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Self-healing of surface cracks in mortars with expansive additive and crystalline additive

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ABSTRACT

This research studies the self-healing potential of cement-based materials incorporating calcium sulfoaluminate based expansive additive (CSA) and crystalline additive (CA). Mortar specimens were used throughout the study. At the age of 28 days, specimens were pre-cracked to introduce a surface crack width of between 100 and 400 μm. Thereafter, the specimens were submerged in water to create a self-healing process. The experimental results indicated that the mixtures with CSA and CA showed favorable surface crack closing ability. The optimal mix design was found to be a ternary blend of Portland cement, 10 wt.% CSA and 1.5 wt.% CA, by which a surface crack width up to about 400 μm was completely closed, and the rate of water passing was dropped to zero within 28 days. It was hypothesized that the amount of leached Ca^{2+} from the matrix plays an important role on the precipitation of calcium carbonate which is the major healing product. The analyses showed that those specimens with CSA/CA additions released more Ca^{2+} than that control specimen. Moreover, those specimens with additives had higher pH value which would favor calcium carbonate precipitation.

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1. Introduction

Self-healing processes in cement-based materials have been investigated for decades. Generally, the phenomenon comprises two major mechanisms. For internal crack healing, the process is currently based on further hydration or swelling of unreacted particles. These particles can be ordinary Portland cement as well as other types of binders, which had not been fully hydrated in the initial stage of hydration, particular in low w/c mixes. However, such a mechanism is not highly promising in healing typical cracks in concrete because of the limited remaining potential and difficulties in optimizing the performance. Generally, the volume of hydration products of cement is not sufficient to close large cracks. The healing is limited to a crack width which is not larger than 50–150 μm. Li and Yang [1] reported that the maximum crack width of 50 μm is necessary to achieve full recovery of mechanical and transport properties in engineered cementitious composite (ECC) material. Between 50 and 150 μm, partial recovery can be attained. In mechanical point of view, the deflection capacity of healed pre-cracked ECCs recovers about 65–105% from original specimens [2]. In addition to the further hydration, another mechanism involves the precipitation of calcium carbonate which is the main process for self-sealing of surface cracks on hardened concrete. The main cause of self-healing was attributed to the formation of calcium carbonate, a result of reaction between calcium ions from the matrix of concrete and atmospheric carbon dioxide dissolved in water [3]. This type of self healing mainly reduces the water permeability and is therefore most important to watertight structures, such as underground structures, reservoir and dams [2]. In view of durability, this type of self healing would improve the resistance of cracked concrete against the migration of undesirable substances. There are various practical experiences and experimental studies [3–5] which have demonstrated that the crack healing in cementitious materials can lead to a reduction of water permeability over time. However, no mechanical recovery has been reported. Apart from two major mechanisms mentioned earlier, pore blocking by impurities in water and loose particles resulting from crack spalling are also considered as possible processes in self-crack healing of concrete [3].

Recently, various alternative cementitious materials were used in the research of self-healing concrete. Hosada et al. [6], Kishi et al. [7] and Sisomphon and Copuroglu [8] investigated the self-healing potential of cement-based materials when calcium sulfoaluminate based expansive agents were used as a cement replacement material. Jaroenratanapirom and Sahamitmongkol [9] evaluated the self-healing performance of mortars with different supplementary cementitious materials namely; fly ash, silica fume and a crystalline admixture. Qian et al. [10] reported the self healing ability of engineered cementitious composite incorporating limestone powder, blast furnace slag and nanoclay.

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Table 1
Chemical compositions of materials used.

Oxide contents (%wt.)	CEM I 42.5N	CSA-α	CSA-β	CA
CaO	63.30	48.09	75.00	73.40
SiO_2	19.50	1.71	1.20	13.72
Al_2O_3	5.60	12.66	3.50	3.66
Fe_2O_3	2.30	0.45	1.70	2.28
Na_2O	0.30	0.05	0.03	1.24
K_2O	0.90	0.06	0.03	0.40
SO_3	2.70	35.48	17.00	3.91
MgO	1.10	0.92	0.49	0.70

Table 2
Mineral compositions of calcium sulfoaluminate based expansive additives.

Mineral composition (%wt.)	CSA-α	CSA-β
Hauyne ($C_4A_3\underline{S}$)	32	10
Free lime (C)	20	50
Anhydrite ($C\underline{S}$)	40	30
Others	8	10

Note: Cement chemistry notations, C = CaO; A = Al_2O_3; $\underline{S}$ = SO_3.

Table 3
Mix design of mortars by mass ratio.

Mix	Description	OPC	CSA-α	CSA-β	CA	Water	Sand
M1	Control	100	–	–	–	25	200
M2	CA1.5	98.5	–	–	1.5	25	200
M3	CA4	96	–	–	4	25	200
M4	CSAα	90	10	–	–	25	200
M5	CSAβ	90		10	–	25	200
M6	CA1.5/CSAα	88.5	10	–	1.5	25	200

In an effort to enhance the self-healing potential of cement-based materials, mortar mixtures incorporating different cementitious materials were evaluated. The effects of additives on surface crack closing ability, water tightness and microstructures of pre-cracked specimens were investigated. Eventually, various hypotheses on surface crack closing phenomena of cement-based materials derived from the experimental results in this study were proposed and discussed.

2. Experimental investigations

Ordinary Portland cement CEM I 42.5 N, crystalline additive and expansive additive were used in this study. Crystalline additive[1] is a synthetic cementitious material which contains reactive silica and some crystalline catalysts. Its reactive components react with $Ca(OH)_2$ to form crystalline products which disconnect pores and fill cracks in the concrete. The crystalline products can only occur when sufficient moisture is present. The main application of crystalline additive is to improve the water tightness and to stop leakage of concrete structures. It is also classified as one of the hydrophilic water-proofing materials [11]. Apart from crystalline additive (CA), a synthesized ternary blend (Hauyne, anhydrite and free lime) calcium sulfoaluminate based expansive additive (CSA) which is a commercial product normally for shrinkage compensation was used. Two types of CSA additives (CSA-α and CSA-β) with different chemical composition were used (Table 1). The mineral compositions are given in Table 2. It has to be noted that CSA-α[2] is an original commercial expansive additive product normally for shrinkage compensation, while CSA-β is a modified one which contains more free-CaO. Based on the advices of the producers and trial mixes, the suitable dosages were set 1.5% and 10% by mass of total cementitious material, for CA and CSAs, respectively.

Mortar specimens were used for all analyses in this study. All mixtures were designed based on water-to-cementitious ratio (w/c) of 0.25 and sand-to-cementitious ratio (s/c) of 2.0 by mass. The mix designs of mortars are demonstrated in Table 3. Superplasticizer, Glenium ACE30, was used to achieve workable condition of mortars. To prepare specimens, the mixing sequence was 2 min low speed followed by 2 min high speed mixing with a commercial Hobart mixer. The disc-shape specimens were cast in plastic containers with 75 mm diameter and a height of about 20 mm. To achieve a large crack width, all specimens had to be reinforced with galvanized wire-mesh which was placed at the mid-height of the specimens. The filled containers were vibrated for 20 s on a vibrating table. After 24 h, specimens were demolded and subsequently damp cured at a controlled temperature of 25 ± 2 °C and 95 ± 5% RH for a 3 day. Eventually, all specimens were exposed to laboratory air for another 25-day period.

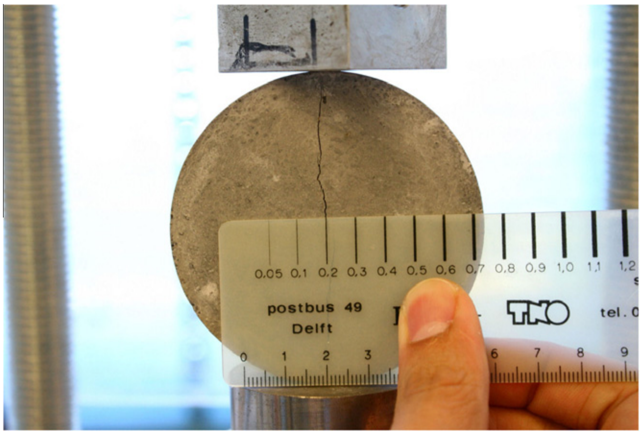

Fig. 1. Specimen cracking.

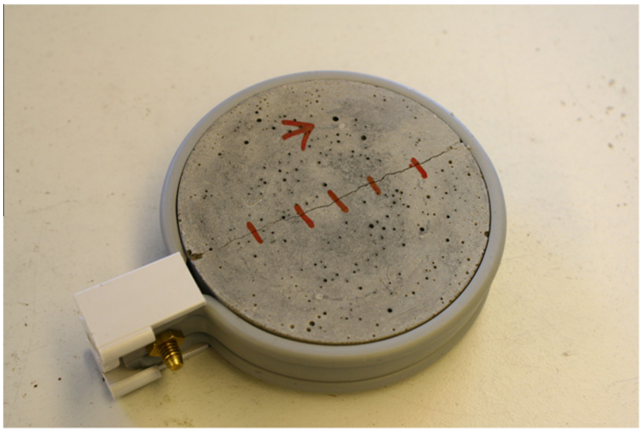

Fig. 2. Specimen with PVC bracket.

The specimens were pre-cracked in the manner of splitting tensile strength test in order to introduce a surface crack width of about 100–400 μm (Fig. 1). After pre-cracking, the specimens were fastened as tightly as possible by a 75 mm diameter PVC pipe bracket to create a confinement. The purpose of this application was to imitate a real condition where hardened concrete is usually under some constraint. A Leica MZ10 stereomicroscope with Leica LAS software was used to measure surface crack widths. The surface crack width was measured at five positions on each surface of specimens. Distance between each position was about 10 mm

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[1] Xypex Admix C-1000NF, Xypex Chemical Corporation, Canada.

[2] Denka CSA#20, Denka Corporation, Japan. NB: These products may not be the only materials which have such performances.

as showed in Fig. 2. For each mix, two pieces of disc-specimens were used for analysis. Hence, there were totally 20 positions of crack which were measured and monitored for each mixture. Initial surface crack widths were measured immediately after bracket installation. Then, all specimens were submerged into water which was replaced once every 7 days. The residual surface crack widths were measured at 4, 7, 14 and 28 days wetting periods. As water was replaced every 7 days, it has to be noted that the crack width measurement was performed at the stage before water replacement. Also, it has to be remarked that specimens with different compositions were submerged in separate curing container throughout the healing phase.

Water passing test was conducted on pre-cracked mortars to investigate the permeability of specimens due to crack progression. The specimen was attached to a plastic cylinder, and tightly fastened with a PVC bracket. Silicone sealant was applied along the seam to prevent water leakage (Fig. 3a). A constant water head of 100 ± 5 mm was controlled throughout the experiment by adding water (Fig. 3b). The specimen was placed on supports to allow free movement of water. The water passing rates were measured at 4, 7, 8, 14, 15 and 28 days wetting periods. The duration of each measurement was 10 min.

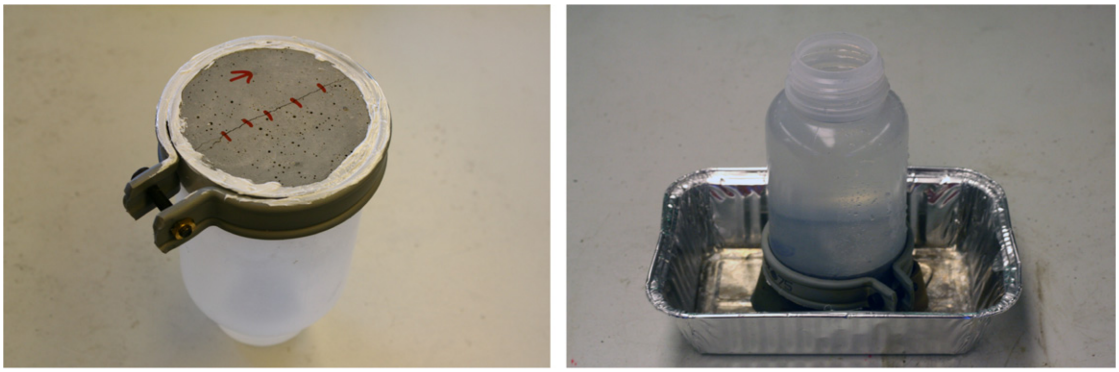
Eventually, the appearance of healed cracks was observed internally. The profile of crack and formation of healing products were studied on polished specimens by using stereo microscope. The integrity of the samples was maintained by impregnation with a low viscosity fluorescent dye epoxy under vacuum. The specimens were vertically sliced perpendicular to the crack direction to a thickness of about 10 mm by a machine saw and dried in the oven at 35 °C for 24 h. Thereafter, the sliced specimens were impregnated in dyed epoxy under vacuum for another round. After the hardening of epoxy, the surfaces of specimens were ground by using DBT Diamond Roller and Grinder/86 thin sectioning unit for initial preparation of polished sections. Finally, specimens were polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond pastes, respectively.

Calcium ions dissolved from the matrix play a role on the precipitation of calcium carbonate. To evaluate the amount of leached calcium ion, the specimens were cast in plastic containers with 33 mm diameter and a height of about 50 mm. The filled containers were vibrated for 20 s on a vibrating table. Thereafter, the specimens were treated in similar manner to those disc specimens. After 28 days, these cylinder specimens were half-broken. The circumference surface and the top (or the bottom) area of specimens were coated with epoxy. The fracture surface was only the area which was subsequently exposed to the environment. Each specimen was immersed into 100 ml deionized water. The pH value and electrical conductivity of the solution were measured regularly. At 7 days, 5 ml of the solution was collected and then diluted with 2% HNO_3 to prevent precipitation. Thereafter, the concentration of calcium ion dissolved in the water for 7 days was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Results and discussion

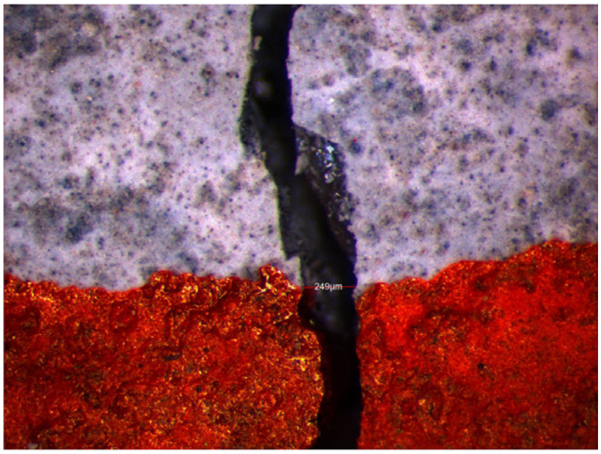
The surface cracks of mortars before and after self healing process were investigated by using stereo optical microscope at 40 × magnification (Fig 4). The reduction of crack width is quantitatively demonstrated in Fig. 5a–f for M1–M6 mortars, respectively. The width of surface crack was measured on 20 different locations at 0, 3, 7, 14 and 28 days wetting period. The initial crack width of all specimens was found in a range between about 50 and 400 μm. The change of surface crack width was used as an indicator of quantitative evaluation of self crack healing. Generally, there was no visible difference of crack closing rates between those on top surface and bottom surface for each particular mix. Hence, the results are not demonstrated individually. For all specimens, it was found that the development of crack closing process with respect to wetting period, however, with different rates. Also, the self crack healing ability can be observed on control mix (M1), while the surface crack up to about 150 μm width has been closed within 28 days. For M2–M5 mixes, cracks with the width up to about 200–250 μm can be completely sealed. Considering at larger crack width (200–400 μm), however, the residual crack width of M3 was still broader than those M2, M4 and M5. It is clearly seen that M6 mixture showed the optimum healing potential where the surface crack up to about 400 μm can be sealed within 28 days. Hence, the ability of crack closing was in the order of M1 < M3 < M2 = M4 = M5 < M6. Compared M3 to M2, there was no benefit to overdose the addition of CA into mortar. In case of CSA, it was found in previous study [8] that the maximum replacement ratio would be limited to 10% which is also a value suggested by manufacturer. The mortar with overdosed CSA-α (20% replacement) was disintegrated after about 7–10 days wetting period due to an excessive expansion.

As demonstrated in Fig. 6a–c, the surface cracks were categorized into three groups of crack width which were for the initial width of <200 μm, 200–300 μm and 300–400 μm, respectively. The results were obtained from the average values of each crack range, and presented in term of relative crack width to the initial values. For small initial cracks (<200 μm), the residual crack width of the control mortar was about 10% of the initial width after 28 days wetting. It can be seen that all mortars with additives can close the small cracks within 14 days. However, only M6 mix has a potential to completely seal medium (200–300 μm) and large cracks (>300 μm) within about 28 days. In this view, it can be

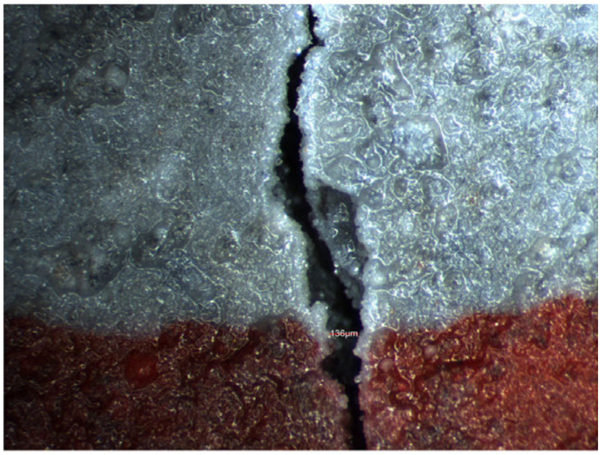

(a) Specimen for water passing test

(b) Set-up of the water passing test

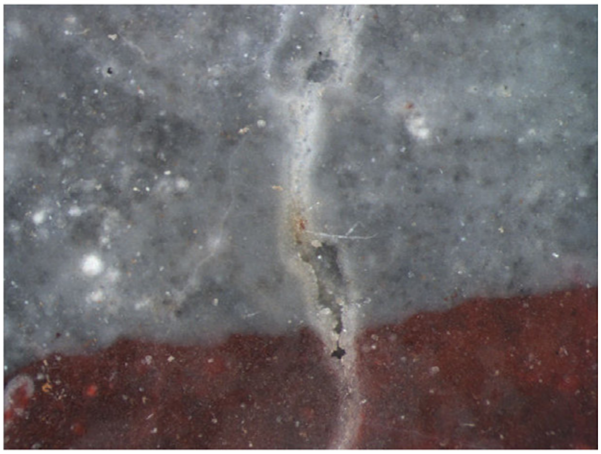
Fig. 3. Water passing test.



(a) Initial



(b) 7 days



(c) 28 days

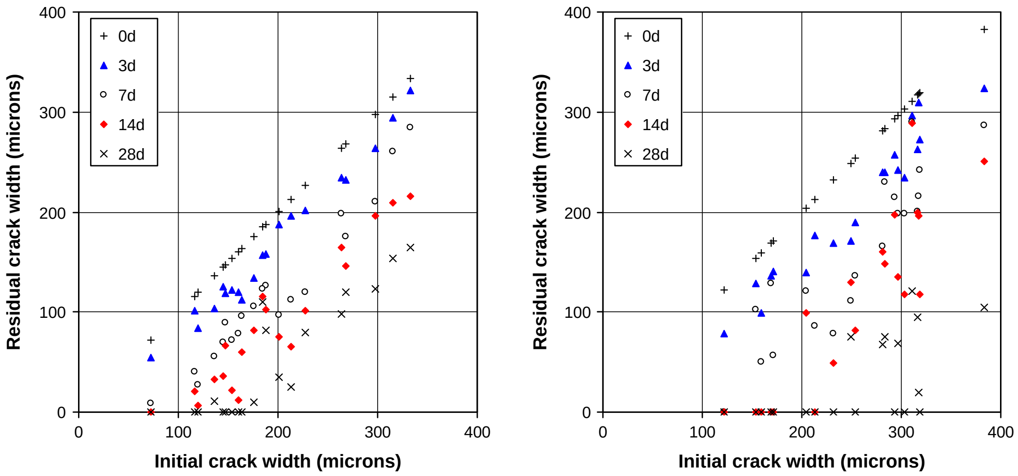
Fig. 4. Reduction of crack width (M6).

obviously seen that M4 mix has a higher healing potential than M2 and M5 mixes at the first 14 days. At 28 days wetting, however, there was almost no difference between M2, M4 and M5 mixes, particularly for large crack healing. However, a more rapid healing ability would be more preferable in practice. Hence, the ability of surface crack closing could be ranked in the order of M1 < M3 < M2 < M5 < M4 < M6. While M6 was completely healed within 28 days, it has to be noted that the surface cracks on M4 and M5 mortars were completely sealed at 56 days wetting period.

Fig. 7a and b shows the result of water passing rate of pre-cracked mortars corresponding to wetting period. At the beginning of the test, the initial water passing rates were measured. The initial rates were found in the range between 22 and 35 g/min. Thereafter, the reduction of water passing rate was presented in relative values to the initial water passing rate. For the control mortar (M1), slight reduction of water passing rate can be observed in the early period, while those mortars with CA or CSA showed rapid reduction of water passing ability during the first 5 days. The rates of reduction were gradually decreased between 5 and 7 days. However, after the water renewal at 7 days, the water passing rates of all mortars expectedly rebounded. From this observation, it can be hypothesized that some healing products formed at early period can be dissolved or decomposed under fresh water exposure. While most concretes in practice are usually exposed to fresh water, it is important to note that the specimens continuously released Ca^{2+} and OH^- to the curing water. Owing to the restricted environment of curing containers in laboratory, the rather high alkalinity of curing water in laboratory experiment may cause the misleading evaluation of concrete self-healing phenomenon, particularly the surface crack closing ability. On the contrary, the dissolved CO_2 in curing containers were consumed and continuously depleted. This may retard the precipitation of calcium carbonate which is a major product of self healing process. Therefore, it is essential that the water in curing containers is frequently replaced in laboratory experiments. It has to be noted that no rebound of water passing rate was observed after water renewal at 14 days and beyond. As healing products became denser, the decomposition rate might be substantially reduced, while the precipitation of calcium carbonate was still continuing.

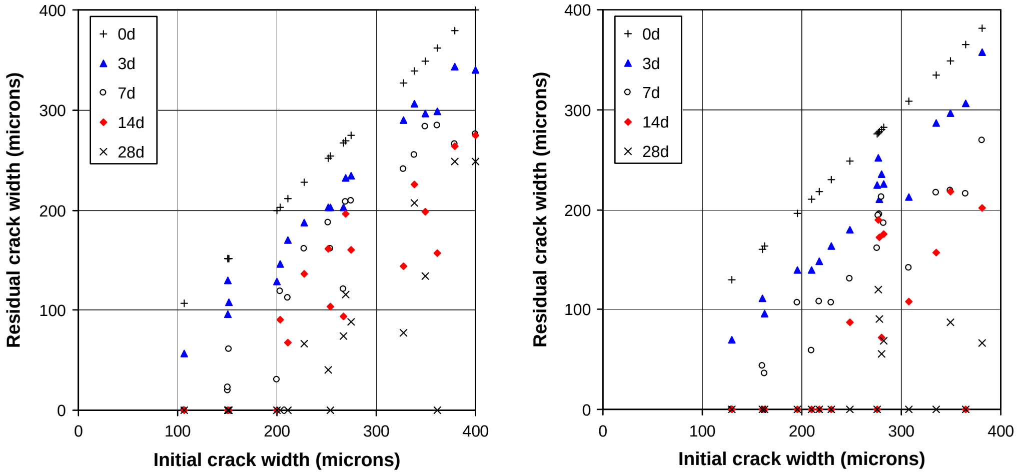
After 56 days, the surface cracks of M4–M6 specimens were completely sealed, and their water permeability rates with 100 mm water head were zero. Therefore, the water passing test was conducted at a higher water pressure. Fig. 8 shows the results of water passing test with a water head of 2000 ± 5 mm compared to the original water passing rates with a water head of 100 mm. As seen in Fig. 7, in the beginning period, it was clearly seen that M4 mortar had a more rapid crack closing ability compared to the M5 mortar. A similar tendency has been obtained from the surface crack closing ability investigated by stereomicroscope. After 28 days wetting, however, it seems that M5 had a slightly lower relative water passing rate than that M4. In addition to surface crack sealing, it seems that matrix swelling and further hydration of cementitious materials would play a role on the reduction of internal crack width and water passing ability. An explanation to this finding could be the slower hydration of free-CaO and consequent expansion compared with the formation of ettringite. The mass fraction among three oxides (CaO, Al_2O_3 and SO_3) indicate that ettringite would be the sole major product of CSA-α reaction. The limited amount of $C_4A_3\underline{S}$ in CSA-β would cause a lower amount of ettringite formation compared with that from CSA-α. It can be hypothesized that the formation of ettringite plays a major role on early healing period, while the presence of excess free-CaO in CSA-β would react at later ages. At 56 days with a higher water head, it is clearly seen that M5 had significantly lower water permeability than M4.

In a previous study [8], similar experiments were conducted on disc-mortars, however, without any confinement. It was noticed that there were numerous macro-cracks in the specimens, particularly at the interfacial transition zones (ITZ) between matrix and aggregate (Fig. 9a). Generally, the size of crack width was about 20–30 μm. This would be due to the effective expansion of the hardened matrix with CSA addition. Cracks would appear, if the expansive strain of the matrix exceeds its tensile strain capacity. Because ITZ is usually weaker than the bulk paste, cracks can be found around sand particles. In this study, the specimens were fastened by pipe brackets to create a confinement and prevent



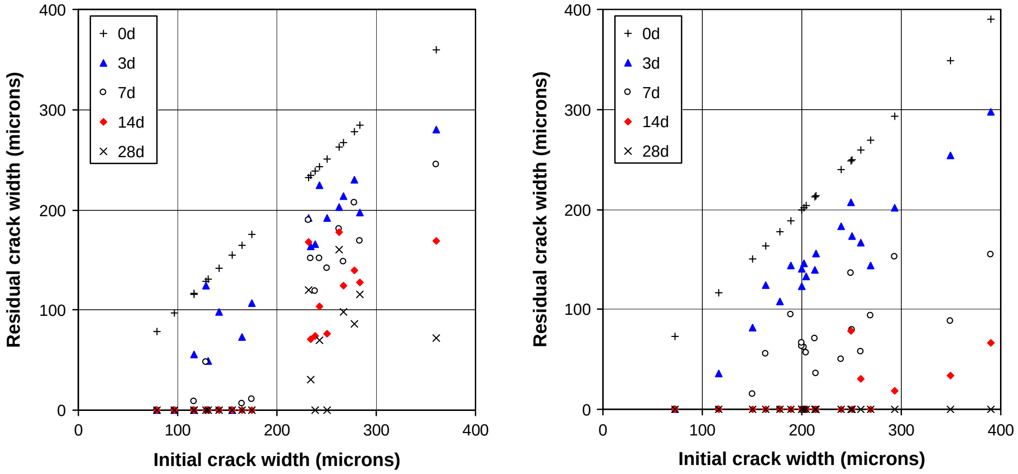
(a) Control (M1)

(b) CA1.5 (M2)



(c) CA4 (M3)

(d) CSAα (M4)



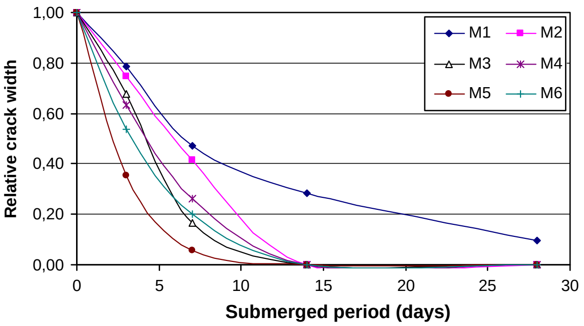
(e) CSAβ (M5)

(f) CA1.5/CSAα (M6)

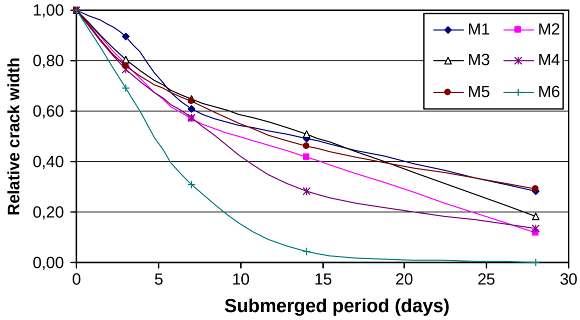
Fig. 5. Crack width analysis.

excessive deformation. The confinement would improve self crack closing ability. Moreover, the specimen could not be excessively expanded; hence, macro-cracks can be minimized (Fig. 9b). Although the residual crack in Fig. 9a seems to be smaller than that in Fig. 9b, it has to be noted that the prior had a smaller initial crack width than the latter.

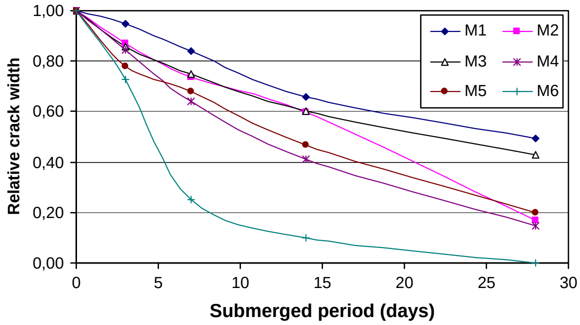
The appearance of surface crack closing products seen on the surface would be majority due to the precipitation of calcium carbonate which deposited on the surface of specimens (Fig. 10). In a previous work [8], the microstructures of crack were also observed on petrographic thin-sections through a polarized light microscope, by which excess formation of calcium carbonate on



(a) <200 μm initial cracks

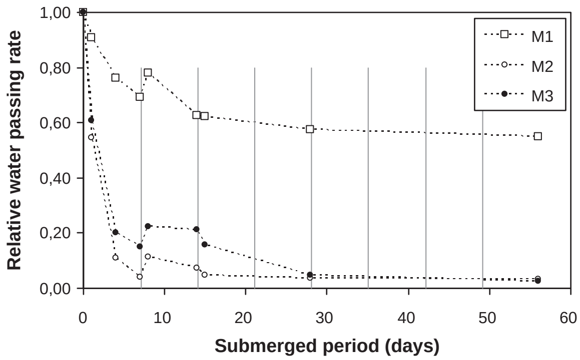


(b) 200-300 μm initial cracks

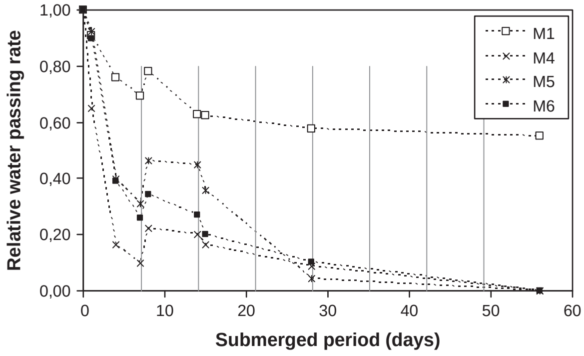


(c) 300-400 μm initial cracks

Fig. 6. Relative crack width of mortars.



(a) Control and mortars with CA



(b) Control and mortars with CSA

Fig. 7. Relative water passing rate of mortars.

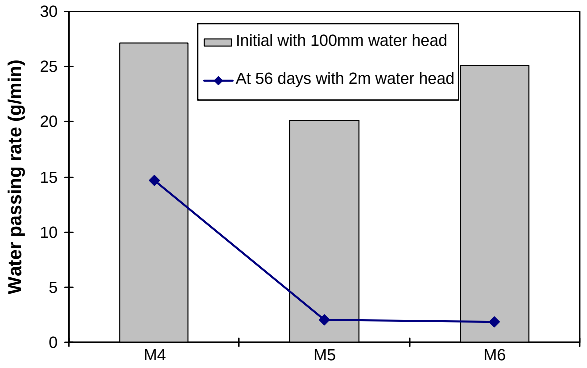
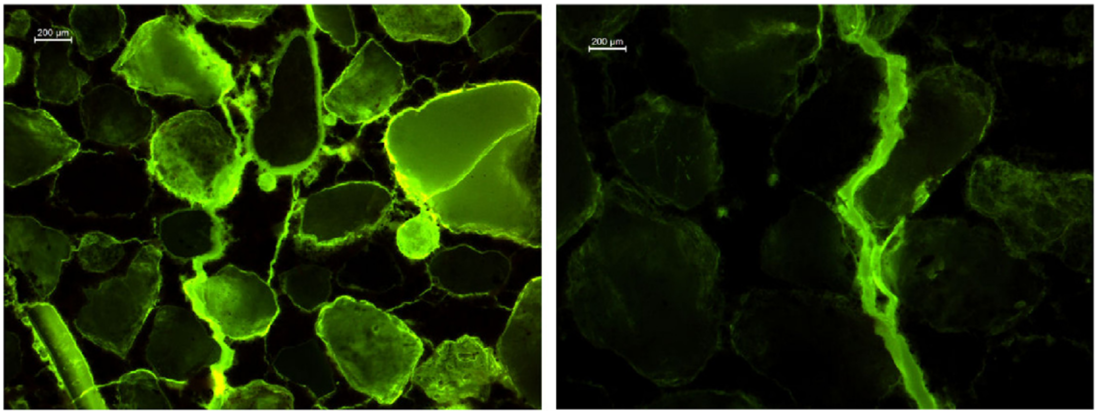


Fig. 8. Water passing rate through cracked mortars.

surface crack of mortar was identified. Apart from the precipitation on crack mouth, minor precipitation of calcium carbonate can be observed inside crack (Fig. 11a). It was hypothesized that the hydration products had been leached and re-crystallized in water that had flown into the crack [12]. The addition of CSA/CA would play a role on the precipitation of calcium carbonate. It is possible that the carbonate products could not be calcium carbonate alone. This could be involved to the reaction of ettringite with carbon dioxide which yield carbonate analog of ettringite. As another hypothesis, the net-like formation of ettringite inside the crack would serve as a quasi-reinforcement, and allow more suitable precipitation sites of calcium carbonate (Fig. 11b).

However, the most promising assumption is that the mixtures with CA and CSA boost the Ca^{2+} dissolution that forms calcium carbonate. To investigate the amount of leached ions from the matrix, the fractured specimens were immersed into deionized water. Fig. 12 shows the pH values and electrical conductivity of water hosting the mortar specimens. For each value, the result was obtained from the average of four specimens. For all cases, the pH value and electrical conductivity of solution were increasing with respect to exposure period. It has to be noted that pH values were directly related to the amount of dissolved OH^- anions in the solution, while the electrical conductivity was dependent on the concentration of total dissolved ions in the solution. Generally, the control specimen (M1) showed the lowest electrical conductivity at all immersion periods. The pH values of M1 and M4 solutions were rather low compared to those M5 and M6. At identical pH values, M1 showed the lowest electrical conductivity, while M5 and M6 gave the highest values. In this point of view, the specimens with CSA/CA would release more calcium ions compared with the control specimen (M1), if OH^- and Ca^{2+} were considered as two major ions dissolved from specimens. As seen in Table 4, the results from ICP-AES confirm that those mortars with additives released more Ca^{2+} than the control mix.

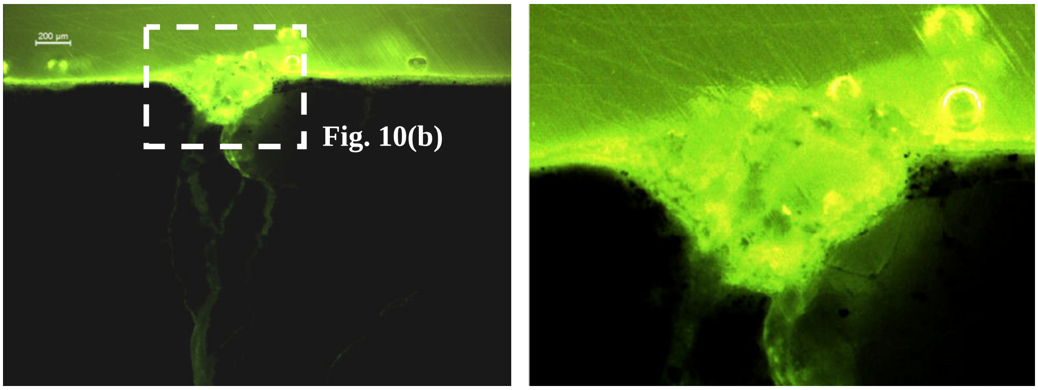
The mechanism of self crack closing of cement-based materials is schematically illustrated in Fig. 13. When the cement-based materials exposed to water, the Ca^{2+} ions is gradually released from the matrix. The water in crack would contain high concentration of



(a) CSA mortar without constraint from previous work (Sisomphon & Copuroglu (2010)

(b) CSA mortar (M4) with constraint in this study

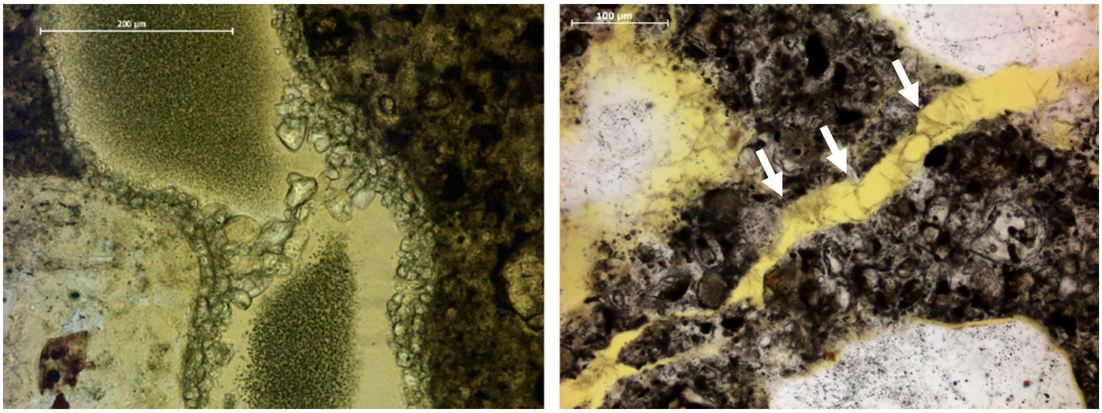
Fig. 9. Effect of constraint on microstructure of mortars with CSA.



(a) Calcium carbonate precipitation

(b) Enlarged view of the precipitation in Fig. 10a

Fig. 10. Precipitation of calcium carbonate (M6 specimen).



(a) Calcium carbonate

(b) Ettringite

Fig. 11. Healing products formation in the mortars with CSA addition [8].

Ca^{2+} ions, while the concentration in the external water on the surface of specimen would be lower due to dilution. On the contrary, carbonate ion released from the matrix itself is minimal. The incoming water would be the only source of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-). Therefore, the concentration of carbonate ions in the water in crack would be not more than that in the

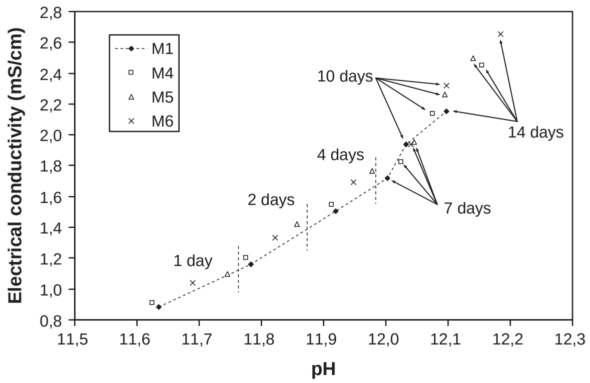


Fig. 12. Electrical conductivity vs pH of water for submersion of mortars.

Table 4
pH values, electrical conductivities and calcium contents in water after 7 days submersion.

Mix	pH	Electrical conductivity (mS/cm)	Ca^{2+} concentration (mg/l)
M1	12.00	1.72	71
M4	12.03	1.82	73.5
M5	12.05	1.95	126.3
M6	12.04	1.94	98.8

surface water. Regarding to this condition, it seems that the location nearby the crack mouth would be the only area which have significant amounts of both calcium and carbonate ions. Due to this reason, plenty of precipitation of calcium carbonate can be observed at the crack mouth, while less precipitation can be seen on other locations (Fig. 14). In view of cementitious types, more Ca^{2+} ions released from the specimens with CSA/CA would promote the precipitation of calcium carbonate. Moreover, the mixtures with CSA or CA had higher pH than the control (Fig. 12). Rising of alkalinity in environment favors a calcium carbonate precipitation [3]. On the other hand, swelling of the matrix would also play a minor role in the reduction of internal crack width. Further study is essentially required to evaluate the effect of matrix swelling on the change of internal crack width. However, regarding to the results in this study, it seems that the reduction of water passing rate was influenced by surface crack healing rather than internal crack healing. Due to the reduction of water passing ability, the healing process prevents the penetration of water and dangerous substances through crack. It is important to remark that surface crack healing usually has no benefit on the mechanical recovery of pre-cracked mortar or concrete. However, using CSA and CA has a potential to heal the internal crack, and recover the mechanical properties of strain hardening cementitious composite (SHCC) which has a tight crack width [13].

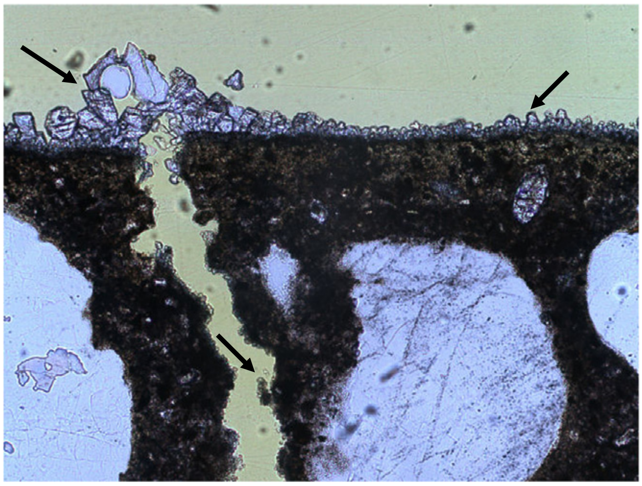


Fig. 14. Precipitation of calcium carbonate at different locations. The specimen was obtained from previous study [8].

4. Conclusions

This paper presents the results on the potential of using calcium sulfoaluminate based expansive additive (CSA) and crystalline additive (CA) for self crack closing mortars. Based on the experimental results in this study, it was found that the uses of CSA and CA as additives are beneficial with respect to surface crack closing phenomenon. In case of control mix, the surface crack up to about 150 μm width has been closed within 28 days. With CSA and CA additions, however, cracks with the width of 250–400 μm can be completed closed. In view of transport property, the rates of water permeability through crack of mortars with additives were considerably reduced with respect to exposure period. After 28 days, M4–M6 showed zero permeability. In this study, calcium carbonate was found to be the major healing product. For those samples with the additives, a significant amount of calcium carbonate precipitation can be observed, particular on the mouth of crack. It has been

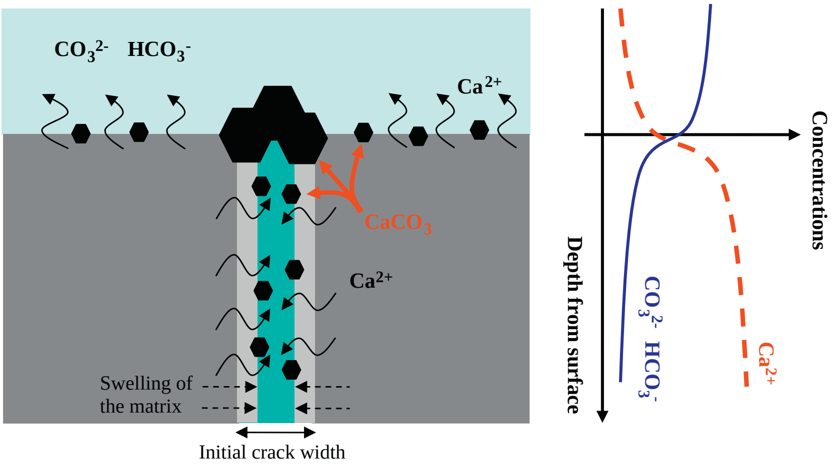


Fig. 13. Schematic illustration of the precipitation of calcium carbonation.

hypothesized that the location nearby crack mouth would be the only area where optimum amounts of both calcium and carbonate ions coexist. In view of mix design, the amount of leached Ca^{2+} from the matrix plays an important role on the precipitation of calcium carbonate. The analysis showed that those specimens with CSA/CA additions released more calcium ion than the control specimen. Moreover, the higher pH of specimens with additives favors the precipitation of calcium carbonate.

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