Self-healing concrete with crystalline admixture – a review

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Abstract. Concrete is the most used construction material for years. However long term serviceability is an issue, when we focus on sustainable building and use of materials. In long term service different types of visual and structural defects can appear in concrete structures. Defects in material enhances due to aggressive factors in outdoor (chlorides, sulphides and carbonates, freeze-thaw) which reduces material properties over a longer period. Mainly defects on visible surfaces of structures are from mechanical impacts, environmental exposure or due to improper maintenance. There are methods to reduce the risks and improve service life. One of them is self-healing materials, like bacteria, crystalline additives, in-capsulated healing agents and other. Use of self-healing material has preference, like lower maintenance costs for inspection, monitoring and complicated repair. Crystalline admixtures have several advantages comparing to other self-healing techniques, like improved concrete water tightness, no need for encapsulation before addition to concrete mix, which reduces sample preparation time.

1. Introduction

There are several chemical and physical factors, which affect aesthetic look and shorten service life of concrete structures. That is concrete structure exposure to aggressive agents as chlorides, sulphides, carbonates; water penetration through pours and small cracks due to absorption or hydrostatic pressure; freeze-thaw cycles [1]. As a result pores and small cracks like hairline cracking can be observed in concrete structures. To prolong service life self-healing materials can be used. Self-healing materials have many advantages: less people work and money saving due to inspection, monitoring and repair. Self-healing of concrete is triggered on its own. Self-healing ability of concrete [1], stainless steel reinforced concrete [2], high-performance concrete [3] and high-performance fibre reinforced concrete (HPFRC) [1], [3] have been researched. Due to healing mechanisms it can be divide in two parts:

- autogenic healing: natural closure of cracks due to un-hydrated cement in concrete and no specific self-healing admixtures are added. But this type of self-healing is not predictable and cannot be controlled [4], [5].
- autonomic healing: engineered closure of cracks with additives which is not a part of a ordinary cement [3]–[7]:
  - Passive – no need for human involving, self-healing starts from external promoters [2], [8].
  - Active – human involved to activate and complete the self-healing mechanisms [2], [8].

A lot of researchers have been investigated autonomic self-healing mechanisms with fibre reinforcement [1], [3], bacteria [9]–[12], crystalline additives [1], [3], [7], [13], [14], absorbent polymers [15], absorbent clay materials [6], incapsulated healing agents [4], [6], [16], expansion agents like sulfo-aluminate [6], [13], [14] and others.
In this review most of interest is focused on chemical additives – crystalline additives (CA), because of their dual positive influence – crack healing and concrete permeability reduction ability. In moist environment CA react with cement and forms calcium silicate hydrates. These additives help to reduce concrete porosity and water permeability as well [4]. Difference between CA (permeability reducing admixtures) and hydrophobic additives are - the first ones have hydrophilic nature apart prom CA [7]. Due to Belie et. al. [17] CA performance is largely influenced by mix design. Better effect can be noticed with HPFRC. But still healing process for 0,2 mm wide cracks is relatively time demanding from few weeks to several months.

2. Autogenous crack healing

Autogenous crack healing mechanisms has been studied almost for forty years. Main conclusions are that crack healing mechanisms changes by concrete age. In case of young concrete main mechanism is hydration of un-hydrated cement particles in concrete in presence of high moisture [1], [3], [4], [18], [19]. In case of concrete with low water:cement ratio, <0,3, even 20-30% of all cement particles can be un-hydrated and participate in self-healing process [5], [20]–[22]. For older concrete calcium hydroxide (Ca(OH)₂) converts to crystallized calcium carbonate (CaCO₃) as a result of exposure to atmosphere with carbon dioxide (CO₂) [1], [4], [7], [18], [19], [23]. This phenomena first was discovered in 1836 by the French Academy [8]. Crack size which can be healed by this mechanism’s varies from 0,05 mm till 0,3 mm, but it can be unpredictable. Much more presence of water, not moisture, is needed [6], [14], [24]. Different additives such as fly ash, blast furnace slag, silica fume, limestone powder promote autogenous crack-healing in later stage in concrete due to un-hydrated binders, which have slower pozzolanic reactions [1], [3], [4], [7], [18], [23], [25]. These pozzolan materials in presence of water reacts with portlandite and produce binding products [25]. Van Tittelboom et al. have done research adding to Portland cement fly ash or blast furnace slag as pozzolanic additives. It was found that concrete crack self-healing rate is 0,015 mm/day, and are influenced by environmental conditions [26]. K. Tomczak et.al. has challenged autogenous healing by making samples with very low w:c ratio 0.28 and 0.23. Pre-cracked samples with crack width 0-0,8 mm was healed in water for 28 days. Cracks below 0,46 was completely healed after 2 months, but wider cracks have healed only for 15-30%. Self-healing speed also changes during time, but most influencing factor is crack width, if cracks are wider healing considerably slows down [27].

3. Autonomous crack healing using crystalline additives

Crystalline additives are mostly water soluble additives which improve concrete properties at fresh and hardened state [24]. As American concrete institute (ACI) writes on their report crystalline additives are one type of permeability reducing admixture. ACI divide permeability reducing additives in two parts. That reduces water permeability at no-hydrostatic conditions and at hydrostatic conditions. In category that reduces water permeability at no-hydrostatic conditions falls typical hydrophobic products. Admixtures that can function under hydrostatic conditions include crystalline admixtures. Some of these additives have a lot of benefits like reducing drying shrinkage, minimize chloride ion penetration to surface, improved frost resistance and autogenous healing properties [28].

Crack width that can be healed with CA variates till 300 μm. [4], [24] but if the techniques are combined, like crystalline additives with expansive admixtures, healed crack width can be increased till 400 μm [7].

Moisture is very important if chemical agents (crystalline additives) is added in concrete to promote deposition and fill the crack. Usually in outside environment it is not an issue [4], [7]. After crack is formed, in presence of moisture tricalcium silicate (C₃S) reacts and Calcium Silicate Hydrate (CSH) is deposited on crack walls and it fill the crack[7]. Quality of concrete self-healing ability can be affected by mix proportion, temperature, environmental humidity and stress in crack region. If stress is too high, at already healed crack area new cracks can appear [4]. Calcium carbonate as an deposit in self-healed
crack can appear in different morphologies – calcite, aragonite, vaterite, monohydrocalcite, ikaite and amorphous CaCO₃. By-product which appeared after concrete self-healing with CA mostly is the same that can be seen after autogenous healing – calcite, brucite and aragonite.

It must be mentioned that self-healing using crystalline additives show better results when samples are immersed in water or subjected to wet-dry cycles [2].

Authors mostly use commercially available crystalline additives, as WT- 250 commercialized by Sika [3] Admix C-1000NF by Xypex [6] Penetron Admix by Penetron [5] or do not specify what crystalline admixture is used. Esscoffres et. al. has mentioned higher Mg content in admixture which can lead to higher amount of healing by-product aragonite [3]. Other authors [1], [5], [6] have mentioned as one of compounds reactive silica or micro silica.

Results that are achieved differs, because of many different parameters used in each research. Starting from mixture: cement type, sand:cement proportion, water:cement proportion, different additives, dosage and type (superplasticizers, viscosity agents). There is a luck of standardized testing method, methods of testing differs almost in each paper. Therefore, it is hard to compare the results. In fallowing text research by different authors will be discussed one by one and summarized in table 1. This problem have mentioned also other authors and standardizations is needed [29]–[31].

Ferrara et. al. [1] used crystalline admixture which consists from cement, sand and micro silica. Admixture were investigated by EDS analyses and compared with Portland cement specimen. Only difference was slightly higher peak of sulphur. Normal strength concrete (NSC) and HPFRCC samples were pre-cracked after 2 months and healed by immersing in water and exposed to an open air. Crack width were 0,2 mm for NSC and deflection till 2mm for HPFRCC. Normal strength concrete and HPFRCC with crystalline admixture showed good healing capacity after 1 month. In both cases better results was achieved if samples were immersed in water. Sample testing continued and showed improvement even after 12 months [1].

Escoffres et. al. [3] used commercially available crystalline admixture from SIKA WT-200. EDS analysis was made, and high amount of Mg were found in this admixture. After 28 days sample prisms of HPC, HPFRC and HPFRC-CA have been exposed to three-point bending test to pre-crack samples with crack width close to 0,2 mm. Part of each material was immersed in water and one part left in air. After 56 days all prisms were tested again with three-point bending test. HPFRC-CA showed by 10-20% better results than HPFRC in air exposure. HP C, HPFRC and HPFRC-CA self-healing ability is discussed during constant loading similar to service conditions [3].

M. Roig-Flores and her team [7] has investigated crack-healing ability of concrete samples with and without crystalline admixture. Pre-cracked 2 days old samples (crack width bellow 0,3 mm) were investigated. Different conditions – water immersion, water contact, humidity chamber and air exposure were used to accelerate crack-healing. Conclusions are that crack healing abilities increase for samples with crystalline admixture that have been immersed in water. Cracks have been healed around 95%, but samples without admixture only 75%. Samples with and without crystalline admixture that have been exposed in humidity chamber and in air have very low crack healing ability. All samples have been compared after 0 and 42 days [7].

Wang et. al. [6] used porous expanded clay aggregates as sodium carbonate container, commercially available crystalline additive from Xypex Admix C-1000NF and sulfoaluminate based expansive additive Denka CSA#20. Crystalline additive mainly consists from crystalline catalysts and reactive silica. Samples were pre-cracked after 7 days and healed in water for 28 days. Best self-healing results showed samples with mix proportions 10-12% of Na₂CO₃, 7-10% of sulfoaluminate based expansive agent, 4,5% of crystalline additive [6].

Sisomphon et.al. [14] used in his research crystalline additive and expansive additive. Crystalline additive consists from reactive silica and crystalline catalysts (hydrophilic water-proofing materials). As an expansive additive calcium sulfoaluminate based commercial product was used with mineral composition of Hauyne, anhydrite and free lime. Samples were pre-cracked after 28 days. Pre-cracked sample crack size was 0,1-0,4 mm. Samples were immersed in water for 28 days. Surface cracks up to 0,15mm can be closed in 28 days [14].
Cuenca et. al. [5] has done research of self-healing of fibre reinforced concrete after several self-healing - pre-cracking cycles. To enhance self-healing crystalline admixture was used. Samples were pre-cracked using Double Edge Wedge Splitting test and crack width was controlled with crack mouth opening displacements (CMOD). Samples were cured after pre-cracking in water, at open air and wet-dry cycles. Samples at air represented low crack-healing ability. Completely crack healed only for samples with crack width less than 0.3 mm, which were immersed in water, doesn’t matter permanently or periodically. Even more showed good repeated crack healing ability over an 1 year after repeated pre-cracking tests.

Coppola et.al. [32] has investigated novel method of self-sealing concrete by adding in concrete mixture fumaric acid-based admixture (WP). It was found that by using WP is possible to precipitate denser crystals comparing with commercially available products. Cracks till 0.4mm is completely filled with white crystal products. No improvement on waterproofing was seen if dosage of WP increased from 1 to 2 % versus cement content. Cracks till 0.4mm was healed already after 7 days after sample immersion in water.

Roig-Flores et.al. [2] has investigated healing in early age concrete, that is, samples were pre-cracked at age 2 days. Crystalline admixture influence on crack healing at different conditions were evaluated: water immersion at 15 °C and 30 °C and wet/dry cycles. Exposure time 42 days. Best results were obtained for samples immersed in water and held at 30°C temperature. Samples subjected to these conditions gained 0.99 average healing ratio with smallest standard deviation in results. Cracks in width to 0.4mm were healed.
Table 1. Summary of concrete types, mix design, used crystalline additives, pre-cracking methods and healing.

| Reference | Concrete type | Cement type | W:C | Additive | Method to crack | Time till Pre-cracking | Crack width | Healing days | Conditions |
|-----------|---------------|-------------|-----|----------|-----------------|------------------------|-------------|--------------|------------|
| [1]       | normal strength concrete | II 42.5 | 0,63 | blend of cement, sand and microsilica | 3-point bending test with COD-controller | 35-42 days | 130 and 250 μm | 1, 3, 6 and 12 months | immersed in water or exposed to open air |
| [6]       | normal strength concrete | Not specified | 0,25 | calcium sulfoaluminate based expansive additive (CSA, Denka CSA#20) and crystalline additive (CA, Xypex Admix C-1000NF) | 3-point bending test, notch in the middle of sample | 7 days | 0–200 μm | 28 days | healing in still water |
| [23]      | normal strength concrete (NSC) | P II 52.5 | 0,45 | calcium sulphoaluminate expansive agent and natural metakaolin with a small amount of additives | compressive strength tests | 7 d | Not specified | 28 d | water |
| [2]       | fiber-reinforced concrete | II/A-L 42.5 R | 0,6 | not Specified | splitting test | 2 days | 100 and 400 μm | 42 days | water immersion at 15 °C, water immersion at 30 °C, and wet/dry cycles |
| [5]       | fiber reinforced concrete | II 42.5 | 0,5 | crystalline admixture (Penetron Admix) | residual flexural tensile strength with CMOD | 3, 7, 28 and 56 days and 4 months | below 300 μm | Till 6 months | submitted to air exposure |
| [7]       | fiber-reinforced concrete | II/A-L 42.5 R | 0,45 | not specified | splitting test | 2 days | below 300 μm | 42 days | water immersion, water contact, humidity chamber and air exposure at laboratory conditions |
| [14]      | fiber reinforced concrete | I 42.5 N | 0,25 | crystalline additive and expansive additive | splitting tensile strength test | 28 days | 100–400 μm | 4, 7, 14- and 28-days | water |
| [3]       | high-performance fiber reinforced concrete | Not specified | 0,43 | crystalline additive (WT- 250 by Sika) | three points bending with RCOD | 28 days | 200 μm | 56 days | immersed in water submitted to air exposure |
| [1]       | high performance fiber reinforced cementitious composites | I 52.5 | 0,18 | blend of cement, sand and microsilica | 4-point bending with COD-controller | 2 months | 130 and 250 μm | up to six months | immersed in water |
4. Conclusion
Overlooking literature research on self-healing concrete has been made for different type of concretes, cements and w:c ratio in recent years. Various pre-cracking time has been investigated which can affect healing rate and results. If pre-cracking has been made at early stage of concrete hardening, autonomic healing goes together with autogenic healing and it is hard to differ these healing processes. Applied healing time differs from healing conditions. One can be concluded, if crystalline additives are used in cementitious materials more important is water then moisture in surrounding. Samples immersed in water gain faster crack healing and quality of healed crack is better, even cracks after repeated pre-cracking can be healed. This limits the use of the crystalline additive in materials for facades, panel constructions and other objects in the outdoor and indoor environment which are not in direct contact with water.

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