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Effect of aggregates and water contents on the properties of magnesium phospho-silicate cement

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Abstract

Properties of magnesium phospho-silicate cement (MPSC) mortars with different fine aggregates, and different water contents were investigated in the present work. Three types of fine aggregates, natural sand, dead burnt magnesia and alumina particles were used. Two types of hard burnt magnesia powder with MgO content 89.51 and 71.50 wt.% were used as binder. Compressive strength of MPSC mortar with different water/binder ratios were determined at ages of 1, 3, 7, and 24 h. The 3, 7, and 28 day compressive strength and modulus of elasticity were also tested. It was found that the compressive strength of MPSC mortar decreases with the increase of sand content, regardless of sand type. However, the strength reduction of MPSC mortars formed with magnesia and alumina sand was much smaller than that of mortars formed with natural sand. Moreover, in spite of the raw materials, compressive strength and elastic modulus of MPSC decreased with the increase of water/binder ratio at all ages. The hydrate products were analysed by XRD and TG-DTA, and the porosity of MPSC mortar was analysed by MIP. Results showed total porosity increased with the increase of water content. The content of hydrate product of MPSC, phosphate hexahydrate, also increased with the increase of water content. However, it seems that the change of mechanical properties of MPSC is mainly controlled by increase of total porosity which was determined by water content.

Keywords: Magnesium phosphate cement; Fly ash; Aggregate; Water content; Microstructure

1. Introduction

Cements made from magnesia have been developed for many years, such as magnesia oxychloride cement (MOC), magnesia oxysulphate cement (MOS), and magnesia phosphate cement (MPC). Among them, MPC now has been attracting more attention due to its higher early age and long-term strengths, and better durability. The traditional MPCs, magnesia ammonium phosphate cement (MAPC) had been investigated by many research workers. It may have potential applications, such as rapid repair of concrete structures, borehole sealant, and for solidification of hazardous waste [1–12]. The reaction products of MAPC mainly include magnesium ammonium phosphate hydrate that is formed by acid–base reaction between magnesia and ammonium dihydrogen phosphate. The reaction initially forms a hydrogel, followed by the crystallization of an insoluble phosphate, magnesium ammonium phosphate hexahydrate ($NH_4MgPO_4 \cdot 6H_2O$). Generally, to reduce reaction rate, the magnesia used in this system is dead burnt magnesia. During the reaction of magnesia and ammonium dihydrogen phosphate, however, some ammonia is liberated as a gas [13,14]. So, the utilization of this cement is limited. The color of dead burnt magnesia is white or light yellow, in practical applications, fly ash is usually added to this system in order to obtain a color similar to the appearance of Portland cement products. At the same time, fly ash can reduce the cost of MPC. However, the strength of MPC may decrease due to the addition of fly ash in this system [1,5].

Recently, a new MPC system based on dead burnt magnesia and potassium phosphate has been developed. It is found that the new MPC can be improved by inclusion of a large amount of fly ash [15,16]. Fly ash mainly consists of alumino-silicate, it is possible that a multi-compositional amorphous binder consisting of

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P_2O_5, SiO_2, Al_2O_3, MgO, and K_2O can be formed from fly ash and magnesium potassium phosphate. The amorphous mass fills the voids and bonds the matrix together, and thus makes the hydrated paste harder than the system without fly ash. Besides the amorphous species, a crystalline, magnesium potassium phosphate hexahydrate ($KMgPO_4 \cdot 6H_2O$) is also formed in the matrix. Fly ash can be added to the system up to 40 wt.% without degrading the mechanical properties of the system, according to the previous studies [16]. Due to fly ash as a main component in the type of magnesium phosphate cement, it can be called magnesium phosphosilicate cement (MPSC). Because large amount of fly ash is utilized in this system, it provides a new way of utilizing fly ash and other similar industrial waste. Therefore, the new binder system has benefits in environmental protection and sustainable development.

In the present research work, the effects of fine aggregate and water content on the properties, including compressive and elastic modulus of MPSC mortar were investigated. Hydrates, porosity and microstructure were also studied in order to clarify the relation between mechanical properties and microstructure.

2. Experimental

2.1. Materials

The fine aggregates used in the current research was natural river sand, dead burnt magnesia sand, and sintered alumina sand. Their particle size distributions and fineness are set out in Table 1. Two types of hard burnt magnesia powder with MgO content of 89.51% and 71.50% respectively were used as the base compound. For convenience, the former is named M9 and the latter M7. The mean particle sizes of M9 and M7 were 30.6 and 59.8 μm, respectively. The chemical composition of Class F fly ash was Al_2O_3, 26.69; SiO_2, 50.54; CaO, 8.07 and Fe_2O_3, 7.76 percent by weight. Chemical reagent monopotassium phosphate (KH_2PO_4) was used as the acid compound and borax ($NaB_4O_7 \cdot 10H_2O$) as a retarder of the cement.

Table 1
Particle size distribution and fineness of aggregate sands

Particle size distribution (mm) and fineness	Natural sand (%)	Magnesia sand (%)	Alumina sand (%)
0–0.15	1.36	0.04	1.28
0.15–0.3	16.19	1.08	1.11
0.3–0.6	61.26	13.81	18.29
0.6–1.18	16.35	22.87	17.60
1.18–2.36	3.71	20.93	43.57
2.36–5.0	0.87	40.93	18.12
Fineness	3.05	4.58	4.54

Table 2
Materials proportions

Materials	Ratios by weight
Natural sand to binder	1:1.0, 1:1.5, 1:2.0, 1:2.5, 1:3.0
Magnesia sand to binder	1:1.0, 1:2.0, 1:3.0
Alumina sand to binder	1:1.0, 1:2.0, 1:3.0
Water to binder	0.16, 0.17, 0.18, 0.19, 0.20, 0.21

The MPSC binder paste was formed by mixing magnesia powder, monopotassium phosphate (MPP) with borax (the addition of borax was 4 wt.% of magnesia), and fly ash (the addition of fly ash was 40 wt.% of dry binder). The MPSC mortar was prepared with different aggregate sand/binder ratios, or by different water/binder ratios. The mixing proportions are listed in Table 2.

2.2. Test methods

40 × 40 × 40 mm mortar cube specimens were cast for compressive strength tests, and 40 × 40 × 80 mm mortar prisms specimens for modulus of elasticity. The MPSC specimens were demolded 1 h after casting, then were cured under the room temperature in lab air (25 ± 2 °C and 50 ± 5% relative humidity). To observe the strength development at early ages, the MPSC mortar specimens were tested at 1, 3, 7, and 24 h. The compressive strength test was conducted on an ELE Auto machine with loading rate 0.375 MPa/s. The test for static modulus of elasticity was carried out on a MTS (material test system) machine with 450 ton capacity at ages of 3, 7 and 28 day, respectively.

The temperature rise during the early reaction in a small (100 g) sample of mortar was recorded by a digital multimeter, METEX, to get the qualitative information of the reaction. The X-ray diffraction (XRD) analysis for the powder specimens was carried out using a Philips PW 1830 X-ray diffractometer, with a scanning rate of 0.5° 2θ/min. Differential thermal analysis (DTA) was carried out using DTA 7 Perlin Elmer. The temperature change in DTA was from 25 to 500 °C with a heating rate of 10 °C/min in air. Mercury intrusion porosity (MIP) analysis was conducted with an AutoPore IV 9500 machine in order to understand the pore distribution of MSPC mortars.

3. Results and discussion

3.1. Mechanical properties

The effects of fine aggregate on compressive strength of MPSC mortar specimens with different binder to sand ratios are shown in Fig. 1. Fig. 1(a) illustrates the results of mortar strength with different amounts of natural

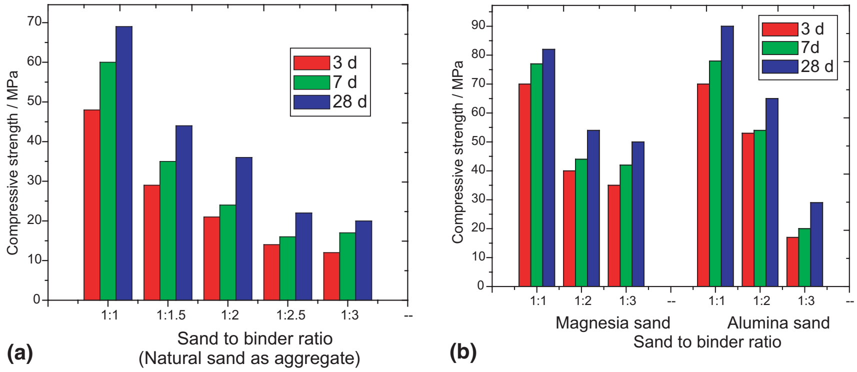


Fig. 1. Mortar strength at different sand/binder ratios.

river sand. Fig. 1(b) is for the mortars with different magnesia sand and alumina sand. They all show that the highest strength occurs at the sand/binder ratio of 1:1. The strength of MPSC mortar decreases with an increase of aggregate content regardless of the curing age and the type of sand. The strength of MPSC mortar highly depends on the effective bonding of sand and paste. An increase in sand content causes a reduction in paste volume increasing the interface region. This causes weak links inside the mortar which lead to lower compressive strength.

Although the strengths of magnesia and alumina sand mortars also decrease with the increase of binder/sand ratio, compared to the specimen made of natural sand, the ratios of reduction are much smaller. Moreover, the strengths of magnesia and alumina mortars are much higher than that of natural sand mortar for all sand/binder ratios. This could be for two possible reasons: (1), magnesia and alumina sand are coarser than natural sand and (2), some reaction between phosphate and magnesia or alumina sand may happen, and a stronger interface may form between the cement paste and magnesia or alumina sand grains.

The effect of water content on the mechanical properties of MPSC mortar was examined with the river sand mortar. The natural sand was passed 2 mm sieve, here. The sand/binder ratio was 1:1, and water/binder (W/B) ratio varied from 0.16, 0.17, 0.18, 0.19, 0.20 and 0.21. The influence of W/B ratio on compressive strength of MPSC mortar at early ages is shown in Fig. 2. Fig. 2(a) is for the M7 series and Fig. 2(b) the M9 series. As expected, the strength of MPSC mortar decreases with the increase of W/B for all ages. At 1 h, only the samples with W/B of 0.16, 0.17, and 0.18 demonstrated a measurable strength. But, the other three samples had no measurable strength. However, at 3 h, all the samples reached about 20 MPa. By comparing Fig. 2(a) and (b), it is noted that the strength of the M7 series mortars is even slightly higher than that of M9 series at age of 3 h, though the former had less MgO content and was much coarser in particle size than the latter.

Fig. 3 shows the strength development of MPSC mortars with different water/binder ratios at age of 3, 7, and 28 days. Compressive strength of the M7 and M9 series samples had an inverse relation with the water to binder ratio at every age. The larger the water/binder ratio, the lower the strength is. This phenomenon is the same as in the products made from Portland cement, which can be attributed to more pores formed inside the

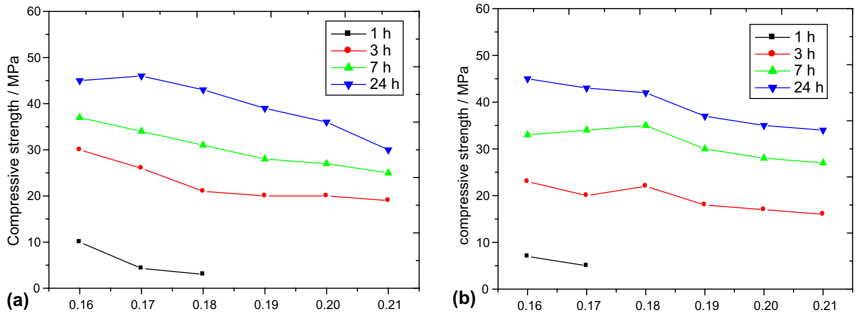


Fig. 2. Early strength development of MSPC mortar with different water content: (a) water/binder ratio (M7 series) and (b) water/binder ratio (M9 series).

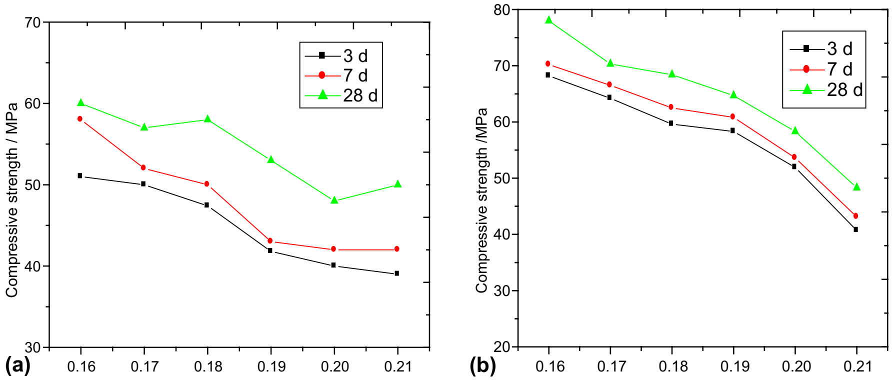


Fig. 3. Strength development of MSPC mortar with different water content: (a) water/binder ratio (M7 series) and (b) water/binder ratio (M9 series).

cement paste due to the larger water content. In the present study, at the three latter ages, the absolute strength of the M9 series is higher than that of the M7 series. At the W/B ratio of 0.16, the strength of the M9 sample is about 20 MPa higher than that of the M7 sample. However, the strength of the M9 series samples shows a sharper reduction than the M7 series does when W/B ratio increases. At the W/B of 0.21, the two series of MPSC mortars have a similar strength.

The modulus of elasticity of MPSC mortars with different water content and different dead burnt magnesia materials has been determined at 3, 7 and 28 days. The values of modulus of elasticity for the M7 and M9 series are shown in Fig. 4(a) and (b), respectively, as a function of water content. The figures show a similar trend of dependency on W/B for modulus of elasticity with the compressive strength. It decreases with the increase of water content at all the ages. However, the extent of decrease in modulus of elasticity is much smaller than that of in compressive strength. Meanwhile, the figure shows the trend of increase of modulus of elasticity at longer ages.

3.2. Physical properties

The initial setting times of MPSC cement at different water contents were almost the same, about 9 min. The apparent densities of MPSC mortar samples were measured during mercury intrusion process (MIP), and all the values were around 2.40 g/cm^3.

The hydration of MPSC was exothermic. According to the previous study of the authors, if no fly ash was added to the MPSC binder, the temperature rise would be over 70 °C during hydration progress (100 g dry sample). When 40 wt.% fly ash was blended into the binder, the temperature was reduced to 40–50 °C [16]. The maximum temperature of mortar samples with different water contents also varied from 40 to 50 °C in this work. The time to reach maximum temperature during hydration of all MPSC mortar samples was almost the same, about 14 min.

3.3. The relationship between mechanical properties and microstructure

Like Portland cement, the strength of MPSC develops with hydration time. After water was blended into the dry binder, the phosphate dissolved into water firstly to form an acidic solution. Then it reacts with MgO at the surface of magnesia particles. After sufficient hydrates were formed, the mortar sets and hardens to a continuum, and the strength increases. However, the strength development of MPSC was achieved more quickly than that of Portland cement. It meant that the

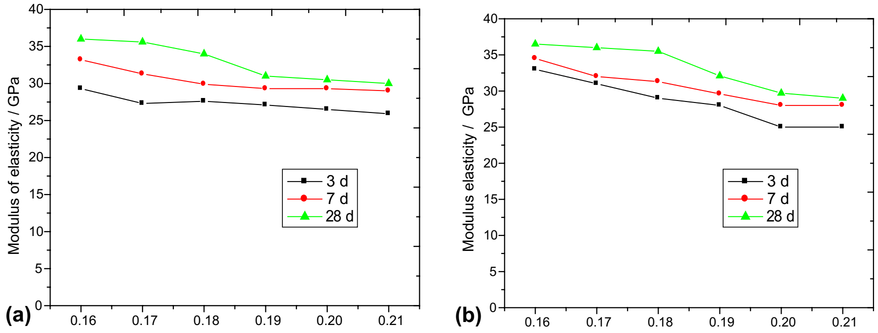


Fig. 4. Modulus of elasticity MPSC mortar with different water content: (a) water/binder ratio (M7 series) and (b) water/binder ratio (M9 series).

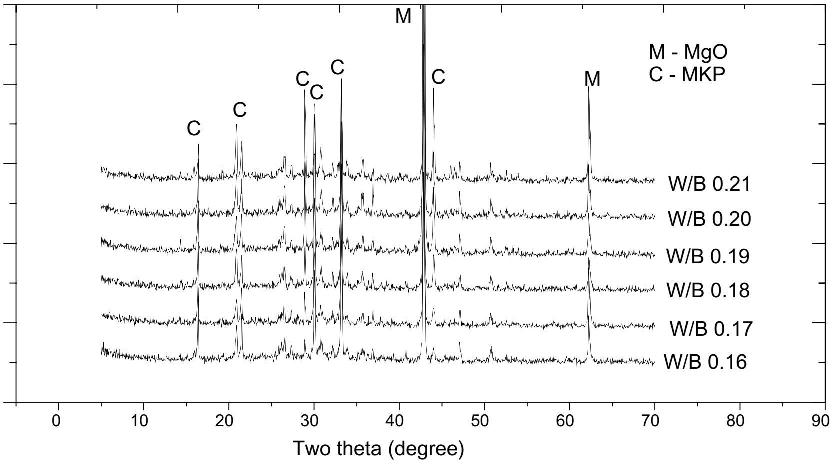


Fig. 5. XRD spectra of M9 series sample with different W/B ratios.

microstructure matured much faster than that of Portland cement. The structural development depends on the chemical reaction. The hydration of MPSC was an acid–base reaction with quick reaction rate. At the same time, a lot of heat evolution would be released within a very short hydration time. This causes a rapid temperature rise, which further accelerated the hydration rate.

XRD (Fig. 5) analysis shows that the main hydration product is magnesium potassium phosphate hexahydrate ($MgKPO_4 \cdot 6H_2O$—MKP). Some of the phosphate hexahydrate product crystallizes (the sharp diffraction peaks) and the residual would remain amorphous or as a cementitous gel (the diffuse peaks). XRD also shows much unreacted magnesia remains in the paste. Thus the solid phase of MPSC paste mainly consisted of unreacted magnesia grains, crystallized MKP, an amorphous mass, and fly ash grains. With the increase of water, it seems that the crystallized MKP also increased according to the diffraction intensity. Due to one molecule of crystallized MKP containing six molecules of water, with increase of water content, the crystallization of MKP would be favorable.

Fig. 6 shows the TG-DTA result of sample M9W6. In a MAPC system, the hydration product was magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), and it could be dehydrated over 50 °C to about 200 °C [17,18]. The structure determination showed that $MgKPO_4 \cdot 6H_2O$ was isostructrual with $MgNH_4PO_4 \cdot 6H_2O$. The NH_4^+ ion was substituted by smaller K^+ ion that lead to minor structural changes [19]. The TG-DTA data indicate that the hydrate product, MKP is also dehydrated at the temperatures over 50 °C. Most weight loss (water) happens during the temperature range around 107 to 115 °C. By comparing the area enclosed by the dehydration values of all curves, it was found that the amount of MKP product increases with water content slightly.

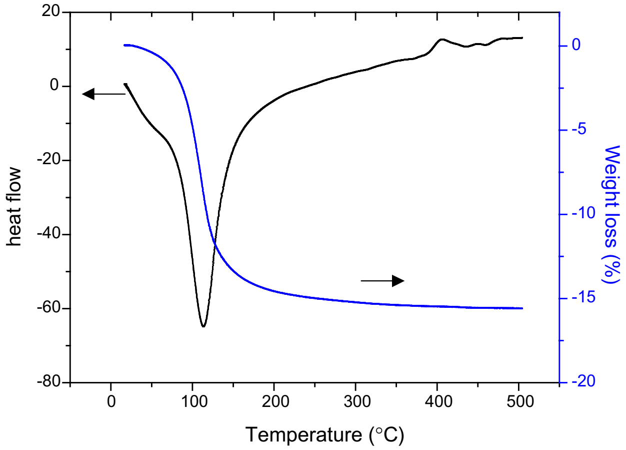


Fig. 6. DTA-TG analysis and the hydrate produced in MPSC paste.

The result of MIP analysis is given in Fig. 7. It shows the pore radius distributions in Fig. 7(a) and cumulative mercury pore volume versus pore size diameter Fig. 7(b). The results indicate that both pore size distribution, Fig. 7(a), and the total porosity are influenced by water content. The cumulative pore volume increases with water content as expected. It can be noted that the influence of water content mainly concentrates on the pores with a diameter less than 2 μm. The relationships between porosity of mortar sample and mechanical property are shown in Fig. 8. Fig. 8(a) is for modulus of elasticity and Fig. 8(b) for compressive strength. The higher water content causes an increase of total porosity in the mortar sample; the increase of porosity causes the degradation of mechanical properties.

Many researches thought that cementing of MPSC are not bonded by interlocking crystallites, because it was not possible to form a crystallites network in very short time [20–22]. It is the amorphous gel that forms a continuum and produces the cementitious properties

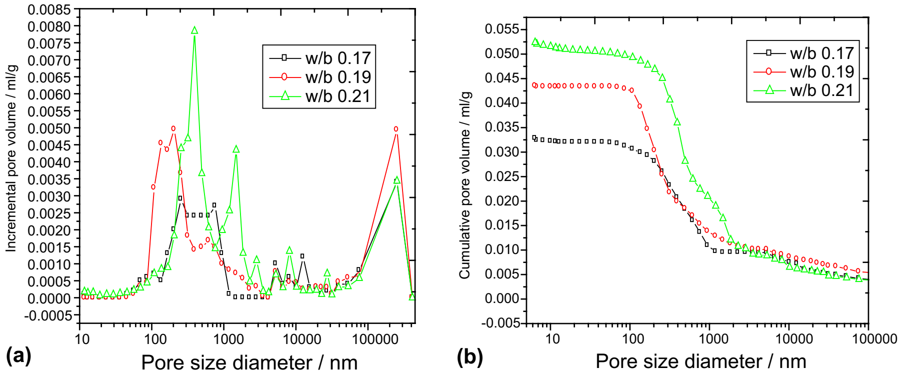


Fig. 7. (a) Pore radius distribution and (b) cumulation.

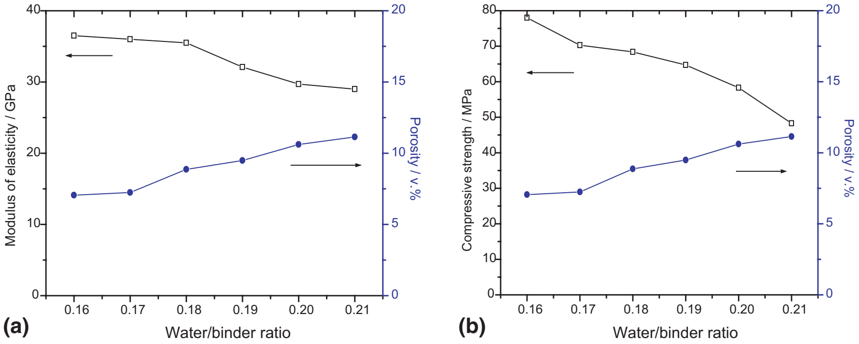
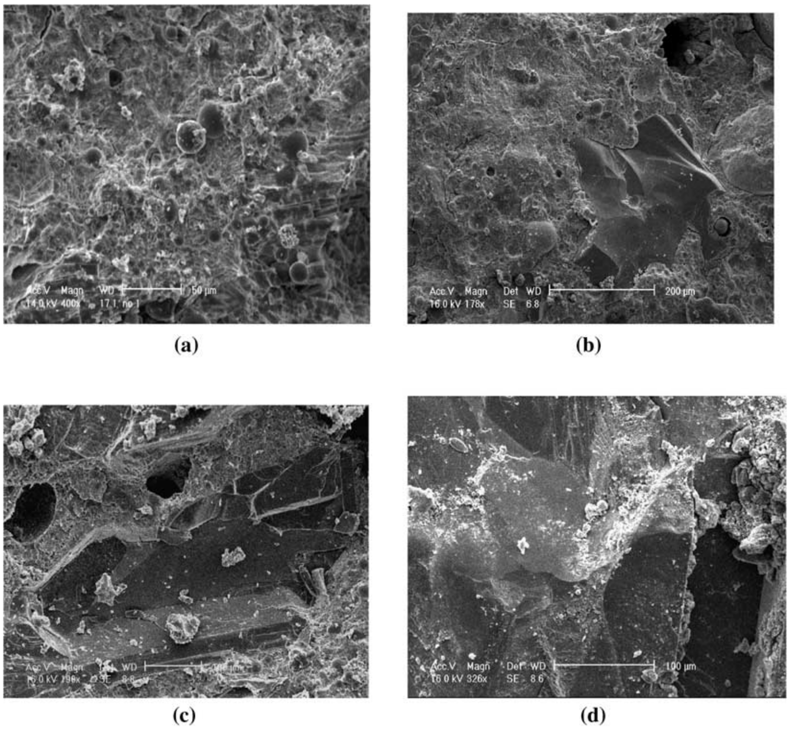


Fig. 8. Relationship between mechanical properties and total porosity of M9 mortars. (a) Modulus of elasticity at 28 day and (b) compressive strength at 28 day.


(a) (b)

(c) (d)

Fig. 9. Microscopy of MPSC paste and mortar with different sands. (a) MPSC paste, (b) MPSC mortar with natural sand, (c) MPSC mortar with magnesia sand and (d) MPSC mortar with alumina sand.

due to its huge specific surface energy. The effect of fly ash in MPSC may be both physical and chemical. The former indicates that fly ash particles fill the voids and make the structure denser, whereas, the amorphous silica and alumina in fly ash might take part in the interaction and form more cementitious gel to make the microstructure denser.

Fig. 9 shows the microstructure of MPSC paste and mortars with different types of sand. According to Kingery [23], cold phosphate bonding could be achieved with cations that had small ionic radii and were amphoteric or weakly basic, such as beryllium, aluminum, iron and calcined magnesia. As the magnesia aggregate was the same as the binder material (the main composition is MgO), chemical reaction certainly happens around the surface of magnesia. Alumina sand, is basic comparing to phosphate (acid mass) and could also react around the alumina particle surfaces. However, the composition of natural sand is quartz, so only physical adhesion occurred at the interface of MPSC paste and natural sand. On the other hand, after the compressive strength tests, the fracture of mortars with magnesia sand and alumina sand passed through some aggregates. This provides support to the idea that some reaction has taken place at the interface between magnesia or alumina sands.

4. Conclusions

The effect of fine aggregates and water content on the mechanical properties of MPSC mortar have been studied. The following conclusions can be drawn from the current research.

(1) The compressive strength of MPSC mortar decreases with the increase of fine aggregate content for the ranges studied here. This may be because the sand content was too high, so there would not be enough cement paste available for bonding and the interlinks between paste and sand grains could be weakened.
(2) At the same binder/sand ratio, the MPSC mortars formed with magnesium or alumina sand show much higher strength than that of mortar formed with natural river sand. This improvement may come from the interaction between phosphate and magnesia or alumina at the surface of aggregates.
(3) For mortars made with either M7 and M9, the compressive strength and modulus of elasticity all decrease with the increase of W/B ratio at all ages, because a higher water content leads to more pores inside the mortar. MIP results have shown that the total porosity increases with an increase of water content.
(4) According to XRD and TG-DTA analysis, the content of the crystallized hydrate product of MPSC, MKP, also increases with increase of water content for the W/B ranges selected in this study.

Acknowledgements

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