Study on magnesium phosphate cement modified by steel slag

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Abstract. This paper mainly studied the influence of steel slag on the setting time, compressive strength, corrosion resistance, microstructure and pore structure of MPC. It was found that the setting time of MPC decreased with the increase of steel slag. The compressive strength was optimum with 15% content of steel slag. The addition of steel slag improved the corrosion resistance of MPC in low concentration alkali solution. With the increase of alkali solution concentration, the hydration product was decomposed, resulting in the increase of crack and harmful pore of MPC.

1. Introduction
Magnesium phosphate cement (MPC) is a new inorganic cementitious material as known chemically-bond ceramics [1]. Due to the excellent properties, such as high early strength, rapid setting time, good bond performance and lower drying shrinking, MPC has been used as the fast repair and reinforcement material in the field of building structures [2]. The formations of MPC are mainly dead burned magnesium oxide, acid phosphate and admixture through acid-base reaction and the hydration product is mainly MgKPO₄·6H₂O [3, 4], as shown in equation (1).

\[
\text{MgO} + \text{KH}_2\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot 6\text{H}_2\text{O}
\] (1)

Previous studies showed that the main influence factors on the properties of MPC included molar ratio of phosphate and magnesium oxide (P/M), water binder ratio (W/C) and some admixtures, the performances were relatively good with the P/M of 1/4~1/5, W/C of 0.14~0.16 [5, 6]. Recently, mineral admixtures, such as fly ash (FA), silica fume and slag, etc. have been used to improve the properties of MPC. Li [7] found that the compressive strength increased 7.6% with the addition of 50% FA. Zheng [8] reported that the compactness and compressive strength of MPC significantly increased with the mixing of 15% FA and 10% silica fume. What is more, Lin [9] and Chen [10] found that the addition of FA and silica fume could improve the water resistance of MPC. However, the effects of steel slag on the properties of MPC is rarely reported.

In this paper, steel slag was used for the modification of MPC and mainly the influence of steel slag on the setting time, compressive strength, alkali resistance and pore structure of MPC, has been studied.

2. Experimental details
2.1. Raw materials
Previous studies indicated that the surface area of magnesium oxide is strictly related to its calcination temperature, which strongly determines the reactivity of this acid-base reaction [11, 12]. Li found that
the setting time of MPC was just 283 seconds with the calcination temperature of 1200 °C [12]. Therefore, at the sintering level of 1600 °C, which will lead to well crystallized MgO crystal of higher mean grain size and reduce the activity of MgO. However, due to the acid-base reaction, the reaction rate of MPC is always fast. In this paper, the used dead burned MgO is calcined by magnesite at 1600 °C and the chemical composition and physical properties are shown in Table 1. The used steel slag was superfine steel slag and the chemical composition and physical properties are shown in Table 2. The used reagents, such as KH2PO4, Na2B4O7·10H2O (Borax) and Ca(OH)2 are analytically pure. The used water was deionized water.

Table 1. Chemical composition and physical properties of calcined MgO.

| Sample | MgO (%) | CaO (%) | SiO2 (%) | Al2O3 (%) | Fe2O3 (%) | Density (g/cm³) | Bulk density(g/cm³) | Specific surface area(cm²/g) |
|--------|---------|---------|----------|-----------|-----------|----------------|----------------------|---------------------------|
| MgO    | 91.7    | 1.4     | 1.6      | 4.0       | 1.3       | 3.46           | 1.67                 | 805.9                     |

Table 2. Physical and chemical properties of steel slag.

| Sample | CaO (%) | Fe2O3 (%) | SiO2 (%) | Al2O3 (%) | MgO (%) | MnO (%) | P2O5 (%) | Loss (%) | Specific surface area (m²/kg) | Density (g/cm³) |
|--------|---------|----------|----------|-----------|---------|---------|---------|---------|-----------------------------|----------------|
| Slag   | 38.2    | 24.9     | 18.3     | 6.8       | 5.1     | 2.5     | 1.4     | 2.8     | 657                         | 3.62           |

2.2. Experimental design

2.2.1. Mixing design of MPC. Based on the previous studies mentioned above, the mix proportion of MPC in this paper is shown in Table 3. Among which, the retarder of borax (B) and steel slag were added by the mass percentage of MgO.

Table 3. Mixing proportion of MPC.

| Sample code | P/M | W/C | B (%) | Steel slag (%) |
|-------------|-----|-----|-------|----------------|
| Control     | 1/4.5 | 0.14 | 5     | 0              |
| M1          | 1/4.5 | 0.14 | 5     | 5              |
| M2          | 1/4.5 | 0.14 | 5     | 10             |
| M3          | 1/4.5 | 0.14 | 5     | 15             |
| M4          | 1/4.5 | 0.14 | 5     | 20             |

2.2.2. Corrosion resistance of MPC. Determine the optimum dosage of steel slag and after 28 days of curing, the control sample and the optimum steel slag content sample were soaked in water and Ca(OH)₂ solution with the pH value 9, 11 and 13 for 30, 60 and 90 days to evaluate the corrosion resistance of modified MPC.

2.3. Testing method

2.3.1. Setting time and compressive strength. The setting time was tested using a modified Vicat needle according to the standard of ASTM C807-05. The MPC paste was cast in the mold of 40×40×160mm for the test of compressive strength. After remolded, the samples were cured at the temperature of 20°C and testing 28 days compressive strength.

2.3.2. Microstructure analysis. The microstructure of MPC was tested by the field-emission scanning electron microscope of SEM, NOVA Nano SEM230) equipped with an energy dispersive spectrometer (EDS).
2.3.3. **Pore structure analysis.** The porosity and pore size distribution were analyzed by Auto Pore IV 9500 mercury injection apparatus instrument with the pressures in the range of 0.2-60,000 psi.

3. **Results and discussion**

3.1. **The influence of steel slag on the setting time of MPC**

The influence of steel slag on the initial setting time of MPC is shown in Figure 1. The result indicated that the setting time of MPC decreased with the increase of steel slag. The retarding mechanism of the control sample is mainly due to the adsorption of $\text{B}_4\text{O}_7^{2-}$ ionized by borax on the surface of $\text{MgO}$ and blocking the hydrolyzation of $\text{MgO}$. As a result, the setting time prolonged. After the steel slag added, the $\text{Ca}^{2+}$ provided by $\text{CaO}$ in steel slag can combine with $\text{B}_4\text{O}_7^{2-}$, which can weaken the retarding effect of borax. Therefore, the setting time decreased with the increase of steel slag.

![Figure 1. Setting time of MPC.](image1)

![Figure 2. Compressive strength of MPC.](image2)

3.2. **The influence of steel slag on the compressive strength of MPC**

For each mixture, there are three samples in each test. The results are the average of three testing values shown in Figure 2. The results displayed that the compressive strength increased first and then decreased with the increase of steel slag. When the content of steel slag was 15%, the enhancement effect of MPC was optimum. With increase in slag content beyond 15%, the compressive strength
decreased. The main reason for this phenomenon can be explained as follows. Steel slag, being an inert material, can act as the filler and make the MPC matrix denser. In addition, as ultrafine powder, the nucleation effect of steel slag can reduce the nucleation barrier of MPC during the reaction process. However, when the slag was excessive, the hydration product generated by MPC decreased. The limited hydration product is not sufficient enough to bind together the slag particles tightly, resulting in the loose matrix and lower compressive strength of MPC. Moreover, the amount of free CaO increased with the increase of steel slag, which could react with water and generate expansive Ca(OH)₂, resulting the cracking of MPC matrix. Therefore, the compressive strength of MPC decreased with the excessive steel slag.

3.3. The corrosion resistance of steel slag modified MPC
The above results indicated that the strength of MPC sample (M3) with 15% steel slag was the best. Therefore, in this section, the control sample and sample with 15% steel slag were selected to evaluate the effect of steel slag on the corrosion resistance of MPC. After soaked the samples in water and Ca(OH)₂ solutions with the pH values of 9, 11 and 13 for 30, 60 and 90 days, the compressive strength were tested, and the results are shown in Table 4.

| Sample code | Soaking time(day) | Compressive strength(MPa) | water | pH=9 | pH=11 | pH=13 |
|-------------|------------------|--------------------------|-------|------|-------|-------|
| control     | 0                | 43.1                     | 43.1  | 43.1 | 43.1  | 43.1  |
|             | 30               | 42.7                     | 41.9  | 39.4 | 27.1  |       |
|             | 60               | 42.1                     | 40.6  | 34.6 | ---   |       |
|             | 90               | 41.5                     | 39.1  | 28.8 | ---   |       |
| M3          | 0                | 47.9                     | 47.9  | 47.9 | 47.9  |       |
|             | 30               | 47.7                     | 47.1  | 44.4 | 33.4  |       |
|             | 60               | 47.2                     | 45.5  | 39.6 | --    |       |
|             | 90               | 46.8                     | 44.2  | 34.4 | --    |       |

The results of Table 4 showed that the compressive strength of the samples slightly decreased in water with the increase of soaking time. When soaked for 90 days, the strength losses of control and M3 samples were 3.7% and 2.3%, respectively. The results indicated the water resistance of steel slag modified MPC was relatively good. When soaked in the Ca(OH)₂ solution, the strength of MPC decreased with the increase of pH values and soaking time. The strength losses of the control and M3 samples after soaked 90 days were found to be 9.3% and 7.7% at the pH value of 9, 33.2% and 28.2% at the pH value of 11, respectively. It showed that the alkali resistance of MPC was relatively good in low concentration Ca(OH)₂ solution. With the concentration of alkaline solution increase, the alkali resistance of MPC was poor. Among which, the alkali resistance of steel slag modified MPC was better than the control sample. However, when the pH values was 13, the samples was corroded seriously after soaked 30 days and the strength could not be measured.

3.4. Microstructure of MPC
The microstructures of the samples after soaked 30 days were tested, as shown in Figure 3.
The microstructure of MPC indicated that the matrix compactness of M3 sample was better than the control sample at the same pH value after soaked, which indicated that the addition of steel slag improved the corrosion resistance of MPC. With the increase of pH value, the morphology of MPC products was changed and the crack size increased. Previous research indicated that the hydration product MgKPO$_4$ of MPC would be decomposed into expansive Mg(OH)$_2$ deposit and soluble phosphate in the alkaline environment [13]. The ionic reaction equation is presented in equation (2).

$$MgKPO_4 + OH^- \rightarrow K^+ + PO_4^{2-} + Mg(OH)_2 \downarrow$$  

With the increase of pH values, the decomposition amount of MgKPO$_4$ increased, resulting in the loose structure and low strength. In addition, the expansive Mg(OH)$_2$ product, which caused the matrix cracking. Due to the mentioned factors, the properties of control MPC sample decreased. However, Steel slag is a kind of alkali activated cementitious material. It has certain activity in alkaline environment. The hydration of steel slag improved the compactness of MPC, as a result, the mechanical properties and corrosion resistance were better than the control sample.

**3.5. Pore structure**

The above results indicated that the resistance of MPC was poor at high concentration of alkaline solution. In this section, the pore structure of the control sample and M3 sample in Ca(OH)$_2$ solution with the pH value of 13 after soaking 30 days were tested. The results were presented in Figure 3 and Table 5.

According to the effects of pore diameter on the properties of cement-based materials, the pore can be divided into the following parts [14]. The pores less than 20nm is harmless, 20~100 nm is the less harmful pore, 100~200nm is the harmful pore and the pore larger than 200nm is the more harmful pore.

After soaked, the pore structure are shown in Figure 4 and Table 5. The results showed that the total porosity and most probable pore size were decreased from 14.67% and 12.54 to 11.83% and 10.74 with the addition of steel slag, which indicated that steel slag could refine the pore size and decrease the total porosity of MPC. Although the addition of steel slag slightly decreased the content of harmless and less harmful pore, the harmful and more harmful pore of M3 sample significantly decreased. Therefore, the compressive strength of M3 sample was bigger than the control sample after soaked in Ca(OH)$_2$ solution 30 days.
Figure 4. Pore structure of MPC after soaking in Ca(OH)₂ solution 30 days ((a) Differential distribution. (b) Cumulative distribution).

Table 5. Pore distribution of MPC.

| Sample code | Total porosity (%) | Most probable pore size (µm) | The pore content (mg/L)×10⁻² |
|-------------|--------------------|------------------------------|-----------------------------|
|             |                    |                              | Aperture size (nm)           |
|             | 1                  |                              | <20 | 20–100 | 100–200 | >200 |
| Control     | 14.67              | 12.54                        | 1.67 | 1.77   | 1.76    | 9.45 |
| M3          | 11.83              | 10.74                        | 1.53 | 1.31   | 1.22    | 7.80 |

4. Conclusions
(1) The addition of steel slag decreased the setting time of MPC.
(2) The compressive strength of MPC increased first and then decreased with the addition of steel slag. The strength was optimal with the 15% content of steel slag.
(3) The addition of steel slag decreased the total porosity, optimized the pore structure and improved the corrosion resistance of MPC.

Acknowledgements
The authors would like to acknowledge the financial support provided by National Natural Science Foundation of China (No.51678011) and Beijing Natural Science Foundation (No.8162005).

References
[1] Roy D M 1987 J. Sci. 235 651-58
[2] You C, Qian J S, Qin J H and Wang H T 2015 J. Cem. Concr. Res. 78 179-89
[3] Viani A and Gualtieri A F 2014 J. Cem. Concr. Res. 58 56-66
[4] Buj I, Torras J, Rovira M and Pablo J D 2010 J. J. Hazard. Mater. 175 789-94
[5] Hou D S, Yan H D, Zhang J R and Li Z G 2016 J. Constr. Build. Mater. 112 331-42
[6] Li Y, Shi T F and Li J Q 2016 J. Constr. Build. Mater. 105 384-90
[7] Li Y and Chen B 2013 J. Constr. Build. Mater. 47 977-83
[8] Zheng D D, Ji T, Wang C Q and Hossain K M A 2016 J. Constr. Build. Mater. 106 415-21
[9] Lin W, Sun W and Li Z J 2010 J. J. Build. Mater. 13(6) 716-21
[10] Chen B and Wang J 2010 J. Cem. 7 14-18
[11] Viani Alberto 2016 J. Ceram. Int. 42 (14) 16310-16
[12] Li Y, Sun J and Chen B 2014 J. Constr. Build. Mater. 29 177-83
[13] Li Y., Shi T F, and Sun J 2015 J. J. Build. Mater. 18(6) 1060-64
[14] Wu Z W 1990 Expansive Concrete (Beijing: Railway Publishing of Beijing)