Study on flexural resistance and hydration mechanism of magnesium phosphate cement

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ABSTRACT: Based on a large number of research data at home and abroad, this paper designed an experiment to complete the research on the mechanical properties and durability of magnesium phosphate cement by the ratio of magnesium phosphorus, fly ash content and pH value. On this basis, the effects of curing methods and different concentrations of hydrochloric acid on hydration products of magnesium phosphate cement were studied, and the mechanism of action was analyzed. Finally, when the M/P ratio was 4, with the increase of curing time, the strength of MPC increases gradually. When M/P is greater than 4, the flexural strength of MPC all shows a certain degree of shrinkage. In addition, fly ash can reduce the shrinkage of magnesium phosphate cement-based materials; The content of K-type struvite ($KMgPO_4 \cdot 6H_2O$) in MPC can be increased under acid curing (pH=2) and water curing conditions.

1. INTRODUCTION

Magnesium Phosphate Cement (MPC) is a kind of cementing material composed of alkaline component magnesium oxide (M), acidic component phosphate (P) and retarder (B) in a certain proportion [9]. As a new type of inorganic cementing material, MPC has many advantages, such as fast setting and hardening, better bonding property, better volume stability, shrinkage and better heat resistance than old concrete [2][8]. MPC is widely used in the rapid repair of roads, Bridges, airport runways and other facilities [6], as well as the solidification of harmful and radioactive substances, and have important civil, military applications, dental cement and bone binder [1][10].

By changing the dosage of M/P and fly ash, the influences of different M/P on MPC's flexural properties and products, the influences of different fly ash dosage on MPC's flexural properties and products, and the influences of hydrochloric acid solution of different pH on MPC's mechanical properties and products were designed and analyzed in this paper.

2. TEST

2.1. Raw material

(1) Copy Magnesium oxide (MgO): The test adopts industrial pure grade of re-fired magnesium oxide, made of magnesite ($MgCO_3$) forged in an industrial kiln at about 1700℃, and then crushed and ground into different particle sizes, the color is brown and yellow.

(2) Potassium dihydrogen phosphate (KH_2PO_4): Industrial grade KH2PO4, white crystal.

(3) Retarder ($NaB_4O_7 \cdot 10H_2O$): Chemical pure, content not less than 99.5%.

(4) Experimental water: laboratory tap water.

(5) Fly ash (FA): Grade II fly ash (FA) from Shenyang Taiouke Chemical Co., LTD was used in this test. Its specific volume is about 280m^2/kg, belonging to low calcium ash.

2.2. Experimental method

(1) The average value of flexural results of a set of three prisms is taken as the test result. When the three strength values exceed the average value by 10%, the average value should be taken as the flexural strength test result.

(2)A side of the test body is placed on the supporting cylinder of the testing machine, the long axis of the test body is perpendicular to the supporting cylinder, and the load is evenly added vertically on the relative side of the prism at the rate of 50N/s ± 10N/s through the loading cylinder, until it is broken. The flexural strength Rf is expressed in Newtons per square millimeter (MPa) and calculated in accordance with Equation (1):

$$R_f = \frac{1.5F_f L}{b^3} \quad (1)$$

Among, F_f represents the load applied to the middle of the prism at breaking, N.L represents the distance between the supporting columns, mm.b represents the side length of a prismatic square section, mm.

(3) Refer to GB/T 17671-1999 "Cement mortar strength test method (ISO method)" determination of flexural strength.

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2.3. Laboratory environment

The temperature of the test molding laboratory should be maintained at 20°C±2°C, and the relative humidity should not be less than 50%. The temperature of the curing box or fog chamber with mold curing shall be kept at 20°C±1°C and the relative humidity shall not be less than 90%.The water temperature of the test curing pool should be within the range of 20°C±1°C.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Effect of M/P on flexural performance of MPC

M/P can significantly affect the development of the flexural strength of MPC. When the M/P ratio is 4, the flexural strength of MPC gradually increases with the increase of curing age. However, when M/P is greater than 4, the flexural strength of MPC decreases by 22.58% at 7d. In addition, an increase in M/P generally increases the early strength of MPC. For example, when M/P is 4, the lowest flexural strength for the first 7 days of MPC is 6.7MPa. When M/P is 5, the lowest flexural strength is 7.2MPa. When M/P is 6, the lowest strength is 8MPa.

3.2. Effect of fly ash on flexural property of MPC

In this paper, different proportions of fly ash were added under the conditions of M/P=4:1, M/P=5:1 and M/P=6:1 respectively to observe the strength of natural curing and water curing and then make a conclusion. FA0 means fly ash content is 0%, FA15 means fly ash content is 15%, and FA25, FA35 and FA45 are the same.

3.2.1. M/P=4:1

It can be seen from Table 1 that when M/P is relatively low (M/P=4), the impact of fly ash on the flexural strength of MPC is not obvious. When the fly ash content increases from 15% to 25%, the flexural strength of MPC increases by 11.29%, and then the increase of fly ash will gradually reduce the flexural strength of MPC. On the one hand, the addition of fly ash improves the pore size distribution of MPC; on the other hand, the increase of fly ash reduces the relative content of cementing material in MPC [4].

Table 1. Flexural strength of MPC under M/P=4:1 (unit: MPa)

Matching	Group	Natural curing		Water storage	
		1 day	7 day	1 day	7 day
M/P=4:1(contain flyash)	FA0	6.6	8.2	9.0	10.3
	FA15	7.6	6.2	9.0	9.1
	FA25	6.4	6.9	8.9	9.5
	FA35	6.2	6.6	9.2	9.2
	FA45	8.2	5.9	10.8	8.2

3.2.2. M/P=5:1

As shown in Table 2, when M/P in MPC is equal to 5, fly ash content has little effect on MPC, and even fly ash can reduce the flexographic strength of MPC, while fly ash does not change the flexographic strength of MPC significantly. Meanwhile, it can reduce the bond strength of MPC in early and middle stages, but can improve the growth rate of bond strength in later stages.

Table 2. Flexural strength of MPC under M/P=5:1 (unit: MPa)

Matching	Group	Natural curing		Water storage	
		1 day	7 day	1 day	7 day
M/P=5:1(contain flyash)	FA0	7.2	8.0	9.6	10.5
	FA15	6.4	6.7	10.0	8.7
	FA25	6.8	6.0	9.7	7.7
	FA35	6.1	7.1	13.2	8.2
	FA45	6.2	6.9	8.7	5.7

3.2.3. M/P=6:1

When M/P in MPC is equal to 6, the effect of fly ash content on MPC is similar to the above M/P is equal to 5, and even the addition of fly ash will significantly reduce the flexural strength of MPC [7].

3.3. Effect of pH value on flexural performance of MPC

3.3.1. Flexural performance test of MPC at different pH values without fly ash

Table 3 shows the influence of different pH values on the flexural strength of MPC. It can be clearly seen that the flexural strength of MPC with M/P at 5 is the highest under strong acid condition. Similarly, when M/P is 4, the flexural strength gradually decreases with the increase of pH value, and the MPC with M/P at 6 also shows a general trend of decline.

Table 3. Flexural Strength of MPC in Hydrochloric acid without fly Ash at Different pH Values (MPa)

Matching	pH	1		15		2		2.5		3	
	Cure time	1d	7d	1d	7d	1d	7d	1d	7d	1d	7d
Pure magnesium phosphate	M/P=4	10.6	11.9	11.1	11.5	13.4	10.8	10.2	10.0	10.5	8.7
	M/P=5	11.0	10.0	14.2	11.0	10.9	11.5	11.3	11.0	11.3	9.7
	M/P=6	10.8	10.1	10.6	9.3	10.4	7.9	10.9	11.4	10.9	10.6

3.3.2. MPC flexural performance test at different pH with fly ash

The addition of fly ash can obviously improve the corrosion resistance of MPC. However, it is worth noting that the hydrochloric acid corrosion resistance of MPC is roughly the same under the same fly ash content. However, in hydrochloric acid solution environment, higher M/P ratio can make MPC obtain better flexural strength. Studies have shown that fly ash can only play its activity in alkaline environment [3].

When M/P is 4, the flexural strength of MPC can be significantly improved only when the fly ash content reaches 35%. At the same time, it is found that when M/P is 6, fly ash will significantly reduce the flexural performance of MPC. In addition, there is a positive correlation between the increase of fly ash content and the decrease of flexural strength. It can be seen from Table 4 that when M/P is 5, MPC without fly ash shows an obvious downward trend with the increase of pH value of hydrochloric acid solution (pH>1.5), that is, low-acid solution has a significant impact on the flexural strength of MPC without fly ash. However, when fly ash is added, the flexural strength of hydrochloric acid solution at different pH values has little change.

Table 4. M/P=5:1 (fly ash) the flexural strength of MPC in hydrochloric acid at different pH values

Matching	pH	1		15		2		2.5		3	
	Cure time	1d	7d	1d	7d	1d	7d	1d	7d	1d	7d
M/P= 5:1 (contain fly ash)	FA0	11.0	10.0	14.2	11.0	10.9	11.5	11.3	11.0	11.3	9.7
	FA15	8.9	7.8	9.1	9.1	10.8	10.6	9.0	9.1	10.8	9.1
	FA25	10.6	8.6	10.1	9.1	7.8	10.2	9.0	10.0	10.3	8.6
	FA35	9.8	7.0	11.0	9.1	9.9	8.0	9.9	8.2	9.7	8.3
	FA45	9.6	8.0	11.4	9.1	11.3	8.0	9.4	8.2	8.7	8.3

4. STUDY ON PHASE COMPOSITION OF MPC

4.1. Appearance study

It can be seen from the observation that the appearance of the cement specimen of 1-day curing with acid soaking has little change, while the appearance and quality of the MPC specimen of 7-day curing with acid soaking have been significantly corroded to different degrees, the surface structure has been destroyed, the surface of the test block has obvious holes, and the volume of the test block has been reduced to different degrees. The quality loss rate of the sample is positively correlated with soaking time, and the stronger the acid is at the same soaking age, the higher the loss rate is.

4.2. XRD analyses

4.2.1. The effect of curing mode

MPC used in acidic environments will not only be affected by the pH value of the solution in the environment, but also cause differences in curing conditions due to different construction sites, which will have different degrees of influence on the strength development of MPC. The development of MPC strength is closely related to its phase composition, so it is very important to study the variation of MPC hydration products under different curing conditions.

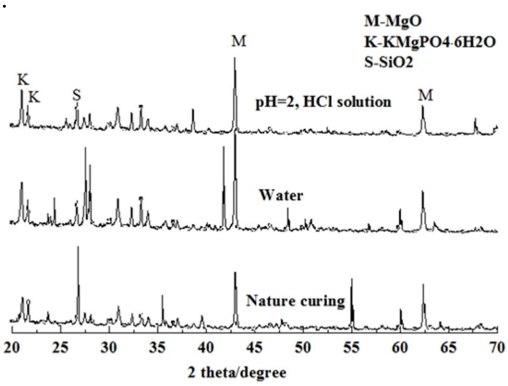

Figure 1. Effect of curing mode on MPC phase composition(fly ash free).

Figure 1 shows the XRD patterns of hydration products of MPC (without fly ash) under different curing conditions. It can be seen from Figure 1 that hydration products of MPC cured in natural curing, water curing and hydrochloric acid solution are mainly K-type guvite ($KMgPO_4 \cdot 6H_2O$), unreacted magnesium oxide and part of silicon dioxide. Among them, MPC produced more K-type struvite ($KMgPO_4 \cdot 6H_2O$) under acid curing and water curing conditions. It can be seen from the production amount of struvite ($KMgPO_4 \cdot 6H_2O$), the main hydration product of MPC, that water curing and hydrochloric acid curing with a certain acidity (pH=2) can increase the number of hydration products of MPC. This also partly explains the phenomenon that the mechanical properties of MPC after hydrochloric acid immersion are enhanced rather than reduced.

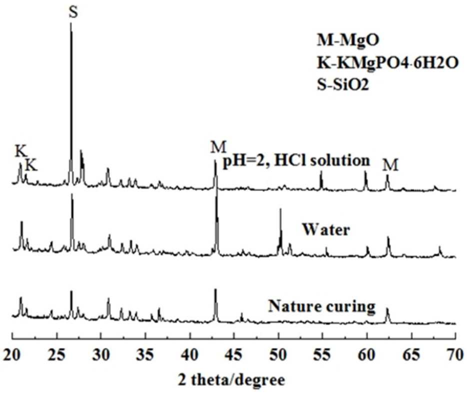

Figure 2. Effect of curing mode on MPC phase composition (fly ash).

FIG. 2 further illustrates the influence of curing mechanism on the mechanical properties of MPC modified by fly ash. In the test, hydration products of MPC mixed with 45% fly ash under different curing conditions were tested and analyzed. As can be seen from Fig.2, hydration products of MPC after mixing fly ash are still mainly K-type struvite, unreacted magnesium oxide and part of silicon dioxide, and the addition of fly ash does not produce significant new hydration products in MPC. However, the addition of fly ash seems to increase the content of SiO_2 in MPC under water curing and hydrochloric acid curing conditions, or it is believed that after the addition of fly ash, MPC can consume more SiO_2 under natural curing conditions than under other curing conditions.

4.2.2. Influence of hydrochloric acid solution concentration

Figure 3 shows the XRD peak spectrum of MPC soaked in hydrochloric acid solution at different pH values (without fly ash). It can be seen from Figure 3 that hydrochloric acid at different pH values will affect the contents of hydration products K-type struvite, residual SiO_2 and residual MgO in MPC. When pH value is 1, the residual MgO content in MPC is the largest, and when pH value is greater than 1.5, the residual MgO content in MPC changes relatively little. This may be related to the different hydration mechanisms of MPC at different pH values. It is worth noting that when pH of hydrochloric acid solution is 2, the amount of K-type struvite ($KMgPO_4 \cdot 6H_2O$), the main hydration product of MPC, is the least; while when pH value is large or small, the amount of K-type struvite ($KMgPO_4 \cdot 6H_2O$) is roughly the same [5]. This may be because the hydration mechanism of MPC is greatly changed in pH=2 of hydrochloric acid, and the content of K-type struvite ($KMgPO_4 \cdot 6H_2O$) generated is relatively small.

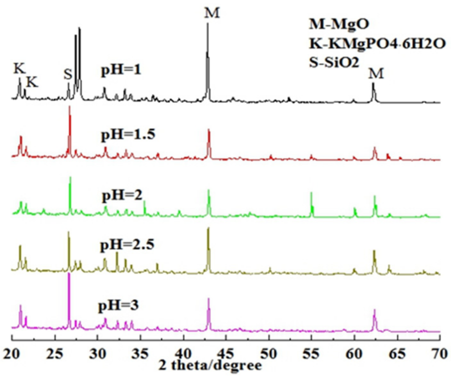

Figure 3. Effect of HCl solution concentration on MPC phase composition (fly ash free)

FIG. 4 shows the influence of hydrochloric acid solutions of different concentrations on the hydration products of MPC doped with fly ash. It can be seen from FIG. 4 that the content of SiO_2 in MPC increased significantly after the addition of fly ash. For further observation, it was found that the hydration mechanism of MPC in hydrochloric acid solutions of different pH changed after fly ash was added. MPC still increased with the increase of pH of hydrochloric acid solution after soaking in high concentration hydrochloric acid solution (pH=1) without fly ash.

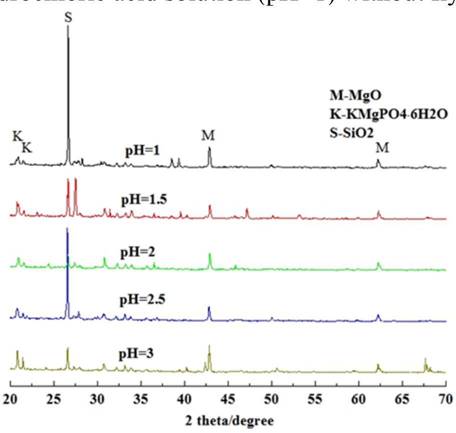

Figure 4. Effect of HCl solution concentration on MPC phase composition (fly ash)

5. CONCLUSION

This paper mainly studied the effects of M/P on the mechanical properties of MPC, fly ash on the mechanical properties of MPC and pH value on the mechanical properties of MPC. On this basis, the effects of curing methods and different concentrations of hydrochloric acid on the hydration products of MPC were studied. The main conclusions are as follows:

(1) M/P can significantly affect the development of compressive and flexographic strength of MPC (without fly ash). When the M/P ratio is 4, the strength of MPC gradually increases with the increase of curing age. When M/P is greater than 4, the flexographic strength of MPC appears to shrink to a certain extent.

(2) Fly ash can improve the flexural performance of MPC with low M/P (M/P=4), but the improvement of compressive strength of MPC with fly ash is not obvious. In addition, the impact of fly ash on the drying shrinkage of magnesium phosphate cement-based materials, fly ash

incorporation will reduce the shrinkage of magnesium phosphate cement-based materials.

(3) Only when pH value of hydrochloric acid solution is less than 1.5, fly ash modified magnesium phosphate cement shows better compressive strength.

(4) The hydration products produced by MPC under different curing conditions are mainly K-type struvite ($KMgPO_4 \cdot 6H_2O$), unreacted magnesium oxide and some silicon dioxide. Acid curing (pH=2) and water curing conditions can increase the content of K-type struvite ($KMgPO_4 \cdot 6H_2O$) in MPC.

REFERENCES

1. Baoguo Ma, Jingran Wang, Xiangguo Li and Chao He. Solidification of lead nitrate by magnesium phosphate cement under different environmental conditions. J. Function materials,2013,44(21):3183-3185+3189.
2. Hongtao Wang, Shihao Zhang, Jianhua Ding and so on. Study on Influencing factors of wear resistance of magnesium phosphate cement repair material J. Functional Materials, 2015, 46(20): 20068-20072.
3. Hongyi Jiang, Lianmeng Zhang. Study on magnesium phosphate cement. Journal of Wuhan University of Technology,2001,23(4):32-34
4. Jiangtao Zhao, Xiangguo Li, Yan Zhang, Huaqing Liu and Xiaopeng Yin. Effect of fly ash on magnesium phosphate cement J. Silicate bulletin,2018,37(02):695-700.
5. Junxia Liu, Zhongyu Li, Maoliang Zhang and Ran Hai. Research progress of magnesium phosphate cement modified by mineral admixtures J. Inorganic Chemicals Industry, 2022,54(01):18-23.
6. Qi Fang, Bingfei Xiao and Zhu Ding. Review on research progress of mineral admixtures in MPC J. Concrete, 2021(06):67-72.
7. Siyu Zhang, Huisheng Shi and Shaowen Huang. Effect of fly ash content on mechanical properties of magnesium phosphate cement based composites. J. Journal of Nanchang University (Engineering Edition), 2009, 31(01):80-82.
8. Weiliang Bai, Ming Li and Qi Xie. Study on preparation and mechanical properties of modified magnesium phosphate cement. J. Industrial buildings, 2021,51(04):161-166+203.
9. Xingwen Jia, Duanke Si, Xin Zhang and so on. Study on mechanical properties of carbon fiber reinforced magnesium phosphate cement mortar. J. Materials Review, 2016, 30(22): 138-142.
10. Zizheng Wu, Jian Zhang, Tongyi Chen, Lijun Li, Changsheng Liu, Han Guo and Zhongwei Chen. Experimental study on magnesium phosphate bone adhesive bonding fracture. J. Chinese Journal of Restorative and Reconstructive Surgery, 2006(09):912-915.