Self-Healing Mechanism of a Concrete Using Chemical Agent

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Abstract

The formation of fissures in cement-based materials and concrete, resulting from both self-induced processes and external forces, presents a major obstacle to the sustained durability and structural integrity of buildings. To address this issue, scientists have created a groundbreaking technique with built-in abilities for self-sufficient crack repair, referred to as self-healing concrete, which holds great potential for improving the lifespan of structures and minimizing environmental harm. This approach provides both a self-regenerating repair mechanism and the possibility for independent restoration, substantially lowering maintenance requirements and simultaneously increasing the lifespan of concrete constructions. This article thoroughly examines the operational principles, manufacturing methods, and self-healing properties particularly in terms of crack restoration and mechanical function—of concrete integrated with chemical-based self-repairing agents. These substances include various materials such as sodium silicate, calcium nitrate, dicyclopentadiene, calcium hydroxide, calcium sulfoaluminate, silica, and superabsorbent polymers. This review considers both self-induced and independent self-healing methods, with literature indicating that cracks can be effectively repaired and mechanical properties can be substantially recovered. The effectiveness of healing and the restoration of mechanical properties can vary considerably depending on the type and concentration of the healing agents. Numerous studies have reported over full restoration of mechanical strength and complete healing of crack depths. Superabsorbent polymers serve as highly efficient self-repair agents, especially when used in conjunction with self-healing agents such as calcium nitrate or CSA. Chemical-based self-repair agents offer an effective method for improving concrete durability, ensuring structural safety, and facilitating their real-world use.

Keywords: Self-healing concrete, Superabsorbent polymers, Sodium silicate, Calcium nitrate, Dicyclopentadiene, Mechanical strength recovery.

1. Introduction

A crack in a component of the structure introduces localized pliability, which may affect the structure's capacity to react to oscillations. This characteristic can be employed to identify and assess the depth of a fracture in a structural element. The local adaptability of a structural component with a crack alters, influencing the response to vibrations from external forces.

1.1. Classification of Structural Cracks.

1.1.1. Transverse crack: These are fractures oriented perpendicular to the beam's axis. These are the most frequent and critical, as they decrease the cross-sectional area and weaken the beam. They induce localized pliability in the beam's rigidity due to strain energy accumulation near the crack tip.

1.1.2. Longitudinal cracks: These are fractures aligned with the beam's axis. Though less frequent, they become hazardous when tensile stress is applied at an angle perpendicular to the crack's orientation, i.e., perpendicular to the beam's axis.

1.1.3. Open cracks: These fractures consistently stay open. They are more accurately referred to as notches. Open fractures are simple to create in a laboratory setting, which is why most experimental studies concentrate on this type of crack.

1.1.4. Surface cracks: These are the fractures that appear on the surface. They can usually be identified through dye penetration or visual examination.

1.2. Defects in Concrete.

Macro Defects: Concrete has limited strength and can deteriorate rapidly if these defects are present, as water and other contaminants can easily penetrate. Eventually, a structure requires maintenance within a few years of construction. Before applying additional precautionary steps, the root causes must be recognized and the defects rectified. Since the inadequate concrete beneath the waterproofing layer has not been addressed to repair the macro/micro defects within the concrete slab, waterproofing is often applied superficially and does not achieve the intended results. These issues are mainly due to flaws in design and/or construction techniques.

1.2.2. Micro Defects: These defects are imperceptible to the unaided eye. They are generally tiny cavities caused by numerous capillary pores due to the use of poor-quality concrete with a high water-to-cement ratio. They can also result from an overuse of water or an elevated water-to-cement ratio in the concrete mixture. Concrete commonly develops small fractures, which can occur due to various factors. As these cracks are usually shallow and intermittent, they do not pose an immediate major threat to concrete degradation. Over time, they expand in depth, length, and width due to variations in temperature, environmental conditions, and applied loads, eventually linking with other minor fractures to create a continuous route for water penetration.

1.3. Carbonation: Carbonation is the process in which atmospheric CO2 reacts with calcium oxide in concrete over time, forming calcium carbonate. This is essentially the reverse of the chemical reaction that occurs in cement kilns to produce the cement used in concrete, which generates most of the CO2 embedded in the material. The gradual, ongoing process of carbonation progresses from the exterior towards the interior. The CO2 footprint of both cement and the concrete it forms will significantly decrease over the life of the cement due to carbonation, which reabsorbs about one-third of the CO2 emitted during cement production. Therefore, it's essential to account for the environmental benefits of carbonation when assessing the life cycle of concrete and the structures constructed from it. The composition of structural concrete is intentionally designed to limit the carbonation rate, preventing this problem from arising during the lifespan of buildings and infrastructure. When the carbonation front reaches the steel reinforcement, it may lead to rusting. However, during the end- of-life stage, when concrete is crushed for reuse as construction waste, a higher level of carbonation occurs. The crushing process greatly increases the material's surface area, facilitating the absorption of CO2. Although the deconstruction and demolition at the end-of-life stage may be relatively fast, the carbonation that takes place during this phase is considerable. Newly crushed concrete aggregate undergoes carbonation due to leaching from rain exposure, along with the direct absorption of ambient CO2. This process significantly speeds up the carbonation rate. When the recycled aggregate is used in various applications during the material's secondary life cycle, additional CO2 absorption occurs. Carbonation progresses more rapidly in low-strength concrete applications without steel reinforcement, such as blocks, because CO2 can penetrate the material more easily. These materials can increase in strength during the carbonation process while absorbing CO2, and without steel reinforcement, their functional lifespan could extend to hundreds of years rather than just a few decades. The Pantheon in Rome, constructed about 1900 years ago, stands as tangible evidence of this.

1.4. Corrosion: When harmful substances to steel, such as CO2 and chlorides from de-icing salts, penetrate concrete and reach the steel reinforcement in the structure, corrosion begins. Electrons flow from the anodic to the cathodic areas due to an electrochemical reaction, releasing ferrous ions at the anode and hydroxide ions at the cathode. Over time, this can cause a differentiation between the anodic and cathodic areas on the surface of the steel reinforcement. Rust is formed as a byproduct of this reaction. Rust creates internal pressure that cracks the surrounding concrete, as it occupies more volume than steel; this allows more CO2 and chlorides to infiltrate the concrete from the surface. The corrosion process accelerates as a result. Structures like bridges, parking garages, and buildings near water—such as piers, dams, docks, and harbors—are often damaged by chloride-induced corrosion of the reinforcement.

1.6. Self -Healing: Concrete capable of healing its own cracks is typically described as having self-repairing characteristics. It is also known as self-healing concrete. Due to concrete's relatively low tensile strength, fractures are common. These voids reduce the durability of concrete as they allow gases and liquids, potentially carrying harmful substances, to penetrate. Both the concrete and the steel reinforcement bars can be damaged if microcracks propagate and eventually reach the reinforcement. Cracks in concrete that self-repair wouldb enhance the material's longevity and extend the service life of concrete structures.

1.7. Degradation:

Future degradation of concrete structures may partly result from mistakes in concrete production, casting, pouring, placement, or compaction. For instance, insufficient curing may lead to the formation of microcracks perpendicular to the surface of the concrete, due to shrinkage from drying. The mixing and segregation process can be assessed by examining areas in the cement paste with fewer or no (fine) aggregates under a microscope, along with the evaluation of cement or binder clumping and the distribution of coarse aggregates at the mesoscale. Using fluorescence, the effects of processes that influence capillary porosity, such as micro bleeding, can be detected. Inadequate compaction may expose localized regions where the cement pastes poorly bonds with aggregate particles, leading to excessive voids.

1.8. Chloride-Induced Corrosion: Chlorides, often derived from deicing salts (used in colder climates), seawater, or industrial processes, can penetrate the concrete and reach the embedded steel reinforcement. Chlorides break down the protective passive film around the steel, initiating rust formation (corrosion). As the rust expands, it exerts pressure on the surrounding concrete, leading to cracking, spalling, and overall degradation.

Impact: Rusting of reinforcement causes expansion, leading to cracking and spalling of the concrete surface, which weakens the structure. Factors: The severity of chloride-induced corrosion depends on the chloride concentration, concrete porosity, and the quality of the concrete mix.

2. Literature review

Caihong Xue et al. 2007, Australia the primary elements of encapsulation-based self-healing technology are healing agents and encapsulation techniques. A variety of experimental and computational studies have been carried out to assess the efficiency of the self-healing method. Polyurethane-based polymers are considered the most promising self-healing agents available today due to their excellent flexibility, relatively fast curing time, and water-free healing mechanism. Further adjustments are necessary to address issues such as stress concentration near the interface, detachment of the solidified healing agent, poor mixing, and premature reactions. Glass and ceramic are the most commonly used capsule materials, especially in laboratory-scale studies. However, capsules have a limited ability to withstand the mixing process. The polymer capsule has the potential to enhance the survival rate and minimize mechanical strength loss, though these benefits may be offset by the complex heating and mixing procedures, low likelihood of breakage, and significant elongation before rupture. Selecting the most reliable and precise assessment method for self-healing behavior is difficult, as there are no standardized indicators or universally accepted evaluation criteria for self-healing efficiency. A more comprehensive understanding of self-healing behavior can be gained by integrating nondestructive testing techniques such as digital image correlation, X-ray computed tomography, neutron radiography, acoustic emission analysis, and numerical simulations. Reaching a consensus on the optimal viscosity, appropriate elastic modulus, strain capacity, and bonding strength of polyurethane-based healing agents will take some time.

Nur Farhayu Ariffina Et Al. Samadia, 2015, To achieve optimal compressive strength, flexural strength, tensile strength, and overall strength development, the epoxy content should be at least 10%. After 28 days, the material's measured compressive, flexural, and tensile strengths were 36 MPa, 3 MPa, and 3.8 MPa, respectively. After 360 days of curing, the strength development of the 10% epoxy self-healing mortar increased by 40%. As a result of inadequate hydroxyl ions to react with the excess epoxy, the hardening process began to slow down as the epoxy concentration rose. The results from the UPV and compressive strength tests indicate that the self- healing mechanism of the epoxy resin is functioning efficiently.

A. Aliko-Benítez a et al. 2015The study included two case examples. The first case allowed us to discuss the influence of different model parameters on the healing process. For the examined range of values, the predicted healing progression closely matches the trends observed experimentally, though additional validation is necessary to confirm the model's predictions. The key factor is to consider both damage and healing when evaluating diffusion coefficients. The crack volume grows as damage increases, leading to higher permeability, a factor directly linked to the diffusion coefficient. Diffusion must decrease in regions where healing is occurring because, as healing advances, the material's permeability reduces as the cracks close. We noted that the work is ongoing, taking into account both mechanical and reaction-diffusion challenges.

Gupta Souradeep et al. 2016, While autogenous self- healing has been widely discussed in research, this study demonstrated that encapsulation-based self-healing has the potential to offer superior healing, owing to its ability to repair a broader range of crack widths and its faster response to matrix fractures. Glass tubes and capsules can significantly weaken the structural integrity of a concrete building. There is insufficient data on the consistency of the self-healing process under repeated loading. There is limited understanding of how bacteria are encapsulated. More critically, there is still a lack of knowledge about how the size and design of the capsules influence their effectiveness in promoting self-healing. Furthermore, while bacteria can survive for up to six months, their longevity must be considerably improved for bacteria encapsulation technology to be practical and viable in construction and civil engineering applications. Lastly, there is still a lack of data on how bacteria-based self-healing can restore the mechanical properties of concrete. The absence of traditional fracture propagation control is one factor that may have hindered the expected effectiveness of self-healing in several cases studied. This essentially means that a crack formed under load continues to propagate, leading to an increase in crack length and width, even as the load decreases. Further research is needed to explore different methods for controlling fracture width while implementing the appropriate self-healing techniques. Considering the advancement of self- healing materials over the past decade, it is reasonable to expect their more widespread use in construction soon. However, the highlighted technological and technical challenges must be addressed before this future can be achieved.

M. Kumarasamy Karur. S. Hemavathi et al. 2017, The sodium silicate microcapsules were synthesized using the in- situ polymerization technique. The produced microcapsules varied in size from 2 to 5 microns. After 28 days of curing, the injection of sodium silicate microcapsules showed no effect on the concrete's strength. The specimens with microcapsules had healed by an average of 9.447% after 14 days and 4.921% after of microcapsules, the specimens showed only limited effectiveness. As 2% was only sufficient to occupy the air voids in the concrete, increasing the volume of microcapsules could enhance efficiency. The specimens with sodium silicate microcapsules exhibited a 254.60% strength increase, while the conventional specimens showed a 24.95% increase in strength. It was confirmed that the healing process was occurring naturally.

P. Bala Murugan, et al. 2019, According to the project results, the self-healing concrete with epoxy resin performs effectively, as evidenced by the ultrasonic pulse velocity test and compressive strength measurements. After extended curing, both the ultrasonic pulse velocity test and compressive strength begin to return to their original values. The capsule- based encapsulation method is capable of filling cracks and preventing further crack propagation. This approach can lower inspection, labor, and maintenance costs. Full-scale cast microencapsulated self-healing concrete has proven successful in maintaining mechanical properties, with the setting and hardening process unaffected by the proper amount of encapsulated healing agent.

Shima Taheri and Simon Martin Clark, 2021 A successful technique for the controlled release of self-healing agents under induced stress conditions in cement-based materials was demonstrated using core-shell nano-capsules composed of an MMA+DMA core (resin and accelerator, Part A) and a BPO core (hardener, Part B), encapsulated by PMMA, produced via the mini-emulsion method. The following key conclusions were drawn from the systematic approach used in the development of nano-capsules and the optimization of formulation and mixing processes to effectively incorporate these self-healing nano-capsules: Among the three synthetic methods tested, encapsulating self-healing agents in PMMA was the only procedure that produced stable nano-capsules with consistent morphology, smooth spherical surfaces, no aggregation, and average diameters of approximately 400 ± 100 nm (Part A) and 900 ± 100 nm (Part B). However, this resulted in increased porosity, greater drying shrinkage, and a reduction in the overall strength of the mortar. The inclusion of D-191 and D-192 dispersing agents helped achieve a uniform distribution of healing agents throughout the mortar matrix.

G. Zhu1, Y. Zhou Based on the idea that the core materials partially harden at the oil/water emulsion interface due to the diffusion of curing agents from the aqueous phase to the oil phase, a new and simple method has been developed to produce epoxy/epoxy microcapsules. The resulting microcapsules can be tailored in terms of size and wall thickness by adjusting the stirring speed and curing temperature. The shell (solidified epoxy) and core (liquid epoxy) are almost identical in composition. The resulting microcapsules will exhibit an ideal spherical shape and smooth surface if the weight ratio of EDA to epoxy E-51 exceeds 1:2 and the reaction time exceeds 20 minutes at 60°C. We found that this technology is easier to industrialize than traditional in situ polymerization methods, where the epoxy core and shell materials differ.

H. M, Jonhers, Microscopic analysis of the cracks revealed that calcium carbonate-based mineral precipitates formed in both conventional and bacterial specimens. In bacterial specimens, however, cracks healed effectively and completely, with mineral precipitation mainly occurring within the crack, while in conventional specimens, precipitation occurred primarily at the crack edges, leaving much of the crack unhealed. The findings indicated that the self-healing ability of bacterial concrete specimens was markedly enhanced compared to the conventional specimens. The inclusion of organic bio-mineral precursor compounds in the concrete mix may reduce compressive strength, except for calcium lactate, which increased the strength by 10% compared to conventional specimens. The study's results suggest that bacterial concrete, which incorporates expanded porous clay particles containing bacteria and calcium lactate, leads to significantly more efficient crack healing than concrete with empty expanded clay particles. This can be attributed to the biological processes involved in bacterial concrete, alongside the purely chemical processes present in conventional concrete. However, the combined use of calcium lactate and bacteria capable of metabolizing this compound remains the most effective strategy to guarantee their presence and the swift initiation of crack-healing action.

Abdul Rahman Mohd. Sam et. al 2017, The study explored the use of epoxy-modified mortars without a hardener for self-healing of cracks. The mortar mix included a cement- to-fine aggregates ratio of 1:3, with 5-20% epoxy resin relative to cement, and a water-cement ratio of 0.48. Both compressive strength and self-healing tests were conducted on mortar cubes and specimens, respectively. The mixing procedure was similar to that of ordinary cement mortar, with the addition of epoxy resin. The primary goal of the study was to identify the optimal epoxy resin percentage for the mortar mix, using a standard mortar mix as the control.

The self-healing potential of epoxy resin without a hardener as a self-healing agent was evaluated using 100 x 100 x 100 mm cube specimens. Non-destructive testing, including ultrasonic pulse velocity (UPV), was employed to assess the propagation of cracks. The microstructure of the specimens was examined using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Further analysis using Field Emission Scanning Electron Microscopy (FESEM) was conducted on fractured pieces of the samples.

The optimal mix ratio was determined based on the compressive strength of the specimens. The highest compressive strength, 36 MPa after 28 days, was achieved with 10% epoxy resin, outperforming the strength of standard mortar. The porosity of the mortars significantly influenced their strength, with reduced porosity leading to improved properties. Additionally, tests were conducted to evaluate the performance of microcapsules in reducing porosity and enhancing strength.

The results showed that the mortar exhibited an apparent porosity of 6% after 28 days. The study also examined the self- healing performance of the epoxy-modified mortar through non-destructive testing and compressive strength measurements. Ultrasonic pulse velocity (UPV) was used to evaluate the self-healing process, with results comparing conventional mortar and epoxy-modified mortar after 12 days. The study assessed the performance of epoxy-modified mortar through non-destructive testing and compressive strength tests.

Ultrasonic pulse velocity (UPV) was employed to evaluate the self-healing capacity, with results compared between conventional mortar and epoxy-modified mortar after a 12- month curing period. The findings revealed that the epoxy- modified mortar exhibited improved performance over time, indicating a denser, less porous material. The use of epoxy resin as a healing agent proved to be effective in enhancing the mortar's self-healing properties.

G. Zhu et al 2013. A straightforward method for preparing epoxy/epoxy microcapsules has been developed, where the core materials are partially hardened at the oil/water (o/w) emulsion interface by the diffusion of the curing agent from the aqueous phase to the oil phase. The resulting microcapsules feature a uniform shell (solidified epoxy) and core (liquid epoxy), with the size and wall thickness being adjustable by controlling the stirring rate and curing temperature. The optimal conditions for producing microcapsules with a perfect spherical shape and smooth surface are a weight ratio of EDA to epoxy E-51 greater than 1:2, with the reaction occurring at 60°C for over 20 minutes. This method is considered more industrially feasible and simpler than traditional in situ polymerization techniques, which use different materials for the shell and core.

M. W. Hussain, 2015, The results of various tests conducted on self-healing epoxy mortar were used to evaluate its mechanical properties. The optimal mortar mix was determined based on its compressive strength. The addition of 10% epoxy resin enhanced the compressive strength, likely due to the alkalis from the hydration process reacting with the epoxy resin. A flexural test was performed to assess the material's resistance to deformation under load, and the 10% epoxy mix exhibited the highest flexural strength across both curing regimes.

The tensile splitting strength test revealed that the 10% epoxy resin provided the highest tensile strength, particularly in specimens subjected to wet-dry curing conditions. The reduction in porosity within the mortar led to increased density, thereby enhancing its strength. Based on the results, the 10% epoxy content with wet-dry curing was selected, as it offered higher compressive strength and favourable conditions for both hydration and polymerization processes.

The self-healing performance of the epoxy-modified mortar was evaluated using non-destructive testing and compressive strength measurements. The 10% epoxy content exhibited the most effective self-healing performance. Overall, the findings demonstrated that epoxy resin without a hardener can serve as a viable additive for mortar.

K. Ramya 2017, The approach combines both natural healing and artificial methods for crack repair. One of the most widely studied techniques is the microcapsule-based self- healing method. This approach involves encapsulating a healing agent, such as sodium silicate, and embedding it within the concrete's polymer matrix. When cracks occur, the microcapsules break open, releasing the healing agent into the crack plane through capillary action. The healing fluid then interacts with a catalyst, triggering a polymerization reaction that bonds the crack surfaces together.

Microencapsulation is used to protect both the healing agent and the catalyst, if both are present. The microcapsules must be months of curing. The findings indicated that the reduced porosity contributed to increased strength. It becomes durable

enough to remain intact until a crack forms, while having minimal impact on the overall properties of the concrete.

Various tests have been conducted to assess the performance of these microcapsules in self-healing concrete, including compression tests, ultrasonic pulse velocity (UPV) tests, rebound hammer tests, and bending tests. The results indicate that the process is effective in enhancing the self-healing capabilities of concrete. The strength of concrete containing microcapsules is comparable to that of conventional specimens, and the healing efficiency is evaluated by inducing cracks and testing the compressive strength after 14 days of healing. The use of self-healing concrete has the potential to extend the service life of structures and reduce the need for costly repairs. This study presents the results and discussion of tests conducted on microcapsules to assess their performance in self- healing concrete. Compression tests on cube specimens were used to determine the ultimate failure load, while the healing efficiency was estimated by testing the compressive strength of cracked cubes after 14 days of healing. Ultrasonic pulse velocity (UPV) tests were conducted before loading, after inducing cracks, and after 7 and 14 days of healing on six prisms and five cubes. Rebound hammer tests were performed to correlate UPV values with rebound hammer readings and compressive strength. The results indicated that the strength of the concrete did not significantly differ from conventional specimens despite the incorporation of microcapsules.

Fernando Cotting et. Al 2019, Microcapsules containing a commercial epoxy resin were synthesized using the in-situ polymerization technique. The size distribution of the microcapsules was analyzed by laser diffraction. These filled microcapsules were incorporated into a three-layer epoxy coating system at varying concentrations (10% to 15%) and with microcapsules distributed across different layers. Electrochemical impedance spectroscopy (EIS) was employed to evaluate the coating system, and a pull-off adhesion test was conducted to assess the coating’s adhesion properties.

The percentage of encapsulated material was calculated using the formula:

$$(^{mass\ of\ filtered\ material})\mathrm{x100}\ total\ mass\ of\ sample$$

The incorporation of microcapsules in the epoxy coating and their application on carbon steel panels showed that the loading of the coating system with self-healing microcapsules resulted in a decrease in the total impedance of the coating. This indicates a certain disruption in the coating system due to the presence of microcapsules. However, the self-healing agent was confirmed to be effective for all samples containing microcapsules, as verified by the electrochemical techniques and corrosion tests employed in this study.

Higher concentrations of microcapsules resulted in improved self-healing films, leading to better anticorrosive performance. Additionally, the pull-off adhesion tests demonstrated that the presence of microcapsules did not compromise the adhesion properties of the coating system in any way.

3. Discussion

The operational process of self-healing materials can differ based on the type of HA. Recently, a range of self-healing agents have been explored. Self-healing processes within cement-based systems can generally be divided into two categories: autogenic and autonomic. Autogenous healing, or autogenic healing, refers to the process in which performance restoration occurs due to the presence of material components that would normally be part of the mix under typical conditions. On the other hand, autonomous healing depends on the inclusion of engineered additives, which, under normal conditions, would not naturally be present in the concrete mix, to support the healing process. Recently, many researchers have examined self-healing cementitious materials using autonomic mechanisms, which involve various factors such as different bacterial strains, crystalline additives, encapsulation, and polymeric substances. The functional principles of self-repairing materials may vary across different types. The process behind the chemical-based HA mechanism is outlined below.

3.1.Calcium nitrate:

Calcium nitrate (CN) is typically encapsulated within concrete through microencapsulation, and when cracks develop, calcium nitrate interacts with unhydrated cement to produce a new hydration byproduct. It is important to mention that calcium nitrate contains cations similar to those found in C2S and C3S, and it can also react with hydroxide to form CSH. Calcium nitrate can also participate in a reaction with unhydrated cement particles. Moreover, the calcium ions (Ca2+) delivered into cracks by calcium nitrate could contribute to the precipitation of calcium carbonate, resulting in an increase in the saturation index Ω of calcite. The hydration byproducts formed on the cracked surface help restore the cracks and improve mechanical properties. The reaction mechanism of calcium nitrate is demonstrated in Eqs. (1) and (2) below.

$Ca(NO_3)_2 + 2Ca(OH)_2 \rightarrow 2Ca(NO_2)_2 + 2H_2O$, $Ca(NO_2)_2 + CO_2 \rightarrow CaCO_3 + 2NO_2$.

3.2.Sodium silicate:

Generally, sodium silicate (SS) is incorporated as a healing agent in cementitious systems during the initial sample preparation stage, usually in the form of microcapsules. As cracks develop, the capsule shell breaks, and sodium silicate interacts with Ca(OH)2 to generate more calcium silicate hydrate (C–S–H) gel. C–S–H, a key hydration product, plays an essential role in influencing the mechanical and durability properties of concrete. The additional formation of C–S–H within cracks in the concrete aids in restoring its mechanical and durability characteristics. The reaction pathway for the sodium silicate-based healing agent is illustrated in Eq. (3).

$XH20$

$2Na^{+} + SiO^{3-}{}_{2} + Ca^{2+} + 2OH^{-} \rightarrow\!\!\longrightarrow CaOSiO_2xH_2O + 2NaOH$.

3.3.Calcium hydroxide:

The self-repair of concrete, cement-based materials, or geopolymers can also be achieved through the use of calcium hydroxide. The primary healing byproducts include calcium carbonate, C–S–H gel, calcium carbonate ettringite, and mono- carboalumination. Research suggests that saturated $Ca(OH)_2$ has been proposed as a healing agent for self-compacting concrete. When $Ca(OH)_2$ is saturated around the unhydrated cement particles in concrete, the unhydrated cement clinker dissolves, releasing $Ca2^{+}$ ions over time. Furthermore, $SiO_2(aq)$ is also discharged. Given that $Ca(OH)_2$ is already saturated, the release of $Ca2^{+}$ ions from unhydrated cement causes solid $Ca(OH)_2$ to promptly precipitate in the crack. Once the necessary concentration of $SiO_2(aq)$ is attained, C–S–H is subsequently formed.

3.4.Calcium sulfoaluminate:

Another expansive mineral additive, calcium sulfoaluminate (CSA), can also serve as a healing agent. The addition of CSA into concrete results in the formation of hydration products like ettringite (AFt) and monosulfoaluminate (AFm), which help to fill the cracks. CSA is primarily incorporated into the concrete mixture in capsule form, preventing concrete expansion and enabling healing when cracks form by releasing the CSA. However, there are certain drawbacks to this approach, including issues with bonding between the capsule and concrete, challenges in capsule preparation, and negative effects on the mechanical performance of concrete when the capsule quantity is high. An alternative method involves granulating the CSA admixture after cracks have formed. Hydration byproducts, including AFt and $CaCO_3$, form and heal the cracks, but ettringite is relatively unstable, limiting the effectiveness of the healing process.

3.5.Silica:

Kendrick et al. described the reaction between calcium hydroxide and micro silica, leading to the formation of C–S–H gel. Baltakys et al. utilized two forms of silica, namely amorphous and crystalline, and found that the reaction between calcium hydroxide and amorphous silica occurred more quickly than with the crystalline form. Latina and Tabbaa investigated silica precursors, specifically an aqueous silica particle solution, as a healing agent that reacts with $Ca(OH)_2$ in the matrix to form C–S–H gel, thereby filling the crack. This aqueous solution is encapsulated using polyurethane microcapsules. As cracks develop, the silica particles react with $Ca(OH)_2$ in the mixture, producing C–S–H gel that ultimately fills the crack.

3.6.Dicyclopentadiene:

In contrast to the previously mentioned healing agents, where the formation of additional cement hydration byproducts facilitates crack self-healing, Dicyclopentadiene is a monomer that polymerizes upon reaction with a catalyst, resulting in the formation of highly cross-linked healing products. Dicyclopentadiene (DCPD) appears as a white crystalline substance or a clear liquid. This compound acts as a monomer in polymerization reactions and has proven to be an effective healing agent for asphalt, polymers, and concrete. The self- healing of concrete involves the polymerization of DCPD through a process known as ring-opening metathesis polymerization (ROMP). The reaction polymerizes DCPD at ambient temperature, creating a strong and highly cross-linked network that helps fill the crack. The shell serves to isolate the healing agent from the catalyst, preventing the polymerization of DCPD in the absence of cracks in the concrete. When a crack forms, the capsule ruptures, releasing the healing agent, which triggers a polymerization reaction.

3.7.Superabsorbent polymers:

Similar to the mechanism of CSA, superabsorbent polymers swell and seal the crack after absorbing water that has penetrated from the wet side. Unlike CSA, however, it does not generate expansive products like Aft instead, it solely expands to fill the crack. Superabsorbent polymers are a class of polymeric materials capable of absorbing large amounts of liquid (roughly 100–500 times their own weight), transforming into watertight, impermeable gels. When a crack forms in the cementitious system containing SAP and the SAP contacts water, it swells, closes the cracks, and restores the permeability of the system. SAP also facilitates internal curing in cementitious systems, enhances autogenous healing, and can aid in strength development. Superabsorbent polymers can be composed of various materials, and their absorbent capacity may vary depending on the material used. Commonly utilized SAPs as self-healing agents include cross-linked copolymers of acrylamide and sodium acrylate; copolymers of acrylamide and acrylic acid, polysaccharides, and others.

4. Role of microcapsules and unaltered healing agents in mechanical behavior:

Research has investigated different techniques for integrating self-healing agents into cement-based materials and geopolymers, with encapsulation being the predominant method. Certain self-healing agents are also incorporated by substituting binders or other components within these materials. The performance of these self-healing agents is strongly affected by their concentration and the techniques used for their incorporation. Replacing cement components with microcapsules typically leads to a decrease in mechanical strength, which depends on factors like the dosage, properties of the material, and size of the microcapsules. As a greater proportion of high-strength materials (such as cement or aggregates) are substituted with higher quantities of microcapsules, the mechanical strength tends to diminish.

As a self-repairing agent, superabsorbent polymers (SAPs) have also been found to decrease the compressive strength of cementitious materials in a way similar to microencapsulated sodium silicate. Hong and Choi noticed a reduction in compressive strength (fc), with a more pronounced decline at higher concentrations. The expansion of SAPs, which absorb and slowly release water, resulting in the formation of voids within the material, is the cause of this reduction in compressive strength. Furthermore, the higher overall porosity caused by the reduced density of dry SAPs also contributes to a decrease in material strength. In another study, Yang et al. examined the effects of SAP on alkali-activated systems.

Previous research indicated that the addition of SAP led to a decrease in compressive strength (fc) of alkali-activated slag (AAS). The rate of decline in compressive strength increased steadily as the dosage increased from 0.3% to 1.0%. The formation of macro voids within the mortar or paste matrix, caused by the release of absorbed water, is responsible for the weakening of the material. Pelto et al. found a significant strength reduction of over 50% with the addition of 1% SAP. However, the strength reduction was less than 25% when SAP was coated with three layers: polyvinyl butyral, cycloolefin copolymer, and an outer layer of zirconium silicon oxide produced through sol-gel. A higher water-to-cement (w/c) ratio is typically employed during the production of fresh cementitious material to compensate for the water absorbed by SAP. This is due to the water-absorbing nature of SAP. However, compared to uncoated SAPs, coatings reduce water absorption, which lowers the required w/c ratio and enhances compressive strength. Advancements in mixture formulation, coating techniques, and material composition could enhance the overall system, allowing for higher SAP doses with a reduced impact on compressive strength (fc).

5. Conclusion

This cutting-edge review article offers an extensive analysis of recent developments in the use of chemical-based self-healing materials in concrete and cementitious composite, emphasizing their sustainability and effectiveness in enhancing the durability of civil infrastructure. The article presents a thorough analysis, comparison, and discussion on the effectiveness of self-healing in cementitious materials incorporating various chemical-based agents, drawing on over 150 research studies. According to previous studies, the most common method for integrating healing agents into cementitious materials is encapsulation.

Researchers have utilized various techniques, including directly mixing healing agents in powder or particulate form during the preparation phase of cementitious materials. Some have also employed lightweight aggregates, treating them by soaking or vacuum methods to embed healing agents before adding them to the cementitious mix. Of all the methods, encapsulation has emerged as the most widely used and successful technique for crack sealing. It was particularly noted that incorporating specific healing agents, such as SAP and SS, can significantly recover compressive strength, potentially up to 100%.

Additionally, the use of calcium hydroxide, SAP, CN, and calcium sulfoaluminate cement has shown potential for crack healing with a complete reduction in their width (100%). The largest crack width healed through autogenous means was 380 μm, while the autonomous method was able to heal cracks up to 750 μm in width. However, it has been noted that sodium silicate is favored by researchers as a healing agent in the literature, in comparison to other healing materials. This review article is expected to function as a well-structured resource, enabling researchers to understand the existing knowledge and pinpoint key areas for future research.

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