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Review Article

Effect of raw materials and proportion on mechanical properties of magnesium phosphate cement

Yangzezhi Zheng [a,b], Yang Zhou [c,d,*], Xiaoming Huang [a,b], Haoyuan Luo [a,b]

[a] School of Transportation, Southeast University, Nanjing 211189, China
[b] National Demonstration Center for Experimental Education of Road and Traffic Engineering, Southeast University, Nanjing 211189, China
[c] School of Materials Science and Engineering, Southeast University, Nanjing 211189, China
[d] State Key Laboratory of High Performance Civil Engineering Materials, Jiangsu Research Institute of Building Science Co., Nanjing 211103, China

HIGHLIGHTS

- Summarized the relationship between phosphate, magnesium oxide and water and the mechanical strength of MPC.
- Some specific mineral admixtures can enhance the strength of MPC.
- Fibers have a positive effect on the strength of MPC matrix.

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ABSTRACT

Magnesium phosphate cement (MPC) cementitious material is a phosphate cement-based material with strength formed by a serious of acid-base neutralization reactions among magnesium oxide, phosphate retarder and water, which has a high early strength and a broad application prospect in the field of pavement rehabilitation. This review collects and organizes the latest progress in the field of research on the influencing factors of mechanical properties of magnesium phosphate cementitious materials worldwide in recent years, and discusses the possibilities of application in airport engineering.

The type of phosphate has a great influence on the reaction products, and the strength of the reaction products of ammonium salt is higher. Borax is the most commonly used retarder, and the retarding effect is related to the ratio of boron to magnesium. However, borax retarders have an adverse effect on the strength of MPC. In terms of the influence of mineral admixtures on the properties of MPC, fly ash, silica fume and metakaolin, as common mineral admixtures, have a positive influence on the mechanical properties of MPC, but the mechanism and degree of the influence of the three materials on the strength of MPC are slightly different; Aggregates can also improve the volume stability and mechanical properties of MPC by forming skeleton structure and slowing down the exothermic reaction. In fiber reinforced MPC matrix, steel fiber is the most widely used and the bonding performance between special-shaped steel fiber and MPC matrix is higher than that of straight fiber; basalt fiber has also been proved to be used to improve the mechanical properties of MPC system.

1. Introduction

Magnesium phosphate cement (MPC) is a cementitious material based on the formation of strength by metal oxides and phosphates through acid-base neutralization reactions in aqueous environments. MPC is a chemically bonded phosphate ceramic, which has some properties similar to ceramics, such as low porosity, high density, excellent compressive strength and bonding strength, and good volume stability. At the end of the 19th century, phosphate cement was used in dental materials (Fan, 2016; Qin, 2019), but due to the severe exothermic neutralization reaction, phosphate cement (ceramic) has obvious disadvantages in the medical field. At the same time, MPC is also a new type of cement material with rapid setting and rapid strength growth. In the mid-20th century, phosphate materials began to be used in the

* Corresponding author. School of Materials Science and Engineering, Southeast University, Nanjing 211189, China.
E-mail addresses: zyzz@seu.edu.cn (Y. Zheng), tomaszy@seu.edu.cn (Y. Zhou), huangxm@seu.edu.cn (X. Huang), luohaoyuan@seu.edu.cn (H. Luo).
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manufacture and research of special embedding materials for casting cobalt-chromium alloys (Earnshaw, 1960; Kingery, 1950, 1952) and refractory materials. The melting point of magnesium oxide is as high as 2800 °C, and its resistance to alkaline oxides is extremely excellent, making it a good choice for refractory materials (Chen and Li, 2005; Wu and Ma, 2007). Based on the good fire resistance of magnesia, MPC has been developed as a porous material for foamed concrete. MPC foamed concrete has the effects of high temperature resistance and sound insulation (Chen et al., 2012; Lai et al., 2018), and is suitable for interlayers of walls, playgrounds and other facilities. With the increase of calcination temperature of magnesia, the crystal structure of magnesia is denser, the grain size is larger, and the active is lower. On the other hand, by substituting phosphoric acid or phosphite with ammonium phosphate or potassium phosphate, the reaction rate between phosphate and metal oxide can also be reduced, so that the reaction between dead-burned magnesium oxide and phosphate can be reduced. At this point, the speed of chemical reaction often depends on the particle size and specific surface area of the solid material, but too large particles are not conducive to the formation of a dense matrix. For magnesium oxide powder, the time of condensation and hardening is still only 2–3 min (Wang, 2006), although the reaction time has been effectively controlled, but there is also a certain distance from the large-scale use. The application of boric acid and borate really solves the problem of too fast reaction of phosphate cement. It is found that boron-containing compounds (borax decahydrate) can effectively control the reaction rate of MPC. The reaction rate of MPC changes sharply with the amount of boric acid or borax, and it can even be achieved without coagulation for 1 h (Qin et al., 2021). Borax (B) is the most common compound of boron element and the most widely used MPC retarder. MPC material has good interfacial bonding properties. With the application of borax, the reaction rate of MPC with extremely high early strength becomes controllable. Therefore, the possibility of MPC as an emergency repair and reinforcement for roads, airport runways, bridges, and military repair materials has also been explored.

Taking airport pavement maintenance as an example, Portland cement pavement surface is often used in airport construction in China, which can not only effectively improve the overall strength and smoothness of the road, but also prolong the service life of the pavement. At present, the effective methods for rapid treatment of traditional airport pavement diseases include: prefabricated spliced boards, fast-hardening Portland cement, fast-hardening sulfate alumina cement, inorganic polymer emergency repair materials, etc. These materials can achieve a compressive strength of over 30 MPa and a flexural strength of over 3.5 MPa within 7–24 h (Wang and He, 2019). However, most of Chinese international airports are densely populated with flights, taking Shanghai Pudong International Airport as an example, the daily commute time of Pudong Airport runway is more than 20 h, and the vacuum period that can be used for repair is only 1–2 h. The traditional repair material has a long hardening period, the early strength is lower than the load-bearing requirements, so it is gradually difficult to adapt to the non-stop repair requirements of large airports. MPC has the characteristics of fast setting and hardening, high early strength, good bonding performance, and self-leveling, which provides the possibility for non-stop maintenance of large airports. Magnesium phosphate cement is used as a fast road repair material, it has to face the repeated action of various loads, so it needs to meet the requirements of compressive strength and flexural strength of the pavement (Ding and Li, 2005; Mestres and Ginebra, 2011; Yang et al., 2000).

MPC cementitious material is a high-performance alternative to traditional repair materials, especially for those repair projects that require opening traffic quickly. However, although magnesium phosphate cements have been invented for more than 100 years, the application of MPC in pavement repair is still developing. Except the factor as high raw material prices, it is also affected by the complex relationship between material properties and mix ratios. Studies by several scholars have shown that the bond strength between magnesium phosphate mortar and old concrete is much higher than that of silicate mortar (Qin et al., 2018; Xie et al., 2020). In conclusion, as a new type of concrete repair material, MPC has the advantages of fast setting and hardening, which can be adjusted by borax content, high early strength and not low late strength (Qin, 2019), good bonding performance with Portland cement (Qian et al., 2014) etc., but also has disadvantages like lack of unique water reducing agent and expensive raw materials. Many scholars try to use cheaper mineral productions or lower purity magnesium oxide to reduce costs, which achieved good results. However, the cost of MPC is still a key factor affecting its large-scale application compared with Portland cement that has been produced on a large scale.

2. Influence of magnesium phosphate cement mix ratio on strength

2.1. The effect of MgO on the performance of MPC

For the MPC pure slurry system, MgO is not only an important reaction raw material, but in the system with excess MgO, most of the residual MgO also acts as aggregates. However, when the content of MgO is too high, it means that the ratio of phosphate and water will be insufficient, which will lead to insufficient hydration products, resulting in insufficient strength or even no strength; when the content of MgO is too low, coarse particle size of hydration products and excessive shrinkage and deformation due to high exotherm of hydration will still affect the performance of MPC. In order to obtain MPC cementitious materials with good performance, the selection of magnesium oxide materials is also critical.

1) Magnesium oxide activity. Due to the high activity of light-burned and medium-burned magnesium oxide, the reaction is violent. Hence, except for some studies on low temperature properties, in the MPC system, the dead-burned magnesium oxide is usually used in the calcination temperature above 1500 °C (Ahmad et al., 2019; Feng et al., 2016; Qin et al., 2021; Sun et al., 2020; Zhang et al., 2018), its purity is affected by raw materials and calcination process, generally between 85% and 98% (Ahmad et al., 2019; Wang, 2006). The higher the calcination temperature and the purity of magnesium oxide are, the lower the reactivity of MgO is. Another important factor that affects the activity of MgO is the specific surface area (fineness). Wang (2006) studied the effect of the specific surface area of MgO on the setting time. Under the condition that other conditions remain unchanged, the larger the specific surface area of MgO, the faster the setting time of MPC. The specific surface area of MgO commonly used today is about 200–300 m^2/kg (Chen et al., 2010; Hu et al., 2015).
2) Magnesium oxide to retarder (borax) ratio. The retarder based on borax is an important means to adjust the setting and hardening time of MPC cementitious materials. Some scholars (Sugama and Kukacka, 1983) believe that the retardation mechanism of borax is that the ions formed after its dissolution will adsorb to the surface of MgO to inhibit the reaction of dissolved phosphate with MgO. Based on this theory, researchers will correlate the dosage of borax with the dosage of MgO, that is, when the dosage of MgO is increased, the dosage of borax is often appropriately increased to ensure the constant B/M ratio. As mentioned earlier, a large number of scholars have studied the borax/magnesium (B/M) value, but the optimal B/M value is affected by many factors such as material quality, mixing time, and ambient temperature, etc. The current B/M values recommended by various scholars are between 5% and 15% (Chen et al., 2012; Liu and Li, 2011; Xue et al., 2011).

2.2. Effect of phosphate type on MPC performance

The hydration mechanism of MPC has always been a hot research direction, and the main theories include Topochemical mechanism and through-solution mechanism. Among them, the through-solution mechanism is recognized by more scholars, and the key elements of this theory are the dissolution of phosphate and magnesium oxide, the aggregation and nucleation of anions, and cations in the solution and continuous expansion (Abdelrazig et al., 1989; Soudée and Péra, 2000). Based on this theory, scholars have proposed different reaction process hypotheses (Lahalle et al., 2016; Qiao et al., 2010; Wagh, 2016; Wagh and Jeong, 2004; Zhang et al., 2017) and the main chemical equations of the reaction (Chong et al., 2017; Feng et al., 2016; Li et al., 2020; Sun et al., 2020; Zhang et al., 2018). However, with the different types of phosphates, the reaction products of phosphate and magnesium oxide are also different. Common types of phosphates are ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP) and sodium dihydrogen phosphate (SDP). Acidic phosphates such as ammonium, dipotassium hydrogen phosphate, and aluminum phosphate are also used to make MPC, but these phosphates are more acidic, have faster hydration, and have more concentrated heat release, so they are gradually abandoned. Ammonium dihydrogen phosphate and magnesium oxide system has relatively controllable setting time and higher early strength, and is more suitable for high-strength magnesium phosphate system. However, ammonium ions combine with hydroxyl in water to form ammonium monohydrate, which is unstable and decomposes into ammonia and water under heating. Hence if the environmental measures are improper, it may lead to a large amount of ammonia gas escape, which would suffer potential environmental problems; and as the potassium dihydrogen phosphate and magnesium oxide system, although the strength of the reaction product is not as strong as the ammonium salt system, the hydration exotherm is not concentrated, and the problems caused by harmful gases are also avoided. Some scholars, such as Wagh (2016) believed that the hydration products of the ammonium salts and potassium salts systems have similar structural systems, so the potassium salt system is also favored. Some scholars have also used SDP to prepare MPC, but the strength of this system after hardening is significantly lower than that of MPC prepared by ADP and KDP (Qin, 2019). In fact, the number of crystalline waters of phosphate hydration products not only increases with the proportion of water in the reaction, but also takes various forms, and when the reaction is carried out in an aqueous environment, hydration products containing 15 to 22 crystalline waters are even produced (Lahalle et al., 2018), and the difference in the number of crystal waters will also lead to different strengths of the hydration products. If the reaction products and hydration mechanism cannot be studied, the application and development of MPC gelling materials will be greatly affected.

On the basis of previous research, the team of Qian and Qin of Chongqing University summarized the relationship between the types and strengths of MPC cement hydration products, as shown in Table 1. From the strength relationship of MPC hydration products in Table 1, it can be seen that the hydration products of ammonium salts and potassium salts are the better choice for phosphate due to their higher mechanical strength. Although potassium-magnesium phosphate and ammonium-magnesium phosphate systems have greater similarity in performance, the latter is more advantageous in formulating high-strength MPC gelling materials; however, due to the exothermic reaction to make ammonia gas escape, if not handled properly, it may lead to high porosity of MPC hardened body thus leading to the loss of strength.

In conclusion, monohydric phosphate is unstable in nature and is rarely used, often as a PH regulator for dihydrogen phosphate (Liu et al., 2020, 2022). Among the dihydrogen phosphate salts, MPC prepared by ADP has the highest strength, but also the most concentrated exotherm, which may bring potential ammonia escape problems; KDP can also prepare higher strength MPC, and MPC prepared by KDP is not concentrated exotherm, does not produce pollution gas, and is the raw material of MPC chosen by more scholars at present; SDP has the lowest strength and soluble reaction products, and is rarely used by scholars SDP has the lowest strength and soluble reaction products, and is rarely used (Fan and Chen, 2014; Ramsey et al., 2020; Yan et al., 2022).

Table 1
Main hydration products of magnesium phosphate cementitious materials (Abdelrazig and Sharp, 1988; Abdelrazig et al., 1989; Ding and Li, 2006; Fan, 2016; Jiang et al., 2002; Liang, 2010; Qin, 2019; Sugama and Kukacka, 1983; Yang and Wu, 1999).

System	Main type of hydration products	Strength
$MgO\text{-}NH_4H_2PO_4$	$MgNH_4PO_4{\cdot}H_2O$ $MgNH_4PO_4{\cdot}3H_2O$ $MgNH_4PO_4{\cdot}4H_2O$ $MgNH_4PO_4{\cdot}6H_2O$ $MgNH_4PO_4{\cdot}8H_2O$ $Mg(OH)_2$ $(NH_4)_2Mg_3(HPO_4)_2{\cdot}8H_2O$ $Mg_3(PO_4)_2{\cdot}4H_2O$	High and ultra-high strength
$MgO\text{-}KH_2PO_4$	$MgKPO_4{\cdot}H_2O$ $MgKPO_4{\cdot}3H_2O$ $MgKPO_4{\cdot}6H_2O$ $MgKPO_4{\cdot}7H_2O$ $Mg_2K(HPO_4)_2{\cdot}15H_2O$	High strength
$MgO\text{-}NaH_2PO_4$	$MgNaPO_4{\cdot}nH_2O$ Non-crystalline products	Medium strength
$MgO\text{-}H_3PO_4$	$Mg(H_2PO_4)_2{\cdot}nH_2O$ ($n = 2,4$)	Soluble, no strength
$MgO\text{-}Al(H_2PO_4)_3$	$MgHPO_4{\cdot}3H_2O$ $AlPO_4{\cdot}nH_2O$	Medium strength

2.3. Mix ratio design of three-phase system

The cementitious material of magnesium phosphate cement is made up of dead-burned MgO, phosphate, retarder and water in a certain proportion, so the mass ratio of MgO to phosphate (M/P), the water-to-binder ratio (W/C) is the index that most affects the performance of MPC. On the basis of previous research, the team of Qian and Qin of Chongqing University summarized the relationship between the types and strengths of MPC cement hydration products, as shown in Table 1 (Qin, 2019). From the strength relationship of MPC hydration products in Table 1, it can be seen that the hydration products of ammonium salts and potassium salts are the better choice for phosphate due to their higher mechanical strength. Although potassium-magnesium phosphate and ammonium-magnesium phosphate systems have greater similarity in performance, the latter is more advantageous in formulating high-strength MPC gelling materials; however, due to the exothermic reaction to make ammonia gas escape, if not handled properly, it may lead to high porosity of MPC hardened body thus leading to the loss of strength. Some scholars believe that struvite with six crystal waters is more stable and has higher mechanical strength than other hydration products, and are also the most important hydration products of MPC under certain water environments (Feng et al., 2013; Liu and Li, 2011; Qin, 2019; Wang et al., 2005), many scholars put forward the following reaction formulas.

$$MgO + NH_4H_2PO_4 + 5H_2O = MgNH_4PO_4 \cdot 6H_2O \tag{1}$$

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O \tag{2}$$

Eqs. (1) and (2) are also an important theoretical basis for the design of the magnesium phosphate cement mix ratio at this stage. Based on this equation, Xu et al. (2018) and Qin et al. (2021) proposed a three-phase system of phosphate-magnesium oxide-water, respectively, as shown in Fig. 1. The high water-cement ratio condition ($W/B > 0.5$) is mainly focused on the study of reaction mechanism, the low water-cement ratio condition ($W/B < 0.5$) is mainly concentrated on the application study.

Xu et al. (2020) paid more attention to the process of the reaction, by arranging the data of multiple researchers, they concluded that the changes in the ratio between MgO, KDP and water with time can lead to different reaction products (Chau et al., 2012; Lahalle et al., 2016; Le Rouzic et al., 2017), which can also lead to changes in the mechanical strength and bulk stability of MPC (Qiao et al., 2010; Wang et al., 2013). Meanwhile, Xu et al. (2020) also studied that the change of water content will lead to the change of the overall character, and divided it into

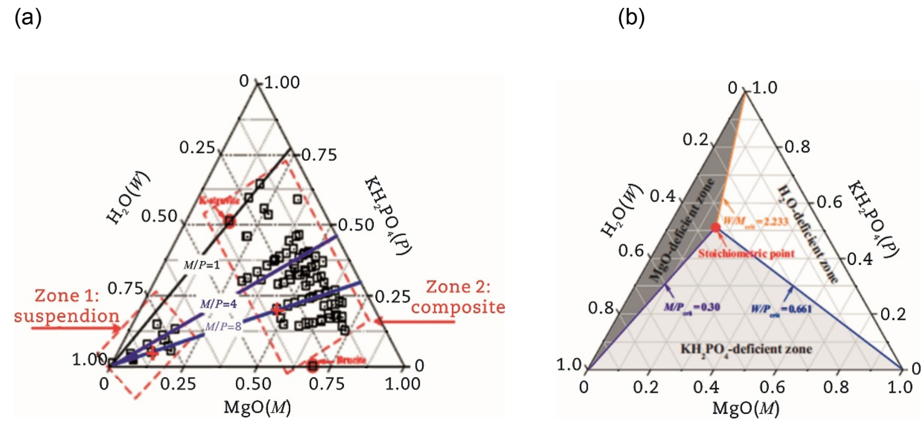

Fig. 1. Phosphate-magnesium oxide-water three-phase system. (a) The relationship between the product state of MPC system and the three raw materials. (b) The best matching ratio of three raw materials.

suspension zone and composite zone. Qin (2019) and others simplified the intermediate process and sought the final reaction product with higher strength. Both yielded the same specific mix ratio for the formation of *K*-struvite according to Eq. (2).

In the *M*, *P*, *W* three-phase system, because the lower price and higher mechanical strength of dead burned magnesia than these of phosphate, dead-burned magnesium oxide is more suitable to become the skeleton of the MPC system, so the dead burned magnesia is often excessive in the actual configuration. Therefore, based on the above chemical reaction equation, the team of Qian proposed the theoretical minimum water consumption hypothesis (Qin, 2019; Qin et al., 2021), that is, when magnesium oxide is in excess, phosphate and water are prepared in a molar ratio of 1:5, and theoretically all phosphate can be converted into struvite or *K*-struvite. Taking the ammonium salts as an example, the mass ratio of water to ADP should be five times of their relative molar mass ratio, namely.

$$\frac{W_{\min}}{\text{ADP}} = N\frac{n_{\text{H}_2\text{O}}}{n_{\text{ADP}}} = 5 \times 18/115 \approx 0.782 \tag{3}$$

where N is multiple relation of H_2O and ADP, which is equal to 5; and n_{H_2O} and n_{ADP} are relative molecular mass of water and ADP respectively.

That is, 0.782 g of water is required for per 1 g of ADP; similarly, 0.662 g of water is required for per 1 g of KDP. However, in the above three-component analysis, the influence of the presence of retarder is not considered. As mentioned above, retarder can delay the reaction rate of MPC system, and is one of the indispensable components of MPC in practical application. At present, in the MPC system, the most commonly used retarders, borax pentahydrate ($NaB_4O_7·5H_2O$) and borax decahydrate ($NaB_4O_7·10H_2O$), both contain a large proportion of crystal water. Since borax will be released into more free water after being dissolved in water, resulting in a significant increase in actual water consumption, the crystal water content of borax should be counted as part of the actual water consumption (Qin, 2019). However, Lahalle et al. (2016, 2018) and Xu et al. (2018) believed that water is the key gelling component of MPC, and the ratio of water determines the amount of crystal water in the final crystal. It cannot be simply considered that struvite is a main product.

At present, many scholars have studied magnesium phosphate systems containing only magnesium oxide and phosphate (and borax). In order to verify the correctness of the three-phase system, combined with a large number of existing research conclusions (Liu et al., 2022), taking the potassium-magnesium phosphate system as an example, the relationship between the ratio of phosphate and the sum of free water and crystal water and the 1 d compressive strength is compiled and calculated in this paper, as shown in Fig. 2. It has converted different *W/C* values, *M/P* values and crystal water in borax into actual *W/P* values. It can be seen from Fig. 2 that the 1 d compressive strength of the MPC cementitious material has a trend of increasing first and then decreasing, but the *W/P* corresponding to the turning point (maximum strength) is slightly lower than the theoretical calculated value ($W/P = 0.662$). Qin (2019) believes that the reason for this difference is that the reaction degree of phosphate is affected by the properties and dosage of MgO and borax.

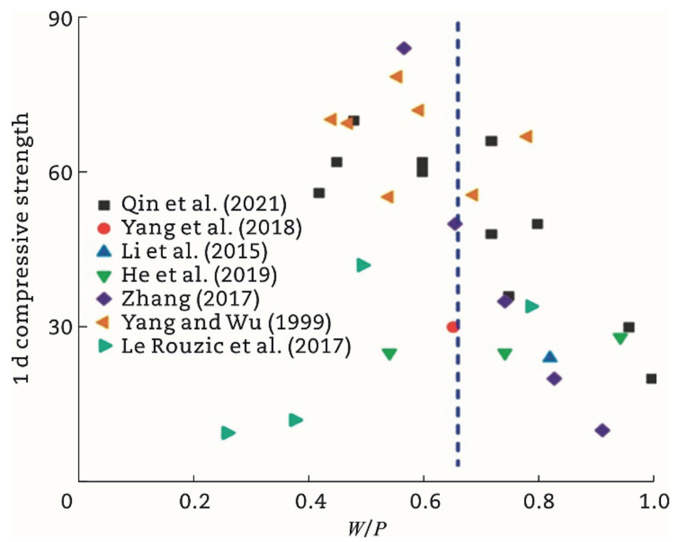

Fig. 2. Relationship between 1 d compressive strength and *W/P* of potassium magnesium phosphate cement paste (He et al., 2019; Le Rouzic et al., 2017; Li et al., 2015; Qin et al., 2021; Yang and Wu, 1999; Yang et al., 2018; Zhang, 2017).

2.4. Borax and other retarders

Many scholars have studied the effect of borax dosage on the reaction rate. Most scholars believe that increasing the dosage of borax can significantly delay the hydration reaction of MPC (Dai, 2019; Wang, 2006; Wang and Cao, 2007; Yang and Qian, 2010). However, Park et al. (2016) and You (2017) observed anomalies as shown in Fig. 3, respectively. With the increase of B content, the setting time of MPC system decreased. In this regard, You (2017) believed that $NaNH_4PO_3OH·4H_2O$ would be formed under a certain mixing ratio, which would lead to the occurrence of abnormal coagulation and shorten the coagulation time. At present, although some scholars believe that boron element will exist in the MPC system in the form of a certain phase, the current research has

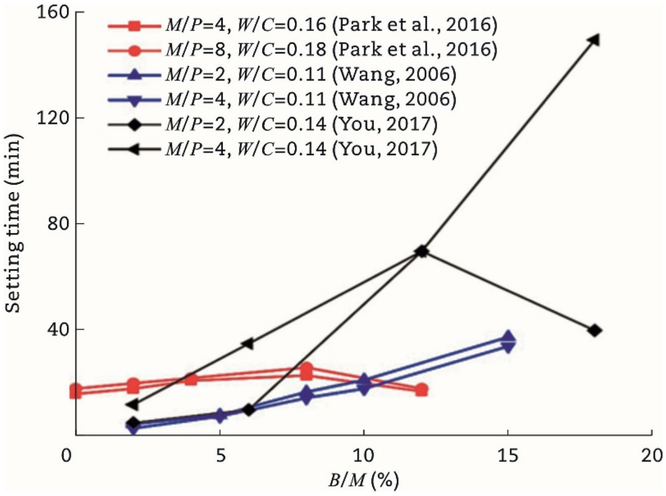

Fig. 3. The effect of borax content on the setting time of MPC (Park et al., 2016; Wang, 2006; You, 2017).

not found that B exists in the form of any crystal phase in the hardened MPC system. Therefore, borax and other boron salts are more like a kind of catalyst in MPC system.

The discovery and application of boric acid and a series of boron salts has greatly improved the use conditions of magnesium phosphate cement and facilitated the large-scale use of MPC. Different scholars hold different views on the effect of borax content on the compressive strength of MPC system. Yang and Qian (2010) showed that when the content of borax is about 7.5%–10% of the mass of magnesium oxide, the compressive strength of MPC hardened body can reach the highest level; Qian and his team believed that the strength of the MPC system would gradually decrease with the increase of borax content (Feng et al., 2016; Liu and Li, 2011; Qin, 2019; Qin et al., 2021). However, it can be agreed that, compared with the effect on the later strength of the MPC system, due to the retarding effect of borax and boric acid, the effect of borax content on the early strength of MPC (within 3 h) is very significant. Because MPC has excellent bonding performance and early strength, it is often used as a repair material for concrete structures in engineering. Therefore, the amount of borax in the actual use process should not be too high, and it should be reduced as much as possible to meet the construction conditions in order to obtain excellent mechanical performance. In addition, in recent years, some scholars have focused on the study of other catalysts that have less influence on the strength of the products in the MPC system. Dai (2019) summed up and compared the effects of various retarders and dosages on the compressive strength of MPC cementitious materials. Although borax can effectively prolong the setting and hardening time of MPC, its strength loss is serious; although $Ca(NO_3)_2{\cdot}4H_20$, $Zn(NO_3)_2$ and borax can effectively prolong the setting and hardening time of MPC, their strength loss is more serious; although $CaCl_2{\cdot}6H_2O$ can delay the hardening of MPC and has less effect on the strength, the chloride ion will destroy the passivation film on the surface of reinforcing steel, which is harmful to the reinforced concrete system. Chen and his team proposed that a new retarder prepared by mixing borax and sodium tripolyphosphate (STP) at a ratio of 1:1 can achieve the best retardation effect in the MPC system (Chen et al., 2010; Hu et al., 2015; Liu et al., 2020; Luo and Chen, 2009). However, borax is still the most important retarder at present, and the effects of various new retarders still need to be promoted and tested.

3. The effect of admixtures on properties

3.1. Mineral admixtures

Due to the high price of magnesium phosphate gelling components, in recent years, many scholars have begun to try to reduce the comprehensive cost of magnesium phosphate systems by adding mineral admixtures. Mineral admixtures are used to replace part of the excess magnesium oxide particles (Ding and Li, 2006; Xie et al., 2020). Admixtures are often added to potassium magnesium phosphate cements as inactive fillers, which not only reduce the production cost of MPC but also reduce the exothermic heat of hydration of MPC, but the effect of different admixtures on the hydration of MPC is not the same (Du et al., 2020; Jiang et al., 2017; Ma et al., 2021; Maldonado-Alameda et al., 2017). These admixtures can fill the pores as physical fillers and assist in the formation of the skeleton structure of MPC. Some cementitious materials can also react with water to form other cementitious substances.

Fly ash (FA) is the powdery ash particles collected in the flue gas of power plant boilers. Davis applied fly ash in cement and concrete as early as the 1930s. With the gradual deepening of awareness, fly ash has become one of the indispensable components of Portland cement concrete system. Yang and Wu (1999), Jiang and Zhang (2001) and others first used fly ash as a toner for magnesium phosphate cement. The color will be close to Portland cement when more than 10% of heavy-burning magnesium oxide is replaced with fly ash. Moreover, different scholars hold different views on the influence of fly ash on the strength of magnesium phosphate cement. It should be noted that although fly ash is blended into MPC cement as an inactive filler, some studies have shown that fly ash may participate in the hydration reaction to generate potassium aluminum phosphate gel in MPC (Liao et al., 2017; Mo et al., 2018). Chen et al. (2010), Li et al. (2008), Zhang and Shi (2009), Zhang et al. (2009) and others believe that fly ash can effectively improve the later strength of MPC cement, and with the increase of fly ash admixture, there is a trend that the strength increases first and then decreases in the later stage, and the water stability of MPC can be improved (Chen et al., 2011; Liu et al., 2022), but the optimum strength of fly ash content proposed by different scholars is not the same. Wang (2006) and Wang et al. (2005) believed that the addition of ordinary fly ash will reduce the strength and fluidity of MPC. Qin (2019) further proposed that the addition of ultra-fine fly ash (UFA) with a particle size of less than 3 μm will act as lubricant which not only improves the fluidity of MPC slurry, but also the strength of MPC at various ages, especially the late strength.

Silica fume (SF) is also a powdery particle collected from industrial smelting fumes. The main component is silicon dioxide. The admixture of silica fume will adsorb a large amount of water, causing the effective water-cement ratio of MPC to decrease, and the flow of MPC will decrease instead. However, some scholars have also indicated that silica fume can improve the flow of MPC and prolong the setting time when the silica fume doping is lower than 15% (Ahmad and Chen, 2018; Xu et al., 2020; Zheng et al., 2016). Li et al. (2015) believed that silica fume has a high pozzolanic effect, which can improve the later strength of the MPC system, but it will increase the water demand and reduce the fluidity. Pan (2018) believed that silica fume can consume OH^- in the system. In order to reduce the alkaline environment of the reaction system, it can also react with free Mg^{2+} in the system to generate $MgSiO_3$ after participating in the reaction, and adjust the concentration of free Mg^{2+} in the system; Chen et al. (2011) and Liu et al. (2020) believed that micro-silica fume or nano-silica can not only improve the strength of MPC system at various ages, but also improve the water resistance and wear resistance of MPC.

Metakaolin has high pozzolanic activity and is often used as an external admixture for construction cement. Mo et al. (2018) believed that the aluminosilicate component in metakaolin will participate in the acid-base reaction of MPC and metakaolin is more active than fly ash. Under the same addition amount, the MPC slurry containing metakaolin is more active than fly ash. The slurry containing fly ash has higher compressive strength; the optimum content of metakaolin is 30%, and the compressive strength of MPC at each age is the highest at the content of 30%. Qin et al. (2020) also believed that the introduction of metakaolin into MPC could significantly improve its compressive strength, volume stability, water resistance and freeze-thaw resistance. Metakaolin has high volcanic ash activity, which can react with $Ca(OH)_2$, the hydration product of OPC, to generate secondary C–S–H gel products, thus improving some properties of OPC (Lu and Chen, 2016; Qin et al., 2020). However, in the MPC system, metakaolin still has no clear reaction mechanism yet.

Improving one or more properties of MPC by adding mineral admixtures has always been one of the research hotspots. In addition to the above common mineral admixtures, many scholars have studied other admixtures (Zhang et al., 2018), has made good progress. However, the reaction mechanism of mineral admixtures participating in the hydration reaction of the MPC system is not clear, and further research on the reaction mechanism is still required in the future.

3.2. Aggregates

The cementitious material will lead to the concentration of hydration exothermic heat and an excessively high total exothermic amount, which is detrimental to the stability, later strength and durability of MPC. Incorporating a certain amount of coarse and fine aggregates can not only improve the exothermic problem of MPC, but also effectively reduce the cost of MPC. However, few scholars have analyzed whether the mineral components in the aggregates participate in the hydration reaction of MPC, and most of them believe that the aggregates are inert substances that participates in the skeleton structure of magnesium phosphate mortar or magnesium phosphate concrete. Park et al. (2016) tested the effect of sand addition on the bond strength of MPC and ordinary concrete, and they believed that the bond strength decreased after sand addition (Fig. 4).

Sand-cement ratio is another important factor affecting the extension of MPC. The admixture of fine aggregates usually has multiple effects on the strength development of MPC mortar. Firstly, the aggregate admixture plays the role of skeleton, which can hinder the expansion of cracks and can improve the strength to some extent. However, as the amount of fine aggregate increases, on the one hand, it will reduce the overall heat release of MPC system, which will affect the early strength development. On the other hand, it will reduce the amount of slurry wrapped with aggregate, which will reduce the workability of mortar and increase the chance of defects in the matrix, which will affect the strength. Affected by the material properties, different scholars have different views on the ratio of the amount of fine aggregate, S:(M+P+B) is about 0.4–1.2 (Chen et al., 2022; Lang et al., 2019; Yu et al., 2021).

Few studies have been conducted on coarse aggregates, because MPC is not suitable for application to large concrete structures due to its high cost. Qin (2019) proposed that coarse aggregates can improve the compressive strength of MPC, which is highest when the amount is about 800 kg/m^3.

3.3. Fibers

As mentioned above, MPC material has the characteristics of rapid development of early strength, high late strength and good bonding performance, and one of the most important uses at present is to be used as a rapid repair and reinforcement material (Qin, 2019). However, the hardened body of the MPC system contains a higher proportion of crystalline phase, exhibits certain ceramic properties, and thus may have higher brittleness and lower strain capacity. Incorporating a certain amount of fiber is the most common measure to strengthen and toughen cement concrete. In general, fibers can be divided into rigid fibers and flexible fibers. Steel fibers of various shapes and sizes are currently the most widely used rigid fibers, while flexible fibers include a variety of polymer fibers, glass fibers, and carbon fibers. In general, an increase in rigid fiber content increases yield stress, while the use of flexible fibers increases viscosity (Khayat et al., 2019). As acicular materials, fibers increase the possibility of mechanical interaction and fiber interlocking between fibers and MPC solid materials. Overall, similar to silicate systems, adding a certain proportion of fibers to MPC systems can increase the strength of MPC (Li et al., 2014; Li and Yi, 2018). However, the properties of fiber-reinforced MPC systems are also affected by fiber content, shape (straight/hook/corrugated), size (length/diameter), material (steel/polymer/glass/carbon), the micromorphology and affinity of the fibers used-the effect of hydrophobicity. Bhutta et al. (2017) believed that the most effective way to reduce brittleness and improve toughness is to add steel fibers to the matrix. Feng et al. (2018) further found that steel fibers can effectively improve the early hydration strength of MPC systems, especially the third day mechanical strength. Qin (2019) studied the influence of the shape and size of steel fibers on the bonding properties of MPC and fibers, and believed that anisotropic fibers facilitate the bonding between fibers and matrix, while the residual MPC matrix on the fiber surface also increases the fiber pullout resistance, as shown in Fig. 5. The increase in fiber length has little effect on the number of fiber roots per unit area (Bhutta et al., 2017; Feng et al., 2022). Decreasing the fiber length-to-diameter ratio increases the effective viscosity of the mix and decreases the drag reduction efficiency, increases the fiber orientation torque, and makes the fibers more inclined to line up along the mix, which is beneficial to the strength of MPC products (Li and Yi, 2018). Qin et al. (2018) researched that the best compressive strength of MPC concrete can be obtained when the content of basalt fiber is 1%, while the flexural strength and tensile strength will increase with the increase of basalt content. And Qin et al. (2018) believe that the performance of basalt fiber in MPC system is better than that of glass fiber. Flexible fibers such as polyethylene (PE) fibers are also used in the MPC system. Different from other fiber materials, these fiber materials have a larger content, which

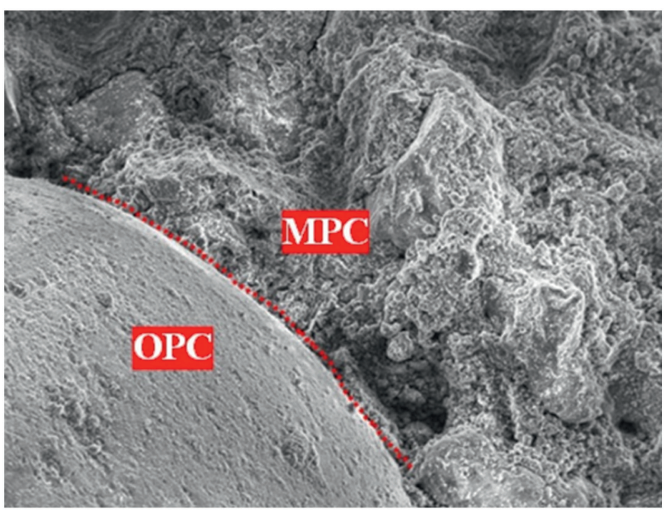

Fig. 4. SEM image of the interface between old concrete and MPC (Jiang et al., 2022).

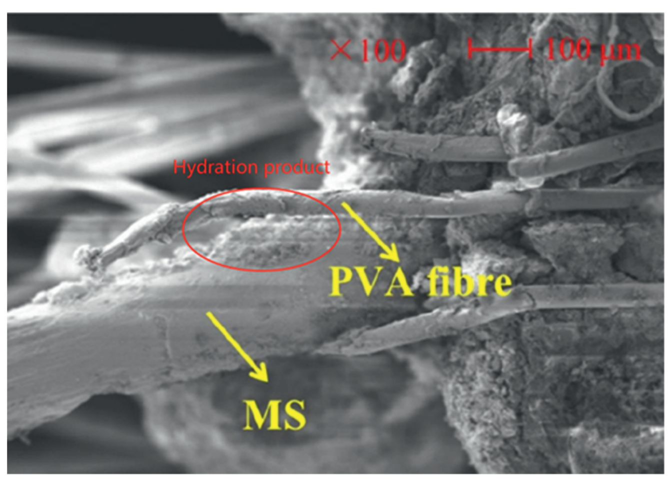

Fig. 5. SEM image of failed specimen with PVA and micro steel (MS) fibers on the fracture surface (Feng et al., 2022).

significantly improves the flexural and tensile properties of the MPC matrix and resists compression. The performance improvement is not enough (Feng et al., 2021). Some scholars have modified plant fibers by certain means (Fan et al., 2015; Jiang et al., 2020; Zhang et al., 2020), and the modified plant fibers can also effectively improve the mechanical properties of MPC.

In summary, similar to fiber-reinforced Portland cement, adding an appropriate amount of fiber will reduce the strength of magnesium phosphate cement, and also enhance the toughness and wear resistance of MPC. The reason is that the addition of fibers will bring in voids and reduce the compressive strength, while the strong toughness of fibers will constrain the flow of the fresh cement base, and make the cracks difficult to expand after the cement base is hardened (Li and Yi, 2018), increasing the embedding between fibers and MPC matrix.

4. Conclusions

(1) Magnesium phosphate cement cementitious material is a phosphate cement-based material that is solidified and hardened to form strength after magnesium oxide, phosphate and retarder are neutralized by acid and alkali under water conditions. The material has high early strength and good adhesion ability to old concrete, borax-based retarder can adjust the setting time of magnesium phosphate system.

(2) The choice of phosphate has a great influence on the reaction products. Due to the difference in the strength of the reaction products, ammonium dihydrogen phosphate and potassium dihydrogen phosphate are the most important phosphate materials in the MPC system. Among them, the reaction product of ammonium salt has higher strength, but is prone to escape of ammonia gas, and is often used in the mixing ratio design of ultra-high-strength ammonium phosphate salt; although the strength of potassium salt is slightly lower, but no gas escapes, so more scholars choose to use potassium dihydrogen phosphate to prepare high-strength magnesium phosphate cement.

(3) Borax is the earliest and most commonly used retarder for MPC cementing materials. The retardation effect of borax is related to the ratio of boron to magnesium. However, borax retarders have an adverse effect on the strength of MPC. Many scholars have proposed that a variety of materials have retardation effects on the MPC gelling system, but most retarders still have negative effect on mechanical strength of MPC, especially at the early stage.

(4) The proportion of water determines the amount of water of crystallization in the hydration product of MPC. Under certain water content conditions, struvite or *K*-struvite is the main hydration product of MPC gelling system, and its strength is higher than other crystals.

(5) Fly ash, silica fume and metakaolin, as common mineral admixtures, all have positive effects on the mechanical properties of MPC, but the mechanisms and degrees of the three materials affecting the strength of MPC are slightly different. With the gradual increase of the content of fly ash, mineral powder and metakaolin, the setting time of magnesium phosphate cement paste shows a shortening trend; most scholars believe that with the gradual increase of the content of fly ash, mineral powder and metakaolin, the compressive strength of MPC specimens will show a trend of increasing first and then decreasing.

(6) Aggregates can also improve the volume stability and mechanical properties of MPC by forming a skeleton structure and slowing down the reaction exotherm.

(7) MPC gelling materials can increase their mechanical properties by fiber reinforcement. In the MPC system, fibers have a more significant effect on the tensile strength and toughness of MPC materials. Steel fibers are still the most widely used fibers, and the shape and ratio of fibers have a significant impact on the bonding properties between fibers and matrix.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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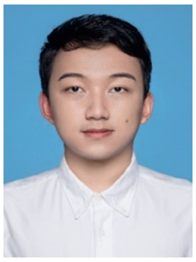

Yangzezhi Zheng is a PhD candidate of Southeast University, China. His main research interests include ultra-high performance cement concrete, magnesium phosphate cement and rapid repair materials for airport pavement surfaces.

Dr. Yang Zhou is an associate professor of Southeast University, China. His main research interests include multi-scale simulation of cementitious composites, microstructure regulation theory and technology of high-performance inorganic non-metallic materials, solid waste resourceization and its application in civil engineering, etc.

Dr. Xiaoming Huang is a professor, and the head of Road and Railway Engineering Department of Southeast University. His main research interests include pavement structure design of high-grade highways, comprehensive application technology of road construction materials, treatment of pavement diseases and comprehensive stabilization technology of roadbed, etc.

Haoyuan Luo is a PhD candidate of Southeast University, China. In past five years, he published more than 20 papers in international and Chinese academic journals and conferences, including 15 SCI/EI retrieved articles.