Research on A3 steel corrosion behavior of basic magnesium sulfate cement

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Abstract: In this paper, Tafel polarization technique is used to study the corrosion behavior of A3 steel basic magnesium sulfate, and then analyzing the ratio of raw materials cement, nitrates rust inhibitor and wet-dry cycle of basic magnesium sulfate corrosion of reinforced influence, and the steel corrosion behavior of basic magnesium sulfate compared with magnesium oxychloride cement and Portland cement. The results show that: the higher MgO/MgSO₄ mole ratio will reduce the corrosion rate of steel; Too high and too low H₂O/MgSO₄ mole ratio may speed up the reinforcement corrosion effect; Adding a small amount of nitrite rust and corrosion inhibitor, not only can obviously reduce the alkali type magnesium sulfate in the early hydration of cement steel bar corrosion rate, but also can significantly reduce dry-wet circulation under the action of alkali type magnesium sulfate cement corrosion of reinforcement effect. Basic magnesium sulfate cement has excellent ability to protect reinforced, its long-term corrosion of reinforcement effect and was equal to that of Portland cement. Basic magnesium sulfate corrosion of reinforced is far below the level in the MOC in the case.

1. Introduction
Basic Magnesium Sulfate Cement (BMSC) is a new type of cementitious material developed on the basis of modified magnesium oxysulphate cement in MgO-MgSO₄-H₂O gas hard gel system. Its main hydration products are insoluble basic magnesium sulfate new whiskers, different from the traditional magnesium sulfide cement and modified Magnesium Oxy sulphate Cement (MOS) completely. BMSC has the advantages of quick setting, early strength, high strength, high bending resistance, high toughness, no carbonation, corrosion resistance and good performance of the ribs. The good performance of the ribs of BMSC is studied specifically in this paper. Reinforcement corrosion is one of the most important factors in the failure of reinforced concrete structures. The cost of maintenance and reinforcement caused by corrosion of steel around the world is $ 100 billion per year. Researchers at home and abroad have studied the corrosion problem of steel in ordinary Portland cement concrete, and the steel bar protection is mainly focused on improving the concrete self-performance, modifying the surface of steel bar, developing new anti-corrosion materials, etc.

Although BMSC containing SO₄²⁻ because of its low alkaline, without Cl⁻, is expected to protect the steel that is not rust, is the key technical issues to determine whether it can enter the construction market as the main building materials.

The strong corrosive effect between Magnesium Oxychloride Cement (MOC) and metal and aluminum is found through a large number of experiments, but there is no detailed study that any strong corrosion behavior of steel bars in magnesium oxysulphate cement. Whether the magnesia cement material can be made of load-bearing components in the use of buildings, reinforcement
corrosion problem is must be solved.

Yu Hongfa\cite{8-9} found that the corrosion resistance of the magnesium oxychloride cement is very serious by studying the corrosion performance and mechanical properties of the steel bars in the reinforced concrete of magnesium oxychloride cement, and an electrochemical corrosion model of corrosion of steel bars in magnesium oxychloride cement was proposed. Qiao Hongxia\cite{10} and others made a different coating of the polarization curve of steel to study the role of various coatings as rust inhibitors on the corrosion of steel bars. If the corrosion degree of rebar in BMSC is less than that of OP cement and MOC, then the future direction of research is applying the basic magnesium sulfate cement gradually to the concrete. After all, reinforcement corrosion is an important factor affecting the durability of concrete.

2. Experiment

2.1. Raw materials

The raw materials using light burned magnesium oxide powder (activity of 58%), the benchmark Portland cement, magnesium sulfate heptahydrate and magnesium chloride hexahydrate are analytical reagents.

The light burned magnesium oxide powder is from Liaoning Haicheng magnesite at 750 ~ 850°C calcined, grinding to get the powder, the chemical composition as shown in Table 1.

| Chemical Components | MgO  | CaO  | SiO₂ | Fe₂O₃ | Al₂O₃ | I.L  |
|---------------------|------|------|------|-------|-------|------|
| Quality Score /%    | 80.20| 1.30 | 6.07 | 0.41  | 0.15  | 11.87|

Magnesium sulfate heptahydrate are flaky crystal, from Tianjin Branch Miao Chemical Co., Ltd.; hexahydrate magnesium chloride as colorless crystals, columnar or needle-like, from Lianyungang Runtai Chemical Co., Ltd.

2.2. Experimental method

2.2.1 Method for determination of A3 corrosion rate: A cement paste sample with a size of 40mm × 40mm × 40mm was used and a A3 steel with a thickness of 1mm was embedded in the diagonal of the specimen. The platinum electrode was used as the auxiliary electrode, and the saturated calomel electrode was used as the reference electrode. The thickness of the protective layer of cement paste 3mm, steel embedded in the surface area of 15cm². In this experiment, the three-electrode linear polarization method\cite{11} was used to determine the natural corrosion current of the steel bar in the cement paste sample, and the corrosion rate was calculated according to the formula (1). The cumulative corrosion thickness is directly calculated using the curve of the corrosion rate - hydration age. Using the instrument for the CHI660C electrochemical workstation, the principle of selection of potential to ensure that the polarization curve of yin and yang covering the Tafir region. The absolute value of the highest potential and the lowest potential and the self-corrosion potential difference is at least 60 mv. Through a large number of debugging, the highest potential of scanning is higher than the open circuit potential of 0.2V, the lowest potential is lower than the open potential of -1.0V.

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\nu = \frac{IM}{FA} \tag{1}
\]

\(\nu\) is the corrosion rate; \(I\) is the natural corrosion current; \(M\) is the molecular weight of the material; \(F\) is the Faraday constant (96500C / mol); \(A\) is the corrosion area; \(\rho\) is the density of the reinforcement.

2.2.2 Selection of Raw Material Ratio of Basic Magnesium Sulfate Cement. In order to study the effect of magnesium sulfate concentration on the corrosion of A3 steel in BMSC, the corrosion rate and cumulative thickness of steel bars were selected when H₂O: MgSO₄ (H) were 20, 22, 24 and 26
respectively; and researched the corrosion rule of A3 steel in BMSC when the molar ratio of MgO to MgSO$_4$ (M) is 6,8,10. The molar ratio of the raw material of the BMSC is a-MgO (light magnesium oxide): MgSO$_4$: H$_2$O = 7: 20, 40% of the fly ash; the water-cement ratio of reference Portland cement slurry is 0.45. The amount of choice is to join 0.3%, 1%, 2.5%, 5% base. Meanwhile, if the magnesium cement as concrete structure, it may be used in humid environment, so it is necessary to study corrosion behavior of A3 steel in BMSC under the dry and wet cycle conditions, the dry and wet cycle will take place in the laboratory. The dry and wet cycle determined by the laboratory was as follows: the cement paste was injected into the A3 cement in the room for 7 days, and then immersed in water for 12 hours. Then the natural drying was taken for 12 hours, the natural corrosion potentials were measured during drying and immersion, and calculate the corrosion rate of steel and cumulative corrosion thickness.

3. Results and Analysis

3.1 Corrosion Regularity of Reinforcement in Basic Magnesium Sulfate Cement

Figure 1 displays steel corrosion rate and cumulative corrosion thickness of BMS, MOC and PO within 1 month. The corrosion rate of rebar in basic magnesium sulfate cement and Portland cement decreased with the increase of hydration age (Fig. 1a), which was due to the prolongation of hydration time. It resulted in increasing cement density, reducing the pore solution, decreasing the dissolved O$_2$ content in the cement, and decreasing the corrosion degree of the steel bar. For magnesium oxychloride cement, the corrosion rate of the steel bars in the first three days was reduced, and then increased rapidly to the maximum at the 7th day, and followed by a downward trend. In terms of basic magnesium sulfate cement, the reinforcement corrosion rate did not increase, therefore, it can be concluded that SO$_4^{2-}$ is less susceptible to adsorption and corrosion than the Cl$^-$. During the early hydration (Fig. 1a for hydration in 10 days), the corrosion rate of steel in the basic magnesium sulfate was significantly higher than Portland cement. The main reason was that the basicity of the pore solution in the basic magnesium sulfate cement was lower to lead corrosion that the surface of the steel is not easy to form passivation film. However, the results of the later hydration were the opposite (the water after 10 days). The reason is that the basic magnesium sulfate cement has low porosity compared with Portland cement, and the liquid-phase conductivity is low, resulting in difficulty in electron transport during the rusting process. It can be seen that the corrosion of steel bars is mainly concentrated in the early stage of hydration compared with Portland cement.

Figure 1b shows the cumulative corrosion thickness of the three kinds of cement hydration in a month, it can see that the reinforcement corrosion of magnesium oxychloride cement is the most serious, its corrosion thickness is 24 times that of BMS, 75 times that of PO.
Fig. 2 Corrosion of steel bars by MOC and BMS (hydration age is one month, left steel bars were removed from BMS and right bars were MOC.)

Figure 2 presents the corrosion situation of two A3 steels buried in magnesium oxychloride cement slurry and basic magnesium sulfate slurry after a month. It can be seen that the reinforcement corrosion of the magnesium oxychloride cement slurry was very serious after a month, the entire surface had been completely covered with rust; but for the basic magnesium sulfate cement slurry, the surface only appeared minor rust point.

In summary, magnesium oxychloride cement on the strongest corrosion of steel, followed by basic magnesium sulfate cement, Portland cement is the weakest. However, in the later hydration, the degree of corrosion of steel bars is similar to that of Portland cement.

3.2 Effect of Proportion of Raw Material on Reinforcement Corrosion Behavior of Basic Magnesium Sulfate Cement

Fig. 3 Change of corrosion rate and cumulative corrosion thickness of the raw material molar ratio with the hydration time (a, c: H = 20 in the magnesium oxide solution; b, d: M = 9)

It can be seen from the figure 3 that when the initial concentration of magnesium sulfate solution was constant, which was H = 20, the corrosion rate of steel bars decreased with the increase of M (Fig. 3a),
the cumulative corrosion thickness of 1 month of hydration also decreases with the increase of M (Fig. 3c). As illustrated that the proper adjustment of M in basic magnesium sulfate cement can slow down the degree of reinforcement corrosion. When the initial concentration of magnesium sulfate solution is constant, the porosity of cement matrix decreased with the increase of M. The basicity of the cement pore solution may increase as the M increases. Both of these factors resulted in a lower degree of reinforcement corrosion.

When the initial M is constant, that is M = 9, the corrosion rate of the steel did not change significantly (3b). As demonstrated in Fig. 3d, the degree of steel bars corrosion was the most serious from the cumulative corrosion thickness when H=26. Meaning is that the corrosion rate of the steel bars is more serious while the concentration of magnesium sulfate solution is too low. The reason is that the ion consumption rate in the solution slows down and the rate of reduction of the pore solution decreases when the concentration of magnesium sulfate solution is low, thus accelerating the corrosion of the steel to a certain extent. However, the concentration of magnesium sulfate solution was not as high as possible. The corrosion of steel in H = 20 was more severe than that of H = 24 (shown in Fig. 3d). The reason may be mainly in the early stage of hydration, the alkaline of the pore solution decreases as the concentration of the initial magnesium sulfate solution increases.

3.3 Corrosion Behavior of A3 Steel in Basic Magnesium Sulfate Cement under Dry and Wet Circulation

![Graphs](image)

Fig. 4 Corrosion rate (a) and cumulative corrosion thickness (b) of steel bars under dry and wet circulation

Figure 4 implies that the corrosion rate of the steel bars in the basic magnesium sulfate cement during the immersion process was higher than that in the drying process. It can calculate the average rate of reinforcement corrosion in the condition of 12 times circulation by the relationship between the cumulative corrosion thickness and the frequency of dry and wet cycles, which is 2.83 times of the reinforcement corrosion rate at the beginning of dry and wet cycle test. With the increase of the frequency of dry and wet cycles, the corrosion rate of steel bars in basic magnesium sulfate cement shown a downward trend, because a small amount of free Mg$^{2+}$ and SO$_4^{2-}$ in the cement pores gradually diffused into the water, which reduced the electrical conductivity of cement. At the same time, with the increase of the number of dry and wet cycles, the cumulative corrosion thickness of rebar in basic magnesium sulfate cement showed a linear growth relationship.
The results illustrate that the corrosion rate of steel bars in the process of immersion is higher than that in the process of drying, but with the increase of the number of dry and wet cycles, the corrosion rate of steel bars in magnesium oxychloride cement is gradually increasing both in immersion and drying.

4. Conclusion
(1) The corrosion behavior of steel bars in basic magnesium sulfate cement was studied. It was proved that the corrosion effect of basic magnesium sulfate cement on steel bars was much lower than that of magnesium oxychloride cement. The corrosion rate of basic magnesium sulfate cement in the early stage of hydration was higher than that of Portland cement, and the corrosion rate of steel bar was gradually reduced at the later stage of hydration, even lower than that of Portland cement.

(2) The effect of the ratio of raw materials on the corrosion of steel bars in basic magnesium sulfate cement was researched. Electrochemical polarization experiments displayed that higher M would reduce the corrosion rate of steel bars. Too high or too low H₂O / MgSO₄ molar ratios may accelerate the corrosion of steel bars.

(3) The effect of wet and dry cycle on the corrosion of steel bars in basic magnesium sulfate cement was studied. The results implied that the corrosion rate of steel bars in basic magnesium sulfate cement showed a decreasing trend with the increase of the number of dry and wet cycles. The cumulative corrosion thickness of rebar in basic magnesium sulfate cement showed a linear growth relationship.

(4) Since the basic magnesium sulfate cement has good barrier properties, it is expected to be the raw material for the preparation of reinforced concrete.

Acknowledgments
This study was supported by the National Natural Science Foundations of China (grants No.51662035, No.U1407104, No.51678304 and No.21401209), Natural Science Foundations of Qinghai Province (grants No.2015-ZJ-947Q and 2015-ZJ-937Q) and foundation teaching and research innovation team project of higher education institution of Qinghai province.

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