Self-healing of Early Cracks in Cement-based Materials by Carbonic Anhydrase Microbiologically Precipitation Calcium Carbonate

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ABSTRACT

This research studies the self-healing potential of early cracks in cement-based materials incorporating carbonic anhydrase (CA) bacteria. CA bacteria can accelerate the CO_2 hydrated reaction then transfer CO_2 to HCO_3^- which can react with soluble $Ca(OH)_2$ on the surface of specimens. Calcium carbonate deposits because of the reaction of HCO_3^- with Ca^{2+}.

Cement specimens were used throughout the study. Specimens were pre-cracked at the age of 7, 14, 28, 60 days, the width of cracks were between 100 and 1000 μm. Thereafter, the specimens were submerged in water exposed to atmosphere.

The experimental results indicated that the CA bacteria showed excellent cracks closing ability to small cracks formed at early age of 7 days, cracks below 400 μm was almost completely closed. Cracks width influenced self-healing effectiveness significantly. Repair ability was restricted when the cracks width were between 500-800 μm and is invalid when the cracks width up to 900 μm.

The transportation of CO_2 and Ca^{2+} controlled the self-healing process. It was hypothesized that the diffusion of CO_2 conformed to Fick law in this study. The computer simulation analyses revealed the self-healing process and mechanism of microbiologically precipitation induced by CA bacteria. The depth of precipitated $CaCO_3$ could be predicted base on valid Ca^{2+}. Moreover, it also explained why cracks closing only occurred on the surface of specimen.

1. INTRODUCTION

Cracking is one of the main factors causing the degradation of concrete durability. Repairing timely or self-healing for cracks may extend the service-life of concrete structures. Since last decade, bio-mineralization has been developed for the treatment of concrete cracks. In recent years, a type of active way, self-healing, for applying bio-mineralization in repairing cracks was developed by several research groups, such as Jonkers in Netherlands [1], De Belie[2] in Belgium and Qian [3] in China. In this paper, a new bio-mineralization technique applying for cracks repair will be addressed. The repair mechanism was shown in Eqs (1)-(4). The repair effectiveness, the influence factors and the mechanism will be discussed.

$$\mathbf{CO_2 + H_2O \leftrightarrow HCO_3^- + H^+} \quad (1)$$

$$\mathbf{HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O} \quad (2)$$

$$\mathbf{Ca^{2+} + Cell \rightarrow Cell - Ca^{2+}} \quad (3)$$

$$Cell - Ca^{2+} + CO_3^{2-} \rightarrow Cell - CaCO_3 \qquad (4)$$

2. MATERIALS

Bacillus mucilaginosus which can produce carbonic anhydrase was used in this study. The concentration of bacterial strain was about 10^9 cells/mL.

Cement specimens were used for all analyses in this study. All mixtures were designed with a water to cement ratio (w/c) of 0.40 by using ordinary Portland cement II 42.5. Five series of specimens were made. Group1 are the specimens without any additions. Group2 are the specimens with nutrient needed for bio-deposition. Group3 are the specimens only with bacteria. Group4 are the specimens with nutrient and bacteria at the same times.

3. METHODS

The self-healing efficiency of bacteria incorporated cement specimens was evaluated by measuring the decrease of water permeability and the area repair rate of cracks. Therefore, two types of cement specimens, cylinders (φ=110mm， H=45mm) for testing water permeability and prisms (40mm×40mm×160mm) for investigating the area repair rate of cracks, were made in each group. Cracks(0.3mm) were made from Group1 to Group4 at the age of 7 days. The cracks with different width between 0.3-1.0mm were pre-made in Group4 at 7 days, for investigating the repair effect influenced by cracks width . All specimens were imerged in water which exposed to atmosphere after cracking. The curing time maintained for 30 days.

The diffusion of CO_2 in concrete conformed to Fick law. In this paper, an equivalent diffusivity of CO_2 in cracked concrete was used accord to the study results by Ha-Won Song et al[4]. The valid Ca^{2+} meant the part of Ca^{2+} which combined with CO_3^{2-}, transferred to $CaCO_3$. It can be tested by the way of EDTA titration. The depth of precipitated $CaCO_3$ could be predicted base on valid Ca^{2+} and then verified by practical experiments.

4. RESULTS AND DISCUSSION

The results showed that specimens (cracks width: 0.3mm) in Group4 had a better repair effect than other group. The coefficient of permeability declined faster and decreaced to 1E-8 after 30d. The cracks could be filled completey at 30 days by testing the area repair rate. (Fig.1)

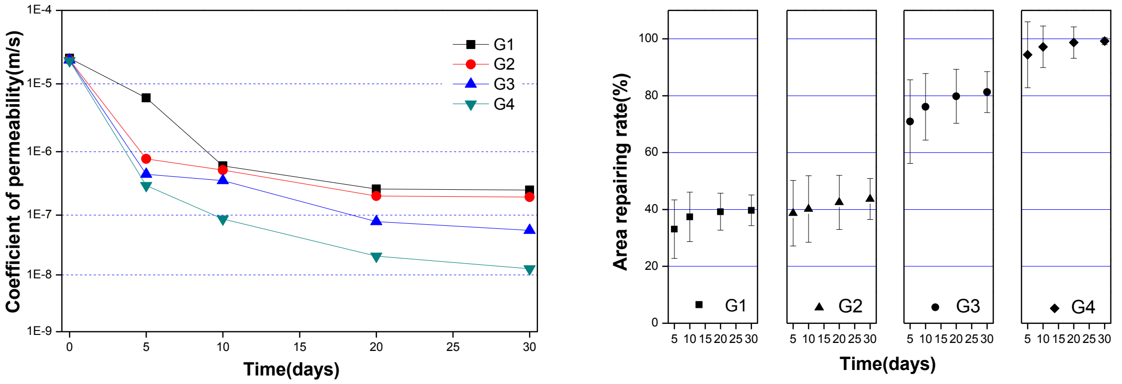


Fig.1 Self-healing effect in different groups

The area repair rate declined with the increasing of cracks width. The cracks below 0.4mm were almost closed completely. Repair ability was restricted when the cracks width were between 500-800 μm and is invalid when the cracks width up to 900 μm.

Further research found that Ca^{2+} escaped outside more easily in large crack. The waste decreased the amount of valid Ca^{2+} and precipitated $CaCO_3$. And large cracks also needed more $CaCO_3$ to fill.(Fig.2)

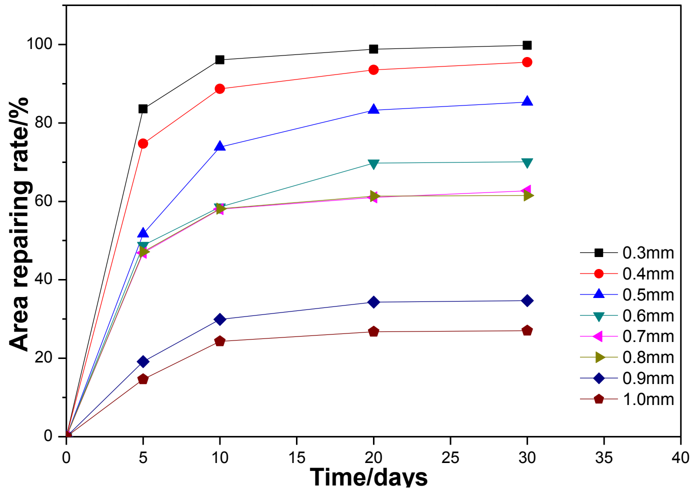
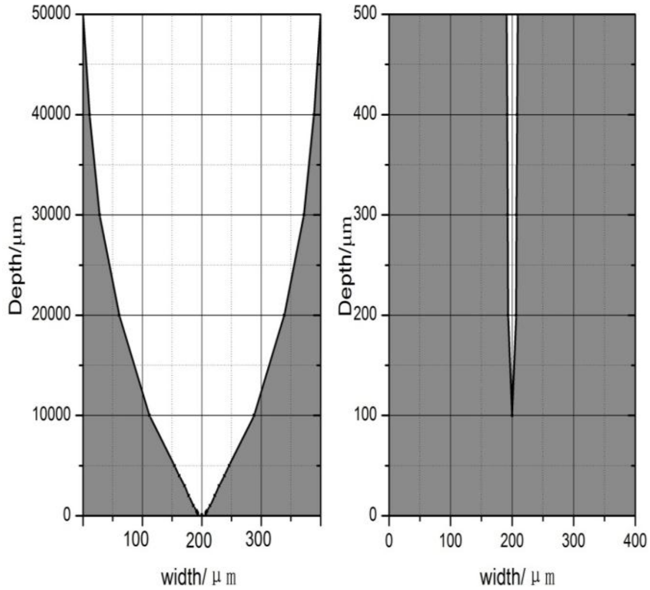


Fig.2 Self-healing effect of cracks with different width

The numerical simulation results showed that the $CaCO_3$ precipitated in cracks was funnel-shaped(Fig.3) High concentration of CO_2 at the surface improved $CaCO_3$ generating faster to fill the crack. The close of surface layer of crack would obstruct the transportation of CO_2 and Ca^{2+}. The depth direction in crack couldn't be repaired by $CaCO_3$.

Fig.3 Numerical simulation results :
$CaCO_3$ deposited in crack(0.4mm, RH80%)



Tab.1 The precipitated depth of $CaCO_3$

Repairing time		Width/mm				
		0.2	0.4	0.6	0.8	1.0
14d	Pre-depth/mm	1.09	0.42	0.23	0.16	0.10
	Exp-depth/mm	0.81	0.42	0.20	0.12	0.11

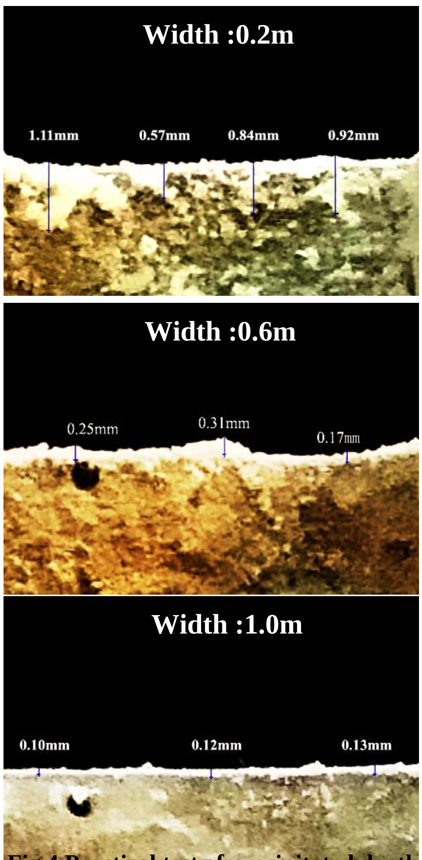


Fig.4 Practical test of precipitated depth

The predicted depth of precipitated $CaCO_3$ base on valid Ca^{2+} was shown in Tab.1.

And practical test results(Exp-depth) fitted well with predicted results(Pre-depth). Fig.4 showed the images of $CaCO_3$ deposited layer in cracks with different width. More $CaCO_3$ could precipitate in the depth direction in smaller crack. The pre-depth was 1.09mm and the exp-depth was 0.81mm in 0.2mm crack. But when crack width increased to 1.0mm, the pre-depth and exp-depth was 0.10 and 0.11 respectively. The result showed that better repair effect often occured in smaller cracks.

5. CONCLUSION

CA bacteria can transfer CO_2 from atmosphere to HCO_3^- which can react with Ca^{2+} in the cracks. Then calcium carbonate deposited to repair the cracks. The experimental results indicated that the CA bacteria showed excellent cracks closing ability to small cracks formed at early age of 7 days, cracks below 400 μm was almost completely closed. Cracks width influenced self-healing effectiveness significantly. Repair ability was restricted when the cracks width were between 500-800 μm and is invalid when the cracks width up to 900 μm. The predicted and experimental depth of precipitated $CaCO_3$ showed cracks closing only occurred on the surface of specimen. The computer simulation analyses revealed the self-healing process and mechanism of microbiologically precipitation induced by CA bacteria.

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REFERENCES

[1] H.M Jonkers, Self-healing of cracks in concrete using a bacterial approach, in: Fronties of Self-healing Materials and Applications, A.N. Shinya(Ed), CMC Publishers, The Netherlands, 2010, pp.194-203.

[2] J. Wang, K. van Tittelboom, N. de Belie, W. Verstraete, Use of silica gel or polyurethane immobilized bacteria for self-healing concrete. Constr. Buil. Mater. 26(2012)532-540.

[3] C. Qian, M. Luo, Q. Pan, R. Li, Mechanism of microbially induced calcite precipitation in self-healing concrete. J. Chin. Ceram. Soc. 41(2013)620-626.

[4] H.W.Song, S.J. Kwon K.J. Byun et al, Predicting carbonation in early-aged cracked concrete. Cem. Concr. Res. 36(2006)979-989.