Corrosion of Steel Fibre Reinforced Mortars - A Microstructural Investigation

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Principal Supervisor: **Dr Ali Nazari**

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A thesis submitted for

Masters of Engineering

Centre for Sustainable Infrastructure

Faculty of Science, Engineering and Technology

Swinburne University of Technology

Australia

Declaration

I hereby declare this thesis to be entirely my own work with relevant attribution to the work of others according to University guidelines

A.N.

Brian Lynch February 2018

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The prospect of undertaking postgraduate studies almost a quarter of a century after completing my undergraduate degree initially filled me with dread. It was, however, the right decision and that change of heart was influenced by exposure to the co-founders of a concrete technology company with whom I worked prior to undertaking my Masters. I am grateful to Jean Desfosses and Aaron Williams, of Descrete, for introducing me to the world of concrete research. I settled in to my studies at Swinburne University remarkably easily with the assistance of Professor Jay Sanjayan and was given wonderful support by my family throughout my candidature. The centrepiece analytical tool used in this project, the optical microscope, was obtained through a research grant I worked on with Yeanette Lizama. Her effort in ensuring a top class microscope was available made a huge difference to the success of this project. The journey to completion was facilitated by my principal supervisor, Dr Ali Nazari, and my associate supervisor, Associate Professor Scott Wade. I am grateful for their encouragement and guidance.

ABSTRACT

Steel fibre reinforced mortars and concrete are growing in demand as specialised applications evolve in both civil and construction fields. Evaluation of steel fibre reinforced mortars where common cementitious binder types are compared directly with geopolymer (the most researched cement alternative) has been strangely absent from the research literature**. In the current study, the first of its kind so far as can be ascertained, samples made with three binders of ordinary Portland cement, a blended cement with 30% fly ash and geopolymer are directly compared when immersed in a corrosive environment of aerated seawater for 6 months.** Changes in electrical resistivity are used as an indicator of corrosion resistance differences between the materials while physical corrosion changes are tracked by degradation of fibres on polished specimens removed from immersion at regular intervals. Microstructural data is collected by permeability, pore and void analyses while micrographs from an optical microscope are used to track changes in the microstructure of each material, namely the paste, over the period of immersion**. Electrical resistivity data, corrosion analyses and the microstructural data suggests there are similarities between the cementitious mortars and that they are quite distinctly different from the geopolymer mortar. Microscopy of the paste in each material over time, however, suggests that the blended cement mortar has more in common with the geopolymer than the standard cement mortar.**

Keywords: Concrete; mortar; geopolymer; fly ash; blended cement; water-cement ratio; electrical resistivity; pitting; optical microscopy; 3D profiling; pores; voids; permeability.

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Chapter 1

Introduction

1.1 Introduction

Concrete has a long history with its origins often traced back to Roman times [2,3]. The modern concrete industry took shape with the invention of ordinary Portland cement (OPC). Widespread usage of OPC coincided with the early stages of the Industrial Revolution in Britain [4]. As the rate of building and construction accelerated at this time, engineers looked for a suitable product to replace traditional masonry and timber construction. The composite of OPC, aggregates and water produced such a product – concrete. Standards and specifications were beginning to take shape by the middle of the nineteenth century. As the Industrial Revolution spread to other parts of the world, so too did the technology of concrete based on OPC. Throughout the twentieth century different types of cement, the evolution of admixtures and the science of reinforcement enabled concrete to be used in almost any construction application imaginable [7]. Its versatility has ensured it maintains a dominance in construction today.

Mortars are a variation of concrete where the large aggregates a[i]re removed, leaving just the smaller aggregates and the paste to form the body of the product [4]. It is more of a niche and specialty product in the construction industry. There is, however, a trend towards high strength concretes where the aggregate size is being reduced to radically alter the rheology to enable self-compaction for instance [7]. These types of concretes are essentially mortars. Therefore, it is quite feasible that the proportion of cementitious materials in the construction market in future compromising different types of mortars may steadily increase.

Concrete is mostly used in conjunction with steel reinforcement [4]. On its own, the hardened mixture of binder and aggregates performs well in compression but can fail in tension or flexure if subjected to significant loading. To overcome this problem, reinforcement is added to concrete so that when it is exposed to either exogenous or endogenous forces the extent of cracking and crack propagation will be curtailed by the reinforcement. This phenomenon has enabled the use of reinforced concrete and mortars in applications that would be well beyond the scope of unreinforced concrete or mortar [3]. While other materials are used to reinforce concrete, by far and away the most common material is steel, predominantly mild steel.

The most common form of steel reinforcement is known as rebar (reinforcement bars) on its own or in combination with steel mesh.

Figure 1. 1: Concrete poured over steel reinforcement (American Concrete Institute)

Figure 1. 2: Typical distribution of steel fibres when concrete fractures (ACI)

Large slabs and precast structural members can be cast with this type of reinforcement (see Figure 1.1). Fibre reinforcement of concrete and mortar (see Figure 1.2) has been used for many decades with its use increasing over this time. It is now viewed as a viable alternative to rebar in many applications such as shotcrete, tunnel linings and complex precast structural elements [1].

The use of steel reinforcement immediately creates a long-term problem of potential corrosion of the steel as the concrete degrades. As it is impossible to create completely impervious concrete, the steel can come under attack either by chloride ingress or carbonation, particularly as cracks propagate over time. How long this attack can be held at bay is influenced by many factors including the type of concrete used [2]. It is this issue that figures most prominently in the current study. By keeping aggregates and water content consistent across all samples and avoiding the use of admixtures it is feasible to analyse the effect of binder type as the main factor affecting the performance of mortars in a corrosive environment.

The corrosion and failure of rebar is naturally of significant concern to engineers and has been studied extensively [2,3,4]. However, the investigation of the corrosion behaviour of steel fibres has merits as well. Ultimately it is the performance of the matrix that matters most as the types of steel reinforcement have become standardised, or at least commonplace, in most structural applications. The study of fibres incorporated into the matrix in comparison to a fibre-free matrix will lead to a more integrated approach where all manner of formulations will be used in the future. This includes the comparative study of fibre-reinforced mortars and concretes based on different binder systems such as the current study.

Figure 1. 3: Typical view of corrosion of steel reinforcement (spalling) in concrete (ACI)

In Broomfield's book [2] the main ways to prevent or minimise corrosion of steel reinforcement in concrete are given as;

(a) Increase cover over reinforcement
(b) Decrease water/ cementitious ratio
(c) Ground granulated blast furnace slag, microsilica, fly ash
(d) Corrosion inhibitors
(e) Coatings and penetrating sealers
(f) Membranes and barriers
(g) Fibre reinforced polymer reinforcement
(h) Stainless steel reinforcement
(i) Cathodic prevention
(j) Epoxy coated reinforcement
(k) Galvanised reinforcement

Of all of these factors, the first three have received the greatest attention in research and are still the most practical steps taken in the field. Cathodic protection is also gaining wider acceptance, particularly on large civil projects. With steel fibre reinforced concrete or mortar the issue of cover of the reinforcement is naturally not a consideration as the random distribution of fibres in the matrix means there will always be fibres near or at the surface [1]. The other two key factors, water/cement ratio and the use of mineral admixtures, certainly are relevant though and are major factors in the current study.

Certain assumptions are made about the expected life span of structures based on how susceptible they are to degradation [4]. While there are other major forms of degradation such as carbonation and alkali silica reaction, the visible sign of corrosion in concrete is spalling (Figure 1.3). It is the most common problem facing many asset owners. Despite the improvement in the research and knowledge base behind corrosion in concrete, most engineers have relied on a handful of methods to monitor the problem. The current study is an attempt to encourage those involved in the concrete industry to embrace new methods.

The study of microstructural changes in concrete would normally be associated with petrography. The techniques and approach being adopted in the current project aim to put a different perspective to what these changes mean in a particular scenario and then draw broader conclusions. While the methodology is certainly not classical petrography, the intent is analogous. A typical cross-section of a corroded concrete rebar sample is given in Figure 1.4.

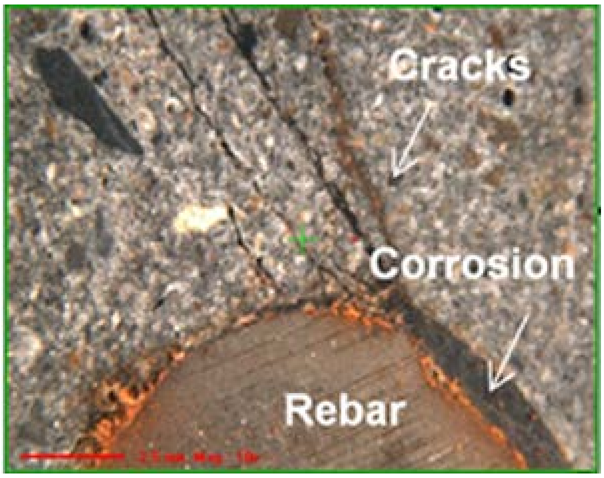


Figure 1. 4: Optical micrograph showing corrosion and cracking around rebar in a concrete matrix (www.asce.org)

1.2 Concrete

At its essence concrete is a relatively simple material. The raw materials can be assembled easily with only the manufacture of cement that has anything more than rudimentary processing. It can be batched, mixed and fabricated in a variety of ways. It is cost effective when compared with feasible alternatives and is the most common manufactured material on the planet [3].

While producing concrete is based on a simple premise, it has become a very sophisticated product with many permutations [2]. Mix designs have evolved taking into account developments such as the move away from natural aggregates, the increased usage of mineral admixtures and the development of more sophisticated chemical admixtures. All of these aspects are ongoing areas for research but the current study is concerned primarily with the effect of binder types.

One hydraulic binder has been largely responsible for the modern concrete industry. By calcining clay and limestone together, a raw product (clinker) is then ground finely with the addition of gypsum and other additives. The resulting product is known as ordinary Portland cement (OPC). When OPC reacts with water it hardens and enables concrete and mortars to be used in a range of applications – concrete being the name given to the final product when a combination of fine and coarse aggregates are used while a mortar refers to a product where only fine aggregates are used. It is inconceivable that the dominance and ubiquity of concrete today would have occurred without OPC. While at times alternatives such as calcium aluminate cements [3], Sorel cements and supersulphated cements have found favour in various places, they have never come close to the prevalence of OPC. Consequently, most concrete research projects use OPC as the control or baseline. That is the case in the current project as well.

Blended cements have been used regularly and extensively for a long time but we are only now seeing long-term studies showing just how beneficial they can be [3]. Adding mineral admixtures such as fly ash, slag and silica fume to OPC to create a blend has many beneficial outcomes – they are generally cheaper, give better rheological properties, minimise the heat of hydration and control shrinkage thereby enabling larger pours. Best of all, they produce more durable concretes [5].

As mentioned earlier, there have been a number of different cements and binders used over time that are not based on the clinker route of OPC. They generally are still referred to as cements though. The main area of research interest into non-cement binders over the past few decades has been geopolymer. Geopolymer is the term commonly used to cover a range of alkali-activated aluminosilicates that have been used as cement-free binders [6]. In the current project, an activator comprising caustic soda (sodium hydroxide) and water glass (sodium silicate) is combined with fly ash. This formulation is used to create a natural transition from the OPC control to a blended cement with fly ash to a cement-free binder (geopolymer) with fly ash as the aluminosilicate backbone.

With the advent of geopolymer technology, concrete technologists are continuing the tradition of constantly seeking alternatives to OPC. Whereas once it was the concerns about OPC's long term stability and suitability for certain applications that drove the quest for alternatives, it is now as much a quest to produce more sustainable binders with superior properties [7].

1.2.1 Mineral Admixtures

Mineral admixtures refer to a range of materials such as fly ash, slag, silica fume and metakaolin. Estimates vary on the total availability and usage of each of these materials but they can be roughly split into two categories – high volume and low volume. The first two materials, fly ash and slag, are classified as high volume as they are by-products of large-scale activities. Fly ash comes from the burning of coal for power generation and slag is a by-product of steel production. Those two activities have been a cornerstone of the industrial age. Silica fume, on the other hand, comes from the production of silicon or ferro-silicon alloys and is produced in far smaller volumes while metakaolin is processed for purpose from kaolin source material. Consequently, the concrete industry and concrete researchers have focussed a lot more time and energy into fly ash and slag [2].

For the current study, fly ash was selected for two reasons;

(1) The blended cement formulation of 30% fly ash is very common in the Melbourne pre-mix market so when mix designs were being considered it was easier to duplicate this design

(2) Geopolymer research in Australia is often based on fly ash, specifically a grade from the Gladstone power station in Queensland

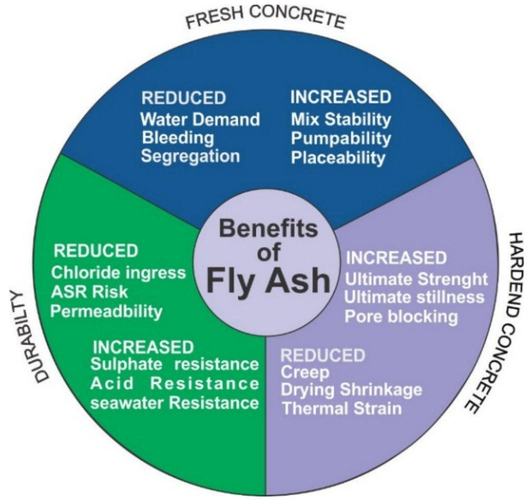


Figure 1. 5: Overview of the benefits of using fly ash in concrete (ADAA)

Fly ash is a pozzolanic material that will combine with lime (calcium oxide) and water to form cementitious hydrated compounds. In a blended cement, such as the 70% OPC (ordinary Portland cement) and 30% FA (Fly Ash) used in the current project, the free lime that is always present in any cement combines with the fly ash to provide additional phases that reduce the permeability of the matrix [5]. This continues as long as there is sufficient moisture in a process known as self-desiccation. The reduced permeability leads to smaller pores in the matrix as well. This in turns means there is less likelihood of pore solution moisture allowing chloride ion diffusion. Without these pathways it becomes harder for chloride ingress to take place deep into the concrete structure where it can attack the rebar or other steel reinforcement [8]. A summary of the benefits of fly ash usage in concrete and mortars is given in Figure 1.5.

1.2.2 Water-Cement Ratio

The equilibrium between the amount of cementitious material, the nature of the matrix and the amount of available water is a key factor in cement and concrete chemistry [9]. It is important that the process of hydration be facilitated but controlled to give the best results. This is why the water-cement (W/C) ratio is such a critical consideration for producing durable concrete. There must be sufficient water to impart a workable rheology to the mix but not too much so as to retard the setting and strength development. The long term effect of getting this ratio right is played out in the pore solution where pores steadily close with age based on reactions involving amorphous silica, free lime and hydrated silicate and aluminate phases all competing for pore solution water. This densification process will prevent the ingress of chlorides and carbon dioxide in a truly durable concrete.

In one key study [10] it was suggested that the chloride to ion ratio was of relatively little importance when compared to the impact of W/C when it came to corrosion protection. The authors showed that corrosion could be contained at a W/C of 0.45 when the pore fluid chloride/ hydroxyl ratio was very high.

While research in recent decades has suggested that both W/C ratio and the type of cement are both important in determining how corrosion resistant a concrete or mortar will be, one of the earliest landmark studies on chloride ingress [11] suggested it was only the latter that plays a part in the long run. In that study OPC and various blended cements (with slag) at different W/C ratios were compared in both a marine environment and a simulated environment. The samples they prepared did not have any steel reinforcement as they just measured chloride penetration.

In the current study two different W/C ratios are used for the two cementitious mortars so that an analysis can be conducted on the differences in corrosion behaviour as related primarily to electrical resistivity changes over the period of immersion in aerated seawater.

1.2.3 Geopolymer

While research into steel corrosion in cement-based concrete has a long history, the same cannot be said for geopolymer concrete. Just over a decade ago, in 2005, authors of a paper stated it “reports the first experimental data available on the subject, comparing corrosion resistance in a Portland cement mortar to the resistance found in two activated fly ash cement mortars" [12]. The mortars referred to here fall under the category of geopolymer. Corrosion resistance was primarily measured by electrochemical corrosion potential and polarisation resistance but reference was also made to changes in microstructure. Their interpretation of microstructural changes is similar to many other geopolymer researchers in that it relates to changes in morphology of fly ash when activated with an alkali source. They did not study the matrix as a whole and the interaction with the embedded steel. The authors concluded that the matrix and pore solution of the geopolymer mortars were sufficiently alkaline to passivate the steel and thereby offer at least equivalent protection to cement-based matrices.

Another study suggests there is a reserve of alkali content in the geopolymer pore solution but the absence of calcium compounds may be a cause for long-term concern and potential depassivation [13]. The paucity of data and information on the behaviour of the geopolymer matrix in the presence of steel reinforcement adds further weight to the need for an investigation such as this one where a geopolymer formulation is compared directly with cementitious ones.

Cement hardens when calcium silicate hydrate forms over time by the reaction of water with the calcium silicate phases in cement, predominantly the alite phase (calcium trisilicate). In tandem, phase transitions occur when the aluminate minerals hydrate in the presence of calcium sulphate (gypsum and other polymorphs). The phase changes of the two systems occur in tandem and have quite different outcomes on the eventual makeup of the matrix over time [4]. While the development of hydrated silicate phases always has beneficial outcomes, the same cannot be said for the hydrated aluminate phases. One phase in particular, ettringite, can be quite deleterious if it develops at the wrong time causing an unwanted expansion to the matrix to become a potential cause of failure of mortars and concrete.

Geopolymers harden by a very different mechanism to cement. Rather than forming discrete hydrated phases, a series of amorphous phases condense along the aluminosilicate backbone to form continuous combinations of sialate and siloxo compounds. Consequently, the curing profile of geopolymers is also quite markedly different with these compounds, rather than phases, forming early and the structure achieving stability and equilibrium at an early stage [6]. While cement hydration evolves over time and can continue to proceed in some form for years in many cases, geopolymers are designed to complete their principal reactions within the first few days of fabrication.

The genesis of geopolymer research is generally acknowledged as the work done by Davidovits in the 1970s [6] and the creation of the Geopolymer Institute thereafter. In the ensuing period, many researchers have looked at a range of formulations where the aluminosilicate backbone can be slag, fly ash or calcined clay for instance and the alkali activator can be any number of reagents based either on sodium or potassium. The fundamental principle of assessing the performance of a cement-free binder as an alternative to cement has driven this work with a view to building a database of performance of these alternatives.

Two problems have arisen over the course of geopolymer research;

(a) very few longitudinal large scale studies of geopolymer structures due to a lack of commercial applications
(b) the slow adoption and adaptation of standards to replicate those in place for cement and cement-based concrete

There is some long term evaluation of geopolymer structures in situ at certain locations in Australia for instance [14] and a few committees looking at standards through bodies such as RILEM but it would be fair to say much work is needed to fully alleviate the concerns held by many in regards to these two issues.

1.3 Corrosion of Reinforced Concrete

Reinforced concrete is a structural material of such importance that engineers must constantly be exploring new ways to protect its integrity. Rebar corrosion can proceed rapidly in some instances once it has been initiated and is then propagated to potential failure (Figure 1.6).

Once corrosion commences it is normally only a matter of time before some repairs will be required. Understanding all aspects of the corrosion cycle and how it impacts steel in any form inside a concrete matrix is valuable information as we constantly seek to achieve the most durable materials.

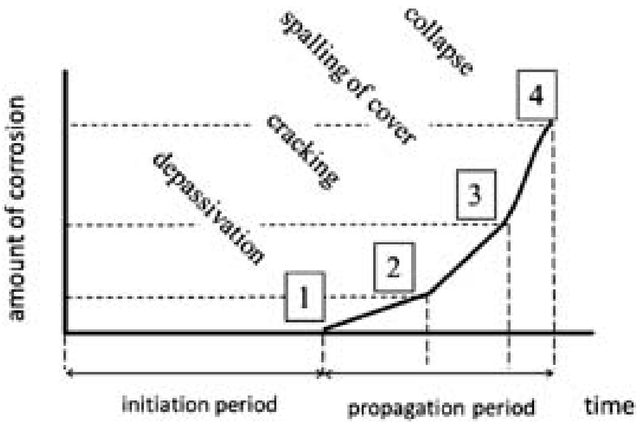


Figure 1. 6: Typical timeline of corrosion development of steel reinforcement in concrete [2]

One of the foundation maxims of reinforced concrete is that chloride attack must be prevented to ensure longevity. However, what concentration of chlorides will do what level of damage to a concrete with a certain mix design and certain reinforcement remains keenly contested.

A review of the literature in 2009 [15] on the effect of chloride content in reinforced concrete contained some interesting observations related to the current project. Under 'Binder Type' they commented "The type of binder influences corrosion initiation by determining the amount of chloride that is available in the pore solution as a result of chloride binding and by affecting the pH of the pore solution. Moreover, certain binders might increase the electrical resistivity of the concrete or improve the characteristics of the steel–concrete interface by forming a denser microstructure." They also stated in their concluding remarks "Regarding reinforcement corrosion, the behaviour of silica fume, fly ash and slag, but also many other upcoming cementing materials, is completely unknown"

A researcher from the University of Newcastle [16] reviewed case studies of various reinforced concrete structures and determined that there was no direct correlation to chloride content and corrosion rates. It was observed that non-reactive aggregates and the use of slag-cement considerably slowed the rate of corrosion but no definitive conclusions were drawn from this analysis.

In another paper [17], the authors looked at a range of cement types in mortars that were exposed to a marine environment for a period of two years. As the length of time of exposure was longer than most studies it is interesting to note the key findings of cements containing silica fume and slag performing better, in terms of corrosion resistance, than those containing fly ash but all three with superior results to OPC.

It can be stated that the most destructive problem (corrosion) in the most common material on the planet (concrete) is still open to conjecture when viewed from the perspective of the key component (binder). This is a great challenge and a key driver for further concrete research.

1.3.1 Techniques for Evaluating Corrosion

There are two main causes of corrosion – carbonation and chloride ingress. Rather than measure corrosion directly via weight loss or pitting, the parameter most often evaluated is chloride ingress and/or chloride permeability. Equally, with corrosion caused by carbonation the most common test is a simple phenolphthalein indicator test to indicate the depth of carbonation rather than attempting to quantify the amount of carbonate directly.

The mechanism of corrosion studied in the current project is chloride ingress. Exposing the samples to aerated seawater exacerbates the degree of chloride ingress and allows a more meaningful comparison between the different materials on their ability to prevent chloride ingress and thereby reduce the impact of corrosion of the steel fibres. Chloride ions are mobile and will diffuse through the matrix in the presence of moisture. The ratio of chloride ions to hydroxyl ions has been found to be a good indicator of the onset of corrosion [18]. It lowers the pH and depassivates the steel making it easier for localised galvanic cells to form and corrosion to commence.

The test methods for measuring chlorides vary from short-term tests such as Rapid Chloride Permeability Test and electrical resistivity to longer term tests such as bulk diffusion (Nordtest) and salt ponding. Chloride levels are often quoted as a percentage of the cement paste and less so as a ratio in comparison to the hydroxyl ion concentration [4]. To obtain a true picture of corrosion resistance in blended cements, the latter approach is more suitable. Hydroxyl ion concentration is generally lower in matrices with blended cements as the mineral admixture reacts with the alkalis in the pore solution and subsequently takes up more hydroxyl ions into the new phases formed in the pores.

Pitting is the main type of corrosion seen in reinforced concrete and mortars for the simple reason that the high pH of the matrix is a natural passivating environment of the steel – usually mild steel – and is thereby prone to localised attack when chloride ions reach a certain concentration. This highly localised, aggressive environment creates a galvanic cell that allows pits to form on the surface of the steel.

The two factors that are most quoted as being the best ways to mitigate the ingress of chloride ions and thereby reduce rebar corrosion are [19]:

(1) Use of mineral admixtures
(2) Lowering the water-to-binder ratio

1.3.2 Electrical Resistivity

A method that takes into consideration the heterogeneity of the material as well as the random orientation of the fibres is electrical resistivity (ER). There are two aspects to consider with ER – the property itself and its relevance.

Electrical resistivity is perfectly suited to concrete and mortar research. It can be measured readily in the laboratory as well as in the field. It takes into account a series of material properties such as porosity, permeability, diffusivity, conductivity and bulk electrical resistance [20]. As it is inherently difficult to ascertain the exact mechanisms of microstructural changes and transport properties within cementitious materials, having a robust analytical method for detecting changes over time is very welcome. While equating a particular ER profile to a corrosion rate is problematic, the same can be said for chloride levels as well.

One researcher [21] reported on work that has been conducted by a RILEM technical committee in comparing different ‘corrosion testing methods’ based on trueness, precision, relevance and convenience and found that ER is as reliable and robust as any other method.

Andrade et al. [22] conducted a thorough comparison of the different techniques for evaluating corrosion and concluded that ER should be used widely in determining the durability of concrete structures. It captures the role of the different pore types and effect of pore solution during the initiation of corrosion stage and also reflects the changing chemical nature of the matrix when corrosion propagation occurs. When Andrade and her team assessed results from all of the available methods in the literature, the analysis showed that ER gave a very good predictor and indicator of the likely onset of corrosion in steel reinforced concrete.

While the figures will vary according to the constituent materials, type of reinforcement and the exposed environment there is a general rule for anticipating the initiation of corrosion based on Table 1.1 guidelines.

Table 1. 1: Relationship of electrical resistivity to expected corrosion rate [2]

Resistivity (kΩ-cm)	Corrosion Rate
Less than 5	Very High
5 – 10	High
10 – 20	Moderate
Above 20	Low

These assumptions naturally must be challenged by detailed analyses of the corrosion rates to determine if any correlation exists [3]. Rebar techniques such as weight loss and half-cell potentials are not suited to fibre reinforcement, so the materials in the current study are analysed for microstructural changes instead. Discrete fibres are assessed for pitting and the fibre-matrix interface observed for changes to determine whether extended exposure to an aggressive environment has caused each of the materials to behave differently and thereby affect the rate of corrosion of the fibres.

1.3.3 Fibre Reinforcement of Concrete and Mortars

In a publication produced by the Concrete Institute of Australia [1] some key points about the purpose of fibres were made. It was noted that fibres "have the effect of controlling the growth and propagation of micro cracks and eventually macro cracks" and their effectiveness is naturally assessed by comparing the properties of reinforced and unreinforced materials. Specifically, they note that fibres will constrain the onset of minor cracks but at the point where macro cracks appear they serve a second function of bridging those cracks to “apply a restraining tension across the crack, an action akin to that of conventional reinforcement”. It is this final statement that ensures the viability of fibre reinforcement as an alternative for conventional rebar reinforcement. Engineers can specify fibre reinforcement for particular applications where fibre offers advantages over rebar knowing that structural considerations will not be compromised. Naturally, it will always be dependent on the application ultimately.

There is a history of certain fibre types becoming very popular at different points in time such as glass, polypropylene, polyvinyl acetate and even natural fibres such as hemp and cellulose. In general, most fibre types impart some critical properties to the matrix such as reduced permeability and reduced plastic shrinkage. In the end, fibres are viewed favourably by many engineers because they provide the flexural or tensile strength or improvement in elasticity to meet a certain specification and can achieve this with a material that can be batched in one plant and fabricated in situ if necessary. This is the case regardless of the material used to make the fibres [3].

If the usage of fibres is to continue to grow all aspects of their performance will need to be scrutinised and researched. It is understandable the mechanical properties are the focus of much of this work. However, if the durability of fibre-reinforced materials is to be viewed in the same light as traditional reinforced concrete the long-term effect of corrosion and general degradation will also have to be understood as comprehensively as possible [4].

Reinforcement with steel fibres will produce a very different outcome to that with rebar. The random, discontiguous nature of the fibres results in fibre orientation patterns that vary with the rheology of the mortar or concrete. The non-Newtonian shear thickening nature of these materials means they can be quite sensitive to the nature of the fibre added (material composition and shape) and the concentration of fibres [23].

This aspect of fibre reinforced materials was considered at the outset of the current study and was a key reason why only one fibre addition rate was considered and why it was set at the lower end of the recommended range.

1.4 Summary of Work on Corrosion of Steel Fibre Reinforced Mortars

When steel fibres corrode it will not induce structural failure in the way rebar corrosion does. However, by studying this phenomenon we will obtain insights into issues beyond corrosion that affect the durability of concrete and mortars. Focussing on microstructure allows the interaction of the matrix, voids, pores, moisture and fibres to be evaluated as a complete relationship. In addition, the differences between surface and bulk effects are easier to explain with this approach.

Regardless of where the fibres appear in the body of the material, they have a role to play in the physical and chemical properties of that body. Variations in corrosion are just a manifestation of this phenomenon. While the body may not fail due to ongoing corrosion of the fibres, it will be directly affected by the corrosion in other ways such as changes to the pore solution and ongoing phase development that occur as a result of self-desiccation [24].

The dosage rate of fibres is kept constant in all formulations in the current study. A previous study [25] looked at different dosage rates of steel fibres in ultra-high performance concretes and found that mechanical properties and durability were altered, but not dramatically, when the dosage rates varied. In regards to corrosion, or degradation as they termed it, they found that exposing these materials to varying chloride rates also had no dramatic or discernible effect on degradation.

Unlike the specification of a minimum concrete cover over rebar, the potential presence of steel fibres at the surface of a reinforced mortar opens one avenue for research – the nature of surface corrosion in these materials. Balouch et al. [26] studied surface corrosion of SFRC and noted that the “literature is mainly focused on corrosion arising from cracks. The only casual results that we could find about surface corrosion are side results reported from studies of corrosion inside the cracks”. They showed that the water-cement ratio needs to be below 0.50 and the fibres covered by at least 0.2mm of paste to avoid surface corrosion.

Fibre reinforcement performs several functions with one of the key ones being to bridge microcracks and prevent crack propagation. Prior to crack initiation the matrix properties and the steel-matrix interface determine the likelihood of chloride diffusion – a precursor to corrosion [27].

The common feature of both rebar reinforced and fibre-reinforced materials is that the steel-paste or steel-aggregate interface plays a key role in determining whether corrosion is likely to occur. The interfacial zone surrounding the steel must be above a threshold pH to maintain passivation of the steel [28]. If the pH drops too low the steel may become depassivated and prone to the onset of corrosion. Concrete and mortar matrices are alkaline and this enables steel reinforcement to be placed inside these matrices in a protective environment. Over time the alkalinity of matrices can be affected by the types of hydration products and this will vary depending on the nature of the matrix, namely the binder type and the amount of free water.

One of the key drivers of changes to the matrix over time is the amount of available portlandite (or calcium hydroxide). It has the dual effect of keeping the pH elevated where natural precipitation of hydrated silicate phases occurs more rapidly and also combining with unreacted amorphous silica to create more calcium silicate phases that densify the microstructure [9]. In regards to the steel concrete interfacial zone (SCIZ), the impact of portlandite is crucial to deterring chloride attack on the steel substrate [29, 30]. This body of work has shown that the presence of portlandite adjacent to steel allows a higher concentration of chloride ions to be present in the paste without inducing corrosion. This has critical implications for the long-term performance of steel reinforced concretes and mortars as it indicates that the service life of structures will be extended where portlandite rich matrices are utilised. The uptake of portlandite by mineral admixtures such as fly ash will reduce the amount available for the ongoing pozzolanic reactions. However, the benefits of pozzolans closing pores and fundamental change to pore chemistry and pore size distribution counteract the depletion issue to still give long-term corrosion benefits [31].

More recent work [32] has shown that the absence of portlandite in specific locations along steel reinforcement will cause an acceleration of chloride-induced corrosion. Voids created by the different compaction rates above and below the steel lead to areas of depleted portlandite and the associated problems.

Other theories have been proposed to explain the phenomenon of ongoing steel passivation provided in the SCIZ [33, 34] where it is not portlandite alone responsible for the ongoing barrier to corrosion. In these studies, it was shown that there was no preferential concentration of portlandite on the steel interface but rather the composition of the hydrated phases was representative of the bulk of the matrix. The significance of this work is that there would be no concern about pozzolans depleting portlandite and potentially affecting the corrosion resistance of the steel. Furthermore, the beneficial impact of the pozzolanic reaction occurs right through the matrix and the steel is protected as a consequence of this phenomenon.

Glass et al. [35] built on previous work that tended to place a lot of emphasis on the presence of reacted and unreacted portlandite at this interface. While their work showed that indeed the presence of portlandite played a role in determining the pH of the interface and thereby the likelihood of corrosion, it was no more prevalent than that observed in the bulk paste. Their work suggested it was a combination of several formed phases at the interface that impacted on corrosion resistance and that it was not portlandite alone that provided this buffering property.

Mangat and Gurusamy [36] looked at different types of steel fibres exposed to two types of environments, with one of them being a local beach, to get a true indication of how the materials behaved in a marine environment. They found that the level of corrosion of the fibres was related to the type of steel used and the chloride ion concentration in the concrete as a function of time and hydroxyl ion concentration.

The two cementitious formulations in the current study were chosen specifically to observe the effects of one mineral admixture (fly ash) at one replacement level (30%) in relation to a baseline mix of OPC. The general improvement in permeability induced by mineral admixtures is well known but data on chloride binding and chloride ingress has only been more recently studied. In a 2010 study [37] a range of different binders were assessed and showed that porosity was not necessarily linear with chloride resistance. Slag additions gave higher resistance than fly ash but it was concluded that the increased permeability of any mineral admixture addition decreased chloride ingress regardless of whether any chloride binding was taking place. This confirms previous studies that report the general benefits of these two main materials [38].

Koleva et al. [39] conducted extensive analyses on the steel-paste interface of mortars containing rebars and exposed to chloride environments. They detected a range of iron chloride compounds that varied according to the nature of the matrix, the concentration of chlorides and whether or not carbonation had occurred contemporaneously.

A state of the art review [27] concluded steel fibre reinforcement has little effect on rebar corrosion other than arresting crack growth. The theme of this review is the consensus that crack width will affect chloride ingress into the concrete matrix but the fibres mitigate structural damage by bridging the gaps and slowing crack propagation. Consequently, the mechanical properties of rebar-reinforced materials will vary depending on whether fibres are present but, ultimately, the corrosion behaviour will vary little.

So far in this section, the work discussed has been focused on cementitious materials. The non-cement material under investigation in the current project, geopolymer, does not have the history of cement-based research and has not often been directly compared in the manner proposed in the current study. Some general comments on geopolymer research follow.

Lloyd et al. [13] looked at the nature of the pore solution in a geopolymer formulation similar to the one used in the current study and uncovered that it is rich in alkali but not in calcium so it therefore has a very different mechanism of pH buffering to prevent steel corrosion.

Prior work [40] explored the relationship between the silicon:aluminium (Si:Al) ratio in various metakaolin geopolymer formulations and how this affected the microstructure. The authors concluded that manipulation of this ratio could optimise mechanical properties with those formulations having a higher silica ratio suffering lower strength due to defect sites.

The interplay between the type of aluminosilicate backbone used for geopolymer and the type and concentration of the alkali activator informs much of the research [6]. Highly specialised analytical techniques, such as nuclear magnetic resonance and inductively couple plasma, have been used to collect this data but what has been missing, as far as this author can tell, has been analysis of the evolution of microstructure over time. Cement chemistry has been based on an understanding that the hydrated phases resulting from cement hardening will change over time. The evolution of ettringite, for instance, has been studied intensively. It is well understood that geopolymer follows a condensation and precipitation model, rather than hydration, and is therefore not susceptible to free hydroxyl ions in the pore solution. It is less clear, however, whether that means there is no time-based reaction kinetics occurring within the microstructure and whether the steel interface will be exposed to varying conditions over time. This is a real hurdle to overcome in ascribing long term characteristics to steel reinforced geopolymer structures when compared to cement-based equivalents.

In order to put the issue of the impact of the host matrix on the steel interface in context it is important to look more closely at the interfacial transition zone (ITZ). Remembering that the current project is based on the comparison of three steel reinforced mortars with different binder systems, the ITZ will largely affect the behaviour and properties of the various materials.

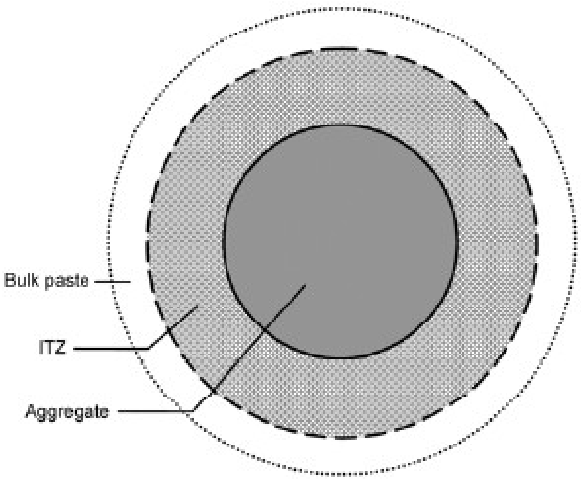


Figure 1. 7: Schematic showing the presence of the interfacial transition zone (ITZ) that forms between the aggregate and the paste in cementitious materials (ACI)

A RILEM report in 1995 [41] was the first to detail the ITZ in a methodical manner by discussing the impact of key parameters like water-cement ratio and the addition of mineral admixtures. The authors showed how the transition zone away from aggregates was affected by these factors in terms of phase formation and porosity. Leeman et al. [42] showed the impact of the ITZ on chloride differences based on binder type and Bentur and Alexander [43] took it further by looking at the engineering properties of various composite materials.

Aligned with the study of the ITZ is the steel-concrete interface zone (SCIZ). There are different theories on the mechanisms at play here in the presence of chlorides but Chris Page has produced a lot of work on it over several decades. In one of his papers [30] he proposed that the buffering effect on pH of cement hydration products helped defer and delay the onset of pitting corrosion and the extent of this effect varied on the nature of the matrix, particularly on the amount of mineral admixtures were present. This work could be related back to a study done over a decade prior where a ranking of how different cements fared in a chloride environment [29] and how that work showed distinct differences in their performance.

Whether it is the interfacial zone, the peculiarity of geopolymer or the nature of the steel interface in relation to the chemistry of the mortars being investigated in the current project a survey of the literature has shown that all of these issues can be viewed from many angles. As is the case with so much in cement and concrete research many theories remain contested [2]. Specifically, the corrosion of steel fibres in mortars has been looked at primarily from the perspective of chloride levels. This is why the current study has been undertaken, namely to investigate this issue from a fresh perspective.

1.5 Problem Statement and Outline

Corrosion of steel reinforcement in concrete is of concern to engineers and researchers because of the devastating consequences it can bring about if not kept in check. Most of the research has dealt with bar reinforcement or ‘rebar’ as it is the most common. Research on fibre reinforcement corrosion is less common.

As far as it can be ascertained, no previous study has directly compared corrosion behaviour of a steel fibre-reinforced non-cement mortar (geopolymer) with cement-based mortars and certainly not by focusing on microstructural changes. Therefore, previous studies on related areas are taken as guides for the current project but most of the techniques are being developed for the first time. It is felt that the results and outcomes will be of significance even if distinct differences in microstructural changes are not detected due to the unique nature of the methodologies.

The mortars made for the current project consist of a binder (cement or cement/fly ash or fly ash/ alkaline activator), sand, water and steel fibres. The first two binder types produce standard mortars as blended cements are commonly used in industrial applications. The third binder type produces the geopolymer mortar. The microstructures of these three mortar types will be quite different, however. The variation of water-cement ratios for the two standard mortars will also affect microstructure.

The matrix that is visible under the microscope is predominantly a combination of the binder and the sand (or fine aggregate). The water added during mixing has turned the binder into a paste and coated the aggregate so that the material fills the mould prior to curing. The steel fibres are also added and settle in the body of the mortar in varying configurations depending on the rheology of the particular mortar.

Once cured and the mortars harden over time the microstructure will change accordingly. The combination of a hardened matrix, voids or pores, water in various states (bound, unbound and pore solution) and fibres oriented randomly provides a multitude of possible microstructures.

After prolonged exposure to a chloride solution (seawater) these different microstructures will change in distinctive ways. This is the premise for the current project.

By using microstructural analysis in tandem with corrosion analysis, it is hoped that the current project will shed valuable light on the complex nature of the behaviour of key mortar formulations over time. With the primacy now given to durability studies, the current project will provide valuable information as it is a direct comparison of three vitally important formulations exposed to the most common corrosive environment over an extended period.

While there will always be debates about what length of time constitutes a durability study, it will be shown that the results in the current study provide clear indications of the contrast between the materials in how they respond to a corrosive environment and that the changes over time are peculiar to each individual material. It would, therefore, be feasible to extrapolate these results to postulate their behaviour over longer timeframes. It is argued that this aspect of the current study means it can be feasibly designated as one of durability.

Chapter 2

Steel Fibre Reinforced Mortars and Electrical Resistivity

2.1 Introduction

In the current study three types of steel fibre reinforced mortar types were exposed to a corrosive environment for 6 months. Weekly electrical resistivity readings were taken and plotted with the results analysed to discern any differences between the three materials.

The history of electrical resistivity as an indicator of corrosion behaviour in steel reinforced concrete can be traced back to the post war period [44]. However, it was not really until the 1970's that it came to be a common technique used by researchers to determine the moisture content in concrete and, thereby, an indicator of corrosion behaviour of reinforced concrete. Woelfl and Lauer published a study in the late 1970's [45] that showed the effects of moisture, aggregate and air content on concrete and how they all play a part in affecting electrical resistivity. Since then, electrical resistivity has been used in research and field applications to help explain the behaviour of concrete and mortars with and without steel reinforcement. However, using electrical resistivity to explain the behaviour of steel fibre reinforced mortars has not been so commonplace.

Buenfeld et al. [46] looked at the resistivity of mortars immersed in sea-water. The authors noted that the large difference in resistivity between saturated and dry concrete was best explained by assuming the conduction method is electrolytic and reliant on microstructure and the composition of the pore solution. It is now widely accepted that these two factors control changes in resistivity and subsequent corrosion resistance of steel reinforced mortars and concrete [21,22].

Hope et al. [47] studied the effect of age and water-cement ratio on electrical resistivity (ER) and found that it increased with age and in concretes with a lower water-cement ratio (W/C). The basis for this work was an underlying assumption that an ER of greater than 10 kΩ-cm was a precondition for the prevention of corrosion. By using pore solution resistivity, mercury intrusion porosimetry and surface examination they determined mechanisms for producing an increase in resistivity as immersion time increased. They showed it was the formation of a discrete aragonite/ brucite layer and a bulk effect related to cement paste pore structure. Of the materials evaluated they found that the blended cements (one with fly ash and one with slag) had the greatest increase in resistance, and thereby resistivity.

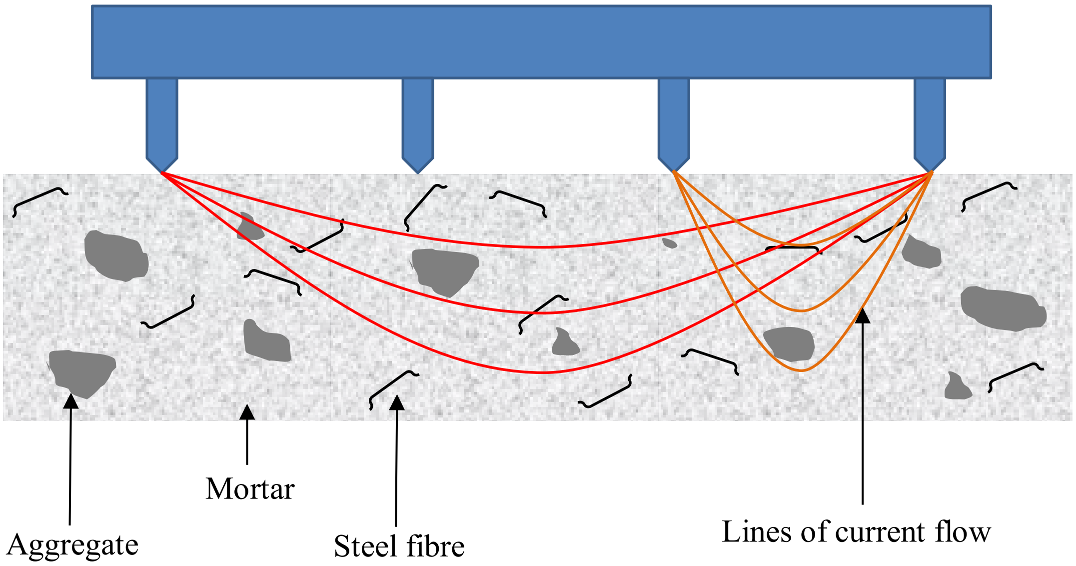


Figure 2. 1: Schematic of the principle of the 4-point Wenner probe [ACI]

The instrument used in the current study to measure electrical resistivity is the Wenner probe (see Figure 2.1). It has been shown that this 4-point measurement method gives accurate apparent resistivity values on field samples [48]. Apparent resistivity is an amalgam of surface, bulk and material resistivities. Resistivity is one of many analytical techniques used to assess corrosion behaviour in steel fibre reinforced mortars. To directly compare the performance of three key binder types in a corrosive environment over an extended period using resistivity and microstructural techniques addresses a gap in the research.

By assessing fibre orientation and distribution in the three mortars and then taking weekly resistivity measurements of the submerged prisms in aerated seawater for six months, the aim of the work outlined in this chapter is to obtain a profile of the resistivity changes. The behaviour of these materials, represented in the profiles, is then related to their expected ability to resist the onset of corrosion of the steel fibres within the matrices.

2.2 Experimental Details

2.2.1 Materials

Each mortar fabricated in the current study is a combination of three components – a binder (cement and water/ cement and fly ash and water/ fly ash and geopolymer activator), fine aggregate and steel fibres. The specifications for each material are given in Table 2.1. Figure 2.2 shows the particle size distribution of the sand used to make each mortar.

Table 2. 1: Composition of Gladstone FlyAsh, ordinary Portland cement and Sodium Silicate

Oxides (%)	Gladstone Fly Ash	ordinary Portland cement	Sodium Silicate
SiO_2	51.1	21.8	29.4
Al_2O_3	25.7	5.80	-
Fe_2O_3	12.5	3.30	-
CaO	4.30	63.0	-
MgO	1.50	2.00	-
MnO	0.20	–	-
K_2O	0.70	0.30	-
Na_2O	0.80	0.50	14.7
SO_3	0.20	2.40	-
TiO_2	1.30	–	-
P_2O_5	0.90	–	-
LOI	0.60	1.00	-

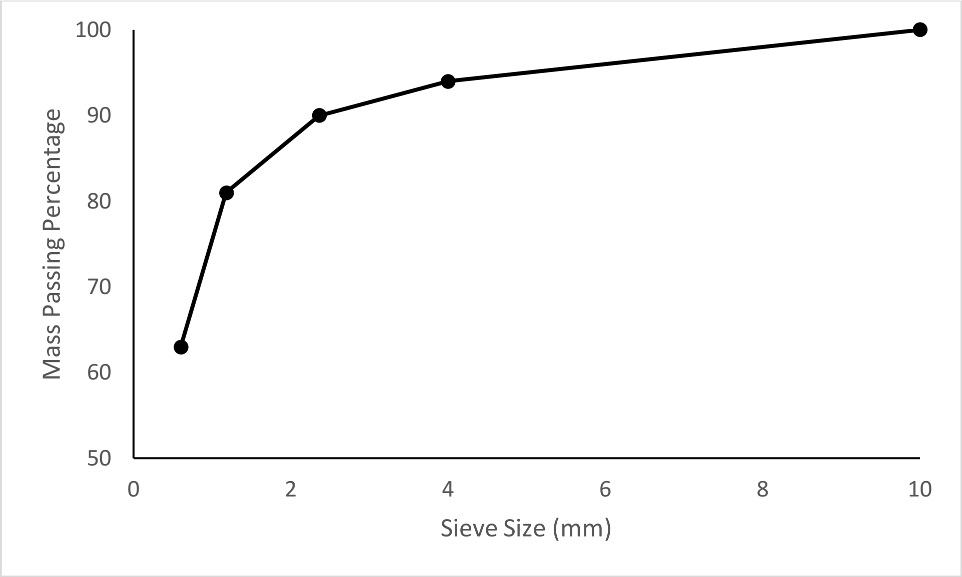


Figure 2. 2: Particle Size Distribution of Mortar Sand

Sodium Hydroxide Solution (8 molar NaOH – a highly concentrated alkaline solution)

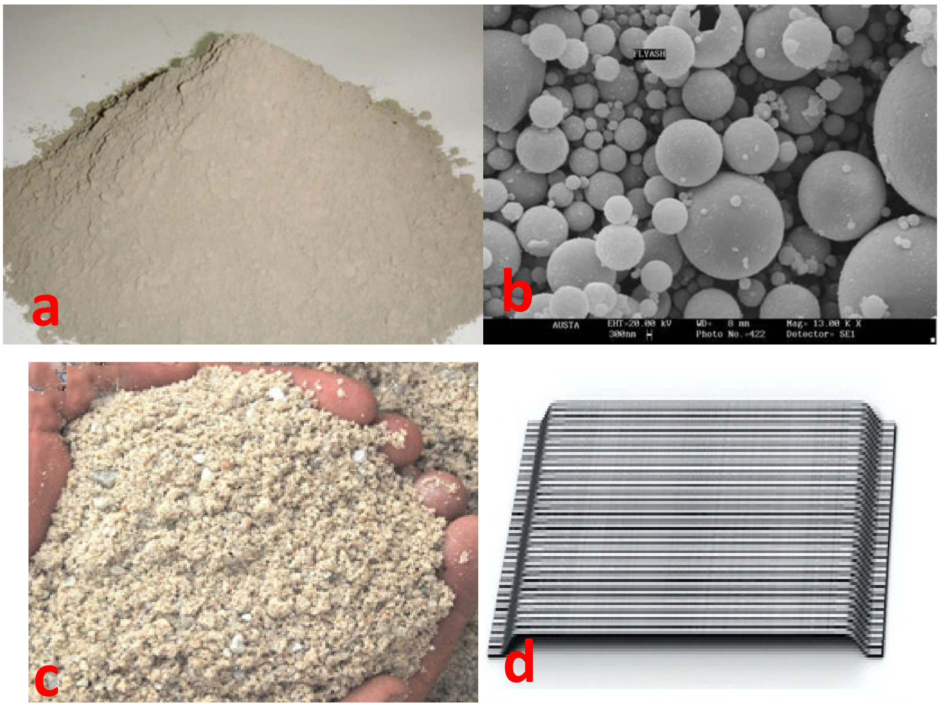


Figure 2. 3: Individual components used to produce the steel fibre reinforced mortars studied in this work, a) cement, b) fly ash (high resolution scanning electron microscope image) [ADAA], c) sand (fine aggregate), and d) steel fibres (Dramix 3D).

2.2.2 Mixture Proportions

To make up individual mortar types the materials were mixed in the proportions outlined in Table 2.2. For all mortars, the fine aggregate and steel fibre amounts were kept constant at values of 710 kg/m^3 and 30 kg/m^3 respectively.

Table 2. 2: Mixture proportions of the mortars made with different binders

Binders	Quantities (kg/m^3)				
	OPC	Fly ash	Sodium silicate	Sodium hydroxide	water
OPC0.4	380	-	-	-	60
OPC0.45	380	-	-	-	67.5
FA0.4	266	114	-	-	60
FA0.45	266	114	-	-	67.5
GEO	-	380	28	72	-

2.2.3 Mixing Process

Two batches of 0.45 water-cement and one batch of 0.40 water-cement mixes were made for OPC and FA. Three batches of the GEO mix were made.

The two water-cement values for OPC and FA were selected for the following reasons;

1. They are close to the threshold where mixes can be feasibly made without the use of chemical admixtures
2. They are common ratios used in industry when durability (and therefore corrosion resistance) is required
3. While they are relatively close in value there is enough of a gap to expect to see sufficient variation in results so that it can be related back to the point made about durability

For all mortar mixes the Dramix 3D steel fibres were added to give a dosage rate of 30 kg/m^3, as per the recommendation of the steel fibre supplier. Based on the 7 kg of dry mortar mix this equated to 154 g of fibres per mix. This type of fibre is used widely in industry, therefore it was assumed that the data collected during the current study could be easily used in commercial applications.

2.2.3.1 OPC Mortars

OPC mortar mixes were made with 5 kg of a commercial sand and 2 kg of ordinary Portland cement for a total of 7 kg of dry material. The dry materials (cement and sand) were placed in a Hobart mixer similar to the one pictured in Figure 2.4. The mixing blade was turned on at a low speed and the dry materials mixed for 30 seconds. The liquid (800 g of water for OPC0.40 and 900 g of water for OPC0.45) was slowly added for the next minute until it was all in the mixing bowl. The wet mix was mixed for a further two minutes at which point the steel fibres were added slowly and mixed at a higher speed for a further two minutes.

2.2.3.2 Fly Ash Mortars

FA mortar mixes were made with 5 kg of a commercial sand, 1.4 kg of ordinary Portland cement and 0.6 kg of Fly Ash for a total of 7 kg of dry material. The dry materials (cement, fly ash and sand) were placed in a Hobart mixer similar to the one pictured in Figure 2.4. The mixing blade was turned on at a low speed and the dry materials mixed for 30 seconds. The liquid (800 g of water for FA0.40 and 900 g of water for FA0.45) was slowly added for the next minute until it was all in the mixing bowl. The wet mix was mixed for a further two minutes at which point the steel fibres were added slowly and mixed at a higher speed was for a further two minutes

2.2.3.3 Geopolymer Mortars

GEO mortar mixes were made with 5 kg of a commercial sand and 2 kg of dry binder material for a total of 7 kg of dry material. All three batches of GEO mixes had to be made at 0.50 liquid-to-binder ratio to enable mixing that resembled the 0.45 OPC and FA mixes, so 1 kg of liquid activator was added. This comprised of 710 g of liquid sodium silicate and 290 g of 8 M sodium hydroxide solution. This 1 to 2.5 parts ratio is a common combination used in geopolymer research. The dry materials (fly ash and sand) were placed in a Hobart mixer similar to the one pictured in Figure 2.4. The mixing blade was turned on at a low speed and the dry materials mixed for 30 sec. The liquid (as outlined above) was slowly added for the next minute until it was all in the mixing bowl. The wet mix was mixed for a further two minutes at which point the steel fibres were added slowly and mixed at a higher speed was for a further two minutes.


Figure 2. 4: Hobart mixer


Figure 2. 5: Cube mould


Figure 2. 6: Prism mould

2.2.4 Sample Preparation

Once each batch had been thoroughly mixed the contents of the bowl was used to fill one lot of cube moulds (Figure 2.5) and three prism moulds (Figure 2.6) of 40 mm × 40 mm × 280 mm.

The cementitious mortars (OPC and FA) were cured by demoulding after 24 hours and placing the cubes and prisms in ambient tap water for 7 days. The geopolymer samples (GEO) were left for 24 hours, then heat cured at 60ºC for 4 hours and then demoulded.

The cubes were used for compressive strength testing (results to be presented in Chapter 4) while the prisms were used for the main part of the experiment – polished specimens for microscopy and whole prisms for electrical resistivity data. The prisms were also used for post-immersion microscopy work.

Three prism samples were selected of each of the five different mixes made – OPC 0.45/ OPC 0.40/ FA 0.45/ FA 0.40 and GEO. A total of 15 prisms and 30 polished specimens (details of their preparation are provided in Chapter 3) were placed in the tank for immersion.

In order to replicate marine conditions, the prisms and polished specimens were placed in a large tank of seawater with an aerator running constantly (see Figure 2.7).

Figure 2. 7: Experimental setup used for immersion of the steel fibre reinforced mortar samples in aerated seawater.

There were 9 full length prisms (280 mm long) and 6 shorter prisms (approx. 230 mm long) used in the current study. The shorter prisms were used to extract the polished specimens and, for the cementitious mortars, were 0.40 water-cement ratio. These shorter prisms were fully submerged while the longer ones had approx. 40mm exposed to the environment.

It was important that the experiment run for a period of time that would give the best opportunity to provide meaningful results where time-related changes were evident and significant. The main guide used for determining test duration was what previous researchers had found about changes to electrical resistivity due to extended exposure to seawater. While many had observed changes occurring after 2 to 3 months [46, 48] it was dependent on sample dimensions and the materials used. To ensure these factors were well and truly covered it was decided that the total period of immersion should be 6 months.

During the 6 months of immersion the only time the experiment was disturbed was for the following;

1. Weekly readings of electrical resistivity of all 15 prisms (with the water topped up to compensate for evaporation)
2. Monthly changing of the seawater with fresh samples retrieved from Port Melbourne

3. Bi-monthly removal of polished specimens (10 after 2 months, 6 after 4 months and the remaining 14 at the end of the 6 months)

The main data being collected throughout the period of immersion was the electrical resistivity of the prisms. This was achieved by first removing the prisms from the tank one at a time. They were then dried with a cloth to removed excess moisture and placed lengthwise on a bench with more cloth underneath the prism. A Proceq Resipod 4-probe Wenner device (Figure 2.8) was used to measure electrical resistivity on each face (excluding the ends). For the cementitious mortars two measurements were taken on each face, giving a total of 8 readings for each prism. For the geopolymer, each face was only tested once. This was because the geopolymer was highly consistent and very little change throughout the immersion whereas the other two materials had more variation from face to face and prism to prism.

Figure 2. 8: The Proceq probe used to take electrical resistivity readings on a typical steel fibre reinforced mortar prism

The electrical conductivity of the water was measured weekly after the prism ER readings. It fluctuated in line with the monthly changing of the seawater in the tank, progressively increasing between changes as evaporation caused a concentration of dissolved solids. An average of 2 litres per week of fresh seawater (taken from the reserve of water collected on each trip) was added to the tank to compensate for the evaporation.

At the end of the immersion period, one prism of each material was selected for dissection. The prisms were cut along their length in three places. The resulting subsections were analysed for fibre distribution by dividing the exposed face into deciles (ten equal spacings along one axis) and counting the number of fibres in each decile. Each fibre was marked with a highlighter and counted manually.

2.3 Results

As described earlier the water in the tank was changed monthly and additional water was added to the tank each week to maintain the same base level and ensure consistent immersion of the larger prisms. The electrical conductivity of the averaged 62.6 milliSiemens over the course of the immersion period with a standard deviation of 5.7 milliSiemens over the full set of weekly readings taken during the immersion period.

2.3.1 Fibre Distribution and Orientation

To ensure that the electrical resistivity readings taken during the main part of the experiment in the current study (the period of immersion) truly reflected a direct comparison of the behaviours of the mortars based on their binder formulation and not other factors it was important to conduct an experiment to eliminate that possibility. The mixture proportions and mixing process were standardised so it was felt there was only behavioural difference between the materials that may affect subsequent analyses – fibre orientation. The rheology of the materials is affected by the binder type, so it is therefore conceivable that the fibres may orient and settle in each mortar type in a manner particular to that material. To ascertain whether that was the case a method had to be developed, as no standard or common technique could be found in the literature.

In the experiment undertaken to evaluate the nature of fibre distribution and orientation across the materials the simplest possible approach was adopted. Sections of materials were taken and a count made of the fibres visible in each section. It was decided to break the prism cross-sections into three zones based on deciles as this would allow an easy breakdown of the face being evaluated by creating upper, middle and lower zones. The top 3 deciles make up the top zone, the bottom 3 makes up the bottom zone while the middle 4 make up the mid-zone. Results are given in Table 2.3 while a typical cross section used for the counting is given in Figure 2.9.

Figure 2. 9: Schematic of the cross sections used to count steel fibres

Table 2. 3:. Distribution of fibres across three sections of the three mortars

Binder	Sample size	Deciles		
		Top 3	Mid 4	Bottom 3
OPC0.45	340	34%	41%	25%
FA0.45	329	29%	32%	39%
GEO	293	30%	33%	37%

Figure 2. 10*:* Typical cross-section used for fibre count. The shiny steel fibres are clearly visible in the mortar.

The distribution of fibres across the length and width of the sections does not appear to follow a pattern that can be ascribed to the particular nature of the host material, namely the binder type affecting the location of fibres. In other words, the fibres are scattered in a manner independent of the material composition themselves as best as can be determined using this rudimentary technique.

2.3.2 Electrical Resistivity Data Reproducibility

When electrical resistivity readings were taken at the start of the immersion period it was noted that those for the OPC and FA prisms fluctuated from face to face, while the GEO readings were very consistent.

In order to understand the impact of these fluctuations in the cementitious mortars, an immersed prism from each of the two cementitious materials was taken for repeated measurements across the four faces. The measurements were repeated 12 times over each of the four faces.

Table 2. 4: Electrical resistivity values for 12 measurements of each face of an OPC prism and an FA prism at 0.45 water-cement ratio

OPC0.45				**FA0.45**			
FACE 1	**FACE 2**	**FACE 3**	**FACE 4**	**FACE 1**	**FACE 2**	**FACE 3**	**FACE 4**
11.5	13.5	10.2	10.0	26.5	33.8	28.9	20.6
10.8	12.5	10.9	11.6	25.5	35.2	28.6	20.4
10.6	12.6	10.1	9.9	25.8	30.8	28.8	19.6
10.2	12.5	8.8	9.1	25.7	32.8	31.0	20.6
10.2	13.6	8.8	10.3	26.3	35.4	31.2	22.3
9.8	12.8	8.9	10.1	26.0	33.6	31.9	21.3
10.1	12.4	10.1	10.8	31.1	36.6	31.4	20.8
9.8	13.5	9.7	8.8	30.3	36.4	32.3	20.8
10.2	13.9	9.6	8.7	28.3	35.6	31.0	20.9
10.1	13.5	8.8	7.8	27.6	34.4	32.9	21.5
10.1	12.7	10.2	10.8	29.9	36.1	31.1	21.1
10.0	12.6	10.7	7.9	30.1	35.2	30.8	23.4
AVERAGE		**10.7 kΩ-cm**		**AVERAGE**		**28.6 kΩ-cm**	
STDEV		**1.6 kΩ-cm**		**STDEV**		**5.2 kΩ-cm**	

From the results in Table 2.4 it can be seen that the higher value for the FA mortar is also accompanied by a higher standard deviation. Clearly, there are differences across faces and across repeated measurements. However, these fluctuations across the four faces of the cementitious prisms was seen throughout the period of immersion as well. The results indicate that the reading taken is contingent on the nature of the surface at the time of reading and the location of the probe. Repeated readings taken over an extended period go a long way to eliminating the uncertainty of particular readings and placing them within a statistical variance.

2.3.3 Electrical Resistivity Data on Immersed Samples

During the 6 months of immersion, the 15 prisms were used for electrical resistivity measurements. The prisms were removed from the tank one at a time and dabbed with a cloth to remove surface moisture. They were laid flat on a bench and the ER measured using the Proceq Resipod. The four faces were measured twice giving a total of 8 values for each prism. The average of these values was taken as the ER value for that prism for that week and the values plotted against the week number.

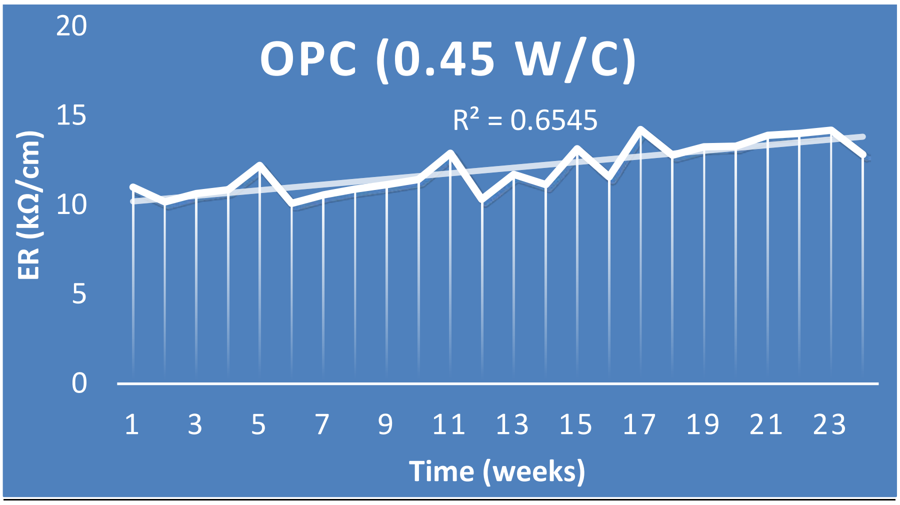


Figure 2. 11: Electrical resistivity readings of OPC0.45 immersed in aerated seawater

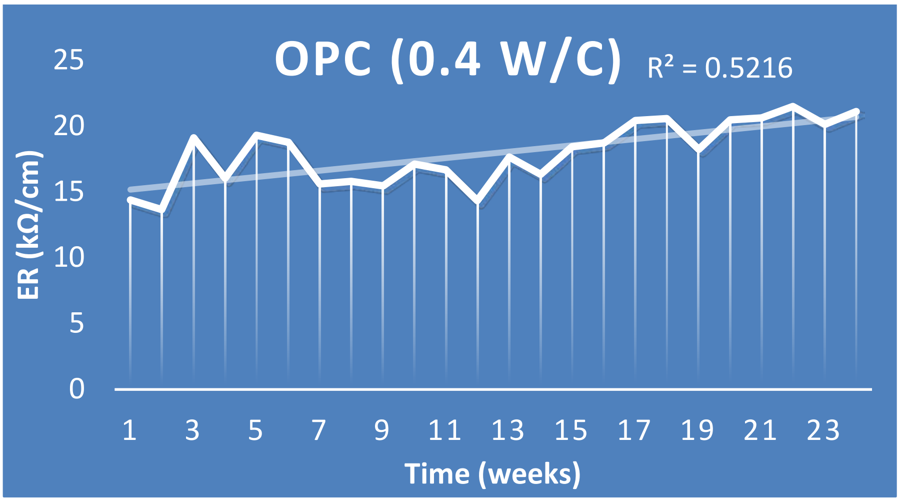


Figure 2. 12: Electrical resistivity readings of OPC0.4 immersed in aerated seawater

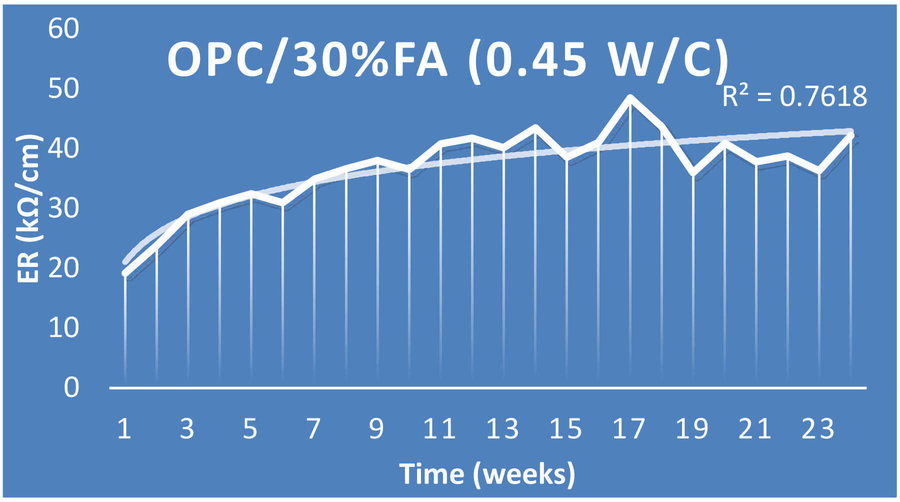


Figure 2. 13: Electrical resistivity readings of FA0.45 immersed in aerated seawater

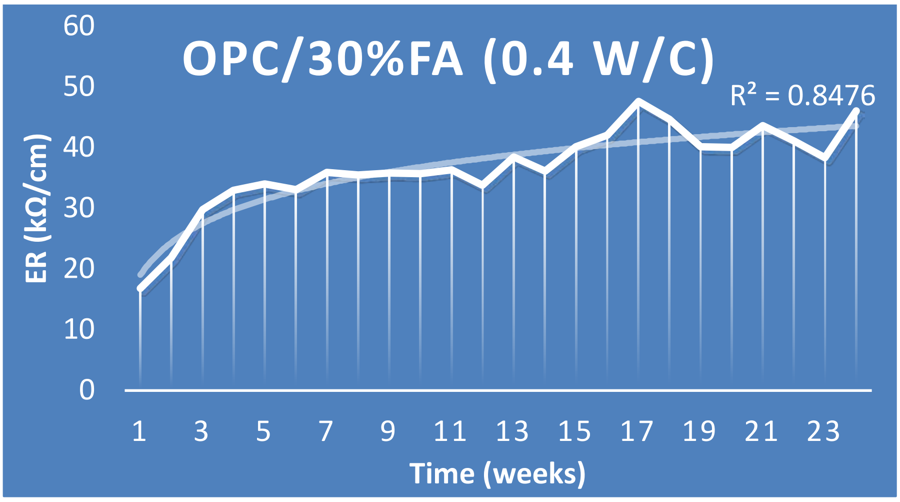


Figure 2. 14: Electrical resistivity readings of FA0.4 immersed in aerated seawater

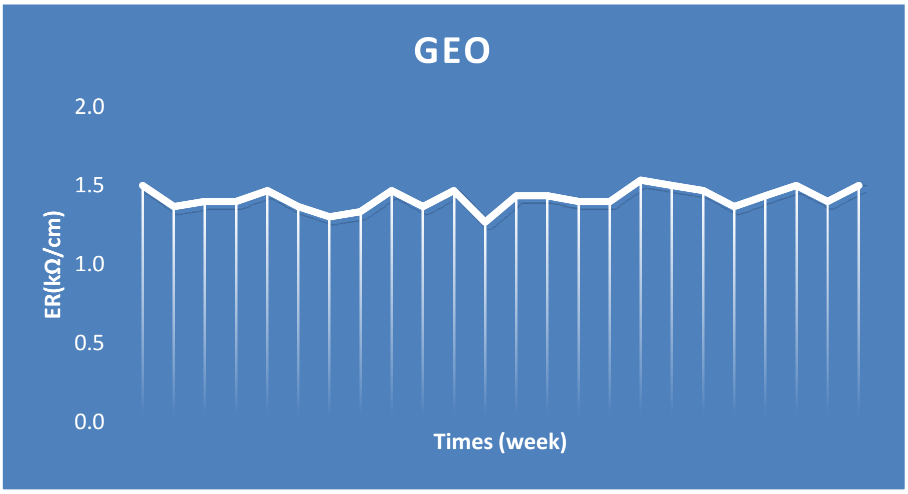


Figure 2. 15: Electrical resistivity readings of GEO immersed in aerated seawater

Electrical resistivity measurements changed in each material throughout the period of immersion in ways particular to each material. Electrical resistivity measurements of the cementitious mortars increased over time. The OPC and blended cement behaved differently overall and also when comparing water-cement (W/C) ratios. The linear nature of the OPC changes occurred in both (Figures 2.11 and 2.12) but the lower W/C ratio had a distinct impact on raising the ER profile. The curvilinear nature of the blended cement profile occurred in both formulation but there was no discernible impact by lowering the W/C from 0.45 to 0.40 (Figures 2.13 and 2.14). The electrical resistivity of the geopolymer remained virtually unchanged for the entire period of immersion, at a low level in comparison to the other mortars (Figure 2.15).

2.4 Discussion of Seawater Immersion of Steel Fibre Reinforced Mortars

Electrical resistivity is measured to compare and contrast the behaviour of the mortars in the current study. The test materials are mortars reinforced with discrete fibres, rather than rebar, and this precludes the use of common potentiometric and galvanic techniques. Within the field of research on corrosion of rebar reinforced concrete the preferred techniques for measuring chloride ingress and the effects of chlorides on corrosion are often variations of electrochemical techniques such as the half-cell potential method [49]. The Rapid Chloride Permeability Test is also very common.

These techniques are well suited when a galvanic cell can be replicated by the continuous nature of the rebar and the distance to the surface of the concrete is well defined. With steel fibre reinforced mortars this is not the case. The random orientation of the fibres do not allow cell methods to be used. The most reliable methods are ones based on measurement of bulk properties that assume this type of mortar to be a heterogeneous material. The interaction of changes in pore distribution, due to the hydration mechanism of the cementitious phases, with its effect on pore solution chemistry and the steel fibres is the main mechanism of corrosion in these bodies [3].

Electrical resistivity is a good indicator of the changes to pore solution chemistry [50] over an extended timeframe. It accounts for the potentially dramatic changes in mix designs between different formulations. The migration of chlorides to sites of corrosion initiation is monitored predominantly by the resistance (or impedance) encountered in the pore solution, as this will change over time. Naturally the materials that make up the matrix have an effect but if they can be standardised except for one component, as has been done with the current study, then comparisons can be made over time that rely heavily on changes to pore solution.

Resistivity readings can be taken quickly and over many samples in a short space of time. This is measured by the electrodes on the resistivity meter and converted to a resistivity reading that factors in the distance across which the resistance is measured. Therefore, it is relatively straightforward to generate a lot of data when comparing a number of samples. Crucially, the changes in resistivity over an extended period in a corrosive environment such as aerated seawater will provide an insight into how prone these materials are to potential failure due to the effect of corrosion of the steel fibres.

While it is well known that electrical resistivity is a good indicator of corrosion resistance, what is less obvious in the literature is how the combination of surface and bulk resistivities are affected across a range of materials. It could be anticipated that a period of 6 months of immersion in a harsh environment like aerated seawater would induce clear observations of the impact of surface effects on each mortar but perhaps the bulk effects would not be so easily discerned simply by one measurement taken on the surface of the test materials. When the first electrical resistivity measurements were made on the immersed samples it was noted that there was a variation in the results from face to face and prism to prism for the cementitious mortars (the geopolymer mortar had a low value and therefore little variation).

It was felt that this variability had to be understood and quantified in order to validate the readings to be taken throughout the period of immersion and ensure the data being recorded was truly representative of the materials being studied. It was to be expected that larger readings would have larger variabilities and so it was the case when this experiment was conducted. The blended cement had a higher ER and higher standard deviation on those readings in comparison with OPC.

In this chapter, three aspects associated with electrical resistivity have been considered;

1. Fibre orientation and distribution
2. Reproducibility of electrical resistivity measurements
3. Electrical resistivity changes of the three materials during six months of immersion in aerated seawater

With an emphasis on the way in which ER is an indicator of the performance of the materials it is vital to present the ER data in such a way that establishes its efficacy and relevance to corrosion behaviour. Therefore, while the experiments conducted to ascertain the results for the first two aspects are covered here it is done so that the longitudinal study of ER will lead to a greater understanding of the material properties addressed in subsequent analyses.

The prism specimens fabricated in the current project are simple mortars of binder, aggregate and liquid with steel fibres added at the mixing stage. The simplicity of the mix designs is to minimise the factors that may bias a direct comparison of the corrosion behaviour of the various mortars. It is a central tenet of the current study that it is the nature of the binder and its impact on the matrix that primarily determines the performance of the mortar in a corrosive environment.

In this section, it has been shown the steel fibres within the various mortars appear to align and orient themselves in a similar fashion and thereby do not appear to impact ER variations across the materials in any preferential way. The fibres have very different properties to the mortar matrix and therefore the total resistivity is affected by their presence. When comparing ER data across the various prisms, however, it is reasonable to assume the differences observed are due to the nature of the mortar materials themselves and in particular the binder [15].

It has also been shown that the reproducibility of ER results across the faces of the prisms reflects the nature of the materials – higher ER giving larger fluctuations of results. Once these readings are normalised via means and standard deviations it can be argued that the technique used for collecting ER throughout the period of immersion (two readings per face and averaged) is valid and sound. For instance, the blended cement prism (FA 0.45) gave a mean of 28.6 kΩ-cm with a standard deviation of 5.2 in the reproducibility study at the start of immersion. Looking at results for this prism at later stages of immersion, the readings were 37.8 and 4.8 at Week 9, 55.5 and 8.3 at Week 18 and 42.5 and 8.6 at Week 24 (the last week of immersion). So while the results continued to be erratic within one prism, the process of averaging the readings out across three prisms per material and over time did produce quite discernible trends using the technique of two readings per face per prism.

By conducting these two experiments – fibre orientation and ER reproducibility – the main data of interest, ER changes over time during immersion, can be confidently used as many concrete researchers do – as a predictor of corrosion behaviour. The veracity of the data is a critical factor to consider when theories are tested and compared by the next major technique of microstructural evaluation.

The stark differences in ER behaviour over the six months of immersion indicate that the various mortars would offer varying resistances to corrosion over extended exposure to a corrosive environment [3]. Therefore, it is argued the ER results will elucidate material differences and how this would be expected to impact on durability of these mortars.

For instance, the unchanged and low ER of the geopolymer mortar suggests that it would be highly improbable that its ER would rise to the generally accepted level of low corrosion likelihood. Based on the accepted theory of how cementitious binders behave such low ER would mean corrosion would be initiated relatively soon after exposure to an aggressive environment. As will be seen later in the microstructural results section this theory does not necessarily hold when comparing geopolymers to cementitious materials. The way the geopolymer binder forms a matrix with the aggregates and fibres clearly differs to the other two binders. Consequently, the way the matrix responds to ingress from chlorides and the barrier layers formed on the prisms is particular to geopolymer. The similarities with the cementitious mortars are not readily obvious. This too is borne out by the microstructural investigation to come in a subsequent chapter.

Work by Buenfeld and his colleagues [46] on mortars exposed to seawater dealt with the changes in the surface layer chemistry as well as bulk effects in relation to pore chemistry. They showed that surface material reacts with the seawater to produce brucite (magnesium hydroxide) and aragonite (calcium carbonate). These compounds form an additional surface layer that increases the overall resistivity of the mortars. As total resistivity is a combination of surface and bulk effects, they also showed that there is an increase in bulk resistivity due to a closing of the larger pores and greater concentration of the smaller pores. It is posited that these effects contributed to the steadily increasing electrical resistivities observed for the two cementitious mortars in the current study.

The results in this section show that while fibre orientation appears to conform to a consistent pattern across all three materials, the various ER values point to distinct differences across the materials and indicate some common features between the two cementitious binders that stand in contrast to the geopolymer binder.

Considering the ER values remain unchanged throughout the period of immersion for the geopolymer binder it will be left for subsequent analyses in the next results chapters to provide more detail of how exactly it behaves in contrast to the other materials. At this point it is sufficient to note that the geopolymer does not change in regards to ER over an extended period of immersion in a corrosive environment while the others do.

The two defining features of the ER graphs are:

1. OPC changes in an ascending linear fashion over time while FA changes in an ascending curvilinear fashion
2. The change in water-cement ratio had an effect on the OPC but not on the FA. Lowering the ratio increased the ER for the OPC while the FA had the same profile for both ratios

Taking immersion and removal of the prisms as the start and end points, the changes observed for each material are given in Table 2.5.

Table 2. 5: Changes in electrical resistivity of the mortars from start (minimum) and end (maximum) of immersion

Binders	ER_{Min} value (kΩ-cm)	ER_{Max} value(kΩ-cm)	ΔER (ER_{Max}-ER_{min}) (kΩ-cm)
OPC 0.40	14.4	21.1	6.7
OPC 0.45	11.0	14.2	3.2
FA 0.40	21.2	41.8	20.6
FA 0.45	20.7	42.5	21.8
GEO	1.5	1.5	-

Within the OPC mortars there was a distinctive difference in the trend of the two water-cement ratios. The OPC 0.40 increased in both net and percentage terms (6.7 kΩ-cm and 47%) compared with the OPC 0.45 (3.2 kΩ-cm and 29%). This was the observation after 6 months of testing, however it is noteworthy that both gradients were increasing at the end of the period of immersion. Over the same period, both blended cement formulations exhibited very similar changes in electrical resistivity. Both increased by approx. 100% (97% for FA 0.40 and 105% for FA 0.45) thereby far outstripping the increases seen with the OPC formulations in both net and percentage terms. The geopolymer did not change at all. The reading obtained at the start of the immersion was the same as that obtained at the end of the immersion.

When the data was plotted and the nature of the changes characterised by the 'goodness of fit' function it was interesting to see a better fit of the higher blended cement values with the estimation of a curvilinear behaviour for both W/C levels. Buenfeld's [46] work on ER changes over time followed this pattern too. The linear behaviour of the two OPC graphs with poorer goodness of fit on lower absolute ER values is an intriguing result.

In regards to the nature of the changes in ER over time between the two cementitious mortars, it may be assumed that it is the nature of the binder and potential phase changes caused by hydration of the binder and/or interaction with the seawater that can explain these observations [50]. Even though the mortars were several months old by the time they were immersed there would still be ongoing changes occurring within the matrix for both types. Then when immersed, surface changes are accelerated as the chlorides in the water react with the paste in particular to form new minerals on the surface. Simultaneously, changes are proceeding internally so when ER is measured it reflects the combination of surface and bulk effects and these changes.

It is not possible to discern the breakdown between the surface and bulk contributions to the total ER values as the Wenner probe takes both into account to give the final reading. Equally, it is not feasible to ascribe one over the other as changing more or less over time. It is known that changes to pore solution chemistry affect resistivity over time [50] and that the addition of fly ash to the binder has an effect on whether the pores close over time. Exposure of the pore solution to the diffusion of ions that resistivity detects will also be affected. In other words, it can be assumed that both contributors to resistivity are changing over time but the rate of change remains unresolved.

The divergence in behaviours of the ER changes over time (linear for OPC and curvilinear for FA) is intriguing. While it is known that fly ash will react with excess portlandite over time and thereby create different pore solution chemistry to a scenario where there is no fly ash but just straight OPC, the extent to which this directly affects ER is contested as stated above.

The conjecture over how different binder systems change over time is also evidenced in the contrast between how the two binders behave at different water-cement ratios. The OPC will change in ways that the blended cement won't, particularly in the slower take up of portlandite and how this affects pore solution pH. However, it is difficult to determine a definitive cause for why one changes with less water present in the matrix while the other doesn't. There could be an effect of the bigger fluctuations (standard deviation) in individual readings masking perhaps a potential difference in the blended cement result going undetected but this is not a conclusion that can be readily drawn on the data available. While it is true that the details of the changes occurring within the four cementitious mortars are difficult to discern with the analytical techniques used in the current study, what can be discussed is the difference in the resistivity values themselves and how that would influence behaviour.

The fact that the ER profiles were essentially identical for the two water-cement blended formulations does not take away from the benefit that the added fly ash gives with consistently higher ER readings than the OPC equivalents. The readings were higher at the start, during and at the end of the immersion period. The results were tapering off at the end so whether they were reaching a peak while the OPC results would keep rising steadily is something, of course, that will remain unresolved. Only results beyond the current study would be able to confirm the behaviour of these materials immersed in aerated seawater for a period longer than six months.

2.5 Conclusions

Steel fibre reinforced mortars are developing and evolving both in terms of their commercial applications and the type of research being conducted. They have interesting properties and their definition can be extended to incorporate the class of materials known as ultra high performance concrete [52].

While it was never the intention in the current study to focus too heavily on the orientation of fibres in the mortars it was evaluated in a rudimentary way so as to provide one more angle for explaining behavioural differences between the mortars. It was shown that the fibres seemed to orient themselves in ways independent of the host matrix. Also, the fluctuations in electrical resistivity readings seemed to conform to a pattern based more on the value of the ER itself rather than the host matrix. This cleared the way to focus on the main data set of this section - the weekly readings of the mortars over the 6 months of immersion. Therefore, the host matrices were compared from the point of view of electrical resistivity as a representation of the composite materials and the differences between them attributed primarily to the differing binders.

The author's exposure to concrete industry bodies in Australia suggests electrical resistivity is becoming more widely used as a tool to determine the long-term performance of all manner of concrete and mortar types. While naturally it has limitations and should not be used in isolation, it is hard to imagine a more versatile technique for producing data in both field and experimental conditions that gives such a clear indication of the performance of materials over extended periods and how they respond to the threat of corrosion and degradation.

The data for the geopolymer mortar suggests that it behaves quite differently to the cementitious mortars. Without prejudicing results to come, perhaps electrical resistivity is not a suitable indicator for the durability of a cement-free material. When cementitious mortars show an increase in ER over time due to both surface and bulk effects but the geopolymer doesn't, it is hard to distinguish whether there aren't any equivalent changes occurring or it is just not being picked up by ER. This dilemma will be addressed in later sections.

The ER data produced interesting findings for the two cementitious mortars. They showed that the two materials display a variation in how ER increases over time and also showed that the difference in water-cement ratios produce different relationships within each material. These differences can be explained in a multitude of ways, starting with surface effects.

Material built up on the surfaces of the cementitious mortars (assumed to be brucite and aragonite [46]) but apparently not on the geopolymer. There is precious little information available in the literature about whether surface compounds will develop on geopolymer mortars and concretes. A cautionary note should be struck here, of course, as geopolymer formulations can vary widely based on the aluminosilicate source and type of activator. Nevertheless, the formulation used in the current study is a common one used in research so not having any information about surface effects is disappointing.

To gauge the impact of the resistivity changes in all of the test materials on the corrosion resistance of each material individually will become more evident in the next sections of results. For the moment, it is noteworthy that the differences are quite stark remembering that this is the first time a comparative study like this has been conducted using this combination of techniques.

Chapter 3

Corrosion Behaviour of Mortars Exposed to Marine Environment

3.1 Introduction

Electrical resistivity differences between the three mortar types suggest the time to corrosion initiation of the steel fibres within their matrices will vary. To undertake this comparison more thoroughly a method had to be developed that would enable evaluation of the differences in surface microstructure of the polished specimens subjected to immersion to complement the ER readings of the prisms from the preceding section of results [3].

Assessing differences in corrosion behaviour between the three materials was always going to be a challenging task. The absence of rebar prevents the use of many standard techniques [4]. With the current project overall having an emphasis on microstructural analysis, it was decided to adapt the common sample preparation technique used in microscopy to suit the current project. Hence, polished specimens exposing steel fibres embedded in the various matrices were exposed to the same conditions as the prisms used for electrical resistivity measurements. The specimens were then removed from the aerated seawater tank at regular intervals and evaluated for pitting of the fibres across the three materials.

As noted earlier, there has been little research done on the surface effects of corrosion in steel fibre reinforced mortars [26]. Therefore, to understand the impact of corrosion in these materials the issue must be looked at from a number of angles. One study [53] observed a series of mortars in an aggressive environment over a 12-month period with different fibre combinations and all containing rebar. They noted that the sacrificial corrosion of the steel fibres helped delay propagation of rebar corrosion.

There are few studies that directly compare geopolymer formulations with standard cementitious ones that evaluate them from a corrosion perspective. Using the standard techniques of measuring corrosion potential (Ecorr) and polarisation resistance (Rp) of electrodes embedded in various mortars with steel reinforcement the authors of one study [54] observed that passivation proceeded at similar rates in the geopolymer mortars as it did in the OPC mortar.

Another study [55] focused on how steel fibres corrode on their own and were not concerned with their performance inside a concrete or mortar matrix. These results provide some insight into the discussion to follow. They found that when pitting occurred it had a dramatic effect on corrosion rates while general mass loss induced slower corrosion. When pitting propagates, it causes brittle failure. Whether a phenomenon like this would be witnessed in the current study depends on whether the type of fibres used were comparable and isolating the impact of the matrix on the corrosion mechanism. Nonetheless, identifying the distinct behaviour of pitting is important as it is assumed as the most dominant and dramatic form of corrosion in the current study.

If the period of immersion was extended perhaps it could be assessed in relation to other mass loss mechanisms, but within the framework of the current study equating the observation of pitting to corrosion rates is the best way to properly evaluate corrosion and garner some idea of the trends across the various mortar types.

Explaining the impact concrete and mortar matrices have on the corrosion properties of steel reinforced structures is the basis of most research into failure and degradation of those materials [3,4]. However, as far as the author is aware, exposing polished specimens of fibre impregnated mortar samples to a corrosive environment and analysing the changes at regular intervals using an optical microscope has not been undertaken before as a means of comparing various mortar combinations.

This section of results will use images from an optical microscope to determine the extent of pitting of fibres within each matrix type. This is an unorthodox method rarely used in this type of research. The qualitative and quantitative observations arising from the micrographs are used to draw conclusions about how each material responds to exposure in a corrosive environment and whether the steel fibres within each matrix are more susceptible to corrosion.

3.2 Experimental Details

3.2.1 Materials

Sections from the prisms made as outlined in Chapter 2 of the 3 mortar types were used for the analyses presented in this chapter.

3.2.2 Methods

Prisms were placed on a concrete saw (Figure 3.1) and sliced through. At least two slices were performed on the prisms selected in order to produce a section of prism that could be fitted to the specimen holder on the fine diamond saw.

Figure 3. 1: Concrete saw for cutting mortar prisms

The finer slicing was performed on a Struers Accutom 50 (Figure 3.2). Approximately 25mm x 25mm x 10mm sections were produced from the 9 prisms (three from each material). A minimum of 5 sections per prism were cut on the Accutom. These small sections were mounted in epoxy resin with the diamond cut surface exposed.

Figure 3. 2: Struers Accutom 50 for cutting thin sections of the prisms

Once the resin had set, the specimens were removed and placed in the automatic polisher (Struers Tegramin) in a turret that holds up to 6 specimens. The sequence for polishing was as outlined below:

Polishing Grade	Time	Force Applied
320 grit SiC	8 mins	10 – 15 N
500 grit SiC	4 mins	25 N
1200 grit SiC	4 mins	25 N
Largo (9 um)	11 mins	25 N
Dac (3 um)	10 mins	30 N
Nap (1 um)	5 mins	25 N

Once the specimens had been polished they were ready for microstructural analyses – optical microscopy and 3D profiling.

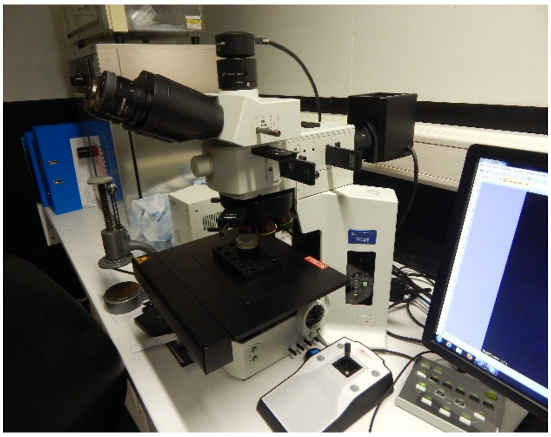


Figure 3. 3: Olympus BX 61 Microscope

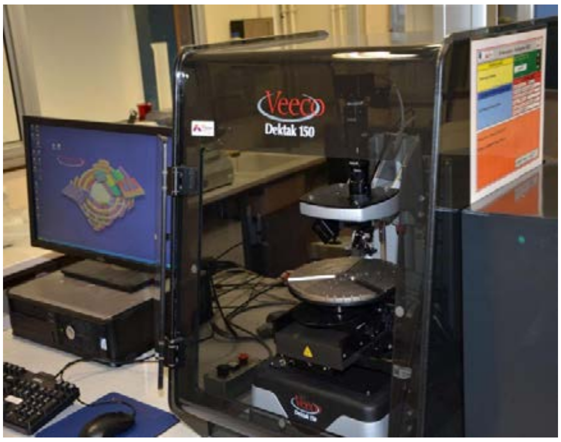


Figure 3. 4: Veeco Dektak 150 Profilometer

Optical microscopy was performed on the Olympus BX61 microscope (left) and 3D profiling was performed on the Veeco Dektak 150 profilometer (right)

At least one optical micrograph and one 3D image was taken of each discrete fibre, some 259 in total across the three materials.

This was the baseline (time zero) data for all of the pitting and microstructural analyses to come during and after immersion.

Several specimens were examined from each material under the optical microscope. Pits within discrete fibres were photographed and then measured. Measurement of pit depths was done by taring the stage height on the optical microscope at zero at the top of the pit (flush with the surrounding matrix) and then increasing the stage height until the bottom of the pit was clearly visible. The reading on the stage height was then taken as an estimation of the pit depth.

If there was too much debris on the fibres to enable a pit depth measurement, the specimen was placed in an ultrasonic bath and cleaned for 3 minutes with dilute (1:10) Clarkes Solution (a metallographic cleaning solution made of hydrochloric acid and inhibitors). This procedure will be covered in more detail in Chapter 4.

3.3 Results

The position and orientation of fibres within the matrix of the polished specimens varied across all of the materials and between different specimens of the same material. It is beyond the scope of the current study to determine what effect the random nature of the fibres has on the corrosion results in outright terms. However, the observations of pit depths in relation to orientation (length and width of exposed fibres) are presented as the main results to provide a comparison across the various materials.

3.3.1 Pitting of Fibres on Polished Specimens

Across all materials it was observed that the type of pitting did not follow a particular pattern based on the nature of the host matrix and this phenomenon became even more pronounced at later stages of immersion. By the end of the period of immersion (6 months) it got to the point where it was not even possible to observe the pitting in the OPC samples as the corrosion product build-up on many of the fibres was not being dislodged by the standard cleaning process employed. Rather than drastically alter the cleaning procedure it was decided to leave the cleaning regime intact so that the dramatic differences in response to the cleaning could be reported in the next section of results on matrix degradation and general microstructural differences.

Specimens that were removed after 2 months and 4 months gave a different set of results again and it was possible to compare across all three materials as the OPC specimens did respond to cleaning by exposing pitting of many of the fibres. Consequently, data on pit depths was collated across all materials for 2 months and 4 months immersion but only for two of the three materials for 6 month immersion.

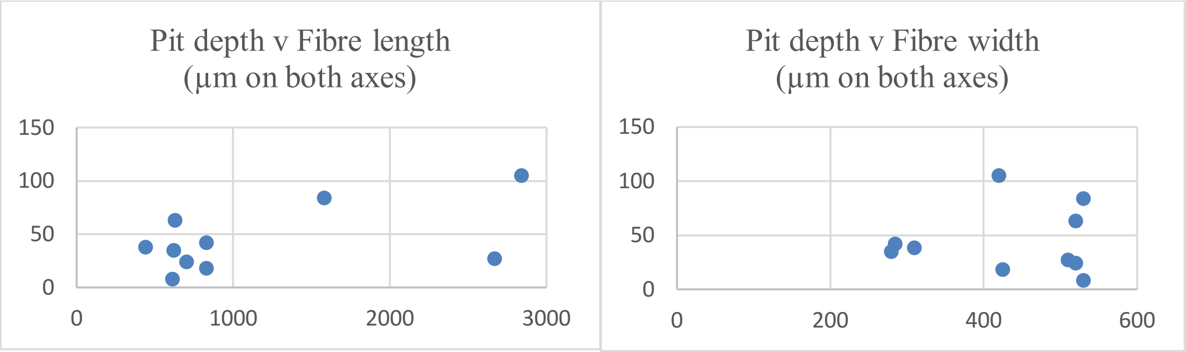


Figure 3. 5: Pit depths of observable pitting in OPC 2 Months samples

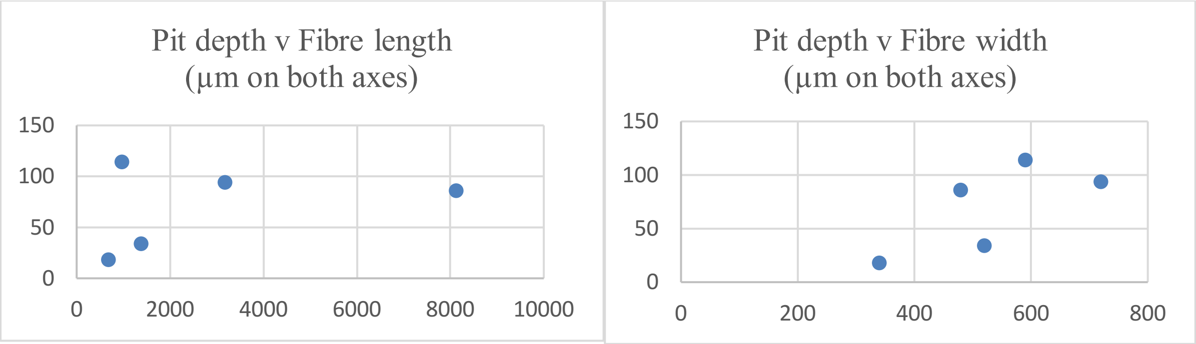


Figure 3. 6: Pit depths of observable pitting in FA 2 Months samples

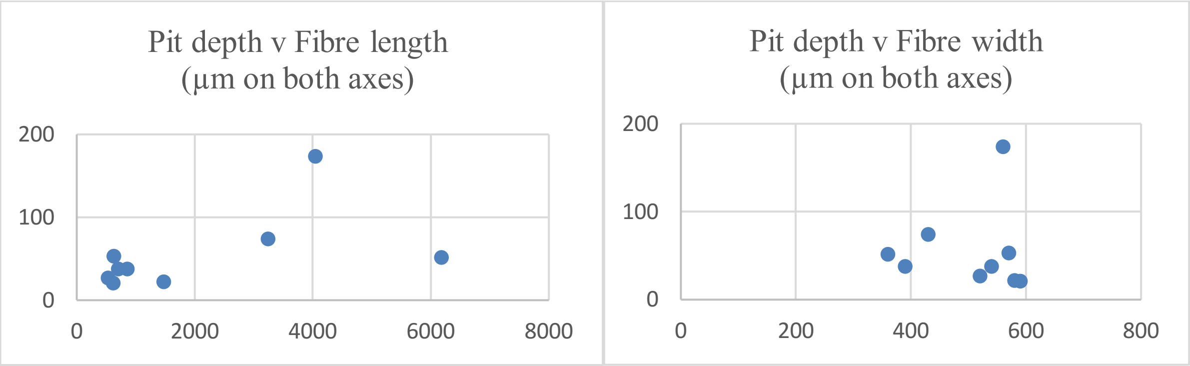


Figure 3. 7: Pit depths of observable pitting in GEO 2 Months samples

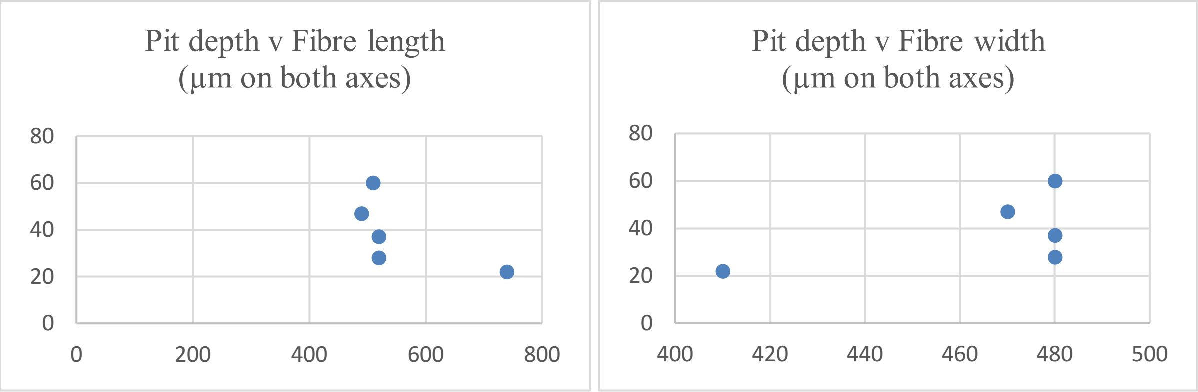
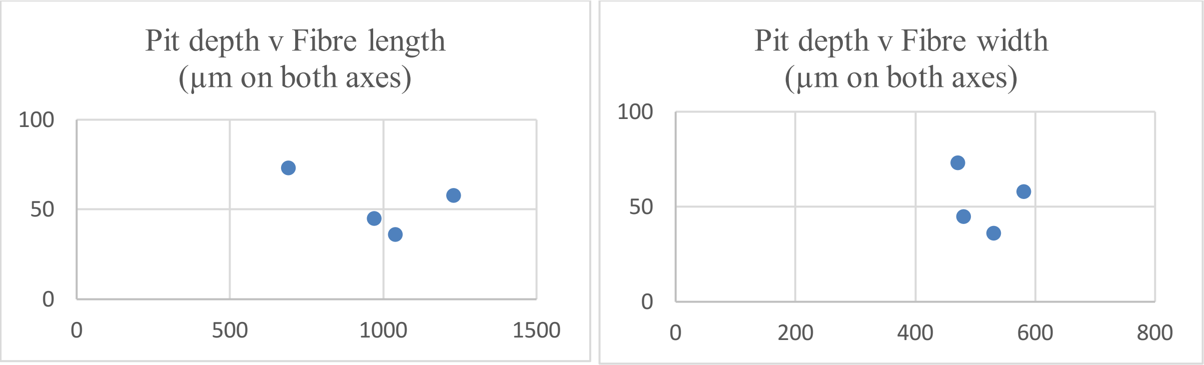
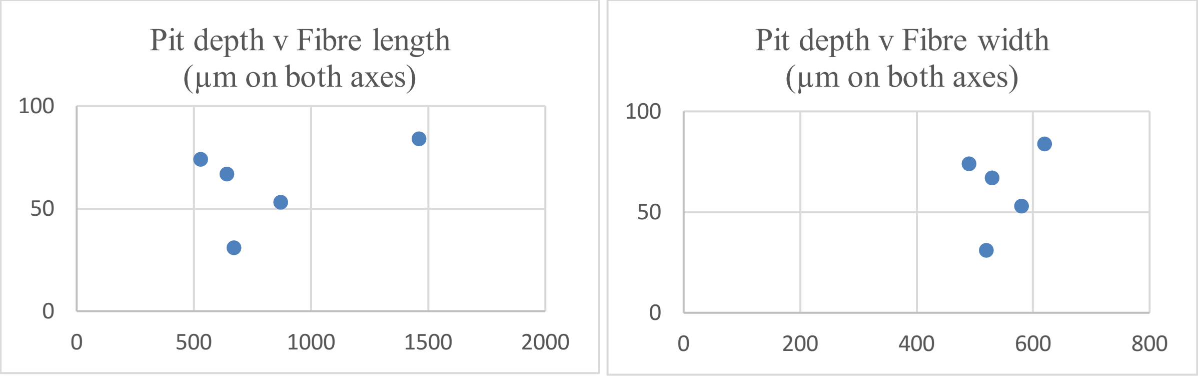


Figure 3. 8: Pit depths of observable pitting in OPC 4 Months samples


Pit depth v Fibre length (µm on both axes)

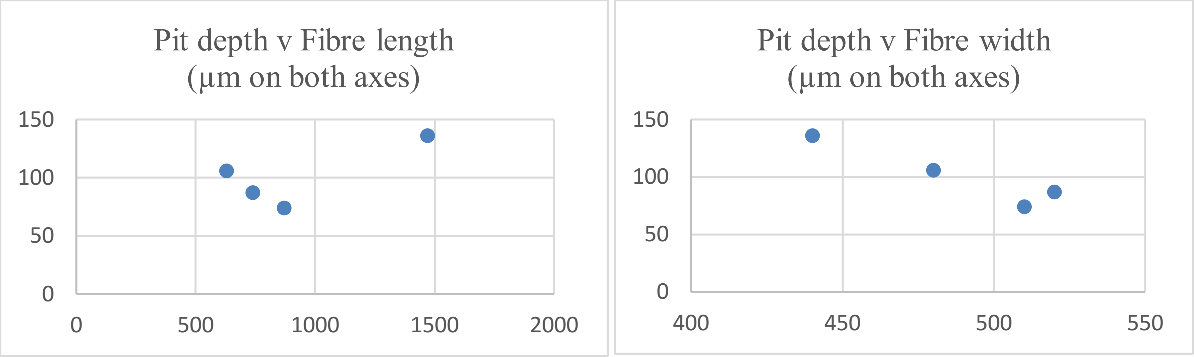
Pit depth v Fibre width (µm on both axes)

Figure 3. 9: Pit depths of observable pitting in FA 4 Months samples


Pit depth v Fibre length (µm on both axes)

Pit depth v Fibre width (µm on both axes)

Figure 3. 10: Pit depths of observable pitting in GEO 4 Months samples


Pit depth v Fibre length (µm on both axes)

Pit depth v Fibre width (µm on both axes)

Figure 3. 11: Pit depths of observable pitting in FA 6 Months samples

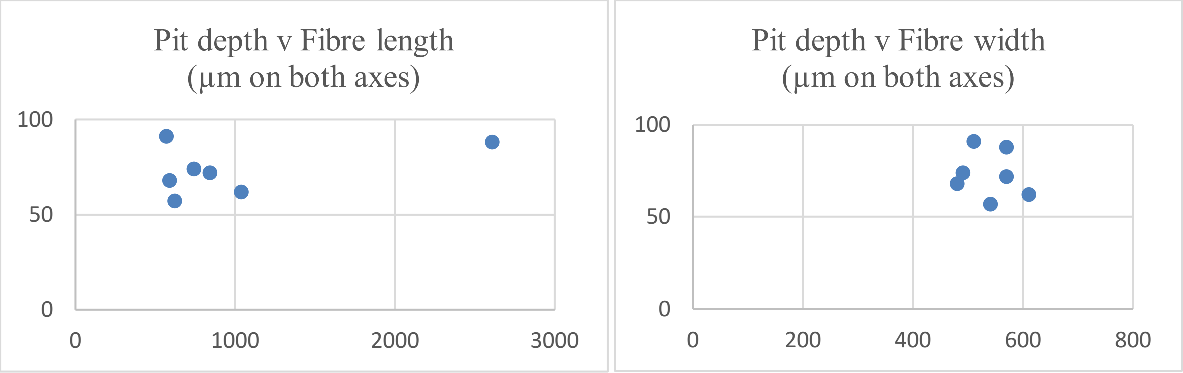


Figure 3. 12: Pit depths of observable pitting in GEO 6 Months samples

The data obtained by estimating pit depths is fragmented and doesn't lead to any direct conclusion about how the fibres behave in each matrix across the period of immersion. It is therefore important to review the data firstly but then adopt some qualitative analysis to complement this outcome. What the pit depth information hasn't conveyed is the changing nature of observed behaviour of the fibres and their surrounding matrices over time and this aspect of the behaviour of these materials is as relevant to the current study overall as the pitting data. In commenting on the data it is useful to compare and contrast the geopolymer with the two cementitious materials as the former behaved in a distinctive manner while the latter shared some common features up until the final stage of immersion.

3.3.2 Pitting of Fibres on Polished Geopolymer Specimens

It was observed that individual fibres on the geopolymer specimens remained intact with only a light covering of debris at the two-month stage (Figure 3.13). The matrix was observed to be holding up well at this stage and there was not a lot of corrosion product visible on the specimens removed from the tank.

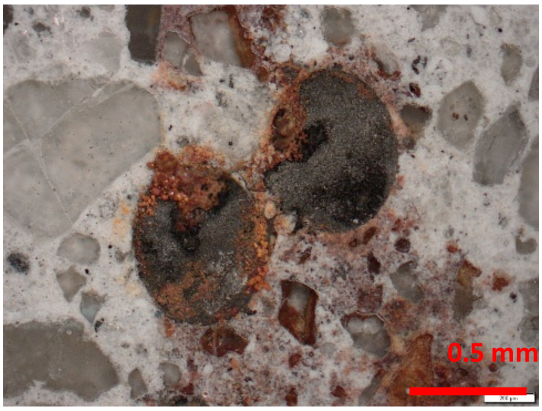


Figure 3. 13: Fibres in the geopolymer matrix after 2 months of immersion

The pitting data for geopolymer at this stage showed that pit depth was possibly related to fibre length but seemingly less so to width as seen in Figure 3.7. The most striking feature generally was that the fibres and matrices of the polished specimens were in better condition than the cementitious ones.

After four months of immersion there was further build-up on the specimens but quite a few of the fibres were still visible (Figure 3.14). There was some localised pitting (Figure 3.10) but many of the fibres seemed remarkably intact. It was noticed at this stage that the orientation of the fibre seemed to play a role in the development of pitting and the propagation of corrosion.

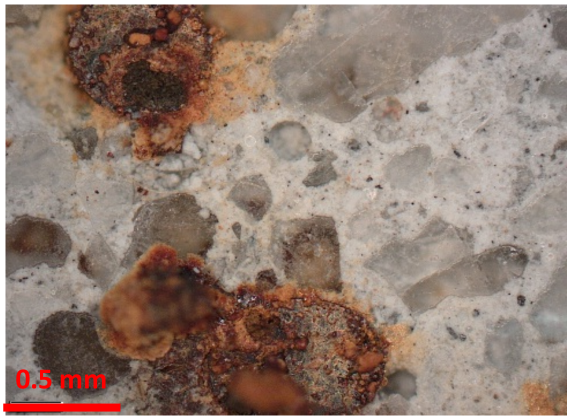


Figure 3. 14: Fibres in the geopolymer matrix after 4 months of immersion

There were less fibres available for pit depth analyses at 4 months than there were at 2 months and as can be seen in Figure 3.10 the results were scattered but the pits were generally quite deep (averaging approx. 60 microns) in comparison to the 2 month values (averaging approx. 40 microns).

Fibres with a greater exposed surface area due to its orientation (the more acute the angle to the plane of the matrix) tended to show less overall corrosion but if a pit did develop it tended to propagate a little more quickly. It would seem a galvanic cell was more likely to develop if there was more space for the anodic and cathodic reactions to occur. This would seem to fit with accepted theory but there has not been any work done on this particular phenomenon, as far as the author is aware, in relation to steel fibres embedded in polished mortar specimens.

By the time the final round of specimens was removed from the tank, the trends observed with the previous batches (2 months and 4 months) were confirmed more or less, particularly in relation to the cementitious samples. It was evident that the surface of the geopolymer specimens had several distinct characteristics in comparison to the others (to be discussed further in Chapter 4). In regards to pitting specifically, the random pitting depths across various samples and fibre orientations seemed to indicate that corrosion was progressing steadily but it was not dramatic (Figure 3.12). It was unclear whether any surface effect was impacting on these observations. In other words, while there were noticeable changes to the observed corrosion occurring on the geopolymer samples as a function of time there did not seem to be a direct correlation with time whereby pit depths got deeper in some systemic fashion the longer the specimens were immersed in aerated seawater (Figure 3.15).

Figure 3. 15: Fibres in the geopolymer matrix after 6 months of immersion (uncleaned left and cleaned right)

3.3.3 Pitting of Fibres on Polished Cementitious Specimens

Taking the two cementitious mortars together, there appears to be some similarities on those samples taken out after two months of immersion in the sense that some surface build-up is starting to occur but also some of the fibres are still visible (Figure 3.16).

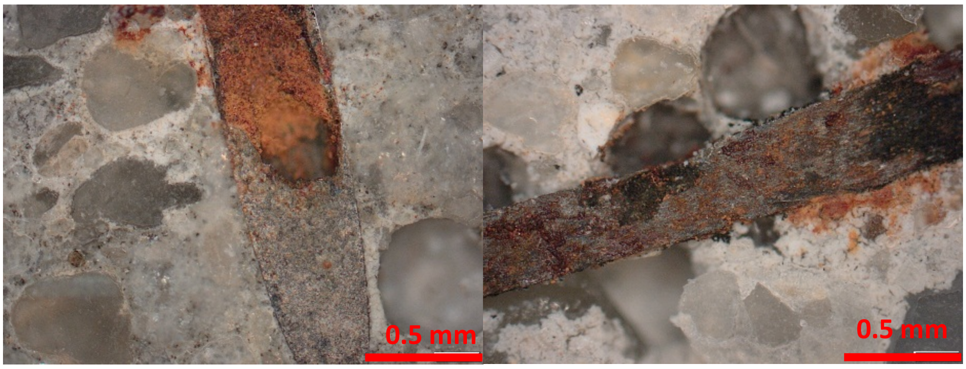


Figure 3. 16: Fibres in the OPC matrix after 2 months of immersion (uncleaned left and cleaned right)

Pit depths ranged quite a lot across the two materials (Figures 3.5 and 3.6) with the longer and wider fibres generally having larger pits of approx. 100 microns.

At the 4 month stage, however, differences appear between the OPC mortar and the FA mortar. The way in which material builds up on the surface of the specimens and then is subsequently removed by cleaning does appear to follow different patterns between the two materials over time. This is especially the case at the end of the immersion period (6 months) where the OPC is much harder to clean and expose the fibres. Consequently, no pitting data was able to be retrieved from these samples. Therefore, only data from the FA and GEO samples are given for the end of immersion (6 months). This facet will be covered in more detail in Chapter 4.

Figure 3. 17: Fibres in the OPC (left) and FA (centre and right) matrix after 4 months of immersion

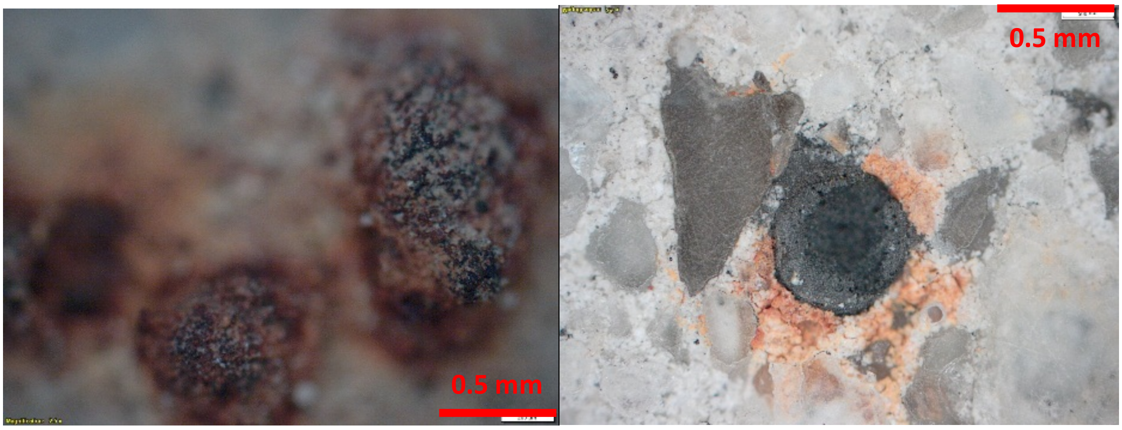


Figure 3. 18: Fibres in the OPC and FA matrix after 6 months of immersion showing that the corrosion product could not be removed from the OPC with the standard cleaning regime (left) while it was removed easily from the FA (right)

3.4 Discussion of Corrosion Behaviour

In this section of results, corrosion behaviour of the various mortars has been assessed via pit depths of the fibres on the polished specimens immersed in seawater for periods up to 6 months. It has been shown that this technique does not produce clear trends or distinctions between the materials. It is not clear that the host matrix plays any particular role in affecting the corrosion rates observed in discrete fibres. The orientation of fibres in the matrix also plays a role in the extent of pitting observed in various fibres.

With these qualifications and shortcomings in mind, it is still worthwhile looking at the observations on pitting and putting them in a broader context in regard to the key to the current study – whether it tell us anything insightful about the nature of the three materials and their respective performance in corrosive environments.

There was some severe pitting in certain fibres within a particular matrix that wasn't replicated in other fibres on the same sample. Equally, it was difficult to discern a clear pattern of behaviour from one material to the next. It would have appeared likely that the geopolymer samples would have distinctive pitting patterns considering they were less affected by surface changes throughout the period of immersion. However, this was not immediately obvious from the observations under the optical microscope of both uncleaned and cleaned samples.

In the preceding section on electrical resistivity, there were distinctive patterns of change over the duration of immersion for each material. Using the guidelines for how resistivity correlates with corrosion, it would be expected to see little corrosion in the blended cement with more expected in the standard cement mortar while the geopolymer mortar would be highly exposed to corrosion.

The extent of corrosion product build-up was noticeably greater for the cementitious mortars than it was for the geopolymer. Comparing the polished specimens removed from the tank at 2, 4 and 6 months it was obvious that there was a steady build-up over time of corrosion product on the OPC and FA specimens while it was quite gradual on the geopolymer specimens. Assuming the concentration of fibres to be fairly uniform across all the materials (taking into account the total number of specimens), there was clearly a difference in the way the cementitious matrices reacted with the seawater compared with the geopolymer. As discussed earlier, the cementitious materials will react with seawater and form surface layers of brucite and aragonite. It is difficult to discern from the literature whether any similar reaction can be attributed to geopolymer. Therefore, it would seem that any build-up of material on the surface of the geopolymer specimens is more a consequence of slow deposition of random material over time rather than a specific reaction that creates a more impermeable barrier. This would help explain the unchanging nature of electrical resistivity as well. Surface resistivity will change with the cementitious mortars as the surface chemistry changes while the geopolymer is not exhibiting these changes.

The range of permutations and different orientations of fibres in each material will become clearer in the next section when more micrographs will be presented to visually document this phenomenon. In this section, suffice to say, we have seen fibres with a lot of surface area exposed to the corrosive environment that have not exhibited a lot of pitting while fibres with the least amount of exposed metal (sitting at right angle to the matrix) have shown some quite severe pitting. These random observations become more erratic too as the length of immersion increases from 2 months to 4 and eventually 6 months. The mechanism of pitting (the creation of a galvanic cell) seems to be affected by factors other than the exposed fibre surface and the host matrix. The erratic pitting data suggests other factors are at play such as the surface products being generated by interaction with the seawater for instance. That aspect will be further explored in the next chapter.

Unfortunately, it was not possible to use the optical microscope to discern features about the bond around the steel fibres and the impact that potentially has on corrosion behaviour. The position of the fibres in the host matrices and the way the fibres bonded varied according to fibre orientation, proximity to aggregates and the nature of the paste. Prior to immersion, reference micrographs of the exposed fibres in all of the polished specimens were taken.

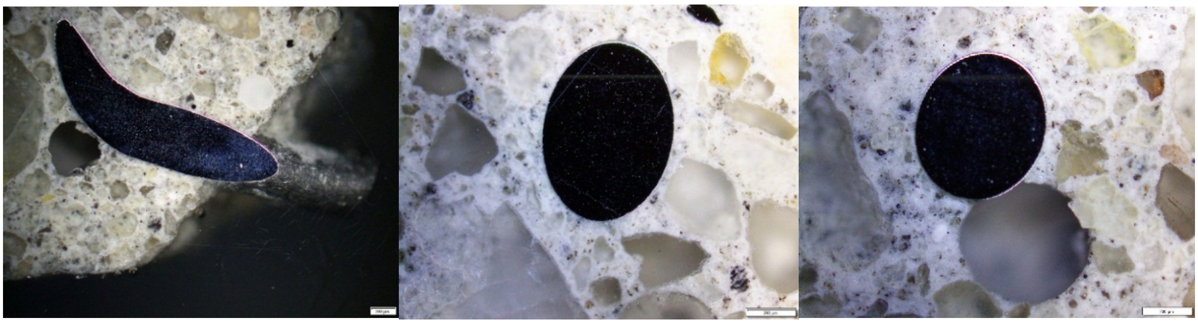


Figure 3. 19: Various orientations of fibres on original polished specimens

The examples in Figure 3.19 illustrate very different fibre positions. The micrograph on the left captures a fibre that has contorted due it being close to the surface and susceptible to the effects of lateral movement and compaction that would not affect fibres deeper within the mortar prisms. The micrograph in the centre, meanwhile, is more representative of a fibre within the bulk of any of the mortars studied. Regardless, of the fibre positioning the surrounding paste will abut the fibre to produce a continuous interface. The most obvious exception to this observation is when a pore or void abuts the fibre as can be seen in the micrograph on the right.

3.5 Conclusions

The current project is based on the premise of assessing corrosion behaviour in steel fibre reinforced mortars based on three different binders. This results section has focussed specifically on the corrosion aspect. It is important to note, however, that studying the corrosion of fibres was always going to produce vastly different observations to what would have been seen had the mortars been reinforced with rebar.

So taking into account the nature of the work being undertaken here it is a notable outcome that despite the lack of clear data several important observations have been revealed. Rather than being a function of area exposed and the orientation within a specific matrix this sections of results has shown that other factors are at play when the fibres on polished specimens corrode over time in a corrosive environment. These observations may feed into a different approach of how the surface layers of fibre reinforced mortars behave in this environment. This, in turn, may open the possibility of rethinking durability issues.

Cementitious mortars are definitely different to geopolymer in the way they respond to a corrosive environment like aerated seawater. The surface build-up is gradual and noticeable over time on the former while that is not necessarily true of the latter. While corrosion product will develop over time on steel fibres in the geopolymer matrix it is not clear whether there is other material that will develop in tandem the way it does with the cementitious mortars.

It is difficult to make the case that the technique employed to assess corrosion behaviour in this section can be described as a performance-based criterion. It is not possible to conclude that one type of mortar will exhibit long-term corrosion resistance over another based on the results presented in this section. Rather, these results confirm the resistivity profiles that each material has particular characteristics.

With the resistivity profiles, the effect of a change in water-cement (W/C) ratio was evaluated for the cementitious mortars. In this section only one W/C ratio of 0.4 was evaluated for the cementitious mortars so that the comparison across the three materials was not complicated by a feature not shared with the geopolymer mortar. The analysis in this section showed that the three types of mortar respond to a corrosive environment in their own distinctive way that differed from the way outlined in the preceding section.

The materials have now been characterised by time-based data - electrical resistivity and pit depths. In the last results chapter the materials will be characterised from a perspective based less on changes recorded over time and a property that defines the material more by its intrinsic nature. The next section will focus on microstructure.

Chapter 4

Microstructural Differences of the Various Mortar Matrices

4.1 Introduction

The overarching premise of the current project is for it to be a comparative study of the corrosion of steel fibre reinforcement in mortars made with three binder types. In this chapter, the comparison is made by analysing microstructural differences. This is a vital consideration in explaining the different behaviours of the various mortars. Data on permeability, voids and pores provide a quantitative comparison that is then taken into the qualitative realm with micrographs of the mortar matrices revealing how the various paste-aggregate interface behave in a corrosive environment [3,4]. Using these techniques, further understanding of the nature of these materials is made.

It has already been seen through electrical resistivity values and the corrosion of fibres within the various matrices that geopolymer behaves very differently to the cementitious materials. We have also seen that the two cementitious materials also have their differences in regards to these parameters. In this section, we will use aspects of microstructure to build on these observations and attempt to put a theory together as to what the true differences are with the matrices and how corrosion variations indicate quite fundamentally that even the simplest mortars can end up being unique in their own way.

Many factors influence the microstructure in mortars and concrete. For instance, the effect of varying the water-cement (W/C) ratios in concretes based on OPC and a blended cement with 20% FA was studied [56] and correlated to the level of corrosion and the degree of permeability of chloride ions. The authors noted that this is also a means of determining porosity and thereby microstructural differences. Another study [57] used back scattered electron imaging to estimate porosity and voids adjacent to a single fibre in a matrix. It was estimated that the porosity found at the fibre interface may increase the air void content of the mortar samples by as much as 1%. Koleva et al. [39] conducted extensive analyses on the steel-paste interface of mortars containing rebars and exposed to chloride environments. The authors detected a range of iron chloride compounds that varied according to the nature of the matrix, the concentration of chlorides and whether or not carbonation had occurred contemporaneously.

Beyond the definitions of microstructural differences, the real importance of much of this referenced work lies in attempting to identify as much as possible how each material behaves in a corrosive environment and using microstructure as a yardstick for long term durability considerations. The contention here is that while the corrosion rates reported earlier may not necessarily offer clear insights into the specific nature of the materials under investigation, the electrical resistivity changes do provide quantitative differences. By now framing the last part of the results around microstructure we will add a qualitative dimension that will offer sufficient insight to support those quantitative differences and complete a rigorous comparison of the mortars under investigation.

Previous studies have referred to microstructure as a means of comparing various mortars but the suite of analyses used in the current project have not been used before so far as can be ascertained. The four different analyses have been carefully selected to unravel and expose key microstructural differences that explain how these materials would be expected to perform in harsh, corrosive environments. Therefore, the aim of this section of results is to clearly articulate the microstructural differences of the three mortars and show that microstructure is a critical parameter to consider when selecting materials subjected to a marine, or similarly corrosive, environment.

4.2 Experimental Details

4.2.1 Materials

The materials used for this section of results are the prisms immersed in aerated seawater (as outlined in Chapter 2) and the polished specimens that were also immersed (as outlined in Chapter 3). New polished specimens were produced from the immersed prisms for determination of voids and the method used will be outlined in the next section. Samples were sent to an external laboratory for pore analysis by mercury intrusion porosimetry (MIP).

4.2.2 Methods

Three cubes cast in the moulds outlined in Chapter 2 were used to obtain compressive strengths for each mortar formulation. The testing was performed on a laboratory scale testing unit.

The fabrication of the steel fibre reinforced mortar prisms, curing and subsequent immersion was covered in Chapter 2. After 6 months of immersion the prisms were removed from the tank and allowed to air dry standing in the same formation they had been in the tank (see Figure 4.1).

Figure 4. 1: The 15 test prisms immersed in aerated seawater for 6 months shown after removal from the tank at the end of the experiment

The only test that was performed prior to sectioning was 24 hour water absorption. Each prism was weighed after air drying for three weeks (dry weight). Each prism was then submerged in tap water for 24 hours and reweighed to determine a wet weight. The difference between these two weights was expressed as a percentage of the original dry weight.

Water Absorption = (Wet weight – Dry Weight)/ Dry Weight x 100%

For the microstructure analyses conducted in this section both polished specimens subjected to immersion and ones taken form the post-immersion prisms were used. The details of preparation of the polished specimens placed in the tank for immersion was outlined in Chapter 3. For the new specimens, small fragments were taken from three of the prisms (one from each binder type) and sent for analysis by mercury intrusion porosimetry (MIP) to an external laboratory. Approximately 1g of each of the three mortar types was used for analysis on the Auto Pore IV 9500.

Figure 4. 2: The Auto Pore IV 9500 mercury intrusion porosimeter

The void analysis was performed on polished specimens taken from sections of the post-immersion prisms using the Dektak Veeco 3D optical profiler. Thin sections were taken of the three binder types and the polished specimens prepared in the same way as outlined in Chapter 3.

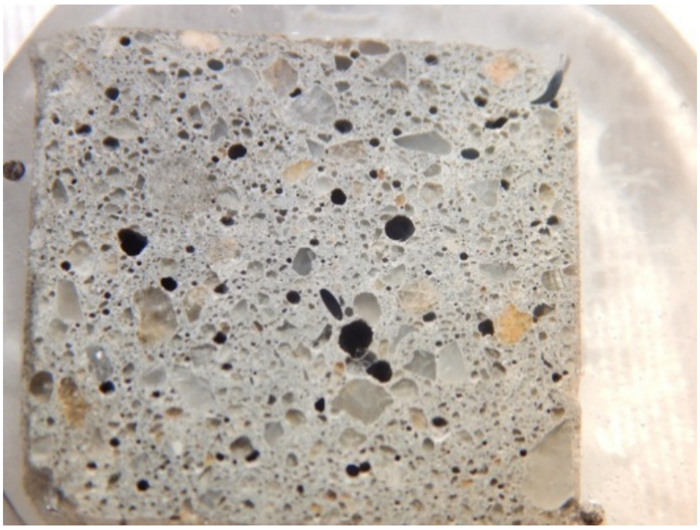


Figure 4. 3: Typical polished specimen used for 3D profiling

The polished specimens were placed on the stand in the 3D profilometer. The microscope was focused onto a region suitable for analysis with the 5X lens. Using the Vision 64 software multiple region analyses were conducted for each material of approx. 2mm x 2mm. As there was no standard procedure for measuring voids in mortar and/or concrete using a 3D profilometer parameters had to be determined based on the appearance of voids once scans were completed of the various matrices. Based on several scans across all of the materials the main parameters were determined as:

- By Threshold – 30 μm (minimum depth of a feature that would be classified as a void)
- Minimum Region Size – 100 μm^2 (minimum area of a feature that would be classified as a void)

For the final analysis in this section, the samples that were used for pitting data in Chapter 3 were also used to assess changes in the host matrix. Rather than focus exclusively on observations of pits in the steel fibres, optical micrographs from the Olympus BX61 microscope were taken of the area surrounding the fibres and also of the general matrix away from the fibres.

The specimens retrieved from the tank after 4 and 6 months of immersion required cleaning to remove reaction products and debris from the surface. This was done by placing the specimens in a beaker and covering them with a dilute (1:10) solution of Clarkes cleaning agent with distilled water as the diluent. Clarkes solution is a combination of hydrochloric acid and inhibitors and is commonly used for removing the corrosion products from steel samples [ASTM Standard G1-03]. Once removed the specimens were washed with distilled water and then air dried. They were then washed again with ethanol and air dried again. This ensured the surfaces were as free as possible form the reaction products and debris that developed with prolonged exposure to the aerated seawater.

4.3 Results

4.3.1 Compressive Strength

Three cubes from each mortar type were tested after 28 days of ambient curing. The results (with error bars) in MegaPascals (MPa) are given in Figure 4.4 for the five different formulations (the two cementitious binders at water-cement ratios of 0.4 and 0.45 along with the geopolymer one).

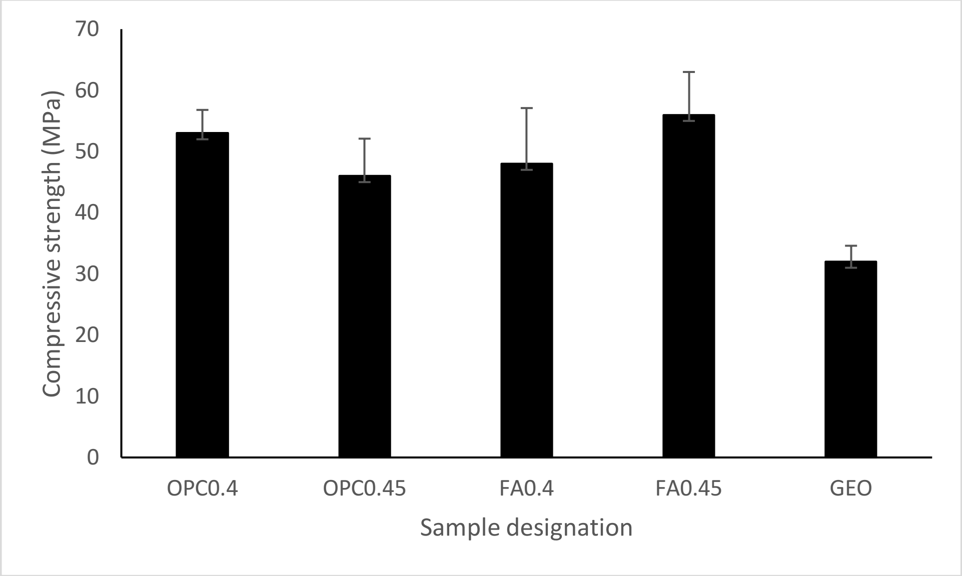


Figure 4. 4: Compressive strength values for each mortar formulation (pre-corrosion)

4.3.2 Water Absorption of Pre- and Post-Immersion Samples

The results for 24-hour water absorption are given in Table 4.1.

Table 4. 1: Water absorption values for the three mortar types

Mixture	Water absorption (%)	
	Pre-Immersed sample	Post-Immersed sample
OPC	3.4	0.2
FA	4.2	0.6
GEO	6.3	5.7

For the two cementitious mortars there was a 94% (OPC) and 86% (FA) reduction in water absorption from pre-immersion to post-immersion, while the geopolymer only reduced by 10%.

4.3.3 Mercury Intrusion Porosimetry of Post-Immersion Samples

The results from mercury intrusion porosimetry (MIP) are given in Table 4.2..

Table 4. 2: Average pore diameters determined by MIP

Sample designation	Average Pore Diameter (µm)
OPC	0.0143
FA	0.0128
GEO	0.0548

As seen with the preceding results on water absorption (Table 4.1), the two cementitious mortars have similar pore size averages. The geopolymer, on the other hand, has an average pore size almost four times that of OPC and more than four times that of the blended cement mortar. In cement chemistry terms, this is a very large discrepancy and shows quite clearly that the microstructure of the geopolymer is significantly different to the other two materials.

4.3.4 3D Microscopy Profiling and Imaging of Post-Immersion Samples

3D profiling was used to estimate the voids content of the three materials with approx. 300 readings taken for each material. This unconventional technique is used to enable data on voids in these materials to be presented as a comparison and reference to the data obtained on the pores by mercury intrusion porosimetry. It is also in keeping with the desire to use microscopy wherever possible in the current study.

Table 4. 3: Void sizes (diameters) as determined by 3D profiling

	Void size (µm)			
Mixture	< 50	50 - 100	> 100	Median
OPC	76%	4%	20%	26
FA	79%	5%	16%	26
GEO	48%	29%	23%	49

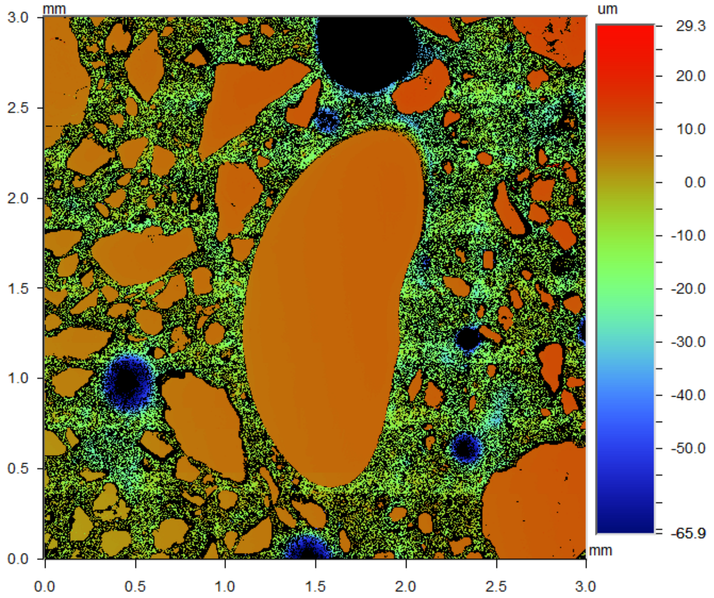


Figure 4. 5: Typical image obtained by 3D profiling when estimating void size and distribution in each material (length and width on axes of main area, depth on colour chart to right)

To illustrate how voids, either caused by entrained or entrapped air, influence properties a study by Wong et al. [58] showed that entrained air at different concentrations within concretes of varying water-cement ratios can have dramatic consequences on transport properties and diffusivities. These properties can be related to resistivity behaviours and therefore how prone the materials will be to chloride ingress and corrosion.

The results in Table 4.3 show similar patterns to the pore size results of Table 4.2. The median void size for the two cementitious materials is the same while the average pore size was also very similar. The median void size of the geopolymer, on the other hand, was much greater than the other materials as was the case with average pore size.

4.3.5 Optical Microscopy of Immersed and Post-Immersion Samples

The sequence of micrographs below (all taken at 50x magnification) illustrate how the various materials responded to the immersion in aerated seawater and subsequent cleaning of the polished specimens to reveal details of the interplay of pitting, corrosion product deposition and the integrity of the revealed, cleaned matrices to withstand these changes.

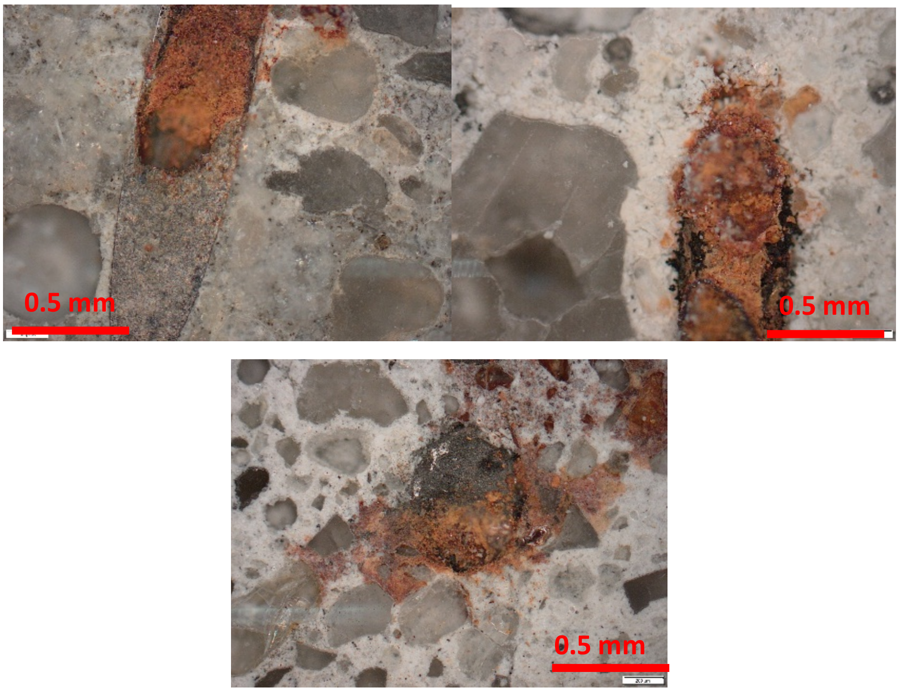


Figure 4. 6: Optical micrographs of OPC, FA and GEO (left to right) after 2 months of immersion – all uncleaned

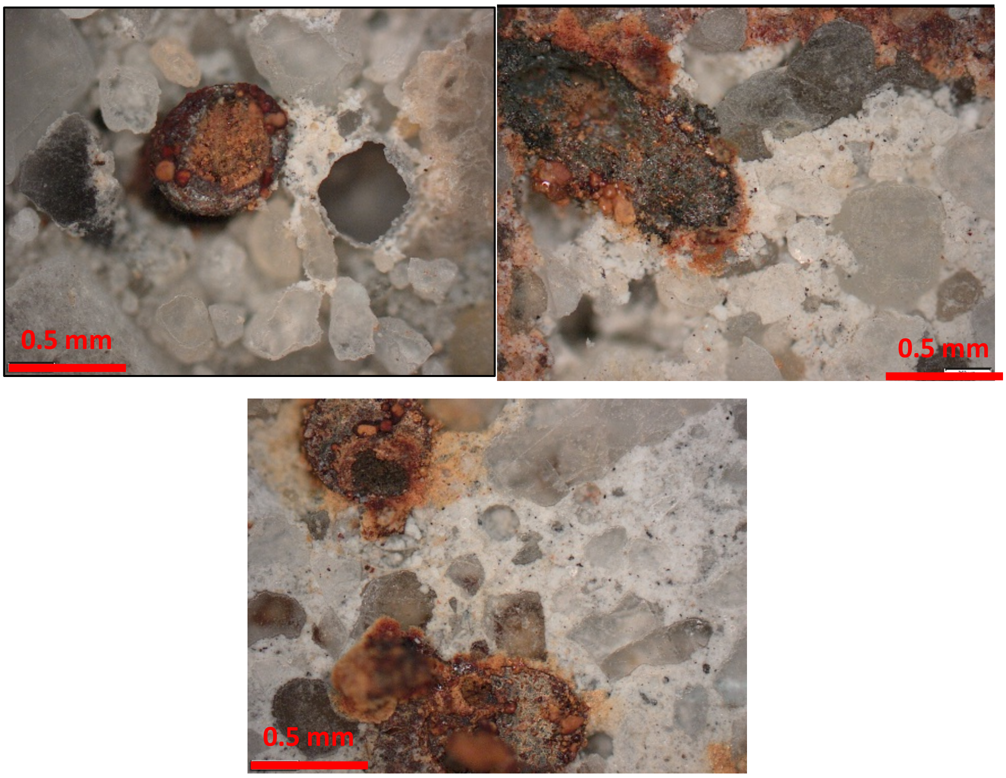


Figure 4. 7: Optical micrographs of OPC, FA and GEO (left to right) after 4 months of immersion – OPC cleaned to reveal fibres but FA and GEO still uncleaned

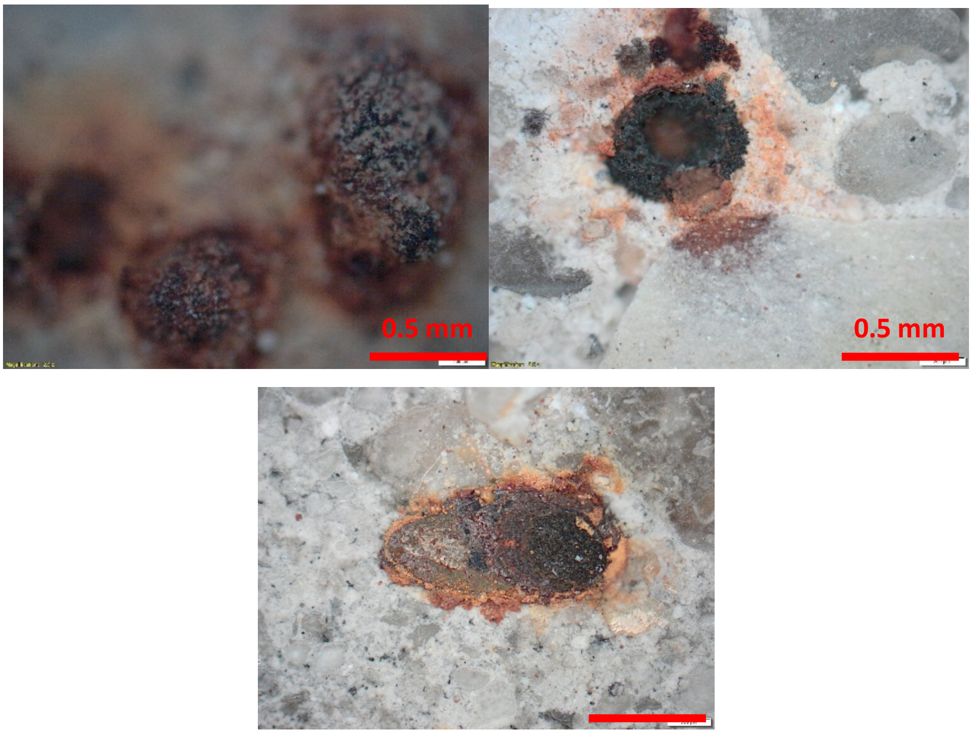


Figure 4. 8: Micrographs of OPC, FA and GEO (left to right) after 6 months of immersion – OPC unable to be cleaned, FA cleaned and GEO uncleaned

In preceding sections, it was clear that the cementitious mortars had far more in common with each other than they did with the geopolymer, in terms of electrical resistivity and microstructural analyses. What makes this set of micrographs, and subsequent ones in the discussion section, so fascinating is that for the first time we are seeing a clear distinction in the performance and behaviour of the OPC mortar in relation to the blended cement mortar, and that, in fact, the blended cement displays properties more closely aligned with the geopolymer than with the standard OPC.

As evidenced in Figure 4.6 the appearance of fibres and the surrounding matrix in all three materials showed some similar characteristics in terms of build-up of corrosion product. After 4 months of immersion the only way fibres were exposed in the OPC specimens was after cleaning. The FA and GEO specimens, on the other hand, still had fibres visible post-immersion in their raw state (uncleaned as evidenced in Figure 4.7). At the end of the immersion period of 6 months, the fibres in the OPC specimens were not responding to the nominated cleaning technique while the FA and GEO were still able to be cleaned with the latter still having some fibres visible on uncleaned surfaces (Figure 4.8).

The results show the contrast between the microstructure of the three materials at various stages of immersion in aerated seawater has been presented in relation to the steel fibres in a manner similar to the way results were presented in Chapter 3 when pitting data was used to highlight the corrosion behaviour of the materials. In the ensuing discussion section, the focus will be on the matrices themselves in order to more fully explain the contrast between the materials in terms of distinct microstructural differences.

The premise of measuring electrical resistivity changes and matching that with corrosion resistance and quantifiable microstructural differences progressed along a line showing that the cementitious materials were similar and the geopolymer was different. However, the final step of qualitative analysis reveals very different results. It is this revelation that changes the whole trajectory of the current study and is a powerful affirmation of prioritising qualitative analysis as much as data collection to ensure that the ongoing mysteries of concrete and mortar research will continue to be pursued.

The changes to the microstructure of the matrices over time were revealing. It was clear that the harsh conditions of aerated seawater were affecting all of the materials but there were clear differences in how each material was behaving and responding to these conditions. While in the preceding section on pitting analyses it was shown that corrosion of the steel fibres proceeded at times randomly and independently of the changes to the host matrix, it was also clear that there were patterns of changes to these host matrices. When debris and corrosion products were cleaned away from the fibres to reveal the extent of pitting, the impact this had on the matrices was noticeable.

The results show when the matrices themselves were the focus of the analyses it was even more noticeable and revealing of the changes occurring over time and the different behaviour of each material. The proceeding discussion will focus on these contrasts and attempt to place these observations in the context of long-term performance and durability of these materials.

4.4 Discussion of Microstructural Differences

The compressive strengths of each of the formulations was presented as the first set of results in this chapter. The values for the cementitious materials varied from the nominal target of 40 MPa with all above that value. While the geopolymer was the only material to have an average compressive strength (over 3 samples tested) below this target it does not affect the analyses conducted in the current study in any substantive manner. In previous chapters, observations of the electrical resistivity profiles and pitting of steel fibres of each material were presented without reference to the differences in compressive strength. Equally, the discussion in this chapter will proceed with that same caveat.

Subsequent to compressive strength, there were four aspects considered in the results section of this chapter and all are related to microstructure;

(1) General permeability represented by water absorption
(2) A measure of porosity by means of mercury intrusion porosimetry
(3) A novel method for measuring voids using a 3D profilometer, and
(4) Finally, observing general changes in microstructure and matrix differences via optical microscopy

While the first two methods are common techniques, two types of microscopy were specifically employed to give the current study a fresh perspective and insights into how the microstructures of these materials would change in a corrosive environment.

The water absorption results show that the two cementitious materials became clearly more impermeable after the extended period of immersion, whereas the effect is much diminished with the geopolymer. This is most likely due to some degree to the way surface materials build up on the cementitious mortars due to reactions between the ions in the water and unreacted hydration products and lack of any corresponding phenomenon with the geopolymer. It is well known that calcium carbonate and magnesium hydroxide [46] form on the surface of concrete and mortars made with cement-based binders. There is very little in the literature about the outcomes for geopolymer formulations, in terms of their performance in a corrosive environment like aerated seawater.

Permeability and permeation are broad concepts within cement and concrete research [2,3]. They give general indications of a materials' susceptibility to attack by chloride ingress and carbonation but always require additional information to determine their true behaviour, particularly when cracking is present [59]. In the current study there are clear trends in reduced permeability of the cementitious mortars as opposed to the geopolymer one but it cannot be deduced from the water absorption figures alone how effective these changes have been in creating a more corrosion resistant material. As with the electrical resistivity changes in Chapter 2, the behaviour of the cementitious mortars seems to be far more time dependent than the geopolymer. In other words, as the length of time of immersion increases we can see an improvement in how the cementitious mortars respond to the corrosive environment – increased electrical resistivity and reduced permeability.

The contrast here with the geopolymer mortar is significant on the measures of electrical resistivity and water absorption, both of which give general indications of performance. Even though more detailed analyses will reveal the degree of nuances between the materials it is very revealing to see the stark differences on these measures. The fact that the geopolymer did not change at all in electrical resistivity while the cementitious ones clearly did stood out during the period of immersion. To then see the way that the geopolymer remained essentially as pervious at the end of immersion as it was at the commencement helps explain the resistivity data [60]. To then also contrast its behaviour with the cementitious materials and see how the water absorption data aligned with resistivity to give us a more complete picture of the way these materials respond to this environment and provides a valuable comparison on the behaviour of these materials.

Even before exploring some of the key indicators of microstructural differences, the first result of this chapter confirms the more general observations of bulk properties of the three materials and how geopolymer appears to be such a different material. These observations place in context the ways in which materials respond to a harsh, corrosive environment. Structural materials like concrete and mortar have long service lives and are affected by their environments throughout that time. Therefore, bulk properties like resistivity and permeability reveal a lot about their behaviour over extended periods.

The average pore size results show that the differences between the cement-based materials and the geopolymer are quite stark at the pore level. These differences will certainly affect the way in which the pore solution changes over time as these are directly related to pore size, along with the chemistry of the pore solution [61]. As geopolymer has fundamental chemical differences with cement-based binders it will naturally follow that the pore solutions, formation of gels and subsequent phase changes will be very different [62,63].

Looking firstly at the results between the OPC and the blended cement, it turns out the latter has a smaller average pore size. It is known that a densification and reduction of pore size will be induced by the reaction of the fly ash in a pozzolanic manner [64]. It is unknown how much of an effect will be seen within a certain timeframe. These analyses were performed on samples that had been cast several months prior to immersion and then undergone 6 months of immersion. It is not possible to discern the effect of curing, hydration, changes to pore chemistry and the build-up of surface layers on the prism to determine one factor over another so we are left to compare materials in the knowledge they have been exposed to the same conditions.

Smaller pores reduce diffusion through the matrix thereby reducing conductivity of the pore solution. This has a direct effect on increasing resistivity [65]. Consequently, there is a correlation between those materials with the smaller average pore size (the cementitious mortars) and a higher resistivity. The noticeably larger pores in the geopolymer and low resistivity are to be expected.

There is a distribution of larger and smaller pores across all three materials. The changes within those pores over time will be a function of their size and the nature of the surrounding matrix. Smaller pores are more stable while larger ones tend to behave like air voids once they reach a certain size [66]. It is those pores between these two extremes that may undergo changes in their chemical composition and subsequently affect properties such as diffusion coefficients and resistivity [50].

It was initially envisaged that 3D profiling would be used to look at the fibre-matrix interfaces and potentially at pitting of the fibres. However, it became clear that the polished specimens immersed beyond 2 months would be unsuited to analysis in this manner due to the deposition of material on the polished surfaces. The images and data obtained on the polished specimens prior to immersion did show that this method was well suited to analysing void sizes. The sensitivity of the microscope was within this range (with a void classified as having a diameter greater than 50 microns) while determining pores sizes was beyond it. Therefore, post-immersion polished specimens of mortar sections were used to assess void size and distribution.

There was no indication in the literature that this approach had been adopted before and yet it was a remarkably simple and effective means of distinguishing the pattern of voids between the cementitious mortars and the geopolymer. There was a study using a similar approach that provides a reference of sort for this work [67]. Confocal microscopy revealed pore structures in hardened cement paste through thin sections. This is important work as it leads into other developments such as x-ray tomography that could provide real 3D rendering of concrete and mortar matrices that provides greater understanding of the interconnectedness of pores, voids, moisture and solid matrices.

The voids analysis presented in the current study reveals a similar pattern as the previous data on pore size. The median void size for the cementitious materials is similar while that for geopolymer is distinctly different. The sensitivity and tolerances of this method are different to mercury intrusion porosimetry (MIP), hence the use of the median figure rather than the average. MIP is a highly sensitive operation of a non-wetting liquid (mercury) being forced into pores with the resistance and surface tension, relative to the force applied, being equated to pore size. The instrument has sufficient sensitivity to accurately measure pores across the size distribution and thereby accurately estimate the numerical average of these pores. With the void analysis by 3D profiling, however, the sensitivity and accuracy can only be estimated by repeat analyses. The data resulting from the sequence of analyses is appraised for its consistency and then presented once discernible, repeatable patterns are noted. It has also been decided to present the median value as the mean is skewed by some very large void sizes.

In the preceding chapter, the corrosion behaviour of the fibres within each matrix was discussed. The nature of the host matrix was also discussed to provide context for the quantitative analysis of corrosion via pit depths in individual fibres. In this chapter the focus is microstructure, rather than direct corrosion as it was in Chapter 3 or an indicator of corrosion as it was in Chapter 2 when electrical resistivity was discussed. With the first three analyses presented in this Chapter providing quantitative distinctions of the microstructural differences between the materials, it is important to deal with the observations of changes to the microstructure throughout the period of immersion from a descriptive, qualitative perspective.

The micrographs presented below chronicle degradations in the matrices of all three mortar types at one stage of immersion (4 months) and at the end of immersion (6 months). The differences at the first removal from immersion (2 months) can be illustrated with reference to micrographs already presented in this chapter and the preceding one.

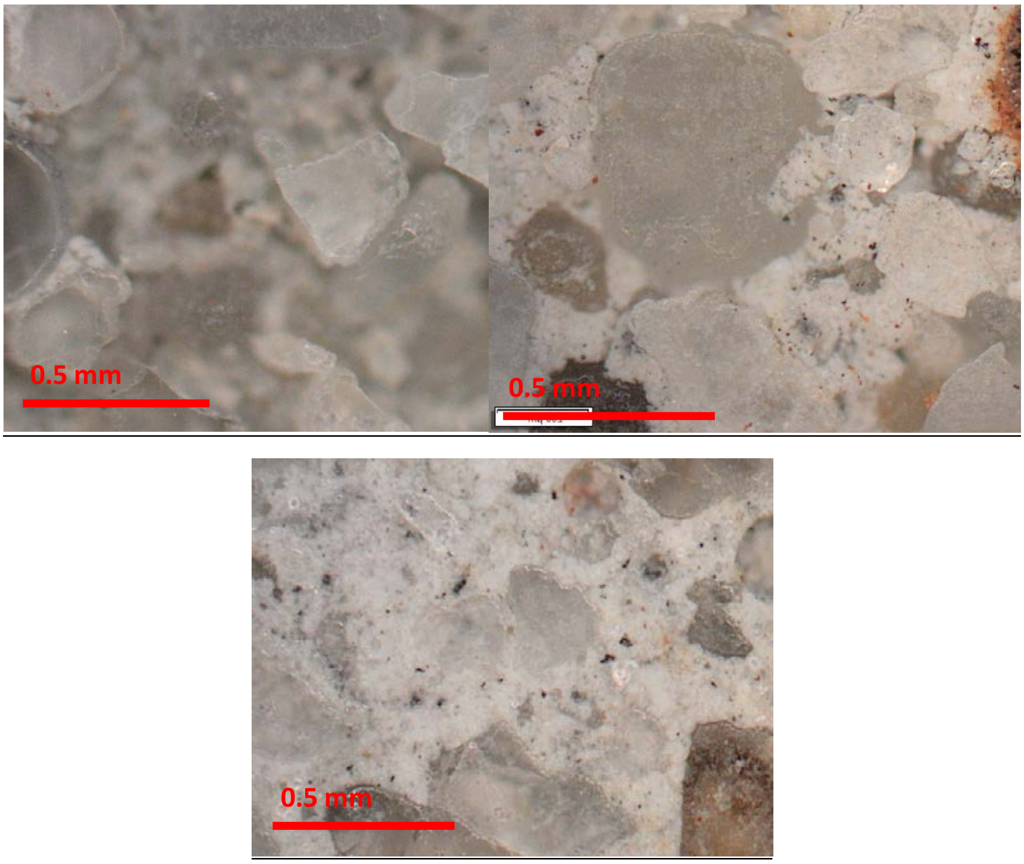


Figure 4. 9: Cleaned matrices at 4 months of OPC, FA and GEO (left to right)

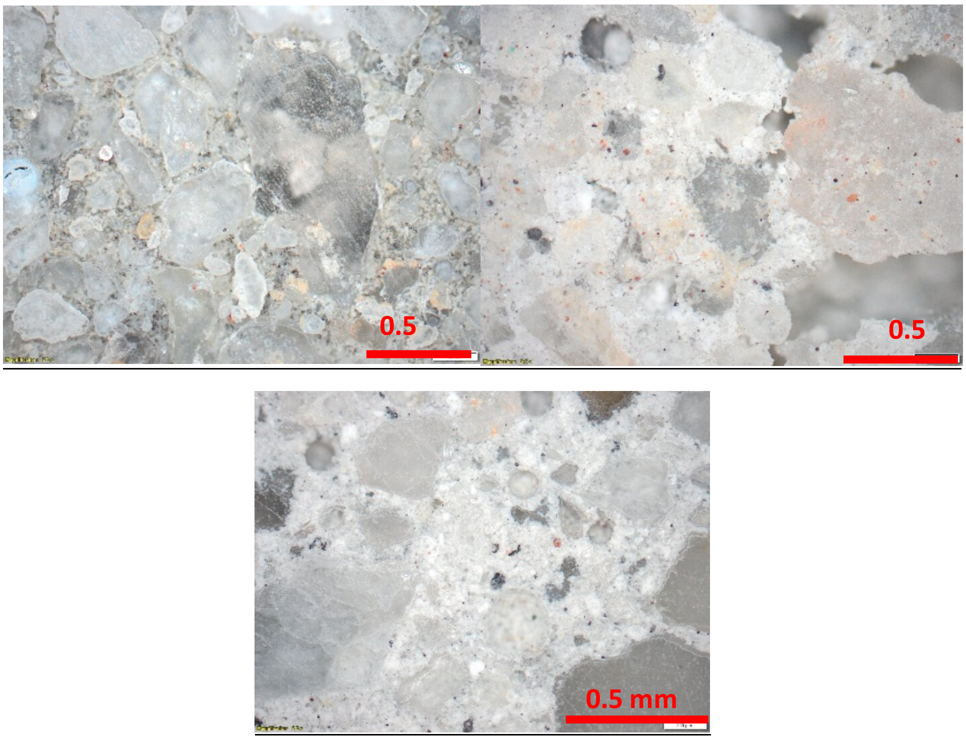


Figure 4. 10: Cleaned matrices at 6 months of OPC, FA and GEO (left to right)

As has been stated earlier, micrographs of the specimens removed after 2 months of immersion showed across the three materials that some deposition of surface material (debris, reaction products and corrosion product) was occurring in a manner where it was difficult to discern a lot of variation between the materials. Certainly, deposition on the geopolymer specimens appeared to be occurring differently to the cementitious mortars but it was not feasible to draw definitive conclusions from these observations.

By the time of the second removal of specimens, after 4 months of immersion in aerated seawater, it was clear that distinctive patterns were emerging. It has been noted earlier in this chapter, and in the last one, that the materials responded to cleaning of the polished specimens in ways peculiar to each material. Fibres in the OPC specimens could be revealed by cleaning but not uniformly or as easily as the FA specimens. This was the first major divergence between these materials from a microstructural perspective. The three quantitative analyses of this chapter (water absorption, average pore size and median void size) and the pitting data of the previous chapter indicated these two materials were similar in terms of microstructural analyses. Now, after a reasonably lengthy exposure time to a harsh environment, the two cementitious materials were behaving differently. The paste in the OPC specimens was being removed by the cleaning solution after 4 months while the paste in the FA specimens was remaining largely intact as can be seen in Figure 4.9. If the comparison is then extended to the GEO specimens, it can be seen that the FA behaves in a manner far more akin to the GEO than the OPC. This too is a distinctive break from the patterns preceding analyses had revealed where similarities were only evidenced between the cementitious materials.

The specimens removed at the end of immersion period of 6 months confirmed the pattern of behaviour seen after 4 months. The micrographs in Figure 4.10 show that the paste in the OPC specimens was removed by cleaning while the paste in the FA and GEO specimens remained largely intact again. This series of micrographs is also revealing when it is remembered that the fibres on the OPC specimens after 6 months did not respond to cleaning and the corrosion product remained in situ at the same time as the paste was being removed.

This series of observations of the behaviour of the three materials throughout immersion in a corrosive environment frames the discussion and conclusions of the entire current study. The aim of the study is to compare and contrast three key building materials from the perspective of corrosion resistance and microstructure. The first chapter of results showed there were clear variations in electrical resistivity profiles throughout immersion but that the corrosion data (pit depths of fibres) presented in the second chapter of results didn’t show these variations. Now in this final chapter of results we are seeing this pattern repeated to some extent where the quantitative analyses suggest a particular pattern but the qualitative analysis suggests something else. Except in this section of results we can see clear evidence of the microstructure of the various materials responding in distinctive ways that we could not in the pitting data analysis. Therefore, the author argues that these microstructural differences are the most important findings of the current study.

Support for the statement about the importance of these microstructural differences can be found when it is considered that the concerns of the long-term durability of reinforced concrete are overwhelmingly to do with the paste. Both chloride ingress and carbonation propagate through the paste. The new types of durable concrete have low permeability based on pastes with low porosity while potentially still maintaining a high level of air voids. This fresh perspective on microstructure also opens opportunities for new materials like geopolymer to be assessed by new guidelines that take into account that not all spaces in the paste are the same. Equally, it is hoped a measure of resilience can be used to discriminate across various binder types that looks beyond standard quantitative measures used currently.

Further to the preceding discussion on changes detected to the microstructure during the period of immersion it is vital to place these observations in the context of a desire to understand surface effects. It has been speculated as to the chemical and physical interactions each material had with the aerated seawater. Putting this in a broader context, the study of surface effects on concrete has an interesting backstory.

A paper published in 2000 by Papadakis [68] presented some findings about the effects of supplementary cementing materials (SCM) and aggregates and their correlation in respect to chloride ingress. Replacement of cement and/or aggregate by the SCM affected chloride ingress with a clear benefit of having an SCM up to a certain level. It was postulated that chloride binding capacity is affected by the amount of calcium silicate hydrate (CSH) near the surface and its subsequent effect on capillary pores. When an SCM is present, such as fly ash, there is more CSH near the surface and this allows chlorides to ingress to a certain depth before their diffusion is arrested by densification of the matrix by ongoing hydration and pozzolanic reactions.

Earlier work by noted researchers Chris Page [69] and Nick Buenfeld [70], among others, looked at the phenomenon of chloride binding too. As analytical techniques become more sophisticated, the interplay of chlorides, pore solution and the solid phases is better understood. In another paper published in 2000 [71] the chloride levels close to the surface of concrete was found to be relatively high as a result of high levels of bound chlorides. Further into the concrete the balance between free and bound chlorides changed such that bound chlorides were not anywhere near as prominent due to changing pore solution chemistry and the effects of diffusion.

Taking these principles into consideration for the current study, it would seem reasonable to suggest that the polished specimens from the cementitious mortars would be subject to chloride ingress of some form and these would be a combination of free and bound chlorides. Optical microscopy will not discern these effects, however, so the explanation for the degradation of the microstructures over time must take into account other considerations, particularly physical. There could be little doubt that the physical abrasion of the surfaces of the polished specimens will have a deleterious effect on their appearance. In order to gauge the extent of this effect it is perhaps best to look at the respective changes to the paste, aggregate and the steel fibres.

An interesting feature of the work in this section of results has been the way fibres have corroded in relation to their host matrix. Three stages of corrosion were evaluated based on varying lengths of immersion in aerated seawater – 2 months, 4 months and 6 months. In most other corrosion studies, the length of time to corrosion initiation is assumed to be that period when chloride ingress is occurring through the covering layer over steel reinforcement. In the current study, that is not the case as it is fibre reinforcement in use and their corrosion is monitored by changes in polished specimens. The fibres are exposed to a harsh environment at the outset of the experiment and it is expected that corrosion would commence almost immediately.

Consequently, when the first lot of specimens were removed after 2 months it was confirmed by optical microscopy that some corrosion of some of the fibres had commenced across all three material types. It appeared that the nature of the geopolymer matrix was having some impact on how prevalent the corrosion was for those specimens while there seemed to be some common characteristics across the two cementitious materials and they were behaving quite differently to the geopolymer. Surface build-up was more noticeable on the cementitious ones as well. This would affect corrosion rates as a galvanic reaction is more likely to proceed once deposition occurs on the steel surface.

Divergence in behaviour began to occur at the 4-month mark. The specimens removed at that point had quite a bit of debris on their surfaces. It was not possible to see the polished fibre, paste or aggregate surfaces on any of the cementitious specimens and was only possible in limited cases for the geopolymer ones. Therefore, it was at this stage that the cleaning of the specimens began to discriminate between the OPC and FA specimens. This was more clearly the case at the end of immersion when the OPC specimens were not responding to the cleaning technique being used, but the FA and geopolymer specimens were with the latter still showing that debris and surface build up was much less noticeable than the FA specimens.

With these observations in mind, it is important to discuss the effect of the host matrices from the perspective of the interfacial transition zone (ITZ). Research on the ITZ has been conducted for several decades but a paper in 2004 is noteworthy [72] as it uses microscopy of polished specimens to discern a mechanism of reducing porosity as hydration products evolve in the paste over time. The nature of the binder, and thereby the paste, plays an important role in this phenomenon. The current study is comparing and contrasting various binder types and thereby various types of ITZ.

The ITZ always has to be considered in relation to the steel-paste interface and the aggregate-paste interface and the distances between all of these features. Pore distribution and the composition of the solid phases will vary across these profiles [73]. This in turn will impact on the properties of the bulk material, whether it be steel fibre reinforced mortars or traditional reinforced concrete. It has been shown that the types of pores are dependent on location within the matrix and proximity to fibres and aggregates [74]. Evaluation of pores and voids in the ITZ and their locational impact on the analyses conducted in the preceding chapters is beyond the scope of the current study.

The distinctive nature of geopolymer has been used to compare and contrast it against the cementitious materials in the current study. In relation to microstructure, geopolymers offer a stark contrast to cementitious materials. The hydration of silicate phases in the presence of a calcium source is the centrepiece reaction in understanding how the microstructures of cementitious materials change over time. The evolution of the aluminate phases present unique challenges as well, particularly with ettringite, but it is the hydrating silicate phases that have the most impact on diffusion and changes in pore structure generally. In contrast, it has long been assumed that calcium plays a minor role in the reaction kinetics of geopolymers. This has been challenged by some researchers [75] who believe it is necessary to establish the exact role of calcium, rather than assuming it is inert or benign.

Behind the science of geopolymer is the theory of alkali activation of an aluminosilicate source. The way in which alkali ions, primarily sodium and potassium, behave within the microstructure has been a common focus of the research. The hardening of the paste by a process of dissolution and condensation and how this varies based on the ratio of silicon to aluminium has also featured prominently [76, 77]. In the current study, data has been presented to show that the pore and void size and distribution of geopolymer in comparison to cementitious materials vary considerably. It has been beyond the scope of the current study to delve into more detail about the differences in pore chemistry of the two systems. Studies have shown that the nature of these differences are strongly dependent on the aluminosilicate source and the activation mechanism [78, 79, 80].

Some of the other results in the current study offer potential insights into microstructural nuances of geopolymer. The low electrical resistivity of the immersed prisms and the high water absorption of the post-immersion prisms indicate the geopolymer microstructure is more permeable and more conductive. The permeability aspect was also borne out in the void analysis. Conductivity, on the other hand, has not been evaluated in the current study by any other method than electrical resistivity (an inverse relationship). The way the steel fibres interact with the geopolymer microstructure may indeed be quite different to the way they behave in a cementitious microstructure. This comment is based on studies of the role of iron in geopolymer.

A recent study claimed to detect for the first time the presence of discrete iron particles within an activated slag geopolymer microstructure [81], however found no evidence of any interactions or reactions with the surrounding matrix. This is an important milestone in geopolymer research as it opens a new line of inquiry on the role of iron, particularly in comparison to cementitious microstructures. Within the field of cement chemistry the role of calcium, the silicate phases and the aluminate phases tends to dominate research but it has been well known that high iron levels in clinker do impact the properties of mortars and concretes made predominantly with cement [2, 4]. A subsequent study [82] showed evidence of diffusion of iron oxide in a geopolymer microstructure under thermal shock. A model was proposed to explain the observed behaviour. This stream of research on iron in geopolymer may help guide future work undertaken to fully comprehend microstructural differences with cementitious matrices.

Aligned with the preceding discussion on iron is a more general observation on the methods employed in the current study that compared geopolymer to the cementitious mortars in terms of surface effects during immersion in aerated seawater. It was noted that the steel fibres within the geopolymer matrix responded differently to the others throughout immersion. It can be postulated the iron reacting on the surface of these fibres did so in a particular way for the geopolymer that was not replicated in the other materials. Consequently, corrosion products and debris developed on the geopolymer also in a different manner. Therefore, despite the limitations of the results outlined in the current study and the conclusions that can be drawn from the micrographs of these surface changes throughout immersion it can be suggested that this general approach may be used in future studies perhaps in tandem with other methods to more fully explain the nature of steel reinforcement within different microstructures.

4.5 Conclusions

A microstructural investigation has revealed quite a lot about the differences between the three mortars. Certain trends are borne out of a series of analyses only to be challenged by the next series. Four different techniques were used in this section in order to provide a thorough perspective on microstructure. Water absorption and mercury intrusion microscopy are common techniques but the use of 3D profiling and optical microscopy to complement these analyses provides a fresh perspective.

The absolute figures obtained from the first three sets of analyses all point to a common thread of the cementitious mortars being less permeable than the geopolymer with smaller pores and smaller voids. Chloride ingress and potential for subsequent corrosion should therefore be less in these materials. As was shown in the preceding chapter measuring surface corrosion across these materials at different lengths of exposure to the corrosive environment of the current study did not follow this pattern necessarily.

The comparison of the three materials in this chapter used the quantitative data mentioned above arising from the three measurements, leading into the final analysis which was more qualitative. Evaluation of micrographs of their respective matrices and how they responded to immersion and cleaning revealed a pattern of behaviour hitherto not revealed by other analyses.

While the first three analyses provide snapshots, the study of the microstructures of the three materials reveal information about their performance under extended stress. Exposure to aerated seawater for 6 months followed by cleaning with an acidic solution can reasonably be classified as placing these specimens under a stressful regime. More importantly, it exposed the materials to forces that would enable a comparison of how the various binders would respond to these conditions. With the aggregates and fibre concentrations consistent across all formulations, the paste that forms from the various binders has to withstand much of the stress.

If any conclusions can be drawn on the relative durability of the materials in the current study it would stem from the observations of the resilience of the paste as seen in the micrographs of the last section of results in this chapter. This is particularly prescient for the cementitious mortars as there are still lingering questions about the direct contrast with geopolymer when so many of its characteristics are at odds with the cementitious materials. The blended cement exhibits a distinctive resilience that supports long standing theories in cement and concrete research of the benefits of using a mineral admixture to partially replace cement.

While it has been repeatedly stated that any conclusions drawn on the behaviour of the three materials from a microstructural viewpoint must be qualified by the nature of the experiment it is important to note that the techniques used did elucidate differences that can be potentially related to long-term durability. The techniques are surface based but reveal important general properties. Particularly, micrographs reveal time based differences that could be used to extrapolate and predict longer-term properties.

Chapter 5

Summary and Future Work

5.1 General Discussion

The current study aimed to evaluate the differences in three steel fibre reinforced mortar types when exposed to a corrosive environment. Results obtained before, during and after 6 months of immersion in aerated seawater showed that these mortars behaved in a manner unique to the binder type used to fabricate the mortars. The effect of the fibres was also distinctive in terms of the respective corrosion behaviours and microstructural differences of each mortar.

The first test generally performed in any concrete or mortar research project is compressive strength. In the current project, the three mortar types were tested under the same conditions so as to get a baseline of information about the materials. The mix designs were based on a 40MPa premix formulation. The results showed that the blended cement was the strongest (average 52 MPa) followed by Ordinary Portland Cement (average 50 MPa) and then by geopolymer (32 MPa). While the values were quite different it has been assumed that all subsequent observations of the materials are based on other intrinsic differences rather than anything related to strength differences. It has been assumed that the blended cement, for instance, behaves in the way observed due to the interaction of cement and fly ash when compared to Portland cement and not the fact that it is approximately 20% stronger than the latter. Similarly, the lower value for geopolymer was not factored into subsequent evaluation of its performance using the other measures employed in the current study.

5.1.1 Concrete and Corrosion

The interface of steel fibres in mortar is an important consideration. In preceding chapters, it has been discussed how pitting and general corrosion occurred in a series of fibres across the different matrices, but it is necessary to note more general observations about the nature of the interface to put this all in context.

Corrosion of steel reinforcement is such a serious concern that research into causes and solutions require ongoing attention. While the main causes (chloride ingress and carbonation) and consequences (concrete spalling and structural failure) are well known, it is remarkable how much still remains contested on the best ways to address this issue. In the current study, the issue has been evaluated in terms of the relationship between the steel and the host matrix. The structural aspect has been deliberately avoided by not using rebar in the samples and assiduously avoiding the structural properties of the steel fibres and/or the host matrices as a factor for consideration.

Steel fibre reinforced mortars are composites of the mortar and the fibres – two distinct materials with quite different properties. When these composites are exposed to a harsh environment like aerated seawater, the two materials respond in their own distinctive way as well. However, the basis of the current study, and indeed all concrete corrosion studies, is that the concrete or mortar as the host material has a direct effect on the steel contained within. It is argued by the author that this perspective validates the nature of the current study – as long as steel is integrated into a matrix, particularly in a manner that would be replicated commercially, the corrosion behaviour of that matrix can be assessed and the results reported that add to the body of research into concrete and corrosion.

Concrete and mortars come in a wide variety of forms with the first parameter of any study being the choice of formulations to evaluate. The current study has deliberately limited the scope of formulations in order to focus on how a cement-free binder compares with two common cement-based formulations. It is the starkness of the contrast between these three formulations that lends immediacy and relevance to the current study, particularly as it is the first of its kind to use the designated analytical techniques to evaluate geopolymer alongside cementitious formulations. It is also believed that the suitability of an alternative material like geopolymer can be assessed most thoroughly when compared with common commercial cement-based materials.

5.1.2 Fly Ash

As a mineral admixture, fly ash has many virtues and beneficial properties. Its wide usage in concrete throughout the world is testament to and affirmation of this observation. When present as a component of a binder formulation it behaves in a pozzolanic fashion reacting with free lime and densifying the matrix when the reaction products fill pores.

In the current study, the impact of fly ash on steel fibre reinforced mortars was evident on several fronts. It clearly had an impact on electrical resistivity. When comparing steel fibre reinforced mortars where all aspects were identical except the binder had been partially replaced by fly ash, it could be seen that the fly ash increased resistivity right from the start of immersion in the corrosive environment. The increase in resistivity over time was greater in the mortars containing fly ash when compared with those without fly ash – from 21 to 42 kΩ-cm for the blended cement while the OPC went from 11 to 14 kΩ-cm for the higher water-cement ratio and 14 to 21 kΩ-cm for the lower ratio. The fly ash based geopolymer is not compared with any other geopolymer formulation so its contrasting behaviour to the cementitious formulations cannot be placed in a context like that noted above on the impact fly ash has when used as a cement replacement.

5.1.3 Geopolymer

A geopolymer formulation was utilised in the current study as it is generally recognised as the most important cement-free concrete. It is also recognised that two aspects of geopolymer research require more work – longitudinal studies and direct comparisons with cement-based formulations. This particular study addresses both of these aspects but only as comprehensively as a project of this size allows.

In terms of its behaviour over an extended period, what became obvious in the current study throughout the period of immersion was that the electrical resistivity trended very differently for geopolymer in comparison to the other two materials tested. The ER value remained almost unchanged at 1.4 kΩ-cm for the entire period of immersion in aerated seawater. This trend was significant because it was taken over a sufficient period that the effect of extended exposure became clear and it was dramatically different to the cementitious materials. By the time micrographs were being observed of the onset of corrosion and the nature of the matrix changes over time, it had become clear that geopolymer behaved differently to the cementitious mortars in terms of electrical resistivity.

The fact geopolymer behaves differently to the cementitious materials allows an analysis of what those differences really mean. Understanding whether the low resistivity value translates to poor corrosion performance, as would be the case with a cementitious material (see Table 1.1), arises from these observations. The corrosion analysis conducted in the current study does not bear that out (see Figure 3.5 to 3.12) but it is a non-conventional technique. It remains unknown whether half-cell potentials, for example, on mortars made in the same fashion but containing rebar would have had an impact on the resistivity profile during immersion.

The diffusivity and permeability of geopolymer in comparison to cement-based materials is a fascinating area of research and will remain so for the foreseeable future. The two main causes of rebar corrosion in concrete and mortar – chloride ingress and carbonation – are directly affected by these properties. The current study has drawn attention to aspects of potential concern in regards to geopolymer but is certainly not sufficiently comprehensive to prove conclusively these concerns are intrinsic to all geopolymer formulations.

5.1.4 Water-Cement Ratio

The experimental template used in the current study was designed to primarily compare and contrast three materials made under the same conditions with just the binder type changed. However, a secondary consideration was to investigate the effect of using two formulations for the cementitious mortars at varying water-cement ratios. It was also decided to keep these ratios reasonably close together so they would be more representative of commercial applications. For instance, no high-quality, durable premix would be made at a W/C ratio of 0.6 while the range of 0.4 and 0.45 used in the current study is quite common.

This seemingly narrow variation did, however, produce interesting results. Specifically, the electrical resistivity profile change in the OPC was not replicated in the blended cement. This indicates quite different dynamic changes occurring in the respective matrices. Longitudinal studies of the effect of varying the water content in a range of cementitious binders, such as that undertaken in the current research, would produce valuable information for engineers as they seek to specify the most durable formulations into the future.

5.1.5 Electrical Resistivity

A consistent theme expounded in this thesis has been that the electrical resistivity data collected during the immersion phase of the experiment has enabled comparison across the three materials using a technique that is well designed to capture subtle changes in behaviour over time. While the period of immersion was only six months for the current study, electrical resistivity measured using the Wenner probe method could feasibly be conducted on these materials indefinitely. By doing so, a long term profile of how surface and bulk resistivities change and whether a peak in impermeability is reached would also feed into the narrative of material selection for highly durable construction products.

5.1.6 Microstructure

Above all else, the author has tried to convey the centrality of microstructure in the current study. It is a concept that embraces so many facets of the behaviour of building materials. In concrete and mortar research, it has particular resonance as it combines all of the constituent elements of the paste, the matrix and aggregate/ steel interfaces and how these change over time. It is precisely for this reason that the author believes microstructural studies should be more prominent in concrete and mortar research.

Viewed in its broadest sense, the differences in microstructure between the materials unfolded over time with a series of analytical techniques that revealed aspects of the materials that offered new perspectives. It initially seemed that the cementitious materials would always align more closely with one another in comparison to the geopolymer. However, as time went by it seemed that having fly ash in common as a constituent material narrowed the gap between the blended cement and the geopolymer in terms of microstructure. Again, this observation highlights the importance of longitudinal studies with a strong microstructural focus in the author's opinion.

Ultimately, it was as a result of the microstructural analyses conducted in the current study that a clear divergence was observed between the two cementitious materials. The addition of fly ash to the cementitious binder produced paste that had far greater resilience than the binder without any fly ash (straight OPC) in the corrosive environment the materials endured for 6 months based on the response of the various microstructures to immersion and subsequent cleaning. Furthermore, while electrical resistivity and quantitative microstructural analyses of the geopolymer suggested it may be susceptible in this harsh environment the qualitative analysis of its matrix indicated that it has a resilience potentially greater than the cementitious matrix with the fly ash addition. This method of determining paste resilience is unconventional so it will remain to be seen whether subsequent research confirms these observations.

5.2 Conclusions

The work conducted for the current study aimed to compare and contrast three mortar types from the point of view of electrical resistivity, corrosion and microstructure. It has been argued that interesting and distinctive patterns of behaviour were discerned through each parameter.

A rudimentary attempt to determine whether fibre distribution and orientation influenced electrical resistivity across the mortar types, in tandem with a simple reproducibility analysis, ensured the electrical resistivity values measured throughout the experiment could reasonably be used as a basis for comparing the different materials. Electrical resistivity was used to discern the nature of the differences of the materials themselves and not any extraneous factors such as the fibres behaving differently in each material.

Pitting of fibres across the various mortars was observed at regular intervals when polished specimens were removed from immersion in aerated seawater. This analysis didn't necessarily reveal discernible differences in the performance of the steel fibres within each material but it did allude to differences between the matrices themselves.

In the final lot of results, permeability of each material was assessed by 24 hour water absorption and revealed that the cementitious mortars were far less permeable than the geopolymer. Pore size analysis by MIP and void size analysis by 3D profiling also bore out this trend.

On the other hand, microstructural differences evaluated by optical microscopy revealed a different dichotomy. There were more similarities between the blended cement mortar and the geopolymer mortar while the standard cement mortar behaved in its own unique manner. While the paste formed in the blended cement and geopolymer mortars are fundamentally different in terms of chemical composition they were analogous in their physical characteristics in this experiment.

Ultimately, it was the physical differences, particularly related to microstructure of the host matrices, of each material in a corrosive environment that was the main outcome of this study.

5.3 Future Work

In the current study, two common cementitious mortar types were compared alongside the developing technology of geopolymer. Using electrical resistivity to characterise their behaviour when exposed to a harsh and corrosive environment, these materials were also then assessed using corrosion and microstructure methods. The end result of the current project has been the development of a unique approach to understanding the performance of steel fibre reinforced mortars, adding to the body of research on durability of key building materials.

Inevitably, important areas for consideration were alluded to but not covered in any detail in the current study. The author therefore would like to suggest potential aspects that may be considered for future work aligned with this study and its outcomes.

The current study followed a particular pattern. A regular reading (electrical resistivity) was taken each week of a 6 month experiment where the materials under investigation were immersed in aerated seawater. The intention was to ascertain a pattern of behaviour peculiar to each material. The results of those tests certainly did reveal intriguing differences. Subsequent analyses were then intended to place these resistivity profiles in context while moving onto the two key aims of the study – corrosion behaviour and microstructural differences. The author contends that this sequence of analyses enabled the benefit of the current study to be clearly elucidated in the last section of results presented on microstructure.

Ultimately, the current study was framed as a microstructural investigation. The results obtained from microscopic analyses showed that the materials behaved in idiosyncratic ways throughout the experiment. If this work is to be extended by future research, the author feels that development of additional microscopy techniques is vital.

5.3.1 Microhardness

In the current study, microstructure has been evaluated primarily from the point of view of the analysis of pores and voids, along with observations from two microscopy techniques. Given that concrete and mortar research is, largely, a structural endeavour it will be important to further the current study by using a microstructural technique that derives from physical characteristics of the microstructure.

Microhardness testing is a potentially useful technique to study microstructural differences of mortars exposed to a corrosive environment. Studies have been conducted that look at the variations in paste microhardness in relation to the distance from aggregates and found that clear patterns can be discerned between cement and blended cement matrices [83, 84]. Other work has shown the benefits along with the limitations of this method [85]. One of the key aspects of the current study has been the role of fly ash. Therefore understanding the impact of fly ash on microhardness properties will also be critical for future work.

Wang et al. [74] provides possibly the most detail about the effect of the interfacial transition zone (ITZ) via a nanoindentation model while another study [86] suggests that the paste can be viewed as a two-phase material depending on its spatial relation to aggregates and the size of those aggregates. This places the study of the ITZ into a different context and, perhaps more importantly, the ongoing debate about pore structures and how they affect chloride ingress and diffusion.

Aligning microhardness with other microstructural techniques will likely provide valuable behavioural data of matrices that are being assessed for durability. Sections can be taken of aged specimens and analysed using these techniques. It is, in essence, an extension to the traditional work of petrography.

5.3.2 Geopolymer Microstructure

Following on from the suggestion of using microhardness to reveal information on how different pastes behave, there also needs to be more investigation of the true nature of the geopolymer microstructure. The modern construction and building materials markets have been developed primarily on a common understanding of how the cement hydration reaction is harnessed to produce durable materials that have properties that can be specified and tested. The uncertainties and ambiguities of geopolymer are limiting commercial opportunities so they must be addressed as a matter of urgency.

There is work being undertaken to document durability concerns of geopolymer and methods to overcome them [14,87]. One aspect the author would suggest requires attention is microstructure. The microstructural techniques used in the current study have provided an interesting baseline of data but much more is needed. While microhardness comparisons with other materials would be useful there needs to be much more analysis done via a technique such as x-ray tomography [88, 89] for instance.

The current study showed that the geopolymer paste behaves quite differently in terms of its distribution of voids and pores, its resistance in a marine environment and surface reactions over time when compared with cementitious materials. The precise reasons why this occurs need to be uncovered, otherwise its suitability in harsh environments will be challenged.

As more results come to light from the durability studies being conducted on in situ geopolymer samples, the author feels that more concerted microstructural analyses done over extended timeframes will be an invaluable accompaniment to studies on chloride ingress for instance.

5.3.3 Surface Properties

It is understandable that the main concerns for researchers and practitioners of the long-term performance of concrete have been chloride ingress and carbonation. These are undoubtedly the main causes of degradation and failure of concrete structures, other than severe physical impact. It is also well established that the main way to prevent or reduce the deleterious effects of these phenomena is to decrease the permeability of the concrete matrix. Hence, durability studies have been dominated by investigation of means of creating ever more impervious concretes where bulk properties are the focus.

It can be argued, however, that surface properties have an important role to play. At the very least, the changing composition of surface reaction products have barrier properties that affect the ingress of chlorides and carbon dioxide. Also, as has been pointed in the current study, if an alternative material such as geopolymer clearly has different surface properties then it is beholden on the concrete research community to clearly identify these differences.

The author believes that simple analytical techniques can be developed to track changes in surface properties for any construction material under investigation. Electrical resistivity readings can be taken over extended timeframes with intermittent samples taken for X-ray diffraction or energy dispersive X-ray spectroscopy for instance to quantify and correlate chemical changes with physical changes such as the densification of the matrix. This approach would be relatively straightforward yet provide a wealth of information on behavioural differences between any number of materials.

Equally, sub-surface properties could be tracked on longitudinal samples by removing a nominated surface depth and then subjecting the exposed surface to the method outlined in this thesis of polishing a specimen and performing 3D profiling and optical microscopy. This would be a simple way to obtain data on changes to voids and the condition of the paste and the interfacial transition zone.

5.3.4 Steel Fibre Corrosion

One burning question remains from the current study and many others alike - does corrosion of steel fibres in a concrete or mortar really matter? It has been argued in the current study that the rate of corrosion of the fibres is not necessarily the aspect that should be a focus. Rather, the way in which the matrix around the fibres responds to the development of corrosion products when fibres corrode is a more pressing concern. Indeed, the nature of the host matrices themselves is equally as pressing.

Suffice to say that as steel fibre usage increases it is vital that researchers evaluate the impact of corrosion from as many angles as possible. It is only by doing so that the complete understanding of how fibre reinforced structures compare to rebar reinforced structures can be achieved.

The importance of corrosion, however, can never be underestimated in any structural application. In years to come, concrete and mortars may be designed with a hybrid mix of reinforcement materials. If steel is present in any form, the long-term degradation of that steel by corrosion and the impact that process has on the surrounding material must always be a key consideration for engineers and researchers alike.

5.3.5 Summary

In this section on suggested future work, four aspects of further research have been considered;

1. Microhardness
2. Geopolymer Microstructure
3. Surface Properties
4. Steel Fibre Corrosion

While many others could have been proffered, the author believes these are the four most pressing based on the outcomes of the current study.

It is hoped that these suggestions will be heeded and advanced at some point in the future. This will enhance our understanding of steel fibre reinforced mortars and their suitability for a range of applications, particularly in regards to other types of geopolymer than just the formulation used in this study.

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