

Control of Crystal Polymorphism of CaCO_3 Generated in Cracks of Cementitious Material by Change of Temperature and pH



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Abstract

Generally, crack is inherent in reinforced concrete structures and leads to serious damage in service period. In there, recurrences of such damages will lead to the enlargement of the cracks, thereby allowing other deteriorating elements such as CO_2 and Cl- to further penetrate the concrete, and this can have serious consequences for the concrete structure. On the other hand, in an environment where there is supply of water, concrete structures display "self-healing," in which some of cracks close up naturally, and this phenomenon is closely associated with the hydrates that are newly generated in the areas of crack formation.

In this study, author aimed to the kind of CaCO_3 generated by self-healing phenomenon. CaCO_3 is crystal polymorphism and it's reported that crystal form can be controlled by the relationship of temperature and pH. Generally, CaCO_3 consist of the three kinds such as calcite, vaterite and aragonite for crystal formation. A vaterite is also generated most densely among these, and self-healing can be expected.

Therefore, an experiment is made for the purpose of establishing the condition to generate a vaterite. The supplied a saturated $\text{Ca}(\text{OH})_2$ solution with CO_2 nano-bubble is used for the effective self-healing. Conditions of the temperature and pH are managed by 20-60°C and 8.5-12 pH. As a result, it was confirmed that the self-healing conditions of saturated $\text{Ca}(\text{OH})_2$ solution, which supplied CO_2 nano-bubbles, displayed the most effective self-healing performance in the surface and internal sections of the cracks.

Key Words: Cementitious material; Crack; Self-healing; CaCO_3 ; $\text{Ca}(\text{OH})_2$; CO_2 ; Nano-bubble; Vaterite

Introduction

It is unavoidable that crack outbreaks in materials such as concrete. Deterioration factors penetrate into the crack, it is concern that leads to fatal damage to the concrete structure. On the other hand, there is a phenomenon called "self-healing" where the relatively small crack that occurred to the concrete under an environment with the water supply blocks up the crack [1-3]. There are three crystal forms in the crystal of CaCO_3 generated by self-

healing. In this study, we focused on the CaCO_3 crystal generated by self-healing and investigated better self-healing conditions by adjusting the temperature and pH, and by CO_2 penetrate fine cracks as nano-ubbles. By controlling crystal polymorphism so that vaterite is formed intentionally, this could lead to the production of finer self-healing substances. Figure 1 shows the process of the self-healing of this study [4,5].

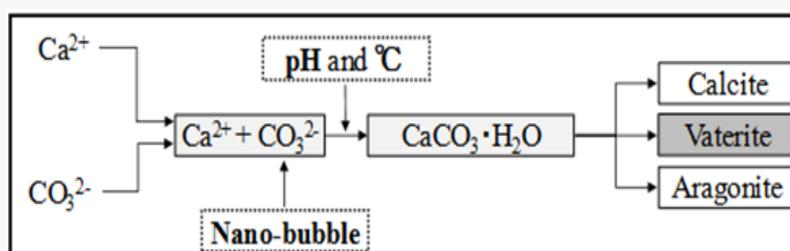


Figure 1: Process of the self-healing [2].

Materials and Methods

Using early strength Portland cement (C, density: 3.14g/cm³, Average particle diameter: 10µm), we made a specimen of water-cement ratio 40%. Cracks with average widths of about 0.15 mm were incorporated by drying for about 24 hours in a drying oven at 105°C, followed by constraining shrinkage of the cement paste to conduct experiments as a specimen "before self-healing. Table 1 shows experimental factors and experimental conditions, Table 2 shows an experimental procedure and content. The self-healing method we used is as follows. After CO₂ micro/nano bubbles were provided for 4 hours, a specimen was left in a water tank of saluted Ca(OH)₂ solution with added CO₂ micro/nano bubbles for 20 hours. This process was counted as 1 cycle (1day).

Table 1: Experimental factors and conditions.

Self-healing condition	Ca(OH) ₂ + Microbubble (CM) Ca(OH) ₂ + Nano-bubble (CN)	pH 9.0
Temperature : 20°C (CM-20, CN-20), 40°C (CM-40, CN-40)		
Self-healing period: 7 days (7 cycles)		

Table 2: Experiment procedure and contents.

Experimental levels	Evaluation	
	Surface and internal section	Substances precipitated
Before	- Microscope- X-ray CT	- Raman spectroscopic analysis - TG-DTA- SEM analysis
After		

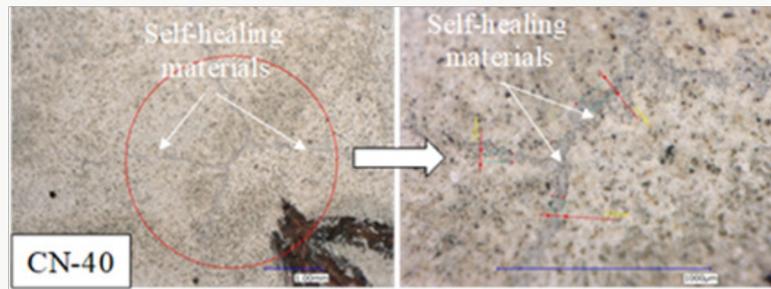


Figure 2: Cracked surface after self-healing.

Results and discussion

Figure 2 shows the observation results of the cracked surface part seen through the microscope. Self-healing precipitates were observed in the surface layer of cracks due to self-healing in both the CN series that supplied nano-bubbles and the CM series that supplied micro-bubbles. Figure 3 shows crack conditions at the time of cracks being introduced and after self-healing (CN-40). As long as 3D analysis images were observed, no clear change of

void structure before and after self-healing was identified. Figure 4 shows the results of void volume of each case before and after self-healing in accordance with the change of temperature condition of self-healing and supply condition of CO₂. As a result, it was considered that CN series with supplied nano-bubbles were more effective than CM series with supplied micro-bubbles and also temperature condition of 40°C was more advantageous for self-healing than that of 20°C.

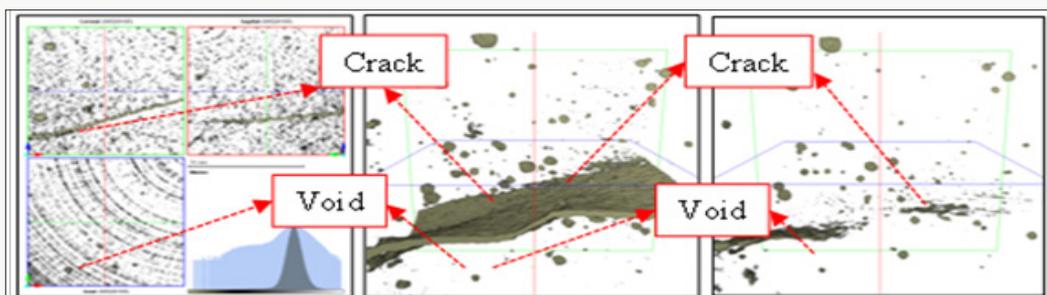


Figure 3: 3D analysis image by X-ray CT.

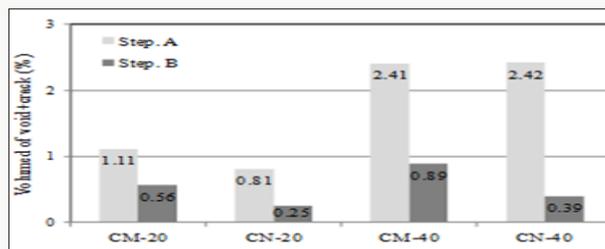


Figure 4: Volume change of (void + crack).

In order to identify crystalline components of precipitates generated by self-healing, we implemented Raman spectroscopy using a specimen obtained from the cracked area, on which a large amount of self-healing precipitates were adhered to (CN-40). Figure 5 shows the result of the measurement. An extremely tiny peak wavelength of CaCO_3 powder on the surface of non-crack area was identified at the same position as the peak wavelength

of CaCO_3 powder. Meanwhile, it was determined that, concerning cracked parts, the obvious peak wavelength corresponding to the peak wavelength of CaCO_3 appeared. Moreover, it was confirmed that the peak wavelength in either case did not correspond to that of Ca(OH)_2 powder. It is, therefore, considered that most of the component substance precipitated after self-healing was CaCO_3 .

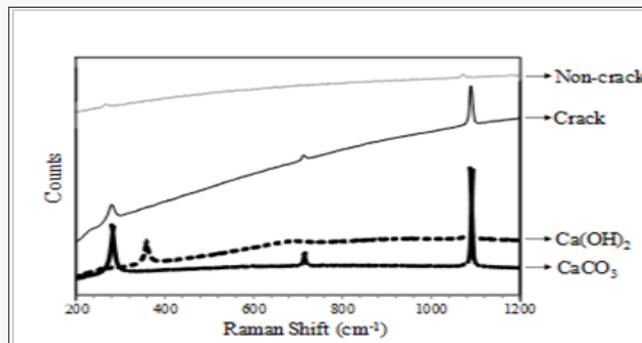


Figure 5: Raman spectroscopy analysis.

In order to chemically evaluate precipitates inside cracked parts by self-healing, we compared and evaluated the change in the amount of Ca(OH)_2 and CaCO_3 between before and after self-healing of individual series, using TG-DTA. Figure 6 shows the results of the analysis. In all of the series, regardless of the change of temperature

condition and supply condition of carbon dioxide for self-healing, compared to Before and Non-crack, the amount of Ca(OH)_2 in crack decreased, while the amount of CaCO_3 in crack increased. The estimated amount of precipitates by self-healing increased in the order of $\text{CN-40} > \text{CM-40} \cong \text{CN-20} > \text{CM-20}$.

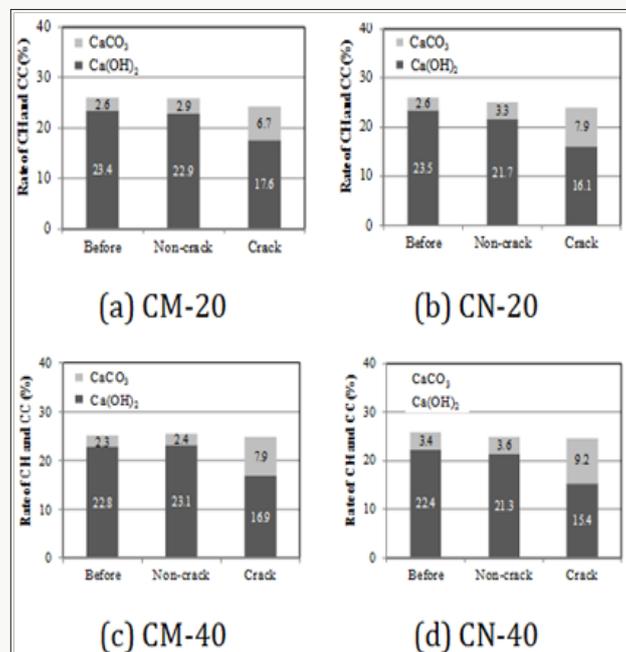


Figure 6: Comparison of the self-healing precipitated substances by TG-DTA.

Finally, SEM analysis was carried out to confirm the shape of the crystals produced under controlled temperature and pH. Figure 7 show SEM image of cracked areas of and CN-40 with nanobubbles. As a result, almost no Ca(OH)_2 was observed in cement solution under CN-40 with self-healing temperature of 40°C and pH 9.0. However, a large amount of C-S-H gel as well as a number

of Vaterite, which were adhered to its' surface, were determined. For this reason, it is considered that controlling the temperature at 40°C and pH at about 9.0 makes it possible to produce self-healing precipitates of Vaterite, which is expected to contribute to more precise self-healing.

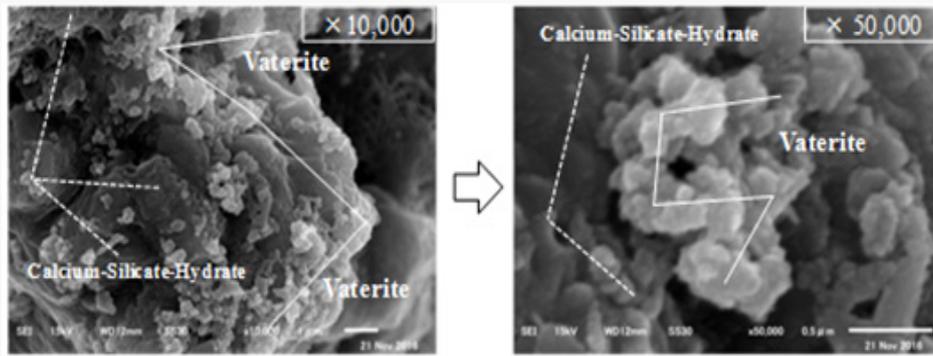


Figure 7: SEM image of cracked areas (CN-40).

Conclusion

It was confirmed that under a self-healing condition that saturated $\text{Ca}(\text{OH})_2$ solution with CO_2 micro/nano-bubbles is supplied into cracked areas, provision of Ca^{2+} and CO_3^{2-} facilitated CaCO_3 reaction. Furthermore, it was determined that even cement material alone could demonstrate more effective self-healing performance in comparatively large cracks of more than 0.1mm. In addition, we could generate Vaterite that contributed to densification of cement matrix from the effect of void filling, by not only providing nano-sized super-fine bubbles that included carbonate ion into saturated $\text{Ca}(\text{OH})_2$ solution but also adjusting water temperature at about 40°C and pH at about 9.0 as self-healing condition.

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