- Technical Paper -

FUNDAMENTAL STUDY ON SELF HEALING OF CEMENT PASTE BY CALCIUM ALMINATE BASED AGENTS

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ABSTRACT

In past researches, self-healing mechanisms by cementitious materials are currently based on the further hydration of unreacted particles, except biological ones. However, such a mechanism never promises maximum healing capacity of agents due to its consumption during mixing. This causes the difficulties in optimizing the performance. In this work, a concept of calcium aluminate based agent encapsulation will be suggested. Attempting to verify its availability, healing agent potential was investigated under several environments. In the results, possibility of the method could be indicated.

Keywords: self-healing, ettringite, encapsulation, computed tomography

1. INTRODUCTION

For the aim of developing self-healing concrete, many researches have been conducted. According to state-of-the-art (STA) report of Technical Committee on Autogenous-healing in cementitious material published by Japan Committee Institute (JCI) [1], all of their mechanisms were classified as shown in Fig.1.

Regarding autogeneous healings, containing cementitious materials, they are currently based on further hydration of unreacted particles, except biological one [2]. They consist of ordinary cement materials as well as some special cementitious additives replaced to cement, which had not been fully hydrated in the initial hydration stage but remained partially unhydrated in hardened concrete. However, such a mechanism does not promise effective self-healing capacity because of consuming the additives during mixing. It seems to be difficult in optimizing and controlling its performance after crack propagation.

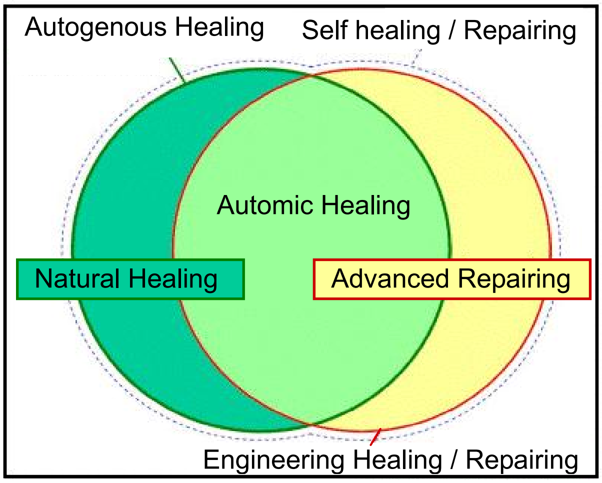

Fig.1 Definition of Self-healing/ Repairing Concrete

On the other hand, as activated repairing methods, non-native (organic) agents such as polymer-based agents coated with non-adequate layer encapsulation or hollow tubes were proposed. They may affect hydration kinetics and strength development. Furthermore, they can be deteriorated by ultraviolet light. Higher cost is also disadvantage.

Based on these points of view, in this research, suitable healing agent was selected. In addition, an alternative encapsulation method to protect the agent during cracking was also proposed. To realize this concept, fundamental properties of the healing agent were investigated. Furthermore, based on this concept, the target of our self healing concrete is defined to deal with stopping water leakage and regaining concrete stiffness.

2. TECHNICAL BACKGROUND

2.1 Material Selection

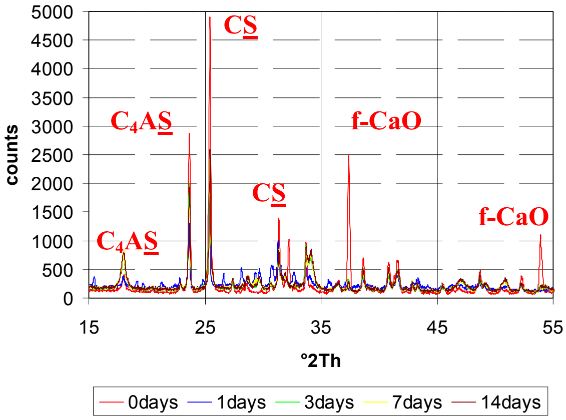

Fig.2 Time variation of the chemical components of the healing agent by XRD (pH=7+1, 20°C for 14 days)

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In this research, a mixture of synthesized CA crystals (e.g. Hauyne, $3CaO.Al_2O_3$, $CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$), anhydrous gypsum and lime - a ternary blend healing agent, which is a commercial product (in this case, density = 2.93 g/cm^3 and specific surface area = 2930 cm^2/g) normally for shrinkage compensation was utilized. The XRD analysis that is the time variation of the healing agent chemical components saturated under natural water (pH=7+1) at 20°C for 14 days is shown in Fig.2. The admixture produces ettringite ($3CaO.Al_2O3CaSO_4.32H_2O$) when it is mixed with water. In calculation, the volume of ettringite is approximately ten times larger than initial CA crystals [3], which has potential for closing a crack (healing). In addition, uncontrolled expansions (e.g. Transformation of AFm to AFt[2nd] due to external sulphate attack and Delayed Ettringite Formation) are also unconcerned.

2.2 Encapsulation method

Currently, several numbers of encapsulation researches have been conducted. For achieving our idea, the encapsulation layer must be a non-aqueous type in order to prohibit early hydration of the healing agent during mixing. An ideal material should be inorganic, insoluble and resistant against high pH environment. In addition, it must be mechanically stable to keep intact layer condition against concrete mixing process.

As a first step, powder granulation of the agent should be realized. To control the healing behavior, the size of the healing agent and the quality of coated layer are very important factors. One of the possible methods is a technique called freeze granulation[4], which is based on spraying suspensions into liquid nitrogen and drying without shrinkage: density and homogeneity retained. The granule size distribution is also well controlled by the suspension rheology (flow properties) and the process parameters (pump speed and air pressure).

As a second step, establishing the encapsulating methodology is more challenging phase. The granules should be preferably coated by inorganic layer that has a lower stiffness compared to the surrounding cement paste, which can make crack propagate through the capsules, and to expose the healing agent into the crack.

Above all, the schematic ideal illustration is shown here as Fig. 3.

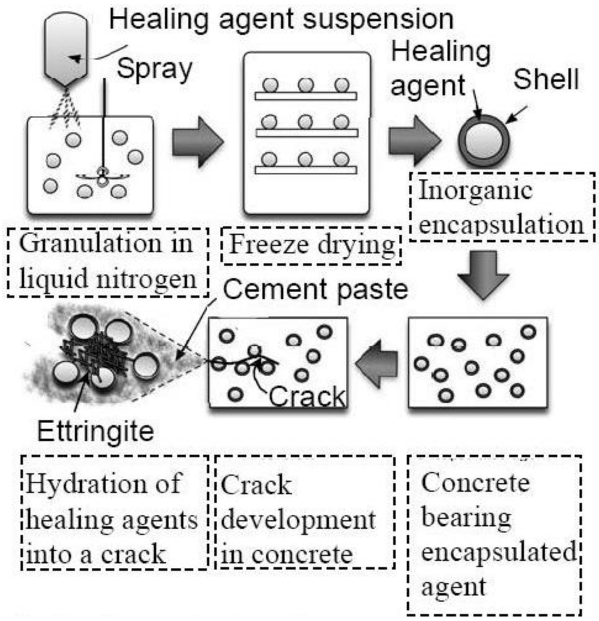

Fig.3 Concept for the granulation and encapsulation of calcium aluminate based agent

3. EXPERIMENTAL SETUP

3.1 Used materials

Ordinary portland cement (CEM I 32.5R) is used. As a resource of healing agent, an ettringite series expanding material is used. As the others, epoxy resin (bisphenol-A type) and hardener (triethylenetetramine type) are utilized.

3.2 Experimental Program

(1)Destructive test

First of all, so as to investigate healing agent potential itself, the specimen made of epoxy was utilized (Fig.4) in different environments.

First, epoxy was casted in a mold, and it was cut into two pieces. Then, their cut surfaces (crack surface) were polished with sandpaper (average abrasive micro grain sizes, 30.2 ± 1.5 in micron by FEPA) to make them appropriate crack roughness (but it is flat surface in macro scale), and two holes with 1 mm diameter were drilled on one piece. In the case of Φ=0.584mm, a certain size of injection needles had been embedded in advance. Finally, the healing agent was packed in the holes by hand. Both discs were combined together with a thin stainless steel plate (200μm thick) in between to create an artificial crack , and eventually tied with a steel wire.

These specimens were immersed under still water

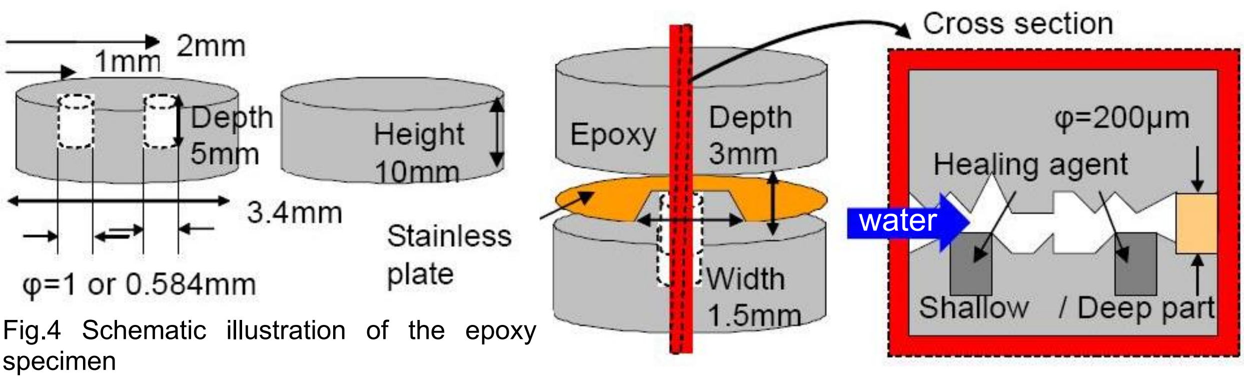

Fig.4 Schematic illustration of the epoxy specimen

or an alkaline solution (pH=13±1, 0.1M/L-NaOH) for curing. To control pH, the solutions were replaced every 12 hours. Three different curing temperatures, 3±1°C (fridge), 20±1°C (chamber), 35±1°C (chamber), were applied. Hole diameters which were simulated capsule size were Φ=1 and 0.584mm. In a certain period, 1, 2, 3, 7 and 14days after curing, specimens on each environment condition were taken from the water for analyses.

After that, so as to investigate healing properties, these specimens were immersed under 95% ethanol to replace water for one day, and they were dried in a chamber (35±1°C) for one day. Then, they were impregnated in epoxy with a fluorescent dye under vacuum. In one day after hardening, they were cut on the appropriate cross section crossing over the healing agent zone (as seen in Fig.4), and the surface was polished. Investigation was conducted by microscope and ESEM-EDX.

Regarding to the microscopic observation, as shown in Fig.5, the healing area was measured by software. The area was compared to a criterion of healing area that we defined; the hole size times crack width(200μm) in the square. On the other hand, for ESEM-EDX, three representative positions, shown in Fig.5, were observed under neutral and alkaline environment. "A" was assumed as the unreacted part, "B" was assumed as the reacted part immediately above the healing agent, and "C" was assumed as the reacted part, which went away to vacant space.

(2)Nondestructive test

In this experiment, the real crack situation exposed to water passing through a crack was assumed. To evaluate the potential of our healing agent on such environment, variation of water flow test is an effective way. In the author's previous research, in the case of a crack up to 0.4mm, the water flow reduction could be remarkably occurred under such situation when the same agent was used as a cement replacement [5]. However, contributing factors to self healing were complicated so that healing agent potential itself could not have been recognized.

To reveal the healing process by the healing agent, the computed tomography (CT) shown in Fig.6 was utilized to visualize the variation of porosity after water passed through the crack. In this research, a mortar was utilized due to restriction of specimen size in the CT. Regarding procedures of making specimens, schematic illustration was shown in Fig.7. First, the mortar was casted with a fishing wire (Φ=500, 234 and 80μm) in the center, which simulated an ideal water path in the mortar. After demolded in 3 days, the specimen was cured under pure water for 4 days. Then, the wire was pulled out, and the specimen was cut into two pieces. Next, these surfaces were polished and dried for 2 days in the 30±1°C chamber. Finally, a plastic plate which contained the healing agent in the middle of the ring was put between the polished surfaces, and all of the parts were fixed together with a plastic tape.

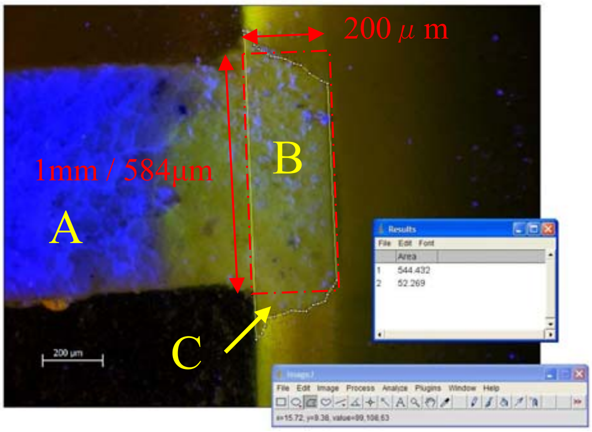

Fig.5 Microscopic & ESEM-EDX observation and healing criteria

Fig.6 Computed tomography

Fig.7 Schematic illustration and a picture of the water flow specimen

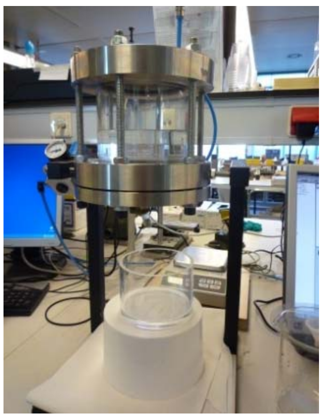
Fig.8 Water flow device

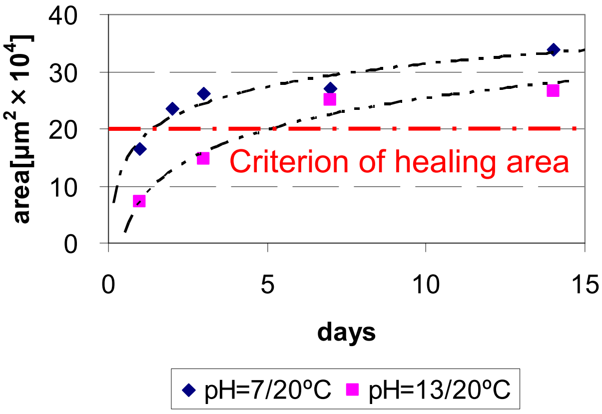

Fig.9 Variation of the healing area depending on pH

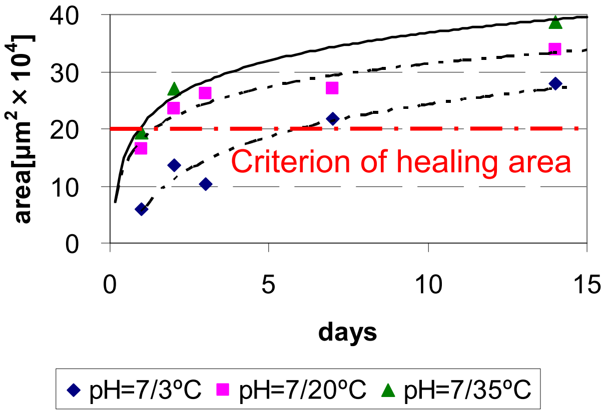

Fig.10 Variation of the healing area depending on TEMP

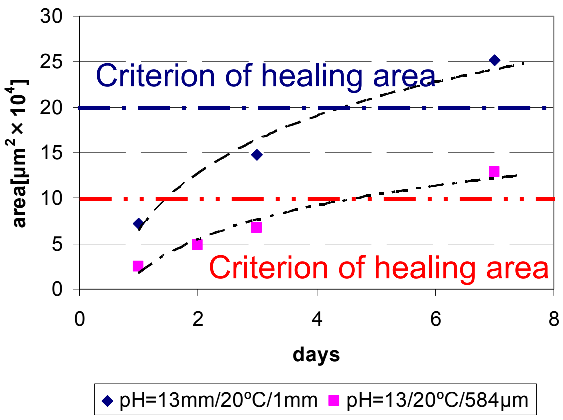

Fig.11 Variation of the healing area by hole size difference

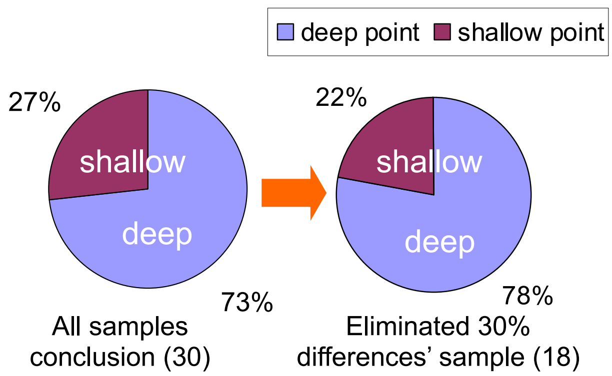

Fig.12 Variation of the healing area by hole size difference

The investigation was carried out by the water flow device, shown in Fig.8, which was controlled approximately 10kPa by air pressure. The water flow was calculated by the water leakage which passed through the hole divided by the cross sectional area of the hole. In 7 (or 3) days after curing started, the specimens were taken from the device and followed the procedure which was as same as in the case of the destructive test to observe with the CT.

4. EXPERIMENTAL RESULTS

4.1 Destructive test

Fig. 9 - 11 show the time variation of the healing area which was defined at previous section 3.1, on each specimen affected by the several environment conditions; curing water pH, temperature and hole (artificial capsual) size, respectively. The red and orange dashed lines are the criterion of healing area of each specimen, Φ=1 and 0.584mm, respectively. From the above, specimens exerted their higher healing potential when the lower pH and higher temperature water came. Additionally, the effect of the hole size simulated for the size effect of capsule was ignorable within this range, which means that each specimen reached to each criterion in the period, 4 -5days. However, further investigation will be needed; relationship between optimization of encapsulation size and the healing effect in future.

A difference of healing effect caused by the influence of the depth of cracked capsule is one of the big interests to reveal the healing mechanism and to apply the mechanism to practical techniques. In Fig. 12, the left circular chart demonstrates summation of the statistic data; which part (crack position from crack surface, deep/shallow, shown in Fig. 4) was healed wider at the same specimen. Parenthetical numbers are the numbers of specimens. It proposed that deeper position was effectively healed compared to the shallow. Furthermore, in the right circular chart, when the data which seemed to have a small difference (30%) between these parts was eliminated, the tendency became more accurate. The selecting process is as follows:

$$|S_a - S_b|/S_a \cdot 100 \geqq 30 \ \& \ |S_a - S_b|/S_b \cdot 100 \geqq 30 \ \rightarrow \ \text{accept} \quad (1)$$

where,

S_a: healing area of shallow part [μ m^2]

S_b: healing area of deep part[μ m^2]

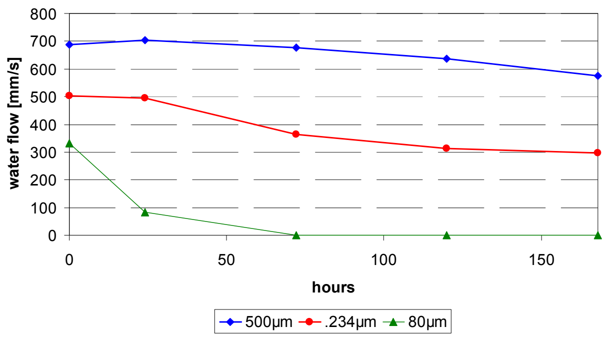

Fig.13 Variation of water flow depending on hole diameter

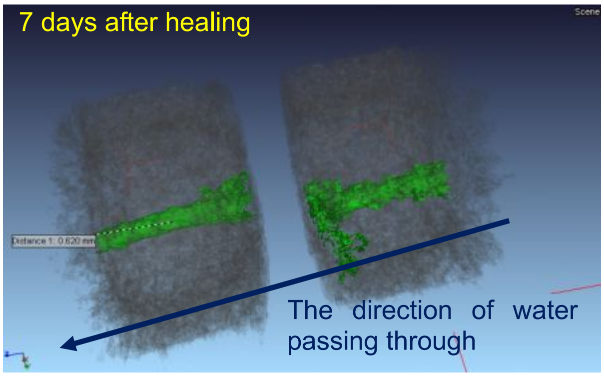

Fig.14 CT image in the case of 500 μ m hole

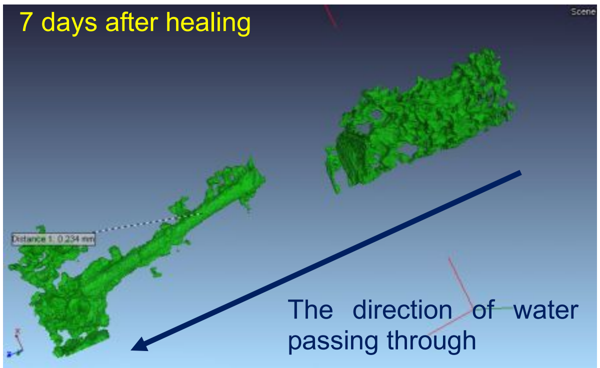

Fig.15 CT image in the case of 234 μ m hole

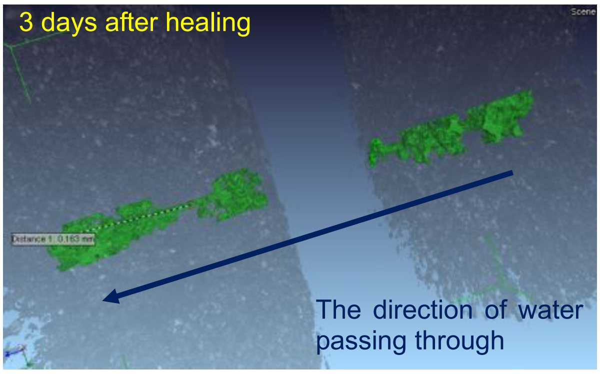

Fig.16 CT image in the case of 80 μ m hole

Further discussion will be conducted at the next section 4.2 with the result of non-destructive test.

In the result of the ESEM-EDX observation, even in the "A" part, under both environments, small ettringite was able to be found, but mainly they were unreacted healing agents. In "C" part, in the case of neutral environment, bigger size of ettringite was able to be observed. On the other hand, the matrix was more porous compared to the other. In "B" part, contrasting to our prediction, no ettringite was able to be found visually under both cases. Also, we could not get any accurate ettringite peak by the EDX analysis. To optimize encapsulation size and to reveal healing mechanism, further investigation should be conducted in future.

Furthermore, regarding to the property of the healing agent, it can be deteriorated once it is subjected to wet and dry cyclic condition. Ettringite itself does not have sufficient stiffness to regain the virgin stiffness of cement matrix, either. Thus, the specific proportion of the healing agent and cement should be optimized in future as well.

4.2 Nondestructive test

Fig. 13 shows the time variation of water flow on each specimen of the hole size. The one with smaller diameter expressed the faster reduction of water flow.

Fig. 14 and 15 show the CT images of 500 μ m- and 234 μ m-hole-specimens in 7days after water passed through the holes, respectively. In the case of the hole diameter, 80 μ m, shown in Fig.16, water flow was stopped after 3 days so that the image was taken at that time.

The gray-colored part is a mortar and the green part is a porous area. When a wire tries to pull out, as a rule of thumb, approximately 100 μ m can be larger than the original value of the wire diameter due to the friction between the wire and the mortar. In addition, at the edge of the specimen, a fracture can be occurred in the passed trials.

In the 500 μ m case, compared to the specimens above and below across the healing agent, the reduction of porous part was nothing remarkable.

However, in the case of 234 μ m, compared the one above to the one below, reduction of the porous part (capillary pores) which mainly surrounded the wire hole was able to be observed. We suppose the healing agent was dissolved in the water which flowed to capillary pores, and then the deeper area below was healed. This is the reason of slight reduction of water flow in this case.

Furthermore, in the case of 80 μ m, another phenomenon was able to be observed. In the below specimen, one narrow point exists there. We suppose in this case, a narrow part became a bottle neck of this specimen, and the significant water flow reduction could be occurred.

According to results above and the results of Fig.12, we suppose that healing in the crack can be occurred due to not by the position of crack depths but by relatively stable positions; water (leakage) reduction can be occurred by the integration of capillary pores and narrow space healing.

5. CONCLUTIONS

In the destructive and nondestructive tests mentioned above, properties of the healing agent are investigated so that the following conclusions are derived;

(1) There is a potential of using expansive additive as a self healing material in concrete.
(2) In the case of lower pH and higher temperature, curing water shows higher healing effect. The size effect of the healing agent was not able to be observed in this research.
(3) This healing mechanism by water passing through is caused by the healing integration effect of capillary pores and narrow space.

6. OUTLOOK

Further investigations are as follows;

(1) Development of suitable encapsulation method and granulation techniques.
(2) Optimize the ratio of the healing agent to cement.
(3) Optimize the capsule size through experimental and modeling studies [6].

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