Scientific paper

Crack Self-healing Behavior of Cementitious Composites Incorporating 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 structure. 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 self-healing phenomenon of autogenous healing concrete using geo-materials for practical industrial application was investigated. Moreover, a self-healing concrete was fabricated by ready-mixed car in a ready-mixed concrete factory, then used for the construction of artificial water-retaining structures and actual tunnel structures. The results show that the crack of concrete was significantly self-healed up to 28 days re-curing. Crack-width of 0.15mm was self-healed after re-curing for 3 days and the crack width decreased from 0.22 mm to 0.16 mm after re-curing for 7 days. Furthermore, it was almost completely self-healed at 33 days. It was founded that this phenomenon occurred mainly due to the swelling effect, expansion effect and re-crystallization. From these results, it is considered that the utilization of appropriate dosages of geo-materials has a high potential for one of new repairing methods of cracked concrete under the water leakage of underground civil infrastructure such as tunnels.

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 (Breugel 2007). 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** (Ahn *et al*. 2009).

Recently, many potential markets of self-healing cement-based materials have been reported by civil engineers from many different countries as follows. First, the cost for reconstruction of bridges, in USA, has been estimated between $20 and $200 billion. The average annual maintenance cost for bridges in that country is estimated at $5.2 billion. Comprehensive life cycle analyses indicate that indirect costs due to traffic jams and associated loss of productivity are more than 10 times the direct cost of maintenance and repair (Breugel 2007). Especially, the average age of U.S. bridges is 42 year, so they were deemed either structurally deficient or functionally obsolete last year by the U.S. Department of Transportation. In March 2009, it is report that the American Society of Civil Engineers gave U.S. infrastructure a grade of "D" reflecting delayed maintenance and chronic underfunding; it estimates that $2.2 trillion is needed over the next five years to bring that grade up to a grade of "B" (Broek 2009).

For the United Kingdom, repair and maintenance accounts for almost 45% of the UK's activity in the construction and building industry. In case of Netherlands, one third of the annual budget for large civil engineering works is spent on inspection, monitoring, maintenance, upgrade, and repair. In case of Japan, East Japan Railway Company reported that maintenance and repair cost of railway bridges and tunnels are estimated at $10 billion. In the point of this, actually, if crack self-healing concrete can minimize cracks, we can get a longer life and more sustainable civil infrastructures (Ahn *et al.* 2007).

The performance of structures with elapse of time is often reported with graphs like that shown in **Fig. 2**. In general, for high durability and normal designs, increasing the volume of cracks in a structure increases the repair costs as shown **Fig. 2(b)**. However, when considering the self-healing design, if a crack occurs, it will be healed autogenously after minor damage, as shown **Fig. 2 (c) and (d)**. This concept is one of the maintenance-free methods which, apart from saving direct costs for

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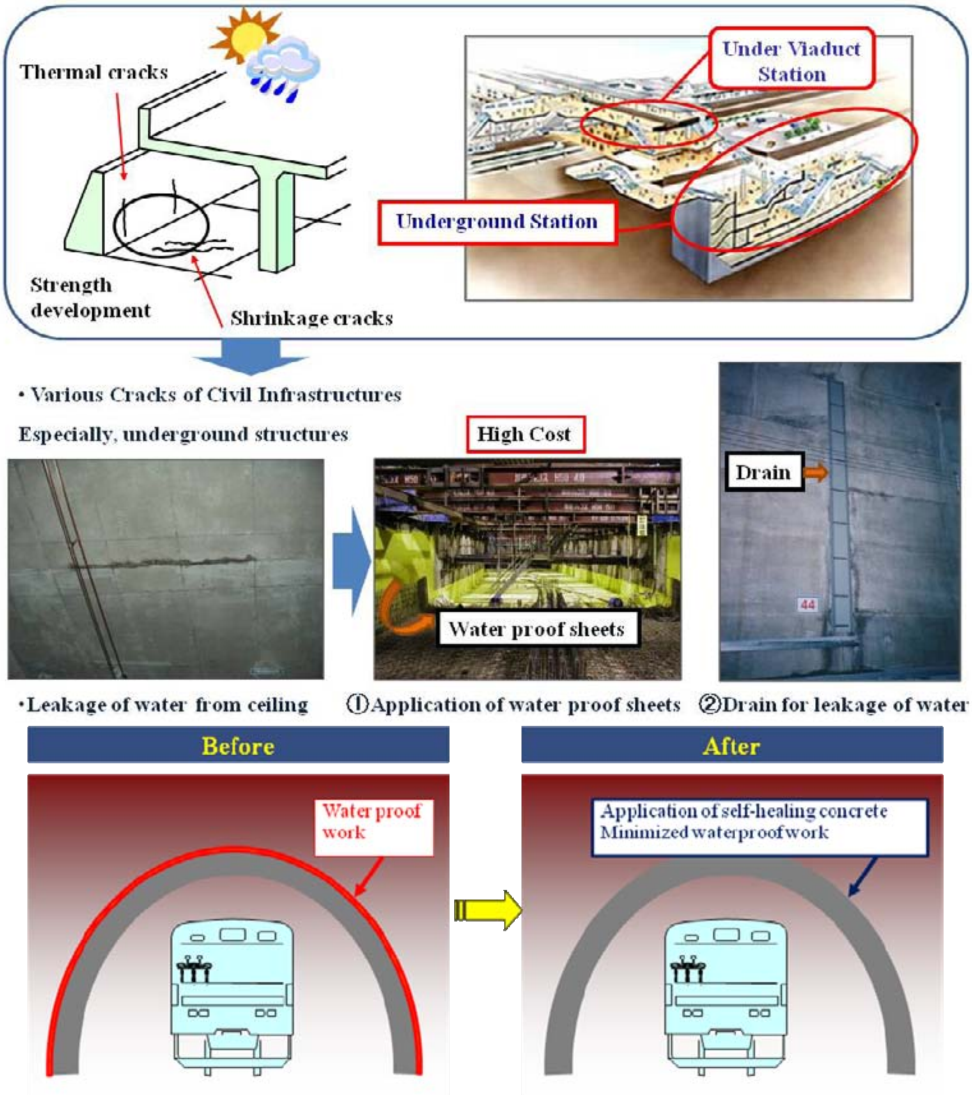
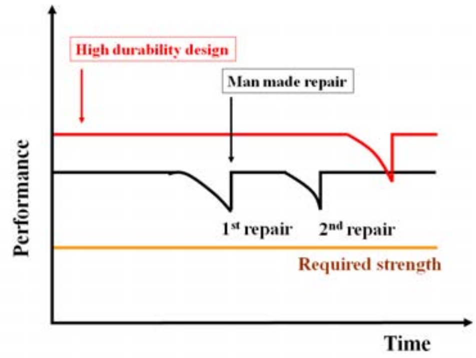


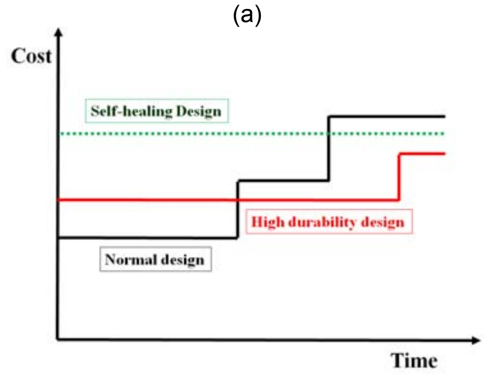
Fig. 1 Application concept of self-healing concrete for the water leakage of underground civil infrastructures as tunnels.

maintenance and repair, reduces the indirect costs – a saving generally welcomed by contractors. Furthermore, general construction philosophy has begun to change from [Design and Construction concept: constructor responsibilities for maintenance and repair of structures are limited] to [Design, Construction and Maintenance concept: constructor has responsibilities including the maintenance, monitoring and repair for life cycle of structures] as shown **Fig. 2**. This trend shows that it is necessary for both the industrial and research fields to develop concrete including self-healing crack concepts in the near future (Breugel 2007).

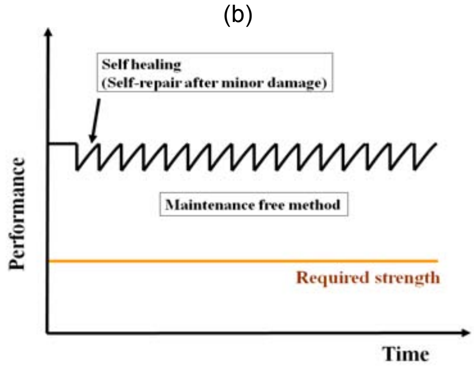
Therefore, the aim of this study is to develop autogenous healing concrete using various mineral admixtures for practical industrial application. Research has been done on the healing of cracks in aged concrete, but it seems that very little is known about the actual healing mechanism and its conditions. 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 (Homma *et al.* 2009). 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 (Kishi *et al.* 2007). 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 abilities to a cementitious composite at normal or high water/cement ratios, the self-healing properties of concrete incorporating geo-materials as a partial cement replacement were investigated in terms of recrystallization on cracked concrete and the effects of various carbonates for the recrystallization.



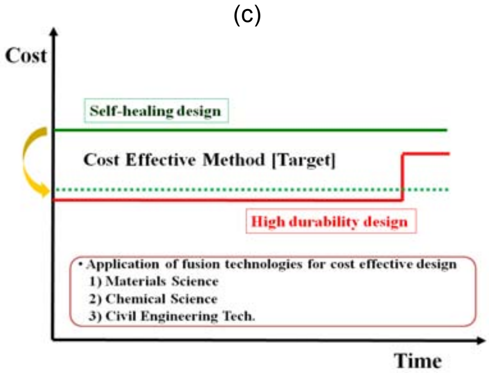
(a)



(b)



(c)



(d)

Fig. 2 (a), (b): Performance (a) and costs (b) over time for normal structures (black line) and high durability design structures (red line). (c), (d): Performance (c) and cost (d) over time of the structure made with self-healing concrete (Breugel. 2007).

Especially, it was investigated based on consideration with self-healing performance of materials and cost effectiveness as shown **Fig. 2(d)**, in order to apply self-healing concrete as a new method for crack control and enhanced service life in concrete structures.

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] (Ahn *et al*. 2008).

2. Experimental methods

2.1 Materials

(1) Cement

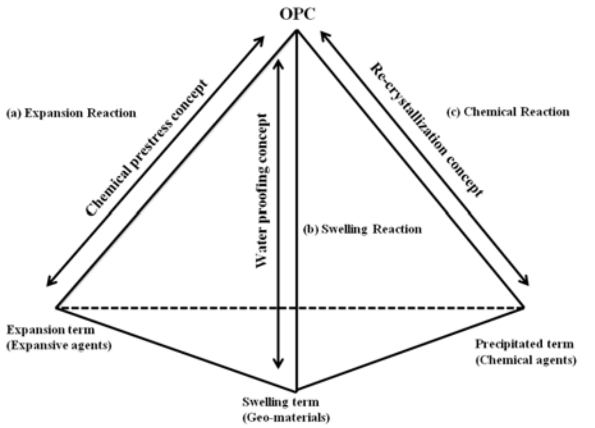
Type I Japan Portland cement was used in all cementitious composite and concrete mixtures.

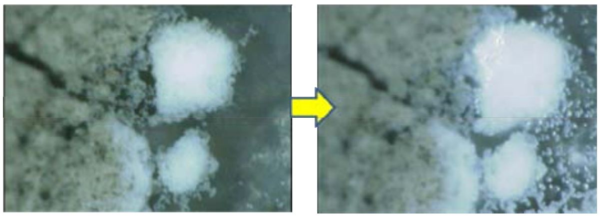
(2) Mineral admixtures & Chemical agents

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 reported in the previous research shown in **Fig. 3** (Ahn, 2008). The expansive agent, two geo-materials (A, B) and chemical agent used were commercial products produced in Japan. K type of expansive agent was used for this investigation. It consists of three mineral admixtures, $C_4A_3\bar{S}$ (hauyne), $CaSO_4$ (anhydrite) and CaO (free lime). Geo-material A was 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. 3(b)**, because the montmorillonite mineral is a 2:1 layer consisting of an octahedral sheet sandwiched between two silica sheets as shown in **Fig. 4**. Chemical structure of geo-material B is also similar to structure of geo-material A, however, its chemical composition is a little bit different. In case of chemical agent, various types of carbonates such as $NaHCO_3$, Na_2CO_3 and Li_2CO_3 (etc.) were selected to supply the effect of cementitious recrystallization with expansive agent in air voids in cracked concrete.

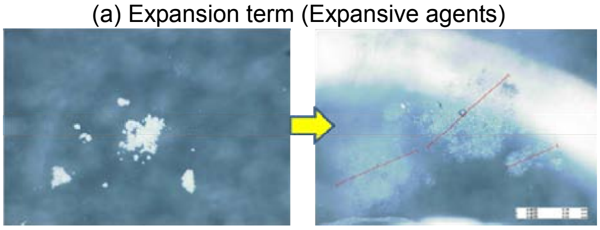
(3) Superplasticizers

Polycarboxylate-based superplasticizer was also used in order to fabricate specimens. Three types of superplasticizer: lignin-based AE plasticizer (SP I), polycarboxylate-based superplasticizer (SP II: standard type), and

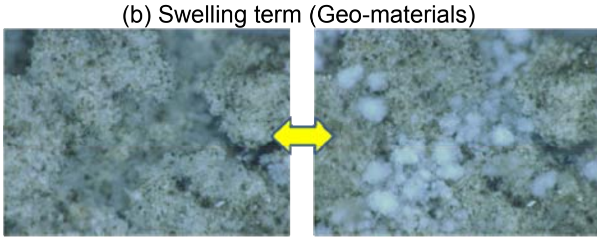




(a) Expansion term (Expansive agents)



(b) Swelling term (Geo-materials)



(c) Precipitated term (Chemical agents)

Fig. 3 Design of cementitious composite materials with self-healing capability.

polycarboxylate-based superplasticizer (SP III: slump retention type) were used in order to clarify the effects of each superplasticizer on the fluidity of paste and concrete which include cementitious composites with self-healing capability.

2.2 Estimation method of mini-slump for fresh properties

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. 200g of cement were used to make the cementitious paste. When the superplasticizer was added, the water content of the superplasticizer was ignored with regards to the mixing water (the solid content of the superplasticizer was around 25%). 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 procedure involves transferring the cement paste in the mini-slump cone, then lifting the cone smoothly and quickly. The area of the paste spread on an acrylic plate is measured and expressed in millimeters. 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.

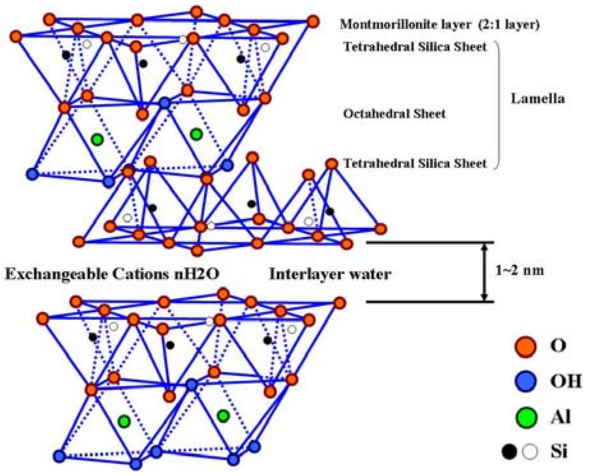


Fig. 4 Chemical structure of geo-material (Li, 1995).

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. 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** and **Table 3** show the mixing proportions of concretes; a W/B ratio

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

Sample	OPC	Expansive agent (CSA)	Geo-Materials (A ,B type)	Chemical additives
I	90%	O	O	
II	90%	O	O	O
III	90%	O	O	O

Table 2 Mixing proportion of concrete.

Binder (kg/m^3)	B	370
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

Table 3 Mix-proportions of binder.

Sample	Binder		
	OPC	Mineral admixtures	
		EA	SHA
Plain Concrete	100%	0%	0%
Expansive Concrete	90%	10%	0%
Self-healing Concrete	93%	5%	2%

EA : Expansive Agent, SHA : Self-Healing Agent

of 47.3% and an 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. The compressive strength of concrete was also measured by JIS A 1108 after 1, 3, 7, and 28 days. Self-healing concrete 10Φ x 20 cm cylinders were prepared after conducting the concrete slump test.

The experiments were divided into two stages. In the first stage, basic properties such as concrete slump and flow, compressive strength, TSTM test and water permeability were investigated in the laboratory. In the second stage, they were cured for 1 month and then artificially cracked in order to clarify the self-healing capability and 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.

3. Results and discussion

3.1 Relationship between the fluidity of basic design materials and the amount of superplasticizer adsorbed

In general, it is not easy to test the compatibility of a particular combination of cementitious composites incorporating new materials and superplasticizer in concrete because performing concrete trial batches consumes time, materials, and energy. Several methods involving smaller amounts of material, which are easier to implement and repeat, have been developed. These are generally based on studying the rheological behavior of a grout. In particular, two methods are widely used: the mini-slump method and the marsh cone method. For the mini-slump test, it requires very little material to conduct and its results match well with concrete slump results. (Jiang *et al*. 2000).

Thus, this method was conducted for the investigation of fresh properties. When conducting the mini-slump test, the saturation point must be found for comparison between new fabricated composite materials and ordinary Portland cement paste (the “saturation point”: the minimum superplasticizer dosage required to achieve constant fluidity at 5 or 60 minutes) Therefore, the effect of superplasticizer types on the fluidity was investigated first in this study.

Figure 5 shows the effect of the addition of superplasticizers on cementitious composite pastes utilizing a two component system. For two-component systems, three materials such as CSA (expansive agent), Geo-material A and Geo-material B (two geo-materials) were added to the cement system. Water/binder ratio of all specimens was fixed at 0.45. When 0.8% of SPI was dosed in OPC and OPC incorporating CSA, the initial flow was measured to be close to the target flow. In case of the addition of CSA 10%, its fluidity is similar to that of OPC at the same dosage of SPI. However, in case of the addition of Geo-material A 10%, it lost its fluidity rapidly compared to other mineral admixtures because of water adsorption due to the swelling effect occurring rapidly and flow could not be measured for 5 mins. This shows that superplasticizers and mineral admixtures with no adsorption effect should be added in order to compensate for slump loss and increase the workability. In case of the addition of Geo-material B 10%, a little initial flow was lost compared to previous OPC test. However, there was no effect on the slump retention. In other words, CSA and Geo-material B are potentially highly useful for the co-mineral admixtures containing Geo-material A. **Figure 6** shows the fluidity results of cementitious composite pastes on the ternary system of OPC90%+CSA5%+Geo-materials5%. As mentioned above, the addition of Geo-material A resulted in rapid flow loss. Therefore, the dosage of SPI was increased to 3.0% in order to increase the fluidity. However, the addition of SPI (AE plasticizer) did not increase the workability. Increasing the dosage of SP I-3.0% resulted in rapid flow loss when compared to SP I-2.28%. Therefore, the superplasticizer type was changed from SPI to SPII for the next stage. SPII is a polycarboxylate-based superplasticizer which is applied normally, similar to the standard type. In case of the addition of SPII-3.0%, it shows similar retention effects of OPC and OPC90%+CSA10%.

From these results, it can be said that at a W/B =0.45, the addition of SPI in the tested ternary system was not effective in solving the incompatibility problem. SPII was more effective than SPI in fresh pastes containing CSA and Geo-material A according to the results of the mini-slump test. Therefore, specimens using this mix proportion were cured, following the previously mentioned test methods, for 120 days in order to check the self-healing capability.

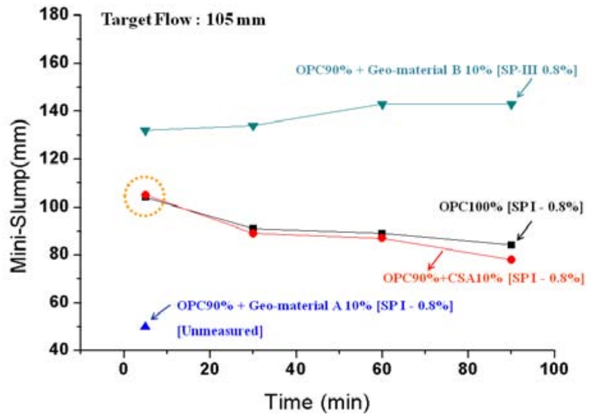


Fig. 5 Effect of the addition of superplasticizers on the mini-slump of cementitious composite pastes (two-component system or Binary system, Water/Binder ratio = 0.45).

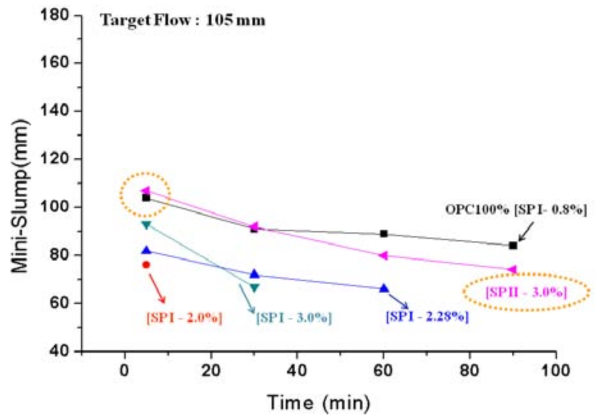


Fig. 6 Effect of the addition of suerplasticizers on the mini-slump of cementitious composite pastes in case of Sample I (OPC 90% + CSA 5% + Geo-materials 5%; three-component system, Water/Binder ratio = 0.45).

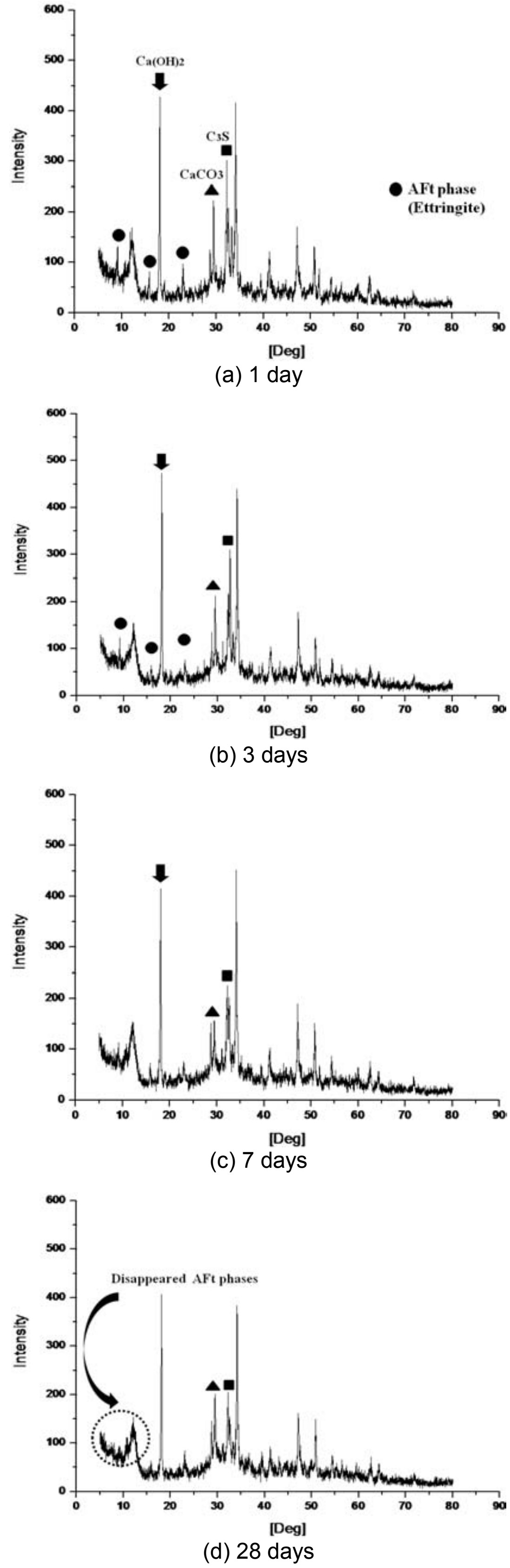


Fig. 7 Main hydration products of sample I [OPC 90% + CSA 5% + Geo-materials 5%] pastes at normal water/binder ratio of 0.45 (the three-component system).

3.2 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 3**. **Figure 7** shows the XRD pattern of [OPC90%+CSA5%+Geo-materials5%] pastes by hydration time. The XRD pattern of cement pastes incorporating CSA and Geo-material A were close to that of the two-component system incorporating expansive agent, except that the AFt phases (Ettringite) peak decreased from 3 days and disappeared after 7 days. This indicates that these phases can be transferred from hydrated aluminate phases to Stratlinigte (C-A-S-H).

Figure 8 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. 8 (f)**.

Figure 9 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-detector were carried out to investigate the morphology, shape, and size of re-hydration products and to clarify re-crystallization.

Figure 10 shows the re-hydration products on the surface of the specimen between the original and self-healing zones in case of sample I. **Figure 10 (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 (CASH) 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(sialate-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. 11**. **Figure 12** 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. 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.

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

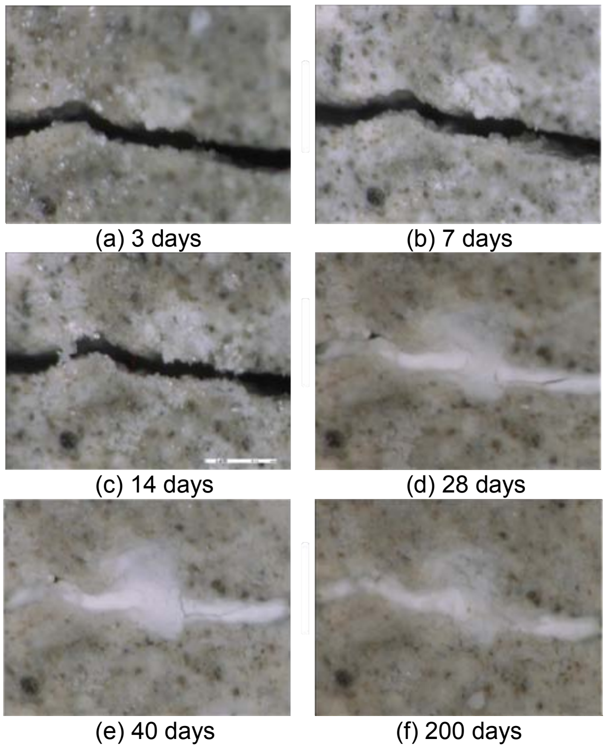


Fig. 8 Process of Self-healing on the sample I pastes at normal water/binder ratio of 0.45 (the three-component system).

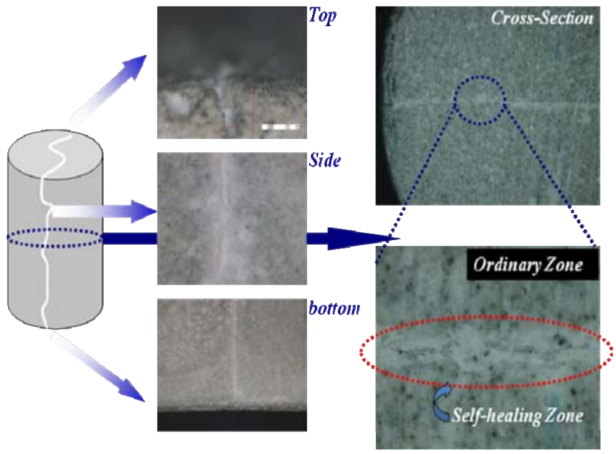
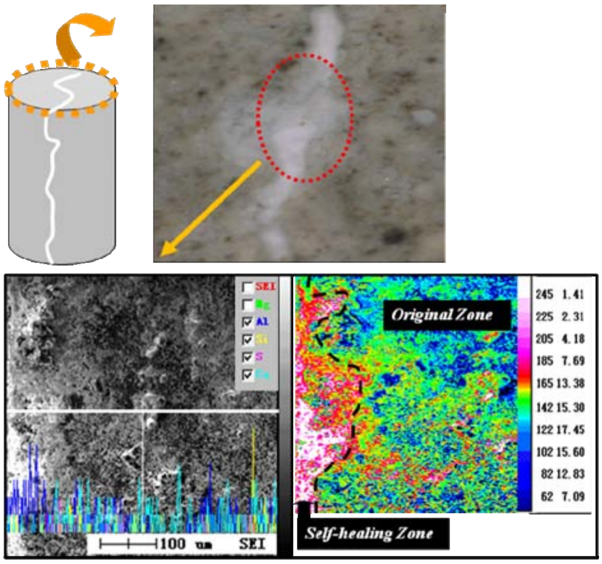
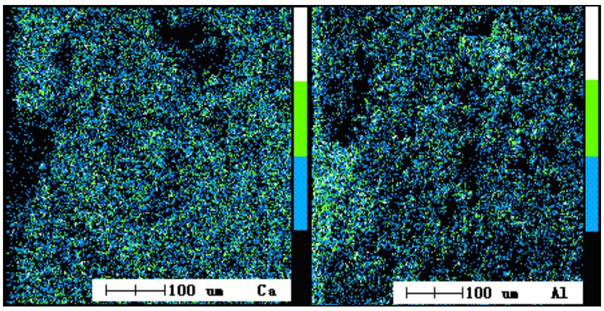


Fig. 9 Self-healed shape of cracked pastes according to regions such as top, side, bottom and cross-section [in case of Sample I].



(a) SEM-EDS image of self-healing area (line analysis)



(b) Comparison X-ray Mapping results between self-healing area and original area

Fig. 10 Self-healing phenomenon of crack by crystallization of aluminosilicate phases on the cementitious pastes incorporating expansive agent and Geo-materials [Surface Analysis of specimen].

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)

Figure 13 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. However, its chemical stability seemed to be weak after re-curing for 7 days, and the crack reopened as shown in **Fig. 13(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.

Figure 14 and **Fig. 15** show 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-H phases and AFt phases as shown in **Fig. 16**.

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. Calcite was then formed between CAH phases by the continuing re-hydration, shown in **Fig. 17**. 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. **Figure 18** 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. 18 (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. Furthermore, it didn't show loss of re-crystallization products compare to sample I after re-curing 3 days as shown in **Fig. 18 (c)**.

These rehydration products were mainly composed of fibrous phases from chemical additives and calcite as shown in Fig. 19. 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.

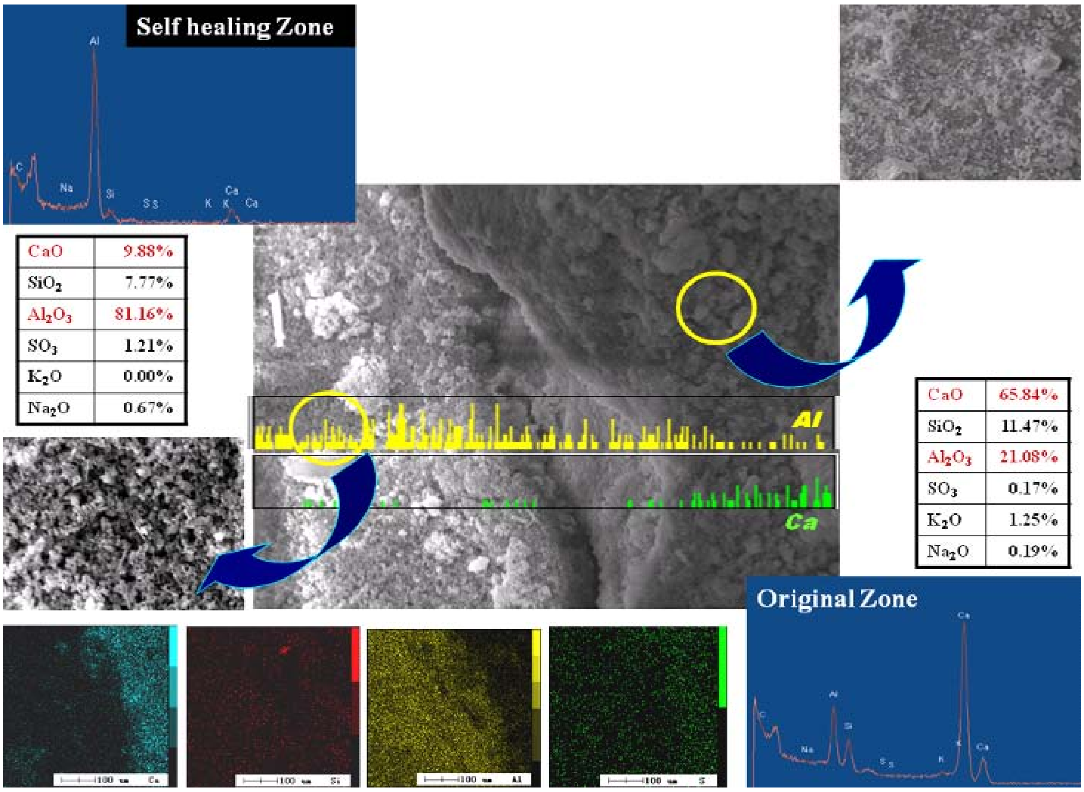
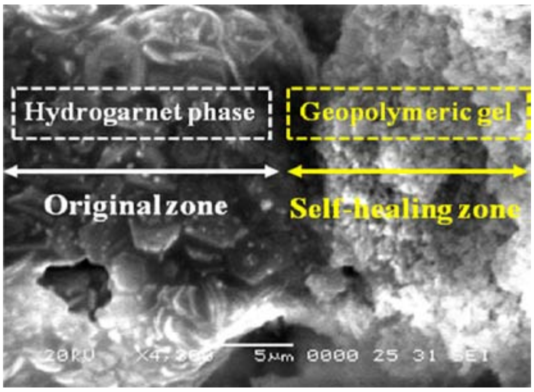
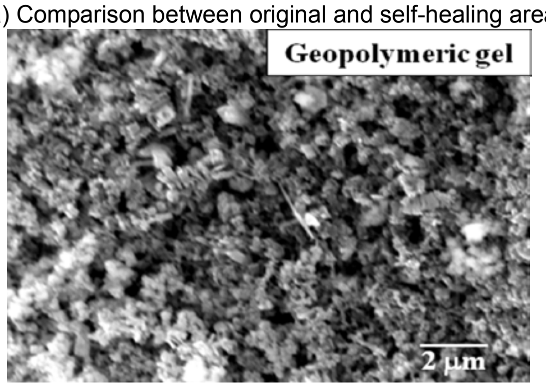


Fig. 11 Comparison X-ray mapping results between self-healing area and original area [Surface Analysis of cementitious pastes incorporating CSA and Geo-materials].

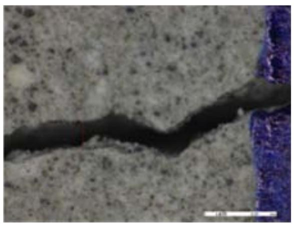


(a) Comparison between original and self-healing area

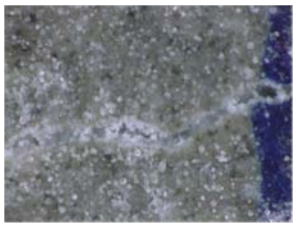


(b) Hydration products of Self-healing area

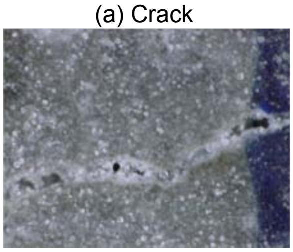
Fig. 12 Comparison between geopolymeric gel phase from self-healing area and hydrogarnet phase from original area



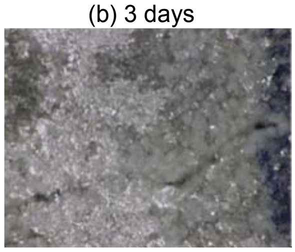
(a) Crack



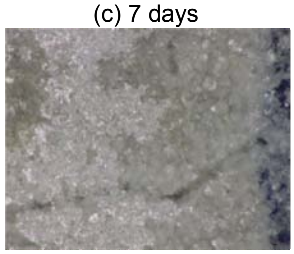
(b) 3 days



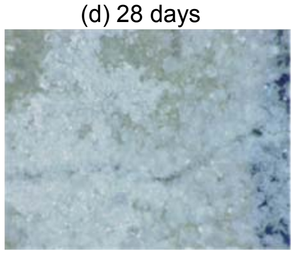
(c) 7 days



(d) 28 days

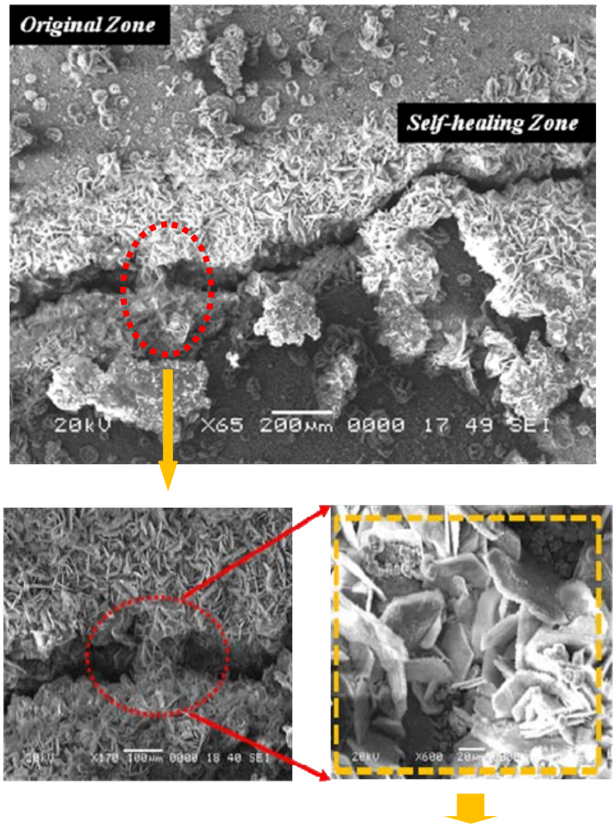


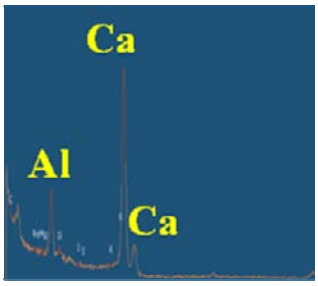
(e) 40 days



(f) 200 days

Fig. 13 Self-healing process of cementitious composite materials based on the upgrade design I (Sample II) [Water/Binder ratio = 0.45].





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

Fig. 14 Self-healed re-hydration products in crack by hydrogarnet phases (C-A-H) and calcite phases ($CaCO_3$) in case of sample II.

3.3 Workability of self-healing concrete

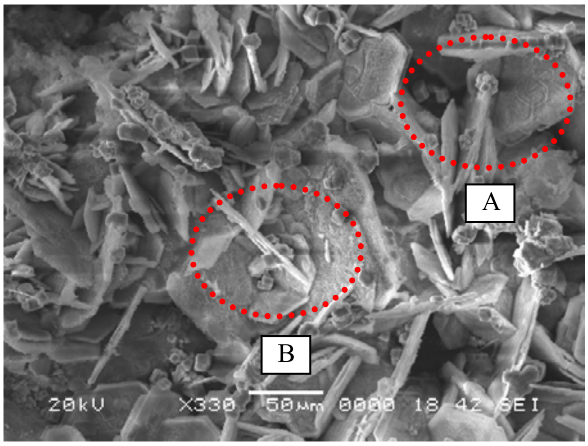
In order to fabricate self-healing concrete using self-healing cementitious composites, the concrete workability test was conducted at a ready-mixed concrete factory in Japan.

All materials except premix products, which were manufactured in the laboratory, were provided from the ready-mixed concrete factory as shown in **Fig. 20**. Concretes were mixed in 30~50 liter batches using materials in the field, including cement, sand, gravel and water. Concrete slump loss and slump flow were estimated as functions of time. The method for testing in the field was the same as in the laboratory.

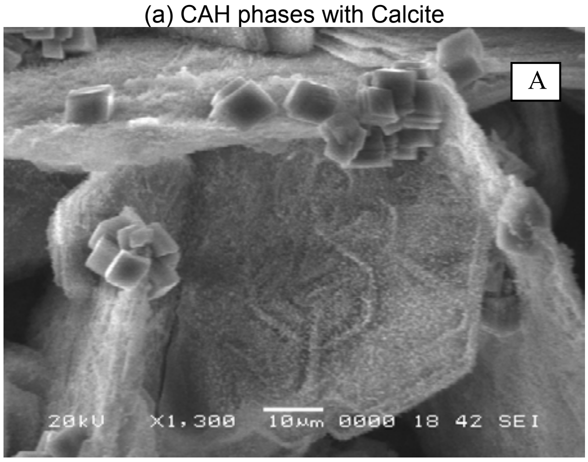
All concrete incorporating premixed products used a W/B ratio of 47.3% and S/A ratio of 46.6%, and premixed products replaced ordinary Portland cement by 7%. The dosage of each superplasticizer was decided in the range of 0.8 – 1.35 % in order to obtain the initial target slump of 21cm (target air: 4.5%). Concrete flow was measured up to 60 minutes at 30 minute intervals.

When 1.20 % of SP II was dosed in self-healing concrete, the initial slump value was measured close to the target slump value (21 cm). However, the target air requirement was not satisfied and the mix lost fluidity rapidly compared to normal concrete. Therefore, SP III was used in order to increase air and slump retention in the next experiment.

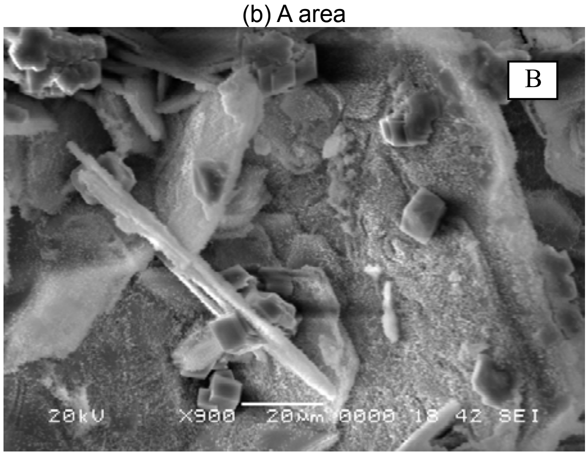
Figure 20 schematically shows the fabrication proc-



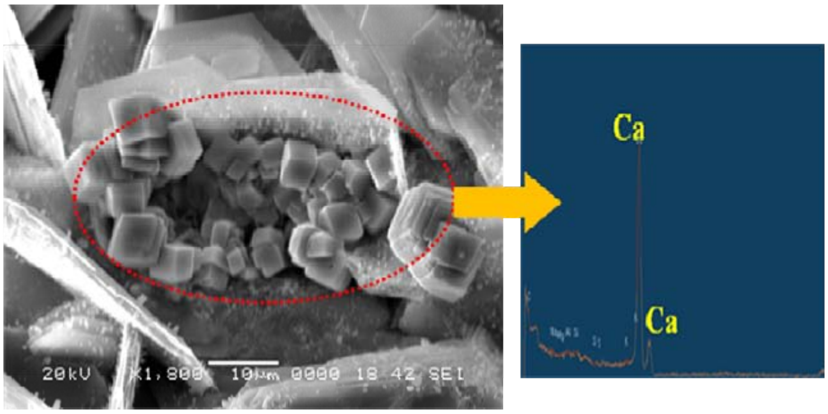
(a) CAH phases with Calcite



(b) A area



(c) B area



CaO	95.02%
SiO_2	0.40%
Al_2O_3	0.89%
K_2O	0.94%
Na_2O	2.14%
MgO	0.60%

Fig. 15 X-ray spectrum of calcite from re-hydration products between cracks in case of sample II.

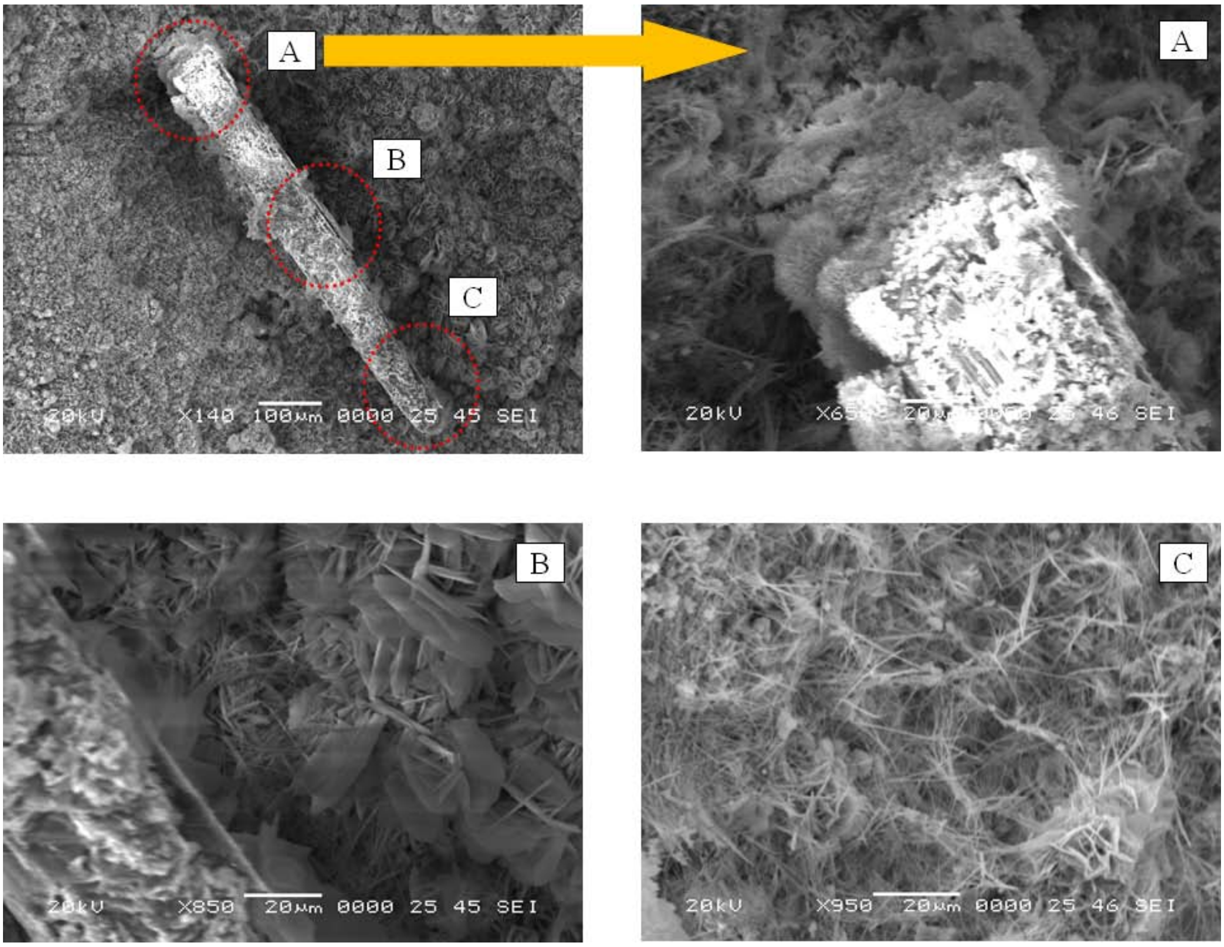
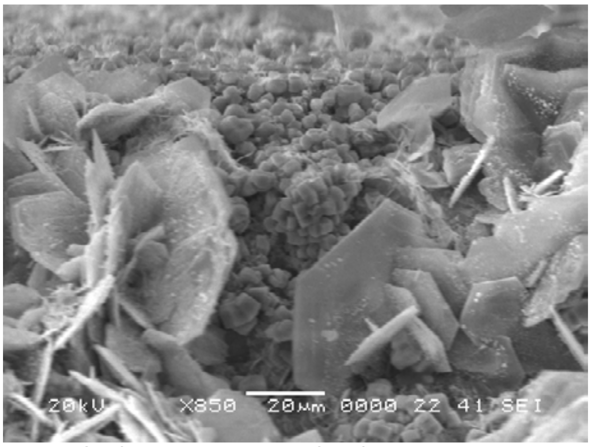


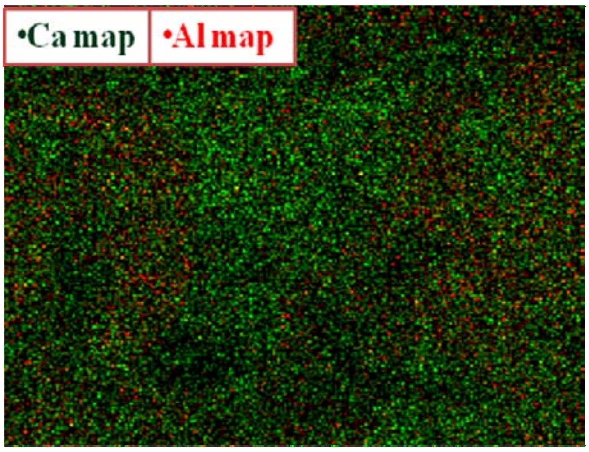
Fig. 16 Formation of hydrogarnet phases and AFt phases from calcium hydroxide.

ess of self-healing concrete in ready-mixed concrete plant. All processes were as the conventional concrete. Premixed products were handled similar to the input process of mineral admixture. A 3 m^3 of concrete was mixed for each artificial water-retaining structure. Mixing lasted about 60 seconds after the input of premixed products (generally, conventional concrete is mixed for 45 seconds).

The concrete was then retained for around 60 min in the ready-mixed car in order to check the slump retention effect. After 30 and 60 minutes, slump, slump flow, and air content were again measured. Slump was main-

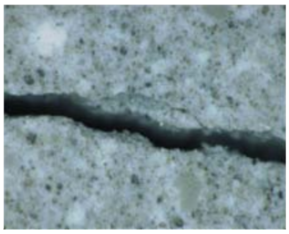


(a) Surface morphology of self-healing products

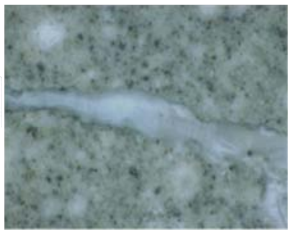


(b) X-ray mapping of Ca (green) ions and Al (red) ions

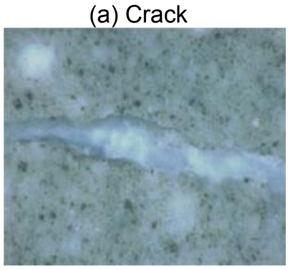
Fig. 17 Formation of $CaCO_3$ and CAH phases in self-healed area (X-ray mapping results of hydrogarnet phases and calcite phases).



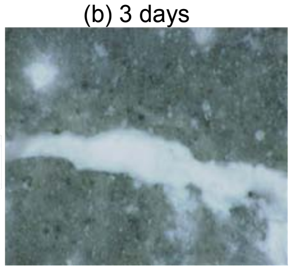
(a) Crack



(b) 3 days



(c) 7 days



(d) 28 days

Fig. 18 Self-healing process of sample III [Upgrade design II, Water/Binder ratio of 0.45].

tained at the target slump value of 21 centimeters and air was 4.5% after 1 hour. Therefore, self-healing concretes incorporating premixed products with target slump, slump flow and air could be fabricated in the actual ready-mixed concrete plant. The workability test satisfied the target slump and air requirements, as shown in **Fig. 21**.

3.4 Physical properties of self-healing concrete

Cement-based materials like concrete and mortar are quasi-brittle materials. These materials show a softening behavior when tested in uni-axial tension. In order to quantify the early age behavior of self-healing concrete as compared to those of conventional and expansive concrete, a temperature-stress testing machine (TSTM) test was conducted. Three types of concrete – plain concrete, expansive concrete (EC) and self-healing concrete (SHC)–were prepared for TSTM test and their experimental results are presented in **Fig. 22**. Under the same semi-adiabatic temperature condition, the temperature evolution of the expansive concrete is slightly higher than normal concrete, and that of self-healing concrete is slightly lower than normal concrete. The first phenomenon was due to the replacement of cement by expansive agent, which has a higher hydration activity, thus the hydration heat on the first day elevated slightly. The second phenomenon was caused by the cement amount, which is 10% less in self healing concrete.

It is well known that expansive concrete can induce extra expansion to compensate for shrinkage. The test results showed this tendency. After 20 hours, the compressive stress of the expansive concrete was 0.8MPa higher than that of normal concrete, whose was 1 MPa. After temperature of specimens returned to room temperature, the tensile stress of expansive concrete was slightly lower than that of normal concrete. This is because the extra expansion of expansive agent becomes stagnant after one day due to the lack of water and the developing stiffness of surrounding hydrated matrix. The restrained stress evolution of self healing concrete is between these two concrete, the maximum compressive stress was 1.4MPa, and the final tensile stress was 1.6MPa. Even though the premix added in the self-healing concrete was composed of many composites, its restraint stress development is similar to that of the expansive concrete. When comparing the Young's modulus, it can be seen that there is not large difference among these types of binders. Based on the above, it could be concluded that the cracking sensitivity of self-healing concrete is similar to expansive concrete and has a better cracking resistance than normal concrete.

Furthermore, in case of compressive strength, it can be seen that SHC exhibits similar compressive strength to Plain as shown in **Fig. 23**. This means that self-healing concrete also passed the minimum field requirement for compressive strength (red line).

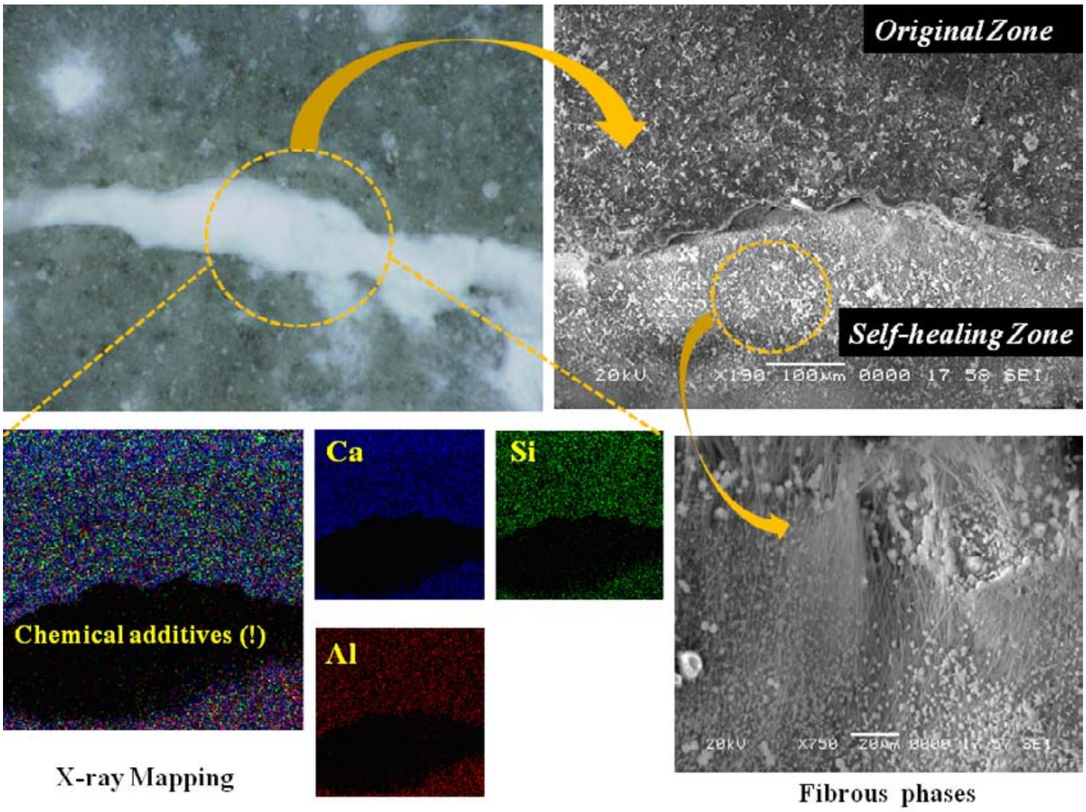


Fig. 19 X-ray mapping results of fabricated fibrous phases and C-A-S-H phases [Upgrade design II, Water/Binder ratio of 0.45].

(a) Check up Ready-Mixed plant

(b) Preparation of materials (input self-healing agent)

(c) Fabrication of self-healing concrete

Fig. 20 Fabrication process of self-healing concrete in the ready-mixed plant for actual application.

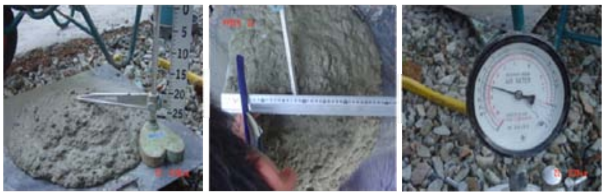


Fig. 21 Initial workability test of fabricated self-healing concrete (Target : slump 21cm, slump flow around 40 cm x 40 cm, Air 4.5%).

For estimating the durability of concrete structures, it is necessary to understand the permeation of water into concrete. Water permeability of self-healing concrete is one of several important concrete properties for the prevention of water leakage from water-retaining or underground structures. In order to measure the permeability of concrete, this research adopted an output method which enables the measurement of the permeation directly by observing the reliability and starting point of hydraulic divergence of permeation in concrete (Okazaki, *et al*. 2006). **Table 4** shows the water permeability test results of self-healing concrete. Generally, the function of water permeability coefficient is as follows.

$$k = q / I \tag{1}$$

Where

K : water permeability coefficient (m/sec),

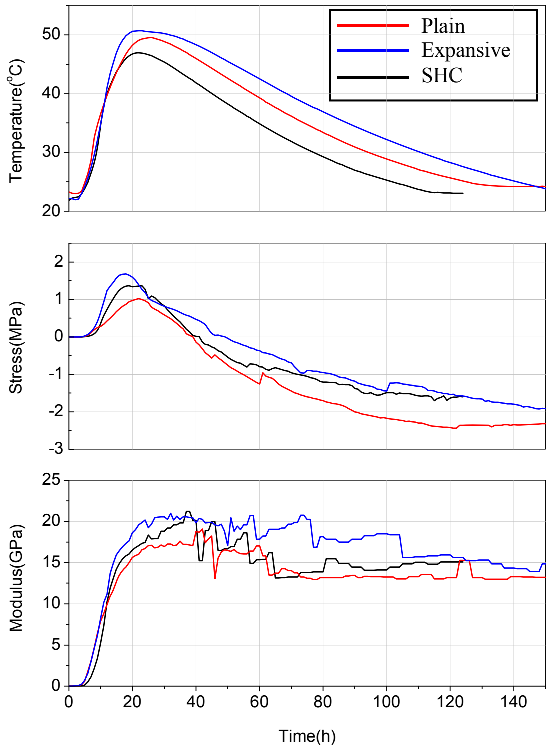


Fig. 22 TSTM results of various concrete.

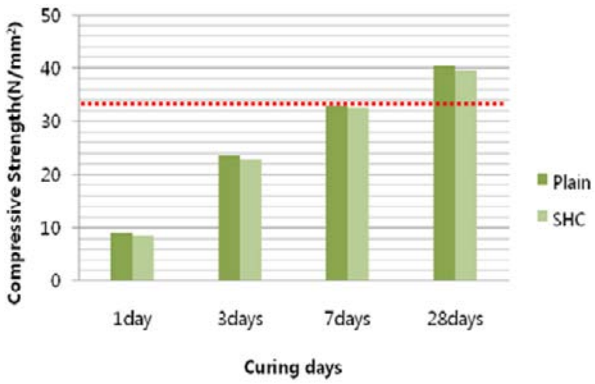


Fig. 23 Compressive strength of self-healing concrete.

q: water flow /unit time and volume ($m^3/m^2/sec$),

i : hydraulic gradient

Water pressure was 2.0 MPa (=2 x 10^6 N/m^2) in this research. Each specimen was cured for 28 days, and then immersed in water again for 2 days in order to estimate the water permeability. The result showed that water permeability coefficient of self-healing concrete was significantly lower than that of conventional concrete. This indicates that self-healing cementitious composite could be used as a mineral admixture for the sealing of water leakage.

3.5 Self-healing capability of self-healing concrete

Figure 24 (a) and **Fig. 24 (b)** show the healing process under water supply of cracked conventional paste and

Table 4 Comparison water permeability between conventional concrete and self-healing concrete.

Sample	Time (s)	V (cm/s)	K (m/s)
Plain	60	0.000294	5.35E-05
SHC	1800	8.69E-06	1.65E-06

cement paste incorporating expansive agent made at water/cement ratio of 45%. Crack width was controlled between 0.1 mm and 0.4mm to satisfy maximum tolerable crack widths. However, after 28 days curing, the crack still remained even though the specimen was re-cured under water immersion condition for 33 days.

This is because sufficient hydration occurred by the supply of surplus water during mixing. In other words, this indicated that the specimen already lost the capability for self-healing using unhydrated particles. This is similar to previous results. In case of cement paste incorporating self-healing agent, it was also self-healed perfectly after re-curing for 3 days, as shown in **Fig. 24 (c)**. In this case, both mineral and chemical additives were significantly affected to form re-hydration products with high chemical stability. Moreover, in case of self-healing concrete, the crack was significantly self-healed up to 28 days re-curing.

Figure 25 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. 25 (b)**. 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. 25 (d)**.

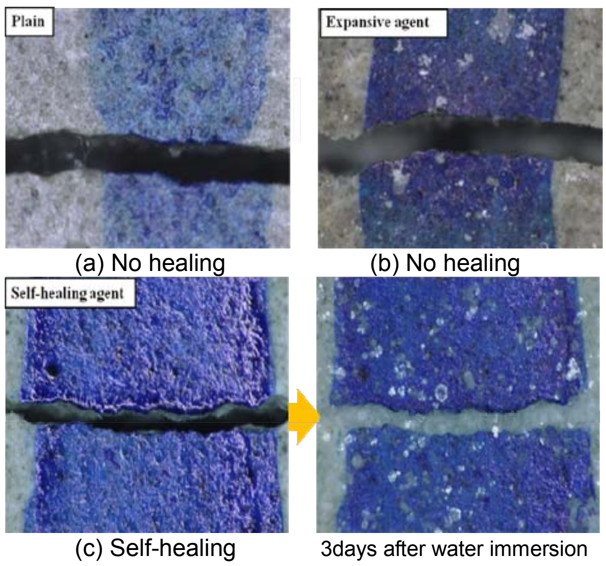
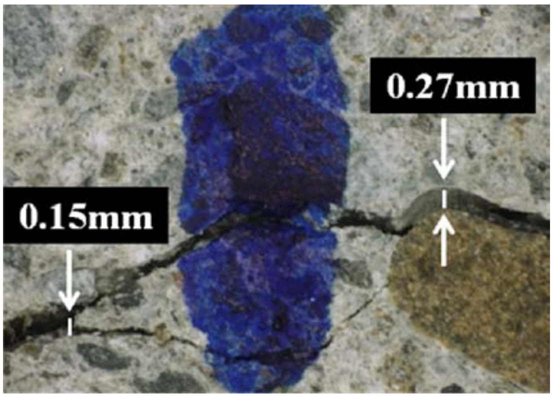
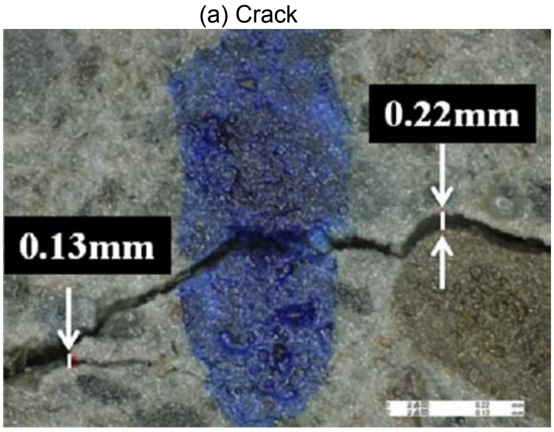


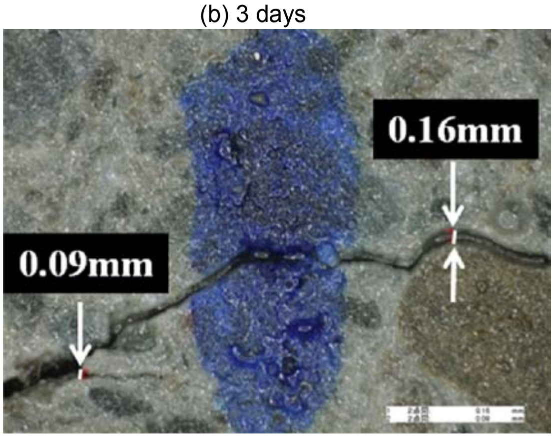
Fig. 24 Self-healing behaviour of cementitious composite materials incorporating geo-materials [Water/Binder ratio = 0.45].



(a) Crack



(b) 3 days



(c) 7 days

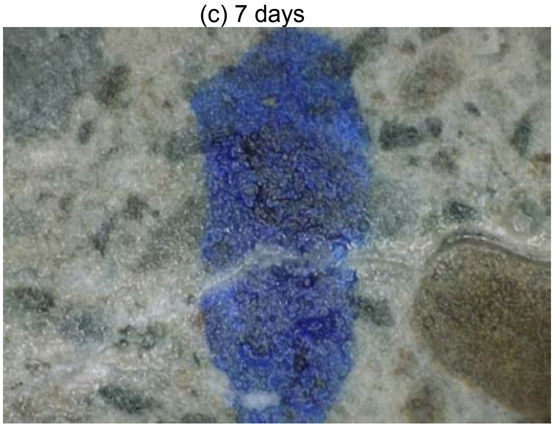
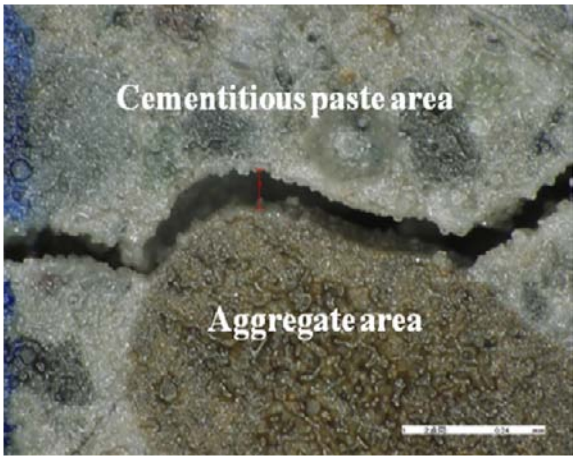

(d) 33 days

Fig. 25 Process of self-healing on self-healing concrete at wter/binder ratio of 0.47.



(a) 3 days

(b) 33 days

Fig. 26 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. 26**, 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 **Fig. 27**. Some re-crystallization structure from the cementitious paste was deposited on the aggregate surface or in the crack between aggregates as shown in **Fig. 27**. Therefore, this indicates that cracks of these types will take more time for self-healing.

4. Conclusions

In this study, the new method of self-healing design to repair cracks in cracked concrete was suggested, and the self-healing properties of cracked concrete using various mineral admixtures were investigated.

(a) Self-healing products on aggregate surface

(b) Diffusion of self-healing products from paste zone

Fig. 27 Self-healing images on crack between aggregate zone and paste zone of self-healing concrete.

1) In order to improve the self-healing capability to the cementitious system at normal water-binder ratio, it is suggested that special terms such as expansion term, swelling term, and precipitation term be considered for the design of materials and practical application.
2) Self-healing capability was significantly affected by aluminosilicate materials and various modified calcium composite materials.
3) In case of Upgrade design II (Improvement of chemical stability and self-healing velocity), it was found that chemical and mineral additives significantly affected the formation of re-hydration products with high chemical stability as well as rapid self-healing velocity. From these concepts, some particular mix-proportions for cementitious composite materials with self-healing capability were suggested.

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