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Review

A comprehensive review on self-healing cementitious composites with crystalline admixtures: Design, performance and application

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ABSTRACT

Crystalline admixture (CA) has garnered attention as a promising self-healing agent for cementitious composites. This paper aims to provide a comprehensive review on the effects of CA on the self-healing behaviours and durability properties of cementitious composites. CA is in powder form, consisting of Portland cement and special chemicals as self-healing stimulants. Since the powder-form CA was directly mixed with the cementitious mixture, CA addition has no significant impact on the properties of fresh concrete but enhances the compressive strength of CA-cementitious composites. Furthermore, self-healing is activated by moisture, resulting in the production of calcium-based self-healing products. In terms of crack closure efficacy, CA-cementitious specimens cured under wet/dry cycle demonstrated a higher crack closure ratio than those cured under water immersion or air exposure. Specimens cured in chloride solution exhibited the best healing recovery. However, reduced mechanical recoveries are observed in specimens exposed to freeze–thaw cycles and those in chloride solution, while better mechanical recoveries are found in specimens exposed to wet/dry cycles. Overall, CA can reduce the sorptivity, permeability, chloride penetration, and the depth of sodium ions penetration, offering favourable protection for cementitious composites. Although some durability properties of CA-cementitious composites have been explored, further studies are required to investigate potential effects on shrinkage, ingress of aggressive ions, carbonation, and alkali-silica reaction (ASR). The application of CA in cementitious composites could be considered as a cost-effective approach for inducing self-healing capability, given its affordable and straightforward construction process.

1. Introduction

1.1. Background

Modern structural design codes require high strength and durable construction materials to satisfy the design needs for complex, high-rise, safer, and durable structures. Concrete is one of the most popular choices as it is strong, durable, and economic. Concrete has been widely used for various infrastructures, such as residential or commercial buildings, bridges, roads and other human-made structures [1–3]. Although concrete has many advantages [4–6], concrete is known as a quasi-brittle material, which cracks under tension impacting the serviceability of concrete structures. Cracks can be caused by shrinkage of cementitious composites under restraint conditions, such as

autogenous, free drying, and carbonation shrinkages [7–9]. Some unwanted cracks may result from unexpected loading, like earthquake, strong wind, and externally high or cold environmental temperatures, etc. [10]. Subsequently, water and aggressive ions can penetrate into the cementitious matrix and promote many other durability-related issues, like frost damage, alkali-silica reaction, corrosion of reinforcement, and sulphate attack [11,12]. Repair of concrete cracks generally requires substantial maintenance costs. Researchers [13,14] have revealed that there was an economic loss of approximately \$13 billion during the repairing and maintenance process of built concrete structures due to corrosion-induced damages in Australia. Appropriate solutions including crack-resistant concrete and crack repairment methods have been widely studied and self-healing concrete is also one of the solutions for cracking control.

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1.2. Recent advances in concrete crack healing

Various strategies have been developed for concrete crack repair, one of the advanced repair techniques is to incorporate self-healing or self-repairing agents into cementitious composites [15–21]. As Huang et al. [22] pointed out, although there were many self-healing techniques, their objective was almost the same, to seal cracks, develop denser microstructural matrix, and improve resistance of the concrete structures to aggressive-ions penetration. Several studies [23,24] divided the self-healing process as autonomous and autogenous healing.

For autonomous self-healing, some researchers [25–27] employed capsule-based healing agents, including bacterial spores [28–32] and vascular networks [33,34], in the cementitious matrix for concrete crack control and repair. The bacterial would induce precipitation of calcium carbonate to heal the cracks after the bacterial carrier is broken during cracking. Zhang et al. [35] found that additional protective strategies or nutrients were required for the survival of bacteria in alkaline cementitious matrix; Otherwise, the healing capacity could not be guaranteed. Some researchers employed hollow glass fibres [36,37] and shape memory alloys [38–40] as healing agents in autonomous healing techniques. The authors also observed that due to the brittle nature of hollow glass fibres, some healing agents were released prior to the crack initiations, lowering the self-healing capacity [35]. Chang et al. [41] reported that, due to the presence of spores or tubes, the workability of the cementitious composites was negatively affected. Shape memory alloys are also used for crack control, but this approach is much more expensive than other healing materials, limiting its real-world applications [42].

Several researchers [43,44] mentioned that autogenous self-healing could be defined as healing due to the continuous hydration of unhydrated cementitious materials or the precipitation of calcium carbonate to fill the cracks. The healing agents include expansive agents [45–56], superabsorbent polymer [57–65], and crystalline admixtures (CAs) [35,66–73]. These agents are widely utilised due to proper compatibility in repairing micro-cracks for cementitious materials. Several studies [66,67] pointed out that expansive agents were directly mixed with Portland cement in preparing the cementitious composites, and the self-healing efficiency was improved when compared with a reference group. Li et al. [57] directly added superabsorbent polymer (SAP) into binder to seal the cracks but found that numerous pores were formed due to the expansion of SAP particles. Furthermore, an advantage of autogenous self-healing of CA lies in its functionality as CA could be added to the cementitious mixture without impacting the workability [4].

1.3. Healing with crystalline admixtures

Typically, CA is mainly used as permeability-reducing agents or waterproofing materials for cementitious materials with low cost and ease of handling [74–78], and CA could be directly added into the cementitious mixture during casting. Xue et al. [79] reported that CA was in powder form, containing Portland cement, activated silicon, and special chemicals as healing stimulator. However, the detailed chemical compositions of CA are not mentioned [5,6,35,66,75,77,80], due to commercial patent protection. According to several studies [81,82], special chemicals in CA particles could react with hydration products to fill pores with crystalline deposits, and these deposits were integrated with the cementitious matrix to form a denser structure with better resistance to aggressive-ions penetration. By combining this fact and crack initiation, many researchers [76,78,83] pointed out that CA presented a high potential to act as a healing agent for repairing shrinkage or load-induced concrete cracking.

Wang et al. [84] suggested that CA can significantly reduce the gas permeability of cementitious composite, and also improve the cracking closure efficiency. Their experimental results were verified by numerical simulations using Abaqus with good agreement [84]. Borg et al. [85]

mentioned that CA addition could reduce shrinkage and creep deformation of the cementitious matrix with recycled aggregates. Several researchers [84,86,87] revealed that the main role of CA was to induce fibrous ettringite as one of the self-repairing products in the cracked zone, improving the healing efficiency. Oliveira et al. [88] pointed out that the application of CA could stimulate further hydration or pozzolanic reactions to repair the cracks, and the healing products based on CA stimulation had similar compositions when compared to hydration products. Based on the experimental study by Wang et al. [89], CA could slightly increase the 28-day compressive strength while reducing the permeability by 17 %. The authors [89] noted that comparing with curing in tap water, the healing efficiency of CA was improved by seawater curing, due to more chemical precipitations including Friedel's salt and $Mg(OH)_2$. Xue et al. [90] carried out self-healing investigations using CA and structural polyurethane. They found that the addition of CA increased recovery efficiency in terms of compressive and flexural strengths. Insoluble products such as C-S-H gel and calcite were found filling the cracking regions [90]. Jaroenratanapirom et al. [91] observed that CA could effectively heal for cracking with width < 0.1 mm in 28-day curing, but the repairing efficiency would be reduced when healing larger crack width. Li et al. [77] compared crack-healing results between control groups and mortars with CA. They suggested that CA significantly improved the self-repairing efficiency of cementitious mortars with only 1.2 % compressive strength loss. Michael et al. [92] applied CA as one of the healing agents in investigating the mechanical properties and resistance to aggressive ions of novel concrete. The authors [92] noted that the application of CA increased the load-bearing capacities of concrete samples, and the samples demonstrated better resistance to chloride-ion penetration [161–163].

1.4. Research significance and scope

Fig. 1 presents the research efforts relating to 'self-healing crystalline admixture' based on primary authors' address and year of publication globally. Based on the above-mentioned literature, many studies have been carried out to investigate the repairing mechanisms of CA in cementitious composites [4–6,83,93], while some studies focused on the self-healing of mortars with CA in different curing conditions [69–71,79]. As an external additive to the cementitious materials, it is required to clearly understand how the healing process happens and characterise the self-healing products. Furthermore, there is an increasing trend to investigate the microstructural analyses of the healing products and the healing efficiency of cracks with different widths in the cementitious composites incorporating CA. However, the research related to self-healing process under various aggressive environment exposure is limited. Meanwhile, experimental results related to the influence of CA on the durability properties of cementitious composites are limited. Hence, a thorough review should be performed to provide insightful understanding of the healing process of CA in aggressive environments and potential effects on concrete durability.

This paper aims to perform a comprehensive review of the potential effects of CA on durability-related aspects of cement-based materials. Firstly, the self-healing of different cementitious mixtures with CA was reviewed. Then, the detailed healing process of cementitious mixtures with CA exposed to different aggressive curing environments was investigated, and the resistance improvements by CA addition to durability issues, including shrinkage, chloride-ion penetration, and permeability, were discussed. Finally, an economic analysis was carried out to summarise the economic aspects of CA [164–166].

2. Properties of different CAs

Various types of CAs have been used as permeability-reducing agents to enhance the resistance of cementitious materials in blocking the access of water into the cementitious matrix. According to some studies [79,94], CA is manufactured in powder form, and most CA particles

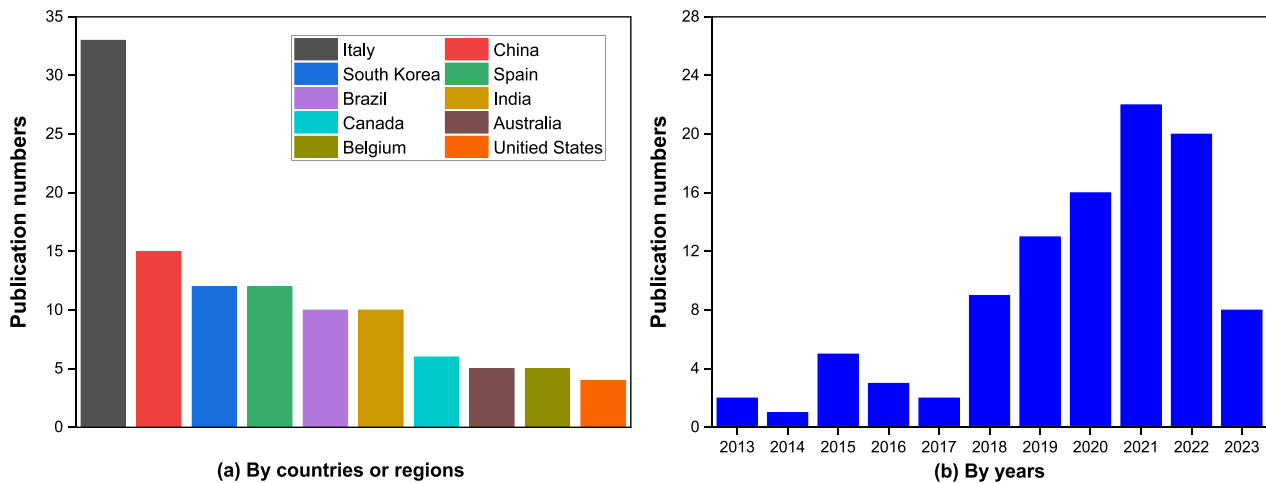


Fig 1. Publication distribution on the topic of self-healing crystalline admixture based on Scopus Database (from 2013 to 2023).

have angular shapes, as presented in Fig. 2. As commercial products, various CAs are available including Xypex and PENETRON [79,95,96]. The composition details of CAs being kept confidential and the diversity in available crystalline admixtures make the predictions of their actual effects on self-repairing process very different.

Based on the available information on CAs' composition, several researchers [35,45,46,76,90,97] agreed that CAs mainly contain calcium oxide, silica, aluminates, and special chemicals for healing stimulation. Similarly, Nasim et al. [98] mentioned that crystalline admixtures could be considered as a mixture of several chemicals and cement binder. Aiming to classify the chemical compositions of CA as a self-healing agent, X-ray fluorescence (XRF) technique was used by many authors [79,93,95–99], as summarised in Table 1.

From Table 1, it can be noted that the main oxides in CAs are calcium oxide and silica, ranging from 51.6 % to 71.2 % in weight percentage to CA content together. Although different types of CAs may have similar oxides, the proportion of the oxides varies significantly [93,98,99]. According to Park et al. [100] and Guan et al. [101], the C/S ratio (calcium to silica ratio) for Portland cement was between 3.0 and 3.4. The CAs listed in Table 1 have a C/S ratio range at 1.55 to 7.38. While the majority of CA content (up to 80 wt%) is cement powder [102], only two studies [79,95] showed that CAs had a similar C/S ratio to that of cement, being 3.5 and 3.79 respectively. Other studies [93,96–98] reported that CAs had a higher C/S ratio ranging from 4.2 to 7.38. The CA used in the study by Alvee et al. [99] had a relatively low C/S ratio,

which was only 1.55, containing higher content of Fe_2O_3 (27.23 %), while the content of Fe_2O_3 in other studies was generally less than 4 %.

For other oxides, Garcia et al. [96] observed TiO_2 , SrO, and P_2O_5 in the Xypex CA powder, ranging from 0.06 to 0.17 %. Park et al. [100] also found SrO, P_2O_5 and MnO below 0.2 % in the Xypex crystalline admixtures. Moreover, a high content of MgO was found in the study by Park et al. [100] and Wang et al. [95], being 15.9 % and 11.3 % respectively. This variation indicates that the composition of CA products varies largely, even produced by the same manufacturer, and the detailed designs highly depend on the trading secret. Further evidence can be obtained by comparing the C/S ratio of Xypex CA in studies conducted by Park et al. [100], Wang et al. [95], and Garcia et al. [96], which was 3.31, 3.79 and 7.38 respectively.

3. Effect of CA on fresh and hardened concrete

Although CA has been widely used as permeability-reducing agents, limited information is available about how the addition of CA may affect the physical and mechanical properties of cementitious composites. Meanwhile, Oliveira et al. [88] pointed out that it was necessary to ensure that the addition of any supplementary cementitious materials (SCMs) did not negatively affect the properties of cementitious composites. Hence, this review aims to investigate the actual effects of CA addition on mortar and concrete samples in both fresh and hardened states.

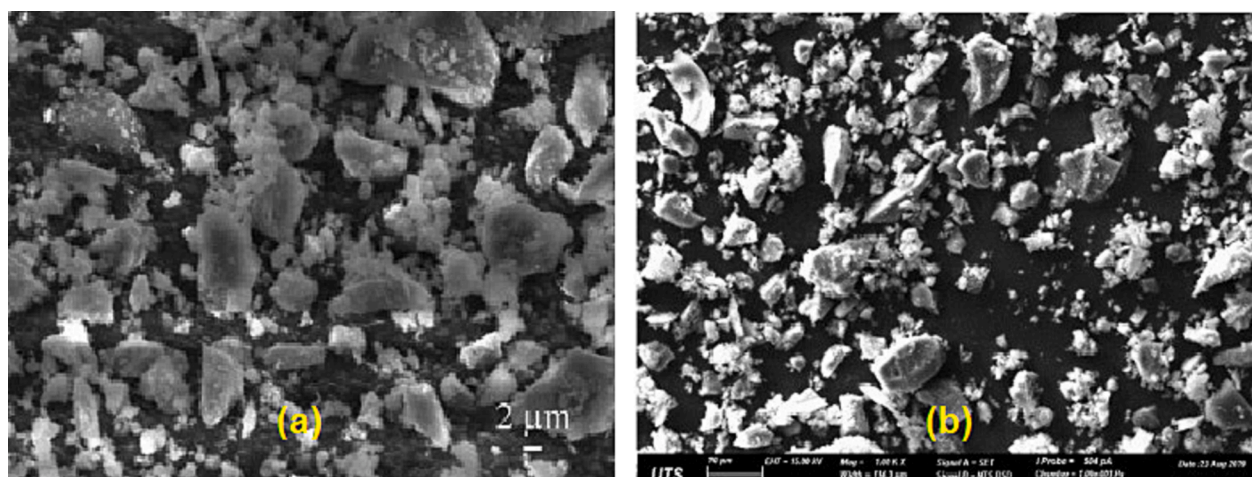


Fig 2. Morphology of CAs in different studies: (a) by Ferrara et al. [94]; and (b) by Xue et al. [79].

Table 1
Chemical composition of different crystalline admixtures.

Oxides	Pentens T-308 CA [99]	CA [93]	CA [98]	PENETRON Admix® [79]	Xypex CA [95]	Xypex CA [96]	CA [97]
CaO	32.58	44.0	67.72	47.26	53.53	59.77	57.5
SiO ₂	21.07	7.6	11.37	13.48	14.1	8.1	13.7
Fe ₂ O ₃	27.23	1.6	3.15	1.44	1.84	2.08	2.81
Al ₂ O ₃	3.46	1.3	8.22	3.7	4.36	1.98	3.45
Na ₂ O	3.51	3.3	1.01	11.02	—	1.29	13.1
K ₂ O	0.26	0.3	1.17	0.74	—	0.44	1.02
SO ₃	2.71	1.5	—	2.05	2.79	2.09	3.77
MgO	—	1	6.02	3.54	11.3	0.82	4.19
LOI	9.18	36.9	1.34	16.77	12.08	23.43	0.46

Note: LOI refers to loss on ignition

3.1. Fresh properties

Munn et al. [103] investigated the potential impact of CA addition on the flowability of CA-cement composites. They found that the addition of 0.8 wt% CA did not affect the flowability of concrete samples, and almost the same slump results were observed. Similarly, Wang et al. [104] compared the flowability of concrete samples with and without additional CA additives, and they observed that CA addition had no obvious impact on slump results when compared with that of CA-free concrete samples. According to Wang et al. [104], since the major content of CA was cement power, the variance of CA addition had no apparent effects on the flowability of cementitious composites. Some studies [80,88] advised that by comparing the chemical compositions of CA and cement, as similar results were obtained by the XRF test, the addition of CA had no obvious negative impact on the workability of CA-cement samples.

For setting times, Munn et al. [103] mentioned that although CA could promote self-healing efficiency, the CA addition delayed the setting times by up to 18 %. They suggested that the addition of CA increased the entrapped air content delaying the setting time, being consistent with the study by Nataadmadja et al. [105]. However, Zheng et al. [106] analysed both initial and final settings for samples with and without CA, and concluded that CA addition did not increase the setting times of cementitious composites. They reported that the setting time of different samples variation was up to 3 %, which indicated that CA had no apparent influence on the setting times of CA-cement composites. Furthermore, several studies [76,83,88] also agreed that there was no clear increment of setting time for CA-cement specimens when compared with CA-free samples. Overall, by analysing the above literature, only marginal differences were found in the workability and the setting time, showing that CA addition has negligible effect on fresh cementitious composite properties.

3.2. Mechanical properties

Wang et al. [104] investigated the effect of CA addition on the compressive strength development of fly ash–cement mortars. 0.8 wt% of CA powder led to strength increments of 8.5 % and 8 % for samples cured for 28 days and 90 days [104]. Several studies [69,104] pointed out that CA can promote pore-blocking deposits of calcite improving the compactness of CA-cementitious matrix, leading to a higher compressive strength when compared to reference mortars. Borg et al. [107] analysed the compressive strength of mortar samples with 1 wt% CA and concluded that 12.6 % of compressive strength increment was observed in CA-cement mortars compared to CA-free samples at 28-day exposure. They suggested that the primary reason for the strength gain lied in the porosity reduction of the cementitious matrix, a denser matrix providing a higher resistance to compressive loads, being in good agreement with other studies [76,83].

For CA-concrete samples, Zheng et al. [106] added 0–1.6 wt% CA into concrete samples, leading to a strength increment of approximately 10 % on concrete samples with 1 wt% CA. Zheng et al. [106] suggested

that CA stimulated the formation of crystalline deposits to positively affect the microstructure of the cementitious matrix. A denser CA-cementitious matrix was formed by sealing the pores. As depicted in Fig. 3, apparently, by adding 0.8 wt% CA, the volume of macropores in the cementitious matrix is significantly reduced compared to that of macropores in CA-free samples, highlighting the benefit of CA addition in protecting internal matrix of structural concrete. Chandra et al. [66] observed that an addition of 1.1 wt% CA promoted 11.45 % strength increase for CA-concrete composites compared to reference samples. They mentioned that special chemicals in CA induced formations of C-S-H gels fill the voids and pores in the microstructure of concrete, leading to a higher compressive strength.

Overall, the studies validate that CA addition can improve the compressive strength of CA-cementitious composites. The primary reason is that CA powder promotes the formation of different insoluble products, including calcite [69,104] and C-S-H gels [66], to fill the pores and voids of cementitious matrix. Thus, a denser cementitious composite is leading to a higher comprehensive strength when compared with CA-free samples. Many studies [88,108] added that the reduction in porosity in CA-cement matrix not only promoted the strength development to resist compressive loads but also provided better protection to internal steel reinforcement, improving overall structural resilience.

However, compared to strength improvement in compressive strength (up to 12.6 % increase), CA addition does not seem to improve tensile strength. Oliveira et al. [88] explained that although the microstructure was denser, negligible improvement in tensile strength was observed, since denser microstructure provides only limited improvement to the tensile plane, observation being consistent with other studies [83,104,106]. For flexural strength investigation, Sisomphon et al. [109] observed a slight improvement of about 4.8 % for the flexural strength of CA-cement specimens. Likewise, other studies [35,81,107] noted that due to the brittle nature of the cementitious matrix, although CA promoted pore-blocking reactions, only a marginal contribution was found in terms of flexural strength enhancement. To sum up, adding CA into cementitious composites can lead to an improvement in compressive strength due to denser microstructure but leads to less improvement in tensile and flexural strength, caused by the inherent brittle nature of concrete.

4. Effect of CA on self-healing efficiency

4.1. Self-healing mechanism

Many previous studies [35,45,46,76,90,97] mentioned several unknown chemicals in CA powder, stimulating the precipitation of different crystalline deposits in the cracked regions. Table 2 depicts the possible reactions in the self-healing process.

For the sample precipitation of healing products, based on the study in [83], these active chemicals as $2nCa(O-R-OH)_2$ in Eq. (1) contained both hydrophilic component ($-OH$) and hydrophobic component ($-R$), and the reactions are described by Eqs. (1) and (2):

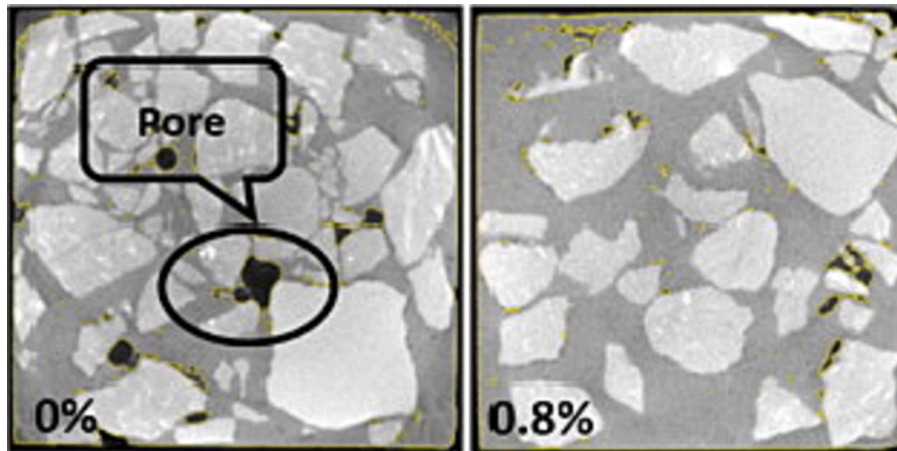


Fig 3. Pore-blocking induced by CA addition [106].

Table 2
Possible self-healing reactions.

Self-healing reaction	Healing products	Refs.
Carbonate precipitation	$CaCO_3$	[83,110,111]
Complex precipitation	C-S-H gels and $M_xCaR_x - (H_2O)_x$	[69,112–115]
Recrystallisation	Mono-carbo-aluminate (MCA), Mono-sulfo-aluminate (MSA)	[4,116–118]

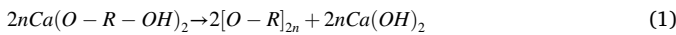
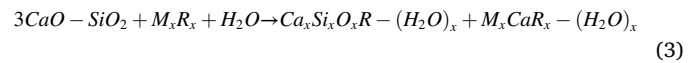


Fig. 4 shows the stimulation of CA on the self-repairing process after cracking. Hu et al. [83] explained that, when the crack occurred, active chemicals permeated into the cracked zone, stimulating the formation of calcium hydroxide and crystals $([O - R]_{2n})$ under a high moisture condition. Calcium carbonate was precipitated in the presence of carbon dioxide, and the crystals $([O - R]_{2n})$ were then accumulated. The authors [83] mentioned that after a reduction in pH of the cementitious matrix, $Ca(O - R - OH)_2$ would form developing a continuous self-healing capacity of CA. Similarly, many other studies [66,101,115,119] suggested a long-term self-healing capability was observed due to the accumulation of active chemicals. Some researchers [79,90,115,118] agreed that

active anions in CA promoted the reaction rate of calcium ion to form various deposits repairing micro-cracks. Sisomphon et al. [46] revealed that high concentration of Ca^{2+} was observed in the healed zone of the cementitious composites, being in agreement with other studies [79,90]. Some other studies [88,120] pointed out that the stimulation of calcium carbonate by CA also improved the density of the cementitious composites, since the crystalline deposits could block the micro-pores of the cementitious matrix. As a result, CA promotes the reduction in permeability of CA-cement matrix.

Likewise, several studies [6,69,114,120] suggested that relatively complex deposition reaction in self-healing process could be expressed as Eq. (3):



where M_xR_x is the indication of active chemicals, $Ca_xSi_xO_xR - (H_2O)_x$ mainly refers to C-S-H gels, and $M_xCaR_x - (H_2O)_x$ refers to the major healing deposit [88].

Based on the chemical reaction in Eq. (3), the addition of CA powder would promote the production of C-S-H gels and insoluble crystalline precipitation. Considering Eqs. (1) to (3), with the stimulation by active chemicals, cement is consumed to form different non-soluble deposits healing micro-cracks as shown in Fig. 5. Similar to reactions described by Eqs. (1) and (2), the presence of water is an important factor for the chemical precipitations. The reason is that continuous moisture

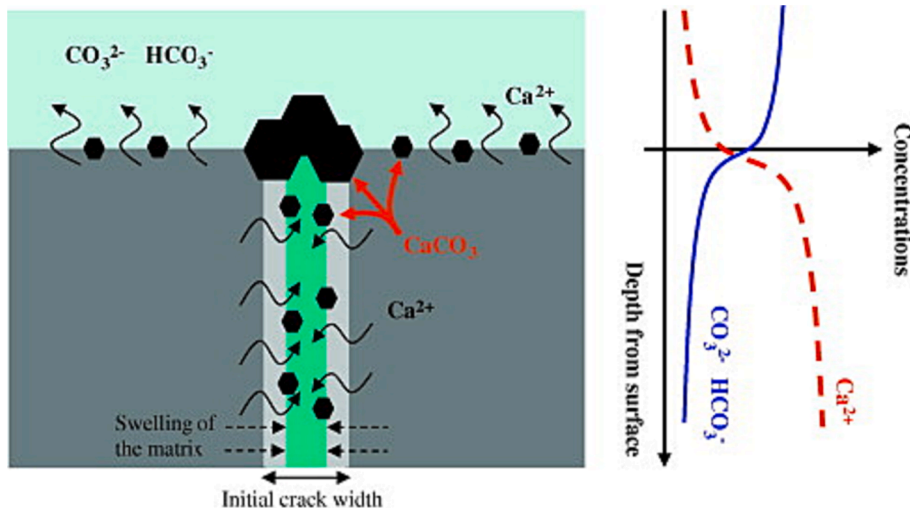


Fig 4. Stimulation of CA on the self-healing process [46].

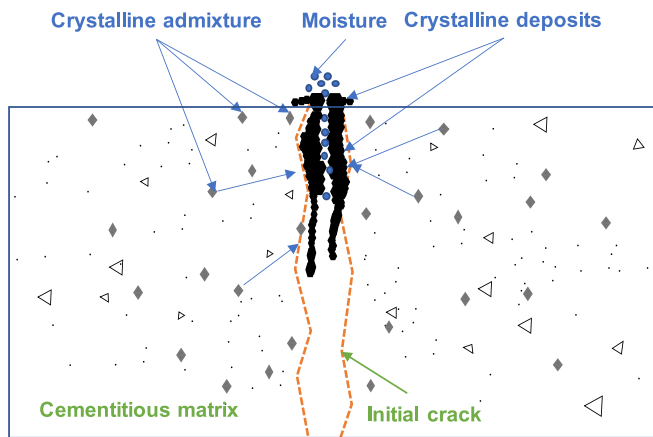


Fig 5. Complex deposit reaction induced by CA in sealing cracks.

accounts for prolonging the self-healing process promoted by CA, as the combination of CA and surrounding moisture stimulates crystalline deposit-blocking micro-cracks [121]. Ferrara et al. [122] stated that C-S-H was found in the self-healing products via SEM-EDS analysis. Similarly, other studies [68,79,90] also revealed the presence of C-S-H gels in the healing products, due to the possible pozzolanic reactions under CA stimulation. Bao et al. [123] mentioned that with the presence of water in cracked regions, CA stimulated the continuous hydration of unhydrated cementitious materials to form C-S-H gel, improving repairing efficiency and compactness. Jiang et al. [121] observed that CA provided better self-healing efficiency, and more C-S-H gels were formed in the healed zone, which was verified by energy dispersive spectrometry analysis (EDS). Meanwhile, they noted that healed zone was denser than the uncracked zone, revealing the fact that CA also induced pore-blocking precipitation to improve the density of CA-cement matrix, being consistent with several studies [66,112]. Guan et al. [101] used CA as the major repairing agent, and it was found that CA induced more C-S-H gels in the healing products compared to healing products of CA-free specimens via analysing TG curves. They also noticed that the percentage of CaCO_3 in self-healing products was higher than that of CA-free mortars, suggesting that CA increased the formation of C-S-H gels and CaCO_3 [101].

Considering the recrystallisation reaction, many studies [4,117,118] reported that the healing process was related to the recrystallisation of the C_3A (tri-calcium aluminate) phase of the cementitious materials or $\text{Ca}(\text{OH})_2$ to Mono-carbo-aluminate (MCA) or Mono-sulfo-aluminate (MSA). Rahhal et al. [124] reported that with the presence of moisture, CH was consumed in the recrystallisation reaction stimulated by crystalline additives to form MSA, and a typical recrystallisation reaction is depicted in Fig. 6. Oliveira et al. [4] suggested that under CA stimulation, part of the unhydrated cementitious materials was recrystallised into MCA, filling the micro-cracks, and refining the cementitious matrix. Huang et al. [22] reported that when crack forms, under the activation by moisture, CA would promote the recrystallisation of $\text{Ca}(\text{OH})_2$ into MCA as crystalline deposits to repair micro-cracks. They also mentioned that the continuous supply of water was the main governing factor for long-term self-healing capacity of CA, and the thermal stability of MCA was higher than that of CaCO_3 . Similarly, Lothenbach et al. [116] revealed that MCA was thermally stabler than CaCO_3 , contributing to the porosity reduction.

By considering three possible reactions in describing self-healing process, the major healing mechanisms by CA stimulation are governed by two aspects: despite different self-healing products are formed in cracked regions, they are generally identified as calcium-based products, which is verified by SEM-EDS analysis [121,122] and TG analysis [79,90,101]. In particular, the result of SEM-EDS analysis indicates that the atomic percentage of Ca^{2+} in healing products is higher

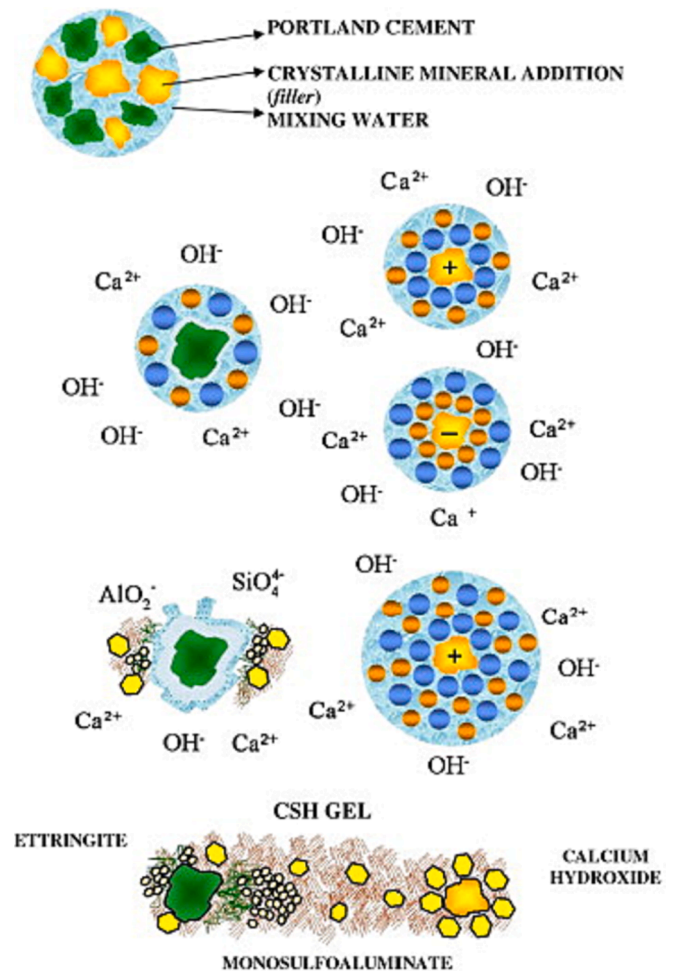


Fig 6. Recrystallisation reaction induced by CA [124].

than that in the uncracked cementitious matrix, while the atomic percentage of Ca^{2+} at some points in healing products were 100 % [90]. Likewise, Xue et al. [79] observed that Ca^{2+} ions were leached from unhydrated cementitious matrix and accumulated to form various crack-blocking deposits. Secondly, Hu et al. [83] mentioned that moisture played a crucial role in activating the special chemicals in CA power, stimulating the repairing process as cracks occurred. Since water could penetrate into the cementitious matrix after crack initiation, the self-healing process could be activated with less limitations, being beneficial for cracking closure.

4.2. Self-healing behaviour

Although the primary purpose of CA addition is to reduce the permeability of the CA-cement matrix, many studies [76,78,83,88] mentioned that, due to the capacity of inducing pore-blocking precipitation, CA has been used as an alternative in repairing the microcracks of cementitious materials. Table 3 summarises the effects of CA addition on healing efficiency in different studies.

Chandra et al. [66] revealed that the curing environment directly affected the self-healing efficiency of CA-cementitious composites, lying on the differences in types and microstructures of crystalline deposits. As a result, it is crucial to carry out a separate review on the self-healing efficiency of cementitious matrix with CA addition subjected to different curing environments.

4.2.1. Non-aggressive curing environment

Chandra et al. [66] added 1.1 wt% CA into the cementitious mixture,

Table 3
Healing efficiency of CA-stimulated self-healing process.

CA content	W/C ratio	Experimental programme	Curing condition	Major conclusions of crack closure	Refs.
Not mentioned (1.1 wt%)	0.45	Mechanical testing, self-healing products analysis (FTIR, SEM-EDS)	Water immersion, wet-dry cycle, air exposure	Completely healed with CA addition	[66]
Not mentioned (0–4.5 wt %)	0.5	Mechanical testing, mercury intrusion porosimetry, SEM-EDS, TGA	Water immersion	Completely healed with CA addition	[35]
Xypex (2 wt %)	0.3	Mechanical testing, shrinkage	Water immersion, wet-dry cycle, air exposure	Completely healed with CA addition	[95]
Not mentioned (2 wt%)	0.53	Mechanical testing	Water immersion, air exposure	CA addition improved healing efficiency	[80]
Not mentioned (2 wt%)	0.43	Mechanical recovery, SEM-EDS	Water immersion, wet-dry cycle, air exposure	CA addition improved healing efficiency	[72]
PENETRON Admix® (0.8 wt%)	0.33	Mechanical testing, shrinkage, visual crack observations, TGA	Water immersion, wet-dry cycle	Completely healed with CA addition	[74]
Not mentioned (0–2 wt%)	0.33	Self-healing products analysis (SEM-EDS, Raman spectroscopy)	Water curing at 60 °C for 7 days and 178 days	Partial and total crack repair	[93]
PENETRON Admix® (1 wt%)	0.4	Mechanical recovery, SEM, TGA	steam curing at 80 °C for 3 days	CA addition improved healing efficiency	[90]
Not mentioned (1.5 wt%)	0.53	Self-healing analysis, Raman Spectroscopy	Water immersion, wet-dry cycle, freeze-Thaw cycles	CA addition improved healing efficiency	[45]
Not mentioned (1 wt%)	0.63	self-healing analysis, ultrasonic testing, SEM	Water immersion, wet-dry cycle, freeze-Thaw cycles	Completely healed with CA addition	[94]
PENETRON Admix® (1 wt%)	0.3	Strength recovery, XFD, FTIR, ESEM-EDS, TGA	0.5 M and 2 M NaCl solution, distilled water	Totally healed in NaCl solution, partially healed in distilled water	[79]

and they found that the addition of CA promoted the self-healing efficiency of CA-cement. Chandra et al. [66] observed that samples cured in water immersion and wet-dry cycle had higher strength recovery than that of samples cured in air exposure. The reason is that due to the continuous supply of moisture, CA could promote formations of crystal deposits and CaCO_3 in repairing micro-cracks [66]. Similarly, Zhang et al. [35] reported that the crack-closure efficiency of CA-cement composites was enhanced due to CA addition, and the concentration of CaCO_3 in self-healing products was increased by 5.22 % compared to control group. They revealed that the primary role of CA addition was to

accelerate the formation of various crack-blocking deposits, including CaCO_3 and C-S-H (in Fig. 7), being consistent with other studies [125,126].

Wang et al. [95] found that CA addition could not only reduce the shrinkage of CA-cement composites, but also improve the self-repairing efficiency compared to the control groups when cured in water immersion and wet-dry cycle. However, several studies [95,127] mentioned that if CA-cement samples were cured in ambient conditions, the healing capacity was insufficient due to the lack of moisture, being in agreement with other studies [22,123]. In the study by Cuenca et al. [74], 0.8 wt% of CA was mixed with cementitious mortars, and they found that CA promoted the healing efficiency of the cementitious materials subjected to multi crack-healing cycle. Cuenca et al. [74] observed the continuous healing capacity of CA after conducting multiple cracking-healing cycles. The evidence is that CA completely heals cracks induced by the first pre-cracking, and it heals up to 70 % of reopened cracks due to second pre-cracking [74]. To accelerate the self-repairing process, Oliveira et al. [93] cured CA-cement composites in water at 60 °C for 7 days and 178 days for the self-healing product analysis, including SEM-EDS, TGA and Raman Spectroscopy. They reported that, in terms of short-term curing, more formations of MCA (Mono-carbo-aluminate) were observed in the cracked regions with 1–2 wt% CA. In terms of long-term curing, Oliveira et al. [93] mentioned that 2 wt% CA addition had better self-healing efficiency, and they noted that CA provided continuous healing capacity, since the repairing process could be activated by the presence of moisture and supply of CH, agreeing with several studies [115,118]. Xue et al. [90] steam cured all pre-cracked samples in steam at 80 °C for 3 days. They observed that after the accelerated healing process, crystalline deposits were precipitated, sealing cracks, and blocking the micropores, as illustrated in Fig. 8. Several studies [90,128] mentioned that high-temperature curing could improve the healing efficiency, as the formation of secondary ettringite was promoted due to the transformation of metastable hydration products, including monosulfate (AFm).

Azarsa et al. [80] cured 2 wt% CA to investigate the self-repairing efficiency and durability properties of concrete samples, and they found that the addition of crystalline admixtures reduced the permeability and improved the healing capacity of CA-cement composites. The micro-cracks were sealed by the formation of deposits compared to control groups, as more crystalline deposits were stimulated in the cracked region [80]. Likewise, Lauch et al. [72] examined the potential effects of CA on sealing efficiency of concrete. They found that the

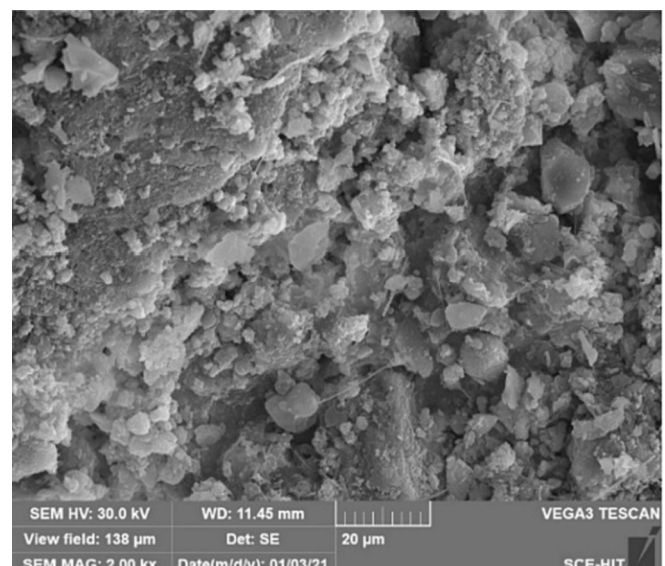


Fig. 7. Ball-shaped crystalline deposit in healed region [35].

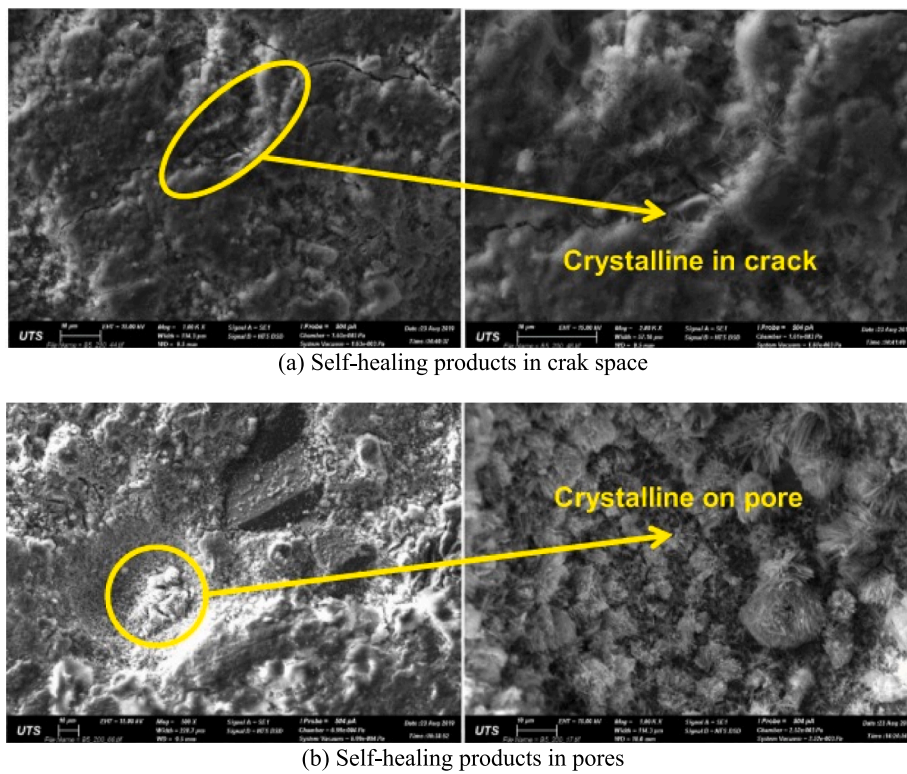


Fig 8. Self-healing products in the cracked region and pores [90].

addition of CA improved both strength regain and recovery rate of CA-concrete samples, and samples cured in wet-dry cycle had 99 % strength regain. As illustrated in Fig. 9, cracked areas found in samples cured in wet/dry cycles had been fully sealed, while that of samples cured in air exposure was slightly healed [72]. Many studies [6,66,72] revealed that

the type of self-healing agents had less impact on strength recovery due to similar healing products, and the compactness of self-healing products was the contributing factor of strength recovery after sealing cracks. Furthermore, several studies [129–131] observed that CA addition could also promote the sealing efficiency of ultrahigh-performance concrete

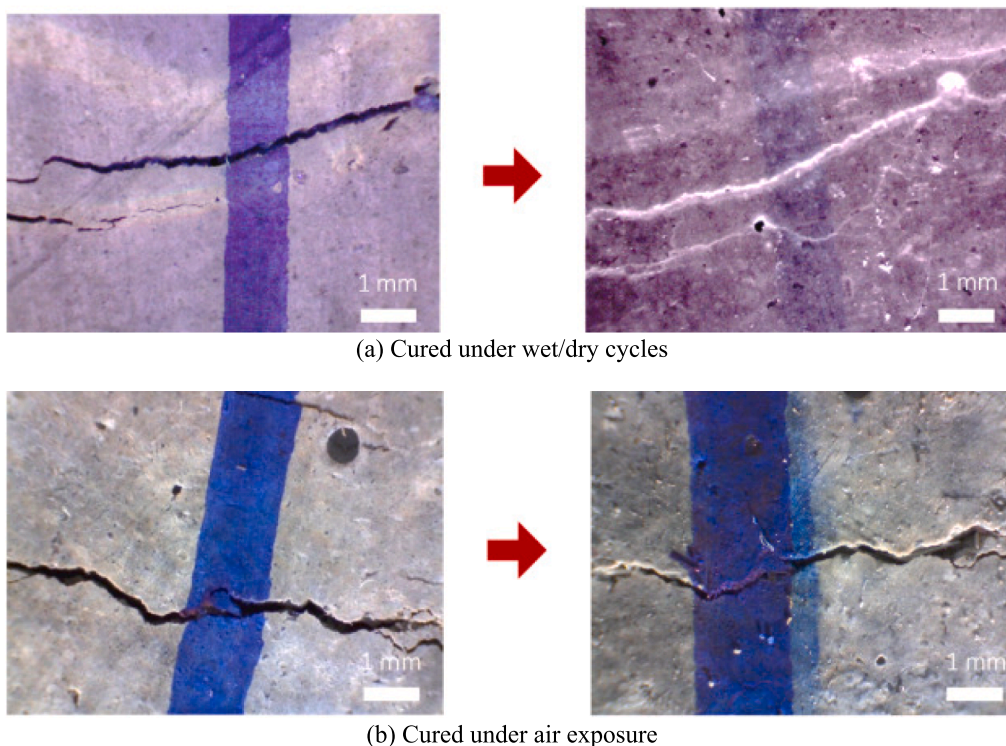


Fig 9. Healing efficiency comparison between samples cured in wet/dry cycle and air exposure [72].

(UHPC) samples.

4.2.2. Aggressive curing environment

Ferrara et al. [94] considered various curing conditions for CA-concrete composites, including water immersion, wet-dry cycle, and freeze–thaw cycles (FTC). For samples exposed to FTC, Ferrara et al. [94] reported that concrete samples with CA addition had faster cracking recovery than CA-free samples, as CA stimulated more formation of CaCO_3 along the cracked region. Unlike the self-healing products with round shapes induced in wet/dry cycle in Fig. 7, needle-like crystalline deposits are produced in Fig. 10, which may be due to the changing temperature. However, they suggested that compared to samples exposed to wet-dry cycles, CA-cement composites exposed to FTC had lower mechanical strength recovery, as the crystalline deposits were negatively affected by the temperature fluctuation. An evidence is that several minor cracks are found in the self-healing product of samples cured in FTC via SEM analysis [94]. Ferrara et al. [94] utilised ultrasonic testing to monitor the damage recovery of CA-concrete samples and CA-free samples. They found that the addition of CA increased the acoustic velocity of samples after the healing process, due to a higher crack closure rate. Ferrara et al. [94] suggested that the findings in ultrasonic testings were in agreement with the findings in mechanical recovery investigation, highlighting the feasibility of CA addition in improving the self-healing efficiency of concrete specimens. Furthermore, Aspiotis et al. [45] conducted self-healing investigations on CA-concrete samples subjected to water immersion and FTC. They observed that the strength recovery of CA-concrete specimens cured in FTC was lower than those cured in water immersion. The reason is that the formation of C-S-H gels and CaCO_3 is interfered when cured in FTC. This delay in the deposit formation has been reported by many studies [45,132].

Considering aggressive environment exposure, Xue et al. [79] investigated the potential effects of chloride ions on the self-healing efficiency of CA-cement samples. 0.5 M and 2 M NaCl solutions were used as the aggressive environment. It was observed that although CA accelerated the formation of pore-blocking deposits, the crack closure rate of samples cured in chloride solutions was higher than that of samples cured in distilled water since chloride ions contribute to increasing the formation of solid deposits in sealing microcracks [79]. Many studies [79,133] believed that AFm phases in the cementitious matrix were consumed by Cl^- ions to form Friedel's salt (Fs), providing additional deposits for crack closure. However, Xue et al. [79] pointed out that, despite the presence of chloride ions improving the crack-closure rate, the flexural strength recovery of samples exposed to Cl^- solution was lower than that of samples cured in distilled water. Several researchers explained [79,134,135] that Cl^- ions interfered with and

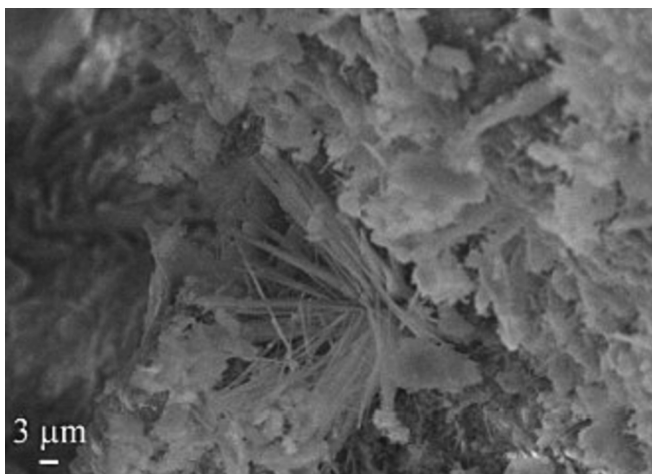


Fig. 10. Self-healing deposits under FTC [94].

weakened the bonding between healing products and cracked surfaces, lowering the resistance to flexural loads. Likewise, Yalley et al. [136] suggested that Cl^- ion changed the mineralogy of the initial repairing products compared to that under water curing, causing a reduction in the flexural capacity of self-healing products.

4.3. Self-healing efficiency comparison

Concerning the efficiency of crack-mouth healing in the self-healing process, many studies [35,66,74,95] verified that CA addition could heal the microcracks up to 56-day exposure. Zhang et al. [35] revealed that 81.5 % crack closure could be achieved for pre-cracked samples (0.118 mm cracking width) subjected to a 28-day wet/dry cycle, whereas Cuenca et al. [74] found that, cured in 30-day wet/dry cycle, pre-cracked samples with 0.11 mm cracking width were healed by 80 % (Fig. 11). In both studies, similar results are obtained, although 1.5 wt% CA was used in the study [35], it did not provide significant improvement compared to 0.8 wt% CA addition. Chandra et al. [66] reported that, after adding 1.1 wt% CA, a 90 % closure rate could be achieved for pre-cracked samples with 0.2 mm crack width exposed to 42-day wet/dry cycles. This result highlights that when prolonging the exposure duration, a higher closure rate can be obtained since CA additives provide long-term repairing capacity for pre-cracked samples. Xue et al. [90] accelerated the healing process by applying 80 °C steam for 3 days. 92 % cracked area could be sealed. Fig. 11 shows that only samples cured in chloride solution for 30 days were fully healed, which is due to the additional formation of Fs and ettringite [79]. Overall, longer exposure time and higher curing temperature could further boost the healing rate of CA-cement composite. However, although FTC curing provides a higher sealing rate, temperature fluctuation negatively affects crack closure [94].

Regarding flexural recovery during the self-healing process, it is completely different from that of the closure rate observed. Although samples cured in a chloride environment have the best closure rate, due to the excessive formation of Fs and ettringite [79,133], Cl^- ions also interfere with the strength recovery of self-healing products, lowering the flexural capacity of healed samples. Similarly, although CA addition improves the repairing efficiency of cementitious composites compared to that of CA-free samples subjected to freeze–thaw cycle curing [94], microcrack formations lower the flexural recovery compared to that cured in wet/dry cycle. Overall, the best curing environment of CA-cement composites is wet/dry cycle, which could provide a faster closure rate and more favourable flexural recovery.

5. Effects of CAs on concrete durability

Many studies [111,137–140] pointed out that there were concerns when adding different supplementary materials to cementitious systems, due to unknown effects on concrete durability properties. As a result, many researchers [35,45,80,119,136,141] carried out parametric studies investigating the potential effects of CA addition on the durability of mortars and concretes. Tables 4–6 depict the potential impacts of adding crystalline admixture powder on the durability properties of CA-cement composites, including sorptivity (Table 4), permeability (Table 5), and chloride-ion penetration (Table 6).

5.1. Water sorptivity

Aspiotis et al. [45] carried out experiments to investigate the potential impacts of CA addition on the sorptivity of concrete samples. 14 % sorptivity reduction could be achieved by adding 1.5 wt% CA to the cementitious matrix after the cracks were sealed. During the curing process, CA powder not only stimulates the formation of crystalline deposits in the cracks but also improves the blocking of macropores near the cracked regions, reducing the sorptivity of CA-concrete samples [45]. Some studies [45,142] explained that the main reason for the

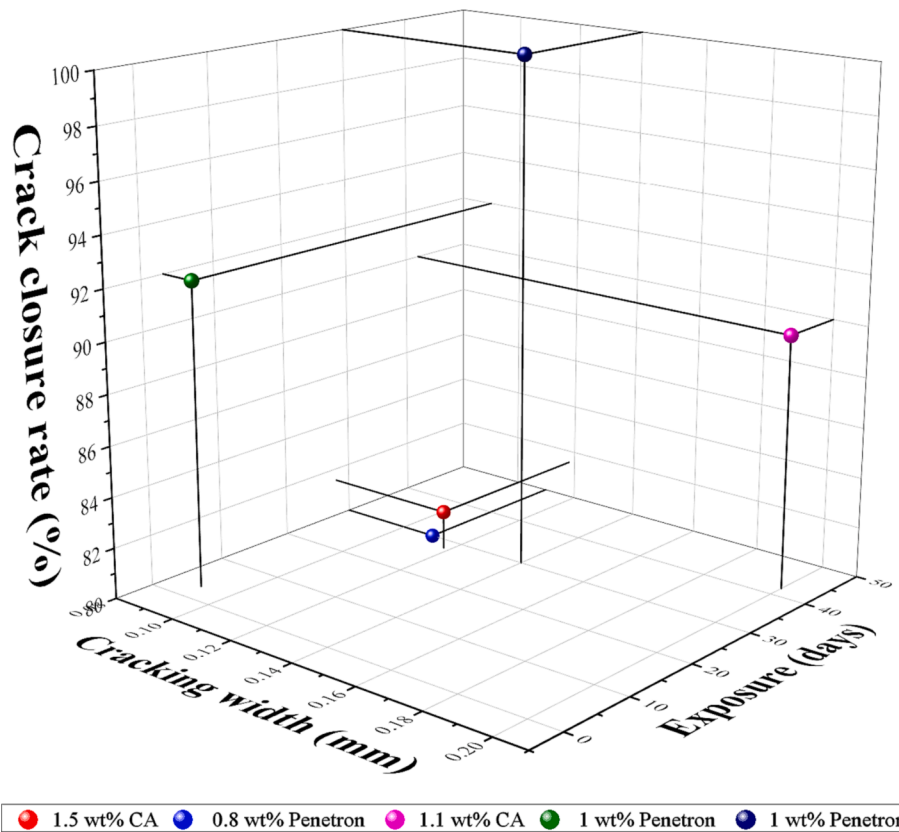


Fig 11. Healing efficiency comparisons (1.5 wt% CA [35], 0.8 wt% PENETRON [74], 1.1 wt% CA [66], 1 wt% PENETRON [90], and 1 wt% PENETRON [79]).

Table 4
Effects of CA addition on sorptivity reduction.

CA content	W/C ratio	Major conclusions	Ref.
Not mentioned (1.5 wt %)	0.53	Sorptivity was reduced	[45]
PENETRON Admix® (1.2 wt%)	0.5	Sorptivity was reduced by 35–45 % at 56 days	[77]
Not mentioned (0–4.5 wt%)	0.5	Sorptivity was reduced by 20.3 % at 28 days (1.5 wt% CA)	[35]

Table 5
Effects of CA addition on impermeability improvement.

CA content	W/C ratio	Major conclusions	Refs.
Not mentioned (0–4.5 wt%)	0.5	18.92 % permeability reduction with 1.5 wt% CA addition	[35]
Not mentioned (0–5 wt%)	0.45	The permeability was reduced with 2 wt% CA addition	[121]
Not mentioned (2 wt %)	0.532	25 % improvement on impermeability	[80]
Not mentioned (2 wt %)	0.43	The permeability was reduced	[72]
Xypex Admix (2 wt %)	0.44	The permeability was reduced	[148]

sorptivity reduction is that less capillary channels existed in cementitious matrix due to crack closure and pore blocking, reducing the overall water permeation. Li et al. [77] carried out sorptivity experiments to test pre-cracked and healed specimens with CA addition. After 56-day curing, compared to the control group, the sorptivity of healed slag-cement specimens with 1.2 wt% addition was reduced by 35–45 %, highlighting the benefit of CA addition to repair microcracks while

Table 6
Effect of CA addition on resistance against chloride penetration.

CA content	W/C ratio	Experimental programme	Major conclusions	Refs.
Not mentioned (2 wt%)	0.532	Rapid chloride permeability test (RCPT)	19 % resistance improvement at 56-day exposure	[80]
Not mentioned (1.5 wt%)	0.53	Rapid chloride permeability test (RCPT)	Higher chloride-penetration resistance	[45]
Not mentioned (0.8 wt%)	0.41	Rapid chloride permeability test (RCPT)	Reduction of chloride permeability	[92]
Not mentioned (0.5–1 wt%)	0.56	Chlorides penetration test	19.3 % reduction of chloride permeability	[6]
PENETRON Admix® (0.8 wt%)	0.5	Chlorides penetration test	14.75 % reduction of chloride penetration	[155]
PENETRON Admix® (1 wt %)	0.2	Chlorides penetration test	Resistance was improved for UHPC	[141]

reducing the water absorption. Li et al. [77] mentioned that chemicals in CA powder induced additional crystalline deposits blocking water-accessing pores, lowering sorptivity, agreeing with other studies [143,144]. Similarly, Zhang et al. [35] investigated the potential effects of CA addition on the water-absorption performance of cement mortars. Adding 1.5 wt% CA into mortars, they observed that approximately 20.3 % reduction in sorptivity after 28-day curing. The reduced sorptivity was beneficial to improve the resistance to aggressive substances penetrating the cementitious matrix.

Fig. 12 compares the sorptivity reduction observed in different studies. For CA-cement composites cured for 28 days, the reduction in sorptivity was 14 % and 20.3 % according to Aspiotis et al. [45] and

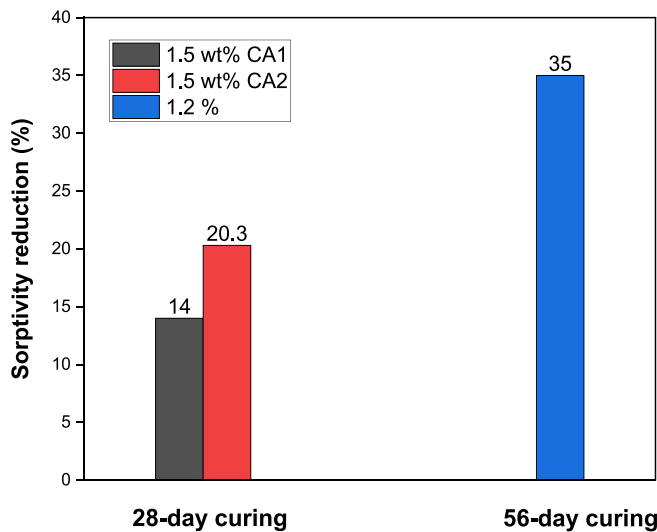


Fig 12. Sorptivity reduction comparison (1.5 wt% CA1 [45], 1.5 wt% CA2 [35], and 1.2 wt% PENETRON [77]).

Zhang et al. [35] respectively (Table 4). A lower reduction in sorptivity was reported by Aspiotis et al. [45] due to a relatively more porous interfacial transition zone in concrete matrix compared to mortar matrix. Although CA stimulates pore-blocking deposits, in a given healing timeframe, chemicals in CA could only partially block the micropores in concrete matrix, resulting in a higher water absorption [101,108]. Concerning the sorption differences of mortar samples reported by Li et al. [77] and Zhang et al. [35], the first reason is that Li et al. [77] cured the CA-mortar specimens for 56 days. Due to the longer curing time, more crystalline deposits are induced by CA powder, providing a denser surface structure. Several studies [82,145] suggested that CA could stimulate a continuous healing process with the presence of moisture, improving the overall compactness of the cementitious matrix due to the additional pore-blocking process. Secondly, Li et al. [77] partially substituted cement with granulated blast furnace slag (GBFS) in sustainable mortars. They suggested that samples with 10 wt% GBFS for cement replacement demonstrated better sorptivity reduction at 56-day exposure. The reason is that, compared to cement, higher silica content of GBFS provided additional formations of C-S-H gels through pozzolanic reaction sealing the cracks and pores [77,121,146].

5.2. Permeability

Zhang et al. [35] observed that the addition of CA positively impacted permeability. They found that after adding 1.5 wt% CA, 18.92 % permeability reduction was achieved compared to that of CA-free mortar samples subjected to 28-day curing, indicating the impermeability enhancement by chelating CA powder. Based on the findings by Zhang et al. [35] and Chen et al. [147], the primary reason for the permeability reduction was due to the filling of the pore structure by crystalline deposits, agreeing with the sorptivity reduction reported by Zhang et al. [35]. Likewise, Jiang et al. [121] compared the permeability coefficient of CA-free mortars and mortars with 2 wt% CA after 28-day curing, they observed that the presence of CA improved the resistance of permeability by inducing more deposits of healing cracks and blocking pores. While there is a 30 % reduction in the permeability of mortars with 2 wt% CA, Jiang et al. [121] suggested that the permeability could be further reduced by replacing cement with silica-rich materials, leading to more formations of C-S-H gels for improving the overall compactness of the cementitious matrix.

Considering the potential effects of CA addition on permeability reduction for concrete samples, Azarsa et al. [80] investigated the permeability of concrete specimens with 2 wt% CA. They noticed that

approximately 25 % reduction in permeability could be achieved compared to CA-free concrete samples as presented in Table 5. Some studies [80,149] highlighted that capillary channels were reduced by the additional formations of crystalline products, having less water penetration depths compared to CA-free samples. Lauch et al. [72] investigated the permeability of different concrete samples with CA addition subjected to various curing environments. They observed that when subjected to wet/dry cycles, concrete samples with 2 % CA showed the most effective reduction in permeability, being 19 % less than that of control groups. Furthermore, Drochytka et al. [148] added 2 wt% Xypex Admix in concrete mixture. The authors [148] found that the permeability of CA-concrete composites was 30 % less than that of the CA-free group after 6-month exposure, as a result of the continuous pore-blocking reactions induced by CA powder.

Fig. 13 compares the permeability reduction for mortar samples (1.5 wt% CA [35], 2 wt% CA1 [121]) and concrete samples (2 wt% CA2 [80], 2 wt% CA3 [72], 2 wt% Xypex [148]). In terms of mortar samples, the permeability reduction (18.92 %) in the study by Zhang et al. [35] is lower than that (30 %) in the study by Jiang et al. [121]. The main reason is that Jiang et al. [121] partially replaced cement with 6 wt% silica fume, increasing the overall compactness of the cementitious matrix leading to less capillary pores, resulting in higher resistance against water penetration. Secondly, the permeability test in the study [121] was performed to analyse the crack recovery of pre-cracked mortar specimens with and without CA, while the other study [35] uses uncracked samples, leading to less permeability reduction.

For concrete samples, the permeability reduction of 19 % and 25 % was observed in the study by Lauch et al. [72] and Azarsa et al. [80], respectively. The better improvement in the latter study [80] lies on the use of Portland limestone cement (PLC). Some studies agreed that [80,150] the higher amount of limestone content in PLC (up to 15 wt%) provided additional filler effects reducing the pore size and interconnectivity in cementitious matrix. As a result, the resistance against water permeation was improved compared to cementitious matrix using only ordinary Portland cement (OPC). The highest permeability reduction (30 %) was measured by Drochytka et al. [148], curing the pre-cracked samples for 6 months. Some studies [148,151] suggested that an increased curing period can allow more crystalline products to be formed from both continuous hydration or recrystallisation of hydrate products, resulting in better a permeability resistance. Yildirm et al. [108,152] agreed that the application of CA promoted long-term hydration, leading to a denser cementitious matrix, being less permeable for water penetration.

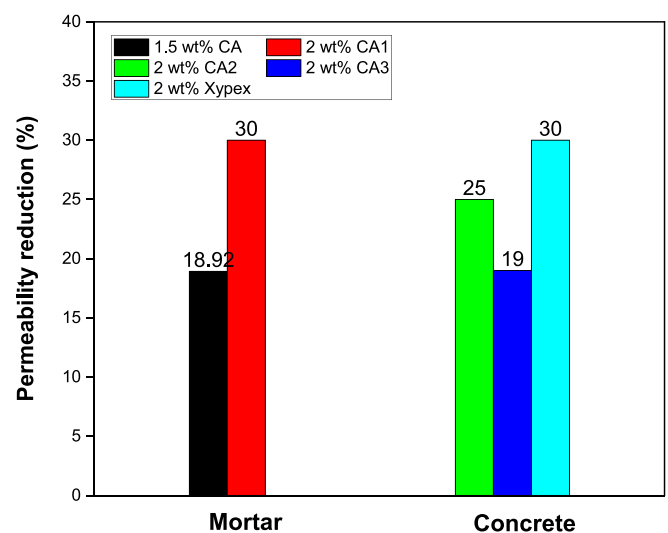


Fig 13. Permeability reduction comparison (1.5 wt% CA [35], 2 wt% CA1 [121], 2 wt% CA2 [80], 2 wt% CA3 [72], 2 wt% Xypex [148]).

5.3. Chloride-ion penetration

Table 6 summarises various experiments investigating the effects of CA on chloride-ion penetration. Azarsa et al. [80] carried out the rapid chloride penetration test (RCPT) for investigating the potential effects of CA addition on the reduction of chloride permeation. The authors [80] found that 2 wt% addition of CA powder altered the microstructure of the CA-cement matrix and reduced the capillarity and pore volumes, resulting in 19 % improvement in resisting chloride-ion penetration. Some studies [80,149] explained that the inclusion of CA promoted the pore-blocking process of the cementitious matrix, and also improved the resistance against chloride penetration. Aspiotis et al. [45] carried out experiments with 1.5 wt% CA addition. They observed that, compared to conventional concrete samples, lower chloride contents were obtained in CA-concrete composites. Many researchers [45,153] mentioned that the crystalline formation induced by active chemicals in CA contributed to refining pore network, reducing the level of chloride ingress. Similarly, Michael et al. [92] reported that 25.7 % chloride penetration reduction could be achieved compared to CA-free samples by adding 0.8 wt% CA into the concrete mixture. CA prolongs the hydration process leading to a denser cementitious matrix, thus improving the overall resistance against chloride ion penetration [92]. Tsampali and Stefanidou [6] carried out chloride-ion penetration tests for concrete samples with and without CA addition. In their study, samples with 1 wt% CA addition led to the highest chloride permeability reduction of 19.3 %. Other studies [6,154] reported that CA led to the recrystallisation of portlandite to form layered double hydroxide (LDH) with the presence of moisture, reducing the porosity of cementitious matrix and improving the resistance against chloride permeability. Likewise, Doostkami et al. [141] suggested that CA addition could increase the resistance of chloride permeability of ultra-high performance concrete (UHPC).

Similar findings are observed by Tsampali et al. [6] (19.3 %) and Azarsa et al. [80] (19 %) as shown in Fig. 14. Although the brands of CA are not mentioned in the two studies, as concrete mixture proportions are similar, similar chloride permeation reductions are recorded, highlighting the feasibility of using CA to improve the durability of cementitious composites. Typically, 2 wt% CA addition may not have better performance than 1 wt% addition. Since special chemicals are accumulated in the cementitious matrix, excessive addition of CA powder does not provide better performance. As a result, the commercial usage recommendation of CA addition is 0.8 wt% [102]. Although 0.8 wt% PENETRON CA was used in the study by Guenca et al. [155], they only

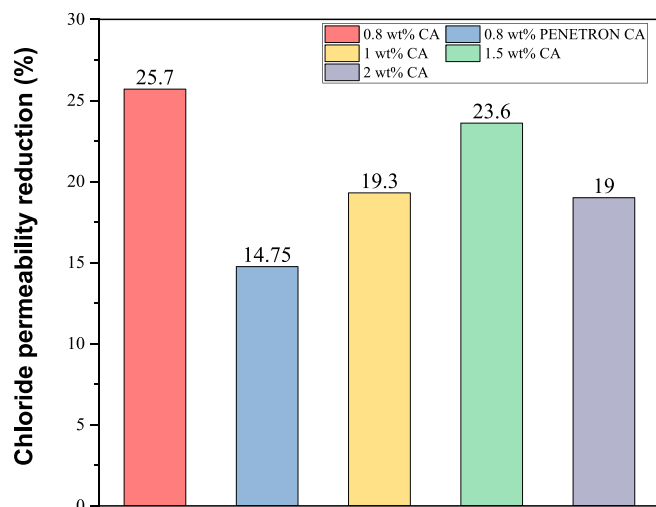


Fig 14. Reduction in chloride permeation with different CA content (0.8 wt% CA [92], 0.8 wt% PENETRON CA [155], 1 wt% CA [6], 1.5 wt% CA [45], and 2 wt% CA [80]).

observed 14.75 % reduction in the chloride mitigation experiment, indicating difference performances of various CAs. In the study conducted by Aspiotis et al. [45], 1.5 wt% CA addition provides 23.6 % reduction in chloride penetration. Higher reduction lies on that Aspiotis et al. [45] substituted Portland cement with 10 % calcium sulfoaluminate (CSA). As CSA provides a relatively fast strength development and low porosity in CSA-cement composites, a higher chloride penetration reduction was achieved. Some studies [45,156,157] revealed that CSA additives could further improve the resistance against chloride-rich environment due to more formations of C-S-H gels and stratlingite. Overall, the combination of CA and CSA could facilitate the promotion of calcium ion dissolution in inducing higher density of C-S-H and more pore-blocking precipitates, resulting in better chloride penetration reduction [45,46]. The highest permeation reduction is found in the study by Michael et al. [92], being 25.7 % reduction compared to the control group. The reason is that Michael et al. [92] added proprietary polypropylene fibres in the cementitious matrix, which could not only act as additional reaction sites for hydration process but also interfere with the permeation of chlorides.

5.4. Alkali-silica reactions

Munhoz et al. carried out an accelerated mortar bar test (AMBT) to investigate the potential effects of CA addition on the resistance of alkali-silica reactions (ASRs) for samples made with reactive aggregates [97]. While adding 1–3 wt% CA to the mortars made with reactive aggregates, Munhoz et al. [97] found that CA significantly reduced expansion by 75.4 % and 64.5 % for the samples immersed for 14-day and 28-day NaOH bath respectively (Fig. 15). It should be noted that when a higher amount of CA powder is added, slightly higher expansions were observed when compared with those of samples containing 1 wt% CA.

Several studies [97,158] noted that the favourable benefit of CA addition in resisting ASR expansion was due to the limitation in alkali ions and water molecules in the CA-cement matrix. Compared to samples with CA addition, a higher penetration depth of sodium ion was observed, resulting in higher expansion [97]. Similarly, Liu [110] observed that the penetration depth of sodium ions was reduced with Xypex CA addition, thus improving the ASR resistance. Likewise, other studies [83,159] agreed that CA induced pore-sealing deposits reduced both the amount and penetration depth of aggressive chemicals,

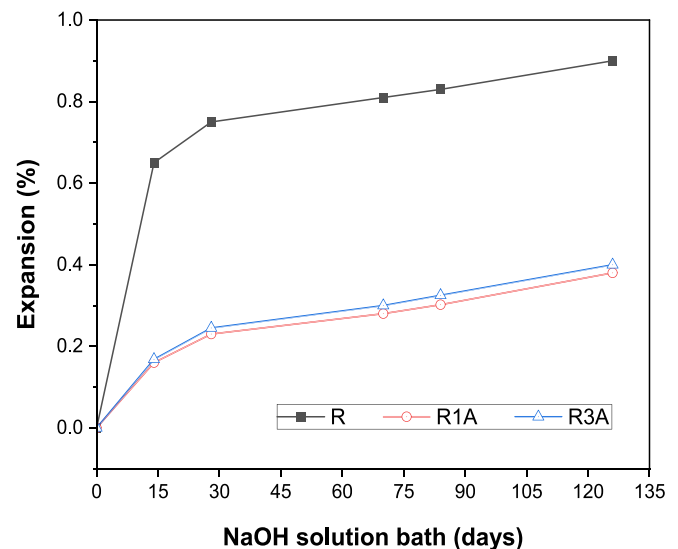


Fig 15. AMBT results of samples with and without CA (Note: R means control group, R1A refers to samples with 1 wt% CA addition, while R3A means samples with 3 wt% CA addition) [97].

providing a durable cementitious matrix. However, experimental data investigating the actual effects of CA ASR are still limited, and more studies are required to fill this gap.

Based on the above-mentioned discussions regarding the effects of CA addition on sorptivity, permeability, chloride-ion penetration, and ASRs of cementitious composites, the favourable effects of CA additives up to 2 wt% addition on CA-cement composites performance are governed by two main aspects. Firstly, CA powder facilitates higher healing efficiency in healing microcracks with denser self-repairing products for pre-cracked samples. As a result, higher resistance against water penetration of CA-cement composites is achieved. Secondly, CA additives generate pore-blocking deposits sealing micropores and capillary channels in a cementitious matrix, preventing the permeation of water and aggressive ions. Thus, a denser microstructure forms in CA-cement admixture, less permeable compared to CA-free samples, providing better protection to the interior cementitious matrix and reinforcement from corrosion.

5.5. Economic analysis

Mainly serving as impermeability-improving agents, CA has gained attention in self-healing studies. The admixtures of CA mainly consisted of cement powder and special chemicals protected by commercial patent, having similar storage requirement to cement binder [5,6,66,98]. Based on the material nature of CA, it has two main advantages as self-healing agent. Firstly, since up to 80 wt% content of CA is cement [102], the cost of CA is inexpensive in terms of raw material cost (unit price of cement is \$0.429/kg), making it a proper alternative in repairing microcracks in the cementitious matrix (Table 7).

Hu et al. [83] reported that although the price of Xypex CA varied from \$5 to \$10/kg, up to 2 wt% CA addition could significantly repair microcrack and reduce the maintenance and labour cost if taking manually repairing of cracking structure into account. Several studies [75,77,79,80,95,96] showed that CA could be directly mixed with binder without any specific treatments, highlighting its practicality. Compared to traditional coating methods, used to improve the resistance to water penetration, Flores et al. [69] pointed out that CA addition had negligible effects on workability, and promoted better durability properties for the cementitious composites.

Huang et al. [22] noted that both healing agents based on CA or encapsulated bacteria provided better healing efficiency compared to other healing agents. By considering the manufacturing process and the cost of two self-healing agents, self-healing stimulator based on crystalline additives had lower cost compared to bacteria-based agents, being close to that of cement [22]. Similarly, Jonkers [160] mentioned that the cost of the bacteria-cement composites was approximately twice that of the conventional cementitious composites. The reason is that the additional costs of bacteria-based healing agents are associated with the technique of encapsulation, being the key factor to ensure the healing efficiency of this type of healing inducer [22]. Furthermore, Xiao et al. [25] revealed that although good repairing capacity was provided by bacteria-based healing agents, the mechanical strengths of bacteria-cement composites were lowered due to encapsulation. The relative weak points interfere the strength development of cementitious matrix, being a major concern when using this repairing technique. However, for CA powder, being of a similar nature to that of cement, no obvious reduction in strength development was observed. On the contrary, pore-blocking precipitation provides denser microstructure, leading to higher compressive strength of CA-cement composites.

Table 7
Price comparison of crystalline admixtures and Portland cement.

Raw material	Unit price (\$/kg)	Addition (%)	Refs.
Cement binder	0.429	N/A	[102]
Xypex CA	5–10	0–2	[83]

6. Conclusion and perspective

The developments and investigations of CA addition in self-healing cementitious composites have been thoroughly reviewed in this paper. This review is conducted to systematically synthesize the effects of CA addition on crack self-healing and durability properties of CA-cementitious composites. The following conclusions can be drawn as:

- (1) CA is a commercial product being produced in a powder form, and up to 80 wt% of CA content is made with cement. As a result, the total weight of calcium oxide and silica in CA ranges from 51.6 wt% to 71.2 wt%, having similar C/S ratio to that of cement. Due to business patent protection, details of special chemicals in CA are kept confidential.
- (2) CA addition has no apparent effects on workability, setting time, tensile and flexural strength of CA-cement composites, while up to 12.6 % compressive strength improvement is observed at 28-day exposure. After crack initiation, special crystals ([O-R]_{2n}) are activated by moisture to induce crystalline deposits in healing microcracks and pores, providing a denser cementitious matrix. There are three possible self-healing reactions, including carbonate precipitation, complex precipitation, and recrystallisation. Despite there are different healing reactions, micro-characterisations have revealed that all self-healing products stimulated by CA are calcium-based products.
- (3) CA-cementitious composites cured in wet/dry cycle have better healing efficiency than those cured in water immersion or air exposure, stimulating ball-like crystalline deposits. CA-concrete specimens cured in freeze–thaw cycles have better healing rate when compared with CA-free samples. Needle-like crystals are formed as self-healing products. In chloride solution curing, CA-cement composites have the best healing rate when compared with other samples, due to additional formation of Fs and ettringite. Longer curing duration and higher curing temperature could boost self-healing process.
- (4) The mechanical recovery of specimens cured in freeze–thaw cycles is lower than that by wet/dry cycle. Moreover, although chloride ions improve the sealing rate, the mechanical recovery of samples cured in chloride solutions is lower than that of samples cured in wet/dry cycle due to a reduced strength development.
- (5) CA addition significantly improves the resistance against sorptivity, permeability, and chlorides penetration, due to favourable pore-blocking processes contributing to a denser cementitious matrix. Meanwhile, CA addition lowers the penetration depth of sodium ions, improving the proper resistance to ASRs with less expansion.
- (6) Application of CA in cementitious composites could be considered as a cost-effective technique in inducing self-healing products, considering low material cost and practicality. Furthermore, CA powder does not negatively affect the strength development, but improve overall compactness.

However, based on recent studies, while the crack closure and durability properties of CA-cement composites have been well-studied, there are still several aspects that require further investigation, as follows:

- (1) More studies should be performed in the potential effects of CA addition on resisting ASR, since limited information is available with conservative conclusions. The studies on potential effects of sulphate ions on self-healing efficiency of CA-cement specimens are very limited. Thus, more research works are encouraged to be carried out.
- (2) It is highly recommended to perform detailed experiments on the interfacial transition zone between healing product and

cementitious matrix, aiming to classify the unknown interactions and differences in hardness and friction coefficient.

- (3) In terms of durability properties, it is necessary to explore how CA addition may affect the shrinkage and carbonation of cementitious materials, and potential effects of CA addition on aggressive-ion ingress subjected to different environments, including sulphate solution and chloride solution curing.
- (4) The influence of CA on corrosion of reinforcement should be investigated in both carbonated concrete and chloride environments.

Moreover, there are various perspectives to consider regarding CA-cement composites:

- (1) Self-healing agents with lower cost and easy construction will continuously attract researchers' attention, which will further advance self-healing concrete technology.
- (2) The demands for improvements in structural concrete performance with lower permeability and better resilience will keep increasing, as the design of durable concretes is required for structural resilience.

CRedit authorship contribution statement

Xuqun Lin: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Wengui Li:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Funding acquisition, Conceptualization. **Arnaud Castel:** Writing – review & editing, Writing – original draft, Validation, Resources. **Taehwan Kim:** Writing – review & editing, Writing – original draft, Validation. **Yuhan Huang:** Writing – review & editing, Writing – original draft, Validation, Supervision. **Kejin Wang:** Writing – review & editing, Writing – original draft, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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