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THE INFLUENCE OF POTASSIUM PHOSPHATE AND FLY ASH ADDITION ON THE SETTING TIME AND MECHANICAL STRENGTHS OF MAGNESIUM PHOSPHATE CEMENTS

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The paper presents the influence of two types of potassium phosphates on the setting time and compressive strengths of magnesium-phosphate cements (MKC). Potassium dihydrogen phosphate KH_2PO_4 (MKP) and dipotassium phosphate K_2HPO_4 (DKP) were used to prepare the MPCs, by mixing with dead burnt magnesia, water and setting retarder (borax). The compressive strengths of MPCs with MKP were higher as compared with those with DKP, for both short (1,3 days) and long (7,28 days) hardening times. The partial substitution of dead burned magnesia with fly ash (10%wt.) increases with 13-24% the mechanical strengths of magnesium-phosphate cements, especially for longer curing ages (28 days). The paper presents also the influence of the setting retarder (borax) dosage on the MPCs mechanical strengths.

Keywords: magnesium phosphate cements, potassium dihydrogen phosphate, dipotassium phosphate, fly ash, mechanical strengths, setting time

1. Introduction

Phosphate cements are obtained by the mixing of a basic component (usually an oxide) with phosphoric acid or a phosphate salt [1,2].

The development of magnesium phosphate cement (MPC) was initial spurred by the need to obtain fast setting cements for dental or bone restorations. Further investigations on MPC showed that this material has several superior properties as compared to normal portland cement, such as rapid setting, high mechanical strength at short and long hardening time, excellent frost strengths, low drying shrinkage and long-term durability [3-9].

Initially MPC was produced using dead burnt magnesia, ammonium dihydrogen phosphate and water [1]. However, during the process of obtaining magnesium-phosphate cement with ammonium dihydrogen phosphate it can be released ammonia, gas which is toxic in high concentration. This serious disadvantage of MPC prepared with ammonium dihydrogen phosphate hindered

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considerably its wider application. For this reason, research have been performed to replace the ammonium dihydrogen phosphate in MPC composition. Recent studies showed that a good substitute for ammonium phosphate is potassium dihydrogen phosphate (KH_2PO_4-MKP) [3,8,10-12]. The reaction kinetics between the calcined magnesia and MKP, as well as the resulted MPC properties are influenced by several factors, such as: calcined magnesia reactivity, magnesia-to-phosphate molar ratio, aggregate-to-binder ratio, water-to-binder ratio and type and dosage of setting retarders [3, 9-13].

In the last thirty years, MPCs were used as fast rapid setting cements for roads and landing strips (airports) rehabilitation, for soil stabilization and recently for toxic waste treatment i.e. for their solidification/stabilization in MPC matrix [1,2].

Some studies reported the manufacture of MPCs in which fly ash was used together with calcined magnesite as main solid component [6, 13-15]. Fly ash addition reduced the heat release during MPC hardening and determined the decrease of production costs. Fly ash, waste resulted in energy industry, contains as main components various types of aluminate-silicates. According to Ding and Li [6], a high amount of amorphous compounds can result in the reaction of aluminate-silicates and magnesium potassium phosphate which together with crystalline magnesium potassium phosphate hexahydrate ($KMgPO_4 \cdot 6H_2O$) resulted in the reaction of MgO with MKP, determines the increase of MPCs mechanical strengths.

In this study was assessed the influence of potassium phosphate type, i.e. potassium dihydrogen phosphate (KH_2PO_4 – MKP) or dipotassium phosphate (K_2HPO_4 - DKP), on the mechanical strengths of MPC. The influence of the partial substitution of dead burned magnesia with fly ash (10 wt.%) as well as the presence and dosage of setting retarder addition (borax) on the MPCs compressive strength is also presented in this paper.

2. Materials and methods

The precursors used for the preparation of magnesium phosphate cements were:

- Dead burnt magnesia (M) obtained by the calcination of magnesite at 1500°C, with the main characteristics presented in table 1.

Table 1

The characteristics of dead burnt magnesia

MgO %	**SiO_2 %**	**CaO %**	**Fe_2O_3%**	**Al_2O_3 %**	**L.O.I %**	**Density g/cm^3**	**Blaine specific surface area cm^2/g**
94.63	2.52	1.40	0.68	0.40	0.37	3.37	3250

- dipotassium phosphate (K_2HPO_4 - DKP) or potassium dihydrogen phosphate (KH_2PO_4 – MKP), chemical reagents;
- setting retarder – borax ($Na_2B_4O_7.10H_2O$) - chemical reagent;
- fly ash (F), waste produced by a coal fired power plant; the main crystalline mineralogical phases, assessed by X-ray diffraction analysis (XRD) are: SiO_2, $CaAl_2Si_2O_8$ and Al_2SiO_5 - Fig. 1.

The setting time of magnesium-phosphate pastes was determined with Vicat apparatus. The pastes were prepared by manually mixing the dead burnt magnesia, fly ash, phosphate salt and borax with water. The resulted pastes were cast into a metallic ring with the inside diameter of 26 mm and a height of 25 mm. The setting time of paste represents the time elapsed from the moment when the solid components were mixed with water until the Vicat needle forms a fine mark on the paste surface.

MPCs compressive strengths were assessed on paste specimens (15x15x60 mm) hardened for 1, 3, 7 and 28 days in air at 20±2°C.

The X ray diffraction (XRD) analysis were performed on a Shimadzu XRD 6000 diffractometer. The XRD spectra were obtained using a monochromatic CuKα radiation (λ= 1.5406 Å).

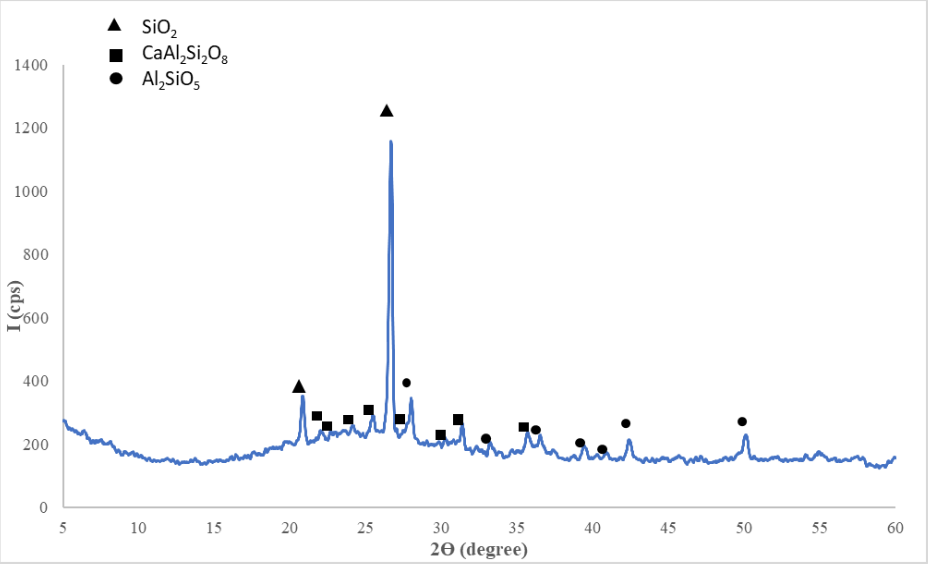


Fig. 1. XRD patterns of fly ash

The compositions of the magnesium-phosphate cements (MPC) are presented in Table 2.

Table 2

Materials dosage (wt.%)

Specimen	MgO (M)	Fly ash (F)	KH_2PO_4 (MKP)	K_2HPO_4 (DKP)	Borax* (%)	Water to solid ratio**
M_MKP	80	-	20	-	-	0.3
M_F_MKP	72	8	20	-	-	0.3
M_F_MKP_ B6.6	72	8	20	-	6.6	0.3
M_MKP_B3.3	80	-	20	-	3.3	0.17
M_MKP_ B6.6	80	-	20	-	6.6	0.17
M_DKP	80	-	-	20	-	0.17
M_DKP_B3.3	80	-	-	20	3.3	0.17
M_DKP_B6.6	80	-	-	20	6.6	0.12

* borax dosage was calculated with reference to the magnesia amount

**was calculated considering the water brought in the system by $Na_2B_4O_7.10H_2O$

The pH and the electrical conductivity of the aqueous solutions containing MPCs were determined using a pH and conductivity metter. First step was the dissolution of phosphate salts (MKP or DKP) in water; the water to MPC ratio was 10:1. This solution was mixed with a magnetic stirrer for five minutes after which the pH and conductivity were assessed. Dead burnt magnesia, borax and fly ash (in some compositions) were added to the solution and the suspension was stirred for another 5 minutes before assessing the pH and conductivity. The solutions were continuously stirred (200 rot/min) during the experiment and the determinations were performed from 10 to 10 minutes up to 110 minutes.

3. Results and discussions

Table 3 presents the values of setting time assessed for the studied magnesium-phosphate cement pastes.

Table 3

Values of setting time for the magnesium-phosphate cement pastes

Specimen	M_MKP	M_MKP_B3.3	M_MKP_B6.6	M_F_MKP	M_F_MKP_B6.6	M_DKP	M_DKP_B3.3
Setting time (min)	-*	4	12	6	13	3	161

*) Flash setting immediately after the mixing of solids components with water.

From the data presented in table 3 it can be observed that in the case of M_MKP composition is compulsory the use of setting retarder (borax); the increase of borax dosage determined, as expected, an increase of the setting time.

Partial substitution of dead burnt magnesia (M) with fly ash (F) produces a delay of the setting time, in correlation with borax dosage.

The use of DKP instead of MKP has a significant influence on the setting time. For M_DKP_B3.3, one can observe an important increase of the setting time as compared with M_MKP_B3.3 (table 3).

The evolution vs. time of pH and electrical conductivity of MPC aqueous solutions can provide additional information regarding the setting and hardening processes.

As it can be seen in Fig.2, after 5 minutes from the moment of phosphate salts mixing with water (MKP and DKP are dosed in the amount corresponding to the studied MPCs), as a result of their dissolution, the pH value:

- decrease up to 4.4 in case of MKP solution,
- increase up to 8.7 in the case of DKP solution.

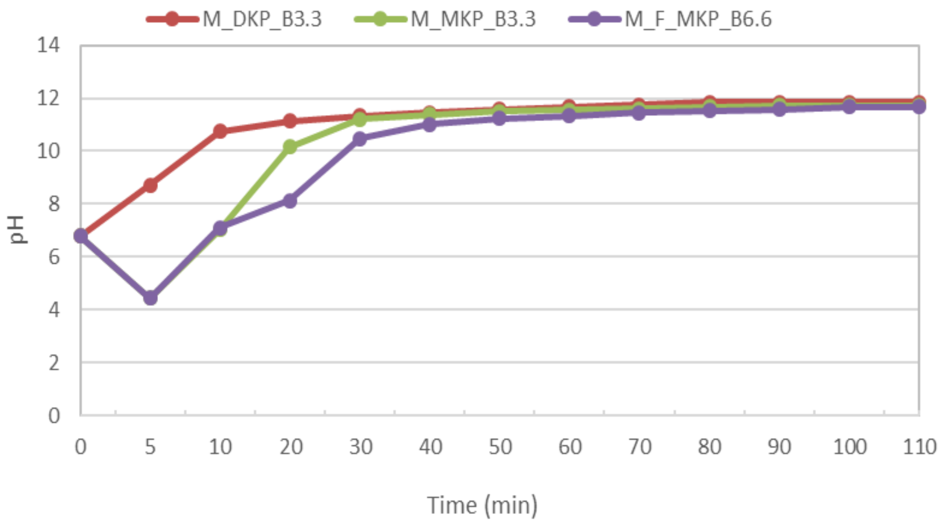


Fig. 2. pH of MPC solutions vs. time

When MgO and borax were added to the solution (minute 5), the pH increases up to approx. 12 in 30 minutes for M_MKP_B3.3 and M_DKP_B3.3 and in 50 minutes for M_F_MKP_B6.6. The slower increase of the pH value in the case of the composition with fly ash (M_F_MKP_B6.6) as compared to M_MKP_B3.3, can be explained by the lower amount of MgO in the system (F substitutes 10 % wt. of M); the pH increase is mainly determined by the MgO dissolution process [16].

The dissolution of DKP and MKP in water, in the first 5 minutes, causes also an increase of the conductivity (Fig. 3). In the case of MPCs with MKP (M_MKP_B3.3 and M_F_MKP_B6.6), one can notice an decrease of conductivity in the first 30 minutes, followed by a stabilization of conductivity at values around 5.3 mS/cm.

In the case of DKP, after its dissolution in water, the conductivity rapidly increases up to 20 mS/cm, followed by a very slow decrease, for the next 60 minutes, up to 17.5 mS/cm.

Le Rouzic *et al.* [16] attributed the decrease of conductivity to a precipitation phenomenon, which begins as soon as MgO is added to the phosphate solution; on the other side, the increase of conductivity is attributed to a dissolution phenomenon. Thus, according to these authors, the first compound formed in the MgO - MKP system, at pH between 6 and 7, is the newberite ($MgHPO_4.3H_2O$); the increase of the solution pH over 7 determines the dissolution of newberite and k-struvite ($MgKPO_4 \cdot 6H_2O$) is formed in the system. In the case of M_DKP_B3.3 sample, the pH of the DKP solution is 8.7, therefore one can presume that k-struvite is directly formed but with a smaller rate or/and in a smaller quantity as compared with MgO-MKP system. Lahalle *et al.* [17] show that in MgO - MKP systems the presence of boric acid does not hinder the initial dissolution of reactants but may delay the precipitation of reaction products. A similar finding was reported by Liu *et al.* [14] for phosphate systems based on calcined magnesite, fly ash and MKP, in which the setting retarder was borax. For a high dosage of borax an inhibition of the k-struvite precipitation process was reported by these authors and explained by the formation of a Mg-containing complex in the solution.

The very small decrease of the conductivity noticed in M_DKP_B3.3 system up to 110 minutes (Fig.3) suggests an important delay of k-struvite precipitation, which correlates well with the long setting time (table 3).

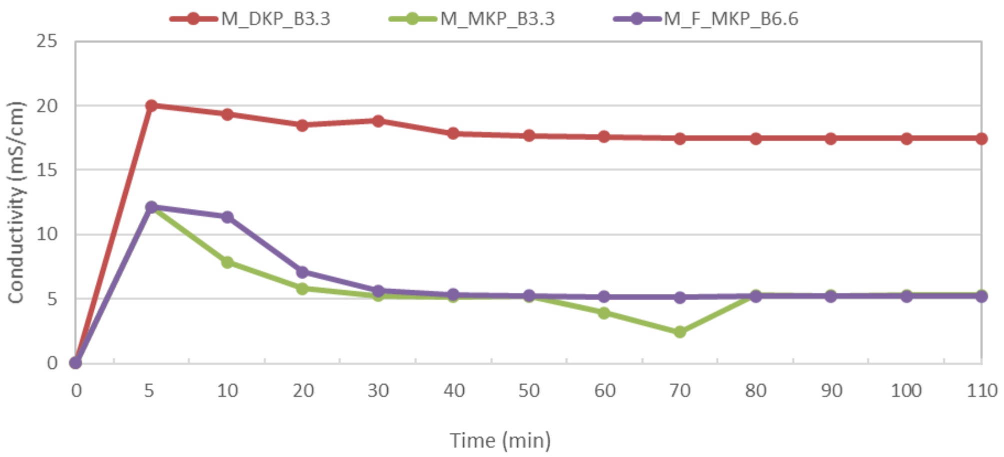


Fig. 3. Electrical conductivity of MPC solutions vs. time

Fig. 4 shows the influence of borax dosage on the compressive strength of cements with MKP. It can be observed that regardless of the hardening period the increase of borax dosage leads to a decrease of compressive strength. This behavior has been also reported in other studies [14,15] and can be explained, as shown above, by a delay of k-struvite precipitation in the borax presence [14], compound which determines the increase of mechanical strength [16].

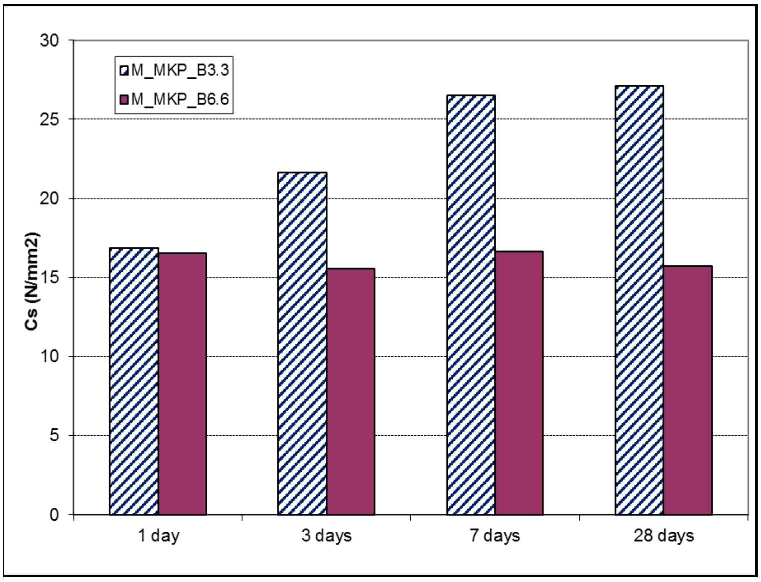
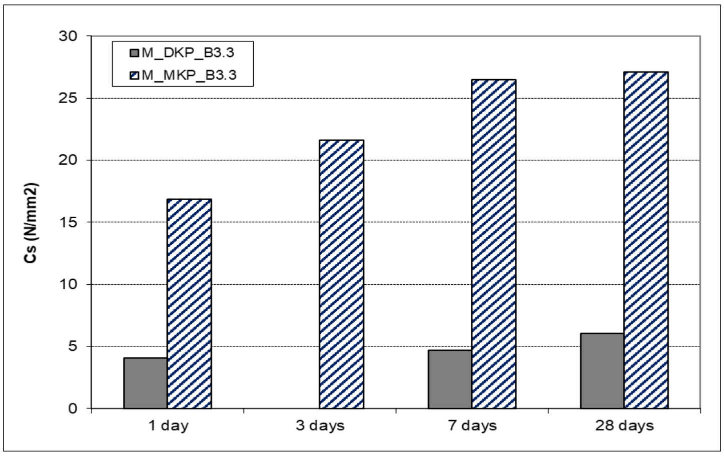


Fig. 4. The influence of borax dosage on the MPCs compressive strength after different hardening times

Fig. 5 shows the influence of the phosphate salt (MKP and DKP) on the MPCs compressive strength.



a

Fig. 5a). Compressive strength vs. time for MPCs prepared with 3.3% dosage of borax

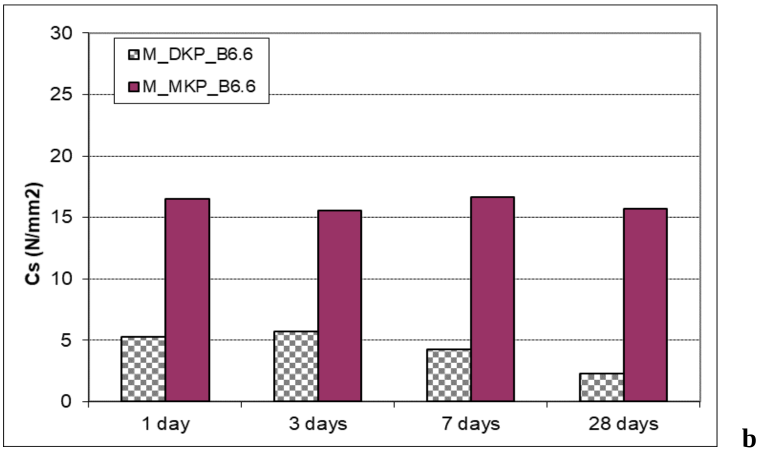


Fig. 5b). Compressive strength vs. time for MPCs prepared with : 6.6% dosage of borax

It can be observed that regardless of the borax dosage, the specimens prepared with potassium dihydrogen phosphate (MKP) have higher mechanical strength as compared with those prepared with dipotassium phosphate (DKP). This could be due to the formation of a higher amount of k-struvite in the cements with MKP as compared with those with DKP. These results are in good agreement with the information obtained by X-ray diffraction analyses (which will be further discussed), that suggest a higher content of non-reacted MgO in DKP pastes as compared to MKP pastes, for the same curing age.

Fig. 6 shows the influence of partial substitution of magnesium oxide with fly ash (10 %wt.) on the MPCs mechanical strengths.

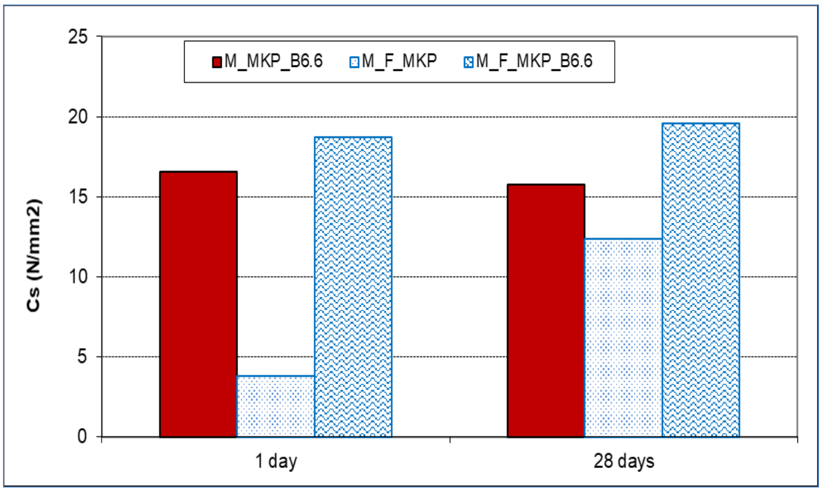
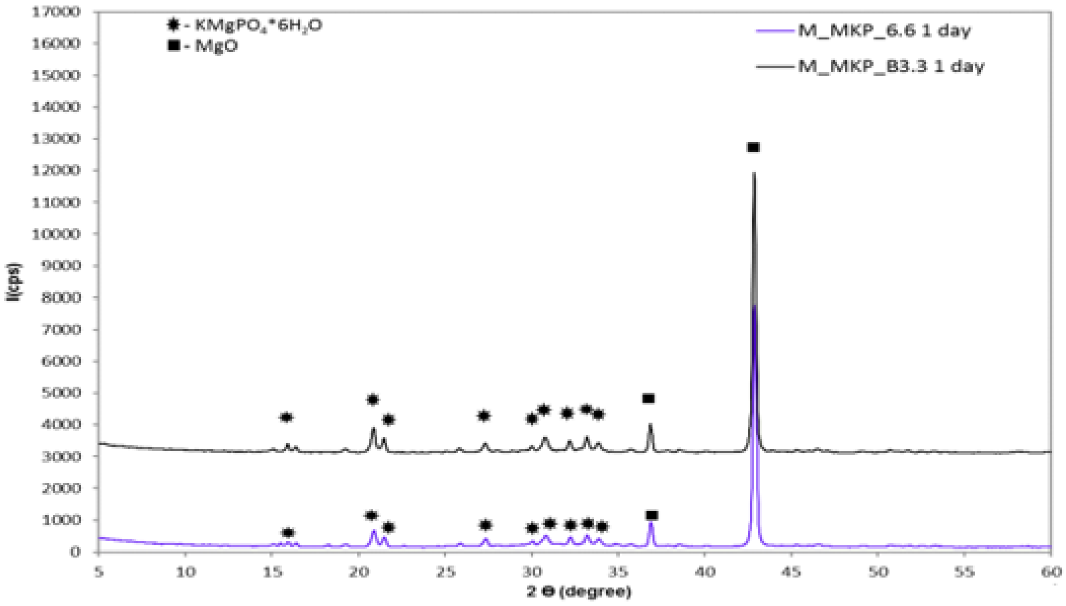


Fig. 6. The influence of MgO substitution with fly ash (10%wt.) on the mechanical strengths of MPCs, hardened or 1 day and 28 days

One can also notice a decrease of the intensity of magnesium oxide peaks with the increase of hardening time, from 1 day to 3 days; this can be due to the consumption of MgO in the reaction with MKP/DKP with k-struvite formation.

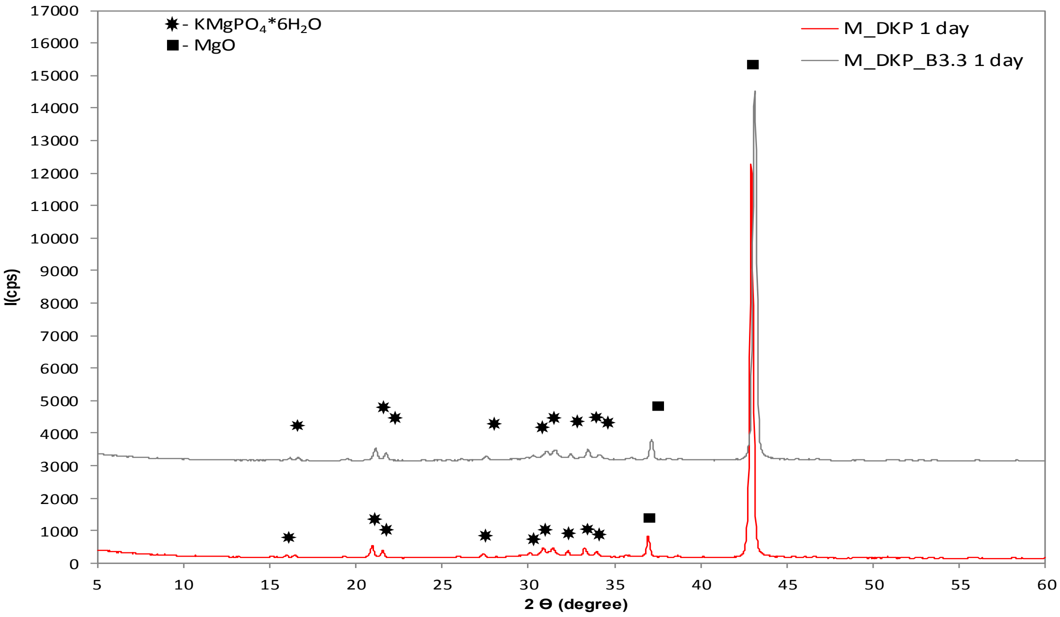
The substitution of magnesia with fly ash in MPC, without the use of retarder (borax), causes a decrease of the mechanical strengths (see M_MKP_B6.6 as compared with M_F_MKP - Fig.6); this is probably due to the rapid setting (see tab.3) which can cause internal stresses. The mechanical strength of M_F_MKP increases with the increase of curing time from 1 day to 28 days, probably due to the reaction of aluminate-silicates, present in fly ash, with potassium ions [14]. The mechanical strength of M_F_MKP_B6.6 (with fly ash) is slightly higher as compared to the one assessed for M_MKP_B6.6, both for short (1 day) and long (28 days) curing ages. This can be explained also by an adequate kinetic of hardening processes when borax is present in the system.

X-ray diffraction analyses of MPC hardened for 1 day and 3 days are presented in Figs.7 and 8. XRD patterns show the presence of magnesium oxide and k-struvite, as main crystalline phases.



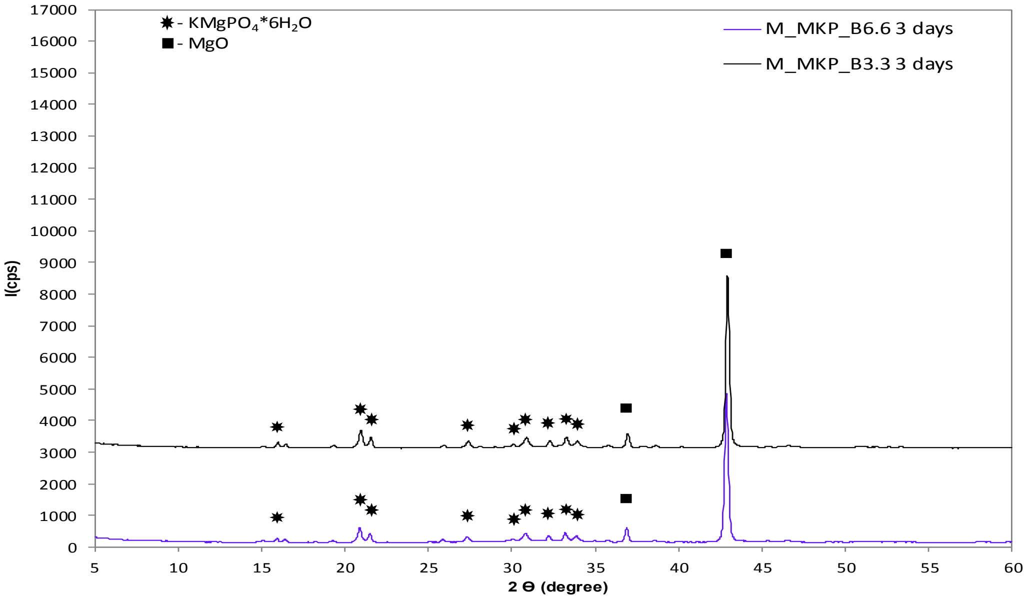
a.

Fig. 7a). XRD patterns of MPCs after 1 day of curing in air, prepared with MKP



b.

Fig. 7b). XRD patterns of MPCs after 1 day of curing in air, prepared with DKP



a.

Fig. 8a). XRD patterns of MPCs after 3 days of curing in air, prepared with MKP

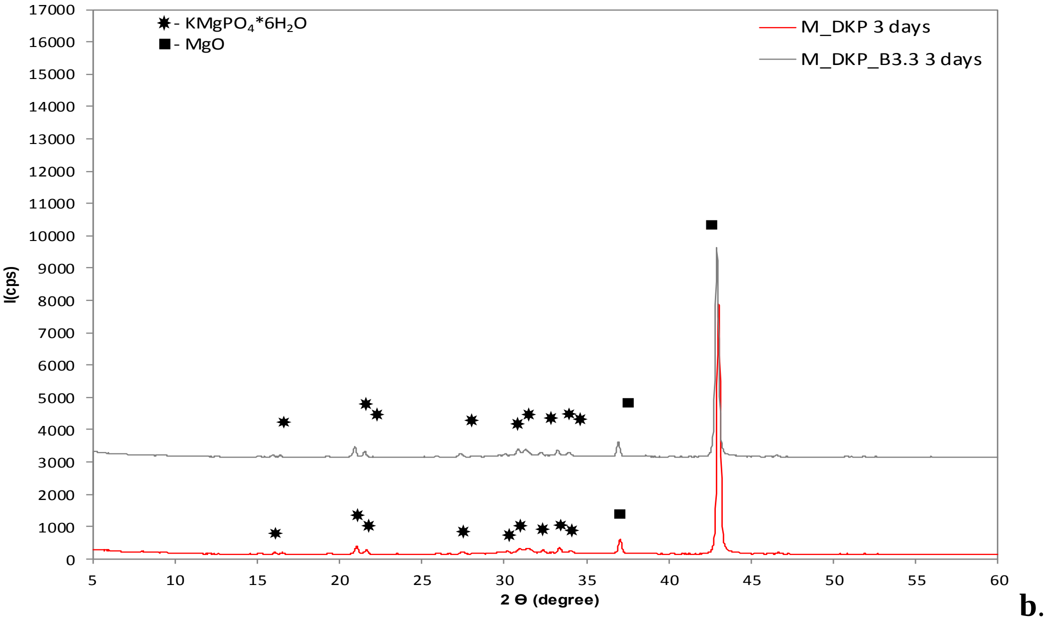


Fig. 8b). XRD patterns of MPCs after 3 days of curing in air, prepared with DKP

On the XRD patterns of MPCs with DKP (Figs. 7b and 8b) the intensities of MgO peaks are higher as compared to those assessed on MPCs with MKP (Figs. 7a and 8a); this suggests the formation of a smaller amount of k-struvite in the systems with DKP, process correlated with MgO consumption.

4. Conclusions

This paper presents the preparation and characterization of magnesium-phosphate cements (MPCs) based on dead burnt magnesia (with/without fly ash addition) and two types of phosphate salts i.e. KH_2PO_4 (MKP) and K_2HPO_4 (DKP). The following conclusions can be drawn:

- The setting time of MPCs is influenced by the type and dosage of phosphate salt (MKP or DKP) as well as the presence and dosage of setting retarder (borax). For the preparation of MPCs with MKP is compulsory to use borax; the increase of borax amount determined, as expected, an increase of the setting time. Partial substitution of dead burnt magnesia with fly ash (10%wt.) does not exert an important influence on the setting time. An important delay of setting was noticed for the MPCs with DKP and borax.
- The compressive strengths of MPCs with MKP were higher as compared with those of MPCs prepared with DKP. This may be due to the formation, precipitation and crystallization of a higher amount of k-struvite in the cements with MKP; k-struvite is the main crystalline compound formed in this type of MPCs and is essential for the hardening process.

- Partial substitution of dead burnt magnesia with fly ash (10%wt.) determines an increase of the mechanical strength in the cements with MKP and borax.
- X-ray diffraction analyses of magnesium-phosphate cements obtained with MKP or DKP, after 1 day and 3 days of hardening, show the presence of k-struvite ($KMgPO_4{\cdot}6H_2O$) as main crystalline reaction product.

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