Investigation on the Corrosion Behavior of Steel Embedded in Basic Magnesium Sulfate Cement Concrete: An Attempt and Challenges

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ABSTRACT: Basic magnesium sulfate cement is a type of green high-performance cementitious material. In order to exert its performance advantages and expand its application field, it is urgent to study the problem of steel corrosion in basic magnesium sulfate cement concrete (BMSCC). In this paper, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) were used to study the corrosion behavior of steel bars in different strength grades of BMSCC in seawater. Based on the relationship between the corrosion current density and the immersion time, the corresponding time-varying model was obtained. The LPR and EIS results show that the corrosion potential and polarization resistance of steel bars in BMSCC decreased with the immersion time in the seawater environment. The fitting analysis indicated concordance between the corrosion rates with the logarithmic function time-varying model. Furthermore, the cracking time of the protective layer of BMSCC was analyzed based on the cracking time prediction model of Portland cement concrete and the mechanical properties of BMSCC.

1. INTRODUCTION

Durability is a major issue and research focus of the world’s concrete structures. There are many factors contributing to the durability of concrete, such as steel corrosion, concrete carbonation, freeze–thaw damage, and destruction of erosive media. Mehta believes that the main source of issues with concrete durability is steel corrosion followed by freeze–thaw cycle damage and physicochemical effects. The corrosion products produced by the corrosion of steel bars requires a larger volumetric space, which leads to the cracking or spalling of the concrete protective layer, thereby reducing the mechanical properties of the concrete structure and seriously affecting the safety performance of the structure. According to statistics, steel corrosion accounts for 80% of concrete durability problems, while marine environments and chloride-containing media, such as deicing salts, are the main cause of steel corrosion in concrete.

In 2012, Yu and Wu successfully prepared basic magnesium sulfate cement (BMSC) with $5\text{Mg(OH)}_2\cdot\text{MgSO}_4\cdot7\text{H}_2\text{O}$ phase as the main strength phase by admixture modification technology. BMSC, a new type of green high-performance cementitious material, has the characteristics of low thermal expansion, no returning to moisture, good frost resistance, high temperature resistance, and no moisture absorption. BMSC also has excellent mechanical properties including high compression resistance, high tensile strength, and high toughness; it has gradually become a research hotspot in the field of building materials. However, up to now, few published articles have focused on the corrosion behavior of steel embedded in basic magnesium sulfate cement concrete (BMSCC) given its novelty as a type of cementitious material. As a result, the durability problem requires further examination to expand the application of BMSCC in engineering applications.

Corrosion of steel in concrete is an electrochemical process. Electrochemical measurement is a powerful means to reflect its essential process. Compared with its analytical or physical methods, electrochemical methods present fast test speed, high sensitivity, continuous tracking, and in situ measurement. Therefore, the electrochemical detection method has paid great attention to the development and characterization of steel bar corrosion behavior in Portland cement. At present, the most commonly used electrochemical detection methods in the laboratory are linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). A typical linear polarization resistance method uses a three-electrode device (working electrode (WE), reference electrode (RE), and auxiliary electrode (AE). A small DC voltage disturbance...
AE (10 mV) was applied to the steel bar (WE) in the concrete. After a certain stabilization time, the polarization resistance was obtained according to the linear relationship near the corrosion potential in accordance with the Stern–Geary formula, thereby quantitatively characterizing the corrosion current density. EIS, which was formerly known as AC impedance spectroscopy (ACIS), is the most important electrochemical research method for studying electrode reaction kinetics and material corrosion and corrosion inhibition mechanisms. EIS has been widely used in the field of reinforced concrete corrosion research since John et al. first tried to use the EIS to carry out the steel corrosion test in concrete. Unlike the time domain method such as LPR, EIS is a frequency domain test method. In addition to the polarization resistance, EIS can also obtain other electrochemical information such as solution resistance, capacitance of the concrete protective layer, and charge transfer resistance of the corrosion system that cannot be obtained by LPR and other methods.

LPR and EIS are currently used as the main means to study the corrosion of steel bars in Portland cement concrete structures. In order to study the corrosion of BMSCC reinforcement, this study combined LPR and EIS methods to systematically study the corrosion behavior of steel bars in different strength grades of BMSCC in simulated seawater and obtain the time-varying regularity of steel corrosion density with time. In addition, based on the time-varying model of steel corrosion in Portland cement, a time-varying model conforming to the corrosion of steel in BMSCC is proposed. According to the ASTM standard for steel corrosion, the initial corrosion time and the cracking time of the protective layer conforming to the corrosion of steel in BMSCC is proposed. Steel corrosion in Portland cement, a time-varying model with time. In addition, based on the time-varying model of steel corrosion in Portland cement, a time-varying model conforming to the corrosion of steel in BMSCC is proposed. According to the ASTM standard for steel corrosion, the initial corrosion time and the cracking time of the protective layer embedded in the BMSCC were calculated. By studying the corrosion behavior of steel bars in BMSCC in simulated seawater and calculating the cracking time of the BMSCC protective layer, a possibility is proposed for the application of BMSCC in marine engineering.

2. RESULTS AND DISCUSSION

2.1. Ultrasonic Pulse Velocity (UPV). The basic principle of the UPV test is that a stress wave is generated in the concrete by an ultrasonic pulse sender, and the wave can be received using a receiving transducer. Then, the UPV values of the concrete can be calculated via the distance and time that the stress wave travels through the concrete. The UPV is closely related to the internal structure of concrete. Generally, the higher the porosity of concrete, the lower the UPV.

Figure 1 plots the relationship between the UPV value and compressive strength of the BMSCC specimen. It can be seen that the UPV of BMSCC gradually increases with the increase in concrete strength grade. It can be explained that the higher the strength grade, the lower the internal defects and porosity of the BMSCC specimens, thus exhibiting a higher compressive strength. The conclusions obtained above confirm that the experimental results of BMSCC and Ordinary Portland Concrete are the same, that is, the greater the water–cement ratio, the more internal defects and the greater the porosity in the concrete.

2.2. Linear Polarization Resistance (LPR). Figure 2 shows the linear polarization curves of the BMSCC samples at different strength levels following exposure to simulated seawater at different ages. According to the test results of Figure 2, corrosion potential values of different grade BMSCC samples exposed to simulated seawater at different ages were obtained (Figure 3). The corrosion potential value of the steel bar in BMSCC gradually decreased with the extension of the exposure age. According to the requirements of ASTM C876, when the \( E_{corr} \) value is greater than \( -0.20 \) V, the corrosion probability of the steel in the concrete is less than 10%, and the steel is basically in a passivated state. Therefore, at a \( E_{corr} \) value of \( -0.35 \) V < \( E_{corr} \) < \( -0.20 \) V, the concrete activation of the medium steel bar was uncertain and had 50% probability of corrosion at this time. Similarly, at a \( E_{corr} \) value of less than \( -0.35 \) V, the probability of corrosion of the steel in the concrete was as high as 90%. The \( E_{corr} \) value of the C20 test block was less than \( -0.35 \) V before the test block was immersed in seawater, and the \( E_{corr} \) value of the C35 and C50 test block was greater than \( -0.35 \) V (Figure 3). These results indicate that the probability of corrosion of C20 and C35 after curing in air was 90% and 50%, respectively. When the C20, C35, and C50 test blocks were immersed in simulated seawater, the \( E_{corr} \) values were all less than \( -0.35 \) V, and the \( E_{corr} \) value decreased with the immersion time.

Figure 4 shows the corrosion current density (\( I_{corr} \)) of reinforcing steel embedded following BMSCC samples exposure in seawater at different strength levels, all of which were tested by the LPR. The \( I_{corr} \) of the reinforcing steel embedded in the BMSCC specimens exhibited a positive correlation with the exposure time. According to the published literature, the steel in concrete is under passive conditions with \( I_{corr} < 0.1 \mu A \cdot cm^{-2} \). In addition, the steel exhibited a high corrosion rate with \( I_{corr} > 10 \mu A \cdot cm^{-2} \). In addition, the steel is in the moderate corrosion condition when \( 1 \mu A \cdot cm^{-2} < I_{corr} < 10 \mu A \cdot cm^{-2} \) and in the low corrosion condition when \( 0.1 \mu A \cdot cm^{-2} < I_{corr} < 1 \mu A \cdot cm^{-2} \). The results in Figure 4 exhibited concordance with the results of the corrosion potential, such that when the steel bars in the BMSCC were in air, the steel bars were not in a passivated state but were instead in a low corrosion state. When the BMSCC test block was immersed in simulated seawater for 30 days, the steel bars in the BMSCC test blocks of the different strength grades were still in a low corrosion state. Prolonged immersion time rapidly increased the corrosion rate of the steel bars in the C20 test block, such that the steel bars were at a medium corrosion rate. When the strength level of BMSCC reached C35 and C50, the corrosion rate of steel in BMSCC were still at a low rust rate before an immersion time of 90 days. However, when the soaking time exceeds 180 days, the steel bars in the BMSCC began to enter a medium rust state. Furthermore, the comparison shows that
the corrosion rate of steel bars in C35 and C50 was lower than the corrosion rate of steel bars in C20 at the same exposure age. H2O and O2 exposure to the surface of the steel bar were the main sources of concrete corrosion following exposure to air, which resulted in corrosion of the steel. The steel bars in the C20 began to rust in the air, while the steel bars in the C35 and C50 were activated in the air. This was mainly because of the difficulty in forming a passivation film in the BMSCC given its pH value of approximately 11. The main reason for the corrosion of steel in C20 is that H2O and O2 reach the surface of the steel bar, which causes corrosion of the steel bar. The matrix of the C35 specimens is more compact compared with the C20 specimens, and the C35 and C50 specimens provide less transmission channels for H2O and O2, resulting in a lower probability of steel corrosion. Prolonged test block placement exposure time in the simulated seawater resulted in corrosion of the steel bar given that Cl− accumulated on the surface of

Figure 2. Linear polarization resistance test curve of BMSCC after different exposure times. (a) C20. (b) C35. (c) C50.
the steel bar, thereby resulting in serious steel bar rust in the BMSCC. Further, it can be found from the corrosion potential and the corrosion current density that an increase in the concrete strength reduced the corrosion probability of steel bars in the BMSCC.

2.3. Electrochemical Impedance Spectroscopy (EIS).
Electrochemical impedance spectroscopy (EIS) was used to assess the electronic conductivity of concrete, which performed as a solid electrolyte in reinforced concrete. The EIS data were presented as a Bode $|Z|_{2}$, $|Z|_{1}$, and a Nyquist plot (Figure 5b,d,f). The Bode $|Z|_{2}$ plot allows the absolute values of the impedance ($|Z|$) to be plotted against the logarithm of frequency (Hz). The Nyquist plot allows the imaginary resistance ($Z''$) to be plotted against the real resistance ($Z'$). Each dot on the Nyquist plot represents the impedance measured at an excitation frequency. The correlations between $|Z|$, $Z_{re}$, and $Z_{im}$ are defined by eq 1:

$$\left[ Z \right] = \sqrt{Z_{re}^{2} + Z_{im}^{2}}$$  \hspace{1cm} (1)

Figure 5a,c,e indicates that the impedance value of the BMSCC gradually decreased with the extension of the exposure time regardless of the concrete grade. However, at the same exposure age, the impedance value of the high-strength BMSCC was higher than that of the low-strength grade BMSCC specimens. For example, when the exposure age was 30 days for seawater immersion, the impedance values of the C20, C35, and C50 specimens were 10,000, 40,000, and 42,007 ohm-cm$^{-2}$, respectively. At an exposure age of 90 days, the impedance value values the C20, C35, and C50 specimens were calculated to be 7360, 28,000, and 32,324 ohm-cm$^{-2}$, respectively.

Two capacitive reactance arcs in the Nyquist curve were observed at the different exposure times, namely, high-frequency capacitive anti-arc and low-frequency capacitive anti-arc. The high-frequency curve characterizes the characteristics of the concrete protective layer. The position of the intersection of the high-frequency capacitive anti-arc, and the low-frequency capacitive anti-arc reflects the resistance of the material passing through the concrete to the surface of the steel. In addition, the electrochemical process related to the corrosion of the steel can be characterized by the low-frequency curve. The extension of exposure time of the different intensity grades BMSCC generated a gradual decrease in the high-frequency capacitive anti-arc diameter of the Nyquist curve and a gradual increase in the low-frequency capacitive anti-arc diameter. As a result, the intersection of the high-frequency capacitive anti-arc and low-frequency capacitive anti-arc gradually shifted to the left. For the same age, the high-frequency capacitive arc radius of the high-strength BMSCC was significantly higher than that of the low-strength BMSCC. These results indicate that, in the C35 and C50 BMSCC, the resistance of the material passing through the concrete to the steel surface was greater than that of the C20 strength grade BMSCC.

Figure 5 shows an equivalent circuit model with the circuit code $R_{c} (Q_{dl} |Q_{dl} , Q_{dl} , W)|$, where $R_{c}$ is the resistance of the test concrete protective layer, respectively, $R_{ct}$ is the charge transfer resistance of the steel bar, and $Q_{dl}$ is the electric double layer capacitance of the steel/concrete interface zone. Due to the non-uniformity of the concrete and steel surface, the ideal electric double layer capacitor ($C_{dl}$) was replaced by the constant phase angle element CPE ($Q_{dl}$). At the same time, in the early stage of corrosion, considering the effect of diffusion control, the Warburg diffusion element ($W$) was added to the equivalent circuit model.

The equivalent circuit simulation results were well in concordance with the original EIS data (Figure 5). The parameters of fitting impedance data are listed in Table 1. The $I_{corr}$ of reinforcing steel tested by the EIS was obtained by combining the $R_{ct}$ values and eq 1, the results of which are shown in Figure 7. The $I_{corr}$ for all the specimens tested by the EIS displayed the same trend with the $I_{corr}$ measured by the LPR. Notably, the $I_{corr}$ measured by the LPR was lower than that tested by the EIS when the steel was out of the passive state, especially for the control specimens. According to Koleva et al., this may be due to the transformations of the corrosion products emerged on the steel surface, which made the $R_{p} > R_{ct}$. Only when there were no mass transport processes could $R_{p}$ be equal to $R_{ct}$.

According to Table 1, a positive correlation was observed between the $R_{ct}$ value and the BMSCC intensity level at the same exposure age. For example, at a BMSCC of C35, the $R_{ct}$ value of the BMSCC after 30 days of soaking in seawater was 32,400 ohm-cm$^{-2}$, and the $R_{ct}$ value of the C20 test piece after 30 days of soaking in seawater was 13,420 ohm-cm$^{-2}$, or a reduction of 30%. These results indicate that improvements in
the BMSCC strength level can significantly improve the rust resistance efficiency of the steel bar. When BMSCC (C35) was immersed in seawater, the $R_{ct}$ was calculated to be 32,400, 16,790, 13,720, and 6610 Ohm·cm$^{-2}$ with exposure times of 30, 90, 180, and 270 days, respectively. Due to the diffusion effect of Cl$^-$, the Cl$^-$ content in the concrete gradually increased, which generated pitting corrosion of the steels, resulting in the gradual decrease in $R_{ct}$ over time. That is, as the exposure time of the ocean increased, the tendency of the steel to corrode gradually increased as well.

2.4. Basic Time-Varying Model of Steel Corrosion Rate. There are many time-varying models for the steel corrosion rate before concrete cracking. Liu and Weyers$^{26}$ believed that after the cracking of concrete and after the
occurrence of steel corrosion, surface corrosion of the steel bar hinders the diffusion of iron ions on the surface of the steel bar, and the corrosion rate slows down with time and eventually stabilizes. The relevant data established the relationship between the corrosion rate and time, and the corresponding corrosion rate model was defined as follows:

\[ I_{\text{corr}}(t) = 0.85 I_{\text{corr}}(t_p) \times (t - t_p)^{-0.29} \quad (2) \]

\[ I_{\text{corr}}(t_p) = \frac{37.8 \times (1 - w/c)^{-1.64}}{C} \quad (3) \]

where \( I_{\text{corr}}(t) \) is the corrosion current density of the steel bar at the time of \( t, \mu A \cdot cm^{-2} \); \( I_{\text{corr}}(t_p) \) is the corrosion current density of the steel bar at the time of \( t_p, \mu A \cdot cm^{-2} \); \( t \) defines the time after the steel bar begins to rust, year (a); \( w/c \) defines the water-to-cement ratio; and \( C \) is the thickness of the protective layer, mm. Vu27 combined Liu and Weyers’ models with their
The relationship between the corrosion current density and time after corrosion was established using relevant data. The corresponding corrosion rate model was defined as follows:

\[ I_{\text{corr}}(t) = I_{\text{corr}}(1) \times e^{-0.402t} \]  

(6)

where \( I_{\text{corr}}(0) \) is the corrosion current density of the first test steel bar, \( \mu A \cdot \text{cm}^{-2} \).

Li\(^{29}\) conducted a large number of model tests on reinforced concrete curved members in the marine environment. A positive correlation was initially observed between the corrosion rate of the steel bars with time, after which it slowed down. The correlation data was used to establish the relationship between the corrosion current density and time after corrosion. The following empirical formula can be defined as follows:

\[ I_{\text{corr}}(t) = 0.3683 \ln(t) + 1.1305 \]  

(7)

The time-varying model of steel corrosion in ordinary concrete for the time-varying model was mainly derived as an exponential function model and a logarithmic function model, indicating that these two functions can accurately predict the service life of ordinary concrete. Based on the data obtained by electrochemistry, the logarithmic function, exponential function, and quadratic polynomial function were all used to nonlinearly fit the corrosion current density of steel bars in the BMSCC after different exposure times (Figure 7). The fitting expressions of different functions are shown in Table 2. The time-varying model obtained by the logarithmic function exhibited the highest fitting degree, specifically at C20 C35 and C50 fitting degrees of 0.913 0.979, and 0.957, respectively. Therefore, for the time-varying model of the BMSCC reinforced concrete in seawater environment, eq 10 (C20), eq 13 (C35), and eq 16 (C50) can be used.

### 2.4.1. Initial Corrosion Time of Steel Bars

The steel bar began to rust when the chloride ion concentration on the steel surface reached the critical value. Usually, the time when the chloride ion concentration on the steel surface reached the critical value was taken as the initial corrosion time \( t_i \) of the steel bar. According to the electrochemical corrosion judgment basis given in GB/T 50344-2004,\(^{30}\) the initial corrosion time of steel bars was calculated by the corrosion current density limit of the steel bars.

### 2.4.2. Cracking Time of the Concrete Protective Layer

Many time-varying models have been established for the reinforced concrete protective layer, such as the Funahashi model\(^{32}\) the Rodriguez model, and the Niu Taotao model.\(^{32,33}\) This paper employed the Youping Liu theoretical model,\(^{34}\) which considers the influence of the corrosion products on the concrete diffusion around the steels and approximates the surrounding concrete pore transition zone to steel. The circumference of the thick ring was inversely proportional to the thickness of the oxide layer. Therefore, as the rust layer thickened, the diffusion distance of the iron ions increased and generated a decrease in the generation rate of the rust products. The amount of steel corrosion can be calculated as follows:

\[ \frac{dW_{\text{rust}}}{dt} = \frac{k_p}{W_{\text{rust}}} \]  

(17)

where \( D \) is the diameter of the steel bar, mm; \( W_{\text{rust}} \) is the corrosion amount, mg/mm; and \( k_p \) is the coefficient related to metal loss rate, such that \( k_p = 0.105 \text{ } t \text{ } (1/\text{ } t) \text{ } D \text{ } I_{\text{corr}}(t) \), \( t \) is the coefficient related to rust \( \alpha = 0.523 \) when the rust product is Fe(OH)\(_2\). Additionally, because corrosion products generally include the above two, \( \alpha \) was taken as the mean value, 0.573.

Integrating (eq 17) yields

\[ W_{\text{rust}} = \sqrt{2 \int_0^t k_p \text{ } dt} \]  

(18)

The critical rust amount, \( W_{cr} \) of the concrete protective layer cracking can be expressed by the following formula:

\[ W_{cr} = \frac{\pi \rho_{st} \rho_{rast}}{4} \left[ \frac{f_t}{E_{st}} \frac{u^2 + m^2}{n^2} + k_1 + d_0 \right] D \]  

(19)

where \( m = (D + 2d_0)/2, n = C + (D + 2d_0)/2; \rho_{st} \) and \( \rho_{rast} \) are the rebar density (7850 kg/m\(^3\)) and rust density (3600 kg/m\(^3\)), respectively; \( f_t \) defines the concrete tensile strength, 2.41 N/mm\(^2\) (C20), 2.97 N/mm\(^2\) (C35), and 4.01 N/mm\(^2\) (C50);\(^{35}\) \( E_{st} \) defines concrete effective elastic modulus, \( E_{st} = E_{st} / \left(1 + \nu_{st} \right) \), such that \( E_{st} \) is the concrete elastic modulus and is equal to 23.36 GPa (C20), 34.56 GPa (C35), and 48.64 GPa (C50);\(^{35}\) \( q_{cr} \) is the concrete creep coefficient, early strength cement takes 2.2, ordinary cement takes 2.0; and \( \nu \) is Poisson’s ratio (test group test: 0.25); and \( d_0 \) is the thickness of the gap between the cement and concrete interface (12.5 μm).\(^{32}\)

### 2.4.3. Initial Corrosion Time of the Steel Bars and Cracking Time of the Concrete Protective Layer

The cracking time, \( t_c \) of the protective layer was calculated by setting the steel corrosion amount, \( W_{\text{rust}} \), to the critical corrosion amount, \( W_{cr} \) of the concrete protective layer.

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**Table 2. Basic Time-Varying Models of Steel Corrosion Rate of BMSCC**

| specimens | models | \( R^2 \) | no |
|-----------|--------|--------|----|
| C20       | \( I_{\text{corr}}(t) = 0.5755 + 0.113t + 0.00009t^2 \) | 0.910 | 9   |
|           | \( I_{\text{corr}}(t) = 64.47 \ln(t + 4553.06) - 542.57 \) | 0.913 | 10  |
|           | \( I_{\text{corr}}(t) = e^{0.0045t-0.5537} \) | 0.848 | 11  |
| C35       | \( I_{\text{corr}}(t) = 0.324 + 0.009t - 1.118t^2 \) | 0.954 | 12  |
|           | \( I_{\text{corr}}(t) = 0.673 \ln(t + 23.938) - 2.061 \) | 0.979 | 13  |
|           | \( I_{\text{corr}}(t) = e^{0.0041t-0.6409} \) | 0.774 | 14  |
| C50       | \( I_{\text{corr}}(t) = 0.320 + 0.008t - 1.278t^2 \) | 0.879 | 15  |
|           | \( I_{\text{corr}}(t) = 0.344 \ln(t + 7.081) - 0.541 \) | 0.957 | 16  |
3. CONCLUSIONS

1) As a new type of green cementitious material, BMSCC and its durability caused by steel corrosion is an important research topic. In the present work, the corrosion behavior of steel bars in BMSCC was studied by the electrochemical method.

2) Linear polarization resistance and electrochemical impedance spectroscopy were used to characterize the electrochemical corrosion behavior of steel bars in the BMSCC at different strength grades. The test results of the LPR show that the corrosion potential of the BMSCC decreased with the immersion time, and the corrosion current density increased with the immersion time. These results suggest that the corrosion rate of steel bars in the BMSCC increased with seawater exposure time. However, the corrosion rate of the steel bars in the high-strength BMSCC was significantly slower than that of the low-strength test blocks.

3) The results obtained by fitting the EIS test data by the equivalent circuit model also show the same rule as the LPR method. Specifically, the polarization resistance of the steel bar in the BMSCC decreased with seawater immersion time, indicating an increase in the corrosion rate. However, the corrosion rate of steel in the C35 and C50 test block was lower than that of the C20 test block.

4) The corrosion current density of the steel bars in the BMSCC was fitted against time using different types of functions. The fitting results indicate that the exponential function reflected the corrosion law of the steel bars in the BMSCC with the immersion time, of which the corrosion of the BMSCC steel bars was obtained with different strengths. In addition, the corrosion time of the two BMSCC strength grades was calculated based on the reinforced concrete cracking time model of the Portland cement. The results exhibited a negative correlation between the strength of the BMSCC with the corrosion rate of the steel bars.

4. MATERIALS AND METHODS

4.1. Raw Materials. The light-burned magnesia powder (MgO) used in this study had a purity of 80% and was obtained from Haicheng Jinsha Magnesium Mining (Liaoning Province, China). The active MgO was 60.0% by the hydration method.20 The magnesium sulfate (industrial-grade, MgSO₄·7H₂O) was produced by Nanjing Reagent Co, Ltd. (Jiangsu Province, China) and had a purity of 99.0%. The magnesium sulfate was ground by a mill grain and passed through a sieve with screen apertures of 75 μm. Citrate (C₆H₅O₇·2H₂O) was sourced from Aladdin China (CAS number 77-92-9, laboratory grade) with a purity of >99.5% and used as a chemical admixture. Additionally, chemical-grade magnesium sulfate (MgSO₄·7H₂O), sodium sulfate (Na₂SO₄), and magnesium chloride (MgCl₂) were used in the experiment, which were obtained from Guangdong Guanghua Sci-Tech (Guangzhou, China). The fly ash (FA) was obtained from the Suizhong power plant and Chaoyang Hongjian Slag (Liaoning Province, China). The chemical compositions of the MgO and FA were analyzed by X-ray fluorescence (XRF) with a PANalytical Axios PW4400 analyzer (PANalytical, Eindhoven, Netherlands), and the results are shown in Table 4. The fine aggregate used was natural river sand with a fineness modulus of 2.72. Crushed basalt aggregate was used as the coarse aggregate with a continuous grade of 5–10 mm.

4.2. Specimen Preparation. The mix proportion of BMSCC and the mixture design and basic mechanical properties of BMSCC (C20, C35, and C50) are listed in Tables 5 and 6, respectively. Three strength grades of reinforced BMSCC specimens with a dimension of 40 × 40 × 200 mm³ were designed, and the schematic diagram rebar location in the BMSCC specimen is presented in Figure 8. The details of the process of mixing BMSCC were as follows: (1) First, the weighted MgO, FA, MgSO₄, and sand were put into the mixer for dry mixing for 5 min and then a well-mixed binder was obtained; (2) Second, weighted water and citrate were added into the binder until evenly mixed; (3) Finally, the crushed basalt aggregate were added and mixed for 5 min. The slump and flow of the concrete mixture were measured after mixing, and specimens were casted and cured under sealed conditions for 24 h. The specimens were then demolded and cured in saturated limewater from 20 ± 5 °C for 28 d. The corresponding physical and mechanical properties of the sample materials are summarized in Table 3. The bottom surfaces (40 × 40 mm²) of BMSCC specimen were not sealed with epoxy resin until the specimen had dried, after which the sealed specimen was immersed in artificial seawater for the exposed test.

Smooth ordinary carbon steel rebars with a diameter of 10 mm and a length of 18 cm were used and embedded centrally.
in mortar specimens with a cover depth of 15 mm. A copper wire was soldered to one end of the reinforcing steel, and both ends were covered with epoxy resin coating. The diagram of steel reinforced mortar is presented in Figure 8.

4.3. Test Method. 4.3.1. Fundamental Theory. The self-corrosion potential ($E_{\text{corr}}$), polarization resistance ($R_p$), and corrosion current density ($I_{\text{corr}}$) of the reinforcement are mostly used to characterize the corrosion degree of reinforcement. The Tafel slope for the anodic and cathodic reactions occurring under an open circuit may be obtained from the linear polarization curve. The current density at that point is $I_{\text{corr}}$ and the potential at which it falls is the $E_{\text{corr}}$. This test method is also useful to assess the $R_p$, which is defined by the ratio of the applied potential to the applied current. Polarization resistance measurement is an accurate and rapid way to measure the general corrosion rate.36,37 The calculation formula is defined as follows:

$$R_p = \frac{\Delta E}{\Delta I} \Bigg|_{\Delta E \to 0}$$  \hspace{1cm} (20)

where $R_p$ is the polarization resistance ($\Omega \cdot \text{cm}^2$); $E$ is the potential (V); and $I$ is the current density (A/cm$^2$). A high value indicates that the material is more resistant to corrosion.

In 1957, Stern and Geary38 derived an equation to calculate the corrosion rate of reinforcement. By applying small differences in the potential around the corrosion potential and measuring the currents associated, the $R_p$ of the electrode can be determined using eq 20. According to this polarization resistance, the $I_{\text{corr}}$ value can be calculated through the Stern–Geary equation as follows:39

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{R_p}$$  \hspace{1cm} (21)

where $\beta_a$ and $\beta_c$ are the Tafel slopes;37 $R_p$ is the polarization resistance ($\Omega \cdot \text{cm}^2$); $I_{\text{corr}}$ is the corrosion current density ($\mu\text{A} \cdot \text{cm}^{-2}$); and $B$ is a constant related to $\beta_a$ and $\beta_c$, the anodic and cathodic slopes of the Tafel curve, respectively. When the rebar is in the passivation stage, $B = 52$ mV, and when the rebar is in the corrosion stage, $B = 26$ mV.40,41

4.3.2. Experimental Setup. For the LPR test, the test principle was to apply a constant potential ($\Delta E < 10$ mV) at the steel bar to ensure that the disturbance signal is small enough to satisfy the linear relationship between voltage and current. The LPR test was conducted using the three-electrode test system, with the saturated calomel electrode as the RE. We used a mercury RE covered with HgCl$_2$ paste, which was saturated with KCl and had a potential of +0.242 V with respect to the standard hydrogen electrode. The stainless steel plate served as the auxiliary electrode (AE), and the steel rebar served as the working electrode (WE) under testing. The potential scanning range was within the range of $-10$ to $10$ mV with respect to the open-circuit potential and at a scanning rate of 0.1667 mV/s. The test instrument was the CHI600D electrochemical workstation produced by Hua Ke Pu Tian Technology Co., Ltd., Beijing. The schematic diagram of the LPR test is shown in Figure 9.

In the EIS test, the EIS measurements were performed in situ using a CHI600D electrochemical workstation. The EIS tests were carried out applying a voltage of 10 mV (r.m.s.) sine wave within a frequency range of 100 kHz down to 1 mHz.

Table 5. Mix Proportion of BMSC

| composition     | MgO/kg·m$^{-3}$ | MgSO$_4$/kg·m$^{-3}$ | FA/kg·m$^{-3}$ | citrate /kg·m$^{-3}$ |
|-----------------|-----------------|----------------------|----------------|---------------------|
| weight          | 270             | 122                  | 138            | 1.35                |

Table 6. Mix Proportion of BMSCC

| no   | BMSC/kg | gravel/kg | sand/kg | water/kg | slump/mm | 3 d/MPa | 28 d/MPa |
|------|----------|-----------|---------|----------|-----------|---------|----------|
| C50  | 530      | 1078.3    | 718.6   | 164.3    | 91        | 40.5    | 49.2     |
| C35  | 530      | 1078.3    | 718.6   | 185.5    | 135       | 22.8    | 35.9     |
| C20  | 530      | 1078.3    | 718.6   | 249.1    | 228       | 12.8    | 23.9     |

Figure 8. Schematic representation of the steel reinforced mortar (a: three-dimensional view; b: front view; c: side view).
measurements were made using two electrodes: the RE and AE were short-circuited and connected to a stainless steel plate and the WE connected to the steel rebar, respectively. The impedance results were fitted using the ZSimpWin software.

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**Notes**

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