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Immobilization of erosion ions in seawater by Fe-Al bimetallic hydroxide

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Immobilization of erosion ions in seawater by Fe-Al bimetallic hydroxide was systematically analyzed. Firstly, Fe-Al bimetallic hydroxide was synthesized in the simulated solution of marine concrete crack area, and immobilization of chloride ion and sulfate ion was studied. The treatment effects of chloride ion and sulfate ion were obviously different, indicating that it had selectivity for ion immobilization. Secondly, immobilization of hydroxyl ion by bimetallic hydroxide was also demonstrated according to the high alkali environment in marine concrete crack area. The pH value of simulated solution decreased significantly, and the more solid products, the greater the decrease. Finally, microstructure and composition of Fe-Al bimetallic hydroxide was studied by SEM and EDS. The crystal presented spherical and spherical accumulation, which provided a natural place for immobilization of erosion ions. In addition to Fe, Al C, O, Na and Mg, chlorine and sulfur were found in Fe-Al bimetallic hydroxides. The simulated solution treated by Fe-Al bimetallic hydroxides was studied by FTIR. Erosion ions entered the interlayer structure of Fe-Al bimetallic hydroxide through ion exchange, while lactate ions were replaced into simulated solution. The results provided a new idea for improving the repair effect of concrete crack based on microbial mineralization.

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Keywords: Immobilization of corrosive ions, Fe-Al bimetallic hydroxide, Chloride ion, Sulfate ion, Marine concrete

1. Introduction

Rich marine natural resources and huge ecosystem service value were the important foundation and guarantee of world economic development. It was an inevitable choice for coastal countries to promote the high-quality development of marine economy by building a modern marine industrial system [1,2]. As the main engineering material in the world, concrete was one of

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the main materials for marine infrastructure construction. As the main engineering material in the world, concrete was one of the main materials of marine infrastructure construction, which was widely used in marine engineering such as ports, docks, sea crossing bridges, subsea tunnels, artificial islands and so on [3,4].

Marine concrete, as an important basic material, had made an important contribution to the development of marine economy. With congenital defects of low tensile strength and easy cracking, marine concrete was damaged by erosion ions in seawater, which seriously affected the engineering durability and service life [5,6]. Chloride ions and sulfate ions were the main causes of marine concrete corrosion, and chloride ion would cause corrosion of reinforcement, while sulfate ion could promote the formation of expansive products and lead to cracks. Therefore, the fixation of erosion ions in seawater was also taken as one of the main directions when studying the repair of concrete cracks [7-12]. Layered bimetallic hydroxide was a new multifunctional two-dimensional material with special layered structure, and it was similar to brucite structurally. With its special interlayer structure, ion exchange between layers could be realized, and the target ion was immobilized. The results showed that almost any type of anion could be intercalated into the interlayer structure through interaction [13-15]. Tattematsu et al. proved that chloride ion was fixed in cement by Ca-Al bimetallic hydroxide, which prevented the corrosion of reinforcement effectively [16]. Yang et al demonstrated the chloride ion concentration in the pore solution was greatly reduced through the synthesis of Mg-Al bimetallic hydroxide with p-aminobenzoic acid, and the released anions played a role in corrosion inhibition [17]. Bimetallic hydroxide, containing amino acids, was directly mixed into mortar or concrete, which could also effectively alleviate the corrosion effect of chloride ion on reinforcement. The adsorption of bimetallic hydroxide on sulfate ion was less studied in concrete, mainly focusing on wastewater treatment. In the synthesis of bimetallic hydroxide, there were some differences in the treatment effect of sulfate ion by changing the proportion of calcium and magnesium. When the molar ratio of Ca and Al was 2:1, the adsorption capacity for sulfate ions was the largest, and the adsorption effect of Ca-Al bimetallic hydroxide was better than that of Mg-Fe bimetallic hydroxide [18]. Ma et al. found that the addition of LDHs could reduce the output of ettringite in cement paste, cut down the expansion characteristics of cement paste, and improve the sulfate corrosion resistance of concrete [19]. Based on the above research results, the synthesis of bimetallic hydroxide in the crack area of marine concrete could fix chloride ions and sulfate ions, and avoid damage to concrete; Through the change of chemical environment in the crack area, it was also conducive to improve the self-healing effect of various concrete agents, such as microbial self-healing agent.

This study, immobilization of erosion ions in seawater by Fe-Al bimetallic hydroxide was systematically analyzed. Firstly, Fe-Al bimetallic hydroxide was synthesized in the simulated solution of marine concrete crack area, and immobilization of chloride ion and sulfate ion was studied. Secondly, immobilization of hydroxyl ion by bimetallic hydroxide was also demonstrated according to the high alkali environment in marine concrete crack area. Through the immobilization of erosion ions, the effect of Fe-Al bimetallic hydroxide on improving chemical environment was clarified. Finally, microstructure and composition of Fe-Al bimetallic hydroxide was studied by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS); The simulated solution treated by Fe-Al bimetallic hydroxides was studied by fourier transform infrared spectroscopy (FTIR). The immobilization mechanism of erosion ions in seawater by Fe-Al bimetallic hydroxide was revealed.

2. Materials and methods

2.1. Materials

The objective of the study was to improve the chemical environment in marine concrete crack area, slow down the corrosion damage to concrete, and create a suitable environment for microbial self-healing agent. In order to carry out experiments easily, relevant experiments were carried out in simulated solution of marine concrete crack area.

Sodium chloride, magnesium chloride and sodium sulfate were purchased to prepare simulated seawater solution, and they were all analytical grade. In simulated solution, the concentration of chloride ion was 0.49 mol/L, while the concentration of sulfate ion was 0.03 mol/L. The interior of concrete was a high alkali environment, and the alkalinity of crack area should also be high. Therefore, in order to be closer to the actual situation, sodium hydroxide was used to adjust the pH value of simulated solution, and the pH value was 14 ultimately. Analytical grade of ferrous lactate and sodium metaaluminate were purchased from Nanjing Keyi Chemical Co., Ltd., and they were used to synthesize bimetallic hydroxides. Deionized water was self-made in the laboratory.

2.2. Experimental method

150 ml of simulated solution was measured, and ferrous lactate and sodium metaaluminate were added respectively. The addition amount was shown in Table 1. After the above solution was fully stirred, it was allowed to stand at a constant temperature of 30±1℃ for 28 days. After filtration, the treated simulated solution and synthetic bimetallic hydroxide were obtained.

Table 1. The addition amount of ferrous lactate and sodium metaaluminate.

No.	ferrous lactate (g)	sodium metaaluminate (g)
FA-1	11.42	4.05
FA-2	13.33	4.73
FA-3	15.23	5.40
FA-4	17.13	6.08
FA-5	19.04	6.75

In order to evaluate the immobilization effect of erosion ions, inductively coupled plasma was used to measure the concentration changes of chloride ions and sulfate ions in simulated solution. At the same time, the pH value of simulated solution was also tracked and analyzed by pH meter, which was used to evaluate the change of hydroxyl ion in simulated solution.

The solid product obtained by filtration was naturally air dried at a constant temperature of 35±1℃. SEM (FEI Company, Netherlands) with a GENESIS 60S energy dispersive X-ray spectroscope (EDS) spectroscopy system with magnification from 1,000 to 10,000 was used to observe the microstructure and to measure the elemental compositions of solid product. The accelerating voltage and spot size of the secondary electron detector were 20 kV and 4.0, respectively. The FTIR spectrum of simulated solution treated by Fe-Al bimetallic hydroxides was recorded using a Nicolet 5700 spectrometer by KBr pellet technique with the resolution of 4 cm^{-1} and scanning the product for 20 times in the range of 4,000~400 cm^{-1}.

3. Results and discussion

3.1. Immobilization of erosion ions

The simulated solution of marine concrete crack area contained chloride ion and sulfate ion, and the immobilization effect of erosion ions by solid product deposition was systematically studied. The results were shown in Fig. 1 and Fig. 2.

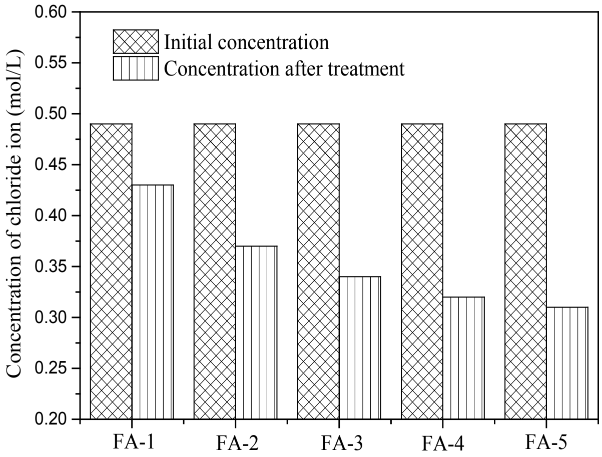


Fig. 1. Concentration of chloride ion treated by bimetallic hydroxide.

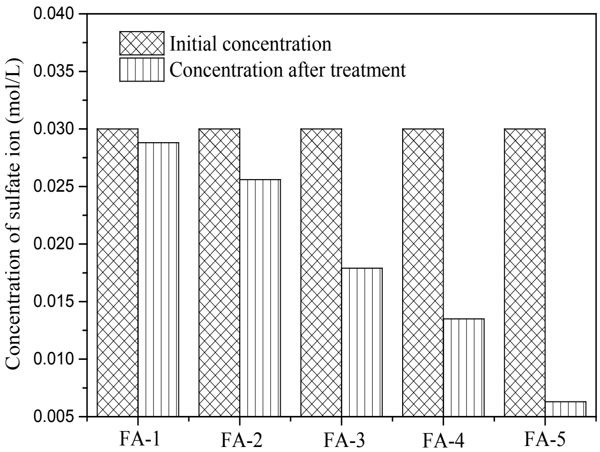


Fig. 2. Concentration of sulfate ion treated by bimetallic hydroxide.

The concentration of chloride ion in simulated solution was shown in Fig.1. It could be seen from Fig.1 that the concentration of chloride ion in simulated solution showed a downward trend. The reason was that with the increase of ferrous lactate and sodium metaaluminate, the solid products deposition would also increase, and the adsorption and fixation of ions will improve significantly. In test groups FA-1, FA-2, FA-3, FA-4 and FA-5, the concentrations of chloride ions were 0.43, 0.37, 0.34, 0.32 and 0.31 respectively. Compared with the initial chloride concentration, the concentration decreased by 12.24%, 24.49%, 30.61%, 34.69% and 36.73 respectively. The concentration of sulfate ion in simulated solution was shown in Fig.2. It was not difficult to find that the concentration of sulfate ion was consistent with the concentration of chloride ion, which both showed a downward trend. The difference was that the decrease range of sulfate ion was greater, and the treatment effect was better. In test groups FA-1, FA-2, FA-3, FA-4 and FA-5, the decrease range of sulfate ions were 4.02%, 14.67%, 40.33%, 55.11% and 79.08% respectively. Comparative analysis of the test results, the treatment effects of chloride ion and sulfate ion were obviously different, indicating that the solid product had selectivity for ion immobilization.

3.2. pH value of simulated solution

As was known to all, concrete was a high alkali environment, and the pH value of crack area was also relatively high. Crack repair technology based on microbial mineralization was considered to be the most promising self-healing technology, and the challenge was the survival and growth of microorganisms in the concrete crack area, which was the decisive factor of the technology. Only on the premise of ensuring the survival and growth of microorganisms, higher enzyme catalytic activity was obtained, and more minerals were deposited to fill and seal the cracks. For this purpose, the immobilization effect of hydroxyl ions by solid products was studied, which was used to evaluate the possibility of reducing the alkalinity in concrete crack area.

The pH value of simulated solution in each test group was systematically analyzed, and the results were shown in Fig. 3. In each test group, the pH value of simulated solution decreased significantly, and the more solid products, the greater the decrease. The main reason was the decrease of hydroxyl ions in simulated solution, which might be immobilized in the interlayer structure by solid products. So, the composition and structure of solid products could be analyzed to verify the above results. In test groups FA-1, FA-2, FA-3, FA-4 and FA-5, the pH value of simulated solution was 13, 12, 11, 11 and 10 respectively. It could be predicted that with the increase of ferrous lactate and sodium metaaluminate, the synthesis of solid products should increase, and the alkalinity of simulated solution would further decrease until it reached neutrality. The results provided a new idea for improving the repair effect of concrete crack based on microbial mineralization.

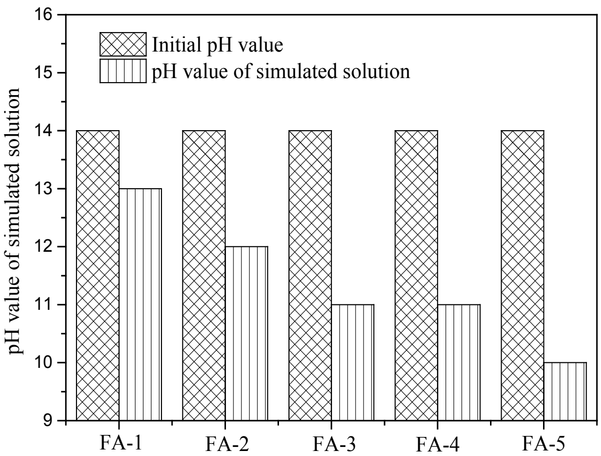
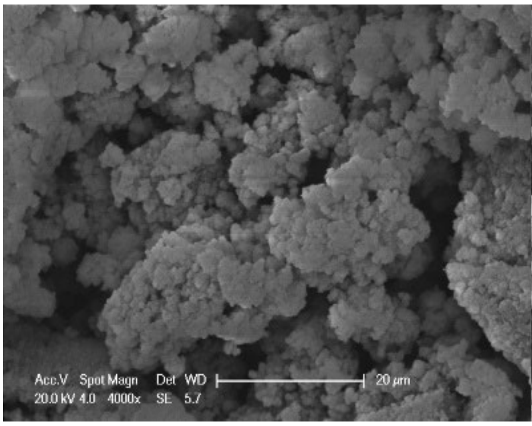


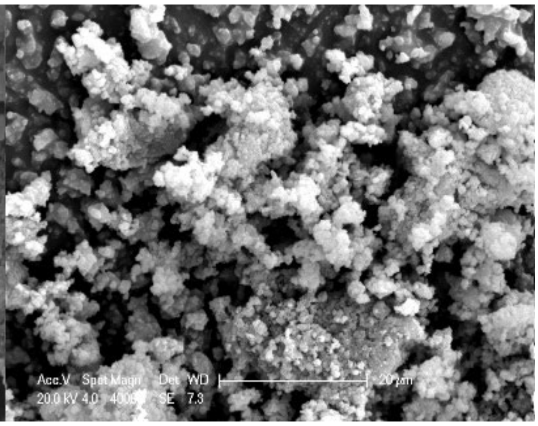
Fig. 3. pH value of simulated solution treated by bimetallic hydroxide.

3.3. Characterization of solid product

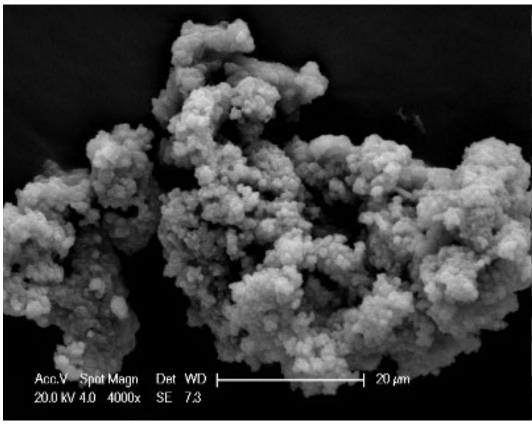
In order to find out the immobilization cause of erosion ions, microstructure and composition of solid product was studied by scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and fourier transform infrared spectroscopy (FTIR), and the results were shown in Fig.4, Fig.5 and Fig.6.



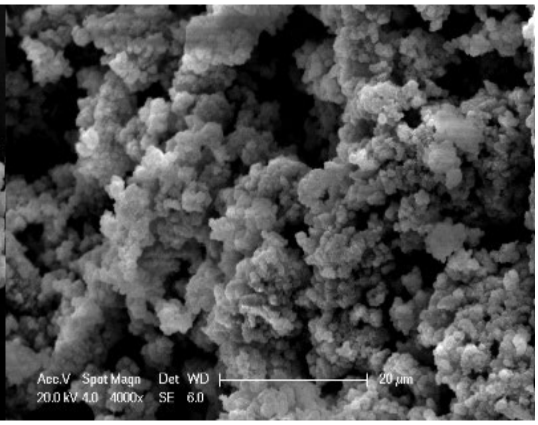
FA-1



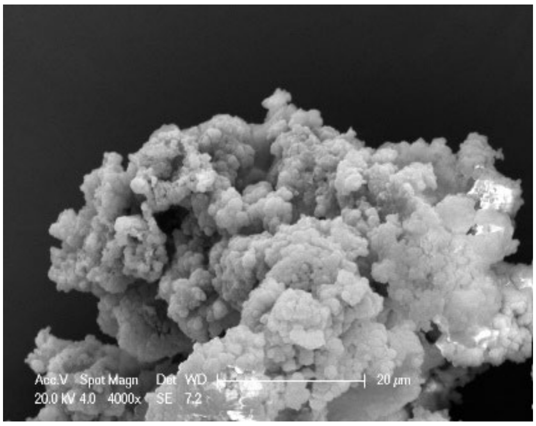
FA-2



FA-3



FA-4



FA-5

Fig. 4. Microstructure of Fe-Al bimetallic hydroxide.

element	wt%	Atomic%
C	29.34	55.06
O	35.23	49.64
Na	9.98	9.79
Mg	0.45	0.42
Al	5.34	4.46
S	0.35	0.24
Cl	1.13	0.72
Fe	18.18	7.34
total	100.00	100.00

FA-1

element	wt%	Atomic%
C	18.35	34.44
O	32.43	45.69
Na	11.22	11.00
Mg	0.96	0.89
Al	6.34	5.29
S	0.86	0.60
Cl	2.46	1.56
Fe	27.38	11.05
total	100.00	100.00

FA-2

元素	wt%	Atomic%
C	11.83	22.20
O	26.26	37.00
Na	16.16	15.85
Mg	1.23	1.14
Al	9.98	8.33
S	1.16	0.81
Cl	5.13	3.26
Fe	28.25	11.40
total	100.00	100.00

FA-3

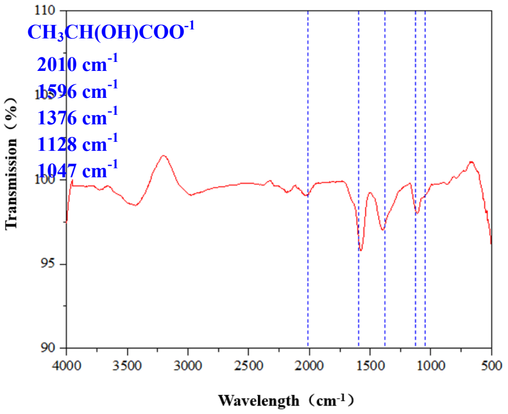
element	wt%	Atomic%
C	9.36	17.56
O	18.76	26.43
Na	19.34	18.97
Mg	1.56	1.45
Al	11.76	9.82
S	1.22	0.85
Cl	5.22	3.32
Fe	32.78	13.23
total	100.00	100.00

FA-4

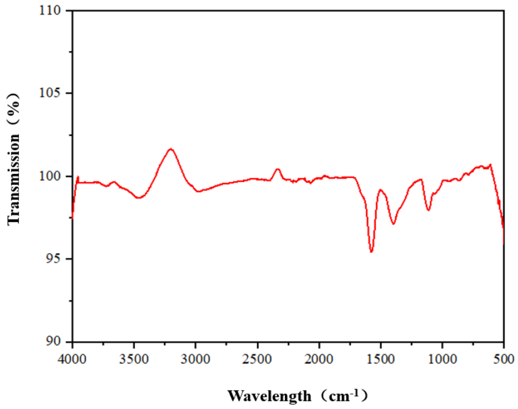
element	wt%	Atomic%
O	27.27	43.56
Na	12.94	14.38
Al	25.62	24.27
S	1.18	0.94
Cl	6.65	4.79
Fe	26.36	12.06
total	100.00	100.00

FA-5

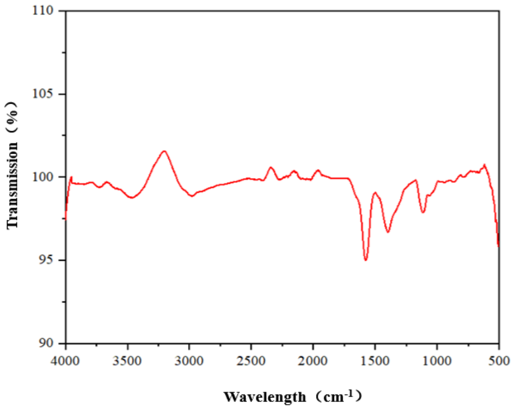
Fig. 5 Element composition of Fe-Al bimetallic hydroxide



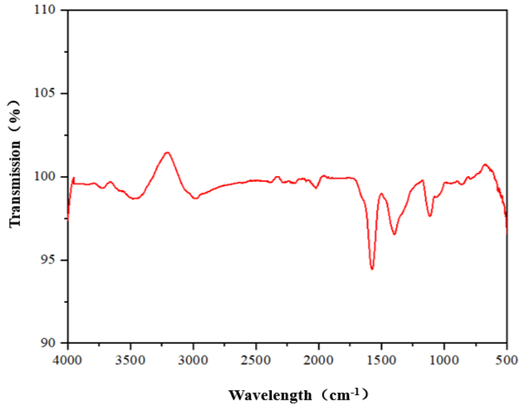
FA-1



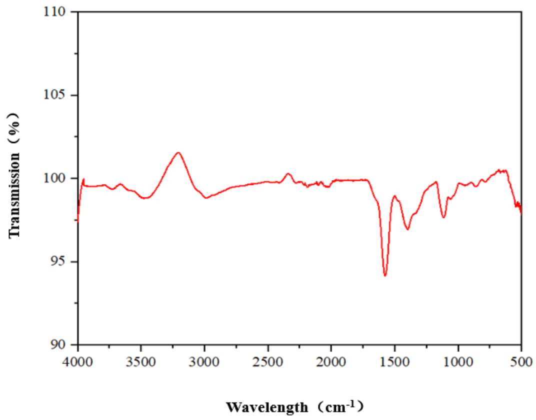
FA-2



FA-3



FA-4



FA-5

Fig. 6. FTIR spectrum of simulated solution treated by Fe-Al bimetallic hydroxides.

Microstructure of solid product was shown in Fig.4, the microstructure of solid product was not uniform; In terms of size, the distribution range of crystal size was from 1 to 20 μm; From the morphology, the crystal presented spherical and spherical accumulation. There was a layered distribution space in the accumulation structure, which provided a natural place for immobilization of erosion ions. Comparative analysis of relevant studies, the structural characteristics of Fe-Al bimetallic hydroxide were basically the same as those of other bimetallic hydroxides. The element composition of Fe-Al bimetallic hydroxide could be obtained from Fig. 5, and it was mainly composed of Fe, Al C, O, Na and Mg. In addition, chlorine and sulfur were also found in Fe-Al bimetallic hydroxides, which proved that Fe-Al bimetallic hydroxides had the immobilization effect of erosion ions. The FTIR spectrum of simulated solution treated by Fe-Al bimetallic hydroxides was shown in Fig.6. As could be seen from Fig.6, the vibrational absorptions of $CH_3CH(OH)COO^-$ were found in all test groups; Through ion exchange, chloride ions, sulfate ions and hydroxyl ions in simulated solution entered the interlayer structure of Fe-Al bimetallic hydroxide, while lactate ions were replaced into simulated solution; Therefore, lactate ions appeared in simulated solution.

4. Conclusions

This study, immobilization of erosion ions in seawater by Fe-Al bimetallic hydroxide was systematically analyzed. Firstly, Fe-Al bimetallic hydroxide was synthesized in the simulated solution of marine concrete crack area, and immobilization of chloride ion and sulfate ion was studied. In test groups FA-1, FA-2, FA-3, FA-4 and FA-5, the concentration decreased by 12.24%, 24.49%, 30.61%, 34.69% and 36.73 respectively, while the decrease range of sulfate ions were 4.02%, 14.67%, 40.33%, 55.11% and 79.08% respectively. The treatment effects of chloride ion and sulfate ion were obviously different, indicating that it had selectivity for ion immobilization. Secondly, immobilization of hydroxyl ion by bimetallic hydroxide was also demonstrated according to the high alkali environment in marine concrete crack area. The pH value of simulated solution decreased significantly, and the more solid products, the greater the decrease. Finally, microstructure and composition of Fe-Al bimetallic hydroxide was studied by SEM and EDS. The crystal presented spherical and spherical accumulation, which provided a natural place for immobilization of erosion ions. In addition to Fe, Al C, O, Na and Mg, chlorine and sulfur were found in Fe-Al bimetallic hydroxides. The simulated solution treated by Fe-Al bimetallic hydroxides was studied by FTIR. Erosion ions entered the interlayer structure of Fe-Al bimetallic hydroxide through ion exchange, while lactate ions were replaced into simulated solution. The results provided a new idea for improving the repair effect of concrete crack based on microbial mineralization.

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