

The Effect of Waterproofing Additives on the Self-Healing of Concrete with Minerals

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"I hereby declare that, except where specifically indicated, the work submitted herein is my own original work."

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1. Introduction

1.1 Motivation

Although concrete can be manufactured to a level where it is almost watertight, a perfectly consistent density is extremely difficult to obtain (Maxwell-Cook, 1967, Russell, 1983). Regardless of the quality, structural concrete will always contain networks of pores and capillaries, which can become pathways for the ingress of water. The movement of water through concrete can be undesirable in watertight structures, such as water tanks, swimming pools, basements and roofs. In particular, if liquid is allowed to enter reinforced concrete, the steel reinforcement bars will corrode. The resulting rust is about three to five times the volume of the original material and exerts a large amount of pressure on the surrounding concrete, causing the formation of cracks (Perkins, 1997).

Traditionally, the transmission of water through concrete has been prevented by lining concrete elements with an impermeable membrane or coating (Cementaid, 2010), however these options are expensive, delay construction time and waste valuable space. In addition, as the impervious lining has no structural strength, the concrete structure, which it is guarding against the infiltration of water, must be designed to protect it from structural distortion and the relative movement of the structural units when loaded (Maxwell-Cook, 1967). When defects do occur in these linings, they can be difficult to repair, and the concrete can be permanently damaged. An alternative option is to use admixtures to create dense, durable concrete that can resist hydrostatic pressure without allowing water to seep through it. Usually these admixtures reduce the permeability of concrete by reducing the number of cracks and voids in the concrete, minimising the passages for water movement (Chan et al., 1999).

While the waterproofing of concrete is a major issue when designing a concrete structure because flaws in the water tightness of buildings can contribute to the corrosion of reinforcing steel, engineers are also concerned about cracks forming during the course of a structure's lifetime. In addition to being detrimental to the structural integrity of concrete constructions, cracks provide new pathways for salts to reach reinforcement bars and therefore also cause corrosion (Lindquist et al., 2006). In the US, it is estimated that the average annual cost of bridge maintenance and repair is \$5.2 billion; meanwhile in Europe, 50% of nations' annual construction budgets is spent on the rehabilitation of existing structures (Sangadji and

Schlangen, 2012). Furthermore, using life cycle analysis, Yunovich et al. (2001) calculated that the indirect costs associated with looking after highway bridges, due to traffic delays and lost productivity, could be ten times the direct costs.

Not only is the economic impact of restoring damaged structures severe, the maintenance work that is undertaken also negatively affects the environment. Sangadji and Schlangen (2012) argued that up to 50% of CO₂ emissions can be associated with the building and construction industry in the UK, and Ghosh (2009) found that the production of cement contributed to 5-7% of annual man-made CO₂ emissions worldwide. Taking this into account, Van Breugal (2007) recognised that self-healing cement could play an important part in “enhancing the longevity of our built infrastructure”, which will “undoubtedly reduce the impact of mankind’s activities on the stability of the biosphere” (Van Breugal, 2007).

The self-healing processes in cement can be classified into two groups, autogenous healing and autonomic healing. Autogenous self-healing is a result of the inherent material properties of cement. Edvardsen (1999) identified that the main mechanism of autogenous healing in 100% PC was the formation of CaCO₃ crystals in the cracks due to un-hydrated CaO present in cement reacting with water and CO₂, which migrates through the cracks. In contrast to the ‘natural’ process of autogenous healing, autonomic healing is manufactured by encapsulating healing agents, such as epoxy resins, superglues, bacteria, expansive components and alkali-silica solutions, in the cement matrix (Joseph et al., 2011, Sangadji and Schlangen, 2012). As a crack propagates through the cementitious material, it eventually reaches a microcapsule or tube filled with a healing agent, which ruptures, releasing the agent into the crack plane, facilitating healing (Joseph et al., 2010). Although research into both autogenous and autonomic self-healing is being performed, van der Zwaag (2007) noted that autogenous healing is more attractive, being more economical. Hence, this project has focused on autogenous self-healing with the addition of MgO, and examined how the presence of waterproofing affected the healing ability, which requires the introduction of water to the crack.

1.2 Aim and Objectives

The aim of this project was to investigate the impact of waterproofing admixtures on the self-healing potential of cement pastes in concrete, which has been enhanced through the addition

of mineral additives. The mineral additive that was used throughout the research was MgO, and the waterproofing admixtures were provided by Cementaid, in the form of their *Everdure Caltite System*.

The objectives were to:

- Investigate the effect of waterproofing additives on 100% PC.
- Investigate the performance of the mineral additive MgO in improving the autogenous self-healing activities of PC when waterproofing admixture is present.
- Identify if there is an optimum amount of MgO for self-healing when cement is waterproofed with an admixture.

1.3 Structure of Report

This report is divided into six chapters. Chapter 1 introduces the project, outlining the motivation behind conducting the research undertaken and setting the aims and objectives. Chapter 2 is a literature review of research covering different methods of waterproofing concrete using admixtures and papers regarding the self-healing potential of concrete. Chapter 3 describes the experimental methodology adopted during this project, while Chapter 4 presents the results of experiments, comparing different mixes by image analysis and mechanical strength regain. Chapter 5 consists of conclusions inferred from the project and future work that can be carried out.

2. Literature Review

2.1 Waterproofing Admixtures

2.1.1 Introduction

Concrete made to an insufficient quality and that is a part of architectural features that are exposed to moisture will require waterproofing. For example, the most common problem that affects the durability of concrete foundations is the ingress of water containing acids, sulphate salts and chloride ions, which can alter the microstructure and chemical composition of the concrete or corrode the reinforcement steel (Mendes et al., 2014). To ensure against the transmittance of water through structures, concrete must be dense and durable, with sufficient resistance against water seepage when subjected to hydrostatic pressure (Chan et al., 1999). Even the highest quality concrete will contain cracks, voids and capillaries for water to collect and travel through. These must be reduced in order to minimise the passage of water.

Concrete is composed of cement and aggregates, and the aggregates are typically dense materials with low permeability. Therefore, it is the permeability of the cement component that controls the water-tightness of concrete. Primarily, it is the pores and capillaries in cement that cause this permeability, but it is also exacerbated by microcracks that allow even more water to pass through. The capillaries and pores formed during the early stages of concrete's life, due to spaces originally filled with water, can be blocked by further hydration of cement particles while curing, however this relies on sufficient hydration products being produced. In order to protect concrete against water seepage, various admixtures can be used to increase its watertightness. (Chan et al., 1999)

2.1.2 Different Types of Admixtures

There is a wide range of admixtures available that reduce the permeability of cement. Water-reducers, superplasticizers, mineral admixtures, polymer admixtures and air-entraining agents are all commonly used to prevent liquids from travelling through concrete. In this section a selection of admixtures will be explored in detail, including ones that will be used in the experiments.

Water Reducing Admixtures

Water reducing admixtures are widely used in water retaining structures. Concrete mixes with water reducers decreases the amount of water required to achieve a desirable workability. This reduction in water/cement ratio allows concrete to have a higher density, and hence lower permeability. The most common chemicals used in water reducing admixtures are lignosulphonates, hydrocarboxylic acids and carbohydrates (Chan et al., 1999).

Rixom and Mailvaganam (1999) explain that, in a normal cement paste, there is a tendency for particles to be attracted to each other due to van der Waal forces acting between them, causing them flocculate. However, with the addition of water reducers, this is not the case. Figure 1 illustrates the difference in cement particle dispersion between a concrete mix with and without a water-reducing admixture. Water reducing agents are adsorbed onto cement particles, and as layers of these substances build up, they repel each other electrostatically, because they have the same negative ionic charge, causing particles to disperse, creating a more cohesive, consistent mix (Chan et al., 1999). The dispersion of particles also results in a reduction of inter-particle friction, so the amount of energy needed to induce a flow in the fresh concrete is also lowered (Rixom and Mailvaganam, 1999). Furthermore, water is released from being trapped among clusters of cement particles, increasing the workability of the concrete (Chan et al., 1999). Therefore a lower water/cement ratio can be used to achieve a similar workability to the mixture without the water reducing agents (Russell, 1983). Figure 2 shows that in the absence of cracks, permeability is a function of water/cement ratio (Rixom and Mailvaganam, 1999).

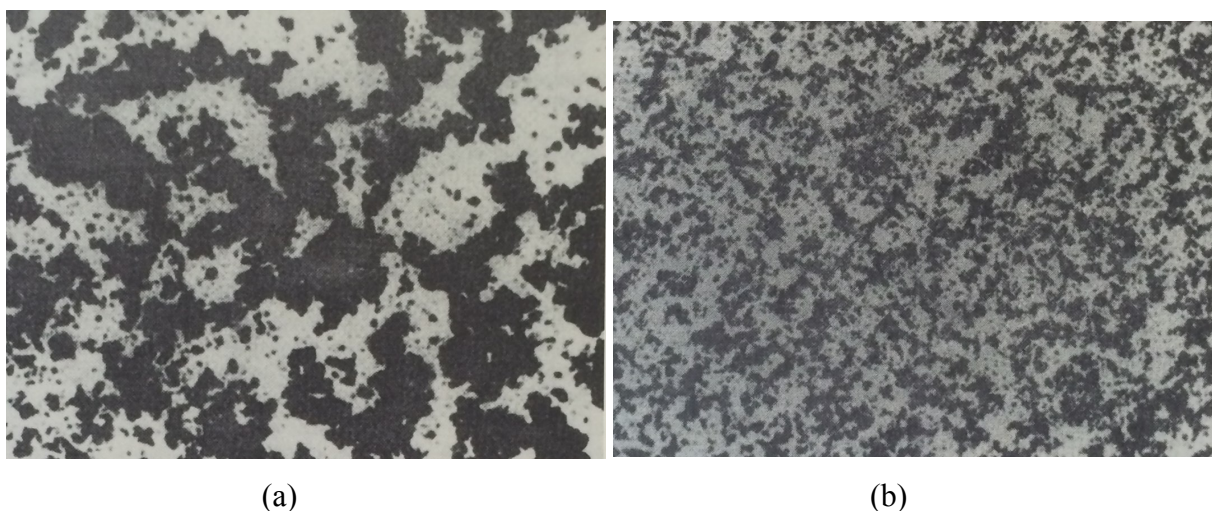


Figure 1: Cement particle dispersion (a) before, and (b) after addition of water-reducing admixture (Rixom and Mailvaganam, 1999).

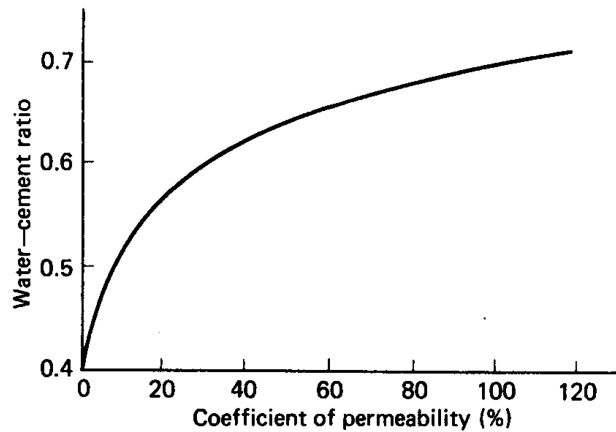


Figure 2: Permeability as a function of water-cement ratio (Rixom and Mailvaganam, 1999).

Superplasticizers

Superplasticizers are high range water reducers that can reduce the water content required by a specific mix by up to 30%, whereas normal water reducers only reduce water required for a workable mix by 10 -15% (Russell, 1983). The two main types of superplasticizer are sulphonated naphthalene-formaldehyde and sulphonated melamime-formaldehyde (Perkins, 1997). Like water reducers, they reduce the water/cement ratio, and hence permeability, by being adsorbed to cement particles and causing repulsion between them, encouraging a more uniformly hydrated cement matrix (Rixom and Mailvaganam, 1999).

Mineral Admixtures

Unlike some other admixtures, minerals are usually added to concrete mixtures in large amounts, replacing a proportion of the PC. They are usually either natural pozzolans or industrial by-products, such as granulated blast furnace slag and fly ash (Chan et al., 1999). Thomas et al. (2012) found that mineral admixtures are extremely advantageous in concretes, reducing the environmental damage, while improving durability.

Mineral admixtures consist of very fine particles, which allows concrete to be mixed with a lower water content to achieve the same workability as a mix with 100% PC. As a result, minerals are usually used in self-compacting concrete, which require a high degree of workability (Ramanathan et al., 2012). In concretes with mineral admixtures, there are fewer large pores and a large number of smaller pores, as the mineral mixtures fill voids and microcracks with products from pozzolanic reaction, which have smaller pores. (Chan et al., 1999). Additionally, there is a lower amount of thermal hydration in mineral concretes,

resulting in fewer micro-cracks caused by thermal stresses, which contributes to a reduction in permeability as well (Wang et al., 2005).

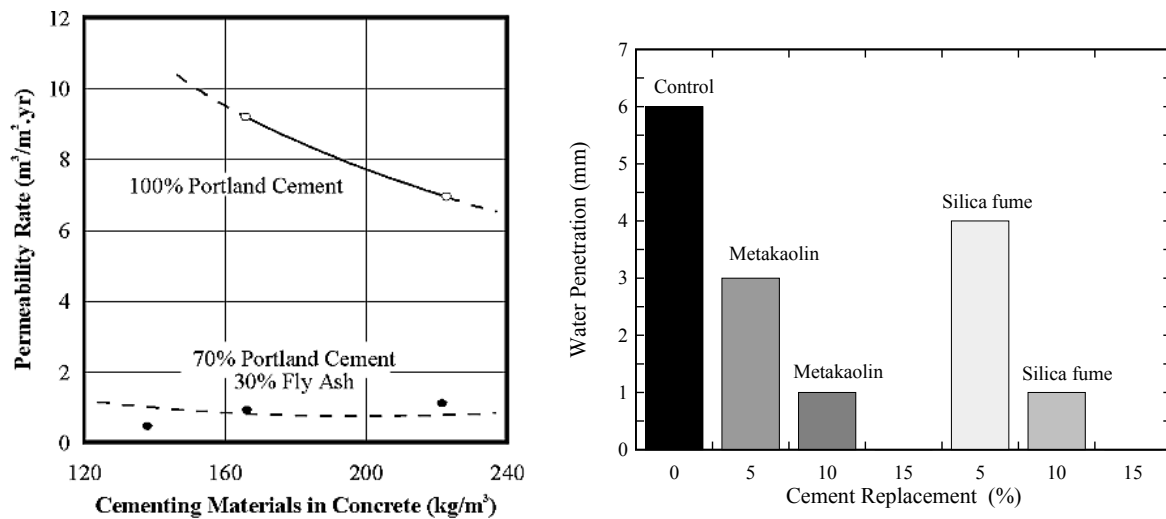


Figure 3: Graphs showing the effect of mineral additives on permeability (Ramanathan et al., 2012).

Dampproofers/Hydrophobers/Water Repellents

Although well-designed concrete should be compact and sufficiently impermeable, imperfections may occur due to errors in handling and execution of tasks. Dampproofers are admixtures that modify concretes so that they become hydrophobic. The chemicals in the admixture are mainly wax emulsions, bitumen, or liquid fatty acids, such as oleic, caprylic and capric. They form thin water repellent layers on the surface and within the networks of capillaries and pores throughout the concrete by (Rixom and Mailvaganam, 1999):

1. Reacting with the cement hydration products.
2. Coalescing.
3. Being incorporated into the cement paste in a very finely divided form.

The layers that line the surface of the concrete and the internal surfaces of its pores causes the contact angle between the concrete and water to increase, weakening the molecular attraction between them (Polder and de Vries, 1997). As a result, the concrete surfaces repel water. In contrast, normal concrete exhibit hydrophilic behaviour as there is molecular attraction between water and cement pastes (de Vries and Polder, 2001). Figure 4 compares the interaction between water and concrete surfaces with and without dampproofing. This treatment has been found to reduce the water absorption of concrete by up to 90% (Polder and de Vries, 1997). Chan et al. (1999) note that, although this group of admixtures is able to

reduce the passage of water through concrete that is a result of capillary action, they cannot resist the entry of water due to external hydrostatic water pressure.

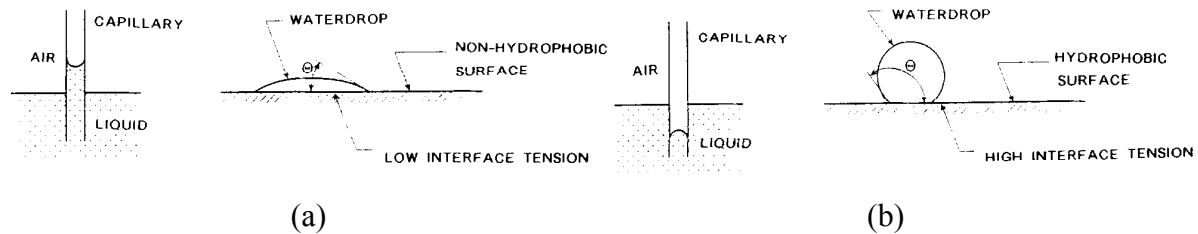


Figure 4: Interaction between concrete and water (a) Concrete with hydrophober; (b) Concrete with hydrophober (Polder and de Vries, 1997).

Pore Blocking Admixtures

Pore blocking admixtures physically are able to prevent the transmission of water when subjected to hydrostatic pressure. They block the pores and capillaries in concrete. They normally consist of bituminous or wax emulsions, which accumulate in capillaries formed by bleed water. When concrete is subjected to hydrostatic pressure, the globules of admixture particles gather as they travel with the water flowing through the capillaries, eventually forming a physical plug preventing water from penetrating the concrete any further. (Chan et al., 1999)

2.1.3 Waterproofing systems

Waterproofing ‘systems’ can use a combination of different admixtures to reduce the permeability of concrete. There are many of these waterproofing admixtures available commercially, and a selection is discussed briefly in this section.

Rheocrete Proof Marine

BASF (2002) describes Rheocrete Proof Marine as a “*hydrophobic pore-blocking ingredient for concrete*”. It is ideal for concrete structures in marine environments and water retaining structures.

FOSROC Conplast WP500

Conplast WP500 is a chloride free, organic liquid that immediately disperses in water. It claims to provide integral protection by causing hydrophobic effects. (MEGA TEC, 2012)

Triton TT ADMIX

Triton TT ADMIX is waterproofing admixture that allows concrete to withstand large amounts of hydrostatic pressure. Chemicals in the admixture react with cement hydrates to cause a catalytic reaction that produces a non-soluble crystalline formation of dendritic fibres throughout the pores and capillaries in the concrete, sealing structures against water. (Triton, 2011)

Cementaid Everdure Caltite

Cementaid's waterproofing system uses three components. It contains a superplasticizer, which reduces the water/cement ratio in concrete, producing a dense low permeability mix. It also contains both a hydrophobic element to reverse capillary suction and a pore blocking admixture to prevent water movement due to hydrostatic pressure. (Cementaid, 2010)

2.2 Self-Healing Concrete

2.2.1 Introduction

Self-healing can be described as the concept of automatic damage repair. In biological systems, self-healing is common. Plants and animals repair themselves and recover functionality after getting injured (Blaiszik et al., 2010). Synthetic self-healing systems are designed to imitate the processes witnessed in animals, where inflammation and blood clotting are triggered by injury, followed by cells gathering at the site of injury, forming a matrix which causes new tissue growth (White et al., 2011).

The self-healing of construction materials is not a new phenomenon. Scientists have been aware of the inherent self-healing abilities of cement for a long time. Hearn (1998) noted that the French Academy of Science noticed self-healing behaviour in water-retaining structures, culverts and pipes in 1836, and Van Breugal (2012) found that the healing phenomena was recognised by Glanville (1931) early in the twentieth century. In their study of several different structures built in the last two centuries, Nijland et al. (2007) found that self-healing of cracks was present in mortars due to the formation of white crystalline CaCO_3 . PC-based concrete mainly heals itself naturally by the same mechanism (Edvardsen, 1999).

2.2.2 Self-Healing

The development of new self-healing composite materials has led the literature to use many terms to differentiate between the various functions they possess. While the healing mechanisms are different, both autogenous healing and autonomic healing materials are classed as materials belonging to smart structures, as shown in Figure 5. They can be further divided into passive materials, which react to external stimuli without human assistance, or active materials, which require intervention in order to complete the healing process (Qureshi, 2013).

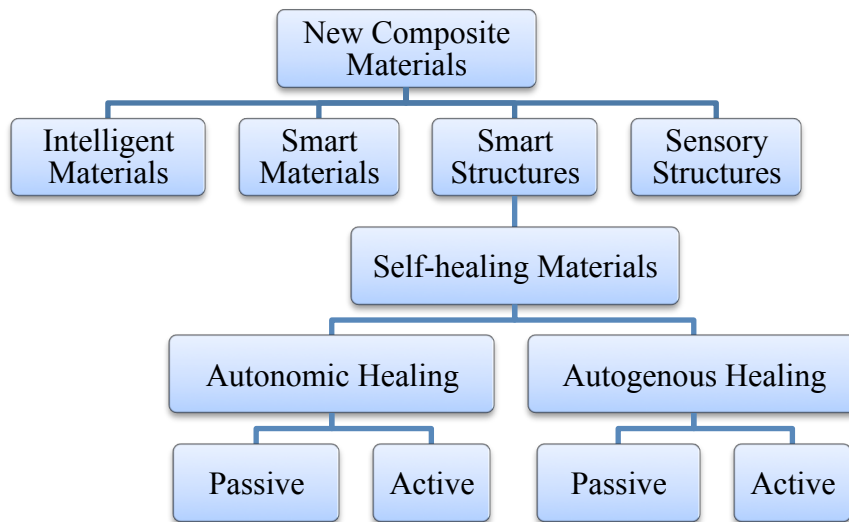


Figure 5: Schematic representation of self-healing terms (Joseph et al., 2011).

2.2.3 Autogenous Self-Healing in Cement

The autogenous healing of cementitious material is a self-repair ability due to the intrinsic properties cement possesses. Yang et al. (2011) determined that for autogenous self-healing to occur, concrete must be exposed to wet-dry cycles or fully immersed in water, and contain adequate concentrations of un-hydrated or partially hydrated cement.

Kishi et al. (2007) identified the main processes involved in autogenous healing as: (a) swelling and hydration of cement pastes; (b) calcium carbonate crystal precipitation; (c) flow paths being blocked by water impurities or by loose particles from the crack surface. Much of the literature available on the subject of the autogenous self-healing of cement admits that the process is not completely understood. Hearn and Morley (1997) deduced that self-sealing in mature concretes is due to dissolution and deposition. Neville (2002) claimed that the self-repair is mainly caused by the hydration of un-hydrated cement particles as moisture

penetrates cracks. Considering that research suggests that over 25% of the cement particles in concrete are un-hydrated (van der Zwaag, 2007), it is possible to see why there is potential for autogenous healing to be effective in concretes. However, this was later found to only apply to early age cracks in concrete, and many scientists have agreed that the most probable cause of self-healing is the precipitation of calcium carbonate crystals in cracks at later ages (Wu et al., 2012, van der Zwaag, 2007, Lv and Chen, 2013).

Edvardsen (1999) observed that almost 100% of the healing material in her research was composed of CaCO_3 crystals. These findings are supported by the fact that white CaCO_3 precipitate is commonly found on the outside surface of cracks, shown in Figure 6 (Wu et al., 2012). As hydrated cement products dissolve in water, the free calcium ions, Ca^{2+} , react with the dissolved carbon dioxide, in the form of carbonates, CO_3^{2-} , or bicarbonates, HCO_3^- . The chemical reaction process is (Edvardsen, 1999):

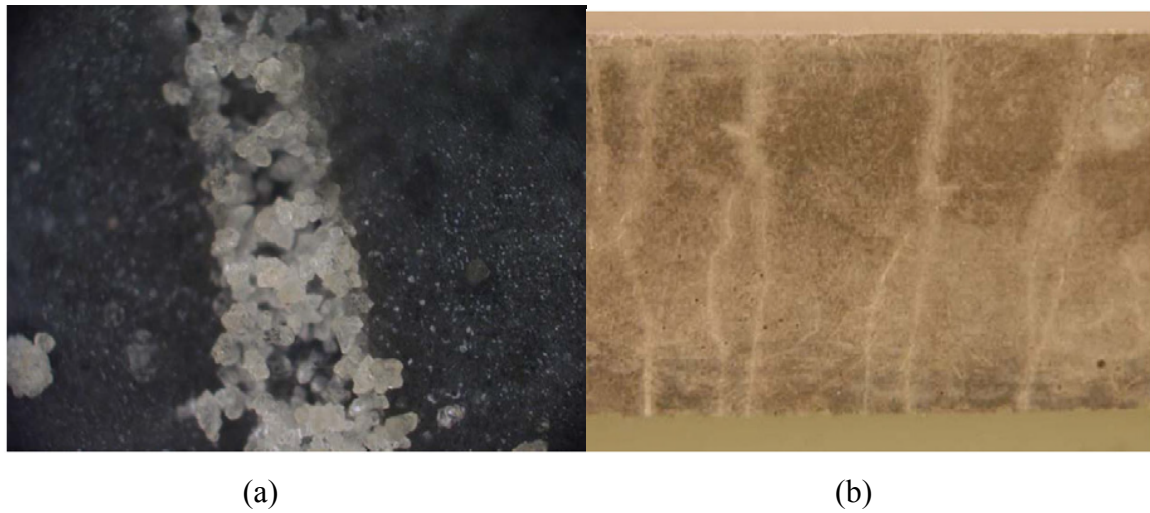
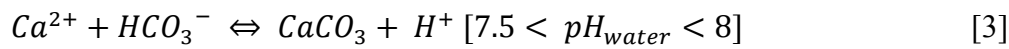
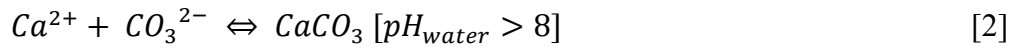
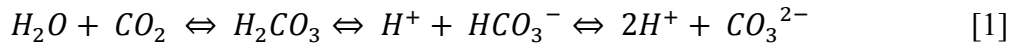


Figure 6: (a) Microscopic image of crystallised products found in a crack with width 100µm (Homma et al., 2009) and (b) Macroscopic image of white residue filling cracks on surface of a specimen (Qian et al., 2009).

It can be inferred that the autogenous self-healing of concrete is almost exclusively due to the hydration and carbonation of cement particles. Both processes require the addition of water to the cracks in order to activate the healing mechanisms.

The self-healing of concrete results in reduced water permeability and the recovery of mechanical strength, however there are several factors that will affect the efficiency of healing. Edvardsen (1999) discovered that the type of cement and type of aggregates used in concrete, as well as the hardness of the water the concrete is exposed to, has no influence on the growth rate of healing substances, whereas the crack width and water pressure can determine how quickly it repairs itself. In addition, she noticed that higher water temperatures, as well as higher pH values of water and lower CO₂ partial pressures, encouraged CaCO₃ precipitation. When investigating permeability and self-healing, Reinhardt and Joos (2003) discovered that the flow rate of water through cracked samples is influenced by the crack width and temperature. Smaller cracks are repaired faster, as are cracks at higher temperatures. The importance of small crack widths in the effectiveness of self-healing is seen in many pieces of literature (van der Zwaag, 2007, Edvardsen, 1999, Yang et al., 2011, Lv and Chen, 2013). The success of Engineered Cementitious Composite (ECC) as a self-healing material is partly because of the fibres bridging cracks and reducing crack widths, and it has been suggested that crack widths must be below 200 µm for successful self-healing (van der Zwaag, 2007).

Recently, Ter Heide and Schlangen (2007) studied the mechanical strength gain and reduction in permeability in early age concrete that was cracked and left to heal. The authors measured the amount of healing in response to various factors, including specimen age at the time of cracking, compressive stress applied during healing, cement type and crack width. The main conclusions from this research were that strength recovery was only observed in specimens stored under water, even at 95% relative humidity no increase in strength or crack healing was seen, and that the extent of strength recovery was greater for samples initially damaged at an early age. In addition, it was established that the compressive stress applied during healing does not affect the self-healing. Specimens were loaded with stresses ranging from 0 N/mm² to 2 N/mm². As long as the applied stress was large enough to close the crack, an improvement in strength and stiffness recovery was witnessed.

2.2.4 Enhancing Autogenous Self-Healing with Mineral Admixtures

It is widely acknowledged that autogenous self-healing in concrete is caused by the formation of CaCO₃ and Ca(OH)₂ crystals (Homma et al., 2009). However, un-hydrated cement grains are required to facilitate healing. This means that high water/cement ratio concretes will have

a low potential for self-healing as a larger proportion of their cement particles will be hydrated. In order to increase the self-repair potential of concretes, researchers are examining the use of mineral admixtures, such as expansive agents. A few admixtures will be explored in this section.

Calcium Sulfo-Aluminate (CSA) Based Minerals

CSA based additives have been used by researchers to create expansive concretes. Hosoda et al. (2007) investigated the self-healing of these expansive concretes. Their mixtures used low heat PC, which has a slow rate of hydration, thereby increasing the potential for self-healing (Yamada et al., 2007). Self-healing was analysed through the examination of crack widths over time, and all samples were cured in water. The mixes incorporating the expansive additives showed signs of self-healing involving the additional expansion of the concrete after cracking and the formation of new hydrate crystals (Hosoda et al., 2007). Figure 7 shows the extent of crack healing, due to expansion and hydration, in a mix with 13.2% CSA based additive.

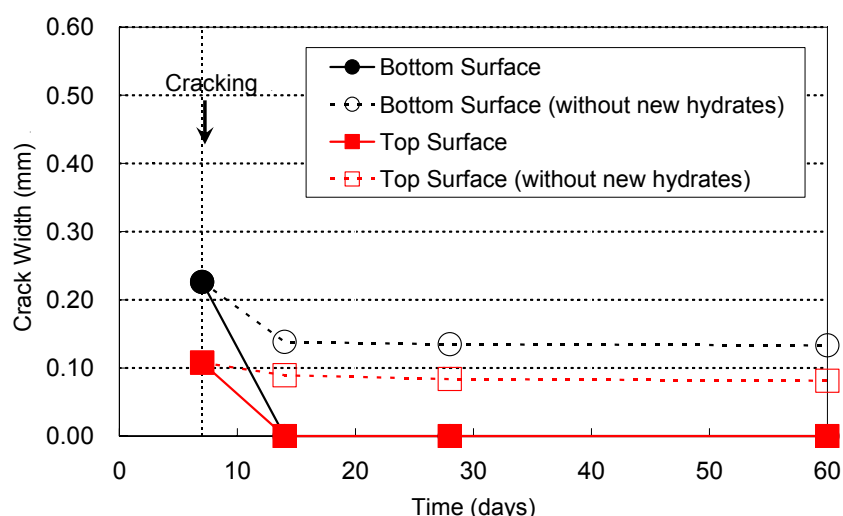


Figure 7: Change in crack width over time (Hosoda et al., 2007).

Following the encouraging results that Hosoda et al. (2007) obtained with regard to using CSA based expansive additives, Yamada et al. (2007) conducted tests using ordinary and high early-strength PC and P-CSA, a newly developed, high performance CSA type expansive additive. Previously, the amount of expansive additive used had varied between 30 and 60 kg/m³ (Hosoda et al., 2007). However, Yamada et al. (2007) chose to use smaller amounts of the additives in their mixes, using 20 to 30 kg/m³. They found that this caused the self-healing

of the crack to be mainly due to the precipitation of CaCO_3 , with “almost zero additional expansion of concrete” being observed. Specimens using both ordinary and high early-strength PC with the expansive additive were compared against a sample composed of low heat without any expansive additives. It was noted that a higher degree of self-healing occurred in the samples with P-CSA.

Further experiments involving expansive agents consisting of CSA were carried out by Ahn and Kishi (2010). The expansive agent comprised $\text{C}_4\text{A}_3\text{S}$ (hauyne), CaSO_4 (anhydrite) and CaO (free lime). This was combined with two geo-materials, both with high SiO_2 contents. Specimens were cured in water following cracking and XRD tests revealed that the chemicals in the healing products were very similar to those produced during the self healing of samples without the geo-materials. However, the XRD pattern, in Figure 8, showed one of the peaks of the AFt phases decreasing and, finally, disappearing after 7 days of curing, indicating that these phases transferred from hydrated aluminate phases to C-A-S-H (Stratlingite). It was also found that one of the geo-materials underwent alkaline activation in the presence of calcium hydroxide, leading to the formation of amorphous calcium aluminosilicate in the cracks, which behaved like a geopolymeric gel. SEM images, in Figure 9, show hydrogarnet phases, formed by CSA, at the crack interface. Further examination also showed that most of the geopolymeric gel phase had grown around dense hydrogarnet phases, demonstrating that the expansive agent had bridged the crack.

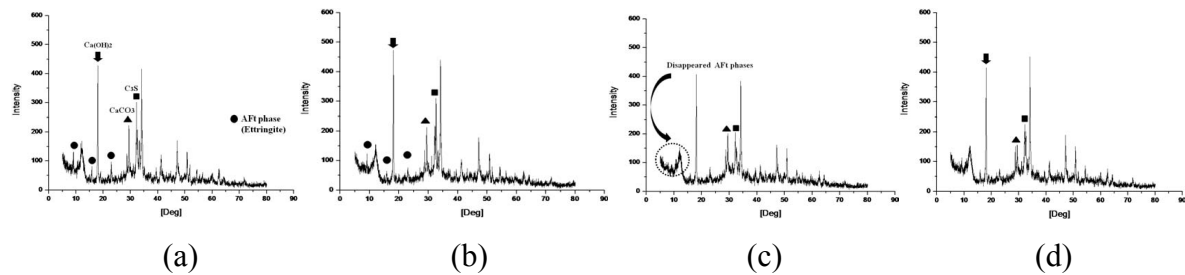


Figure 8: XRD pattern showing main hydration products of sample containing 90% OPC, 5% CSA and 5% geo-materials during healing on: (a) Day 1; (b) Day 3; (c) Day 7; (d) Day 28 (Ahn and Kishi, 2010)

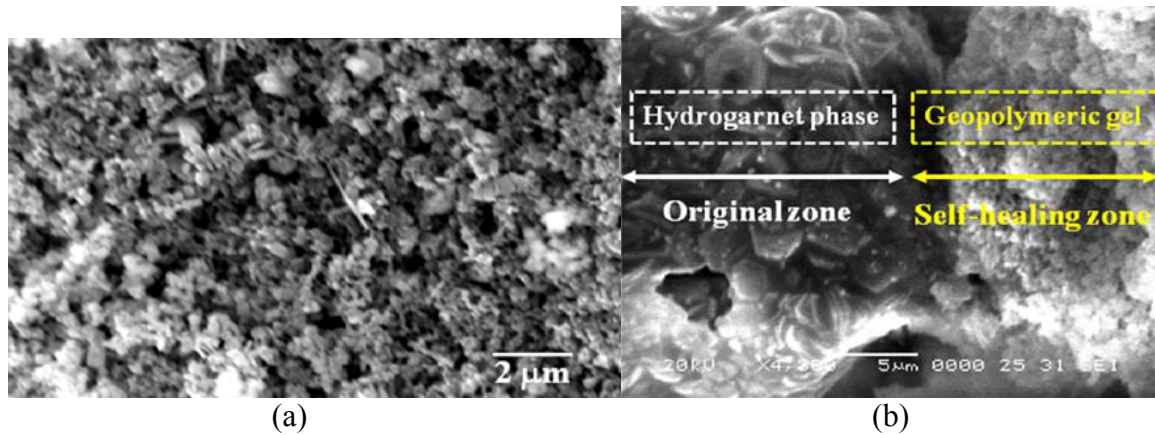


Figure 9: (a) Image of geopolymeric gel; (b) Comparison between geopolymeric gel and hydrogarnet phases (Ahn and Kishi, 2010).

More recently, Sisomphon et al. (2012) used mixtures of OPC, CSA additives and a crystalline additive. Tests involved two CSA additives, both were synthesized blends of hauyne, anhydrite and free lime, similar to the expansive additive used by Ahn and Kishi (2010). After cracks were induced in disk shaped specimens, they were cured in water. Self-healing was assessed by using a stereo optical microscope examine crack width and water permeability tests. Various different sizes of initial crack width were used to determine the optimum proportion of additives, which was found to be 10% CSA and 1.5% CA (crystalline additive). A large amount of CaCO_3 precipitates was found at the surface cracks of these samples. It was hypothesized that CSA and CA enhance self-healing in concrete by boosting the Ca^{2+} dissolution that is required for CaCO_3 formation. This was supported by the fact that when fractured specimens were immersed in deionised water and the electrical conductivity of the water was tested, the mixtures with CSA and CA had the highest conductivities, which is dependent on the amount of dissolved ions in the water. Figure 10 demonstrates the importance of a larger number of Ca^{2+} ions in the water. As calcium ions are released by the cement matrix, they interact with carbonate and bicarbonate ions in the incoming water, causing calcium carbonate formation. The crack mouth is the only location where there are significant numbers of both calcium and carbonate ions, which explains why CaCO_3 precipitates formed there.

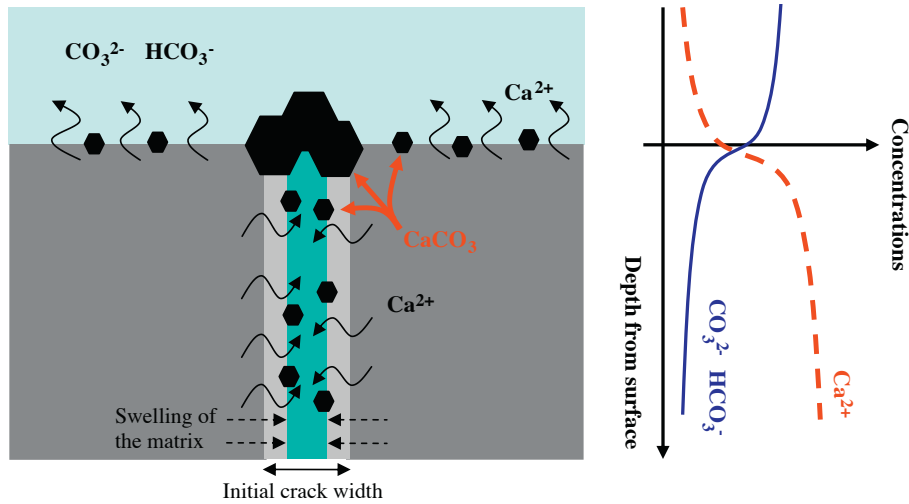


Figure 10: Illustration of precipitation on calcium carbonate (Sisomphon et al., 2012).

It has also been found that the surrounding environmental conditions can have a large effect on the self-healing of cements including CSA and CA. A study carried out by Sisomphon et al. (2013) showed samples subjected to wet and dry cycles exhibited signs of better self healing in terms of deflection capacity, flexural stiffness and flexural strength under four-point bend tests, when compared against healing in air and tap water. In addition, the difference between curing samples tap water and boiled water was explored. Figure 11 contains images of samples cured in both conditions. The samples cured in tap water show visible CaCO_3 precipitation, whereas the samples cured in boiled water do not due to the lack of carbonate ions present in cooked water. Tests revealed that even though CaCO_3 formation at the crack mouth improved water tightness, mechanical strength recovery was less evident because the precipitates at the crack opening decreased the hydration of particles inside the crack.

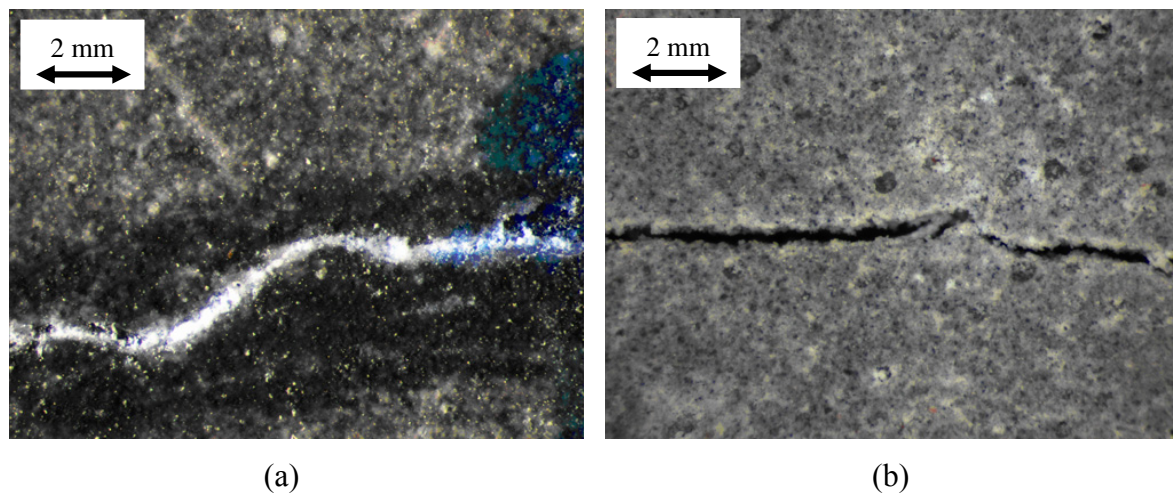


Figure 11: Image of crack after 28 days of curing in (a) tap water and (b) boiled water (Sisomphon et al., 2013).

Blast Furnace Slag (BFS)

Qian et al. (2009) investigated the self-healing behaviour of fibre-reinforced strain hardening cementitious composites with blast furnace slag and limestone powder. Their samples were tested using a four-point bend test. One set of samples was tested until failure 28 days after demoulding, while another two sets of samples of each mixture tested were deflected 2.4 mm before being left to cure in water or air before bent till failure 28 days later. The samples cured in water with BFS and LP were found to reach about 60-80% of the deflection capacity of the samples that failed on day 28, which was significantly higher than the recovery of specimens cured in air. Olivier et al. (2013) recently compared the self-healing of 100% PC specimens with ones where 50% of the PC was replaced with BFS. Using tomography and gas permeability tests, they concluded that 50% BFS samples had slower self-healing in an early age than 100%PC, however in the long term the 50% BFS samples had a greater healing capacity, demonstrated by Figure 12.

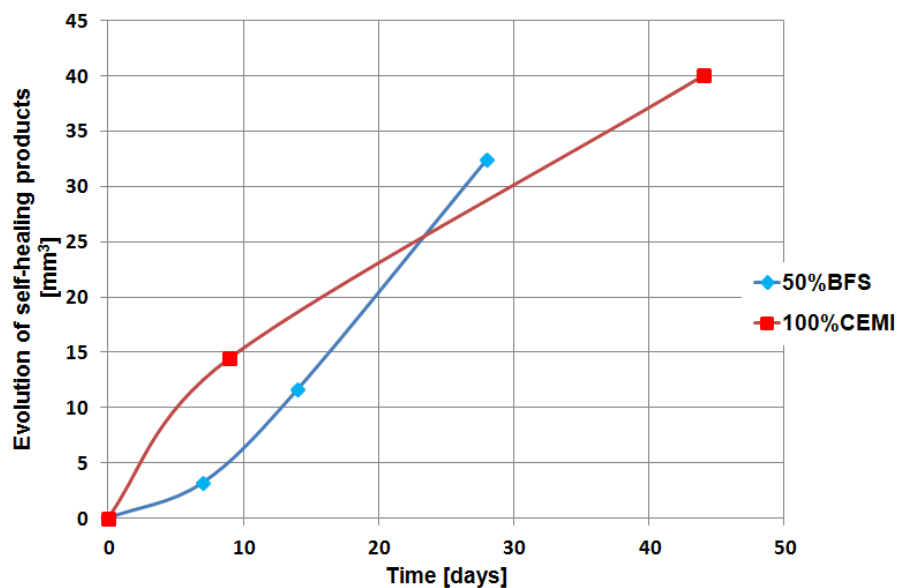
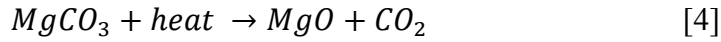


Figure 12: Growth of self-healing products in cracks after a splitting test (Olivier et al., 2013).

2.2.5 MgO

The slow hydration of MgO, which is an intrinsic component of cement, has been known to cause expansion (Mehta, 1978), and currently, MgO is commonly used as an expansive additive (Qureshi, 2013). Compared to expansive additives that use CSA, the hydration and hence expansion of MgO requires less moisture and its hydration products are more chemically stable in the cement paste (Mo et al., 2010).

MgO is mainly produced from the calcination of magnesite ($MgCO_3$), by the following reaction:



Higher calcination temperatures cause the formation of larger crystals of MgO, shown in Figure 13. The larger the MgO crystals are, the slower the hydration process will be, causing delayed expansion, which is used to counteract shrinkage.

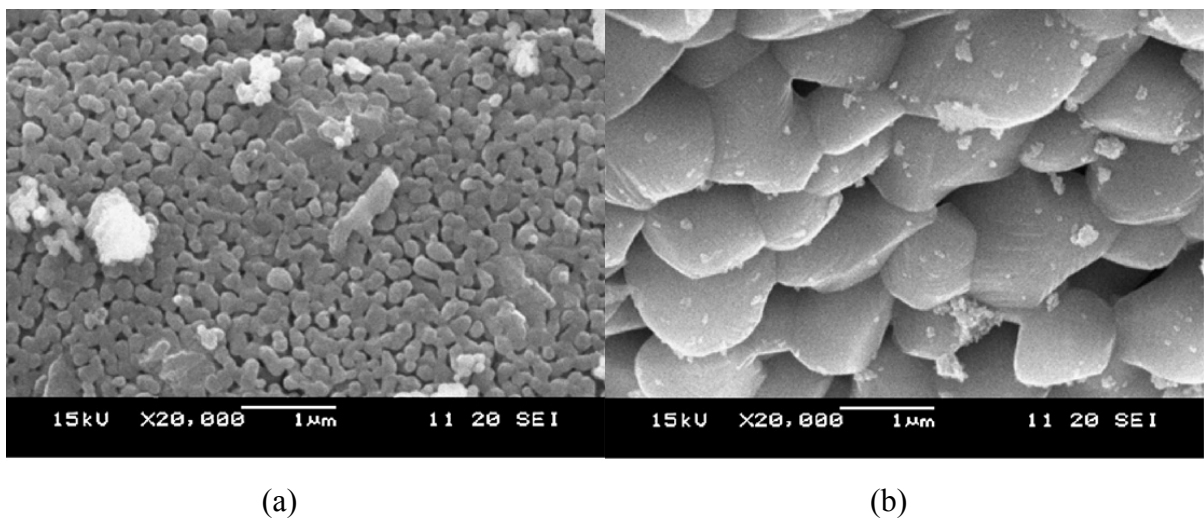


Figure 13: Microstructure of MgO produced (a) at 1100C for 1 hour; and (b) at 1300C for 1 hour (Mo et al., 2010).

There has been an increasing interest in using MgO in cements as engineers look to make the production of cement more environmentally friendly. Although the production of MgO emits more CO_2 than PC production, MgO blocks have the potential to reabsorb more CO_2 and enhance the strength of concrete when subjected to accelerated carbonation curing (Liska and Al-Tabbaa, 2009). The use of MgO as an additive to enhance the autogenous self-healing of concrete is a relatively new idea. Small amounts of MgO are present in many mineral additives that are used to increase the self-healing potential concrete, such as FA (fly ash), SF (silica fume) and CA (crystalline additive) (Jaroenratanapirom and Sahamitmongkol, 2010). Qureshi (2013) explored the use of MgO as a potential mineral for aiding autogenous self-healing based on its effectiveness as an expansive agent. Using three point bend tests and microscopic image analysis, he found that mixes including MgO exhibited better mechanical strength recovery and crack sealing than samples without MgO. Prisms were tested till failure

after 1 day of curing, before being cured in a water tank and tested again 28 days later. Figure 14 shows that specimens with 5% MgO and 5% bentonite showed an average mechanical strength recovery of 68% after 28 days of curing, while mixes with 5% MgO recovered by 33.6% in the same time period. Image analysis in Figure 15 shows that the crack in a sample with 5% MgO was fully sealed after 28 days of curing.

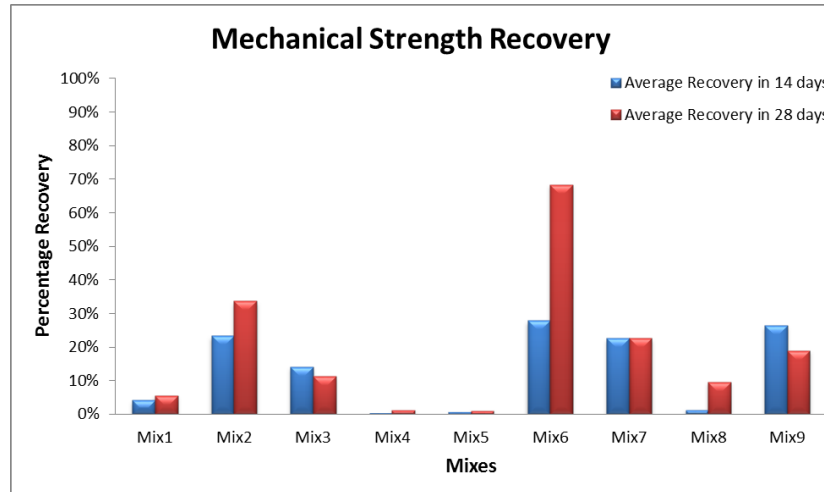


Figure 14: Mechanical strength recovery of different mixes, where mix 1 consists of 100% OPC, mix 2 consists of 95% OPC + 5% MgO, and Mix 6 consists of 90% OPC + 5% MgO + 5% bentonite clay (Qureshi, 2013).

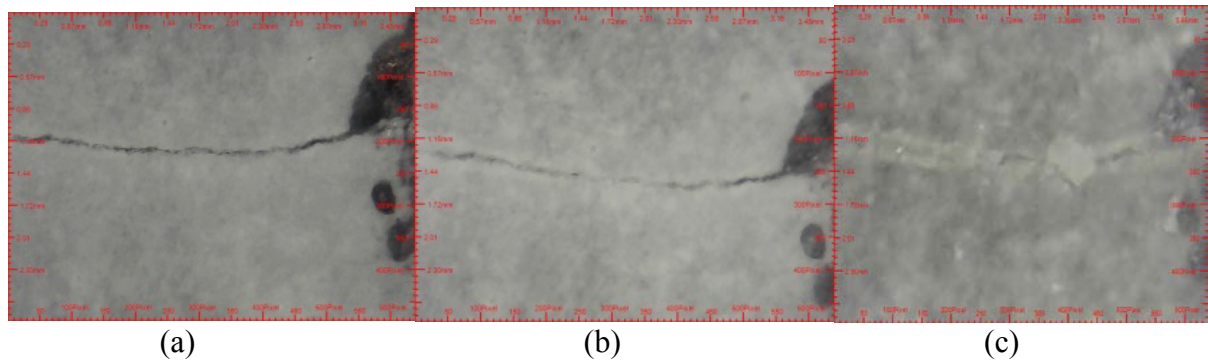


Figure 15: Images of crack healing after (a) 7 days, (b) 14 days and (c) 28 days of curing (Qureshi, 2013).

The addition of MgO to mixes improves both the crack healing and crack sealing properties of PC. It is thought that the volumetric expansion of MgO during hydration is a critical factor in this remarkable enhancement. During hydration, Mg^{2+} ions react with OH^- ions to form $\text{Mg}(\text{OH})_2$, which is approximately 2.2 times the volume of MgO (Chen, 2011).

2.3 Conclusions

In this section waterproofing admixtures and mineral admixtures that can enhance the autogenous self-healing of concrete have been reviewed. The importance of both qualities in a well-designed, durable structure has been discussed. Water and hydration are critical for the autogenous self-healing of concrete, so the question that arises when one combines the two is how will they interact? Will the self-healing ability of concrete be inhibited?

3. Experimental Work

In the literature, many different tests for examining the extent of self-healing in concretes have been suggested. Sisomphon et al. (2013) used a four-point bend test to investigate self-healing, whereas Yang et al. (2011) uses resonant frequency measurements to quantify autogenous healing in ECC. Some researchers have also employed permeability tests to evaluate self-healing, expecting to observe a reduction in permeability due to the hydration of particles in cracks. (Ter Heide and Schlangen, 2007). In this project, research focused on using compressive strength tests, three-point bend tests and microscopic image analysis to compare the autogenous self-healing of different mixtures. In addition, XRD tests were run on a small selection of the mixtures' self-healing products to identify their chemical compositions.

3.1 Materials

The main materials used in these experiments were Ordinary Portland Cement (OPC), two different types of magnesium oxide (MgO), a superplasticizer and a waterproofing admixture. Information about the materials is provided in Table 1 and their chemical properties of OPC and the two types of MgO are documented in Table 2.

Table 1: Materials and information.

Materials	Information
Cement	CEM 1 52.5N Portland Cement supplied by Hanson, UK and conforms to BS EN 197 – 1.
Magnesium Oxide	MgO N50 and MgO 92/200 supplied by RBH Ltd., UK.
Superplasticizer	MasterGlenium 123 (formerly Glenium 123) is a BASF product and was supplied by Cementaid, UK. It satisfies BS EN 934 – 2.
Waterproofing Admixture	Everdure CALTITE Hydrophobic Pore-Blocking Ingredient (HPI) supplied by Cementaid, UK.

Table 2: Chemical properties of PC and MgO from supplier information.

Chemicals	PC	MgO N50	MgO 92/200
SiO₂ (%)	19.50	N/A	2.0
Al₂O₃ (%)	4.90	N/A	N/A
CaO (%)	63.60	1.0	1.6
Fe₂O₃ (%)	3.10	N/A	N/A
MgO (%)	0.90	97.5	91.5
SO₃ (%)	3.30	0.85	N/A
Fe (%)	N/A	0.07	N/A
Cl (%)	N/A	0.2	N/A
R₂O₃ (%)	N/A	N/A	1.0
Mn (%)	N/A	0.006	N/A
Loss on Ignition (%)	2.10	8.0	4.0

3.2 Mixes

During the course of this project, twelve different mixes were made, six with the waterproofing system and six without the waterproofing system. The water/cement ratio of each mix was kept within the standard consistency limits. The amount of superplasticizer used was equal to 0.7% of the cementitious material by weight, and the waterproofing admixture was dosed at 30 litres/m³ of concrete. The mix designs are outlined in Table 3.

Table 3: Mix design of cementitious composites by percentage weight, where 100% is dry mass of OPC and MgO.

Mix	OPC	MgO N50	MgO 92/200	Water	Superplasticizer	Waterproofing Admixture
1	100	0	0	26.0	0.7	0
2	100	0	0	25.6	0.7	1.2
3	97	3	0	30.0	0.68	0
4	97	3	0	29.8	0.68	1.2
5	95	5	0	30.8	0.67	0
6	95	5	0	30.2	0.67	1.2
7	97	0	3	28	0.68	0

8	97	0	3	28	0.68	1.2
9	95	0	5	28.4	0.67	0
10	95	0	5	27.8	0.67	1.2
11	93	0	7	28.4	0.65	0
12	93	0	7	28.2	0.65	1.2

3.3 Preparation

For all the mixes in this project, mixing was performed using a high-powered food mixer at a rotational speed of 190 rpm. Additionally, a palette was used to mix the cement paste manually to ensure its cohesiveness and uniformity as the beater of the food mixer did not reach the bottom of the mixing bowl, leaving some of the binder untouched. The masses of all the necessary components for each mix were measured using a top pan balance with an accuracy of 0.01g.

3.3.1 Standard Consistency Tests

Before cubes and prisms of cement could be made, standard consistency tests needed to be carried out, in accordance with ASTM C 187 and BS 4550, to determine a suitable water/cement ratio for each mix. Every test involved using 500g of binder. The binder was mixed for 1 minute, before water and the admixtures were added according to the mix proportions. Mixing then continued for 30 seconds and then the mixture was mixed manually for 30 seconds. Finally, the mixer was switched on for another two and a half minutes. Once mixing was complete, the paste was moulded into a ball and thrown from hand to hand, a distance of 150 mm, six times to vibrate the paste, reducing the amount of air voids in it. The standard consistency test was then performed on the cement paste using Vicat's apparatus, shown in **Figure 16**. The cement paste was put into the cylindrical mould and excess paste was removed. The mould was placed centrally under the plunger and the plunger was brought down to its surface before being released. Once the plunger had stopped moving, the reading on the apparatus was noted. The water/cement ratio was considered adequate if the reading was between 5 mm and 7 mm. The consistency test was repeated until values within the consistency limits were obtained for each mix.

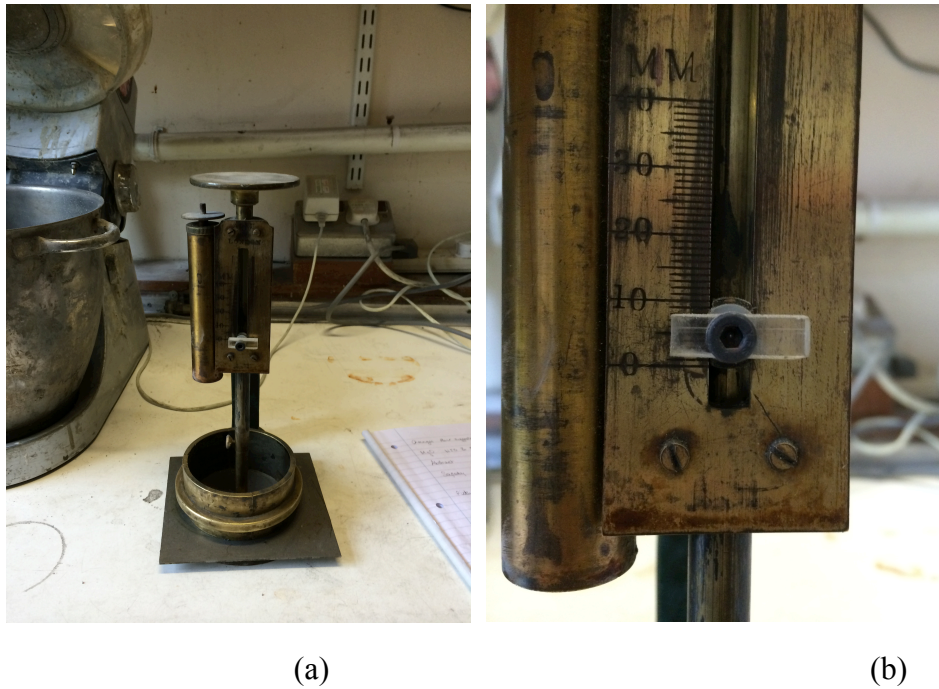


Figure 16: (a) Vicat's apparatus; (b) Vicat needle showing height of the plunger above the bottom surface of the apparatus.

3.3.2 Preparing Samples for Testing

Once suitable water/cement ratios had been determined, nine cubes (40 x 40 x 40 mm) and six rectangular prisms (40 x 40 x 160 mm) were prepared for the compressive strength tests and three-point bend tests respectively. To make enough cement paste for these specimens, 4000g of binder and the corresponding amounts of water and admixtures were used. The following procedure was used to make these samples:

1. The binder, water and admixtures were mixed together. The mixing process is summarised in Figure 17.

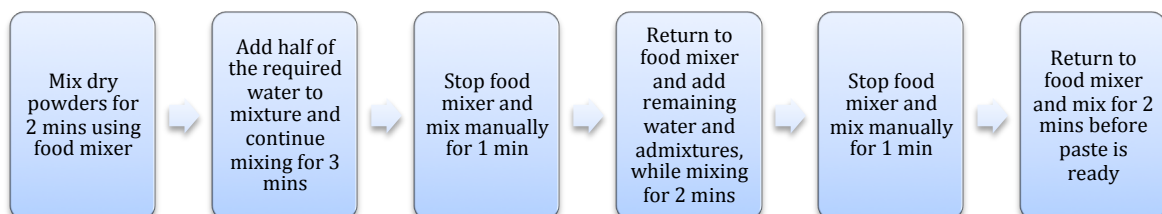


Figure 17: Mixing process.

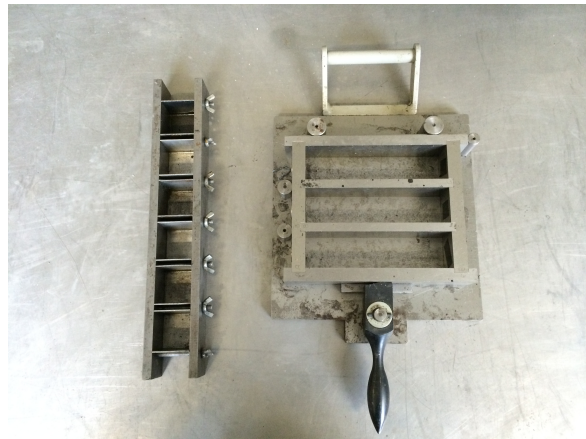
2. Clean steel prism and cube moulds were lubricated with ado-strike oil, which reduces the risk of cement sticking to the moulds, making it easier to de-mould. Moulds were

then filled with the cement paste in two layers. After each layer was added, the paste was agitated with a palette knife in order to displace air bubbles. When the moulds were full, they were manually vibrated by being lift up 5 cm off the table top and dropped 60 times to further remove air voids and aid compaction. Finally, a palette knife was used to level the surface of the cement and remove any excess cement. Then the moulds were covered in cling film and left for 24 hours at laboratory temperatures of $20\pm1^{\circ}\text{C}$, and 60% RH.

3. After 24 hours, the specimens were de-moulded and either tested or left to cure in tanks of tap water at laboratory temperatures of $20\pm1^{\circ}\text{C}$. The water in the tanks was replaced once a week so that continuous hydration of the cement was possible.



(a)



(b)

Figure 18: (a) High-powered food mixer; (b) Steel moulds.

3.4 Experimental Method

3.4.1 Compressive Strength Test

Compression tests were conducted in accordance with BS EN 196-1:2005. Before the compression tests were performed on the cubes their masses were measured using a top pan balance and their dimensions were recorded using digital callipers. If the cube samples were taken from the curing tank then they were dried at the laboratory temperature before any measurements were taken. Once this was finished, compressive strength tests were conducted.

A 40 mm testing core was attached to a 250 kN compressive strength test cell and the cube specimens were placed in between the two plates. The test cell was set to a loading rate of 2.4

kN/s. Once the specimen had been crushed, the machine stopped and the maximum compressive strength of the specimen was shown on the console in Figure 19. These tests were conducted immediately after de-moulding on day 1, then next on day 3 and day 15 to compare the development of compressive strength among the different mixes. During each phase of testing, three cubes of each sample were crushed.

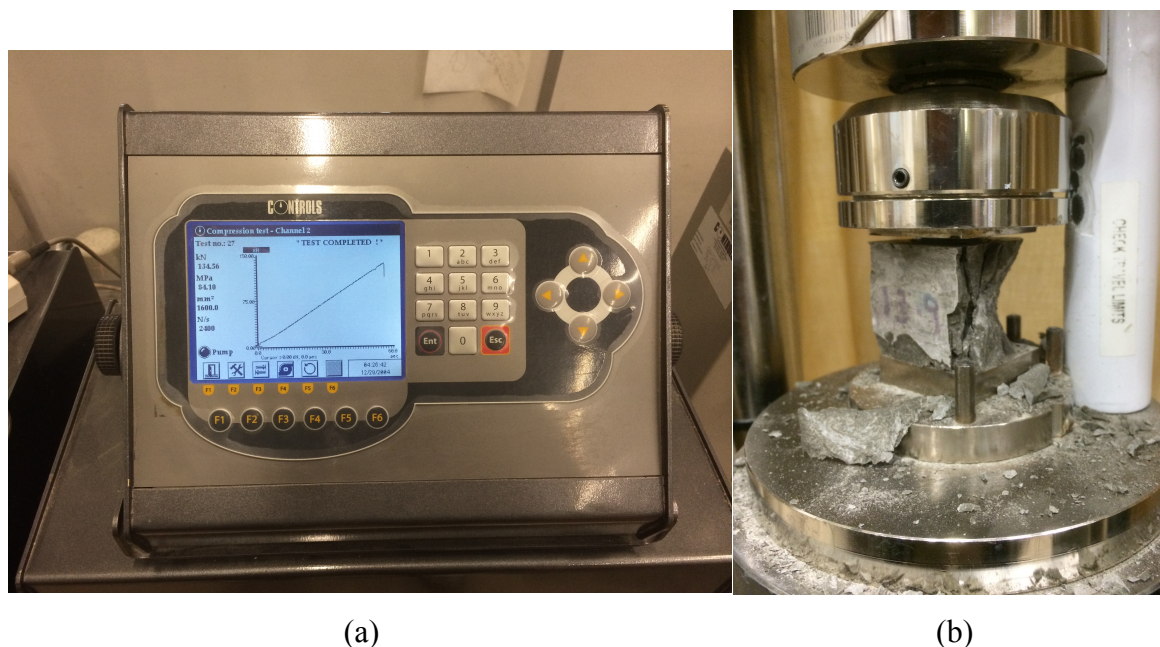


Figure 19: (a) Console that operates the compressive strength test cell; (b) Cement cube at failure.

3.4.2 Three-Point Bend Test

For the three-point bend tests, the dimensions and masses of the prisms were recorded prior to testing. If they were being taken from the water tanks then they were air-dried first. The three-point bend tests were carried out using Instron machines, with supports 135 mm apart. Specimens were placed on the supports such that the load acted through its mid-span and each support was equidistance from the end of the prism. The ramp speed was set at 0.05 mm/min, the cyclic loading was not switched on and the sensitivity was adjusted to 4%. The specimen was then loaded till failure, when it was unable to resist loading any further and the load registered by the loading shaft began to decrease. The test data, including the load and the central displacement of the prism, was recorded. The cracked samples were then placed vertically in the water tanks for curing. For each mix, there were two groups of samples, group A and group B. For group A, cracks were induced in three prisms on day 1, immediately after being de-moulded, using a 2 kN capacity Instron machine. Afterwards, these cracked samples were placed in a tank of tap water for curing at a laboratory temperature of $20 \pm 1^\circ\text{C}$. They were then tested till failure 14 days later. For group B, the three

specimens was first cured in tap water at $20\pm 1^\circ\text{C}$ for 14 days after de-moulding. These prisms were then tested until final failure in the 30 kN capacity loading cell Instron machine. The data that was collected during these three-point bending tests included load and central displacement. For group A, the two sets of loading data were used to analyse the self-healing potential of the mixes.

During testing, the crack width was not controlled. The crack widths recorded ranged from 0.01 mm to 0.5 mm, however this included some samples that entirely separated. All samples were cured in water and placed upright in the curing tank, including the samples that were separated. This was done so that the self-weight of the samples would push their cracks closed as research has suggested that, although the application of a compressive stress does not influence the strength recovery in concrete, a small compressive stress is required to close cracks. Once the two crack faces touch each other, or the distance between the crack faces is minimal, self-healing occurs (Ter Heide and Schlangen, 2007).

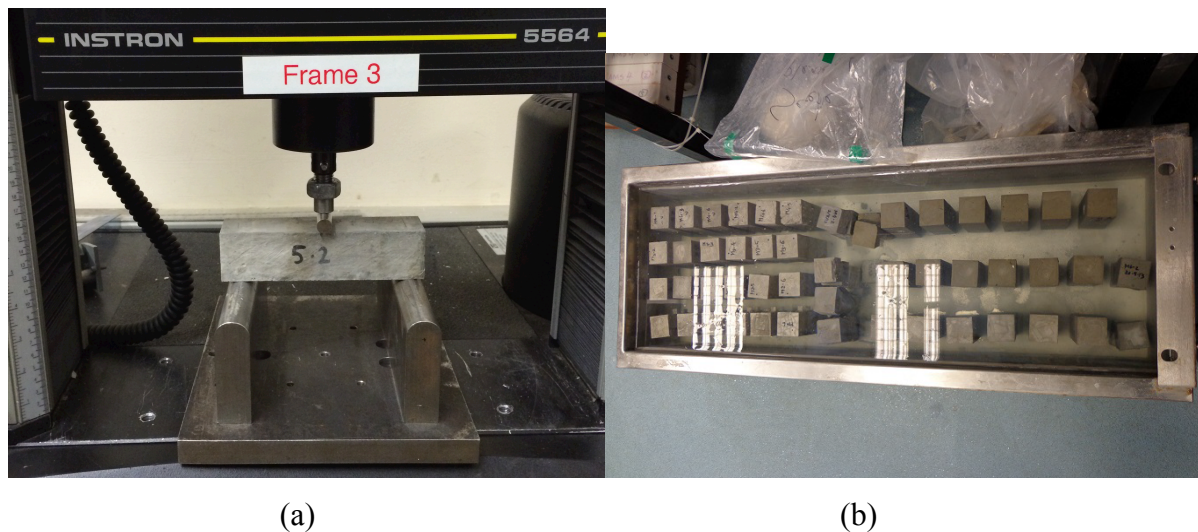


Figure 20: (a) Instron machine performing three-point bend test; (b) Prism specimens curing in an upright position.

3.4.3 Image Analysis with Digital Microscope

Digital microscope analysis was used to analyse the crack healing in specimens as a result of being cured in water for 14 days. The GXCAM 1.3 type digital microscope, supplied by GT Vision Ltd., was used to observe crack widths. Cracks were examined immediately after crack formation on day 1 and immediately before samples were re-cracked on day 15. The reduction in crack width was used as an indicator of self-healing.



Figure 21: Digital microscope analysis equipment.

3.4.4 XRD

XRD tests were performed to investigate the self-healing products of cement with waterproofing admixtures, and compare them with healing products formed in cement mixtures that do not have waterproofing. The tests were performed on samples with 5% MgO N50 and 5% MgO 92/200, mixes 5, 6, 9 and 10. The 100% OPC mixtures were not tested because they had to be disposed of, as there was limited space in the curing tank. Samples that had been cured for 56 days were used in these experiments. To prepare the samples for the XRD tests, the prisms were broken apart at their cracks and the healing products were scraped off the inside surface of the crack using a toothbrush and a metal spatula. The healing products were then gathered and ground into a fine powder that was passed through a 75 μm sieve. Next, the powder was placed in a container and covered in acetone for three days. They were subsequently placed in an oven at 60°C for 24 hours before being tested in the machine shown in Figure 22. The scanning values were between 2 θ values of 5 and 60° at 1 secs/step.

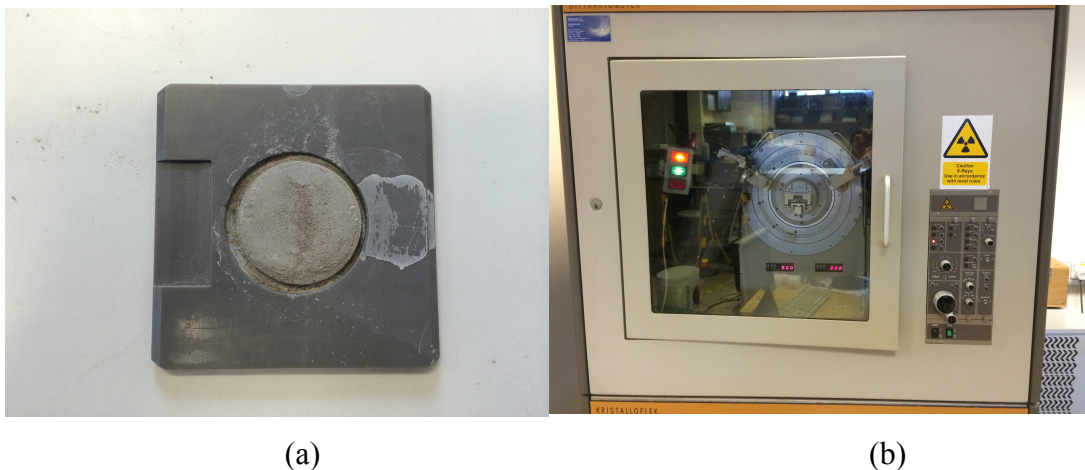


Figure 22: (a) XRD sample; (b) XRD machine

4. Results and Discussion

4.1 Results

4.1.1 Compressive Strength Test

The compressive strength development of the all the mixes has been summarised in Figure 23. In the majority of the mixes the addition of waterproofing additives has reduced their compressive strength. However, by comparing mixes 7 and 8, it is possible to see that waterproofing admixtures have had a beneficial effect in the mixes with 3% MgO 92/200.

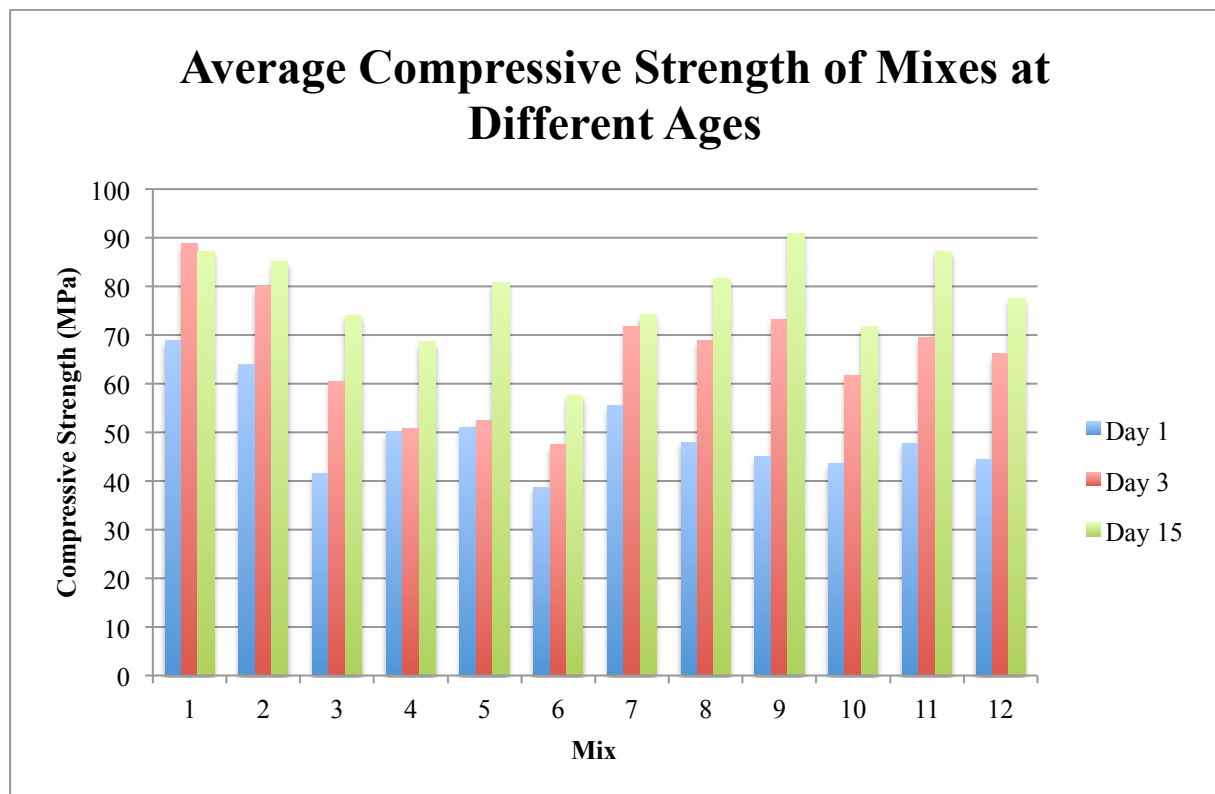


Figure 23: Development of compressive strength as specimens age.

Most of the mixes gain strength in a very similar way as they age; Figure 25 shows that all mixes with MgO 92/200 and the 100% OPC mixes exhibit a large improvement in strength between day 1 and day 3 and then a much smaller increase in strength over the next 12 days. In contrast, MgO N50 mixes (Figure 24), with the exception of M3, show more gradual gains in strength. In addition, substituting OPC for MgO, both N50 and 92/200 has decreased the compressive strength of mixes. The only two mixes with similar strengths to 100% OPC are 5% MgO 92/200 and 7% MgO 92/200 mixes.

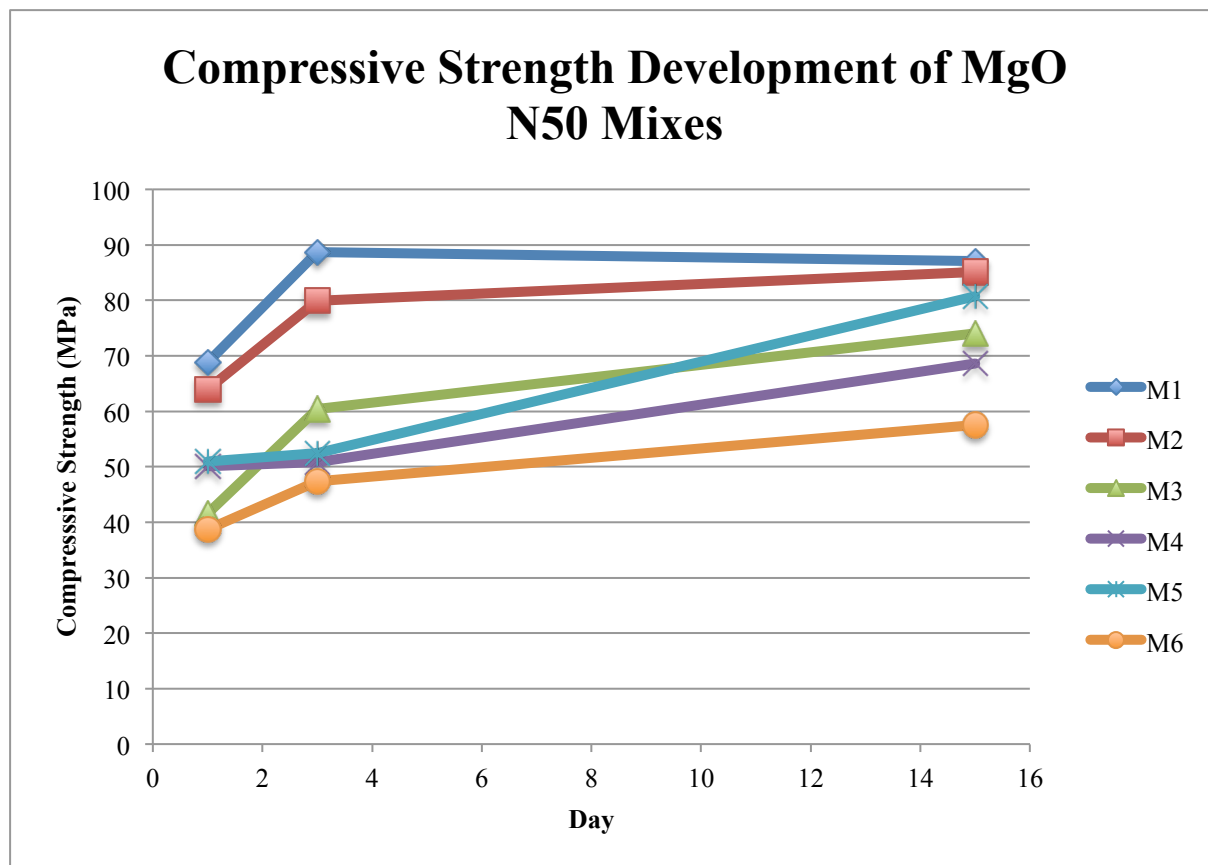


Figure 24: Compressive strength development of MgO N50 mixes.

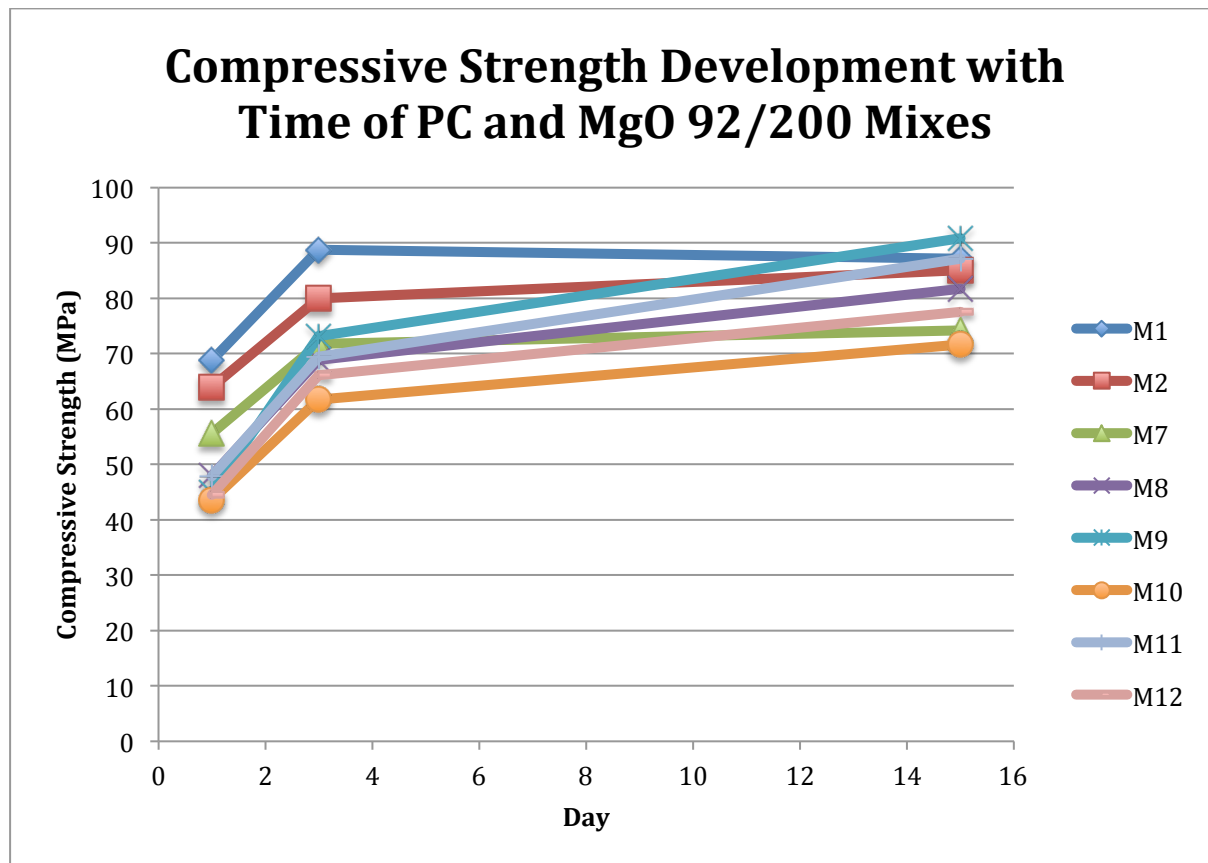


Figure 25: Compressive strength development of MgO 92/200 mixes.

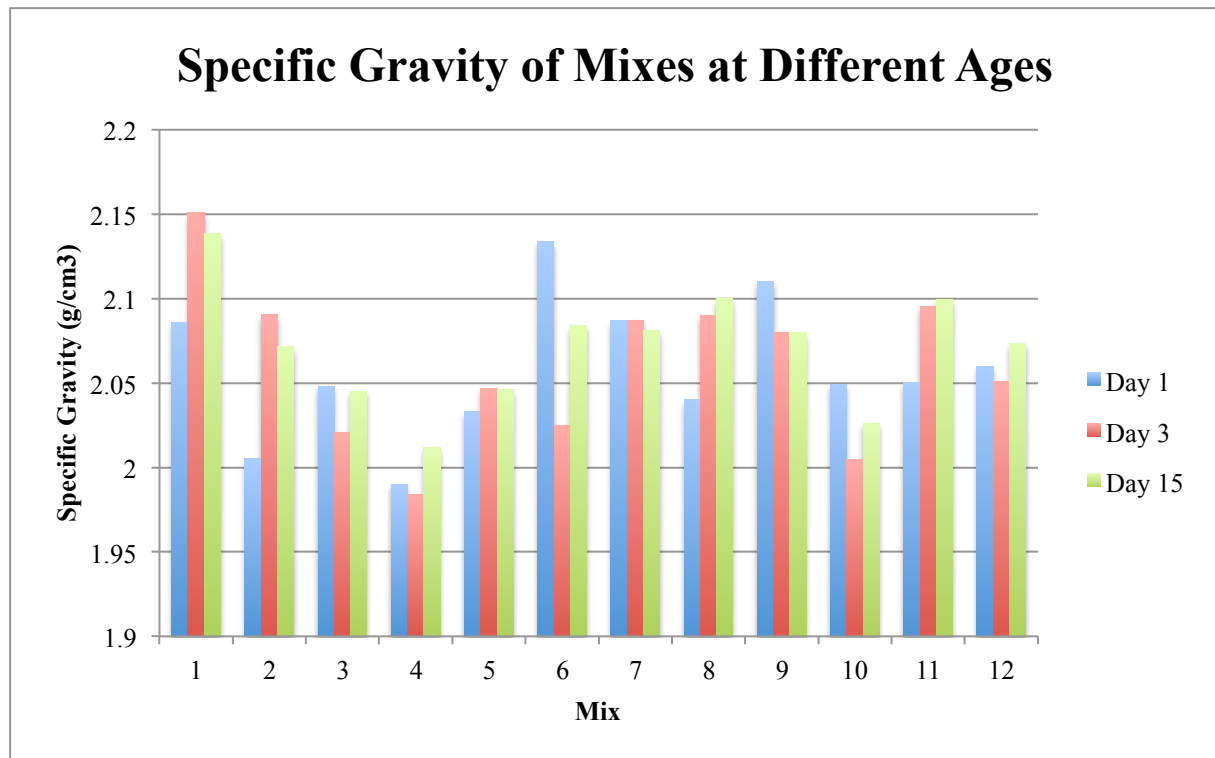


Figure 26: Average specific gravity of mixes.

Figure 26 shows that the addition of waterproofing additives has caused the specific gravity of mixtures to decrease apart from the mixes with 5% MgO N50 and 3% MgO 92/200.

4.1.2 Three-Point Bend Test

The three-point bend tests were used to induce cracks in one-day specimens in order to monitor the mechanical strength recovery of early age cement pastes. The day 1 cracking load has been compared to the load at which the specimen failed on day 15 when it was reloaded, in order to see if there is any evidence of recovery and hence self-healing. Figure 27 and Figure 28 contain graphs that plot the mechanical strength regain of samples with the original loads required to create cracks on day 1. The blue bars represent Day 1 loading, whereas the red bars represent the reloading of samples on day 15:



Figure 27 shows that mixes with 100% OPC exhibit no signs of mechanical strength recovery with and without water proofing. Although they do not display any self-healing abilities based on the three-point bend test, the 100% OPC mixtures M1 and M2 did have higher failure loads than most of the others.

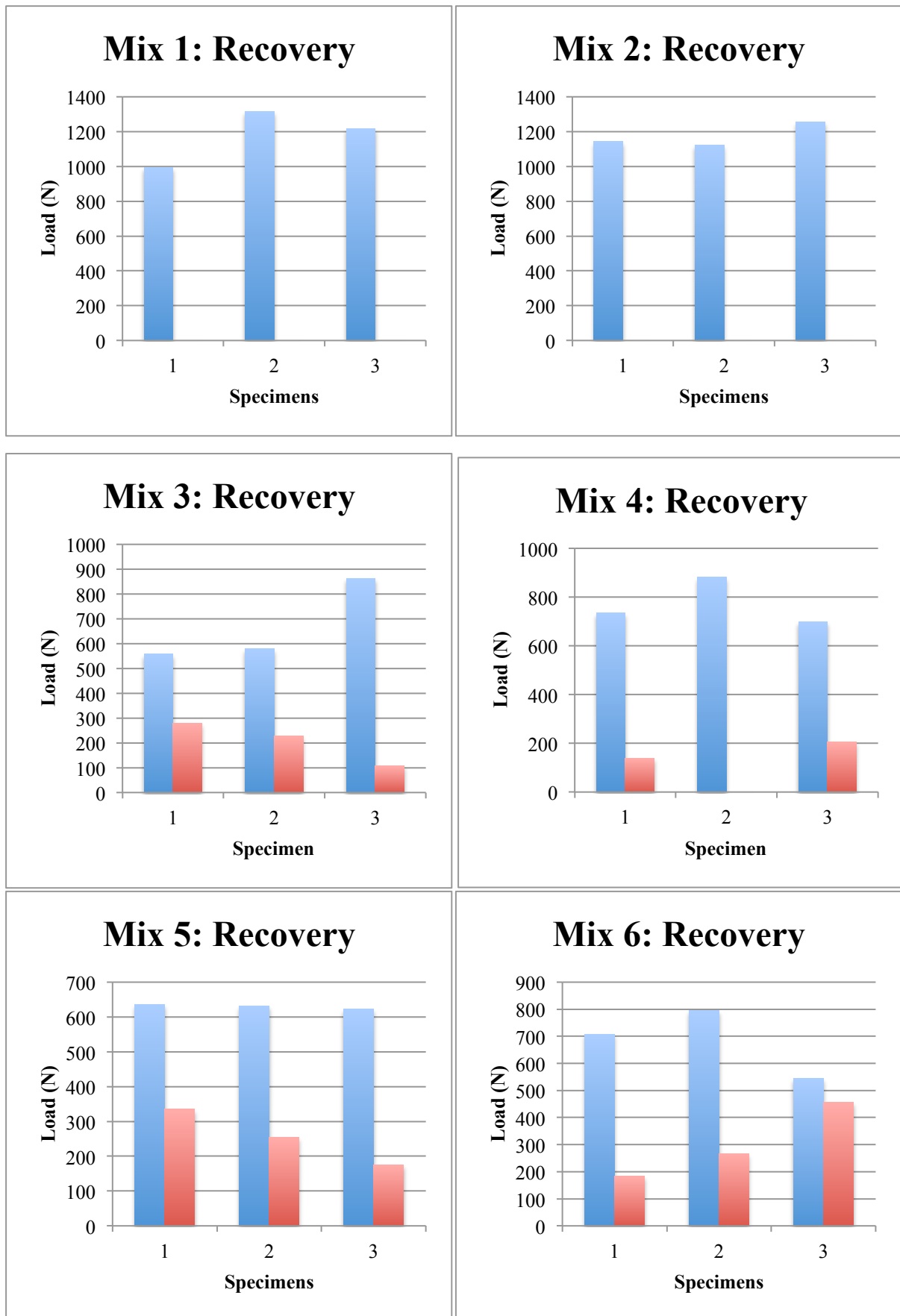


Figure 27: Three-point bend test failure loads for specimens tested on day 1 and their recovery loads after 14 days of curing for mixes 1, 2, 3, 4, 5 and 6.

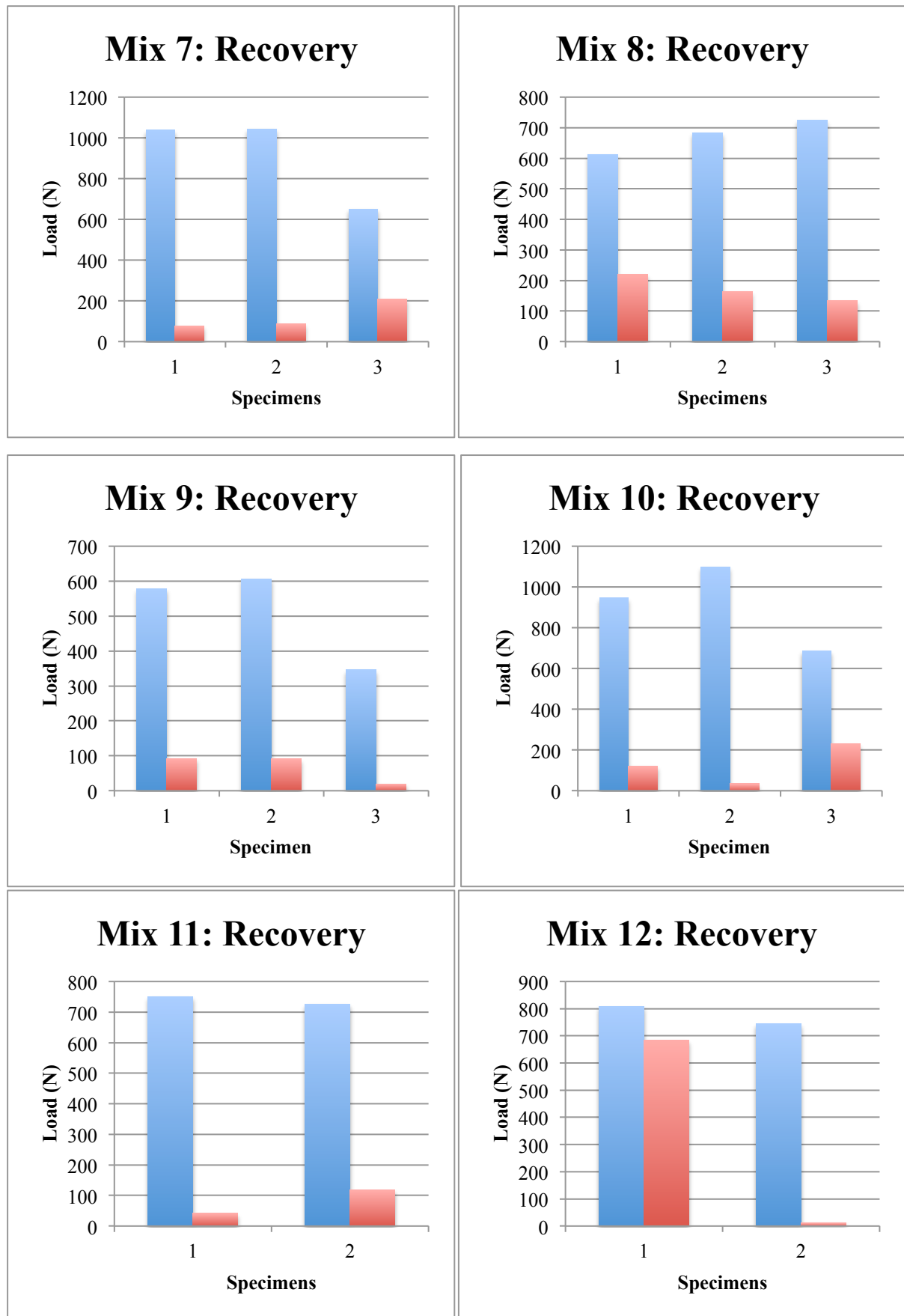


Figure 28: Three-point bend test failure loads for specimens tested on day 1 and their recovery loads after 14 days of curing for mixes 7, 8, 9, 10, 11 and 12.

The recovery of mechanical strength with the addition of MgO is very promising. The addition of MgO N50 in both 3% and 5% doses has caused recoveries in mechanical strength of up to 50% in samples. In one 5% MgO N50 sample including waterproofing, as much as 84% of the original strength had been recovered as shown in M6 in Figure 27. The strength recovery displayed by samples with MgO 92/200 does not show the same level of strength recovery as their N50 counterparts. Although M12 appears to have had one sample that has had a phenomenal recovery, it may be an anomaly, and had there been more time more specimens would have been cast and tested as only two samples of M11 and M12 are documented in Figure 28 as there was an accident during the handling of specimens.

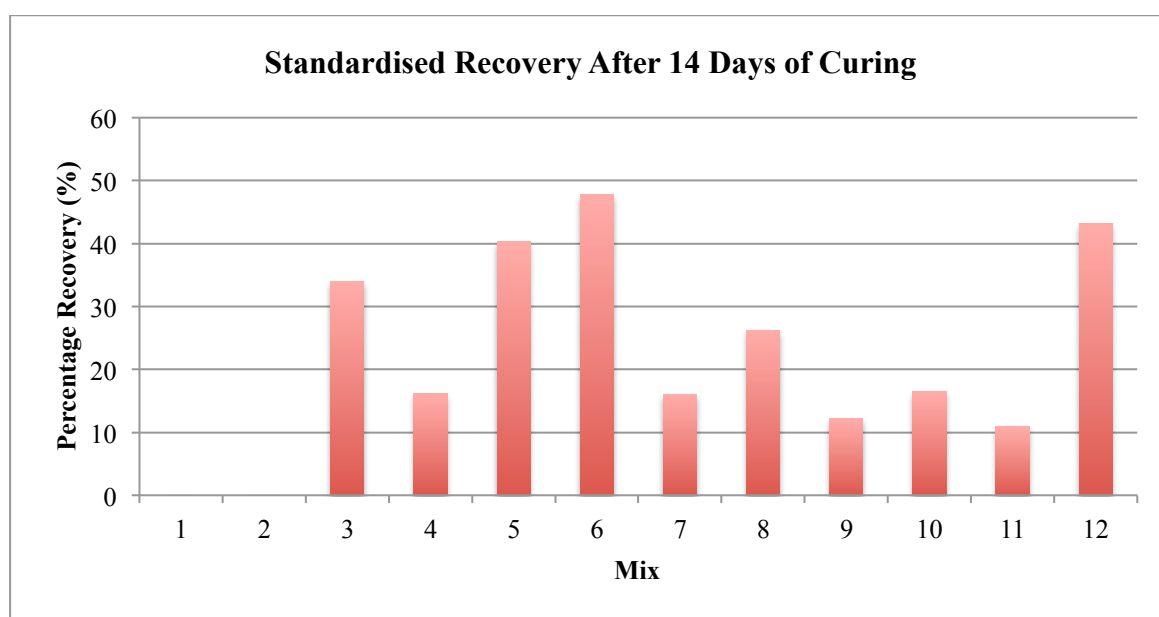


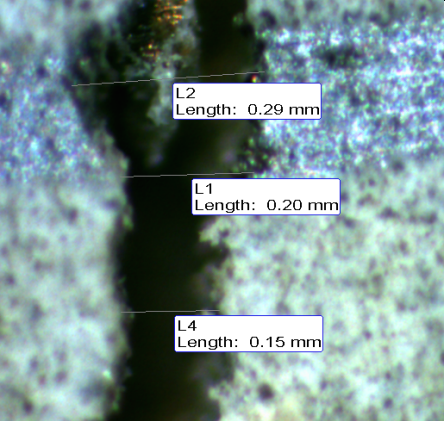
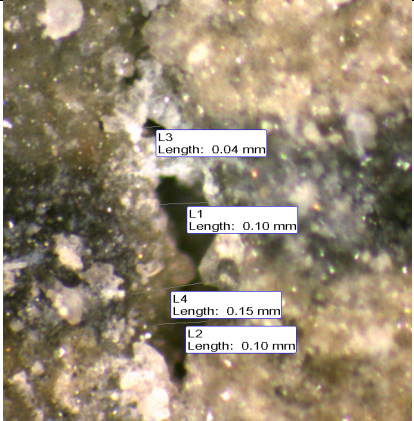
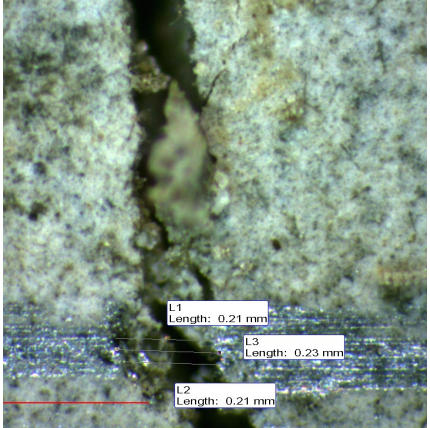
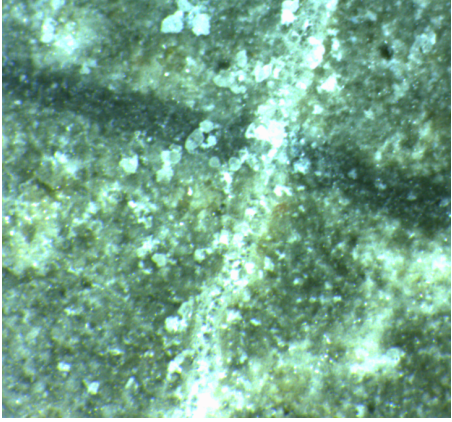
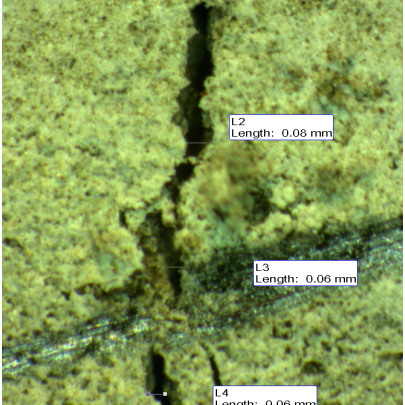
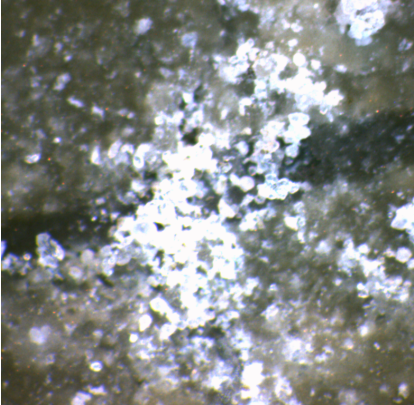
Figure 29: Average percentage of mechanical strength recovery of mixes in 14 days.

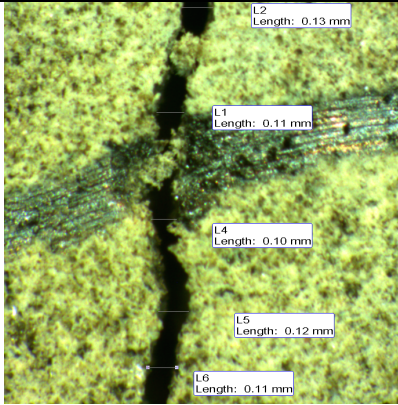
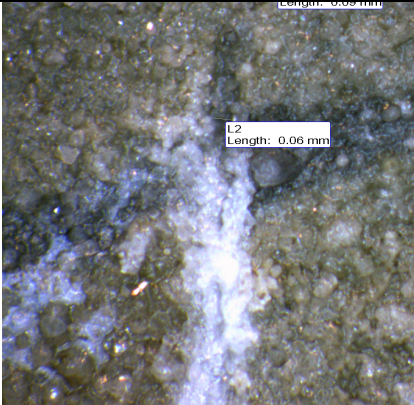
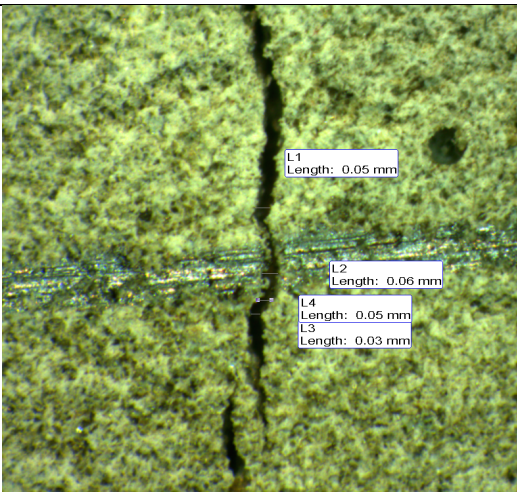
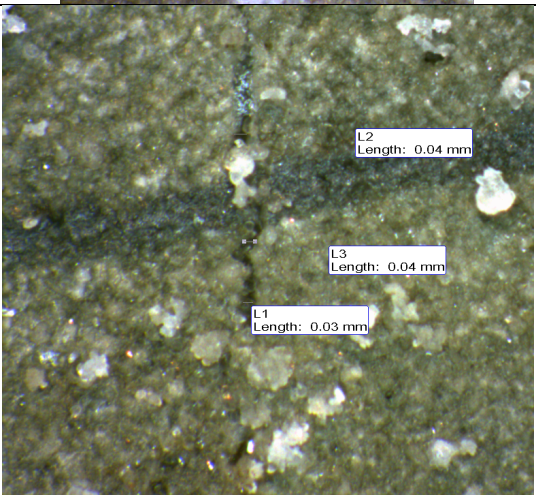
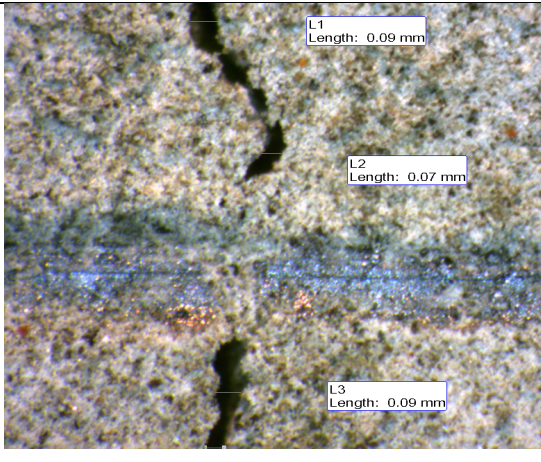
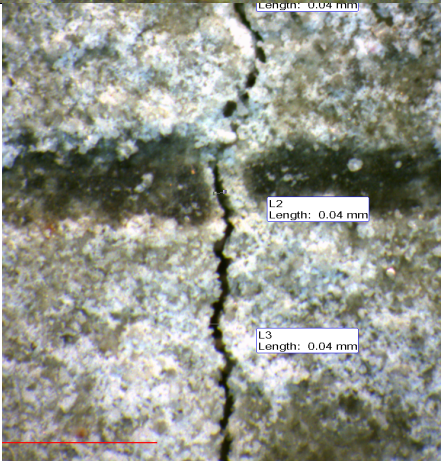
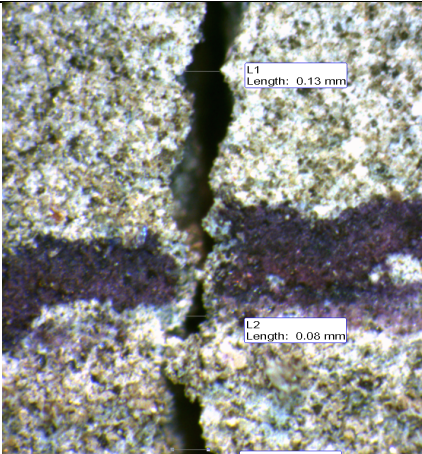
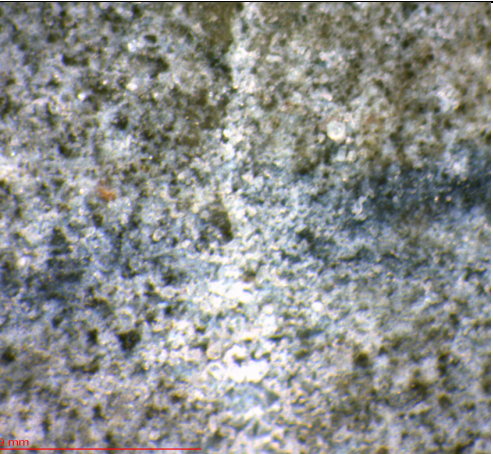
A comparison of the average strength recovery is illustrated in Figure 29. In terms of mechanical strength regain, M6 healed the most, closely followed by M12 and M5. The addition of waterproofing additives seems to have been beneficial for the self-healing of certain mixes. The average mechanical strength recovery of M6 was 47.8%, whereas M5 recovered by 40.4% on average showing that waterproofing additives may improve the self-healing of concrete. A similar effect was observed in mixtures with MgO 92/200. Comparing the two different types of MgO, N50 is much more effective than 92/200 at the same dose of 5%. Without waterproofing, 92/200 samples recovered by a maximum of 16%. In contrast, the N50 equivalent recovered by as much as 53%. When samples included waterproofing, the result was similar; N50 samples showed a maximum strength regain of 84%, while the 92/200 samples recovered by as much as 33%.

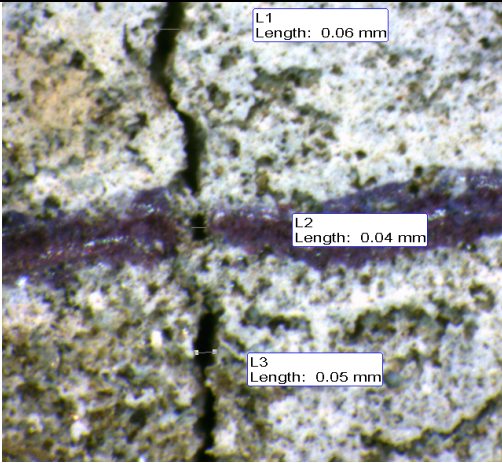
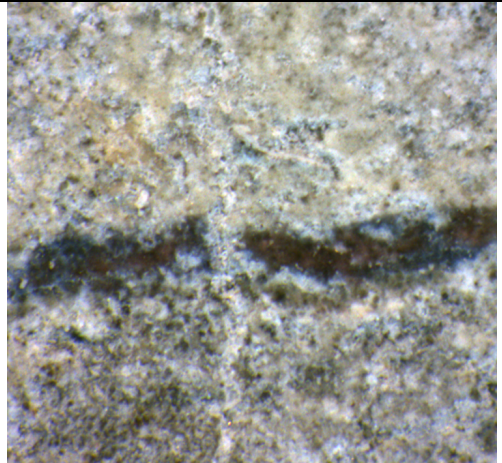
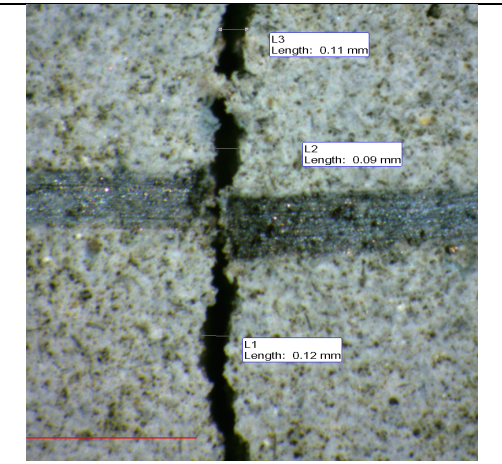
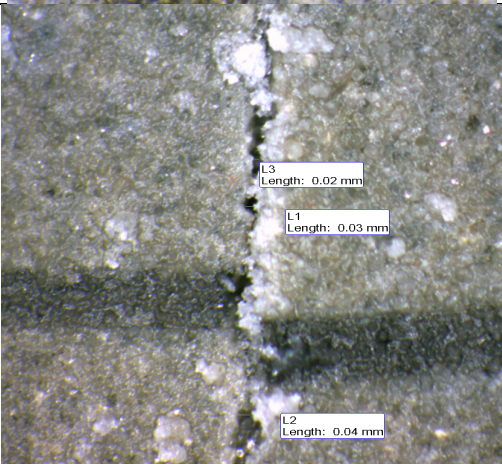
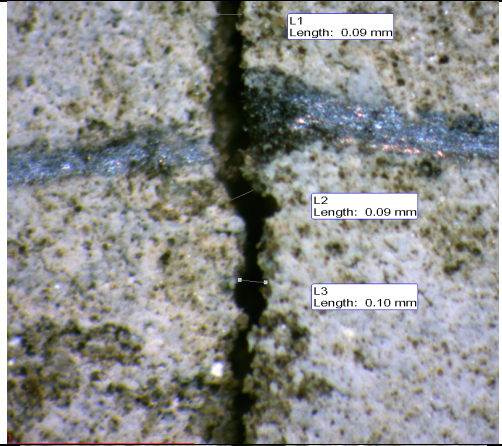
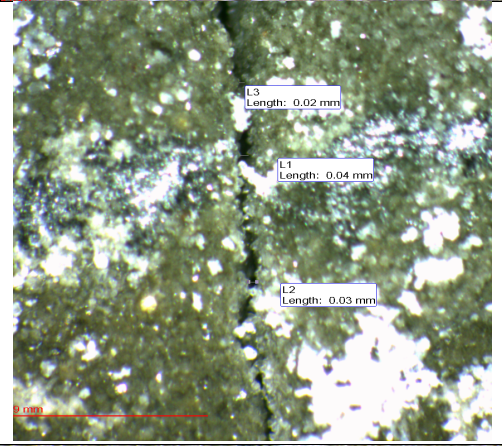
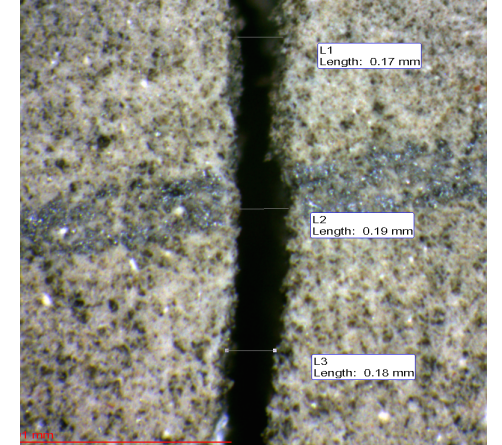
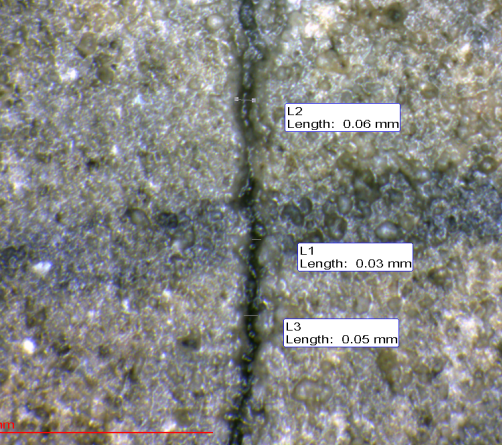
4.1.3 Image analysis with Digital Microscope

Image analysis was conducted to measure the change in crack width over time. This has been documented in Table 5. Images for these crack width calculations were taken of the bottom of the crack. Although not all samples exhibited self-healing through mechanical strength regain, every sample's crack width decreased as time past. Table 4 shows some digital microscope images of cracks.

Table 4: Digital microscope image of cracks on day 1 and day 15.

Mix	Image on Day 1	Image on Day 15
1		
2		
3		

4	 L2 Length: 0.13 mm L1 Length: 0.11 mm L4 Length: 0.10 mm L5 Length: 0.12 mm L6 Length: 0.11 mm	 Length: 0.06 mm L2 Length: 0.06 mm
5	 L1 Length: 0.05 mm L2 Length: 0.06 mm L4 Length: 0.05 mm L3 Length: 0.03 mm	 L2 Length: 0.04 mm L3 Length: 0.04 mm L1 Length: 0.03 mm
6	 L1 Length: 0.09 mm L2 Length: 0.07 mm L3 Length: 0.09 mm	 Length: 0.04 mm L2 Length: 0.04 mm L3 Length: 0.04 mm
7	 L1 Length: 0.13 mm L2 Length: 0.08 mm	 mm

8		
9		
10		
11		

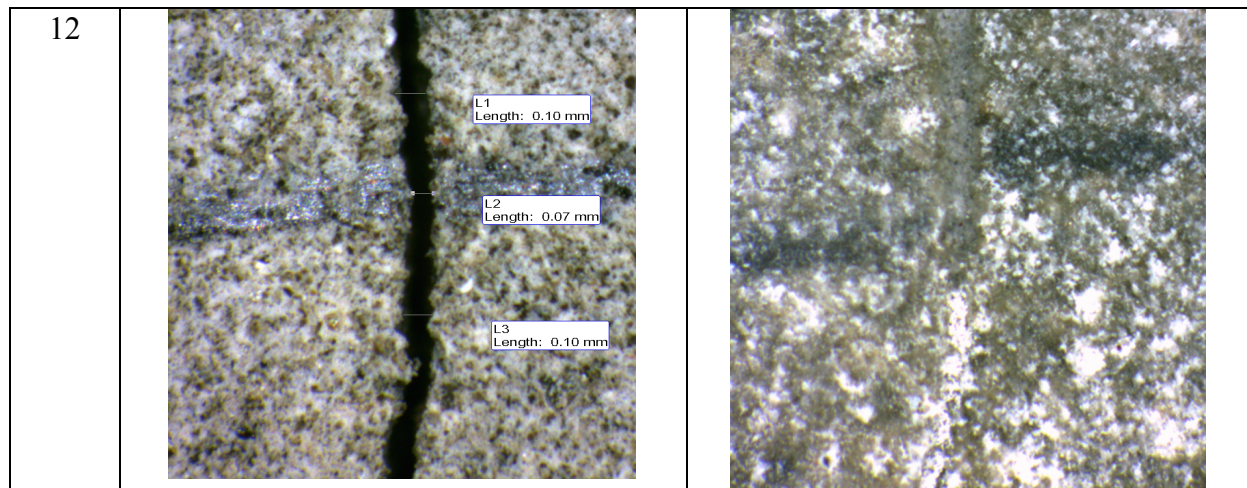


Table 5: Change in crack width over time.

Mix	Specimen	Average Crack Width (Homma et al.)	
		Day 1	Day 15
1	1	0.21	0.06
	2	0.2	0.13
	3	0.26	0.08
2	1	0.22	0.11
	2	0.25	0.08
	3	0.25	0
3	1	0.09	0.02
	2	0.07	0.01
	3	0.09	0.01
4	1	0.09	0.04
	2	0.11	0.06
	3	0.07	0.04
5	1	0.06	0
	2	0.06	0.02
	3	0.04	0.03
6	1	0.09	0.03
	2	0.07	0.04
	3	0.06	0.05
7	1	0.2	0.02
	2	0.13	0.02
	3	0.06	0
8	1	0.06	0
	2	0.06	0
	3	0.09	0
9	1	0.06	0
	2	0.06	0
	3	0.09	0

10	1	0.09	0
	2	0.11	0.03
	3	0.07	0
11	1	0.02	0
	2	0.18	0.04
	3	0.02	0
12	1	0.05	0
	2	0.09	0
	3	0.11	0.03

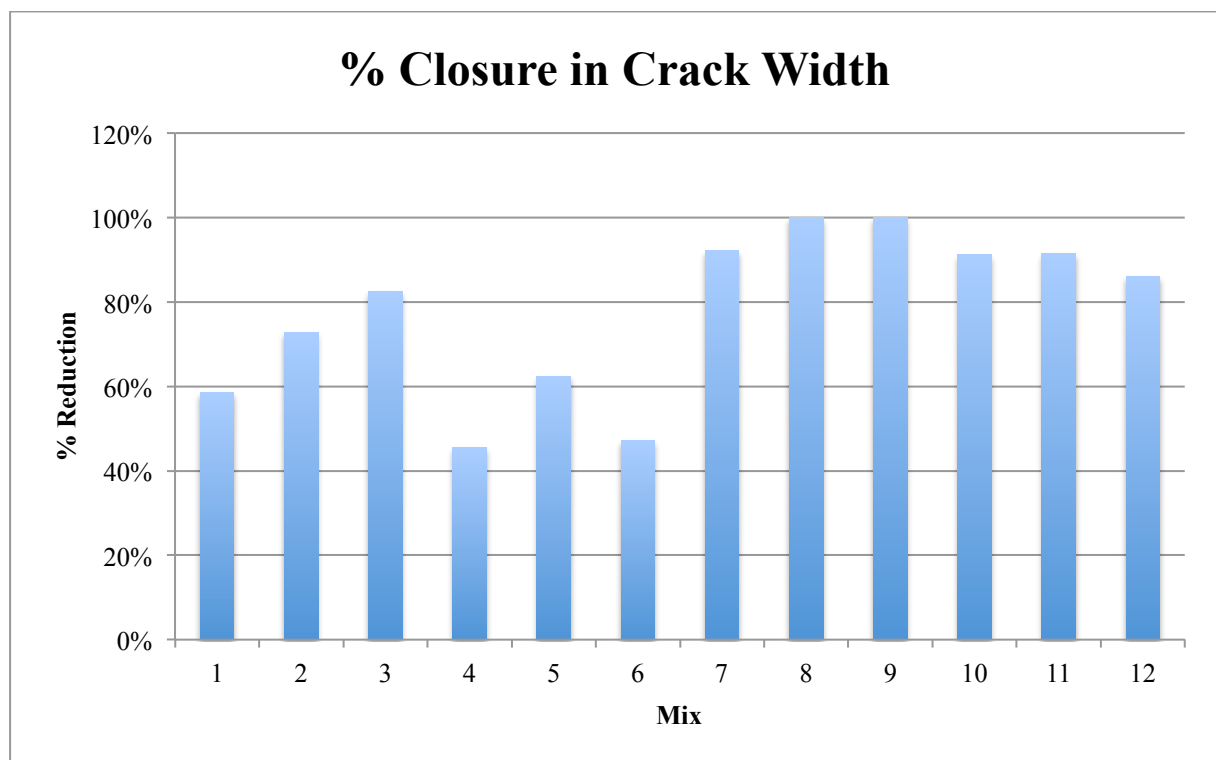


Figure 30: Closure of crack width over 14 days as a percentage.

Healing was found to occur in all the samples, but it was particularly effective for sealing cracks in cement pastes with MgO 92/200. In addition, a lower proportion of larger cracks healed. None of the cracks wider than 0.1 mm healed completely. Healing of the crack also seems to be independent of waterproofing in cements with MgO 92/200. On the other hand mixtures with MgO N50 seem to be affected by the waterproofing admixture as the samples with waterproofing healed less than those without it.

4.1.4 XRD

XRD tests were performed on the healing products in cracks in M5, M6, M9 and M10 to determine what hydration products were contributing towards the self-healing of the cement

pastes and to examine whether waterproofing affected the formation of certain products. The results of the XRD tests are shown below.

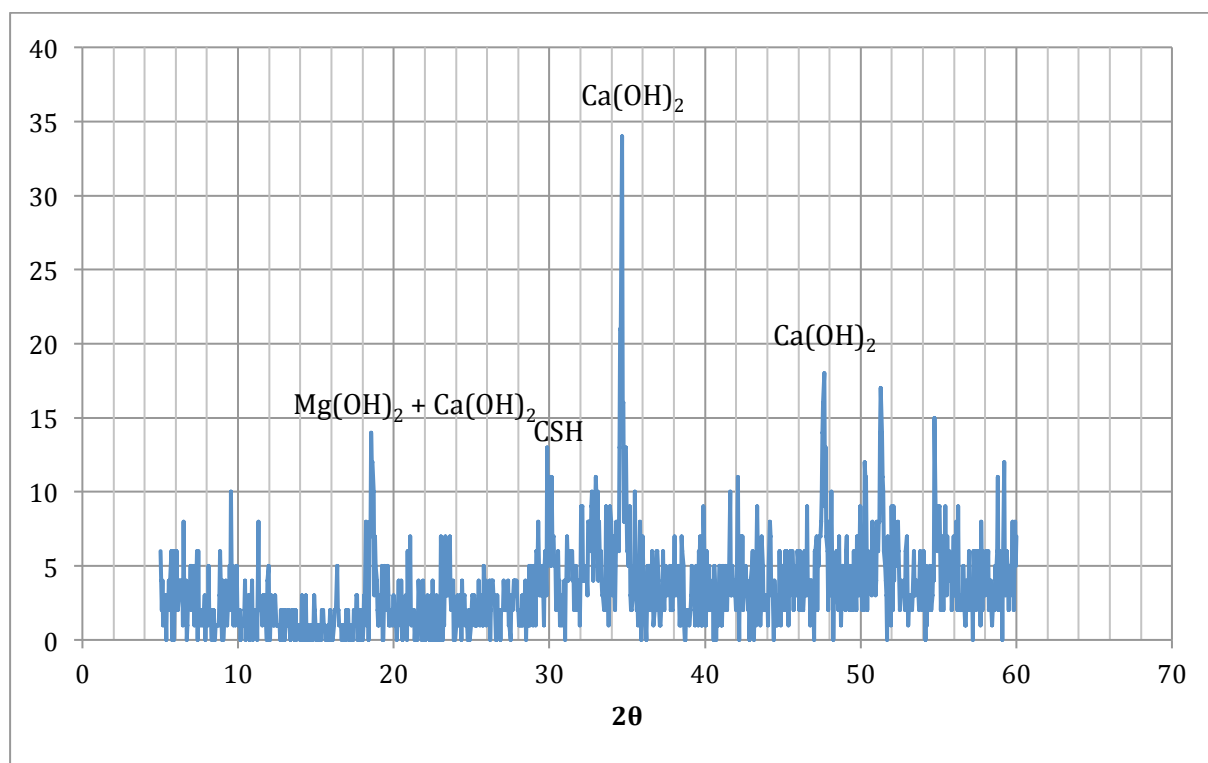


Figure 31: XRD result for M5.

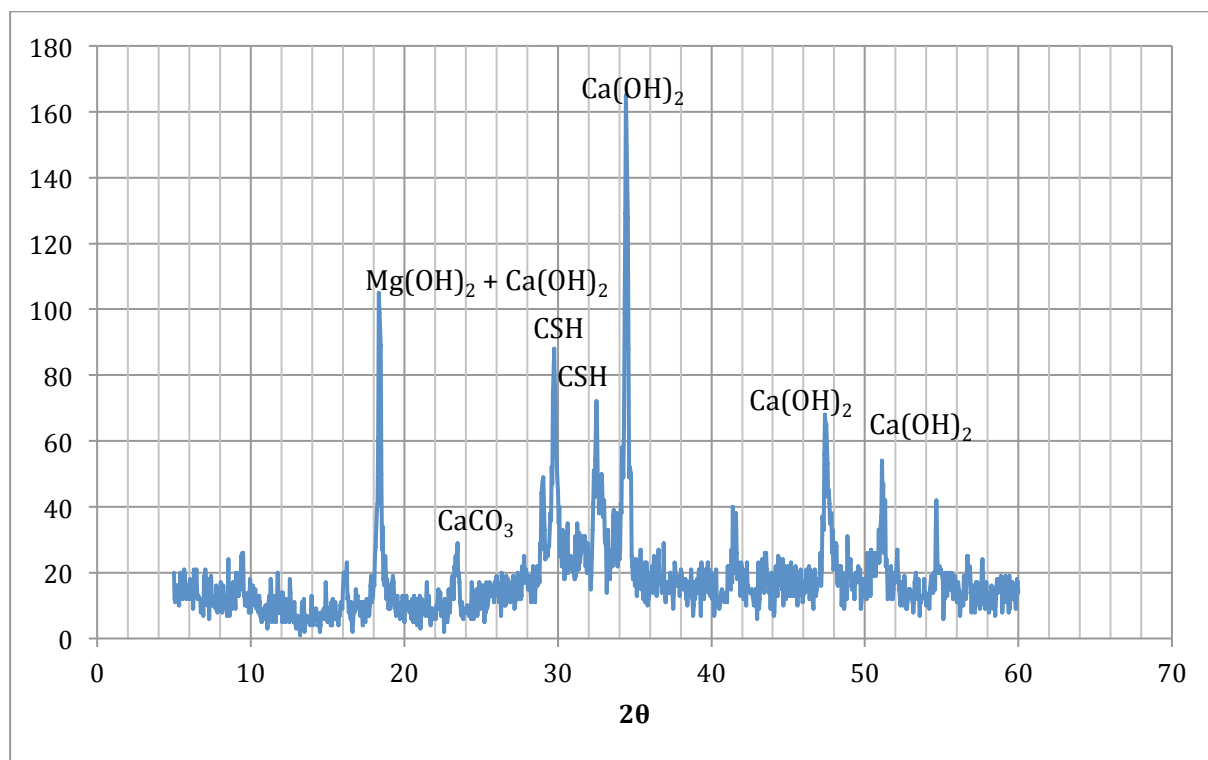


Figure 32: XRD result for M6.

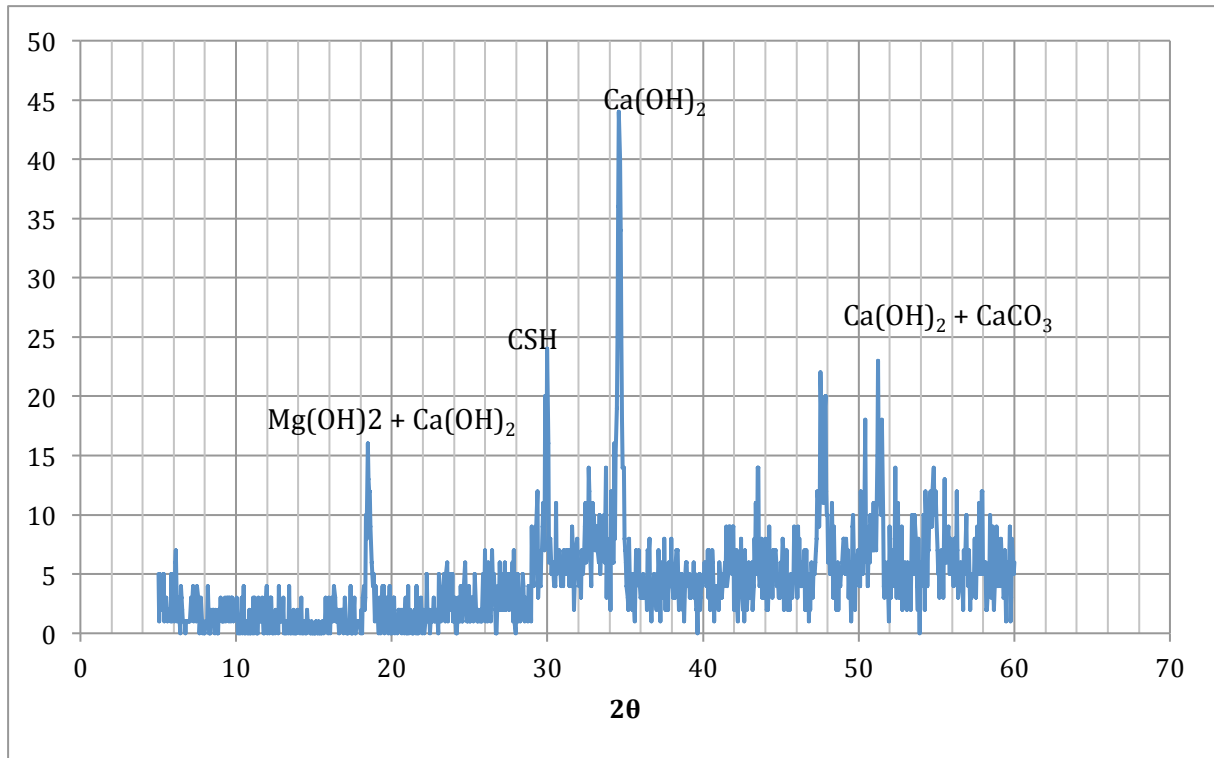


Figure 33: XRD result for M9.

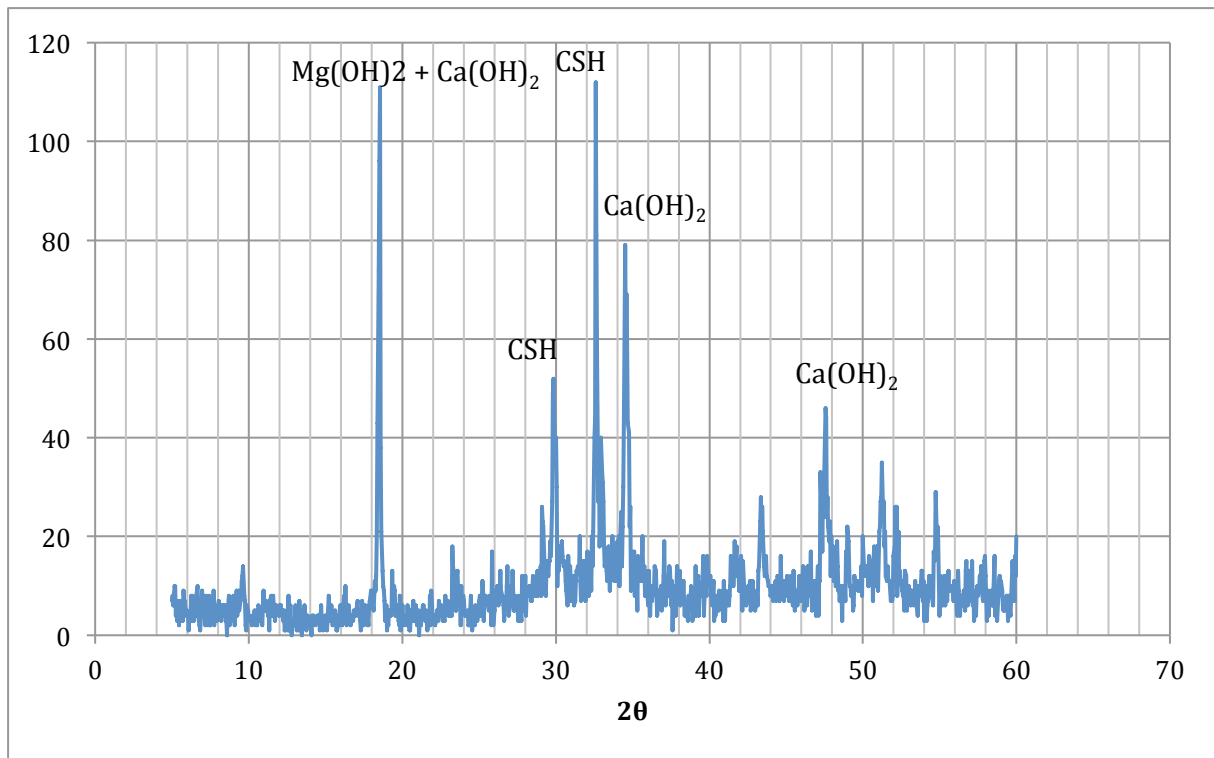


Figure 34: XRD result for M10.

The results of the XRD tests show that the healing products collected mainly consist of two chemicals, portlandite and CSH, but there is also some brucite as a result of the presence of MgO in the mixes.

4.2 Discussion

In the previously mentioned tests, the addition of waterproofing admixtures to the cement paste mix has not been found to negatively affect the self-healing potential of these cement pastes. The presence of waterproofing additives did not affect the cement mixture's ability to close cracks greatly. There was a small reduction in the percentage of the crack that was healed during the image analysis. However, in the case of mechanical strength, three-point bend tests showed that some mixtures of waterproofing additives and MgO increased the amount of strength recovered during curing. In some of these cases it was identified that the cracks had not even closed fully by the time the samples were exhibiting their recoveries. This could perhaps relate to the fact that if the crack is still open then more water can flow into the crack and hydrate unhydrated cement and MgO particles, whereas if the crack is closed quickly, the sealing of the crack could block off particles of cement from water that could potentially hydrate it and increase the cement structure's strength.

These experiments were carried out in ideal curing conditions where the damaged cement blocks were subject to water tanks, and this will have helped the cement hydrate with waterproofers in their mix. In the real world, if concrete or cement was not subject to hydrostatic pressure for a prolonged period of time, moisture may not be able to penetrate it and its particles may not be able to hydrate quite as freely. Further research would need to be conducted to see if this has any value for real world application.

The results of the XRD tests indicate that there is no remarkable difference between the self-healing products produced in cement with and without waterproofing. Both contain portlandite, CSH and brucite. It is thought that the presence of brucite enhances the self-healing of cement in two different ways. Firstly as an expansive agent it helps with self-healing, and secondly, the formation of brucite delays the hydration of cement particles around it, and therefore more un-hydrated cement particles are available to hydrate and improve self-healing.

5. Conclusions

5.1 Conclusions

Waterproofing admixtures and admixtures that enhance the autogenous self-healing of concrete are two extremely important components in the design of a durable, good quality structure. As such it is vital that they do not interfere with each other when they are a part of the same structure. During the course of this project cement pastes, which include waterproofing admixtures and mineral additives that enhance the autogenous self-healing of concrete have been investigated. From the research and the experimental work, the main findings are that:

- The main mechanisms by which waterproofing admixtures work is by reducing the amount and the size of pores by decreasing the water/cement ratio required for a workable mix, by using hydrophobers and by using pore-blocking additives.
- Cement has an intrinsic autogenous self-healing ability, which can be enhanced by the addition of mineral additives.
- When combined with MgO, which is used as a mineral admixture to improve the self-healing of concrete, waterproofing admixtures do not affect the concrete's self-healing abilities when cured under ideal conditions.
- MgO N50 cement mixes exhibit the most mechanical strength recovery with waterproofing additives.

5.2 Further Work

Although this project is now over, a large number of possible future directions are available to those who wish to further the study of self-healing concrete with waterproofing additives. Had there been more time, it may have been useful to conduct experiments inducing cracks in concrete that have been aged and observing the effects of self-healing and waterproofing on the specimens. Another option is the use of different additives to enhance the self-healing of concrete, such as blast furnace slag and fly ash. In a world where citizens are becoming more and more environmentally conscious, using these waste products to develop durable structures would be of great benefit.

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Appendix

Safety Retrospective

I think that the risk assessment that was conducted at the beginning of this academic year that considered the dangers of working in the geotechnical laboratory was very accurate. One of the main health and safety risks that was identified was the need to wear a safety mask to avoid inhaling the dust from cement and magnesium oxide powder. I also worked with potentially hazardous equipment, such as the high-powered food mixer and the instron machine and was aware that I needed to act with extra care and attention when doing so.