# Crystalline Admixtures for Autonomous Healing in Concrete: The Past, Present and Future

**K. H. Kong and C. Q. Lye**

**Abstract** The development of chemical admixtures for concrete used marked a significant milestone in construction industry, and they have now become an essential component in modern concrete, due to the capability of designing desirable fresh and hardened properties. The effects on the latter, particularly durability, is important as it allows longer structural service life and hence lower associated environmental impact. However, concrete is prone to crack formation which threatens its durability. One way of dealing with this issue is to impart autonomous healing ability in concrete through the use of crystalline admixtures for repairing or sealing microcracks fully by the concrete itself. This paper provides a comprehensive overview on the past and current research on the autonomous healing in concrete using crystalline admixtures, studying the types, mechanism, performance and technology involved. The research gap and potential limitations are discussed to support future development in this area.

**Keywords** Autonomous healing · Self-healing · Cracks · Crystalline admixtures · Sustainability

## 1 Introduction

Cracking in concrete is an inevitable phenomenon, which can take place at early age when concrete is in the fresh state and throughout its service life due to various reasons such as shrinkage, weathering and loading. The presence of cracks in concrete facilitates transportation of fluids and gases into its core, potentially leading to the corrosion of reinforcement in structural concrete, and thus affecting its integrity. As continuous repairing and maintenance of concrete can be cost and labour intensive, the development of crack treating technology in the form of self-healing has gained much attention in the field of concrete technology.

K. H. Kong (✉) · C. Q. Lye
Civil and Environmental Engineering Department, National University of Singapore, Singapore, Singapore
e-mail: ceekkh@nus.edu.sg



K. K. Hau et al. (eds.), *Recent Advances in Structural Engineering and Construction Management*, Lecture Notes in Civil Engineering 277,
https://doi.org/10.1007/978-981-19-4040-8_1

Chemical admixtures have become one of the main ingredients in the modern concrete to enhance its properties in fresh and hardened state. Since the beginning of the 2010s, the potential use of crystalline admixtures to recover the performance and repair cracks in concrete in an autonomous manner has been actively studied. Based on ACI 212.3R-10 report [1], crystalline admixtures are categorised as permeability-reducing admixtures, which are normally used to prevent water migration in structural concrete. Crystalline admixtures are also known to be hydrophilic, and they react with water and cement particles in concrete to produce modified C-S–H gel and pore-blocking precipitate in microcracks and capillaries.

This paper provides an in-depth analysis on the self-healing effect derived from crystalline admixtures on the performance recovery and crack sealing in concrete, mortar and paste mixes, reported by various researchers globally (mainly Europe) since the beginning of the 2010s. The recent studies tended to focus on the autogenous healing of fibre reinforced concrete containing crystalline admixtures [17, 18, 24].

## 2 Characteristics of Crystalline Admixtures

Crystalline admixtures are irregularly shaped powdered material with particle size similar to that of cementitious materials. The density of crystalline admixtures is within the range of 2.0–2.9, lower than that of typical Portland cement (PC) at 3.15. Table 1 compares the chemical composition between crystalline admixtures and typical PC. Given that crystalline admixtures are commercial products with proprietary chemical technology, their chemical composition content is expected to vary in a wide range. Notwithstanding this, calcium oxide (CaO) and silica oxide ($SiO_2$) are the major components, making up at least 50% in the total content. Some

**Table 1** Chemical composition of crystalline admixtures

| Oxide | Crystalline admixtures | | | Typical Portland cement [25], % |
|---|---|---|---|---|
| | Average, % | Std. Dev, % | Range, % | |
| CaO | 51.0 | 13.3 | 30.9–73.4 | 63 |
| $SiO_2$ | 14.4 | 4.0 | 7.6–20.3 | 20 |
| $Fe_2O_3$ | 2.6 | 0.9 | 1.58–4.3 | 3 |
| $Al_2O_3$ | 2.9 | 1.0 | 1.3–4.36 | 6 |
| $SO_3$ | 2.4 | 1.1 | 1.0–4.43 | 2 |
| MgO | 7.8 | 7.2 | 0.55–19.4 | 1.5 |
| $K_2O$ | 0.44 | 0.33 | 0.15–1.22 | 1 |
| $Na_2O$ | 6.41 | 5.57 | 1.2–15.22 | |
| MnO | 0.097 | 0.072 | 0.06–0.241 | – |
| LOI | 21.0 | 9.6 | 8.57–36.9 | 2 |

Data from [10, 16, 17, 19, 20, 22, 26, 29, 34, 36–38, 40]

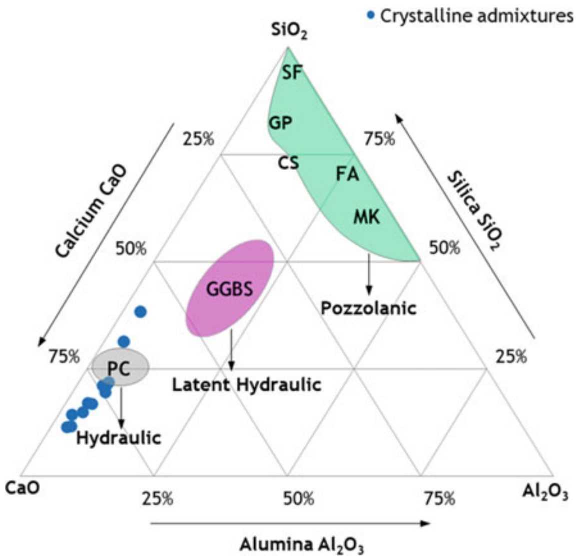


**Fig. 1** Ternary plot of crystalline admixture in comparison with other cements [11] (GGBS, ground granulated blast furnace slag; FA, fly ash; SF, silica fume; MK, metakaolin; C-S, copper slag; GP, glass powder)

crystalline admixtures tend to carry high significant amount of either magnesium oxide (MgO) or sodium oxide ($Na_2O$). The rest of the oxide content of crystalline admixtures is not too different to that of PC, but their loss on ignition (LOI) content is found to be very high.

The ternary diagram of the $SiO_2$, $Al_2O$ and CaO contents of crystalline admixtures is given in Fig. 1, along with other established cements. It can be seen that crystalline admixtures are mainly in the region of hydraulic, suggesting that they have similar chemical reactivity to PC. In addition, the main mineral compositions commonly present in crystalline admixtures are alite, belite, ferrite, calcite, portlandite and quartz, and in a few cases, gypsum is found [10, 16, 18, 26, 35]

## 3 Recovery of Mechanical Properties of Cracked Mixes

### *3.1 Compressive Strength*

The recovery of compressive strength is tested by introducing cracks to concrete/mortar specimens through either controlled crack width method [29] or loading up to 90% of its compressive strength [36]. The specimens are then subjected to different curing conditions (in the form of moist, air and alternate moist-air curing) for a period of time. The recovery is determined as the percentage ratio between strength at tested age and strength before cracking. Figure 2 presents the recovery results of various cracked concrete/mortar specimens commonly containing less than

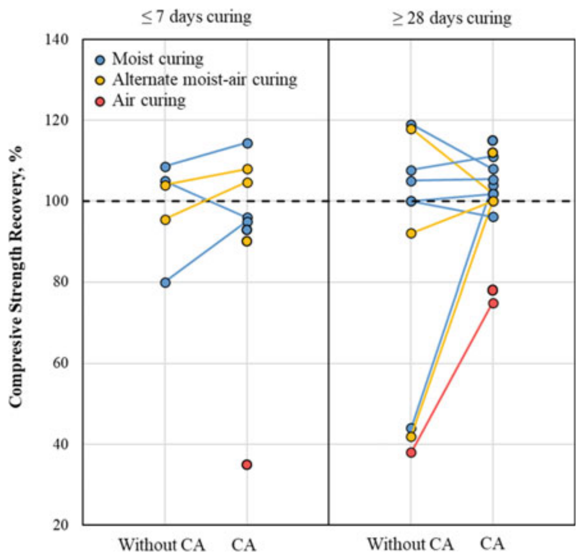


**Fig. 2** Recovery of compressive strength of cracked concrete/mortar specimens made with and without crystalline admixtures at different curing conditions [6, 8, 21, 28, 29, 36]

3% crystalline admixtures by mass of cement (only one case at 16%) and the corresponding reference specimens made without crystalline admixtures. Comparing the results of mixes made with or without crystalline admixtures, there is no strong evidence to suggests that the use of crystalline admixtures shows a clear advantage in compressive strength recovery. However, the effect of crystalline admixtures on the recovery is more pronounced when mixes were subjected to at least 28 days curing than that of 7 or less days curing. Both moist curing and alternate moist-air curing methods are found to be important to realise the recovery.

### 3.2 *Stress/Load-Controlled Mouth Opening Displacement Relationship*

Three point bending tests are commonly used to investigate the recovery of mechanical properties of self-healing concrete in terms of its stress or load (sometimes stiffness) and controlled mouth opening displacement (CMOD) relationship. The beam specimens are loaded to a targeted crack width then released and reloaded after curing for self-healing to take place. In general, the results tend to fall into two categories: either no significant recovery [7, 12, 35] or improved recovery [5, 13–15] due to the use of crystalline admixtures. In the latter category, the effect of crystalline admixtures on recovery is more effective when specimens are exposed to moist condition, longer curing days and having cracks width less than 100 μm.

## 3.3 Permeability and Absorption

The permeability and absorption of cracked concrete is one of the most commonly used methods to evaluate its self-healing ability. However, given that crystalline admixtures are normally used permeability-reducing admixtures, the assessment can be favourable for their inclusion in concrete. Figure 3 shows the compilation results for the recovery of permeability and absorption for mixes containing up to 4.5% crystalline admixtures which are subjected to controlled crack width and exposed to various conditions. As to be expected, mixes containing crystalline admixtures tend to show better recovery than reference mixes, except for the absorption test results obtained from a single study. In some cases, a full recovery (i.e. cracks are fully sealed) is reported as seen in the water permeability tests. The exposure conditions have an effect on the recovery of both cracked mixes made with and without crystalline admixtures, where the moist environment is shown to be conducive for self-healing (except for one case) and air exposure works the opposite. The effect of wet-dry cycle exposure is inconclusive due to limited study, but it is expected less effective than moist environment. It shall be mentioned that mixes containing combination of crystalline admixtures and expansive agent do not show greater recovery improvement than crystalline admixtures containing crystalline admixtures only, although the combination still performs better than the reference.

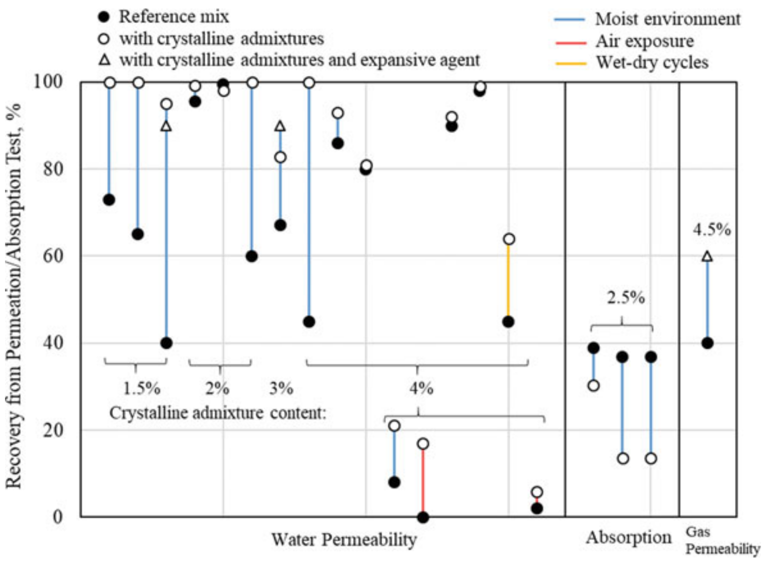


**Fig. 3** Recovery of permeation/absorption of cracked mixes made with and without crystalline admixtures for various exposure conditions [2, 3, 5, 12, 26, 27, 31–34, 36, 37]

# 4 Effect of Crystalline Admixtures on Crack Sealing

## 4.1 Crack Recovery

One of the main features of self-healing in concrete is the ability to seal or repair microcracks through chemical reactions, which helps to prolong the service life of structural concrete. Figure 4 shows the average recovery of crack width of mixes containing up to 4% crystalline admixtures and the corresponding reference mixes with different initial crack width and subjected to different healing conditions. The healing period (after crack is induced) varies from 28 days to 6 months, but generally less than 3 months.

The overall results suggest that the recovery of crack is affected by the inclusion of crystalline admixtures, as well as initial crack width and healing conditions. Comparing the results of mixes exposed to moist environment, the average recovery of crack of mixes made without crystalline admixtures decreases as the crack width increases, from 95% for ≤ 1 mm cracks to about 80% for 0.2–0.3 mm cracks. On the other hand, the average recovery of crack of mixes made with crystalline admixtures consistently fluctuates in the region close to 95% for up to 0.3 mm crack. Although the data beyond 0.3 mm cracks for mixes exposed to moist environment during

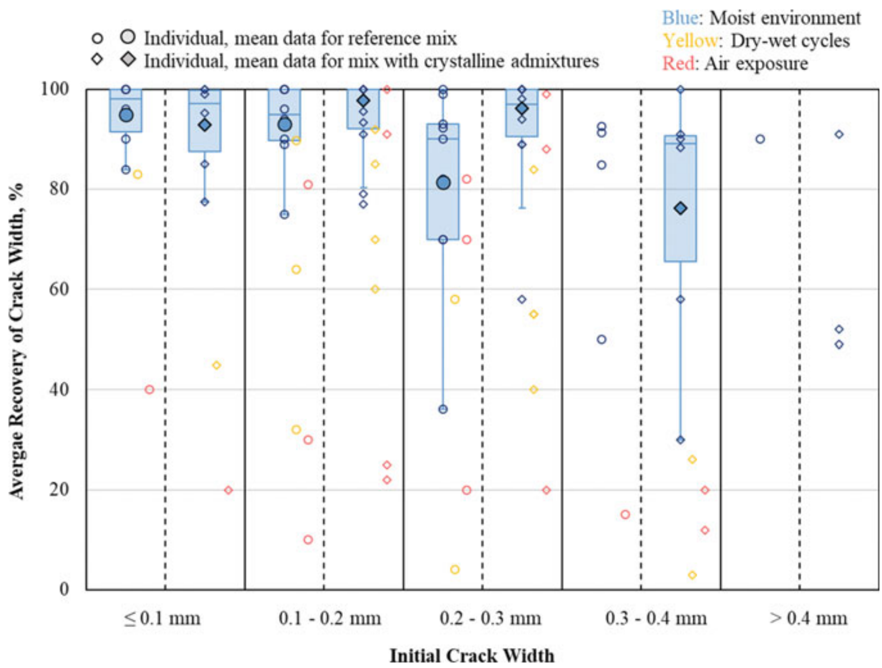


**Fig. 4** Crack recovery of mixes made with and without crystalline admixtures subjected to different healing conditions. (Data from [4, 7, 9, 17, 20, 23, 26, 32, 34])

healing are limited, it is speculated that the cracks are not likely to be repaired fully even when crystalline admixtures are used. As for healing conditions in the form of dry–wet cycles and air exposure, the sample is small and the data are scattered, as seen for both mixes made with and without crystalline admixtures. Notwithstanding this, the general trend suggests that the crack recovery decreases as the crack width increases for both mixes regardless of healing conditions. Lastly, the overall results also suggest that for a given crack width, the recovery of cracks is the highest in moist environment, followed by dry–wet cycles, and air exposure does not seem to promote significant recovery.

### *4.2 Microstructural Studies*

Microstructural studies allow better understanding on the mechanism involved in self-healing process when crystalline admixtures are used. The results from energy dispersive spectroscopy (EDS) analysis suggest that calcium, oxygen, carbon and silicon are the main elements present in mixes containing crystalline admixtures, whilst aluminium, magnesium and potassium are found in minor amounts [2, 5, 8, 9, 14, 15].

Based on scanning electron microscope (SEM) observations, needle-like/acicular/fibrous crystals are known to be commonly found self-healing products in mixes containing crystalline admixtures [2, 9, 14, 38]. In one case, the healing products appear in a scab form with amorphous structure [8]. More specifically, C-S–H gels [18, 26, 30]; calcium carbonate [18, 30] and calcium carbonate in aragonite polymorphic form have been identified [12]. This is also aligned with the findings using Fourier transform infrared spectroscopy (FT-IR), which show the presence of calcium carbonate and C-S–H in mixes made with crystalline admixtures.

According to X-ray diffraction (XRD) analysis on mixes containing crystalline admixtures, the main phase detected is AFt, calcite, C–A–S–H, portlandite, quartz and cement compounds [10, 17, 21]. The present of portlandite and calcite is confirmed from thermogravimetric analysis [10, 39]. It shall be mentioned that monocarboaluminate is detected in mixes containing crystalline admixtures, which is thought to be the product resulting from the interaction between limestone filler and $C_3A$ [10].

The overall results suggest that the healing mechanisms of crystalline admixtures mainly involved further hydration for the formation of C-S–H gels, carbonation for the formation of calcium carbonate. Other mechanisms such as formation of highly expansive Mg-rich hydro-carbonate and generation of portlandite have also been suggested, which require further evaluation.

## 5 The Verdict on the Future of Crystalline Admixtures

The autonomous healing ability discovered in crystalline admixtures is an added advantage in addition to its originally intended permeability-reducing feature. However, the experimental results shown in Sects. 3 and 4 tend to suggest that the autonomous healing ability of crystalline admixtures is more prominent when concrete is in contact with moisture. Therefore, the use of crystalline admixtures for water-retaining and marine structures can be beneficial for both low permeability and self-healing ability. However, its application in indoor structures with low humidity is unlikely to provide any significant self-healing ability due to the lack of moisture to undergo further chemical reactivity for unhydrated cement particles in concrete.

Comparing with other autonomous healing technologies developed in the recent years, the use of crystalline admixtures is relatively straightforward as they do not require encapsulation, vascular systems and microbial involvement. Crystalline admixtures can be easily specified in concrete design, and the production process of concrete made with crystalline admixtures is similar to that of normal concrete, simply by adding them into the concrete during production, similar to the process of introducing superplasticiser and retarding admixture.

At present, the research on the effect of autonomous healing ability derived from crystalline admixtures is still much in an exploratory stage. Future studies on crystalline admixtures may emphasise on its long-term effect on autonomous healing with at least of one year monitoring, repeated cracking–healing cycles and upscaling to real-life concrete applications in order to substantiate the reliability and validity of its autonomous healing mechanisms.

## 6 Conclusions

This study reveals the current research knowledge on the autonomous healing ability of crystalline admixtures, which are originally intended for use for water-proofing feature, to provide performance recovery and crack sealing in concrete. In general, the inclusion of crystalline admixtures for autonomous healing tends to show favourable results. Further investigation is required to gain better understanding of the characteristics of crystalline admixtures and their chemical mechanisms in order to realise their full potential in self-healing.

The main findings of the study are given below:

- Crystalline admixtures usually have high calcium, silicon and LOI contents. They also have similar chemical reactivity like Portland cement, suggesting that crystalline admixtures require water for reactions.
- The mechanical and durability performance recovery of mixes containing crystalline admixtures are found to be dependent on the exposure conditions, in which moist environment is the most favourable whilst the dry environment is the least favourable.

- Similarly, crack sealing ability due to the use of crystalline admixtures is more prominent when exposed to moist environment. Crystalline admixtures are shown to be effective to seal microcracks with width less than 0.3 mm (service limit crack width), which could be beneficial to protect concrete from damaging.
- The main self-healing mechanisms involved in crystalline admixtures are further hydration of unhydrated cement particles in forming C-S–H gels and carbonation in forming calcium carbonate.

## References


1. ACI (Ameircan Concrete Institute) 212. (2010). *Report on chemical admixtures for concrete*, Farmington Hills.
2. Azarsa, P., Gupta, R., & Biparva, A. (2018). Crystalline waterproofing admixtures effects on self-healing and permeability of concrete. In *1st International Conference on New Horizons in Green Civil Engineering*,(pp. 1–10).
3. Azarsa, P., Gupta, R., & Biparva, A. (2019). Assessment of self-healing and durability parameters of concretes incorporating crystalline admixtures and Portland limestone cement. *Cement and Concrete Composites, 99*, 17–31.
4. Borg, R. P., et al. (2018). Crack sealing capacity in chloride-rich environments of mortars containing different cement substitutes and crystalline admixtures. *Journal of Sustainable Cement-Based Materials, 7*(3), 141–159.
5. Buller, A. et al. (2019). Mechanical recovery of cracked fiber-reinforced mortar incorporating crystalline admixture, expansive agent, and geomaterial. In *Advances in Materials Science and Engineering* (pp. 14).
6. Cuenca, E., et al. (2018). Influence of self-healing stimulated via crystalline admixtures on chloride penetration. *ACI Special Publication, 326*, 10.
7. Cuenca, E., & Ferrara, L. (2017). Repeatability of self-healing in fiber reinforced concretes with and without crystalline admixtures: Preliminary results. *ACI Special Publication, 319*, 18.
8. Cuenca, E., et al. (2021). Crystalline admixture as healing promoter in concrete exposed to chloride-rich environments: Experimental study. *Journal of Materials in Civil Engineering, 33*(3), 14.
9. Cuenca, E., Tejedor, A., & Ferrara, L. (2018). A methodology to assess crack-sealing effectiveness of crystalline admixtures under repeated cracking-healing cycles. *Construction and Building Materials, 179*, 619–632.
10. de Souza Oliveira, A., et al. (2020). Crystalline admixture effects on crystal formation phenomena during cement paste's hydration. *Journal of Thermal Analysis and Calorimetry, 139*, 3361–3375.
11. Dhir, R. K., et al. (2019). *Sustainable construction materials: Recycled aggregates*. Woodhead Publishing.
12. Escoffres, P., Desmettre, C., & Charron, J. P. (2018). Effect of a crystalline admixture on the self-healing capability of high-performance fiber reinforced concretes in service conditions. *Construction and Building Materials, 173*, 763–774.
13. Ferrara, L., & Krelani, V. (2014). Engineering self healing capacity of cement based materials through crystalline admixtures. In *5th International Conference on Self-Healing Materials*, (pp. 4).
14. Ferrara, L., Krelani, V., & Carsana, M. (2014). A '"fracture testing"' based approach to assess crack healing of concrete with and without crystalline admixtures. *Construction and Building Materials, 68*, 535–551.

15. Ferrara, L., Krelani, V., & Moretti, F. (2016). On the use of crystalline admixtures in cement based construction materials: From porosity reducers to promoters of self-healing. *Smart Materials and Structures, 25*, 1–17.
16. Garcia-Vera, V., et al. (2019). Influence of crystalline admixtures on the short-term behaviour of mortars exposed to sulphuric acid. *Materials, 25*, 1–17.
17. Govejevic, A., et al. (2021). The effect of crystalline waterproofing admixtures on the self-healing and permeability of concrete. *Materials, 1860*, 14.
18. Guzlena, S., & Sakale, G. (2021). Self-healing of glass fibre reinforced concrete (GRC) and polymer glass fibre reinforced concrete (PGRC) using crystalline admixtures. *Construction and Building Materials, 267*, 14.
19. Helene, P. et al. (2018). Evaluation of the chloride penetration and service life of self-healing concretes activated by crystalline catalyst. *IBRACON Structures and Materials Journal 11*(3).
20. Jaroenratanapirom, D., & Sahamitmongkol, R. (2010). Effects of different mineral additives and cracking ages on self-healing performance of mortar. In *Proceedings of Annual Concrete Conference 6*: Phetcha Buri, Thailand. (pp. 551–556).
21. Jiang, Z. et al. (2014). Self-healing of cracks in concrete with various crystalline mineral additives in underground environment. *Journal of Wuhan University of Technology-Material Science Education, 29*(5), 938–944
22. Jo, B. W., et al. (2015). Effect of incorporation of self healing admixture (SHA) on physical and mechanical properties of mortars. *Journal of Ceramic Processing Research, 16*(1), 138–143.
23. Krelani, V., & Ferrara, L. (2013). Self healing capacity of concrete with crystalline additives: natural versus accelerated exposure conditions. In *Proceedings of the 4th International Conference on Self-Healing Materials*, Ghent, Belgium, (pp. 426–430).
24. Lo Monte, F., & Ferrara, L. (2021). Self-healing characterization of UHPFRCC with crystalline admixture: Experimental assessment via multi-test/multi-parameter approach. *Construction and Building Materials, 283*, 1–12.
25. Neville, A. M. (2011). *Properties of concrete* (5th ed.). Longman.
26. Park, B., & Choi, Y. C. (2018). Self-healing capability of cementitious materials with crystalline admixtures and super absorbent polymers (SAPs). *Construction and Building Materials, 189*, 1054–1066.
27. Park, B., & Choi, Y. C. (2019). Prediction of self-healing potential of cementitious materials incorporating crystalline admixture by isothermal calorimetry. *International Journal of Concrete Structures and Materials, 13*(36), 14.
28. Reddy, T., & Ravitheja, A. (2019). Macro mechanical properties of self healing concrete with crystalline admixture under different environments. *Ain Shams Engineering Journal, 10*, 23–32.
29. Reddy, T., Ravitheja, A., & Sashidar, C. (2020). Micromechanical properties of self-healing concrete with crystalline admixture and silica fume. *ACI Materials Journal, 117*(3), 63–74.
30. Reddy, T., Ravitheja, A., & Sashidhar, C. (2018). Self-healing ability of high-strength fibre-reinforced concrete with fly ash and crystalline admixture. *Civil Engineering Journal, 4*(5), 971–979.
31. Roig-Flores, M., et al. (2015). Self-healing capability of concrete with crystalline admixtures in different environments. *Construction and Building Materials, 86*, 1–11.
32. Roig-Flores, M., et al. (2016). Effect of crystalline admixtures on the self-healing capability of early-age concrete studied by means of permeability and crack closing tests. *Construction and Building Materials, 114*, 447–457.
33. Sisomphon, K., & Copuroglu, O. (2011). Self healing mortars by using different cementitious materials. In *International Conference on Advances in Construction Materials through Science and Engineering*, Hong Kong, (pp. 8).
34. Sisomphon, K., Copuroglu, O., & Koenders, E. A. B. (2012). Self-healing of surface cracks in mortars with expansive additive and crystalline additive. *Cement and Concrete Composites, 34*, 566–574.
35. Sisomphon, K., Copuroglu, O., & Koenders, E. A. B. (2013). Effect of exposure conditions on self healing behavior of strain hardening cementitious composites incorporating various cementitious materials. *Construction and Building Materials, 42*, 217–224.

36. Takagi, E. M., et al. (2018). Self-healing of self-compacting concretes made with blast furnace slag cements activated by crystalline admixture. *International Journal Materials and Product Technology, 56*(1/2), 169–186.
37. Wang, X., et al. (2018). A self-healing cementitious composite with mineral admixtures and built-in carbonate. *Cement and Concrete Composites, 92*, 216–299.
38. Weng, T. L., & Cheng, A. (2014). Influence of curing environment on concrete with crystalline admixture. *Monatshefte fuer Chemie, 145*, 195–200.
39. Xue, C., et al. (2020). Self-healing efficiency and crack closure of smart cementitious composite with crystalline admixture and structural polyurethane. *Construction and Building Materials, 260*, 15.
40. Ziegler, F., et al. (2020). Evaluation of internal and superficial self-healing of cracks in concrete with crystalline admixtures. *Materials, 13*, 18.