ENHANCEMENT OF AUTOGENOUS HEALING IN CONCRETE THROUGH INTERNAL CARBONATION

by

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Abstract

Self-healing of micro-cracks in cement composites have been widely investigated by cement and concrete researchers in the past two decades. Indeed, most research findings suggest that the self-healing technique could potentially mitigate concrete structure deterioration. Among the various approaches to achieve self-healing in concrete, some involve altering the constituents to enhance the autogenous healing mechanism while others involve incorporating additional healing agents (bacteria, adhesives, crystalline additives). The suitability of these approaches has been discussed in this thesis. The primary contribution to autogenous self-healing is via carbonation, a reaction between hydrated products in concrete with atmospheric carbon dioxide. However, autogenous carbonation-based self-healing has some significant limitations; reduced matrix pH, insufficient carbonation penetration and non-uniform deposition of precipitants in cracks. To offset these limitations, a mechanism that involves the utilization of Sodium Carbonate ($Na_2CO_3$) solution as a healing agent has been proposed in this study. Multiple aspects of concrete performance, such as compressive strength, tensile strength, permeability and fiber-matrix bond strength were used as parameters to assess whether the proposed solution works better than autogenous healing. To replicate the different types of damages and internal cracking that could arise during the service life of concrete structures, the effects of drying shrinkage, single fiber bond slip and mechanical stresses on the self-healing proclivity of cement-based materials were also explored. A novel technique to measure self-healing under constantly applied stress has also been introduced for better assessment of self-healing.
Lay Summary

Concrete is after water, the most used material in the world today. However, concrete structures around the world degrade and develop cracks over time. This allows deleterious substances to enter concrete and cause further deterioration, possibly leading to collapse. Thus, structures frequently require repair, which raises the total cost of maintenance. Self-healing mechanisms in concrete attempt to reduce the need for regular repair in structures. One such mechanism, carbonation, is a reaction between concrete constituents and atmospheric $CO_2$ to produce new precipitate in cracks, leading to self-healing. However, with the just aforementioned precipitant deposition, crack filling is neither complete nor sufficient to reduce the need for repairs. In this thesis, a self-healing mechanism whereby the need for atmospheric $CO_2$ is replaced by using sodium carbonate ($Na_2CO_3$) solution is investigated. The proposed self-healing approach was assessed using specimens subjected to different types of internal deformations and applied stresses.
Preface

This thesis presents the original, unpublished work carried out by the author, Anupam Choudhary, under the supervision of Dr. Nemkumar Banthia. In this research work, specimens have been produced and tested by the author according to the ASTM standards and experiments were performed in the Material Laboratory at UBC, Vancouver.
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Chapter 1: Introduction

1.1 Background

Concrete like other materials developed by humans (metals, ceramics, etc.), is susceptible to permanent damage from which it cannot revert to its original state. This life cycle of concrete is in stark contrast to materials found in nature like skin tissues or plants, which can recover cuts and heal themselves when exposed to damage. Table 1 summarizes the key features of natural and man-made structural materials, from which one can understand the limited self-healing ability of concrete. Very few innovative man-made materials have self-healing ability like ‘lime cements of the Roman empire’ or the healable oxide film to prevent corrosion of aluminum [1].

<table>
<thead>
<tr>
<th>Man-made Structural Materials</th>
<th>Structural Materials of Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on the entire periodic table</td>
<td>Based on few elements (C, N, O, Ca, Si, etc.)</td>
</tr>
<tr>
<td>Thermo-chemistry (high temperature) processing</td>
<td>Ambient temperature processing</td>
</tr>
<tr>
<td>Fast production rate</td>
<td>Slow growth rate</td>
</tr>
<tr>
<td>Largely monolithic or simple composite structures</td>
<td>Complex, hierarchical structures</td>
</tr>
<tr>
<td>Unchanging structure once fabricated</td>
<td>Continuous replacement and renewal</td>
</tr>
<tr>
<td>No ability to adapt to change of environment</td>
<td>Ability adapt to an evolving environment</td>
</tr>
<tr>
<td>No capacity, in general, for self-repair</td>
<td>Ability to sense damage and self-repair</td>
</tr>
<tr>
<td>Thus: requiring &quot;worst-case&quot; design with</td>
<td>Thus: allowing optimal design to match current conditions without penalty of large safety factor</td>
</tr>
<tr>
<td>additional safety factor</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1: Comparison of key features of man-made and natural structural materials (adopted from [1])*

Concrete is designed to crack up to serviceable limits. Even under these limits, the presence of cracks in concrete could lead to the ingress of deterioration inducing water and other deleterious substances. Due to structural reasons or shrinkage, further cracking also occurs and leads to connectivity between previously segmented micro-cracks and pores, thereby increasing the permeability of concrete structures. In marine environment, crack formation will accelerate the penetration of chlorides, thereby initiating rebar corrosion and reducing the service life of structures. Due to such deterioration, around 50% of construction budget in Europe is being spent on regular maintenance and repairs required for concrete structures through their service life [2]. In United States alone, the cost of bridge maintenance and repair is estimated to be $5.2 billion. In addition to these direct costs, there are significant indirect costs due to loss in productivity and traffic jams during repairs. Thus, there is a need for self-healing research to drive down
maintenance costs. Building more sustainable structures will also help drive down the volume of concrete needed for repairs and thus reduce the carbon footprint of the construction industry in the long term. Figure 1 below indicates how a high-quality material incorporating self-healing can lead to lower eventual cost even though initial cost of construction is higher. A possible barrier to the implementation of self-healing technologies would thus be the too high initial cost of current technologies. The focus of new research studies should therefore be on reducing the initial cost of construction via self-healing concrete while also elongating the period before a first structural repair is required.

Concrete, being a cementitious material, does possess some self-healing ability due to its ongoing hydration. During the past two decades, significant research has been conducted to enhance the self-healing ability of concrete, either by altering the constituents or introducing external healing agents [3]. In the literature review section of this thesis, an overview of previous research studies on self-healing, and an assessment of their feasibility concerning durability issues like corrosion is provided. Potential research areas that could enhance self-healing without reducing the mechanical performance or durability of concrete structures are also highlighted. Studies on 2000-year-old Roman Concrete piers have also revealed repeatable self-healing mechanism present in those structures [4]. The research on healing mechanisms in Roman concrete and its applicability to modern concrete used in industry is also discussed.

The current thesis focuses on enhancing the autogenous healing in concrete, specifically carbonation, using low-cost mechanisms. The lower cost of implementing self-healing is essential

\[ \text{Figure 1: Performance and cost, including direct repair cost, versus elapse time for (A) normal and (B) self-healing high quality infrastructure which requires less iterations of repair [1].} \]
in keeping the initial construction cost low. This will ensure that concrete structures incorporating self-healing are more economically viable relative to structures subjected to regular repairs. Autogenous healing is concrete’s innate ability to partially fill cracks caused during service life of a structure. It was first observed in water retaining and underwater structures, which customarily maintain a moist environment conducive for autogenous healing. Ter Heide [5] explained that the possible causes for autogenous crack healing in these structures can be classified into physical and chemical processes. Physical processes like pore blocking and matrix swelling are temporary while chemical processes such as hydration of unhydrated particles or precipitation of calcium carbonate are permanent.

Among the two chemical processes, precipitation of carbonate in cracks has previously been reported to be the predominant autogenous healing mechanism [6], especially at later ages when little unhydrated material is available in concrete [7]. According to Neville [8], if crack takes place at an early age, when the degree of hydration is low, continued hydration is the primary mechanism while for cracks at later ages like 28 or 56 days, carbonation takes over as the primary mechanism. However, the experimental results from literature do not seem to follow this trend always. In some studies [9-10], the major product found in the cracks is a white precipitate Calcium Carbonate (CaCO$_3$), even when continued hydration was expected to be the dominating mechanism. The mechanism for precipitation of CaCO$_3$ in cracks is the reaction between dissolved calcium ions from the matrix and dissolved carbon dioxide from the atmosphere. However, the reaction is limited by the small quantity of dissolved carbonate (CO$_3^{2-}$) ions and the minute concentration of CO$_2$ in the atmosphere [11]. In addition, previous studies have reported that precipitation inside cracks is non-uniform, and thus, while surface can be sealed at the crack mouth, most of the crack volumes remain empty [12]. The reasons for non-uniform filling of cracks is that the dissolved CO$_2$ from the atmosphere can only diffuse up to a certain depth from the surface. Thus, only a small region close to the surface has enough CO$_3^{2-}$ ions to cause precipitation of calcium carbonate. Further, carbonation inside concrete reduces the pH of concrete leading to depassivation of protective rebar film and initiation of corrosion in steel reinforcement.

An attempt has been made in the past by Wang et al. [13] to overcome these limitations of natural atmospheric carbonation by utilizing sodium carbonate (Na$_2$CO$_3$) for internal carbonation. In their study [13], ceramsite infused with Na$_2$CO$_3$ enhanced the self-healing process, especially deeper
inside the cracks than just on the surface. This improvement in self-healing was traced to the presence of carbonates that led to a uniform precipitation in cracks and higher self-healing potential than natural carbonation using dissolved CO₂. However, given that [13] also used expansive mineral additives in conjunction with the Na₂CO₃-infused ceramsite for self-healing, more studies on the crack-healing potential of internal carbonation are needed. Moreover, given that the self-healing investigation by [13] was performed on unloaded samples, the present study is extended to samples exposed to varying degrees of applied stress during healing.

In the present study, the influence of Na₂CO₃ on the self-healing performance of cement composites is further investigated. Specimens are submerged in 0.95M Na₂CO₃ solution to provide healing after cracking. Given that the reduction of pH during carbonation occurs during the conversion of dissolved CO₂(g) to carbonate (CO₃²⁻) ions according to the mechanism in Equation 1.1 below, the use of Na₂CO₃ directly in the system should allow for introduction of carbonate ions without reducing pH in concrete as highlighted in Equation 1.2 below. The efficacy of the proposed internal carbonation mechanism would be evaluated by subjecting cement composites prepared with and without Na₂CO₃ powder to different levels of damages, and measuring the degree of mechanical strength, bond strength and durability property recoveries.

\[
CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (1.1)
\]

\[
Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaOH \quad (1.2)
\]

Multiple aspects of concrete performance, such as compressive strength, tensile strength, permeability and fiber-matrix bond strength were used as parameters to assess whether the proposed solution works better than autogenous healing. A variety of assessment techniques are needed since damage and cracks also occur in multiple ways. Different ways of introducing internal cracking into the system such as shrinkage cracks, bond slipping and mechanical stresses, have thus been explored to ensure applicability of this mechanism in structures. A novel technique whereby permeability evolution of concrete specimens subjected to different levels of compressive stresses was used for a better assessment of self-healing was also introduced. In the later part of the thesis, the measured permeability coefficient and service life models available in literature were also used in performing Service Life Predictions. Results from comparison of predicted service
life indicate that healing with internal carbonation using $Na_2CO_3$ solution could lead to an increase in service life of concrete.

1.2 Outline of thesis

The objective of this thesis was to study the internal carbonation mechanism for enhancing autogenous healing in concrete. The thesis comprises of five chapters as listed below:

- Chapter 1: Introduction  
- Chapter 2: Literature Review  
- Chapter 3: Methodology  
- Chapter 4: Results and discussion  
- Chapter 5: Conclusion and future work

Chapter 1 lays out the background for the research work. It also embodies an outline of the thesis with short discussion on each chapter.

Chapter 2 provides a review of current research on self healing mechanisms with insights into the feasibility of the different approaches to self-healing. Several research gaps are discussed which should be explored in future work.

Chapter 3 covers the methodology adopted in the research work and the details about the materials required. It also includes the details on the mixture design and proportions. Various damage and assessment techniques used in current work are discussed with reasons on why they are suitable for measurement of damage and healing.

Chapter 4 presents the results of the assessment tests discussed in the previous chapter and inferences are drawn from the experimental observations.

Chapter 5 summarises the conclusions of the thesis and offers recommendations for future work.
Chapter 2: Literature review

This chapter contains a discussion of the different approaches that researchers have taken to achieve self-healing in cementitious materials. The approaches can be classified into autogenous, autonomous and vascular self-healing mechanisms. The purpose of this chapter is not to provide an exhaustive review or comparison of the available approaches to introduce self-healing in concrete. Recent review papers have covered that aspect [3, 9, 11] in detail. Rather, the goal is to provide an overview of the research being done on self-healing, assess their feasibility with respect to durability issues like corrosion and to explore potential research areas which can enhance self-healing without reducing the mechanical performance or durability of concrete structures.

2.1 Autogenous self-healing

2.1.1 Mechanisms of autogenous healing

Self-healing properties in concrete were first observed in water retaining structures [10] and underwater structures, which has been observed to be an ideal condition for self-healing [14-15]. Such crack healing, which occurs in ordinary concrete without any intervention, has been termed as autogenous healing as per RILEM committee [16]. Ter Heide [5] explained that the possible causes for autogenous crack healing in these structures can be classified into physical and chemical processes, which are shown in Figure 2. The chemical causes, i.e. carbonation and continued hydration, have been observed to be the major contributors to the autogenous healing process. However, among these, the primary mechanism for autogenous healing has not been clear to date. Edvardsen [6] in his study on permeability of cracked concrete found $CaCO_3$ precipitation as the primary effect of self-healing. Other researchers like Granger et al [17], have detected Calcium-Silicate-Hydrate ($CSH$) in the healed crack. According to Neville [8], if crack takes place at an early age, when the degree of hydration is low, continued hydration is the primary mechanism while for cracks at later ages like 28 or 56 days, carbonation takes over as the primary mechanism. However, the experimental results from literature don’t seem to always follow this trend. In most investigations like Yang et. al. [18] and Qian et al. [19], the major product found in the cracks is a white precipitate $CaCO_3$, even when sometimes, continued hydration was expected to be the dominating mechanism. This contradiction was explored in detail by Huang et al. [11]. This research revealed that the continued hydration in a crack is different from initial hydration.
reactions. Portlandite, which is the minor product in cement hydration, was almost 80% of the reaction products in cracks. This research, however, did not consider natural concrete cracks but simulated artificial cracks using two slices of concrete pressed together [12]. Thus, more research is needed to understand the mechanism of crack healing in natural cracks caused by loading or shrinkage.

![Figure 2: Possible causes of self-healing: (a) formation of calcium carbonate or calcium hydroxide, (b) sedimentation of particles, (c) continued hydration, (d) swelling of the cement matrix [5].](image)

2.1.2 Carbonation of CH

For decades, there has been confusion among researchers as to which mechanism of autogenous healing is more prevalent and has more potential [12]. Continued hydration in a crack as noted before, is reported to have different hydration products than original hydration reaction, producing only about 15% Calcium Silicate Hydrate (CSH) [11]. Therefore, the precipitation of CSH alone will not be able to completely fill cracks. Also, continued hydration tends to densify the region around a crack, thus reducing the leaching of ions and slowing down the healing kinetics [11]. Earlier research studies [6, 20] also indicated that precipitation of CaCO₃ by reaction of atmospheric CO₂ with Calcium Hydroxide (CH) is more prevalent in healed cracks and thus, has more potential for complete crack healing. Literature survey also reveals that in Portland Cement (OPC) concrete as well as concrete blended with Supplementary Cementitious Materials (SCM), the most prominent self-healing material in absence of any specialized additive is calcite. Thus, carbonation as a self-healing process is discussed in more detail in this review. The reactions that take place during carbonation of portlandite by atmospheric CO₂ are as follows:

\[
H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (2.1)
\]
\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3 \]  

While there are lots of studies on self-healing by carbonation, the negative effect of carbonation in reducing the pH of concrete has received meager attention. As we can see from above reactions, the introduction of \( H^+ \) ions will reduce alkalinity in concrete, which can result in de-passivation of protective film on rebars and earlier initiation of corrosion. Thus, promoting carbonation for self-healing can have a negative impact on durability of reinforced concrete. Also, since the \( CO_2 \) will diffuse from the outside, \( CaCO_3 \) is likely to precipitate near the crack mouth and cracks will not be filled uniformly, as observed in literature [11, 13]. One of the approaches to get around these issues is to provide carbonate ions as salts inside the concrete matrix. This could be done either directly by adding carbonate ions as a powder or encapsulated to prevent a reaction before cracking. Wang et. al [13] introduced sodium carbonate in porous aggregates and obtained a deeper and more uniform precipitation of \( CaCO_3 \), resulting in lesser permeability of filled crack. Thus, adding carbonate ions to concrete via soluble salts has a potential to improve self-healing and further investigation is needed. However, once portlandite is consumed, carbonation of CSH can have the negative effect of increasing the pore volume [12]. Thus, more research is needed to optimize the amount of carbonate salts to improve self-healing effects.

2.1.3 Need for water for healing mechanisms

For decades, many researchers have recognized water as a primary component needed to heal cracks, especially via autogenous healing. Water serves as the solvent to enable both carbonation and continued hydration mechanisms for autogenous healing and its presence is essential inside a crack. Hence, self-healing was first observed in underwater structures. According to Qian et al. [20], multiple wet and dry cycles is the ideal condition for self-healing and insignificant healing was observed in open air. Lauer and Slate [21] also reported that healing in an atmosphere at 95% relative humidity gave healing strengths as much as 85% lower than those obtained by healing under water. Apart from autogenous healing, water is also crucial to bacterial self-healing and any other approach that involves precipitation of healing products in cracks. Even though the need for water has been recognized, theoretical and experimental research is lacking as to quantifying the amount of water required to initiate different self-healing mechanisms for a certain crack width. Innovative solutions have been introduced, like porous aggregates [22], hydrogels [22-23], super-absorbent-polymers [24-25], etc., which can hold on to water until cracking and release it to
activate self-healing. However, significantly more research is needed to find the optimal amount of water needed, finding ways of its preservation in concrete and its utilization during healing of cracks.

2.1.4 Autogenous healing in pozzolanic portland cement (PPC)

Adding a pozzolanic material like fly ash and slag in concrete, which have slow pozzolanic reactions, will result in latent hydraulic material being present at later ages in concrete. This hydraulic material can then react with $CH$ to produce more $CSH$ to fill up the cracks. Termkhajornkit et. al. [27] indicated a higher healing of shrinkage cracks with a higher replacement of fly ash. However, fly-ash and other pozzolanic materials consume $CH$, thus reducing the possibility of carbonation as a means of self-healing. Also, kinetics of pozzolanic reactions are too slow to provide effective healing of cracks. One of the alternatives is to use highly reactive pozzolana like Silica Fume but due to high rate of pozzolanic reaction, Silica Fume may already be consumed even before cracking occurs. Further theoretical and experimental research is therefore needed to utilize the pozzolanic reaction as a means of self-healing in concrete.

2.2 Encapsulated self-healing agents

Due to the limitations of small crack width for complete autogenous healing, researchers have tried to modify the healing approach to obtain higher expansion to fill larger cracks, for e.g. use of bacteria in concrete [28], microencapsulated healing agents [29-30] and crystalline admixtures [31]. The healing agents can vary from mineral admixtures like expansive cements and silica to adhesive agents like epoxy [32].

2.2.1 Bacterial self-healing

2.2.1.1 Mechanism of healing by bacterial spores

Since the carbonation by autogenous mechanisms has been shown to be able to fill cracks up to a limited crack width, there is a need to look for other potential methods for crack filling. One potential method with a larger capacity of crack filling is to utilize bacterial spores to precipitate carbonate in cracks and pores.

Two mechanisms or pathways have been used for carbonate precipitation by bacterial spores, namely:
1. **Hydrolysis of urea** – In these methods, the bacterial cell walls become negatively charged and attract positive calcium ions (Ca$^{2+}$) to their surface. These ions can then react with carbonate ions dissolved in water to produce carbonate precipitation building from the cell walls. The bacterial cell acts as a host for this carbonation in the following way:

$$\text{Ca}^{2+} + \text{Cell} \rightarrow \text{Cell} - \text{Ca}^{2+}$$

$$\text{Cell} - \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Cell} - \text{CaCO}_3 \downarrow$$  \hspace{1cm} (2.3)

Its higher potential for crack-filling than atmospheric carbonation is due to hydrolysis of urea which produces hydroxyl ions (OH$^{-}$). This encourages spontaneous formation of more carbonate ions than natural carbonation as can be seen from reaction mechanism below. However, the byproduct ammonium ions affect concrete matrix negatively. Also, after first precipitate coating on cell wall, bacterium dies and self-healing stops.

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$$  \hspace{1cm} (2.5)

2. **Utilizing carbon dioxide by bacterial respiration** – This mechanism avoids the by-product ammonium formation by utilizing CO$_2$ from bacterial respiration. However, to account for lack of OH$^{-}$ ions from urea hydrolysis, it requires a Ca-rich environment and high pH. This necessity of high pH is to maintain the spontaneity of conversion of carbonic acid to carbonate ions.

Ca-rich environment for bacterial spores in both mechanisms is usually provided as Calcium lactate, which acts as a nutrient rich food source for bacteria. This reaction is as follows:

$$\text{Ca(C}_3\text{H}_4\text{O}_3)_2 + 6\text{O}_2 \rightarrow \text{CaCO}_3 + 5\text{CO}_2 + 5\text{H}_2\text{O}$$  \hspace{1cm} (2.5)
Carbon-dioxide produced by bacterial respiration aids in self-healing by reacting with portlandite hydration product. This reaction below is similar to atmospheric carbonation, just the source of $CO_2$ is different. The second mechanism is thus limited by $pH$ and amount of portlandite available.

2.2.1.2 Limitations of bacterial healing

Although self-healing by bacterial spores have a higher potential in terms of being able to fill up larger cracks than autogenous healing, there are many challenges facing their implementation for structural concrete. Bacterial spores in dry state have been proven to last for decades, but the environment in concrete is adverse and limits their lifetime to a few months only. This is due to ever-reducing concrete pore size. When, pore size becomes smaller than size of spores, spores are subjected to stresses leading to their death. Also, surviving the harsh concrete mixing process is difficult for these spores. Thus, the bacterial spores need encapsulation for their protection. Encapsulation using clay pellets can protect bacteria, but it leads to a reduction in concrete strength and other problems associated with encapsulation. Since bacterial self-healing requires two phases, namely bacteria and food sources, there is a problem of optimization of nutrient and bacteria to ensure ubiquitous presence in concrete.

2.2.1.3 Application of bacteria based self-healing in structures

To introduce this concept in structures, large scale demonstration project is required. One such demonstration was done by researchers at Delft University in Netherlands. The idea was to construct a self-healing building is applied by "Innergy", designed by Marcus architects and Department of Self-Healing Materials at Delft University. These bacteria are harmless, to both human and animal life. They are responsible for the development of limestone, promoting cracks repair without any additional or external assistance. The closure of the cracks will maintain the reinforcement unaffected by the aggressive agents and the concrete will have thus a longer life. Till now there have been no subsequent publications on this demonstration project. In the next few years it will be examined by TU Delft in which circumstances the bacteria remain alive and how exactly the restoration of the concrete proceeds [33].

Another interesting project has been applied in Andean Mountains in Ecuador: an irrigation canal about 500 meters long has been constructed. A collaboration between researchers from TU Delft and Universidad Catolica de Santiago de Guayaquil in Ecuador has applied concrete self-healing
techniques to prevent irrigation canals from cracking, thus preventing expensive repair operations and seriously diminishing the chance of crop failure. A research group, headed by Jonkers and Wiktor, decided to use natural fibers together with bacteria as healing agent to improve the concrete performance, control the crack widths and guarantee the crack healing. The chosen fibers were Abaca, indigenous to Ecuador. After five months, the cast concrete showed no sign of cracking or deterioration and therefore its healing performance could not be evaluated [33]. The performance reports of these buildings will demonstrate the self-healing provided by bacteria. Precise service life estimation can be achieved only through an in-depth knowledge of the self-healing efficiency and its variability, and this is the key to promoting this concept among contractors and owners.

2.3 Self-healing by expansive mineral admixtures

Expansive admixtures for self-healing are usually added during concrete mixing and can be classified into two types of additives with different mechanisms: expansive additives and crystalline additives. Expansive additives will include calcium sulfo-aluminate, free lime and other minerals which react directly with water to produce expansive products and aid in filling of cracks. Crystalline additives on the other hand, may include reactive silica or other chemicals which can react with $\text{CH}$ in hydration products to produce crystals capable of reducing permeability of cracks. These minerals have potential to fill wider cracks and accelerate crack healing kinetics. However, since these admixtures are added during the mixing, they may have already reacted before crack occurs and may not be available for self-healing. Thus, encapsulation is necessary to protect the agent and preserve the healing ability of these agents.

2.4 Self-healing by adhesives

Adhesives that have been used as glues in manufacturing have the potential to fill cracks by hardening inside the cracks. These agents can be based on a single component, two-components or multiple components [32]. The number of components and the type of adhesive affect the mechanism of filling cracks. For example, in a two-component epoxy protected by capsules, it is difficult to obtain the correct ratio of both components in a crack, thereby significantly reducing the self-healing efficiency. One component epoxy on the other hand is more efficient as it only
needs air to expand, harden and fill cracks. Again, to preserve one-component epoxy till cracking age, encapsulation is necessary.

2.5 Encapsulation

Since the healing agents like bacteria and adhesives must be protected till the cracking time, encapsulation is a promising solution. When a crack occurs and breaks through a capsule, self-healing is achieved by release and reaction of healing agent. Critical parts of the mechanism are the breaking of capsule and successful release of healing agent. Also, these capsules, if present in large amounts, can start affecting the mechanical performance of concrete [3]. Significant research has been done on finding the ideal healing agent for encapsulation, but there has been little focus on the ideal capsules [34]. They should be breakable during cracking but also not reduce the compressive strength of concrete. Capsules should also be able to resist the mixing process and should have reduced capillary forces to improve release of healing agent [34]. A lot of research has also been done on the ubiquity of capsules in concrete, just to increase the probability of a crack passing through. More modelling research and control on the mixing process is needed to ensure the ubiquitous presence of healing capsules in concrete.

In terms of encapsulated healing agents, due to the sophisticated approach requiring careful mixing and optimum distribution of capsules, these technologies are currently too expensive for industrial use. Significant amount of research on capsule and healing agents is needed before external healing agents can be implemented in structural concrete.

2.6 Vascular self-healing approaches

In place of capsules, it is possible to use vascular system to provide external healing agents to cracks in concrete. In terms of biomimicry, this is an approach similar to natural materials like skin. When there is a cut on human skin, healing is achieved by obtaining healing agents from other parts of the body. A similar approach in concrete would require pipes inside the structure which are connected to one healing reservoir [3]. In the event of a crack breaking through this pipe, healing agents will be released to fill the crack. In this way, repeatable self-healing can be achieved if enough healing agent is present in the reservoir just like natural materials. Having an external supply is however expensive due to the variability in the types of concrete structures as can be seen in Figure 3 below. Such implementation increases complexity and cost of casting.
Recent research has also suggested an interconnected hollow fiber network to escape the need for external supply [35]. These interconnected fibers can provide healing agents for many repeated cracking cycles. Vascular self-healing technology in its current embryonic state, is still too expensive to be used in structural concrete and more research is needed to find innovative ways to drive down the economics of this bio-inspired approach. Possibly, a core of reactive self-healing agent with shell around it as the structure can be explored as a method of construction of columns, making a structure similar to self-healing biomaterials in plants.

2.7 Learning from the past: roman maritime concrete

Studies on Roman Maritime structures have revealed a potential for self-healing mechanisms that can work on larger time scales over hundreds of years [4]. The interest in this material stems from the fact that concrete piers developed by Romans have survived over 2000 years in sea water [4], which is considered to be a harsh environment for durability of Portland Cement Concrete. Therefore, careful analysis of Roman Cementitious microstructures and properties and provide insights to improve self-healing mechanisms in modern concretes.

2.7.1 Cementitious processes

Research suggests that Ancient Roman Concretes could gain chemical and mechanical resilience over centuries, which arises from their ability to arrest micro-crack propagation and seal the cracks
via crystallization [4]. Hydration reaction here is different from OPC concrete as the cementing processes evolve over time. The first stage of hydration reactions in Roman Concrete takes place between hydrated lime (\(Ca(OH)_2\)) and alkali-rich volcanic glass (containing silica and alumina) and produces calcium-aluminate-silicate-hydrate (\(C-A-S-H\)), which binds the large coarse aggregates (deci-centimeter sized) used in Roman concrete. The pozzolanic reaction stops after almost all the hydrated lime is consumed, which happens within 5-10 years.

After the initial hydration, interaction with seawater percolating through the structures causes slow dissolution of residual amorphous volcanic ash and volcanic aggregates. This changes the percolating fluid composition and it becomes locally supersaturated in Calcium, Silicon, Sodium and Potassium; which leads to crystallization of more cementitious products like ‘Al-tobermorite’ and ‘strätlingite’ [36]. They crystallize in interfacial zones and pores to improve the mechanical resilience of the structure. This is analogous to water-rock reactions that take place in volcanic rocks with water [4]. Roman Marine concretes were therefore capable of healing cracks in presence of sea water.

2.7.2 Key features of microstructure

Studies on the microstructure of 2000 year old Roman Marine mortar show dense intergrowths of platey crystals that enhance cohesion and obstruct crack propagation at the micron scale [37]. These intergrowths of crystals are a result of crystallization over centuries through seawater exposure. Crystallization of Al-Tobermorite in Roman Maritime Concrete is the crucial to crack healing and development of cohesion over time. Key features observed in studies on the microstructure of Al-tobermorite found in the Roman samples [38] were:

1. Isothermal Bulk modulus, \(K_0\), of Al-tobermorite in Roman concrete microstructure was observed to be substantially higher than \(C-A-S-H\) in slag concrete used today.

2. NMR studies also indicate long-silicate chain lengths and a low \((Ca/(Si + Al))= 0.8\) ratio, which is an indicator of higher degree of polymerization and a larger \(Si^{4+}\) binding energy. Higher polymerization usually indicates stronger cement paste for modern concrete.

3. Al-tobermorite structure was observed to be cross-linked and possessing high \(Al^{3+}\) substitution in concrete as recorded by Raman Spectra. The higher substitution of Silica ions by Aluminum ions enhances the bonding in the structures while also provides
vacancies for absorption of $Na^+$ and $K^+$ ions to be absorbed in chemical exchange with seawater.

The above properties indicate high endurance of Al-tobermorite crystals in comparison to the binder present in OPC and alkali-activated slag concrete used today. Therefore, although the initial pozzolanic reaction is slower than hydration of OPC and thus leads to slower strength development, post-pozzolanic processes ensure that the material keeps getting denser and stronger over time when Al-tobermorite crystals reinforce the pores in the matrix.

2.7.3 Role of temperature in crystallization

While cementing minerals like Al-tobermorite can also be produced in alkali activated slag concretes, they usually require high temperatures in laboratory synthesis. Laboratory synthesis of Al-tobermorite is a form of pozzolanic reaction between $CaO$, $SiO_2$ and $Al_2O_3$ and requires a temperature of 150°C to crystallize Al-tobermorite in days. The process involves internal restructuring of the more commonly found poorly crystalline C-A-S-H precursor to produce a phase transformation of crystalline Al-tobermorite [39]. Alkali-activated synthesis has been able to produce crystals of Al-tobermorite at lower temperatures of 80-85°C [40] in weeks. However, the Roman marine mortar was able to produce crystalline Al-tobermorite just by itself without external heat supply [36]. Thermal modelling on Roman piers have indicated that the temperature was high (around 85°C) for months after building the structure before cooling down to sea temperature. This high temperature was caused by the exothermic pozzolanic reaction and the large sizes of concrete in structures. These high internal temperatures aided in restructuring the C-A-S-H phase partly to crystalline Al-tobermorite phase [37]. However, as discussed before, the post pozzolanic crystallization of Al-tobermorite and other zeolites occurs just due to dissolution of volcanic glass and supersaturation of the percolating fluid and happens at ambient seawater temperatures. This second phase of crystallization of Al-tobermorite at ambient temperature is helpful in self-healing of cracks and densification of the ITZ. This is similar to rock-water reactions in volcanic rocks exposed to water place such that cementing processes can take place over long periods of time without needing external heat supply.
2.7.4 Adoption of roman self-healing model for modern concretes

The most important differentiating factor in Roman self-healing concrete is that it was designed to thrive in chemical exchange with seawater while OPC marine concrete is designed to stay leakproof and withstand the deleterious reactions with ions in seawater. Therefore, while designing concrete capable of autogenous healing in modern concretes, research should also focus on utilizing the ambient environment of the structure instead of just avoiding interaction completely. Also, another important property of Roman concrete is the long-term cementitious process which last hundreds of years [4]. Therefore, Research in modern self-healing concrete should also focus on possibilities of utilizing long term cementitious process (like carbonation) for healing cracks and strengthening the structure.

Modern concretes also utilize supplementary cementitious materials to reduce the porosity of concrete. Natural pozzolanas (pumice, metakaolin) are a class of such SCMs that partially replace Portland Cement to reduce CO₂ emissions and enhance certain performance aspects. Durability of modern concrete relies on low porosity and minimal aggregate reactivity (to reduce possibility of Alkali Silica Reaction). Also, the presence of portlandite at later ages in OPC concrete and even in blended systems, ensures a high pH system required to sustain a passivation layer on steel reinforcement in concrete. The pH of Roman concrete system on the other hand, is lower than that required to sustain a steel reinforcement passivation, and thus could lead to earlier initiation of corrosion. Thus, more research is needed on preventing corrosion when a mix similar to Roman marine mortars is used. However, there are some benefits of lacking CH as Roman Maritime Concretes are no longer susceptible to leaching. While modern concretes prefer aggregates to be unreactive and largely insoluble in fluids, Roman Concrete thrives in active dissolution of remaining volcanic aggregate. In fact, reactivity of large volcanic aggregates aids in crystallization in the interfacial transition zone (ITZ) and thus strengthening of the weakest link in concrete [4]. Further research is needed to explore the possibilities of using reactive aggregates in modern concretes to provide crack healing.
Another challenge to implement Roman concrete principles is that the lime cement mortar with volcanic ash as the pozzolan has lesser strength than required for modern structural concrete. Moreover, the gain in strength is slow as the pozzolanic reaction is slower than hydration in OPC concrete [4]. However, the crystallization process and the ionic exchange reactions that take place in the self-healable lime mortar need to be studied. This will help determine if it is possible to replicate the process by using volcanic ash in modern concrete or obtaining ionic exchange with CSH to fill up pores. Further theoretical and experimental studies are needed to enhance understanding the self-healing mechanisms in Roman concrete and implement them with alternative materials in concrete.

2.8 Assessment and evaluation of self-healing

Although a lot of recent research has been devoted to understanding the mechanisms and reaction products in self-healing, quantitative assessment of its effects on the engineering properties of concrete and cement-based materials needs a more comprehensive investigation. In the following sections, major issues of the current evaluation methods for self-healing technologies are analyzed with suggestions to make healing evaluation robust.
2.8.1 Impact of stress level on evaluation of self-healing

Literature review reveals that to evaluate self-healing in research, damage is first introduced to concrete specimens by various methods of pre-cracking. Some of the common pre-cracking methods include compression, direct tension, beam bending and split tensile test [42]. Choice of pre-cracking method is dependent on the test chosen to evaluate self-healing. Literature review reveals two classes of tests that are popular for assessment of healing. One is to assess permeation properties after healing and the other to assess recovery of mechanical properties like strength and stiffness. Several experimental setups, either standard permeability tests or specialized setups (for e.g. water flow test developed in European project HEALCON [43]) have been used in literature for assessment of change in permeability due to self-healing [42]. For permeability tests, pre-cracking is just to introduce cracking to significantly increase permeability and the choice is dependent on the type of specimen (for e.g. 3 point-bending method for a beam-shaped plane concrete specimen). To evaluate recovery of mechanical properties, common research practice has been to repeat the pre-cracking method and compare the response after self-healing to the original specimen response. Other innovative techniques like NDT’s have also been used to evaluate self-healing response [42].

However, most of these assessment techniques fail to represent the actual structural situation on site where concrete is subjected to a stress both during the damaging and healing stage. In most of self-healing research, specimens are unloaded after pre-cracking and healed in a stress-free state in ideal under-water conditions. Sustained loads during healing can result in through crack stresses, which should affect the kinetics of certain self-healing mechanisms. Compressive stress results in a mechanical crack closure, while a tensile stress will result in a mechanical crack opening which can lead to unstable cracking, thereby disrupting the healing process. Small compressive stresses (2-4 MPa) have been reported to be beneficial for self-healing [44], however the impact of higher compressive service loads found in real situations on self-healing has not yet been explored. Tensile stress and flexural stress on the other hand, have been reported to adversely affect self-healing in Engineered-Cementitious-Composites (ECC) [45-46]. Therefore, research on the impact of level and type of stress is necessary before self-healing technologies can be incorporated into design for structural concrete.
2.8.2 Crack volume evaluation vs. crack width

Most studies to date have considered crack width as the primary parameter to determine the extent of damage as well as the extent of healing. In most studies, this value of crack width is only the width at the surface, for e.g. the Crack-Mouth-Opening-Displacement (CMOD) for flexural test is the width which is controlled during the test. This however is not representative of the width along the whole length and depth of crack [42]. Crack widths even at the surface, are variable along their length as can be seen in Figure 5 below. In such cases, average of multiple observations along the length is usually considered as the crack width [47-48].

Since a similar variability exists along the depth under the surface of crack, it does not make sense to just use a single parameter to study the extent of damage in a crack [42]. Crack area on the surface can be evaluated by image processing of micrographs [50]. Calculating area instead of average width can improve evaluation of damage and self-healing efficiency. However, the variability of crack depth is still not considered in this approach. Thus, it can be concluded that crack volume in three dimensions is the ideal parameter to recognize the extent and efficiency of self-healing. Measurement of crack volume is extremely difficult to obtain through microscopy. Modern techniques like Computerized Tomography, which utilizes several 2-D X-ray images to simulate 3-dimensional image, can be used for evaluation of crack volume. Micro CT scans (μCT) have been used previously to create 3-dimensional microstructural image of voids [51] and internal cracks in concrete [52]. 3D images of internal cracks were used as way to obtain volume of crack healed. Especially in tests considering recovery in permeability as a measure of self-healing,
incorporating CT scan and 3D microstructural imaging to observe the closing of crack connectivity via self-healing as a validation and extension to their studies. More research studies incorporating μCT and other volume-methods for self-healing evaluation are needed. These studies will help eliminate ambiguities associated with crack width.

2.8.3 Evaluation of the bond-strength between self-healing products and concrete

Even if self-healing products (CaCO$_3$, adhesives, etc.) completely fill a structural crack, studies are lacking on the bond strength between the precipitate produced in cracks and neighboring concrete. This will provide an important perspective on the mechanical integration and computational modelling, for which knowledge of the bond strength is essential [53]. Furthermore, the absence of research findings has made it unclear whether failure takes place in the healed material or otherwise. Hence, questions such as is the weakest link located in the bond or the healed material are yet to be addressed [42]. If bond fails before the failure of healing product matrix, focus should be on selecting a product with better bond strength. A study similar to the bond and compatibility studies between fibers and concrete is needed for various additives and their healing products with native concrete. For e.g. the bond strength between calcite and C-S-H needs to be tested to find out the mechanical recovery possible with each self-healing mechanism.

2.9 Conclusion from literature

In the last two decades, extensive research has taken place and a variety of approaches have been explored to enhance self-healing in concrete. Some of these approaches are for now, too expensive to be used in industry. Chemical healing agents like adhesives are too expensive to be used in large volumes in structural concrete. Also, they pose problems of bond and compatibility with the native concrete. Bacteria as a healing agent are not expensive if directly added to concrete, but for them to survive till the time of cracking, encapsulation is generally needed, which creates problems as discussed in section 2.5. Autogenous healing on the other hand, comes at little additional cost and needs to be optimized and utilized to its fullest potential. Theoretical and computational modelling of carbonation and continued hydration as self-healing mechanisms is needed to explore if and how these mechanisms can provide suitable healing for different kinds of cracks that occur in concrete. Most researchers place their cracked samples under water or in air but without any stress level. The impact of stress level on various self-healing mechanisms has not been studied till now.
Roman Maritime concrete is capable of repeatable self-healing over centuries and can serve as a prototype for developing effective healing in OPC concrete. The key to the long-term healing is the positive interaction of the Roman marine concrete with its ambient environment (seawater). The principle of durability by reactivity in Roman concrete vs. durability by minimal porosity in OPC is something that should be explored for modern self-healing concretes. More theoretical and modelling studies are needed to better understand the Roman mortar healing mechanisms and look for alternatives within the current spectrum of cementitious materials. The use of hydration heat for crystallization of other minerals is also an interesting property that needs to be explored in modern concrete. Romans used specific instances of volcanic ash that is not available at most locations around the world. Research is also needed to look for possible alternatives to volcanic ash to produce reinforcing crystals like Al-tobermorite in modern concretes.

Major experimental techniques for assessment of self-healing are either permeability tests or mechanical property tests to evaluate recovery in durability and strength. Research on self-healing in the last decade has a possible missing link for applicability in the industry. The missing link is to study the influence of stress on the self-healing of cracks in an in-service concrete structure. 3-dimensional imaging of cracks can go a long way in providing a better evaluation of healing efficiency and understanding of the mechanisms of segmentation of cracks during healing. Tests for calculating bond strength and compatibility of healing products with neighboring concrete also need to be developed. All these improvements will help make the assessment methods robust enough to allow self-healing technologies to be used for structural processes.

Self-healing research also needs to be broadened into considering other forms of damages as well, for e.g., large plastic deformation, corrosion or salt-scaling. Anything which alters the chemical or physical conditions inside concrete matrix is potentially a damage, that needs to be taken care of in one way or another. More research is needed on these alternative forms of damages as they are equally important in the integrity of the structure. Smarter detection of damage through sensors will obviously help gather crucial data to create better self-healing concrete and increase the life cycle and sustainability of structures.

For the purpose of this thesis, the objective is to study a low-cost enhancement of autogenous healing by using \( \text{Na}_2\text{CO}_3 \) and introducing it directly into matrix for carbonation. Nonetheless, the introduction of carbonates needs to be optimized as too much carbonate can be detrimental by
reacting with clinker phases or CSH directly and affecting strength. In the following chapters, experiments are conducted to verify damage and then healing using 0.95M Na$_2$CO$_3$ solution and conclusions have been drawn on the feasibility of this mechanism in filling cracks and recovering performance of concrete.
Chapter 3: Materials and testing

3.1 Material composition

Canadian Standard Association (CSA) Type 10 general-use (GU) Portland cement (ASTM Type I), natural river sand, coarse aggregate with maximum size of 12 mm and potable water were used for the mixing. Chemical composition of the GU cement used in the study is shown in Table 2. Specific gravities of sand and coarse aggregates were 2.62 and 2.7 respectively. Sodium carbonate (Na$_2$CO$_3$) powder with a purity of 98% was used to provide carbonate ions for healing. Na$_2$CO$_3$ concentration of 0.95M, which is close to the concentration required for saturation was used. This will ensure ample availability of carbonate ions such that the carbonation reaction in equation (2) will only be limited by availability of calcium ions in the matrix. While testing single fiber-pullout, straight steel fibers of length 50 mm and diameter 1 mm are used. The mix proportions of concrete and mortar used in the test program are given in Table 3.

<table>
<thead>
<tr>
<th>Table 2: Chemical composition of GU cement used in current study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Item</strong></td>
</tr>
<tr>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>SO$_3$</td>
</tr>
<tr>
<td>LOI @ 950 °C</td>
</tr>
<tr>
<td>LOI @ 550 °C</td>
</tr>
<tr>
<td>Insoluble residue</td>
</tr>
<tr>
<td>NaEq</td>
</tr>
<tr>
<td><strong>Physical properties</strong></td>
</tr>
<tr>
<td>Blaine Fineness (m$^2$/kg)</td>
</tr>
<tr>
<td>Passing 45 µm (%)</td>
</tr>
<tr>
<td>Autoclave Expansion (%)</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concrete</th>
<th>Mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>414 kg/m³</td>
<td>400 kg/m³</td>
</tr>
<tr>
<td>Water/Cement ratio</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Water</td>
<td>207 kg/m³</td>
<td>200 kg/m³</td>
</tr>
<tr>
<td>Coarse Aggregate</td>
<td>736 kg/m³</td>
<td>-</td>
</tr>
<tr>
<td>Fine Aggregate</td>
<td>951 kg/m³</td>
<td>867 kg/m³</td>
</tr>
</tbody>
</table>

All samples were moist-cured at a temperature of 23°C and Relative Humidity of 95%. The three different environments used for healing during this research study are 1) laboratory air (at room temperature), 2) submerged in water and 3) submerged in 0.95M Na₂CO₃ solution.

3.2 Tests for assessment of self healing:

For assessment of healing, different techniques for introducing cracks/damage into the system were used to replicate a real structural application where cracking may occur from various sources. The different kinds of testing used are shown in Figure 6. Mechanical recovery was assessed using splitting tensile test while durability recovery was investigated by testing water permeability under applied stress. Single fiber pullout test was used to test recovery of bond between steel-fiber and mortar.

![Figure 6: Schematic showing the different types of tests conducted to assess performance recovery due to self-healing.](image)

3.2.1 Splitting tensile strength

Sixteen cylindrical concrete samples of diameter 75 mm and height 150 mm were prepared for this test. After 14 days of moist-curing, tensile strength recovery evaluation of these samples was performed in three stages. Firstly, split tensile strength was determined on 14th day after casting by testing four samples as per ASTM C496 [54]. The next stage was to pre-damage the remaining 12 samples by loading up to 90% of the ultimate load before removing the load to introduce internal
After pre-loading damage, five samples each were left under three different environmental conditions for healing as mentioned in section 3.1 (laboratory air, submerged in water and $Na_2CO_3$-saturated water) for a period of 7 days to heal. A period of 7 days was selected to give ample time for the carbonation process in cracks to be completed. After healing, the samples were reassessed for split-tensile strength via the same tests used for pre-cracking the samples.

### 3.2.1.1 Level of preloading for adequate damage

To ascertain the optimum damage inducing preload on samples, 3 different pre-loading percentages were tried to see if they cause a loss in strength. As can be observed from the Figure 7 below, pre-loading at 90% for these samples caused a loss of strength of approximately 12% while loading at 60% or 80% of ultimate load showed insignificant loss in strength. For initial compression test, five samples were used to determine compressive strength and four samples each were tested for each level of pre-load. Finally, 90% of the ultimate strength as a preload was selected for introducing internal cracks in the system.

![Figure 7: Charts showing a comparison of loss in strength at different levels of pre-loading in splitting tensile tests.](image)

### 3.2.2 Early age exposure to dry air

This test was designed to investigate whether the proposed self-healing mechanism can help heal damage or shrinkage cracks caused by samples being exposed to improper curing and a constant flow of dry air at an early age. For this test, after casting and demolding, cylindrical concrete samples of diameter 75 mm and height 150 mm are separated into two groups from the same casting:
• The first group of samples was subjected to a constant airflow of 820 CFM (cubic feet per minute) using a rotating table fan for a specified time period. The samples were kept equidistant from the fan at a radius of approximately 30 cm (~1 ft).
• The second group of samples was covered with plastic sheets to prevent any moisture evaporation.
• After the dry-air exposure period of 2 days, the compressive strength of four samples from each concrete batch was determined as per ASTM C39 [55].

After the determination of compressive strength of the two concrete sample groups, the remaining samples in each group were subjected to two different healing environments: submerged in tap water and submerged in $Na_2CO_3$ solution (0.95M concentration). After healing for 7 days, the samples were again tested in compressive strength to compare recovery in the three different environments.

3.2.3 Single fiber-pullout test

Tensile tests on dogbone shaped mortar specimens was conducted to investigate the bond between steel fiber and concrete and to check if the bond can be repaired. Quasi-static single fiber pull-out test was performed using a table mounted assembly machine while both load, pullout distance and energy under the P-Δ curve were observed. The setup, shown in Figure 8, allows an observation of all stages of the pullout process from initial elastic deformation to the end of the test as the fiber is pulled-out.

![Figure 8: Typical dog-bone shaped specimen and test-setup for quasi-static single fiber pullout](image-url)
Figure 9: Schematic of a dogbone sample

The dogbone shaped specimen, as shown in Figure 9, consists of two halves, which are separated by a 0.5 mm thick plastic separator. The dog bone molds have a partition where each side of the mortar must be separated by a thin plastic film so that the mortar is not in contact with anything else except for a single steel fiber. A steel fiber was inserted into a central hole created in the plastic film before placement in the mold. The same procedure was repeated to make 20 replicas of plastic films with steel fibers at their centers.

The mixing and placing the cement mortar was as per ASTM C305 [177]. Water is first poured into the mixing bowl, after which cement is added. They are mixed for about 30 seconds to get a consistent cement paste, after which gradually sand is added while the mixer is rotating. Once all the sand is added, it is allowed to mix for another 30 seconds. The speed of the mixer is then increased, and mixing continued for about 30 seconds. The mixer is then stopped, the excess mortar collected on the sides is scraped off and allowed to stand for another minute. Mixing is resumed, and the process is completed after another 60 seconds of mixing ensuring a uniform mortar is obtained. A spatula or a small steel spoon is used while casting order to fill the mold. First, the mortar was placed in the mold such that it is only half filled on either sides so that the orientation and the alignment of the steel fiber can be adjusted. It was ensured that the fiber was placed straight and exactly at the center of the mold. Then, the rest of the mold was filled with mortar. The above step was repeated for the rest of the molds and then covered all the mortar filled molds filled were covered with a plastic sheet. The moulds were vibrated slightly on a Table vibrator for about 90-100 seconds, care is taken so that the fibre is still in position and alignment during and after vibration.
To conduct this test, two separate methods for assessing damage and recovery of bond strength were used. First method was to leave the samples under constant flow of dry air at early age and assess damage using pullout tests like the procedure in section 3.2.2. The second damage method specific to the pullout test was to pre-load the samples to a fixed value of fracture energy to obtain similar level of bond slip in all samples before subjecting them to different healing conditions. Loading was stopped manually once the peak load was observed in the load displacement curve and a fixed value of fracture energy was reached.

3.2.4 Permeability test under applied stress

To assess durability recovery due to self healing, most of the research till date has been focussed on measurement of water permeability. Several experimental setups, either standard permeability tests or specialized setups (for e.g. water flow test developed in European project HEALCON [43]) have been used in literature for the assessment of change in permeability due to self-healing [42]. However, in previous studies on self-healing, concrete samples are given a healing period without any imposed applied stress. In an on-site structural element, it is rare for a concrete to experience stress-free state after cracking. Crack healing can be different in stressed and unstressed environments and also depends on the nature of the stress [44]. Small compressive stresses (2-4 MPa) have been reported to be beneficial for self-healing [44], however the impact of higher compressive service loads found in real situations on self-healing has not yet been explored. Tensile stress and flexural stress on the other hand, have been reported to adversely affect self-healing in Engineered-Cementitious-Composites [45-46].
In this study, a water permeability setup developed by Banthia and Bhargava [54], which can measure permeability under an applied compressive stress was adopted. A schematic for this test is shown in Figure 10. In this setup, two permeability cells are assembled, one of which is kept under no stress and the other is kept in a Universal Testing Machine under an applied compressive stress. The concrete samples are 102 mm in diameter and 204 mm long with a 50 mm diameter hollow cylindrical core. For the estimation of the 14-day compressive strength, three solid cylindrical samples of 102 mm diameter and 204 mm length were cast. Three hollow cylinders used for the permeability tests at different levels of stress were also prepared. At the age of 14 days, the hollow cylindrical specimens were taken out of curing room, assembled into separate permeability cells either under stress or free of load. Readings of the weight of water permeating radially through the samples were taken continuously. To allow adequate time to achieve steady-state flow in samples, water was allowed to permeate through samples for 2 days. Thereafter, the water in the test system was replaced with water saturated with $Na_2CO_3$ powder (0.95M). Readings were taken for a further two days, and permeability vs. time plots were compared for the total test duration of 4 days.

Two stress levels of $0.15f_u$ and $0.35f_u$, where $f_u$ represents the compressive strength was applied in the experiment. A 15% compression stress is expected to reduce permeability by compression.
while a 35% stress level is expected to increase permeability via internal cracks based on previous studies on critical stress level in this setup [54]. The coefficient of water permeability was calculated by applying Darcy’s law in a radial flow [55]:

\[
K_W = \frac{Q \ln \left( \frac{r_2}{r_1} \right)}{2\pi h \Delta H}
\]  

(3.1)

Where, \(K_W\) is the coefficient of water permeability; \(Q\) is the flow rate of water through the sample; \(r_2\) and \(r_1\) are the outer radius and inner radius of the hollow cylinder respectively; \(h\) is the height of specimen and \(\Delta H\) is the difference in hydraulic head between inner and outer sides of the specimen. Darcy’s law is only valid after equilibrium (inflow = outflow) and thus, only readings after 1 hour of starting the test were analysed for permeability as suggested in an earlier research on this setup [57].
Chapter 4: Results and discussion

4.1 Splitting tensile test

Figure 11 shows a comparison of tensile strengths observed before and after healing under the three different conditions. Each strength recorded in the figure is an average of four samples. From the graph, it can be observed that healing in a saturated solution of \( \text{Na}_2\text{CO}_3 \) (0.95M) led to the highest gain in strength followed by water and laboratory air healing. However, when samples were left in the laboratory air, the strength is statistically similar to the 90\% pre-loaded strength. In water, due to self-healing via innate autogenous mechanisms, pre-damage strength of 3.7 MPa was recovered. The highest strength of 4.8 MPa observed when healing with \( \text{Na}_2\text{CO}_3 \) solution shows that ample availability of carbonate ions is beneficial to gain back the lost strength by filling cracks and voids with \( \text{CaCO}_3 \).

Previously, other studies on bio-based self-healing concretes using calcite-producing bacteria have also shown higher compressive and tensile strength due to \( \text{CaCO}_3 \) precipitation in cracks [58-59]. Although their mechanisms for calcite precipitation is different from that of the current study, it is clear that as \( \text{Na}_2\text{CO}_3 \) helped fill cracks with \( \text{CaCO}_3 \), the splitting tensile strength was improved.

![Graph showing the comparison of Split Tensile Strength among the 3 different healing conditions and the initial tensile strength before and after pre-loading](image-url)
4.2 Recovery after damage from early age exposure to dry air

Following the testing procedure outlined in section 3.2.2, tests were conducted on both concrete and mortar specimens. To assess the damage caused towards compressive test due to dry-air curing of samples for 2 days at an airflow of 820 CFM from the table fan, compressive strength was first compared after 3 days and the plots are shown in Figure 12 below. From the plots, it can be observed that loss of strength due to dry-air curing is more in mortar than concrete. Quantitatively, dry-air mortar samples while 30% lesser strength than control group, while in concrete, the difference is only 10%. This can be attributed to the higher possibility of shrinkage in mortar due to higher volume fraction of cement paste. However, from the error bars (standard deviations) in plot, in both cases, the difference is statistically significant and there is a quantifiable damage. One limitation of this test is that it is not exactly clear if the damage is due to internal cracks, shrinkage cracks or just from the slowing down of hydration. From the fact that mortar has more damage, it can be qualitatively stated that at least some extent of the damage is in internal cracks, otherwise, similar slowdown of hydration is to be expected in concrete as well.

![Figure 12: Plots showing the loss in compressive strength caused by dry-air flow at an early age in both concrete and mortar.](image)

After 7 days of healing for both concrete and mortar in either water or sodium carbonate solution, compressive strength tests were again conducted to compare strength evolution. Healing in these two environments is then plotted and compared in Figure 13. All Compressive strengths recorded at stages of damage and post-healing were compiled together for all groups and shown as overall strength development plot in Figure 14.
Figure 13: Bar-plots comparing the compressive strength at the 10th day after 7 days of healing in each of the 4 groups of samples. All 4 plots have the same limits on the y-axis (0-45 MPa) for easier comparison among the plots.

All strength values shown in graph are average of five samples for each healing condition. After healing, it is obvious that in all groups, more strength was gained in $Na_2CO_3$ solution than in water curing. Careful evaluation of results in Figure 13 and Figure 14 also shows that the percentage strength development is higher in samples previously exposed to flow of dry air, before a subsequent exposure to a healing condition. One possible explanation for this is that since the reaction in equation (2) is expansive in nature, the reaction will be more pronounced when there are more cracks or voids available. The reaction stops when the $CaCO_3$ concentration in solution becomes large enough to achieve equilibrium and stop equation (2). Larger spaces will take a longer time to reach a critical concentration of $CaCO_3(aq.)$ required to stop precipitation. Thus, increasing the potential for more carbonation. In addition, diffusion of carbonate ($CO_3^{2-}$) ions to crack locations is easier due to enhanced permeability. This is especially relevant for the current study whereby the ions permeate samples from the healing solution. In addition, diffusion of carbonate ($CO_3^{2-}$) ions to location of cracks is easier due to enhanced permeability and this is especially relevant for the current study where the ions come inwards from the solution in which concrete specimens are submerged for healing. Figure 13, it can also be observed that the difference between the effects of water and sodium-carbonate healing on compressive is lower in concrete and least in undamaged concrete. This is because the initial difference between damaged dry air-cured and control samples was lesser in concrete and thus, there is lesser potential for
healing. One interesting observation highlighted in Figure 14 is that at the 10th day, the highest strength is observed in samples initially dry-air cured and then healed in 0.95M Na$_2$CO$_3$ solution. A higher carbonation in previously damaged samples here can be attributed to faster diffusion of carbonate ions into the matrix, thereby leading to more carbonation in cracks and voids. No such observation is observed in mortar samples. In fact, at the 10th day, the control samples healed in water still had a higher strength relative to both batches of damaged samples. In mortar, the initial loss was too large to recover using the proposed internal carbonation mechanism. Whereas at the 10th day, the pre-damaged mortar samples reached only a compressive strength of 24 MPa, the undamaged and water cured samples attained a strength of 27.7 MPa. Nonetheless, compared to the 18.2 MPa strength of pre-damaged samples exposed to water-curing at the 10th day, strength recovery was significantly higher in pre-damaged samples exposed to Na$_2$CO$_3$ solution.

![Figure 14: Comparison of development of strength in concrete and mortar after exposure to different conditions. 'undamaged' in the legend refers to the samples in the control group not exposed to damage via. dry-air curing.](image)

### 4.3 Fiber pullout test

#### 4.3.1 Recovery of bond properties after damage from early age air-flow exposure

Similar to the compression strength test in section 4.2, peak load and fracture energy of single fiber pullout samples were calculated. Calculations were made for both pre-damaged samples and pre-damaged samples subsequently cured in either water or Na$_2$CO$_3$ solution. Given that variability in the fiber-pullout test is usually higher than in compression strength test, the reported values in Figure 14 are an average of 8 samples. It is observable from the plots that an exposure to flowing
Dry air from a fan causes a loss of bond strength development in the early age. This can be attributed to both shrinkage cracks caused by evaporation of water and stunted hydration process leading to a weaker bond between the steel fiber and matrix. From Figure 14, it is also clear that dry air-cured samples subsequently exposed to Na$_2$CO$_3$-based healing performed better than their counterpart samples cured in plain water.

In previously undamaged and well-covered specimens, the fracture energy is similar irrespective of the curing solution. However, the fiber-pullout peak load is observed to be lower for specimens exposed to Na$_2$CO$_3$ solution. Overall, compared to the compressive strength results, differences in fiber bond properties were smaller. This is to be expected since it's highly unlikely that the precipitation of carbonates took place at the fiber-matrix interface, especially when the bond is undamaged.

![Graphs comparing the development of peak load and fracture energy for steel-fiber matrix bond as observed in fiber-pullout tests across damage and healing periods](image)

4.3.2 Recovery of bond properties after partial fiber-pullout

The results from the pullout test are summarized in Table 4. After 14 days of curing at room temperature and 98% relative humidity, the single steel fiber is pulled out partially until a fixed value of fracture energy (N-mm) was achieved for each sample. While this fixed value was determined from preliminary tests, post peak slipping means that the adhesion bond between fiber and matrix is lost. After healing for 7 days, Table 4 shows that while the fiber pullout peak load was similar for both sets of water and Na$_2$CO$_3$-healed samples, it was still lower than that of
undamaged samples. Conversely, fracture energy is shown to be higher for samples healed in $Na_2CO_3$ solution. This suggests that for $Na_2CO_3$-healed samples, fiber bond was somewhat stronger such that more energy was required to pull the fiber. It can also be concluded that the full strength of adhesion bond cannot be fully recovered using the internal carbonation mechanism.

Table 4: Peak load and Fracture Energy from fiber pullout tests during partial slip at 14th day and complete pullout at 21st day

<table>
<thead>
<tr>
<th>Age (days)</th>
<th>Peak Load (N)</th>
<th>Fracture energy (N-mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>damage +</td>
<td>damage +</td>
</tr>
<tr>
<td></td>
<td>water-healing</td>
<td>$Na_2CO_3$-healing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>146.9</td>
<td>146.9</td>
</tr>
<tr>
<td>21</td>
<td>135.7</td>
<td>139.5</td>
</tr>
</tbody>
</table>

4.4 Recovery of permeability under stress due to self healing of internal cracks

From the setup explained in section 3.2.4, the weight of permeated water was recorded with time. Using the weight of permeated water, and equation (3), radial permeability of the hollow cylinders was measured at different levels of stress on the sample. The average permeability-time plots of samples are shown in Figures 16-18. One highlight apparent from the permeability plots of the unstressed samples shown in Figure 16 is that irrespective of the infiltration solution, the permeability of samples decreased until a steady state was achieved. This phenomenon is unsurprising given that some time is required for all the pores and micro-cracks in samples to be fully infiltrated by water. The water infiltration process typically starts with the filling of large pores and micro-cracks, and then followed by the smaller pores. Some pores get blocked due to loose particles carried by water. The flow stabilization process should typically complete within few hours of beginning the test. After saturation of all pores, unhydrated cement particles present in the vicinity of pores/cracks hydrate and fill cracks. This is partly the reason for the gradual decline in sample permeability as pores are progressively filled, and the samples attain flow equilibrium. Indeed, it took about 15 to 20 hours after test commencement to achieve steady state flow in these unstressed samples. Nonetheless, once the flow had stabilized, Figure 16 equally shows that the permeability of samples infiltrated by $Na_2CO_3$-saturated water was slightly lower than that of samples exposed to the plain water. Since in the above test, $Na_2CO_3$-saturated water was only permeated after exposure to plain water for 48 hours the permeability vs. time curve is already flattened, it can be assumed that most of the unhydrated particles close to pores/cracks
have already hydrated. Moreover, given that the age of samples prior to testing is 14 days, no further hydration induced reduction in permeability is expected when Na$_2$CO$_3$-saturated water is permeated through the samples. Hence, any further refinement of pores or cracks will be as a result of carbonation between CO$_3^{2-}$ ions and hydrated concrete constituents. Thus, the permeability reduction reported in Table 5 and Figure 16 is a proof of CaCO$_3$ precipitation in cracks and pores.

**Figure 16: Permeability vs. time for stress-free sample**

**Figure 17: Permeability vs. time for sample loaded at 15% of its ultimate strength**
Figure 17 and Figure 18 show the permeability plots of samples subjected to two different degrees of compressive stress. Similar to the unstressed samples, they show that the permeability of samples decreased until the steady flow was established. However, initially the samples start from a different value of permeability. For instance, the 14.0% $f_a$ stress constricted the pores and reduced the initial value of permeability in the first hour of the test. Conversely, Figure 18 indicates an increase in initial permeability which may have resulted from stress induced pore opening. The most important highlight of the data shown in Figure 17 and Figure 18 is the fact that the permeability of samples is clearly dependent on the influence of the applied stress level on the pore structure.

Table 5: Permeability values recorded at 48th hour various levels of compressive load for water and Na$_2$CO$_3$ saturated water

<table>
<thead>
<tr>
<th>Load (lbs)</th>
<th>Stress (MPa)</th>
<th>Stress (%$f_a$)</th>
<th>Permeability ($\times 10^{-11}$) at 48th hour</th>
<th>Percentage permeability reduction in Na$_2$CO$_3$ vs. water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Water</td>
<td>Na$_2$CO$_3$ saturated water</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>1.59</td>
<td>1.14</td>
</tr>
<tr>
<td>4000</td>
<td>3.02</td>
<td>14.4%</td>
<td>1.12</td>
<td>0.97</td>
</tr>
<tr>
<td>10000</td>
<td>7.55</td>
<td>35.9%</td>
<td>2.17</td>
<td>1.15</td>
</tr>
</tbody>
</table>
Table 5 gives a summary of the permeability coefficient of stressed and unstressed samples. For the unstressed samples, Table 5 shows that while final permeability of the sample exposed to plain water was $1.59 \times 10^{-11}$ m/s, that of the samples infiltrated with the $Na_2CO_3$-saturated water was $1.14 \times 10^{-11}$ m/s. According to Sugiyama et al. [58], decrease in the permeability of samples at low stress is traceable to the compression of large voids and cracks. Thus, pore compression and closure of internal cracks happens with compressive stress. However, with further increase of the applied stress level to 36% of $f_u$, the permeability coefficient of plain water and $Na_2CO_3$-saturated water infiltrated samples increased to $2.17 \times 10^{-11}$ and $1.15 \times 10^{-11}$ m/s, respectively. The increase in permeability as the applied stress became higher was attributed to increased crack width [59] and increased crack coalescence/pore connectivity [60]. The mixed effects of stress levels on the water permeability of cement composites has been previously reported [57, 63]. Based on high coefficient of variation (c.o.v.) of roughly 7-50% as reported in previous study [54], it can be concluded that permeability values observed here are not distant enough to compare absolute values of one sample from another. However, since plain water and $Na_2CO_3$-solution are passed consecutively through the same sample, the relative difference in the two values (% permeability reduction) is a useful parameter that could be compared across the three stress levels. To verify this, a series of tests were conducted on three concrete samples under no applied stress by permeating plain water and $Na_2CO_3$-solution through them and comparing the drop in permeability. The results are reported in Table 6. Even though the initial permeability values differ a lot (c.o.v. of 44%), the variation in percentage permeability reduction is much lesser at a c.o.v. of 15.43%. The standard deviation of 4.56% shown in Table 6 is significantly lesser than the differences in percentage reduction reported in Table 5.
Table 6: Permeability values recorded at 48th hour for three samples under no applied stress.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Permeability (×10⁻¹¹) at 48th hour</th>
<th>Percentage permeability reduction in Na₂CO₃ vs. water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plain Water</td>
<td>Na₂CO₃ saturated water</td>
</tr>
<tr>
<td>1</td>
<td>1.59</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>4.12</td>
<td>2.69</td>
</tr>
<tr>
<td>3</td>
<td>2.83</td>
<td>2.10</td>
</tr>
<tr>
<td>Mean</td>
<td>2.85</td>
<td>1.98</td>
</tr>
<tr>
<td>σ (std. dev.)</td>
<td>1.27</td>
<td>0.78</td>
</tr>
<tr>
<td>c.o.v.(%)</td>
<td>44.44%</td>
<td>39.65%</td>
</tr>
</tbody>
</table>

The positive influence of the Na₂CO₃-saturated water on the permeability of samples is a new development traced to internal carbonation. Compared to the samples subjected to plain water infiltration, the permeability of samples exposed to Na₂CO₃-saturated water reduced by about 28.3%. With the application of 14.0%\(f_u\) stress on samples, Table 5 shows that the initial positive impact of Na₂CO₃-saturated water in reducing sample permeability was vitiated, declining from 28.3% to 13.4%. It does seem that with pores and fine micro-cracks already compressed at a low applied stress of 14%\(f_u\), the influence of internal carbonation induced precipitation of CaCO₃ in reducing the permeability of samples was made slightly redundant. However, with an applied stress level of 36%\(f_u\), the reduction in permeability is higher at 47.0% as volume of micro-cracks initiated in samples increased. Diffusion of ions is made easier due to microcracks and increased continuous water passages. Therefore, as Na₂CO₃-saturated water percolates though these micro-cracks, enhanced diffusivity of \(CO_3^{2-}\) ions and the extended interaction with \(Ca^{2+}\) ions leached from the matrix led to an increased precipitation of \(CaCO_3\) in cracks. One benefit of using Na₂CO₃-saturated water to enhance self-healing in cement composites is that the deposition of \(CaCO_3\) will occur all through the length of cracks, unlike a few millimetres from the surface typically observed with the external carbonation process. This effect was also observed in previous study on internal carbonation [13]. Note, the possibility of continued hydration filling cracks was eliminated by first exposing sample to water for two days before passing Na₂CO₃-solution.
4.5 Service life prediction with internal carbonation

The analysis for prediction of service life of concrete using permeability coefficient was adopted from the research by Banthia and Bhargava [61]. In their analysis, empirical relationships obtained by Hedegaard et al. [62] and Hansen et al. [63] were used to predict values of coefficient of permeability, $K_w$ and chloride ion diffusion coefficient, $D$ respectively, as shown in equations (4.1) and (4.2) below.

$$K_w = 2.8 \times 10^{-10} \left(\frac{W}{c}\right)^5$$  \hspace{1cm} (4.1)

$$D = 1.7 \times 10^{-\left(\frac{c+0.3f}{w}+7.0\right)}$$  \hspace{1cm} (4.2)

Where, $K_w$ = water permeability coefficient (m/s), $D$ = chloride ion diffusion coefficient (cm$^2$/s), $c$ = cement content of concrete (kg/m$^3$), $w$ = water content of concrete (kg/m$^3$), and $f$ = fly-ash content of concrete (kg/m$^3$) which is 0 for the current mix. By substituting values of concrete composition from Table 3 in equations (4.1) and (4.2), one can obtain $K_w = 0.875\times10^{-11}$ m/s and $D = 1.7\times10^{-13}$ m$^2$/s.

A relation between $K_w$, $D$ and effective pore-radius $r_{eff}$ (defined as the radius of the effective pores in a cross-section which take part in transport) was also developed in the study by Banthia and Bhargava [63], which has been shown in equation (4.3) below. In this equation it is assumed that the effective pore-radius $r_{eff}$ is the same for both permeability and diffusion. $C$ is a constant which will be calculated empirically later.

$$K_w = \left(\frac{r_{eff}^2 \rho g}{8D_0\eta}\right)D = C \ast D$$  \hspace{1cm} (4.3)

Where, $K_w$ as before is the water permeability coefficient (m/s), $D$ is the diffusion coefficient (m$^2$/s), $r_{eff}$ is the effective pore radius (m), $\eta$ is the viscosity of water (N-s/m$^2$), $\rho$ is the density of water (kg/m$^3$) and, $g$ is the gravity (m/s$^2$). Equation (4.3) can be modified further to include the effect of stress and Na$_2$CO$_3$-saturation in water, by defining two more coefficients to account for them as $S$ and $N$ respectively. These coefficients were defined here as a ratio of permeability coefficient $K_w$ for each sample with respect to the value at zero-stress and water permeation as shown in equations (4.4) and (4.5). These factors can be calculated from the values in Table 5.
Collectively, they can be used to account for the effect of both stress and Na$_2$CO$_3$-saturation as shown in equation (4.6).

\[ S = \frac{K_{w_{stressed}}}{K_{w_{unstressed}}} \]  
\[ N = \frac{K_{w_{Na_2CO_3-solution}}}{K_{w_{water}}} \]  
\[ K_{normalized} = N * S * K_{w_{unstressed-water}} \] 

Given that coefficient of permeability is proportional to the fourth power of effective pore-radius \( (K_w \propto r_{eff}^4) \) as per Hagen-Poiseuille’s law, therefore using equation (4.7), the effective pore radius can also be modified to consider the effect of stress and Na$_2$CO$_3$-saturated water as follows:

\[ r_{normalized} = N^{0.25} * S^{0.25} * r_{eff_{unstressed-water}} \] 

where, \( r_{normalized} \) is the effective pore radius corresponding to normalized permeability values. Substituting equation (4.7) into equation (4.3), a modified relation between \( K_w \) and \( D \) can be obtained for normalized values as:

\[ K_{normalized} = C * N^{0.5} * S^{0.5} * D \] 

The above relationship can then be used to calculate chloride ion diffusion coefficient, \( D \) for each condition using the values for \( K_{normalized} \), \( N \), \( S \) and \( C \). To evaluate constant \( C \), we can use equation (4.8) for the condition of no stress and water permeation where \( N = S = 1 \).

\[ K_{normalized} = K_{w_{unstressed-water}} = C * D \] 

Substituting the empirically obtained values of \( K_w = 0.875 \times 10^{-11} \) m/s and \( D = 1.7 \times 10^{-13} \) m$^2$/s calculated earlier, the value of constant \( C \) for the concrete used in permeability experiments can be evaluated as \( C = 5.12 \) m$^{-1}$.

Calculations for \( N \), \( S \) and \( D \) for each condition are presented in Table 7. Using these values and adopting the implemention of Tuutti’s model for service life-prediction [64] from Banthia and Bhargava [61] as shown in equation (4.10), we can obtain a prediction of time, \( t_i \) (in years) for initiation of chloride corrosion. For the initiation of chloride corrosion, the service life depends on \( x^2 \), the concrete cover in mm and is inversely proportional to \( D \). The
durability factor, \( d.f. \) is the ratio of service life of current stress and liquid type to the service life with water permeation and no applied stress as shown in equation (4.11).

\[
t_i = \frac{x^2}{0.2678D}
\]  
(4.10)

\[
Durability Factor, d.f. = \frac{t_{current}}{t_{unstressed-water}}
\]  
(4.11)

<table>
<thead>
<tr>
<th>Stress ((% f_u))</th>
<th>Permeating liquid</th>
<th>( K_w ) ((*10^{-11} m/s))</th>
<th>( N )</th>
<th>( S ) ((*10^{-12} m/s))</th>
<th>( t_i ) (\text{(years)})</th>
<th>Durability Factor, d.f.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Water</td>
<td>1.59</td>
<td>1</td>
<td>1</td>
<td>3.11</td>
<td>30.1</td>
</tr>
<tr>
<td>0</td>
<td>( Na_2CO_3-sol )</td>
<td>1.14</td>
<td>0.72</td>
<td>1</td>
<td>2.63</td>
<td>35.5</td>
</tr>
<tr>
<td>14.4%</td>
<td>Water</td>
<td>1.12</td>
<td>1</td>
<td>0.7</td>
<td>2.61</td>
<td>35.8</td>
</tr>
<tr>
<td>14.4%</td>
<td>( Na_2CO_3-sol )</td>
<td>0.97</td>
<td>0.87</td>
<td>0.85</td>
<td>2.21</td>
<td>42.3</td>
</tr>
<tr>
<td>35.9%</td>
<td>Water</td>
<td>2.17</td>
<td>1</td>
<td>1.36</td>
<td>3.63</td>
<td>25.7</td>
</tr>
<tr>
<td>35.9%</td>
<td>( Na_2CO_3-sol )</td>
<td>1.15</td>
<td>0.53</td>
<td>1.01</td>
<td>3.07</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Table 7: Computation of service life and durability factor, d.f.

![Figure 19: Influence of stress level and Na\(_2\)CO\(_3\) on (a) durability factor, d.f. and (b) service life](image)

Table 7 presents the value of service life, as per equation (4.10) assuming a concrete cover of 25 mm for each condition. The exact values of service life predicted here are not that significant since the permeability values themselves possess a high coefficient of variation. However, we can do a relative comparison using the durability Factor, \( D \) on the effect of permeating \( Na_2CO_3 \) solution instead of water through the same concrete. From Table 7, we can see that a 36% stress level in
concrete reduced the service life, leading to a durability factor, d.f. of 0.85. Conversely, the exposure of concrete samples to 0.95M Na$_2$CO$_3$ solution did not only counteract the effects of sustained high compressive stress, the original durability was almost recovered (d.f. = 1). Figure 19 shows the durability factor and service life as a function of the compressive stress level on concrete. For both water and Na$_2$CO$_3$ solution permeation, Figure 19 shows that while the d.f. is highest at 14.4% fu applied stress, it dropped as the stress level increased to 35.9%. This observation of a critical stress above which durability starts to decrease was also reported in previous studies on permeability under stress [56-57, 63]. As a sample is loaded in compression, both pore compression and internal cracks start to affect its permeability. However, at lower levels of stress (~20%), pore compression is more pronounced and after a certain critical value of stress, the effect of internal cracks becomes more prominent leading to a decrease in durability.

Relative to plain water infiltrated samples, Figure 19 also shows that for all stress levels, the permeation of Na$_2$CO$_3$ solution through concrete samples led to higher d.f. and predicted service life. While percentage reduction in permeability due to permeation with Na$_2$CO$_3$ solution was significantly different at the three levels of stress (28.3%, 13.4% and 47%), the percentage increase in service life was much closer at all levels of stress (18%, 19% and 12% for 0 fu, 0.14 fu and 0.36 fu respectively). For example, even though the reduction in permeability was the highest at 0.36 fu, the percentage increase in service life is the lowest. This is to be expected from equation (4.10), since service life is inversely proportional to the diffusion coefficient, $D$ a relation which is asymptotically infinite as $D$ approaches 0. Thus, a change in values closer to 0 has more impact than a change farther away. Therefore, even in concretes where there is no significant damage or internal cracks, pore refinement using internal carbonation is likely to contribute significantly to an increase in service life of a structure. Curing with Na$_2$CO$_3$ solution can be applied to existing structures where service life extension is a big priority. The observed Na$_2$CO$_3$ solution induced enhancement of concrete durability is similar to the positive effect of fiber reinforcement and silica fume addition on durability as shown in previous research studies [57, 63]. Thus, internal carbonation could be utilized as a viable lower-cost alternative for some of the expensive methods of pore refinement such as silica fume and fiber-reinforcement in concrete.
Chapter 5: Conclusions and suggestions for future work

5.1 Conclusions

This study aims to propose and validate a modification of carbonation as a self-healing mechanism in cement composites. From the various assessment tests conducted, it’s concluded that modified carbonation using Na$_2$CO$_3$ solution can help restore internal crack induced degradation of the mechanical and durability properties of cement-based materials.

1. Using splitting tensile tests, it was observed that recovery of tensile strength was highest when samples were submerged in 0.95M Na$_2$CO$_3$ solution. This shows that localized internal cracks can be healed such that the overall mechanical strength is recovered.

2. When concrete or mortar is damaged by exposure to dry-air curing at an early age, strength evolution is also highest in Na$_2$CO$_3$ solution. The inference from this test is that the modified internal carbonation mechanism works significantly better when partially damaged samples are placed submerged in Na$_2$CO$_3$ solution, since the diffusion of ions would be faster into the matrix in samples with internal cracks.

3. For single fiber pullout test, it was observed that while pre-damage peak load could not be recovered, fracture toughness of the bond was improved when samples were immersed in 0.95M Na$_2$CO$_3$ solution. However, compared to the improvement observed in mechanical properties, internal carbonation induced improvement of single fiber-matrix bond property is lesser.

4. Water permeability measurement of samples subjected to different levels of compressive stress indicated that the infiltration of these samples with 0.95M Na$_2$CO$_3$ solution instead of water led to reductions in permeability coefficient. However, these reductions in permeability coefficient were dependent on the applied stress level, with the highest healing occurring at a stress level capable of inducing internal cracks. Self-healing becomes more pronounced in the presence of internal cracks because the diffusion of carbonate ions into crack locations was easier and more reactions took place. Furthermore, Service Life Predictions indicated that healing with 0.95M Na$_2$CO$_3$ can enhance the durability of concrete and lengthen its useful service life at all the compressive stress levels investigated.
Based on findings from this study, the proposed enhancement of autogenous healing using $\text{Na}_2\text{CO}_3$ solution appears to be helpful in sealing internal cracks in cement composites thereby improving mechanical and durability properties of pre-damaged mortar and concrete samples.

5.2 Practical implications

In this thesis, the mechanism of crack healing and performance improvement with internal carbonation was investigated. Two techniques of providing healing were explored. While in the first technique, pre-damaged samples were submerged in $\text{Na}_2\text{CO}_3$ solution, a permeability setup whereby the $\text{Na}_2\text{CO}_3$ solution was permeated under pressure through concrete was the second technique. For practical application, the first technique will correspond to ponding the surface of cement composites with the $\text{Na}_2\text{CO}_3$ solution for a given time interval. On the other hand, the second technique is analogous to infusing the $\text{Na}_2\text{CO}_3$ solution under pressure, similar to the polymer impregnation procedure routinely used for concrete repairs. Given that these two methods can be utilized for accessible parts of a structure, the use of $\text{Na}_2\text{CO}_3$ solution for durability and strength improvement of old structures is a potential application. One more application maybe during concrete repairs, where the substrate surface is ponded to enhance the substrate-repair overlay bond. During this process, a replacement of water with $\text{Na}_2\text{CO}_3$ saturated water could lead to the precipitation of $\text{CaCO}_3$ in micro-cracks created at the interface during surface preparation. The feasibility of these suggested practical applications needs to be explored further in future studies.

The benefits of the current study are also similar to carbonation curing of concrete. The current internal carbonation mechanism has an advantage over $\text{CO}_2$ curing in that it doesn’t reduce the $p\text{H}$ of a cement composite during carbonation. Thus, the period of corrosion initiation should not be affected unless the hydroxide ions produced during reaction in equation (1.2) leached out of the matrix completely. Furthermore, in precast construction where operation control is possible, a similar mechanism to carbonation curing whereby $\text{Na}_2\text{CO}_3$ solution is used to infuse carbonate ions into cement composites thereby improving service life could be developed.
5.3 Suggestions for future research

Preliminary experimental results and previous research has indicated a loss of strength if Na\textsubscript{2}CO\textsubscript{3} or any other carbonate powder is directly added during the initial mixing of concrete [65]. This is because the carbonates if added during the mixing stage reacts directly with clinker phases like C\textsubscript{3}S and C\textsubscript{2}S impeding the hydration and strength development in concrete. However, from experimental results obtained in this study, one can observe that the same material when introduced at 3 days or 7 days in a damaged material leads to an improvement in mechanical and durability properties. However, for true self-healing without any intervention, mechanisms like encapsulation need to be developed to transport carbonates into the matrix without allowing them to react before internal cracks develop. Proper methods of encapsulation need to be investigated in future such that carbonate ions can be introduced into the system without the capsules affecting the strength of concrete. Further research is also needed to investigate whether the modified carbonation method is effective at avoiding initiation of corrosion as theoretically proposed in this thesis. As evident from the results of the permeability under stress tests performed in this study, the stress level on concrete is critical during healing. Therefore, further investigation is needed to establish a relationship between permeability and applied stress levels. Such a relationship will help optimize the design and maintenance of concrete structures.
References


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