

INFLUENCES ON THE TRANSPORT PROPERTIES OF A RANGE OF SOUTH AFRICAN MARINE CONCRETES

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Declaration

I declare that this dissertation is my own work. It is being submitted as partial fulfilment for the degree of MSc. (Engineering) to the University of Cape Town. It has not been submitted before for any degree or examination at any other University.

Signed by candidate

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March, 2010

Abstract

It is widely understood that the transport properties of marine concretes affect their potential durability in their service environment. The critical deterioration effect on such concretes is corrosion of embedded steel promoted by chloride ion ingress into the concrete. The occurrence of such deterioration and the rate at which it occurs depends on the quality of concrete, the aggressiveness of the particular marine environment and the coupling between the two.

This dissertation presents the results of an experimental study done to compare different South African marine concrete making materials sourced from Cape Town, Port Elizabeth and Durban. The materials are typically specified for reinforced concrete structures in these urban marine regions. In Cape Town, ground granulated corex slag (GGCS) and fly ash (FA) blended with ordinary Portland cement (OPC) are the two binder blends used to produce concrete. The most commonly used aggregate is greywacke. In Port Elizabeth, FA blended with OPC is used in marine concretes with quartzite aggregate. In Durban, Slagmore (a factory blend of ground granulated blast furnace slag with a small proportion of FA) interground with OPC clinker is used with the available tillite aggregate. In addition plain OPC mixes with each aggregate type were also produced to act as reference mixes. Two water/binder (w/b) ratios of 0.40 and 0.55 were used for all mix combinations. To enable comparison between the different mixes, the assumption was made that concretes of w/b ratio, binder type, aggregate type and age period have comparable transport properties.

The objective of the study was to find the effect of above variables on apparent chloride diffusion coefficient (D_a), chloride conductivity, oxygen permeability water sorptivity and compressive strength on concrete from the three urban marine South African regions. Characteristic bulk diffusion (42 and 182 days), durability index (28, 91 and 182 days) and cube (28, 91 and 182 days) compressive strength tests were done on concrete specimens to determine properties from which potential durability is inferred. Emphasis is placed on the first two tests. The applicability of the different tests done in characterising marine concretes is also done. The information should inform service life modelling allowing material design to be done more effectively.

Results indicate that w/b ratio significantly affects the transport properties of concrete, with mixes at the lower w/b ratio having improved properties. Differences of up to 40 % were observed in D_a values for each mix combination at the two tested water/binder ratios. Chloride conductivity values showed differences of up to 25 % at the sample ages tested for both w/b ratios. Oxygen permeability values are seen to have between 50 % and 80 % between the two w/b ratios. Water sorptivity values show a reduction range of between 17 % and 35 % for all mixes at the two w/b ratios at all sample ages.

Binder type is found to have a notable effect on the transport properties of the concrete mixes tested. The chloride ingress test results show that slag blended mixes D_a values are greater than D_a values of FA blended, and FA blended D_a values are greater than plain OPC mixes. The decrease in D_a values ranges from 50 % to 80 % between each binder type variation. A similar ranking is seen for chloride conductivity results with differences of up to 70 % between slag blended mixes and plain OPC mixes and 25 % between FA blended mixes and plain OPC mixes. Oxygen permeability values show the following ranking in order of decreasing values: FA blended mixes > Slagmore blended mixes > plain OPC mixes > GGCS blended mixes. Water sorptivity values show the following ranking in order of decreasing values: FA blended mixes > Slagmore blended mixes > GGCS blended mixes > plain OPC mixes.

Aggregate type was seen not to have an appreciable influence on the measured transport parameters. Results also indicate that all the transport properties measured reduce with continued curing (and sample age).

Of the durability index tests done, the chloride conductivity test was found to have a good correlation with bulk diffusion test data. A discussion is given on the application of the chloride conductivity test in service life modelling.

Dedication

To my parents, for their wisdom

Work hard for your living (Pauline Njeri, 1953 -)

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Abbreviations and Notations

CEM I 42.5N	Class 42.5 normal hardening Portland cement
CEM II A-S 42.5N	Class 42.5 normal hardening portland-slag cement
C_s	Chloride surface concentration
CCI	Chloride conductivity index
CSF	Condensed silica fume
CT	Cape Town
D_a	Apparent chloride diffusion coefficient
D_c	Chloride diffusion coefficient
DB	Durban
DI	Durability index
FA	Fly ash
$f_{cu,28}$	28-day cube compressive strength
GGBS	Ground granulated blast-furnace slag
GGCS	Ground granulated corex slag
ITZ	Interfacial transition zone
k	D'Arcy coefficient of permeability
OPC	Ordinary Portland cement
OPI	Oxygen permeability index
PE	Port Elizabeth
R^2	Linear regression correlation coefficient
RC	Reinforced concrete
SCM	Supplementary cementitious material
w/b	Water/binder ratio (by mass)
WSI	Water sorptivity index
P	Plasticiser

Chapter One

Introduction

1.1 Background

Reinforced concrete (RC) is one of the most widely used materials for structural construction owing to its economic and durability aspects. In use, it is exposed to various aggressive agents which must be resisted during the service life of a structure. Chloride ions are one of the most common agents to which RC structures are exposed. Industries such as abattoirs use chloride solutions in their activities, road structures in cold climates are exposed to de-icing salts which are laden with chloride ions, while other coastal structures such as jetties, breakwater and harbours are in direct contact with the marine environment (Poulsen and Mejlbro, 2006). The marine environment is one of the most damaging physical and chemical environments that an RC structure can be subjected to. As over three-quarters of the earth's surface is covered by sea water, a large number of RC structures are subjected to the marine environment either directly or indirectly (Mehta and Monteiro, 2005).

RC structures exposed to sea water may deteriorate through physical and chemical mechanisms that involve interactions between the concrete and its environment. Chemical deterioration occurs from the salt compounds of sea water which are largely sulphates and chlorides, as well as from the magnesium content. Sulphate and magnesium ions attack and deteriorate the concrete system by reacting with the binder phase. The reaction products formed create expansive forces causing cracking and eventual spalling of the concrete. When reactive aggregates are used in concrete, alkali-aggregate expansion can also occur. Chloride ions themselves are not aggressive to the concrete material, but break down the protective oxide layer on the surface of embedded steel in a process known as depassivation. Carbonic acid produced by marine organisms can also permeate into concrete and lead to depassivation (Eglinton, 1998). Depassivation of steel makes it susceptible to corrosion which leads to subsequent reduction in the ultimate capacity, serviceability and aesthetics of a structure.

Physical deterioration occurs through crystallization pressure of salts within concrete subjected to cyclic wetting and drying conditions. It also occurs due to frost action in cold climates and mechanical abrasion due to wave action and floating objects (Bungey and Millard, 1996, Ballim et al, 2009, Mehta and Monteiro, 2005, Mehta, 1991). Figure 1.1 is a schematic representation of the factors that cause the deterioration of marine concretes and affect their potential durability.

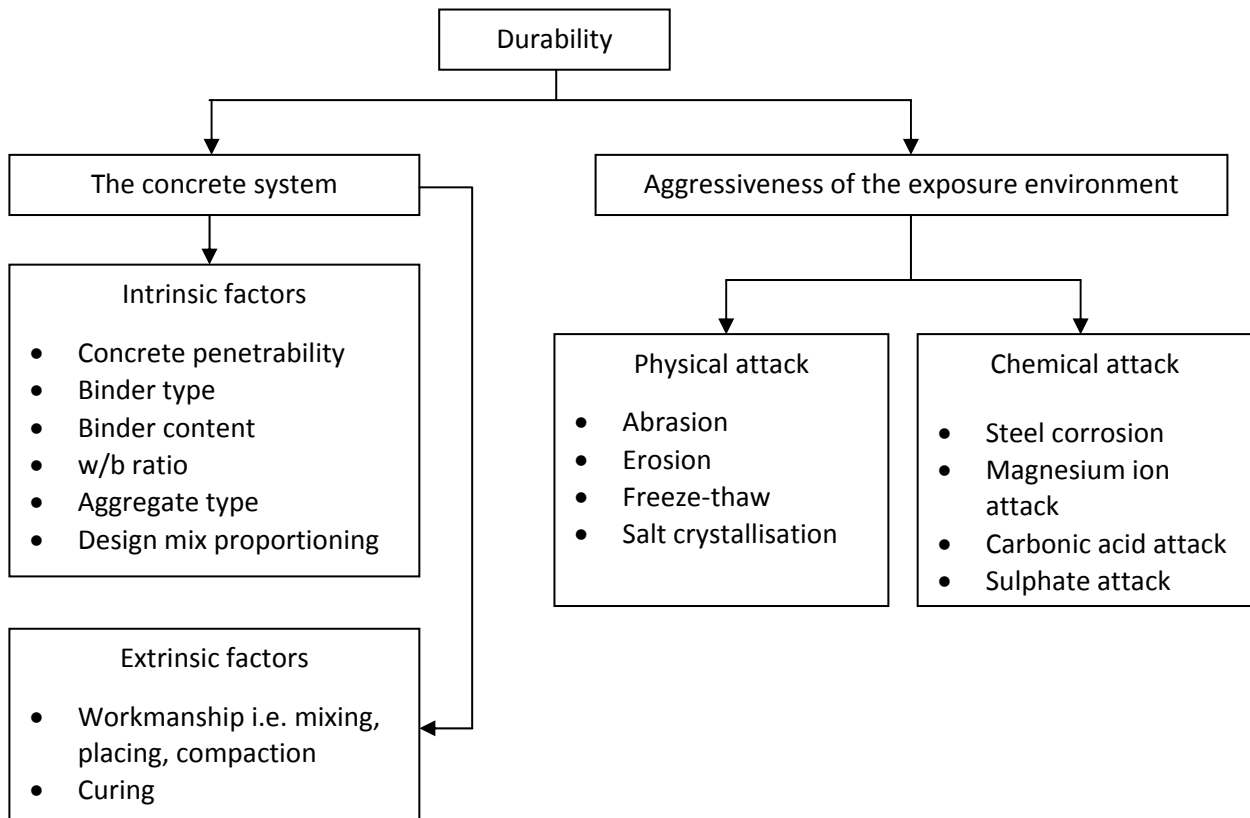


Figure 1.1: Schematic representation of factors influencing durability of marine concretes (Adapted from Ballim et al, 2009)

Corrosion of steel promoted by chloride ion ingress is the most common durability problem of RC structures in the marine environment. Worldwide, corrosion of reinforcement represents over 40 % of the total damage in marine RC structures (Ballim et al, 2009, Broomfield, 2007, BRE Centre for Concrete Construction, 2004, Federal Highway Administration, 2001, Bungey & Millard, 1996, Mehta, 1991).

In order to improve the service life performance of concrete in chloride-rich marine environments, it is necessary to understand the transport properties of concrete. This refers

to the penetrability of concrete which is influenced by the chemical and physical composition of concrete. Penetrability of concrete is defined as the degree to which its pore and micro-structure permits the passage of fluids or ionic species through it. It is a function of the pore size and structure, degree of pore inter-connectivity and tortuosity, as well as the nature of the cement hydrates. A concrete with low penetrability offers better protection to embedded reinforcing steel than one with high penetrability. Factors that affect the penetrability of concrete are w/b ratio, binder type and degree of hydration of the binder phase (Richardson, 2002).

1.2 Concrete characterisation in the marine environment

Given the action of chloride ions in promoting corrosion of embedded steel, concrete must be able to perform one or both of the following functions: first, restrict the penetration of chloride ions (and other aggressive species) to the level of embedded reinforcement; second, retard the corrosion rate once depassivation has occurred and the corrosion process has begun. Reduction of the corrosion rate may be done by restricting the access of oxygen and moisture (necessary for corrosion to occur) through the concrete to the level of embedded steel. However, as concrete is porous in nature, this cannot be easily achieved. It is nevertheless controllable through appropriate design aimed at limiting the ingress of the deleterious species. As to restricting the penetration ability of aggressive agents, no reliable methods of doing this exists. It therefore becomes essential that RC structures be made to withstand the service conditions of the marine environment (Cerny and Rovnanikova, 2002, Mackechnie, 1996).

The transport mechanisms of fluids and ionic species to penetrate and move within a concrete matrix needs to be understood to adequately determine the potential durability of RC in the marine environment. Ingress of any species into concrete occurs via the system of concrete pores, cracks and defects in the concrete. In un-cracked and intact concrete with a saturated pore system, diffusion driven by a concentration gradient is the primary mechanism driving the movement of chloride ions. Other mechanisms, such as migration and convection of ionic species also occur. Oxygen penetrates concrete primarily by permeation while moisture/water is carried into concrete from its environment by capillary

suction. In deeply submerged elements, transport of aggressive species occurs by permeation (Kropp and Alexander, 2007, Cerny and Rovnanikova, 2002).

All the aforementioned transport mechanisms are a function of the concrete material constituents, mix proportions and the quality of the cover region of concrete. In characterising concrete in the marine environment, it is fundamental to understand how these various parameters interact (Ballim et al, 2009, Poulsen and Mejlbro, 2006, Mackechnie, 1996).

1.3 Motivation and research significance

Currently, most of the information on the potential durability of South African (SA) marine concretes stems from studies on Western Cape concrete materials and RC structures. Thus, there is a need to do actual characterisation of the transport properties of concrete mixes from different regions in SA exposed to the marine environment. This should provide further understanding and knowledge into the potential durability they offer to RC structures. Further, it would allow for a more general use of service life prediction models for other SA marine conditions.

Studies on characterising the potential durability SA concretes have mainly taken two approaches:

1. The direct durability testing approach.
2. The durability index (DI) approach.

The direct durability testing approach involves exposing samples to a deleterious agent and quantifying the rate of ingress of the agent through the samples. Tests done on the exposed samples prove the adequacy or lack thereof of a concrete type to resist penetration of the aggressive agent. For concrete exposed to a marine environment, service life prediction models have been developed from these tests. Examples of such models are; LIFE-365 (ACI committee 365, 2005), UCT Service Life Model, (Mackechnie, 2001), Duracrete, (Duracrete, 1998) and Clinconc (Tang, 1996).

The DI approach considers the transport mechanisms of the deleterious species through concrete and quantifies its rate of penetration. Alexander et al (2007) describe the DI approach as a tool for controlling the potential durability of marine concrete, and as giving two design-for-durability specifications for given marine exposure conditions. The first of these is the binder type which impacts on the penetrability of the concrete system. The binder types used for SA marine concretes are normally restricted to blended cements which potentially offer sufficient resistance to chloride penetration compared to plain Portland cement (OPC) concretes. The second specification given is the minimum depth to the level of embedded steel. For all periods of desired service life and for marine environment exposure conditions, the minimum cover thickness is 50 mm.

The DI approach also applies limiting index values obtained from tests that are used to characterise the transport properties of the cover region of concrete. The values are used as potential durability indicators that an as-built structure should meet to be considered inherently durable (Ballim et al, 2009, Alexander et al, 1999a).

Each of the two approaches is sensitive to the material constituents (binder and aggregate) and proportions (binder content and water/binder ratio) that influence the transport mechanisms of concrete. They are thus considered appropriate for this study in characterising the different South African marine concretes.

1.4 Experimental tests

Direct durability testing was done using the bulk diffusion test described in ASTM C-1556-04 (2004). It was used to determine the rate of penetration and content of chloride ions in concrete exposed to a saline rich environment. The test is appropriate for understanding chloride ion transport as it allows for the movement of chloride ions within the concrete to be primarily by diffusion. It is important to note that, as chloride ions penetrate through the concrete, they interact with the binder matrix in a process termed chloride binding. Chloride binding reduces the concentration front of available ions in a concrete mix. The bulk diffusion test takes cognisance of this. From the test, the apparent chloride diffusion coefficient is determined which is a measure of chloride ion transport in concrete. Diffusion

coefficients are used in Service Life Prediction models to predict the potential durability of an RC structure in a chloride laden environment.

Durability was index measured using a suite of three characterising tests known as the South African Durability Index test methods. These provide a means of measuring concrete transport parameters which are related to concrete performance in service and to inherent durability as explained by Alexander et al (2007). As the resistance of concrete to chemical and environmental attack and the protection of embedded steel are directly related to penetrability, the tests focus on the transport processes and hardened properties of concrete. The tests are; chloride conductivity index (CCI), oxygen permeability index (OPI), and water sorptivity index (WSI). The CCI test is used to characterise chloride ion movement through a concrete sample. Its index value is further related to the diffusivity of chloride ions in concrete by the diffusibility relationship. The OPI test is used to characterise fluid flow by permeation and the penetration of a carbonation front while the WSI test is used to relate moisture ingress (Ballim et al, 2009, Alexander et al, 1999b, Mackechnie, 1996, Streicher and Alexander, 1995).

1.5 Objective

This experimental study explores the comparability of geographically different South African marine concrete mixes. It investigates the influences on the transport properties of concrete mixes that are typically produced for actual RC structures in the marine environment. This is in order to better improve the understanding of the inherent durability of “real” South African marine concretes and the factors influencing chloride penetration. This will lead to more accurate service life prediction for reinforced concrete structures in a marine environment

1.6 Aims

To show the influences of concrete material types and proportions on the transport characteristics of the different concrete types, the aims of this study are to:

1. Compare nominally equivalent marine concretes from different geographical areas. The term equivalent is used to relate concrete mixes of similar w/b ratio, material type (binder and aggregate), material quantity and exposure condition.
2. Obtain chloride ingress values for the marine concretes by measuring the rate and content of chloride ion penetration i.e. apparent chloride diffusion coefficient (D_a) and apparent surface concentration (C_s) values.
3. Obtain characteristic Durability Index values for the marine concretes and compare them to prescribed Durability Index values for marine concrete.
4. Explore the effect of w/b ratio, concrete constituent type (both binder and aggregate) and sample age on the transport properties of the marine concretes.
5. Draw conclusions as to the concrete material and proportion influences on the transport properties.

1.7 Scope of experimental study

This experimental study investigates concrete mixes typically supplied by large scale ready-mix concrete companies to the marine urban areas of Cape Town, Port Elizabeth and Durban. Figure 1.2 is a map of South Africa with the three urban regions shown. South Africa has a temperate sub-tropical climate with considerable regional variations caused by differences in elevation, wind systems ocean currents. Durban and Port Elizabeth, in the eastern and south-eastern coasts respectively, are influenced by the warm south-flowing Mozambique Current blowing across the Indian Ocean and generally experience higher temperatures. Cape Town, in the Western Coast, is influenced by the cold north-flowing Benguela Current blowing across the Atlantic Ocean which contributes to the cooler temperatures and general air dryness (MS Encarta Premium Suite, 2005).

Materials for use in the study were sourced from these areas. The influences of material type and proportion influences on the transport mechanisms were determined for each concrete type. Further, the transport properties of the concrete mixes will be compared to each other and to those reported in other South African studies.



Figure 1.2: Regional map of South Africa (MS Encarta Premium Suite, 2005)

1.8 Experimental methodology

The research experimentation has five binder types, three coarse aggregate types and two w/b ratios, all sourced from the different geographic regions. In order to compare the different concretes types produced, the concrete mixes need to be standardised as much as possible. This is done so as to determine the sensitivity, effect and interactions of the material type and proportions on the penetration of deleterious species. The following general limitations were thus applied to the concrete mixes:

1. Two water/binder ratios (by mass) of 0.40 and 0.55.
2. Water content limited to 165 l/m^3 which is within ready-mix plant recommendations
3. Workability achieved by use of a water reducing admixture to give an average slump of 75 mm.
4. 19 mm coarse aggregate.
5. Coarse aggregate content kept at 1170 kg/m^3 .
6. Yield of the mixes achieved by adjusting the fine aggregate content.
7. A CEM I 42.5N OPC used as the reference cement.

1.9 Experimental materials and variables

The materials used in this experimental study were sourced from the geographical urban areas mentioned and are typically used for reinforced marine concrete construction in the respective geographical regions. The concrete mix variables investigated were; w/b ratio, binder type, aggregate type and sample age.

1.10 Outline of dissertation

This dissertation is divided into six chapters as follows:

Chapter 1 is a general introduction with emphasis on the performance of marine concretes. An overview of what characterises durability in the marine environment is covered.

Chapter 2 gives a literature review of the transport mechanisms in concrete exposed to the marine environment. The focus is on chloride ion ingress largely present in this environment and which portends serious durability implications on marine structures. The effects of chloride ion ingress and the factors affecting its penetration are discussed in detail. This is looked at with regard to the properties of concrete and its constituent material type and proportion that might have an impact on inherent durability in the marine environment. Existing test methods that are used to characterise concrete exposed to the marine environment are also presented.

Chapter 3 describes the experimental details and methodology of this study.

Chapter 4 gives the experimental results of this study and discusses and evaluates the results.

Chapter 5 is a discussion on the existence of relationships and correlations between the test results that indicate the applicability of the tests in determining the durability performance of marine concretes.

Chapter 6 presents the findings of the experimental study conducted giving a conclusion to the analysis and discussions made of the results. Recommendations for further study are also given.

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Chapter Two

Literature review

2.1 General

This chapter covers the fundamentals of reinforced concrete (RC) deterioration with special emphasis on the durability of RC in the chloride-laden marine environment. A background of the structure of concrete and of the transport mechanisms of ionic species in concrete is first given, followed by a review of the deterioration mechanisms of RC in the marine environment. The different concrete materials aspects that affect RC durability in the marine environment are also covered. Finally, a review of the analysis of the chloride content of contaminated concrete is covered including the test methods used to assess durability of RC in the marine environment.

2.2 The structure of concrete

2.2.1 General

Concrete is a three-phase composite system of binder paste, aggregate particles and an interfacial transition zone between the two. The structure of concrete in association with these components is discussed here under the heading; the pore structure of concrete. The interfacial transition zone is discussed separately. The cover layer of concrete is also discussed in relation to its influence on the durability of concrete.

2.2.2 The pore structure of concrete

In freshly mixed concretes all voids exist as water filled spaces that become filled, partially or totally with hydrating binder. The binder which consists of various phases of calcium silicates and aluminates reacts with water forming fibrous calcium silicate hydrate (CSH) sheets. These interlock into a particulate network with interstitial spaces between them referred to as gel pores. At the boundaries of the CSH sheets, larger spaces known as capillary pores with diameters of up to about 5 μm are formed. Gel pores are generally fine and have a

diameter of about $0.015 \mu\text{m}$ and are considered virtually impenetrable (Cerny and Rovnanikova, 2002).

As binder grains hydrate they occupy more space than the original size of the binder grain. This expansion moves into the capillary pores decreasing the capillary pore volume and increasing the gel pore volume. This eventually causes the reduction of the spaces in freshly mixed concrete forming a dense and relatively impenetrable matrix. Air voids also occur in concrete. In well compacted concretes, they generally occupy about 1 % of the total volume and have little influence on the penetrability of the concrete. They are also typically isolated from other entrapped voids. Figure 2.1 illustrates the relative sizes of the pores within the concrete pore structure.

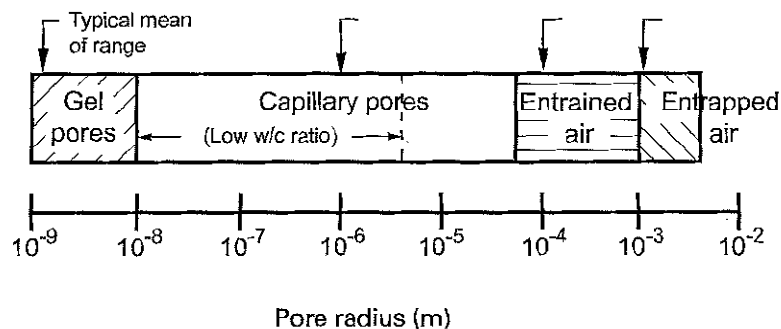


Figure 2.1: Relative size of the pore types found in concrete (Richardson, 2002)

Aggregate particles also have voids within their structure and discontinuities at the surface of embedded steel also contribute to the void volume. However, such voids are isolated from the permeability network of well cured and compacted concrete by the surrounding binder paste (Mehta and Monteiro, 2005, Richardson, 2002, Neville, 1995).

The penetration of deleterious species into concrete occurs mainly through the capillary pores with the size and interconnectivity of the capillary pores inherently determining the resistance of concrete to the penetration of deleterious substances. As such, the pore structure is fundamental to the durability of concrete in its environment (Mackechnie, 1996, Haynes, 1982).

2.2.3 The interfacial transition zone

The ITZ is a zone of finite thickness (10 - 50 μm) around coarse aggregate particles that results from particle packing inefficiencies i.e. one-sided hydration product growth and water entrapment. Figure 2.2 illustrates this together with the other main phases found in a concrete matrix. The ITZ has been reported by Mehta and Monteiro (2005) to have far greater influences on the mechanical and durability properties of concrete than is reflected by its size. The process of formation of the ITZ occurs as follows; in freshly compacted concrete, a thin film of water surrounds the aggregate particles. This results in a localised increase of the water/binder (w/b) ratio. As the binder grains hydrate, they encounter the “wall” of the aggregate. Owing to the higher local w/b ratio, the hydration products form relatively larger crystals resulting in a region of higher porosity and permeability than the bulk binder paste (Mehta and Monteiro, 2005, Liao et al 2003, Cerny and Rovnanikova, 2002, Scrivener and Nematy, 1996, Garboczi and Bentz, 1996, Neville, 1995). Figure 2.3 illustrates this porosity as a function of distance from an aggregate particle. Nearer the aggregate-paste interface, there is significantly higher porosity compared to the bulk binder paste.

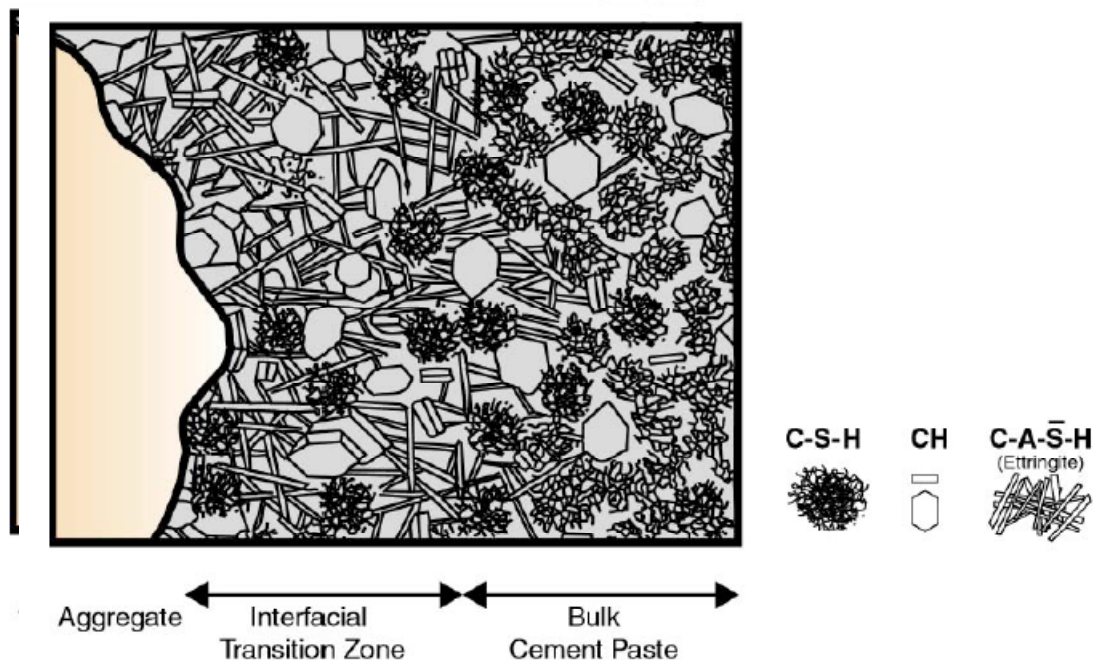


Figure 2.2: The three main phases in a concrete matrix (Mehta and Monteiro, 2005)

Scrivener (2004) reported that the ITZ can make up some 20 – 30 % of the total paste volume in a typical concrete. As such, the ITZ has a significant influence on the properties of

concrete particularly, elastic modulus, compressive strength, chloride and sulphate diffusivity, electrical and thermal conductivity, shrinkage and creep (Garboczi and Bentz, 1996).

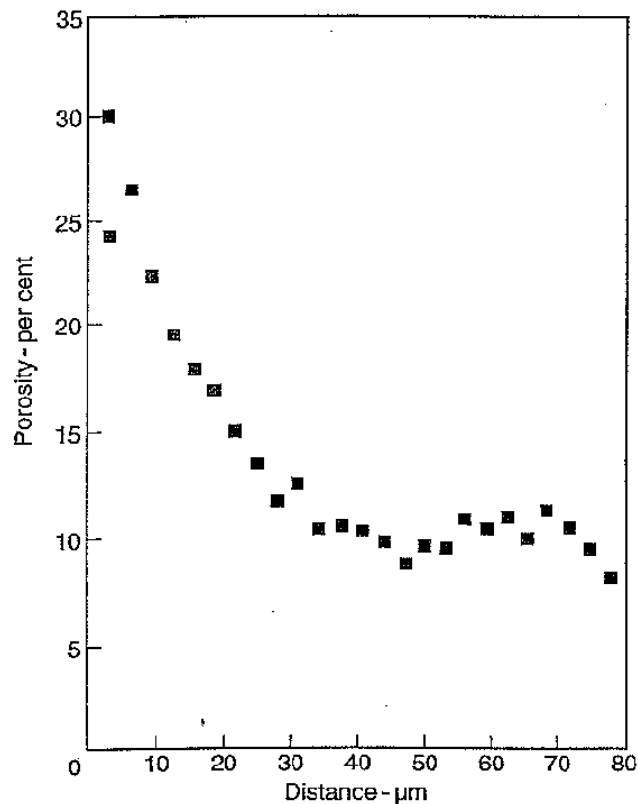


Figure 2.3: Porosity as a function of distance from a coarse aggregate particle (Neville, 1995)

In addition, the connectivity of the ITZ has an influence on the transport properties of concrete and its inherent durability. A more pronounced and connected ITZ causes a higher transport potential of the concrete. The connectivity of the ITZ is influenced mainly by two factors (Scrivener et al, 2004, Mehta, 1988):

1. Concrete material constituents volume. The higher the binder paste volume, the more aggregate particles are dispersed within the concrete matrix resulting in decreased occurrence and connectivity of the ITZ. Similarly, the higher the volume of coarse aggregate particles in relation to the binder paste, the larger the area of contact between the coarse aggregates. This greater area of contact results in greater connectivity of the ITZ around the aggregate particles.
2. The quality of coarse aggregates in the concrete matrix. Limestone and dolomitic aggregates compared to quartz, sandstone or feldspar aggregates form strong chemical bonds with the binder paste thus a less pronounced ITZ. The influence of the ITZ and

aggregate particles shall be further discussed in section 2.6.5 in relation to the durability of RC in the marine environment.

2.2.4 The cover layer of concrete

The cover layer of concrete is defined as “the thickness of concrete between the face of the concrete, as cast, and the outer face of ... embedded steel” (SANS 10100-2:2009). The cover layer is the first line of defence of RC structures against the environmental influences it is exposed to protecting the embedded steel and the bulk concrete structure itself. Figure 2.4 is an illustration of the cover region of concrete showing the influences on the quality of the cover region and the deleterious species that penetrate through the cover region causing deterioration. However, the cover layer of concrete is generally of lower quality than the bulk of the concrete. The cause of this shall be described next.

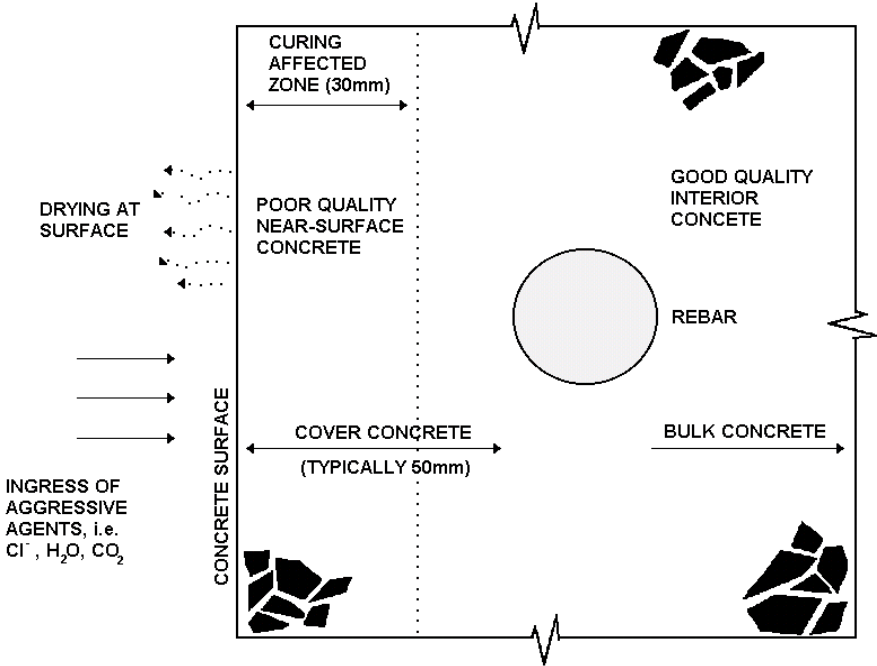


Figure 2.4: Illustration of the cover region, showing influence of environment and curing (Alexander et al, 2007)

As freshly cast concrete cures, moisture loss to the ambient environment occurs leading to a loss of water for hydration. Premature drying occurs, potentially causing micro-cracking of the cover layer. This inherently causes the gradient of concrete quality from the interior to the exposed surfaces of the concrete mass. Other causes of the reduced quality of the cover

layer are the quality of workmanship i.e. placing and compaction, bleeding and segregation effects (Alexander et al, 2007).

The deleterious processes that lead to RC deterioration are advantaged by a poor quality of the cover region. It thus becomes important that good concrete design must focus on engineering the quality and condition of the cover region with an effort to reduce its penetrability. This can be achieved by making the cover layer of adequate thickness and quality (Alexander et al 2007).

SANS 10100-2:2009 gives typical cover thicknesses that range from 25 mm to 80 mm depending on the severity of the environment that the concrete is exposed to. For concrete exposed to a saline environment, the cover thickness recommended by Alexander et al (2007) is 50 mm. It is imperative that adequate cover be achieved in an RC structure as its thickness is proportional to the ingress of deleterious species such as carbon dioxide, oxygen and moisture. As will be discussed in sections 2.4 and 2.5, the presence of these species at the level of embedded steel is necessary for corrosion to occur.

2.3 Transport mechanisms of concrete

The passage of deleterious species through the concrete cover layer potentially leads to deterioration. Deterioration usually involves the movement of substances and fluids (liquids, gases, ions) through the pore structure of the concrete. The fluid-transport mechanisms of the concrete are therefore important parameters in determining the rate of deterioration and are discussed next (Ballim et al, 2009, Kropp and Alexander, 2007, Poulsen and Mejlbro, 2006, Glass, 2003, Richardson, 2002, Costa and Appleton, 1999).

1. **Capillary suction.** Capillary suction (also referred to as absorption), occurs on a concrete surface subjected to cyclic wetting and drying and refers to the movement of fluids into the concrete pore structure. Capillary suction is dependent on the pore geometry and the degree of saturation of concrete. This mechanism is responsible for the accumulation of ionic species on the surface of concrete.
2. **Convection.** Convection (also called wick action), occurs within the concrete structure as a result of differential moisture gradients. Water containing ionic species moves across

the gradient towards the drier regions. Evaporation of moisture close to the concrete surface also causes convection.

3. **Permeation;** occurs as a result of an external pressure gradient that is present on one face of a concrete structure. This mechanism mainly occurs in structures that are submerged in deep sea waters with one face exposed to air or lower pressure. The permeability of concrete is dependent on the concrete microstructure, the moisture condition of the material and the characteristics of the permeating fluid.
4. **Migration;** occurs as a result of an electrical potential present across one face of a concrete structure causing a movement of ions. This mechanism is determined by the mobility of the penetrating ionic species.
5. **Diffusion;** occurs in a continuous liquid phase of the concrete as a result of a concentration gradient of ions producing a chemical potential. Diffusion rates are dependent on temperature, moisture content of concrete, type of diffusant and the inherent diffusibility of the material.

The rate of any of the above transport process depends on the volume fraction, tortuosity and connectivity of the pores in the concrete structure. The rate is also determined by other factors such as the w/b ratio, binder type, binder content, binder fineness and degree of hydration. Reducing w/b (which controls the original spacing of the binder grains) and continued hydration may, for example, result in the capillary pores becoming blocked by gel and isolated so that they are interconnected solely by gel pores. Transport is very slow through the gel pores thus inhibiting the penetration of potentially deleterious species (Glass, 2003).

2.4 The deterioration of reinforced concrete in the marine environment

2.4.1 General

To properly design, specify and produce durable concrete it is essential to understand the deterioration mechanisms that RC structures in the marine environment are subjected to and the processes that lead to their deterioration. Such deterioration is discussed here with reference to the cover layer of concrete and its penetrability. Penetrability is defined as the degree to which the pore structure permits the passage of fluids or ionic species through it.

Broadly speaking, the general principles in regard to the mechanisms of deterioration of concrete, their rate and extent of deterioration is much reduced by the provision of good quality dense and well compacted concrete, particularly in the cover region of concrete. The following are leading causes of RC deterioration that stem from the use of poor concrete (Berke et al, 1994):

1. Poor mix design and material selection: High w/b ratios, dilution of concrete mixtures with the addition of too much water or over-dosage of concrete workability aids generally yield penetrable concretes. Poor particle size grading of aggregate particles is also a source of lack impenetrability.
2. Poor construction practice: Inadequate compaction and placement causes the segregation of aggregate particles and bleeding of mix water leading to penetrable concretes.
3. The ingress of moisture into sufficiently cured concrete further promotes deterioration. Water, essential for hydration, turns from hero to villain as it is also essential for deterioration processes to occur. Water carries and sustains deleterious species into concrete and is itself involved in undermining the integrity of RC structures. Almost all forms of deterioration involve the presence of water in the surrounding environment and in the internal pore structure of the concrete. Concrete in a dry environment generally shows a lower rate and extent of deterioration than concrete in a wet or humid environment.

Figure 2.5 illustrates the different deterioration mechanisms that can play a role in the deterioration of an RC structure in the marine environment.

The mechanisms that can cause deterioration of RC structures are broadly defined here into two categories:

1. Deterioration primarily caused by chemical mechanisms
2. Deterioration primarily caused by physical mechanisms

Common forms of deterioration in each category are discussed next. The corrosion of embedded steel reinforcement is discussed under a separate heading, because of its

importance as a mechanism of deterioration, as well as being both a physical and chemical mechanism of deterioration.

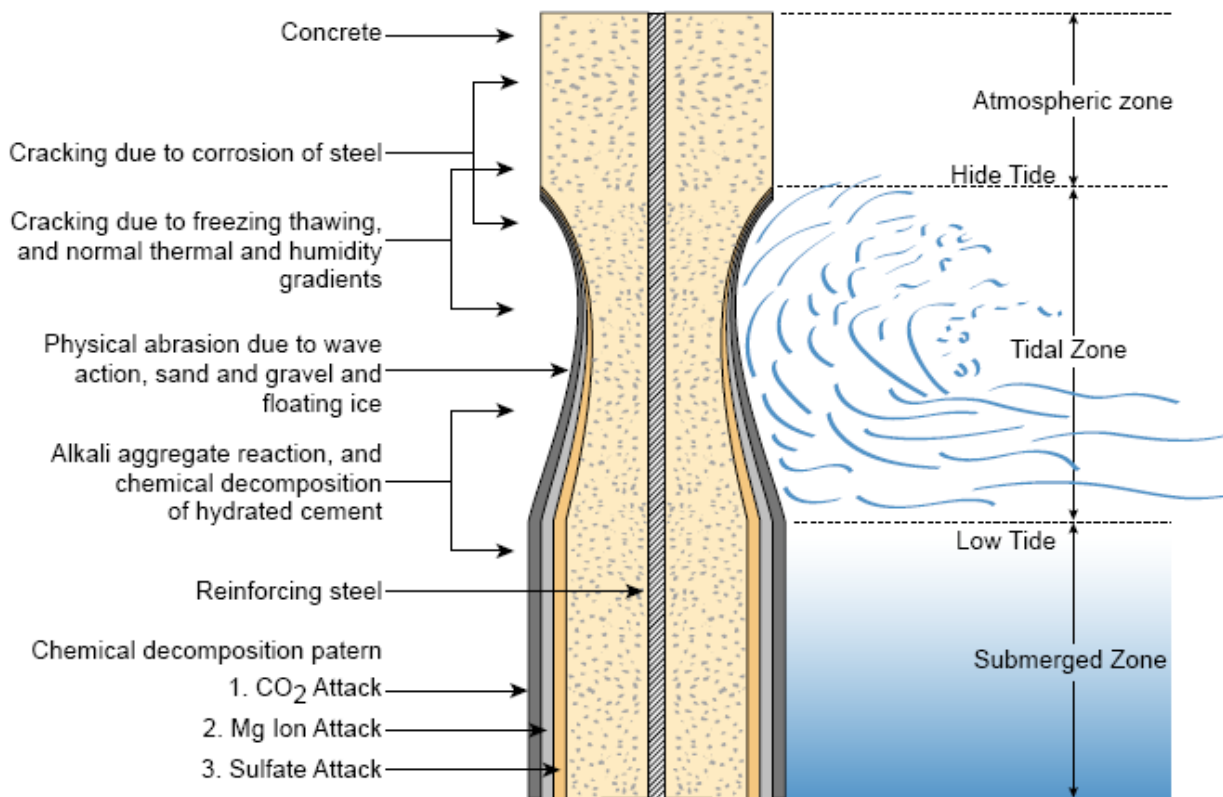


Figure 2.5: Illustration of deterioration of a concrete cylinder exposed to seawater (Mehta and Monteiro, 2005)

2.4.2 Chemical deterioration of reinforced concrete in the marine environment

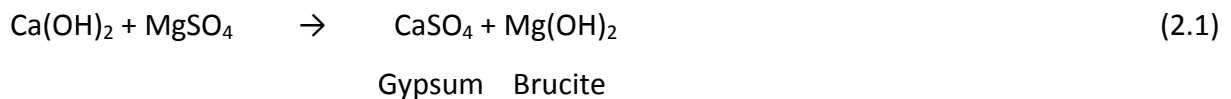
The world's oceans are fairly uniform in chemical composition and typically contain about 3.5 % soluble salts by mass comprising ionic salts of sodium chloride, magnesium chloride and magnesium sulphate (Mehta and Monteiro, 2005, Eglinton, 1998). Sodium and chloride ions have the highest ionic concentrations; typically 11,000 and 20,000 mg/litre, respectively. Sodium and chloride ions are themselves not aggressive to the concrete matrix but the latter contribute to the corrosion of embedded steel. Magnesium and sulphate ions are aggressive to the binder paste and have typical ionic concentrations of 1400 and 2700 mg/litre, respectively. Sea water pH varies between 7.5 and 8.4, with the average value in equilibrium with atmospheric carbon dioxide being 8.2 (Mehta and Monteiro, 2005, MacInnis, 1991). In sheltered bays marine organisms that produce carbon dioxide and/or hydrogen sulphide can lower the local pH value to below 7.0 (Mackechnie, 1996). This

section looks at several forms of the deterioration of reinforced concrete mediated by the ionic species present in sea water.

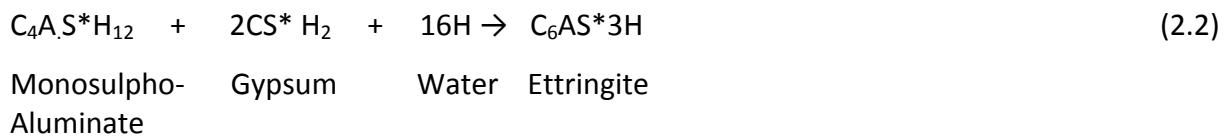
1. Magnesium ion attack

Magnesium sulphate and magnesium chloride cause deterioration of marine concretes through ion-exchange and ion-addition reactions with the calcium hydroxide component of binder paste (Eglinton, 1998).

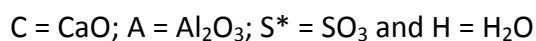
The first anion reaction proceeds as shown in equation 2.1 with magnesium sulphate reacting with the binder matrix forming calcium sulphate and magnesium hydroxide (Ballim et al, 2009):



This is followed by the calcium aluminates in the binder paste reacting with the sulphate ions and gypsum present in binder to produce ettringite which is potentially expansive in a predominantly sulphate rich environment. This is shown in equation 2.2. The action of the formation of brucite shall be discussed later.



where:



In an alkaline environment, the formation of ettringite in concrete is accompanied by a large increase in the concrete solid volume, causing a build up of internal stresses that lead to cracking and eventual spalling of concrete. However, the chloride ions in sea water have an ameliorating effect of suppressing ettringite formation by replacing the hydroxide ions to form calcium sulphate and calcium sulpho-aluminate (Ballim et al, 2009, Mehta and Monteiro, 2005, Richardson, 2002). These products are soluble in sea water and are leached away leading to an eventual loss of solid components from the concrete mass. In submerged concrete this is not a problem as such leaching occurs by diffusion which is in itself a slow

process. In the tidal and splash zones however, the leaching process is accelerated by tidal and wave action (Mackechnie, 1996). Leaching nevertheless leads to a strength loss and increased penetrability of the concrete matrix exposing it to more severe forms of attack (Ballim et al, 2009, Mehta and Monteiro, 2005). As such, it becomes evident that in the chloride laden marine environment, the influence of the chloride ions on the concrete system is more influential on the potential durability of RC structures and the deterioration mechanism(s) that compromise such durability.

The magnesium cation accompanying the sulphate ion itself reacts with the calcium hydroxide component of binder paste forming brucite as given in equation 2.1. Brucite, is a white deposit precipitated on the surface of concrete that has a low solubility. It further reacts with the calcium silicate hydrates to produce magnesium silicate hydrates. These reactions are beneficial to concrete as they form a protective layer on the concrete surface in addition to blocking the surface pores. Such concrete would suffer less deterioration (Mehta and Monteiro, 2005).

2. Carbonic acid attack

Normally, the low concentration of atmospheric carbon dioxide, its low solubility in water at atmospheric pressure and ambient temperature as well as the ineffectiveness of the gas transport mechanism across the air/water interface is responsible for the protection afforded by water to submerged structures (Ballim et al, 2009).

However, in sheltered bays and estuaries, sea water usually contains a higher concentration of dissolved carbon dioxide. Additionally, when microbiological and other organic mechanisms in sea water that form carbonic acid are in proximity to the structure, deeply submerged structures are vulnerable to carbonic acid attack (Eglinton, 1998). The initial reaction of carbonic acid with the calcium hydroxide of the binder paste is the formation of almost insoluble calcium carbonate, but this is rapidly followed by the conversion of the carbonate aragonite to the more soluble calcium bicarbonate accompanied by accelerated leaching.

Carbonation can cause the pH values of sea water and concrete to fall to 7.5 presenting a potentially harmful situation to concrete. This effect of lowered pH on reaching the level of

embedded steel causes the passive gamma-ferric oxide layer on the surface steel to become depassivated. In oxygenated sea water, corrosion will start. In unreinforced concrete, the action of carbonation is not potentially a durability problem. In such structures, carbonation has the effect of refining and improving the near surface pore structure of the concrete (Ballim et al, 2009).

3. Attack by marine sediments

In deep RC structures, where marine sedimentation may occur, the decay of sulphide-producing bacteria occurring under anaerobic conditions, leads to the formation of hydrogen sulphide. If in the adjacent moist areas sufficient oxygen is present, the hydrogen sulphide is oxidized to sulphuric acid. Under the appreciable pressure from the overlying burden of marine sands and hydrostatic head, the corrosive acid permeates into the concrete initiating the corrosion of embedded steel (Ballim et al, 2009).

2.4.3 Physical deterioration of reinforced concrete in the marine environment

1. Wave action

In the tidal and splash zones, waves driven by wind, tidal surges, ocean currents and abnormal weather can exert impact loads of up to 300 kPa (Mehta, 1991). Wave action on concrete marine structures such as dolphins and sea walls can cause local damage of the protective brucite and aragonite layers on the concrete surface or stability failure (Mackechnie, 1996).

2. Abrasion damage

Occurring together with wave action, abrasion damage refers to movement of sea water relative to the concrete surface where the sea water has sediments or solid loads. The abrasive action of suspended solids causes wearing of the concrete surface. Wind-borne sand particles can also cause the same. Abrasion leading to the erosion of material from the concrete surface accelerates concrete deterioration and creates a potentially hazardous situation that abrasion damage and other forms of deterioration take advantage of (Ballim et al, 2009).

3. Salt crystallization

Wetting and drying of the cover concrete zone, such as encountered in the tidal and splash zones, are responsible for soluble salts being carried into the concrete pores during the wet periods. On drying, the salts crystallize creating expansive pressures, which in turn can lead to cracking and eventual spalling of concrete. This phenomenon is also known as salt weathering (Ballim et al, 2009, Mehta and Monteiro, 2005, Richardson, 2002).

4. Alkali-silica reaction

When aggregates susceptible to alkali attack are used in concrete, sea water accelerates alkali-silica reaction due to the presence of sodium and chloride ions which act as catalysts to the reaction (Ballim et al, 2009, Mehta, 1991).

5. Frost action

Problems caused by freezing of concrete are encountered in sea waters in cold climates. Sea water that penetrates the concrete pore structure freezes and on turning to ice increases in volume. This expansion induces tensile stresses in the concrete and microcracking of the binder paste occurs. In freeze-thaw cycles, the cracks are propagated by the cyclic freezing and thawing actions (Ballim et al, 2009).

2.5 The corrosion of reinforcing steel in the marine environment

2.5.1 General

Corrosion is an electrochemical process mediated by the formation of anodic and cathodic areas on the surface of steel where ferrous steel is oxidized to hydrated iron oxides and rust in the presence of oxygen and moisture. Figure 2.6 is an illustration of the corrosion process.

At the anode, electrons are released forming metal ions which pass into solution, while at the cathode the electrons are consumed by reduction (Broomfield, 2007, Poulsen and Mejlbro, 2006, Richardson, 2002, Mackechnie and Alexander, 2001, Bungey and Millard, 1996). Equations 2.3 and 2.4 give the ionic reactions.

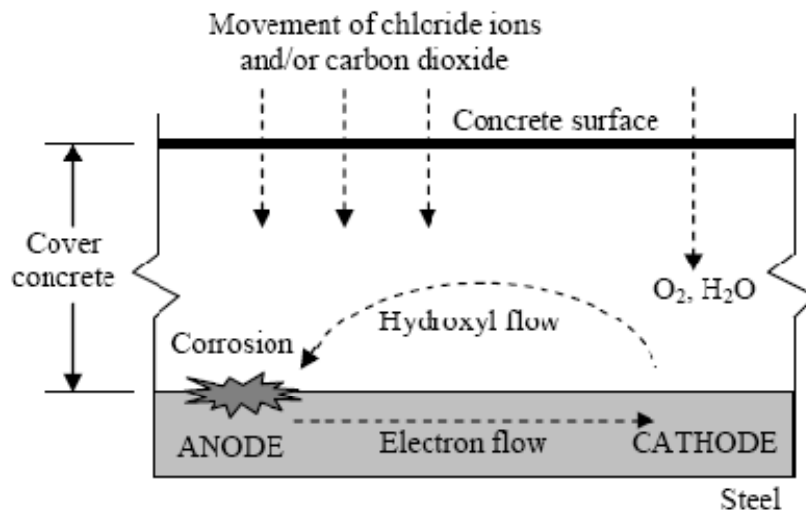


Figure 2.6: Schematic diagram of corrosion of reinforcement in concrete (Mackechnie and Alexander, 2001)



Interestingly, in submerged structures where the rate of oxygen diffusion into concrete is very low, corrosion also occurs. Corrosion occurs as a result of the cathodic curve moving back to intersect the anodic curve at a low potential. This is however not significant in terms of the overall service life of the structure (Richardson, 2002).

2.5.2 Corrosion induced damage

The first consequence of corrosion is a reduction in the cross section of the reinforcement from the dissolution of embedded steel. Second, corrosion products have a lower density than the parent material and hence are expansive. This induces stresses within the concrete leading to cracking, subsequent delamination and eventual spalling of concrete around embedded steel. Figure 2.7 is an illustration of the stages in this process. Ultimately, the result of corrosion in RC structures is a reduction in the ultimate bearing capacity (Broomfield, 2007, Richardson, 2002).

2.5.3 The loss of passivation

Typically, steel embedded in marine concretes is protected from corrosion by the following means (Ballim et al, 2009, Broomfield, 2007):

1. The high pH conditions present at the concrete-steel interface due to the alkaline nature of concrete. This promotes the formation of a protective film of gamma ferric oxide on the surface of the steel i.e. passivation.
2. The absence of deleterious species such as chloride ions and carbon dioxide capable of destroying the protective passivating film.
3. The insufficient availability of oxygen to sustain corrosion reactions.

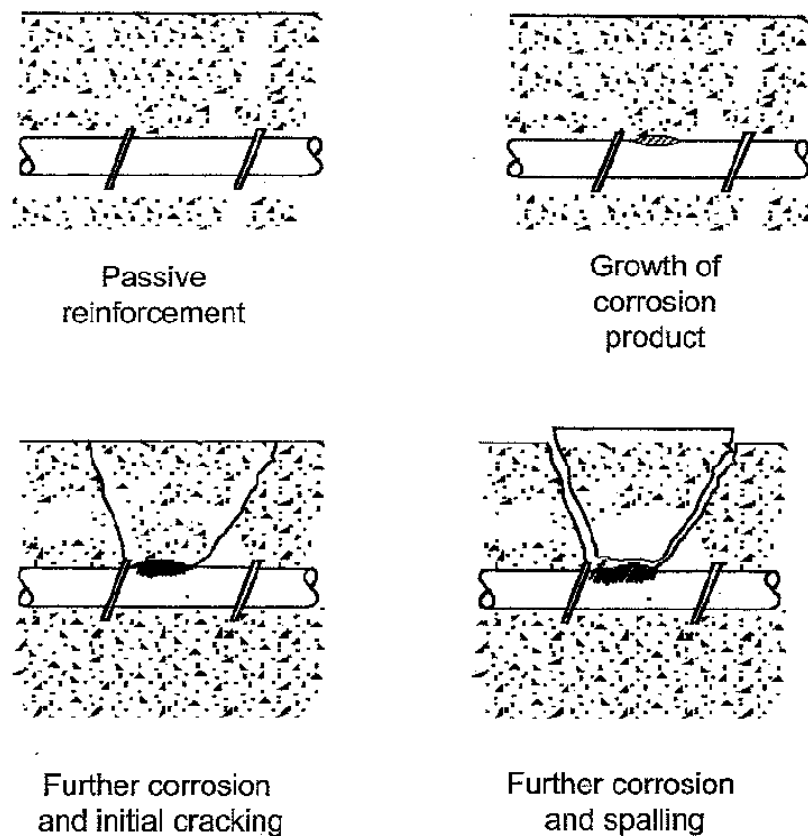


Figure 2.7: Stages in corrosion induced damage (Richardson, 2002)

The loss of passivation, and subsequent corrosion of embedded steel in concrete, occurs in the marine environment as a result of one or both of the following factors (Ballim et al, 2009, Mehta and Monteiro, 2005):

1. Carbonic acid attack of the concrete penetrating the concrete to the steel surface with a resultant altering of local alkaline conditions essential for maintaining passivation.
2. Ingress of chloride ions to the steel surface with a resultant disruption of the passivation layer.

Both these processes require some time to penetrate through the cover layer of concrete and render the embedded steel liable to corrosion i.e. depassivation. The initiation and actual rate of steel corrosion is thus determined by the concentration of the ions that reach the steel as well as the concentration of oxygen that diffuses to the steel surface. In the marine environment, chloride ions have a much higher concentration and it is in this regard that this experimental study focuses on chloride induced corrosion (Ballim et al, 2009, Broomfield, 2007, Poulsen and Mejlbro, 2006, Bungey and Millard, 1996).

2.5.4 Chloride ions in concrete

1. Chloride ion contamination

Chloride ion contamination of concrete leading to reinforcement corrosion may arise from both internal and external sources. Internal sources of chloride ions include contamination of the mix materials and the use of admixtures such as calcium chloride as a set accelerator in construction. Codes of practice, limit the acceptable levels of chloride ion contamination resulting from the use of contaminated mix materials. The use of admixtures containing chloride ions for reinforced concrete is generally not permitted. External sources of chloride ions include de-icing salts applied on concrete surfaces and sodium chloride in the marine environment (Eurocode ENV 1992-1-1, EN 206-1, 2002, Broomfield, 2007, Glass, 2003, Schiessl, 1987).

2. The ingress of chloride ions

The ingress of chloride ions into the concrete surface occurs in the liquid phase and can be summarised as follows; high surface chloride ion concentrations are initially developed by capillary suction; the chloride ions then migrate by diffusion towards the lower concentration areas of the internal material. The latter is the main transport mechanism of chloride ions within the concrete matrix under saturated or semi-saturated conditions

(Ballim et al, 2009, Kropp and Alexander, 2007, Poulsen and Mejlbro, 2006, Mehta and Monteiro, 2005, Glass, 2003, Costa and Appleton, 1999, Tang, 1996).

Chloride ion diffusion is affected by the concrete pore structure and occurs through these three paths within the concrete matrix:

1. Interconnected pores in the binder phase.
2. Interconnected pores in the coarse aggregate particles.
3. Interconnected pores in the ITZ.

Other mechanisms such as migration, permeation, convective flow and electro-osmosis (movement of water under the influence of an electric field) also occur. The exposure condition, the concrete moisture content and the pore structure however largely determine the penetration mechanism that occurs (Glass, 2003, Costa and Appleton, 1999).

2.5.5 Chloride induced corrosion in the marine environment

Chloride ion induced corrosion is generally focussed on a small area forming a pit on the surface of reinforcing steel i.e. pitting corrosion as illustrated in Figure 2.8. This can lead to a rapid loss of cross-section resulting in a critical reduction in the load bearing capacity of a reinforced concrete member. This form of deterioration is more severe than cracking leading to spalling as the evidence of distress is usually not apparent on the concrete surface (Broomfield, 2007, Richardson, 2002).

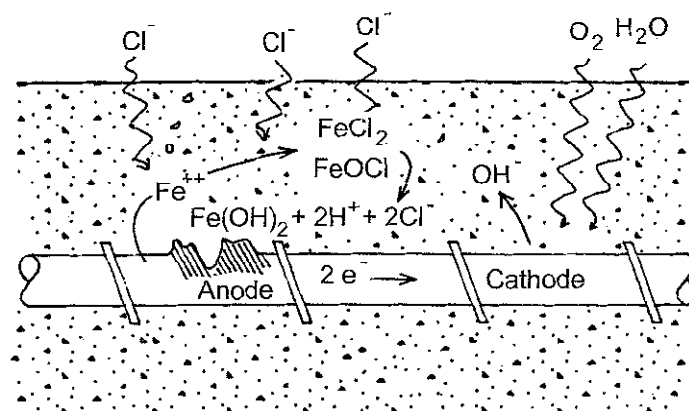


Figure 2.8: Pitting corrosion in a chloride-laden environment (Richardson, 2002)

The anodic reaction illustrated in Figure 8 is particularly damaging as it is self-propagating due to the local acidic conditions and the recycling of chloride ions by hydrolysis. The reaction proceeds as shown in equation 2.5 – 2.7:



The increased acidity of the anodic area prevents precipitation of corrosion products and encourages further oxidation of the steel. This accounts for the severe damaging effects of pitting corrosion.

2.5.6 Chloride binding in concrete

Within the concrete system, the chloride ions may exist in the following three forms (Richardson, 2002, Glass et al, 1996, Kropp, 1995):

1. Free chloride ions in the pore solution.
2. Loosely bound chloride ions.
3. Strongly bound chloride ions.

Free chloride ions are mobile ions that may be introduced from external sources. They are the most significant contributors to corrosion risk as their presence at the level of the reinforcing steel causes localised depassivation. This may occur despite the concrete pH being generally alkaline. The reinforcing steel is then susceptible to corrosion (Ballim et al, 2009, Broomfield, 2007, Poulsen and Mejlbro, 2006, Bungey and Millard, 1996).

Bound chlorides, in general are defined as chloride ions removed from the concrete pore solution by physical and/or chemical interaction with the binder paste. The aluminate components of the binder paste loosely bind internally or externally introduced chloride ions. The term loosely is given to them as a carbonating front moving into the concrete releases some of these bound chlorides into the pore solution. Such physical binding is postulated to be the result of sorption of the loosely bound chloride ions on the interior

pore surfaces of concrete. Strongly bound chloride ions are chemically combined with the aluminate components of the binder (Richardson, 2002, Boddy et al, 1999, Glass et al, 1996, Arya and Newman, 1990).

The chloride binding capacity of a concrete mix is dependent on a number of factors: the alkalinity of the binder used; its fineness and its tri-calcium aluminate and tetra-calcium alumina-ferrite contents (Richardson, 2002). The higher aluminate content in slag and fly ash blended concretes has been found to increase the chloride binding capacity of such concretes compared to an OPC concrete (Oh and Jang, 2007, Harrison, 1995, Arya and Xu, 1995, Rasheeduzzafar et al, 1990). However, this becomes less significant with high chloride ion concentrations. The tri-calcium aluminate content in hydrating binder has been found to influence the chloride binding capacity of concretes with concretes made with binders containing high amounts of tri-calcium aluminate showing more chloride binding capacity (Harrison, 1995).

Chloride binding results in the reduction of chloride ion concentration levels. Inherently, there is a reduction in a concentration potential and amount of migrating ions, which slows the deterioration processes. Additionally, there are less available chlorides to depassivate embedded steel (Glass and Buenfield, 1995, Schiessl & Raupach, 1990).

The chloride binding capacity of concrete must be quantified when studying chloride transport to better understand the deterioration process and the expected durability of concrete in the marine environment. This is done by chloride profiling followed by acid solubility of the pore liquid (pore water extraction) of the concrete or binder (Poulsen and Mejlbro, 2006).

Figure 2.9 illustrates the significant benefit of using slag and fly ash as cement extenders to minimise the effects of chlorides in corroding embedded steel compared to OPC concretes. The effect of using these cementitious extenders is clearly shown in reduced chloride conductivity values of a range of concrete grades tested at 28 days.

2.5.7 The threshold value of chloride ions in reinforced concrete

The depassivation of embedded steel takes place when a critical concentration of chlorides in concrete is reached at the level of the steel. This concentration, defined as the threshold value of chloride ions, is the total acid soluble chloride content of the concrete at which corrosion of embedded steel initiates in concrete exposed to a chloride laden environment (Ballim et al, 2009, Mejlbro and Poulsen, 2006).

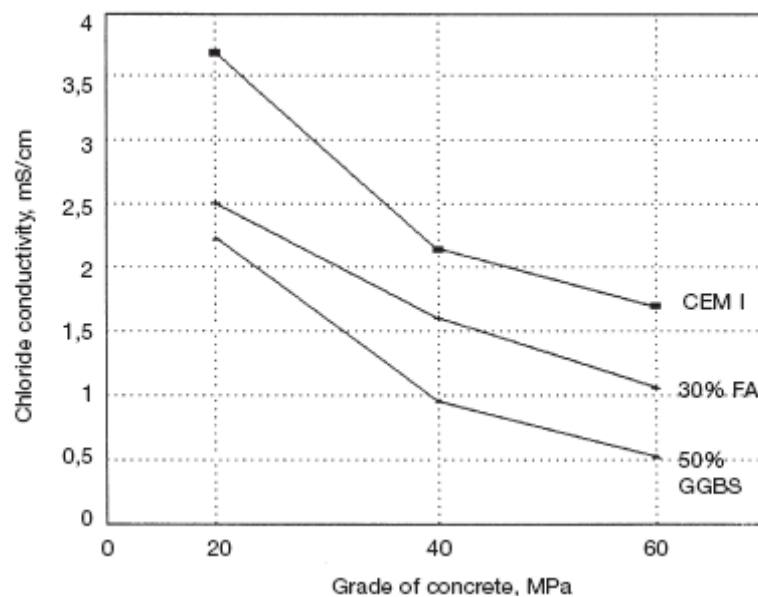


Figure 2.9: Effect of FA and GGBS in reducing the chloride conductivity of concretes over a range of strength grades (Alexander et al, 1999a)

Corrosion initiation and the critical chloride threshold value are dependent on the following factors (Broomfield, 2007, Richardson, 2002, ACI 222, 1994):

1. Binder type and its tri-calcium aluminate content.
2. Proportion of free chlorides to the total chloride content.
3. Chloride ion to hydroxyl ion ratio.
4. Water/binder ratio.
5. Hydroxyl ion concentration.
6. Temperature and relative humidity.
7. Electrical potential of the reinforcement.

The interaction of these factors is such that a critical chloride threshold value has not been uniquely established. Severally and jointly the above factors are also dependent on the properties of the particular concrete and its exposure environment. Table 2.1 shows the scatter of critical chloride threshold value results obtained by different researchers ranging from 0.06 to 2.5 for different concrete types.

Table 2.1: Published critical chloride threshold values

Chloride threshold value (% mass of binder)	Reference
0.06 – 2.2	Bamforth, 1996
0.17 – 2.5	Glass and Buenfield, 1995
0.06 – 2.5	Pettersson, 1992
1.6 – 2.5	Lambert et al, 1991
0.5 – 2.0	Schiessl and Raupach, 1990
0.5 – 1.4	Tuutti, 1982

As a design guide, the Comite Euro-International du Beton has published a possible relationship between critical chloride content, relative humidity and concrete quality illustrated in Figure 2.10.

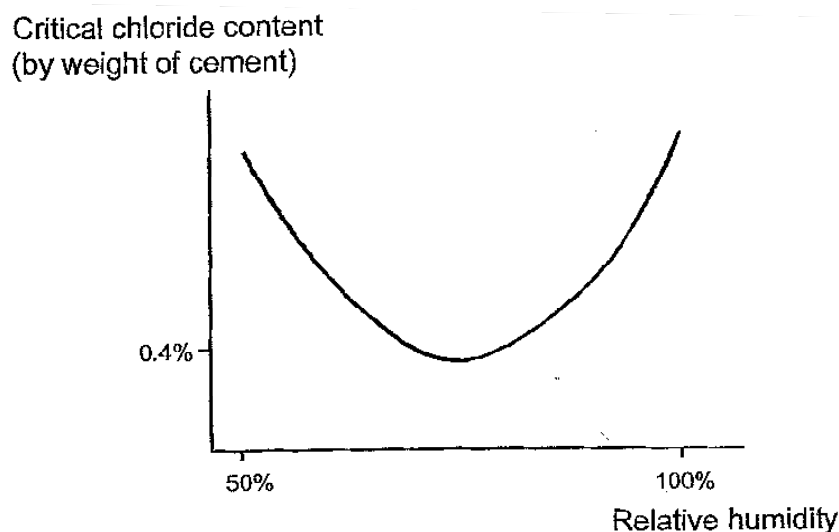


Figure 2.10: Typical critical chloride content for good quality un-carbonated concrete (adapted from Richardson, 2002)

The range of values covered by the graph shows a critical chloride level of 0.4 % by mass of binder for good quality un-carbonated reinforced concrete. The slope of the curve depends on the quality of the concrete and extent of carbonation. The better the concrete and lower the carbonation level, the higher the critical chloride level (CEB, 1989).

2.6 Factors influencing the chloride resistance of reinforced concrete in the marine environment

2.6.1 General

In the marine environment, durability of reinforced concrete is achieved when it is able to withstand the service conditions during its design life without significant deterioration. The South African National Standard SANS 10100-2, 2009, gives the following definition for durable reinforced concrete, *“when subjected to potentially destructive exposure (other than wear or loading), it protects the embedded metal from corrosion and performs satisfactorily for the life-time of the structure”*. The code of practice further describes this durability as a function of three factors that are attributed to the concrete system (SANS 10100-2, 2009);

1. **Impenetrability:** The concrete must be sufficiently impervious to deleterious species present in the environment that lead to deterioration. This is achieved with the use of normal density aggregates a sufficiently low water content, water/binder ratio , complete compaction of the concrete, and sufficient hydration of the binder.
2. **Binder type and content:** The rate of transport of deleterious species in concrete is largely dependent on the characteristics of binder paste. The binder component in concrete determines the degree of resistance the concrete system has against deterioration.
3. **Structural detailing:** It is important to note that durability is not achieved by engineering the concrete constituent materials alone, but also by structural design through the provision of adequate concrete cover to embedded steel. As most deterioration processes occur in reinforced concrete within the cover region, it is imperative that the cover region be designed to be of sufficient thickness so as to resist the penetration of deleterious species present in the environment.

The above factors and others associated with reinforced concrete durability in the marine environment shall be discussed here with reference to the penetrability and chloride resistance of concrete. The influences of these factors were investigated in this experimental study.

2.6.2 Binder type

The main influence that binder type has on concrete is on the rate of strength development with the main binder type in use in South Africa being a plain CEM I, 42.5N binder. This is an ordinary Portland cement (OPC) that is however not recommended for use on its own in the marine environment. The composition of OPC offers limited resistance to the ingress of chloride ions (Ballim et al, 2009, Alexander et al, 2007, Baweja et al, 1999). As such, blending OPC with supplementary cementitious materials i.e. extenders, is common practice for marine concretes and the extender types in this section shall be discussed as blends with OPC. These extenders have cementitious properties that increase the chloride ingress resistance and chloride binding capacity of a concrete mix. High chloride ingress resistance and binding results in less accumulation of chloride ions at depth within the concrete matrix and hence low diffusion coefficient values (Oh and Jang, 2007, Page and Vennesland, 1983).

The use of these supplementary cementitious materials (SCM) also has an economic and environmental benefit. Materials used as cementitious extenders to OPC in South African marine concretes are ground granulated blast-furnace slag (GGBS), ground granulated corex slag (GGCS), fly ash (FA) and condensed silica fume (CSF). They increase the performance of marine concrete by changing its chemistry and microstructure. It is therefore important to consider the composition of these materials and their effect on chloride ingress in comparison to OPC concretes. Their chemical constituent properties of these materials are given in the Table 2.2.

The increased performance against chloride ingress that blended concretes have has been researched extensively. Harrison (1995) gives the following ranking in decreasing order of the chloride ingress resistance that different concretes made with different binder types: OPC: GGBS < OPC: FA < OPC.

Table 2.2: Typical percentage compositions of oxide analyses of South African cement and extenders (Grieve, 2009a)

Oxides	OPC	GGCS	GGBS	FA	CSF
CaO	67.2	37.2	34.0	4.7	0.6
SiO ₂	22.3	30.8	35.5	54.1	92
Al ₂ O ₃	4.4	16.0	15.4	32.9	1.5
MgO	1.01	13.7	9.4	1.3	0.6
TiO ₂	0.22	0.51	1.2	1.7	-
Fe ₂ O ₃	3.4	0.87	0.98	3.3	1.2
MnO	0.08	0.09	0.88	-	-
K ₂ O	0.56	0.35	0.87	0.6	0.6
Na ₂ O	0.21	0.12	0.16	0.6	-
SO ₃	0.58	3.19	2.49	0.4	-

1. Ground Granulated Blast Furnace Slag (GGBS)

GGBS, a product of the blast furnace process used to produce iron, is a latent hydraulic binder that is comprised of mainly silica and alumina ions. GGBS produces concretes that offer excellent chloride binding properties when substituted for OPC. The higher aluminium oxide content in a GGBS concrete compared to an OPC concrete increases its chloride binding potential and decreases chloride diffusion (Glass et al, 1997, Dhir et al, 1996, Arya et al 1990). Figure 2.11 illustrates this.

Increased GGBS content also decreases the porosity of the concrete system. The higher silica content contained in GGBS leads to improved hydration resulting in more of the capillary pores being filled with hydrated binder paste. The reduction was reported by Soroka (1993) as being dependant on the amount of GGBS substituted but has an optimum range as substitutions greater than 60 %, results in increased permeability. This is illustrated in Figure 2.12.

The use of GGBS in concrete also leads to improved resistance to sulphate attack and a reduction in expansion in the occurrence of alkali silica reaction (Ballim et al, 2009)

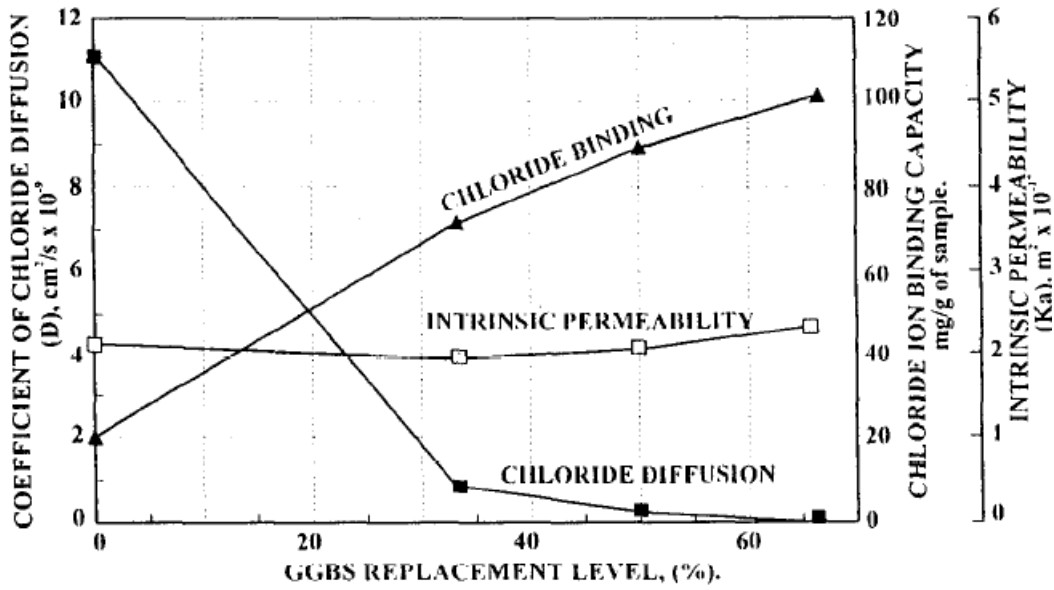


Figure 2.11: The effect of GGBS replacement on the permeability, chloride binding capacity and chloride diffusion of concrete (Dhir et al, 1996)

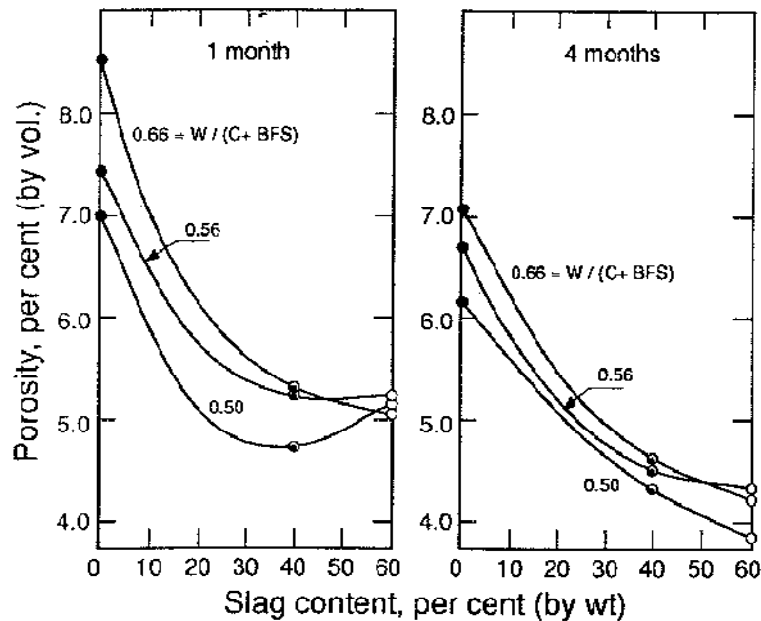


Figure 2.12: Effect of GGBS content and w/b on concrete capillary porosity (Soroka, 1993)

2. Ground Granulated Corex Slag (GGCS)

GGCS used in the Western Cape Province, South Africa is a by-product of the Corex™ iron production process. Its chemical characteristics and mode of action are similar compared to GGBS, but the former is faster reacting. GGCS concretes have been found to have a denser microstructure and improved chloride binding capacities similar to GGBS concretes. Figure

2.13 shows chloride iso-conductivity curves for GGCS and GGBS concretes which exhibit similar chloride transport characteristics (Mackechnie et al, 2003, Alexander et al, 1999a).

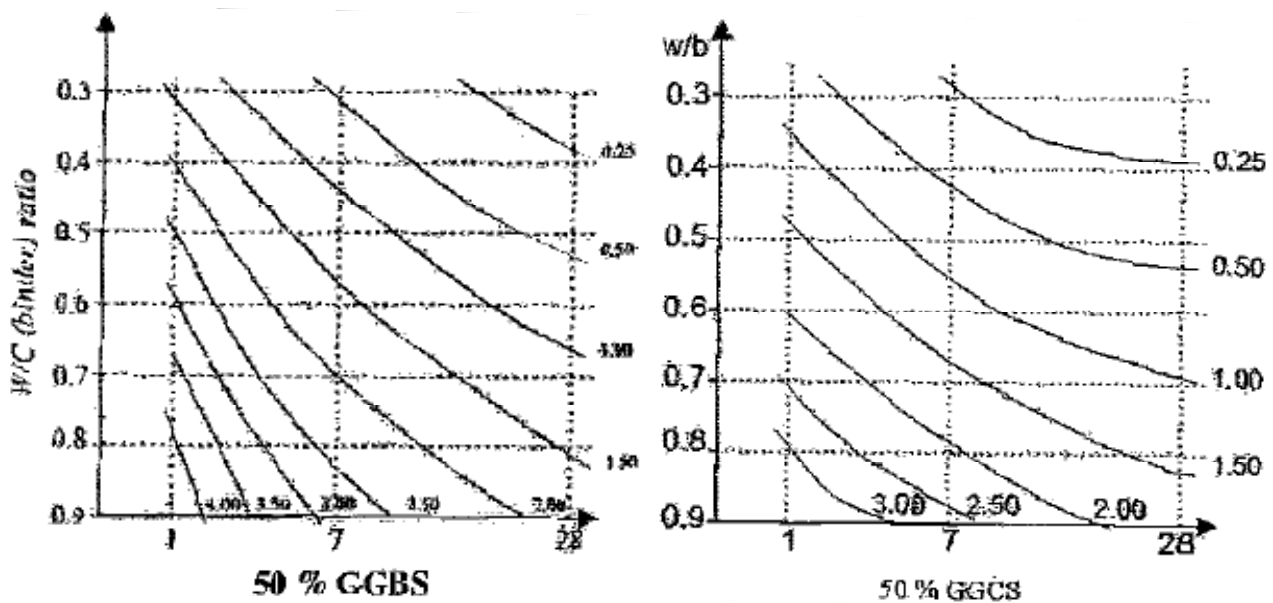


Figure 2.13: Chloride iso-conductivity curves for GGBS and GGCS concretes (Mackechnie et al 2003, Alexander et al, 1999a)

In marine concretes, for optimum chloride resistance, the substitution of OPC by GGCS is generally 50 % as proposed by Mackechnie et al (2003). Gardner (2006) showed that 50 % GGCS substitution of OPC concrete reduced diffusion coefficient values after 90 days of diffusion testing by up to 77 %. Table 2.3 shows values obtained by Gardner (2006).

Table 2.3: 90 day diffusion tests results for 0.65 w/b ratio concretes (Gardner, 2006)

Concrete type	Diffusion coefficient
OPC	10.2×10^{-12}
50 % GGCS	2.28×10^{-12}

3. Fly Ash (FA)

FA is pale grey/white pozzolanic material formed during coal combustion where the flue gases comprising fused clay and quartz particles are collected by electrostatic precipitators in glassy spherical shapes. Its chemistry is mainly comprised of silica and alumina ions which give fly ash its pozzolanic properties. The lack of a CaO component in it is nevertheless countered by the production of calcium hydroxide in the hydration of OPC. The silica content

of fly ash reacts with the calcium hydroxide produced from OPC hydration to form additional CSH gel which densifies the concrete matrix. Additionally, the spherical shape and high fineness of fly ash particles improves the particle packing of FA concretes and ultimately slows the ingress of chloride ions (Chalee and Jaturapitakkul, 2008). Figure 2.14 illustrates the effect of FA substitution on the pore size diameter of binder paste.

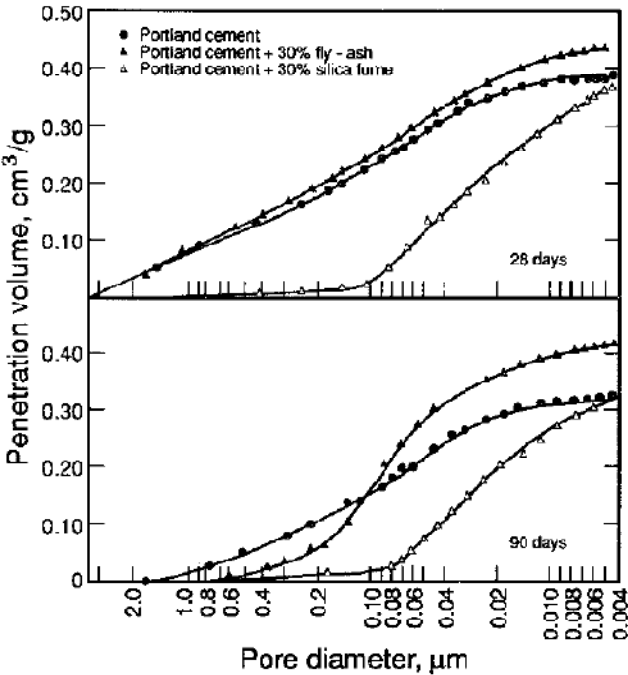


Figure 2.14: The effect of FA and CSF substitution on the pore size distribution of binder paste (Soroka, 1993)

The high alumina content of fly ash increases its chloride binding potential and decreases chloride ingress as illustrated in Figure 2.15 by the chloride profiles of FA concretes. The samples were exposed to a chloride rich environment for 10 years under continuous cyclic wetting and drying conditions (Ngala et al, 1995, Thomas and Mathews, 2004, Thomas and Bamforth, 1998).

Fly ash concretes have slower and extended hydration periods and at 28 days have been found to have similar chloride transport characteristics as plain CEM I concrete types. Mackechnie, (1996) reported that increased performance characteristics of FA blended concretes is developed at later ages. The delayed hydration characteristic fly ash concrete blends have is however beneficial in large concrete pours where they exhibit reduced heat of hydration.

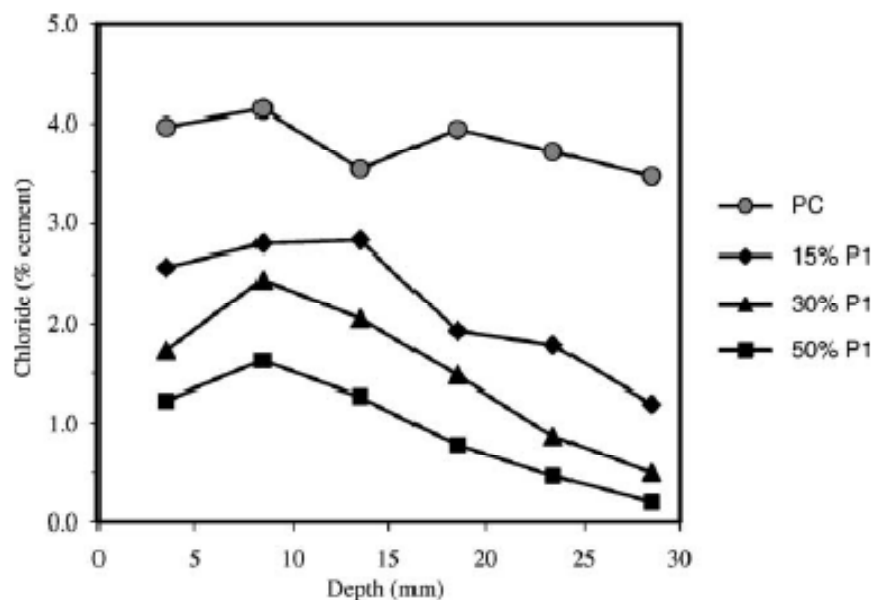


Figure 2.15: The effect of FA on chloride profiles in concretes exposed to marine conditions (Thomas and Mathews, 2004)

4. Condensed Silica Fume (CSF)

CSF also known as microsilica (MS) is a by-product of the ferrosilicon alloys smelting process. It is largely made up of silica of fine amorphous nature making it a highly active pozzolanic binder with the small particles providing numerous nucleation sites for hydration. This in addition to CSF having a pore filler effect thereby reducing the permeability of CSF concretes. The result is a dense binder matrix that has fewer capillary pores. Figure 2.14 illustrates this. The fine particle size distribution also improves workability and reduces water demand (Ballim et al, 2009, Alexander et al, 1999a, Hussain and Rasheeduzzafar, 1994, Soroka, 1993).

Silica fume concretes have shown significant reduction in chloride conductivity compared to OPC concretes. Table 2.4 gives chloride conductivity results of CSF concretes where OPC has been substituted with 5 % and 10 % CSF. Ternary blends of CSF and GGBS show further improved values of chloride conductivity (Alexander and Magee, 1999).

However, several researchers have shown that CSF concretes exhibit poor chloride binding characteristics (Delagrave et al, 1997, Mangat and Molloy, 1995, Arya and Xu, 1995, Arya et al, 1990). Figure 2.16 illustrates this in CSF concretes compared to other concrete mixes. CSF concretes are therefore not recommended for use in reinforced concrete structures in the marine environment.

Table 2.4: 28 day chloride conductivity results for 0.56 w/b CSF concrete blends (Alexander and Magee, 1999)

Concrete mix	Chloride conductivity (mS/cm)
OPC	1.93
5 % CSF	0.95
10 % CSF	0.68
50% GGBS	0.81
5 % CSF/45 % GGBS	0.50
10 % CSF/40 % GGBS	0.36

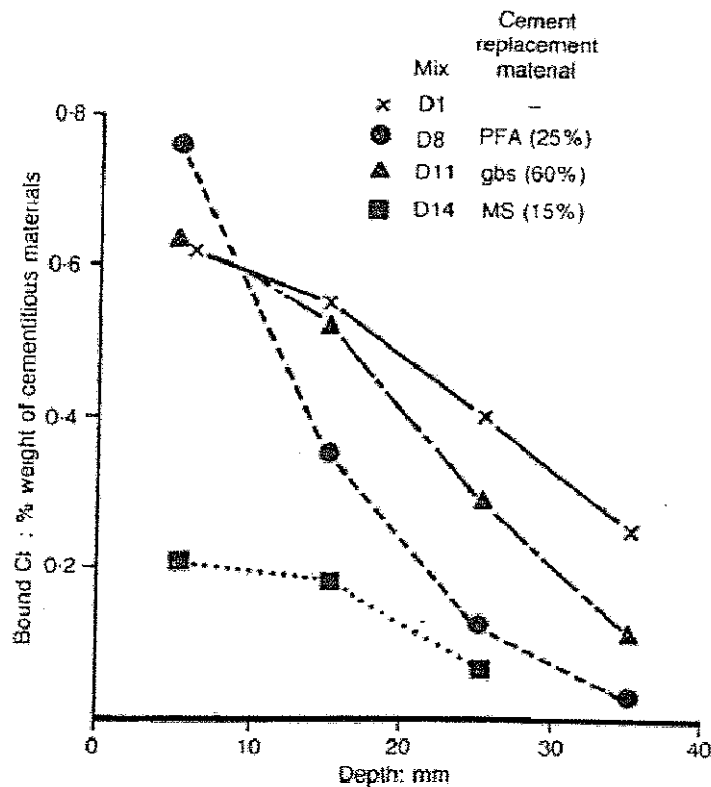


Figure 2.16: Chloride binding capacity of silica fume concretes compared to other concrete types (Mangat and Molloy, 1995)

2.6.3 Water/binder ratio

Water/binder (w/b) ratio has an inversely proportional influence on the strength and durability characteristics of concrete. As a function of the capillary pore volume, w/b ratio controls the spacing between binder grains themselves and between the binder phase and

aggregate particles (Glass, 2003). Richardson (2002) gives three requirements of w/b ratio necessary to produce durable concrete:

1. The w/b ratio must be low enough to limit the initial volume of the capillary pore network produced by the mix water.
2. The w/b ratio must be high enough to provide a water-filled capillary pore network with an initial volume at least twice that of the un-hydrated binder.
3. The w/b ratio chosen combined with the curing regime must be sufficient to enable the capillary network to remain water-filled long enough to ensure sufficient hydration.

A study by Mehta and Manmohan (1980) investigated the influence of w/b on penetrability and reported that decreasing w/b ratio and increasing the degree of hydration by proper and extended curing had the effect of reducing the volume and size of the pores within the concrete microstructure. The net effect is the 'beneficial' reduction in penetrability of the hardened binder paste. The same result has been reported by Richardson (2002) and Soroka (1993) as an increase in permeability with increasing w/b ratio as illustrated in Figure 2.17.

Similar studies by Arya et al (1990) concluded that with increasing w/b ratio, chloride binding increased as a result of an increasing degree of hydration at higher w/b ratios. Macdonald and Northwood (1995) obtained an exponential relationship between diffusivity and w/b ratio as illustrated in Figure 2.18.

Hobbs and Mathews, (1998) studied the relationship between effective diffusion coefficient and w/b ratio and reported that chloride diffusion increases with increasing w/b ratio. Using equation 2.8, from the study, the effective diffusion coefficient can be determined for plain OPC concretes.

$$D_{\text{eff}} = 0.04(1166^{w/b}) \times 10^{-12} \text{ (m}^2\text{/s)} \quad (2.8)$$

where:

D_{eff}	effective diffusion coefficient
w/b	water/binder ratio

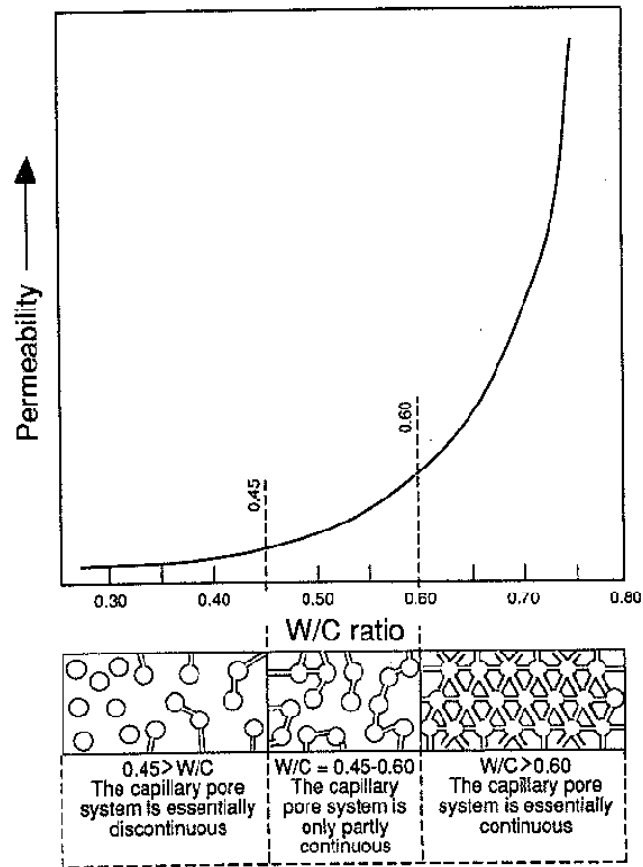


Figure 2.17: Influence of w/b ratio on permeability (Soroka, 1993)

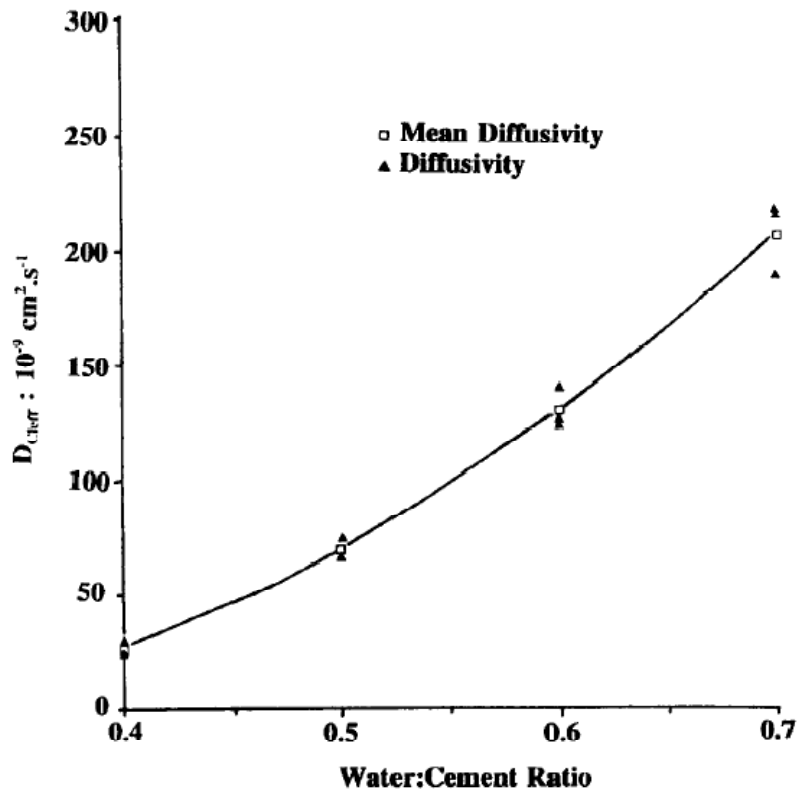


Figure 2.18: Diffusivity as a function of w/b ratio (Macdonald and Northwood, 1995)

2.6.4 Curing

The curing process where sufficient moisture is provided to the concrete for continued hydration such that it attains sufficient impenetrability is a primary durability factor. Increased hydration of binder particles leads to a decrease in the capillary pore structure as more gel products are formed to block the capillary pores. The result illustrated in Figure 2.19 is a reduction of the transport of deleterious substances through the concrete as similarly reported by Glass (2003) and Costa and Appleton (1999).

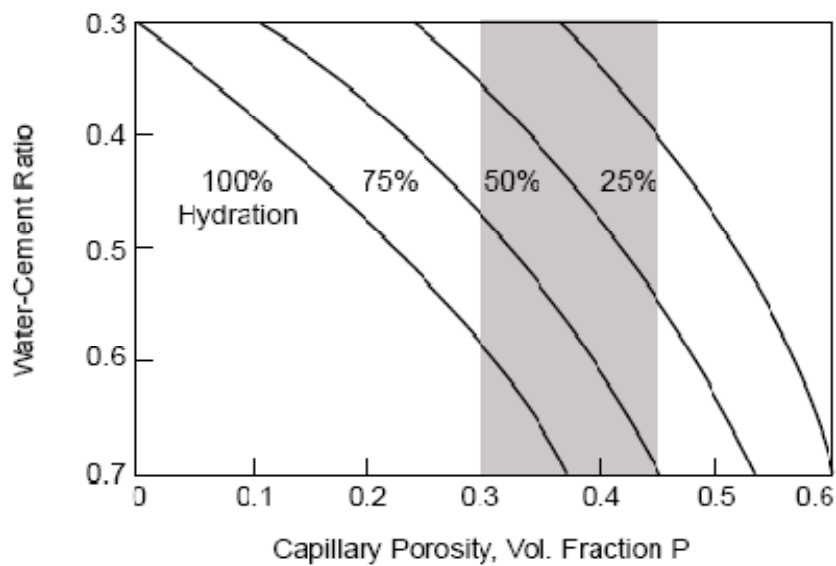


Figure 2.19: Reduction of permeability of binder paste by hydration level (Mehta and Monteiro, 2005)

Dhir et al (1986) reported that curing during the early days after concrete placing has a crucial effect on the absorption properties of the cover layer of concrete as this region is highly susceptible to the loss of moisture for hydration. Figure 2.20 illustrates this.

Boddy et al (1999) and Mangat and Molloy (1994) showed that hardened cement paste increased its resistance to chloride ingress with increased maturity as hydration continued to occur verified by a recorded decrease in D_c . Mangat and Molloy (1994) showed the relation between the diffusion coefficient and time can be expressed by a power function as shown in equation 2.9:

$$D(t) = D_1 t^{-m} \quad (2.9)$$

where:

$D(t)$ diffusion coefficient after exposure time t

D_1 diffusion coefficient at one year

t time (years)

m empirical coefficient

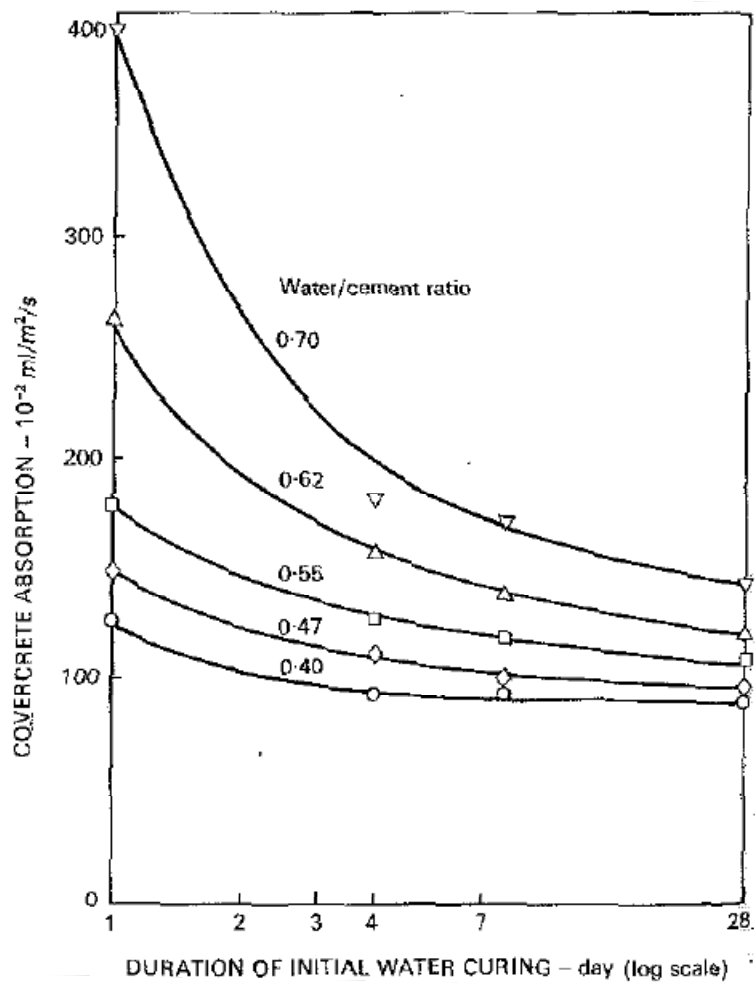


Figure 2.20: The influence of initial moist curing on the absorptivity of concrete (Dhir, et al, 1986)

The empirical coefficient, m , is a function representing the effect of continued hydration in concrete as well as a parameter representing the pore blocking effect of the brucite layer on the surface of concrete exposed to sea water.

Regarding the influence of curing on the surface concentration of chlorides, C_s , many researchers report that increases with continued curing (Hong and Hooton 1999,

Mackechnie 1996, Mangat and Molloy 1994, Bamforth and Price, 1993). It was further found that blended concretes hydrate much slower than OPC concretes making them much more sensitive to the curing duration and methods used. Figure 2.21 illustrated this effect as a reduction in chloride conductivity values of concrete tested after 28 days moist curing.

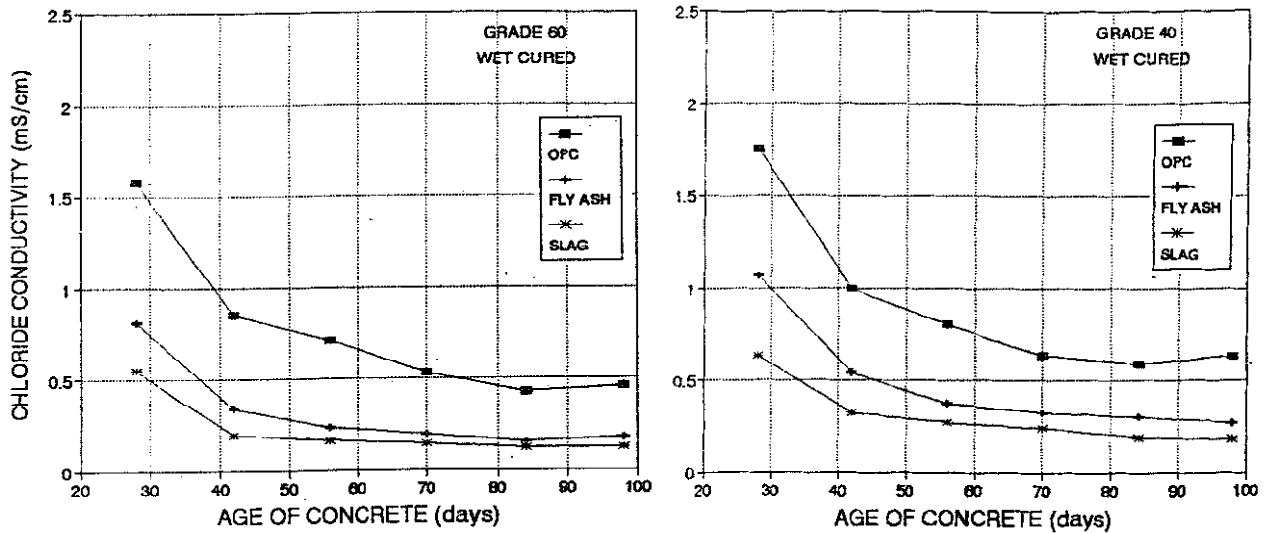


Figure 2.21: Reduction in chloride conductivity after immersion in chloride solution at 28 days (Mackechnie, 1996)

2.6.5 Aggregate type

Aggregate particles in concrete are surrounded by a layer of binder gel that isolates the aggregates from the permeable network in concrete rendering them sufficiently impermeable to the ingress of deleterious species (Richardson, 2002). As such, chloride transport does not usually occur through aggregates, but through the ITZ which has a higher porosity than both the binder paste and the aggregate particles (Mehta and Monteiro, 2005, Scrivener, 2004, Caré, 2003, Garboczi and Bentz, 1997, Scrivener and Nematy, 1996, Scrivener et al, 1995).

Mehta (1988) and Cerny and Rovnanikova, (2002) advise that the selection of aggregate type is an important factor so that the aggregate type chosen does not have a detrimental impact on the chloride resistance of marine concretes. Limestone and dolomitic aggregates should be preferred over quartz, sandstone or feldspar aggregates as they form a stronger chemical bond with the hydrating binder paste. Additionally, the latter have compatible coefficients

of thermal expansion with the bulk binder paste which minimises the potential to micro-cracking. Quartz aggregates have been reported by Mehta and Monteiro (2005) as having higher permeability than granitic aggregates by up to 1000 times. These two are the main rock types of the coarse aggregate types used in this study.

Preferentially, smaller sized coarse aggregates are preferred in concrete. They provide more local restraint to dimensional changes (from temperature and humidity variations) that induce microcracking within the aggregate particle itself and/or the bond it has formed with the binder paste.

The fine aggregate content of concrete has been reported to have an impact on the ingress of chloride ions. Known as the percolation effect, Halamickova et al (1995) studied its impact on the effective diffusion coefficient (D_{eff}) and reported that for an increase in the sand volume there was a subsequent decrease in effective diffusion coefficient. Table 2.5 shows results of 0.5 w/b ratio water-cured mortars from the study.

Table 2.5: Effect of sand content on effective diffusion coefficient (Halamickova et al, 1995)

Sand volume (%)	Degree of hydration (%)	Average D_{eff} ($m^2/s \times 10^{-12}$)
0	55 – 56	29.6
35	70 – 73	9.6
45	70 – 72	17.9
55	70 – 73	8.4

An irregularity occurs between 35 and 55 % sand content where the effective diffusion coefficient doubles. This is postulated to be the point where percolation occurs resulting from a negative effect on the pore structure by relatively impermeable aggregate particles replacing binder paste.

Ultimately, mix design should find a balance of aggregate content that provides a dense impenetrable concrete matrix.

2.6.6 Other factors influencing chloride action in marine concretes

1. Carbonation

As earlier discussed carbonation causes depassivation of embedded steel. Where carbonation and chloride ingress occur simultaneously, apart from accelerating the depassivation, the pH lowering effect of carbonation causes some of the bound chlorides to be set free. This increases the chloride content of the pore solution which in effect accelerates chloride diffusion through concrete (Ballim et al, 2009, Arya and Xu, 1995).

2. Degree of environmental exposure

The performance of reinforced concrete in the marine environment is also a characteristic of the severity of the exposure conditions. These vary considerably from a wide range of factors such as micro and macro-climate, position relative to the sea, orientation and prevailing winds (Mackechnie, 1996). Table 2.6 summarises the natural environmental classes considered in South Africa for the marine environment.

Table 2.6: Natural environmental classes (adapted from SANS 10100-2: 2009)

Environmental class	Description of the environment
XS1	Exposed to airborne salt but not in direct contact with sea water
XS2a(b)	Permanently submerged (exposed to abrasion)
XS3a(b)	Tidal, splash and spray zones (exposed to abrasion)

3. Cracks

In most cases the occurrence of cracks on a concrete surface has an impact on the serviceability of a structure. Nevertheless the susceptibility to penetration of concrete by deleterious substances increases tremendously once cracks develop, even if the concrete is of good quality or proper workmanship. Common causes of cracking are excessive deflection due to load, drying shrinkage, thermal shrinkage, freeze-thaw cycles and expansive chemical reactions (e.g. alkali-silica reaction, ettringite formation). In the marine environment, the width and depth, interconnectivity, frequency and orientation (relative to embedded steel) of cracks may affect the structural integrity and inherent durability of reinforced concrete by

providing easy access to the ingress of chloride ions. Design codes hence provide guidelines to limit crack widths in reinforced marine concretes.

2.7 Detection and analysis of the chloride ion content of concrete

2.7.1 General

This section discusses detection and analysis methods of the chloride content of concrete. The dominant mechanism of chloride ingress into concrete is diffusion for which an important parameter to be determined is the apparent chloride ion diffusion coefficient (D_a). D_a is a measure of the chloride resistance capacity of the concrete and is dependent on the pore structure of the concrete matrix. The accumulation of chlorides on the concrete surface which gives the diffusion process a driving potential is similarly an important measurable quantity defined as surface concentration (C_s). The two values D_a and C_s are characteristic properties and are used in service life prediction models to predict the time to corrosion initiation and the inherent durability of reinforced concrete exposed to chloride ions (Stanish and Thomas, 2003).

2.7.2 Bulk diffusion testing and chloride profiling

A common method used to determine the apparent chloride diffusion coefficient of concrete is through bulk diffusion testing described in the ASTM C1556-04 (2004) manual. Sealed and saturated concrete samples are exposed to a saline environment that allows for chloride ions to penetrate the concrete solely by diffusion. The purpose of the test is to obtain the chloride concentration of concrete at different profile levels which are then analysed to give the surface chloride concentration (C_s) and the corresponding apparent chloride diffusion coefficient (D_a). The test is most representative of fundamental chloride ion diffusion through a concrete matrix though it is time consuming.

Kropp and Hilsdorf (1995) describe the distribution of chloride ions in concrete as a function of the exposure conditions and time and with ingress of the chloride ions occurring through diffusion. Concentration profiles are obtained as illustrated in Figure 2.22. With increasing penetration depth and duration of exposure the relative change in concentration are used to estimate the progress of the ingress of chloride ions with time.

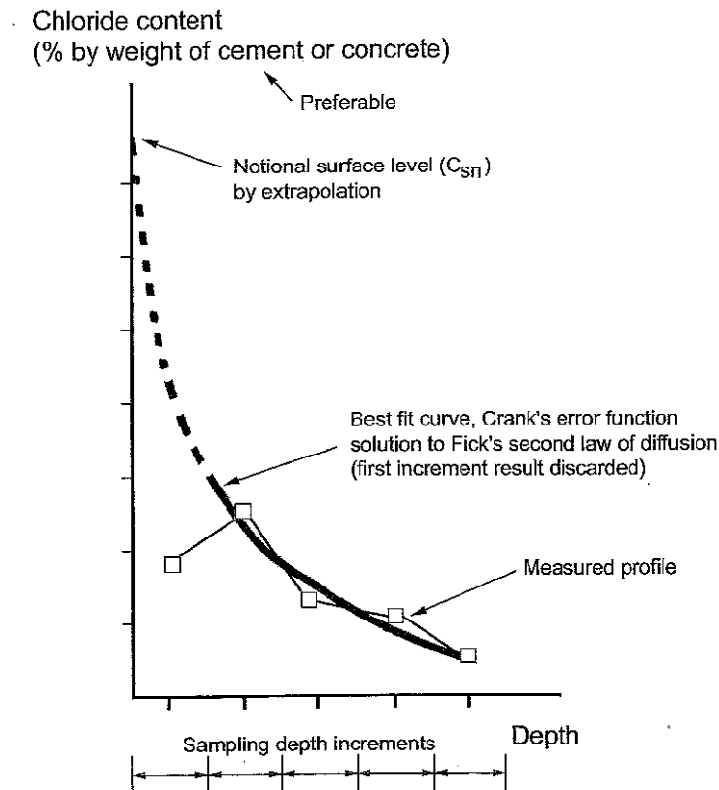


Figure 2.22: Chloride concentration profile (Richardson, 2002)

2.7.3 Chloride content analysis

Determination of the chloride ion content of concrete is generally found by different measurement and test methods. The total amount of chloride ions in concrete is found using acid-soluble content techniques whilst the free chloride content is found using water-soluble chloride content techniques. The bound chloride content can then be determined as the difference between the total and free chloride ion contents. The results of both test methods are expressed as single point values of percentage chloride by mass of binder from which diffusion coefficients are determined (Poulsen and Mejlbro, 2006, Richardson, 2002).

The acid-soluble content technique is predominantly used in the analysis of the chloride content of concrete, though it overestimates the durability threat posed by the chloride ions in concrete. Nevertheless, it should be noted that bound chlorides can be released within the concrete by processes such as carbonation. As such, specification clauses for reinforced concrete in the marine environment impose chloride content limitations based on total chloride contents (SANS 10100-2:2009, Richardson, 2002).

Total chloride ion content measurement is usually done by obtaining dust samples of concrete surfaces drilling which are then analysed for their chloride ion content by several test methods; Rapid Chloride Test method, Quantab- method, Volhardt titration, Potentiometric titration or X-ray fluorescence (Poulsen and Mejlbro, 2006, Richardson, 2002).

The chloride content measured is then used in Fick's laws of diffusion. This is described in the following section.

2.7.4 Mathematical modelling of chloride ion ingress and calculation of the apparent diffusion coefficient

Modelling of chloride ion ingress through diffusion is based on Fick's diffusion theories whose first law describes diffusion as a steady state process giving equation 2.10 (Crank, 1975). It describes diffusion as a flux of ionic species per unit of concentration gradient.

$$F = -D_c \frac{\partial C}{\partial x} \quad (2.10)$$

where:

F mass transport rate (g/m²s)

D_c chloride diffusion coefficient (m²/s)

$\frac{\partial C}{\partial x}$ concentration gradient measured normal to the surface (g/m⁴)

The negative sign denotes that the diffusion of chloride ions occurs in the direction opposite that of increasing concentration gradient. The chloride diffusion coefficient is important in reinforced marine concrete design as it enables the modelling of the progress of a chloride front in concrete exposed to a chloride-laden environment.

However, as chloride ions diffuse into concrete, the concentration at any time changes at every point x making the diffusion process a non-steady state process. The time dependency of the diffusion coefficient is shown in equation 2.11 (Takewaka and Mastumoto, 1988).

$$D_c(t) = D_0 \left(\frac{t_0}{t} \right)^m \quad (2.11)$$

where:

D_c	chloride diffusion coefficient (m^2/s)
D_0	chloride diffusion coefficient at time $t = 0$ (m^2/s)
t	time of exposure (s)
t_0	time $t = 0$ (s)
m	parameter that defines the evolution of D_c with time

To simplify this, Fick's second law of diffusion further models chloride ingress as a one-dimensional mass balance equation. This is given in equation 2.12 (Poulsen and Mejlbro, 2006).

$$\frac{\partial C}{\partial t} = -D_a \frac{\partial^2 C}{\partial x^2} \quad (2.12)$$

where

C	concentration of chloride ions (g/m^3)
t	time of exposure (s)
D_a	apparent chloride diffusion coefficient (m^2/s)
x	depth measured normal to the surface (m)

The equation defines the concentration of chloride ions in time changing along a pre-defined direction. It is solved with the following boundary conditions as the diffusion coefficient is dependent on the testing conditions:

1. at the concrete surface; $C(x=0, t=0) = C_s$
2. at depth within the concrete; $C(x=\infty, t>0) = 0$

Figure 2.23 illustrates a one-dimensional chloride profile modelled from Fick's second law of diffusion that expresses the change in chloride ion content per unit time.

The nature of the chloride profile shows that chloride ions penetrate progressively into the concrete matrix with time. This trend is typical of all concrete types but the slope varies as influenced by the various factors discussed earlier. From a chloride profile, the concentration of chlorides that can significantly initiate corrosion at depth can be determined.

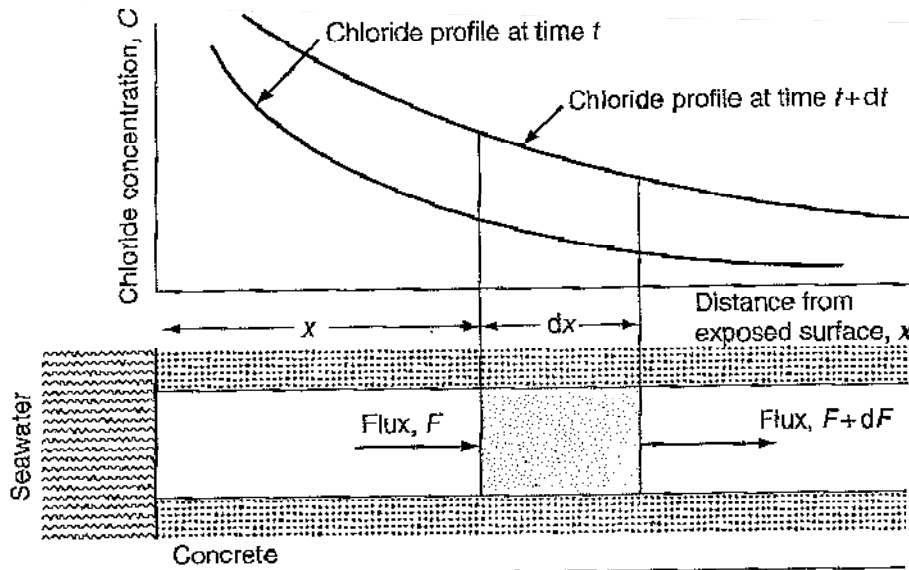


Figure 2.23: Change in chloride ion content per unit time as expressed by Fick's second law of diffusion (Poulsen and Mejlbro, 2006)

The solution to Fick's second law of diffusion is obtained using Crank's error function solution which assumes that D_a is a constant value for a specific exposure time (Richardson, 2002). The apparent chloride diffusion coefficient is then calculated using equation 2.13:

$$C_{x,t} = C_s - (C_s - C_i) \operatorname{erf} \left(\frac{x}{2\sqrt{D_a t}} \right) \quad (2.13)$$

where:

$C_{x,t}$ concentration at depth x measured normal to the section at time t
expressed by % weight of binder (g/m^3)

C_s projected surface chloride concentration determined by regression
analysis expressed by % weight of binder (g/m^3)

C_i initial chloride-ion concentration of the binder prior to immersion in
the exposure solution by % weight of binder (g/m^3)

erf error function

x depth measured normal to the surface (m)

D_a apparent chloride diffusion coefficient (m^2/s)

t time of exposure (s)

Diffusion does not occur through a homogenous solution and other factors come into play interfering with the interpretation of chloride diffusion data. The concrete matrix is porous having both liquid and solid components though diffusion through the latter is negligible compared to the diffusion through the pore structure. The rate of diffusion is primarily controlled by the diffusion coefficient through the pore solution and by the physical characteristics of the capillary pore structure (Stanish et al, 2001).

2.7.5 Reported values of chloride diffusion coefficient of concrete mixes

A sample review of a wide range of published values of diffusion coefficients from experimental studies is given in Table 2.7. The values are from samples exposed to a chloride rich environment in the laboratory. From the table it is clear that OPC concretes generally yield values of the order of 10^{-12} m²/s with of fly ash and slag concretes yielding values lower by a factor of 10. The information given in the table includes the exposure time concrete types used and reference. A discussion on the main findings of the studies related to this experimental study is then given.

In an experimental study on the effect of w/b ratio and fly ash blending of concrete on chloride diffusion coefficient (D_c), Chalee and Jaturapitakkul (2008) report that a decrease in w/b ratio resulted in a decrease in diffusion coefficient, D_c . They also reported that FA replacement of OPC resulted in lower D_c values than plain OPC concrete subjected to the same conditions by up to 15 %. However, w/b ratio had more effect than fly ash replacement on reducing D_c . Their study also investigated the effect of exposure time on reducing D_c by subjecting concrete to a chloride laden environment for 2, 3, 4 and 5 years.

Chalee and Jaturapitakkul (2008) also found that increased exposure time resulted in a decrease in D_c results from the study of the effects of material and environmental parameters on chloride penetration profiles in concrete, Oh and Jang (2007) investigated the effect of OPC replacement by fly ash on D_c . Their results indicate that the fly ash replacement reduced D_c values by 15 % - 50 %.

Yang (2004) studied the transport properties of concrete subjected to a chloride rich environment by ponding tests. The experimental variables of the study were w/b ratio and the concrete constituent materials. D_c was found to increase with increasing w/b ratio. The

addition of supplementary cementitious materials, fly and slag, resulted in a significant decrease of D_c . A look at the values given in Table 2.7 however shows only marginal increase in D_c between the w/b ratios of 0.45 and 0.55. A similar behaviour is seen from the study by Chalee and Jaturapitakkul (2008).

Table 2.7: Published diffusion coefficient values

D ($\times 10^{-12}$ m ² /s)	Exposure time (days)	Concrete mix		Reference
		Binder	w/b	
5.00	730	OPC	0.45	Chalee And Jaturapitakkul, 2008
1.40		15 % FA	0.55	
5.70		OPC		
1.60		15 % FA		
6.44	105	OPC	0.40	Oh and Jang, 2007
5.66		20 % FA		
10.20	90	OPC	0.65	Gardner, 2006
2.28		50 % GGCS		
16.39	90	OPC	0.45	Yang, 2004
6.13		20 % GGBS		
3.51		20 % FA	0.55	
23.35		OPC		
7.13		20 % GGBS		
5.24		20 % FA		
5.53	180	OPC	0.50	Stanish and Thomas, 2003
1.56		25 % FA		
1.53		56 % FA		
3.46	120	25 % GGBS	0.40	Hong and Hooton, 1999
2.01	365			
52.3	28	OPC	0.58	Mangat and Molloy, 1994
23.8	90			
10.0	270			

Part of the study by Stanish and Thomas (2003) used bulk diffusion testing to determine the effect of fly ash replacement on D_c values. The results given in Table 2.7 indicate that there is

a significant decrease in D_c values when OPC is substituted for OPC. It is also evident that fly ash addition has an optimum value on the margin of decrease in D_c values.

Two experimental studies by Hong and Hooton (1999) and Mangat and Molloy (1994) studied the dependence of concrete age on D_c . The former reported results that indicate significant decrease in D_c values with increased concrete age in GGCS blended concretes by up to 42 % within a period of 8 months. Mangat and Molloy (1994) reported a more significant decrease in D_c values of plain OPC concretes of up to 80 % within a similar period of 8 months.

2.8 Characterising the durability of reinforced concrete in the marine environment

This section looks at the various methods used to characterise the inherent durability of reinforced concrete in the marine environment based on performance specifications. Two approaches are presented here. The first is a nomogram developed by Mackechnie (2001) to predict the chloride diffusion resistance of concrete. The second developed by Alexander et al (2009) is a suite of tests based on durability index tests that considers the transport properties of concrete.

2.8.1 Prediction of chloride diffusion

A Service Life Prediction model of specifying concrete performance in respect of chloride resistance has been developed Mackechnie (2001). The model, known as the UCT Service Life Model, is based on Ficks's second law of diffusion. It provides an empirical means for predicting the time rate at which the concentration of chlorides increases at any point below the surface of concrete exposed to external chlorides. Using early age measured D_a and C_s values, the South African model predicts long-term chloride diffusion coefficients for marine concretes. The format of the prediction model is illustrated in Figure 2.24 showing a graphical prediction of 50-year diffusion coefficients for marine concretes.

In application of the model, a modified form of Fick's second law of diffusion is used to allow for reducing diffusion coefficients with time based on binder type. Slag and fly ash concretes

have larger reductions than OPC and silica fume concretes. Equation 2.14 illustrates the modified Fick's second law of diffusion:

$$C_x = C_s \left(1 - \operatorname{erf} \left[\frac{x}{2\sqrt{D_i t^{1-m}}} \right] \right) \quad (2.14)$$

where:

C_x concentration at depth x measured normal to the section at time t
expressed by % weight of binder (g/m^3)

C_s projected surface chloride concentration determined by regression
analysis expressed by % weight of binder (g/m^3)

erf error function

x depth measured normal to the surface (m)

D_i diffusion coefficient at one second (m^2/s)

t time of exposure (s)

m empirical material coefficient relating to the reduction in diffusion coefficient D_c with
time t

The model allows for long-term effects such as chloride binding and continued hydration. Validation of the prediction model has been done using chloride content results from a range of reinforced concrete structures in the marine environment ranging in age from 3 to 75 years.

Dhir et al (1991) have also developed a similar nomogram also based on Fick's second law of diffusion that specifies the performance of concrete against chloride resistance. It relates the intended service life, environmental chloride content, concrete cover, chloride threshold value for corrosion and the required chloride diffusion coefficient.

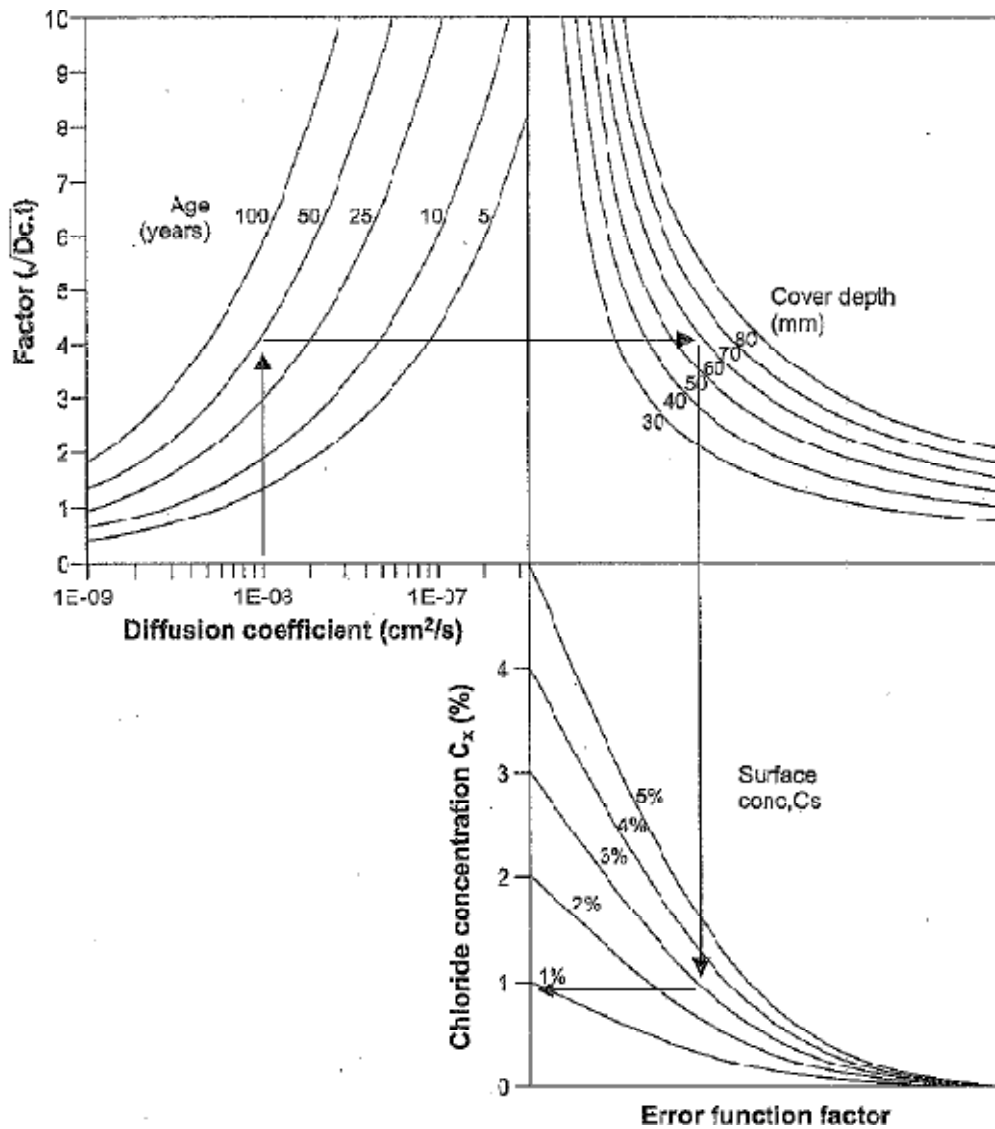


Figure 2.24: Nomogram format of the South African chloride prediction model (Mackechnie, 2001)

2.8.2 Estimation of time to corrosion activation

Once chloride levels at the level of embedded steel have been predicted, an estimate of the time to corrosion activation can be made. Using 0.4 % - 0.5 % by mass of binder as a chloride threshold value, typical times for the time to corrosion activation can be determined. Figure 2.25 illustrates the prediction model on different moderately cured concretes with 60 mm concrete cover. The model allows for different binder types thus allowing continuing hydration and chloride binding in the concrete. Environmental exposure conditions are also defined by the model.

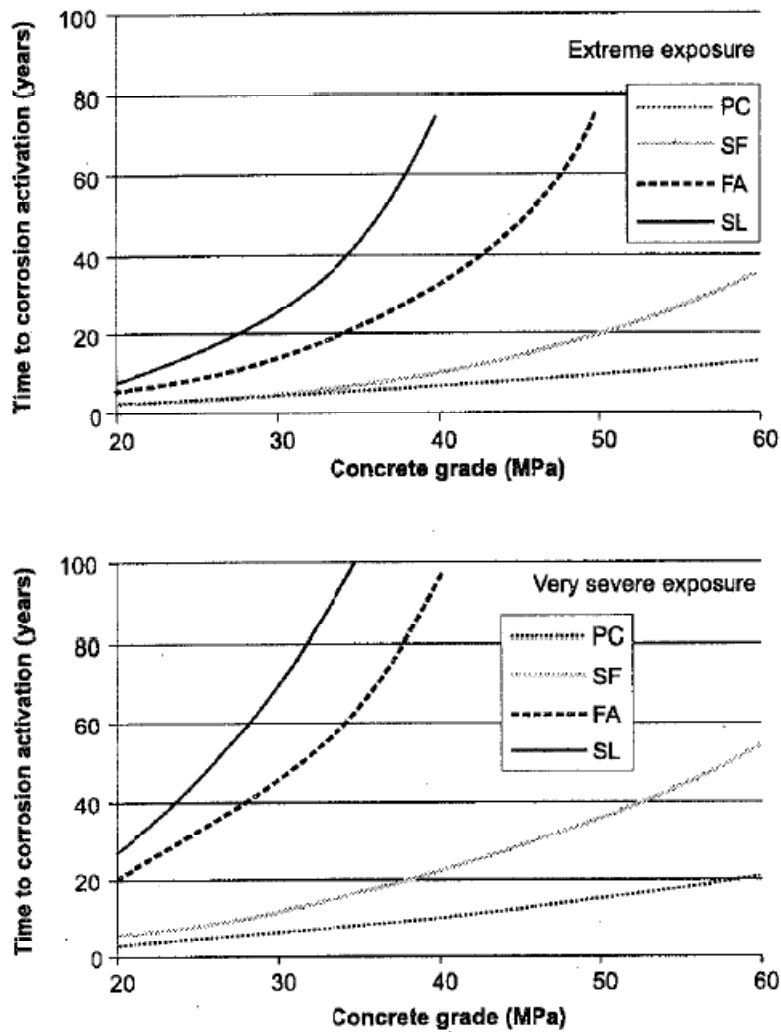


Figure 2.25: Time to corrosion activation for different moderately cured concretes with 60 mm concrete cover (Mackechnie, 2001)

2.8.3 The South African durability index approach

A range of test methods exist in different parts of the world for control of the durability properties of concrete. Most of the test methods investigate the gas permeability, sorptivity and electrical conductivity (electrical resistance) of concrete the results of which constitute what is commonly referred to as durability indicators. The tests measure transport parameters that principally reflect the pore structure, pore connectivity and pore chemistry of the concrete. These transport mechanisms can be linked to deterioration processes through calibration and/or modelling thus providing a useful and practical measure of the potential durability of the concrete (Beushausen and Alexander, 2009).

The South African durability index approach is one such suite of test methods whose results are used as potential durability indicators of reinforced concrete construction. Based on the measurement of the transport related properties of the cover layer of concrete, the durability index tests give a reflection of the dual aspects of material potential and construction quality. The tests characterise the cover layer of concrete with physical and engineering parameters that are sensitive to the various concrete constituent materials, their ratios, the production methods and curing regimes used.

The durability index approach is applicable for use in the laboratory and in situ, to determine the performance of concrete based on the tested concrete achieving certain minimum requirements in respect of the three index tests at a sample age of 28 days (Alexander et al, 2007). The South African construction industry applies the approach to:

- Control the quality of concrete delivered to the site
- Optimise concrete mixes for durability
- Specify durability based on previous performance
- Predict long-term performance based on service life models and testing of the as-built structure

The durability index values are also used as a means of predicting the performance of reinforced concrete in a particular environment when used on service life prediction models (Ballim et al, 2009, Alexander et al, 2007, Mackechnie, 2001, Alexander et al 1999a).

2.8.4 The South African Durability Index tests

Given the complex nature of reinforced concrete deterioration mechanisms in the marine environment and their varied transport processes, no single test parameter can be used as a measure of the inherent durability of marine concretes. The three durability index tests cover the range of transport mechanisms in concrete and can particularly be applied to the chloride resistance of concrete. As was described, chloride transport through concrete occurs through a series of transport mechanisms. Initially, absorption and capillary suction cause the development of high surface chloride ion concentrations. Diffusion then causes the migration of the chloride ions within the concrete matrix. In deeply submerged

structures permeation occurs where the chloride ions move into the concrete matrix under a pressure gradient (Ballim et al, 2009, Kropp and Alexander, 2007, Poulsen and Mejlbro, 2006, Mehta and Monteiro, 2005, Glass, 2003, Costa and Appleton, 1999, Tang, 1996).

The three durability index tests are applicable to the series of transport mechanisms and are:

1. Chloride conductivity index test.
2. Oxygen permeability index test.
3. Water sorptivity index test.

Samples for testing are typically disks of 70 mm diameter by 30 mm thick cored and sliced from the cover layer of concrete cubes or in-situ construction. They are then conditioned in an oven set at 50°C for a period of 7 days before testing. A summary of the durability index tests and their relevance to this experimental study is described next.

1. Chloride conductivity index (CCI) test

As the natural diffusion of chloride ions into concrete is an extremely slow process, the chloride conductivity index test provides an alternative accelerated measurement that is an indication of concrete's resistance to the penetration of chloride ions. The test relies on the electrical acceleration of ions by applying a voltage across a concrete sample. The voltage and current are used to calculate the concrete's conductivity, which in turn can be related to the concrete's resistance to chloride ion ingress. The chloride conductivity value is expressed as velocity per unit of electric field. Low chloride conductivity values represent greater chloride resistance of concrete. A relationship also exists between the chloride conductivity index value and the chloride diffusivity of concrete, known as the diffusibility relationship (Ballim et al, 2009, Mackechnie, 1996, Streicher and Alexander, 1995). Equation 2.15 gives the diffusibility relationship.

$$Q = \frac{D}{D_0} = \frac{\sigma}{\sigma_0} \quad (2.15)$$

where:

- Q diffusibility of concrete
- D diffusivity of chloride ions through concrete

D_0 diffusivity of chloride ions through concrete pore solution

σ_0 conductivity of concrete

σ conductivity of pore solution

The CCI value is sensitive to changes in the pore structure and concrete chemistry as well as binder type, w/b ratio and continued curing and curing regimes. Sensitivity to the binder type is postulated to be linked to the chloride binding characteristics exhibited by different binder types. Figure 2.26 illustrates typical test results for chloride conductivity values, measured on water-cured samples at 28 days of age, in relation to w/b ratio and binder type.

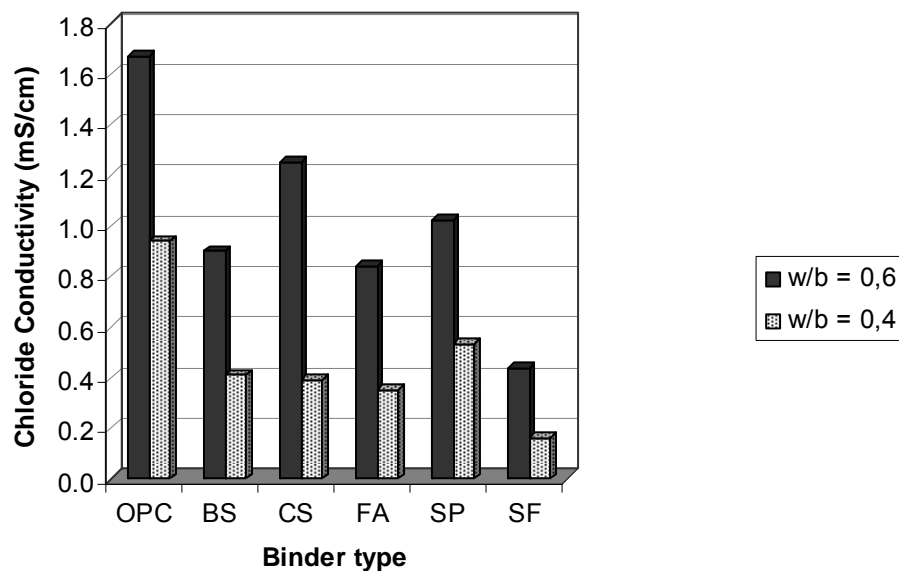


Figure 2.26: Typical 28-day chloride conductivity index test results (Ballim et al, 2009)

The drawback of the chloride conductivity index test result is that the applied electric current causes rapid mobility of chloride ions that the binding effect of the binder paste is over-ridden. The test is used to specify the performance of concrete in the marine environment and Table 2.8 shows characteristic values used by South African concrete designers for marine concretes.

The chloride conductivity test is also used to predict a long term D_a and C_s from which chloride levels at the level of embedded steel are determined. If chloride threshold levels have been reached, the time to corrosion activation is then obtained from this (Mackechnie, 2001).

In this experimental study, the chloride conductivity index test is used to characterise the concrete produced at 28 days and the continued development of chloride resistance in continuously moist cured concrete. The influence of the concrete mix constituents and proportions on the chloride conductivity index value is also determined.

Table 2.8: Typical 28 day CCI values for various concrete grades normally specified for the marine environment (Alexander et al, 2007)

Environmental class		70:30	50:50	50:50
		CEM I:FA	CEM I:GGCS	CEM I:GGBS
XS1	C*	3.00	4.00	3.50
	M [#]	2.50	3.50	2.80
XS2a	C	2.45	3.25	2.60
	M	2.15	2.90	2.30
XS2b/XS3a	C	1.35	1.95	1.60
	M	1.10	1.60	1.35
XS3b	C	1.10	1.55	1.25
	M	0.90	1.30	1.05

* Buildings and other common structures with a design service life of 50 years

[#] Monumental structures, bridges and other civil engineering structures with a design service life of 100 years

2. Oxygen permeability index test (OPI)

The OPI test is indicative of the concrete pore structure. It measures the permeability of concrete by measuring the pressure decay oxygen of gas through a concrete sample placed in a falling head permeameter. The coefficient of permeability is determined from the slope of the line produced when the natural log of the ratio of initial pressure to pressure at any time is plotted against time. The oxygen permeability index is defined as the negative log of the coefficient of permeability. Typical logarithmic values of OPI range over three orders of magnitude i.e. from 8 to 11, the values on the upper end correspond to concrete of higher impermeability and of higher quality (Ballim et al, 2009).

The OPI test assesses the overall micro- and macrostructure of the outer surface of cast concrete, and is particularly sensitive to macro-voids and cracks, which act as short-circuits for the permeating gas. Thus the test is very useful to assess the state of compaction, presence of bleed voids and channels, and the degree of interconnectedness of the pore

structure. OPI values are also sensitive to w/b ratio, binder type and curing regimes as illustrated in Figure 2.27 (Ballim et al, 2009, Mackechnie, 1996).

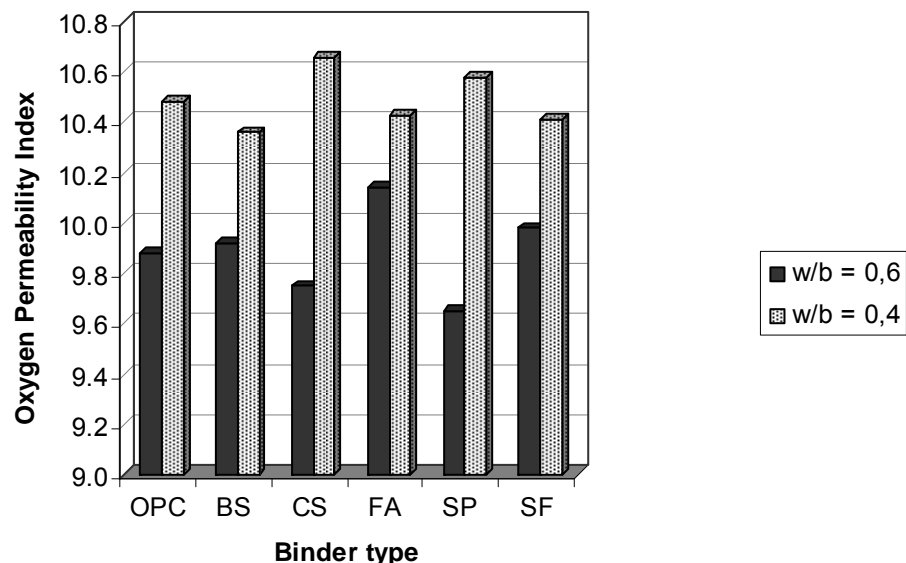


Figure 2.27: Typical 28-day oxygen permeability index test results (Ballim et al, 2009)

Correlations also exist between OPI values and carbonation depths in concrete. The test is primarily designed to characterise a concrete mix against carbonation induced corrosion. In the marine environment, it is applicable in where carbonic acid attack may be introduced from organic mechanisms in sea water. The OPI values obtained in this study are used to compare the different concrete types produced and to determine the influences. The values could be used as indicative of the potential of similarly produced marine concretes.

3. Water sorptivity index (WSI) test

The WSI test uses the rate of absorption of water by a dry concrete sample as a measure of the sorptivity of the concrete sample. This occurs under capillary action where a fluid is drawn into a porous, unsaturated material. The rate of movement of a wetting front through a porous material under the action of capillary forces is defined as sorptivity. A linear relationship exists between the mass of solution absorbed and the square root of time. The slope of the line is defined as the sorptivity index.

Sorptivity is dependent on the pore geometry and the degree of saturation of the concrete matrix. The WSI test has been found to be sensitive to the grade of concrete and the nature and extent of early curing of the cover concrete and is thus mainly be used to assess

construction quality. In general, the higher the water sorptivity value, the more permeable the concrete and the lower the concrete quality. Sorptivity is also influenced by compaction, aggregate orientation and distribution. Moist cured concrete blends of GGCS and FA have been found to have considerably lower values than plain OPC concretes. This is indicative of the beneficial use of cementitious extenders which improve the micro-structural porosity properties of such concretes (Alexander et al, 2007, Mackechnie, 1996). Figure 2.28 illustrates typical test results for water sorptivity, measured on water-cured samples at 28 days of age, in relation to w/b ratio and binder type.

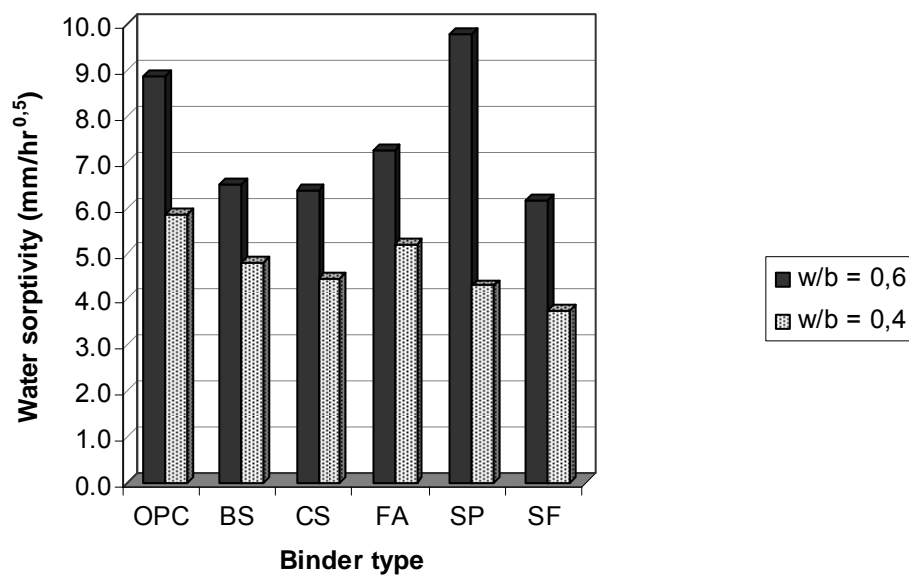


Figure 2.28: Typical 28-day water sorptivity index test results (Ballim et al, 2009)

The WSI is not directly related to any reinforced concrete deterioration mechanism. In this experimental study, the sorptivity test is used to characterise and compare the concrete mixes produced at the respective testing ages. The influence of the concrete mix constituents and proportions on the WSI value is also determined. The values obtained could be used as indicative of similarly produced concretes potential values.

2.9 Closing remarks

Durability of reinforced concrete in any given environment is governed by certain general prescriptive requirements; good material type and detailing design, an upper limiting w/b ratio, a lower limiting binder content, a limiting minimum cover to the level of reinforcement and good construction practice. In the aggressive marine environment, these factors are

critical in ensuring the impenetrability of chloride ions into concrete, which potentially promote and lead to corrosion of embedded steel. The factors were extensively covered in this chapter. Other deterioration mechanisms in the marine environment such as magnesium ion attack, carbonic acid attack, wave action, abrasion damage and salt crystallisation were also comprehensively presented.

The transport properties that contribute to concrete deterioration in the marine environment were discussed in relation to chloride ion induced deterioration. The ability of chloride ions to enter and move within concrete is a major factor in determining its potential durability. As a consequence, concrete with low chloride ion transport properties has a potentially enhanced service life. The ease of entry of deleterious chloride ions into concrete is influenced by the penetrability of the concrete pore structure which is a factor of both material type (primarily binder type) and w/b ratio.

The transport of chloride ions into concrete driven by a concentration difference occurs primarily by diffusion. Analysis of the diffusion of chloride ions is done using Fick's second law of diffusion which presents chloride transport with two parameters; the apparent chloride diffusion coefficient (D_a) and the apparent surface concentration (C_s). These two parameters are a measure of chloride ion transport in concrete.

In the marine environment, concrete materials for use are normally restricted to blended concretes which have been found to have good chloride action mitigating properties. The SCM typically used are slag and fly ash which refine the pore structure of a concrete matrix thereby slowing the ingress of chloride ions. Further, these materials have good chloride binding properties which reduce the chloride ion concentration front. Slag and fly ash concretes have been reported to have low D_a values which indicate better chloride ion resistance. This is compared to plain OPC concretes which have characteristically high D_a values. High values of D_a translate to increased rates of diffusion of chloride ions into concrete and hence an accumulation of chloride ions within the concrete matrix. An accumulation above a threshold level (normally taken as 0.4 % by mass of binder) increases the susceptibility to corrosion of steel. The optimum replacement levels of each SCM to obtain good chloride resistance were given as up to 30 % and 50 % for fly ash and slag to OPC respectively.

Concrete grade governs the inherent durability of marine concretes by controlling the density and penetrability of concrete. W/b ratio controls the spacing between binder grains themselves and between binder grains and aggregate particles thereby limiting the pore volume through which chloride ions can penetrate through. In the marine environment, w/b ratios between 0.40 and 0.55 have been found satisfactory in limiting the ingress of chloride ions.

The influence of adequate concrete cover on transport of chloride ions should not be overlooked in prescribing potentially good concrete for the marine environment. By increasing the transport distance that chloride ions have to be transported through to reach the level of embedded steel; potentially durable concrete can be attained. In the marine environment, typical cover thicknesses range from 50 mm to 80 mm.

Two approaches that are used in characterising the potential durability of marine concretes were also covered in this chapter. These are the deterioration mechanism approach and the Durability Index tests approach. The first approach involves exposing samples to a chloride-laden environment and quantifying the rate of ingress of chloride ions through the samples. The bulk diffusion test described was presented as a test method used in the deterioration mechanism approach. The latter approach, quantifies the quality of the cover layer of concrete where the transport of deleterious species occurs. The tests describe potential durability using limiting values based on the transport properties of concrete. Both approaches are further linked to service life prediction models and performance specifications.

The two concrete transport mechanism characterisation approaches are sensitive to the concrete type and grade influences on the transport mechanisms of concrete. They are thus considered appropriate for investigation for this study. The next chapter will cover the experimental details and methodology used in characterising the concrete mixes produced in this study using the above criteria.

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Chapter Three

Experimental details: Materials and tests

3.1 General

This chapter presents the details of the experiments performed for the experimental study conducted at the UCT Concrete Laboratories. Figure 3.1 gives an experimental flow chart. Details of the material constituents and proportions, exposure conditions and tests conducted are given in this chapter.

3.2 Materials

The materials were sourced from the marine urban areas of Cape Town, Port Elizabeth and Durban and are what are typically used by concrete ready mix companies supplying concrete to the marine environment. There were five binder types and three coarse aggregate types.

3.2.1 Binders

Codes and standards give guidelines for binder types for use in reinforced marine concretes to ensure durability. BS EN 206-1 (2002) provides that blended cement concretes be used in marine concretes. SANS 10100-2:2009 also provides that marine concretes should contain supplementary cementitious materials. Alexander et al (2007) report that reinforced unblended concretes i.e. OPC only, are insufficient in resisting chloride ingress in marine concrete compared to blended binder concretes. As a result, South African marine concretes are restricted to blended concretes. Five available South African binder types were used with each type coming from a single production batch. The binder types used are described below with Table 3.1 giving oxide analyses for the binder types. The values given are averages from the particular production run from which the binders were obtained. All the binders were obtained in single, bulk deliveries and stored in airtight drums in the laboratory to prevent deterioration with time.

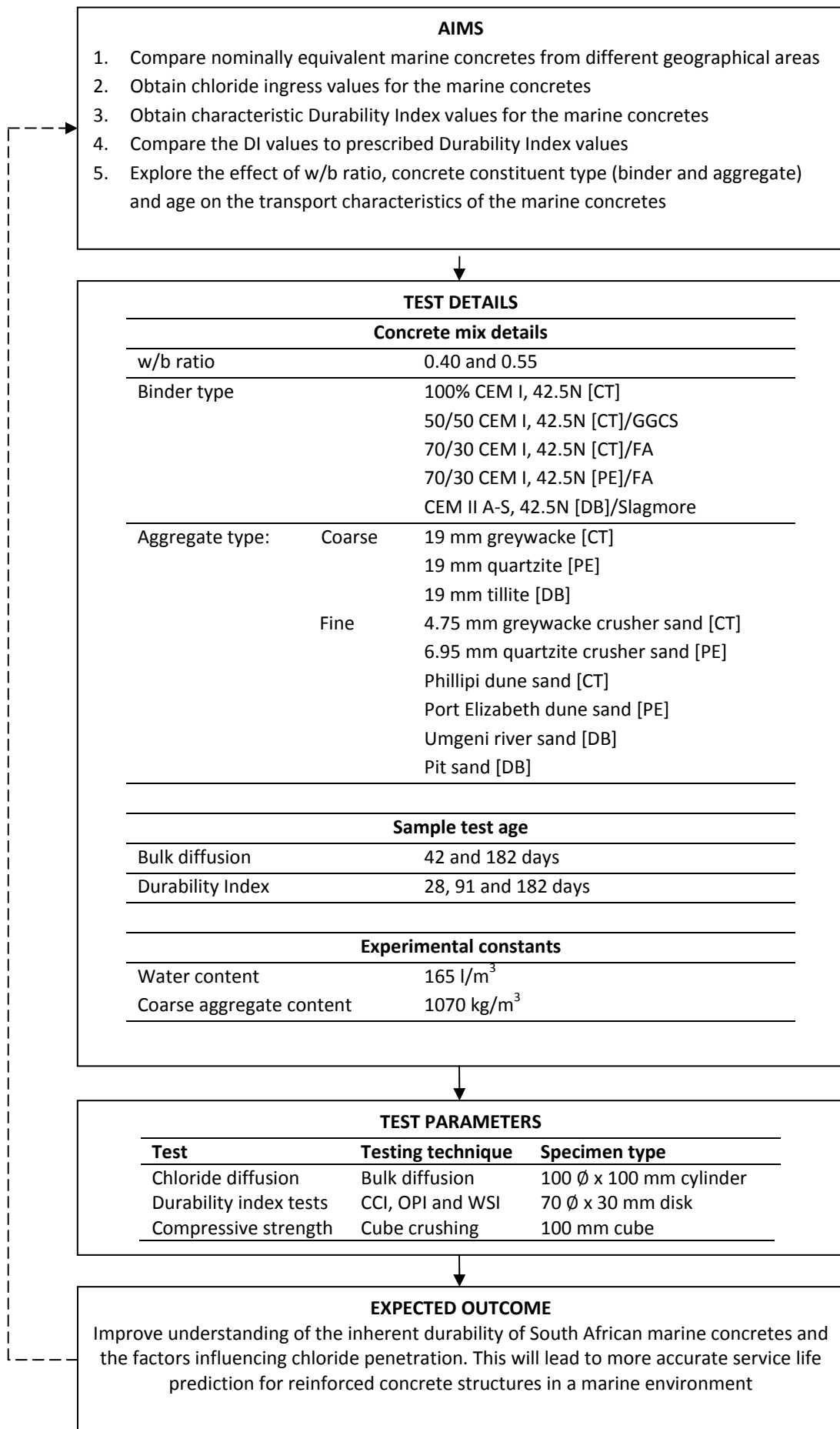


Figure 3.1: Experimental Flow chart

Table 3.1: Chemical compositions: Oxide analyses of binders (%)

Oxides	CEM I	CEM I	CEM II A-S	GGCS ⁴	FA ⁵	Slagmore ⁶
	[CT] ¹	[PE] ²	[DB] ³			
CaO	65.29	63.52	59.08	37.12	4.40	35.03
SiO ₂	21.59	24.22	24.40	34.10	52.80	35.79
Al ₂ O ₃	4.54	3.54	6.00	13.94	34.10	13.67
Fe ₂ O ₃	3.47	4.87	2.59	1.06	3.60	0.71
SO ₃	2.21	1.83	2.50	4.94	0.10	N/A
MgO	1.24	1.86	4.55	11.59	1.10	9.76
K ₂ O	0.68	0.38	0.59	0.69	0.50	0.30
TiO ₂	0.29	0.42	N/A	0.61	1.60	N/A
Na ₂ O	0.12	0.36	N/A	-	0.40	N/A
Mn ₂ O ₃	0.11	0.04	N/A	4.94	0.10	N/A
P ₂ O ₅	0.11	0.03	N/A	0.00	0.30	N/A
Cl	0.01	0.00	N/A	-	-	-
C	-	-	-	-	0.80	N/A

N/A - Not available

¹ - CEM I [CT]: Riebeek West PPC

² - CEM I [PE]: Port Elizabeth PPC

³ - CEM II A-S [DB]: Durban NPC

⁴ - GGCS: Saldanha Steel Plant

⁵ - FA: Lethabo Thermal Power Station

⁶ - Slagmore: Durban NPC

1. CEM I, 42.5N

Two types of ordinary Portland cement binder complying with the requirements of SANS 50197-1:2000 were used, viz:

1. CEM I, 42.5N (CEM I [CT]) from Riebeek West PPC factory in the Western Cape Province.
2. CEM I, 42.5N (CEM I [PE]) from Port Elizabeth PPC factory in the Eastern Cape Province.

2. CEM II A-S 42.5N

CEM II A-S 42.5 (CEM II A-S [DB]) complying with the requirements of SANS 50197-1:2000 from Durban NPC factory in the KwaZulu Natal Province. The binder is a factory blend, marketed under the brand name NPC premium, which is constituted of 85 % CEM I, 42.5N clinker inter-ground with 15 % Slagmore.

3. Ground granulated corex slag (GGCS)

GGCS from Saldanha Steel Plant in the Western Cape, is a latent hydraulic binder complying with the requirements of SANS 1491-1:2005. Typical substitutions of GGCS for OPC in marine concretes are 50 %.

4. Fly ash (FA)

FA from Lethabo Thermal Power Station in the Northern Free State, is a pozzolanic binder complying with the requirements of SANS 1491-2:2005. Typical substitutions of FA for OPC in marine concretes are 30 %.

5. Slagmore

Slagmore is a brand name of a cementitious extender from Durban NPC factory. It is a blend of 92 % GGBS and 8 % FA complying with the requirements of SANS 1491-1:2005. Typical blending substitutions of CEM II A-S 42.5N by Slagmore are in the range of 40 - 50 %.

3.2.2 Aggregates

The principle adopted for the concrete mixes was that both coarse and fine aggregates should be representative of the materials commonly used for ready mix marine concretes in the particular geographical region. In two series of concrete mixes (Cape Town and Port Elizabeth) both coarse and fine aggregates were crushed from the same rock source with a proportion of finer blending sand used. In the third series (Durban) the fine aggregates were natural sands from different sources. Details of each aggregate type are given next. All the aggregates were obtained in single, bulk deliveries and stored indoors.

1. Coarse aggregate

In this study, 19 mm coarse aggregates conforming to SANS 1083:2006 were used. Their typical characteristics are given in Table 3.2. The values are typical ranges obtained from studies on the properties of South African aggregates reported by Alexander and Davis (1991). The aggregates were received at the UCT Concrete Laboratories and stored dry until they were required for the concrete mixes.

Table 3.2: Typical characteristics of aggregates (Alexander and Davis, 1991)

Aggregate property	Aggregate type	Value		
		Greywacke [CT]	Quartzite [PE]	Tillite [DB]
Relative density		2.64 - 2.78	2.65	2.68 - 2.72
10 % Fines Aggregate Crushing Value (kN)		299	244	270
Unconfined compressive strength (MPa)		297 - 308	354 - 394	180 - 300
Elastic Modulus (GPa)		68 - 77	47 - 83	68 - 79
Coefficient of thermal expansion ($\times 10^{-6}/^{\circ}\text{C}$)		10.9	12.4	6.5
Water absorption (%)		0.4	0.52	0.6

Choice of aggregate for use in South Africa is determined mainly by the transportation cost and distance from the quarry to the construction site. A further but not decisive factor is the susceptibility of the aggregate to alkali-silica reaction. The aggregates chosen for this experimental study take cognisance of both. Two of the aggregate types, greywacke and tillite are washed to reduce their dust content. The grading curves of the coarse aggregate types used in the marine urban areas are given in Figures 3.2 - 3.4.

Greywacke from the Peninsula Quarry in the Western Cape is the commonly available coarse aggregates for use in Western Cape marine construction. It is a fine-grained glassy rock consisting of quartz, feldspar, mica and iron oxides formed by thermal metamorphism of argillaceous rocks of the Malmesbury group. Greywacke particles are dark/grey-coloured and angular (Grieve, 2009b, Brink, 1979, Truswell, 1970).

Quartzite is the coarse aggregate available in Port Elizabeth for marine construction. It is a hard greyish-white rock formed by re-crystallisation and silica cementation of sedimentary sandstone to quartzite (Grieve, 2009b, Brink, 1979 and Truswell, 1970).

Tillite mined in the Umgeni Quarry in Durban is one of two available coarse aggregates for use in the KwaZulu Natal province for marine construction. It is a greyish-blue rock formed by glacial sedimentation of argillaceous rocks consisting essentially of quartz, feldspars and clays. Tillite particles are usually angular (Grieve, 2009b, Brink 1979 and Truswell, 1970).

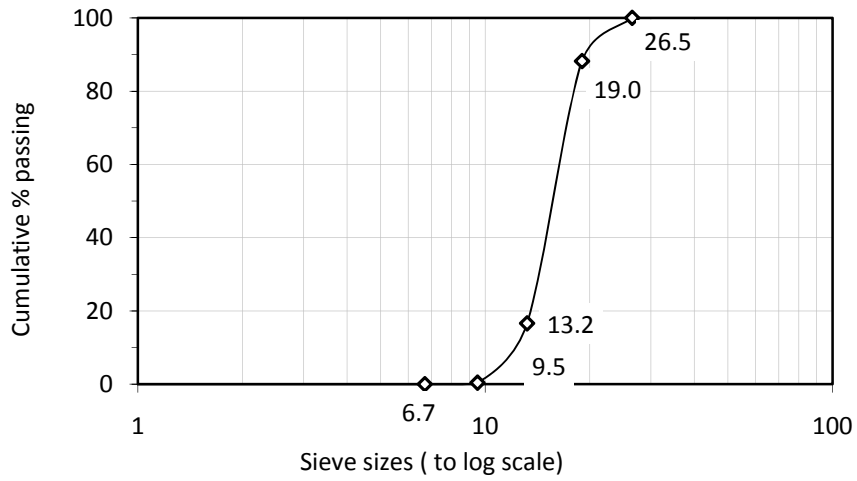


Figure 3.2: Grading curve for 19 mm Cape Town greywacke aggregate

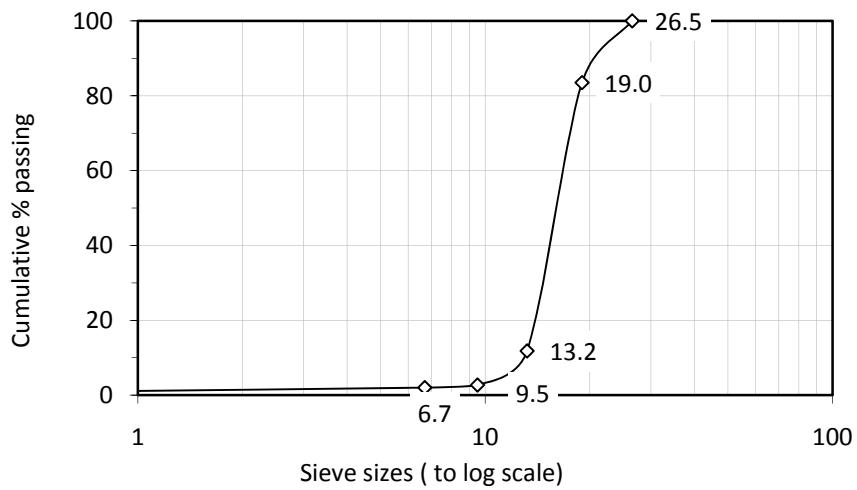


Figure 3.3: Grading curve for 19 mm Port Elizabeth quartzite aggregate

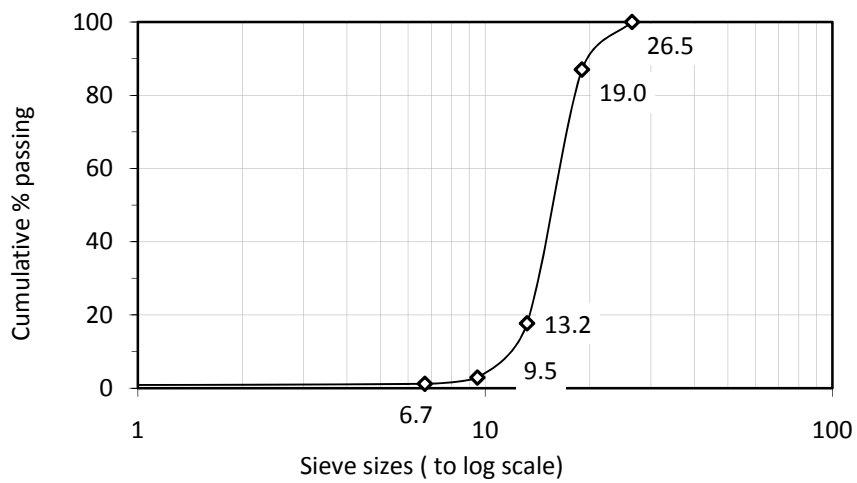


Figure 3.4: Grading curve for 19 mm Durban tillite aggregate

2. Fine aggregate

Fine aggregates conforming to SANS 1083:2006 were used. The fine aggregates were oven dried at 100 °C for 24 hours and air cooled for another 24 hours before being used for the concrete mixes. This was done as the fine aggregates were delivered to the UCT laboratories in a moist condition.

In the Cape Peninsula area, a blend of Philippi dune sand and crushed 4.75 mm greywacke sand is often used to make up the fine aggregate component of marine concretes. Philippi sand particles are smooth and well rounded providing for a low water demand and workability but are poorly graded causing bleeding problems of concrete mixes produced. As such 4.75 mm crushed greywacke is used to substitute for the dune sands by up to 50 %.

In the Port Elizabeth area, a blend of dune sand and crushed 6.95 mm quartzite sand is used to constitute the fine aggregate component of marine concretes. The dune sands are well rounded providing for workability but are poorly graded causing bleeding problems of concrete mixes produced. As such 6.95 mm crushed quartzite is used to substitute 50 % of the dune sands in concrete.

In Durban, a blend of river sand and pit sand is used to comprise the fine aggregate component of marine concretes. River sands are slightly “bunch graded” so the finer pit sands are usually substituted for river sands by up to 10 % to improve the fines content of marine concretes.

The grading curve and typical characteristics of the fine aggregate types used in the marine urban areas are given in Figures 3.5 - 3.7.

3.2.3 Water

Cape Town Municipal tap water was used for concrete production and testing.

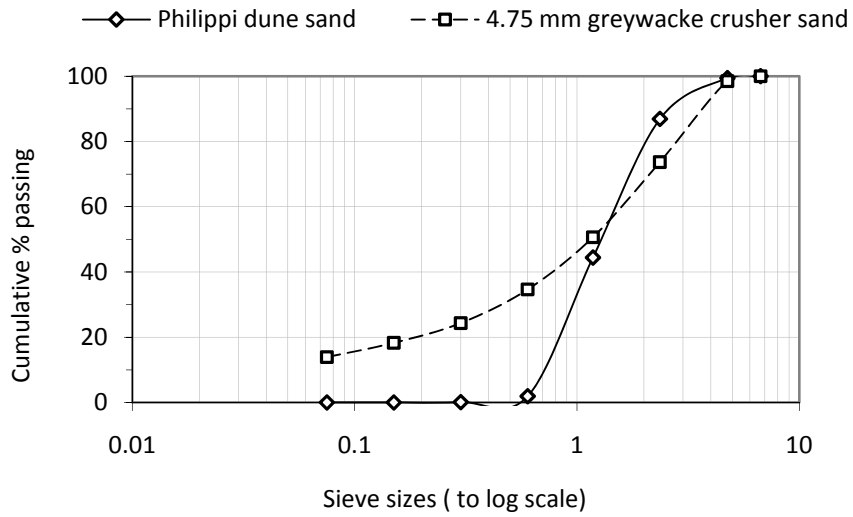


Figure 3.5: Grading curves of Cape Town fine aggregates

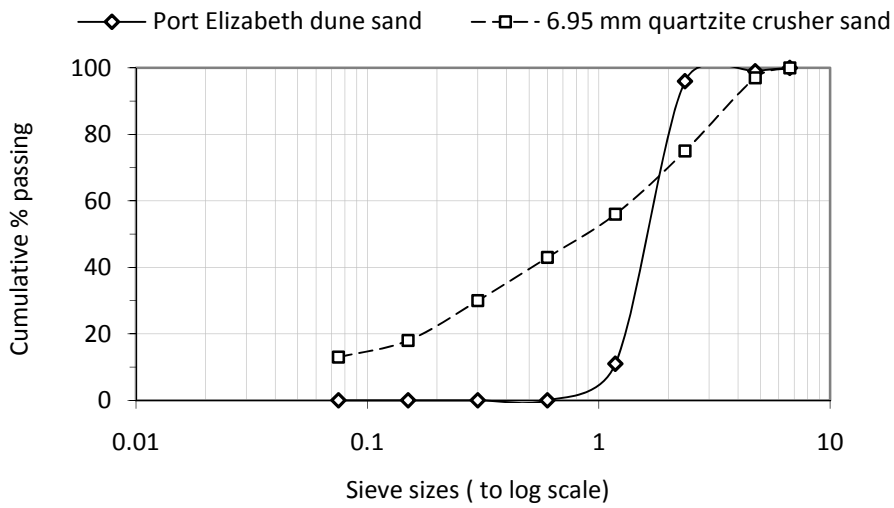


Figure 3.6: Grading curves of Port Elizabeth fine aggregates

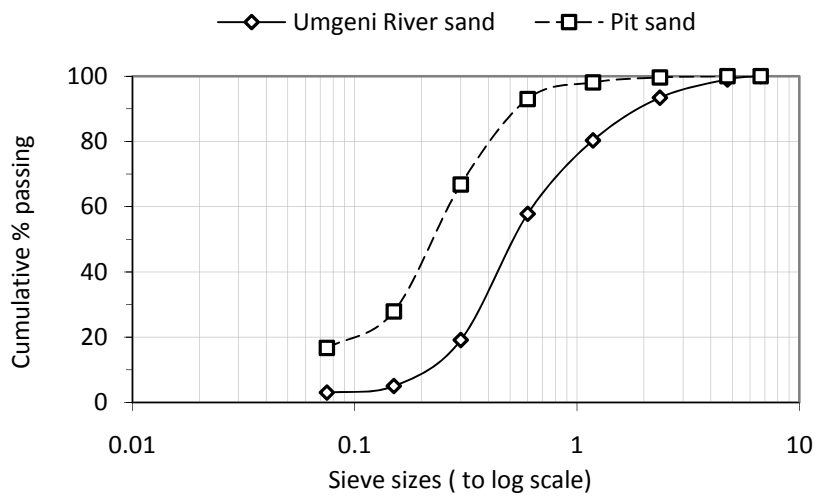


Figure 3.7: Grading curves of Durban fine aggregates

3.2.4 Water reducing admixture

A water reducing admixture (plasticiser), Chryso Plast Omega 101 manufactured by Chryso Chemicals, was used was added to provide workability. Its use was recommended by the ready-mix concrete companies in the marine urban areas of Cape Town, Port Elizabeth and Durban (Abrahams, 2008, Dawneerangen, 2008, Schutte, 2008, Venier, 2008).

3.2.5 Exposure solution for bulk diffusion tests

A NaCl solution was prepared from laboratory grade salt with a concentration of 165 g NaCl per litre of solution (2.8 M concentration) and used as the exposure solution to simulate a chloride laden environment. Municipal tap water was used to prepare the solution.

3.3 Experimental details

3.3.1 Mix proportions

The concrete material combinations considered in each region are shown in Table 3.3. They are the materials typically used by large scale ready mix concrete suppliers in the urban areas as indicated.

Table 3.3: Regional material combinations

Region	Binder type	Fine aggregate type	Coarse aggregate type
Cape Town [CT]	CEM I, 42.5 N	Philippi dune &	
	CEM I, 42.5 N: 50 % GGCS	greywacke crusher	19 mm greywacke
	CEM I, 42.5 N: 30 % FA	sand	
Port Elizabeth [PE]	CEM I, 42.5 N: 30 % FA	PE dune & quartzite crusher sand	19 mm quartzite
Durban [DB]	CEM II A - S, 42.5 N: Slagmore	Umgeni River & pit sand	19 mm tillite

The concrete mixes were designed using the Cement and Concrete Institute volumetric mix design method (Addis and Goodman, 2009). The details of the various concrete mixtures are shown in Tables 3.4 - 3.6.

Table 3.4: Concretes mix proportions with Cape Town aggregates

	Binder content (kg/m ³)						w/b ratio	Fine aggregate content (kg/m ³)			Slump (mm)	f _{cu,28} (MPa)		
	CEM I [CT]	CEM I [PE]	CEM II A-S [DB]		GGCS	FA		Slagmore	Total	Philippi dune sand			Greywacke crusher sand	Total
(1)	412	-	-	-	-	-	412	0.40	471	324	795	0.60	70	60.0
	300	-	-	-	-	-	300	0.55	530	365	895	0.40	70	42.0
(2)	206	-	-	206	-	-	412	0.40	471	324	795	0.50	70	69.0
	150	-	-	150	-	-	300	0.55	530	365	895	0.40	75	51.0
(3)	289	-	-	-	124	-	412	0.40	471	324	795	0.30	80	56.0
	210	-	-	-	90	-	300	0.55	530	365	895	0.30	85	37.0
(4)	-	289	-	-	124	-	412	0.40	471	324	776	0.30	85	58.0
	-	210	-	-	90	-	300	0.55	530	365	876	0.25	95	36.5
(5)	-	-	237	-	-	175	412	0.40	471	324	786	0.45	75	60.0
	-	-	210	-	-	90	300	0.55	530	365	883	0.25	90	40.0

(1) Cape Town binder control mixes - 100 % CEM I [CT]

(2) Cape Town binder regional mix - CEM I [CT]/50 % GGCS

(3) Cape Town binder regional mix - CEM I [CT]/30 % FA

(4) Port Elizabeth binder mix - CEM I [PE]/30 % FA

(5) Durban binder mix - CEM II A-S [DB]/Slagmore

Water content = 165 l/m³

Greywacke coarse aggregate content = 1070kg/m³

P* Plasticiser dosage (% mass of binder)

Table 3.5: Concretes mix proportions with Port Elizabeth aggregates

	Binder content (kg/m ³)							w/b ratio	Fine aggregate content (kg/m ³)			P*	Slump (mm)	f _{cu,28} (MPa)	
	CEM I [CT]	CEM I [PE]	CEM II A-S		GGCS	FA	Slagmore		Total	PE	Quartzite				
			[DB]							dune sand	crusher sand				Total
(6)	412	-	-	-	-	-	412	0.40	388	388	776	0.60	100	55.5	
	300	-	-	-	-	-	300	0.55	438	438	876	0.60	65	41.0	
(7)	206	-	-	206	-	-	412	0.40	388	388	776	0.35	100	59.0	
	150	-	-	150	-	-	300	0.55	438	438	876	0.25	100	41.0	
(8)	-	289	-	-	124	-	412	0.40	388	388	776	0.40	100	60.5	
	-	210	-	-	90	-	300	0.55	438	438	876	0.30	90	46.0	

(6) Cape Town binder control mixes - 100 % CEM I [CT]

(7) Cape Town binder control mix - CEM I [CT]/50 % GGCS

(8) Port Elizabeth binder regional mix - CEM I [PE]/30 % FA

Water content = 165 l/m³

Quartzite coarse aggregate content = 1070kg/m³

P* Plasticiser dosage (% mass of binder)

Table 3.6: Concretes mix proportions with Durban aggregates

	Binder content (kg/m ³)						w/b ratio	Fine aggregate content (kg/m ³)			Slump (mm)	f _{cu,28} (MPa)	
	CEM I [CT]	CEM I [PE]	CEM II A-S		Total	Umgeni River sand		Durban pit sand	Total	P*			
			[DB]	GGCS FA		Slagmore							
(9)	412	-	-	-	-	412	0.40	708	78	776	0.45	90	60.0
	300	-	-	-	-	300	0.55	796	87	876	0.45	75	41.0
(10)	206	-	-	206	-	412	0.40	708	78	776	0.55	90	67.0
	150	-	-	150	-	300	0.55	796	87	876	0.45	70	50.0
(11)	-	-	237	-	-	175	0.40	708	78	776	0.40	65	57.0
	-	-	210	-	-	90	0.55	796	87	876	0.40	70	40.0

(9) Cape Town binder control mixes - 100 % CEM I [CT]

(10) Cape Town binder control mix - CEM I [CT]/50 % GGCS

(11) Durban binder regional mix - CEM II A-S [DB]/Slagmore

Water content = 165 l/m³

Tillite coarse aggregate content = 1070kg/m³

P* Plasticiser dosage (% mass of binder)

Table 3.4 gives the mix constituents and proportions of the concrete mixes produced with aggregates used in Cape Town. The coarse aggregate type is 19 mm greywacke. To make up the fine aggregate content, two sands were blended, viz: Philippi dune sand and greywacke crusher sand. For this series, three binder types were used with the plain CEM I binder with greywacke aggregate used as a control non-marine mix. The aim of this was to establish the performance of the Cape Town binders in comparison to each other and the control mix.

Table 3.5 gives the mix constituents and proportions of the concrete mixes produced with aggregates used in Port Elizabeth. The coarse aggregate type is 19 mm quartzite. To make up the fine aggregate content, two sands were blended, viz: Port Elizabeth dune sand and quartzite crusher sand. For this series, the blended binder type typically used in the Port Elizabeth marine environment was used i.e. CEM I: 30 % FA. Plain CEM I and CEM I: 50 % GGCS binders were used with quartzite aggregate to act as control mixes. The aim of this was to establish the performance of the Port Elizabeth binder in comparison to the Cape Town binders.

Table 3.6 gives the mix constituents and proportions of the concrete mixes produced with aggregates used in Durban. The coarse aggregate type is 19 mm tillite. To make up the fine aggregate content, two sands were blended, viz: Umgeni River sand and Durban pit sand. For this series, the blended binder type typically used in the Durban marine environment was used i.e. CEM II A – S: Slagmore. Plain CEM I and CEM I: 50 % GGCS binders were used with tillite aggregate to act as control mixes. The aim of this was to establish the performance of the Durban binder in comparison to Cape Town binders.

Cross comparison was also done between mixes produced with the regional aggregate types and plain CEM I and CEM I: 50 % GGCS binders. This was to determine the effect of coarse aggregate type on the transport properties being investigated.

All the concrete mixes were proportioned to give a consistent water content of 165 l/m³ with two w/b ratios of 0.40 and 0.55 respectively yielding two ranges of cement contents of 300 kg/m³ and 412 kg/m³. The water content used was within ready mix plant recommendations (Abrahams, 2008, Dawneerangen, 2008, Schutte, 2008). Reducing the water demand of a mix by as much as 15 % has been found to give concretes that achieve

higher strengths and improved durability potential (Whitney, 2008). A slump of 75 ± 25 mm was achieved in all mixes using a water reducing admixture (plasticiser). A plasticiser is used to achieve and maintain workability. Details of the amount of plasticiser added and slump achieved are given in Tables 3.4 - 3.6. The dosage is given as percent of total binder content by mass.

The coarse aggregate content of all mixes was fixed at 1070 kg/m^3 with the fine aggregate contents adjusted in each mix to maintain yield and comparability. The quantity of cementitious extender substituted for the primary binders was 50 % for GGCS, 30 % for FA and 42 % for Slagmore. All mix constituents were mass batched. Details of the 28 day strengths are given in Tables 3.4 - 3.6 rounded off to the nearest 0.5 MPa.

3.3.2 Control mixes

In each regional series, control specimens were produced at the two w/b ratios of 0.40 and 0.55 containing CEM I, 42.5N Western Cape Portland cement and the regional aggregate. These are essentially non-marine concrete mix types. This was done so as to find the behaviour of plain OPC concrete, the influence of using supplementary cementitious materials and the influence of aggregate type.

The Cape Town CEM I mix was used as a control so as to determine the effect of using supplementary cementitious materials in concrete. The Cape Town CEM I: GGCS mix was used as a reference mix. This was due to its proven ability to produce potentially durable marine concretes (Ballim et al, 2009).

3.3.3 Concrete specimens and production

Concrete was produced using a horizontal forced action pan mixer of 0.05 m^3 capacity. The batch masses were 50 kg. The pan mixer was charged with coarse aggregate, fine aggregate and binder respectively and the constituents dry mixed for roughly 30 seconds. Water mixed with the water reducing admixture was slowly added until the mix was visually consistent. The total mix time was about 3 minutes. Slump measurements were then taken.

3.3.4 Number of specimens and ages of testing

For each of the 22 concrete mixes, the following specimens were used:

For bulk diffusion tests:

2 № 100 Ø x 100 mm cylinders for each mix sampled at the two testing ages of 42 and 182 days i.e. 88 № cylinders in total.

For durability index tests:

4 № cubes for each mix sampled at each of the three testing ages of 28, 91 and 182 days i.e. 264 № cubes in total.

For compressive strength:

3 № cubes for each mix sampled at each of the three testing ages 28, 91 and 182 days i.e. 198 № cubes in total.

3.3.5 Curing and test conditions

After testing for slump, moulds were filled, compacted on a vibrating table then covered with polythene sheets for about 24 hours at room temperature before demoulding. Samples for durability index and compressive strength testing were then placed in a water bath maintained at 23 ± 2 °C for continuous curing in accordance to SANS 5861-3:2006 until their respective test ages.

The cylindrical samples for bulk diffusion testing were cured in a Ca(OH)_2 water bath solution for 27 days after demoulding after which they were coated with epoxy resin on the cylindrical sides. They were then immersed in the NaCl exposure solution as per the provisions of the ASTM C1556-04 test for 42 and 182 days before chloride profiling. The bulk diffusion samples were kept in an environment room maintained at a temperature of 23 ± 2 °C for the entire duration of exposure.

3.4 Experimental tests

3.4.1 Bulk diffusion

Bulk diffusion tests were conducted on all concrete mixes exposed to a saline environment for 42 and 182 days. Two specimens were tested per mix as per the provisions of the test described in ASTM C1556-04 (2004) manual. The specimens were saturated in lime water after an initial 28 days moist curing. They were then coated with epoxy resin except for the exposure face. The samples were immersed in 2.8 M salt solution. Dry-profile grinding to 5 mm and dry-slicing to 16 mm of the specimens was done at increment depths from the exposed surface to obtain five powder samples. Table 3.7 gives the sampling depths. Potentiometric titration was then done to determine the total acid-soluble chloride contents at the profile levels. A detailed procedure of the test extracted from ASTM C1556-04 (2004) manual is given in Appendix B. (B.1.1).

Table 3.7: Sampling depths for chloride content analysis (Adapted from ASTM C1556-04)

	Sampling depth (mm)	Average depth (mm)
Depth 1	0 - 1	0.5
Depth 2	1 - 3	2
Depth 3	3 - 5	4
Depth 4	5 - 9	7
Depth 5*	11 - 17	14

* 2 mm was lost from the saw blade width between depths 4 and 5

3.4.2 Durability Index tests

The Durability Index (DI) tests characterise the cover layer of concrete by measuring different transport properties in concrete. The tests are predominantly used to predict the potential durability performance of reinforced concrete.

The DI tests typically done on uncontaminated concrete samples comprise:

1. Chloride conductivity index (CCI) test.
2. Oxygen permeability index (OPI) test.
3. Water sorptivity index (WSI) test.

The DI tests were done in this experimental study to track the influence of continued curing on the transport properties of concrete measured and to act as a control for the samples for characterising the specimens exposed to a chloride-laden environment.

Procedures for the three DI tests are given in Appendix B, extracted from the UCT Durability Index Testing Manual (Alexander et al, 2009).

3.4.3 Compressive strength

The cube compressive strength test is a measure to establish the quality of hardened concrete by testing the ability of concrete to withstand load. The test described in SANS 5863: 2006 is a bulk property index indicator of concrete that is sensitive to material type, material proportions, as well as compaction and curing regimes. For a given concrete type produced with proper workmanship and certain material ratio specifications, concrete should attain its desired target strength.

The compressive strengths of the concrete mixes were obtained by performing standard cube (100 mm cubes) compressive strength tests. The specimens were tested at 28, 91 and 182 days to SANS 5863:2006. All the tests were performed using a manually-operated hydraulic AMSLER compression machine at a loading rate of 0.3 ± 0.1 MPa/sec.

3.5 Closing remarks

This chapter gave an outline of the experimental programme. Details of the materials used and their proportions were given. Details of the tests were also given. These are bulk diffusion testing, durability index testing and compressive strength. The variables as outlined in this chapter are: w/b ratio, binder type, aggregate type and sample age. They are the factors that are under investigation in this study. The next chapter presents the results of the tests done. Discussion of the results and cross comparison between the different mixes will be made on this basis of the variables under investigation. These are w/b ratio, binder type, aggregate type and sample age.

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Chapter Four

Experimental results and discussion

4.1 General

This chapter presents the results, analysis and discussion of the experiments on the concrete specimens. These comprise chloride ingress using the bulk diffusion test, the three durability index (DI) tests, and compressive strength. The form of presentation of this chapter is done with reference to the tests themselves and the variables being investigated. The variables as outlined in Chapter 3 are: w/b ratio, binder type, aggregate type and sample age. Evaluation of the concrete transport properties measured in the tests and the influences of materials and mix proportion are made on the basis of the test results. Results of tests done on the regional mixes are also presented and compared to each other and the Cape Town plain OPC mix. Figure 4.1 illustrates a schematic of the experimental programme.

The discussion follows the assumption made in Chapter 1 that that concretes of similar w/b ratio and binder type are ideally comparable. For all the evaluations, the Cape Town plain OPC and GGCS blended mixes are used as controls.

The results of the experiments done are presented in the following format:

1. Chloride ingress - bulk diffusion test.
2. Chloride conductivity index test.
3. Oxygen permeability index test.
4. Water sorptivity index test.
5. Cube compressive strength.

At the end of each section discussing each of the above results, a summary is given of the influences established by each test. These are then drawn into specific conclusions at the end of the chapter.

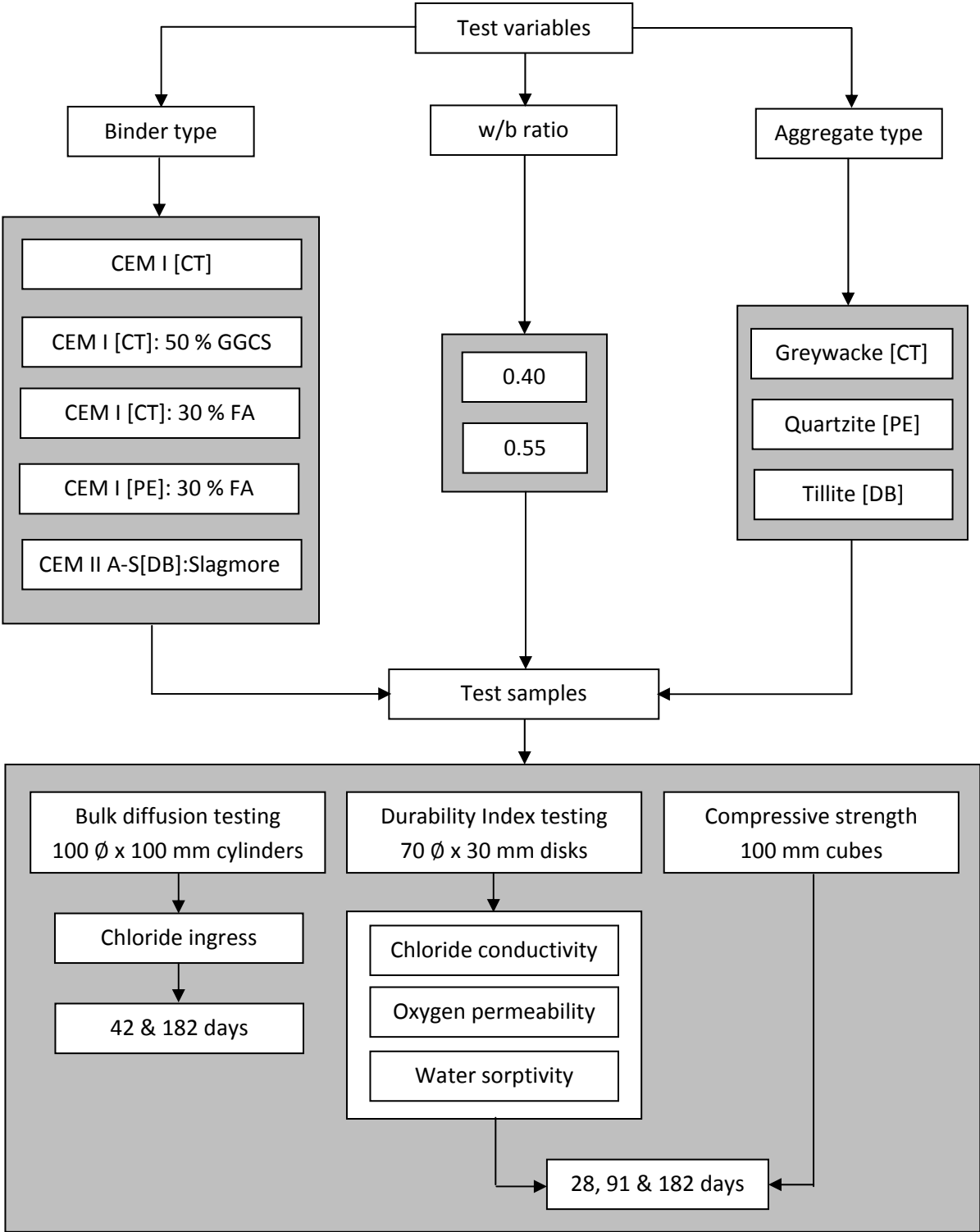


Figure 4.1: Summary of experimental programme

CT - Cape Town
PE - Port Elizabeth
DB - Durban

Each main section begins with an outline of the governing mechanism of the test and the factors being considered. The main sections are further divided into sub-sections where the experimental variables are analysed. The first sub-section presents the results and discussion of the regional trend and the influence of w/b ratio. On the former, a holistic appraisal of their performance is given with the differences between the different regional mixes being drawn out. The regional trend is discussed in this section. The second sub-section focuses on the influence of binder type on the transport properties of concrete. For these, concrete was produced using Cape Town aggregates as controls. The binders are typically those used in the three urban marine regions. The third sub-section discusses the influence of aggregate type on the transport properties of concrete. Here, the regional aggregates were used with two replicate binder types typically used in Cape Town (GGCS blended, and plain OPC). The last sub-section assesses the influence of sample age. For chloride ingress, the chloride profile results are presented here. For the DI tests, the influence of continued moist curing is discussed.

Statistical analysis at a 95 % confidence interval was done on the results of the tests to determine the reliability of the data obtained from this study. The analysis was used also to determine the significance of the variables and to quantify the influences. Details of this are in Appendix A. The statistical procedure used is detailed in ASTM E178 -02: Standard practice for dealing with outlying observations. An extract from the manual outlining the procedure is given in Appendix C.

It should be noted that there exists a degree of repetition in the presentation and discussion of results, particularly the influences of w/b ratio and binder type. These influences are consistently seen through the results and the reiteration of their influences is done so as to fully explore and draw comparisons between them.

4.2 Chloride ingress – Bulk Diffusion Test

Concrete samples that had been cured for 28 days in lime water were exposed to a 2.8 M NaCl solution as specified in the Bulk Diffusion test (ASTM C1556-04, 2004). Two samples per mix were retrieved at 42 and 182 days. Profile grinding was done at different depth levels from the surface to a total depth of 16 mm. The powder samples were then chemically

analysed to determine their chloride content. For each test age and sample, the total chloride content obtained from the powder samples was plotted against the corresponding depth to obtain a chloride profile. The apparent diffusion coefficient (D_a) and the surface chloride concentration (C_s) were calculated from the profiles of each sample using a non-linear curve fitting method described.

Determination of the chloride transport values, D_a and C_s , was using a curve fitting computer programme that applies the error function in Fick's second law (Equation 2.14) to the measured chloride-ion contents. The programme applies a non-linear regression analysis by means of least squares. The method with an example calculation is also described in ASTM C1556-04 (2004).

Using the two factors, extrapolation of the chloride profiles to a depth where the chloride content was 0.4 % by mass of binder was also done. This is referred to as $X_{0.4}$ (mm). It is a composite parameter that incorporates both D_a and C_s , and is an engineering measure of the needed cover depth. The curve fitting technique was used to determine this. Further, given the relatively limited (16 mm) depth profiling done, the $X_{0.4}$ allows for comparison of chloride content values at deeper depths.

For some of the chloride profiles, the first sample depth had lower chloride content than the second depth or subsequent depths. This was anomalous as it was expected that the closer to the exposure face, chloride content values would be much higher. The reason for this result could not be explained as the samples were fully saturated prior to being immersed in the salt solution. In such cases, the first chloride content result for such samples was discarded in determining the chloride transport properties.

Chloride profiles for all the concrete mixes were analysed so as to note the overall shape of the profiles. Good correlation was found ($R^2 > 0.80$, see Table A.1.1 and A.1.2 in Appendix A) for the chloride content values used to plot the profiles.

The following sections describe the bulk diffusion test results in detail based on the various influences being investigated. Only the later age (182-day) results shall be discussed for the variables of regional trend, w/b ratio and concrete material constituent. The 42-day chloride ingress values were premature for a deterministic analysis, but were used to show the

change in chloride ingress with time. The 42- and 182-day results shall be discussed together under the heading of sample age.

4.2.1 Regional trend and influence of w/b ratio

Figure 4.2 gives a summary of the 182 day bulk diffusion test results for the different regional concretes compared at the two w/b ratios of 0.40 and 0.55. Cross comparison is made between the different regional concrete types.

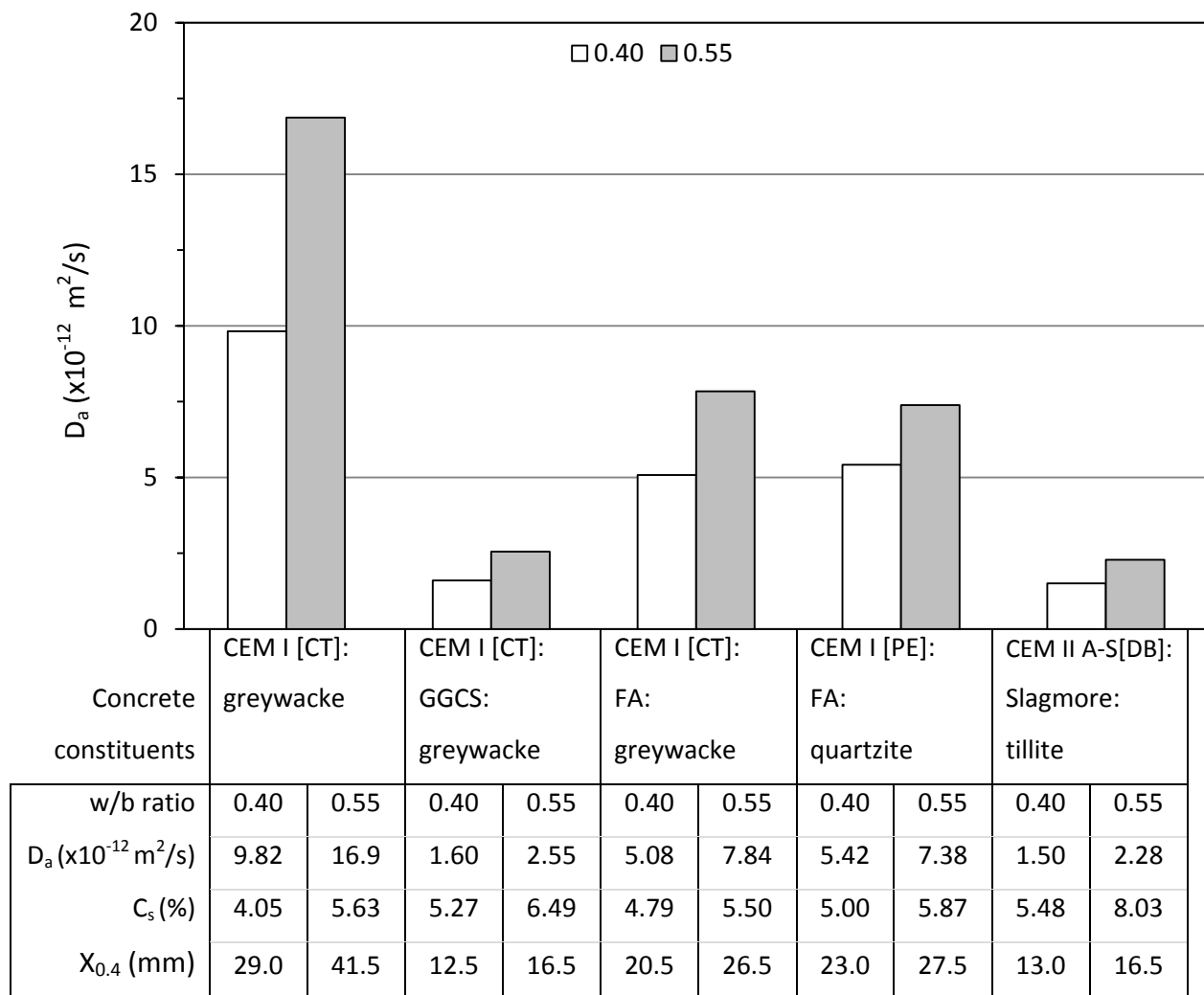


Figure 4.2: 182-day bulk diffusion test results of different regional marine concretes

From Figure 4.2, at 182 days, it is evident that a decrease in w/b ratio is effective in reducing chloride transport values. The Cape Town plain OPC concrete mixes have the largest reduction of 41 % in D_a values between the two w/b ratios. The Cape Town CEM I [CT]: GGCS: greywacke and the Durban CEM II A-S [DB]: Slagmore: tillite mixes show a decrease in

D_a values from the 0.55 w/b ratio to the 0.40 w/b ratio of 37 % and 34 % respectively. The Cape Town FA blended regional mixes exhibit a 35 % decrease. The Port Elizabeth CEM I [PE]: FA: quartzite mixes have a corresponding decrease of 26 %. The results reported by Chalee and Jaturapitakkul (2008) have a similar reduction trend for the FA blended and plain OPC concretes.

From the data table it is also clear that the low w/b ratio concretes have lower C_s and $X_{0.4}$ values. The trend of w/b ratio influencing the rate of chloride transport has been reported by many researchers (Chalee and Jaturapitakkul, 2008, Yang, 2004 and Mackechnie, 1996). The lower w/b ratio concretes having lower chloride transport values translates to better chloride resistance. This trend is also seen in the other concrete types (Figures 4.4 and 4.5).

From the data table in Figure 4.2, it is observed that C_s results for the 0.40 w/b ratio concretes are lower than for the 0.55 w/b ratio concretes. Further, it is observed for each binder type that there is a clear cluster of results. It is seen that the slag (GGCS and Slagmore) blended mixes have higher values at both w/b ratios, followed by the FA blended mixes. The plain OPC mixes have the lowest C_s values. Though Mackechnie, (1996) points out that C_s is influenced by binder type, no particular trend can be established as a comparison between all C_s values gives a poor correlation coefficient. This is illustrated in Figure 4.3. It is thought that the chloride binding capacity between the different w/b ratio and binder types which has an impact on the penetration rate could have affected the C_s values.

Mackechnie (1996) advises that C_s values for concretes younger than 2 years are inconclusive as chloride transport has not yet stabilised. Analysing the C_s results would therefore be misleading owing also to the curve fitting technique used and the fact that for some of the concrete mixes the first chloride content depth result was discarded. The C_s results shall therefore not be further discussed.

From the data table in Figure 4.2, it is also apparent that the slag blended concrete mixes have lower chloride transport values than both the FA blended and plain OPC concretes. This influence of binder type is discussed in the next section.

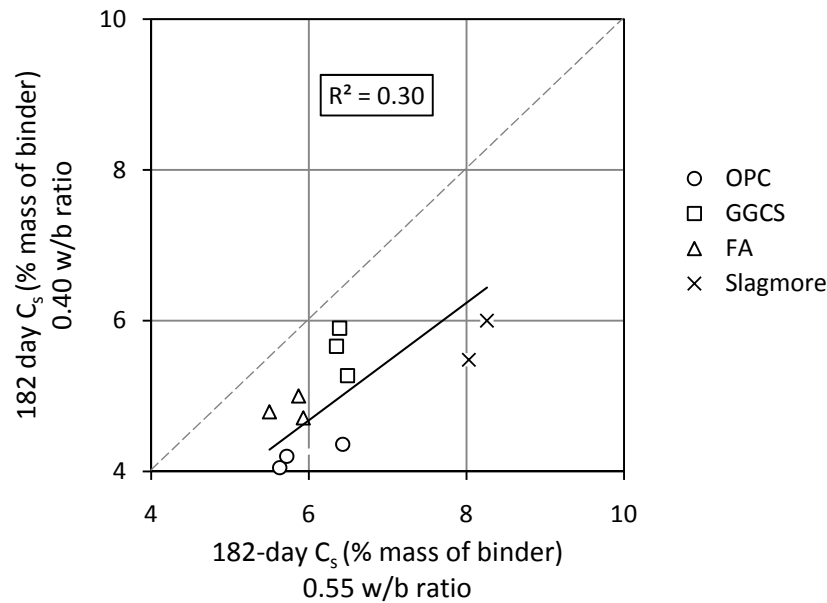


Figure 4.3: Comparison of 182-day C_s values for 0.40 and 0.55 w/b ratio concretes

At both w/b ratios the different concrete mixes are ranked as follows in order of increasing D_a values at 182 days: slag blended mixes < FA blended mixes < plain OPC mixes. The differences within the binder types are small and the order is adopted for practicality. The $X_{0.4}$ depth extrapolations also follow the same trend and clusters are seen between the groups. The slag blended mixes have lower values than either the FA blended or plain OPC mixes at both w/b ratios.

4.2.2 Influence of binder type

Figure 4.4 gives a summary of the 182-day bulk diffusion test results for the different concrete types produced with Cape Town aggregates and the different regional binders. This is done to determine the influence of binder type on chloride penetration at the two w/b ratios of 0.40 and 0.55. Cross comparison is therefore made between the different binder types.

From the data table it is apparent that the concrete mixes containing a slag component have low chloride transport values compared to the FA blended and plain OPC mixes. Figure 4.5 also shows this trend for plain OPC mixes compared to GGCS blended mixes. Mackechnie (1996) reported the same behaviour for a range of concrete grades. Slag blended mixes have

increased chloride binding characteristics compared to FA blended and plain OPC mixes. These results are also in agreement with the findings of Gardner (2006) and Dhir et al (1996).

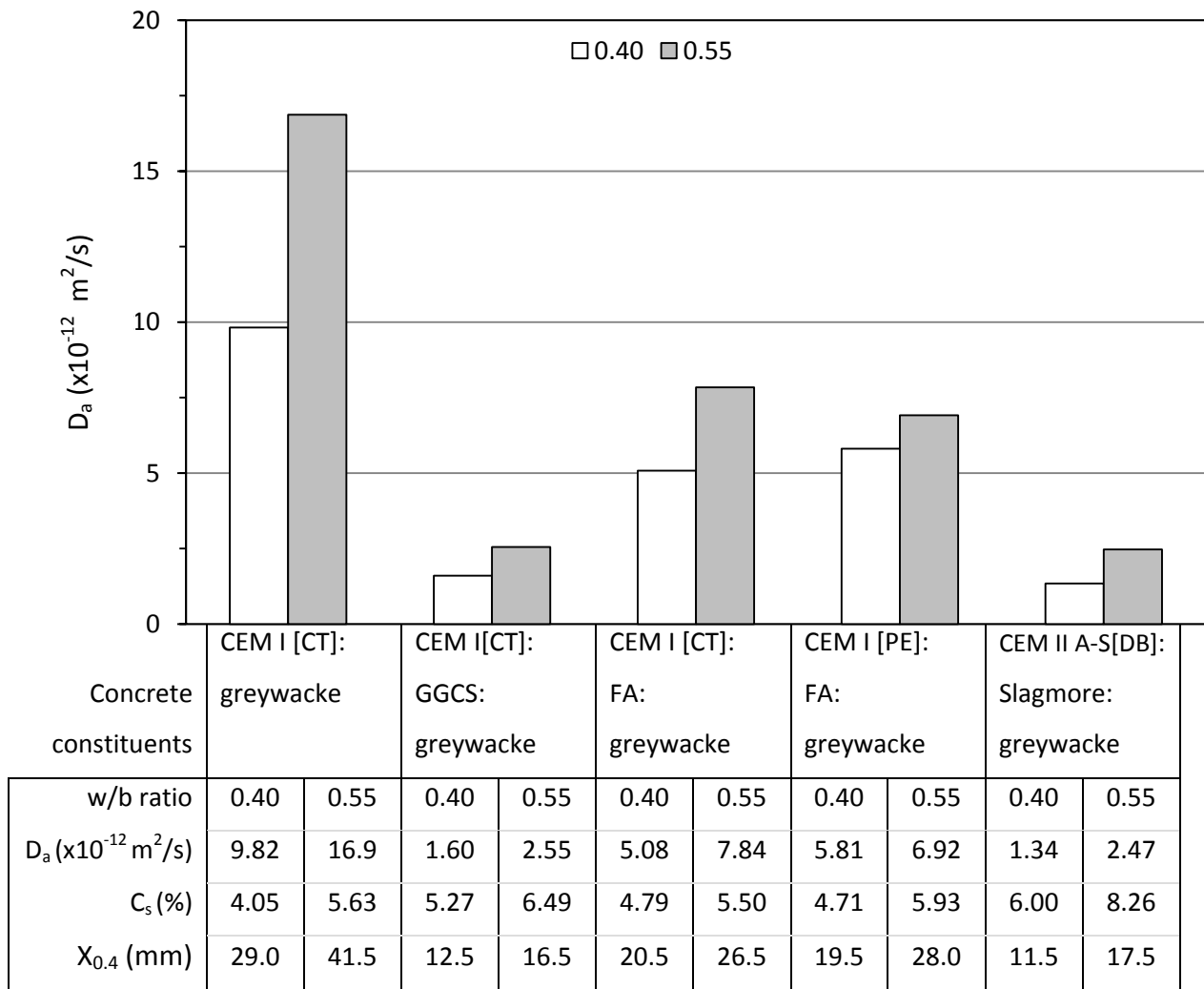


Figure 4.4: 182-day bulk diffusion test results of different mixes made with Cape Town aggregates and different regional binders

The reduction in chloride ingress values is attributed to the chloride binding capacity of the supplementary cementitious materials (SCM) used in the concrete as similar behaviour was noted by Stanish et al (2001) and Rasheeduzzafar et al (1990). Considering the mixes with CEM I [CT] binder, the inclusion of GGCS resulted in a large decrease in D_a values of up to 80 % at both w/b ratios. The FA blended mixes show a reduction of up to 50 %. Given the reduction range, it is clear that the inclusion of SCM in an OPC mix is more effective in lowering D_a values than reducing w/b ratio as was seen in Section 4.2.1. Generally, the rate of penetration of chlorides into concrete is dependent on the pore structure and the

chloride binding capacity of the binder paste (Stanish et al 2001). From the results, the low D_a values of the blended mixes attest to improved pore structure and better chloride binding in comparison to the plain OPC mix.

It is noted that the CEM I [CT] and CEM I [PE] binders blended with FA have a similar range of values. The chemical analyses of the two CEM I binders given in Table 3.1 shows that they are comparatively similar. As the FA used was from the same batch, this would inherently indicate that CEM I [CT] and CEM I [PE] impart similar chloride transport characteristics to concrete. The two slag blended mixes also have values that have a similar range which also indicates that the binder types used impart similar chloride transport characteristics to concrete.

From the chloride ingress results presented, the ranking of D_a values adopted earlier is seen again, i.e. slag blended mixes < FA blended mixes < plain OPC mixes. The decrease in D_a values ranged from 50 % to 80 % between each binder variation. The $X_{0.4}$ depth extrapolations also follow the same trend and clusters are seen between the groups. The slag blended mixes have lower values than either the FA blended or plain OPC mixes at both w/b ratios.

4.2.3 Influence of aggregate type

The influences of w/b ratio and binder types shown in Figure 4.5 were discussed in the previous sections. Significant differences are seen of w/b ratio and binder type for all concrete types with similar coarse aggregate composition.

From the chloride ingress results in Figure 4.5, no significant trend is evident between the different aggregate types. It appears that aggregate type does not have a dominant influence on chloride-ion penetration. For each set of mixes with similar binder composition, all the chloride ingress values are statistically similar (see Appendix A). Also from an engineering viewpoint, differences in the chloride ingress values for each set of mixes with similar binder composition were insignificant.

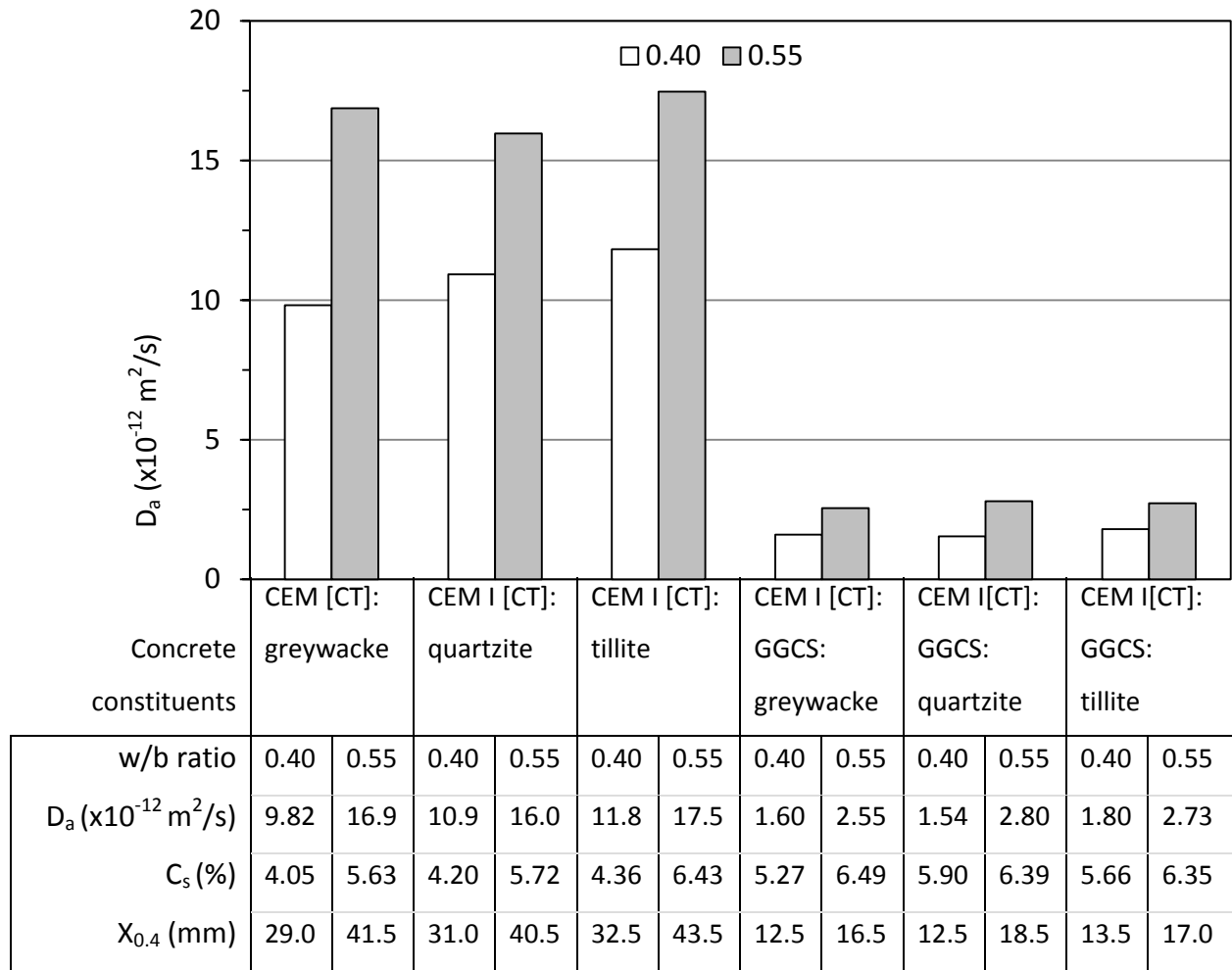


Figure 4.5: 182-day bulk diffusion test results of different mixes made with Cape Town binders and different aggregates

4.2.4 Sample age

Table 4.1 gives the chloride transport values of concrete specimens sampled at 42 and 182 days. Typical profiles for the regional concrete types are given in Figures 4.6 - 4.10 for illustrative purposes. The other chloride profiles for the mixes are presented in Appendix A. Plain CEM I mixes with Port Elizabeth quartzite and Durban tillite aggregate were however not sampled at 42 days due to a scheduling oversight.

From the table it is clear that chloride content values increased with increasing duration of exposure to a chloride environment. This is seen for all concrete types and is attributed to ongoing diffusion.

The slag blended mixes have the lowest chloride transport values, which points to the good chloride binding capacity of slag. The plain OPC mixes have higher chloride transport values. Such mixes have been reported by many researchers as having poor resistance to chloride ingress. The FA blended mixes have lower chloride transport values than the plain OPC concrete mixes indicating improved chloride resistance.

Table 4.1: Chloride transport values

Ref:	Concrete mix constituents	Sample age		42 days		182 days	
		w/b	D _a	C _s	D _a	C _s	
Fig. 4.6	CEM I [CT]:	0.40	88.0	1.64	9.82	4.1	
	greywacke	0.55	90.0	1.70	16.9	5.6	
Fig. A.5	CEM I [CT]:	0.40	-	-	10.9	4.2	
	quartzite	0.55	-	-	16.0	5.7	
Fig. A.6	CEM I [CT]:	0.40	-	-	11.8	4.4	
	tillite	0.55	-	-	17.5	6.4	
Fig. 4.7	CEM I [CT]: GGCS:	0.40	3.0	2.23	1.60	5.3	
	greywacke	0.55	9.8	3.41	2.55	6.5	
Fig. A.1	CEM I [CT]: GGCS:	0.40	3.7	2.91	1.54	5.9	
	quartzite	0.55	10.8	3.58	2.80	6.4	
Fig. A.2	CEM I [CT]: GGCS:	0.40	3.3	2.53	1.80	5.7	
	tillite	0.55	11.2	3.94	2.73	6.4	
Fig. 4.8	CEM I [CT]: FA:	0.40	26.0	2.95	5.08	4.8	
	greywacke	0.55	42.7	2.20	7.84	5.5	
Fig. A.3	CEM I [PE]: FA:	0.40	24.6	2.34	5.81	4.7	
	greywacke	0.55	46.9	3.67	6.92	6.0	
Fig. 4.9	CEM I [PE]: FA:	0.40	24.5	2.60	5.42	5.0	
	quartzite	0.55	48.3	3.64	7.38	5.9	
Fig. 4.10	CEM II A-S [DB]: Slagmore:	0.40	3.2	2.56	1.50	5.5	
	tillite	0.55	9.3	3.48	2.28	8.0	
Fig. A.4	CEM II A-S [DB]: Slagmore:	0.40	5.0	2.48	1.34	6.0	
	greywacke	0.55	11.9	3.87	2.47	8.3	

D_a x 10⁻¹² m²/s

C_s % mass of binder

It is seen that mixes blended with supplementary cementitious materials (SCM) have lower D_a values compared to the plain OPC mixes. These mixes exhibit steep chloride profiles and have higher near-surface chloride concentrations.

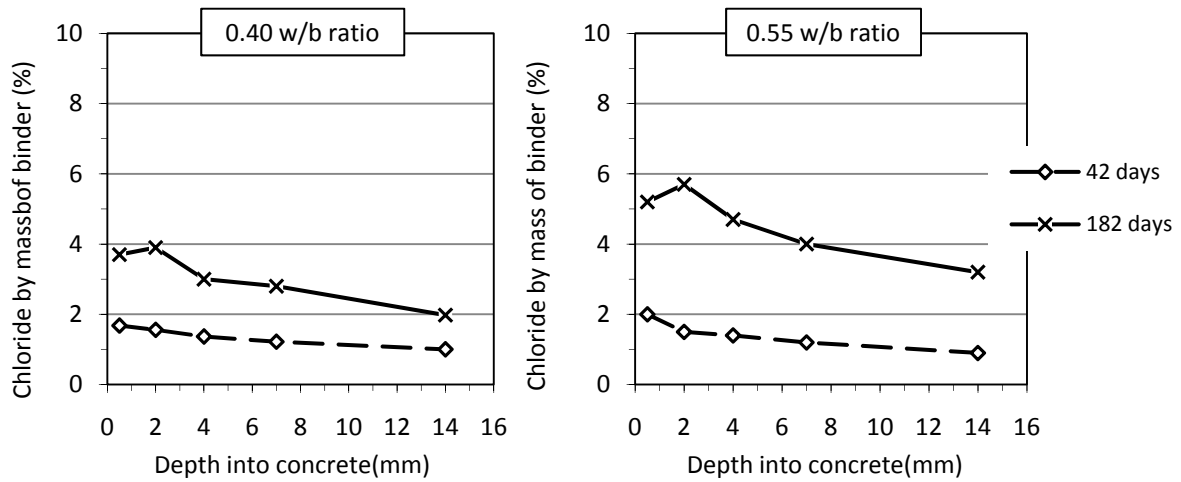


Figure 4.6: Chloride profiles CEM I [CT]: greywacke

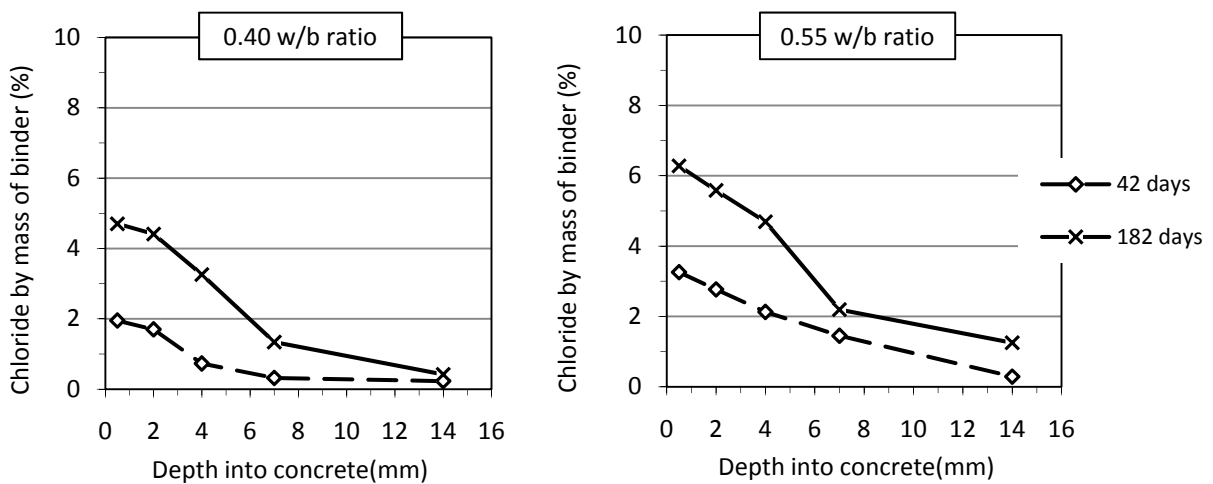


Figure 4.7: Chloride profiles CEM I [CT]: GGCS: greywacke

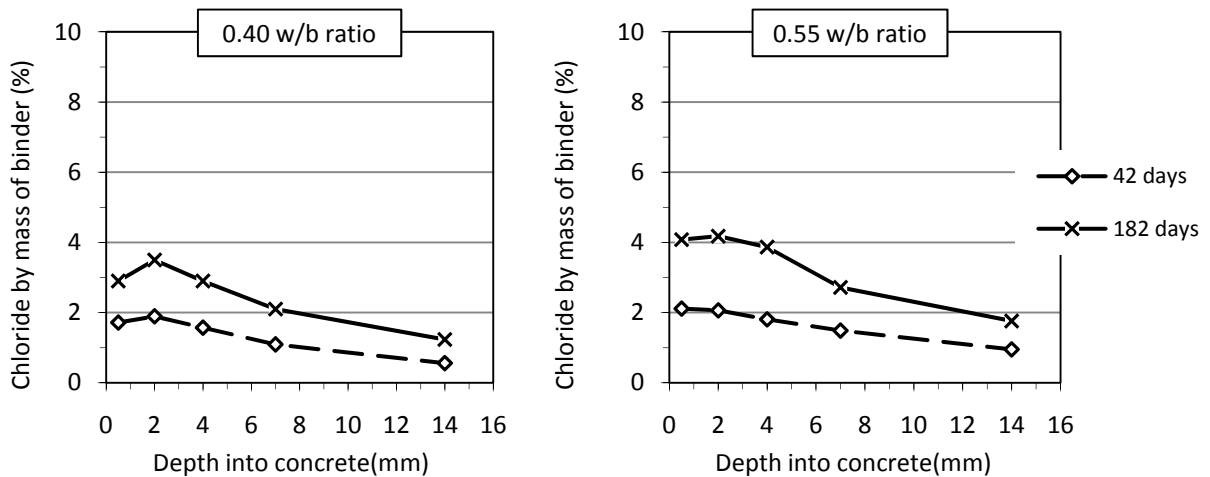


Figure 4.8: Chloride profiles of CEM I [CT]: FA: greywacke

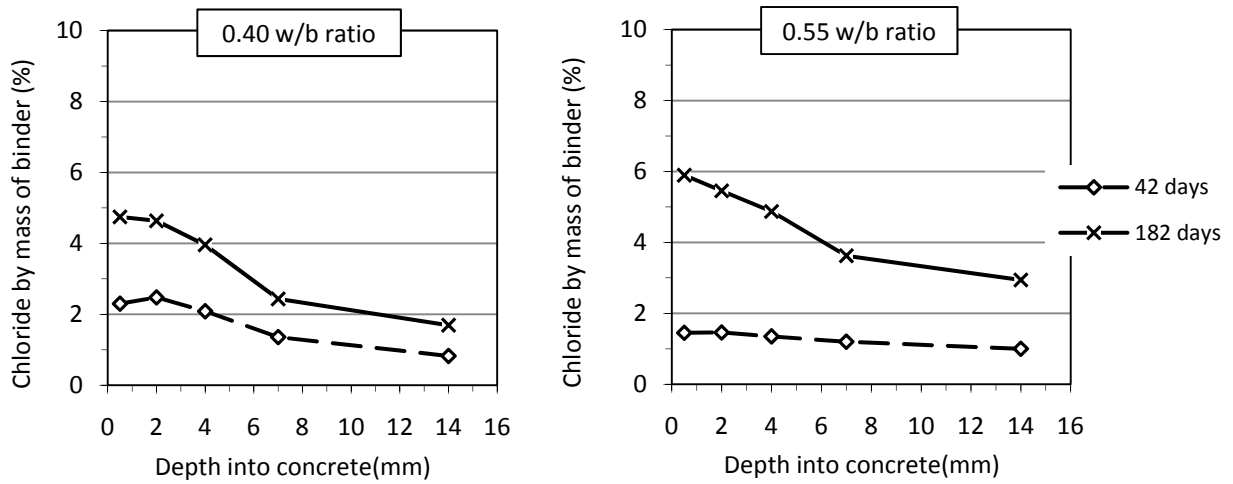


Figure 4.9: Chloride profiles CEM I [PE]: FA: quartzite

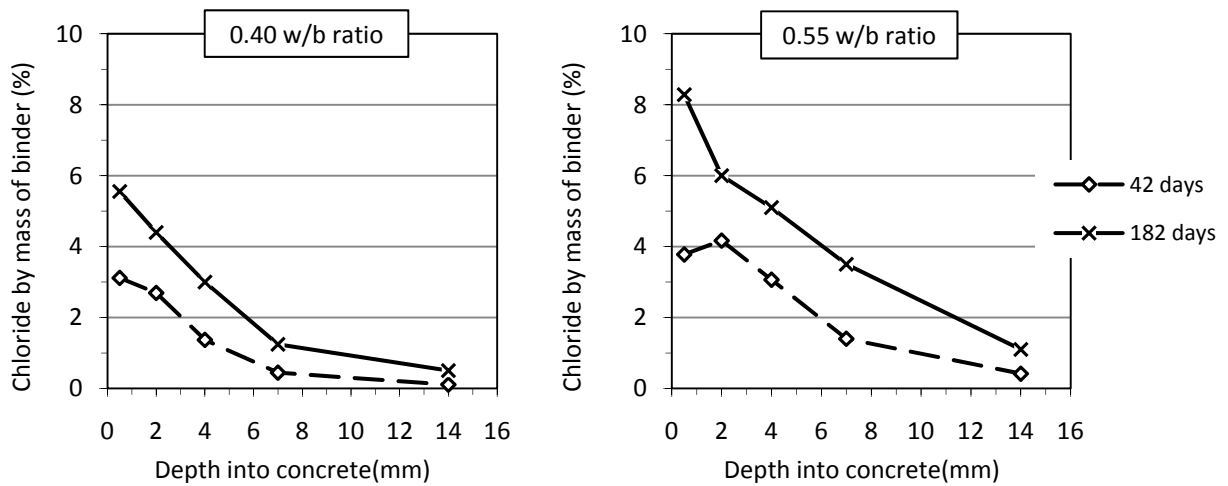


Figure 4.10: Chloride profiles CEM II A-S [DB]: Slagmore: tillite

The plain OPC mixes exhibit comparatively poorer resistance to chloride transport at all sample ages. The concrete mixes with plain OPC exhibit shallow chloride profiles and high chloride concentrations throughout the profile depths. This denotes the poor resistance to chloride penetration of unblended binder mixes.

At both sample ages, the slag blended mixes show lower chloride transport values than the FA blended mixes. However, FA blended mixes show a higher reduction range of up to 85 % between 42 days and 182 days. The slag mixes have a reduction range of between 45 % and 75 % for both GGCS and Slagmore blended mixes. Interestingly, the plain OPC mixes also exhibit a large reduction range of up to 88 %. This is attributed to the chloride binding capacity of the SCM which slows chloride ion transport. Penetrating chloride ions are immobilised by physical and chemical means which decreases the free ion concentration

thus slowing the diffusion process (Song et al, 2008). This reduction behaviour is also thought to be due to continued binder hydration making the pore structure denser and inaccessible to the chloride ions.

4.2.5 Summary remarks

From the bulk diffusion results presented, it is seen that plain OPC mixes have the least resistance to chloride ion ingress and have the highest transport values. This is in comparison to the blended binder mixes of slag (GGCS and Slagmore) and FA. The slag blended mixes have near-similar and the lowest transport values. This is attributed to the higher chloride binding capacity of slag. The FA blended mixes from Cape Town and Port Elizabeth also have near-similar chloride ingress resistance values which are higher than for the slag blended mixes, but considerably lower than for the plain OPC mixes. This behaviour of FA blended mixes is attributed to the packing effect and pozzolanic reaction of FA in concrete.

With regard to w/b ratio, the lower 0.40 w/b ratio mixes have lower chloride transport properties in comparison to the relatively 'poorer' 0.55 w/b ratio mixes. The pore structure of the lower w/b ratio mixes is more closed resulting in decreased penetrability. Further, it is seen that reducing w/b ratio is more effective in plain OPC mixes than in blended binder mixes.

Aggregate type does not have a dominant influence on chloride ion ingress, as no considerable difference is seen between mixes of similar binder type.

Comparing the effect of binder type and w/b ratio for common aggregate mixes, it is evident that the addition of SCM is more effective in reducing chloride transport values in OPC mixes than reducing w/b ratio or changing aggregate type respectively.

From the results it is also evident that chloride content values increased with increasing duration of exposure to a chloride environment. This is seen for all concrete types and is attributed to ongoing diffusion.

4.3 Chloride conductivity index

The chloride conductivity index (CCI) is a durability prediction and an early age durability characterisation parameter. It measures the resistance of a concrete matrix to the transport of ionic species. The CCI index test relies on electro-migration of chloride ions through a concrete matrix with the index value being the durability characterisation parameter. The test is appropriate in providing an indication of the overall ionic transport process of concrete exposed to a chloride rich environment. Low CCI values are indicative of a concrete’s pore structure’s resistance to ionic ingress. Conversely, high CCI values are indicative of reduced resistance to ionic transport (Mackechnie, 1996).

Comparison of CCI values is made on the basis of regional concrete type, grade of concrete, mix constituents (aggregate and binder) and the duration of moist curing. All the concrete mixes are compared to the plain OPC control concrete mixes at the respective w/b ratios of 0.40 and 0.55.

4.3.1 Regional trend and influence of w/b ratio

Figure 4.11 illustrates 28-day CCI values of test specimens from the different regional marine mixes.

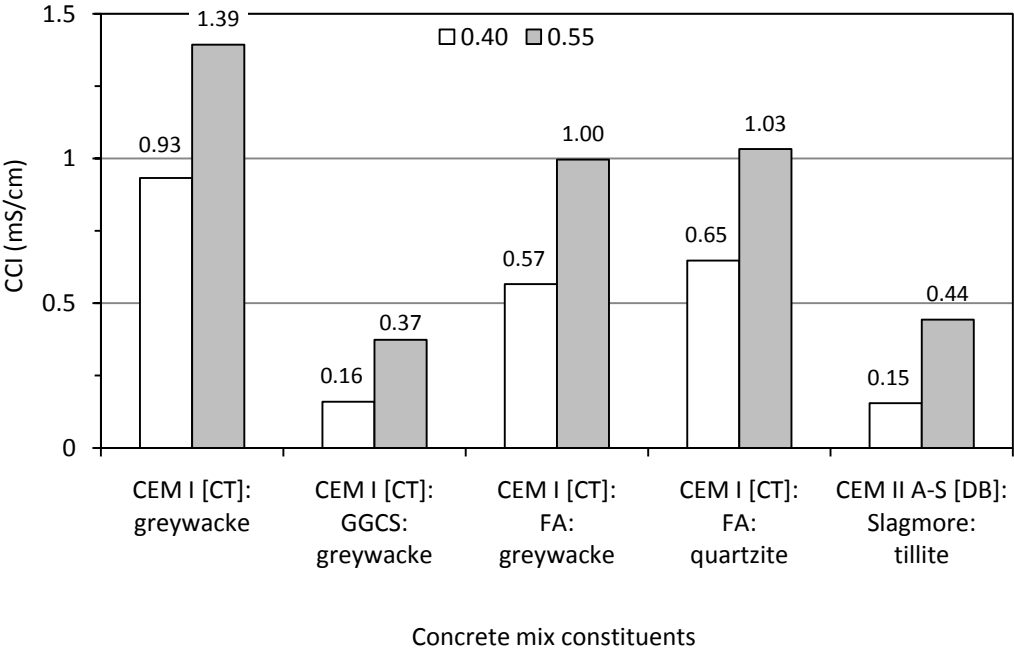


Figure 4.11: 28-day CCI values of the regional concrete mixes

From the figure, it is seen that concretes at the lower 0.40 w/b ratio have lower 28-day CCI values than concretes at the higher 0.55 w/b ratio. The other concrete mixes also exhibit this trend as shown in Figures 4.12 and 4.13. The effect of binder type seen is discussed in the next sub-section.

The Slagmore and GGCS blended mixes respectively have the greatest reduction of 66 % and 56 % between the two w/b ratios. The FA blended mixes from Port Elizabeth and Cape Town respectively have reduced values of up to 43 % and 37 % between the two w/b ratios while the plain OPC mix has a reduction range of 33 %. Chloride transport in concrete is largely dependent on the nature, amount and continuity of the concrete pore structure. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in a reduction of the ionic transport properties as explained by Glass (2003). This magnitude of reduction in CCI values for slag blended mixes is also attributed to the higher chloride binding capacity of slag compared to the FA blended and plain OPC mixes.

From the chloride conductivity results of the regional mixes presented in this section, the ranking of D_a values adopted earlier for chloride ingress is also seen for CCI values, i.e. slag blended mixes < FA blended mixes < plain OPC mixes.

4.3.2 Influence of binder type

Figure 4.12 illustrates 28-day CCI values of samples from concrete made with Cape Town aggregates and the different regional binders. This is done to determine the influence of binder type on chloride resistance at the two w/b ratios of 0.40 and 0.55.

From the figure, it is apparent that concretes at 0.40 w/b ratio have lower CCI values than concretes at the 0.55 w/b ratio. As discussed earlier, chloride transport in concrete is largely dependent on the nature, amount and continuity of the concrete pore structure. The slag (GGCS and Slagmore) blended mixes have the greatest reduction of 82 % and 70 % at the 0.40 and 0.55 w/b ratios respectively. This magnitude of reduction in CCI values for slag blended mixes is attributed to the higher chloride binding capacity of slag compared to OPC. Both FA blended mixes also have lower chloride conductivity values than the plain OPC mixes. Their reduction is up to 25 % at both w/b ratios. Generally, the chloride binding

nature of the extenders is attributed with the decrease in chloride conductivity values in comparison to the plain OPC mixes (Alexander et al, 1999a, Mackechnie, 1996). The chloride binding capacity of a binder is dependent on the aluminate content of the binder type. In the blended binder types used, their Al₂O₃ content is higher than for the plain OPC binder (Table 3.1) (Richardson, 2002, Boddy et al, 1999, Glass et al, 1996, Soroka, 1993, Arya and Newman, 1990).

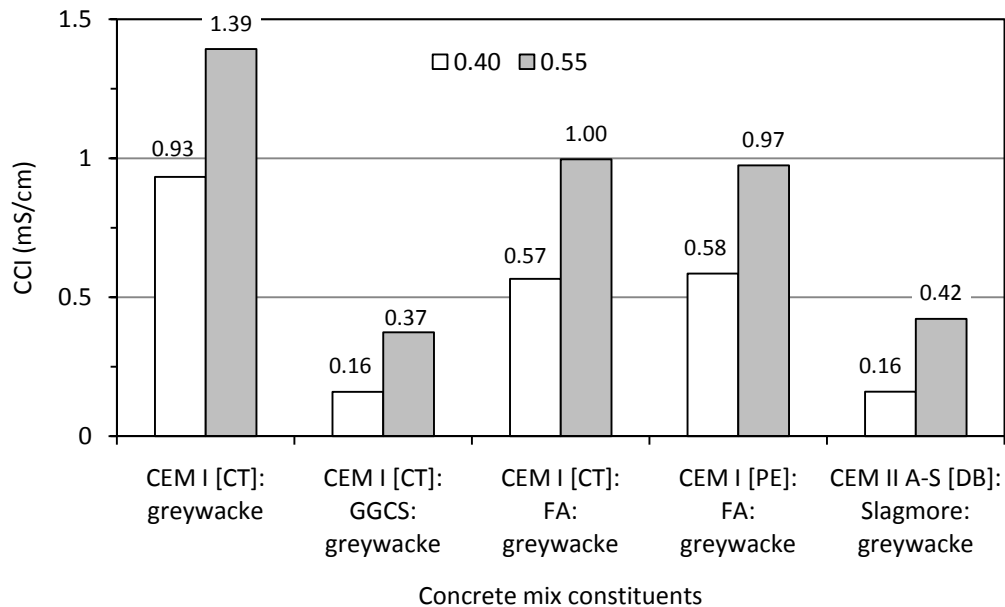


Figure 4.12: 28-day CCI values of a range of concrete types made with the regional binders and Cape Town aggregates

Mackechnie, (1996) reported that the chloride conductivity test shows sensitivity to the pore structure of blended mixes. In Figure 4.12 the pore refining nature of GGCS and FA in blended Cape Town concrete mixes is seen to cause a decrease in chloride conductivity values in comparison to the plain OPC concrete mixes. Inherently, this impedance to ionic transport leads to a reduction in corrosion susceptibility, occurrence and propagation (Richardson, 2002). This is also seen in Figures 4.11 and 4.13 where all the blended mixes have lower CCI values than the plain OPC mix. In the latter figure, the beneficial effect of using GGCS in a mix is clearly evident. From the two foregoing figures, 4.11 and 4.12, it is clear that binder type has a more significant effect on reducing CCI values than reducing w/b ratio.

Compared to the values reported by Ballim et al (2009) and Mackechnie (1996) of Cape Town mixes, the values obtained in this study are favourably lower. This is thought to be possibly a result of the use of crushed rock as fine aggregate which improves the packing density of the aggregate phase and reduces ionic transport through the ITZ. The void content of the mix would also be reduced which inherently means more durable concrete (Mehta and Monteiro, 2005). Another reason could be change in binder properties. As such, the concrete mixes are deemed appropriate for use in the marine environment given the limiting 28 day CCI values recommended by Alexander et al (2007). Sufficient cover depth must also be provided. The limiting values are given in Table 2.8.

From the results, the ranking of chloride conductivity results is the same as that given earlier for chloride ingress; is seen again; slag blended mixes < FA blended mixes < plain OPC mixes.

4.3.3 Influence of aggregate type

To determine the influence of aggregate type on the chloride conductivity characteristics of concrete, samples were made with Cape Town binders and the different regional aggregate types. Figure 4.13 illustrates 28-day CCI values of test samples at the two w/b ratios of 0.40 and 0.55.

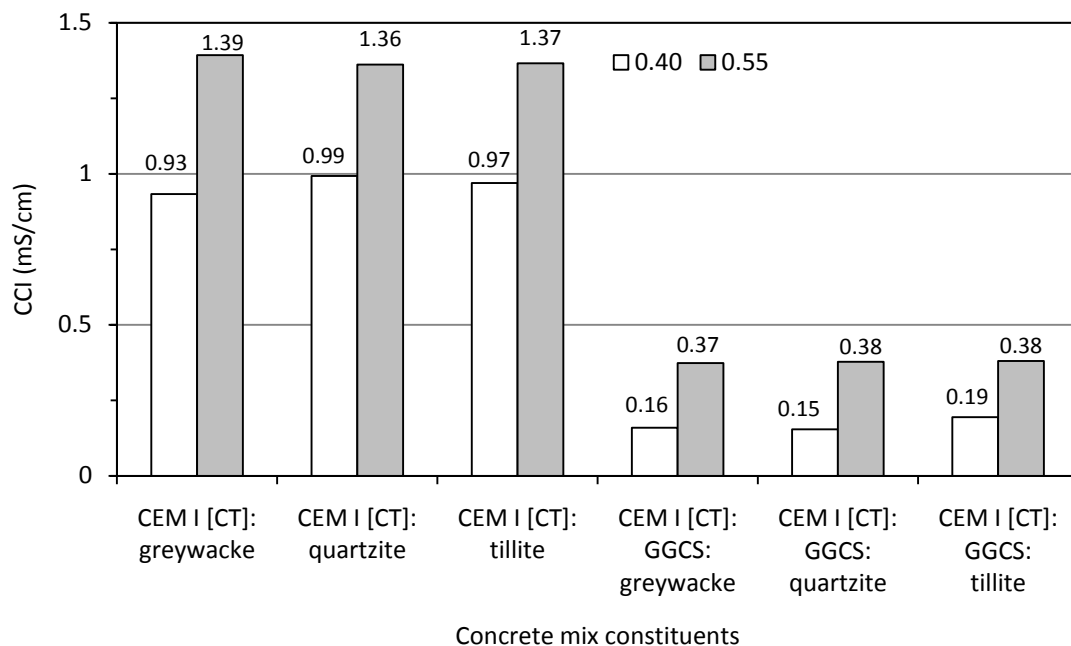


Figure 4.13: 28-day CCI values of a range of concrete mixes made with the regional aggregates and Cape Town binders

The influences of w/b ratio and binder type evident in the figure were discussed earlier. From the figure, it is noted that, for each binder type, chloride conductivity values are not significantly different, and from a practical point of view are independent of aggregate type.

4.3.4 Influence of continued moist curing

Figures 4.14 - 4.16 show the effect for all the concrete mixes of continued moist curing on chloride conductivity. The figures show CCI test values for 0.40 and 0.55 w/b ratio mixes respectively at 28, 91 and 182 days. The effects of w/b ratio, binder type and aggregate type seen in the figures were discussed earlier.

Between 28 and 91 days, the slag blended mixes exhibit a reduction of up to 30 % at the lower 0.40 w/b ratio and 50 % at the higher w/b ratio. The FA blended mixes have a reduction of up to 30 % at the lower w/b ratio and 40 % at 0.55 w/b ratio. The plain OPC mixes have a higher reduction range in chloride conductivity of up to 49 % at 0.40 w/b ratio and 36 % at 0.55 w/b ratio. From this it is clear that that at higher w/b ratios, the blended mixes are more sensitive to continued moist curing.

At 182 days, the 0.55 w/b ratio FA blended mixes provide similar values of chloride conductivity as the 0.55 w/b ratio slag blended mixes. This shows that given sufficient moist curing, at this w/b ratio, the two binder types offer comparable chloride transport resistance to concrete in the long term. The 0.40 w/b ratio FA blended mixes have higher chloride conductivity values at 182 days than similar w/b ratio slag blended mixes. The reduction in values between 91 and 182 days for the FA blended mixes is however considerable. The behaviour exhibited by the FA blended mixes points towards FA being classified as a slow reacting pozzolanic binder requiring an extended period of moist curing. Mackechnie (1996) also reported that increased performance of FA blended mixes is developed at later ages. The plain OPC concrete mixes show poorer resistance to chloride conductivity compared to the blended mixes at 182 days.

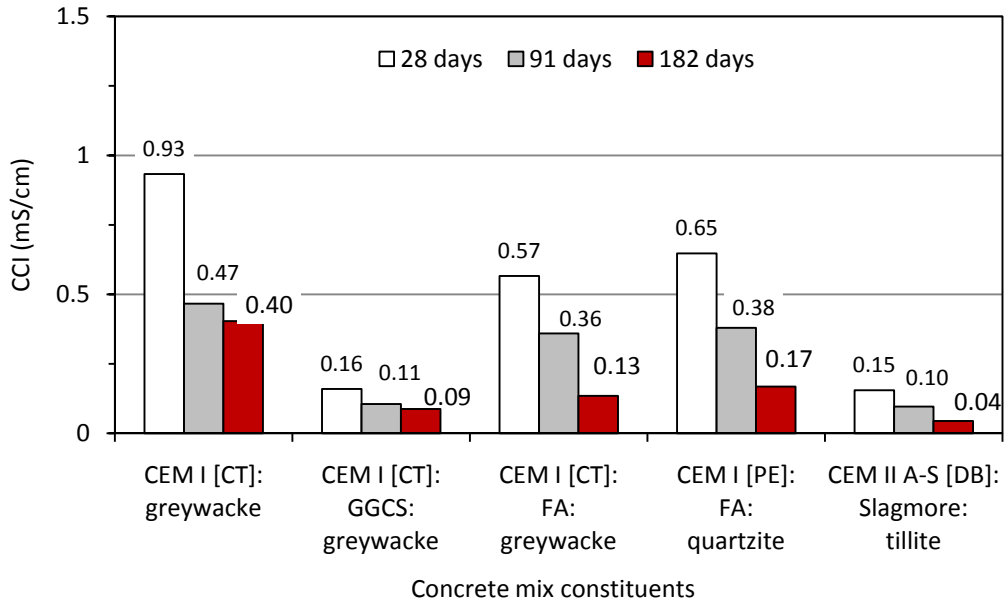


Figure 4.14 (a): 0.40 w/b ratio CCI values of regional concrete mixes at 28, 91 and 182 days

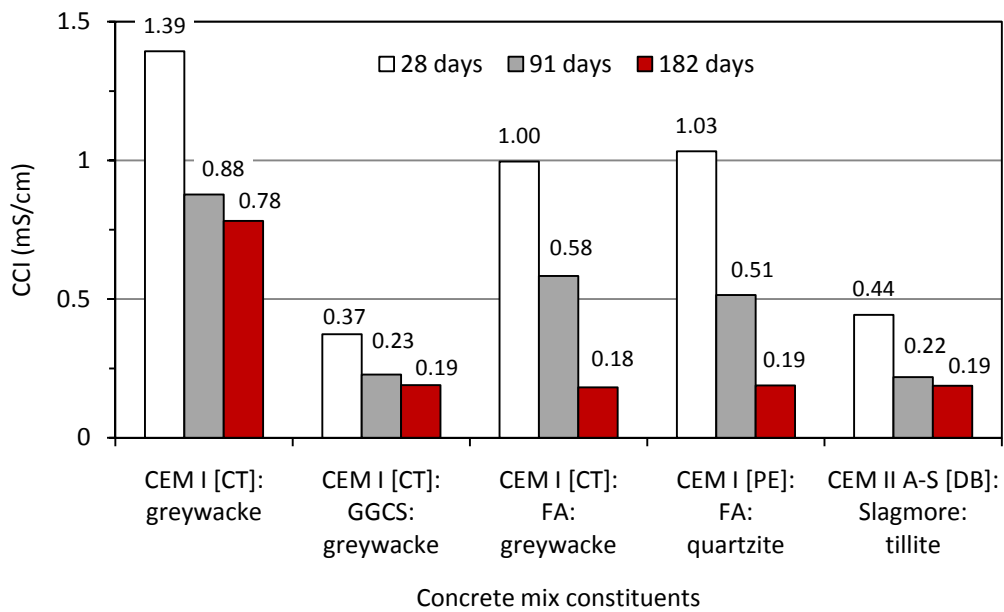


Figure 4.14 (b): 0.55 w/b ratio CCI values of regional concrete mixes at 28, 91 and 182 days

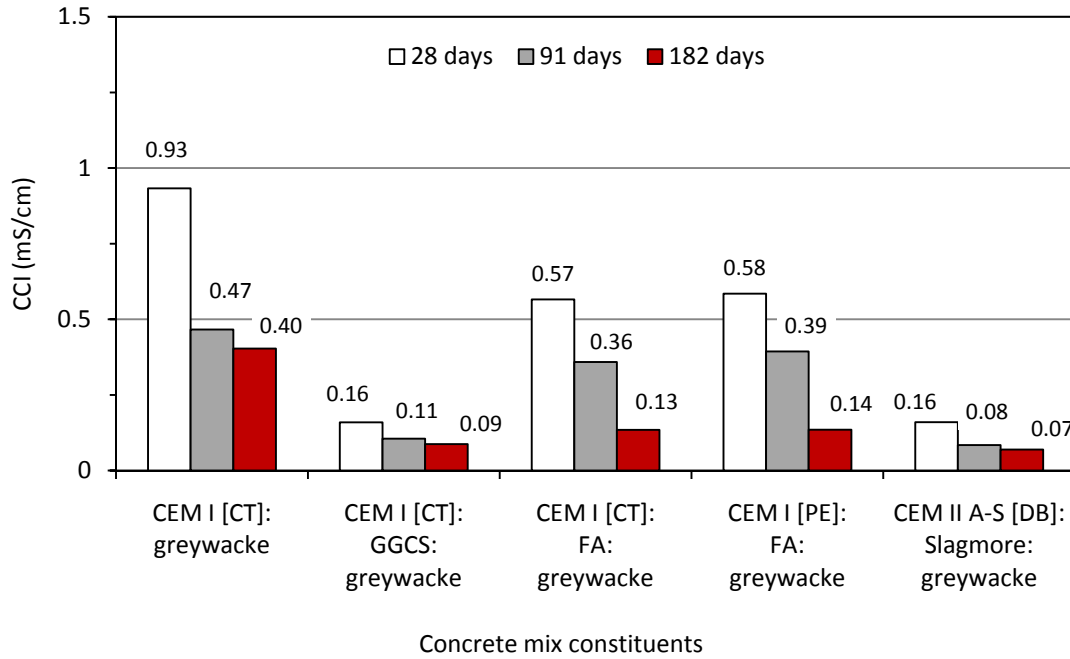


Figure 4.15 (a): 0.40 w/b ratio CCI values of a range of concrete mixes made with the regional binders and Cape Town aggregates at 28, 91 and 182 days

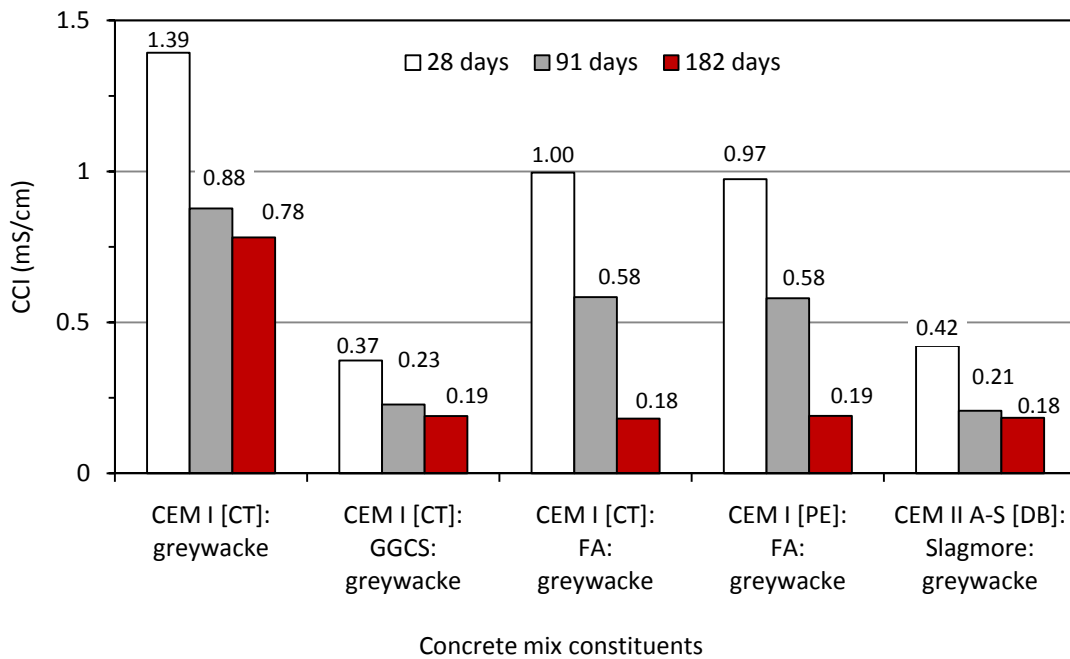


Figure 4.15 (b): 0.55 w/b ratio CCI values of a range of concrete mixes made with the regional binders and Cape Town aggregates at 28, 91 and 182 days

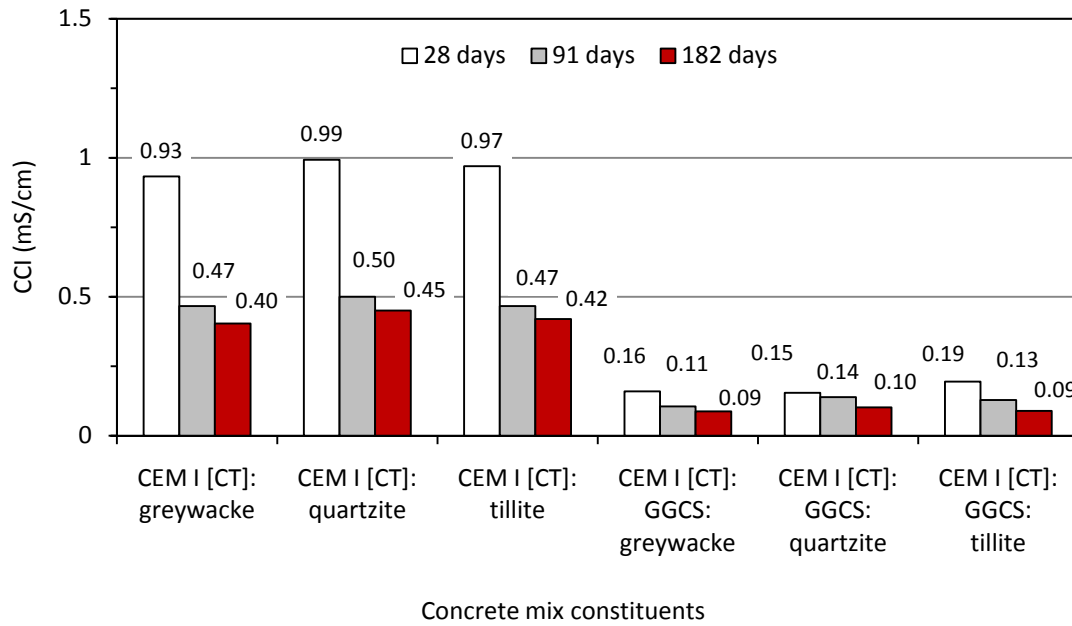


Figure 4.16 (a): 0.40 w/b ratio CCI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

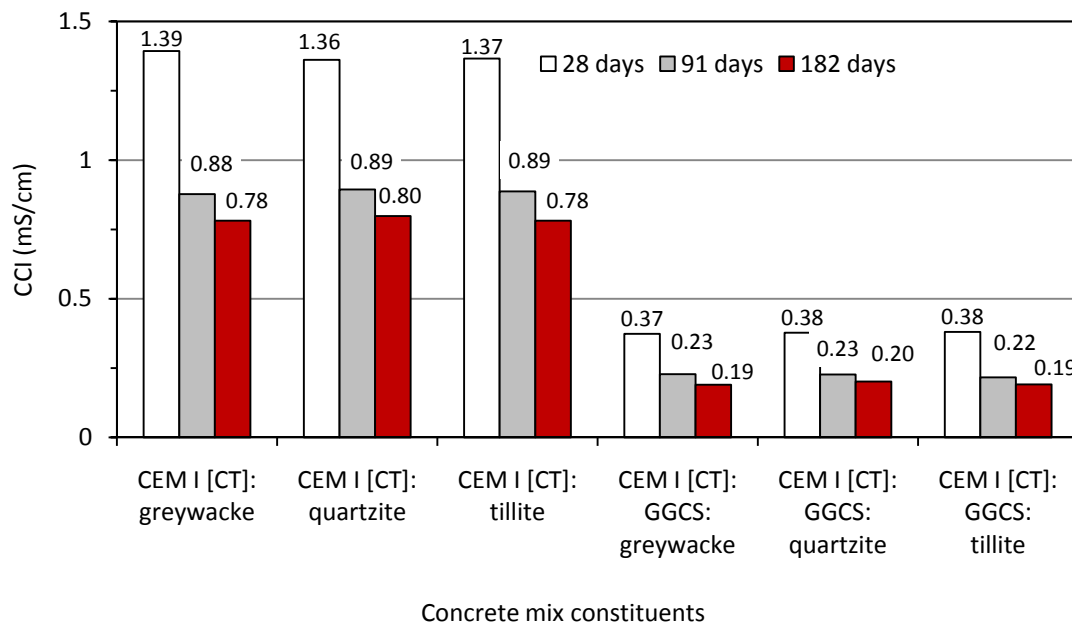


Figure 4.16 (b): 0.55 w/b ratio CCI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

4.3.5 Summary remarks

From the chloride conductivity results presented, it is seen that plain OPC mixes have the least resistance to ionic transport and have the highest CCI values. This is in comparison to

the blended binder mixes of slag (GGCS and Slagmore) and FA. The slag blended mixes have near-similar and the lowest transport values. This is attributed to the pore refining nature of slag which reduces the interconnectivity between penetrable pores in concrete. The FA blended mixes from Cape Town and Port Elizabeth also have near-similar chloride ingress resistance values though they are higher than for the slag blended mixes, but which are lower than for the plain OPC mixes. This behaviour of FA blended mixes is also attributed to the pore refining nature of FA in concrete.

With regard to w/b ratio, the lower 0.40 w/b ratio mixes have lower ionic transport properties in comparison to the relatively 'poorer' 0.55 w/b ratio mixes. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in a reduction of the ionic transport properties.

Aggregate type does not have a dominant influence on ionic transport, as no significant difference is seen between mixes of similar binder type.

From the results it is seen that the effect of inclusion of SCM in a mix is more effective in reducing ionic transport in a mix than the reduction of w/b ratio, continued moist curing or changing aggregate type respectively. It is also appreciated that ionic transport values for the tested mixes decreased with continued curing. This is attributed to continued hydration.

4.4 Oxygen permeability index

The oxygen permeability index (OPI) test characterises the transport of gases by permeation through a concrete matrix. The test is indicative of the concrete pore structure through which permeation occurs. The pore structure is sensitive to changes in w/b ratio, binder type and curing. In addition, the level of compaction, presence of bleed voids and channels also influence the degree of connectivity of the pores within the concrete matrix (Alexander et al, 1999). A concrete with a low degree of connectivity of its pore structure would have a high OPI value (and conversely a low coefficient of permeability). In an RC structure with adequate cover, the penetration of deleterious species such as oxygen and carbon dioxide through the cover region would be slowed by the provision of such concrete. (Ballim et al, 2009).

It should be noted that analysis of the permeability characteristics of concrete is done on the coefficient of permeability (k) values, as these are the measured test values. Details of the statistical analysis done are given in Appendix A. The OPI values are transformed k values and are used and presented for their practical usefulness.

Comparison of permeability characteristics is made on the basis of regional concrete type, grade of concrete, mix constituents (aggregate and binder) and the duration of moist curing. All the concrete mixes were also compared to the plain OPC control mixes at the two w/b ratios of 0.40 and 0.55.

4.4.1 Regional trend and influence of w/b ratio

Figures 4.17 and 4.18 illustrate 28-day OPI and coefficient of permeability (k) values of samples of different South African marine concrete mixes respectively.

From Figure 4.17, it is apparent that concretes at the 0.40 w/b ratio have lower k values than concretes at the 0.55 w/b ratio. The same trend is seen in Figures 4.20 and 4.22. Permeability is dependent on the nature, amount and continuity of the concrete pore structure where flow occurs by permeation. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced which results in the 'beneficial' reduction of permeability as explained by Mehta and Manmohan (1980).

From the k values given in Figures 4.18, 4.20 and 4.22, it is clear that the difference in all values between the two w/b ratios of 0.40 and 0.55 falls between 30 % and 40 %. It is also evident that there are clusters between mixes of the same binder type at each respective w/b ratio. This is attributed to the pore filling nature of each binder type. The reduction in permeability values between the two w/b ratios is attributed to a reduction in pore connectivity through hydration.

From the results it also seen that the FA blended mixes exhibit slightly lower but not statistically different k values than the OPC reference mixes. Permeability results reported by Mackechnie, (1996) of wet cured plain OPC and FA blended concrete mixes support this. The Cape Town GGCS blended mixes however have considerably higher k values at both w/b

ratios compared to the plain OPC control mixes and the other regional concrete mixes. Ballim et al (2009) and Du Preez (2002) reported a similar trend.

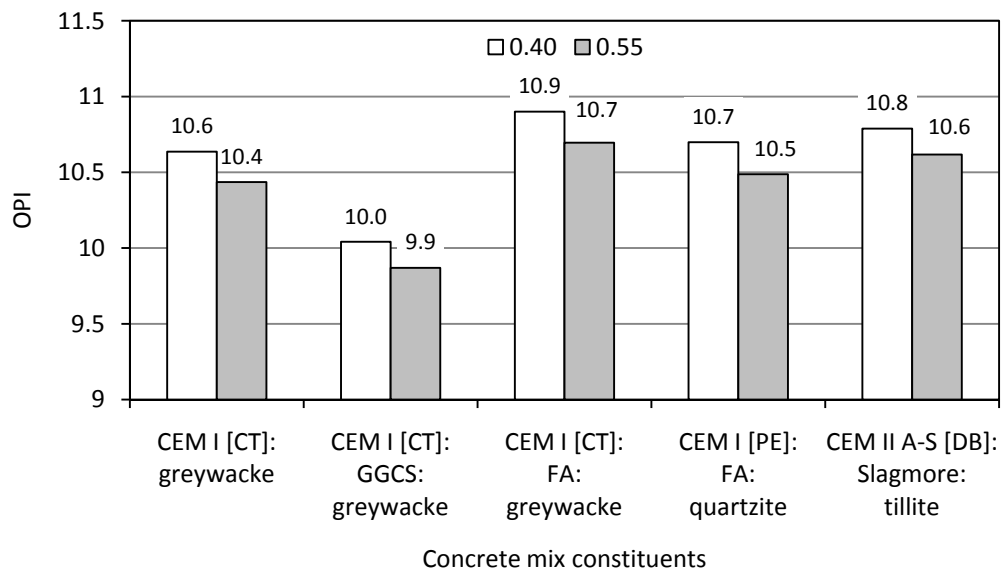


Figure 4.17: 28-day OPI values of the regional concrete mixes

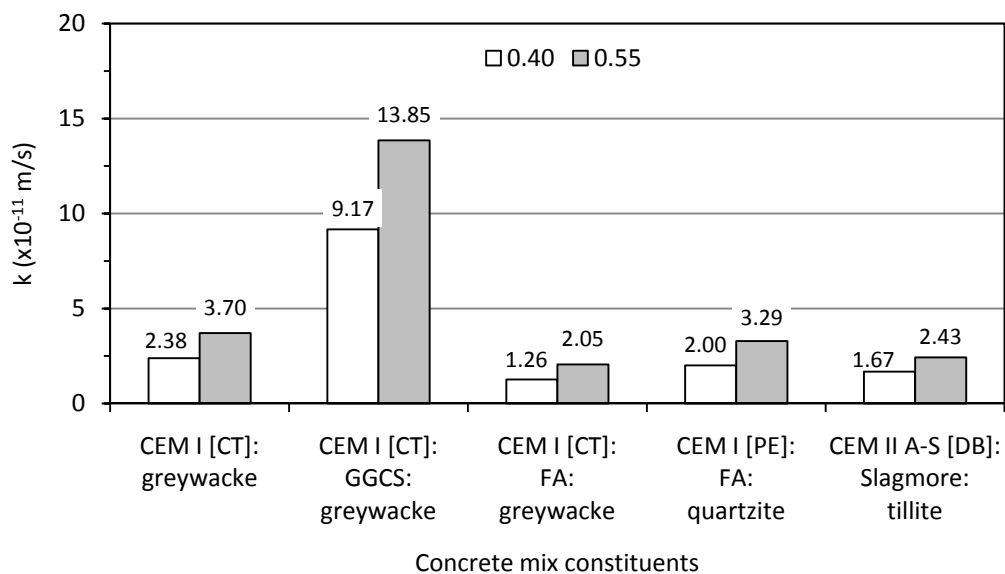


Figure 4.18: 28-day k values of regional concrete mixes

The transformed 28 day OPI values illustrated in Figure 4.17 are however higher than values reported by Mackechnie (1996) and Ballim et al (2009) for the concrete mixes containing greywacke. The use of crushed rock as fine aggregate which improved the density and probably the particle packing efficiency could have caused the improved OPI values.

Considering the OPI values for the concrete mix containing Durban CEM II A-S [DB]: Slagmore: tillite mix, it would be expected that the mix would show similar permeability

characteristics as the Cape Town GGCS blended mix. The Durban binders are largely composed of CEM I clinker and GGBS with a small 8 % proportion of FA. However, the k values for this concrete mix are in the range of the concrete mixes containing 30 % FA as an extender. Interestingly, the same mix also shows good chloride resistance in terms of CCI values as seen in Figures 4.11 and 4.12. This synergistic effect was also reported by Aïtcin (2008). The favourable chloride resistance behaviour is attributed to the chloride binding capacity of the slag component. The low permeability is thought to be a result of the pore filling nature of FA. This however requires further investigation with varying amounts of FA being substituted in ternary blended concrete mixes for validation.

In comparison with OPI values reported by Mackechnie (1996) and Ballim et al (2009), the values obtained in this study are favourably better. It is thought that the use of crushed rock as fine aggregate in concrete mixes of this study could have contributed to the general decreased permeability characteristics of the concrete mixes. As discussed earlier, the use of crushed rock improved the packing density of the aggregate phase thereby reducing ionic transport through the ITZ and the void content of the mixes.

The OPI values obtained from samples tested in this study are also found to be favourably higher than those recommended by Alexander et al (1999a), as satisfactory for adequate performance in the marine environment provided sufficient cover depth is provided.

At both w/b ratios the regional mixes are ranked as follows in order of decreasing OPI values at 28 days: FA blended mixes > Slagmore blended mixes > plain OPC mixes > GGCS blended mixes. The differences within the FA and Slagmore blended binder types are nevertheless small and the order is adopted for practicality.

4.4.2 Influence of binder type

Figures 4.19 and 4.20 illustrate 28-day OPI and coefficient of permeability (k) values of samples of concrete made with Cape Town aggregates and the different binder types typically used in the urban marine regions. This is done to determine the influence of binder type on permeability at the w/b ratios of 0.40 and 0.55.

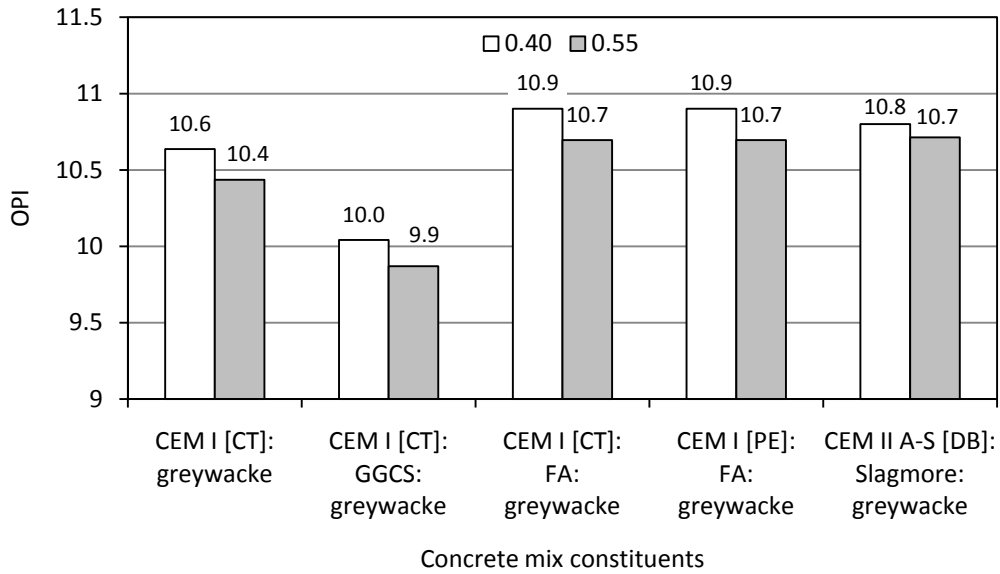


Figure 4.19: 28-day OPI values of a range of different mixes made with Cape Town aggregates and different regional binders

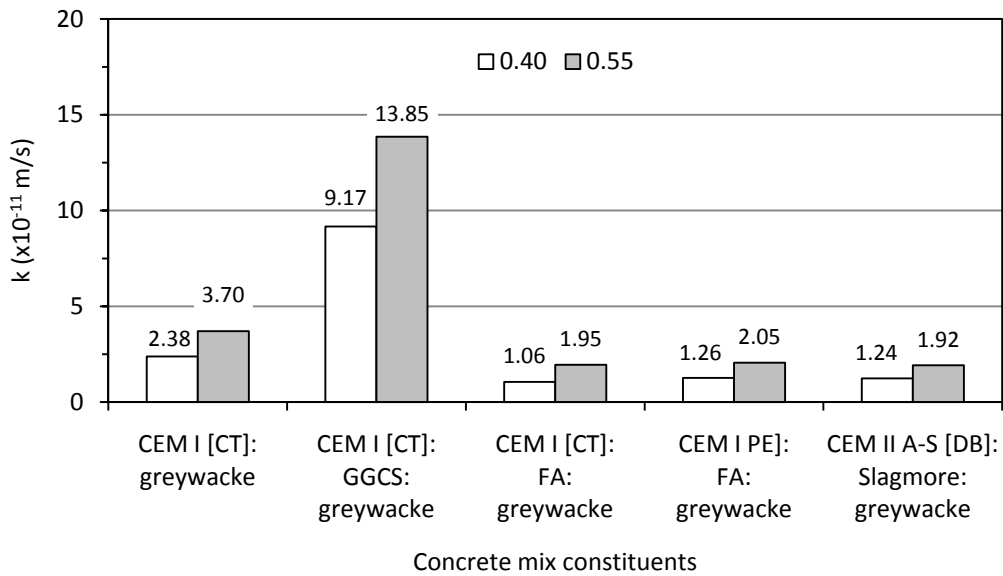


Figure 4.20: 28-day k values of a range of concrete mixes made with Cape Town aggregates and different regional binders

The concrete mixes made with GGCS as an extender have comparatively higher k values and hence higher permeability characteristics than the other concrete mixes. This is consistent with the results illustrated in Figures 4.22. The increase in permeability is on average 80 %. A similar trend was seen in the results reported by Ballim et al (2009) and Mackechnie (1996) on wet cured samples.

Moranville-Regourd (1998) and Taylor (1990) explain that this is characteristic of certain hardened slag mixes. The use of slag in concrete results in larger pore sizes than equivalent w/b ratio plain OPC mixes. Though the general pore structure may be discontinuous, it is thin-walled resulting in a more permeable concrete matrix. The concrete pore structure is related to the calcium hydroxide (CH) content of a binder phase. In slag mixes, the CH content is reduced leading to a highly permeable pore structure. It is concluded, that the use of GGCS as an extender results in concrete of relatively higher permeability than concrete mixes made with plain OPC binder or OPC binder extended with FA.

The FA blended mixes have lower k values than the plain OPC mixes at both w/b ratios by up to 50 %. This is attributed to the pore filling nature of FA. As was seen for the chloride conductivity values, it is also noted that the CEM I [CT] and [PE] concrete mixes blended with FA have similar values. As the FA used was from the same batch, this would portend that CEM I [CT] and [PE] impart similar permeability characteristics to concrete. This means that plain OPC cements from Cape Town and Port Elizabeth are similar from a permeability perspective.

Concrete mixes made with Durban CEM II A-S [DB]: Slagmore binder have k values that were within the range of concrete produced with FA only as an extender. These values are also much lower compared to those obtained with concrete blended with GGCS. GGCS has a chemical composition similar to GGBS hence it would be expected that both concrete mixes would have comparable permeability characteristics. This is however not seen. It is thought that FA refines the pore structure of the concrete mix making it more impermeable than the concrete mix blended with GGCS. This synergistic effect was discussed earlier.

From the permeability results given in Figures 4.18 and 4.20, it becomes evident that the inclusion of FA and Slagmore in a mix has a greater reduction effect of up to 50 % in lowering permeability values than reducing w/b ratio. W/b ratio was found to reduce k values by up to 40 %.

From the permeability results presented, the ranking of OPI values adopted earlier is seen again, i.e. FA blended mixes > Slagmore blended mixes > plain OPC mixes > GGCS blended mixes.

4.4.3 Influence of aggregate type

Figures 4.21 and 4.22 illustrate OPI and coefficient of permeability (k) values of samples from different concrete types made with GGCS and CEM I [CT] at 28 days respectively, and at two w/b ratios. This is done to find the influence of aggregate type on permeability. The influence of w/b ratio and binder type seen in the figures was discussed earlier.

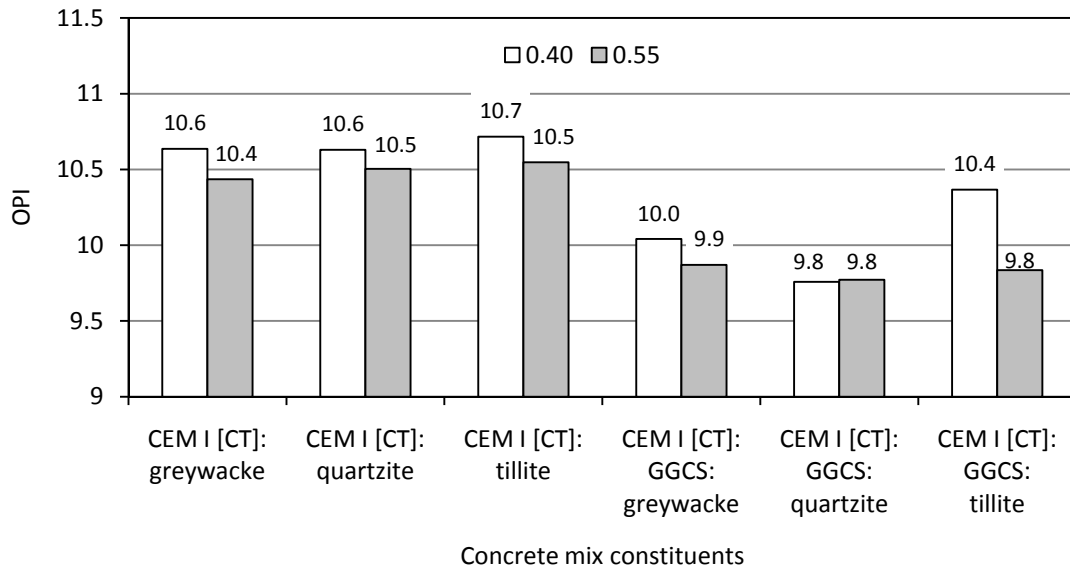


Figure 4.21: 28-day OPI values of concrete of different mixes made with Cape Town binders and the regional aggregates

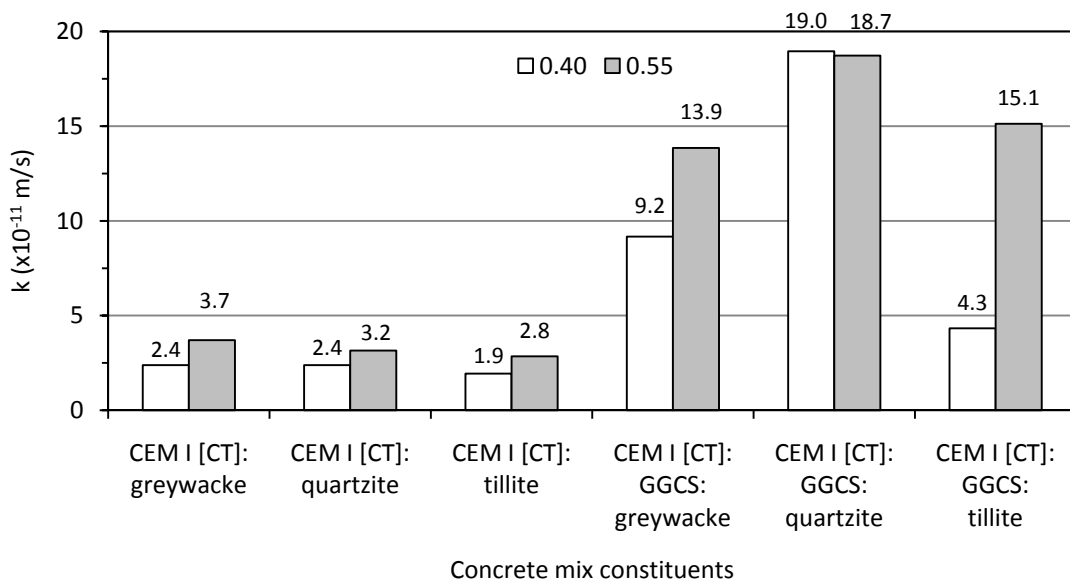


Figure 4.22: 28-day k values of concrete of different mixes made with Cape Town binders and the regional aggregates

From Figures 4.21 and 4.22, the GGCS blended mixes with quartzite aggregate exhibit anomalous results that cannot be explained. However, ignoring these anomalous results, permeability results show consistency and are comparable at each w/b ratio. This indicates that aggregate type has no appreciable influence on permeability.

4.4.4 Influence of continued moist curing

Figures 4.23 - 4.25 show the effect of continued moist curing on OPI values of all the 0.40 and 0.55 w/b ratio mixes concrete mixes.

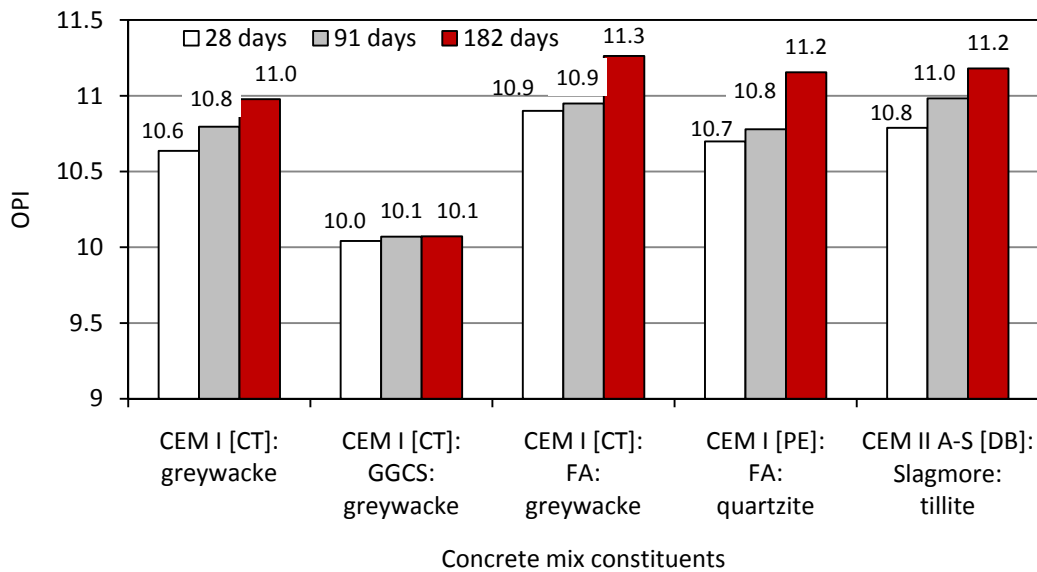


Figure 4.23 (a): 0.40 w/b ratio OPI values of the regional concrete mixes at 28, 91 and 182 days

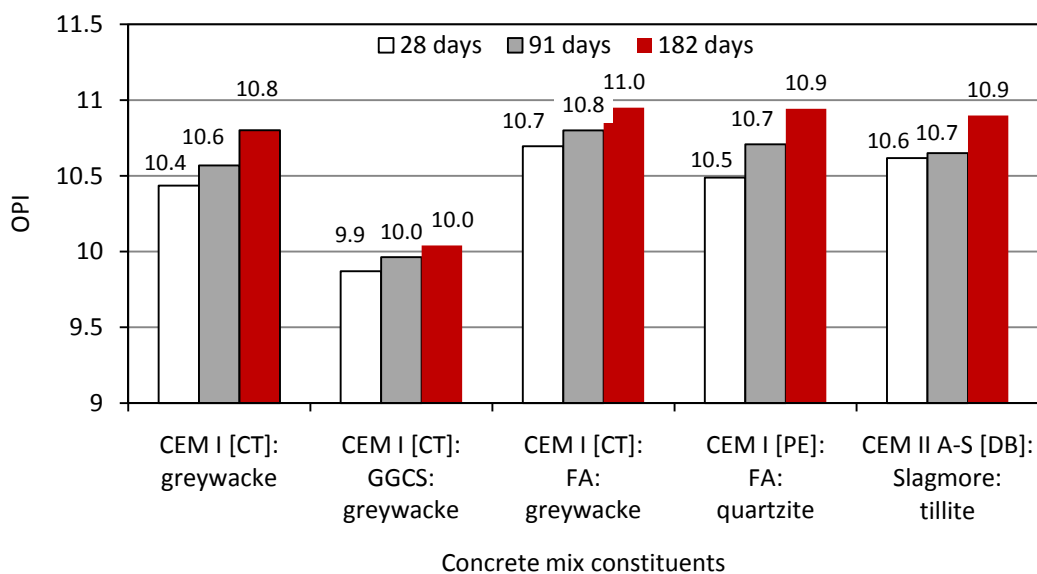


Figure 4.23 (b): 0.55 w/b ratio OPI values of the regional concrete mixes at 28, 91 and 182 days

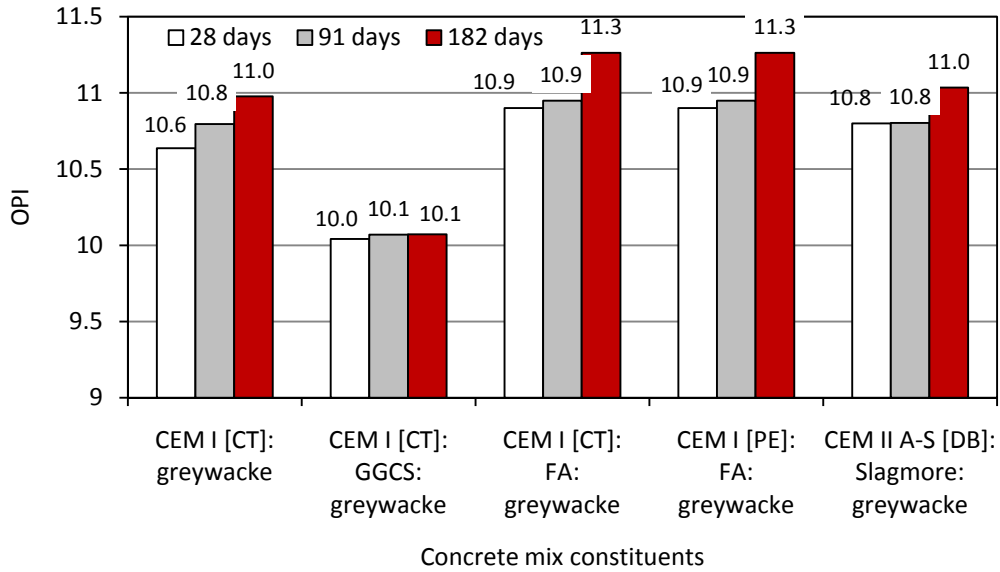


Figure 4.24 (a): 0.40 w/b ratio OPI values of concrete mixes made with Cape Town aggregates and the regional binders at 28, 91 and 182 days

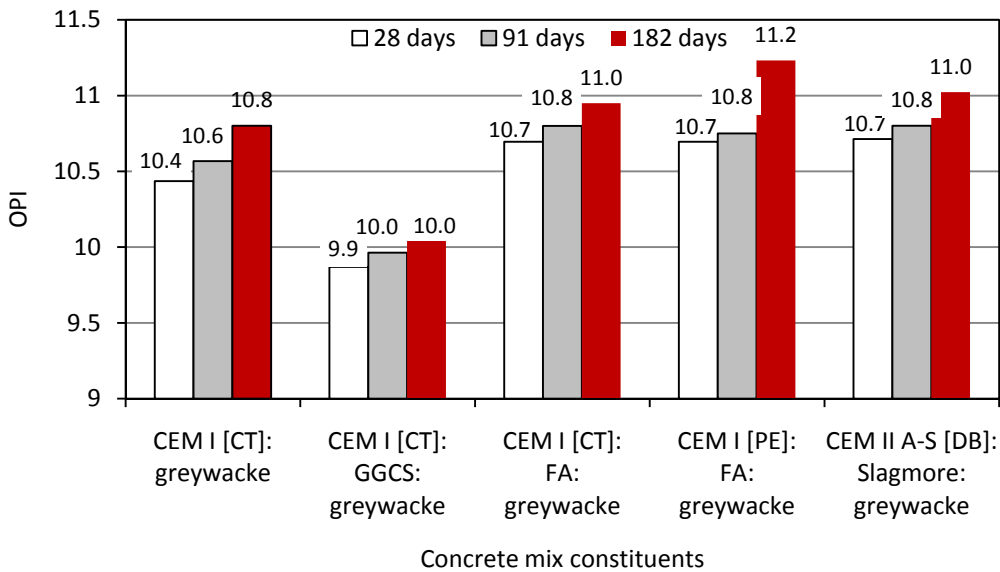


Figure 4.24 (b): 0.55 w/b ratio OPI values of concrete mixes made with Cape Town aggregates and the regional binders at 28, 91 and 182 days

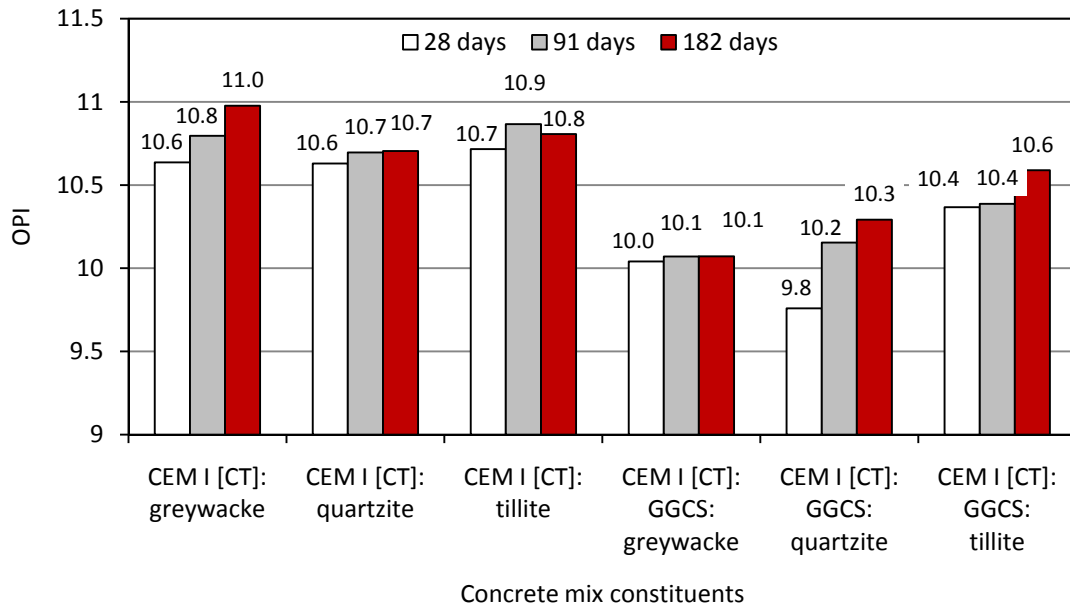


Figure 4.25 (a): 0.40 w/b ratio OPI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

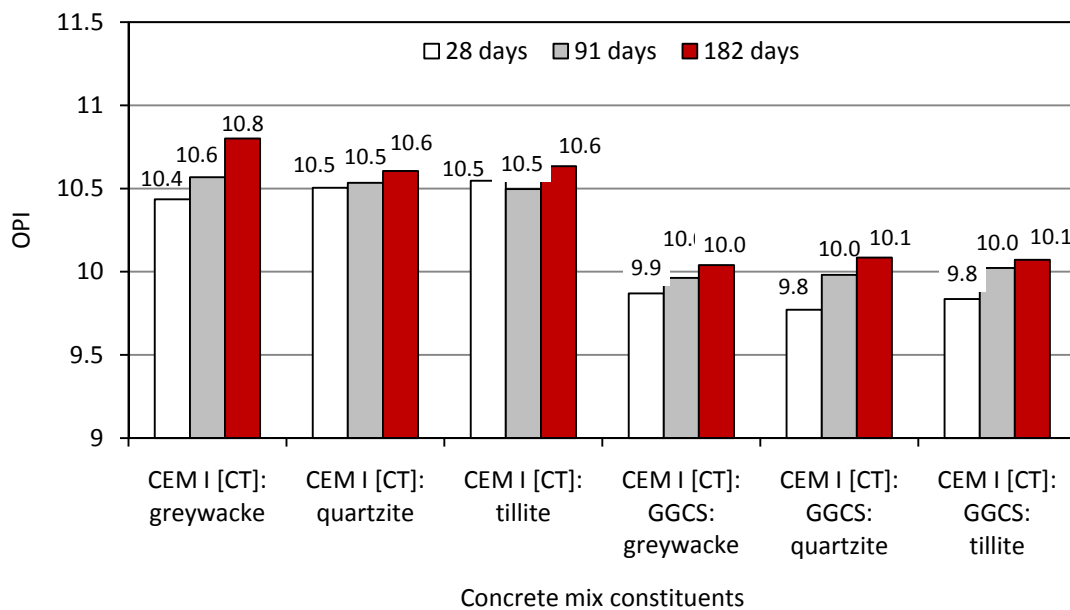


Figure 4.25 (b): 0.55 w/b ratio OPI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

From an engineering perspective, given the extended period of moist curing, no significant difference on OPI values is evident for the slag blended mixes. It is thought that development of the permeability characteristics of the pore structure of slag blended mixes occurs within the first 28 days. The plain OPC and FA blended mixes exhibit an appreciable

increase in OPI values with time. With FA being a slow reacting pozzolanic binder, this increase in OPI values shows that with continued curing, hydration continues in FA blended mixes after 28 days.

A statistical analysis of the k values (see Appendix A) of the concrete mixes did not show any significant difference between the values. From this it is concluded that continued moist curing after 28 days does not cause any appreciable improvement in the permeability characteristics of the concrete mixes.

4.4.5 Summary remarks

From the permeability results presented, it is seen that the mixes containing FA in their binder composition have the lowest permeability coefficient values (and conversely high OPI values). This is attributed to the pore filling nature of FA when used as an extender. The plain OPC mixes also exhibit similar permeability values while the GGCS blended mixes show the least resistance to oxygen permeability.

With regard to w/b ratio, the lower 0.40 w/b ratio mixes have higher resistance to oxygen permeability in comparison to the relatively 'poorer' 0.55 w/b ratio mixes. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced which results in the 'beneficial' reduction of permeability.

Aggregate type does not have a prevailing influence on permeability results, as no appreciable influence on permeability is seen between mixes of similar binder type. The results show consistency and are comparable at each w/b ratio.

Looking at the extended period of moist curing, no significant difference in OPI values is evident for the GGCS blended mixes. It is thought that development of the permeability characteristics of the pore structure of GGCS blended mixes occurs within the first 28 days. The plain OPC, Slagmore and FA blended mixes however exhibit an appreciable increase in OPI values with time. With respect to the latter two blended mixes which contain FA, the FA component is a slow reacting pozzolanic binder requiring an extended period of hydration. This was facilitated by the continued curing done, hence the change in permeability values for these mixes after 28 days.

From the permeability results given, it is seen that the inclusion of FA and Slagmore in a mix has a greater reduction effect in lowering permeability values than reducing w/b ratio. The addition of GGCS in a mix however has the effect of increasing permeability values more than changing w/b ratio, continued moist curing or changing aggregate type respectively.

4.5 Water sorptivity index

The water sorptivity index (WSI) is described by Alexander et al (1999) as characterising the rate of movement of a wetting front through concrete under the action of capillary forces. The WSI test uses the mass of water absorbed from the bottom face (exposed face) as a measure of sorptivity of a concrete sample. As a rule, lower sorptivity values represent more impermeable and high quality concrete. Ballim (1993) found the test to be sensitive to the nature and degree of early curing of the cover concrete which affects the micro-structure. The test is recommended for use to assess construction quality of on-site concrete. Comparing the curing regimes, Mackechnie (1996) reported significant differences of between 25 % and 70 % in sorptivity values for wet and dry cured concrete.

Comparison of sorptivity values is made on the basis of regional concrete type, grade of concrete, mix constituents (aggregate and binder) and the duration of moist curing. All the concrete mixes are compared to the Cape Town plain OPC control mixes at the two w/b ratios of 0.40 and 0.55. Details of the statistical analysis done on the WSI test values are given in Appendix A.

4.5.1 Regional trend and influence of w/b ratio

Figure 4.26 illustrates 28-day WSI values of test specimens from the different regional South African marine mixes.

From the figure, it is clear that concretes at the lower 0.40 w/b ratio have lower WSI values than concretes at the higher 0.55 w/b ratio. The other concrete mixes also exhibit this trend as shown in Figures 4.27 and 4.28. For the plain OPC and GGCS blended mixes, the reduction in values is up to 5 %, while for the FA and Slagmore blended mixes, the reduction in sorptivity values is up to 14 %.

Sorptivity is largely dependent on the pore geometry and the degree of saturation of the concrete matrix. Low WSI values translate to less permeable concretes of improved quality. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in a reduction of the sorption characteristics as explained by Glass (2003) and Mackechnie (1996).

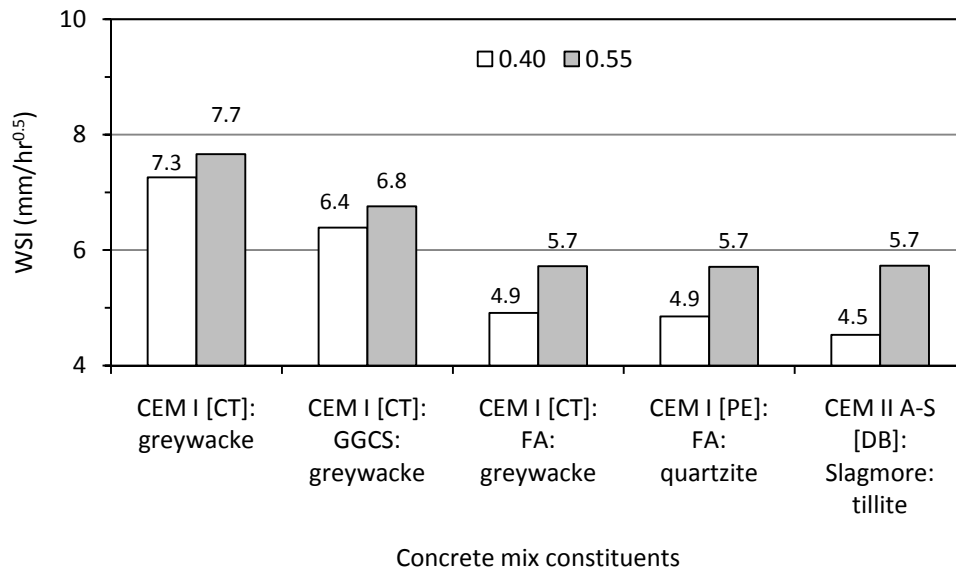


Figure 4.26: 28-day WSI values of the regional concrete mixes

Considering the different blended regional mixes, they exhibit lower sorptivity values than the Cape Town plain OPC control mix. Mackechnie (1996) reported that moist cured concrete blends of GGCS and FA have lower sorptivity values than plain OPC mixes. This is indicative of the beneficial use of cementitious extenders which generally improve the micro-structure properties of extended concretes. This effect of binder type will be discussed further below.

At both w/b ratios the regional mixes are ranked as follows in order of increasing sorptivity values at 28 days: FA blended mixes < Slagmore blended mixes < GGCS blended mixes < plain OPC mixes. The differences between the FA and Slagmore blended binder mixes are however small.

4.5.2 Influence of binder type

Figure 4.27 illustrates 28-day WSI values of samples from concrete made with Cape Town aggregates and the different regional binders. This is done to find the influence of binder type on sorptivity at the two w/b ratios of 0.40 and 0.55. The influence of using SCM in concrete mixes is also seen in Figure 4.26 and 4.28.

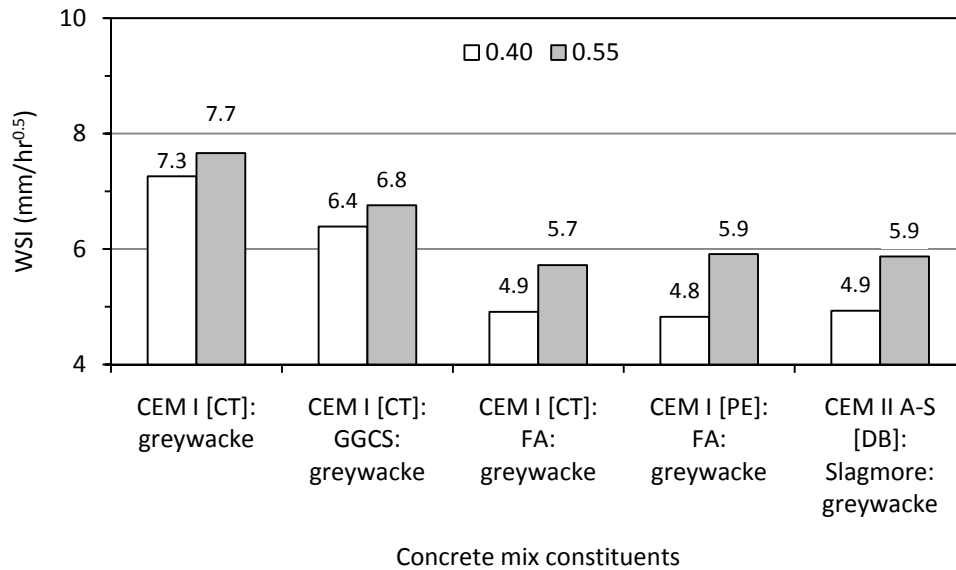


Figure 4.27: 28-day WSI values of a range of different mixes made with Cape Town aggregates and different regional binders

All the blended mixes have lower WSI values than the plain OPC mixes. From the figure, three distinct classes of binder type appear, similar to those in Figures 4.19 and 4.20 for permeability results. The FA blended concrete mixes have the same range of lower WSI values in one group. The inclusion of these extender types in an OPC mix results in a reduction in values of up to 34 % for the 0.40 w/b ratio mixes and up to 24 % for the 0.55 w/b ratio mixes. This is attributed to the pore filling nature of FA. The GGCS blended concrete mixes have higher WSI values than these two blended binder types. This trend is seen at both w/b ratios. Figure 4.28 also illustrates the effect on sorptivity of blending an OPC mix with GGCS. Mixes with GGCS have comparatively lower sorptivity values than plain OPC concrete mixes by an average of up to 11 % at both tested w/b ratios. With regards to the CEM II A-S [DB]: Slagmore mixes, their range of sorptivity values is similar to the FA only blended mixes. It is surmised that the inclusion of FA in the mainly slag binder has resulted in

the reduction of the sorptivity characteristics. This synergistic effect was also observed for the Durban blended binders where they exhibit good chloride ingress resistance (Figure 4.4), low chloride conductivity values (Figure 4.12) and low permeability characteristics (Figures 4.19 and 4.20).

In the foregoing discussion, it becomes evident that the influence of SCM in a mix is more effective in reducing sorptivity values than the effect of reducing w/b ratio. FA and Slagmore blended mixes exhibit this trend far much more than GGCS blended mixes at both w/b ratios.

At both w/b ratios the regional mixes are ranked as follows in order of decreasing sorptivity values at 28 days: FA blended mixes < Slagmore blended mixes < GGCS blended mixes < plain OPC mixes. The differences within the FA and Slagmore blended binder types are nevertheless small and the order is adopted for practicality.

4.5.3 Influence of aggregate type

To determine the influence of aggregate type on the sorptivity characteristics of concrete, samples were made with Cape Town binders and the different regional aggregate types. Figure 4.28 illustrates 28-day WSI values of samples at the two w/b ratios of 0.40 and 0.55. The influences of w/b ratio and binder type were discussed earlier.

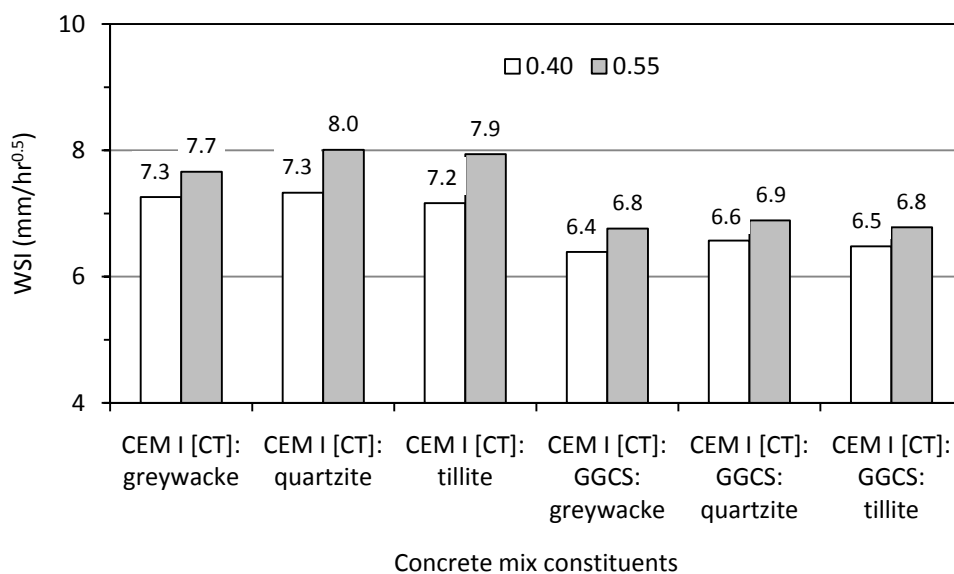


Figure 4.28: 28-day WSI values of concrete of different mixes made with Cape Town binders and the regional aggregates

Similar to the CCI and OPI results, the WSI results show that for each binder type sorptivity values are not significantly different, and more essentially independent of aggregate type.

4.5.4 Influence of continued moist curing

Figures 4.29 - 4.31 show the effect of continued moist curing of all the concrete mixes on OPI values. The figures show the values for 0.40 and 0.55 w/b ratio mixes respectively at 28, 91 and 182 days.

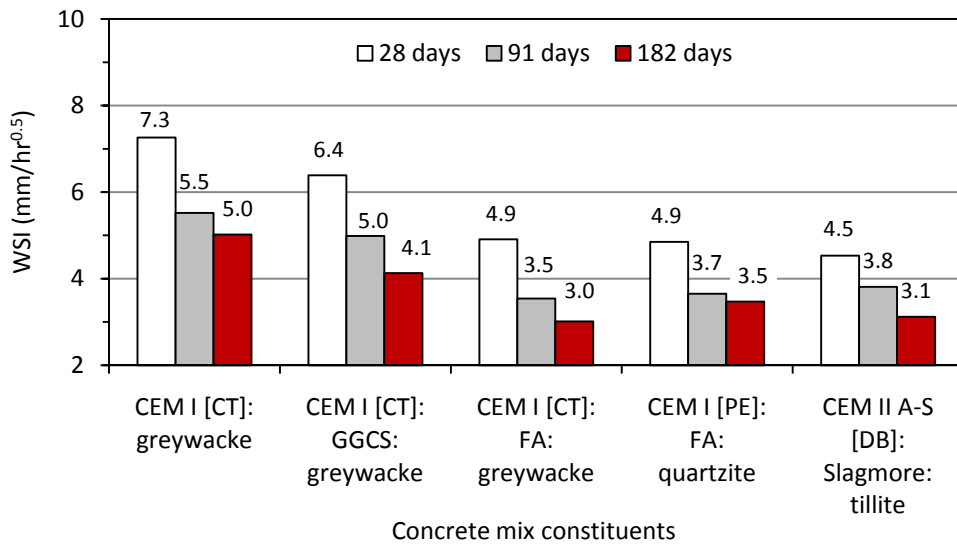


Figure 4.29 (a): 0.40 w/b ratio WSI values of the regional mixes at 28, 91 and 182 days

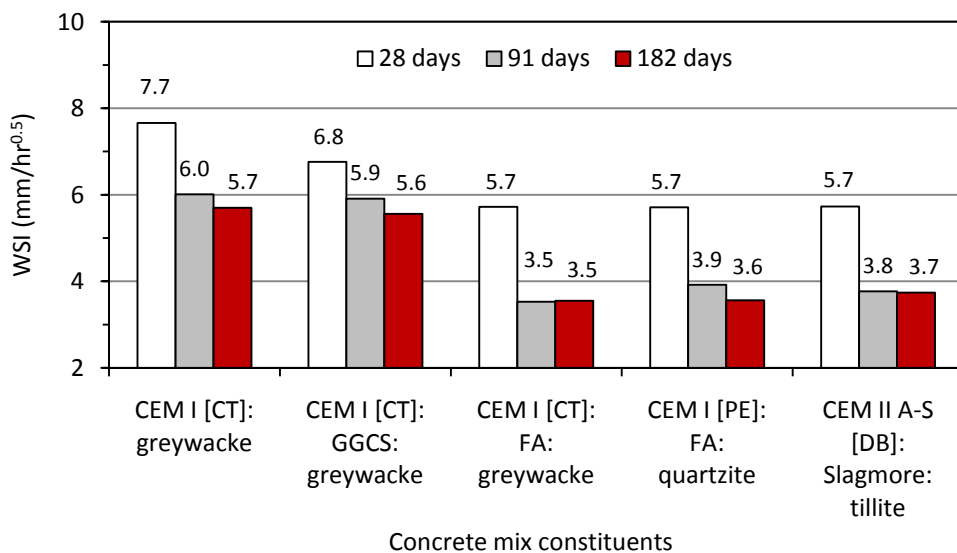


Figure 4.29 (b): 0.55 w/b ratio WSI values of the regional mixes at 28, 91 and 182 days

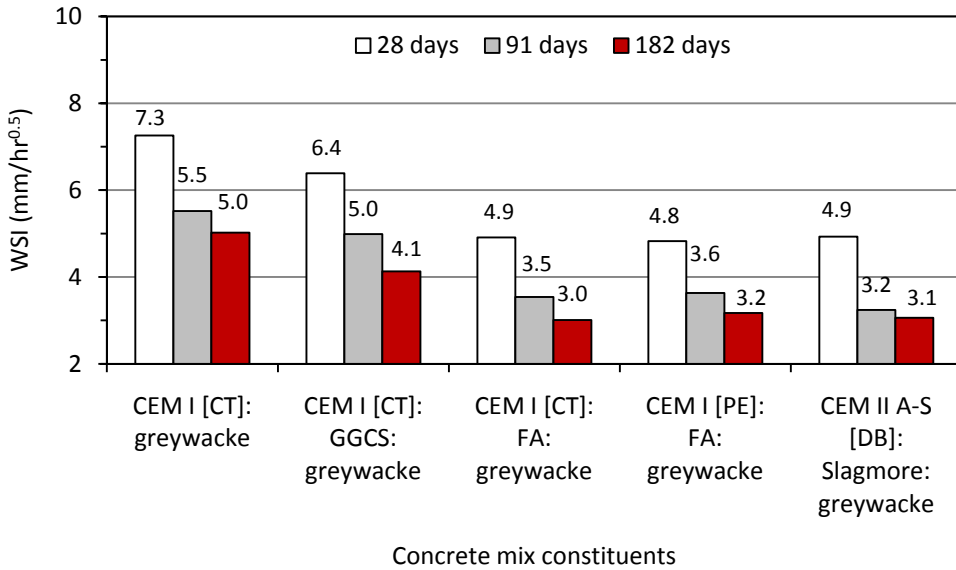


Figure 4.30 (a): 0.40 w/b ratio WSI values of concrete mixes made with Cape Town aggregates and the regional binders at 28, 91 and 182 days

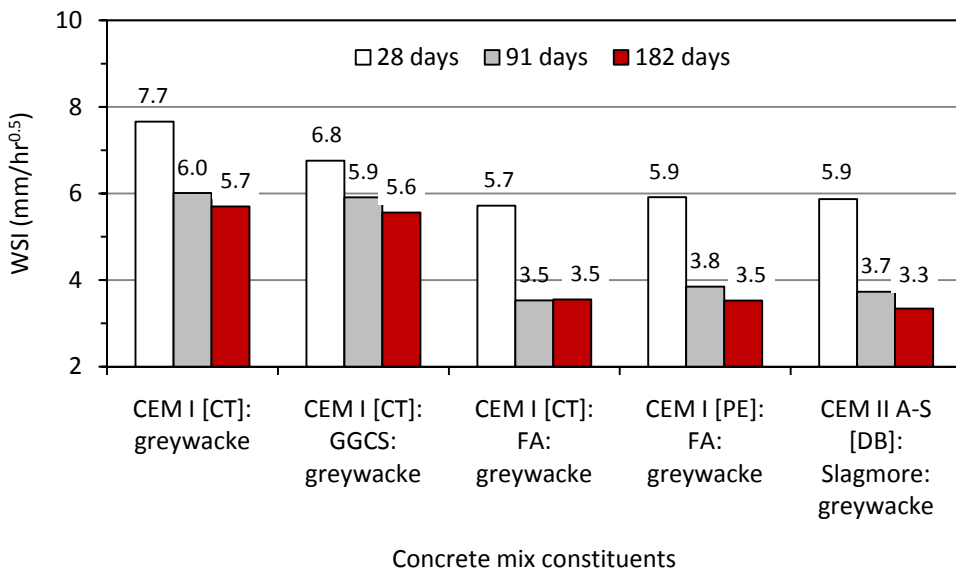


Figure 4.30 (b): 0.55 w/b ratio WSI values of concrete mixes made with Cape Town aggregates and the regional binders at 28, 91 and 182 days

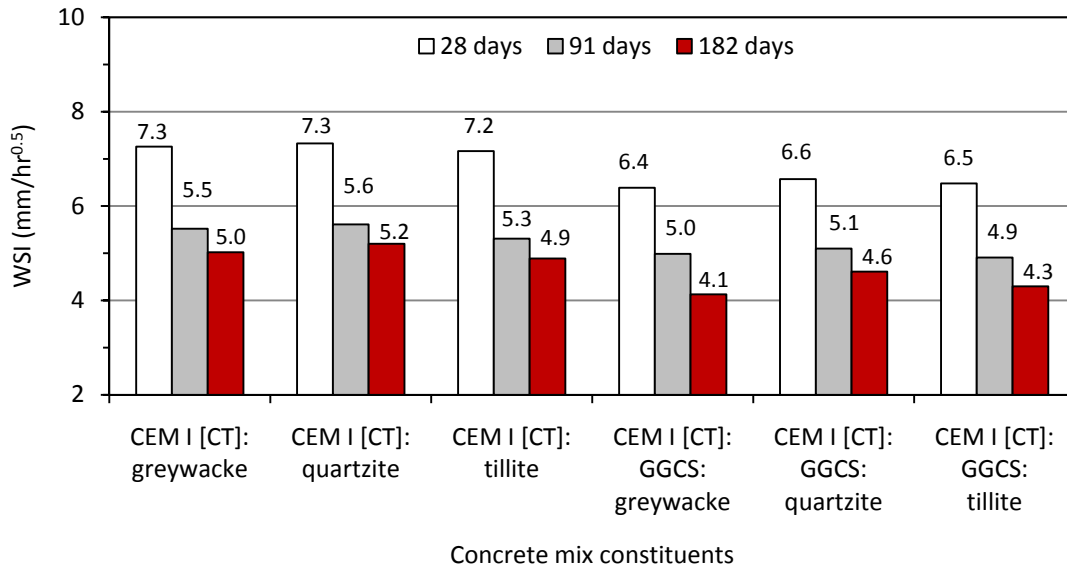


Figure 4.31 (a): 0.40 w/b ratio WSI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

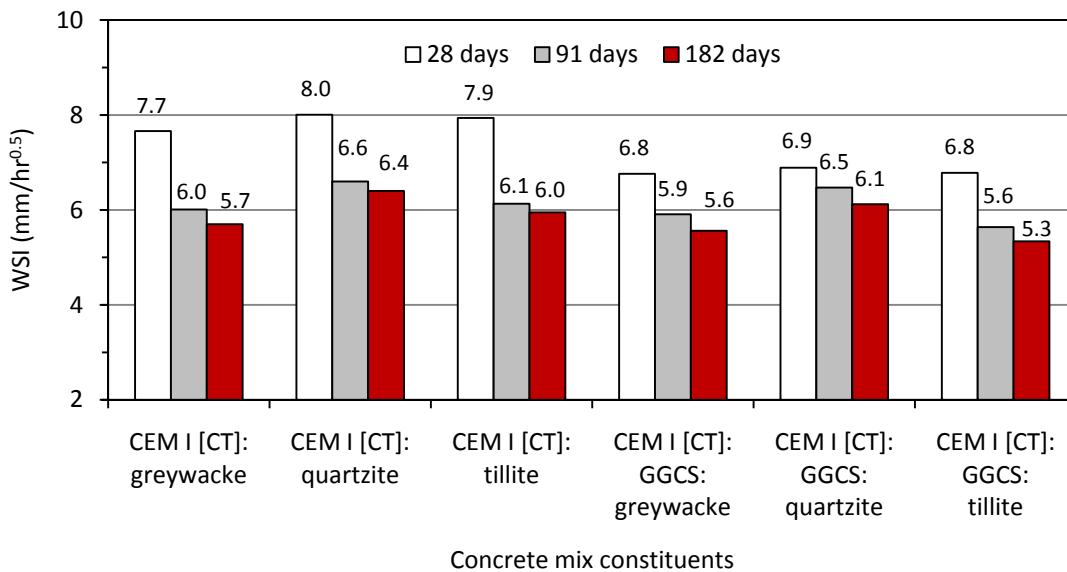


Figure 4.31 (b): 0.55 w/b ratio WSI values of concrete mixes made with Cape Town binders and the regional aggregates at 28, 91 and 182 days

It is clear that with continued moist curing there is a decrease in sorptivity values. The FA and Slagmore blended mixes show a reduction of up to 35 % between the ages of 28 and 91 days. This is indicative of continued hydration leading to a reduction in porosity. The GGCS blended mixes exhibit a reduction of 22 % at the lower 0.40 w/b ratio and 12 % at the higher w/b ratio between 28 and 91 days. The plain OPC control mixes have a reduction of 17 % and 32 % at the 0.40 and 0.55 w/b ratios respectively.

Between 91 and 182 days, the blended concrete mixes showed little appreciable reduction in sorptivity values. At this age, all the concretes offer similar sorption resistance to concrete.

4.5.5 Summary remarks

Considering the different binder types, it is seen that the blended binder mixes exhibit lower sorptivity values than the plain OPC control mixes. The beneficial use of cementitious extenders is to generally improve the micro-structure properties of extended concretes. This effect is mainly due to the finer particle nature of the extenders which improve the pore structure of a concrete matrix making it inaccessible to penetration.

With regard to w/b ratio, the lower 0.40 w/b ratio mixes are of improved quality compared to 0.55 w/b ratio mixes as the latter have higher sorptivity characteristics. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in a reduction of the sorption characteristics.

Aggregate type does not have a prevailing influence on the sorptivity characteristics of the mixes tested, as no significant difference is seen in WSI values between mixes of similar binder type. The results show consistency and are comparable at each w/b ratio.

With the extended period of moist curing, it is evident that sorptivity values decrease with time particularly between the ages of 28 and 91 days. This is indicative of continued hydration leading to a reduction in porosity. FA and Slagmore blended mixes show the greatest improvement followed by the GGCS blended mixes and plain OPC mixes respectively.

From the sorptivity results given, it is evident that the inclusion of FA and Slagmore in a mix has a greater reduction effect in lowering sorptivity values than reducing w/b ratio, continued moist curing or changing aggregate type respectively. The addition of GGCS in a mix is much lower than for the other two blended binder mixes.

4.6 Cube compressive strength

It should be noted that though cube compressive strength is a fundamental factor as regards structural design, it is not a reliable durability performance indicator. This is especially so in the marine environment where design against corrosion deterioration is a key consideration (Aïtcin, 2008). As such, though compressive strength results are presented, it is not intended to link them to potential durability. It is however appreciated that the same influences that control the transport processes also weigh on compressive strength development and thus deserve mention. These are w/b ratio, binder type and sample age in addition to aggregate type. The scope of discussion is therefore limited to giving a generalised assessment of trends only.

4.6.1 Regional trend and influence of w/b ratio

Figures 4.32 (a) and (b) respectively illustrate the gain in compressive strength with time for the 0.40 and 0.55 w/b ratio regional concrete mixes.

From the figures, it is evident that concretes at the lower w/b ratio have significantly higher strength values than concretes at the higher 0.55 w/b ratio at all sample ages. This is also seen for the other concrete mixes produced as shown in Figures 4.33 and 4.34. The Powers model relates the gel: space ratio as controlling the compressive strength of concrete. At the lower w/b ratio, the overall gel volume is larger resulting in higher strength values (Perrie, 2009).

It is also seen that the Cape Town GGCS blended mixes have the highest strength values while the Durban Slagmore blended mixes have the lowest strength values for a given w/b ratio at all sampled ages. The two FA blended mixes have comparable strength values across all sample ages. The Cape Town plain OPC mixes have comparatively better performance regarding strength compared to the transport processes discussed. Three distinct bands are seen in each figure. At the top end, is concrete containing CEM I [WC]: GGCS: greywacke. At the lower end, the Durban mix containing CEM II A-S [DB]: Slagmore: tillite exhibits lower strength values. In between are the FA blended concrete mixes and the plain OPC reference mix.

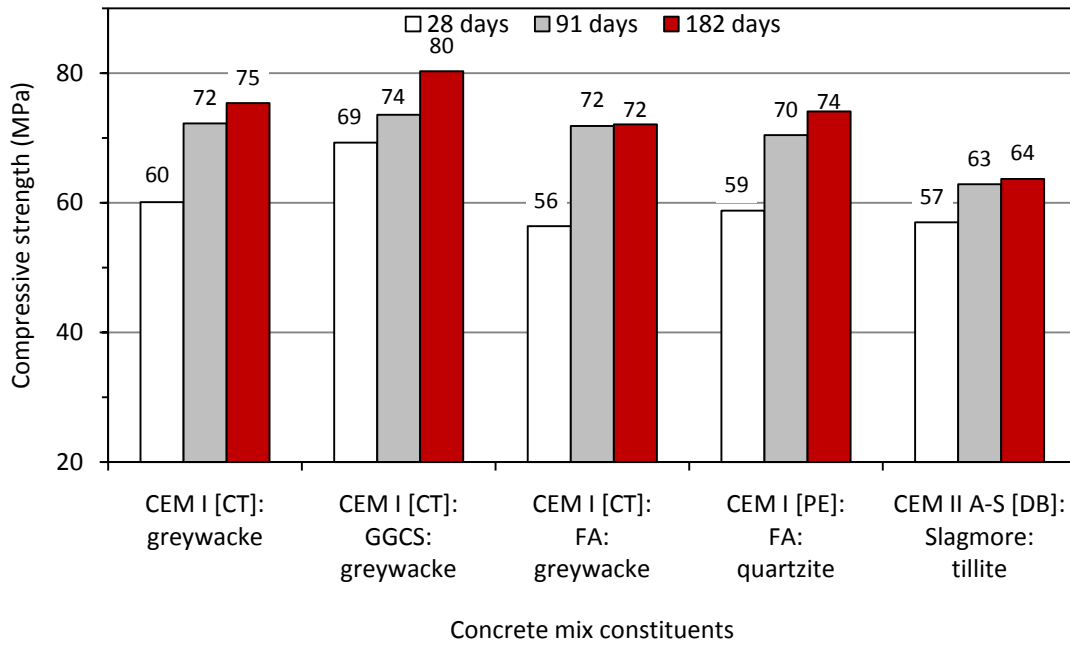


Figure 4.32 (a): Compressive strength development of the regional concrete mixes - 0.40 w/b ratio

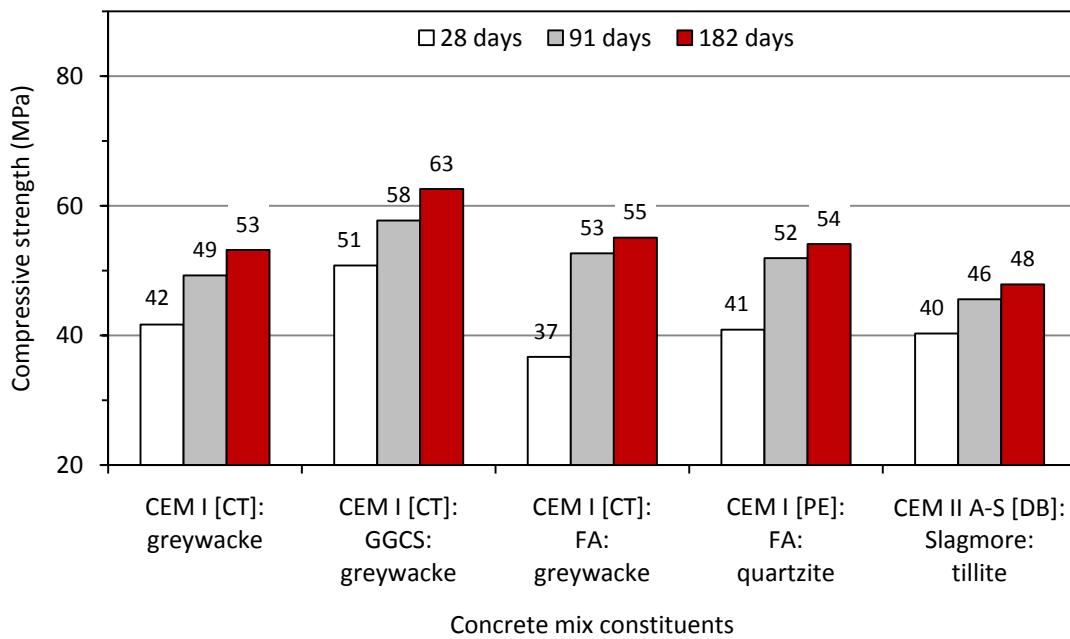


Figure 4.32 (b): Compressive strength development of the regional concrete mixes - 0.55 w/b ratio

4.6.2 Influence of binder type

Figures 4.32 (a) and (b) respectively illustrate the gain in compressive strength with time for the 0.40 and 0.55 w/b ratio concrete mixes produced with different regional binders and Cape Town aggregates.

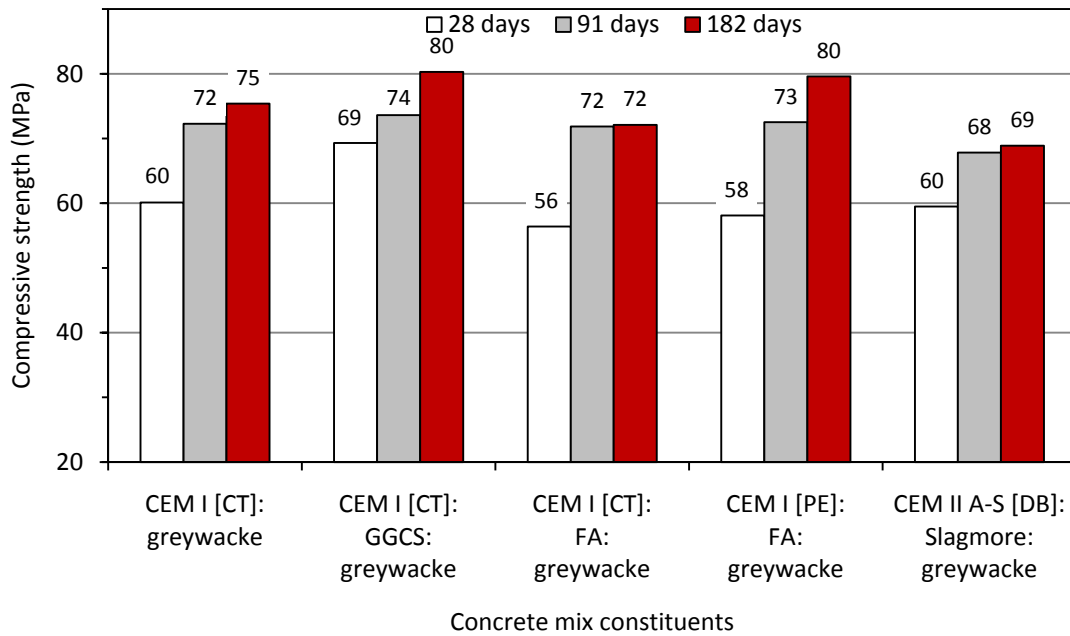


Figure 4.33 (a): Compressive strength development of different mixes made with Cape Town aggregates and the different regional binders - 0.40 w/b ratio

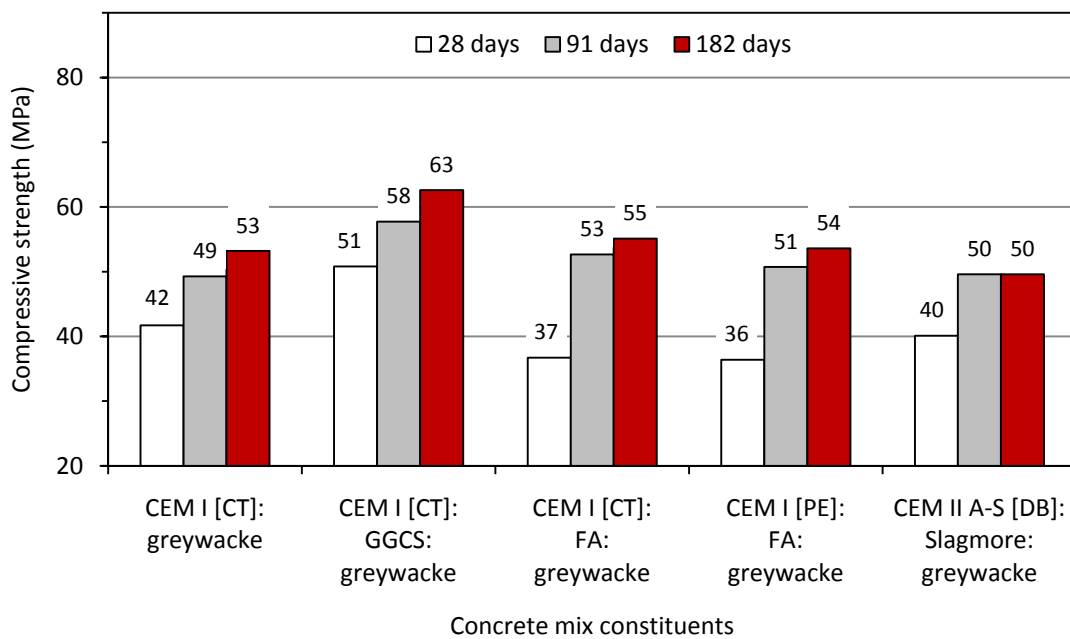


Figure 4.33 (b): Compressive strength development of different mixes made with Cape Town aggregates and the different regional binders - 0.55 w/b ratio

From the figures, the influence of w/b ratio discussed earlier is clearly evident. On the influence of binder type, the behaviour exhibited by the GGCS blended mixes, has also been reported by Alexander et al (2003) who attributed it to its higher reactivity. Figure 4.36 also shows this trend, where the inclusion of GGCS in a plain OPC mix results in higher strength values at all sample ages. The FA blended mixes have lower 28-day strengths which increase by more than 20 % after 91 days of continued moist curing. FA is a slow reacting pozzolanic binder with much slower and extended hydration periods. The extended moist curing period is beneficial in terms of these concrete mixes attaining higher strength values. At the later 182-day sample age, the Durban CEM II A-S [DB]: Slagmore mix has the lowest strength values. This is attributed to the lower CaO content in the blended binder compared to the other blended binders and plain OPC binder (Table 3.1).

4.6.3 Influence of aggregate type

Figures 4.34 (a) and (b) respectively illustrates the gain in compressive strength with time for the 0.40 and 0.55 w/b ratio concrete mixes produced with different South African aggregates and Cape Town binders.

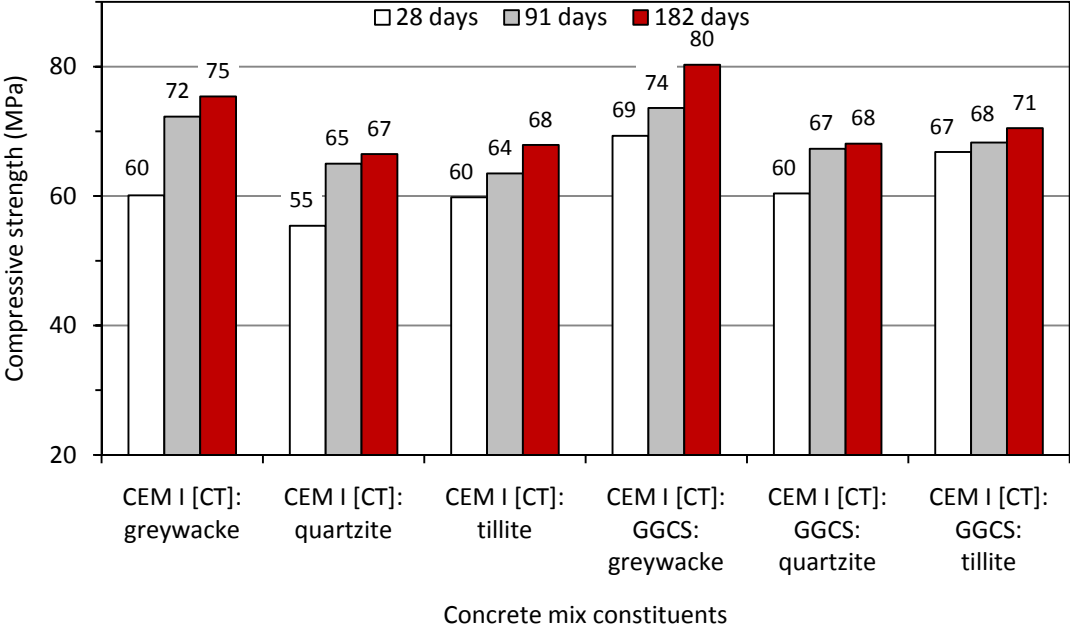


Figure 4.34 (a): Compressive strength development of concrete of different mixes made with Cape Town binders and the regional aggregates - 0.40 w/b ratio

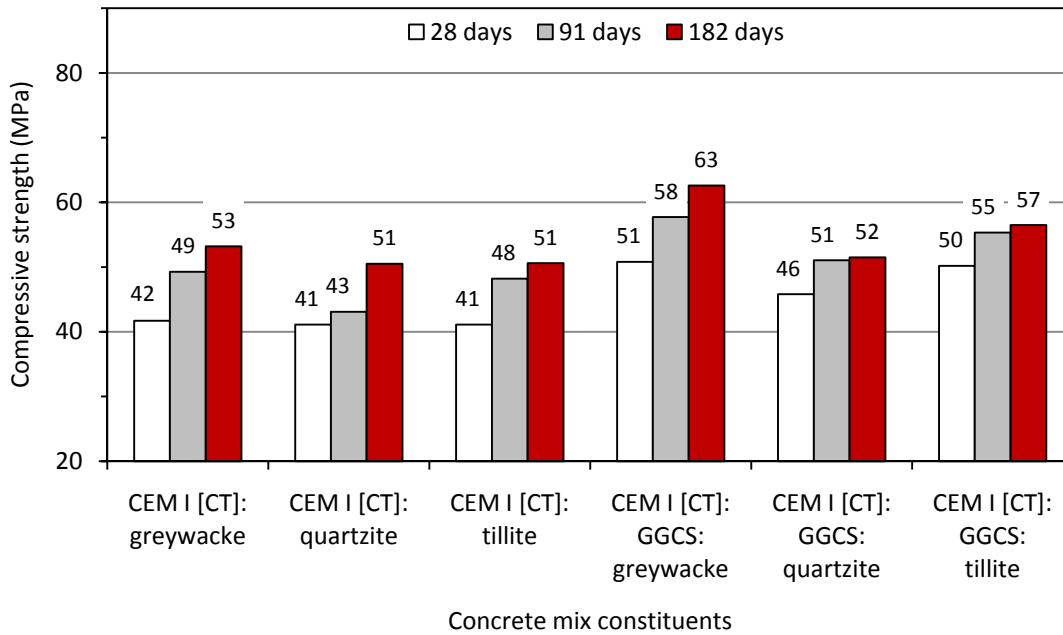


Figure 4.34 (b): Compressive strength development of concrete of different mixes made with Cape Town binders and the regional aggregates - 0.55 w/b ratio

From the figures it is clear that greywacke aggregate produced concrete with slightly higher strength values than tillite and quartzite respectively at both w/b ratios. Using the 10 % fines aggregate crushing values given in Table 3.2 as a measure of aggregate strength, a similar order is seen. Perrie (2009) however points out that this is only significant in low w/b ratio (high strength) concretes.

4.6.4 Summary remarks

From the cube compressive strength results, it is clear that the GGCS blended mixes have the highest strength values at all sample ages. This is attributed to its higher reactivity. The FA blended mixes have lower 28-day strength values which increase considerably after this. The slow reacting pozzolanic nature requiring an extended hydration period is considered to cause this. Slagmore blended mixes have the lowest strength values at all sample ages.

It is also seen that the 0.40 w/b ratio mixes have higher strength values than the 0.55 w/b ratio mixes. The lower w/b ratio mixes have a larger overall gel volume resulting in higher strength values.

From the compressive strength results, it is evident that mixes produced with greywacke aggregate had consistently higher strength values than binder mixes with tillite and quartzite respectively at both w/b ratios. This is attributed to its higher 10 % fines aggregate crushing values which as a measure of aggregate strength.

From the results it is also evident that compressive strength values increased with continued curing. This is seen for all concrete types at both w/b ratios and is attributed to continued hydration.

4.7 Specific conclusions

Based on the results presented and the discussion done, the following specific conclusions are made with regard to the variables investigated and the transport properties established by the experimental tests done.

1. In general, the influence of binder type is greater than the influence of reducing w/b ratio, continued moist curing or changing aggregate type in reducing the transport properties of a concrete mix.
2. At both w/b ratios the different concrete mixes are ranked as follows in order of increasing chloride penetration resistance: slag blended mixes < FA blended mixes < plain OPC mixes.
3. At both w/b ratios the regional mixes are ranked as follows in order of decreasing permeability characteristics: FA blended mixes > Slagmore blended mixes > plain OPC mixes > GGCS blended mixes.
4. At both w/b ratios the regional mixes are ranked as follows in order of increasing sorptivity characteristics: FA blended mixes > Slagmore blended mixes > plain OPC mixes > GGCS blended mixes.
5. Decrease in w/b ratio results in the decrease of the apparent diffusion coefficient (D_a) of the marine concretes.
6. The inclusion of ground granulated corex slag (GGCS) increases the chloride ingress resistance of marine concretes. This results in blended GGCS mixes having low D_a and chloride conductivity values.
7. The use of GGCS in a mix results in concrete with high permeability characteristics.

8. The use of Slagmore binder results in concrete of low penetrability. The binder has good chloride ingress resistance, low permeability and sorptivity characteristics.
9. The inclusion of FA in a mix results in lower permeability and sorptivity characteristics of the marine concretes.
10. FA and Slagmore blended mixes have low permeability and sorptivity characteristics than slag blended mixes.
11. When continued moist curing is done, fly ash (FA) blended mixes have near equivalent chloride conductivity resistance as the slag blended mixes.
12. Continued moist curing reduces the permeability characteristics of FA blended mixes.
13. Plain OPC mixes have poorer resistance to chloride ingress and chloride conductivity than blended binder mixes.
14. Plain OPC concretes have comparable permeability characteristics with FA and Slagmore blended mixes.
15. Aggregate type does not appreciably affect the transport properties of the marine concretes tested.
16. Greywacke aggregate results in mixes of higher strength values than mixes with tillite and quartzite respectively.

4.8 Closing remarks

The extensive series of tests detailed in this chapter have provided valuable information on the influences on the transport properties of the marine concrete mixes produced. W/b ratio and binder type are found to have significant influence on the transport properties of the marine concretes produced while aggregate type and continued moist curing do not have appreciable influences. Lower w/b ratio concretes are found to give less penetrable concretes. At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in a reduction of the transport properties.

The use of supplementary cementitious materials is also found to reduce the penetrability of the mixes tested. Slag (GGCS and Slagmore) blended mixes offer the greatest resistance to chloride ingress and chloride conductivity followed by FA blended mixes. Plain OPC mixes offer the least resistance to chloride ingress and chloride conductivity. This is seen at the two tested w/b ratios and at all sample ages. Resistance also increased at later sample ages and

is attributed to continued hydration. With respect to chloride ingress, the order is ascribed to the chloride binding capacities of the different binder types resulting in the immobilisation of penetrating chloride ions which reduces the total free chloride ion concentration.

With regard to the permeability test, plain OPC mixes and mixes containing FA have the lowest permeability characteristics while GGCS blended mixes have higher permeability characteristics. The order is attributed to the pore refining nature of the binder type used and development of the pore structure as a result of hydration. Looking at the sorptivity characteristics of the tested mixes, FA and Slagmore blended mixes have the lowest characteristics followed by GGCS blended and plain OPC mixes respectively. This order is seen at the two tested w/b ratios and all sample ages. With continued moist curing, the sorptivity resistance characteristics of the mixes improved and this is concluded to be a result of continued hydration causing an improvement in the concrete pore structure.

Aggregate type was found not to have an appreciable influence on the transport properties of the mixes tested. All the values obtained from each test are not significantly different, and show that the transport properties of the marine mixes tested are essentially independent of aggregate type.

In general, binder type was found to have a greater influence on the transport properties of a mix than w/b ratio, continued moist curing and aggregate type respectively.

The following chapter is a discussion on the existence of relationships and correlations between the test results that indicate the applicability of the tests in determining the durability performance of marine concretes.

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Chapter Five

Discussion on application of test results

5.1 General

Consistent trends were revealed in Chapter 4 of the influences of w/b ratio and binder type on the transport properties of concrete. It would thus be beneficial to investigate any relationships between the test results and any correlations that might exist. Such relationships and correlations would indicate the applicability of the tests in determining the potential performance of marine concretes. This chapter therefore presents and investigates the reliability of the experimental tests done in characterising concrete with particular reference to the marine environment. It first looks at the guiding principles behind each test then establishes a basis for determining any correlations that might exist between the results. The discussion then presents the use of the DI tests, which are early age tests, as indicative of durability performance. It is important to appreciate that though the tests measure different concrete transport properties that produce varying responses, the existence of a correlation would also indicate the consistency of results and strength of the trends seen.

5.1.1 Chloride ingress

Mackechnie, (1996), gives four factors that influence the rate of penetration of chlorides into concrete. In order of increasing importance they are; period of initial moist curing, w/b ratio, level of chlorides in the environment and binder type. The results outlined in the previous chapter show a similar trend for three of the variables; w/b ratio, binder type and sample age. Coarse aggregate type was seen not have an appreciable on chloride ingress.

Establishing the influence of w/b ratio and binder type on D_a is done by comparing all the values obtained at 182-days against each other as illustrated in Figure 5.1. The points are for each binder type independent of aggregate type.

The values plot under the line of equality showing a clear bias of high D_a values for concrete mixes at the 0.55 w/b ratio. Mixes at the lower 0.40 w/b ratio concretes have lower D_a . This is attributed to the lower w/b ratio concretes having a more closed pore structure which slowed chloride ion ingress.

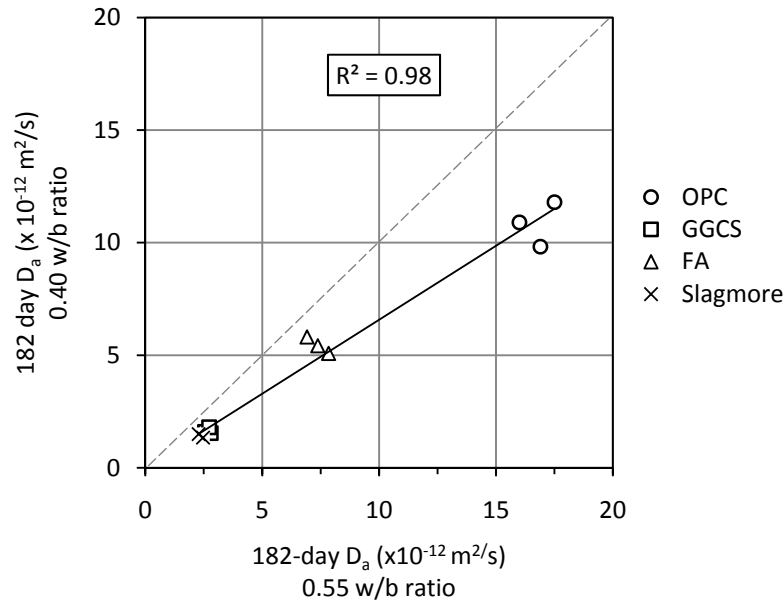


Figure 5.1: Comparison of 182-day D_a values for 0.40 and 0.55 w/b ratio concretes

It is also apparent that mixes with supplementary cementitious materials (SCM) have lower D_a values compared to the plain OPC mixes. This is attributed to the chloride binding capacity of the SCM which slows chloride ion transport. Penetrating chloride ions are immobilised by physical and chemical means which decreases the free ion concentration thus slowing the diffusion process (Song et al, 2008). The good correlation coefficient of 0.98 between mixes of the same binder type means there is a strong consistency of values.

D_a values obtained from the curve fitting exercise decreased with sample age. This follows trends observed by Chalee and Jaturapitakkul (2008), Hong and Hooton (1999) and Mangat and Molloy (1994). Differences noted between the values were attributed to the different w/b ratio and binder types used. This change in chloride transport values is 'beneficial' for resisting long term chloride ingress.

5.1.2 Chloride conductivity index

Generally, it was found that CCI values were influenced by w/b ratio, binder type and duration of curing. Coarse aggregate type does not have a significant influence on chloride conductivity. Establishing the influence of w/b ratio on chloride conductivity is done by comparing all the values obtained at each test age against each other as illustrated in Figure 5.2. The values plot under the line of equality showing a clear bias of higher CCI values for concrete mixes at the 0.55 w/b ratio. Good correlation coefficient of 0.94 between the two w/b ratios is found. The figure also helps to show that the CCI test behaves consistently and reliably across the different binder types.

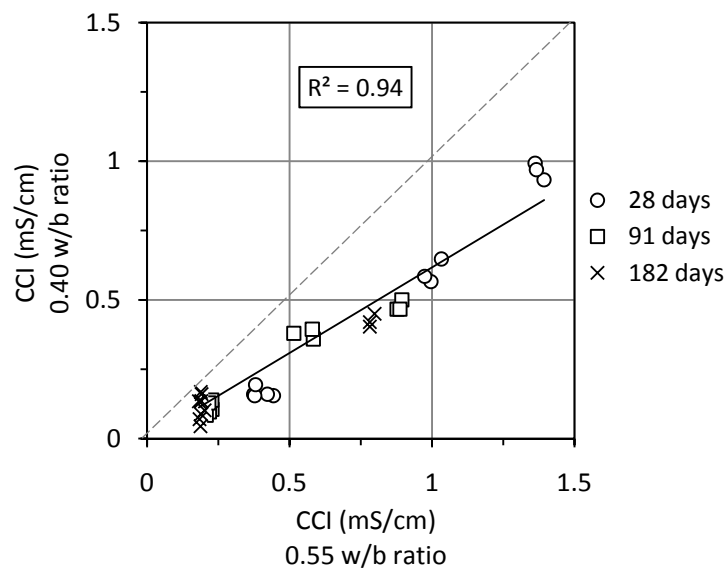


Figure 5.2: Comparison of CCI values for 0.40 and 0.55 w/b ratio concretes

In Chapter 4, the influence of binder type was seen with the blended mixes exhibiting lower values than the plain OPC control mixes. As reported by Alexander et al (1999a), binder type, use of SCM in concrete increases the chloride ingress resistance and chloride binding capacity of a concrete mix. The slag mixes have favourably low CCI values at all ages and w/b ratios indicating good resistance to ionic transport. FA blended mixes have lower values than the plain OPC mixes, but in comparison with the slag blended mixes, their values were higher. The higher CCI values of plain OPC mixes indicates their poor resistance to chloride ions.

Establishing the influence of binder type on chloride conductivity is done by comparing all the CCI values at each age as shown in Figures 5.3 (a) - (c). The values are classified under binder type. The good correlation found at each sample age is indicated. Of interest, is the behaviour that the FA blended mixes exhibit with continued moist curing. It is seen that the values reduce significantly. In Figure 4.43 (c) the values “collapse” into the slag results at 182 days.

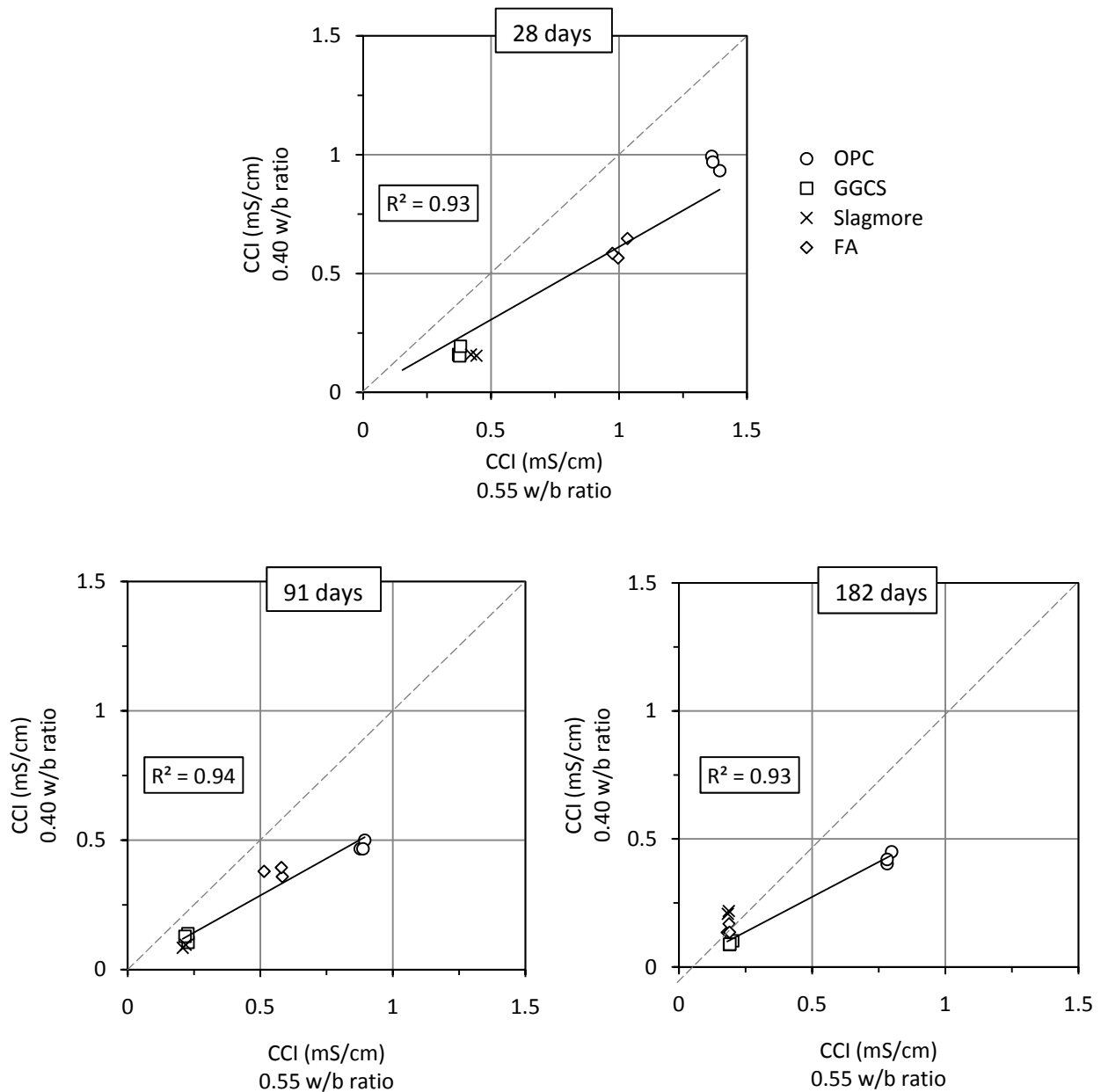


Figure 5.3: (a) – (c): CCI correlations per binder type and sample age

5.1.3 Oxygen permeability index

From Chapter 4, it was seen that the permeability of a concrete mix was primarily influenced by w/b ratio and binder type. Coarse aggregate type did not have an appreciable influence on the permeability. Continued moist curing was seen to have an influence only on the FA blended mixes.

Establishing the influence of w/b ratio on permeability is therefore done by comparing all the values obtained against each other as illustrated in Figure 5.4. The values plot under the line of equality showing a clear influence of high k values (higher permeability) for mixes at the 0.55 w/b ratio. A reasonable correlation coefficient of 0.61 is also found (Other factors such as binder type and sample age also affects k values, therefore it would be pedantic to be critical of the R² value found). As reported by Glass, (2003) w/b ratio governs the capillary pore volume that controls the spacing between binder grains and between the paste and aggregate particles.

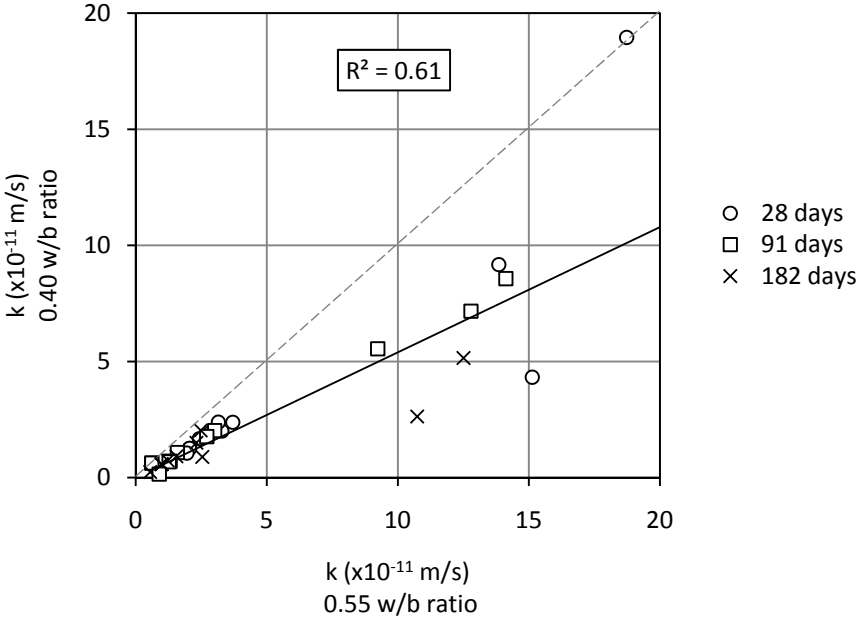


Figure 5.4: Comparison of k values for 0.40 and 0.55 w/b ratio concretes

The use of SCM in the mixes was seen to have a varied effect. The inclusion of GGCS in concrete results in mixes with increased permeability (higher k values). This is in comparison to plain OPC and FA blended mixes which exhibit reduced permeability. Interestingly, the Slagmore blended mixes show low permeability characteristics. The binder contains both

GGBS and FA and appears to derive favourable properties from the two SCM. The binder exhibits a synergistic effect of good chloride transport resistance and low permeability characteristics. Establishing the influence of binder type on permeability is done by comparing all the k test values at each sample age as shown in Figures 5.5 (a) - (c). The points are for each binder type independent of aggregate type. The correlation found at each sample age is indicated.

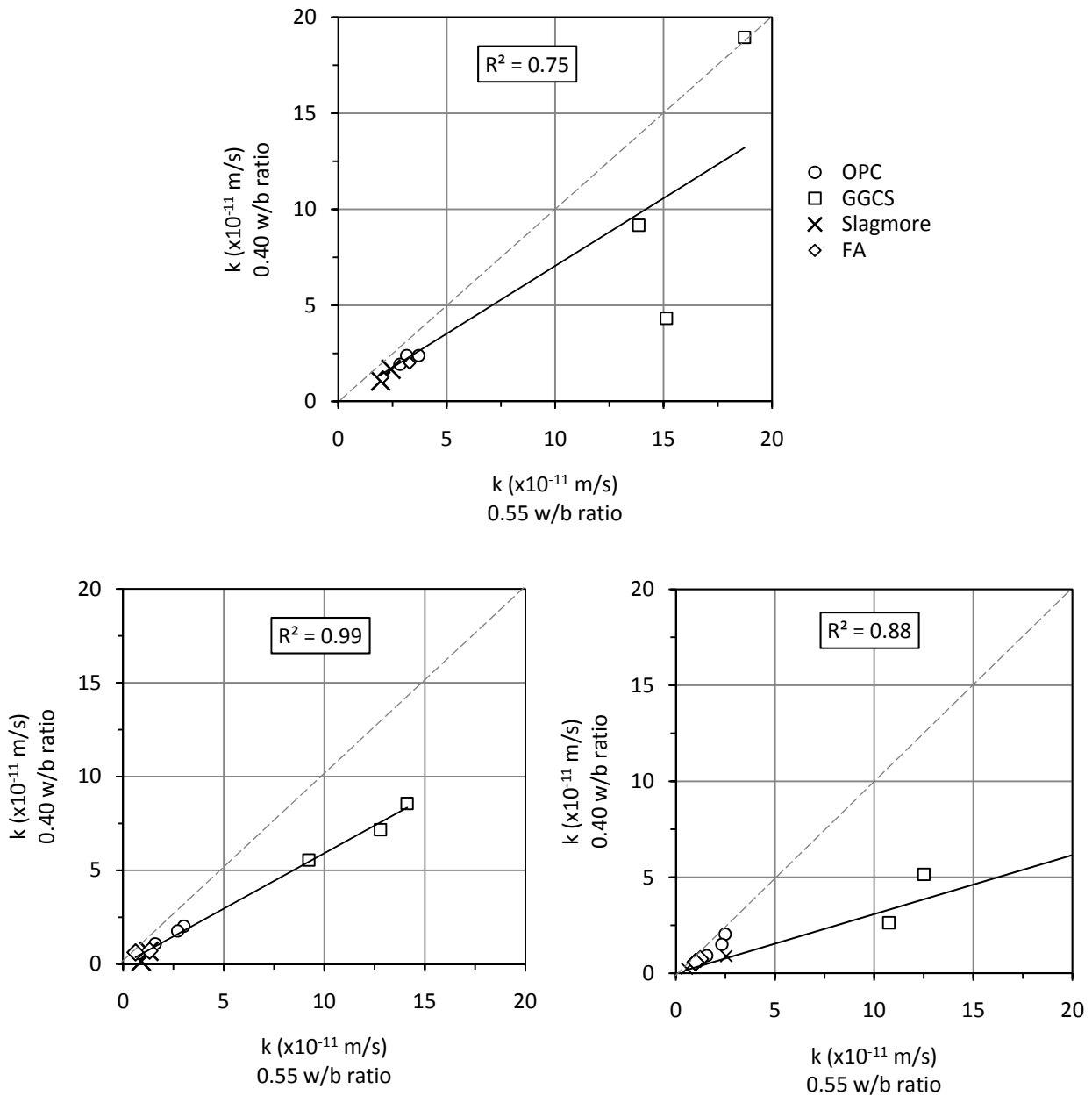


Figure 5.5 (a) - (c): OPI correlations per binder type and sample age

5.1.4 Water sorptivity index

Sorptivity results show a strong influence of w/b ratio. The 0.40 w/b ratio mixes consistently exhibit lower WSI values than the higher 0.55 w/b ratio mixes. At the lower w/b ratio, the pore volume and average size of the pore is reduced resulting in lower WSI values. The pore geometry largely controls the sorptivity characteristics of a concrete with low WSI values translating to less penetrable concretes of improved quality (Mackechnie, 1996).

Establishing the influence of w/b ratio on sorptivity is done by comparing all the values obtained at each test age against each other as illustrated in Figure 5.6. Good correlation of 0.85 is found between the two w/b ratios. The values plotting close to the line of equality also shows that w/b ratio has a lesser effect on well cured concretes.

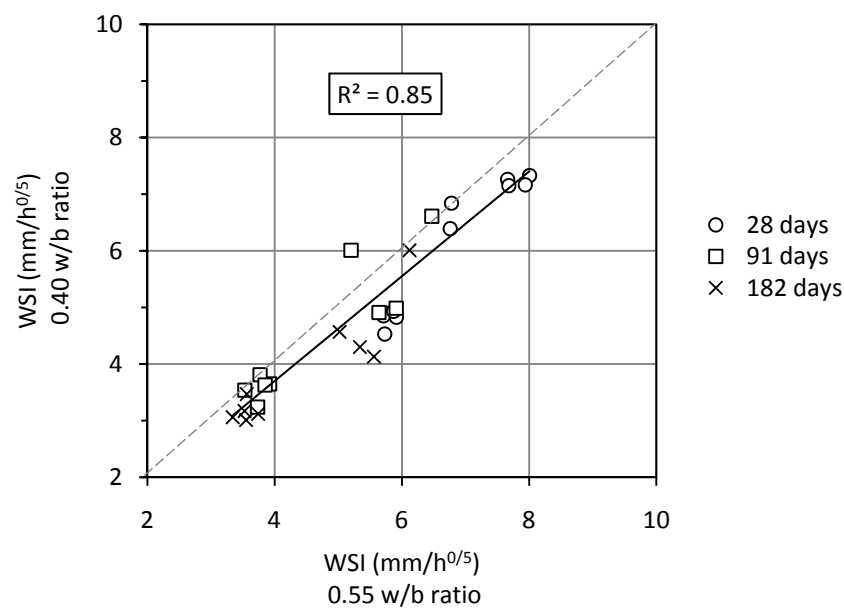


Figure 5.6: Comparison of WSI values for 0.40 and 0.55 w/b ratio concretes

The influence of binder type is also seen with the blended binder mixes giving lower WSI values than the plain OPC concrete mixes. The FA and Slagmore blended mixes have the lowest values while GGCS blended mixes have slightly higher values. The synergistic effect of GGBS and FA earlier seen in the Slagmore blended with regards to chloride conductivity and permeability is seen again with sorptivity.

Establishing the influence of binder type on sorptivity is done by comparing all the WSI test values at each sample age as shown in Figure 5.7 (a) - (c). The points are for each binder type independent of aggregate type. Good correlation is found at each sample age as indicated in the figures.

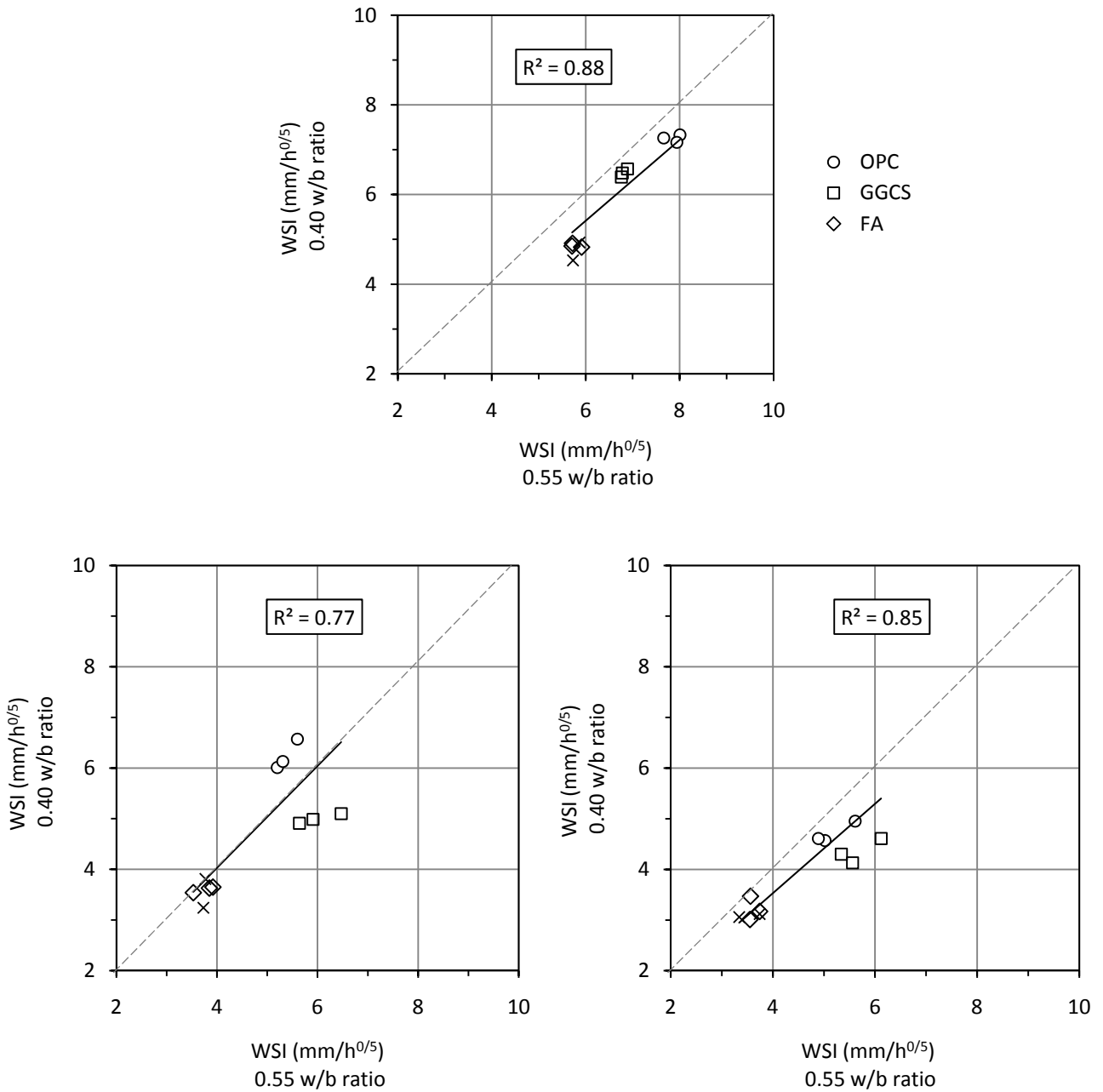


Figure 5.7 (a) – (c): WSI correlations per binder type and sample age

5.1.5 Cube compressive strength

Generally it was seen that w/b ratio and the material constituents of concrete have an influence on cube compressive strength. The GGCS blended mixes give higher strength concretes while the Slagmore blended mixes give concretes with lower strength values. With regards to aggregate type, the use of greywacke results in concrete with higher strength values than concretes with the other two aggregate types. With the extended period of moist curing to sustain hydration, the later age compressive strength values increased.

5.2 Basis of correlations between tests and results

Looking at the tests conducted, the bulk diffusion test, from which chloride ingress values are obtained, is impractical from an engineering perspective due to the length of time and resources required to determine the test values. The DI tests on the other hand are early age tests that are comparatively fast and simpler to conduct. As such it would be worthwhile to investigate the existence of a potential deterministic relationship between results from the DI tests and the bulk diffusion test. Such a relationship would enable the performance and potential durability to be predicted from an early age property.

It should be noted that the existence of a relationship does not necessarily mean that only one of the tests is required to evaluate the properties measured by both tests. Each test is sensitive to the effects and variables under investigation to different degrees (Mackechnie, 1996). In the marine environment, as chloride transport is the critical mechanism, the chloride conductivity test is considered appropriate.

The OPI test provides information on the permeability characteristics of the cover layer of concrete and the quality of workmanship. It is not an indicator of the chloride resistance of concrete (Mackechnie, 1996, Alexander et al, 1999, Ballim et al, 2009). Similarly, the WSI test which Ballim (1993) found to be a good indicator of the level of curing, is not an indicator of the chloride resistance of concrete. Further, the two tests are relatively insensitive in well cured concretes compared to the chloride conductivity test.

The CCI test is essentially an indicator of cover concrete potential material quality, in regard to the penetration of chloride ions. By quantifying the conductivity of a sample, inherent

durability is inferred from the index value obtained. Currently, it has been established by Streicher and Alexander (1995) that there is a relationship between the CCI value and the chloride diffusivity of concrete, known as the diffusibility relationship.

This discussion therefore looks at the applicability and reliability of the chloride exposure tests done in characterising chloride transport. Additionally, the applicability and reliability of the tests for use on marine concretes would be established. The discussion outlined here shall only focus on the aforementioned trends and influences of w/b ratio (0.40 and 0.55) and binder type (plain OPC (OPC), GGCS blended (GGCS), FA blended (Fly ash), Slagmore blended (Slagmore)).

Good correlation is found between the 182-day D_a values and CCI values at all ages and both w/b ratios. This illustrated in Figures 5.8 - 5.10. The linear regression correlation coefficients are given in the figures.

What is clear from the figures is that the slag blended mixes consistently have low chloride transport values. The plain OPC mixes have higher values than either the slag or FA blended mixes. Though the particular binders (and aggregates) used are geographically different, the differences in values noted in each of the six figures between mixes of the same binder type are thought to be small and may be considered to be within the accuracy of the test methods.

The shift of values and lines of correlation towards the upper left of the diagrams with increasing age of CCI can be attributed to continued hydration and improvement of microstructure with time.

From the results, it is seen that the R^2 value does not necessarily improve with age. The 28-day chloride conductivity value can therefore be taken as a good indicator value of concrete performance in the marine environment. Engineering design can take advantage of this early age property by using it as a test to evaluate the potential durability of different mixes. This is in addition to the test being an index test for quality control of as-built concrete.

Influences on the transport properties of a range of South African marine concretes

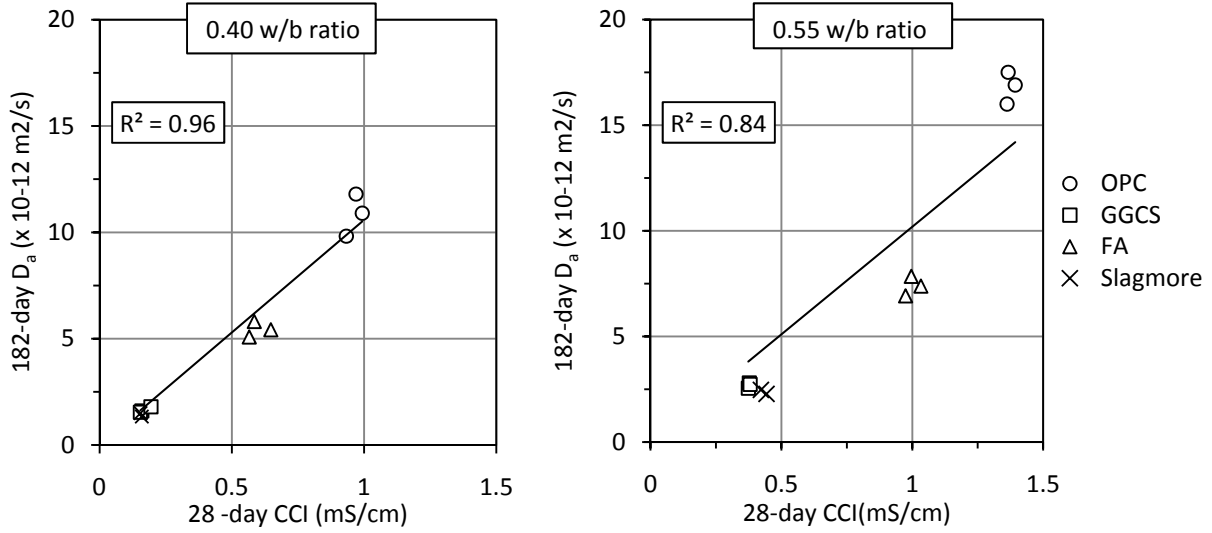


Figure 5.8: Relationship between 28-day CCI and 182-day D_a

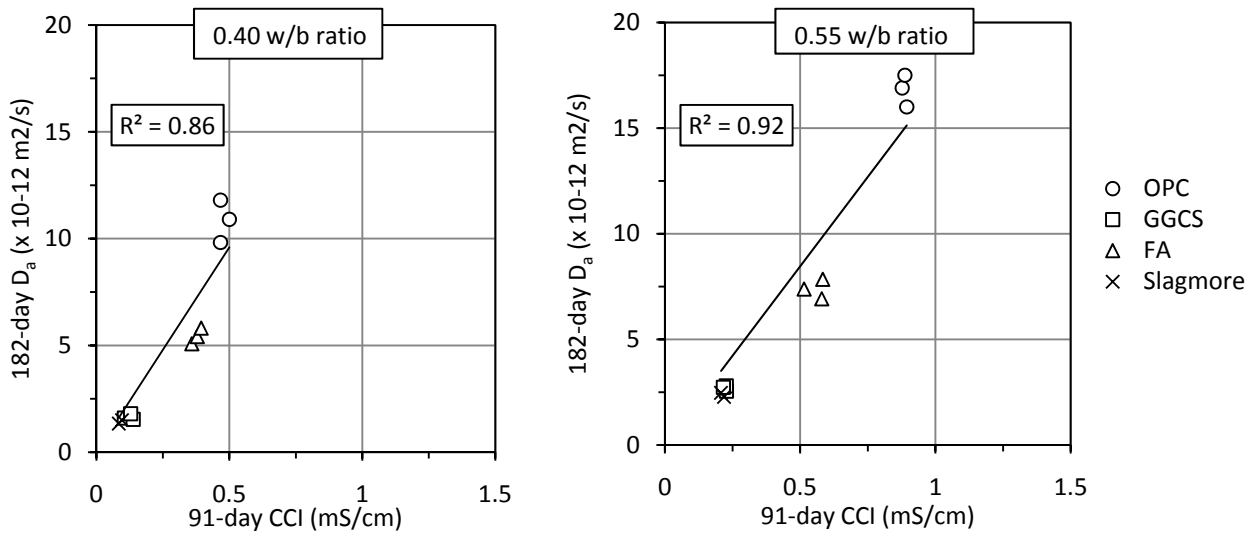


Figure 5.9: Relationship between 91-day CCI and 182-day D_a

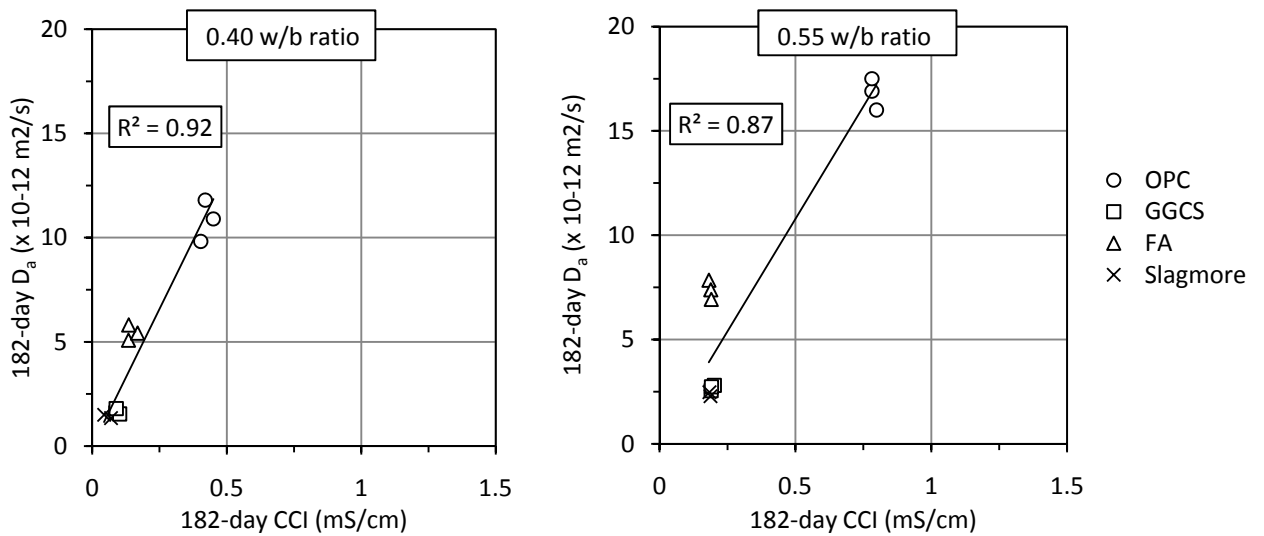


Figure 5.10: Relationship between 182-day CCI and 182-day D_a

Mackechnie (2001) through the South African chloride prediction model reliably showed that the chloride conductivity index values can be used to predict long term D_a values. Based on Fick's second law of diffusion, the model provides an empirical means of predicting chloride ion ingress from a modified 28-day CCI value. The model also estimates a time to corrosion activation from a prediction of the concentration of chlorides levels at the reinforcement level. Figures 2.24 and 2.25 illustrate the format of the prediction model.

Looking at the 28-day CCI values and 182-day D_a correlation in Figure 4.35, good correlation is seen. This result therefore strengthens the SA prediction model which as mentioned is based on the chloride conductivity test. It is important to note that the correlations seen here and those allowed for in the model are essentially binder specific. As also mentioned, the regional material effects (more so binder effects) are minimal. It is therefore concluded that the model is applicable across the different SA marine zones.

5.3 Discussion on the use of the CCI test

The Durability Index (DI) tests have shown sensitivity to the materials and mix proportion variations in the experiments done. Though they measure distinct transport mechanisms they are considered suitable in optimising the transport properties of a concrete mix by appropriate mix design. As explained by Ballim et al (2009) the DI test values have been related to existing service life models indicating the expected durability performance of concrete in its service environment. For marine concretes, the CCI test as discussed and as established by Mackechnie (1996, 2001) is appropriate for durability predictions.

Characteristic performance tests on concrete are normally done at an early age (typically 28 day), from which inherent durability is predicted. However, as was seen, FA blended mixes are prejudiced at this early age. With continued moist curing, hydration continues in FA blended mixes and it is seen that they attain near equivalent chloride conductivity resistance properties as the slag concretes at later ages. It thus becomes incumbent to test the CCI values with age in order to draw conclusions about the use of early age test values for prediction.

Figures 5.11 and 5.12 illustrate the correlations between early age and later age CCI test values. The values are classified under binder type.

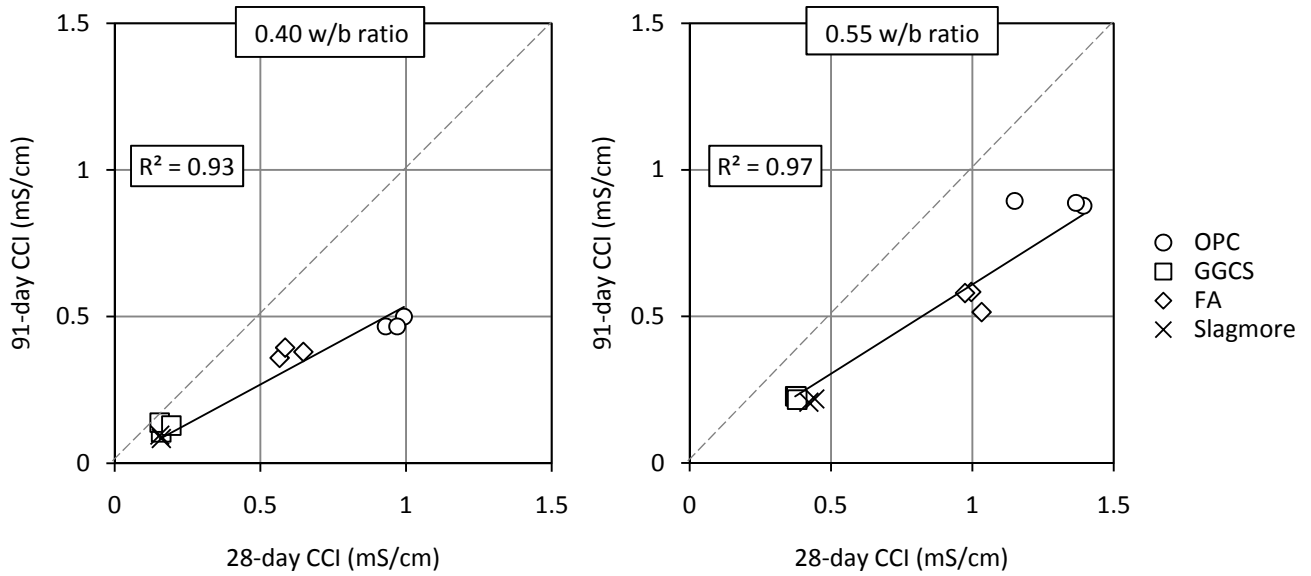


Figure 5.11: 28- and 91-day CCI correlations with binder type

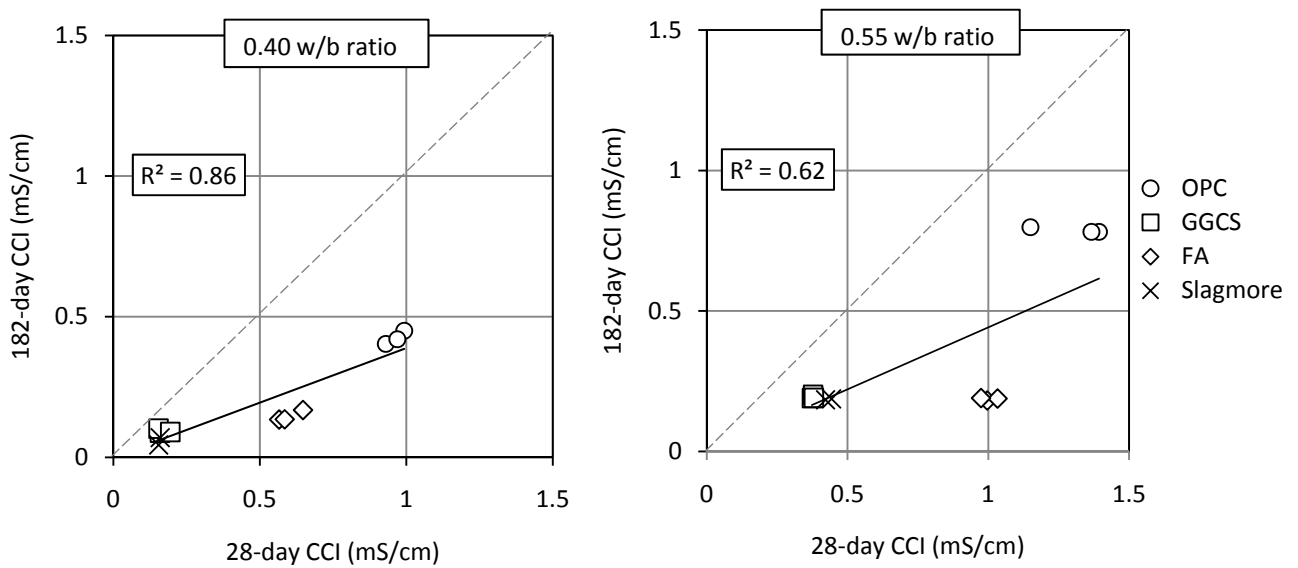


Figure 5.12: 28- and 182-day CCI correlations with binder type

It is clear that good correlation exists between 28- and 91-day CCI values as indicated in the Figure 5.11. The lower correlations between 28- and 182-day CCI values, in Figure 5.12, are attributed to change in binder chemistry due to continued hydration, particularly for the 0.55 w/b ratio FA blended mixes. Test results of these mixes show a clear shift in values towards the lower part of the figures.

The current UCT Service Life Model for concrete in the marine environment (Mackechnie, 2001) is currently being re-calibrated and a proposed format of the model is shown in Figure 5.13. The proposed model relates the intended service life from the environmental exposure condition, concrete type and grade, concrete cover, measured CCI value, chloride threshold value for corrosion and a given chloride diffusion coefficient. Mackechnie (1996) points out that early age CCI values should however be modified for service life prediction to allow for chloride binding and environmental exposure conditions. This is illustrated in Figure 2.24.

In its application the model has the following input variables:

1. Concrete cover depth
2. w/b ratio
3. Environmental exposure condition
4. Binder type
5. Measured or prescribed CCI value

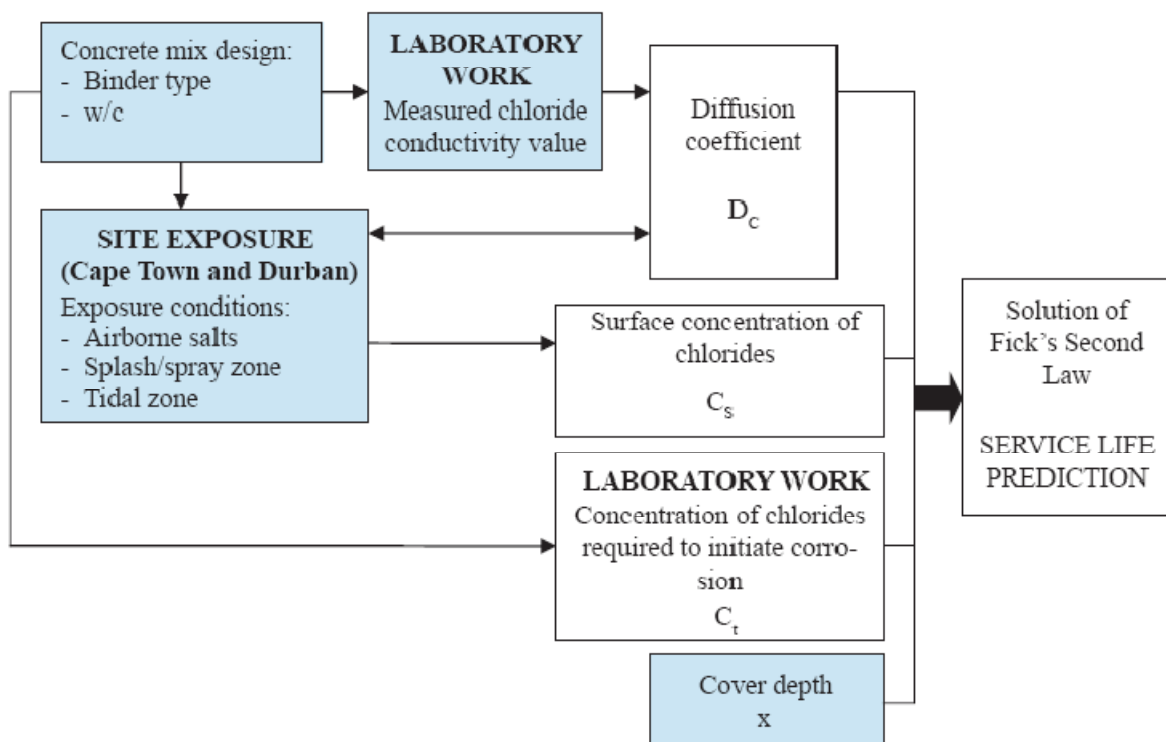


Figure 5.13: Proposed format of UCT Service Life Model (Heiyantuduwa and Alexander, 2008)

CCI values and apparent diffusion coefficient values are fundamental input parameters for the model. As such, the results obtained in this study can be used to strengthen the model and further inform service life modelling of reinforced concrete marine structures. Allowance for long-term effects such as chloride binding and continued hydration should however be allowed for the results of this study to validate the proposed model.

5.4 Closing remarks

With reference to the marine environment where the resistance of a concrete mix to the diffusion of chloride ions is of utmost importance, the CCI test showed results that have good correlation with bulk diffusion data. It was shown that the test is an appropriate indicator of potential durability in the marine environment. Additionally, it also quantifies chloride conductivity. Mackechnie (2001) similarly found good correlation from which a prediction model was developed that predicts a 2-year diffusion coefficient value based on 28-day CCI test values. It was also seen that the test is a reliable indicator of the inherent durability of a marine concrete.

The next chapter presents the main findings and conclusions of this experimental study based on a critical evaluation and discussion of the experimental results given. Recommendations for further study are also given.

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Chapter Six

Conclusions and recommendations

6.1 General

The objective of this experimental study was to explore the comparability of different South African marine concrete mixes. The focus was on the transport properties of concrete types typically produced for RC structures in the marine environment by ready mix plants. Materials were sourced from the urban marine areas of Cape Town, Port Elizabeth and Durban. The aim was to improve the understanding of the potential durability afforded to marine concretes by the geographically different concrete making materials available and their mix proportioning. Chloride ingress and durability index (DI) values were obtained using appropriate testing techniques used in South Africa. The tests give an indication of the penetrability of concrete. Less penetrable concretes are generally considered as having greater potential durability.

The results presented and evaluated in Chapter 4 indicate that w/b ratio and binder type significantly affect the penetrability of concrete. Aggregate type was seen not to have appreciable influences on concrete transport mechanisms. The effect of continued moist curing beyond 28 days had an appreciable effect on fly ash (FA) blended mixes.

The applicability of the experiments in characterising marine concretes was also done so as to establish a relationship that would enable concrete performance to be predicted from an early age transport property.

This chapter presents the main findings of the factors investigated in a more critical sense. They are presented in terms of the results of the experimental tests done and the concrete materials and proportion influences determined by the experiments done. Plain CEM I 42.5, N ordinary Portland cement (OPC) was used as control mixes at the two tested w/b ratios of 0.40 and 0.55.

6.2 Chloride ingress – bulk diffusion tests

Chloride ingress values, apparent diffusion coefficient (D_a) and surface concentration (C_s) were determined from the bulk diffusion testing of 42- and 182-day concrete samples. The values are indicators of the resistance to chloride ion diffusion in concrete

6.2.1 Regional trend and influence of w/b ratio

The 42-day chloride ingress values were determined to be premature for a deterministic analysis, but were used to show the change in chloride ingress with time.

The 182-day chloride ingress values for the different regional concretes showed a strong influence of binder type. The slag (GGCS and Slagmore) blended mixes clearly had the lowest chloride transport values which indicated the good chloride binding capacity of slag concretes. Chloride binding is a physical and chemical immobilisation of chloride ions which reduces the free ionic concentration resulting in a decrease in the diffusion process (Song et al, 2008). The FA blended mixes from Cape Town and Port Elizabeth had comparable chloride penetration values. The Cape Town plain OPC control mixes exhibited the highest chloride ingress values. The above trends were seen at both w/b ratios and are similar to what has been reported by other researchers (Chalee and Jaturapitakkul, 2008, Yang, 2004, Baweja et al, 1999, Thomas and Bamforth, 1999).

C_s values also showed a strong influence of binder type and the same trend as D_a values. The slag blended mixes had lower values than both the FA blended and plain OPC mixes respectively. The slag blended mixes had higher C_s values than both FA blended and plain OPC mixes respectively. This indicates the higher resistance to chloride ion penetration of slag mixes.

With regard to w/b ratio, the concrete mixes produced at the lower 0.40 w/b ratio exhibited lower D_a values than those produced at the 0.55 w/b ratio. Glass (2003) explains that w/b ratio controls the capillary pore size and volume through which chloride transport occurs. Concretes at the lower w/b ratio have a more closed pore structure resulting in an increased resistance to chloride ion penetration.

6.2.2 Influence of binder type

As was pointed out, chloride transport values varied substantially with binder type. The concrete mixes blended with supplementary cementitious materials (SCM) were found to have lower chloride ingress values than plain OPC mixes. This was attributed to the superior chloride binding characteristics of SCM compared to the plain OPC. This was indicated by the steep chloride concentration fronts that the blended mixes exhibited across the sampled profile depths. Chloride binding results in the reduction of the free chloride ion concentration front which reduces the total free chloride ion concentration. The plain OPC mixes exhibited shallower chloride concentration profiles and higher chloride content concentrations throughout the sampled profile depths.

The D_a values of the slag blended concrete mixes were significantly lower by up to 80 % in comparison with the plain OPC concrete mixes. The FA blended mixes had D_a values up to 50 % lower than the plain OPC mixes. The SCM refine the pore structure and improve the chloride binding capacity of blended binder pastes which was exhibited as reduction in the rate of chloride ion diffusion..

6.2.3 Influence of aggregate type

The apparent chloride diffusion coefficient (D_a) values obtained from the bulk diffusion test did not show any significant influence of coarse aggregate type on chloride penetration. Regardless of aggregate type all the D_a values for the each set of common binder mixes were near equivalent. It is therefore concluded that aggregate type does not affect chloride ion ingress. Additionally, the aggregate types from the three geographic South African regions impart near-similar chloride transport characteristics to concrete.

6.2.4 Sample age

Chloride ingress values showed clear time dependence between the first test age of 42 days and the second of 182 days. With continued exposure to a chloride environment, chloride contents and C_s values of all the concrete samples increased, and D_a values significantly decreased. The reduction in D_a was up to 85 % for the FA blended mixes and between 45 % and 75 % for the slag blended mixes. The plain OPC concrete mixes also exhibited a large

decrease of up to 88 %. This was ascribed to the chloride binding of the binder phases' which immobilises penetrating chloride ions. It was also attributed to continued binder hydration which makes the concrete pore structure denser and more inaccessible to the ingress of chloride ions. Measured chloride contents of all the concrete mixes tested also increased between the two sampled ages through the sampled profile depths. This was also attributed to chloride binding.

6.3 Chloride conductivity index

6.3.1 Regional trend and influence of w/b ratio

Similar to the chloride ingress values, the regional mixes also exhibited significant influence to binder type with respect to chloride conductivity. The slag blended mixes exhibited the lowest 28-day CCI test values. The FA blended mixes from Cape Town and Port Elizabeth had comparable 28-day chloride transport values while the Cape Town plain OPC control mixes exhibited the highest values.

From the CCI tests, it was also clear that w/b ratio had a significant influence on ionic transport into concrete. Mixes produced at the 0.40 w/b ratio generally had lower CCI values than concrete mixes at the 0.55 w/b ratio. This was noted for all sampling ages and for all mixes. The trend was attributed to the nature, amount and continuity of the pore structure which is controlled by the spacing between binder grains themselves and between binder grains and aggregate particles. This spacing is a function of w/b ratio (Glass 2003). At the lower w/b ratio, the volume and size of the pores within the concrete microstructure are reduced resulting in the reduction of the chloride transport properties.

6.3.2 Influence of binder type

Chloride conductivity values were found to decrease with the inclusion of SCM compared to plain OPC concrete mixes. The SCM used in this study, GGCS, Slagmore and FA, refine the pore structure of a binder phase (Grieve, 2009a, Aïtcin, 2008). Blending OPC with these extenders results in a decrease in the size, volume and nature of penetrable pores. The CCI test is sensitive to the pore structure where low values indicate reduced ionic transport on concrete. The slag blended mixes had the lowest values followed by the FA blended mixes. The plain OPC mixes showed comparatively poorer resistance to chloride conductivity.

6.3.3 Influence of aggregate type

The CCI test values obtained did not show any influence of aggregate type on ionic transport of concrete. Regardless of aggregate type all the CCI values for the each set of common binder mixes were comparable. It is therefore concluded that aggregate type does not appreciably affect ionic transport mechanisms of concrete. Moreover, the aggregate types from the three geographic South African regions do not appear to influence the ionic transport characteristics of concrete.

6.3.4 Influence of continued moist curing

With continued curing, it was noted that CCI values for all the mixes reduced. The greatest reduction was seen in the FA blended and the plain OPC concrete mixes. The slag concrete mixes were found to have quite low favourable CCI values at the early age of 28 days. At the last testing age of 182 days, the FA mixes had statistically comparable CCI values to the slag blended mixes. This reduction was ascribed to the slow reacting pozzolanic nature of FA having an extended hydration period. The extended moist curing period was beneficial to the FA blended mixes in terms of the mixes attaining low ionic transport characteristics. Ultimately, this means that with sufficient curing, the inclusion of FA and/or slag in a mix would yield concretes offering comparable resistance to chloride ingress. It is therefore concluded that with sufficient moist curing, all the regional concretes of similar w/b ratio and binder content are nominally equivalent.

6.4 Oxygen permeability index

6.4.1 Regional trend and influence of w/b ratio

The regional trend of permeability characteristics of the regional concrete mixes was of the FA and Slagmore blended mixes having lower permeability values than either the plain OPC mixes or GGCS blended respectively. The FA and Slagmore binders had comparable permeability characteristics. The behaviour of the GGCS blended mixes having increased permeability characteristics was attributed to an increase in the pore size. Moranville-Regourd (1998) points out that the use of slag causes an increase in the pore size of slag blended mixes resulting in increased permeability compared to plain OPC mixes.

Of particular interest, was the behaviour of the Durban Slagmore blended mixes. Though the binder is largely made up of GGBS with an 8 % proportion of FA, the mix exhibits low permeability characteristics. This was attributed to the inclusion of FA in the binder. FA fills the pores of a concrete matrix thereby reducing the permeability of the mix as was seen in the FA only blended mixes from Cape Town and Port Elizabeth. A similar synergistic behaviour has been reported by Aïtcin (2008).

Permeability is also a function of w/b ratio as explained by Mehta and Manmohan (1980). w/b ratio determines the nature, amount and interconnectivity of a concrete pore structure where flow occurs by permeation. It was noted that concretes at the 0.40 w/b ratio had lower 'beneficial' measured permeability characteristics compared to those at the 0.55 w/b ratio. The volume and size of the pores within the microstructure of the lower w/b ratio concretes was reduced.

6.4.2 Influence of binder type

As mentioned, binder type significantly influenced the permeability characteristics of a concrete mix. Of the binder types used, it was found that GGCS blended mixes had higher measured permeability values than either FA or Slagmore blended or plain OPC mixes. The first two concrete types had comparable D'Arcy coefficient of permeability (k) values. The use of slag was seen to cause an increase in the permeability characteristics of a mix. Nevertheless, it should be appreciated that in the marine environment chloride induced corrosion is the critical design issue and GGCS blended mixes offer relatively better resistance to chloride ingress.

6.4.3 Influence of aggregate type

The OPI test values obtained did not show any influence of aggregate type on the permeability characteristics of concrete. Regardless of aggregate type all the permeability values for the each set of common binder mixes were comparable. It is therefore concluded that aggregate type does not appreciable affect permeability. Further, that the aggregate types from the three geographic South African regions impart near-similar permeability characteristics to concrete.

6.4.4 Influence of continued moist curing

With an extended period of moist curing, only the FA blended mixes exhibited a decrease in the coefficient of permeability values. This was attributed to the slow reacting pozzolanic nature of FA requiring an extended hydration period than the GGCS blended mixes. The GGCS blended and plain OPC mixes showed no significant improvement in their permeability characteristics after 28 days. It is therefore concluded that development of the permeability characteristics of the pore structures of the slag blended and plain OPC mixes occurred within the first 28 days.

6.5 Water sorptivity index

6.5.1 Regional trend and influence of w/b ratio

The regional trend of the mixes was of the blended mixes exhibiting lower sorptivity values than the plain OPC control mix. This was attributed to the pore filling nature of the SCM which improve the microstructure of concrete. Of the blended mixes, the FA and Slagmore blended mixes were seen to have lower sorptivity characteristics than the GGCS blended mixes. This was attributed to the finer particle size nature of FA which refines the pore structure of concrete to a greater degree as explained by Grieve (2009a).

Sorptivity results also showed a strong influence of w/b ratio. The 0.40 w/b ratio mixes consistently exhibited lower WSI values than the 0.55 w/b ratio mixes. This behaviour was attributed to the pore geometry of concrete which controls the sorptivity characteristics of a mix as explained by Mackechnie (1996). At the lower w/b ratio, the pore volume and average size of the pore is reduced resulting in lower WSI values which translate to less penetrable concretes of improved quality.

6.5.2 Influence of binder type

As previously stated, the blended binder mixes showed lower sorptivity characteristics than the plain OPC control mixes at the two tested w/b ratios. The FA and Slagmore blended binder mixes had the lowest WSI test values. The inclusion of FA in the Durban Slagmore binder was attributed with imparting the low sorptivity characteristics of the Slagmore blended mixes. It was also seen that the GGCS blended mixes had higher sorptivity values

than either FA or Slagmore blended binder mixes. As was seen for the permeability results, the GGCS blended mixes exhibited increased permeability. This was attributed to the characteristic of slag causing an increase in the pore size of a concrete mix, leading to a higher degree of pore network connectivity. As a consequence, the capillary pore structure of concrete would exhibit increased sorptivity.

6.5.3 Influence of aggregate type

The WSI test values obtained did not show any influence of aggregate type on the sorptivity characteristics of concrete. Regardless of aggregate type all the sorptivity values for the each set of common binder mixes were comparable. It is therefore concluded that aggregate type does not appreciable affect sorptivity. Moreover, the aggregate types from the three geographic South African regions impart near-similar sorptivity characteristics to concrete.

6.5.4 Influence of continued moist curing

Continued moist curing resulted in a decrease in sorptivity values for all mixes at both w/b ratios. The greatest reduction was seen between the testing ages of 28 and 91 days. This was indicative of continued hydration leading to a reduction in porosity.

6.6 Cube compressive strength

6.6.1 Regional trend and influence of w/b ratio

The regional trend had the Cape Town GGCS blended mixes showing the highest strength values while the Durban Slagmore blended mixes had the lowest strength values. The two FA blended mixes and the plain OPC mixes had comparable strength values.

Lower w/b ratio concretes had higher strength values than concretes at the higher 0.55 w/b ratio. This was seen for all the concrete mixes produced. The gel: space ratio controls the compressive strength of concrete. At the lower w/b ratio, the overall gel volume is larger resulting in higher strength values

6.6.2 Influence of binder type

The GGCS blended mixes exhibited higher strength values than the other blended binder and plain OPC mixes. This was attributed to the higher reactivity of GGCS. The Durban Slagmore binder mixes exhibited the lowest strength values.

6.6.3 Influence of aggregate type

Concrete made with greywacke aggregate was found to produce concrete with higher compressive strength values than both tillite and quartzite aggregate concretes respectively at both w/b ratios. This was ascribed to the higher 10 % fine aggregate crushing value of greywacke aggregate.

6.6.4 Influence of continued moist curing

With continued moist curing, compressive strength values increased. The effect was more noticeable in the FA blended mixes which have an extended hydration period. The compressive strength values for the slag blended and plain OPC mixes also increased for the slag blended and plain OPC mixes with continued curing, but to a lower degree. At the last testing age of 182 days, all the concretes had comparable strength values. It is thus concluded that with continued curing, all the regional concretes have near-similar compressive strength characteristics.

6.7 Concrete characterisation in the marine environment

Of the experiments carried out only the chloride conductivity test and the bulk diffusion test simulate the marine environment. Considering the two tests, consistent trends were established on the influences of w/b ratio and binder type on the transport properties of concrete. A relationship was also established at the two test ages between the two tests. Though the tests measure different concrete transport properties that produce varying responses, they showed consistent results that indicated the existence of a correlation.

The CCI test, which is essentially an indicator of cover concrete potential material quality to the penetration of chloride ions, quantifies the inherent durability through an index value. The index values were seen to have good correlation with data from the bulk diffusion test.

A format of a proposed model that uses the CCI values as one of the input variables that indicate potential durability was presented.

6.8 Practical implication of the DI tests

The DI tests have shown sensitivity to the materials and mix proportions variations in the experiments done. Though they measure distinct transport mechanisms they are considered suitable in optimising the transport properties of a concrete mix by appropriate mix design. As explained by Ballim et al (2009) the DI test values have been related to existing service life models indicating the expected durability performance of concrete in its service environment. In this study, the influences of material type and proportion have been established using the DI tests. Binder type and w/b ratio have been seen to have significant influences on concrete transport properties at all sample ages.

Characteristic DI performance tests on tests are typically done at the early age of 28 days, from which inherent durability is predicted. However, as was seen, FA blended mixes are prejudiced at this early age. With continued moist curing, hydration continues in FA blended mixes and it is seen that they attain near equivalent chloride conductivity resistance properties as the slag concretes and lower permeability characteristics. The sorptivity characteristics of the concrete types were also found to improve with age and continued curing. It thus becomes incumbent to modify the DI values with age in order to draw conclusions about the use of early age test values for prediction.

6.9 Closing remarks

This experimental study has made strides into understanding the behaviour of geographically different South African concrete mixes exposed to a chloride environment. The influences of w/b ratio, binder type, aggregate type and continued curing and exposure to a chloride-laden environment were explored. Generally it was found that in decreasing order the following had the greatest influence on potential durability of marine mixes; binder type, w/b ratio, continued curing and aggregate type. This was done using various characterising experimental tests.

It is important to note that the conclusions made from the results, particularly in respect of aggregates, are specific to the materials tested, and may not be universally applicable across all aggregate types.

Nevertheless it is imperative to note that, compressive strength, durability indexing and chloride profiling of concrete mixes are not the only factors that are considered when specifying the potential durability of concrete in the marine environment. Other factors such as shrinkage and creep are of equal importance. In conjunction with selection of suitable materials and good construction practice, optimisation of all material and structural design factors should ensure that potential durability of marine concretes is achieved.

6.10 Recommendations

The following recommendations are made for further work based on the findings of this experimental study:

1. Ternary blends of slag, FA and OPC

Of the binder types produced in this study, one range was of a ternary blend of GGBS, FA and OPC. These mixes showed extremely good resistance to the measured transport characteristics measured compared to blends of either one of the two supplementary cementitious materials or plain OPC mixes. Further work should be done to quantify the optimum level of substitution of each of the materials to obtain the lowest transport characteristics.

2. On-site behaviour of regional concrete mixes

It would be valuable to observe the on-site transport characteristics of the marine concrete mixes produced in this study particularly chloride ingress. This would mean exposing samples to a natural marine environment and determining chloride profiles after specified exposure periods.

3. Further laboratory experimental work

This study can be extended by carrying out long term laboratory experiments of the concrete mixes produced to determine their transport characteristics at later ages.

4. Optimum level for use of crushed rock as fine aggregate

Similarly, of the concrete mixes produced in this study, two of the range of mixes had crushed rock making up a percentage proportion of the fine aggregate component. The transport characteristic values of these concrete mixes were improved compared to values obtained in other studies which didn't use crushed rock. It would be beneficial to also quantify the optimum level of substitution of crushed rock in concrete as well as the particle size.

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Appendix A

Experimental results

Notation

The following table gives the notation used to describe the concrete mixes.

Table A.1: Concrete mix labels

w/b ratio	0.40	0.55
Concrete mix constituents	Mix label	
CEM I[CT]: greywacke	M1	M12
CEM I[CT]: quartzite	M2	M13
CEM I[CT]: tillite	M3	M14
CEM I[CT]: GGCS: greywacke	M4	M15
CEM I[CT]: GGCS: quartzite	M5	M16
CEM I[CT]: GGCS: tillite	M6	M17
CEM I[CT]: FA: greywacke	M7	M18
CEM I[PE]: FA: quartzite	M8	M19
CEM I[PE]: FA: greywacke	M9	M20
CEM II A-S: Slagmore: tillite	M10	M21
CEM II A-S: Slagmore: greywacke	M11	M22

Statistical tests and terminology

Statistical analysis at a 95 % confidence interval was done on the test results to determine the reliability of the data obtained from this study. The statistical tests done are:

1. Standard deviation: Gives the spread of values around the mean value obtained.
With respect to the chloride ingress results, the standard deviation values given relates to the apparent diffusion coefficient, D_a . For the DI tests, the standard deviation values given relates to the index value for each respective index test.
2. Coefficient of variation: Measure of the disparity between individual test results.
3. R^2 : Statistical measure of how well a regression line approximates real data points . An r-squared of 1.0 (100%) indicates a perfect fit.

4. T-test: Assesses whether the means of two data sets are statistically different from each other.

The procedure for the statistical tests is described in ASTM E178 -02, Standard practice for dealing with outlying observations. An extract from the manual is given in Appendix C.

A.1 Chloride ingress test results

A.1.1 Bulk diffusion results

Table A.1 (a): 42-day Bulk Diffusion test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
D_a ($\times 10^{-12}$ m ² /s)	88.30	-	-	3.01	3.71	3.25	26.00	24.50	24.60	3.24	4.99	
C_s (%)	1.64	-	-	2.23	2.91	2.53	2.95	2.60	2.34	2.56	2.48	
R^2	0.90	-	-	0.97	0.97	0.95	0.94	0.94	0.93	0.93	0.98	
Standard deviation	1.03	-	-	0.06	0.13	0.23	0.50	0.33	0.48	0.05	0.68	
Coefficient of variation (%)	0.01	-	-	0.02	0.04	0.07	0.02	0.01	0.02	0.02	0.14	
Range ($\times 10^{-12}$ m ² /s)	Min.	87.27	-	-	2.95	3.58	3.02	25.50	24.17	24.12	3.19	4.31
	Max.	89.33	-	-	3.07	3.84	3.48	26.50	24.83	25.08	3.29	5.67

Table A.1 (b): 42-day Bulk Diffusion test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
D_a ($\times 10^{-12}$ m ² /s)	90.40	-	-	9.83	10.80	11.20	42.70	48.30	46.90	9.34	11.87	
C_s (%)	1.70	-	-	3.41	3.58	3.94	2.20	3.64	3.67	3.48	3.87	
R^2	0.89	-	-	0.92	0.95	0.92	0.97	0.94	0.95	0.91	0.95	
Standard deviation	0.32	-	-	0.53	0.04	0.31	1.01	0.36	0.79	0.38	0.21	
Coefficient of variation (%)	0.00	-	-	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Range ($\times 10^{-12}$ m ² /s)	Min.	90.08	-	-	9.30	10.76	10.89	41.69	47.94	46.12	8.96	11.66
	Max.	90.72	-	-	10.36	10.84	11.51	43.71	48.66	47.69	9.72	12.08

Table A.2 (a): 182-day Bulk Diffusion test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
D_a ($\times 10^{-12}$ m ² /s)	9.82	10.90	11.80	1.60	1.54	1.80	5.08	5.42	5.81	1.50	1.34	
C_s (%)	4.05	4.20	4.36	5.27	5.90	5.66	4.79	5.00	4.71	5.48	6.00	
$X_{0.4}$	29.0	31.0	32.5	12.5	12.5	13.5	20.5	23.0	19.5	13.0	11.5	
R^2	0.90	0.93	0.99	0.97	0.97	0.95	0.94	0.94	0.93	0.93	0.98	
Standard deviation	0.01	0.07	0.16	0.09	0.13	0.03	0.45	0.03	0.18	0.00	0.02	
Coefficient of variation (%)	0.00	0.01	0.01	0.05	0.08	0.02	0.09	0.01	0.03	0.00	0.01	
Range ($\times 10^{-12}$ m ² /s)	Min.	9.81	10.83	11.64	1.51	1.41	1.77	4.63	5.39	5.63	1.50	1.32
	Max.	9.83	10.97	11.96	1.69	1.67	1.83	5.53	5.45	5.99	1.50	1.36

Table A.2 (b): 182-day Bulk Diffusion test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
D_a ($\times 10^{-12} \text{ m}^2/\text{s}$)	16.90	16.00	17.50	2.55	2.80	2.73	7.84	7.38	6.92	2.28	2.47	
C_s (%)	5.63	5.72	6.43	6.49	6.39	6.35	5.50	5.87	5.93	8.03	8.26	
$X_{0.4}$	41.5	40.5	43.5	16.5	18.5	17.0	26.5	27.5	28.0	16.5	17.5	
R^2	0.89	0.86	0.96	0.92	0.95	0.92	0.97	0.94	0.95	0.91	0.95	
Standard deviation	0.61	0.15	0.07	0.06	0.04	0.03	0.95	0.04	0.01	0.38	0.03	
Coefficient of variation (%)	0.04	0.01	0.00	0.02	0.01	0.01	0.12	0.00	0.00	0.17	0.01	
Range ($\times 10^{-12} \text{ m}^2/\text{s}$)	Min.	16.29	15.85	17.43	2.49	2.76	2.70	6.89	7.34	6.91	1.90	2.44
	Max.	17.51	16.15	17.57	2.61	2.84	2.76	8.79	7.42	6.93	2.66	2.50

A.1.2 Chloride profiles

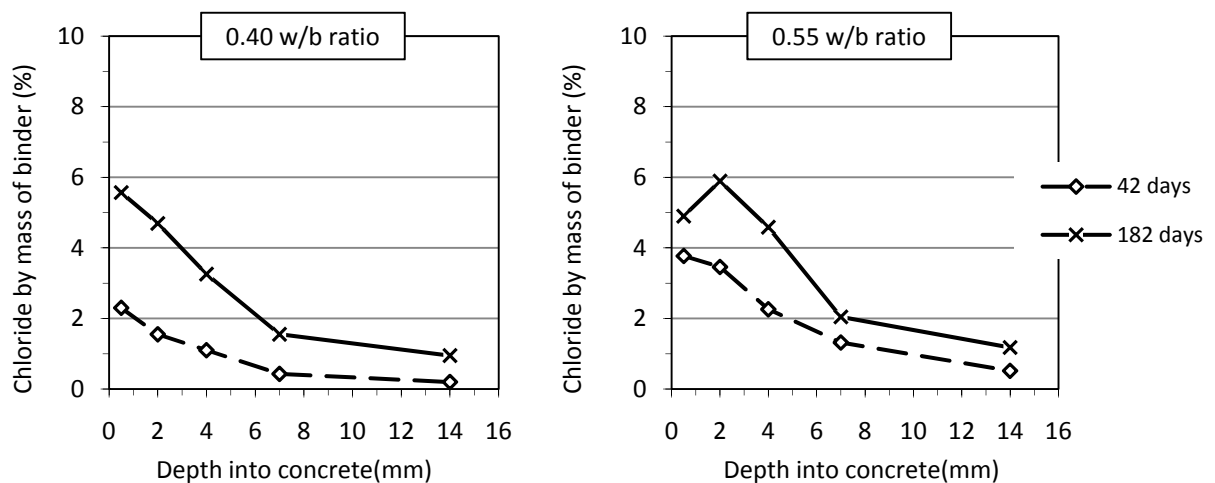


Figure A.1: Chloride profiles: CEM I [CT] : GGCS : quartzite

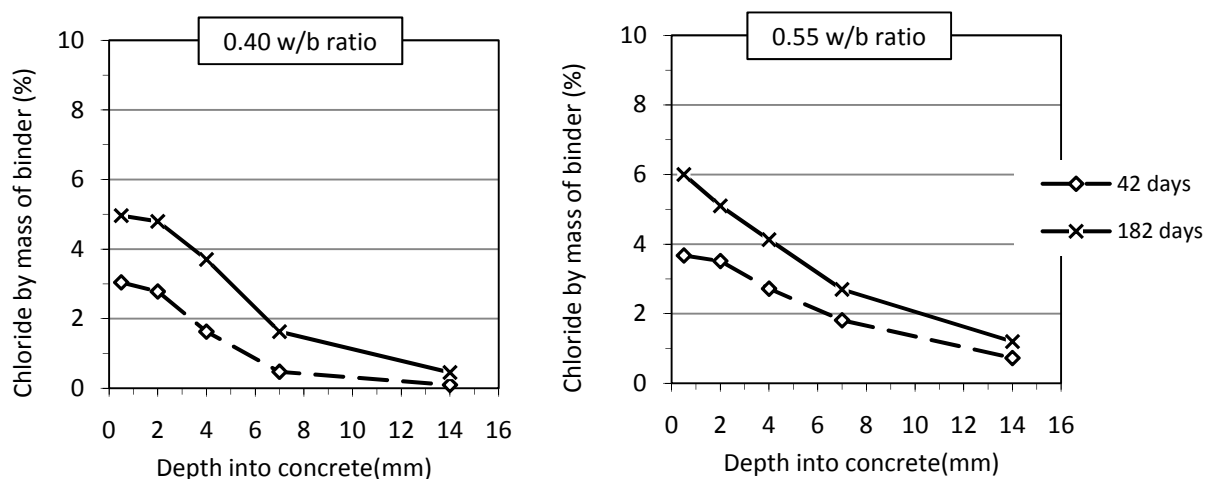


Figure A.2: Chloride profiles: CEM I [CT] : GGCS : tillite

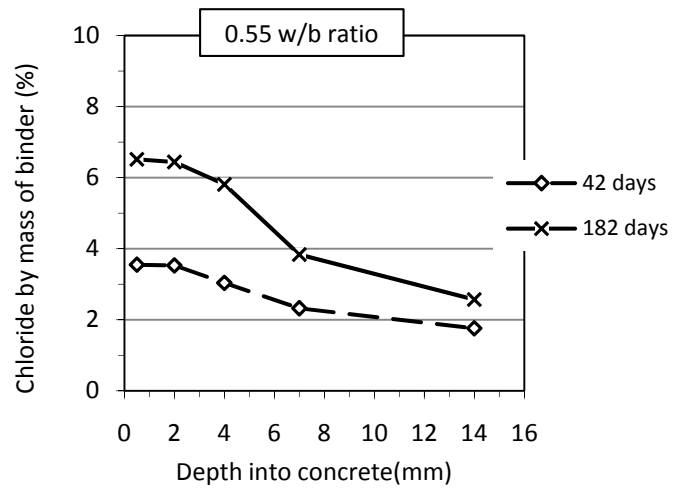
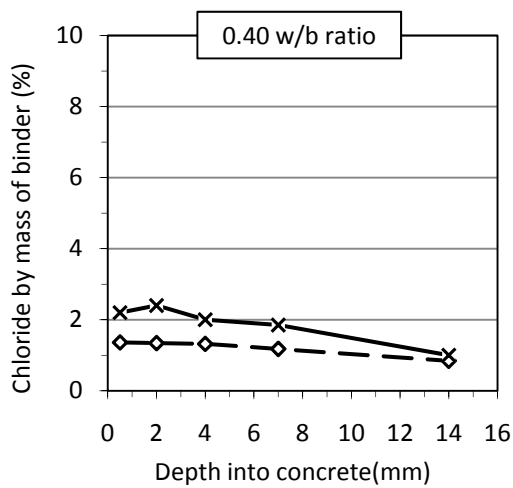


Figure A.3: Chloride profiles: CEM I [PE] : FA : greywacke

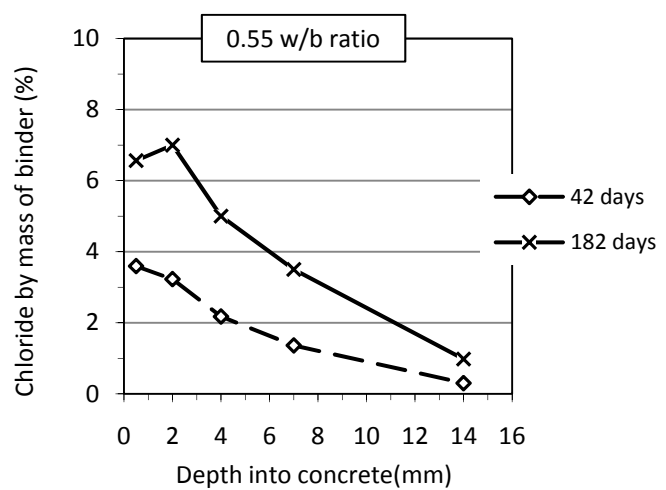
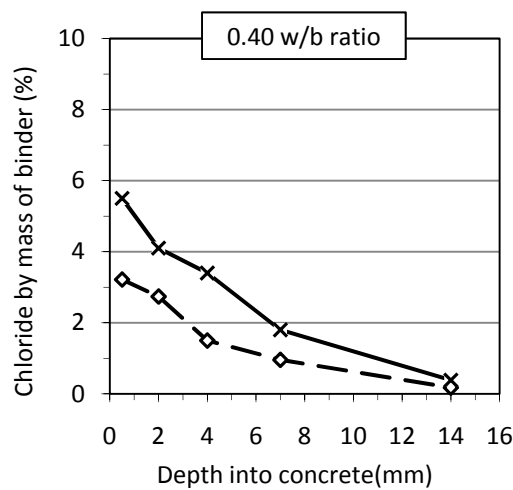


Figure A.4: Chloride profiles: CEM II A-S [DB]: Slagmore: greywacke

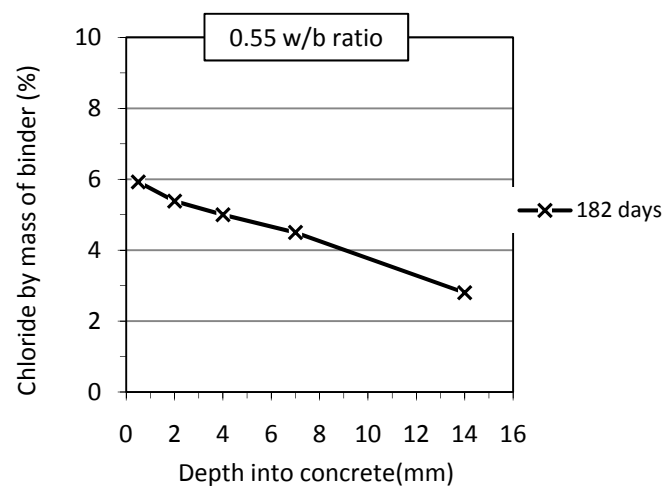
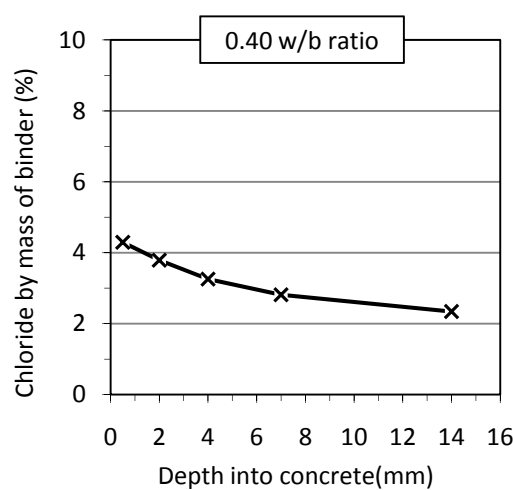


Figure A.5: Chloride profiles: CEM I [CT]: quartzite

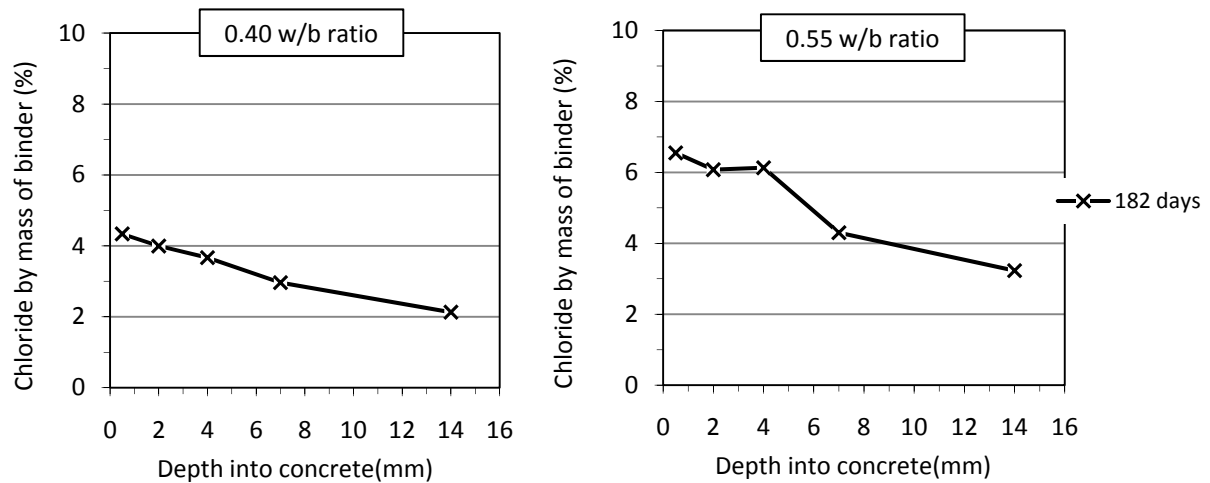


Figure A.6: Chloride profiles: CEM I [CT]: tillite

A.2 Durability index test results

A.2.1 Chloride conductivity index

Table A.3 (a): 28-day CCI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11
Average CCI (mS/cm)	0.93	0.99	0.97	0.16	0.15	0.19	0.57	0.65	0.58	0.15	0.16
Standard deviation	0.18	0.02	0.03	0.03	0.01	0.00	0.04	0.02	0.04	0.03	0.02
Coefficient of variation (%)	0.19	0.02	0.03	0.17	0.06	0.03	0.07	0.03	0.07	0.17	0.10
Deviation (t-value - 3.182)	0.26	0.03	0.05	0.04	0.01	0.01	0.06	0.03	0.06	0.04	0.02
Range (mS/cm)	Min.	0.67	0.96	0.92	0.12	0.14	0.19	0.50	0.62	0.53	0.11
	Max.	1.19	1.02	1.02	0.20	0.17	0.20	0.63	0.68	0.64	0.19

Table A.3 (b): 28-day CCI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22
Average CCI (mS/cm)	1.39	1.36	1.37	0.37	0.38	0.38	1.00	1.03	0.97	0.44	0.42
Standard deviation	0.07	0.02	0.00	0.04	0.10	0.00	0.01	0.04	0.04	0.02	0.02
Coefficient of variation (%)	0.05	0.02	0.00	0.10	0.26	0.01	0.01	0.04	0.04	0.04	0.06
Deviation (t-value - 3.182)	0.11	0.03	0.00	0.05	0.14	0.01	0.01	0.06	0.06	0.03	0.04
Range (mS/cm)	Min.	1.28	1.33	1.36	0.32	0.23	0.37	0.98	0.97	0.41	0.39
	Max.	1.50	1.39	1.37	0.43	0.52	0.39	1.01	1.10	0.47	0.46

Table A.4 (a): 91-day CCI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average CCI (mS/cm)	0.88	0.50	0.47	0.11	0.14	0.13	0.36	0.38	0.39	0.10	0.08	
Standard deviation	0.02	0.02	0.02	0.01	0.01	0.01	0.04	0.01	0.02	0.00	0.01	
Coefficient of variation (%)	0.02	0.03	0.05	0.13	0.04	0.11	0.10	0.02	0.06	0.03	0.14	
Deviation (t-value - 3.182)	0.03	0.02	0.03	0.02	0.01	0.02	0.06	0.01	0.03	0.00	0.02	
Range (mS/cm)	Min.	0.85	0.48	0.43	0.09	0.13	0.11	0.30	0.37	0.36	0.09	0.07
	Max.	0.90	0.52	0.50	0.13	0.15	0.15	0.41	0.39	0.43	0.10	0.10

Table A.4 (b): 91-day CCI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average CCI (mS/cm)	0.47	0.89	0.89	0.23	0.23	0.13	0.58	0.51	0.58	0.22	0.21	
Standard deviation	0.02	0.01	0.01	0.06	0.01	0.01	0.03	0.01	0.07	0.01	0.02	
Coefficient of variation (%)	0.05	0.02	0.01	0.27	0.04	0.11	0.06	0.03	0.11	0.03	0.09	
Deviation (t-value - 3.182)	0.03	0.02	0.01	0.09	0.01	0.02	0.05	0.02	0.10	0.01	0.03	
Range (mS/cm)	Min.	0.43	0.87	0.88	0.14	0.21	0.11	0.53	0.49	0.48	0.21	0.18
	Max.	0.50	0.91	0.90	0.32	0.24	0.15	0.63	0.54	0.68	0.23	0.24

Table A.5 (a): 182-day CCI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average CCI (mS/cm)	0.78	0.45	0.42	0.09	0.10	0.09	0.13	0.17	0.14	0.04	0.07	
Standard deviation	0.05	0.01	0.01	0.00	0.01	0.02	0.02	0.01	0.01	0.00	0.00	
Coefficient of variation (%)	0.06	0.02	0.01	0.04	0.11	0.23	0.12	0.04	0.06	0.03	0.05	
Deviation (t-value - 3.182)	0.07	0.01	0.01	0.01	0.02	0.03	0.02	0.01	0.01	0.00	0.01	
Range (mS/cm)	Min.	0.71	0.44	0.41	0.08	0.09	0.06	0.11	0.16	0.12	0.04	0.06
	Max.	0.85	0.46	0.43	0.09	0.12	0.12	0.16	0.18	0.15	0.05	0.07

Table A.5 (b): 182-day CCI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average CCI (mS/cm)	0.40	0.80	0.78	0.19	0.20	0.09	0.18	0.19	0.19	0.19	0.18	
Standard deviation	0.00	0.02	0.05	0.00	0.00	0.02	0.00	0.01	0.00	0.02	0.01	
Coefficient of variation (%)	0.01	0.03	0.06	0.01	0.01	0.23	0.01	0.07	0.02	0.12	0.03	
Deviation (t-value - 3.182)	0.01	0.03	0.07	0.00	0.00	0.03	0.00	0.02	0.01	0.03	0.01	
Range (mS/cm)	Min.	0.40	0.77	0.71	0.19	0.20	0.06	0.18	0.17	0.18	0.15	0.18
	Max.	0.41	0.83	0.85	0.19	0.20	0.12	0.18	0.21	0.20	0.22	0.19

A.2.2 Oxygen permeability index

Table A.6 (a): 28-day OPI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average OPI	10.6	10.6	10.7	10.0	9.8	10.4	10.9	10.70	10.9	10.79	10.8	
Standard deviation	0.07	0.09	0.05	0.06	0.21	0.04	0.04	0.02	0.17	0.12	0.13	
Coefficient of variation (%)	0.01	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.02	0.01	0.01	
Deviation (t-value - 3.182)	0.10	0.13	0.07	0.10	0.31	0.06	0.06	0.04	0.26	0.18	0.19	
Range	Min.	10.54	10.50	10.64	9.95	9.45	10.31	10.84	10.66	10.64	10.61	10.61
	Max.	10.74	10.76	10.79	10.14	10.07	10.43	10.96	10.73	11.16	10.97	10.99

Table A.6 (b): 28-day OPI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average OPI	10.4	10.5	10.5	9.9	9.8	9.8	10.7	10.49	10.7	10.62	10.7	
Standard deviation	0.13	0.06	0.04	0.11	0.25	0.15	0.09	0.07	0.07	0.05	0.17	
Coefficient of variation (%)	0.01	0.01	0.00	0.01	0.03	0.02	0.01	0.01	0.01	0.00	0.02	
Deviation (t-value - 3.182)	0.19	0.09	0.07	0.17	0.37	0.22	0.14	0.11	0.10	0.08	0.25	
Range	Min.	10.25	10.41	10.48	9.70	9.40	9.61	10.56	10.38	10.60	10.54	10.46
	Max.	10.62	10.60	10.61	10.04	10.14	10.06	10.84	10.59	10.79	10.69	10.96

Table A.7 (a): 91-day OPI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average OPI	10.8	10.7	10.9	10.1	10.2	10.4	10.9	10.78	10.9	10.98	10.8	
Standard deviation	0.05	0.05	0.00	0.02	0.11	0.20	0.27	0.09	0.17	0.09	0.13	
Coefficient of variation (%)	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.02	0.01	0.01	
Deviation (t-value - 3.182)	0.08	0.07	0.00	0.03	0.16	0.30	0.39	0.13	0.25	0.13	0.19	
Range	Min.	10.72	10.63	10.87	10.04	9.99	10.09	10.55	10.65	10.69	10.85	10.62
	Max.	10.88	10.76	10.87	10.10	10.32	10.69	11.34	10.91	11.20	11.12	10.99

Table A.7 (b): 91-day OPI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average OPI	10.6	10.5	10.5	10.0	10.0	10.0	10.8	10.71	10.8	10.65	10.8	
Standard deviation	0.12	0.01	0.00	0.19	0.30	0.24	0.14	0.31	0.12	0.08	0.14	
Coefficient of variation (%)	0.01	0.00	0.00	0.02	0.03	0.02	0.01	0.03	0.01	0.01	0.01	
Deviation (t-value - 3.182)	0.18	0.01	0.00	0.29	0.44	0.36	0.21	0.46	0.18	0.12	0.21	
Range	Min.	10.38	10.53	10.50	9.68	9.54	9.66	10.59	10.24	10.57	10.53	10.60
	Max.	10.75	10.54	10.50	10.25	10.42	10.39	11.01	11.17	10.93	10.77	11.01

Table A.8 (a): 182-day OPI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average OPI	11.0	10.7	10.8	10.1	10.3	10.6	11.3	11.15	11.3	11.18	11.0	
Standard deviation	0.04	0.12	0.08	0.17	0.06	0.12	0.17	0.05	0.04	0.19	0.25	
Coefficient of variation (%)	0.00	0.01	0.01	0.02	0.01	0.01	0.02	0.00	0.00	0.02	0.02	
Deviation (t-value - 3.182)	0.06	0.18	0.11	0.25	0.09	0.18	0.25	0.07	0.06	0.28	0.37	
Range	Min.	10.92	10.53	10.69	9.82	10.20	10.41	11.01	11.09	11.20	10.90	10.67
	Max.	11.03	10.88	10.92	10.32	10.39	10.77	11.51	11.22	11.32	11.46	11.40

Table A.8 (b): 182-day OPI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average OPI	10.8	10.6	10.6	10.0	10.1	10.1	11.0	10.94	11.2	10.90	11.0	
Standard deviation	0.08	0.01	0.00	0.01	0.29	0.30	0.01	0.04	0.18	0.09	0.33	
Coefficient of variation (%)	0.01	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.02	0.01	0.03	
Deviation (t-value - 3.182)	0.11	0.01	0.00	0.02	0.43	0.44	0.02	0.06	0.26	0.14	0.49	
Range	Min.	10.69	10.59	10.63	10.02	9.66	9.63	10.93	10.89	10.97	10.76	10.53
	Max.	10.91	10.62	10.64	10.06	10.51	10.52	10.97	11.00	11.49	11.03	11.51

Table A.9 (a): 28-day oxygen permeability coefficients (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average k (m/s^2)	2.3	2.3	1.9	9.1	17.4	4.3	1.3	2.0	1.3	1.6	1.2	
Standard deviation	0.70	0.09	0.05	1.38	0.21	0.04	0.12	0.02	0.39	0.12	0.61	
Coefficient of variation (%)	0.31	0.04	0.03	0.15	0.01	0.01	0.09	0.01	0.31	0.07	0.38	
Deviation (t-value - 3.182)	1.04	0.13	0.07	2.05	0.31	0.06	0.18	0.04	0.58	0.18	0.90	
Range (m/s^2)	Min.	1.26	2.22	1.85	7.05	17.13	4.24	1.08	1.97	0.68	1.45	0.68
	Max.	3.35	2.48	2.00	11.14	17.75	4.35	1.43	2.04	1.84	1.80	2.49

Table A.9 (b): 28-day oxygen permeability coefficients (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average k (m/s^2)	3.7	3.1	2.8	13.5	16.9	14.6	2.0	3.3	2.0	2.4	1.9	
Standard deviation	0.56	0.46	0.28	3.67	8.01	4.97	0.47	0.56	0.30	0.30	2.45	
Coefficient of variation (%)	0.15	0.15	0.10	0.27	0.47	0.34	0.23	0.17	0.15	0.12	1.27	
Deviation (t-value - 3.182)	0.82	0.69	0.42	5.44	11.87	7.36	0.69	0.83	0.44	0.44	3.63	
Range (m/s^2)	Min.	2.85	2.44	2.42	8.06	5.06	7.25	1.33	2.42	1.57	1.98	-1.69
	Max.	4.49	3.81	3.25	18.94	28.79	21.96	2.71	4.08	2.46	2.85	5.56

Table A.10 (a): 91-day oxygen permeability coefficients (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average k (m/s^2)	1.6	2.0	1.4	8.5	7.0	4.1	1.1	1.7	1.1	1.0	1.1	
Standard deviation	0.27	0.24	0.36	1.54	1.69	2.17	0.36	0.13	0.04	0.19	0.30	
Coefficient of variation (%)	0.17	0.12	0.26	0.18	0.24	0.53	0.32	0.08	0.04	0.18	0.19	
Deviation (t-value - 3.182)	0.40	0.36	0.53	2.28	2.50	3.21	0.53	0.19	0.06	0.28	0.44	
Range (m/s^2)	Min.	1.20	1.66	0.83	6.23	4.52	0.89	0.60	1.48	1.06	0.76	1.13
	Max.	2.00	2.37	1.89	10.78	9.51	7.31	1.65	1.85	1.19	1.32	2.02

Table A.10 (b): 91-day oxygen permeability coefficients (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average k (m/s^2)	2.7	2.9	3.2	10.9	10.4	9.5	1.6	2.0	1.8	2.2	1.6	
Standard deviation	0.17	0.96	0.47	7.47	1.23	3.96	0.21	0.85	0.22	0.21	0.23	
Coefficient of variation (%)	0.06	0.33	0.15	0.69	0.12	0.42	0.13	0.43	0.13	0.09	0.15	
Deviation (t-value - 3.182)	0.26	1.42	0.69	11.06	1.82	5.86	0.32	1.26	0.33	0.31	0.34	
Range (m/s^2)	Min.	2.45	1.50	2.49	-0.18	8.62	3.63	1.27	0.70	1.45	1.93	1.24
	Max.	2.96	4.34	3.87	21.94	12.26	15.36	1.90	3.21	2.11	2.55	1.92

Table A.11 (a): 182-day oxygen permeability coefficients (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average k (m/s^2)	1.1	2.0	1.6	8.5	5.1	2.6	0.5	0.7	0.5	0.7	0.9	
Standard deviation	0.13	0.55	0.26	3.16	0.81	0.64	0.30	0.09	0.09	0.07	0.23	
Coefficient of variation (%)	0.13	0.28	0.17	0.37	0.16	0.25	0.54	0.12	0.16	0.10	0.25	
Deviation (t-value - 3.182)	0.20	0.82	0.38	4.67	1.19	0.95	0.44	0.13	0.13	0.10	0.34	
Range (m/s^2)	Min.	0.86	1.16	1.18	3.80	3.91	1.63	0.11	0.57	0.42	0.56	0.58
	Max.	1.25	2.79	1.94	13.15	6.30	3.52	0.98	0.83	0.67	0.76	1.26

Table A.11 (b): 182-day oxygen permeability coefficients (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average k (m/s^2)	1.6	2.5	2.3	9.1	8.2	8.5	1.1	1.1	0.6	1.3	0.9	
Standard deviation	0.11	0.04	0.01	8.54	9.16	6.41	0.03	0.25	0.03	0.65	0.20	
Coefficient of variation (%)	0.07	0.02	0.00	0.94	1.11	0.76	0.02	0.22	0.05	0.52	0.21	
Deviation (t-value - 3.182)	0.16	0.06	0.01	12.64	13.57	9.50	0.04	0.36	0.05	0.96	0.29	
Range (m/s^2)	Min.	1.42	2.42	2.30	-3.52	-5.34	-1.02	1.08	0.78	0.54	0.30	0.66
	Max.	1.74	2.54	2.33	21.76	21.80	17.98	1.16	1.51	0.63	2.23	1.24

A.2.3 Water sorptivity index

Table A.12 (a): 28-day WSI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average WSI (mm/hr ^{0.5})	7.26	7.33	7.16	6.39	7.15	6.84	4.91	4.85	4.83	4.53	4.93	
Standard deviation	0.47	0.18	0.53	0.19	0.20	0.39	0.27	0.48	0.12	0.23	0.28	
Coefficient of variation (%)	0.07	0.02	0.07	0.03	0.03	0.06	0.06	0.10	0.03	0.05	0.06	
Deviation (t-value - 3.182)	0.70	0.26	0.78	0.28	0.30	0.58	0.40	0.70	0.18	0.34	0.41	
Range (mm/hr ^{0.5})	Min.	6.56	7.07	6.38	6.11	6.85	6.26	4.51	4.15	4.64	4.19	4.52
	Max.	7.96	7.59	7.94	6.67	7.45	7.42	5.31	5.55	5.01	4.87	5.34

Table A.12 (b): 28-day WSI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average WSI (mm/hr ^{0.5})	7.66	8.01	7.94	6.76	7.68	6.78	5.72	5.71	5.91	5.73	5.87	
Standard deviation	0.21	0.18	0.17	0.37	0.36	0.41	0.04	0.30	0.18	0.25	0.13	
Coefficient of variation (%)	0.03	0.02	0.02	0.05	0.05	0.06	0.01	0.05	0.03	0.04	0.02	
Deviation (t-value - 3.182)	0.31	0.27	0.25	0.55	0.53	0.60	0.06	0.44	0.27	0.37	0.20	
Range (mm/hr ^{0.5})	Min.	7.35	7.74	7.69	6.21	7.15	6.18	5.66	5.27	5.65	5.36	5.67
	Max.	7.97	8.28	8.19	7.31	8.21	7.38	5.78	6.15	6.18	6.10	6.07

Table A.13 (a): 91-day WSI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11
Average WSI (mm/hr ^{0.5})	5.52	5.61	5.31	4.99	6.61	4.91	3.54	3.65	3.63	3.81	3.24
Standard deviation	0.36	0.20	0.48	0.27	0.28	0.13	0.13	0.39	0.00	0.11	0.35
Coefficient of variation (%)	0.06	0.04	0.09	0.05	0.04	0.03	0.04	0.11	0.00	0.03	0.11
Deviation (t-value - 3.182)	0.53	0.30	0.71	0.40	0.41	0.19	0.19	0.58	0.00	0.16	0.52
Range (mm/hr ^{0.5})	Min.	4.99	5.31	4.60	4.59	6.20	4.72	3.35	3.07	3.63	2.72
	Max.	6.05	5.91	6.02	5.39	7.02	5.10	3.73	4.23	3.63	3.76

Table A.13 (b): 91-day WSI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22	
Average WSI (mm/hr ^{0.5})	6.01	6.60	6.13	5.91	6.47	5.64	3.53	3.92	3.85	3.77	3.73	
Standard deviation	0.34	0.09	0.04	0.03	0.13	0.36	0.07	0.29	0.39	0.37	0.08	
Coefficient of variation (%)	0.06	0.01	0.01	0.00	0.02	0.06	0.02	0.07	0.10	0.10	0.02	
Deviation (t-value - 3.182)	0.50	0.13	0.07	0.04	0.19	0.53	0.10	0.43	0.57	0.55	0.12	
Range (mm/hr ^{0.5})	Min.	5.51	6.47	6.06	5.87	6.28	5.11	3.43	3.49	3.28	3.22	3.61
	Max.	6.51	6.73	6.20	5.95	6.66	6.17	3.63	4.35	4.42	4.32	3.85

Table A.14 (a): 182-day WSI test results (0.40 w/b ratio)

Mix label	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	
Average WSI (mm/hr ^{0.5})	5.02	5.20	4.89	4.13	6.01	4.30	3.01	3.47	3.17	3.12	3.06	
Standard deviation	0.33	0.29	0.32	0.15	0.19	0.34	0.20	0.17	0.22	0.28	0.08	
Coefficient of variation (%)	0.07	0.06	0.07	0.04	0.03	0.08	0.07	0.05	0.07	0.09	0.03	
Deviation (t-value - 3.182)	0.49	0.43	0.47	0.22	0.29	0.50	0.30	0.26	0.33	0.42	0.12	
Range (mm/hr ^{0.5})	Min.	4.53	4.77	4.42	3.91	5.72	3.80	2.71	3.21	2.84	2.70	2.94
	Max.	5.51	5.63	5.36	4.35	6.30	4.80	3.31	3.73	3.50	3.54	3.18

Table A.14 (b): 182-day WSI test results (0.55 w/b ratio)

Mix label	M12	M13	M14	M15	M16	M17	M18	M19	M20	M21	M22
Average WSI (mm/hr ^{0.5})	5.70	6.40	5.95	5.56	6.12	5.34	3.55	3.56	3.53	3.74	3.34
Standard deviation	0.16	0.06	0.05	0.22	0.19	0.35	0.22	0.37	0.31	0.34	0.17
Coefficient of variation (%)	0.03	0.01	0.01	0.04	0.03	0.07	0.06	0.10	0.09	0.09	0.05
Deviation (t-value - 3.182)	0.24	0.10	0.07	0.33	0.28	0.52	0.33	0.54	0.46	0.51	0.25
Range (mm/hr ^{0.5})	Min.	5.46	6.30	5.88	5.23	5.84	4.82	3.02	3.06	3.23	3.09
	Max.	5.94	6.50	6.02	5.89	6.40	5.86	3.88	4.10	3.99	4.25

A.3 Compressive strength and density results

Table A.15: Compressive strength test results

Concrete mix constituents	w/b	0.40			0.55		
	Age (days)	Average		s.d	Average		s.d
		Density (kg/m ³)	f _{cu} (MPa)		Density (kg/m ³)	f _{cu} (MPa)	
CEM I[CT]: greywacke	28	2462	60.1	3.0	2439	41.7	1.0
	91	2477	72.3	1.6	2492	49.3	2.0
	182	2440	75.4	1.4	2417	53.2	0.7
CEM I[CT]: quartzite	28	2434	55.4	1.6	2409	41.1	0.6
	91	2438	65.0	0.3	2409	43.1	0.4
	182	2421	66.5	1.1	2375	50.5	0.5
CEM I[CT]: tillite	28	2425	59.8	0.8	2414	41.1	1.9
	91	2462	63.5	3.0	2412	48.2	4.8
	182	2447	67.9	5.1	2383	50.6	2.2
CEM I[CT]: GGCS: greywacke	28	2447	69.3	3.9	2429	50.8	0.6
	91	2458	73.6	2.6	2423	57.7	0.9
	182	2500	80.3	0.7	2382	62.6	0.7
CEM I[CT]: FA: greywacke	28	2433	56.4	1.2	2433	36.7	2.9
	91	2408	71.9	1.4	2373	52.7	1.2
	182	2389	72.1	2.1	2381	55.1	2.8
CEM I[PE]: FA: quartzite	28	2410	58.8	3.5	2377	40.9	2.0
	91	2404	70.5	4.1	2413	51.9	0.6
	182	2334	74.1	1.3	2392	54.1	2.4
CEM II A-S: Slagmore: tillite	28	2414	57.0	2.8	2369	40.3	2.0
	91	2398	62.9	0.8	2315	45.6	0.6
	182	2373	63.7	2.8	2333	47.9	0.5
CEM I[PE]: FA: greywacke	28	2452	58.1	3.3	2425	36.4	1.3
	91	2419	72.5	6.9	2441	50.7	4.9
	182	2389	79.6	0.9	2386	53.6	3.5
CEM II A-S: Slagmore: greywacke	28	2429	59.5	1.9	2440	40.1	1.5
	91	2454	67.8	1.0	2451	49.6	2.9
	182	2380	68.9	2.4	2405	49.6	1.2
CEM I[CT]: GGCS: quartzite	28	2492	60.4	4.0	2432	45.8	0.9
	91	2411	68.1	6.5	2393	51.1	2.1
	182	2393	67.3	5.9	2387	51.5	1.5
CEM I[CT]: GGCS: tillite	28	2449	66.8	2.8	2404	50.2	0.8
	91	2419	68.3	4.6	2388	55.3	2.4
	182	2408	70.5	4.3	2370	56.5	2.5

Appendix B

Experimental test procedures

B.1 Diffusion coefficient tests – ASTM C1556-04

B.1.1 Bulk diffusion testing

The Nordic Standard NT Build 443 immersion test described in ASTM C1556-04 (2004) was applied for bulk diffusion testing. Figure B.1 illustrates a schematic diagram of the bulk diffusion test. The test procedure was applied as follows in as far as was practical with the specifications provided for the test:

1. Surface-dry 100 Ø x 100 high cylindrical concrete specimens were coated with an impermeable epoxy resin except for the exposure face.
2. The exposure faces were cleaned with tap water and the specimens then saturated in lime water after which they were removed, scrubbed with a stiff brush and rinsed with tap water.
3. The specimens were exposed to 2.8 M NaCl solution continuously for 42 and 182 days in sealed containers placed in an environment room maintained at $23 \pm 2^\circ\text{C}$.
4. At the sampling ages, samples were removed, cleaned with a stiff brush and rinsed with tap water and stored in an environment room maintained at $23 \pm 2^\circ\text{C}$ for 24 hours.
5. Profile dry-grinding and dry-slicing of the specimens was done at parallel increment depths from the exposed surface to 20 mm to obtain six powder samples. Table 3.7 gives the sampled profile depths.

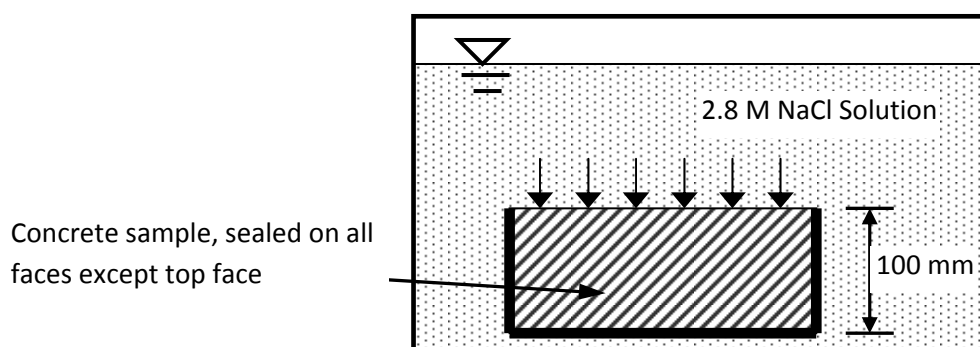


Figure B.1: Schematic of the Bulk Diffusion Test (Ballim et al, 2009)

B.1.2 Chloride potentiometric titration

Determination of the total acid soluble chloride content of each powder sample was done by potentiometric titration to obtain the chloride penetration profiles. A brief outline of the procedure is given here.

1. 2 ml of nitric acid was added to decompose the powder samples and release the chlorides into solution
2. The titrants, sodium acetate and silver nitrate, were added to the solution after half an hour
3. The automatic titrator computes the chloride concentrations from the inflection point of a potential vs. titrant volume plot
4. The chloride concentrations obtained at each profile level were then plotted to obtain the surface chloride concentration (C_s) and the corresponding apparent chloride diffusion coefficient (D_a)

The lowest concentration value obtained was taken to be the background chloride content of the concrete.

This experimental study deals only with the total acid soluble chloride content of powder samples from concrete exposed to a chloride environment. The apparent chloride diffusion coefficient, D_a , is obtained by curve-fitting the chloride penetration profile to Fick's second law as described in Chapter 2 section 2.7.

B.2 Durability Index tests

B.2.1 Chloride conductivity index test

The South African chloride conductivity test involves measuring a concrete sample's electric conductivity. The test procedure was applied as follows (Alexander et al, 2009):

1. Concrete disks (typically 70 mm diameter by 30 mm thick) were cored and sliced from continuously moist cured cube specimens at ages of 28, 91 and 182 days
2. The samples were preconditioned by oven drying at 50°C for a minimum period of 7 days
3. After this, the samples were vacuum pre-saturated with a 5 M NaCl solution for 18 hours
4. The samples were then placed between two conduction cells containing 5 M NaCl solution (Figure B.3)
5. A potential difference of 10 V was applied across the sample and the corresponding current measured

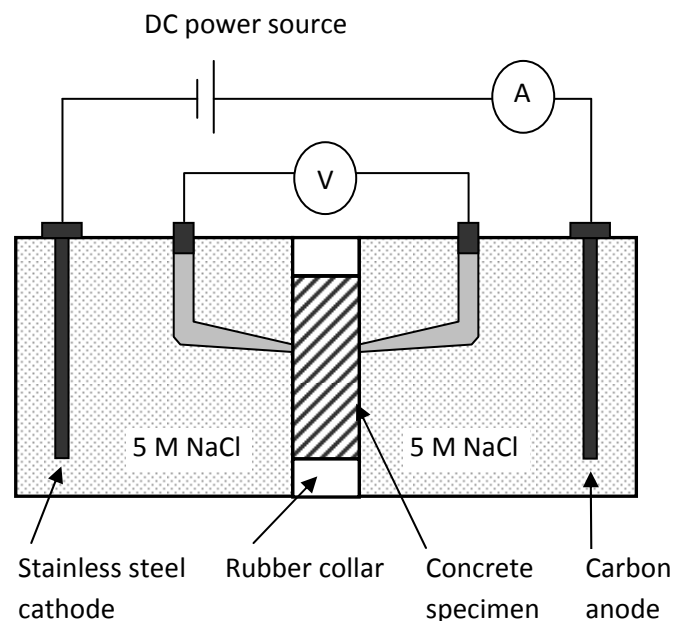


Figure B.3: Schematic of chloride conductivity cell (Ballim et al, 2009)

The chloride conductivity of the samples was calculated using equation B.1:

$$\sigma = \frac{it}{VA} \quad (\text{B.1})$$

where:

σ conductivity of the specimen (mS/cm)

- i electric current (mA)
- V voltage (V)
- t average thickness of specimen (cm)
- A cross-sectional area of specimen (cm²)

B.2.3 Oxygen permeability index test

The oxygen permeability index (OPI) test, developed in South Africa, comprises determining the D'Arcy coefficient of permeability by measuring the pressure decay of oxygen gas passed through a concrete disk. The test procedure was applied as follows (Alexander et al, 2009):

1. Concrete disks (typically 70 mm diameter by 30 mm thick) were cored and sliced from continuously moist cured cube specimens at ages of 28, 91 and 182 days
2. The samples were preconditioned by oven drying at 50°C for a minimum period of 7 days
3. After this, the samples were placed in a falling head permeameter and a pressure gradient applied across the test sample. The pressure decay in the pressure cell was subsequently monitored over time (Figure B.4)

The oxygen permeability coefficient was calculated from the slope of the log of pressure head versus time using equation B.3.

$$k = \frac{\omega V g d}{R A \theta t} \ln \frac{P_o}{P} \quad (\text{B.3})$$

where:

- k coefficient of permeability (m/s)
- ω molecular mass of permeating gas (kg/mol)
- V volume of the pressure cylinder (m³)
- g acceleration due to gravity (m/s²)
- d average specimen thickness (mm)
- R universal gas constant (Nm/Kmol)
- A cross-sectional area of the specimen (mm²)
- θ absolute temperature (K)
- P_o pressure at start of test (kPa)

P pressure at time t (kPa)

The coefficient of permeability (k) is an exponential number and therefore is simplified by defining the permeability index (OPI) as the negative log of k as given in equation B.4

$$\text{OPI} = -\log_{10} k \quad (\text{B.4})$$

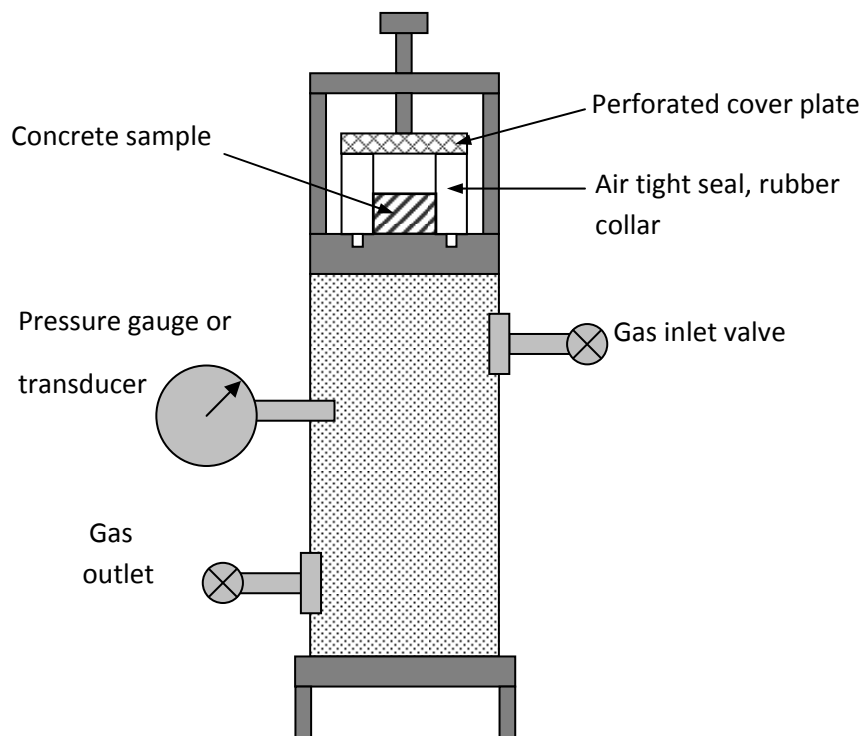


Figure B.4: Schematic of an oxygen permeameter (Ballim et al, 2009)

B.2.4 Water sorptivity index test

The water sorptivity index test (WSI) test, developed in South Africa, comprises measuring the mass change of concrete disk specimens placed in a calcium hydroxide solution over time. The test procedure was applied as follows (Alexander et al, 2009):

1. The concrete disks (typically 70 mm diameter by 30 mm thick) from the OPI test were used
2. The samples were preconditioned by oven drying at 50°C for a minimum period of 7 days
3. The samples were sealed on the circumferential surfaces with tape and exposed to the solution with the test surface facing downwards (Figure B.5)

4. At regular time intervals, the specimens were removed from the water and the mass of water absorbed was determined using an electronic balance
5. Measurements were stopped before saturation was reached and the concrete was then vacuum-saturated in calcium hydroxide solution for 18 hours to determine the effective porosity

A linear relationship is observed when the mass of absorbed solution was plotted against the square root of time. The sorptivity of the concrete was determined from the slope of the straight line produced. Equation B.5 shows this relationship.

$$S = \frac{M_{sat}}{t^{1/2}} \left(\frac{d}{M_{sat} - M_0} \right) \quad (B.5)$$

where:

S	sorptivity
M_{sat}	mass of saturated surface dry concrete (g)
M_0	mass of oven dried mass (g)
t	period of absorption (hr)
g	acceleration due to gravity (m/s^2)
d	average specimen thickness (mm)

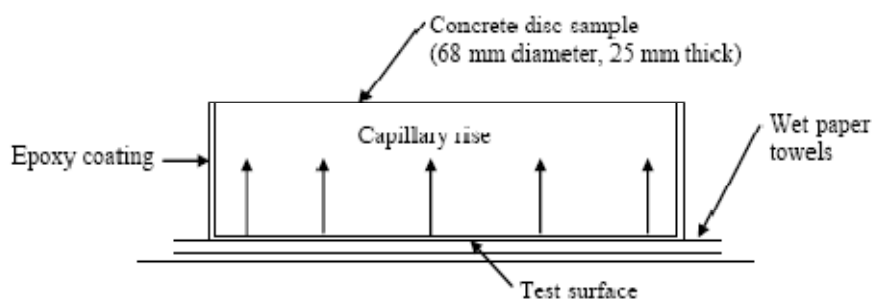


Figure B.5: Schematic of water sorptivity test (Alexander et al 2006)

References

Alexander, M. G., Ballim, Y., and Mackechnie, J. R. (2009), Concrete durability index testing manual, *Research monograph No 4*, University of Cape Town.

Alexander, M. G., Stanish, K. and Ballim, Y., (2006), Performance-based durability design and specification: Overview of the South African Approach, Proceedings of the International RILEM workshop on *Performance based evaluation and indicators for concrete durability*, 19 - 21 March, Madrid, Spain.

American Society for Testing and Materials, ASTM C1556 - 04, (2004), *Standard test method for determining the apparent chloride diffusion coefficient of cementitious mixtures by bulk diffusion*, Philadelphia.

Appendix C

C.1 Statistical analysis

The following is an extract from the American Society for Testing and Materials, ASTM E178 - 02, Standard practice for dealing with outlying observations. It was used to determine the statistical reliability and reproducibility of the data obtained from this experimental study.

1. Scope

1.1 This practice covers outlying observations in samples and how to test the statistical significance of them. An outlying observation, or outlier, is one that appears to deviate markedly from other members of the sample in which it occurs. In this connection, the following two alternatives are of interest:

1.1.1 An outlying observation may be merely an extreme manifestation of the random variability inherent in the data. If this is true, the value should be retained and processed in the same manner as the other observations in the sample.

1.1.2 On the other hand, an outlying observation may be the result of gross deviation from prescribed experimental procedure or an error in calculating or recording the numerical value. In such cases, it may be desirable to institute an investigation to ascertain the reason for the aberrant value. The observation may even actually be rejected as a result of the investigation, though not necessarily so. At any rate, in subsequent data analysis, the outlier or outliers will be recognized as probably being from a different population than that of the other sample values.

Equations C.1 and C.2 below were used to test the statistical significance of the test results and the values obtained checked against Table C.1 to determine their reliability and reproducibility:

$$T_u = \frac{x_u - \bar{x}}{\sigma} \tag{C.1}$$

$$T_i = \frac{x - x_i}{\sigma}$$

(C.2)

where:

- x_u, x_l data point
- \bar{x} sample average
- σ sample standard deviation

Table C.1: Critical values for outlier analysis

No of observations	1 %	2.5 %	5 %	10 %
3	1.155	1.155	1.153	1.148
4	1.492	1.481	1.463	1.425
5	1.749	1.715	1.672	1.602
6	1.944	1.887	1.822	1.729

References

American Society for Testing and Materials, ASTM E178 -02, (2008), *Standard practice for dealing with outlying observations*, ASTM International, Philadelphia.

EBE Faculty Research Ethics Form

**EBE Faculty
Assessment of Ethics in Research Projects**

Name of Student: **KUNG'U GITHACHURI**

Supervisor: **PROF. MARK ALEXANDER**

Department: **CIVIL ENGINEERING**

Degree: **MSc. (Eng.)**

Research Project Title: **INFLUENCES ON THE TRANSPORT PROPERTIES OF A RANGE OF SOUTH AFRICAN MARINE CONCRETES**

Overview of ethics issues in your research project:

Question 1:	Is there a possibility that your research could cause harm to a third party (i.e. a person not involved in your project)?	YES	NO ✓
Question 2:	Is your research making use of human subjects as sources of data? If your answer is YES, please complete Addendum 2.	YES	NO ✓
Question 3:	Does your research involve the participation of or provision of services to communities? If your answer is YES, please complete Addendum 3.	YES	NO ✓
Question 4:	If your research is sponsored, is there any potential for conflicts of interest? If your answer is YES, please complete Addendum 4.	YES	NO ✓

If you have answered YES to any of the above questions, please append a copy of your research proposal, as well as any interview schedules or questionnaires (Addendum 1) and please complete further addenda as appropriate.

I hereby undertake to carry out my research in such a way that

- there is no apparent legal objection to the nature or the method of research; and
- the research will not compromise staff or students or the other responsibilities of the University;
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative interpretations will be considered;
- the findings could be subject to peer review and publicly available; and
- I will comply with the conventions of copyright and avoid any practice that may be considered plagiarism.

Signed by:

	Full name and signature	Date
Student:	KUNG'U GITHACHURI	25/11/2009
	Signed by candidate	

This application is approved by:

Supervisor:	PROF. MARK ALEXANDER	27/11/09
Head of Department	PROF. ALPHOSE ZINGONI	02/12/09
Chair : Faculty EIR Committee For applicants other than undergraduate students who have answered YES to any of the above questions.	NOT APPLICABLE	