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The control of self-healing time of granulated expansive agent by water-soluble film coating

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Although various self-healing methods have been suggested until recently, these methods have merits and demerits. The utilization of expansive agents and mineral admixtures in various methods may be appropriate due to their good healing efficiency, compatibility with the cement matrix, and low cost, but the efficiency of healing products generated by necessity is not guaranteed. In this study, granulation/coating methods are applied to expansive agent. The self-healing time of materials can be controlled via water-soluble film thickness until cracks occur, and healing products will be formed because materials react with moisture via the crack faces after water-soluble film was dissolved by moisture. It was verified through various tests that the granulated expansive agent with water-soluble film coating can control the time of self-healing and can prevent water migration via crack closing.

Key words: Self-healing, Expansive agent, Water-soluble film, Crack.

Instructions

The crack reduction, maintenance/repairing with respect to the durability of concrete structures have a great interest. In particular, maintenance/repairing costs of concrete structures, which constructed in a period of high growth, are increasing so that interest of sustainable structures is growing up. In concrete, cracking is a common phenomenon due to the relatively low tensile strength so that smart/intelligent concrete structures are growing to an international interest. In particular, materials, which have a self-healing capability of cracks in damaged concrete, carried out by many researchers. However, level of practical does not meets yet.

In Korea, self-healing of concrete have been conducted in very common studies such as self-healing properties of cement matrix, development of polymer composite and self-healing by using bacteria and so on. On the other hand, various self-healing strategies such as hollow fiber, microcapsule, expansive agent/mineral admixture, bacteria, and shape memory materials have being conducted in Europe and Japan. In 1969, self-healing properties were for the first time built-in inside polymeric materials. In 1979 and 1981 publications about self-healing in thermoplastic and cross-linked systems appeared. In the 90's, work on self-healing concrete has started by Dry. Although, it was only in 2001 when White *et al.* published their paper in Nature about self-healing in polymer based materials that the research on self-healing materials started to attract a lot of attention [11].

Although various self-healing methods have been suggested until recently, these methods have merits and demerits. The utilization of expansive agents and mineral admixtures in various methods may be appropriate due to their good healing efficiency, compatibility with the cement matrix, and low cost, but the efficiency of healing products generated by necessity is not guaranteed [1, 6]. And the utilization of microcapsule is effective due to releasing of healing agent on necessity, response to many damage locations at the same time, and possible effectiveness under multiple damage events. It, however, has a disadvantages such as difficulty in preparing capsules and in casting, concern of bond between capsules and the matrix, and poor compatibility with the cement matrix because healing agent is organic matter [12]. Table 1 indicates features of microcapsule and expansive agent /mineral admixture.

In this study, granulation/coating methods are applied to CSA expansive agent. The self-healing time of materials can be controlled via PVA film thickness until cracks occur, and healing products will be formed because materials react with moisture via the crack faces after PVA film was dissolved by moisture. Application of granulation/coating method on cementitious material is combined of advantage of microcapsule and expansive agent /mineral admixture. The crack widths and images were obtained via microscopy investigation depending on the elapsed time. At the same time, a water passing test was conducted. Also, healing products, which were formed on crack faces, were evaluated by SEM analysis.

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Table 1. Microcapsule and Expansive agent /mineral admixture (Min *et. al*., 2012).

Type	Advantage	Disadvantage
Microcapsule	• Healing agent release on necessity • Response to many damage locations at the same time • Possible effectiveness under multiple damage events	• Difficulty in preparing capsules and in casting • Limited amount of healing agent • The bond between capsules and the matrix is a concern • Negative effect on the mechanical properties of the cement matrix if too many capsules adapted
Expansive agent and mineral admixture	• Good healing efficacy • Good compatibility of the generated healing products with the cement matrix	• Undesirable expansion if not well treated • Healing products generated on necessity is not guaranteed

Experimental Procedure

Granulation/coating for controlling response time of CSA expansive agent

When crack occurs, self-healing time is able to control by controlling thickness of water-soluble film so that healing products will be formed since materials react with moisture in the crack faces after water-soluble film was dissolved. Therefore, the purpose can be achieved though granulation/coating method. Expansive agent that used commonly is to include lime or CSA. The CSA-based expansive agent consists of hauyne ($3CaO \cdot 3Al_2O_3 \cdot CaSO_4$), free lime (CaO), and anhydrite ($CaSO_4$). They mainly provide ettringite ($3CaO, Al_2O_3, 3CaSO_4, 32H_2O$), which is a micrometer-sized acicular crystal, due to hydration. In particular, ettringite fills the micro pores of concrete and is induced the expansion of concrete. Also, the CSA-based expansive agent is formed crystalline calcium hydroxide by reaction between free lime (CaO) and water, and then the expansion occurs by grows of crystalline calcium hydroxide. However, calcium hydroxide is reduced by calcium aluminate hydrate (C-A-H) that is formed due to reaction with hauyne. Subsequently, acicular ettringite, which induced expansion, is formed by reaction with anhydrite ($CaSO_4$) [5]. Chemical formula of CSA-based expansive agent is as follow;

$$C_4A_3S + 8CaSO_4 + 6CaO + 96H_2O \rightarrow 3(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O) \quad (1)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

In this study, CSA-based expansive agent, whose effect is stable and superior, is used. Table 2 indicates chemical composition and physical properties of CSA-based expansive agent.

CSA-based expansive agent was granulated through a process involving kneading, wet granulation, and drying. And then the surface of the granule was coated with a water-soluble polymer substance using polyvinyl alcohol (PVA) for controlling self-healing time. By repeating coating process, the coating thickness was increased [8]. The PVA coating was 0.064-0.0082 mm thick when the process was repeated at least twice. Table 3 indicates features of the granulated CSA-based expansive agent and coating material and Fig. 1 shows Granules which are coated with PVA film in a pan and close-up image of coating material.

Table 2. Chemical composition and physical properties of CSA-based expansive agent.

MgO (%)	K_2O (%)	Na_2O_{eq} (%)	Cl^- (%)	Ig. loss (%)	Specific gravity (g/cm^3)	Surface area (cm^2/g)
1.3	0.05	0.03	0.03	1.1	2.93	3220

Table 3. The granulated CSA-based expansive agent and coating material.

Type	Features
The granulated CSA-based expansive agent	• Shape: Cylindrical • Diameter: 0.5 mm, Length: 0.3 ~ 0.5 mm • Volume: 0.1963 mm^3 • Granulation method: Wet method
Coating materials	• Water-soluble film: Polyvinyl alcohol (PVA) • Polyvinyl alcohol(PVA) to water ratio = 1 : 10 • Coating thickness : 0.064~0.082 mm • Coating method : Pan-coating

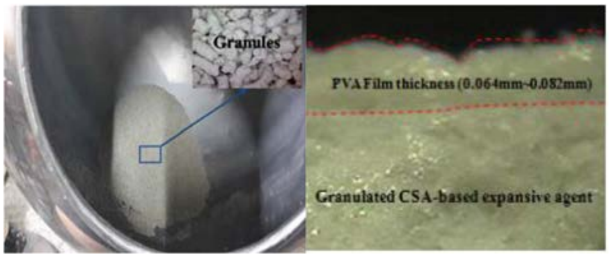


Fig. 1. Granules which are coated with PVA film in a pan and close-up image of coating material.

Materials and mix proportion

This study for controlling self-healing time was used materials for mortar. In particular, coarse aggregate was excluded in this study because test was conducted via mortar. Table 4 summarizes properties of cement and fine aggregate, which are mainly used in this study.

Mortar mixtures to evaluate self-healing efficiency were designed based on W/C = 0.4 and with a cement-to-sand ratio of 1 : 3, according to ISO 679. Also, the replacement ratio of the granules with PVA coating was limited to 10% by mass cement because some researchers

Table 4. Properties of cement and fine aggregate.

Component	Properties
Cement	• Physical: Specific gravity-3.14 g/cm^2, Surface area-3460 cm^2/g, Ignition loss-1.2% • Chemical : SiO_2 (20.6%), Al_2O_3 (6.1%), Fe_2O_3 (3.4%), CaO (62.1%), MgO (2.9%), SO_3 (2.1%)
Fine aggregate	• G_{max} : 5 mm, Density : 2.60 g/cm^3, Absorption : 1.05%, F.M. : 2.78, Chloride contents : 0.01%, Unit weight : 1.565 kg/L

noted the occurrence of unexpected expansion [9]. At the age of 28 days, cracks (range: 0.1-0.35 mm) were created in the mortar specimens by means of a three-point bending test. Then the crack widths and images were obtained via microscopy investigation. Also, self-healing efficiency was evaluated by a water passing test. Finally, healing products, which were formed on crack faces, were evaluated by SEM analysis.

Experimental method

Crack width is able to divide into micro crack (below 0.1 mm), mezzo crack (0.1 ~ 0.7 mm), and macro crack (over 0.7 mm). Because most of crack is factor of degradation of load carrying capacity and durability, It is important to control crack width within allowable range via uniformly distribution of micro crack instead of macro crack. Crack width for durability is limited to below 0.3 mm. Also, Crack width, which is able to undergo risk of water leakage, is 0.06 mm usually. In particular, crack width for waterproof should be below 0.2 mm because water leakage occurs over 0.2 mm undoubtedly. In this study, all the mortar mixtures were placed into the 40 × 40 × 160 mm moulds in different layers. First, a 10 mm mortar layer was brought into moulds and was compacted via vibration. Two Φ2 mm reinforcement bars were placed onto this layer. Afterwards, the moulds were further filled with mortar. After casting, mortar prisms were cured at 20 ± 2 °C and in a 95 ± 5% humidity chamber until the testing time. At the age of 28 days, cracks (range: 0.01-0.35 mm) were created in the mortar prisms by means of a three-point bending test. Fig. 2 indicates a view of three-point bending test for introduction of crack and specimen that was introduced to crack.

Microscopy investigation is common measures for qualitative evaluation. In this study, all the specimens were immersed in water after the introduction of cracks. Afterwards, the crack widths and images were obtained via microscopy investigation depending on the elapsed time. Healing functions and resultant improvements in performances of concrete greatly depend on the environment, where the concrete is located. Therefore, it is crucial to decide a condition of re-curing after inducing damage in investigations or experiments for examining healing behavior. Condition that exits in a real life of concrete structure must be

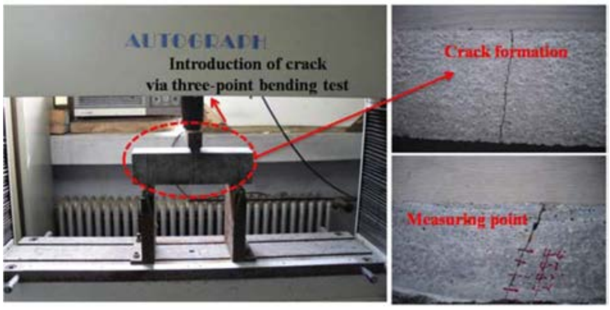


Fig. 2. Views of three-point bending test for introduction of crack and crack formation.

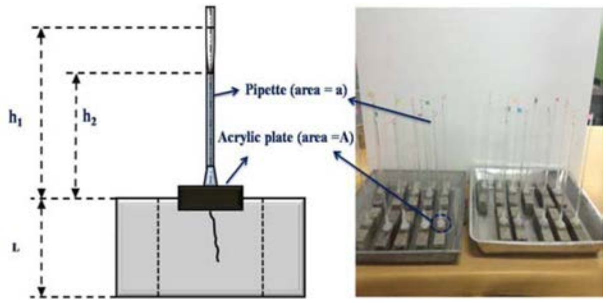


Fig. 3. A schematic and views of water passing test.

carefully chosen for representing the real healing situation [7]. The parameters for evaluating healing ability are divided into two groups, one concerned with mechanical properties such as strength or stiffness, and the other related to a transport substance such as ion or water. It is agreed that the improvement by a healing function is more pronounced in the latter than in the former [3].

Therefore, a water passing test, which evaluated prevention of aggressive agents such as the migration of water due to crack propagation, was conducted at same time, when microscopy investigation was conducted. Fig. 3 shows schematic and views of water passing test.

Results and Discussion

Microscopy investigation

Changes in the crack width and image by microscopy investigation are qualitative evaluation. Therefore, many researchers were attempted various quantitative evaluations for self-healing efficiency. Self-healing closing ratio (β(t)), which was suggested by Dechkhachorn, was introduced [4]. Self-healing closing ratio (β(t) at specific time can be calculated by using follow equation.

$$\beta(t) = 1 - \frac{A_t - A(t)}{A_t} \quad (3)$$

Where, A_i is an initial area of crack before self-healing, A_t is a area of crack-closing at specific time. β = 0 means that no crack-closing occurs while β = 1 means that complete crack-closing has been achieved. Table 5 indicates self-healing closing ratio (â(t) of the

Table 5. Self-healing closing ratio of each mixture (1 : < 0.1 mm, 2 : 0.1 mm ~ 0.2 mm, 3 : > 0.2 mm).

Type	Self-healing closing ratio (β(t))					
	0	7day	11 day	14 day	16 day	28 day
Control-1	0	0.30	0.39	0.51	0.54	0.78
Control-2	0	0.12	0.21	0.24	0.26	0.35
Control-3	0	0.06	0.08	0.10	0.11	0.16
Granule-1	0	0.63	1.00	1.00	1.00	1.00
Granule-2	0	0.53	0.88	1.00	1.00	1.00
Granule-3	0	0.50	0.85	0.96	1.00	1.00

*Granule: The granulated CSA-based expansive agent.

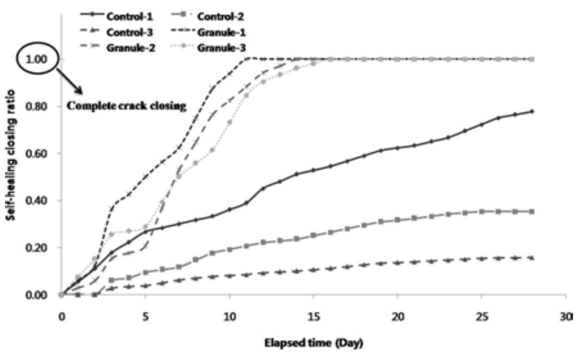
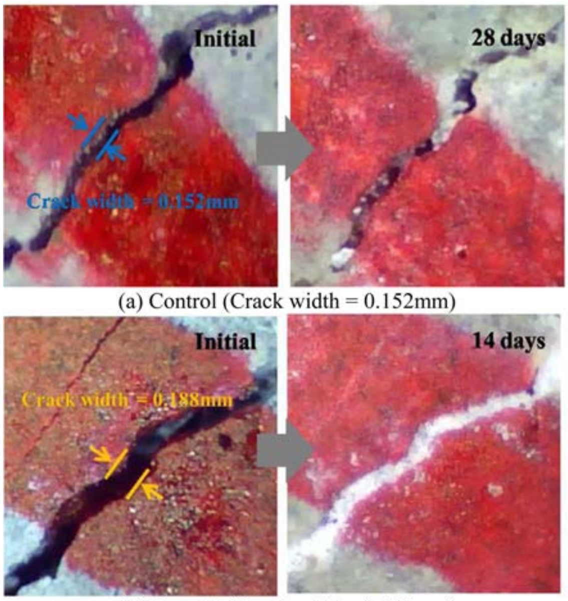


Fig. 4. Self-healing closing ratio depending on elapsed time.



(a) Control (Crack width = 0.152mm)

(b) Granule (Crack width =0.188mm)

Fig. 5. Crack closing process: (a) Control (b) Granule.

specimens, which hold 0.05-0.35 mm crack width, at specific time. Fig. 4 indicates self-healing closing ratio of each mixture depending on elapsed time.

In Fig. 4, self-healing was not achieved because self-healing closing ratio of Control is 0.16-0.78 at 28-days. On the other hand, self-healing closing ratio of the others indicate 1.0 within 11-16 days. Therefore, it can be noticed that self-healing was achieved. Also, tt was verified self-healing efficiency of Granule, which was protected by PVA film, for crack-closing.

Fig. 5 indicates the process of crack-closing via self healing with regard to the typical specimens of Control and the Granule with PVA film coating, which involved 0.1-0.2 mm crack widths in the crack width range. For Control, crack-closing was observed in some parts of the crack after 28-day immersion. The specimen incorporating Granule was observed to have formed crystals and it showed complete crack-closing after 14-day immersion. Therefore, it can be supposed that crack-closing was achieved because the CSA-based expansive agent had reacted due to the removal of the PVA film coating by the migrated moisture via the crack faces.

Evaluation of water migration

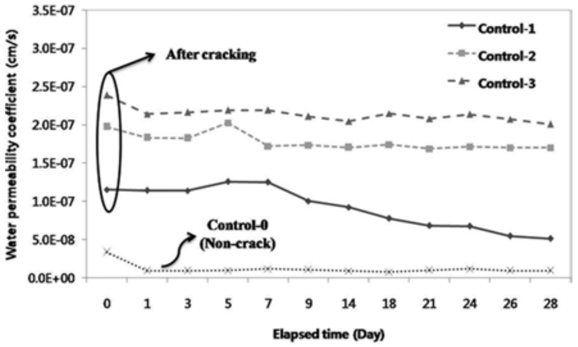
A water passing test, which evaluated prevention of aggressive agents such as the migration of water due to crack propagation, was conducted at same time when microscopy investigation was conducted. Subsequently, water permeability coefficient in each mixture was calculated. Table 6 indicates mean water permeability coefficient of specimens which, hold the crack width range of (< 0.1 mm, 0.1-0.2 mm, > 0.2 mm).

In Table 6, after cracking, water permeability coefficient of the specimens, which hold crack widths of < 0.1 mm, is 1.15, 1.20×10^{-7}, and that of the specimens, which hold crack widths of < 0.1 mm and > 0.2 mm are 1.94, 1.97×10^{-7} cm/s and 2.39, 2.80×10^{-7} cm/s, respectively. Therefore, it was verified that a similar water permeability coefficient was indicated depending on crack width. Also, water permeability coefficient was increased with increasing crack width. Because water permeability coefficient of all mixtures, except for Control-2 and 3, was significantly decreased at 28-days, the permeability resistance was improved.

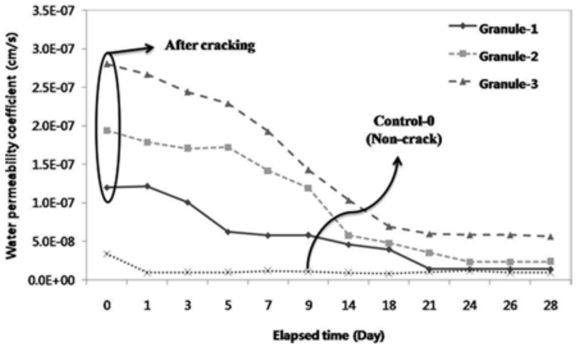
Fig. 6 indicates comparison of water permeability coefficient on each crack width range in each mixture. In Fig. 6, it indicates that a similar water permeability coefficient shows for each crack width range of (< 0.1 mm, 0.1-0.2 mm, > 0.2 mm). In particular, the water permeability coefficients of Control-2 and 3 did

Table 6. Water permeability coefficient depending on elapsed time ($\times 10^{-7}$ cm/s) (1 : < 0.1 mm, 2 : 0.1 mm ~ 0.2 mm, 3 : > 0.2 mm).

Type	After cracking	3 day	7 day	14 day	21 day	28 day
Control-1	1.15	1.14	1.25	0.92	0.682	0.514
Control-2	1.97	1.83	1.72	1.70	1.69	1.70
Control-3	2.39	2.16	2.19	2.05	2.08	2.01
Granule-1	1.20	1.00	0.58	0.46	0.14	0.139
Granule-2	1.94	1.71	1.42	0.58	0.35	0.234
Granule-3	2.80	2.44	1.92	1.03	0.60	0.563



(a) Control



(b) Granule

Fig. 6. Water permeability coefficient on each crack width range in each mixture.

not significantly differ in state after the introduction of cracks, and that of Control-1 slightly decreased. Water permeability coefficient of Granule significantly decreased with increasing of immersion period. In particular, although water permeability coefficient differed at the initial crack, Granule-1 and 2 showed similar values after 24 days. Also, they have gone close to Control-0 (Non-crack). Therefore, the efficacy of crack closing, which prevents water migration through the self-healing of Granule with PVA film coating, was verified.

Analysis of healing products

In most of the literatures studied, the primary mechanism of self-healing is believed to be attributed to the crystallization of calcium carbonate and calcium hydroxide [10]. This view is supported by the fact that precipitated calcium carbonate can often be observed at the outside surfaces of the crack as some white residue. This view is supported by the fact that precipitated calcium carbonate can often be observed at the outside surfaces of the crack as some white residue. As one of the cement hydration products dissolved in water, the calcium hydroxide is liberated and dissipated along the cracking surfaces and then free calcium ions from cement hydration react with dissolved carbon dioxide. Consequently, the crystals are formed, growing at both surfaces of the cracks and finally filling into the gaps [2]. The CSA-based expansive agent mainly provide ettringite (3CaO, Al_2O_3, $3CaSO_4$, $32H_2O$), which is a

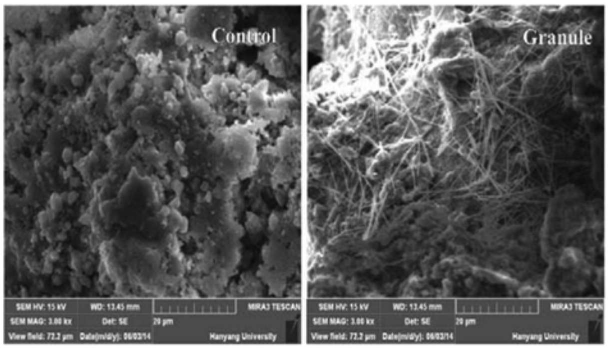


Fig. 7. SEM micrographs of healing products that are formed at crack face.

micrometer-sized acicular crystal, due to hydration. In particular, ettringite fills the micro pores of concrete and is induced the expansion of concrete. Also, They is formed crystalline calcium hydroxide by reaction between free lime (CaO) and water, and then the expansion occurs by grows of crystalline calcium hydroxide. Thus, CSA-base expansive agent causes the expansion, which occurs by ettringite, calcium hydroxide that were formed due to hydration reaction.

Fig. 7 indicates SEM micrographs of healing products of the Control, which has not incorporated anything, and the specimens, which incorporated the granulated CSA-based expansive agent with PVA film coating (Granule). $CaCO_3$, which was indicated short hexagonal-prism morphology or layer morphology that was piled up them, was shown in SEM micrographs of Control. Also, in SEM micrographs of Granule, ettringite, which is needle-shaped prismatic crystals, and CaCO3, which is short hexagonal-prismatic crystals, was shown. Therefore, it was verified that clack-closing was achieved by healing products.

Conclusions

Granulation/coating methods are applied to healing material, which is CSA expansive agent. The self-healing efficacy of healing materials can be maintained via PVA film thickness until cracks occur, and healing products will be formed because materials react with moisture via the crack faces after PVA film was dissolved by moisture. In this study, healing efficiency was evaluated by testing. The following conclusions were arrived at:

1. In self-healing closing ratio, self-healing was not achieved that of Control is 0.16-0.78 at 28-days. On the other hand, that of the other indicates 1.0 within 11-16 days. Therefore, it can be noticed that self-healing was achieved.

2. In the process of crack-closing via self healing with regard to the typical specimens of Control and the Granule, crack-closing for Control was observed in some parts of the crack after 28-day immersion. The

specimen incorporating Granule was observed to have formed crystals and it showed complete crack-closing after 14-day immersion.

3. In Water passing test, the water permeability coefficients of Control-2 and 3 did not significantly differ in state after the introduction of cracks, and that of Control-1 slightly decreased. Water permeability coefficient of Granule significantly decreased with increasing of immersion period.

4. In SEM micrographs, $CaCO_3$, which was indicated short hexagonal-prism morphology or layer morphology that was piled up them, was shown in SEM micrographs of Control. Also, in SEM micrographs of Granule, ettringite, which is needle-shaped prismatic crystals, and CaCO3, which is short hexagonal-prismatic crystals, was shown.

Therefore, it was verified that the granulated CSA-based expansive agent with PVA film coating can maintain the self-healing efficacy until cracks occur and can prevent water migration via crack closing.

Acknowledgments

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References

1. Ahn, Tae-Ho, and Toshiharu Kishi. Crack self-healing behavior of cementitious composites incorporating various mineral admixtures. Journal of Advanced Concrete Technology 8.2 (2010) 171-186.
2. Edvardsen, Carola. Water permeability and autogenous healing of cracks in concrete. ACI Materials Journal 96.4 (1999) 448-454.
3. Jacobsen, Stefan, Jacques Marchand, and Luc Boisvert. Effect of cracking and healing on chloride transport in OPC concrete. Cement and Concrete Research 26.6 (1996) 869-881.
4. Jaroenratanapirom, Dechkhachorn, and Raktipong Sahamitmongkol. Self-crack closing ability of mortar with different additives. J Met Mater Miner 21.1 (2011) 9-17.
5. Lee, Yong-Soo, and Jae-Suk Ryou. Self healing behavior for crack closing of expansive agent via granulation/film coating method. Construction and Building Materials 71 (2014) 188-193.
6. Li, Victor C., and Emily Herbert. Robust self-healing concrete for sustainable infrastructure. *Journal of Advanced Concrete Technology* 10.6 (2012) 207-218.
7. Neville, Adam. Autogenous healing: A concrete miracle?. Concrete International 24.11 (2002) 76-82.
8. Ryou, Jae-Suk, and Yong-Soo Lee. Use of tabletting & coating accelerator for the prevention of early-frost of concrete in cold weather. *Cold Regions Science and Technology* 87 (2013) 1-5.
9. Sisomphon, K., O. Copuroglu, and E. A. B. Koenders. Self-healing of surface cracks in mortars with expansive additive and crystalline additive. Cement and Concrete Composites 34.4 (2012) 566-574.
10. Van der Zwaag, Sybrand. Self healing materials. Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science 1 (2008).
11. Van Tittelboom, Kim, and Nele De Belie. Self-healing in cementitious materials-A review. *Materials* 6.6 (2013) 2182-2217.
12. Wu, Min, Björn Johannesson, and Mette Geiker. A review: Self-healing in cementitious materials and engineered cementitious composite as a self-healing material. Construction and Building Materials 28.1 (2012) 571-583.