Research Article

Yanfang Zhang, Anhui Wang*, Qiwei Zhan, Juanlan Zhou, Yongsheng Zhang, and Weiyang Gu

Influence of ettringite on the crack self-repairing of cement-based materials in a hydraulic environment

https://doi.org/10.1515/rams-2022-0012
received September 17, 2021; accepted December 28, 2021

Abstract: As a green and environmental protection method, the self-repairing technology has great expectations to be met. In this study, the influence of ettringite on the crack self-repairing of cement-based materials in a hydraulic environment was systematically analyzed. First, the composition and pore characteristics of the self-repairing carrier was studied by XRD, XRF, and the mercury injection method. The composition was basically consistent with cement-based materials, and the structure of the self-repairing carrier was relatively dense. Second, the products were analyzed by SEM and EDS, and it was found that the distribution range of crystal size was from 1 to 20 µm, the cube and flocculent accumulation was calcite, while the rod and flake crystals were ettringite. Finally, the repair effect on the surface and inside of the crack was demonstrated by the crack area repair rate and water permeability resistance. Compared with single microbial mineralization, the synergistic repair effect of microbial mineralization and ettringite formation was better in water permeability resistance. With the further increase of water pressure, its advantages would be more obvious.

Keywords: crack, self-repairing, microbial mineralization, ettringite

1 Introduction

Cement-based materials were the most used structural materials in construction projects, and the congenital defects of low tensile strength would lead to cracking, which seriously affected engineering durability and service life [1,2]. In order to solve the global problem that cracks greatly shorten the service life of construction projects, passive repair was usually used but there were a series of problems, such as difficulty to timely monitor cracks, labor consumption, and the normal service of the project affected during repair [3–5]. Therefore, the self-repairing technology was inevitable but there was a lack of low-cost and efficient engineering application of self-repairing technology at home and abroad.

As a green and environmental protection method, the self-repairing technology based on microbial mineralization had the advantages of fast repair speed, strong timeliness, low cost, and convenient process, and has great expectations to be met [6–9]. The preparation of the self-repairing material was relatively complex and the ideal material had to meet certain requirements. First, it was compatible with cement-based materials and did not have a negative impact; second, it should be used as a component of cement-based materials, which could actively repair cracks and maintain its repair effect for a long time and has a reasonable economy. In addition, the measurement of the self-repairing ability should also include accurate positioning and rapid response to cracking sites. Based on the above requirements, the application of the self-repairing technology in the crack repair of cement-based materials had been explored. When cracking occurred, microorganisms could revive from a dormant state in time, maintain active state, and induce mineralization to repair cracks with the entry of oxygen and water [10–12]. Jonkers et al. found that an appropriate amount of microorganisms and the external calcium source would not affect the properties of cement-based materials, which also confirmed the feasibility of
repairing cracks based on microbial mineralization to a certain extent [13,14]. Wiktor et al. used porous lightweight aggregate to immobilize microorganisms and calcium lactate to repair cracks, and the results showed that microbial immobilization was more efficient on the crack surface area. The maximum width of repairing crack could reach 470 µm, but the width of repairing crack without microorganisms was only 210 µm [15]. De Koster et al. proposed that the substrate and spore solid powder were mixed and pressed into a flake particle and it was wrapped with a brittle and easily cracked geopolymer shell to prevent the self-repairing agent from dissolving during mixing [16]. The results showed that this method could reduce the amount of porous carrier, solve the problem of strength decrease, and expand the application range of the self-repairing material. In conclusion, microbial mineralization technology could be used for repairing the crack. However, there were still some problems, and the key problem was that the repair depth was not enough and needed to be solved urgently [17–19].

In this study, the influence of ettringite on the crack self-repairing of cement-based materials in a hydraulic environment was systematically analyzed. First, the composition of the self-repairing carrier was studied by X-ray diffraction (XRD) and X-ray fluorescence (XRF), and pore characteristics of the self-repairing carrier were also studied by the mercury injection method. Second, the feasibility of repairing cracks with the self-repairing carrier was verified, and the composition and microstructure of products were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). Finally, the repair effect on the surface and inside of the crack was demonstrated by the crack area repair rate and water permeability resistance.

### 2 Materials and methods

#### 2.1 Materials

*Bacillus mucilaginosus*, a microbial strain with mineralization ability, was screened from high calcium soil. It was suitable to grow in a neutral and weak alkaline environment, and the suitable growth temperature was 10–40°C. Cultivation of *Bacillus mucilaginosus* was conducted in sucrose culture (10 g of sucrose and 3 g of sodium hydrogen phosphate were dissolved in deionized water to 1 L, and the pH value was adjusted to about 7.0) at 30°C for 24 h. A high concentration of the microbial solution was obtained through proliferation culture and then the microbial powder was prepared by spray drying at 110°C, which was stored in a low-temperature and dry environment before use.

#### 2.2 Preparation of the self-repairing carrier

Aluminum sulfate, calcium nitrate, and aluminate cement were purchased from Sinopharm Group Pharmaceutical Co., Ltd. In the preparation of the self-repairing carrier, microbial powder and aluminum sulfate were used as the core and aluminated cement as the shell. First, microbial powder and aluminum sulfate were mixed in equal proportion to prepare spherical particles by the sugar coating machine, and the particle size was controlled at about 2.0–2.5 mm. Second, a layer of aluminated cement was coated on the outer layer of the particles as a protective layer, and the thickness of the protective layer was 1.0–1.5 mm. Finally, the particles were cured under standard conditions (RH = 90 ± 5%, T = 20 ± 3°C); so far, the preparation of the self-repairing carrier had been completed until the mechanical properties were stable.

#### 2.3 Characterization of the self-repairing effect

Cement, sand, and water were used to prepare cement mortar specimens with dimensions of φ100 mm × 100 mm. In the initial rate, the amount of cement, sand, and water was 450, 1,350, and 225 g, respectively. Then, sand was replaced by the self-repairing carrier, and the replaced rate was 3%. The amount of cement and water remained unchanged in the contrast experiment. In addition, the amount of calcium nitrate accounted for 3% of cement. Then, microcracks were prepared by pressurization, and nails of different diameters were inserted into the microcracks. In this experiment, the width of the artificially prepared crack was 300 µm. In the process of repairing a crack, the specimen was cured in the water environment in the temperature range of 20–25°C for 56 days.

The repair effect was evaluated by the crack repair rate, which was crucial. The area repair rate of the crack surface was calculated by the image method, and the overall repair rate of the crack was obtained by water permeability resistance.

The images of cracks before and after repairing were collected, and they were processed by Image-J software.
The gray threshold was set by the upper limit of the gray value of the crack area, and the repaired and unrepaired crack images could be obtained by threshold segmentation. The area repair rate of the crack surface was calculated by counting the number of pixels of repaired and unrepaired images, respectively. The repair effect of the crack surface was evaluated by this method, and the repair rate of the crack surface was obtained according to the following equation:

$$\eta = \frac{N_i}{N_0} \times 100\%,$$

where $\eta$ was the area repair rate of the crack surface, %; $N_0$ was the number of initial crack pixels; and $N_i$ was the number of repairing crack pixels at the repair time $i$.

When there were cracks in the specimen, water could easily pass through the specimen by the cracks, and the water permeability would increase with the increase of crack width. When the internal crack was repaired, the permeability decreased with the filling of cracks. Therefore, the self-repairing effect of cracks could be characterized by water permeability resistance, which reflected the repair effect of the whole crack (Figure 1). During the test, the specimen was connected to a diameter of $\varphi 100$ mm $\times$ 1,000 mm PVC pipe and the water in the pipe was kept at a constant height of 600 mm. Before the test, the joint between the specimen and the PVC pipe was sealed with epoxy resin to avoid leakage.

The water seepage rate of the initially cracked specimens before the repair was measured, and the water seepage rate of specimens after repairing the crack was obtained. Moreover, constant water pressure was maintained during the test. The repair rate was obtained according to the following equation:

$$y = \frac{V_0 - V_i}{V_0} \times 100\%,$$  \hspace{1cm} (2)

where $y$ was the repair rate, %; $V_0$ was the water seepage rate of the initially cracked specimens before repair; $V_i$ was the water seepage rate of specimens after repair of cracks at a repair time $i$.

### 3 Results and discussion

#### 3.1 Composition and structure of the self-repairing carrier

In the preparation of the self-repairing carrier, microbial powder and aluminum sulfate were used as the core and aluminate cement as the shell. The composition of the self-repairing carrier shell was studied by XRD and XRF, and the results are shown in Table 1 and Figure 2. As a protective layer of the self-repairing carrier, the shell was in direct contact with the matrix of cement-based materials, which required good compatibility so as not to cause negative effects. As seen from Table 1 and Figure 2, the shell was mainly composed of $\text{SiO}_2$, $\text{CaO}$, $\text{Al}_2\text{O}_3$, $\text{SO}_3$, $\text{MgO}$, $\text{Fe}_2\text{O}_3$, and other substances. In the curing process of the self-repairing carrier, a variety of products such as hydrated calcium silicate and hydrated calcium aluminate would be produced, which were basically consistent with the cement-based materials. Therefore, this would not have a negative effect (Figure 3).

In terms of composition, the self-repairing carrier basically had good compatibility with cement-based materials. In addition, it was also necessary to study the microstructure of the self-repairing carrier. The self-repairing carrier should have a relatively dense structure, which would not affect the working performance and durability of cement-based materials. The pore size distribution and cumulative

| Composition | $\text{SiO}_2$ | $\text{CaO}$ | $\text{Al}_2\text{O}_3$ | $\text{SO}_3$ | $\text{MgO}$ | $\text{Fe}_2\text{O}_3$ | $\text{TiO}_2$ | $\text{K}_2\text{O}$ | Other |
|-------------|---------------|---------------|------------------|-------------|------------|-----------------|----------|----------|-------|
| Amount (wt%) | 31.50         | 27.50         | 22.77            | 7.90        | 3.58       | 2.86            | 0.96     | 0.90     | 2.03  |
porosity of the self-repairing carrier are shown in Figure 4. From the figure, it is evident that the pore size was mainly distributed below 100 nm and no large pore size was found; moreover, the cumulative porosity was about 26.3%. It could be seen that the structure of the self-repairing carrier was relatively dense.

### 3.2 Characteristics of products in the crack area

The self-repairing of the crack based on microbial mineralization included a series of processes such as microbial growth, enzymatic chemical reaction, and mineralization product deposition, and microorganisms played an important role in the whole process. However, microorganisms were subject to temperature, humidity, air, and many other factors. Therefore, the repair depth of this method was insufficient. It was found that ettringite was deposited in the crack area of cement-based materials, so as to improve the crack repair depth.

The visual and intuitive repair of cracks is shown in Figure 5. As seen from Figure 5, the initial crack was clearly visible and there was no product filling in the crack. After curing for 14 days, the crack area changed greatly compared with the initial crack; A large number of products accumulated in the crack area, and almost completely filled the crack. From the repair effect of the crack surface, it was superior. To determine whether microbial mineralization and ettringite formation played an important role in the repair process, it was necessary to analyze the products.

In order to further clarify the process of repair crack, the microstructure of the products was analyzed and is shown in Figure 6. The microstructure of the products
was not uniform; in terms of size, the distribution range of the crystal size was from 1 to 20 µm, and, in terms of morphology, the crystal presented cubic and rod-shaped, with flake and flocculent accumulation. It was preliminarily judged that the products were composed of a variety of substances. The EDS spectrogram of the products in the crack area is shown in Figure 7, and it is clear that the products were mainly composed of C, O, Ca, S, and Al, which might be a mixture of calcite and ettringite. When distinguishing different crystal forms, cube and flocculent accumulation was calcite and the rod and flake crystals were ettringite.

Compared with the simple microbial mineralization, the products’ composition of the composite repair method of microbial mineralization and ettringite formation was also analyzed by XRD, and the results are shown in Figure 8. As shown in Figure 8(a), the XRD pattern of the mineralization product is in good agreement with the results for the standard (JCPDS card number 47-1743), and the mineralization product was ultimately characterized as calcite. However, the XRD pattern in Figure 8(b) is obviously different; in addition to the characteristic peak of calcite, there were other characteristic peaks. Through comparative analysis, the new characteristic peak was determined as ettringite. Combined with the analysis results of SEM, EDS, and XRD, there was a superposition effect of microbial mineralization and ettringite formation in the repair process, and the formation of ettringite was conducive to improving the repair depth.

3.3 Self-repairing effect of cracks

The repair effect on the surface and inside of the crack was demonstrated by the area repair rate and water permeability resistance, and the results are shown in Figures 9 and 10.

Compared with single microbial mineralization, the synergistic repair effect of microbial mineralization and ettringite formation had little difference; when the repair times were 7 days and 14 days, the repair effect of microbial mineralization was slightly better. The main reason was that air and water at the crack surface were abundant, which was conducive to the microbial mineralization process. For a simple microbial mineralization repair, the addition of microorganisms was greater, and the early surface repair effect was better. For the synergistic effect of microbial mineralization and ettringite formation, more ettringite was formed with the extension of repair time, which made up for the defect of relatively small microbial content. Therefore, the repair effect of the two methods was basically equivalent in the later stage of repair. The formation process of ettringite is as follows:

1. $\text{Al}^{3+} + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_6$,
2. $\text{Al(OH)}_6 + \text{Ca}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ca}_6\text{Al(OH)}_6\cdot24\text{H}_2\text{O}$,
3. $\text{Ca}_6\text{Al(OH)}_6\cdot24\text{H}_2\text{O} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3\cdot3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$.

The formation process of calcite is as follows:

1. $\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$,
2. $\text{Ca}^{2+} + \text{Cell} \leftrightarrow \text{Cell-Ca}^{2+}$,
3. $\text{Cell-Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Cell-CaCO}_3$.

The crack area repair rate reflected the repair of the crack surface, while water permeability resistance reflected the repair effect of the whole crack. As seen from Figures 9 and 10, the synergistic repair effect of microbial mineralization and ettringite formation was better compared with that...
Figure 6: SEM photograph of the products in the crack area.

Figure 7: EDS spectrogram of the products in the crack area.
of single microbial mineralization. It was easier to carry out the microbial mineralization process at the crack surface, and ettringite formation could be easily realized in any area of the crack. So, the whole crack was well repaired including the area inside the crack. In terms of the surface repair effect, the two methods were basically the same. However, it had certain advantages in water permeability resistance. Due to the small size of the specimen, this advantage was not obvious. However, with the increase of the specimen size and water pressure, this advantage would be significant. It can be predicted that this advantage will be more obvious in large-scale specimens and mass concrete.

4 Conclusion

In this study, the influence of ettringite on the crack self-repairing of cement-based materials in a hydraulic environment was systematically analyzed. First, the composition of the crack self-repairing carrier was studied by XRD and XRF, and the pore characteristics of the crack self-repairing carrier were also studied by the mercury injection method. The shell was mainly composed of SiO₂, CaO, Al₂O₃, SO₃, MgO, Fe₂O₃, and other substances, which were basically consistent with cement-based materials. The pore size was mainly distributed below 100 nm, and the cumulative porosity was about 26.3%. Second, the products were analyzed by SEM and EDS. The distribution range of the crystal size was from 1 to 20 µm, cube and flocculent accumulation was calcite, while the rod and flake crystals were ettringite. Finally, the repair effect
on the surface and inside of the crack was demonstrated by the crack area repair rate and water permeability resistance. Compared with single microbial mineralization, the synergistic repair effect of microbial mineralization and ettringite formation was better in water permeability resistance. With the further increase of water pressure, its advantages would be more obvious. The research provided a new method to improve the crack repair depth, which was conducive to the engineering application of self-repairing technology.

Funding information: This work was supported financially by the National Nature Science Foundation of China (Grant No. 51908253), the Zhenjiang key research and development plan project, and the Dantu key research and development plan project.

Author contributions: Yanfang Zhang: conceptualization, put forward technical concept, Design experiment, Formal analysis, Data curation, Analyze data, Reveal mechanism, Writing – original draft. Anhui Wang: conceptualization, put forward technical concept, design experiment, formal analysis, data curation, analyze data, reveal mechanism, project administration, writing – original draft, writing – review & editing. Qiwei Zhan: conceptualization, put forward technical concept, design experiment, formal analysis, data curation, analyze data, reveal mechanism, project administration. Juanlan Zhou: design experiment, formal analysis, data curation, analyze data, reveal mechanism, project administration. Yongsheng Zhang: design experiment, formal analysis, data curation. Weyiang Gu: design experiment, formal analysis, data curation, analyze data.

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Lin, J. Z. and S. X. Zhou. Experimental study on mix design, self-healing, and mechanical properties of concrete. Journal of Guizhou Normal University (Natural Sciences), Vol. 39, No. 5, 2021, pp. 104–107.

[2] Miao, C. W. and S. Mu. Development and Prospect of Concrete Technology. Bulletin of the Chinese Ceramic Society, Vol. 39, No. 1, 2020, pp. 1–9.

[3] Loser, R., B. Lothenbach, A. Leemann, and M. Tuchschmid. Chloride resistance of concrete and its binding capacity—Comparison between experimental results and thermodynamic modeling. Cement and Concrete Composites, Vol. 32, No. 1, 2010, pp. 34–42.

[4] Ma, H. H., H. F. Yu, and W. Sun. Freezing - thawing durability and its improvement of high strength shrinkage compensation concrete with high volume mineral admixtures. Construction and Building Materials, Vol. 39, 2013, pp. 124–128.

[5] Luzio, G. D. and G. Cusatis. Hygro-thermo-chemical modeling of high performance concrete. Cement and Concrete Composites, Vol. 31, No. 5, 2009, pp. 301–308.

[6] Dejong, J. T., M. B. Fitzgess, and K. Nusslein. Microbially induced cementation to control sand response to undrained shear. Journal of Geotechnical & Geoenvironmental Engineering, Vol. 132, No. 11, 2006, pp. 1381–1392.

[7] Dhami, N. K., M. S. Reddy, and A. Mukherjee. Biominalization of calcium carbonates and their engineered applications: a review. Frontiers in Microbiology, Vol. 4, 2013, id. 314.

[8] De smuyck, W., D. Debrouwer, N. Debelie, and W. Verstraete. Bacterial carbonate precipitation improves the durability of cementitious materials. Cement and Concrete Research, Vol. 38, No. 7, 2008, pp. 1005–1014.

[9] Ercole, C., P. Cacchio, and G. Cappuccio. Deposition of calcium carbonate in karst caves: role of bacteria in Stifflies Cave. International Journal of Speleology, Vol. 30A, No. 1/4, 2011, pp. 69–79.

[10] Belie, N. D., W. Verstraete, and W. D. Muynck. A synergistic approach to microbial presence on concrete: cleaning and consolidating effects. Structural Concrete, Vol. 7, No. 3, 2006, pp. 105–109.

[11] Ferris, F. G., L. G. Stehmeier, A. Kantzas, and F. M. Mourits. Bacteriogenic mineral plugging. Journal of Canadian Petroleum Technology, Vol. 36, 1997, pp. 56–61.

[12] Hammers, F. and W. Verstraete. Key roles of pH and calcium metabolism in microbial carbonate precipitation. Revies in Environmental Science and Biotechnology, Vol. 1, No. 1, 2002, pp. 3–7.

[13] Jonkers, H. M. Bacterial-based self-healing concrete. Heron, Vol. 56, No. 1/2, 2011, pp. 1–12.

[14] Jonkers, H. M., A. Thijssen, G. Muyszer, O. Copuroglu, and E. Schlangen. Application of bacteria as self-healing agent for the development of sustainable concrete. Ecological Engineering, Vol. 36, No. 2, 2010, pp. 230–235.

[15] Wiktor, V. and H. M. Jonkers. Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement and Concrete Composites, Vol. 33, No. 7, 2011, pp. 763–770.

[16] De Koster, S. A. L., R. M. Mors, H. W. Jungers, H. M. Jonkers, G. M. H. Meesters, and J. R. van Ommen. Geopolymer coating of bacteria-containing granules for use in self-healing concrete. Proceedings of Construction and Building Materials, Vol. 32, 2015, pp. 715–733.

[17] Phillips, A. J., R. Gerlach, E. Lauchnor, A. C. Mitchel, D. B. Cunningham, and L. Spangler. Engineered applications of ureolytic mineralization: a review. Biofuelling, Vol. 29, No. 6, 2013, pp. 715–733.

[18] Wang, Q., W. J. Zhang, L. Y. He, and X. F. Sheng. Immobilizing bacteria in expanded perlite for the crack self-healing in concrete. Construction and Building Materials, Vol. 148, 2017, pp. 610–617.

[19] Van Tittelboom, K., N. De Belie, W. De Muynck, and W. Verstraete. Use of bacteria to repair cracks in concrete. Cement and Concrete Research, Vol. 40, No. 1, 2010, pp. 157–166.