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Study on Preparation and Properties of Modified Magnesium Oxysulfate Cements

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In this paper, the author researches on the preparation and properties of modified magnesium oxysulfate cements. The best basic ratio for magnesium oxysulfate cements is chosen by adjusting the concentration of magnesium oxysulfate and water binder ratio at the room temperature. Based on this ratio, five kinds of additives (phosphoric acid, sodium dihydrogen phosphate, Organic Acid Salt A, Organic Acid Salt B and compound additive) are selected to modify the cements. Experimental results show that all additives could improve the performances of magnesium oxysulfate cements. But compared with other additives, the compound additives could effectively improve the strength and water resistance of magnesium oxysulfate cements. In this experiment, this paper carries out the phase analysis of magnesium oxysulfate cements by means of SEM and XRD methods. The results show that the additives could improve the degree of cross-linking of the crystals, and there is a new phase in the cement with Organic Acid Salt A, Organic Acid Salt B and compound additives.

1. Introduction

The magnesium oxysulfate cement is the gas hardness cementations' material which is formed by active magnesium oxide and magnesium oxysulfate solution. China possesses the advantages of developing magnesium oxysulfate cements, especially in Liaoning. But due to the low early strength, poor water resistance and other technical defects, magnesium oxysulfate cements are limited to be used in many areas, which is necessary to do further research to improve magnesium oxysulfate cements. Traditional magnesium oxysulfate cements are made of light-burned magnesia and magnesium sulfate solution, which is with poor physical and mechanical properties, poor water resistance, poor volume stability, and easy crystallization (Dale et al., 2016; Beaudoin and Ramachandran, 1978). Magnesium oxysulfate cements have characteristics of good volume stability, light weight, fire-proofing, low alkalinity, good decorative effect, suppressing frost and well rebar-protection performance, which make they have more advantages in producing decoration materials. However, large-scale applications of magnesium oxysulfate cements in civil engineering have been restricted by its defects such as low strength, long setting time and low water resistance. The fly ash can improve the physical and mechanical properties and water resistance of magnesium oxysulfate cements. There are many similar characteristics between the fly ash and the CFBC fly ash, but now the CFBC fly ash is with large annual discharge. Therefore, this study aims to study the influence of the CFBC fly ash on the magnesium oxysulfate cements' properties. It is expected that the production of lightweight partition wall panels is prepared with magnesium oxysulfate cements modified by the CFBC fly ash (Wu et al., 2015).
The ranges of Mg O/Mg SO4 molar ratio, H2O/Mg SO4 molar ratio, and the citric acid content are determined by single factor experiments. Mg O/Mg SO4 molar ratio, H2O/Mg SO4 molar ratio, and the citric acid content are determined by the orthogonal experiment, therefore, the fiducial mix pro portion of magnesium oxysulfate cements could be determined. For further improving properties of magnesium oxysulfate cements, some industrial by-products are mixed in this system. The study shows the CFBC fly ash can well improve the performances of magnesium oxysulfate cements. In order to achieve high performances magnesium oxysulfate cements with the CFBC fly ash, we study the influences of the fineness, content and chemical composition of the CFBC fly ash on the properties of magnesium oxysulfate cements. Therefore, the optimal mix proportion of magnesium oxysulfate cements is determined. Exploration and production process

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parameters of lightweight partition board made of magnesium oxysulfate cement foamed concrete (Beaudoin and Feldman, 1977; Wu et al., 2014).

2. Basic properties of modified magnesium oxysulfate cements

The shape scheme for modified magnesium oxysulfate cements is shown in figure 1. Pure basic magnesium sulfate crystal is synthesized and characterized as needle rod-shaped 5 Mg (OH) 2·Mg SO4·7 H2O by XRD, through chemistry and thermal analysis. 5 Mg (OH) 2·Mg SO4·7H2O crystal is confirmed to be monoclinic crystal and belongs to space group C121 with specific cell parameters and density (a=15.14, b=6.31, c=10.26, β=103.98 o, ρ=1.87 g/cm3) by simulated annealing method in the software Topas 4.2. 5 Mg (OH) 2·Mg SO4·7H2O crystal layer structure is constituted of Mg-O octahedron as framework and SO42-, H2 O, and OH- as filling ion (molecule) in the interlayer.

Figure 1: The Shape Scheme for Modified Magnesium Oxysulfate Cement

Additives adopted in this work such as K2, K7, K8, K19, K21, K27, K30, K31, K32, and K34 obviously improve the strength of basic magnesium sulfate cements. Moreover, the strength of basic magnesium sulfate cements increases as Mg O/Mg SO4 molar ratio increases with the same magnesium sulfate concentration. At the same raw molar ratio, basic magnesium sulfate cements with higher strength, lower hole solution concentration, and lower specific resistance are more difficult to absorbing moisture and scumming than magnesium oxychloride cements. Furthermore, the porosities of basic magnesium sulfate cements are lower than that of Portland cements (Wu et al., 2017). Complete hydration and a mass of needle rod-shaped 5 Mg (OH) 2·Mg SO4·7H2O in the interior structure of basic magnesium sulfate cements are the main reason for the fact that the strength of basic magnesium sulfate cements is higher than that of magnesium oxychloride cements.

Magnesium oxysulfate cements have crazed completely after 28-day soaking in water, and the reason is that excess Mg O in magnesium oxysulfate cements hydrate and lead to crystallization stress which destroys the cement structure. Basic magnesium sulfate cements display an excellent water resistance based on the fact than the water resistance coefficient of basic magnesium sulfate cements without mineral admixture after 180-day soaking in water more than 0.85 and that with the coal fly ash even reached 0.98. The main reason for this phenomenon is that additives in basic magnesium sulfate cements can inhibit the hydration of Mg O to weaken the crystallization stress, and strength phase 5 Mg (OH) 2·Mg SO4·7H2O in basic magnesium sulfate cements with a low solubility (0.034 g/100 g).

Basic magnesium sulfate cements possess better hydrothermal resistance, salt resistance, carbonization resistance, and steel-protection performance than magnesium oxysulfate cements. Slag-adulterated basic magnesium sulfate cements have not crazed yet after 14-day 80 °C hydrothermal treatment. The strength of basic magnesium sulfate cements increases instead of decreasing after soaking in Mg Cl2 solution for 8 months. Additionally, this cement has not even been carbonized in accelerating carbonation setting. Rebar corrosion degree in basic magnesium sulfate cements is much lower than that in magnesium oxychloride cements. Though the rebar corrosion rate in basic magnesium sulfate cements is faster at the earlier stage than that in Portland cements, the rebar corrosion rate at the later stage declines gradually and tends to be slower even than that in Portland cements (Wu et al., 2016). Basic magnesium sulfate cements adulterate with a small amount of nitrites as corrosion inhibitor hardly corrode rebar.

Thermal insulation materials with high strength, low density, good thermal insulation property, and fireproofing are obtained using basic magnesium sulfate cement mortar as a binding material by chemical and physical foaming methods. The 28-day compressive and flexural strength of basic magnesium sulfate cement mortar adulterated with 40% coal fly ash are respectively 57.7 Mpa (equivalent to that of 52.5 R Portland cements) and 16.2 MPa which is two times of that of 62.5 R Portland cements. Concrete of different strength degrees is prepared by basic magnesium sulfate cement mortar, and the frost resistance of the concrete is better than that of Portland cement concrete. Reinforced concrete member with high tenacity and large bearing capacity is prepared by basic magnesium sulfate cement mortar. In the reinforced concrete member, rebar corrosion rate for four months is only 2‰~3.5‰, which is about 2‰ of that in magnesium oxychloride cement concrete and about 6‰ in slag Portland cement concrete. According to the above results, basic magnesium sulfate cements have been believed to be a promising cement material in a large-scale civil engineering application. The basic structure for modified magnesium oxysulfate cements is shown in Figure 2.

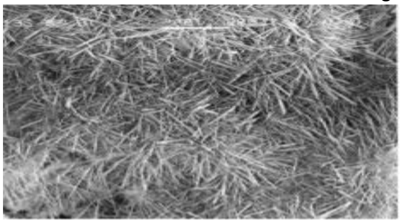


Figure 2: The Shape Scheme for Modified Magnesium Oxysulfate Cement

3. Algorithms and experiments

The pore structure of magnesium oxysulfate cements has been studied through the tests of absorptivity. The microstructure, phase composition, and morphology of magnesium oxysulfate cements have been investigated through the X-ray diffraction analysis, as well as the scanning electron microscopy and EDS analysis. The basic algorithm for the data processing for the EDS analysis is shown as (Siqueira et al., 2015; Chang et al., 2015; Prohens et al., 2015),

$$\begin{aligned}\hat{f}_H^{\alpha}(x) &= \frac{1}{\Gamma(1+\alpha)}\int_{-\infty}^{\infty}\frac{f(t)}{(t-x)^{\alpha}}(dt)^{\alpha} \\ &= \frac{1}{\Gamma(1+\alpha)}\int_{-\infty}^{\infty} f(t)g(x-t)(dt)^{\alpha} \\ &= f(x)*g(x),\end{aligned} \tag{1}$$

The equation is as follows:

$$\partial_j(C_{ijkl}\partial_k u_l + e_{kij}\partial_k\varphi) - \rho\ddot{u}_i = 0 \tag{2}$$

Under the linear theory, that is:

$$\partial_j(e_{ijkl}\partial_k u_l - \eta_{kij}\partial_k\varphi) = 0 \tag{3}$$

The linear equation can be expressed in the following simplified forms:

$$L(\nabla,\omega)f(x,\omega) = 0\,,\ L(\nabla,\omega) = T(\nabla) + \omega^2\rho \mathrm{J} \tag{4}$$

In which,

$$T(\nabla) = \begin{Vmatrix} T_{ik}(\nabla) & t_i(\nabla) \\ t_k^T(\nabla) & -\tau(\nabla) \end{Vmatrix},\ \mathrm{J} = \begin{Vmatrix} \delta_{ik} & 0 \\ 0 & 0 \end{Vmatrix},\ f(x,\omega) = \begin{Vmatrix} u_k(x,\omega) \\ \varphi(x,\omega) \end{Vmatrix} \tag{5}$$

Consider the delay, the L can be expressed as:

$$L^0 = \begin{Vmatrix} C_{ijkl}^0 & e_{kij}^0 \\ e_{ikl}^{0T} & -\eta_{ik}^0 \end{Vmatrix} \tag{6}$$

These functions can be expressed in the following form:

$$C(\mathrm{x}) = C^0 + C^1(\mathrm{x}),\quad e(\mathrm{x}) = e^0 + e^1(\mathrm{x}),\quad \eta(\mathrm{x}) = \eta^0 + \eta^1(\mathrm{x}),\quad \rho(\mathrm{x}) = \rho_0 + \rho_1(\mathrm{x}) \tag{7}$$

The value with superscript of 1 represents the difference below:

$$C^1 = C - C^0,\ e^1 = e - e^0,\ \eta^1 = \eta - \eta^0,\ \rho_1 = \rho - \rho_0 \tag{8}$$

Local fractional integral of f(x) defined by Eq. 9.

$$
{}_aI_b^{(\alpha)}f(t)=\frac{1}{\Gamma(1+\alpha)}\int_a^b f(t)(dt)^{\alpha}
=\frac{1}{\Gamma(1+\alpha)}\lim_{\Delta t\to 0}\sum_{j=0}^{j=N-1} f(t_{\mathrm{j}})(\Delta t_{\mathrm{j}})^{\alpha} \tag{9}
$$

Its local fractional Hilbert transform, denoted by $\int_x^{H,a}(x)$ is defined by:

$$
H_{\alpha}\left\{f(t)\right\}=\hat{f}_H^{\alpha}(x)
=\frac{1}{\Gamma(1+\alpha)}\int_R \frac{f(t)}{(t-x)^{\alpha}}(dt)^{\alpha} \tag{10}
$$

The different factors on properties of magnesium oxysulfate cements have been discussed from the aspect of composition and structure respectively. It shows that citric acids could properly improve the properties of magnesium oxysulfate cements such as the strength, water resistance, acid, alkali resistance and volume stability. The properties of magnesium oxysulfate cements could be adjusted by changing the citric acid content, the ratio of MgO/MgSO4 and H2O/MgSO4. The optimal mixing proportion is as follows: MgO/MgSO4=1.7, H2O/MgSO4=1, and citric acid content=1.3%. The 28-day compressive and flexural strength of this kind of magnesium oxysulfate cement could be up to 60.7 MPa and12.5 MPa, respectively. By the mixed design method, the best mixing proportion of admixtures is made as follows: citric acid=65.8%, sucrose=17.8%, and boric acid=16.4%. The strength and durability of Magnesium oxysulfate cements could be further improved by mixing with modified additives. The tests of absorptivity values show that the porosity of the small capillary pore increases, while the average size of capillary pore becomes smaller, and the cement stone structure could be denser by citric acids and other admixtures, improving the properties of magnesium oxysulfate cements. Through XRD, magnesium oxysulfate cements will generate a new phase composition, which is the pin rod of crystal by incorporating citric acids and other admixtures through SEM. The new phase has changed the composition and structure, and improved the properties of the magnesium oxysulfate cements.

This experiment is based on the normal temperature of sulfur magnesium oxychloride cement's basic mixture ratio test, finding the initial ratio of raw materials with excellent performance. At the same time, we test the magnesium oxychloride cement age, bending strength, compressive strength, a series of performance indicators, and the incorporation of different and mineral admixtures to improve its performance in this benchmark ratio of the magnesium oxychloride cements. For this benchmark ratio on the magnesium oxychloride cement age, a detailed analysis conducts with the bending strength, compressive strength, a series of performance indicators, and the incorporation of different and mineral admixtures with improved performances, drawing that when MgO: MgSO4 is the same, with the increase of water, the initial and final setting time are extended, and when the amount of water is the same, the initial and final setting time are shorten with the increase of MgO:MgSO4. When MgO: MgSO4=3, 3-1-8 phase is the main hydration phase, and a large number of MgSO4 don't react. When MgO: MgSO4=5, 5-1-7 phase is the main hydration phase, which can increase the cement's strength significantly. When MgO: MgSO4>5, Mg (OH) 2 will constantly increase with the strength decreases. Through analyzing the modified magnesium cement concrete with gravel and sand by a certain percentage, it is found that, the strength of concrete with different degrees increases by adding slags and fly ashes to the magnesium in cement concrete It also provides the basis in the future Production. It is observed that the 517-phase crystal shape, which is the main hardened product, uses the XRD test method to analyze the sulfur magnesium oxychloride cement phase's change rule, and uses the SEM to analyze the different factors. It is found that the salt phase is a small needle like crystals, which makes the salt phase with good density, and improves the water resistance of sulfur magnesium oxychloride cements. Compared with the slags, the influence of the fly ash on magnesium cement gravel concrete strength is more obvious. The main reason is the active components contained in the fly ash are more than the slag. As the active mixture, the fly ash and slag's pozzolanic effect and the late hydraulic characteristics play a certain role in promoting the magnesium cement sand and increasing the gravel concrete strength.

4. Results and discussions

The results show that: the citric acid can significantly improve the physical and mechanical properties of magnesium oxysulfate cements. The optimal mix proportion: Mg O/Mg SO4 molar ratio is 20, Mg O/Mg SO4 molar ratio is 12 and the citric acid content is 1.5%. Magnesium oxysulfate cements with the citric acid provides very well performances. The CFBC fly ash can reduce the heat of cement hydration in the early stage, the shrinkage rate of magnesium oxysulfate cements, and the porosity of cement stone, as well as improve the density of cement stone and the physical and mechanical properties. When the CFBC fly ash contains 20% light-burned magnesia, the comprehensive strength at 28 days achieves 78.7 MPa, improved 12.3 MPa and the rate of 18.45%. When the CFBC fly ash is grinded into a median diameter of 15.88 μm, and the CFBC fly ash composes 8%, the comprehensive strength at 28 days achieves 80.7 MPa, improved 14.3 MPa compared with the blank control group, and the rate of 21.55%. Increasing the lower contents of active Si O2, f-Ca O, SO3 in the CFBC fly ash will extend the setting time and improve the comprehensive strength. With the increase of the contents of active Si O 2, f-Ca O, SO3 in the CFBC fly ash, it will have an opposite effect. The optimally technical parameters of lightweight partition board made of magnesium oxysulfate cement foamed concrete are the dilution ratio of foaming agent 1:20, foam formation rate 20, drying environment maintenance at 20°C, and the content of foaming agent 1.11% of the light-burned magnesia quality. The samples satisfy the requirements of the standard GB/T 23451-2009, and the comprehensive strength and water resistance of samples are better

The thermal expansion coefficients of the specimens with different magnesia additions at different tem patterns are shown in Fig. 3. It shows that as the temperance increases, the thermal expansion coefficients of specimens M4 and M6 rise slowly. For the specimen M8, the thermal expansion coefficient increases slowly before 1050°C and climbs dramatically till reaching a peak at 1350°C, then declines. The phenomenon can be explained that for alumina magnesia materials, MA forms at about 1050°C. The higher the magnesia fines additions, the larger the unground of the spinal. As the temperature keeps increasing, MA forms in the specimen, CaO reacts with Al2O3 in the matrix forming CA6 and the expansion increases. When the temperature teaches 1350°C and the formation of MA completes, the shrinkage takes the major role.

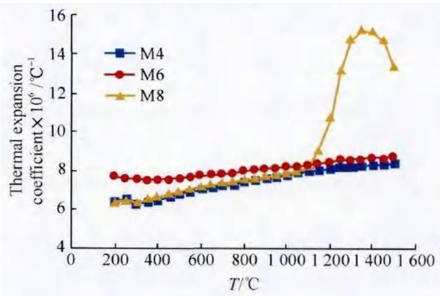
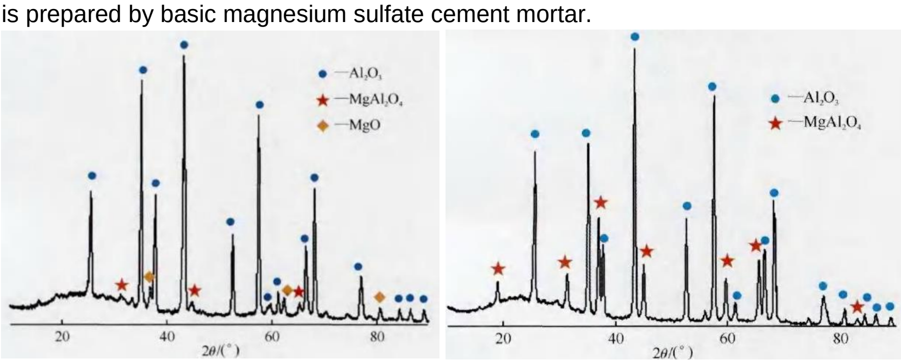


Figure 3: Thermal Expansion Coefficients of Specimens with Different Magnesia Additions

Figure 4 shows the XRD patterns of specimens M6 treated at different temperatures. The main crystal phases of specimens M6 treated at 1100°C and 1500°C for 3 hours are corundum and MA. The former also contains a little magnesia. The specimens M6 treated at 1500°C for 3 hours contains more MA, which means that the reaction of MgO+A12O3->MgAl2O4 (MA) occurs at 1100°C. With the temperature rises, the larger amount of MA forms. Because the formation of MA accompanies with the volume expansion and MA has a high strength in certain conditions. The 28-day compressive and flexural strength of basic magnesium sulfate cement mortar adulterated with 40% coal fly ash are respectively 57.7 Mpa (equivalent to that of 52.5 R Portland cements) and 16.2 MPa which is two times of that of 62.5 R Portland cements. Concrete of different strength degrees is prepared by basic magnesium sulfate cement mortar, and the frost resistance of the concrete is better than that of Portland cement concrete. Reinforced concrete member with high tenacity and large bearing capacity is prepared by basic magnesium sulfate cement mortar.



(a) (b)

Figure 4: XRD Patterns of Specimens M6 Treated at Different Temperatures

5. Conclusion

Traditional magnesium oxysulfate cements are made of light-burned magnesia and magnesium sulfate solution, which is with poor physical and mechanical properties, poor water resistance, poor volume stability, and easy crystallization. Magnesium oxysulfate cements have characteristics of good volume stability, light weight, fire-proofing, low alkalinity, good decorative effect, suppressing frost and well rebar-protection performance, which make they have more advantages in producing decoration materials. The paper studies phase compositions, compressive strength and water resistance of magnesium oxysulfate cements modified by the organic acid CA. A mass of new phases appear and the content of Mg (OH) 2 decreases in the modified cements. This new phase can be expressed by 5Mg (OH) 2.MgSO4.5H2O (515-phase) determined by the chemical element analysis. The SEM analysis proves that the microstructure of the 515-phase is a needle-like crystal. The law of thermal decomposition of this new phase is studied by the TG-DSC method. The process of 515-phase formation is studied by the data of XRD tracking and the modification mechanism of the additives on the magnesium oxysulfate cements which are discussed based on the influence of additives CA on pH changes of magnesia hydration. The compressive strength and water resistance can be improved by the additions of CA. Experimental results show that all additives could improve the performances of magnesium oxysulfate cements. But compared with other additives, compound additives could effectively improve the strength and water resistance of magnesium oxysulfate cements. In this experiment, this paper carries out the phase analysis of magnesium oxysulfate cements by means of SEM and XRD methods.

Acknowledgments

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Reference

Beaudoin J.J., Ramachandran V.S., 1978, Strength development in magnesium oxysulfate cement, Cement & Concrete Research, 8(1), 103-112, DOI: 10.1016/0008-8846(78)90063-7.

Beaudoin J.J., Feldman R.F., 1977, The flow of helium into the microspaces of magnesium oxysulfate cement paste, Cement & Concrete Research, 7(5), 585-596, DOI: 10.1016/0008-8846(77)90120-X.

Chang Y.H., Chenruei K., Wu B.Y., Lu H.L., 2015, Using sustainable landscape overwater equipment for improvement of aquatic ecosystem, Ecological Engineering, 83, 496-504, DOI: 10.1016/j.ecoleng.2015.04.092.

Dale V.H., Kline K.L., Buford M.A., 2016, Incorporating bioenergy into sustainable landscape designs, Renewable & Sustainable Energy Reviews, 56, 1158-1171, DOI: 10.1016/j.rser.2015.12.038.

Prohens R., Barbas R., Portell A., Fontbardia M., Alcobé X., Puigjaner C., 2015, Expanding the crystal form landscape of the antiviral drug adefovir dipivoxil, Crystal Growth & Design, 15(1), 475-484, DOI: 10.1021/cg501542h.

Siqueira D.S., Jr J.M., Pereira G.T., Teixeira D.B., Vasconcelos V., Júnior O.A.C., 2015, Detailed mapping unit design based on soil–landscape relation and spatial variability of magnetic susceptibility and soil color, Catena, 135(341-8162), 149-162, DOI: 10.1016/j.catena.2015.07.010.

Wu C., Chen W., Zhang H., Yu H., Zhang W., Jiang N., 2017, The hydration mechanism and performance of modified magnesium oxysulfate cement by tartaric acid, Construction & Building Materials, 144, 516-524, DOI: 10.1016/j.conbuildmat.2017.03.222.

Wu C., Yu H., Dong J., Zheng L., 2014, Effects of material ratio, fly ash, and citric acid on magnesium oxysulfate cement, Aci Materials Journal, 111(3), 291-297, DOI: 10.14359/51686723.

Wu C., Yu H., Zhang H., 2015, Effects of phosphoric acid and phosphates on magnesium oxysulfate cement, Materials & Structures, 48(4), 907-917, DOI: 10.1617/s11527-013-0202-6.

Wu C., Zhang H., Yu H., 2016, Preparation and properties of modified magnesium oxysulfate cement derived from waste sulfuric acid, Advances in Cement Research, 28(3), 1-11, DOI: 10.1680/jadcr.15.00011.