Influence of Environmental Factors on the Chloride Binding Ability of Cement-carbonated Red Mud Composite Cementing System

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Abstract

The chloride environment is complex and common in engineering, and the corrosion of steel bar caused by chloride ion erosion is one of the main factors that damage the reinforced concrete structure. In this paper, cement-carbonized bayer red mud-carbonized sintering red mud ternary composite cementing system was prepared by carbonated bayer red mud (CBRM) and carbonated sintering red mud (CSRM) as auxiliary cementing materials. The effects of chloride ion concentration, chloride salt type and sulfate on the chloride binding ability of cement-CBRM-CSRM cementing system were studied. The binding isotherm of chloride ions was determined by equilibrium method and the phase composition of cement-CBRM-CSRM cementing system was analyzed by XRD. The results show that the content of bonded chloride in cement-CBRM-CSRM cementing system increases with the increase of chloride concentration in erosion solution. Freundlich binding can well describe the relationship between binding chloride ion content and free chloride ion concentration in NaCl solution. In addition, the order of influence of cations on the chloride binding capacity of cement-CBRM-CSRM cementing system is Ca^{2+}>Mg^{2+}>Na^{+}. In addition, the presence of SO_4^{2-} is unfavorable to the binding of chloride ions in cement-CBRM-CSRM cementing system, and the higher the concentration of SO_4^{2-} in the erosion solution, the greater the adverse effect.

Keywords

Chloride Binding; Carbonated Sintering Red Mud (CSRM); Carbonated Bayer Red Mud (CBRM); Friedel's Salt (FS).

1. Introduction

Concrete is currently the world's largest use of building materials, often used in house construction, roads and bridges and all kinds of marine infrastructure construction [1]. With the development of China's Marine economy, marine engineering concrete construction is also increasing. However, many aggressive ions in the ocean will destroy the durability of reinforced concrete structures, especially chloride ion erosion. Chloride ion erosion can cause steel corrosion, resulting in cracking of reinforced concrete structures, seriously weakening the functionality and safety of reinforced concrete structures during the service period [2].

However, not all chloride ions will cause steel corroson, when the chloride ions into the reinforced concrete, part of the chloride ions will be cement components and cement hydration products combined, this part of the chloride ions are called bound chloride ions [3]. Binding chloride ions include physical adsorption chloride ions and chemical binding chloride ions, and binding chloride ions will not cause corrosion of steel bars [4]. It is very important to study the chloride binding capacity of cement-based materials to improve the chloride erosion resistance of it. In addition to chloride ion erosion, environmental factors such as cation type and sulfate concentration in the erosion environment also have a great influence on the chloride ion binding ability of cement-based materials [5-7]. For example, buildings eroded by deicing salt in winter may be eroded by calcium and magnesium chloride in addition to sodium chloride, and different types of chloride salts have different levels of erosion on reinforced concrete [7-8]. However, buildings in coastal areas and saline-alkali lands are mainly attacked by chlorides and sulfates. When chloride ion and sulfate exist in the corrosive environment, sulfate ion will promote the corrosion of steel bars and cause expansion damage to reinforced concrete structures [9].

Therefore, in this paper,CBRM and CSRM were used as SCMs to partially replace cement to prepare cement-CBRM-CSRM ternary composite cement-CBRM-CSRM cement-forming system, and the free chloride ion content of cement-CBRM-CSRM cement-forming system was measured by automatic ion titrator. The hydration products of cement-CBRM-CSRM cementing system were analyzed by XRD. The influence of external environmental factors such as chloride ion concentration, chloride salt type and sulfate concentration on the ability of cement-CBRM-CSRM cementing system to bind chloride ion was studied.

2. Experiment

2.1 Materials

The Portland cement used in the study (PO 42.5) came from Jiaozuo Qianye Cement Co., LTD. The bayer red mud (BRM) and sintering red mud (SRM) used in this paper were provided by Zhongzhou Aluminum Co., LTD. BRM and SRM were pretreated by wet carbonation and designed as CBRM and CSRM [10].

The chemical composition of cement, BRM and CBRM was determined by X-ray fluorescence (XRF, Axios advanced, PANalytical b.v., Netherlands). The results are shown in Table 1. The mineral composition of BRM and CBRM was analyzed by X-ray diffraction (XRD), and the results were shown in Figure 1 and Figure 2.

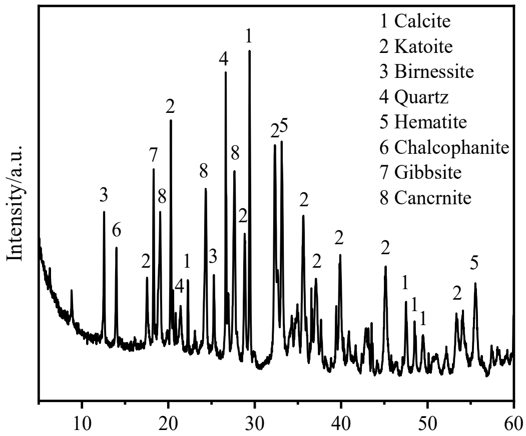

Figure 1. XRD spectrum of CBRM

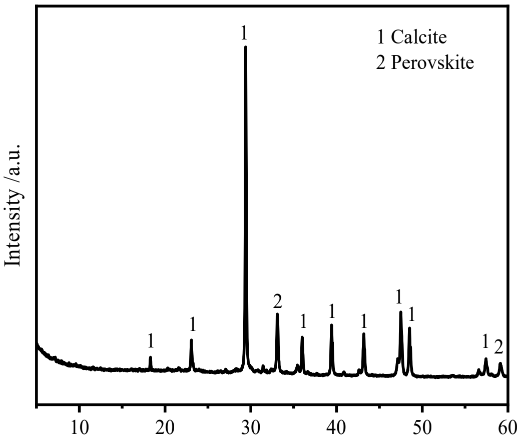

Figure 2. XRD spectrum of CSRM

Table 1. Chemical compositions of main materials (wt. %)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
Cement	18.47	5.76	3.95	62.42	3.69	3.16	0.497	1.00	1.053
CBRM	19.45	24.69	11.99	13.85	1.22	1.03	8.59	0.90	18.28
CSRM	17.33	6.89	18.89	46.55	1.02	1.07	1.29	0.87	6.09

2.2 Preparation of Cement Paste

In this study, different doses of CBRM and CSRM were used to prepare cement paste. The mixing ratio is shown in Table 2. The water-binder ratio of all mixtures was 0.50. Mix the different mixture evenly and pour it into a mold with a size of 20mm × 20mm × 20mm. After pouring vibration, the paste surface wwas sealed with plastic film to prevent water evaporation. After curing in the standard curing room for 24 h, the mold was removed and cured in saturated calcium hydroxide solution for 28 days. After curing to a certain age, the broken specimen was screened, and particles with a particle size between 0.3mm and 1.18mm were collected with a screen of 0.3mm and 1.18mm. After being fully mixed and uniform, these particles were dried in a vacuum drying oven at 50°C for 7 days to remove most of the water in the particles and thus terminate hydration.

Table 2. Mix proportions of paste(% by mass)

	Cement(%)	CBRM(%)	CBRM(%)	w/b
Cement-CBRM	70	30	0	0.5

2.3 Test Methods

2.3.1. Bound Chloride Ion Test

Take 10g (m_0) of the pre-vacuum-dried particles and place them in the dried conical bottle, then use the pipette to accurately weigh 40ml (V) of the erosion solution of known concentration (C_0) prepared with saturated lime water, as shown in Table 3. The lid of the conical bottle was tightly closed and placed in a standard curing room for 10 days. Tang [11] believed that after 7 days of soaking, the concentration of the erosion solution could reach a dynamic equilibrium with the concentration of the pore solution in the particles. Then the supernatant in the conical bottle was poured into the dry weighing bottle. This was the volume of the first balanced liquid and was denoted as V'. At this time, the chloride ion concentration in the first equilibrium solution was titrated by an automatic ion titrator, denoted C_1. Then 200ml (V") of saturated lime water was added to the original conical bottle and seal it for 10 days. Ten days later, the erosive solution and the pore solution in the sample particles reached dynamic equilibrium again, at which time the chloride ion concentration in the supernatant was titrated with the automatic ion titrator, which was the second equilibrium chloride ion concentration in the liquid, recorded as C_2.

The amount of chloride ion reduced in the original erosion solution at the first equilibrium was the total chloride ion curing amount of the sample, which was denoted as C_b; According to the calculation, the physical adsorption chloride ion quantity of the sample was obtained, which was denoted as C_{bc}; According to the total chloride ion curing amount of the sample and the chemical binding chloride ion amount of the sample, the physical adsorption chloride ion amount of the sample can be calculated, which was denoted as C_{bp}. The calculation method is shown in formula (1), (2) and (3). Where 34.45 in the formula is the relative molecular mass of chlorine.

$$C_b = \frac{35.45\times(C_0-C_1)}{m_0} \tag{1}$$

$$C_{bc} = \frac{35.45\times[C_0V-C_1V'-C_2(V+V''-V')]}{m_0} \tag{2}$$

$$C_{bp} = C_b - C_{bc} \tag{3}$$

Table 3. Three schemes comparing erosion solution combination design and numbering

Abbreviation	Concentration of exposed solutions	Chloride ion(mol/L)
0.1NC	0.1mol/L NaCl	0.1
0.5NC	0.5mol/L NaCl	0.5
1.0NC	1.0mol/L NaCl	1.0
1.5NC	1.5mol/L NaCl	1.5
2.0NC	2.0mol/L NaCl	2.0
0.25CC	0.25mol/L $CaCl_2$	0.5
0.25MC	0.25mol/L $MgCl_2$	0.5
0.5NC-0.5NS	0.5mol/L NaCl+0.5mol/L Na_2SO_4	0.5
0.5NC-1.0NS	0.5mol/L NaCl+1.0mol/L Na_2SO_4	0.5

2.3.2. X-ray Diffractometer (XRD)

The mineral phase composition of the sample was conducted by X-ray diffraction (SmartLab (9 kW)). The sample was step scanned from 5° to 60° at a scanning rate of 5°/min at 0.02° 2θ steps integrated.

3. Results and Discussion

3.1 Effect of Chloride Ion Concentration on Chloride Binding Ability of Composite Cementing Cementing System

Figure 3 shows the bound chloride ion curve of cement-CBRM-CSRM cementing system. It can be clearly seen from the figure that the content of bonded chloride ions in cement-CBRM-CSRM cementing system increases with the increase of chloride ion concentration in the erosion solution. Table 4 shows the fitting parameters a, b and correlation coefficient R^2 of Freundlich fitting and Langmuir fitting of cement-CBRM-CSRM cementiting system. As can be seen from Table 4, the correlation coefficients (R^2) of Freundlich fitting and Langmuir fitting for cement-CBRM-CSRM cementiting system were 0.9944 and 0.9679, respectively. It can be seen that the correlation coefficient (R^2) of Freundlich fitting is larger in the two kinds of nonlinear fitting of cement-CBRM-CSRM cementification system, and the fitting result is better.

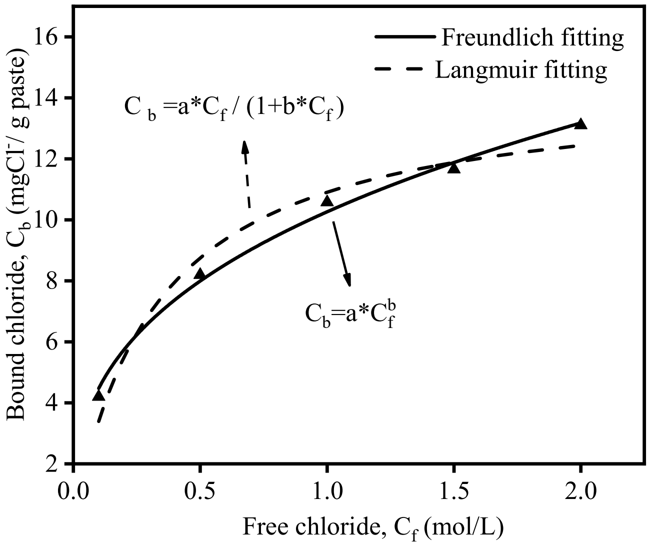

Figure 3. Bound chloride ion curve of samples

Table 4. Chloride ion binding fitting parameters of samples

	a	b	R^2
Freundlich fitting	10.26	0.36	0.9944
Langmuir fitting	44.30	3.06	0.9679

Figure 4 is the XRD pattern of cement-CBRM-CSRM cementing system under the attack of different concentrations of sodium chloride solution. It can be obviously observed from the figure that when the concentration of Cl^- in the erosion solution is 0.1mol/L, the diffraction peak of FS in the cement-CBRM-CSRM cementing system is almost non-existent, and the diffraction peak of KS appears. When the Cl^- concentration in the erosion solution is greater than 0.1 mol/L, the diffraction peak of KS in the cement-CBRM-CSRM cementing system disappears, and the diffraction peak of FS becomes stronger, and the change is very obvious. This indicates that KS in cement-CBRM-CSRM cementing system is formed at low Cl^- concentration (< 0.5mol/L), and when Cl^- concentration in erosion solution increases (> 0.5mol/L), KS will be transformed into FS [12]. In addition, it is worth noting that the diffraction peak of FS in cement-CBRM-CSRM cementing system increases first and then decreases with the increase of chloride ion concentration in the erosion solution. When the concentration of Cl^- in the erosion solution is 1.0mol/L, the diffraction peak of FS is the strongest. It can be seen that the FS formed in cement-CBRM-CSRM cementing system will decrease at higher Cl^- concentration.

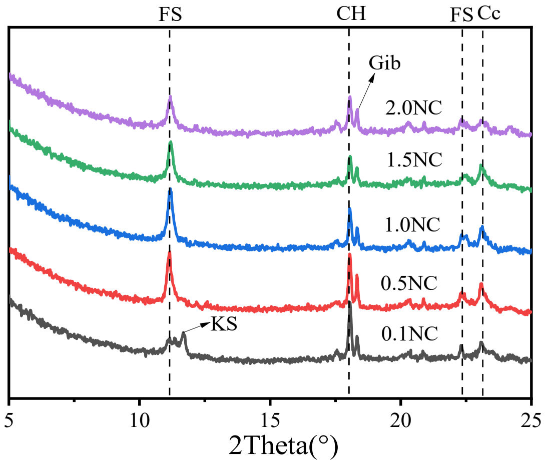

Figure 4. XRD patterns of cement-CBRM-CSRM cementing system under different concentrations of sodium chloride solution (FS: Friedel's salt; KS: Kuzel's salt; CH: $Ca(OH)_2$; Gib: $Al(OH)_3$; Cc: Calcite)

3.2 Effect of Cation Type on Chloride Binding Ability of Composite Cementing Cementing System

Figure 5 shows the content of bound chloride ions in cement-CBRM-CSRM cementing system under the attack of different chlorine salt solutions at different ages. It can be clearly seen that the content of bound chloride ions in cement-CBRM-CSRM cementing system is also different with different types of cations in the erosive solution. The contents of total bound chloride ions, chemically bound chloride ions and physically bound chloride ions in $MgCl_2$ solution were increased by 14%, 12% and 20%, respectively, compared with those in NaCl solution. The content of total, chemically and physically bound chloride ions in the paste soaked in $CaCl_2$ solution was 22%, 18% and 36% higher than that in the paste soaked in NaCl solution, respectively. It can be seen that the order of influence of cations in erosion solution on the chloride binding ability of cement-CBRM-CSRM cementing system is $Ca^{2+}>Mg^{2+}>Na^+$. In addition, the increase in the content of physically bound chloride ions in the paste soaked in calcium chloride and $MgCl_2$ erosion solution was almost twice that of chemically bound chloride ions. This indicates that Ca^{2+}>Mg^{2+} improves the overall chloride binding ability of cement-CBRM-CSRM cementing system mainly by improving the physical binding ability of chloride ions.

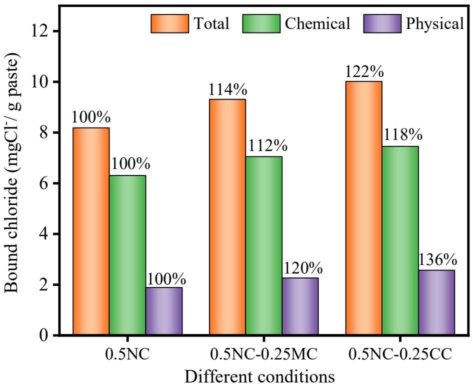

Figure 5. Content of bonded chloride ions in cement-CBRM-CSRM cementing system under the attack of different chloride salt solutions

Figure 6 is the XRD pattern of cement-CBRM-CSRM cementing system under the attack of different chlorine salt solutions. It can be clearly seen that the FS diffraction peak of the paste soaked in $MgCl_2$ and $CaCl_2$ erosive solution is stronger than that of the paste soaked in NaCl erosive solution. Compared with the paste soaked in $MgCl_2$ erosion solution, the FS diffraction peak of the paste soaked in $CaCl_2$ solution is stronger. It can be seen that Mg^{2+} and Ca^{2+} promote the cement-CBRM-CSRM cementing system to generate more FS than Na^+. In addition, in the $MgCl_2$ erosion environment, CH diffraction peak is not observed in the cement-CBRM-CSRM cementing system, which indicates that the presence of Mg^{2+} will lead to the dissolution of CH in the cement-CBRM-CSRM cementing system, resulting in the disappearance of CH diffraction peak [13].

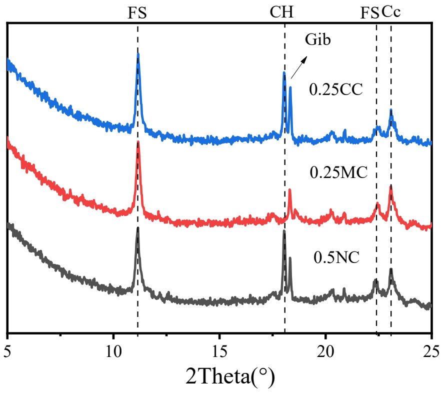

Figure 6. XRD pattern of cement-CBRM-CSRM cementing system under different chloride solution erosion (FS: Friedel's salt; CH: $Ca(OH)_2$; Gib: $Al(OH)_3$; Cc: Calcite)

3.3 Effect of Sulfate on Chloride Binding Ability of Composite Cementing Cementing System

Figure 7 shows the content of bonded chloride ions in cement-CBRM-CSRM cementing system under sulfate attack of different concentrations. It can be found that the content of bound chloride ions in cement-CBRM-CSRM paste decreased significantly after the introduction of SO_4^{2-} into the NaCl erosion solution. When the concentration of SO_4^{2-} in the erosive solution is 0.5mol/L, the total bound chloride ion content, chemical bound chloride ion content and physical bound chloride ion content of cement-CBRM-CSRM gel system decrease by 62%, 63% and 58%, respectively. When the concentration of SO_4^{2-} in the erosive solution is 1.0mol/L, the total bound chloride content, chemical bound chloride content and physical bound chloride content of the cement-CBRM-CSRM cementing system decrease by 70%, 71% and 67%, respectively. It can be seen that the higher the concentration of SO_4^{2-} in the erosive solution, the greater the decrease in the content of binding chloride ions in the cement-CBRM-CSRM cementing system, and the worse the binding chloride ion ability of the cement-CBRM-CSRM cementing system.

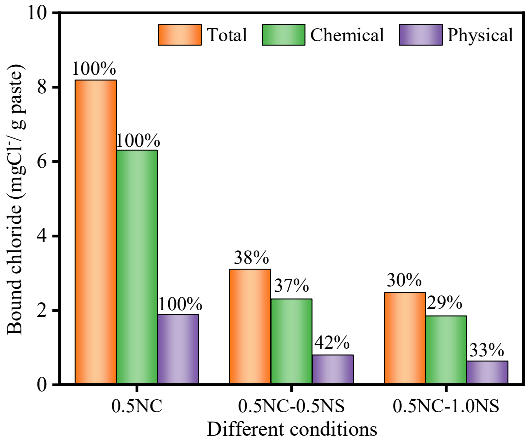

Figure 7. Content of bonded chloride ions in cement-CBRM-CSRM cementing system under attack by sulfate solution of different concentrations

Figure 8 shows the XRD pattern of cement-CBRM-CSRM cementing system under sulfate attack of different concentrations. It can be clearly seen from the figure that when the concentration of SO_4^{2-} in the erosive solution is 0.5mol/L, the diffraction peak of FS in the cement-CBRM-CSRM cementing system is significantly weakened and almost disappears. When the concentration of SO_4^{2-} in the erosive solution is 1.0mol/L, the diffraction peak of FS can hardly be observed in the cement-CBRM-CSRM cementing system. This indicates that the introduction of SO_4^{2+} in NaCl erosion environment will not only reduce the formation of FS, but also affect the stability of FS, which is not conducive to the binding of chloride ions in cement-CBRM-CSRM cementing system. At the same time, CH diffraction peak was not observed in the cement-CBRM-CSRM cementing system in the erosion environment containing SO_4^{2+}. In addition, AFt diffraction peak appeared in cement-CBRM-CSRM paste when SO_4^{2+} concentration was 0.5mol/L. However, the diffraction peak of AFt in the cement-CBRM-CSRM gel system disappeared when the concentration of SO_4^{2+} in the erosive solution increased from 0.5mol/L to 1.0mol/L. This is because ettringite induced by sulfate attack transforms into AFm at an early stage and reverses at a later stage, and the synergistic effect between CBRM and CSRM may accelerate this reversal [14].

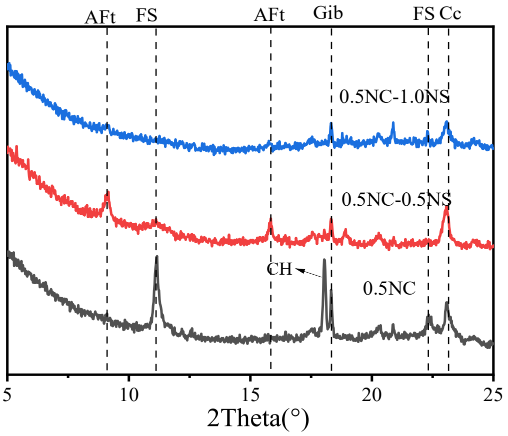

Figure 8. XRD pattern of cement-CBRM-CSRM cementing system under different concentration sulfate solution attack (AFt: Ettringite; FS: Friedel's salt; CH: $Ca(OH)_2$; Gib: $Al(OH)_3$; Cc: Calcite)

4. Conclusion

In this paper, CBRM and CSRM were used as SCMs to prepare cement-CBRM-CSRM ternary composite cementing system. The effects of chloride ion concentration, metal cation type and sulfate on the chloride binding ability of cement-CBRM-CSRM cementing system were studied. The conclusions are as follows:

(1) The content of bonded chloride in cement-CBRM-CSRM cementing system increases with the increase of chloride concentration in erosion solution. Freundlich binding can well describe the relationship between binding chloride ion content and free chloride ion concentration in NaCl solution.

(2) The presence of Ca^{2+} and Mg^{2+} can improve the ability of cement-CBRM-CSRM cementing system to bind chloride ions, and the order of influence is $Ca^{2+}>Mg^{2+}>Na^{+}$. In addition, Ca^{2+} and Mg^{2+} can improve the overall chloride binding ability of the complex cementing system mainly by improving the physical binding ability of chloride ions.

(3) The presence of SO_4^{2-} is adverse to the binding of chloride ions in cement-CBRM-CSRM cementing system, and the higher the concentration of SO_4^{2-} in the erosion solution, the greater the adverse effect.

Acknowledgments

This work was financially supported by the Science and Technology Project of Henan Province (232102321145) and the National Natural Science Foundation of China (U1704148).

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