The Influence of Curing Conditions on the Physical and Mechanical Properties of Magnesia Phosphate Cements

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The paper brings information on the influence of curing conditions such as humidity, variable temperature and chemical solutions, on the compressive strength and weight variation of the magnesia phosphate binding materials, obtained from magnesite, mono-ammonia phosphate, borax and sand having a granulation ranging between 0.1-1 mm, with or without fly ash addition. The XRD and SEM–EDX analysis were made for obtaining information concerning the reaction products formed in phosphate magnesia binding materials cured in conditions of variable humidity.

Key words: magnesia phosphate binder, compressive strength, durability, struvite

The magnesia phosphate binders, made from sintered magnesia and a solution of phosphate salt, harden quickly in air as result of the acid–base reaction. They represent the principal component of certain composite materials, which can be used to carry out rapid repairs to certain works that can be put out of service only for short periods of time [1–11]. Such repair works may involve roads and motorways, runways, industrial floors etc. However, there is little information regarding the durability of such materials [6, 8–10]. Our paper brings some data concerning the durability of some magnesia phosphate mortars cured in variable humidity and temperature conditions and also into aggressive solutions of hydrochloric acid, lactic acid or natrium sulphate.

Experimental Part

To obtain the magnesia phosphate mortars the following materials were used:

– magnesia, from the Serbian Republic, sintered at 1550°C, containing approx. 96% MgO, ground up to a fineness of 2860 cm^2/g Blaine specific surface area;

– mono ammonia phosphate, chemically grade, $NH_4H_2PO_4$;

– fly ash, ground up to a fineness of around 7200 cm^2/g Blaine specific surface area; it was employed as a substitute for magnesia du to costs and colour of the hardened binding materials (the magnesia phosphate binders have a lighter colour than Portland cement);

– borax, to regulate the setting time and the rate of hardening of the binders;

– fine quartz sand, with the particle size between 0.1 mm and 1 mm.

The magnesia to phosphate salt ratio in the magnesia phosphate binders was 3:1. The mortars included also 4% borax which was proportioned related to the amount of magnesia phosphate binder.

Table 1
COMPOSITION OF THE OBTAINED MORTARS

Mortar symbols	Binder composition (%)			Binder / aggregate ratio	Water/ solid
	MgO	$NH_4H_2PO_4$	Fly ash		
M1	75	25	-	1/1	0.10
M1-C10	67.5	25	7.5	1/1	0.10

Table 1 presents the composition of the mortars.

The magnesia phosphate mortars were obtained by adding water to the previously well-mixed solid constituents—sintered magnesia, mono ammonia phosphate, sand and fly ash—, followed by a supplementary mixing. In order to carry out the mechanical tests, 15 x 15 x 60 mm specimens were prepared and compacted on the jolting table. The specimens were demoulded 30 min after casting and cured for 7 days in air at 20 ±2°C. Then, the specimens were cured for 28, 60 and 90 days in various conditions, as follows:

–in the laboratory atmosphere with a relative humidity of approx. 60%. These specimens were taken as reference specimens;

–in a wet air container with a relative humidity of approx. 92%;

–immersed in potable water;

–immersed in a 0.2 m solution of hydrochloric acid (pH = 1.5);

–immersed in a 5% solution of lactic acid (*p*H = 2.5);

–immersed in a 5% solution of natrium sulphate (*p*H = 6.4).

A series of specimens underwent 60 cycles of temperature variation, where one cycle consisted in keeping the specimens for 4 h at –10°C and 4 h in an oven at 40°C; abeing aftewards kept for 16 h at 20°C in the laboratory.

The influence of the thermal strain was appreciated by the changes in the compressive strength as calculated with equation (1).

$$\Delta R = \frac{Ri - Rs}{Ri} \times 100 , \qquad (1)$$

where:

Ri is the compressive strength of the reference specimens cured at 20°C in the laboratory atmosphere;

Rs - the compressive strength of the specimens after *n* cycles of positive/negative temperatures.

The durability of these magnesia phosphate mortars under conditions of variable humidity and aggressive solutions was determined by:

–visual examination of the specimens;

–determination of the compressive strength of the specimens and calculation of the relative modifications in the compressive strength of the specimens according to equation (2).

$$\Delta R = \frac{R_e - R_a}{R_e} \times 100 , \qquad (2)$$

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where:

R_e is the compressive strength of the reference specimens cured for a period of time *t* in the laboratory atmosphere;

R_a - the compressive strength of the specimens cured for a period of time *t* in aggressive environment.

– determination of the weight loss in relation to the weight of the specimens hardened 7 days in air and calculated with the equation (3).

$$\Delta m = \frac{m_0 - m_t}{m_0} \times 100, \qquad (3)$$

where :

m_0 is the initial weight of the specimens (from each mortar composition) hardened for 7 days in air;

m_t - the weight of the specimens (from each mortar composition) kept for a period of time *t* in the already mentioned curing conditions.

In order to obtain information regarding the formation and evolution of the reaction products under conditions of variable humidity, XRD analysis was conducted on samples cured for 28 and 60 days into variable humidity conditions. In addition, SEM/EDX analysis was carried out on selected samples.

Results and Discussion

The behaviour of the magnesia phosphate mortars depends significantly on one hand, on the curing conditions of the specimens and, on the other hand, on their composition.

Table 2

COMPRESSIVE STRENGTH OF THE COMPOSITE MORTARS HARDENED FOR 7 DAYS IN AIR

Mortar symbols	Compresive strenght (MPa) after:				
	1hr	3hrs	24hrs	72hrs	168hrs
M1	20.0	21.7	31.5	36.8	44.3
M1-C10	15.7	20.7	31.4	35.4	42.0

The compressive strength modifications

Table 2 presents the compressive strength of two mortars hardened for up to 7 days in air.

In general, the two mortars show close values for the 7-day compressive strength, except for the first hardening hour when the mortar without fly ash (M1) had a slightly higher compressive strength value. This is justified by the higher content of MgO that is essential for the rapid development of the compressive strength (by its reaction with the phosphate salt solution). Figures 1 and 2 illustrate the evolution of the compressive strengths after the curing in environments with variable humidity. The figures reveal that the 90-day compressive strength of the specimens cured in air with a relative humidity of 60% increases slightly as compared with the 7-day compressive strength of the same specimens. The 90-days compressive strength is obviously higher under conditions of curing in air than under wet atmosphere.

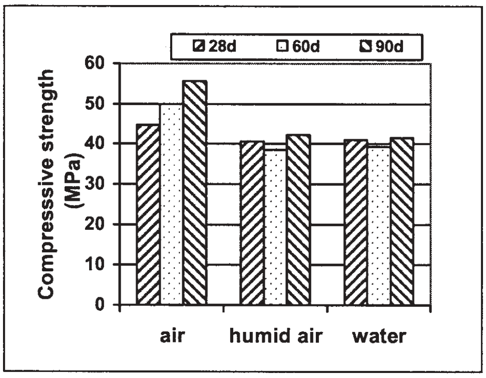

Fig. 1. Compressive strength of mortar M1 related to the humidity of the curing environment

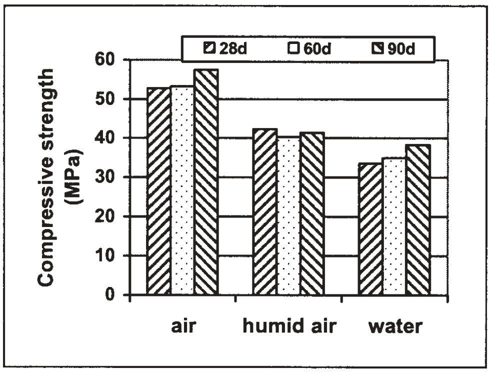

Fig. 2. Compressive strength of mortar M1-C10 related to the humidity of the curing environment

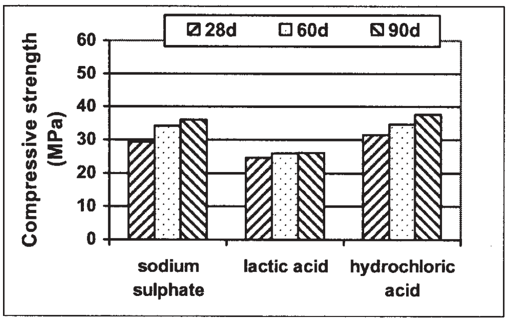

Fig. 3. Compressive strength of mortar M1 samples cured in acid solutions

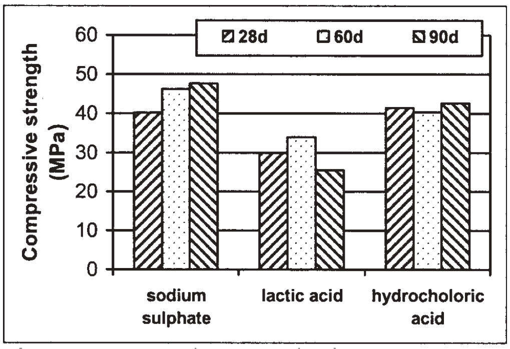

Fig. 4. Compressive strength of mortar M1–C10 cured in acid solutions

Although the mortar M1 had 28-day compressive strength value of the reference specimen higher than that of mortar M1–C10, it presents a clear decrease of the compressive strength in conditions of curing in wet air and especially in water, as shown in figure 1. The compressive strength decreases of the mortar versus the reference specimen (cured in air) are around 20–28% in air with a relative humidity (R.H) of 92% and depending on the curing time, of 34–36% for the curing in water.

For the mortar sample containing 10% fly ash (M1–C10) cured in 92% R.H. air and in water respectively, the compressive strength decreases were obviously smaller (Figure 2). At 92% R.H. or in water, the 90-day compressive

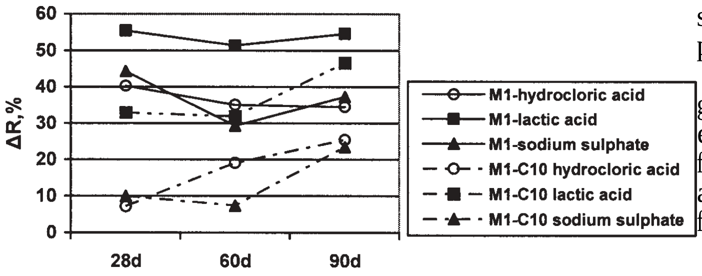

Fig. 5. The compressive strength loss of the mortars in time in relation to the acid curing solution

strength decreases were of 25% as compared with the reference specimen.

Figures 3 and 4 reveal that the curing of magnesia phosphate mortar samples in acid solutions determine decreases of the compressive strength. The compressive strength values of the samples cured in 0.2 m solution of hydrochloric acid, 5% solution of lactic acid and 5% solution of natrium sulphate are lower for both mortar compositions as compared with the samples cured in air. The strength decreases were of approximately 30–55% for the mortar M1, higher than those of the mortar M1–C10 of approximately 6–45% (fig. 5).

The most severe compressive strength decreases, of 45–55%, were found for the mortar samples cured in lactic acid solution with a more pronounced decrease in the case of mortar M1 without fly ash.

In time, the compressive strength decreases for the specimens cured in acid solutions became more noticeable to a certain extent, especially in the case of mortar (M1–C10) with fly ash.

In the table 3 are presented the compressive strength changes of the two mortars samples, after curing for 30 and 60 days in different conditions of temperature (30 and 60 cycles of negative and positive temperatures).

Table 3

THE COMPRESSIVE STRENGTH LOSS AFTER CURING UNDER ALTERNATE POSITIVE AND NEGATIVE TEMPERATURE CYCLES

Mortar symbols	DR (%), after:	
	30 cycles	60 cycles
M1	5.64	-9.42
M1-C10	-6.95	- 12.26

The data reveals a good behaviour of both mortars, especially of the mortar with fly ash. In general, the specimens have presented 6.95%–12.26% compressive strength increases after the curing at alternately –10°C and +40°C. The negative temperature—however, not very low—seems to have no effect on the compressive strength of such mortars, while the cure at +40°C may favour a possible pozzolana reaction of the fly ash and partly even of SiO_2 in the fine sand with MgO.

The weight modifications

Figures 6 and 7 present the weight modifications of the magnesia phosphate mortar samples cured under different conditions of humidity and in aggressive solutions.

The weight changes over time at the curing of the two magnesia phosphate mortars in air were very small (approx. 0.2%), suggesting a good stability of the mortars compositions in the laboratory atmosphere (RH = 60%). At relative humidity higher than 92%, both mortars sample present relatively similar weight increase, of 2.3–3.7%. The values were a little smaller for the curing in water than that for wet air curing. In the first case a process of solubilisation probably overlaps the water retention in the pores.

In the case of samples cured in acid solutions, in general, a weight increase of approx. 1-6% occurs. Few exceptions have been noticed in terms of weight decrease, for the mortar M1 samples cured for 90 days in hydrochloric acid solution and for the mortar M1–C10 samples cured for 28 days in lactic acid solution.

The data regarding the weight modifications and the visual observations may lead to a series of assessments concerning the durability of magnesia phosphate mortars, as follows:

– in general, both mortars M1 and M1–C10 underwent weight loss in humid conditions and in chemical/acid solutions that suggests certain superficial interactions between samples and liquids with formation of products which precipitate on the samples;

– in the case of the samples cured for 60 days in solutions of hydrochloric acid, lactic acid and natrium sulphate, it was observed a very thin white layer on the surface and in some pores of the lateral sides. The thin layer was clearer in the case of the samples immersed in the natrium sulphate solution, in which case the weight increase was also greater. At the same time, the thickness of the layer increased over time, especially in the case of the mortar M1 samples. In the case of the samples prepared with mortar M1–C10, the layer was very thin, almost imperceptible and interspersed with very fine needle-shaped crystals;

– after 90 days of curing in lactic acid solution it was found that large and rounded white crystals appeared on the upper side of the specimens made of mortar containing fly ash (M1-C10). The samples made of mortar M1 cured in a solution of lactic acid presented rare white fine needle-shaped crystals in the pores of the sides;

– at the curing of the samples in a solution of hydrochloric acid, there are visible rare, white and rounded crystals.

It is worthy to note that no deterioration, such as scaling of the specimens made of the two magnesia phosphate mortars was noticed within 90 days of curing in chemical solutions.

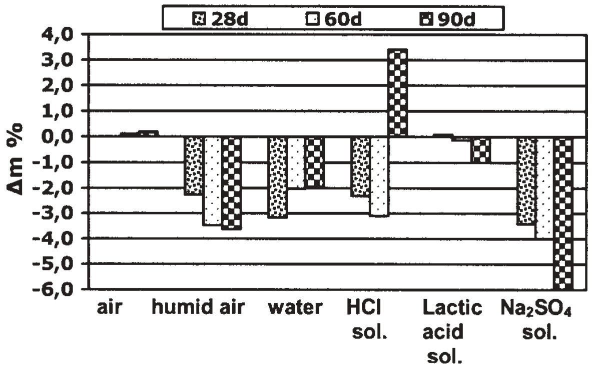

Fig. 6. The mass variation of mortar M1 over time in relation to the curing environment

The occurrence of the thin whitish layer on the surface of the samples could result from an interaction between MgO and solution; the white crystals visible with the naked eye could represent struvite especially, which could change the solubility and the morphology of the crystal , depending on the *p*H in the liquid phase and the time [12, 13].

The hydration products under conditions of variable humidity

Significant information regarding the influence of the environment on the composition characteristics of the

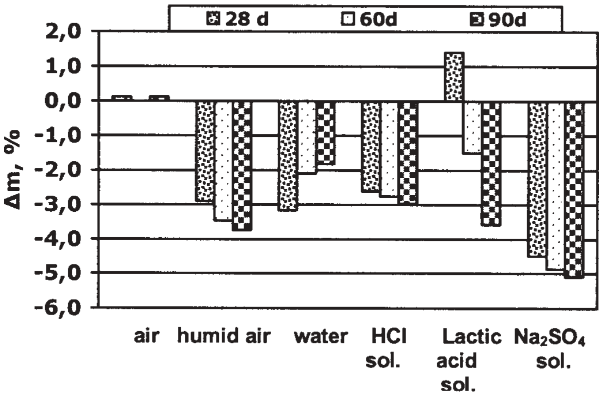

Fig. 7. The mass variation of mortar M1-10 over time in relation to the curing environment

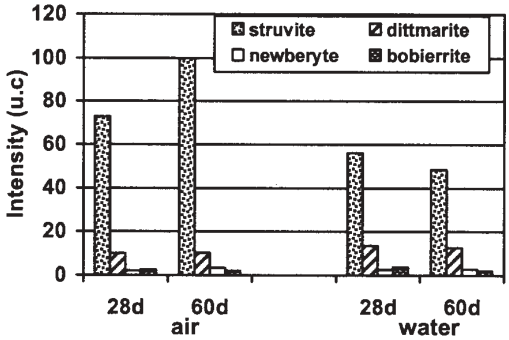

Fig. 8. XRD peaks intensity for the main phosphate hydrates in mortar M1 samples hardened in air and in water

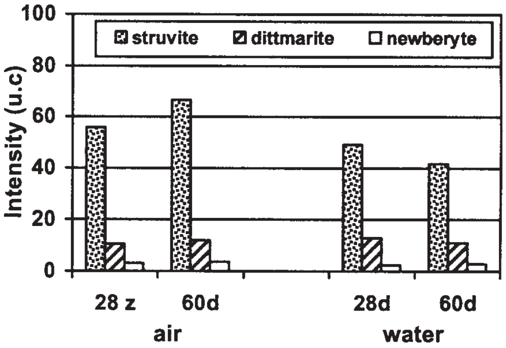

Fig. 9. XRD peaks intensity for the phosphate hydrates in mortar M1-C10 samples hardened in air and in water

hardened magnesia phosphate mortars was obtained by XRD analysis on samples immersed for 28 and 60 days in potable water and on the samples cured in the laboratory atmosphere. The main phosphate hydrocompound identified was struvite, $NH_4MgPO_4\cdot 6H_2O$, beside small amounts of dittmarite, $NH4MgPO4\cdot H_2O$, newberite, $MgHPO_4\cdot 3H_2O$, and bobierite, $Mg_3(PO_4)_2\cdot 8H_2O$. Moreover, quartz and non-reacted MgO were identified. The proportion of the different hydrophophates and their evolution in time present certain characteristics correlated with the curing environment as can be seen in figures 8 and 9.

When curing the mortar samples in the laboratory atmosphere, it was found that the characteristic XRD peak of struvite, $NH_4MgPO_4\cdot 6H_2O$ (4.26 Å) underwent an increase in intensity and the characteristic peak of MgO (2.10 Å) underwent a decrease from 28 to 60 days. This evolution in time of the struvite determines a resistant structure which justifies the favourable evolution of the compressive strength.

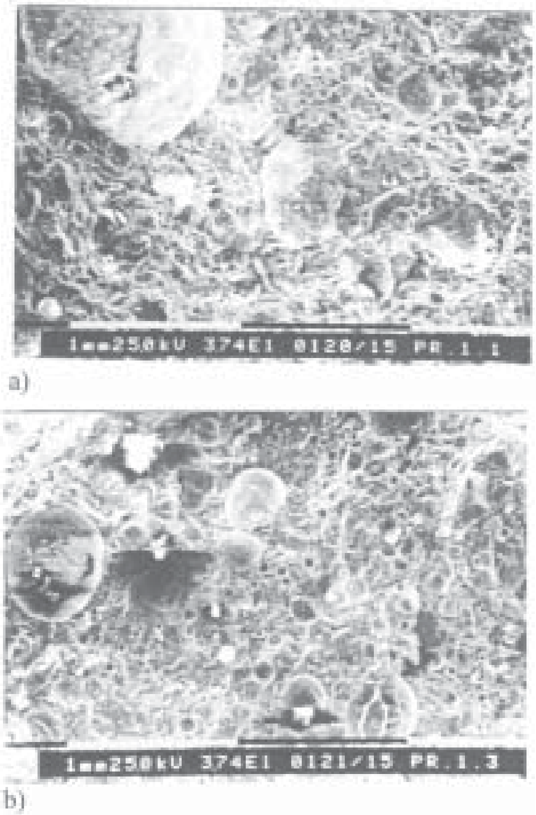

Fig. 10. SEM images of mortars M1 and M2 after 2 months of curing: a) in air, b) in water

The presence of fly ash in the magnesia phosphate mortar diminishes the intensity of the specific peaks for the hydrates (fig. 9).

For the M1 sample immersed in potable water, a diminish of the intensity for characteristic peak of struvite, $NH_4MgPO_4\cdot 6H_2O$ (4.26 Å), was observed from 28 to 60 days, at the same time with the increase of the intensity for characteristic peak of MgO (2.10 Å). This suggests certain instability of struvite, its partial decomposition with releasing of MgO and a possible formation of small basic compounds, slightly crystallised. The instability in water of struvite was also pointed out in some literature data [14], where its slow transformation into newberite was mentioned.

Some information regarding the microstructure of mortar M1 in relation to the curing environment was obtained by SEM/EDX analysis on samples cured for 60 days in air (RH = 60%) and in potable water. Figure 10 shows the obtained images.

The SEM image of mortar M1 cured in air (fig. 10a) shows struvite crystals grown on the surface of the sand grains and a relatively significant volume of pores resulted from the partial release of ammonia. The diameter of the pores

Table 4

THE QUANTITATIVE MICROANALYSIS OF MORTAR M1 UPON 2 MONTHS OF CURING UNDER CONDITIONS OF VARIABLE HUMIDITY

Curing medium	Mg %	Si%	P%	Ca%	Fe%
air	21.14	15.58	60.14	1.75	1.39
water	20.97	19.64	56.09	2.3	1.0

varies from 50 µm to 1 mm, with more pores having the diameter between 50 µm and 200 µm. In the case of the sample cured in potable water (fig. 10b), microcrystals of struvite and porosity comparable with that of the reference sample (cured in laboratory atmosphere) were found.

The quantitative microanalysis of M1 samples mortar (EDX) cured in the laboratory atmosphere and in water for 2 months has shown the elemental composition summarised in table 4.

The data indicates significant changes of the P and Si content when the samples were cured in water comparatively with the curing in air. The P content decrease and the Si content increase confirm a certain solubilisation of the double magnesium and ammonia phosphate hydrate, struvite, in good correlation with the data obtained by of XRD analysis (fig. 8).

Conclusions

The curing of magnesia-phosphate binders in wet environment or in water leads to lower compressive strengths of the binders as compared with those cured in air. The compressive strength decrease in the wet environment is more pronounced in the case of mortar M1 (without fly ash). The substitution of MgO with 10%fly ash leads to an improvement of the compressive strength values for the curing in humidity saturated environment.

The magnesia phosphate mortars type MgO+ $NH_4H_2PO_4$ + water - with or without fly ash have shown a good stability under conditions of variable, alternate, negative and positive temperatures.

The addition of fly ash brings a favourable effect in terms of stability of the magnesia phosphate binders in conditions of curing in acid solutions. The compressive strength decrease is significantly lower in the case of mortar M1–C10 (approx. 10–45%) as compared with the compressive strength decrease values of mortar M1 (approx. 25–55%). This is probably due to the filler effect of the fine fly ash particles, which improves the compactness of the mortar. Introducing of the fly ash in the composition of magnesia phosphate binders, a positive effect on their performances and reduces of the cost of the binders is realised.

The XRD analysis revealed certain instability of struvite when curing of the binders in humid environment, more evident in the case of M1 mortar. This may be correlated with the evolution of the compressive strengths. The SEM/EDX analysis carried out on M1 mortar samples confirmed the instability of struvite when curing in water.

Data regarding the processes taking place at the magnesia phosphate binders–chemical solutions interface, useful in assessing the physical and mechanical properties of such type of binders, will be discussed in a future paper.

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