Self-healing of hardened cement paste affected by additional Ca$^{2+}$ and CO$_{3}^{2-}$ ions with temperature control

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Abstract. A self-healing phenomenon, in which the cracks become partially refilled as a result of rehydration of cement particles and deposition of CaCO$_{3}$, has been observed in narrow cracks under a constant supply of moisture. Also, according to previous studies, the self-healing performance can be maximized by changing the temperature and pH to control the crystal form of CaCO$_{3}$. In this study, attention was paid to the crystal form of CaCO$_{3}$ generated in the self-healing process of a cement-based composite material and, in order to generate denser crystal of CaCO$_{3}$, the change in the crystal form of CaCO$_{3}$ generated in the hardened cement paste by changing the temperature condition was observed and analyzed. Also, to increase generation of CaCO$_{3}$ which is a self-healing precipitate, nano-sized ultrafine CO$_{3}^{2-}$ bubbles using CO$_{2}$ gas were used along with effective supply of Ca$^{2+}$ through adjustment of aqueous solution. As a result, the possibility for effective generation and control of denser vaterite together with calcite was confirmed by adjusting the temperature to about 40°C under the condition of pH 12.

1. Introduction

Crack formation in concrete structures significantly increases ion diffusivity and permeability inside the material and allows chloride ions, and water, oxygen, and carbon dioxide molecules to penetrate the structure repeatedly, causing deterioration at an accelerated rate. In other words, cracks in concrete have an adverse impact on the safety, usability, durability, and aesthetics of structures; therefore, it is important to prevent harmful cracks, including microcracks, to ensure long lifespan and high performance of concrete structures. In Japan, microcracks, whose widths fall below the allowable crack width in building standards, pose no significant problems in most structures in terms of structural durability[1]; however, microcracks can become the originating point of structural deterioration, and one could argue that fundamental prevention of microcrack formation is highly important.

Meanwhile, in the case of narrow cracks, a self-healing phenomenon, in which the cracks become partially refilled as a result of rehydration of cement particles and deposition of calcium carbonate (CaCO$_{3}$), has been observed when there is a constant supply of moisture [2]. Products of self-healing are closely associated with CaCO$_{3}$ formed on the crack surface, as well as calcium silicate hydrate (C-S-H), ettringite, and calcium hydroxide (Ca(OH)$_{2}$) [3-5]. In the self-healing mechanism in concrete, Ca$^{2+}$ in concrete reacts with CO$_{3}^{2-}$ dissolved in water, producing CaCO$_{3}$, a carbonate compound that does not readily dissolve in water; this phenomenon results in refilling of the crack. Equations (1)-(3) represent the calcite crystallization reaction [6].
Among the many studies related to self-healing, Choi et al (2016-2018) reported that carbon dioxide was produced as ultrafine nano-sized bubbles due to the self-healing mechanism under aqueous conditions. The CO₂ precipitated large amounts of CaCO₃ in the surface layer and inside the micro-cracks due to the self-healing of cement-based composite materials, with most of the precipitates identified as vaterite [7-9]. Representative crystals of CaCO₃ can be classified into 3 types including calcite, vaterite, and aragonite, and almost all CaCO₃ produced as Ca(OH)₂ in the hardened specimen of cement combined with CO₃²⁻ in the pore water can be classified as calcite [8-12]. Since vaterite has low density and large volume as a hexagonal crystal, it exhibits excellent pore-filling effects, superior to the other CaCO₃ crystals [10, 11]. Thus, it can contribute to improved water tightness and strength of concrete, allowing self-healing substances with a denser crystal structure than calcite to form [10, 11]. The generation of the 3 types of CaCO₃ crystal forms can be controlled by temperature and pH [11, 12]. According to previous studies, control of polymorphism scale formation is possible to the calcite at water temperature of 15-20 °C, vaterite at 30-50 °C, aragonite at >60 °C, respectively [11, 12].

The objective of this study is to pay attention to the crystal forms of CaCO₃ generated in the self-healing process of the hardened cement paste and determine the effect of the temperature condition on the change in the crystal forms of CaCO₃ which is a self-healing product. Namely, for generation of denser CaCO₃ crystal, an optimum temperature condition of the aqueous solution that enables a large quantity of vaterite to be generated together with calcite among the crystal of CaCO₃ generated in the hardened cement paste. Also, to increase the product of CaCO₃ that is a self-healing precipitate, an evaluation was carried out on application of nano-sized ultrafine CO₃²⁻ bubbles using CO₂ gas in addition to effective supply of Ca²⁺ through adjustment of the aqueous solution. The self-healing process of this study is shown in figure 1.

![Diagram](image)

**Figure 1.** Process of the self-healing by Temperature control.

### 2. Experimental overview

#### 2.1. Materials and specimen overview

In the self-healing of cement-based composite materials, evaluating the change in crystal forms of CaCO₃ produced in the hardened cement paste through temperature adjustment was performed. The major reacting species depend on hydration products according to the hydration reaction of water [6]. Cement paste specimens (φ10 × 30 mm) with a water-cement ratio of 0.4 were produced using ordinary Portland cement (C, density: 3.16 g/cm³, average particle diameter 10 μm) according to the ASTM C 150. To prevent dissipation of water in the specimens, suture curing was conducted at a
constant temperature and humidity of 20±1 °C and 60%, respectively, from immediately after dispensing for 1 day. Subsequently, the demolded specimens were subjected to underwater curing in a water tank at 20±1 °C for 28 days under various temperature conditions for the specimens cut to sizes of φ10 × 3 mm, as shown in figure 2.

2.2. Experimental method

Table 1 shows the experimental factors and conditions of this experiment and figure 2 shows the schematic diagram of this experiment method. As to the self-healing condition, an aqueous solution of saturated Calcium Hydroxide (CH; Ca(OH)₂ solution) and an aqueous solution prepared by mixing calcium oxide (CaO) and ethanol (CH₂H₅OH) (CE; CaO+ethanol solution) are used with the purpose of additionally supplying Ca²⁺. According to previous studies [13], when the aqueous solution prepared by mixing calcium oxide and ethanol, the reaction between Ca²⁺ and CO₃²⁻ is promoted by delaying the reaction between Ca²⁺ and OH⁻, as a result of which, it is thought that, generation of calcium carbonate can be promoted. Here, the CE aqueous solution was prepared by mixing ethanol with calcium oxide first to make 0.5mol-ethanol/mol-CaO and agitating it with distilled water [13]. Also, to increase supply of CO₃²⁻, author applied the method of supplying nano-sized (average particle diameter 50 mm) ultrafine CO₃²⁻ bubbles using an ultrafine bubble generating device that uses the cavitation phenomenon [7-9]. Also, under the condition of pH 12, the experiment was carried out using the two temperature levels [11, 12], 20°C at which calcite is mainly generated and 40°C at which vaterite is mainly generated, referring to the temperature at which each crystal form of CaCO₃ is generated as stated in the existing literature.

As to the experiment method, specimens cut in the size of φ10×3mm were first immersed in a 20°C and 40°C aqueous solution respectively for a prescribed time as shown in figure 2 and then immersed all the specimens equally in an aqueous solution for 4 hours in which nano-sized CO₃²⁻ were generated. Here, the experiment was carried out for 4 cases, 5, 10, 15 and 20 hours of immersion times in CH and CE aqueous solutions respectively, irrespective of the temperature condition. (Refer to table 1.)

Table 1. Experimental factors and conditions.

| Specimen : | Hardened cement paste (water/cement ratio: 0.4) |
|--------------------------|-------------------------------------------------|
| Self-healing condition  | Temperature: 20 °C, and 40 °C Ca(OH)₂ + CO₂ Nano-bubble (CH) |
| [11,12]                | (constant pH of 12) CaO+ethanol+CO₂ Nano-bubble (CE) |
| Self-healing period    | CH, CE(5h) + CO₂ Nano-bubble (4h) I |
|                       | CH, CE(10h) + CO₂ Nano-bubble (4h) II |
|                       | CH, CE(15h) + CO₂ Nano-bubble (4h) III |
|                       | CH, CE(20h) + CO₂ Nano-bubble (4h) IV |

Note: CH: Ca(OH)₂ solution; CE: CaO+ethanol solution.

Figure 2. Schematic diagram of the preparation of the cement samples.
2.3. Measurement item
Table 2 shows the sequence and method of experiment. To evaluate the change in the physical properties of the hardened cement paste resulting from self-healing and the self-healing precipitate, a comparative evaluation was carried out on each condition prior to self-healing (A) and after self-healing (B).

First, to evaluate the self-healing performance depending on the type of aqueous solution, the weight change and weight change rate were calculated from the absolute dry weights of the specimens prior to and after self-healing in all the cases depending on the immersion time change. Also, among the crystals of CaCO₃ that are the main precipitates of self-healing, to grasp the Polymorphisms scale formation control into vaterite that has denser and stable crystal structure than calcite [11, 12], SEM and XRD analyses of each case following changes in the temperature condition were carried out. Here, for SEM and XRD analyses, a test piece of size about 5mm×5mm×5mm was taken from each specimen, of which the hydration reaction was stopped by immersing it in acetone for 4 hours and longer, and then the hydration products and self-healing precipitates of each case were observed and measured.

![Figure 3. Schematic of the self-healing method.](image)

Table 2. Experiment procedure and evaluation.

| Step | Experimental sequence | Subject and method of evaluation | Self-healing substances |
|------|-----------------------|----------------------------------|------------------------|
| A    | Prior to self-healing | Absolute dry weight              | SEM                    |
| B    | After self-healing    | Absolute dry weight ratio        | XRD                    |

3. Results and discussion

3.1. Absolute dry weight change by self-healing
To identify changes in the physical characteristics of the hardened cement paste according to the type of aqueous solution and temperature, the absolute dry, surface-dried, and underwater weights prior to and after self-healing were used to calculate the absolute dry weight ratio (%), porosity reduction by self-healing (%).

Table 3 shows the results of increased absolute dry weights of CH and CE series with three times of each specimen by self-healing. In this section, using the results of the specimen performed at the first data of table 3, comparison and evaluation of absolute dry weight ratio, porosity reduction by self-healing of CH and CE series were conducted.
Table 3. Result of the increased absolute dry weight of CH and CE series by self-healing.

| Temp. | Type  | Increased absolute dry weight (g) |
|-------|-------|----------------------------------|
|       |       | 1st | 2nd | 3rd | 1st | 2nd | 3rd | 1st | 2nd | 3rd | 1st | 2nd | 3rd |
| 20°C  | CH20  | 0.018 | 0.026 | 0.046 | 0.076 | 0.016 | 0.023 | 0.044 | 0.076 | 0.018 | 0.024 | 0.047 | 0.077 |
|       | CE20  | 0.025 | 0.060 | 0.078 | 0.090 | 0.021 | 0.058 | 0.074 | 0.088 | 0.024 | 0.059 | 0.080 | 0.089 |
| 40°C  | CH40  | 0.024 | 0.046 | 0.078 | 0.088 | 0.025 | 0.045 | 0.080 | 0.087 | 0.026 | 0.047 | 0.077 | 0.091 |
|       | CE40  | 0.035 | 0.072 | 0.096 | 0.123 | 0.033 | 0.070 | 0.095 | 0.119 | 0.033 | 0.069 | 0.101 | 0.124 |

Note: CH: Ca(OH)₂ solution; CE: CaO+ethanol solution

Figure 4 and figure 5 show the change in the weight depending on the type of aqueous solution and self-healing period. Here, the weight change in each case was calculated based on the absolute dry weight of the specimen prior to self-healing. As a result of the experiment, the specimen of each aqueous solution showed a trend of weight increase as a whole, irrespective of the aqueous solution temperature, in comparison to the weight prior to self-healing as the self-healing period increases. Also, the weight of the case where the temperature of the aqueous solution was 40°C increased, as a whole, 1.2 times that of the case where the temperature of the aqueous solution was 20°C. In particular, as shown in figure 5, when the temperature of the aqueous solution was 40°C, the CE aqueous solution prepared by mixing calcium oxide (CaO) and ethanol (CH₂H₅OH) showed a trend of weight increase to about 1.3 times that of the CH (calcium hydroxide; Ca(OH)₂) aqueous solution as a whole.

Figure 6 shows the result of calculating the rate of weight increase after self-healing in each condition. In general, as the self-healing period increased, the rate of weight increase showed an increasing trend and, in the case of self-healing period IV(24h) particularly, it could be seen that the rate of weight increase changed in the order of CE40>CE20>CH40>CH20.

From such a result, it can be seen that, when the temperature of the aqueous solution is 40°C, the higher the temperature is, the more the speed of the reaction between Ca²⁺ and CO₃²⁻ grows, even if the amount of Ca²⁺ supplied to each aqueous solution is fixed, in comparison to the specimen of which the self-healing is carried out in the 20°C aqueous solution. Accordingly, it is supposed to have led to increase in the amount of calcium carbonate which is a self-healing precipitate generated due to the increase in the aqueous solution temperature. Also, the increase in the weight was shown to be much bigger in CE series than in CH series as the reaction between Ca²⁺ and CO₃²⁻ was more promoted by using calcium oxide and ethanol as the self-healing solution, and it is thought to be more advantageous to improvement in the self-healing performance.

Figure 4. Absolute dry weight (20°C).

Figure 5. Absolute dry weight (40°C).

Figure 6. Absolute dry weight ratio.

3.2. Crystallographic change in calcium carbonate compound (CaCO₃) by SEM and XRD

In this experiment, to confirm the possibility to generate and control vaterite which is a CaCO₃ compound by controlling the temperature of the aqueous solution during self-healing, an SEM and
XRD analyses were carried out in each temperature condition using the CE series based on the case of self-healing period IV(24h) case.

First, as an SEM experiment, in the case self-healing was carried out using an aqueous solution prepared mixing ethanol and calcium oxide (CE), the SEM images of the specimens after self-healing in the aqueous solution temperature conditions of 20°C and 40°C are shown in figures 7-9 respectively in comparison to the specimens prior to self-healing. The SEM observation was carried out for the cleavage surface of the φ10×3mm specimen (inside the specimen), and the crystal forms of CaCO₃ were evaluated and estimated comparing the crystal form, crystal size, etc. of CaCO₃ identified in the existing literature [11, 12] with the crystal structure obtained in this study.

As a result of the SEM analysis, in the case of the specimen prior to self-healing in figure 7, almost no CaCO₃ was observed among the cement hydrates, and mainly only Ca(OH)₂ and C-S-H were observed. Meanwhile, in the case of the specimen after self-healing in figure 8 for which the temperature of the aqueous solution was adjusted to 20°C, calcite which is a CaCO₃ compound is observed in many parts along with C-S-H. Also, in the case of the specimen after self-healing in figure 9 for which the temperature of the aqueous solution was adjusted to 40°C, vaterite, a CaCO₃ compound, which was the target of this study was mainly generated, and was found to be attached mainly to the surface of calcite.

![Figure 7. Self-healing substances of Prior to self-healing (A).](image1)

![Figure 8. Self-healing substances at Temp. 20°C (CE specimen of IV series).](image2)
To quantitatively evaluate the crystal of CaCO$_3$ compound of the specimen after self-healing identified by the above SEM analysis, an XRD analysis was carried out using the same specimens as those of SEM. Also, in this XRD analysis, referring to the existing literature where peaks of crystal polymorphism of Ca(OH)$_2$ and CaCO$_3$ (Calcite and Vaterite) are reported [14, 15], identification of hydration products and self-healing precipitates was carried out in the range from 15° to 55°.

As shown in figure 10 and figure 11, it was conformed through the XRD analysis that the crystal forms of CaCO$_3$ identified in the SEM analysis were mostly calcite in the case of 20°C and were a large quantity of vaterite along with calcite in the case of 40°C. Also, in the case the self-healing aqueous solution temperature was 40°C, as peaks of vaterite were measured at many points when compared to the case of 20°C and the peak intensity of each crystal was found to be high, it is thought that generation of vaterite increased along with calcite among the CaCO$_3$ compound which is a self-healing precipitate.

Figure 9. Self-healing substances at Temp. 40°C (CE specimen of IV series).

Figure 10. XRD patterns at Temp. 20°C (CE specimen of IV series).

Figure 11. XRD patterns at Temp. 40°C (CE specimen of IV series)
Accordingly, as a result of the above SEM and XRD analyses, it is thought that, if self-healing is carried out by controlling the temperature of the aqueous solution, the crystal forms of CaCO\text{3} generated in the cement matrix are mostly calcite in the case of 20°C and, in the case of 40°C, they can be controlled to be a large amount of vaterite along with calcite. In particular, in the pH 12 condition, vaterite which is a denser CaCO\text{3} compound can be effectively generated and controlled by adjusting the temperature of the aqueous solution to about 40°C. Also, it is thought that the structure can be made denser through a denser structure and the self-healing performance can be improved by attaching vaterite on the surface of calcite of which the crystal size is larger than that of vaterite.

4. Conclusions
In this study, attention was paid to the crystal form of CaCO\text{3} generated in the self-healing process and the possibility for controlling the crystal form of CaCO\text{3} generated in the hardened cement paste by controlling the temperature of the aqueous solution to generate denser crystals of CaCO\text{3} was confirmed. Also, through this, author intended to present the temperature condition that enables generation of a large amount of vaterite along with calcite among the crystals of CaCO\text{3}. In addition, the result of a review on increase in CaCO\text{3} generation by effectively supplying Ca\text{2+} through adjustment of the aqueous solution and applying nano-sized ultrafine CO\text{3}\text{2-} bubbles is put in order as follows:

1. In the case the temperature condition of aqueous solution is 40°C, when compared to the case where self-healing is carried out in a 20°C aqueous solution, though the amount of Ca\text{2+} supplied to each aqueous solution is fixed, it has been confirmed that, the higher the temperature is, the more the rate of reaction between Ca\text{2+} and CO\text{3}\text{2-} grows. For this reason, generation of CaCO\text{3} after self-healing is supposed to have increased.

2. Also, in the case self-healing is carried out using the aqueous solution prepared by mixing ethanol and calcium oxide, as the rate of reaction between Ca\text{2+} and CO\text{3}\text{2-} grows when compared to the case of Ca(OH)\text{2} aqueous solution, generation of CaCO\text{3} after self-healing has increased irrespective of the temperature condition. Due to such a reason, it is thought that the absolute dry weight ratio increase and more effective healing is possible.

3. In the case of self-healing using the aqueous solution prepared by mixing ethanol and calcium oxide, it has been confirmed that the crystal forms of CaCO\text{3} generated in the cement matrix can be changed to mostly calcite in the case of 20°C and to a large amount of vaterite along with calcite in the case of 40°C by controlling the temperature. In the pH 12 condition particularly, it has been confirmed that vaterite which is a denser crystal of CaCO\text{3} can be effectively generated by controlled by adjusting the temperature of the aqueous solution to about 40°C.

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