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Study on Modification of Magnesium Oxychloride Cement

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Abstract. In recent years, magnesium oxychloride cement (MOC) has drawn more and more attention, but its disadvantages of poor water resistance, brittleness, easy to absorb moisture limited its uses. Waste glass fiber reinforced plastic (GFRP) and additives were added into the MOC to improve its performance. The results show that waste GFRP fiber with the length of 5-10 mm has remarked contribution to the softening coefficient of the cement paste. When the addition is 2%, the softening coefficient of the cement increases by 24.95%. Compared to the blank, proper dosages of phosphoric acid, ferric phosphate and citric acid increase the softening coefficient of MOC from 0.461 to 1.026, 0.797 and 0.993 respectively.

1. Introduction

MOC is typical cementing material, which is also known as the Sorel cement or magnesium cement [1]. It is an air-hardening binding material prepared from a certain concentration of magnesium chloride and magnesium oxide, which has the advantages of high mechanical strength and high stiffness. However, it is a brittle material after hardening, and possesses the disadvantages as poor water resistance, easily deformation, moisture absorption and halogenation and other shortcomings. In order to overcome these defects, some additives are used to improve the performance of MOC.

Fiber can significantly improve the mechanical strength of MOC. Li Congbo et al. [2] studied the effects of chopped and continuous arrangement of two kinds of glass fibers on the toughening effect of MOC. It was found that the chopped fiber had better toughening effect of the continuous fiber to MOC matrix. Ma Hui [3] mixed polypropylene fiber, steel fiber and with magnesium mortar and found that the toughening effect of mixed fiber mortar is higher than that single-fiber mortar. The use of additives can also significantly improve the water resistance of MOC. Yu Hongfa [4] and Xiao Liguang [5] found that phosphoric acid can improve the water resistance of MOC.

In this paper, MOC was modified by using waste GFRP fiber and some additives in order to improve the mechanical strength and water resistance. In the same time, we try to find a reasonable utilization approach for waste GFRP.

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2. Experimental

2.1. Materials
The MOC specimens were prepared by mixing various amounts of light-burned magnesia powder (MgO) and a bischofite ($MgCl_2 6H_2O$), which were available on the market. Phosphoric acid, citric acid, and ferric phosphate are all analytical pure, which were offered by the Tianjin Chemical Reagent Co., Ltd.The waste GFRP is from Hengshui, China. By means of crushing, the waste GFRP fiber of different sizes, 0.3mm, 1-5mm, 5-10mm and 10-15mm, is obtained.

2.2. Methods

2.2.1. Sample preparation. The magnesium chloride is dissolved in water to form a certain concentration of solution, mixing with magnesium oxide and admixture according to a certain proportion, pouring into 40mm× 40mm×160 mm mould, demolded after 24 hours, and then natural cured for 7 days. Some samples were used to test bending and compressive strength, and the other samples were placed in water, soaked to age.

2.2.2. Test method. The bending and compressive strength are tested according to GB/T17671-1999. The softening coefficient is used to characterize the water resistance of the specimens. After cured for 7 days, some specimens are used to test compressive strength (Rco), the others are soaked in water for 7 days, whose average compressive strength is Rcw. The softening coefficient Kcn of the specimen is calculated according to the formula:

$$Kcn=Rcw/Rco \quad (1)$$

3. Results and discussion

3.1. Effect of waste GFRP on MOC
The waste GFRP fiber with the length of 0.3mm, 1~5mm, 5~10mm and 10~15mm, are used to modify magnesium oxychloride cement. The compressive strength values were tested. See Figure 1.

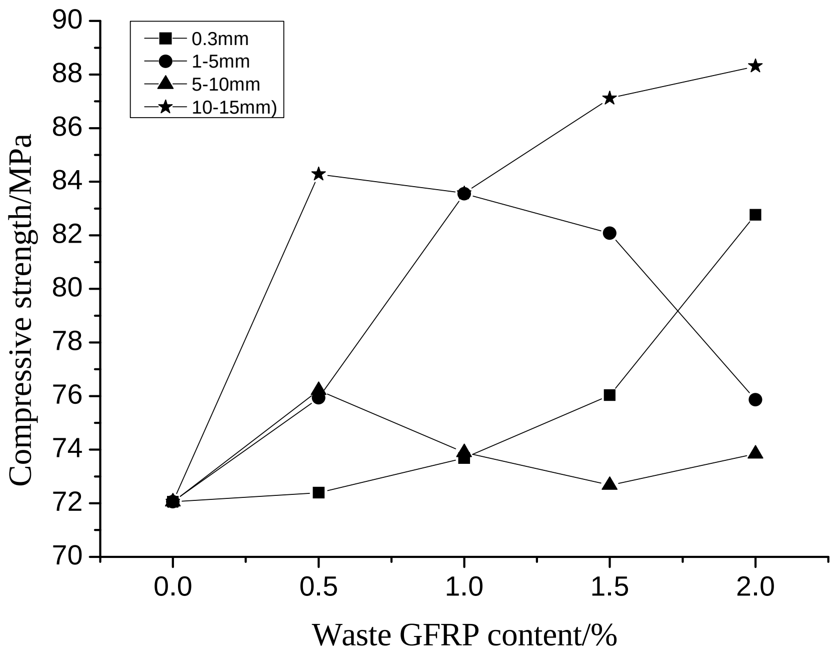

Figure 1. Effect of waste GFRP on compressive strength of the block.

As is shown in the Figure 1, the compressive strength of block increases roughly with the increase in waste GFRP fiber. It can be seen that the waste GFRP fiber of 10-15mm has remarked influence on compressive strength of the block. When the content is 2%, the compressive strength is up to 88.31MPa, increased by 22.55% compared to the blank.

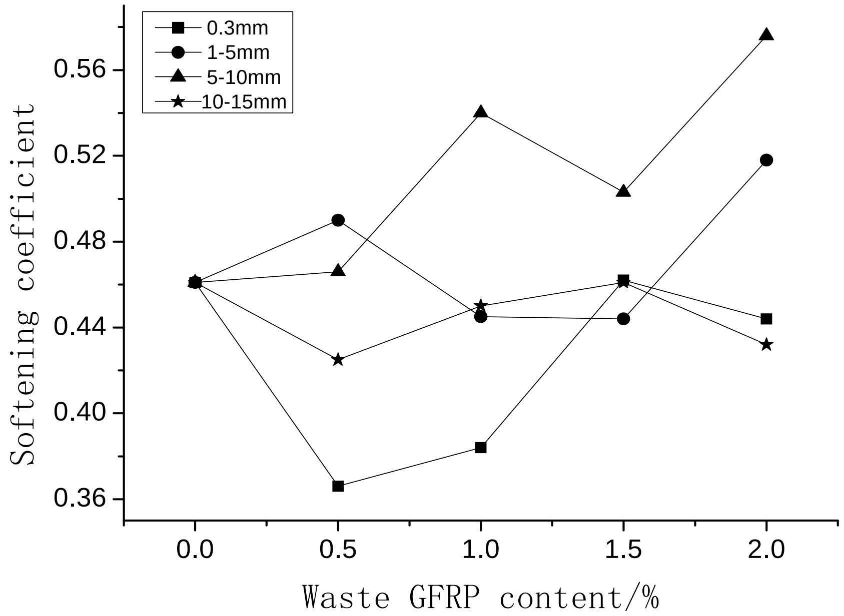

Figure 2. Influence of waste GFRP on softening coefficient of the block.

From Figure 2 we can see that the incorporation of waste GFRP fiber has some influence on the water resistance of magnesium oxychloride cement block. The softening coefficient of 5-10mm fiber increases by 24.95% higher than that of the blank. It is illustrated that waste WGFP fiber of certain size can be used in the test block, which is beneficial to improve the water resistance of the matrix.

3.2. Influence of additives on water resistance of MOC

The major disadvantage of magnesium oxychloride cement is its poor water resistance, moisture absorption, and halogenations, which draws much attention [6, 7]. Additives can be added to improve the structure stability of the material, improving the waterproofing performance and mechanical properties [8-10].

3.2.1. Posphoric acid. Phosphoric acid was used as modifier to increase the water resistance of MOC [11]. The performance is evaluated by the addition of 0%, 0.4%, 0.8%, 1%, 1.2% and 1.6% based on the mass of MOC. The results are shown in Table 1.

Table 1. Effect of phosphoric acid on strength and water resistance of MOC.

Number	Addition of phosphoric acid /%	Compressive strength/MPa		Softening coefficient
		Curing 7d	Soaked in water 7d	
1	0	72.06	33.22	0.461
2	0.4	52.65	44.37	0.844
3	0.8	45.75	44.56	0.974
4	1	43.75	42.61	0.974
5	1.2	41.19	35.18	0.854
6	1.6	38.86	39.87	1.026

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The results show that the softening coefficient increases with the increase of the addition of phosphoric acid. However, the addition of phosphoric acid results in loss in compressive strength. Considering cost and effect, the proper dosage of phosphoric acid is 0.8%.

3.2.2. Iron phosphate. The water resistance performance is evaluated by the addition of 0%, 0.5%, 1%, 1.5%, 2%, 3% of iron phosphate based on the mass of MOC. The results are shown in table 2.

Table 2. Effect of iron phosphate on strength and water resistance of MOC.

Number	addition of iron phosphate /%	Compressive strength/MPa		Softening coefficient
		Curing 7d	Soaked in water 7d	
1	0	72.06	33.22	0.461
2	0.5	79.30	33.70	0.425
3	1.0	77.49	50.68	0.654
4	1.5	73.97	46.59	0.630
5	2.0	69.95	55.75	0.797
6	3.0	69.52	53.32	0.767

From Table 2 we can see that the softening coefficient and compressive strength increase with the increase of the addition of iron phosphate. The proper dosage of iron phosphate is 2 % of the mass of MOC. In this case, the softening coefficient increased from 0.461 to 0.797.

3.2.3. Citric acid. As an additive, citric acid was added into MOC to improve water resistance [12-14]. The performance is evaluated by the addition of 0%, 0.5%, 1%, 1.5%, 2%, 3%, 4% based on the mass of MOC. The results are shown in Table 3.

Table 3. Effect of citric acid on strength and water resistance of MOC.

Number	Addition of citric acid /%	Compressive strength/MPa		Softening coefficient
		Curing 7d	Soaked in water 7d	
1	0	72.06	33.22	0.461
2	0.5	63.16	47.30	0.749
3	1.0	59.66	52.80	0.885
4	1.5	62.85	51.67	0.822
5	2.0	50.95	50.58	0.993
6	3.0	49.43	44.79	0.906
7	4.0	46.15	38.42	0.833

As can be seen from Table 3, with the increase of citric acid content, the softening coefficient increases first and then decreases. The addition of citric acid results in loss in compressive strength. When the citric acid content is 2%, the softening coefficient reached the maximum of 0.993.

4. Conclusion

Waste GFRP fiber has positive contribution to the mechanical strength and water resistance of MOC. When the addition of waste GFRP fiber of 5-10 mm is 2%, the softening coefficient of MOC increases by 24.95%. When the addition of waste GFRP fiber of 10-15mm is 2%, the compressive strength of MOC increases by 22.55%. It is a reasonable utilization approach for waste GFRP.

Effects of various additives to the water resistance of MOC were evaluated. The results showed that the addition of phosphoric acid and citric acid improved water resistance remarkably; the softening coefficients are up to 1.026 and 0.993, respectively. However, there are compressive strength value losses in both cases. The addition of iron phosphate increased the water resistance as well as improved the water resistance of MOC, but also enhanced the trend of the compressive strength within certain range.

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References

[1] Sorrel S, On a new magnesium cement, J. Comptes Ren-dus Sciences. 65 (1867) 102-104.
[2] Congbo Li, Zhenfeng Zhan and Xiaobo Liu, Effect of glass fiber morphology on the mechanical properties of composite materials of magnesium oxychloride cement, J. glass fibre. 3(2005) 5-8.
[3] Hui Ma and Bowen Guan, Research on flexural toughness of fiber reinforced magnesium oxychloride cement mortar, J. nonmetallic ore. 39 (2016) 53-56.
[4] Liguang Xiao, Yanping Liu ,Yandi Zhao and Jiguo Chang, Effect of phosphoric acid on properties of magnesium oxychloride cement, J. Journal of Jilin Architectural and Civil Engineering Institute. 2 (2000) 37-40.
[5] Hongfa Yu, The microstructure and properties of magnesium oxychloride cement admixture. J. New building materials. 4 (1995) 38-41.
[6] Kezhi Huang, Study on urea formaldehyde resin composite additive modified magnesium oxychloride cement. J. Journal of Wuhan University of Technology. 24 (2002) 9-11.
[7] Luming Wang, Study on phosphoric acid / polymer composite to improve the water resistance of magnesium oxychloride cement and mechanism. J. Functional materials. 13 (2015) 66-69.
[8] Zhenguo Li and Zesheng Ji, Progress in research on deformation and cracking of magnesium oxychloride cement products. J. Silicate notification. 31 (2012) 291-300.
[9] Li Yang, Effects of different additives on the waterproof properties of magnesium oxychloride cement. J. Oil refining and chemical engineering. 250 (2014) 17-18.
[10] Kejing Xu*, Jintao Xi, Yanqing Guo and Shuhua Dong, Effects of a new modifier on the water-resistance of magnesite cement tiles. J. Solid State Sciences. 14 (2012) 10-14.
[11] Sglavo V M, Dc Gcnua F, Conci A, et al, Influence of curing temperature on the evolution of magnesium oxychloride cement.J. Journal of materials science. 46 (2011) 6726-6733.
[12] Huijun Xu, Qian Wang and Sen Li, Study on water resistance of magnesium oxychloride cement by proportioning and additives. J. Journal of Shandong University of Technology. 30 (2016) 49-51.
[13] Hualei Su and Yijun Jiang, Study on modification of citric acid on magnesium oxychloride cement. J. Shandong Industrial Technology. 2017, 36-37.
[14] Zhi Zheng and Binggen Zhan, Preparation and properties of new magnesia cement *D*. Hefei University of Technology. 2012.