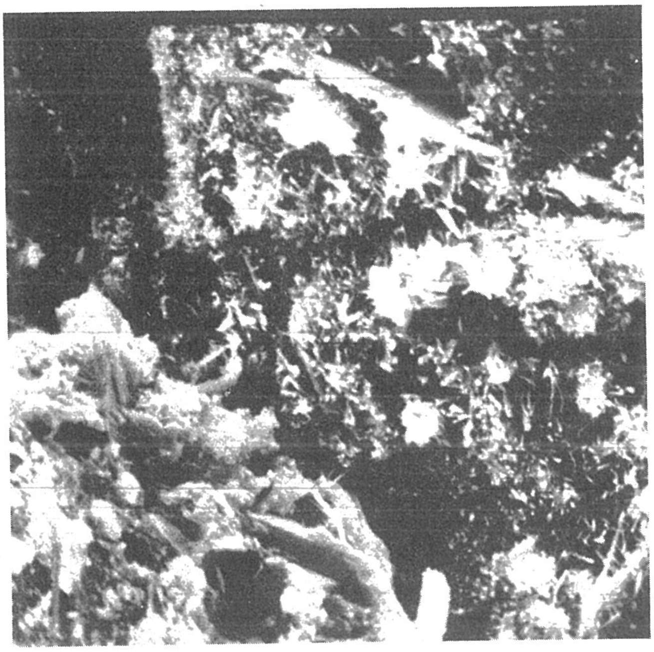

Fig. 10 — *SEM picture of portland cement Type III paste of water-cement ratio = 0.35 at 1 day; magnification: 2000x*

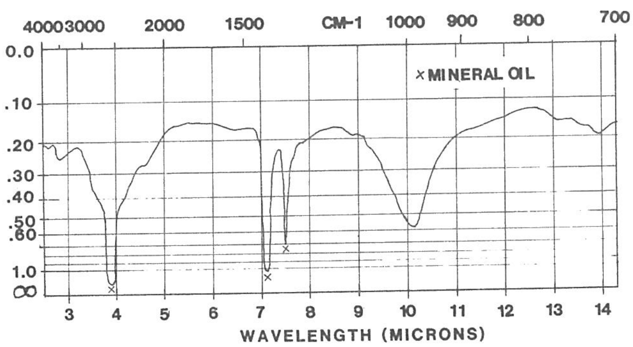

Fig. 11 — *Infrared absorption spectrum of MPH paste of high water content (w/c = 0.525 by weight) at 7 days*

amination described earlier. The following cements were used with w/c = 0.525 by weight: MPC, MPH, MPC + 1.7 borax, and 50 percent MPC + 50 percent MPH.

The infrared spectra obtained show that similar problems are encountered with the spectra of these pastes as with portland cements. The resolution is very low and therefore not much information is provided. Nevertheless, they seem to support the x-ray pattern interpretation. For instance, comparing the infrared spectrum of MPH paste with the infrared spectrums of MPC paste, it is obvious that the broad absorption band with its maximum around 1000 cm^{-1} for the former sample is symmetrical and for the latter is asymmetrical (Fig. 11 and 12). The symmetrical band implies that only one hydration product is formed. The asymmetrical band with a shoulder implies that at least two hydration products are formed. The main peak is assigned to hexahydrate and the shoulder to monohyrate of ammonium magnesium phosphate. The paste made

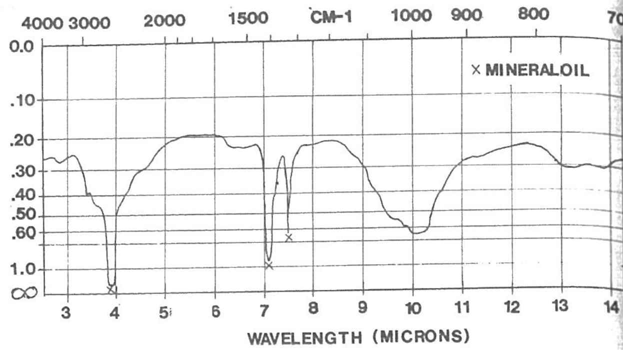

Fig. 12 — *Infrared absorption spectrum of MPC paste of high water content (w/c = 0.525 by weight) at 7 days*

of 50 percent MPC and 50 percent MPH cements also shows asymmetrical band in its infrared spectrum indicating two hydration products. An addition of borax does not change the infrared spectrum of MPC paste.

COMPARISON OF THE TESTED MATERIALS

Based on the results obtained up to this point of testing, the technical advantages and disadvantages of each material under investigation can be summarized as follows:

1. The same water content under identical conditions produces the highest fluidity in MPH formula, and the lowest fluidity in the MAP mixtures (Table 1).

2. The MPC formula has the shortest setting times: initial set is less than 10 min; final set is less than 15 min at room temperature. The MPH formula has the longest ones. The setting times of the other tested mixtures fall between these two extremes (Fig. 2).

3. The highest compressive strengths at the ages of 1 and 3 hr are developed by MPC mortar. The measured 1-hr strength, for instance, was more than 5000 psi with 10 percent water (flowing consistency) at room temperature, which is perhaps unnecessarily high strength for repair. Another advantage is that this material does not require wet curing. On the other hand, its setting times are the shortest, initial setting being less than 10 min at room temperature and probably much less at elevated temperatures.

4. MPH mortar has longer setting times and develops less heat due to the presence of boric acid. However, it produces lower strengths at room temperature at early and late ages. It is very likely that at elevated temperatures the early strengths as well as setting and heat development will be similar to those of the cold-weather formula at room temperature.

5. The modified MPC mortars, that is, the 50-50 blends of cold-weather-hot-weather formulas, as well as the MPC formula with borax addition, seem to combine the advantages of the two individual formulas.

6. The MAP mortars can reach compressive strengths in excess of 3000 psi at the age of 3 hr, despite the fact that their 1-hr strengths are quite low. The setting times are similar to those of the modified MPC mortars.

7. The RS cement mortars can develop about 1500 psi strengths at the age of 3 hr, and considerably less in 1 hr at room temperature. The setting times are similar to those of the MAP mortars.

CONCLUSIONS

The tests revealed that the magnesium phosphate base cements, that is, the MPC and MPH formulas, develop compressive strengths the most rapidly among the tested cements. For instance, the MPC formula can produce compressive strength in excess of 10,000 psi at the age of 1 hr with low water content. Even with high water content, enough to produce flowing consistency, its 1-hour strengths are regularly over 2000 psi. On the other hand, its setting time is short. The early age strength of MPH formula is lower but still considerable and its setting time is somewhat longer. The other two tested cements also develop strengths much faster than Type III cement, even with an accelerator.

Physicochemical investigations provided limited information about the nature of the hydration processes of these cements. For instance, the main hydration products of the MP cements are ammonium magnesium phosphate monohydrate ($NH_4MgPO_4 \cdot H_2O$) and ammonium magnesium phosphate hexahydrate ($NH_4MgPO_4 \cdot 6H_2O$). It reveals that monohydrate (mono) is the main product when the hydration is rapid, and hexahydrate (hexa) is the main product when the hydration is slow.

There are quite a few other properties besides compressive strength that are needed for a cement to be suitable for repair. These are: satisfactory behavior under various temperature and humidity conditions; durability; bond to old concrete; volume stability; frost resistance; chemical resistance including chloride solutions; and others. Investigation of some of these properties is in progress and the results will be presented in another paper.

ACKNOWLEDGMENTS

The authors gratefully acknowledge that the research reported was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR 83-0245. The U.S. Government is authorized to reproduce and distribute reprints for governmental purposes, notwithstanding any copyright notation thereon.