- Technical Paper -

DESIGN OF SELF-HEALING CONCRETE BASED ON VARIOUS MINERAL ADMIXTURES

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ABSTRACT

This study aims to develop and apply self-healing concrete as a new method for crack control and enhanced service life in concrete structures. This concept is one of the maintenance-free methods which, apart from saving direct costs for maintenance and repair, reduces the indirect costs – a saving generally welcomed by contractors. In this research, the effect of various mineral admixtures on the self-healing of cracked cementitious composites and concrete was investigated. The essential properties such as expansion, swelling and re-crystallization for self-healing design were discussed.

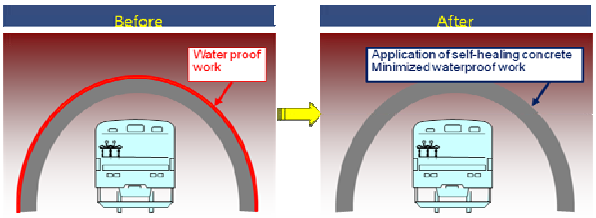
Keywords: crack, self-healing, mineral admixtures, repairing, re-crystallization

1. INTRODUCTION

The serviceability limit of concrete structures is primarily governed by the extent of damage. Cracks, one of various types of damage, play an important role in the serviceability limit. However, if it were possible to know the reason for differing behavior of concrete structures exposed to largely similar conditions, we might have the key for designing high-durability structures with low or negligible maintenance and repair costs. Furthermore, the serviceability limit of concrete structures by cracking might be overcome by crack control methodologies; the enhanced service life of concrete structures would reduce the demand for crack maintenance and repair. In particular, the utilization of self-healing technologies has high potential as a new repair method for cracked concrete under the water leakage of underground civil infrastructure such as tunnels, as shown in Fig. 1.

The aim of this study is to develop autogenous healing concrete using various mineral admixtures for practical industrial application. Research has been done on the healing of cracks in aged concrete, but it seems that very little is known about the actual healing mechanism and its conditions. The mechanism is generally attributed to the hydration of previously unhydrated cement grains and may be aided by carbonation, since the bonding material so formed contains crystals of calcium carbonate and calcium hydroxide. Recently, several researchers have observed the formation of cementitious products such as AFt, AFm and $CaCO_3$ in cracks and calcium hydroxide crystals in air voids in cracked concrete [1]. It was hypothesized that these hydration products had been leached and recrystallized in water that had flown through the crack. However, although it is generally acknowledged that unhydrated cement grains affect the recrystallization of cracked concrete, no detailed examinations have been reported on the healing conditions for this cementitious recrystallization. For plain concrete with a normal or high water/cement ratio, which does not have any self-healing ability, the self-healing phenomenon is mainly controlled by the amount of mixing water. Therefore, in order to give self-healing capabilities to a cementitious composite at normal or high water/cement ratios, the self-healing properties of concrete incorporating various mineral admixtures as a partial cement replacement were investigated in terms of recrystallization on cracked concrete and the effects of various carbonates for the recrystallization.

This study focused on two primary issues: (1) experimental and analytical design of cementitious materials with self-healing capabilities, (2) development of a self-healing concrete using new cementitious materials at normal water/binder ratio [over W/B=0.45] [1, 2].



(a) (b)

(a) Normal concrete (with waterproof work)
(b) Self-healing concrete (without waterproof work)

Fig.1 Application concept of self-healing concrete for the water leakage of underground civil infrastructures as tunnels

2. TEST PROGRAMS

2.1 Materials

(1) Cement

Type I Japan Portland cement was used in all cementitious composite and concrete mixtures.

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(2) Mineral admixtures & Chemical agents

In order to compare the self-healing capability of cementitious composite with various compositions, mineral admixtures such as expansive agent, geo-materials and chemical agents were used. These materials were prepared based on self-healing performance as shown in Fig. 2. The expansive agent, two geo-materials and chemical agent used were commercial products produced in Japan. Geo-materials were used for this investigation; It has an SiO_2 content of 71.3% and an Al_2O_3 content of 15.4%. It shows the XRD pattern of geo-material, which reveals that it is mainly SiO_2 and sodium aluminum silicate hydroxide $[Na_{0.6}Al_{4.70}Si_{7.32}O_{20}(OH)_4]$. It also contains montmorillonite, feldspar, and quartz, and its swelling is mainly caused by the swelling of montmorillonite, which is a swelling clay mineral. This type of geo-material swells 15-18 times its dry size when wetted by water as shown in Fig. 2(b). Polycarboxylate-based superplasticizer was also used in order to fabricate specimens.

2.2 Specimens

Table 1 shows the mix proportions of cementitious composite materials in this research. All cementitious composite pastes in this research were made at a constant water/cement ratio of 0.45. 200grams of cement were used to make the cementitious paste. All the prepared cementitious composite pastes were mixed manually for 5 minutes at ambient temperature. The slump test was then conducted on a small volume of paste using the mini-slump cone. The dosage of each superplasticizer was set in the range of 0.8 – 2.50% in order to obtain the initial target flow. Paste flow was measured at 30 minute intervals up to 90 minutes from mixing.

Table 1 Mix-proportions of cementitious composite materials based on the self-healing design

Sample	OPC	Expansive agent	Geo-Materials	Chemical additives
I	90%	O	O	
II	90%	O	O	O
III	90%	O	O	O

2.3 Estimation method of cementitious composites for crack healing

Cementitious composite pastes cylinders 5Φ x 10 cm in size were prepared following the mini-slump test. They were cured for 120 days and then artificially cracked in order to clarify the self-healing process as shown in Fig. 3. Crack width was controlled between 0.1 and 0.3 mm in consideration of the maximum tolerable crack widths according to construction codes. After cracking, the specimens were again water cured for 200 days.

2.4 Verification of self-healing capability on fabricated self-healing concrete

All cementitious composite materials with self-healing capability [called pre-mixed products] in this research were manufactured in the laboratory. Table 2 shows the mixing proportions of concretes; a W/B ratio of 47.3% and a S/A ratio of 46.6% were applied to all concretes. Slump flow of concrete was measured at the initial point and after 30 and 60 minutes. Self-healing concrete 10Φ x 20 cm cylinders were prepared after conducting the concrete slump test.

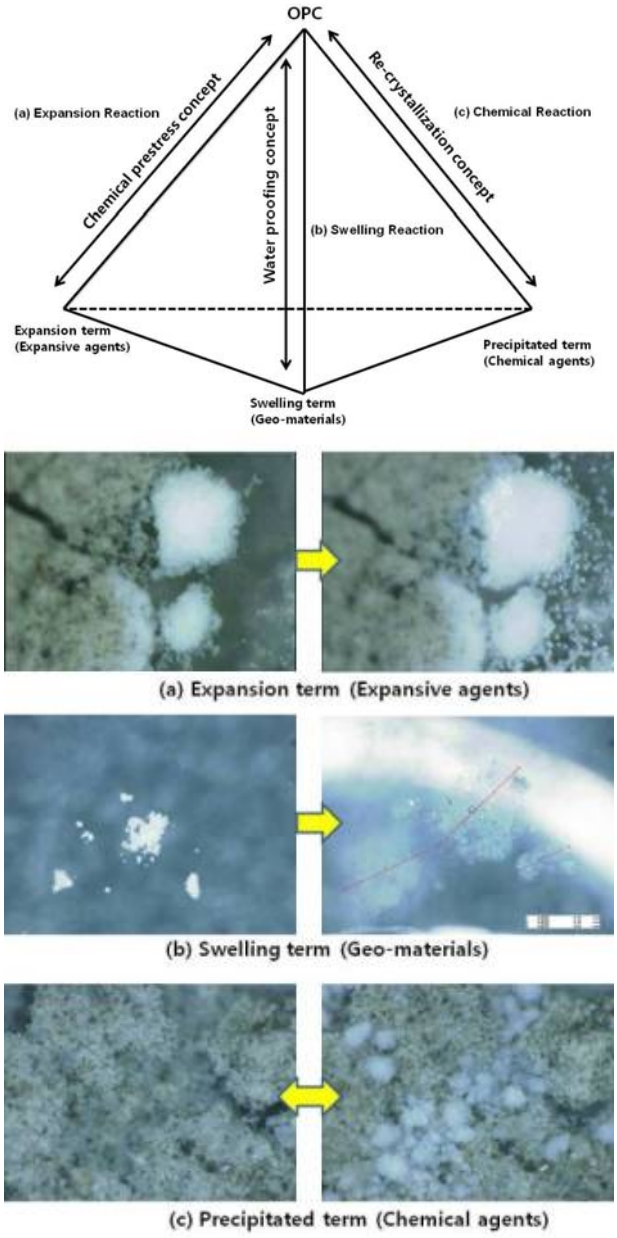


Fig.2 Design of cementitious composite materials with self-healing capability

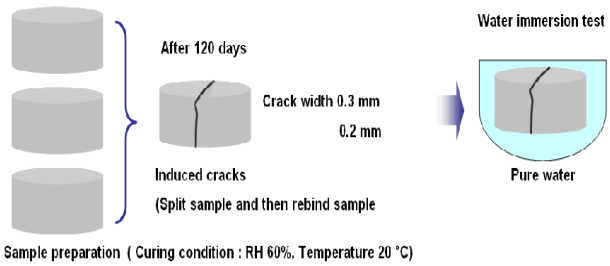


Fig.3 Assessment of self-healing through cracks (experimental method)

They were cured for 1 month and then artificially cracked in order to clarify the self-healing process. Crack width was controlled between 0.1 mm and 0.3 mm according to the maximum allowable crack widths dictated by construction code. The specimens were then water cured for another 1 month after cracking.

Table 2 Mixing proportion of concrete

Binder (B) (kg/m^3)	OPC (93%)	344.1
	Pre-mixed Products (7%)	25.9
Water/Binder (kg/m^3)	W (W/B= 47.3%)	175
Sand (kg/m^3)	S	809
Gravel (kg/m^3)	G	920
Superplasticizer (% B by weight)	SP (1.15~1.35%)	4.26~4.99

3. RESULTS AND DISCUSSION

3.1 Self-healing capability of cementitious composite materials

(1) Effect s of geo-materials on the self-healing

In order to develop cementitious composite materials with self-healing capability compared to normal cement without self-healing capability at the normal W/C ratio, sample I [OPC + Expansive agent + Geo-materials] was investigated considering expansion and swelling terms as shown Fig 2.

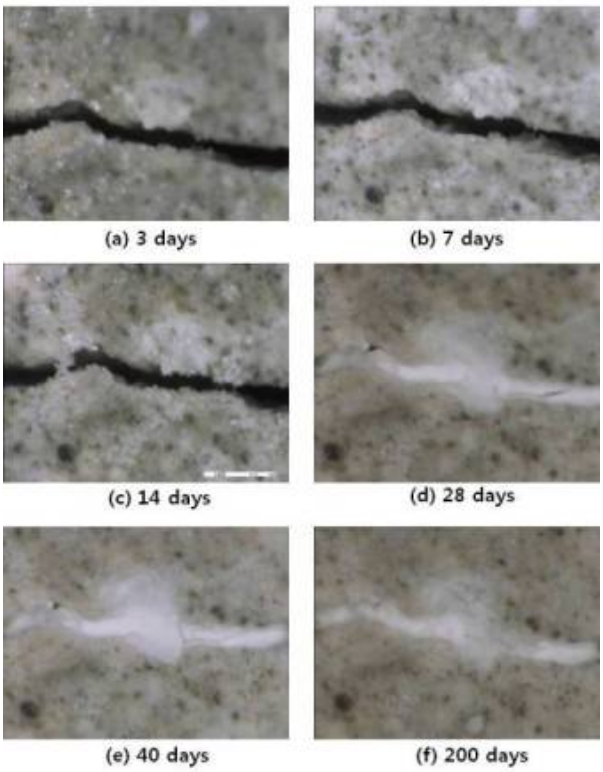


Fig.4 Process of Self-healing on the sample I pastes at normal water/binder ratio of 0.45 (the three-component system)

Fig.4 shows the healing process of the cracked three-component system under water supply. In this case, the crack with an initial width of 0.2 mm was almost healed after 28 days. Rehydration products between cracks were clearly observed after 14 days, and the cracks self-healed perfectly even though there were small cracks between the rehydration products after 200 days, as shown in Fig.4 (f). Fig.5 shows the entire self-healed shape of the cracked specimen by top, side, bottom and cross-section. It was composed of different phases between the original and self-healing zone. Therefore, microscopy and SEM with EDS (Energy Dispersive X-ray Spectroscopy)-detector were carried out to investigate the morphology, shape, and size of re-hydration products and to clarify re-crystallization.

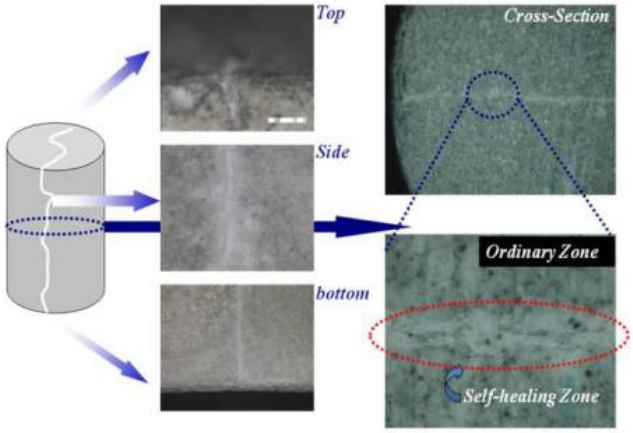
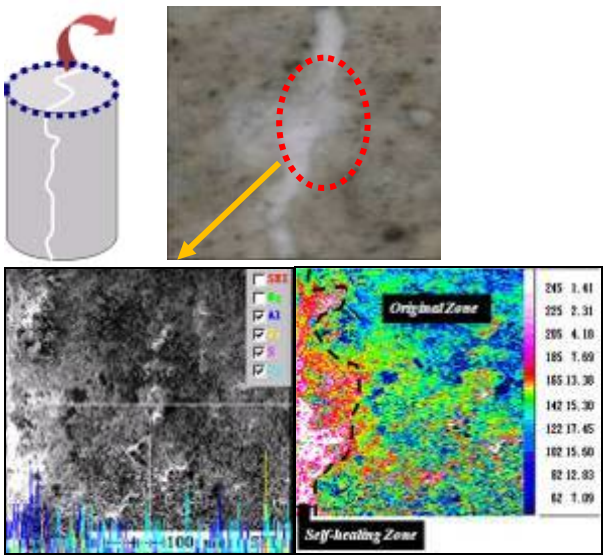


Fig.5 Self-healed shape of cracked pastes according to regions such as top, side, bottom and cross-section [in case of Sample I]



(a) (b)

Fig.6 Self-healing phenomenon of crack by crystallization of aluminosilicate phases on the cementitious pastes incorporating expansive agent and Geo-materials [Surface Analysis of specimen]

Fig. 6 shows the re-hydration products on the surface of the specimen between the original and self-healing zones in case of sample I. Fig. 6 (b) shows

the X-ray map and spectra taken from rehydration products. It was found that the re-hydration products were mainly composed of high alumina silicate materials as shown in the X-ray mapping results. The self-healing zone was composed of modified gehelite phases (C-A-S-H) with high alumina ions compared to original zone. This self-healing phenomenon seems to be related to the crystallization by aluminosilicate with calcium ion.

In general, geopolymers are formed by the polymerization of individual aluminate and silicate species, which are dissolved from their original sources at high pH in the presence of alkali metals. These structures can take one of three types: poly(sialate) (-Si-O-Al-O-), poly(sialte-siloxo) (Si-O-Al-Si-O) and poly(sialate-disiloxo) (Si-O-Al-O-Si-O-Si-O). Typical geopolymer composition can be expressed as $nM_2O \cdot Al_2O_3 \cdot xSiO_2\ y \cdot H_2O$, where M is an alkali metal. In terms of chemical composition, the major difference between geopolymers and Portland cement is calcium.

In this research, it was found that the alkaline activation of Geo-material A in the presence of calcium hydroxide led to the formation of an amorphous calcium aluminosilicate between cracks, which had the same characteristics as a geopolymeric gel in a highly alkaline environment as shown in Fig.6. Fig.7 shows a detailed comparison between geopolymeric gel phase from the self-healing area and hydrogarnet phase from the original area by SEM images. This geopolymeric gel size was smaller than 2μm and the crack interface phases of the original zone formed several hydrogarnet phases made with CSA(expansive agent). This indicates that hydrogarnet phases or AFt phases, which were formed from expansive agent, play an important role in crack-bridging materials. EDS analysis also revealed that most of the modified geopolymeric gel was structured by dense phases as compared to hydrogarent phases.

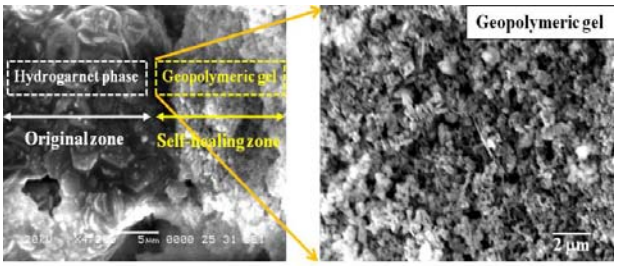


Fig.7 Comparison between geopolymeric gel phase from self-healing area and hydrogarnet phase from original area

This seems effective for sealing against water leakages. From these results, it was concluded that application of geo-materials are desirable for the application of self-healing concrete. However, self-healing velocity for rapid water proof effect of water leakage needs to be improved in order to apply for underground civil infrastructures. Therefore, sample II and sample III have been tested in order to improve this. These results are reported and discussed in the following section.

(2) Effects of chemical additives on the self-healing (Upgrade design I)

Fig. 8 shows the healing process of cracked parts based on upgrade design I (sample II) under water supply. In this case, the crack with an initial width of 0.2 mm was self-healed after re-curing for 3 days. It was found that the self-healing velocity improved remarkably by re-crystallization.

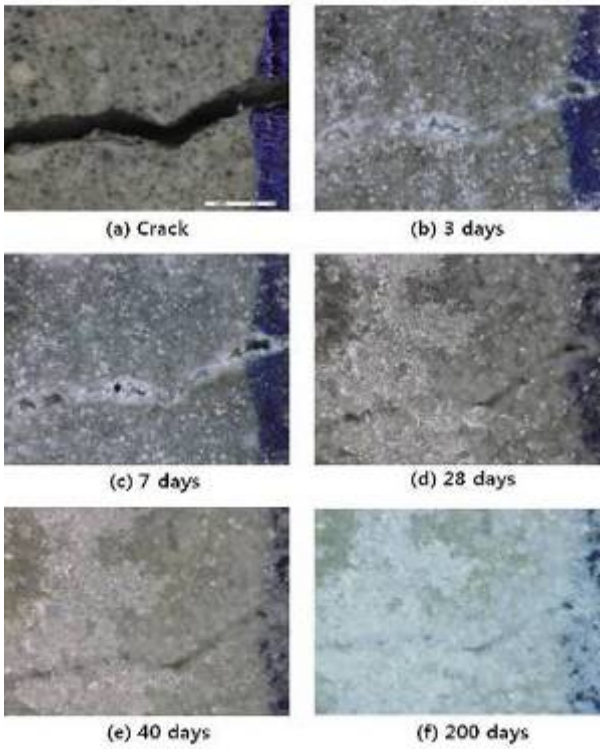
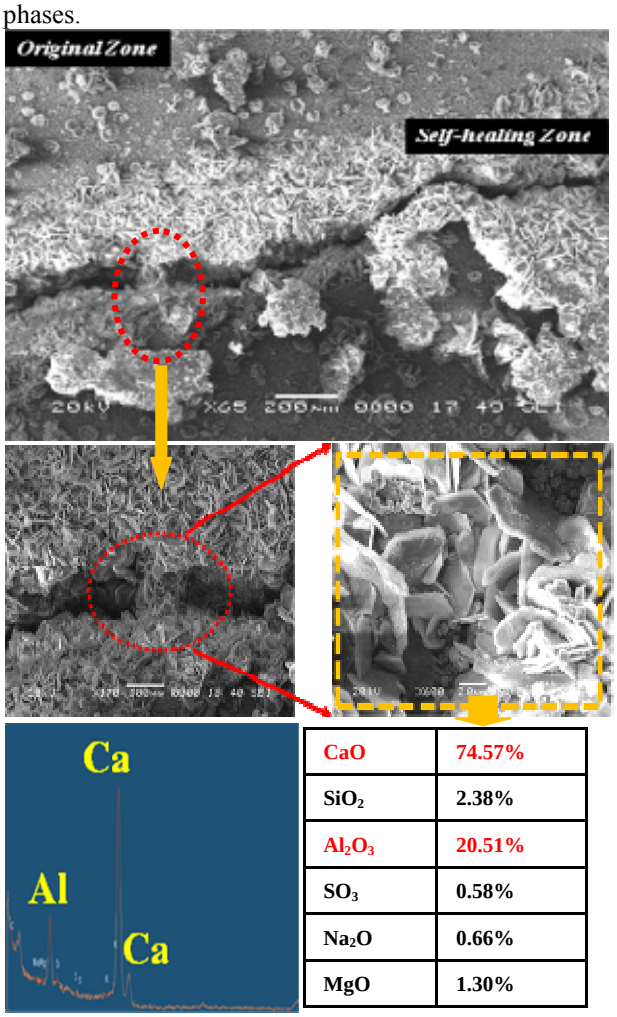


Fig.8 Self-healing process of cementitious composite materials based on the upgrade design I (Sample II) [Water/Binder ratio = 0.45]

However, its chemical stability seemed to be weak after re-curing for 7 days, and the crack reopened as shown in Fig.8 (c). This phenomenon indicates that these products are sensitive to the pH condition and the water solubility; in other words, its chemical durability should be also improved for the long time durability. After 28 days re-curing, the crack closed again by formation of self-healing products. Fig. 9 shows SEM images, X-ray map, and spectra taken from re-hydration products. It was observed that re-hydration products were mainly composed of hydrogarnet phases (C-A-H) and calcite ($CaCO_3$) phases, as shown in the X-ray spectra results. It was also found that re-hydration products on the surface of the specimen between the original zone and self-healing zone were different compared to that of sample I. This formation reaction seems to be related to the improvement of self-healing velocity and chemical stability of re-hydration products. As mentioned above, the formation of self-healing products was faster than that of the previous test case due to the of formation of calcium hydroxide[$Ca(OH)_2$:CH]phases and C-A-H phases at

the initial re-curing stage. However, in general, chemical stability of CH was lower than that of C-A-H. CH phases were consumed in order to form C-A-S-H, C-A-H phases and AFt phases as shown in Fig.10. This indicates that chemical stability of re-hydration products can be decreased at the initial re-curing stage by the volume change of CH in order to transfer other phases.



CaO	74.57%
SiO_2	2.38%
Al_2O_3	20.51%
SO_3	0.58%
Na_2O	0.66%
MgO	1.30%

Fig.9 Self-healed re-hydration products in crack by hydrogarnet phases (C-A-H) and calcite phases ($CaCO_3$) in case of sample II

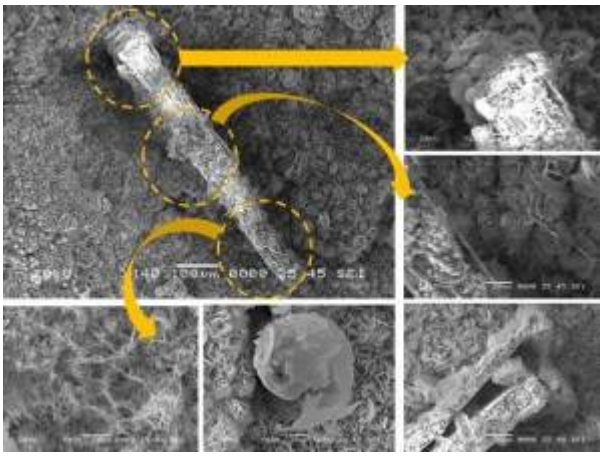


Fig.10 Formation of hydrogarnet phases and AFt phases from calcium hydroxide

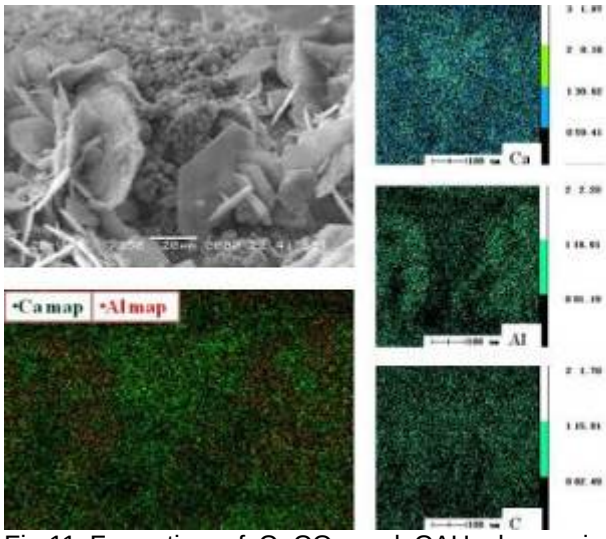


Fig.11 Formation of $CaCO_3$ and CAH phases in self-healed area (X-ray mapping results of hydrogarnet phases and calcite phases)

Calcite was then formed between CAH phases by the continuing re-hydration, shown in Fig. 11. It was found that this was the main mechanism of the upgrade design I for self-healing. Therefore, in order to improve the physical and chemical stability of these re-hydration products and precipitated products as calcite or calcium salts in initial term period, upgrade design II (sample II) was suggested and studied in detail in the following section.

(3) Effects of chemical additives on the self-healing (Upgrade design II)

The objective of upgrade design II was to consider the chemical stability as well as the improvement of self-healing velocity for the cementitious composite materials. Fig.12 shows the process of self-healing of sample III under water supply. In this case, the crack was healed after re-curing for 3 days, as shown in Fig.12 (b). It was found that this design had greater chemical stability compared to sample II. Chemical additives significantly affected the formation of re-hydration products with high chemical stability as compared to the previous design.

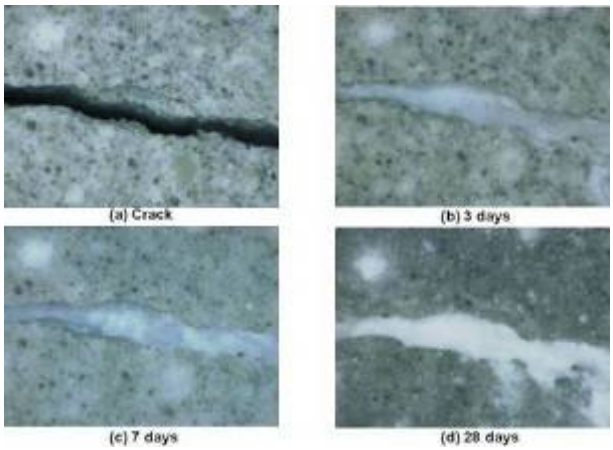


Fig. 12 Self-healing process of sample III [Upgrade design II, Water/Binder ratio of 0.45]

Furthermore, it didn't show loss of re-crystallization products compare to sample I after re-curing 3 days as shown in Fig. 12 (c).

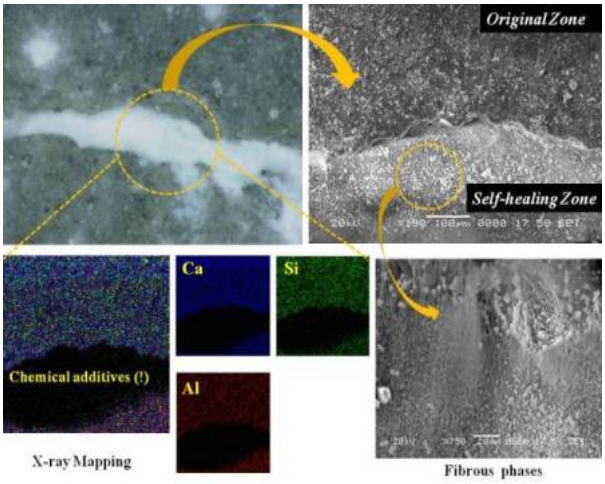


Fig.13 X-ray mapping results of fabricated fibrous phases and C-A-S-H phases [Upgrade design II, Water/Binder ratio of 0.45]

These rehydration products were mainly composed of fibrous phases from chemical additives and calcite as shown in Fig.13. This indicates that these fibrous phases, which were formed from chemical additives, play an important role in crack bridging between cracks. From these results, it was concluded that various composite upgrade designs are desirable for the application of self-healing concrete. Premix cementitious composite materials based on these results were prepared for concrete mixing in order to give self-healing capability. These results are reported and discussed simply in the following section.

3.2 Self-healing capability of self-healing concrete

In case of self-healing concrete, the crack was significantly self-healed up to 28 days re-curing. Figure 12 shows the healing process of cracked self-healing concretes made at the same mixing condition as the conventional concrete. A 0.15 millimeter crack was self-healed after 3 days re-curing, as shown Fig. 14 (b).

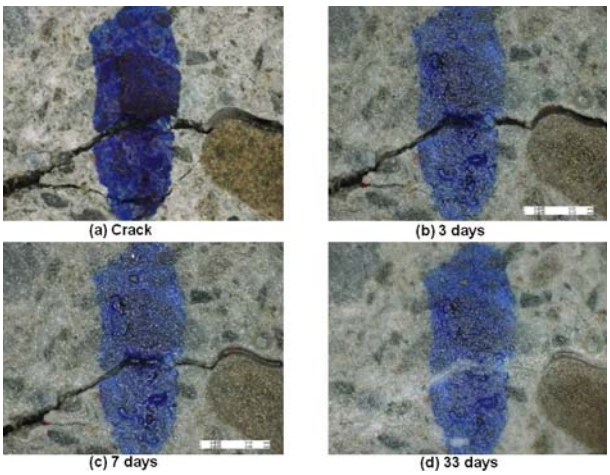


Fig.14 Process of self-healing on self-healing concrete at water/binder ratio of 0.47

After re-curing for 7 days, the crack width decreased from 0.22 millimeters to 0.16 millimeters. Furthermore, it was almost completely self-healed at 33 days as shown in Fig. 14 (d).

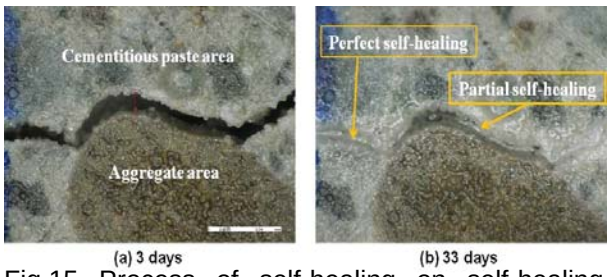


Fig.15 Process of self-healing on self-healing concrete at water/binder ratio of 0.47

This recovery appeared to include self-healing phenomenon such as the swelling effect, expansion effect and re-crystallization as mentioned above. However, in general, it should be considered that cracked aggregate didn't heal by itself. Self-healing at the initial stage occurred in the cementitious paste area between cracks as shown in Fig. 15, resulting in the healing between the cementitious paste and surface of aggregate. However, this type of crack did not perfectly self-heal at the same time as shown in Figure 15. Some re-crystallization structure from the cementitious paste was deposited on the aggregate surface or in the crack between aggregates. Therefore, this indicates that cracks of these types will take more time for self-healing.

4. CONCLUSIONS

In this study, the self-healing properties of concrete using various mineral admixtures were investigated.

(1) Self-healing capability was significantly affected by aluminosilicate materials and various modified calcium composite materials.

(2) The essential properties such as expansion, swelling and re-crystallization for self-healing design were analyzed and discussed.

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