

Effect of reinforcement spacers on concrete microstructure and durability

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Declaration

I hereby declare that this thesis, submitted for the degree of Doctor of Philosophy and Diploma of Imperial College London is the result of my own work, and that all else is appropriately referenced.

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Date: November, 2015

Abstract

Reinforcement spacers (i.e. bar supports, chairs) are crucial elements of reinforced concrete, but their influence on the microstructure and long-term durability is not clear. This study investigates the effect caused by plastic and cementitious spacers, and steel wire chairs combined with different aggregate sizes, curing and conditioning regimes on the transport properties, microstructure and chloride-induced corrosion of concrete structures. Concrete cylindrical samples were prepared with 25 and 50 mm high plastic, steel and cementitious spacers. Samples were then cured, conditioned and tested for oxygen diffusivity, oxygen permeability, water sorptivity and chloride diffusivity.

Selected samples were pressure impregnated with fluorescent epoxy to study the extent and spatial distribution of epoxy intrusion. The interfacial zone between the spacer and concrete was examined using field-emission scanning electron microscope in the backscattered electron (BSE) mode. The ingress of chloride, particularly near the interface between spacers and concrete matrix was studied using micro X-ray fluorescence (μ XRF). The effect of plastic and cementitious spacers on chloride-induced corrosion via capillary rise and cyclic wetting/drying was investigated using small reinforced concrete beams. The feasibility of improving the bond between spacer and concrete by increasing surface roughness of plastic spacers was also investigated.

Results show that concrete samples containing plastic spacers consistently gave the least resistance to transport and the highest epoxy penetration followed by samples with cementitious spacers, and then steel spacers. The control samples (samples without spacers) had the highest resistance to transport in all cases. The epoxy penetration occurred mainly through the spacer-concrete interface. The microstructure of the spacer-concrete interface showed significantly lower cement content and higher porosity compared to 'bulk paste' farther away from the interface. Higher penetration of chloride ions was detected along spacer-concrete interface compared to the control sample or the bulk paste farther away. It is evident that spacers initiate early corrosion and this may reduce the service-life of reinforced concrete structures. The implications of these findings on durability of concrete structures are discussed. Several recommendations to improve the bond at the interface between spacer and concrete are presented.

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Notation

Roman letters

A	Fitting constant
A	Cross-sectional area of sample (m^2)
BSE	Backscattered electron microscopy
C	Concrete
Co	Control sample (sample with no spacer)
C1	Cementitious spacer
CN ₁	Concentration of oxygen in the oxygen stream at 1 bar (m^3/m^3)
CN ₂	Mean concentration of oxygen in the nitrogen stream at 1 bar (m^3/m^3)
CA	Concentration of oxygen (mol/m^3)
C-S-H	Calcium Silicate Hydrate
C ₃ S	$3\text{CaO}.\text{SiO}_2$
C ₂ S	$2\text{CaO}.\text{SiO}_2$
C ₃ A	$3\text{CaO}.\text{Al}_2\text{O}_3$
C ₄ AF	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$
Cs	Concentration of chlorides at surface
C (x, t)	Concentration of chlorides at a distance x from the concrete at surface
D	Diffusion coefficient (m^2/s)
D _{eff}	Chloride diffusion coefficient (m^2/s)
ERF	Error function
g	Gravity acceleration (m/s^2)

G_0	Percentage of oxygen in the initial nitrogen stream
G_1	Percentage of oxygen in outflow stream
GGBS	Ground granulated blastfurnace slag
h	Capillary rise height (m)
h_{eq}	The equilibrium capillary rise height (m)
HPC	High- performance concrete
i	Cumulative absorbed water per unit area of the inflow face (g/m^2)
I	Current through the sample
ITZ	Interfacial transition zone
J_A	Oxygen transport rate ($\text{kg/m}^2.\text{s}$) or ($\text{moles/m}^2.\text{s}$)
k	Coefficient of permeability (m/s)
k_{int}	Intrinsic permeability of the material (m^2)
k_g	O_2 permeability coefficient (m^2)
m	Mass of a sample in the preconditioned state (g)
m_d	Mass of sample at 105°C oven-dried condition (g)
m_{SSD}	Mass of sample at SSD condition (g)
MSA	Maximum size of aggregate (mm)
n	Number of replicates
OM	Optical microscopy
P1	Plastic spacer
P2,P3	Modified plastic spacer
P_1^*	Pressure of oxygen stream (bar)
P_2^*	Pressure difference oxygen stream (bar)
P_1	Absolute pressure on the inlet face (N/m^2)

P_2	Absolute pressure on the outlet face (N/m ²)
P_m	Mean pressure of the inlet and outlet streams
p_h	The hydrostatic pressure (Pa)
p_c	Capillary pressure (Pa)
Q	Oxygen diffusion rate at 1 bar (m ³ /s)
Q^*	Oxygen permeation rate (m ³ /s)
r	Radius of the capillary (m)
$r.d.$	Relative density
R^2	Correlation coefficient
R_1	Flow rate of nitrogen stream (mL/min)
R_2	Flow rate of oxygen stream (mL/min)
RH	Relative humidity (%)
S	Sorptivity coefficient (g/m ² .min ^{1/2})
S1	Steel wire spacer.
SCMs	Supplementary cementitious materials
SEM	Scanning electron microscopy
SE	Standard error
SF	Silica fume
SSD	Saturated-surface dry
t	Thickness of sample
t/MSA	Sample thickness to maximum size of aggregate
UV	Ultraviolet
v	The volume of sample (mm ³)
w	Water content (%)

w_{air}	Weight of sample in air (g)
w_{water}	Weight of sample immersed in water (g)
w/c	Water to cement ratio
$\Delta W/A$	Mass of absorbed water per unit inflow area
x	Distance (m)
μXRF	Micro X-Ray Fluorescence

Greek letters

θ	Accessible porosity
ρ	The density of water (g/mm^3)
ρ^*	The density of fluid (g/mm^3)
η	Dynamic viscosity of the fluid (N.s/m^2)
η_g	Dynamic viscosity coefficient of the fluid (N.s/m^2)
β	A constant
σ	Standard deviation
Φ	Diameter (mm)

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Chapter 1 Introduction

1.1 Research motivation

Worldwide, concrete is the most heavily-used construction material and it has been estimated that around 12 billion tonnes are manufactured annually. In the United Kingdom, 100 million tonnes of concrete are produced every year [Frost, 2005]. The performance of concrete structures, in particular durability, is related not only to design, detailing and specification of materials but also to the quality of construction work [Gjørv, 2011; King and Dakin, 2001]. Positioning of the reinforcement with the correct cover of concrete is essential to protect the reinforcement from corrosion and to ensure that the required structural and fire performances are achieved. Low quality or inadequate concrete cover is a major factor causing premature degradation of concrete structures all over the world and a considerable portion of construction budgets are used for either repair or replacement of degraded structures [Mehta and Monteiro, 2013].

The lack of concrete cover is often due to incorrect placement of the reinforcement in the formwork. Prior to the 1960s, it was common to use practically any available material on-site such as brick and wooden pieces to support steel reinforcement during concreting. Gradually, manufactured spacers made from plastics cementitious materials and steel wires were introduced to achieve better quality control and more accurate provision of the concrete cover. Spacers are also known as bar supports, steel support, wire chairs, bolsters, continuous runners and sidewall spacers. Their function is to hold reinforcing bars securely in proper position prior to concreting and to ensure correct concrete cover between the reinforcement and formwork or blinding in the finished structure. The main potential problems with the use of spacers are the quality control of the produced spacer, the decision on spacer type for a given application and incorrect installation of spacers on site [King and Dakin, 2001].

The introduction of standards and design codes provided guidance for spacer's classification, placement and testing in Europe and United States. However, at present there is a lack of guidance on the manufacture, shape and material of the spacer. Also, no guidance is available for testing the spacer bond to concrete, spacer's hydrothermal deformation

characteristics and transport properties of cementitious spacer. In general, there is lack of technological advancement in the construction industry including the use of spacers in third world countries [Chemrouk, 2008] despite a high demand for concrete infrastructure.

Even with the availability of standards for spacers, designers seem to be more focussed on ensuring the correct amount of reinforcement, strength of the concrete and concrete cover; then the method for obtaining the required cover [Rayner, 2005]. It is still not a common practice for designers to specify spacers or include them on the drawings or contract documents. Contractors are usually in charge of determining what spacers to use and cost seems to be the dominant factor over other attributes.

Many publications [Clark et al., 1997;Jahren, 1994;Kawahigashi et al., 1999;Kenai and Bahar, 2003;Poulsen and Mejlbro, 2010;Tang and Utgenannt, 2009;Vik, 2002] reported issues and concerns over the use of spacers and its effect on concrete durability, in particular reinforcement corrosion. However, a search of the literature found that only limited studies [Concrete Society, 1981;Levitt and Herbert, 1970;Shaw, 2008] have been carried out to establish the effect of spacers on reinforcement corrosion and concrete durability in general. Available studies are based mainly on subjective visual inspection of reinforcement corrosion.

There is lack of research to understand the effect of spacers on the molecular and ionic transport properties of concrete. In essence, the durability of concrete depends on the ease with which fluids and gases can enter into and move through concrete [Neville, 2011a]. Concrete degradation processes such as chloride-induced reinforcement corrosion are rate-controlled by the transport of oxygen, water and chloride ions into concrete [Buenfeld, 1995].

Also, no research has been carried out to study the microstructure of the interface of spacers with the concrete matrix. The properties and performance of reinforced concrete are significantly influenced by its heterogeneous and highly complex microstructure [Mehta and Monteiro, 2013]. Although the microstructure-property relationships are not yet fully developed, understanding the essential elements of the microstructure would help to understand factors influencing important engineering properties of concrete such as durability [Mehta and Monteiro, 2013].

Though spacers seem small and inconsequential, they are left permanently in the structure and their presence could interrupt the microstructure of the concrete cover. Potentially, this

provides easy access of aggressive agents through spacer or its interface with concrete, and compromise the durability and long-term performance of concrete structures. Thus, it is essential to examine the microstructure of spacers and its interface with concrete and investigate the transport properties, to understand the influence of spacers on the properties of concrete. Durability is one of the most researched topics in the area of cement and concrete science. However, the effect of spacers, which is vital for concrete cover integrity, has largely been ignored.

1.2 Objectives and scope

The overall aim of this project is to enhance the understanding of the effect of reinforcement spacers on the microstructure and durability of reinforced concrete. This will be achieved by:

- Establishing the effect of spacers on the transport properties of concrete.
- Studying the microstructure of the spacers and its interface with concrete
- Investigating how spacers affect chloride-induced reinforcement corrosion and service life.

More than 200 concrete specimens with single cover plastic and cementitious spacers and steel wire chairs combined with different aggregate size, curing, and drying regimes are tested to determine its effect on transport properties (138 specimens), microstructure (8 specimens), chloride-induced corrosion and service life (70 specimens). Backscattered electron (BSE) microscopy, micro X-ray fluorescence (μ XRF) spectroscopy and image analysis will be applied to characterise spacer and its interface with concrete. The results from microstructure will be correlated to the measured transport properties.

1.3 Thesis outline

The thesis consists of seven chapters. Chapter 1 outlines the research motivation, objectives and scope of the study. Chapter 2 covers the development of spacers and presents a review of previous research related to the scope of the thesis. Chapter 3 presents the spacers and materials used for this experimental work, set-up and sample preparation procedures.

Chapter 4 covers the effect of spacers on transport properties. It presents the methodology of the experimental work, which includes molecular transport testing, fluorescent epoxy impregnation, imaging techniques and image analysis. Results from specimens made using different types and sizes of spacers that have been subjected to different curing and drying

regimes to simulate site conditions are presented. Image analysis was used to analyse the extent of fluorescent epoxy intrusion. The results show that concrete samples containing plastic spacers consistently gave the least resistance to transport, followed by samples with cementitious spacers, then steel spacers. Image analysis found that epoxy penetration occurred mainly through the spacer-concrete interface and samples containing plastic spacers had the highest epoxy penetration depth compared to samples containing cementitious or steel spacers. The control samples (samples without spacers) had the highest resistance to transport in all cases and the lowest epoxy penetration.

Chapter 5 studies the microstructure of the spacer-concrete interface using Euclidean Distance Mapping to determine the spatial variability of porosity and unreacted cement. Results indicate that the spacer-concrete interface contain significantly lower cement content and higher porosity compared to 'bulk paste' farther away from the interface. Spacers disrupt the packing of cement grains and increase the heterogeneity of the paste microstructure. The width of the interface is around 50 μm from the spacer boundary.

Chapter 6 deals with the effect of spacers on chloride-induced corrosion. Reinforced concrete specimens were exposed to salt solution via capillary rise and wetting/drying cycles. μXRF was used to collect profiles of chlorides versus depth and the data were fitted to Fick's 2nd Law to estimate the non steady-state diffusion coefficient and chloride concentration at the exposed surface. Results were then used to estimate service life (i.e. time to corrosion initiation) of concrete with and without spacers. The location of initial corrosion products was determined by visual inspection of sectioned samples. The results show that spacers provide a preferential path for ingress of chlorides that subsequently accelerate time to reinforcement corrosion.

Finally, the key findings from this thesis are summarised in Chapter 7. The implications of these findings are discussed and recommendations for further research are given. The overall experimental program is illustrated in Fig.1.1.

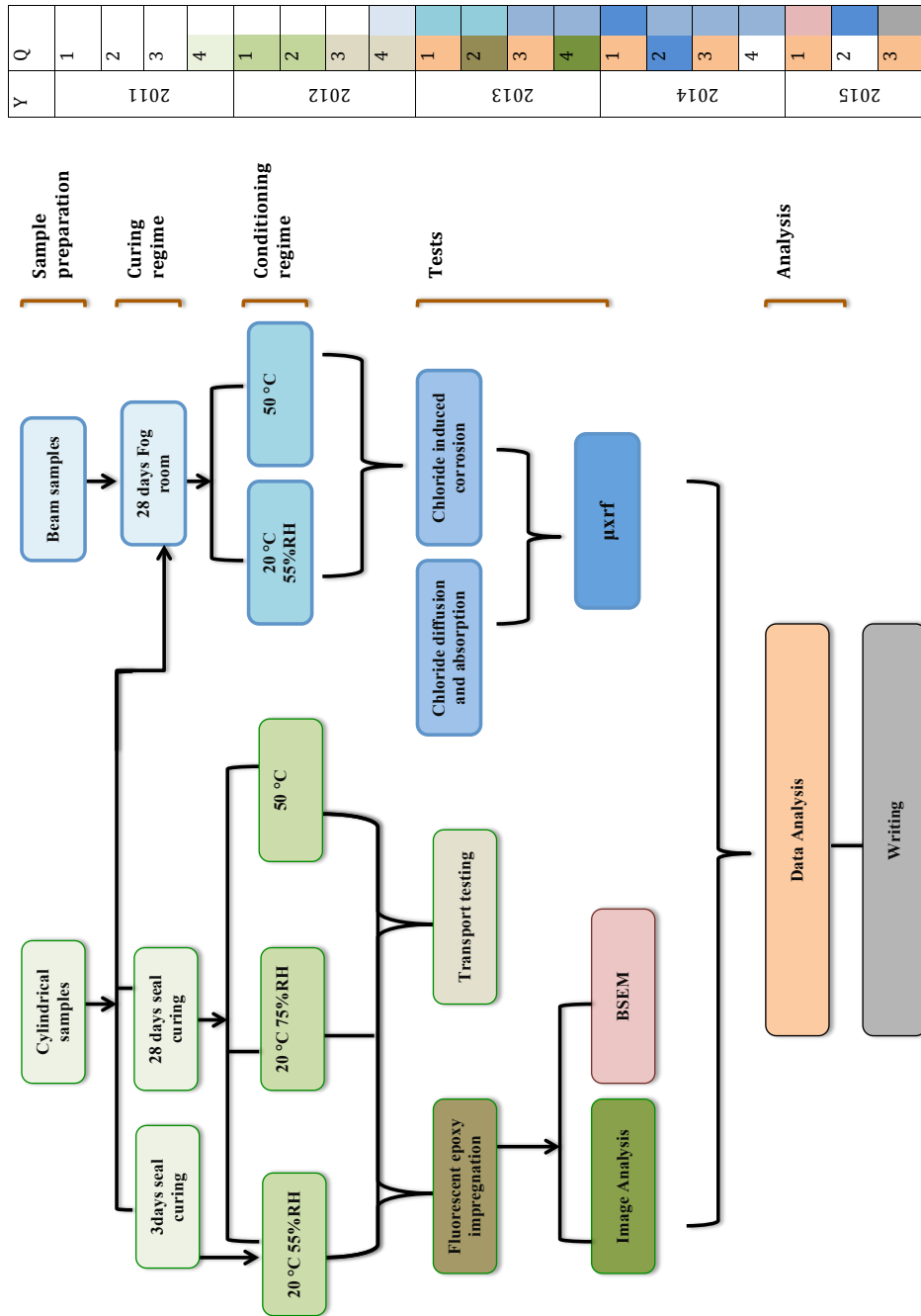


Figure 1.1 Overall experimental program

Chapter 2 Literature review

This chapter presents a literature review on the topics relevant to the scope of this thesis. Firstly, the development, design and types of spacers are presented. Subsequently, available standards and codes of practices on the use of spacers are reviewed. Findings from previous studies on the effect of spacers on concrete microstructure and durability are critically reviewed. Finally, the implication of spacers on concrete microstructure and durability are discussed. Other topics relevant to this study including concrete transport properties, chloride induced corrosion and concrete microstructure will be reviewed and presented in Chapters 4, 5 and 6 respectively.

2.1 Development of spacers

Before 1960, it was common to use bricks, rocks, timber pieces, tiles or practically any available material to support steel reinforcement off formwork or blinding during concreting. Gradually, different shapes and sizes of concrete, plastic spacers and steel wire chairs and methods of attaching reinforcement were introduced to give exact covers [Rayner, 2005].

Spacers provide the specified cover between the steel reinforcement and the concrete surface. The reinforcement may be horizontal as in slabs and beams, vertical as in columns and walls or inclined. Spacers are also used to separate layers of reinforcement. Multiple types of spacer are used for one structure. Spacers must be fixed to reinforcement and have sufficient structural strength to resist reinforcement weight without buckling or overturning [American Concrete Institute, 2004; British Standards Institution, 2001a; Deutsches Institut für Normung (DIN), 2011].

2.1.1 Spacer types

Spacers and chairs are manufactured from three basic materials: plastic, cementitious material or steel wire. Spacers are also classified as either single (point) or continuous (linear) spacers according to their application.

Plastic spacers

Plastic spacers are manufactured from recycled plastic of different strength grades depending on their application. For example, higher strength plastic spacers are used for supporting

heavier and larger size of reinforcement. Plastic spacers are versatile [Shaw, 2008] because they can be used in vertical, inclined or horizontal members without requiring any tying to the reinforcement, thus saving time and cost on site. Plastic spacers are classified into two main shapes: clip-on spacer (“A” spacer or tower spacer), and wheel spacer (circular spacer). Examples of plastic spacer types from various manufacturers are shown in Figure 2.1.

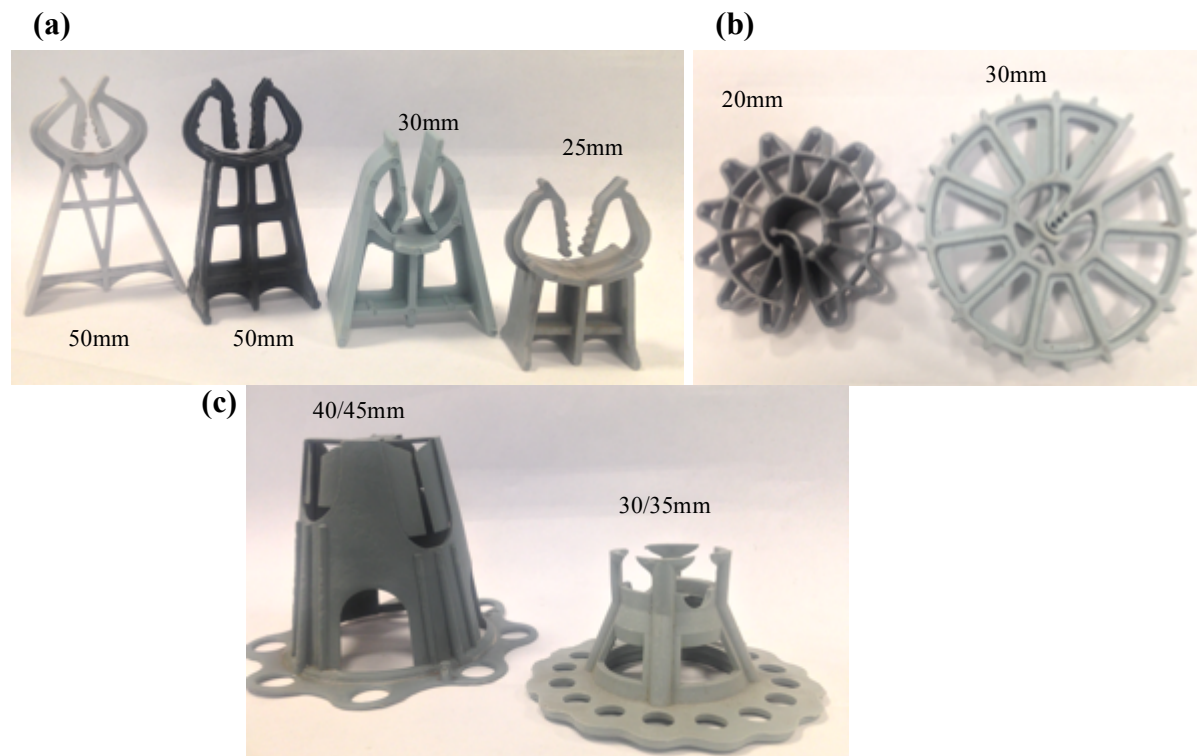


Figure 2.1 Examples of clip-on spacers: a) A-spacers, b) wheel spacers and c) tower spacers.

Clip-on spacers are used in a wide range of structural members including foundations, columns, beams, slabs, and walls. They are also designed for use with conventional formwork and a range of reinforcement size. Tower spacers are for heavy-duty applications where a double or triple cover is required. Tower spacers have a wider base compared to that of clip-on spacers so that the weight of reinforcement can be transferred to formwork without punching the insulation or sinking into soft ground [Shaw, 2007]. Circular (or “wheel”) spacers are used mainly for vertical concrete members such as walls, columns and pile cages.

Generally, plastic spacers have a more complicated shape compared to cementitious spacers or steel wires chairs. This may affect the distribution of aggregates around and within the spacer. On the other hand, the large surface area of plastic spacers can promote a better bond

with concrete. Openings in plastic spacers must be large enough to allow the maximum aggregate size to nestle comfortably in these voids. The workability of concrete must be high enough to permit easy flow of the mix into the openings [Levitt and Herbert, 1970]. Plastic spacers should satisfy the condition that any cross-section perpendicular to the bar has at least 25% voids within the enclosed perimeter to be filled with concrete so that a good bond is achieved [British Standards Institution, 2001a;Concrete Reinforcing Steel Institute, 2009]

However, the coefficient of thermal expansion and contraction of plastic spacers is very different to that of the concrete. This can be as high as 16 times that of concrete The spacer might soften to the extent of deformation under load as concrete internal temperature can reach up to 80°C [Rayner, 2005]. It has also been suggested that plastic spacers may undergo ageing under exposure to the sun and in a marine environment [Rostam, 2005]. However, it should be noted that there have been no experimental studies to support these claims.

Cementitious spacers

Cementitious spacers are made from concrete, mortar or fibre-reinforced concrete. Fly ash, slag and silica fume are usually incorporated in the mix to improve durability performance of the spacer. Cementitious spacers are classified as either single cover spacer or line spacers. Examples of these are shown in Figure 2.2.

Single cover spacers are widely used for horizontal reinforcement to provide a range of cover (15-75 mm) to reinforcement depending on application. Single cover spacers can also be used for vertical reinforcement by tying the spacers to reinforcement using 16-18 gauge soft iron wire. Stainless steel or epoxy coated wires are used for exposure to harsh environments [British Standards Institution, 2001b;Concrete Reinforcing Steel Institute, 2011]. Line spacers are mainly used for bridge decks and heavily reinforced foundations. They are manufactured in variable lengths and sizes. However, all available standards [American Concrete Institute, 2004;British Standards Institution, 2001a;Deutsches Institut für Normung (DIN), 2011;European Concrete Societies, 2001] limit the length of line spacers to 350mm and require bar spacers to be spaced at around 1m and staggered. This prevents the creation of a continuous weakness path along concrete cover in tensile stress direction. The quality of cementitious spacers should be equal to or better than that of the concrete cover [British Standard Institution, 2010;British Standards Institution, 2001a]. To ensure quality control, site made spacers are not permitted by all standards. According to BS7973-1 [British

Standards Institution, 2001a], the mix used for spacers shall have cube strength of at least 50 N/mm² at 28 days. Cementitious spacers have some advantages over other types of spacers in that they have a similar coefficient of expansion to the concrete matrix, can sustain higher loads and have higher abrasion resistance compared to steel or plastic spacers [Rayner, 2005;Rostam, 2005;Vik, 2002]

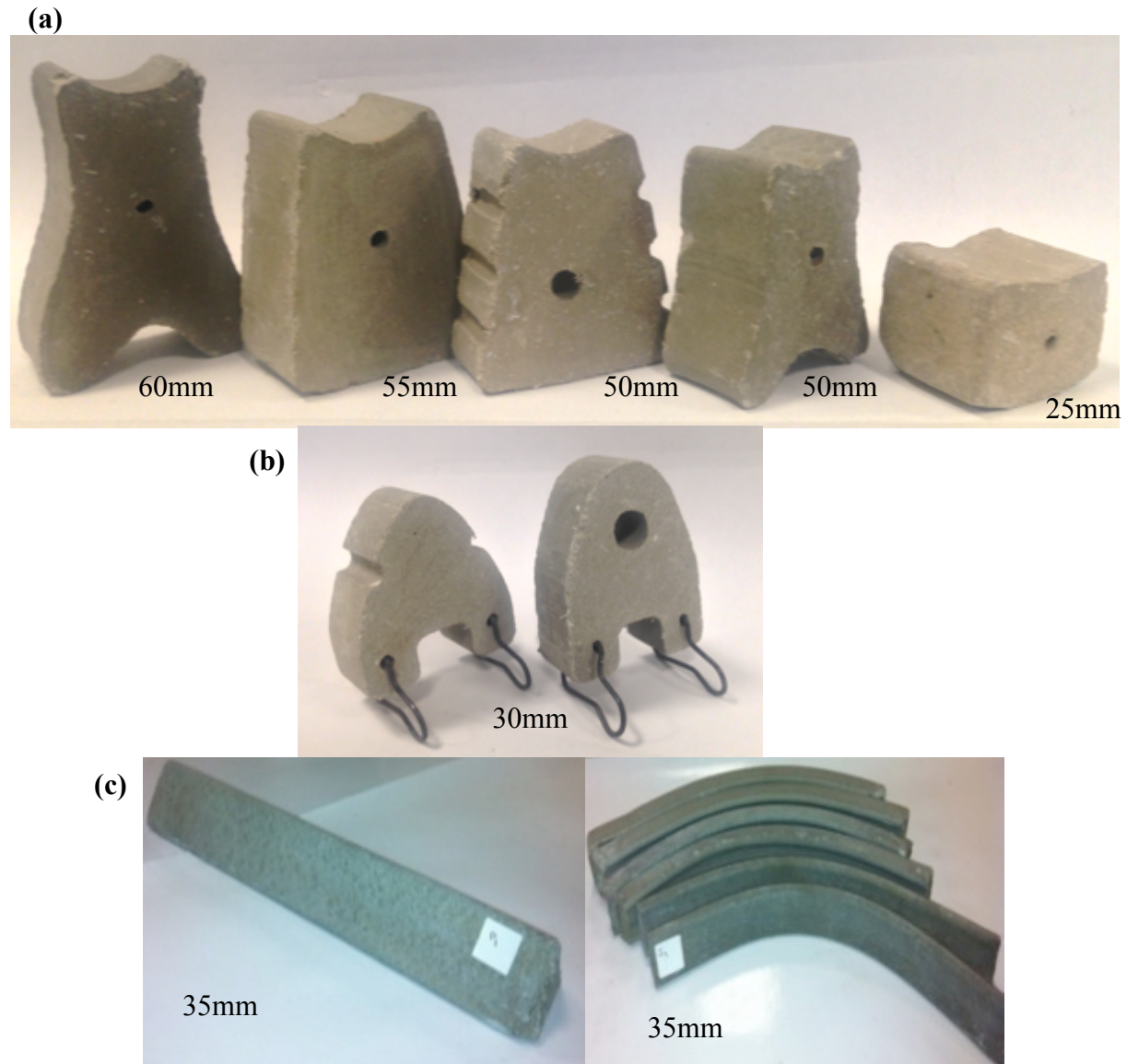


Figure 2.2 Selection of cementitious spacers types: single spacers with centre opening for tie wire (a & b) and line spacer (c).

Steel wire chairs

Steel spacers are classified into two categories: single wire chairs and continuous chairs. Examples of wire chairs are shown in Figure 2.3. Wire chairs are typically used for supporting mesh reinforcements in slabs [British Standards Institution, 2001a]. Continuous chairs are used to support the top reinforcement from the bottom reinforcement [British Standards Institution, 2001a], and are available in heights ranging from 50 mm up to 200 mm. If the chair is higher than 150 mm, strengthening with additional transverse and lattice wires may be required to achieve stability and load bearing capacity requirements of BS7973-1 [British Standards Institution, 2001a].

Single wire chairs are mainly used in cantilever slabs where there is no bottom reinforcement to support a continuous chair [Shaw, 2007]. There are two types of continuous wire chairs: lattices and circular continuous chairs (Figure 2.3). These are manufactured from welded longitudinal steel or stainless steel wires of the same diameter (3.5 or 5 mm). Because plain wire chairs can corrode easily if exposed to chloride ingress or carbonation, the legs of chairs used in exposed faces are cased in plastic protective tips for a distance of at least 40 mm [British Standards Institution, 2001a]. For harsh environments, steel wire chairs require additional corrosion protection for example the use of stainless steel or epoxy coating [American Concrete Institute, 2004; Concrete Reinforcing Steel Institute, 2009]. Further details are given in Table 2.1.

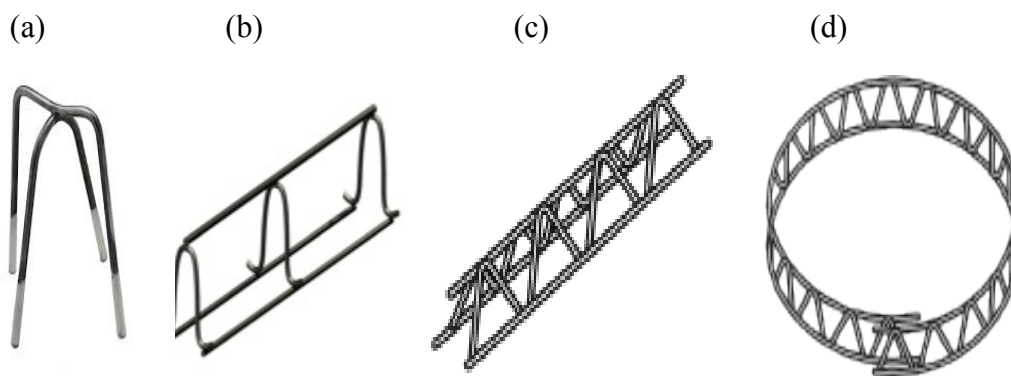


Figure 2.3 Steel wire chairs types: single chair (a), continuous chair and lattice (b & c) and circular chair (d).

2.1.2 Use of spacers

The Concrete Society Report CS101 [1989] was the first published national guidance in the UK on the use of spacers to achieve specified concrete cover. This was superseded by the

British Standard BS 7973 “Spacers and Chairs for Steel Reinforcement” [British Standards Institution; British Standards Institution] that provides guidance on the material, dimension, stability, fixity and application of spacers, BS EN 13670 :Execution of concrete structures [2010] also refer to spacers use on site. In North America, the ACI 315 “Manual of Standard Practice for Detailing Reinforced Concrete Structures” [2009] in conjunction with Concrete Reinforcing Steel Institution (CRSI) “Placing Reinforced Concrete Manual” [2011] provide the required guidance on spacers and application. Other guidance on spacers available in Europe includes the European Concrete Societies Network “Best Practice Guide ” [2001], the DIN EN 13670:2011-03 “Execution of Concrete Structures” [2011] and Deutscher Beton-Und Bautechnik-Verein E.V. [Deutscher Beton-Und Bautechnik-Verein E.V. (DBV)], Leaflet “Spacers According to Eurocode 2” [2011] which is based on the DIN EN 13670:2011-03 . Table 2.1 summarise the recommended classification and placement of spacers from these guidance documents.

It should be noted that there are no standards available that cover the manufacture, testing and use of spacers in Australia [Mackey and Januszke, 1995] and third world countries [Chemrouk, 2008].

Strength and stability: Spacers must be able to support the reinforcement and additional loading from workers and equipment during concreting [American Concrete Institute, 2004; British Standards Institution, 2001a; Deutsches Institut für Normung (DIN), 2011; European Concrete Societies, 2001], without crushing the cementitious spacers or excessive deformation in the case of wire or plastic spacers. Spacing of the spacers is dependent on its strength. Spacers and chairs should be stable and fixed securely to reinforcement to avoid displacement during placing and compacting of the concrete [British Standards Institution, 2001a; British Standards Institution, 2001b; Concrete society, 1989; Deutsches Institut für Normung (DIN), 2011; Shaw, 2007]. Both the DIN EN 13670 [2011] and BS 7973[2001a] classify spacers into categories according to strength and stability. BS 7973 requires the testing of spacers and chairs load capacity prior to site use.

Table 2.1 Summary of various codes of practice on spacer classification and placement

Standard	Spacer classification	Placing reinforcement spacers
ACI 315-99 [2004] CRSI [2011]	Steel wire spacers are classified into: Class 1: Epoxy, vinyl or plastic coated for moderate to maximum exposure; Class 2: Stainless steel protected wire bar supports Class 3: Bright basic wire-provide no corrosion protection Plastic and concrete spacers can be used for moderate to high exposure –grade (c) of [American Concrete Institute, 2011]. i.e.when concrete is exposed to condition requiring additional corrosion protection from chloride Concrete spacers provide maximum corrosion protection	Spacers to be sufficient in number and strength to support the required reinforcing steel. Spacers cast in ground to be spaced at 1200 mm in each direction Spacers spacing depends upon the size and placing of the reinforcing bar being supported. The tolerance of spacer dimension to provide the required cover $\pm 3\text{mm}$
DIN EN 13670:2011-03 [2011] DBV [2011]	Choice of the spacer depends on exposure classes of DIN 1045-1, whether the structure is subjected to freeze- thaw, temperature stresses, water and chemical attacks. Spacers are classified into two categories (L1 and L2) according to capacity and stability.	Spacers to have sufficient capacity and stability depending on load and temperature exposure. Line spacers to be staggered under the main reinforcement to minimise risk of crack formation under tension/compression zones. Tolerance: $<5\text{mm}$.
BS 7973-1 BS7973-2 [British Standards Institution, 2001a;British Standards Institution, 2001b]	Spacers and chairs should have equivalent durability to concrete used. Spacers are classified according to their application and reinforcement loading into four categories: Light (L), Normal (N), Heavy (H) and Chairs (C). Spacers to pass fixity, load bearing	Spacers spacing should not exceed $50d$ and or 1000 mm for solid slabs bottom reinforcement. Spacers shall be staggered Spacers spacing for top and other types of slabs are listed in Part 2 Tolerance: $\pm 1\text{mm}$ for cover less than 75mm and $\pm 2\text{mm}$ for cover greater than 75mm.

and stability tests	
BS EN 13670 [2010]	Cementitious spacers should have at least the same strength and corrosion protection as the concrete in the structure. Steel spacers can be used for exposure class X0 and XC1 of EN 206-1 The chairs and spacers should not lead to enclosure of air, crack formation, penetration of water or damage the reinforcement over the design service life of the structure.

Deformation: Spacers might deform under reinforcement and concreting loads. Although these loadings are for a short period, the deformation cannot be reversed due to hardening of the concrete. Plastic spacers can also deform due to high temperature resulting from the heat of hydration of concrete which can reach up to 80°C [Rayner, 2005], or due to changes in the external environmental temperature that can be as low as -15 °C and as high as 50°C. This is a concern in the case of plastic spacers rather than cementitious spacers because plastic spacers have low elasticity modulus [Rayner, 2005;Rostam, 2005;Shaw, 2008;Vik, 2002]. Cementitious spacers are unlikely to deform significantly under load unless they are crushed (i.e. loaded beyond their ultimate strength). BS 7973-1 [2001a] demands initial testing of spacers for deflection and recovery. In addition, BS 7973-2 considers the effect of temperature variation and recommends testing plastic spacers at -5 °C and 30 °C.

Spacer material: Existing standards [American Concrete Institute, 2004;British Standards Institution, 2001a;Deutsches Institut für Normung (DIN), 2011;European Concrete Societies, 2001] demand that the durability of spacers must be equal to or better than that of the concrete cover. If low quality spacers are used, then the spacers would act as conduits that facilitate access of moisture and other deleterious agents through the cover. Plastic is non-corrosive, but the interface and bond between plastic spacer and concrete can be an issue [Rostam, 2005;Shaw, 2008;Vik, 2002] if differences in volumetric changes occur due to temperature variation or drying shrinkage of the concrete. Wire chairs have the potential to corrode if exposed moisture and oxygen. To overcome this issue, it is recommended that wire

spacers are to be dipped in plastic [Concrete Reinforcing Steel Institute, 2009] or to have plastic tips covering the bottom 40 mm of spacer legs [British Standards Institution, 2001a] when in contact with exposed concrete surfaces. In harsh environments such as de-icing salts or seawater, stainless steel and epoxy coated steel wire spacers should be used [Concrete Reinforcing Steel Institute, 2009].

ACI 315-99, CRSI's Manual of Standard Practice and DIN EN 13670:2011-03 [American Concrete Institute, 2004;Concrete Reinforcing Steel Institute, 2009;Deutsches Institut für Normung (DIN), 2011] provide guidance on specifying spacers according to exposure conditions. However, ACI 315-99 recommendation on the use of plastic spacers in harsh exposure environments (category C- requirement for corrosion protection [American Concrete Institute, 2011]) is surprising considering the reports in the literature that the use of plastic spacers (Section 2.2) may initiate local corrosion. BS 7973 [British Standards Institution, 2001a;British Standards Institution, 2001b] provides no guidance on specifying spacers according to exposure conditions

It should be emphasised that none of the available standards provide details on ensuring that spacers do not impair the durability performance of concrete. For instance, there are no requirements for testing the durability of concrete with spacers, in contrast to the performance-based testing required for load capacity. Also, there is no requirement for testing the durability of cementitious spacers.

Shape and surface profile: The shape and surface characteristics of a spacer might affect its bond with concrete and the compaction of the surrounding concrete. However, none of the standards provide specifications or requirements for the shape or surface texture of spacers. Cementitious spacers with modified surface profiles are commercially available such as the spacers used in this study. It has been shown that increasing the surface roughness can improve the bond between new and existing repaired concrete [Garbacz et al., 2006;Julio et al., 2004;Santos and Julio, 2007]. However, surface profiling of plastic spacers is not an industry practice.

Load transfer: Spacers with a widened base ease the transfer of reinforcement load and any additional loading into ground, blinding or formwork without penetrating the insulation or sinking into soft ground.

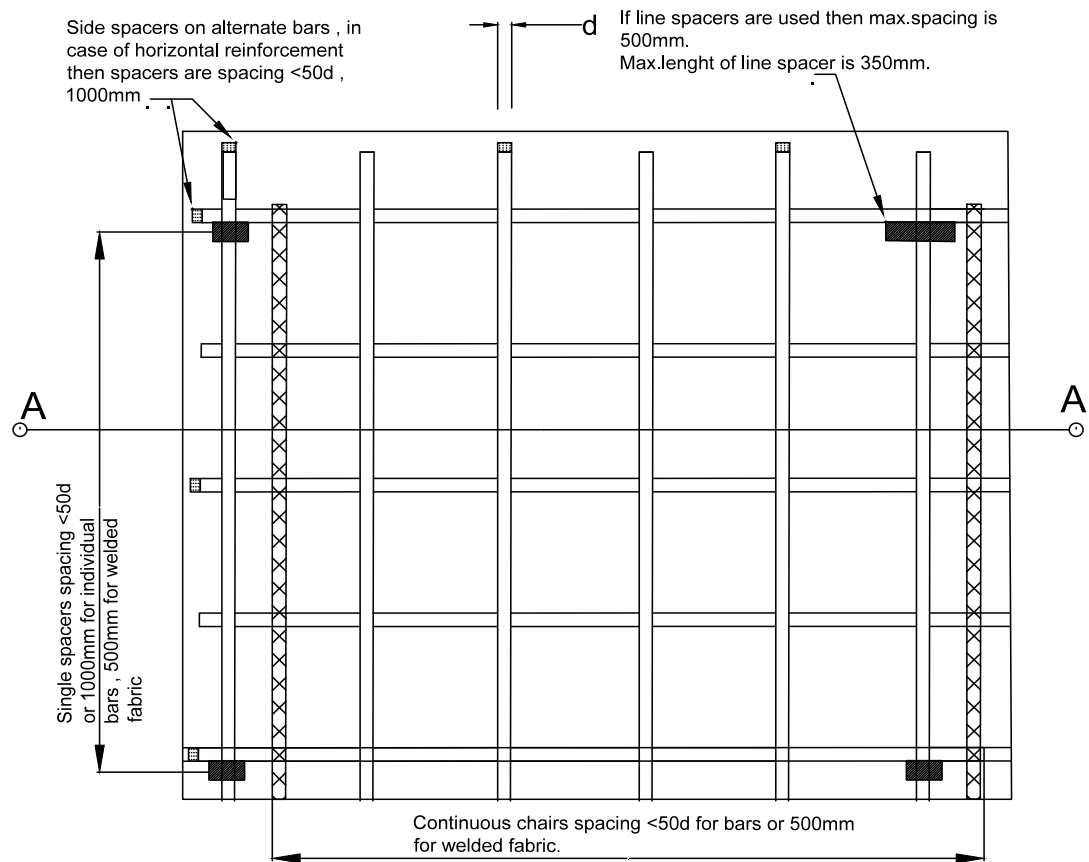
Aesthetics: The underside of spacers will be visible externally, thus architecture specifications exist on the colour and base size for visual concrete. In addition, the underside of spacers may be subjected to surface finishes such as sandblasting and bush hammering.

Cost: Typically, the choice of spacer depends on the sum of its material and labour costs for laying and fixing. Labour cost for laying and fixing spacers to reinforcement appears to be the dominant factor since this can be several times that of the value of the spacer itself, as shown in a study by the Institute of Ergonomics and Construction Economics in Leonberg reported by Max Frank [Max Frank, 2015].

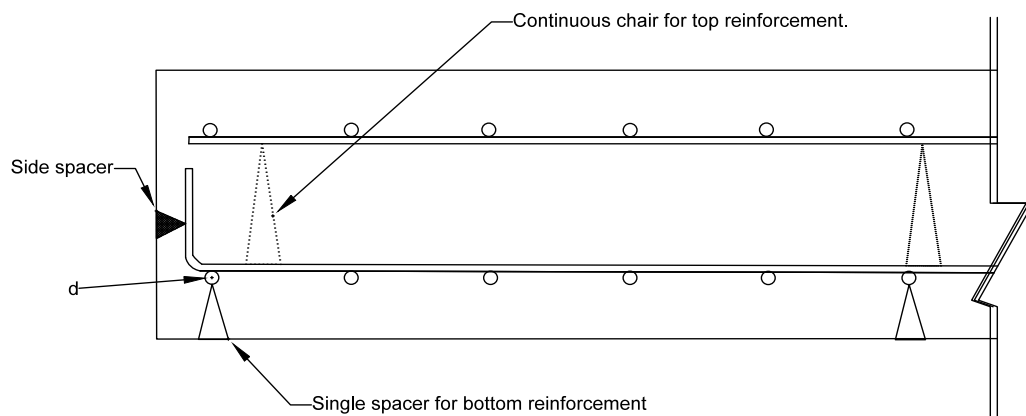
Fig. 2.4 shows the fixing of A-shaped plastic spacers for ground floor slab in accordance to BS 7973-2. Figure 2.5 presents a schematic drawing showing the placement and spacing of different types of spacers in slabs according to BS 7973-2.



Figure 2.4 Fixing of spacers in accordance to BS 7973-2 [Shaw, 2007]



Plan of Slab



Section A-A

Figure 2.5 Schematic drawing showing placement of spacers in slabs according to BS 7973-2.

2.2 Current knowledge on the effect of spacers on the microstructure and properties of concrete

The overall durability of a given structure is influenced by a host of factors beyond that of the cover size and these must also be considered. This section reviews available studies that have reported the effect of spacers on the durability of concrete, in particular on reinforcement corrosion. Past studies on the effect of spacers on the properties of concrete are critically reviewed.

The BRE carried out a study entitled “The specification and achievement of cover to reinforcement in concrete structures” [Seymour et al., 1997] that was summarised by [King et al., 2001]. The study investigated the causes of concrete cover defects in 25 construction sites in the UK. The study showed that concrete cover was not achieved in a large number of locations due to several factors listed in Figure 2.6. Many of these defects are linked to the use and placement of spacers on site, as summarised in Table 2.2. Failure to achieve concrete cover is not considered a priority by site engineers even though about half the total number of defects are caused by site operatives [Clark et al., 1997].

Several field observations have reported a link between spacers and reinforcement corrosion damage. For example, Jahren [1994] reported several cases of reinforcement corrosion damage on Norwegian bridges that have occurred at the locations of spacers. Poulsen and Mejlbro [2010] reported preferential ingress of de-icing salts into concrete at plastic spacers position causing severe local corrosion of reinforcement in columns of road bridges. Shaw et al. [2003] observed severe local corrosion at the location of mortar spacers of inlet culverts in Barseback nuclear power plant reactor resulting in 25% reduction of reinforcement.

Kenai and Bahar [2003] reported similar damage during visual inspection of Algiers airport building. In the study of Kenai and Bahar [2003], six mortar spacers of different dimensions were retrieved from the structure, dried and tested for water absorption. They found that the water absorption ranged from 10-13%, which indicates high porosity and hence, low durability. This was attributed to the fact that the spacers were made on-site and did not conform to standard requirements. It should be noted that site-made spacers are no longer acceptable by current standards. The study proposed that repair works should involve removal of the spacers and application of repair mortar.

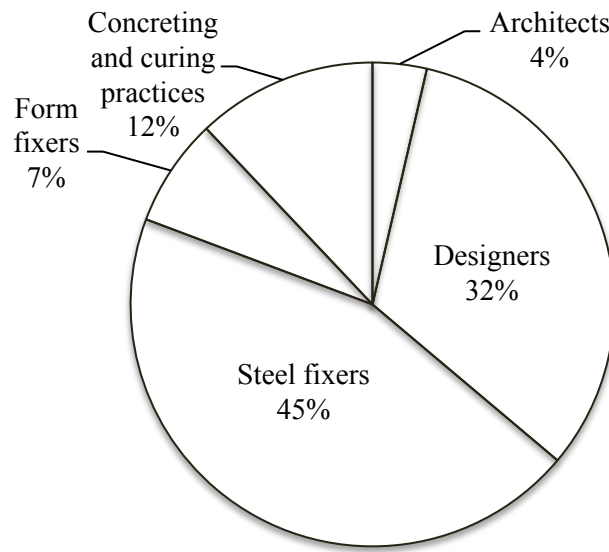


Figure 2.6 Causes of concrete cover defects observed in 25 construction sites in the UK [King et al., 2001]

Table 2.2 Types of concrete cover defects and their influence on spacers [King et al., 2001]

Cause of defect	Relation to spacers
Architect	Use of spacer is difficult in sharp corners, curved members or other complicated/impractical design shapes.
Designers	Crushing of spacers due to reinforcement congestion leading to overloading spacers
Steel fixers	• Missing spacers • Unstable spacers due to inadequate positioning and tying of spacers to reinforcement • Failure to install spacers opposite each other in either face of a member
Form fixers	Displacement of spacers
Concreting	Damage and displacement due to vibrating poker and additional loadings.

Rostam [2005] and Vik [2002] reported that plastic spacers may facilitate chloride ingress along the spacer-concrete interface due to the difference in thermal coefficient of expansion

of concrete compared to plastic spacer. However, no experimental investigation on this effect was carried out. Vik [2002] also stated that spacers made from inferior-quality concrete and steel spacers are, to varying degrees, likely to encourage corrosion, although no experimental evidence was given. Figure 2.7 show local chloride-induced corrosion adjacent to plastic spacer observed by Rostam [2005], however no further field investigation was carried out.



Figure 2.7 Local chloride-induced corrosion adjacent to plastic spacer location.
[Rostam, 2005]

Tang & Utgenannt [2009] investigated the chloride penetration and reinforcement corrosion in five concrete slabs of w/b ratio 0.3 to 0.40 and air contents of 3% to 6.6%. Concrete covers to reinforcements were 10, 15 and 20 mm; these were achieved by mortar spacers at the edges of the slabs, but the mix composition of the spacers was not given. Samples were exposed to a marine environment and the half-cell potential, corrosion rate and resistivity were monitored. After 13 years of exposure, chloride content was determined using titration. Figure 2.8 shows an example of visual examination carried out to establish the location of corrosion. Corrosion was found near the interface between concrete and end mortar spacer. The authors explained that this was due to presence of cracks at or near the concrete-spacer interface or a relatively porous interfacial zone, but the microstructure of the interface was not examined in this study. It should also be pointed that there was no mention of sealing of

the ends of the reinforcement. This is an important issue because the absence or poor sealing of bar ends could have contributed to the corrosion at the bar ends which coincide with spacer location.

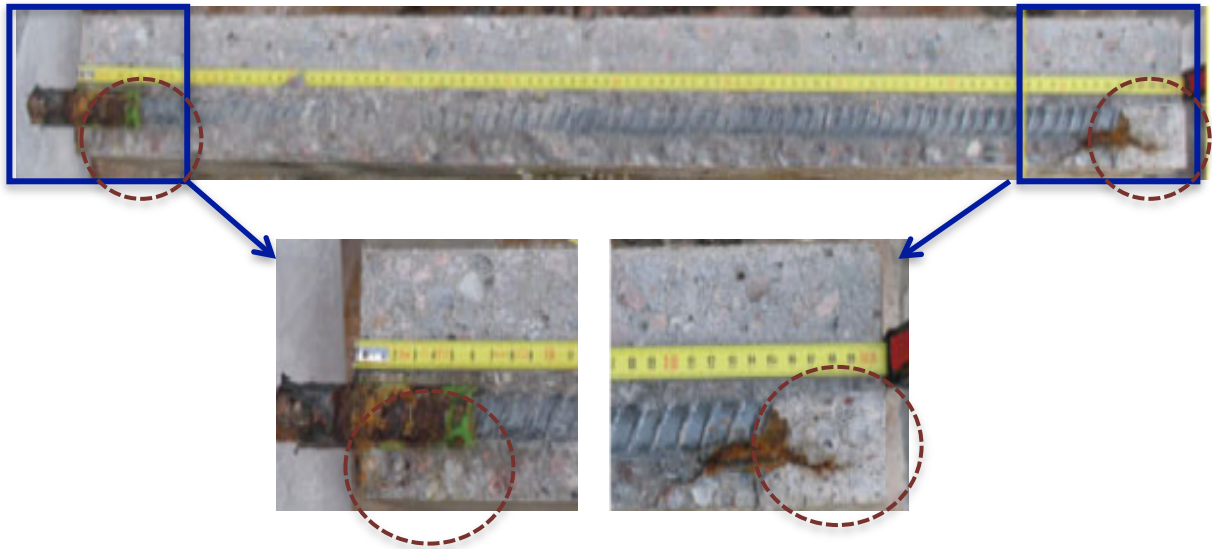


Figure 2.8 Corrosion at the interface between mortar spacer and concrete. Circles indicate location of corrosion that coincided with the location of the mortar spacers.
[Tang and Utgenannt, 2009]

In another study, Kawahigashi et al. [1999] placed reinforced concrete beams of w/c ratio 0.4 with concrete covers of 25 and 50 mm in the splash zone at three locations in Japan. During exposure, the beams were visually inspected for cracking and roughness. Corrosion was monitored using electrochemical methods. The authors observed longitudinal cracks caused by reinforcement corrosion near the end spacers, while other parts of the beam showed no indication of cracking. This observation was supported by the measurements of half-cell potential and chloride penetration that found to be higher at the end spacers compared to that of the center of the beam. The authors suggested that these results were due to bond failure between the mortar spacer and concrete, but no evidence was presented and no further investigation of the spacer-concrete interface was carried out.

The Concrete Society [1981] reported tests on concrete cubes containing steel rebar supported on plastic or dry-press mortar spacers that were subjected to cyclic wetting and drying (4 days in sea water, 3 days drying) for over two years. Hand moulded asbestos

cement was used in the concrete mix. It should be pointed out that asbestos is no longer used in concrete due to its hazardous effects. The composition of the mortar spacers and the shape of plastic spacer were not given. The study observed significant rust deposits on the sample containing plastic spacer (Figure 2.9). In contrast, the sample containing mortar spacer did not show any signs of corrosion. However, no explanation was provided for this.

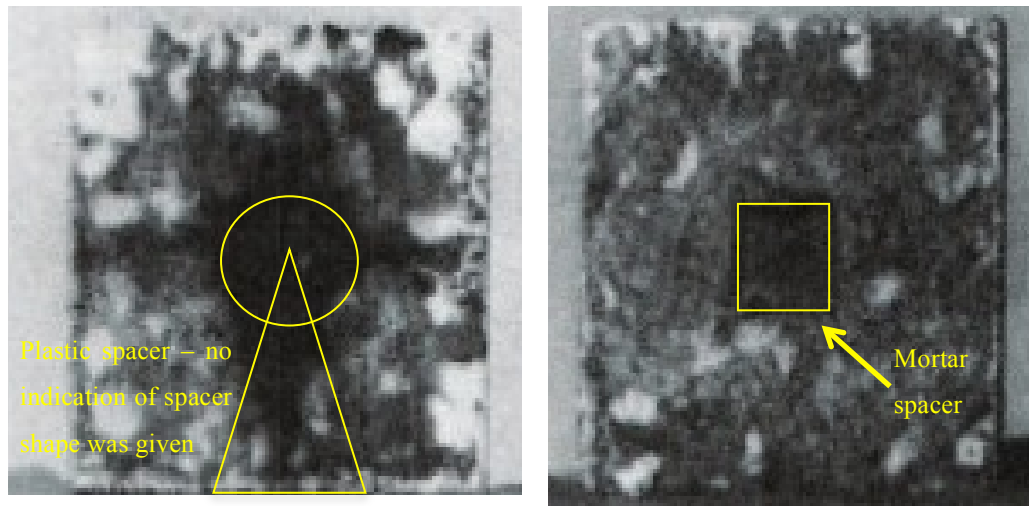


Figure 2.9 Significant rust deposits observed on the sample containing plastic spacer (left), but no corrosion was observed on the sample containing mortar spacer (right). [Concrete Society, 1981]

In another study, Shaw [2008] retrieved 103 plastic spacers and during the demolition of a 36-year-old multi-story car park. 100 A-shaped spacers were deemed suitable for testing in accordance to BS 7973 [2001a] for fixity, stability and load capacity. The spacers were made from medium density polyethylene and the specified concrete cover was 19 mm. The study found that all retrieved spacers passed the fixity, stability and load capacity test. For the latter, the spacers were tested at 50° C and 20°C in accordance with BS 7973-1 [2001a] giving an average deflection of 1.25 mm and 1.03 mm respectively within 10 seconds of load application. Although these values satisfy the requirements of the BS 7973, the effect of the deflection and recovery on the bond between spacers and concrete was not investigated. Several high tensile reinforcement bars were visually inspected for corrosion. It was found that corrosion of the reinforcement adjacent to the position of the spacer was similar to that along the bars far from spacer and in some cases the spacers were still attached to the reinforcement despite after concrete removal as shown in Figure 2.10. The concrete cover

was 20 mm.



Figure 2.10 A-shaped spacer still attached to reinforcement with no sign of corrosion after 36 years of use in car park.[Shaw, 2008]

Levitt and Herbert [1970] studied the performance of spacers in concrete after 10 years of weathering. Concrete beams of dimensions 75 x 75 x 150 mm containing plastic A-shaped spacers (with no opening), wheel plastic spacers and mortar spacers were prepared using a 0.45 w/c ratio concrete. The beams were loaded for 24 hours to simulate reinforcement loads. Visual observations indicated considerable local reinforcement corrosion at the locations of mortar spacers and this was assumed to be due to either the poor quality of the spacer itself or the poor interface between concrete and spacer. For beams containing A-shaped plastic spacers (with no opening), corrosion was observed within a few months of exposure leading to spalling of the concrete cover. Samples with circular plastic spacers performed better because the openings within the spacer allowed the large aggregate particles to nestle within and this promoted adhesion with surrounding concrete. It should be pointed that this study is very old and some types of spacers used are no longer manufactured or used such as the A-shaped spacer with no openings (Figure 2.11).

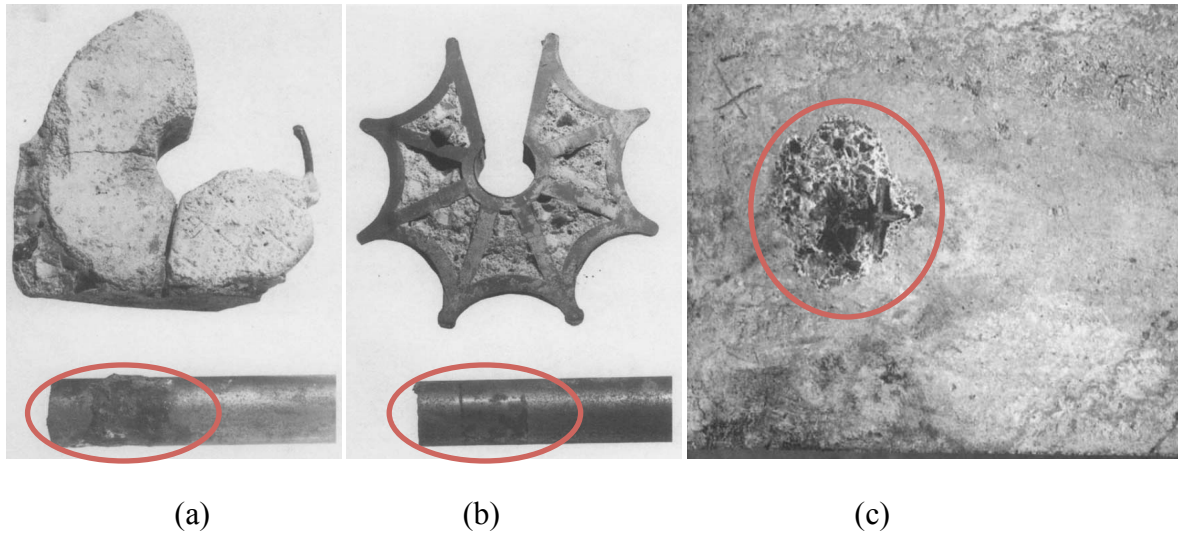


Figure 2.11 Close up steel reinforcement bar after ten years of weathering a) mortar spacer with extracted steel bar showing rust at spacer location, b) wheel plastic spacer with extracted steel bar showing minor rust deposits at spacer location, c) spalling in case of A shape spacers with no openings leading to bar exposure and severe corrosion.[Levitt and Herbert, 1970]

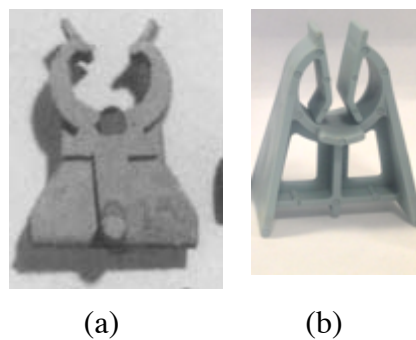


Figure 2.12 Difference between un-pierced A-shape plastic spacer used in [Levitt and Herbert, 1970] (a) and current A-shaped spacers with 25% void requirements by all available standards (b). Plastic spacers with no voids are longer available or used.

2.3 Summary

Existing standards and studies on spacers were reviewed in this Chapter. It is evident that there is a lack of systematic and thorough studies on the influence of spacers on the properties of concrete. Current standards provide little guidance on spacer material, manufacture and shape. There is also no guidance on performance testing of the durability of

spacers or concrete containing spacers. Limited studies have investigated the effect of spacers on reinforcement corrosion. There is also a lack of research on understanding the possible effect of spacers on mass transport properties and the microstructure of the concrete cover. Understanding these effects may be an important link to improving the durability of concrete structures and developing more accurate service-life modeling. This thesis aims to contribute towards these issues.

Chapter 3 Materials and setup

This chapter introduces the materials and experimental setup used in this thesis. Details of spacers and material used, sample preparation, curing, conditioning, and test set up are presented.

3.1 Spacers

Samples of cementitious, plastic and steel spacers were requested from all leading manufacturers and distributors in the UK to explore the available range of products. Approximately, 110 spacer samples were obtained. The spacers vary in terms of material, shape, height as shown in Table 3.1, Figure 2.1 and Figure 2.2 show some of the main spacer types obtained for this thesis. The spacers were examined, measured and tried in the moulds.

Table 3.1 Spacer samples obtained for this thesis.

Spacer Material	Shape	Cover depth (mm)
Plastic spacers	A-Shape (3 types)	15, 25, 30, 50
	Circular shape (4 types)	10, 15, 25, 50, 60
	Tower shape (3 types)	50, 60, 75
Cementitious spacers	Single cover (no tying wire - 4 types)	15, 20, 25, 40, 50, 55, 60
	Single cover (no tying wire - 4types)	15, 20, 25, 40, 50, 60
	Line spacer (2 types)	35, 50
Steel wire chairs	Circular (1 type)	50, 75
	Continuous (2 types)	50, 75
	Single (1 type)	50, 75

There are a number of factors that need to be considered when choosing the type of spacers to be investigated for this study. The spacer size determines the size of the concrete cover to reinforcement, which is dependent on exposure environment and durability requirements. Typical concrete cover size for structures designed to BS EN 1992-1-1 [2004] and ACI 318-11 [2011] ranges from 25 to 60 mm. For this study, spacers that provide a cover of 25 mm

and 50 mm were selected so that the investigation includes both ends of the durability requirements of cover.

In order to facilitate transport testing and microstructural studies, only single cover spacers made of plastic or concrete were investigated. Bar or line spacers were rejected because these require the preparation and testing of large concrete specimens, which would be problematic and impractical for the properties of interest to this thesis. Furthermore, the single cover spacers used in this study are of the highest commercial demand according to two of the main spacer distributors in the UK. However, the availability of single cover steel wire chairs is limited. Therefore, continuous lattice chairs were used for this study. These were sectioned at the node into 100 mm long segments. Plastic spacers contain openings that might trap aggregate particles and block the movement of fresh concrete. Therefore, the openings were measured to ensure that the selected spacer had sufficiently large openings so that the largest aggregate size could nestle in them.

The properties of the selected spacers are listed in Table 3.2. The selected spacers are shown in Figure 3.1. Dimensioned technical drawings of 50mm spacers used in this study are presented in Appendix 1. All spacers used for this study were from leading spacer manufactures and distributors in the UK. The “volume fraction” in Table 3.2 denotes the fraction of the cylindrical sample steel mould that will be occupied by the spacer (Section 3.2.3). The total porosity (θ) of the cementitious spacer was estimated by measuring the volume of water absorbed by the spacer from 105°C oven dry to a vacuum saturated-surface dry condition, then dividing it by the sample volume:

$$\theta = \left(\frac{m_D - m_{SSD}}{\rho V} \right) \times 100\% \quad \text{Eq.3.1}$$

Where:

m_D = mass of a sample at 105°C oven-dried condition (g)

m_{SSD} = mass of a sample at vacuum saturated-surface dry (SSD) (g)

ρ = density of water (g/mm³)

V = spacer volume (mm³)

In latter experiments, the plastic spacer P1 was modified to increase its surface roughness in

order to improve its adhesion and bond to concrete matrix. The modified P1 spacers are designated as P2 and P3 in Table 3.1. P2 was surface roughened using a 120-grit sand paper while P3 had its surface modified by cutting four 1 mm deep groves along the flanges followed by grinding with a 120-grit sand paper. The effect of the modification is shown in Figure 3.2. Prior to use, the plastic spacers were cleaned and dried, while the steel chair segments were sand blasted to remove any rust from the surface. The cementitious spacers were used in a dried condition. The spacers were stored in the laboratory and any moisture or temperature variations were prevented. The term “spacer” will be used throughout this study to describe both spacers and wire chairs.

Table 3.2 Properties of spacers used in this thesis

Spacer ID	Cover size (mm)	Material	Porosity (%)	Volume fraction (%)	Surface area (m ²)
C1-25	25	Fibre-reinforced mortar made with Portland cement containing 50% GGBS at 0.35 w/cm ratio. Contains sand and polypropylene fibres.	15.85	25.6	0.00472
C1-50	50		16.21	25.1	0.00963
P1-25	25	Recycled plastic	0	13.2	0.00165
P1-50	50		0	14.1	0.00256
P2	50	Recycled plastic	0	14.1	-
P3	50	Recycled plastic	0	14.1	-
S1	50	Made from three 5 mm dia. cold reduced wire to BS 4482, came in 2 m lengths.	0	6.1	0.00041

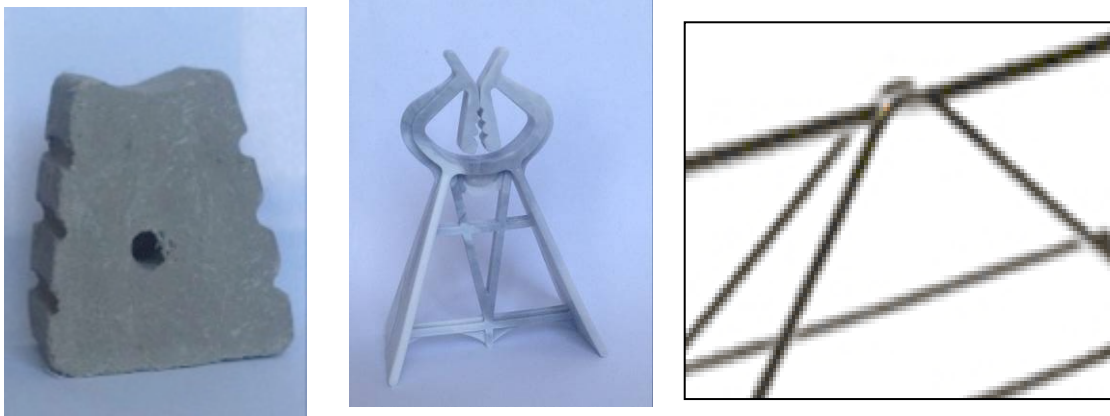


Figure 3.1 Photos of the 50 mm spacers used in this study. Left to right: C1, P1 and S1.

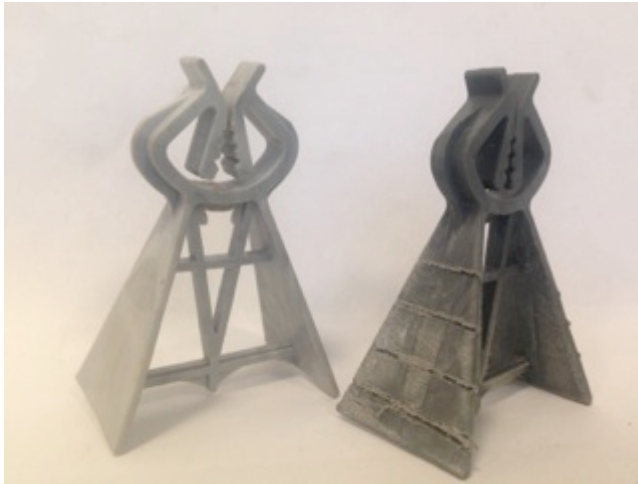


Figure 3.2 Photo of plastic spacers showing the increased surface roughness of P3 (right) relative to the original spacer P1 (left).

3.2 Sample preparation

3.2.1 Materials

Portland cement CEM I was used for all mixes. The oxide composition and loss on ignition are shown in Table 3.3. The calculated Bogue composition of CEM I was 53.1% C_3S , 19.1% C_2S , 10.8% C_3A and 7.2% C_4AF by mass. The specific gravity and fineness of the CEM I cement were 3.06 and 2905 cm^2/g respectively.

Table 3.3 Oxide composition and ignition loss of CEM I

Oxide composition (%)									Ignition
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	Cl-	loss (%)
63.4	20.8	5.4	2.4	1.5	0.3	0.7	2.9	<0.01	2.1

Thames Valley sand and gravel were used as fine aggregates and coarse aggregates respectively. The maximum particle size was 5 mm for sand. For gravel, the maximum particle size was either 10 or 20 mm. The particle size distributions and physical properties of the fine and coarse aggregates are shown in Figure 3.3 and Table 3.4 respectively. The sieve analysis results show that the gravel complied with BS EN 12620:2002+A1 overall grading, and the sand complied with BS 882:1992 medium grading. 10 mm diameter ribbed high yield steel (500B) reinforcing bars were used for producing concrete beams for corrosion testing.

Table 3.4 Specific gravity at saturated and surface dry condition (SSD), moisture content and absorption of the aggregates used.

Property	Sand	Gravel (10 mm)	Gravel (20 mm)
Specific gravity (SSD)	2.6	2.51	2.56
Moisture content (%)	0.25	0.40-0.43	0.41-0.46
24-hr absorption (%)	0.62	0.82-0.86	0.80-0.84

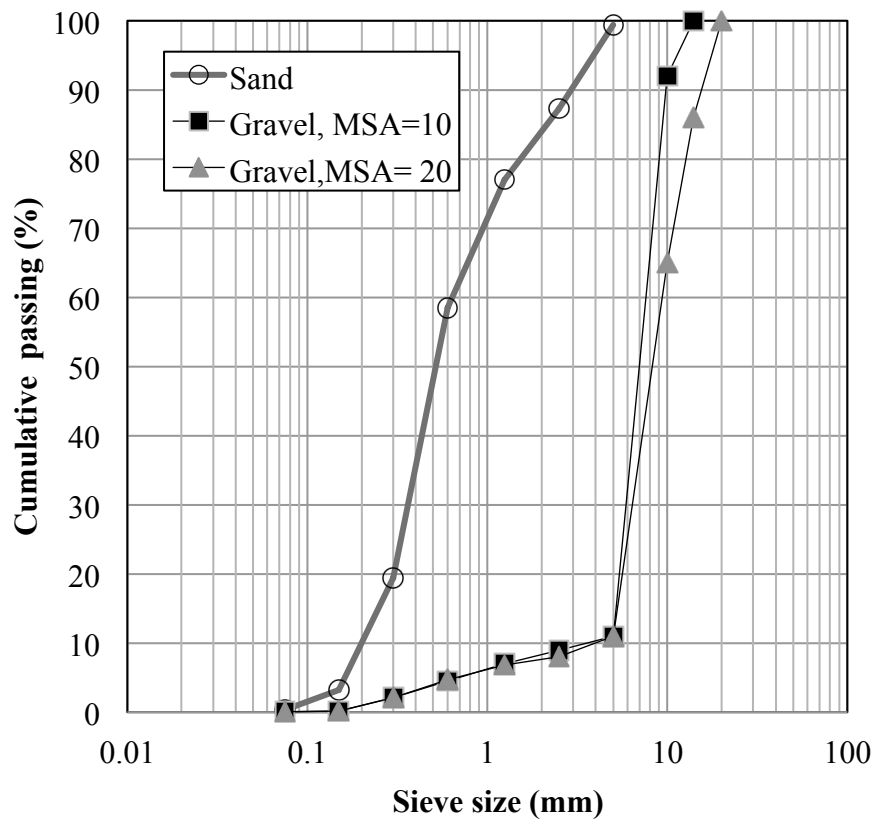


Figure 3.3 Grading curves for the aggregates used (MSA = maximum size of aggregate, mm).

3.2.2 Mix proportions

The proportions of the concrete mixes prepared in this thesis are tabulated in Table 3.5. The proportions of cement, tap water, and aggregates were calculated based on absolute volume method. This method assumes that the volume of a fully compacted concrete sample equals the sum of the volumes of all ingredients [Neville, 2011b]. The mix design also considered the amount of water absorbed by the aggregates when the concrete is in a fresh state to ensure that the targeted free water/cement (w/c) ratio is achieved. The additional water required to bring aggregates to SSD condition is the difference between the 24-hr absorption and actual moisture content. The total aggregate volume fraction was 70% and sand-to-total aggregate ratio was 0.4. The measured slump values for the concrete mixes were in the range of 90 to 100 mm, indicating high workability.

Table 3.5 Mix proportions.

Mix ID	Free w/c ratio	Cement (kg/m ³)	Sand (kg/m ³)	Gravel (kg/m ³)	MSA: (mm)	Aggregate vol. fraction %
C10	0.4	345	726	1090	10	70
C20	0.4	345	733	1098	20	70

3.2.3 Samples set up

Cylindrical samples of 100 mm diameter were prepared for transport testing. The heights of the cylindrical samples were either 25 mm or 50 mm depending on the cover size provided by the chosen spacer. Samples were either cast directly or cored from a larger sample, depending on the maximum size of aggregates. Cylinders from Mix C10 were cast in 100 mm diameter steel moulds while cylinders from Mix C20 were cored from 1500 mm x 600 mm slabs. During initial trial tests, it was found that casting concrete with 20 mm aggregates in 100 mm diameter steel moulds containing spacers resulted in poor compaction and large entrapped air voids. Therefore, a different setup was used to ensure proper compaction of concrete with 20 mm aggregates. A Hilti DD 120 diamond corer was used to extract the 100 mm diameter cores from the slab.

In real practice, the weight of reinforcement should be sufficient to hold spacers in place during concreting and compaction. However, the samples prepared in the laboratory are relatively small and so do not contain sufficient weight of reinforcement to hold spacers in place. Therefore, timber pieces along with steel bars were used to fix the spacers in place while pouring and compacting fresh concrete as shown Figure 3.4 for cast cylinders and Figure 3.6 for slabs. Figure 3.5 shows typical cross sections of cylindrical samples containing cementitious and plastic spacers.

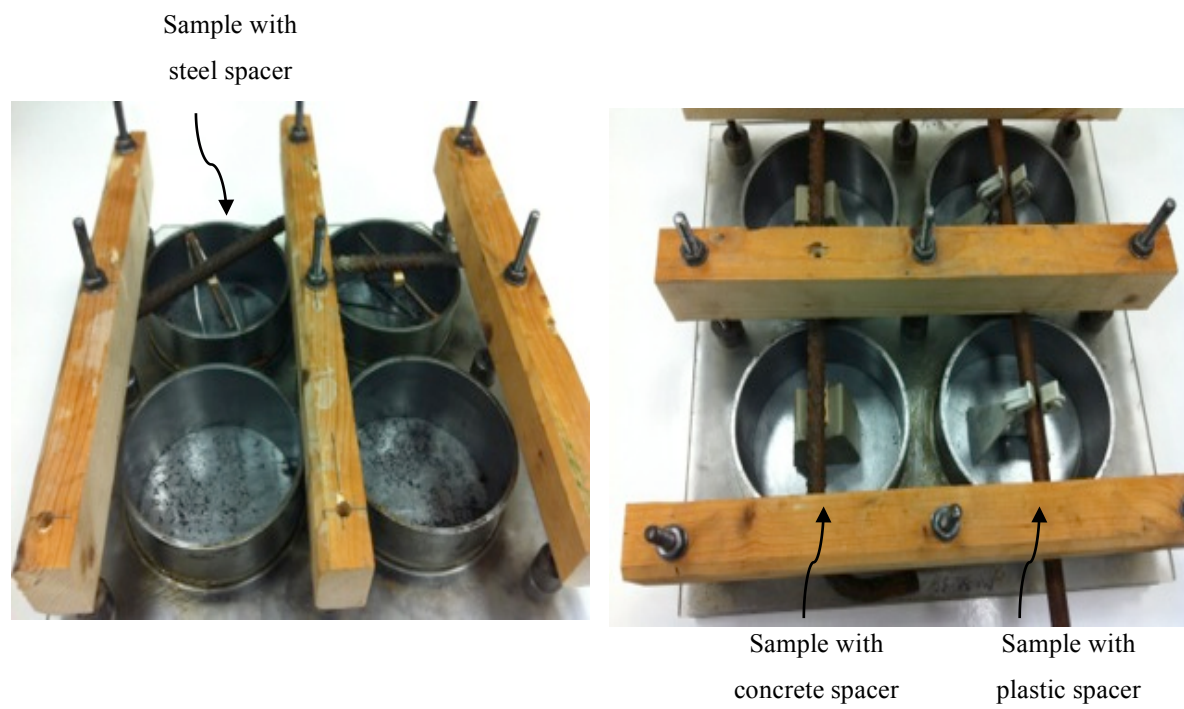


Figure 3.4 Set up for casting 100 mm diameter cylindrical samples

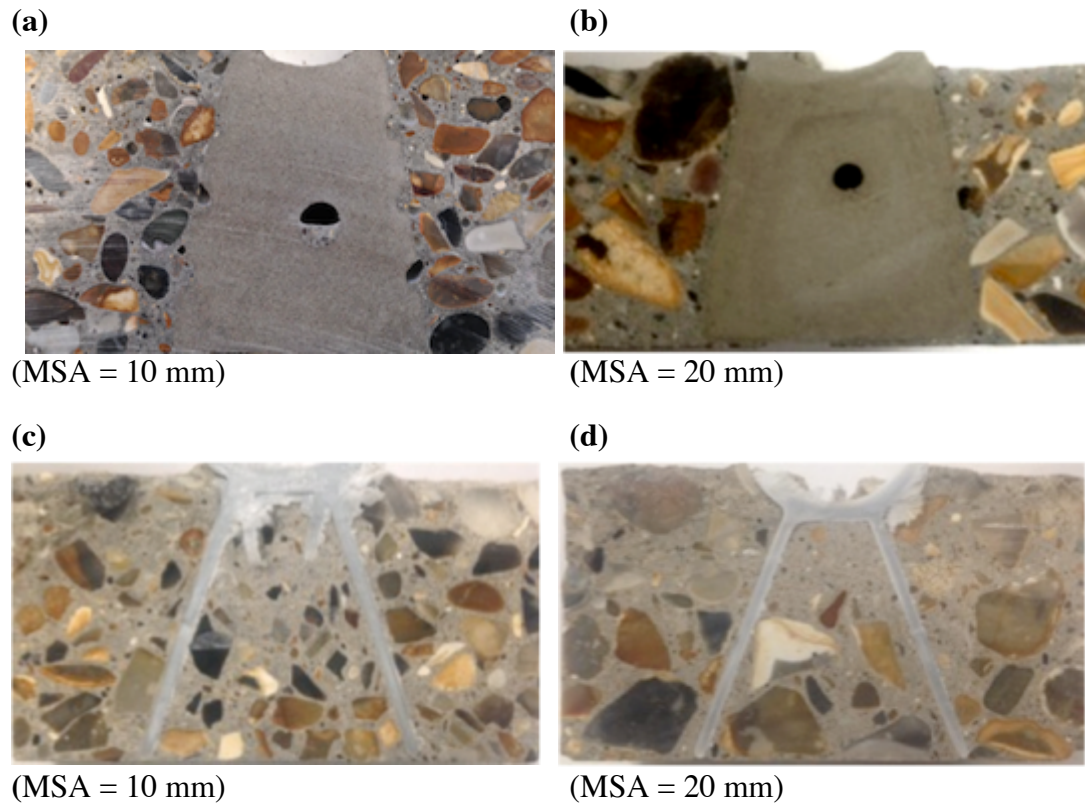


Figure 3.5 Cross-section of 50 mm high cylindrical samples with cementitious spacers (a & b) and plastic spacers (c & d).

For corrosion testing, reinforced concrete beams of 100×100×200 mm were prepared. The beam contains a single 10 mm diameter high yield reinforcing steel bar placed on either a 50 mm cementitious or plastic spacers at mid-length as shown in Fig. 3.8. Control beam samples will also be prepared with the same cover depth, but without spacer. The region for steel corrosion was limited to the middle 100 mm of the steel bar to minimise leakage of corrosion products along the longitudinal direction. To achieve this, both ends of the steel bar were coated with a layer of cement paste ($w/c = 0.3$) and epoxy as shown in Figure 3.7. A superplasticizer (Sika ViscoCrete 20RM) was used to prepare the cement paste at a dosage of .75% by weight of cement. Once hardened, an additional epoxy coat was applied to exposed edges of reinforcing steel bar before exposure.

Steel moulds of 100×100×500 mm were used to cast two beams in each mould. Timber pieces placed in the middle and sides of the mould were used to hold steel bar and spacer in place during concreting and compaction, similar to the approach shown in Figure 3.4. This method was chosen to replicate site use of spacers.

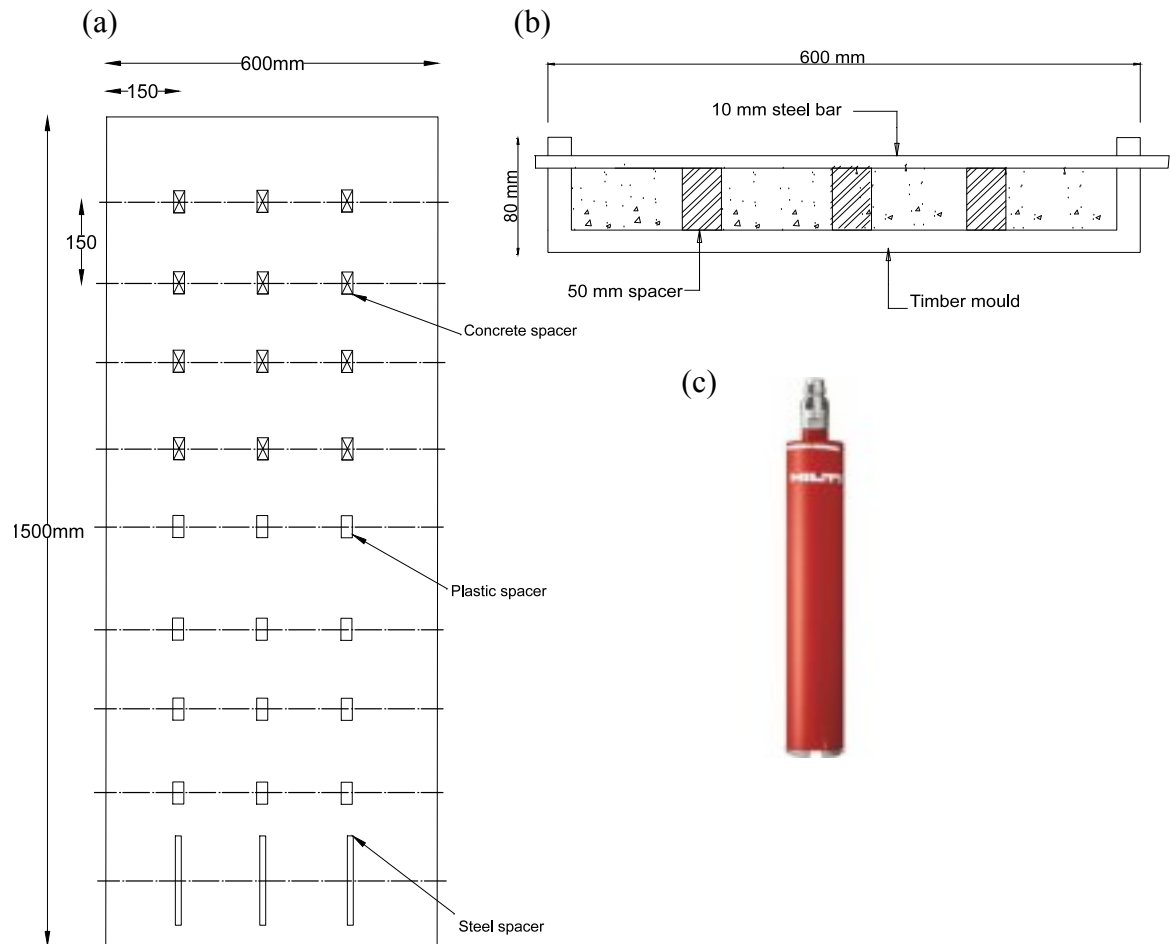


Figure 3.6 a) Plan view of the slab sample showing the position of spacers and reinforcement, b) typical cross-section, and c) coring device.

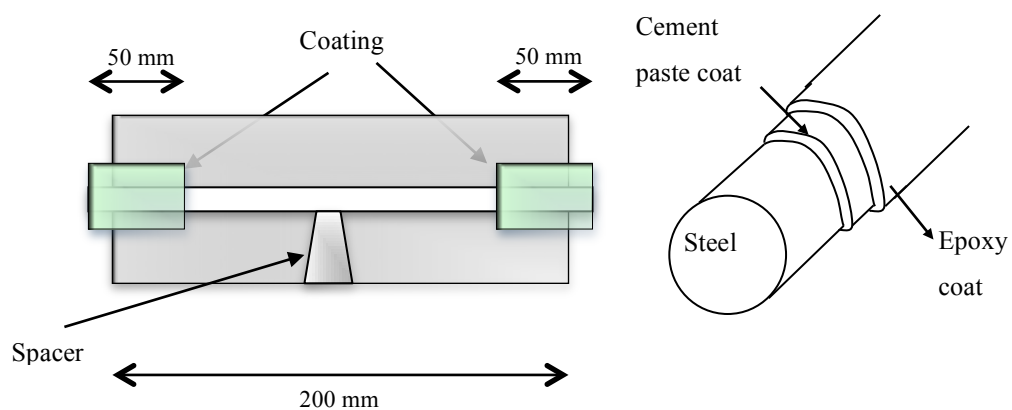


Figure 3.7 Schematic showing beam sample setup for corrosion testing and end coating.

3.2.4 Mixing and curing

Materials were batched by weight. Cement and aggregates were first dry mixed in either a 30 or 50-liter capacity mixer depending on the volume of the cast. Water was then added and mixed for 3 min. A vibrating table with adjustable intensity was used for compaction. The intensity of the vibrating table was adjusted in accordance with workability of the mix. The 25 mm tall samples were compacted in one layer while the 50 mm tall samples were compacted in two layers. Each layer was vibrated until no significant release of air bubbles was observed. All mixes produced were easily compacted and showed no indication of excessive voidage, segregation or bleeding in the cross-section (Figure 3.5). The compacted samples were covered with plastic sheet and wet hessian at room temperature for the first 24 hours and then de-molded.

Density of the hardened concrete was measured and compared against the theoretical density based on mix design as an indication of the degree compaction. The density was measured by weighing cylindrical samples (100 mm dia. x 50 mm high) in air and dividing it by sample volume in accordance with [British Standards Institution, 2009]

$$\rho = \frac{\text{sample weight (kg)}}{\text{sample volume (m}^3\text{)}} \quad \text{Eq. (3-1)}$$

The theoretical density was calculated by summing the weight of mix ingredients per 1 m³ volume. The average measured density of three replicates and the theoretical density are presented in Table 3.6. The measured density results ranged from 2331 to 2340.4 kg/m³, which were slightly higher than expected theoretical density by 1 to 1.2% . Values in brackets represent standard error ($S.E = \sigma / \sqrt{n}$), where σ and n are the standard deviation and number of replicates respectively.

Samples for mass transport testing were sealed cured in cling film and plastic bags at 20° C for a predetermined curing period of 3 or 28 days. A short curing of 3 days was chosen in addition to the standard 28 days curing to replicate typical curing on site. After curing, samples were unwrapped and labeled. Samples for chloride diffusion testing, capillary rise and wetting/drying cycle were cured in a fog room (20°C, 100% RH) for 28 days.

Table 3.6 Measured relative density

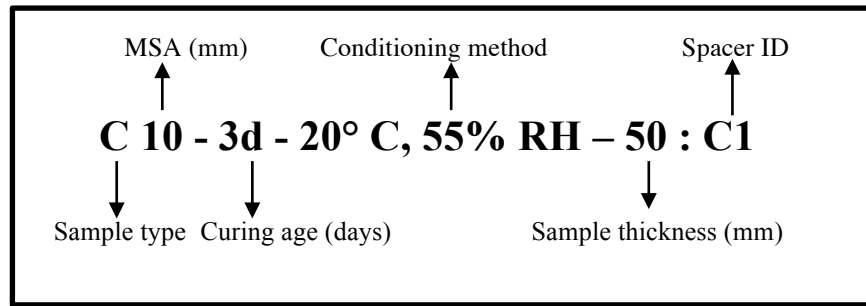
Mix ID	Measured Density (kg/m ³)	Theoretical density (kg/m ³)
C 10 - 3d- 50 : Co	2331.0 (0.002)	2299.0
C 10 - 3d- 50 : C1	2342.1 (0.003)	
C 10 - 3d- 50 : P1	2338.7 (0.002)	
C 10 - 3d- 50 : S1	2342.4 (.003)	
C 20 - 28d- 50 : Co	2341.2 (0.003)	2314.0
C 20 - 28d- 50 : C1	2352.1 (0.004)	
C 20 - 28d- 50 : P1	2339.5 (0.003)	
C 20 - 28d- 50 : S1	2340.4 (.003)	

3.3 Samples

In total, the following samples were prepared:

- I. CEM I concrete at w/c: 0.4 using aggregate of 10 or 20 mm MSA, sealed cured for 3 or 28 days and then conditioned at 20°C 55% RH, 20°C 75% RH or 50°C. Cylindrical samples containing the following spacers were prepared: cementitious spacer (25 or 50 mm), plastic spacer (25 or 50 mm), and steel chair (50 mm). These were used to study the effect of spacers on mass transport properties (Chapter 4).
- II. CEM I concrete at w/c: 0.4 using aggregate of 10 mm MSA, sealed cured for 28 days and conditioned at 20°C 55% RH or 50°C. Cylindrical samples containing 50 mm cementitious or plastic spacers, or steel chairs were prepared. These were used to study the microstructure of the spacer-concrete interface (Chapter 5).
- III. CEM I concrete at w/c: 0.4 using aggregate of 10 or 20 mm MSA, cured in a fog room for 28 days and conditioned at 20°C 55% RH or 50°C. Beam samples containing 50 mm cementitious or plastic spacers were prepared. These were used to study the influence of spacers on reinforcement corrosion (Chapter 6).

The sample designation used in this thesis is shown in Figure 3.8.



Notations:

C = concrete

d = curing age (days)

MSA = maximum size of aggregates

°C = conditioning temperature

RH = relative humidity

C1 = cementitious spacer

Figure 3.8 Sample designation

3.4 Summary

The materials used in this thesis were described in this chapter. Details of spacers, materials, mix proportions, and sample preparation were presented. Details of methods and procedures for sample conditioning, transport and corrosion testing, imaging techniques and image analysis will be presented in Chapters 4 to 7.

Chapter 4 Effect of spacers on mass transport properties

This chapter investigates the effect caused by different types of spacers on the mass transport properties of concrete. Cylindrical concrete samples were prepared with plastic, steel chair and cementitious spacers with thickness of 25 and 50 mm, and maximum aggregate size (MSA) of 10 and 20 mm. Samples were sealed cured for 3 and 28 days, then conditioned to mass equilibrium at 20°C 55% RH, 20°C 75% RH or 50°C oven prior to oxygen diffusivity, oxygen permeability and water sorptivity tests. Selected samples were then pressure impregnated with fluorescent epoxy to study the extent and spatial distribution of epoxy intrusion. Concrete samples containing plastic spacers consistently gave the least resistance to transport, followed by samples with cementitious spacers, then steel spacers. The control samples (without spacers) had the highest resistance to transport in all cases. Image analysis found that a greater epoxy penetration depth was achieved in the samples containing plastic spacers compared to samples containing cementitious or steel spacers. The epoxy penetration occurred mainly through the spacer-concrete interface.

4.1 Introduction

At least ten different concrete deterioration processes have been identified [Buenfeld, 1995], all of which are related to the transport of aggressive agents into concrete, with the exception of mechanical deterioration due to abrasion and spalling [Neville, 2011b]. The transport of liquids, gases and ions into concrete are directly related to concrete durability [Neville, 2011b]. The main transport mechanism involved in concrete deterioration include diffusion, permeation and absorption [Buenfeld, 1995].

It is reasonable to suspect that the presence of spacers may potentially facilitate the ingress of aggressive agents such as water, chloride, oxygen and sulphates, either through the spacer itself or its interface with concrete. If this is true, then spacers would act as weak links, accelerating deterioration and compromising the durability of concrete structures. However, a review of the literature shows that the influence of spacers on mass transport properties has not been investigated before.

Chloride-induced corrosion is rate-controlled by the transport of oxygen, moisture and chloride ions. Determining transport rates are crucial to assessment of durability performance and modelling of remaining service-life. Therefore, oxygen diffusion and permeation, water absorption tests were selected because these are relevant to reinforcement corrosion. Water

ingress via capillary suction plays an important role in transport in non-saturated concrete and it is also relevant to corrosion.

This chapter aims to study the influence of spacers combined with different aggregate MSA, curing and conditioning regimes on transport properties. Concrete samples with plastic, cementitious and steel wire spacers were prepared. Variables include spacer height (sample thickness), maximum aggregate size, curing and conditioning methods. To maintain consistent porosity at the time of testing, all samples had the same free w/c ratio, aggregate volume fraction and curing time. Selected samples were pressure impregnated with fluorescent epoxy and then characterised using image analysis. Results of this chapter will be compared to concrete microstructure and presented in Chapter 5. This chapter aims to establish how spacer type and height affect the transport within the concrete cover and whether spacers provide preferential path for transport along its interface with concrete or within the spacer itself.

Table 4.1 summarises the overall sample preparation programme. A brief description of the materials, mix proportions, sample conditioning, transport tests and image analysis is presented below.

4.1.1 Samples

Two concrete mixes with w/c 0.4 and total aggregate volume fraction of 70% were prepared according to the proportions given in Table 3.5. The main variable in the mix design was the maximum size of aggregate (MSA) of 10 and 20 mm. Properties of the spacers, cement and aggregates are available in Sections 3.1 and 3.2.

138 cylindrical samples with 100 mm diameter and thickness of 25 or 50mm were cast in steel moulds or cored from 1500 x 600 mm slab as described in Section 3.2.3. The samples were then sealed cured in cling film and plastic bags at 20°C for 3 or 28 days to produce samples with different levels of maturity. Three replicates were prepared for each sample.

Table 4.1 Experimental programme

Series	Spacer	Thickness (mm)	MSA (mm)	Curing (days)	Conditioning	Type	No. Samples
I	Co, C1, P1	25	10	3	20°C, 55% RH	Cast	9
	Co, C1, P1	25	10	28	20°C, 55% RH	Cast	9
	Co, C1, P1, S1	50	10	3	20°C, 55% RH	Cast	12
	Co, C1, P1, P2, P3, S1	50	10	28	20°C, 55% RH	Cast *	18
II	Co, C1, P1, P2, P3, S1	50	10	28	20°C, 55% RH	Cast *	18
	Co, C1, P1, P2, P3, S1	50	10	28	50°C	Cast *	18
	Co, C1, P1, P2, P3, S1	50	10	28	20°C, 75% RH	Cast *	18
III	Co, C1, P1, S1	50	20	28	20°C, 55% RH	Core d*	12
	Co, C1, P1, S1	50	20	28	50°C	Core d	12
	Co, C1, P1, S1	50	20	28	20°C, 75% RH	Core d	12

Samples marked with * will be used for imaging and image analysis

4.1.2 Conditioning regimes

Different conditioning regimes were used to produce samples with different moisture states prior to transport testing so that the influence of spacers can be examined under different environmental conditions. The first conditioning regime was drying at 20°C, 55% RH to constant mass. This is a gentle technique and is expected to produce the least damage, but it is a lengthy processes that required about 6 months for the 50 mm thick samples and 4 months for the 25 mm thick samples. Saturated $\text{Mg}(\text{NO}_3)_2$ solution was used to produce the targeted RH.

The second conditioning method was drying at high RH (75%) at 20°C using saturated NaCl solution to produce the required RH. This conditioning regime required about 4 months to achieve constant mass, and it replicates exposure to a humid weather condition. The third regime is drying at a higher temperature of 50° C, which replicates a hot weather condition. This required about 3 months for the samples to achieve constant mass.

Drying was carried out either in an enclosed chamber at room temperature (20°C) or in a 50°C oven. Both contained fans to generate circulating air and soda lime to minimise carbonation. Samples were assumed to have reached equilibrium when the mass loss was no more than 0.01% per day. Figure 4.1 shows an example of the mass loss curves for 50 mm thick control samples that were cured for 3 days before being subjected to the different conditioning regimes. Samples dried at 50 °C were cooled to room temperature in a vacuum desiccator for 24 h prior to transport testing to prevent moisture from re-entering the samples during cooling. Checks by weighing found negligible mass increase.

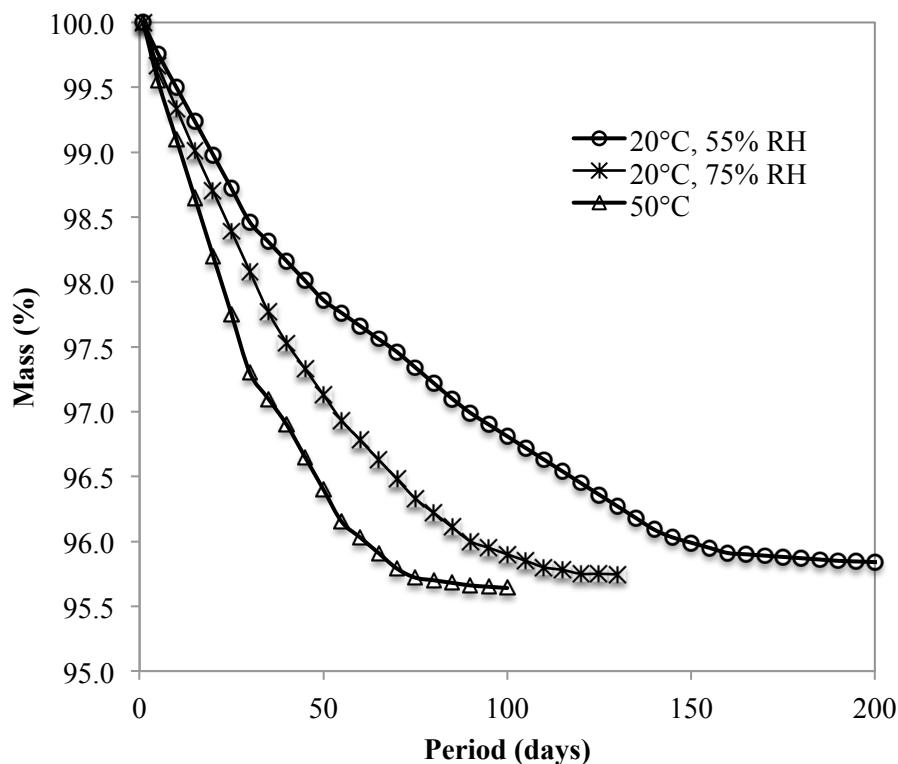


Figure 4.1 Change in mass of control concrete sample (C10-3d-50:C₀) subjected to different conditioning regimes.

4.2 Molecular transport measurements

Transport testing was carried out following the sequence of oxygen diffusion, oxygen permeation and water absorption on three replicate samples. The same sample was used throughout because the results of each test are not influenced by the previous test. These tests were chosen because oxygen transport is relevant to reinforcement corrosion and water ingress plays an important role in many degradation processes.

4.2.1 Oxygen diffusivity

In this test, two streams of gas (oxygen and nitrogen) of equal pressure and temperature are passed through the opposite sides of the sample. The concentration of oxygen is measured in the outflow stream to measure the rate of gas diffusion through the specimen. At steady-state condition, Fick's first law of diffusion can be used to determine the gas diffusion coefficient:

$$J = -D \frac{dc}{dL} \text{ Eq. (4-1)}$$

Where D is the diffusion coefficient in m^2/s , J is the mass transport rate in $\text{kg}/\text{m}^2 \text{ s}$ or $\text{moles}/\text{m}^2 \text{ s}$, and dc/dL is the concentration gradient in kg/m^4 or moles/m^4

The test samples are disk shaped and sealed on their curved surface, and so the oxygen and nitrogen gas streams are passed on opposite parallel faces. Figure 4.2 shows the oxygen diffusion test set up by Wong [2006]. The test sample is placed in the diffusivity cell with the curved surface sealed by applying a 15 kN load on the steel plate cover and silicon rubber ring using a hydraulic jack. This causes the silicon rubber ring to expand laterally and confine the sample to ensure gas flows only through the sample without any leakages through the side. The pressure of the oxygen and nitrogen stream was adjusted to be approximately equal and the set up was allowed to reach equilibrium condition, which typically took about 30 minutes to 1 hour.

The concentration of oxygen in the stream of nitrogen is measured continuously with a zirconia gas analyzer. When a steady-state condition is achieved, the diffusion coefficient D (m^2/s) is calculated by means of Fick's first law of diffusion given by the following equation [Lawrence, 1984]:

$$D = \frac{Q \times L}{A \times (CN_2 - CN_1)} \quad \text{Eq. (4-2)}$$

Where Q is the oxygen diffusion rate at 1 bar (m^3/s) expressed as:

$$\frac{R_1 \times (G_1 - G_0)}{60 \times 10^6} \times \frac{P_1 - P_2}{100} \quad \text{Eq. (4-3)}$$

Where, R_1 = flow rate of nitrogen stream (mL/min), R_2 = flow rate of oxygen stream (mL/min), G_1 = percentage of oxygen in outflow stream, G_0 = percentage of oxygen in the initial nitrogen stream, P_1 = pressure of oxygen stream (bar), P_2 = pressure difference between the oxygen and nitrogen stream (bar), A = cross-sectional area of specimen (m^2), L = thickness of specimen (m), CN_2 = concentration of oxygen in the oxygen stream at 1 bar (m^3/m^3) expressed as:

$$\left[100 - \left(\frac{R_1}{R_2} \times \frac{(G_1 - G_0)}{2} \times \frac{\sqrt{32}}{\sqrt{28}} \right) \right] \times \frac{P_1}{100} \quad \text{Eq. (4-4)}$$

And CN_1 is the mean concentration of oxygen in the nitrogen stream at 1 bar (m^3/m^3) expressed as:

$$\frac{(G_1 + G_0)}{2} \times \frac{(P_1 - P_2)}{100} \quad \text{Eq. (4-5)}$$

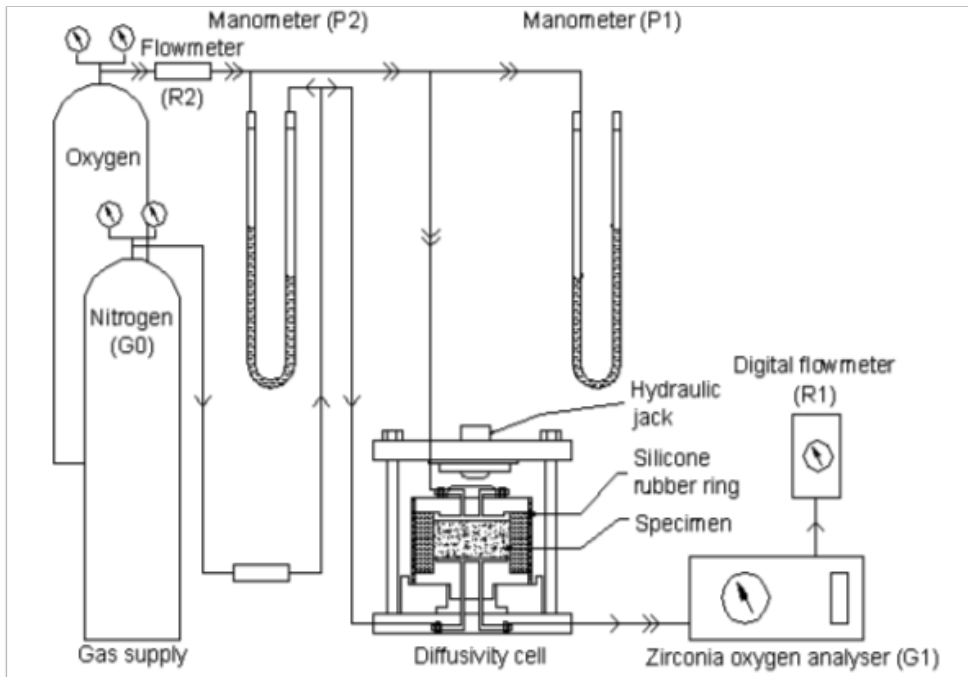


Figure 4.2 Oxygen diffusion test set up [Wong, 2006]

4.2.2 Oxygen permeability

Permeability is the property that measures how fast a fluid flow through a porous material under an applied pressure gradient. This is particularly relevant in some types of structures such as dams, basements, foundations and tunnel linings that experience external water pressure. The significance of this is not only to do with water leakage, but also the ingress aggressive species such as chlorides and sulphates dissolved in the water, which can accelerate degradation [Claisse, 2014]. One of the easiest and fastest techniques for measuring the permeability of concrete directly is the differential pressure technique using a gas [Cabrera and Lynsdale, 1988].

Permeation is described by Darcy's law for incompressible fluids under laminar flow through a porous medium. At steady-state condition, it can be stated as:

$$Q = K \cdot A \cdot \Delta h / L = \frac{K' \rho g}{\eta} \cdot A \cdot \Delta h / L \quad \text{Eq. (4-6)}$$

Where Q = flow rate in m^3/s , K = coefficient of permeability in m/s , A = cross-sectional area of the sample in m^2 , Δh = pressure difference in m , L = sample thickness in m , K' = intrinsic permeability of the material in m^2 , ρ = density of fluid in kg/m^3 , η = dynamic viscosity of the fluid in Ns/m^2 , and g = gravity acceleration in m/s^2 .

The coefficient K' is an intrinsic property of the material, independent of the type of fluid used in the test. However, since gaseous oxygen is compressible, Eq. (4-6) is therefore not valid. Another form of Darcy's law has been developed for compressible fluids by considering that the pressure-velocity product is constant throughout the sample at isothermal and steady state conditions:

$$Q = k_g \frac{A}{2\eta_g L} \left(\frac{P_1^2 - P_2^2}{P_2} \right) \quad \text{Eq.(4-7)}$$

Where k_g (m^2) is the gas permeability coefficient, η_g (Ns/m^2) is the dynamic viscosity coefficient of the fluid ($= 20.2 \times 10^{-6} \text{ N s/m}^2$ for oxygen at 20°C), L (m) is the flow length, P_1 and P_2 (N/m^2) are the absolute pressures on the inlet and outlet faces respectively.

Figure 4.3 shows the test set-up for the oxygen permeation test. A cylindrical specimen is placed in the permeability cell and its curved side is sealed by applying a 15 kN load on the steel plate cover and silicon rubber ring using a hydraulic jack. This creates lateral confining pressure that prevents gas leakage through the side and ensures that oxygen can only pass through the sample from the high-pressure to the low-pressure side. Oxygen gas was then applied to the inlet face to produce a pressure difference across the sample. Three oxygen pressures of 0.05, 0.15 and 0.25 MPa above atmospheric pressure were applied. The outflow rate at each applied pressure was measured at steady-state condition, which is normally achieved within 20 to 40 minutes. Four readings were taken for each applied pressure to calculate the average flow rate. The recorded sample mass before and after test shows negligible change (less than 0.1g). The sample dimensions, the outflow rate, pressure gradient were then used to calculate the oxygen permeability according to Eq.4.7.

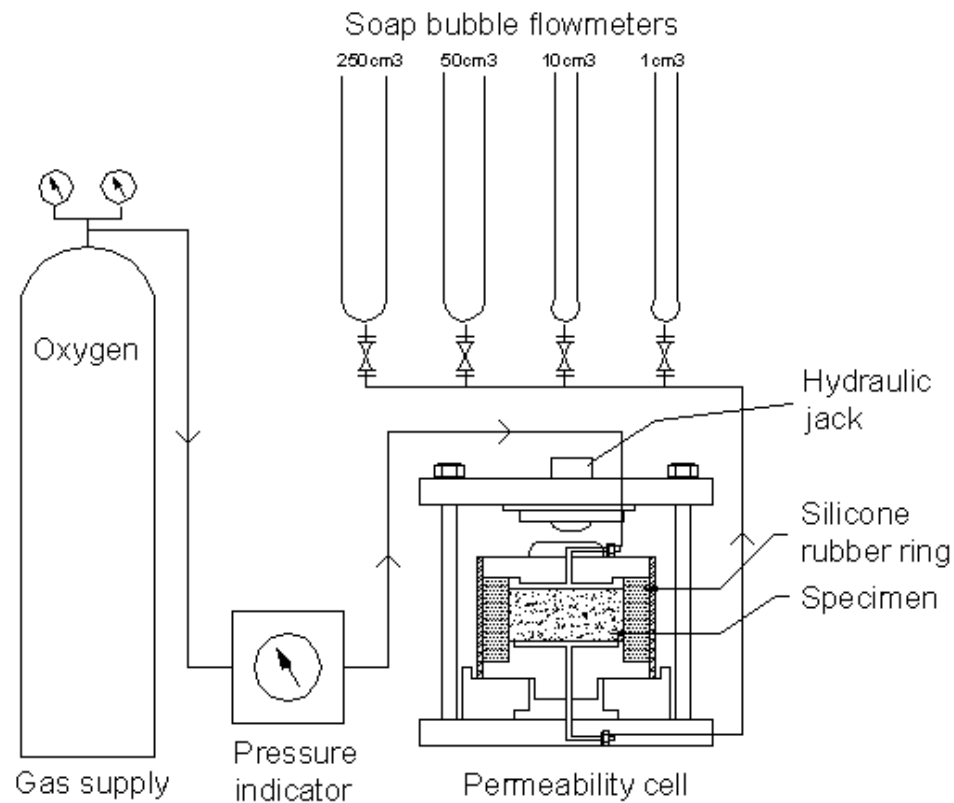


Figure 4.3 Oxygen permeability test apparatus [Wong, 2006]

The obtained permeability k_g at each pressure is an apparent permeability, which is dependent on the applied gas pressure. This is because gas molecules slip at the walls of pore channels, a phenomenon known as gas slippage [Klinkenberg, 1941]. This effect is significant when the mean-free path of the gas molecules is of comparable magnitude to the

pore size. Hence, for very fine capillaries, substantial gas slipping would occur and the gas flow rate is larger than would be expected. Klinkenberg [1941] provided a method to correct for this effect and obtain an intrinsic permeability, which is pressure-invariant. It is noted that the Klinkenberg correction method has been extensively used to calculate the gas permeability of porous medium. The intrinsic gas permeability is obtained via:

$$k_g = k_{int} \left(1 + \frac{\beta}{P_m}\right) \quad \text{Eq.(4-8)}$$

Where

k_g = apparent permeability coefficient (m^2)

k_{int} = intrinsic permeability coefficient (m^2)

β = fitting constant

P_m = mean pressure of the inlet and outlet streams = $(P_1 + P_2)/2$

The mean-free path of gas molecules approaches zero when a very high inlet pressure is applied. Therefore, the capillary pores are much bigger than the mean-free path of the gas molecules and so gas flow predominantly takes place via a viscous mechanism, in contrast to Knudsen diffusion. When such condition is met, the measured intrinsic permeability coefficient depends only on the pore structure of the sample and is independent of the fluid characteristics and applied pressure. To obtain this, an apparent permeability coefficient is calculated from Eq. 4-7 for each of the three input pressures. These are plotted against $1/P_m$ and the intrinsic permeability is obtained from the y-intercept of the best-fit line. An example of typical plot of apparent permeability k_g against $1/P_m$ is shown in Figure 4.4. The coefficient of regression for the least-squares fit was always greater than 0.99.

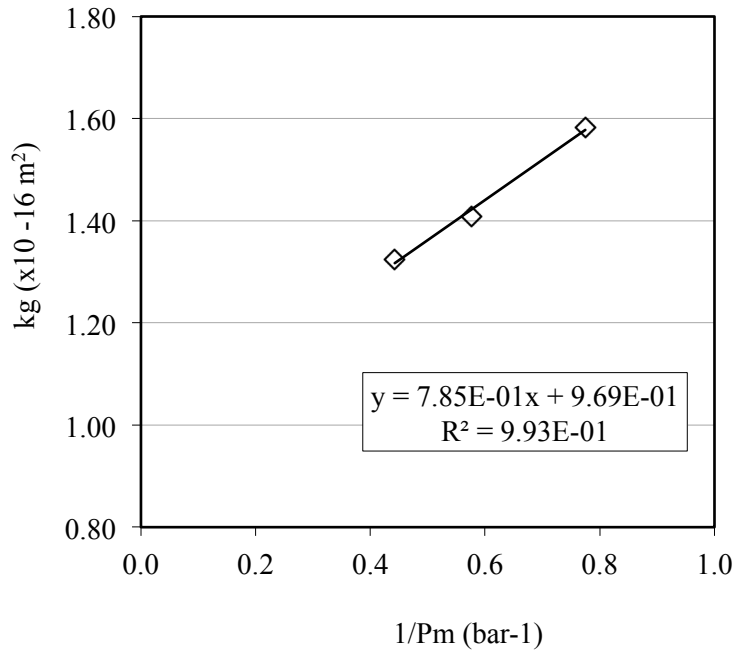


Figure 4.4 A typical plot for Klinkenberg correction to obtain intrinsic permeability. Sample is C10-28d-20°C 55% RH-50:P1.

4.2.3 Water sorptivity

Sorptivity defines the ability of concrete to absorb water by capillary suction. Sorptivity is obtained by exposing the sample to uni-direction absorption under negligible applied pressure and measuring either the rate of inflow or the depth of water penetration over time [Hall, 1977] . The sorptivity coefficient S can be obtained from the following equation:

$$A = C + St^{1/2} \quad (4-8)$$

Where A , t and C are the mass of water absorbed per unit cross-sectional area, elapsed time, and constant from curve fitting, respectively. The constant is considered to be due to the effect of surface finish and open porosity on the absorption at the beginning of the test.

There are several methods for testing sorptivity. Usually, a test specimen of uniform cross section is pre-conditioned by drying to constant mass and then placed with one surface just in contact with water. The weight of water absorbed by capillary rise is measured at fixed intervals. After obtaining at least five data points, a graph is plotted between the mass of water absorbed per unit area of inflow surface against square root of time. The slope of this plot is reported to be the sorptivity of the material.

The test setup is shown in Figure 4.5. Two plastic strips (5 x 5 mm) are used to support the sample in a shallow tray. The sample is immersed in distilled water at a depth of approximately 2 to 3 mm. The mass of absorbed water is measured at suitable intervals (5, 10, 20, 30, 60 minutes, and every 30 minutes thereafter) using an electronic balance accurate to 0.01g. Any surface water on the sample should be wiped off with a dampened tissue before weighing, and each weighing should be completed within 30 seconds. A lid is used to cover the tray to prevent the sample from drying; however, care is taken to ensure that condensates do not form underneath the cover that may drop on to the sample. The weight measurement is performed until the sample is fully saturated.

The sorptivity coefficient was obtained from the slope of the regression line of absorbed water per unit flow area against square root of time according to the classical unsaturated flow theory [Hall, 1977]. The best-fit regression line was drawn across at least 10 readings taken during the first 7 hours of measurement. The coefficient of regression of the least squares fit R^2 was always above 0.98.

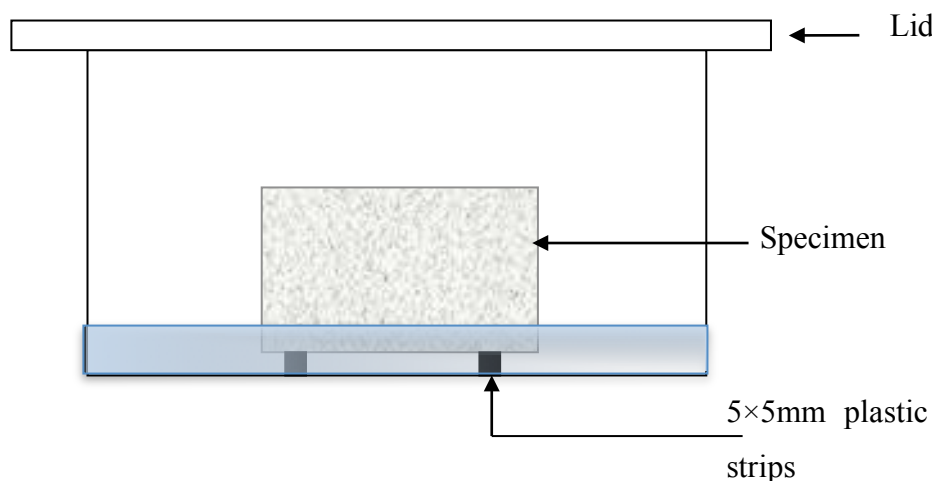


Figure 4.5 Sorptivity test set-up.

4.3 Fluorescent epoxy impregnation

Samples were pressure impregnated with fluorescent epoxy to study the extent and spatial distribution of epoxy intrusion. This would indicate areas of porous regions that act as preferential transport paths. The fluorescent epoxy was prepared by adding a fluorescent dye (Struers Epodye) to epoxy resin (Araldite AY103) at 5g/litre resin. Then, a magnetic stirrer was used to mix the fluorescent resin for one day to ensure that the dye was uniformly dispersed in the resin. The fluorescent epoxy was then heated up to 40°C prior to mixing with

the hardener and toluene. The proportion of epoxy to hardener to toluene used was 25: 3: 1.5 respectively. Toluene was used to reduce the viscosity of the resin.

The curved side of each cylindrical sample was sealed with two layers of waterproof adhesive tape to prevent leakage of the fluorescent epoxy at the start of the impregnation process. Samples were placed in a cell similar to the permeability cell, and then sealed by applying a 15 kN load on the steel plate cover and silicon rubber ring using a hydraulic jack. Subsequently, fluorescent epoxy was poured onto the bottom surface and compressed air at 0.7 MPa above atmospheric pressure was then applied and maintained for 6 hours to force the epoxy into the sample. Figure 4.6 shows a schematic of the test set-up.

The impregnated sample was allowed to harden at room temperature for 2 days. The sample was then sectioned with a diamond saw in half from the centre so that the amount of fluorescent epoxy impregnation can be observed on the cross-section, along interface and within the spacer. Each section was then ground using a 120-grit sand paper to remove excess resin from the surface.

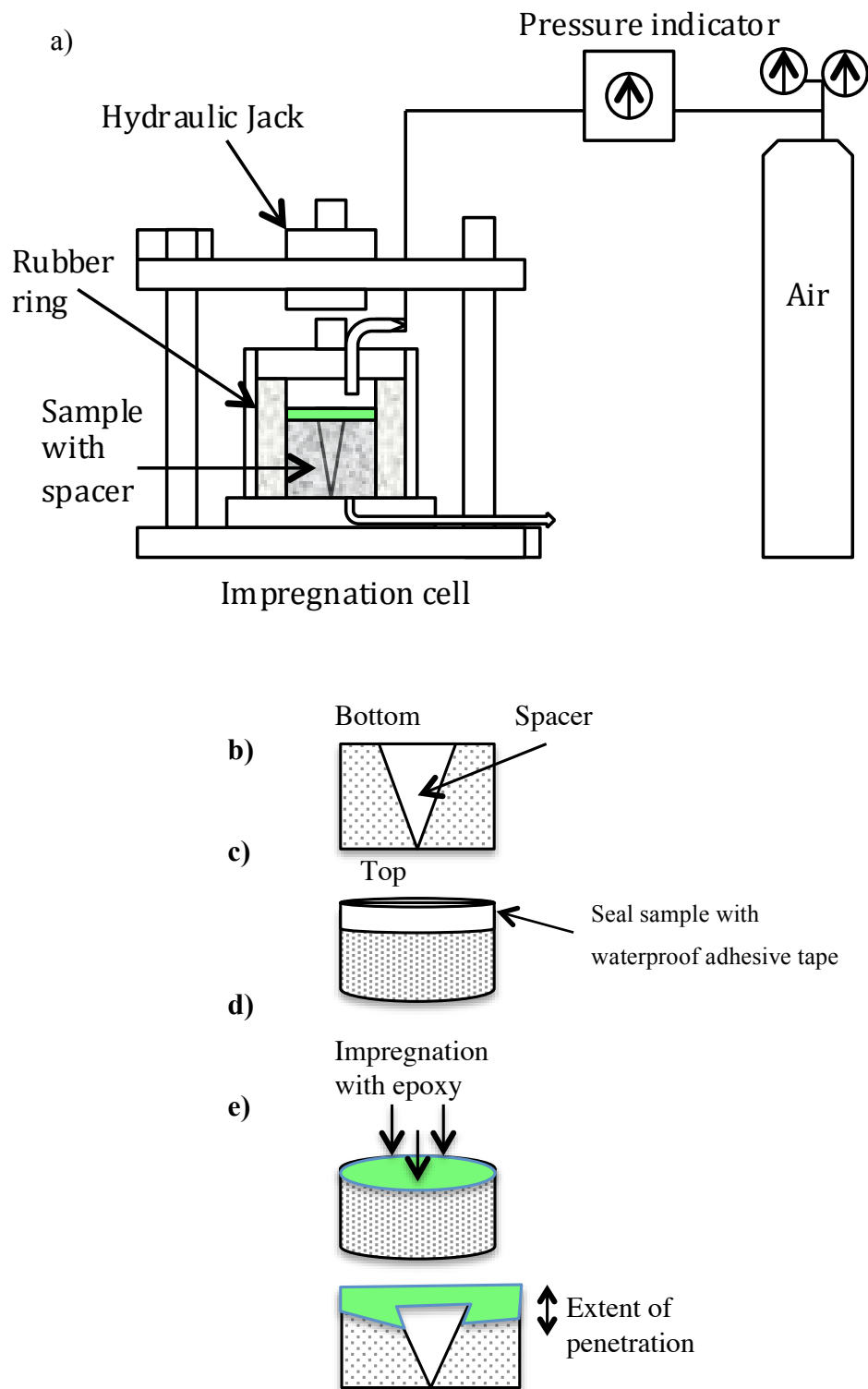


Figure 4.6 Schematic showing a) epoxy impregnation cell, b) cross-section of sample containing spacer, c) sample, d) epoxy impregnation, and e) extent of epoxy penetration.

4.3.1 Digital camera imaging

The sample was illuminated using a 15W ultraviolet (UV) lamp (25 cm length) with a power source of 230-240 V and 50 Hz to induce fluorescence. The UV lamp was situated 3.5 cm above the sample and parallel to the sample edge to give a uniform lighting condition. A digital colour camera (Canon, Power Shot G3) connected to a PC was used to acquire fluorescence images at 2177×1085 pixel resolution in TIFF format without compression. The camera was located at a distance of 20 cm from the sample surface. Imaging was carried out in a dark room to avoid stray light reflection and to achieve a good contrast. Examples of fluorescence images taken with the digital colour camera of samples with and without spacer are shown in Figure 4.7.

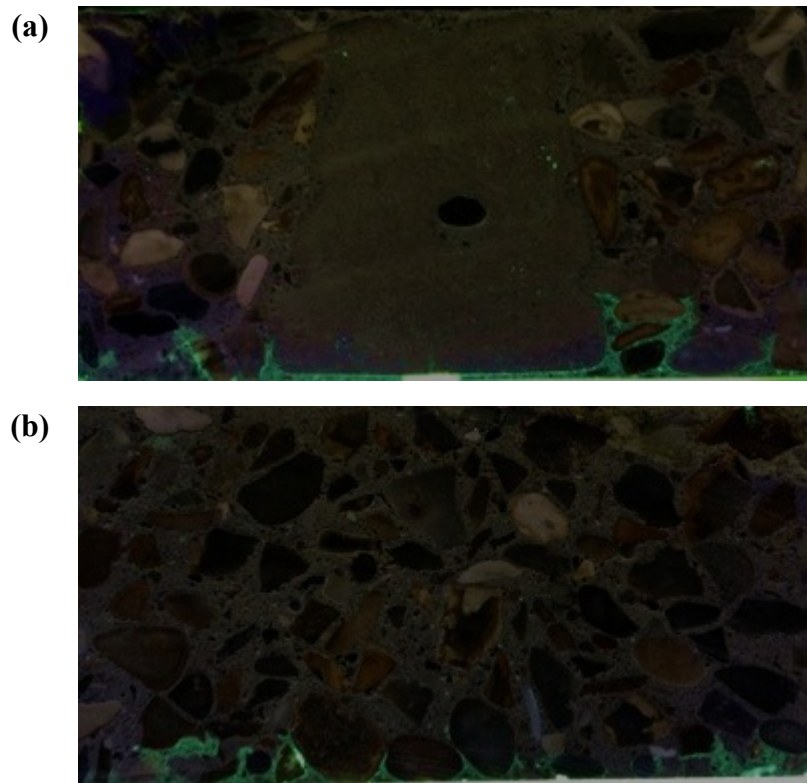


Figure 4.7 Examples of fluorescence images taken with a digital camera showing the extent of epoxy penetration on sample a) C10-28d-20°C 55% RH-50: C1, and b) C10-28d-20°C 55% RH-50: Co.

4.4 Image analysis

An image analysis software (ImageJ) was used to measure the extent and maximum depths of epoxy impregnation from the fluorescence images. Colour thresholding using hue, saturation and brightness settings was carried out to isolate the impregnated area and to generate a binary image as shown in Figure 4.8. For all samples, the hue threshold range was set at 60-180 which corresponds to the green colour angle on the hue circle. The entire brightness and saturation histograms (0-255) were utilised so that all shades of the green colour were included. The same thresholding settings were applied to all samples. The accuracy of the segmentation was checked by cross-referencing the binary images with the original fluorescence images. Original and binary images of all samples are presented in Appendix 3. A screenshot of the applied threshold settings is shown in Figure 4.9.

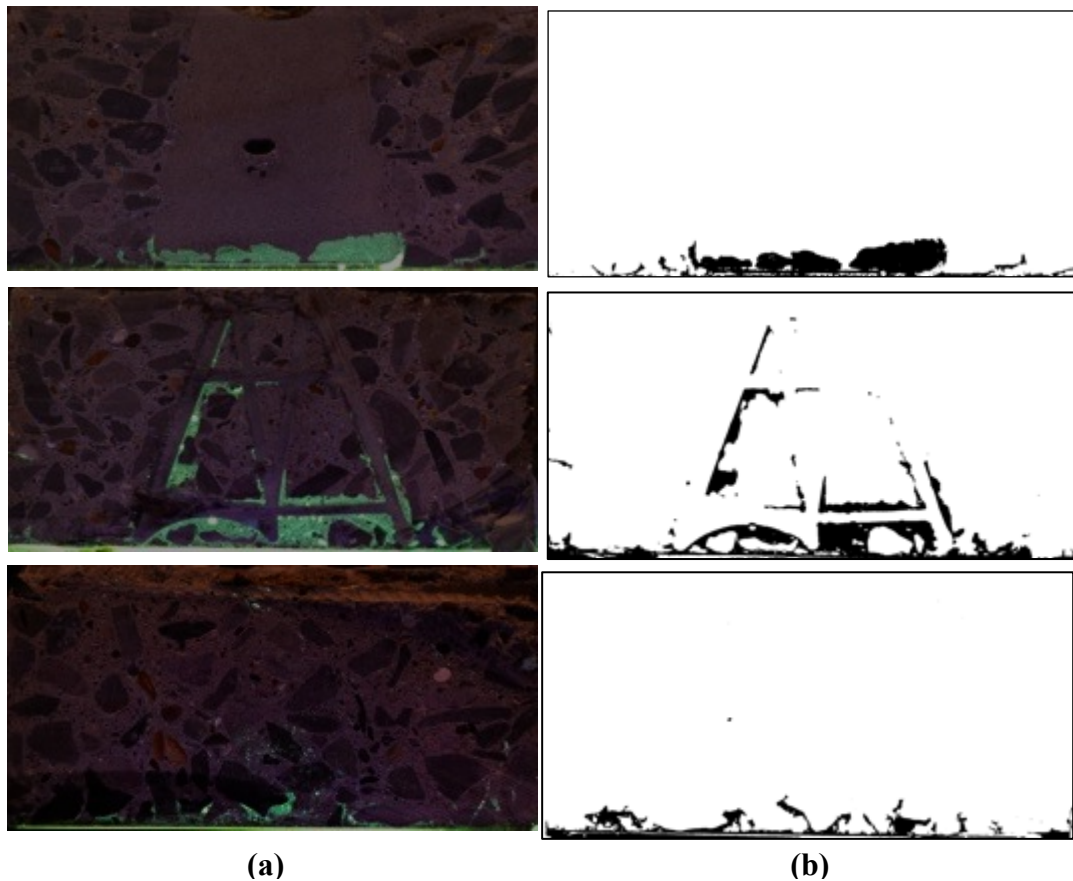


Figure 4.8 a) Cross-sections of the epoxy impregnated samples imaged under UV light and, b) their respective binary images after thresholding. Samples are C10-28d-50°C-50:C1, C10-28d-50°C-50:P1 and C10-28d-50°C-50:S1 (top to bottom).

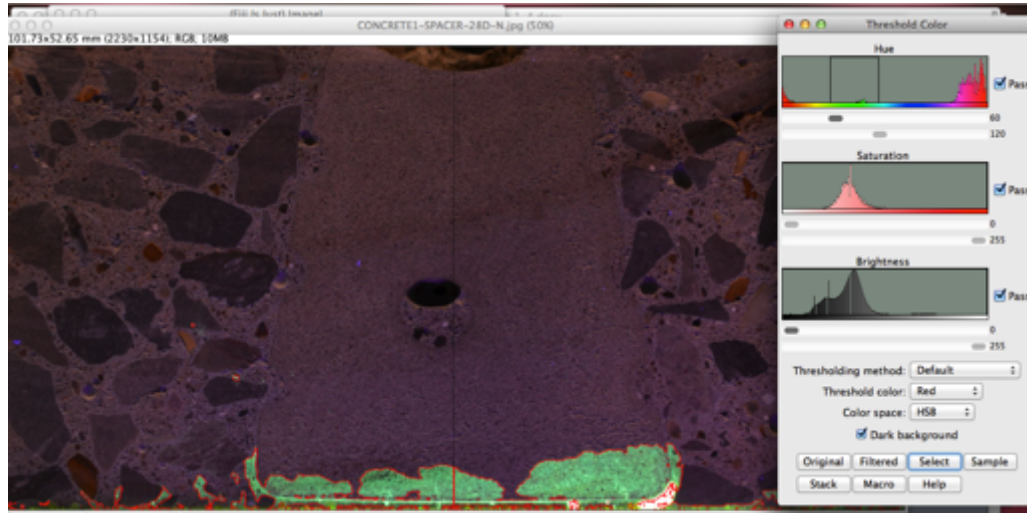


Figure 4.9 Screenshot of ImageJ showing the applied colour threshold settings to segment the fluorescent regions.

4.5 Results

4.5.1 Transport properties

The measured oxygen diffusivity, oxygen permeability and water sorptivity coefficients are presented in Figures 4.10 to 4.13 and tabulated in Appendix 2. Each data point represents the average of three replicate measurements and the variation is presented as the standard error ($S.E = \sigma / \sqrt{n}$), where σ is the standard deviation and n is the number of replicates. It is noted that the variation within the replicates (standard error) was relatively small compared to the variation between the control sample and samples with spacers. Hence, comparison can be made to establish the effect of spacers.

In general, the transport properties of samples with spacers were about 10 to 300% higher than the control samples (without spacers). Concrete samples containing plastic spacers consistently gave the highest diffusivity, permeability and sorptivity coefficients followed by samples with cementitious spacers, then steel spacers. The control samples had the lowest transport coefficients in all cases.

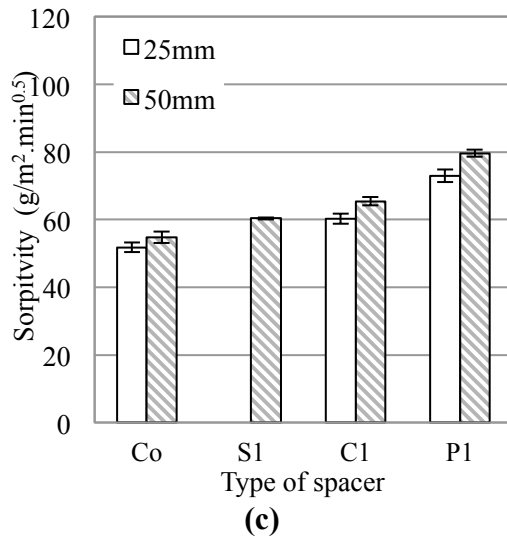
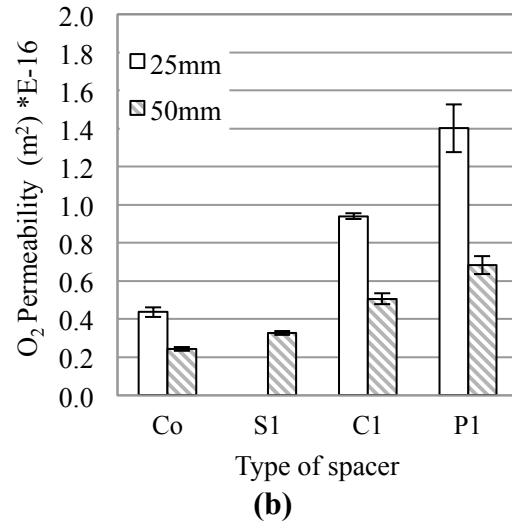
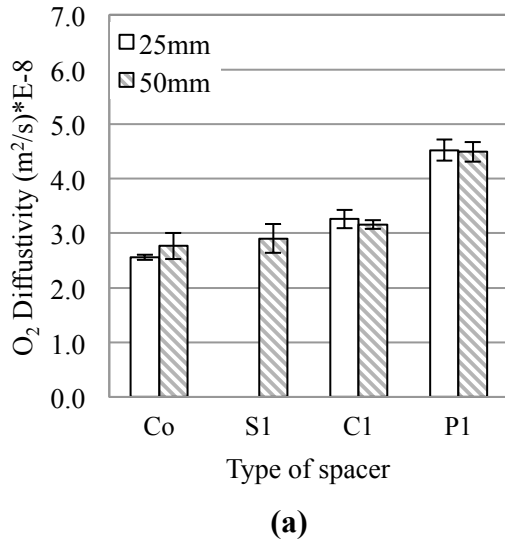


Figure 4.10 Effect of spacer type and height on a) oxygen diffusivity, b) oxygen permeability, and c) water sorptivity after 28 days curing and conditioning at 20°C, 55% RH. MSA is 10 mm.

The results show that increasing the curing age from 3 to 28 days caused a reduction in transport properties in all cases as expected. Transport properties decreased by a factor of 0.65 to 0.70 when comparing the data shown in Figure 4.10 and Figure 4.11. It is also evident that the height of spacer (sample thickness) has an influence on oxygen permeability, but not the measured diffusivity and sorptivity. The 25 mm thick samples consistently gave much higher oxygen permeability compared to the 50 mm thick samples. This is due to the size effect on permeability as reported in Wu et al. [2015].

Conditioning regime prior to testing has a major influence on the measured transport properties. However, samples with plastic spacers were the most sensitive to condition regime; this is reflected in the data shown in Figure 4.12 and Figure 4.13. Oven drying at 50 °C produced the highest transport coefficients. The diffusivity, permeability and sorptivity of samples with plastic spacers were higher than of the control samples by a factor of 2.8, 3.4 and 1.5 respectively. Also, fine cracks were observed in the edge of the base of six samples, with crack widths ranging from 4.4-6.1µm). The cracks appear to be parallel to the spacer location (Figure 4.14). On average, samples with plastic spacer conditioned at 20 °C, 75% RH and 55% RH showed higher transport coefficients by a factor of 1.4 and 1.6 respectively compared to the control. It is evident that conditioning method greatly influences the transport property and this is reflected in the data. Drying at 20 °C, 75% RH consistently gave the lowest coefficients for followed by drying at 55% RH all samples regardless of spacer type, thickness and MSA. The measured transport properties after drying at 50°C were up to a factor of 1.5-2.5 higher than that at 20°C, 75%RH, and up to a factor of 1.2-2 that measured after drying at 20°C, 55%RH,

The results in Figure 4.12 also show that samples containing the modified plastic spacer (P2 and P3) gave a slight improvement in transport properties, which decreased by a factor of 1.1 - 1.2 compared to samples containing unmodified spacer P1.

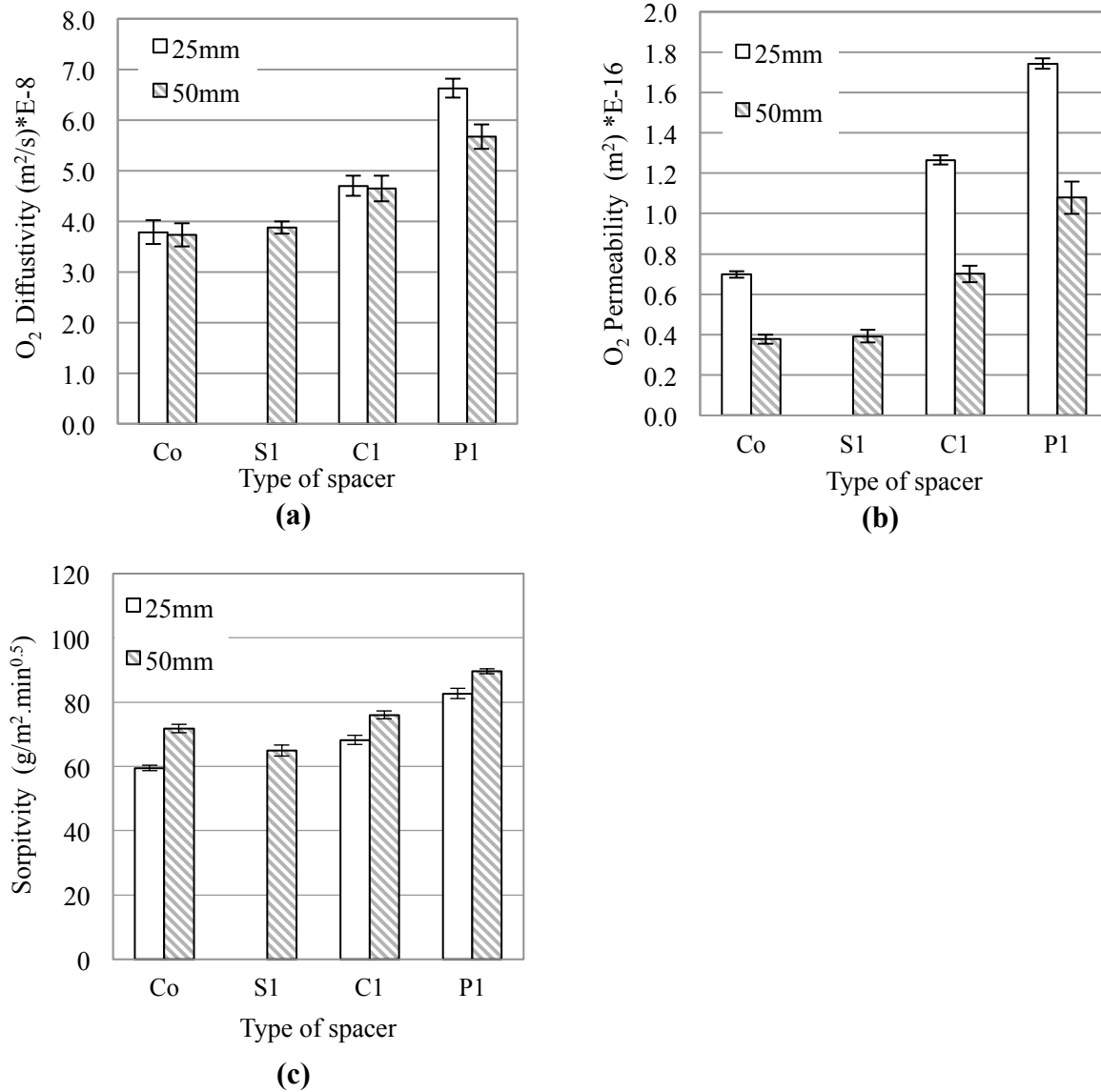


Figure 4.11 Effect of spacer type and height on a) oxygen diffusivity, b) oxygen permeability, and c) water sorptivity after 3 days curing and conditioning at 20°C, 55% RH. MSA is 10mm.

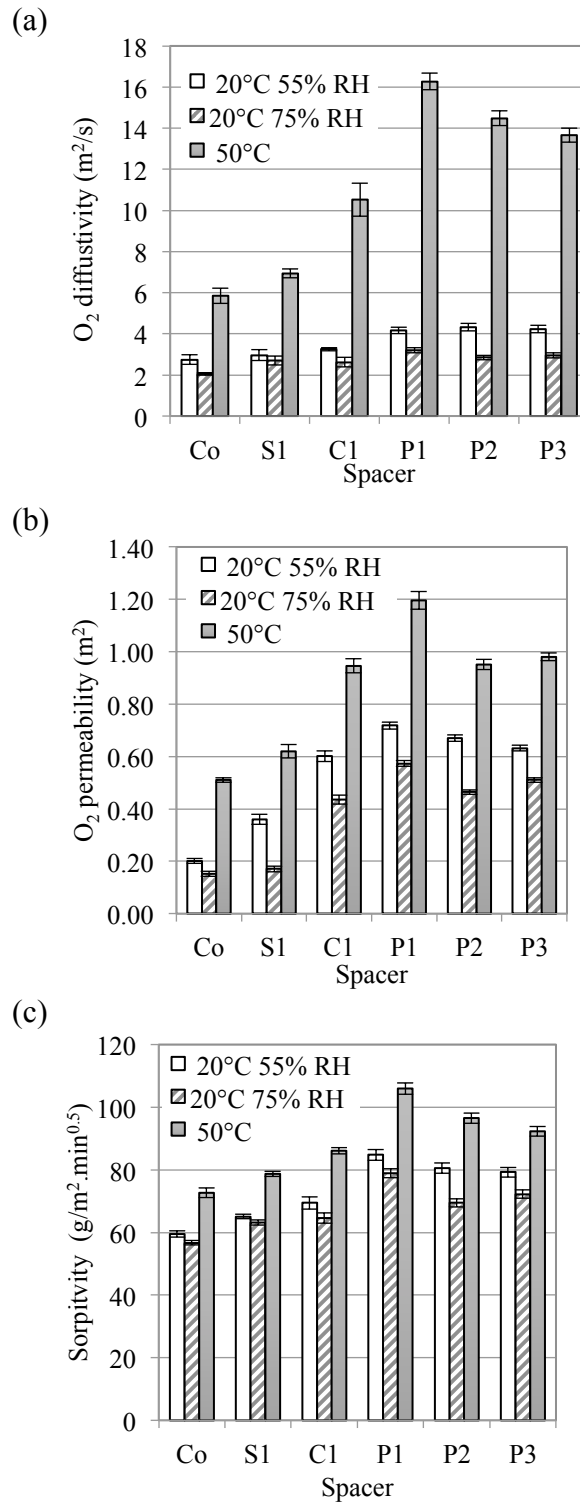


Figure 4.12 Effect of spacer type and height on a) oxygen diffusivity, b) oxygen permeability, and c) water sorptivity after 28 days curing and conditioning at 20°C, 55% RH, 20°C, 75% RH and 50°C. MSA is 10mm.

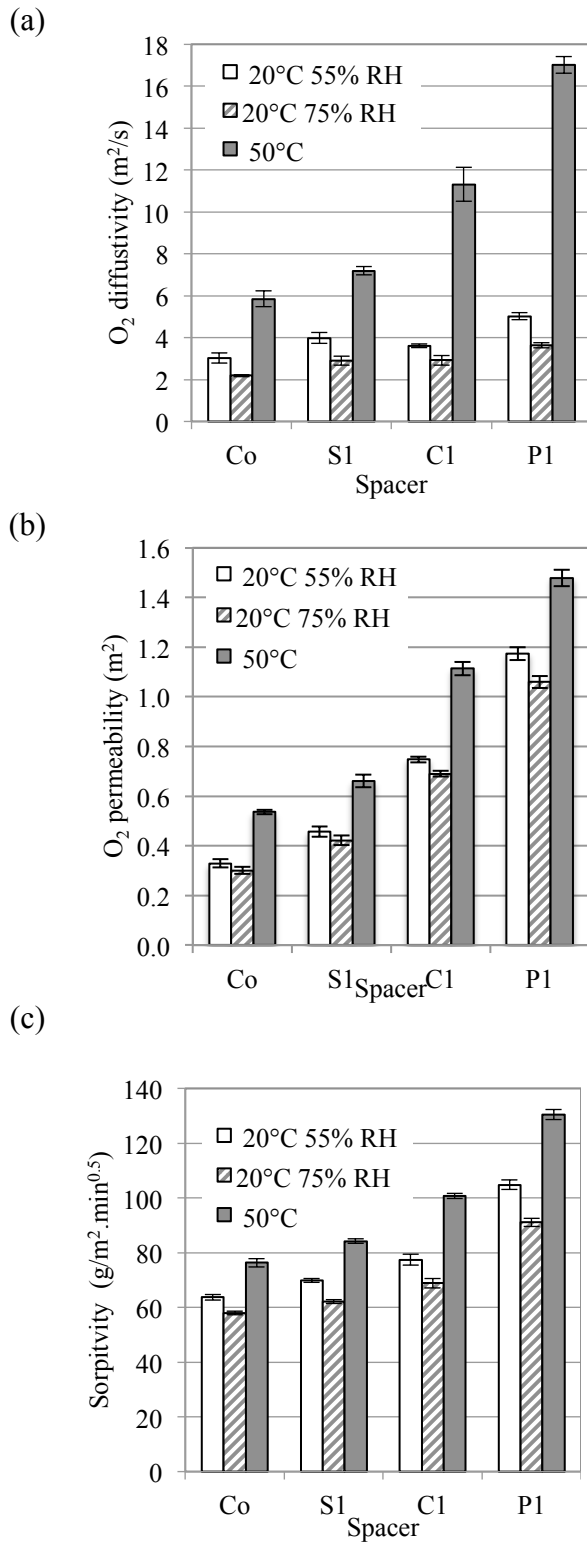


Figure 4.13 Effect of spacer type and height on a) oxygen diffusivity, b) oxygen permeability, and c) water sorptivity after 28 days curing and conditioning at 20°C, 55% RH, 20°C, 75% RH and 50°C. MSA is 20mm.

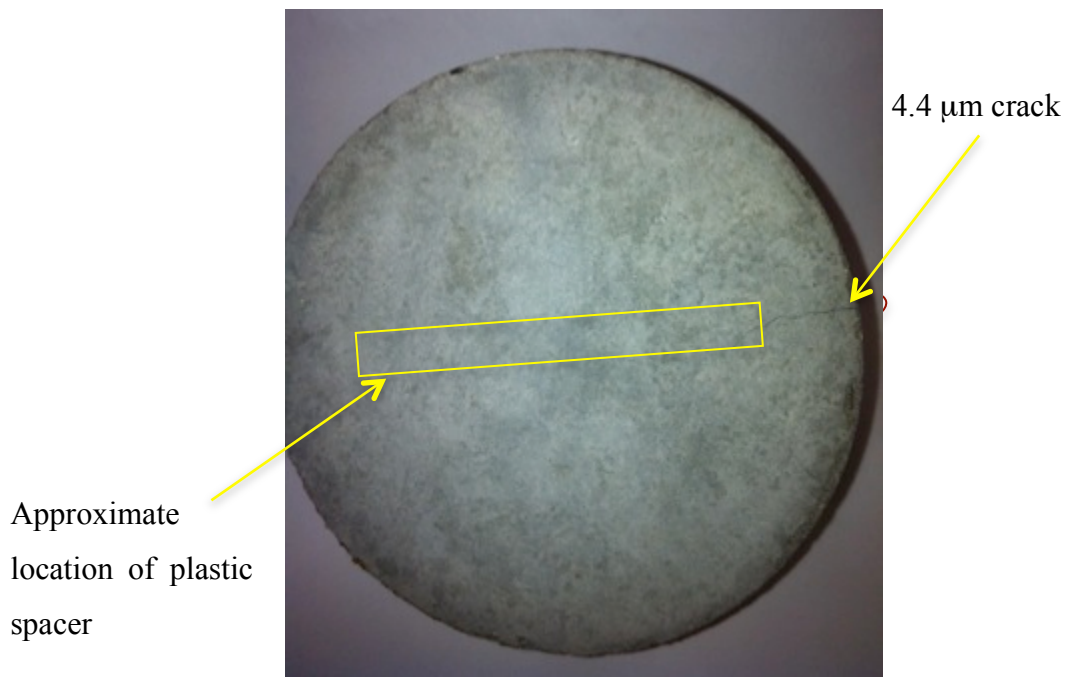


Figure 4.14 Fine cracks appearing on the base of samples with plastic spacers conditioned at 50 °C.

Samples with cementitious spacers had diffusivity and sorptivity coefficients higher than the control sample by a factor of 1.8, and permeability coefficient higher by a factor of 2.4 when conditioned at 50 °C. Additional testing was carried out to determine the absorption of the cementitious spacer. Figure 4.15 shows water absorption per unit area of the cementitious spacer. It was found that the sorptivity of the cementitious spacer ($31.9 \text{ g/m}^2 \cdot \text{min}^{0.5}$) was around 39% of that of the control sample. The total absorption of the cementitious spacer was 18% of that of the control sample. This suggests that the increase in water transport when the cementitious spacer is cast in concrete is due the porous concrete-spacer interface rather than the spacer itself. This will be verified by examining the microstructure gradient along the interface and results presented in Section 5.3.1

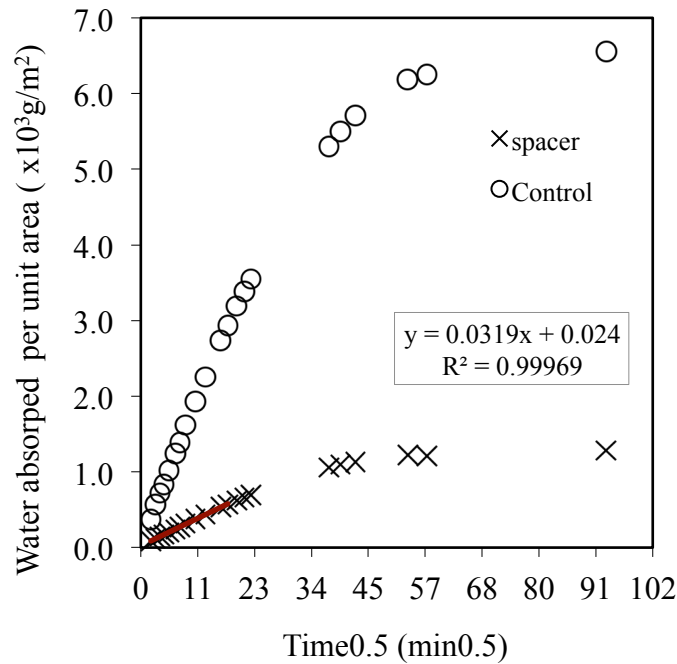


Figure 4.15 Water absorbed per unit area vs. square root of time for cementitious spacers.

The presence of steel spacers had the least effect on transport properties compared to control. On average, the transport coefficients of samples containing steel spacers were higher by 10% in all cases. This suggests that there is a good bond between the steel spacer and concrete. Furthermore, the steel spacer occupies the least volume in the sample and has the smallest surface area in contact with concrete as shown in Table 3.2.

The effect of MSA (10 and 20 mm) for 50 mm thick samples was small for diffusivity (factor of 1.05-1.20) and sorptivity (factor of 1.02-1.23), but much higher for permeability (factor of 1.1-2) as shown in Figures 4.12-4.13. The results show that oxygen permeability for samples with t/MSA of 5 were almost twice that for samples of t/MSA of 2.5 (Figures 4.10 and 4.11) regardless of curing age. On the other hand, the measured diffusivity and sorptivity were relatively constant for samples regardless of spacer type and curing age. The overall trend indicates that diffusivity and sorptivity are independent of t/MSA despite the slight scatter in the data.

Using a coring device to extract samples was a concern because of the possibility of sample damage during coring. If this occurred, then it would be expected that the cored samples would have higher transport properties than the cast samples. However, the transport results of cored samples were relatively similar to those of cast samples which in essence indicate good coring setup that minimised damage.

4.5.2 Image analysis

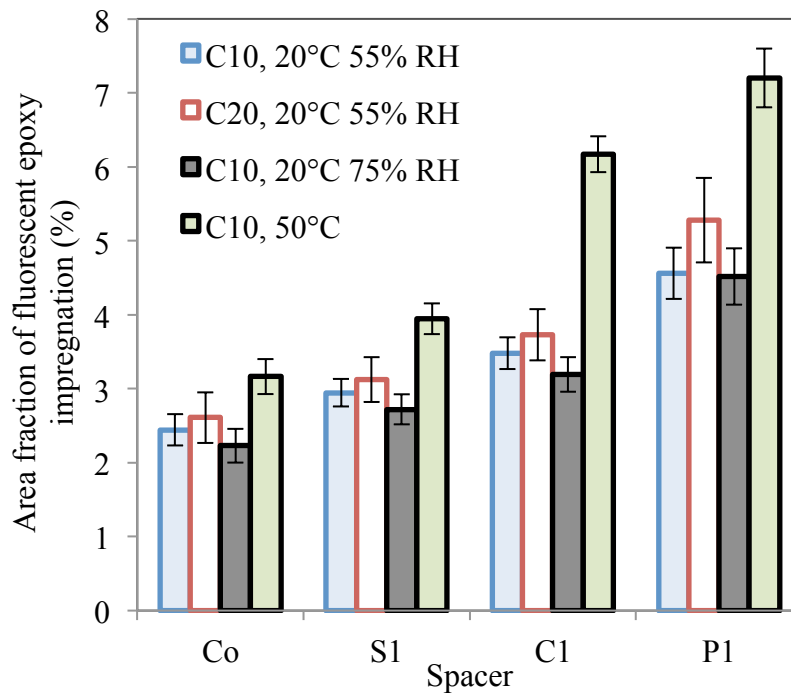
The fraction area and maximum depth of fluorescent epoxy penetration for samples with different spacers, MSA and conditioning regimes are presented in Figure 4.16. The results are average of three replicate measurements and the error bars shown on the figure represent +/- one standard error of the average.

Samples containing plastic spacers consistently showed highest epoxy penetration followed by samples with cementitious spacers and then steel spacers. The control samples had the lowest amount of epoxy penetration. Conditioning regime had a significant effect on the extent of epoxy intrusion. Samples conditioned at 50 °C showed consistently higher area fraction and depth of impregnation followed by samples conditioned at 20°C, 55%RH and then samples conditioned at 20°C, 75%RH. These trends are similar to those observed for mass transport properties presented in Chapter 4.6.1.

Samples with plastic spacer showed epoxy impregnation covering the entire depth of the spacer when conditioned at 50°C. The area fraction and depth of impregnation were greater than those of the control sample by a factor of two and five respectively. Figure 4.8 shows that most of the epoxy intrusion occurred along the spacer-concrete interface and within the concrete inside the plastic spacer. The microstructure of these areas will be further investigated using backscattered electron microscopy in Chapter 5. Depth of impregnation for samples with concrete spacer were higher than the control by a factor of 3, 1.3 and 1.5 when conditioned at 50°C, 20°C 75%RH and 20°C 55%RH respectively. An interesting observation is that samples dried at 50°C showed greater epoxy impregnation within the cementitious spacer than the surrounding concrete (Figure 4.8). This is unexpected because the w/c ratio and sorptivity coefficient for the cementitious spacer were lower than that of the concrete. Therefore, the microstructure of the cementitious spacer will also be examined by backscattered electron microscopy in Chapter 5 to investigate this further.

The presence of steel spacer had a minimal effect on the depth and area of epoxy impregnation, both increasing by only a factor of 1.05 to 1.1 relative to the control. Referring to the results from the C10 and C20 samples ($t/MSA = 5$ and 2.5 respectively), it can be observed that the effect of t/MSA was not consistent through the samples. Its effect on area fraction of samples with plastic spacer was higher than the other samples. This does seem to be an experimental error since the trend is not repeated for different samples and limited number of samples were tested.

(a)



(b)

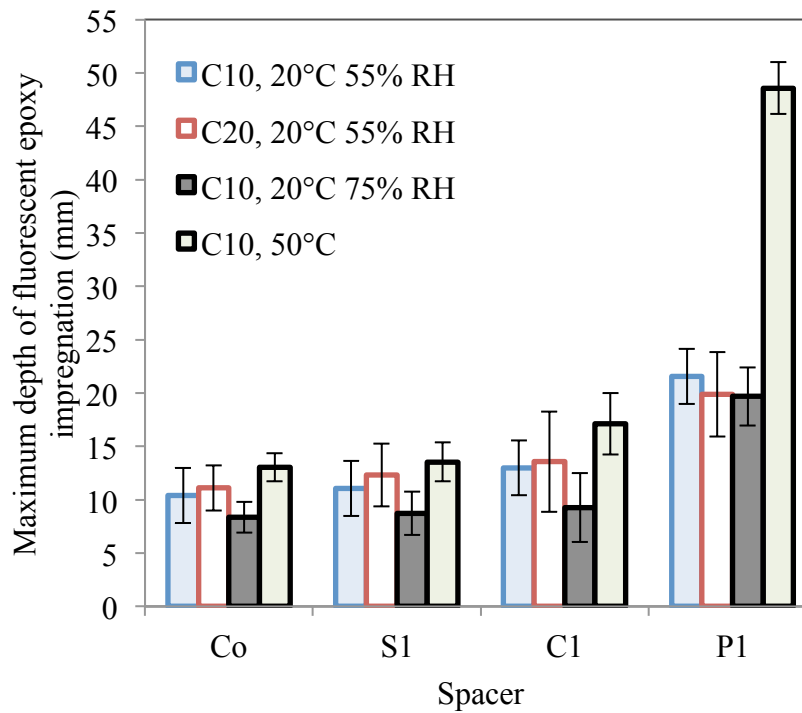


Figure 4.16 Effect of spacer, MSA and conditioning regime on the a) area fraction and b) maximum depth of epoxy penetration.

4.6 Discussion

The results presented in this Chapter shows that the inclusion of spacers increases the bulk transport properties of concrete. The net effect depends on the type of spacer, its thickness and the conditioning method prior to transport testing. The results clearly show that spacers facilitate gaseous and water transport where the aggregate fractions, MSA, curing, w/c ratio and conditioning regime were held constant. Concrete samples containing plastic spacers consistently gave the highest diffusivity, permeability and sorptivity coefficients, and epoxy intrusion followed by samples with cementitious spacers, then steel spacers. The control samples had the lowest transport coefficients in all cases. It should also be noted that the transport results of control samples show good agreement with available experimental data such as [Wong, 2006; Wong et al., 2011; Wu et al., 2015].

There have been no previous studies on the effect of spacers on transport properties. However, the effect of spacers on transport properties can be compared to the influence of aggregates. Normal weight aggregate particles have much lower porosity than the cement paste and so act as obstacles to transport by increasing the transport path tortuosity and reducing the cross-sectional area available for flow. However, the cement paste in the vicinity of the each aggregate particle, known as the “interfacial transition zone” (ITZ), has a significantly different microstructure to that of the bulk cement paste region farther away. On average, the ITZ contains higher porosity and lower cement content [Scrivener et al., 2004; Struble, 1987] and a higher local transport properties [Wong et al., 2009] compared to the bulk paste farther away. However, it has been shown that the net effect of the ITZ on bulk transport properties is small, even when the ITZs are overlapping. Studies have shown that increasing aggregate fraction results in a decrease in bulk transport properties. This shows that the effect of increasing ITZ fraction and percolation is balanced by the reduction in the cross-sectional area available for flow and the increase in cement paste tortuosity and bulk paste impenetrability [Abyaneh et al., 2013; Buenfeld and Okundi, 1998; Wong et al., 2009].

Spacers are either impermeable (plastic and steel spacers) or have lower porosity (cementitious spacers) than the cement paste around it. Therefore, spacers should act as obstacles to transport by reducing the cross-sectional area available for flow, but the results from this Chapter suggest otherwise. The substantial increase in transport properties for samples with spacers can be attributed to the porous interface zone between the spacer and concrete. The porous interface forms a continuous link that span the entire depth of the sample providing an easy path for mass/ionic transport. Fluorescent epoxy impregnation

results in Chapter 4.5.2 and the images shown in Chapter 4.3.1 confirm that the presence of spacer provides preferential path for transport along its interface with concrete. For samples with plastic spacers conditioned at 50°C, it was evident that the fluorescent epoxy penetration occurred through the full depth of spacer mainly along its interface with concrete. Samples with cementitious spacers also showed a similar behaviour. Further details about the microstructure of spacer interface with concrete will be presented in Chapter 5.

Conditioning regime prior to testing has a major influence on the measured transport property. It is clear that samples with plastic spacers were the most sensitive to condition regime and when dried at 50°C, produced the highest transport coefficients. Furthermore, fine cracks were observed in the base of sample parallel to the spacer location. This is due to the difference in thermal expansion and drying shrinkage characteristics between plastic spacer and surrounding concrete as reported by [Rostam, 2005] and [Vik, 2002]. An ambient temperature of 50°C can be reached in places such as the African continent or the Arabic peninsula. Also, the hydration of cement can cause the internal concrete temperature to reach 50°C and higher.

Oxygen permeability results of samples with 10 mm aggregates were affected by the depth of spacer (sample thickness). The sample thickness to maximum size of aggregates ratios (t/MSA) ranged from 2.5 to 5. However, both diffusivity and sorptivity remained relatively constant regardless of the change in t/MSA ratio. These results are in line with the reported effect of t/MSA by [Wu et al., 2015]. The increase in permeability at decreasing t/MSA ratio from 5 to 2.5 is linked to the presence of drying induced microcracks. Samples with smaller t/MSA ratio had higher microcrack density, widths and lengths, hence higher permeability coefficients [[Wu et al., 2015].

4.7 Conclusions

The mass transport properties of concretes with plastic, cementitious and steel spacers at various cover depth (25 and 50mm), maximum size of aggregate (MSA: 10 and 20 mm), curing ages (3 and 28 days) and conditioning regimes (50°C, 55% RH; 50°C, 75% RH, and 50°C oven drying) were investigated. Results were compared to that of control samples without spacers. Samples were prepared at constant free w/c ratio (0.4) and aggregate volume fraction (70%) to ensure similar porosity at the time of testing.

Results show that spacers consistently increased transport properties relative to the control. Samples containing plastic spacers consistently gave the least resistance to transport, followed by samples with cementitious spacers, then steel spacers. The control samples had

the highest resistance to transport. The extent of the effect of spacers on transport properties depends on the curing age, MSA and drying method. Overall, spacers increase gaseous diffusivity, permeability and water sorptivity by up to a factor of 1.3 to 3.4, depending on the spacer type, curing age and conditioning regime.

It was also evident that fluorescent epoxy penetration occurred mainly along the interface of the spacer and concrete, and also within the concrete inside plastic spacers. As expected, drying at 50 °C prior to testing increases the severity of the effect of spacers on mass transport. This is due to the difference in thermal coefficient of expansion and drying shrinkage characteristics between the spacer and the surrounding concrete, in particular for the case of plastic spacers.

Chapter 5 Microstructure of the spacer-concrete interface

This chapter aims to quantify the microstructure of the spacer and its interface with surrounding concrete. Euclidian Distance Mapping [Edmond] method was applied to investigate the effect of spacer on the porosity and unreacted cement distribution, and their spatial variability. Concrete samples with plastic, steel chair and cementitious spacers at thickness of 50 mm and maximum aggregate size (MSA) of 10 mm were studied using SEM and image analysis. The microstructure of the spacer-paste interface showed on average, significantly lower cement content and higher porosity compared to 'bulk paste' farther away. However, this is highly variable from location to location. Samples with plastic spacers had the highest porosity at interface followed by samples with concrete and steel space. The porosity at spacer interface was higher than that of aggregate-paste "interfacial transition zone" (ITZ). The porosity within the bulk cement paste was the lowest. No unreacted cement content was detected near the interface, however the cement content increased sharply to reach a relatively steady value at 50 μm away from the spacer interface for all samples. With respect to both unreacted cement and porosity, the width of the affected zone is around 50 μm from the interface for all spacer types. This value is in the range typically reported for the aggregate ITZ.

5.1 Introduction

At a basic level, the concrete cover can be viewed as consisting of several phases as shown in Figure 5.1. There is a huge amount of research dedicated to study the microstructure of the first three phases, i.e. the bulk cement paste, aggregates and the aggregate-paste ITZ. However, there is no mention of the microstructure of spacers or its interface in any published literature although spacers are left permanently in the concrete cover.

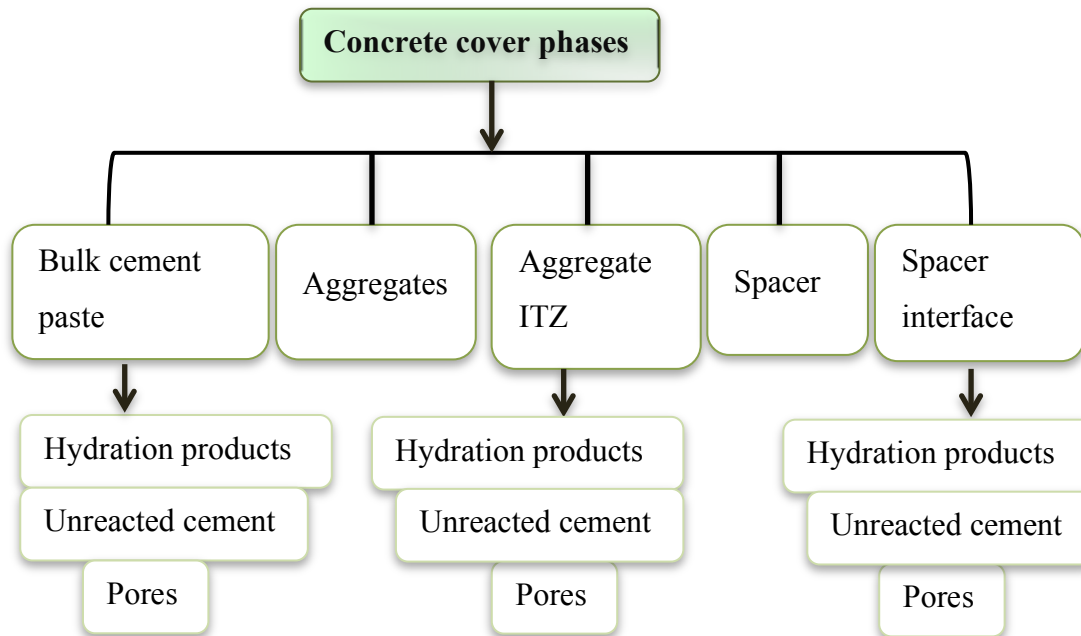


Figure 5.1 Phases within the concrete cover.

The spacer-paste interface can be compared to the aggregate-paste interfacial transition zone (ITZ) as discussed in Section 4.7. The ITZ is a 20 to 50 μm wide region of cement paste that envelops each aggregate particle. Its microstructure is significantly different from the cement paste located farther away due to particle-packing effect and bleed water accumulation on the underside of aggregate particles. Cement particles are unable to pack closely against the larger aggregate particles during concrete batching. Also, bleed water tends to accumulate on the aggregate surface during compaction. These results in higher w/c ratio, thus higher porosity and lower cement content near the aggregate-paste interface compared to the bulk paste farther away.

Over the last thirty years, backscattered electron (BSE) imaging of polished surfaces has become a well-established method for studying the microstructure of cementitious materials [Scrivener et al., 2004]. In BSE imaging, the intensity of backscattered electrons increases with the mean atomic number of the imaged solid phase [Echlin, 2011; Stutzman and Clifton, 1999]. The phase with the largest mean atomic number appears brightest in a BSE image. In a hydrated cement paste, the anhydrous cement phase has the highest brightness intensity, followed by calcium hydroxide, calcium silicate hydrates and finally the resin-filled pores and cracks. Hence, pores and cracks appear as the darkest phase, and this feature of BSE

imaging enables quantitative analysis of spacer–cement paste interface to be conducted. Euclidean Distance Mapping [Edmond] is a quick and efficient image analysis procedure developed by [Wong and Buenfeld, 2006a] to investigate the porosity and unreacted cement distribution, and their spatial variability at the interfacial transition zone. Therefore, this procedure will be employed in this Chapter.

5.2 Experimental

5.2.1 Samples

Eight block samples were prepared as listed in Table 5.1. These blocks were sectioned from samples impregnated with fluorescent epoxy (Section 4.4). Fluorescent epoxy impregnated samples were used because the hardened epoxy provides atomic contrast for BSE imaging and it protects the sample from preparation damage. For example, it eliminates the possibility of sectioning or additional drying-induced cracks. If the sample preparation produces artefacts, these would not be epoxy-filled, therefore not imaged and will be excluded from image analysis.

Concrete samples at w/c ratio 0.4 was prepared, cured for 28 days and conditioned at 20°C, 55% RH and at 50°C. Details of the materials and sample preparation are described in Section 3.2. After curing and drying at the required conditioning regime, the samples were impregnated with fluorescent epoxy as described in Section 4.4. Once the epoxy has hardened, the sample was photographed and a block sample (40 x 20 x 8 mm) was sectioned to include both spacer and surrounding concrete. Block samples for the control samples (i.e. no spacer, Co) were sectioned at the mid-point of the bottom half of the sample. Locations of the block samples are shown in Figure 5.2.

Table 5.1 Samples for microstructure characterisation.

Spacer	Thickness (mm)	MSA (mm)	Curing (days)	Conditioning	Type
Co, C1, P1, S1	50	10	28	20°C, 55% RH	Cast
Co, C1, P1, S1	50	10	28	50°C	Cast

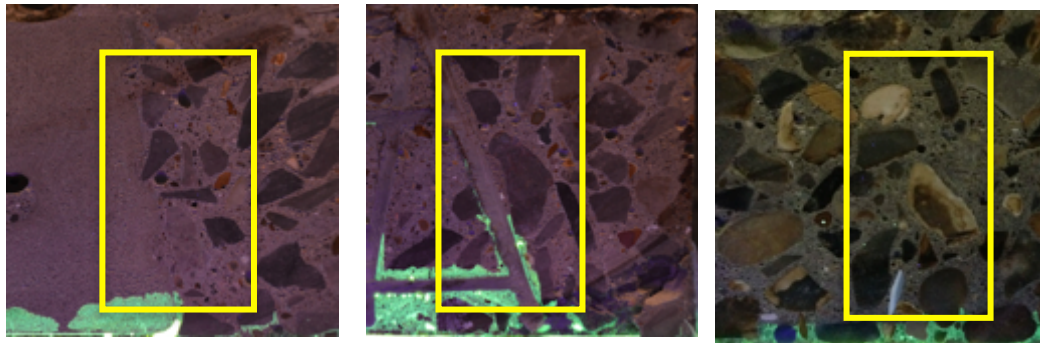


Figure 5.2 A 40 x 20 x 8 mm block is extracted from each cylindrical sample for microstructure characterisation. Locations of the blocks are shown above. Samples (L-R) are C10-28d-50°C-50:C1; C10-28d-50°C-50:P1 and C10-28d-50°C-50:S1.

5.2.2 Sample preparation for microscopy

The sample preparation process for backscattered electron microscopy is according to the method established by [Wong, 2006]. The main procedures include sectioning, full impregnation with epoxy followed by grinding and polishing to a $\frac{1}{4}$ μm finish. As mentioned earlier, the fluorescent epoxy impregnated cylindrical samples were sectioned to produce blocks (40 x 20 x 8 mm) to include both spacer and surrounding concrete. Sectioning was done with a diamond abrasive cutter operated at a slow feed rate of 0.3 mm/s. The blocks were then fully vacuum-impregnated with fluorescent epoxy to highlight pores, cracks and interface between spacer and concrete matrix. The fluorescent epoxy supports and preserves the microstructure from damage during grinding and polishing, and provides atomic contrast so that the pores and cracks are visible in BSE images.

The fluorescent epoxy was prepared by adding a fluorescein dye (Struers Epodye) to epoxy resin (Araldite AY103) at 5 g/litre resin, which is then mixed using a magnetic stirrer for at least 24 hours to ensure that the dye was uniformly dispersed in the resin. The fluorescent epoxy was then heated up to 40°C prior to mixing with the hardener and toluene. The proportion of epoxy: hardener: toluene used was 25: 3: 1.5. Toluene was used to reduce the viscosity of the epoxy and to increase impregnation depth.

Two layers of waterproof adhesive tape were used to seal the sides and bottom of the sectioned block. The resin-hardener mixture was de-aired in vacuum for four hours and then the fluorescent resin was poured onto the sample whilst under vacuum to cover the entire

surface. The vacuum was gradually released to force the epoxy into the sample. A 2.5 bar pressure was further applied on the impregnated blocks to ensure deep penetration [Wong and Buenfeld, 2006b]. The sample was then allowed to cure for two days to achieve sufficient hardness.

The epoxy impregnated blocks were ground at successively finer grades using a series of silicon carbide papers (grit sizes 68 μm , 30 μm , 18 μm and 14 μm) and then polished using diamond abrasives (grit sizes 9 μm , 6 μm , 3 μm , 1 μm and 0.25 μm) to achieve a flat and well-polished surface. The sample needs to be well-polished because surface roughness as produced from saw cutting interferes with the signal generation/collection process, and compromises image quality by reducing contrast and feature definition. The grinding and polishing was carried out using a Struers LaboPol-5 at a speed of 70rpm, with an approximately 7 N force applied onto each sample. A non-aqueous solution was used as a coolant and lubricant during grinding and polishing. The samples were cleaned in ultrasonic bath with acetone to remove grit and abrasives.

A petrographic microscope (Olympus BX 51) with ultraviolet light in reflected mode was used to inspect the surface quality of samples during grinding and polishing stages to achieve bright sample surface with sharp boundaries and good feature definition. The polished blocks are imaged under high vacuum; therefore it was carbon coated using an evaporative coater (EMITECH K550X sputter coater with K250 attachment) to avoid build up of negative charge on the sample surfaces. Samples were then kept in vacuum desiccator until required for imaging.

5.2.3 Scanning electron microscopy

BSE images were collected using a Camscan Apollo 300 field emission SEM operated at 10 kV accelerating voltage and 10 mm working distance. Fifty images were collected per sample for those containing plastic and cementitious spacers. For samples with steel spacer, the number of images collected per sample was forty one and thirty six for those conditioned at 50°C and at 20°C, 55% RH respectively. The decrease in number of images captured is due to the small size of steel wire (5 mm) spacer which limits the available area for observation. All images were captured at a magnification of 500x. The images were digitised to 2560 x 2048 pixels, giving a field of view of $240 \times 192 \mu\text{m}$ and a pixel spacing of 0.094 μm . This magnification was chosen for this study to obtain a decent sampling area and high resolution to locate the phases of interest. This magnification is commonly used for studying pore structure of cement-based materials. Smaller magnifications of 50x and 100x were used for

general viewing of the microstructure. The pixel spacing and field of view of each magnification used is tabulated in Table 5.2 . In order to ensure random and unbiased sampling, the microscope stage was moved at equally spaced distance along the interface of the spacer (around 1 mm increments) ensuring both bulk paste and spacer are imaged. To isolate the effect of aggregate particles on the microstructure, images were selected such that they were located at least 50 μm away from the nearest aggregate particle to avoid sampling the aggregate ITZ. If an image contains aggregate particle close to the spacer interface, the image will be replaced by another image within the surrounding interface. Also, areas near the sample edge were not imaged to avoid the probability of sampling saw- damaged areas.

Table 5.2 Pixel spacing and field of view of images digitised to 2560 x 2048 pixels, captured at various magnifications.

Magnification	Field of view (μm)	Pixel spacing (μm)
50x	2400 x 1920	0.940
100x	1200 x 960	0.470
500x	240 x 192	0.094

Acquiring high-quality images is vital for accurate segmentation of features and subsequent quantification steps. Brightness and contrast settings of the SEM can have a substantial effect on the appearance of the microstructure, specifically the apparent porosity. Therefore, the brightness and contrast settings should be calibrated prior to image capture to optimise the image brightness histogram and to ensure consistent results. An optimised brightness histogram fully utilises the entire dynamic range of available grey scale (0-255) where 0 represent black pixels and 255 represent white pixels. Image detail will be lost in the low and high regions of the grey scale if the contrast setting was too high, thus creating a distorted histogram with artificial peaks at both ends. Overly contrasted images cannot be improved by image processing, as this will only compress the histogram, but not remove the artificial peaks [Russ, 2002]. For this study, the brightness and contrast settings of the SEM were adjusted by trial and error to achieve the optimum BSE image and histogram as shown in Figure 5.3. The optimum settings were then applied to all subsequent images captured for the particular sample to ensure a faithful reproduction of grey values.

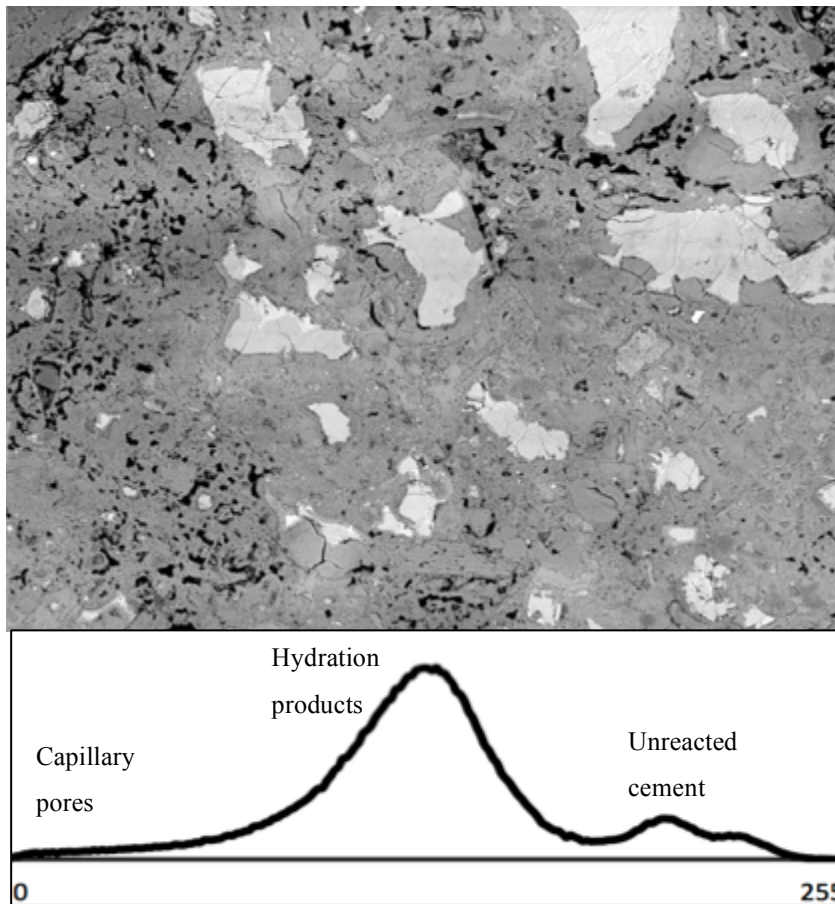


Figure 5.3 Example of BSE image and greyscale histogram obtained when the brightness and contrast settings of the SEM are set at optimum. The sample is C10-28d-20°C, 50%RH-50:Co. Image was captured at 500x magnification giving a field of view of 240 x 198 μm .

5.2.4 Image analysis

Spacer and aggregate segmentation

A significant challenge for accurate quantitative microscopy is in the segmentation of the phases of interest, which for this study are the spacer, aggregates, pores and unreacted cement. However, automated detection and segmentation is often unreliable [Wong and Buenfeld, 2006a]. Therefore, in this thesis, a careful manual tracing operation was applied to detect and segment the spacer and aggregate particles. The tracing was done on an enlarged image using an image analysis software (ImageJ). The boundaries of spacers and aggregate particles are clearly visible, allowing their exact location to be accurately traced. Also, this procedure can detect bond cracks which are preparation artefacts and therefore, should not be

measured as part of the original pore structure for the purpose of this study. The procedure requires about 2 minutes per image to perform, and is shown in Figure 5.4 and Figure 5.5. Although relatively time consuming, it is necessary for accuracy and statistical significance. Once the spacer and aggregate boundaries are accurately marked, subsequent image operations can be automated as described in the following section.

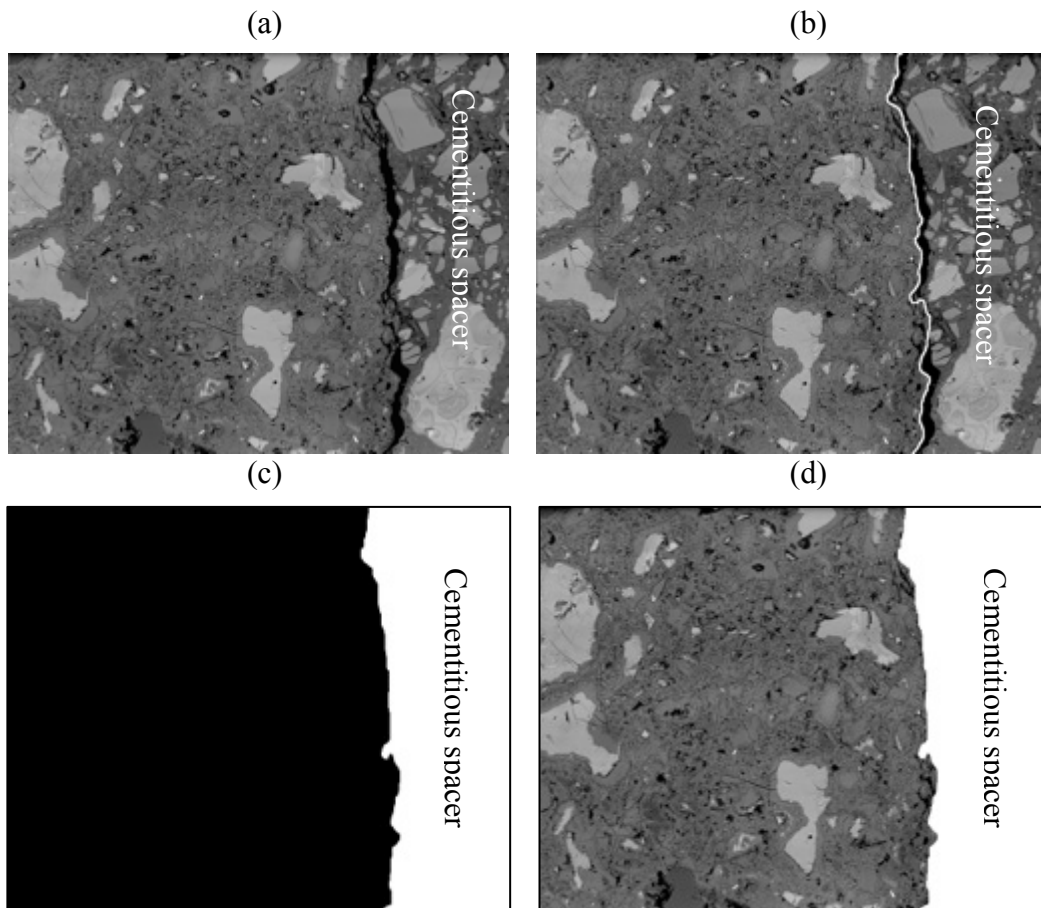


Figure 5.4 Segmentation of cementitious spacer: (a) original BSE image at 500x magnification; (b) spacer boundary is manually traced with a white line; (c) thresholding, particle detection and hole filling to produce spacer binary mask; (d) final image with the spacer removed (field of view: 240 x 192 μm , sample is C10-28d-20°C, 55% RH-50: C1).

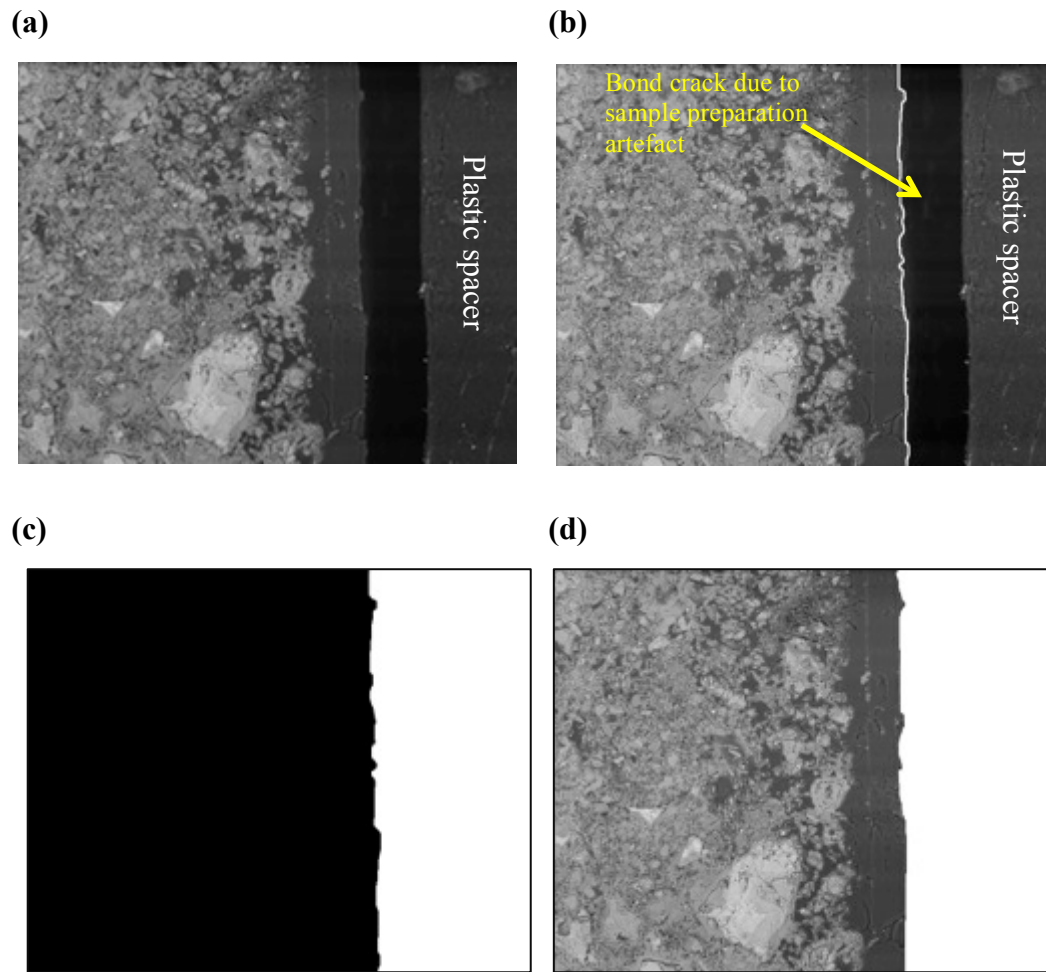
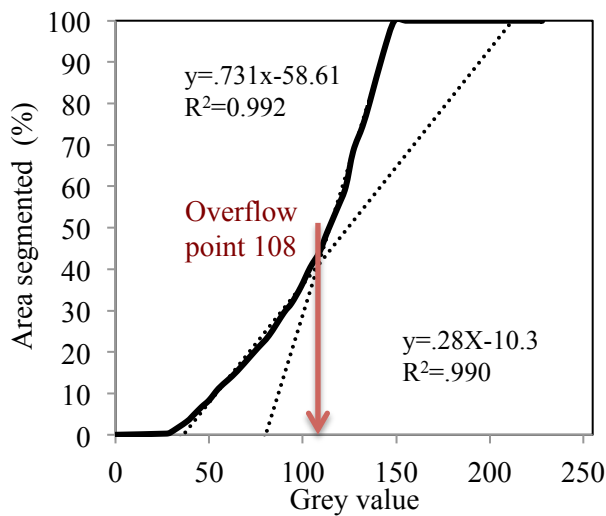


Figure 5.5 Segmentation of plastic spacer: (a) original BSE image at 500x magnification; (b) spacer boundary is manually traced with a white line; (c) thresholding, particle detection and hole filling to produce spacer binary mask; (d) final image with the spacer removed (field of view: 240 x 192 μm , sample is C10-28d-50°C - 50: P1).

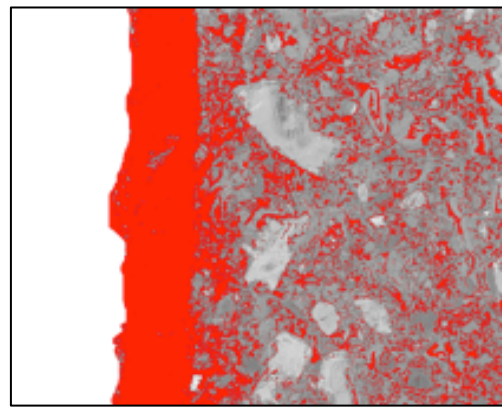
Pore segmentation

The most important characteristic of the microstructure that is to be investigated is the porosity. Herein, the term porosity includes the capillary pores and microcracks. This can be measured using image analysis by carrying out a greyscale thresholding to segment the pores and cracks. For thresholding, the lower threshold value can be set to zero because the pores and cracks are the darkest phase in a BSE image. However, the determination of the upper threshold value needs careful consideration because of ambiguity in the exact location of the pore-solid boundary. In this study, the upper threshold value was determined using the “overflow” method proposed by [Wong et al., 2006]. In this method, the upper threshold value is determined from the inflection point of the cumulative brightness histogram of the

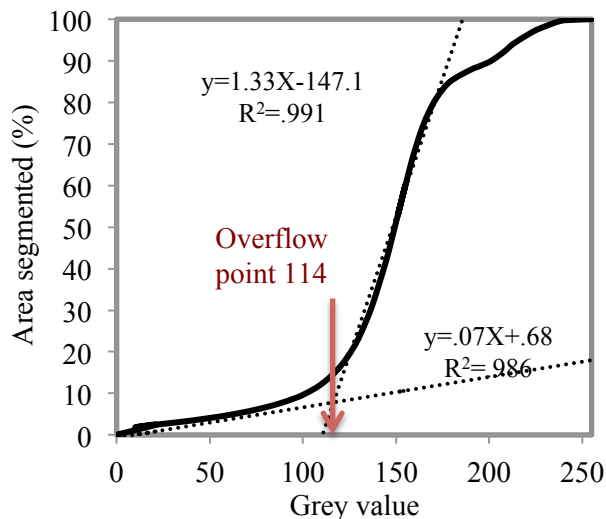
BSE image. This represents a critical point where a small increment in the threshold value will cause a sudden increase in the segmented area, indicating that the pore-solid boundary is reached. The inflection point is obtained from the intersection of two best-fit lines in the cumulative brightness histogram as shown in Figure 5.6 (a, c, e). It can be seen that the obtained upper threshold values varied slightly from one image to another. This is because the overflow method compensates for small and unavoidable fluctuations in beam conditions, sample surface roughness and brightness/contrast settings during image capture. As such, the method provides a consistent and reliable means of segmenting porosity.



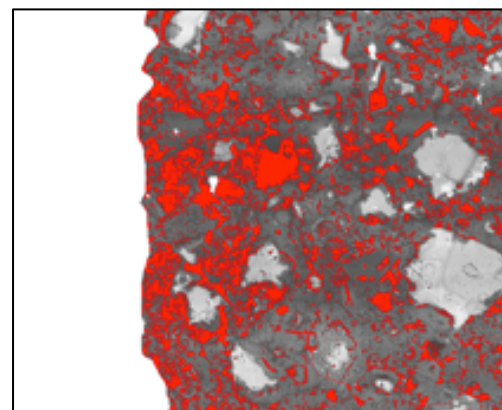
(a) Cumulative grey scale histogram for C10-28d-50°C-50:P1



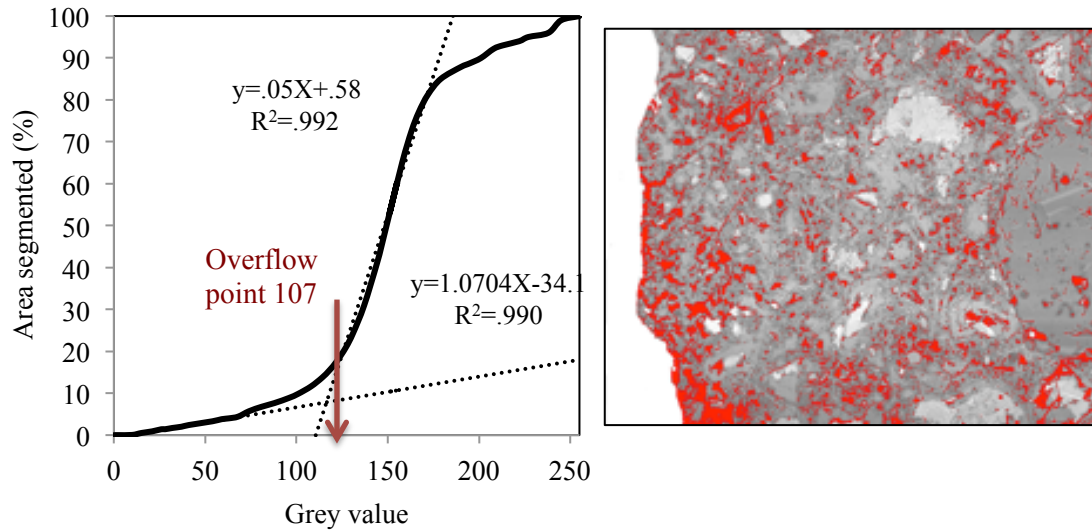
(b) Pores segmented at threshold level 108. Porosity of paste = 43.7%



(c) Cumulative grey scale histogram for C10-28-50°C-50:C1



(d) Pores segmented at threshold level 114. Porosity of paste = 19.9%



(e) Cumulative grey scale histogram for C10-28-20°C, 55%RH-50:S1

(f) Pores segmented at threshold level 107. Porosity of paste = 13.4%

Figure 5.6 Application of the overflow method to determine the upper threshold level for pore segmentation.

Unreacted cement segmentation

In a BSE image, the unreacted cement particles appear the brightest and are highly contrasted from other phases that exist in the microstructure. As such, the brightness histogram tends to show a peak at the far right end that represents the unreacted cement. Therefore, segmentation of the unreacted cement can be carried out by selecting the minimum grey value between the peaks for hydration products and unreacted cement as the lower threshold value (Figure 5.7). The exact location of the minima is determined from the first derivative of the brightness histogram. The upper threshold level for unreacted cement is set at 255.

5.2.5 Euclidean Distance Mapping [Edmond]

The spatial distributions of porosity and unreacted cement at a distance of up to 100 μm from the spacer or aggregate interface were measured using a method known as Euclidean Distance Mapping [Edmond] [Wong and Buenfeld, 2006a].

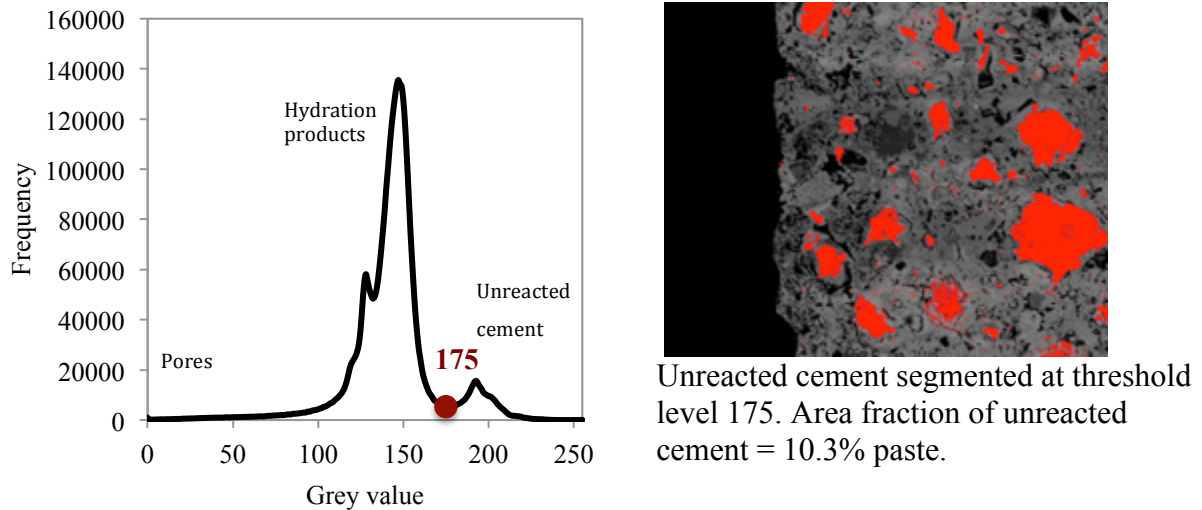
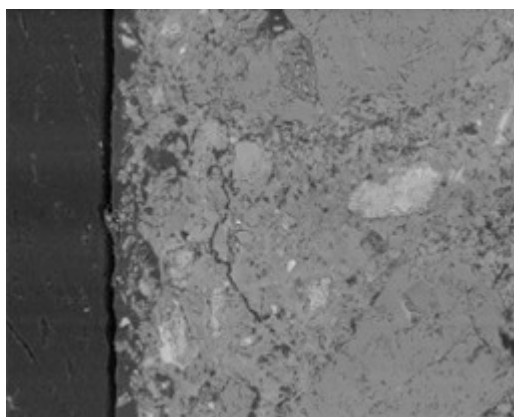


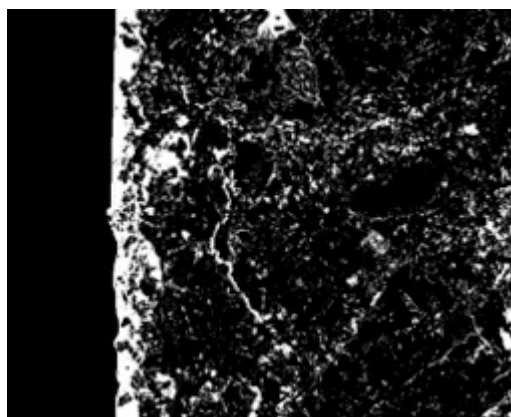
Figure 5.7 The threshold for unreacted cement is selected from the minimum between peaks for hydration products and unreacted cement on the brightness histogram.

Sample is C10-28-20°C, 55%RH-50: S1.

Figure 5.8 shows an example application of the EDM method on a BSE image of the paste region adjacent to a plastic spacer. To determine the porosity gradient from the spacer boundary, a pore binary mask (Figure 5.8b) and spacer binary mask (Figure 5.8c) are first created from the original image by segmentation as discussed in the preceding section. Next, an EDM of the paste (Figure 5.8d) is generated from the spacer binary mask, which is then multiplied with the pore mask to give a distance map of the pore phase only (Figure 5.8e). This effectively transforms the brightness of each pore pixel in the original image to a grey value that has a numerical value equal to its linear distance to the nearest spacer boundary. Finally, the porosity distribution (Figure 5.9c) is obtained by normalising the brightness histogram of the pore EDM (Figure 5.9b) to the paste EDM (Figure 5.9a), and converting the grey values to actual distances by factoring with the pixel spacing value ($0.098 \mu\text{m}/\text{pixel}$). The above steps are repeated three times to get the required porosity distribution over a distance of $100 \mu\text{m}$ (Figure 5.9d). To eliminate the influence from aggregate particles outside the image, the distance maps are cropped by $50 \mu\text{m}$ from all sides. Figure 5.10 shows another example application of the EDM method to obtain the porosity distribution in the paste region adjacent to a cementitious spacer. This process is repeated for a large number of images to obtain an averaged porosity distribution along the spacer-concrete interface.



(a) Original image at 500x magnification.



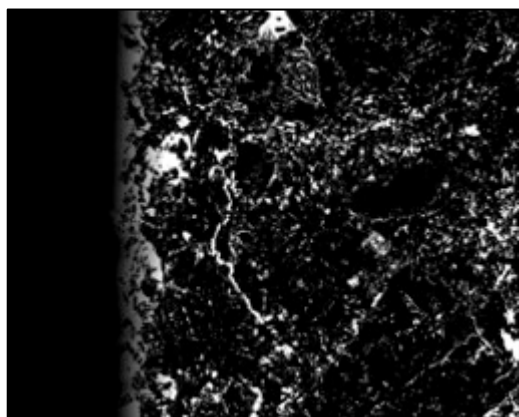
(b) Pore binary mask.



(c) Spacer binary mask.



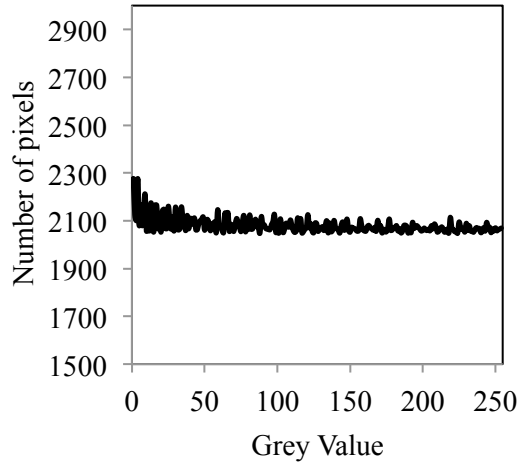
(d) EDM of paste from spacer boundary.



(e) Distance map of pores from spacer boundary.

Figure 5.8 Using EDM to generate distance map of pores from spacer boundary.

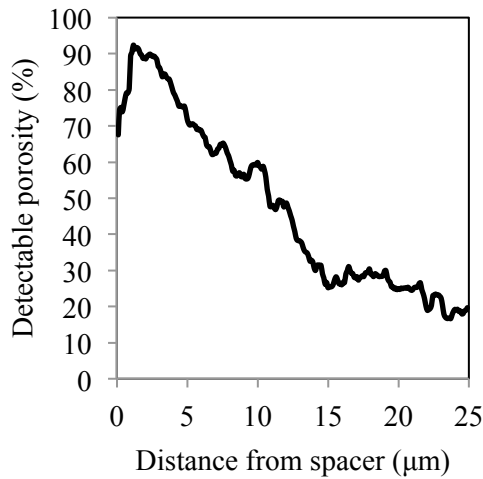
Sample is C10-28d-20°C, 55%RH-50: P1. (Field of view: 240 x 192 μm).



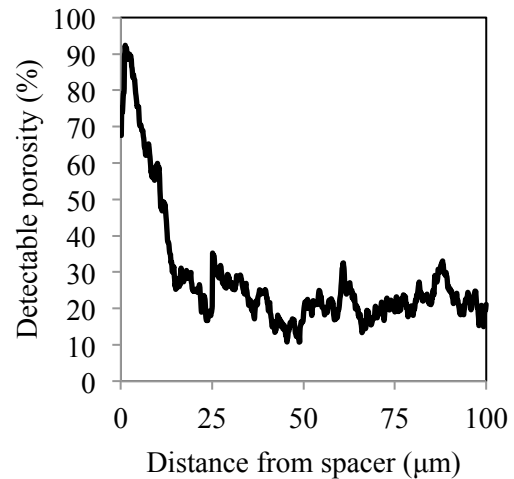
(a) Brightness histogram of paste distance map from spacer boundary (Figure 5.8d). The grey value 255 (white) representing the spacer is not plotted.



(b) Brightness histogram of pore distance map from spacer boundary (Figure 5.8e). The grey value 0 (black) representing the solid phase is not plotted.

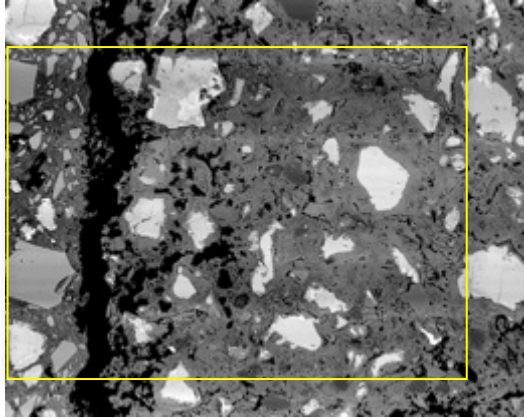


(c) Porosity distribution from spacer boundary at 1 pixel (0.094 μm) strip width.

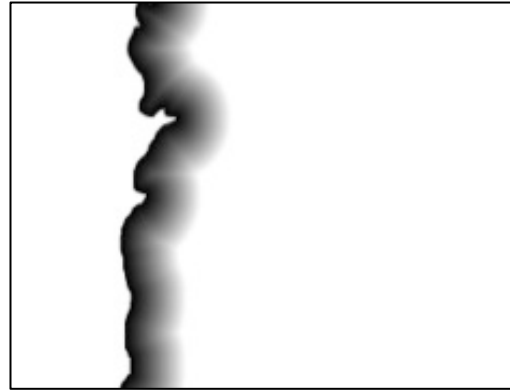


(d) Porosity distribution (up to 100 μm) from spacer boundary at 1 pixel (0.094 μm) strip width.

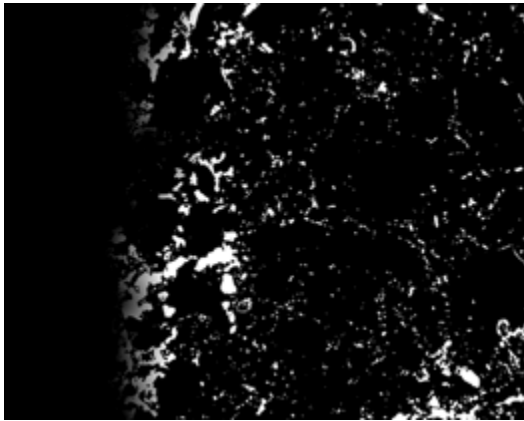
Figure 5.9 Quantifying porosity distribution at the spacer-paste interface using brightness histograms of the pore and paste distance maps.



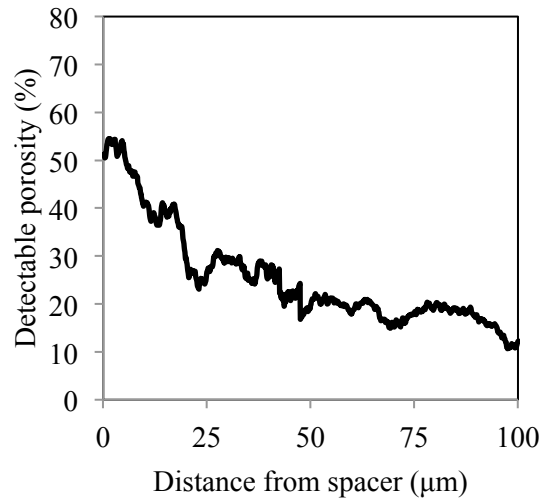
(a) Original BSE image from sample C10-28d-50°C-50: C1 (field of view: 240 x 192 μm). Image was cropped by 50 μm to isolate aggregates ITZ.



(b) EDM of paste from spacer boundary.



(c) Distance map of pores.



(d) Porosity distribution

Figure 5.10 Applying the EDM method on a concrete sample with cementitious spacer (C10-28d-50°C-50: C1) to the obtain porosity distribution from the spacer-paste interface.

5.3 Results and discussion

5.3.1 Spacer-concrete interface

The distribution of unreacted cement and porosity up to 100 μm from the spacer-concrete interface are shown in Figures 5.11 and 5.12. The results are compared with the observed distributions at the aggregate-paste interface (ITZ) and bulk paste of the control sample. Results are average of fifty frames and expressed as area percentage of the cement paste. At

pixel spacing (0.094 μm), the variation is presented as the standard error ($S.E = \sigma / \sqrt{n}$), where σ is the standard deviation and n is the number of replicates.

The porosity shows a general trend of decreasing with increasing distance from the interface. Beyond about 50 μm from the interface, the porosity for all samples becomes relatively stable and reaches the bulk paste porosity value. The results also show that the porosity at the interface increased when the conditioning regime became more severe. For example, the porosity at the plastic spacer-paste interface is around 4 times that of the bulk paste when the sample is conditioned at 20°C 55% RH prior to testing. When conditioned at 50°C, the porosity at the plastic spacer interface increased and is around 5 times that of the bulk paste (Figure 5.11a and Figure 5.12a). It is also interesting to note that the porosity at the plastic spacer-paste interface is greater than the porosity at the aggregate-paste interface by a factor of 2 when conditioned at 20°C 55% RH and by a factor of 3 when conditioned at 50°C.

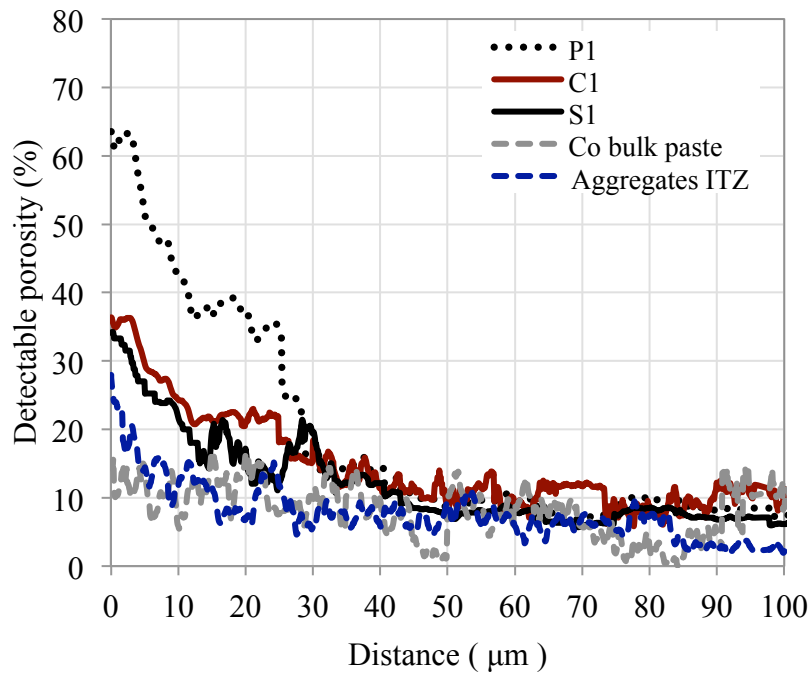
In comparison, samples with cementitious spacer conditioned at 20°C 55%RH had a porosity at spacer-paste interface around 2 times of the bulk cement paste and 1.2 times of the aggregate-paste interface. When conditioned at 50°C, the porosity at the cementitious spacer-paste interface was around 2.5 times the bulk paste and 1.5 times the aggregate-paste interface. Samples with steel spacers showed the lowest porosity at the spacer-paste interface compared to samples with plastic or cementitious spacer. The porosity at the steel spacer-paste interface was 1.5 - 1.8 times higher than the bulk paste porosity.

The anhydrous (unreacted) cement fraction increased steadily from 1% at the spacer-paste interface to around 15% at the bulk cement paste (50 μm away from the spacer boundary) for all spacer types as shown in Figure 5.11(b) and Figure 5.12(b). Samples conditioned at 50°C showed slightly higher values of unreacted cement compared to samples conditioned at 20°C 55% RH. The control sample has the highest unreacted cement content and lowest porosity compared to samples with spacers in all cases. It seems that the zone of microstructure affected by the presence of spacer extends to around 50 μm away from the spacer boundary, with respect to both anhydrous cement and detectable porosity gradients. This value is similar to the typical range of 20–50 μm reported for the aggregate-cement paste interface [Lutz et al., 1997]. The standard error range for each sample is presented in Table 5.3. Error bars are not shown on Figures 5.11-5.12 for clarity.

Table 5.3 Standard error range (+/-) at pixel spacing of (0.094μm),

Sample	Conditioning	Standard error range (+/-).	
		Porosity	Anhydrous cement
Co bulk paste	20°C 55% RH	2.06-2.46	1.88-2.01
	50°C	2.12-2.65	1.92-2.12
Aggregates ITZ	20°C 55% RH	1.98-2.36	1.88-2.73
	50°C	2.12-2.41	1.71-1.93
P1	20°C 55% RH	2.16-2.36	1.54-2.33
	50°C	2.03-2.61	1.67-2.31
C1	20°C 55% RH	2.98-3.33	1.71-2.13
	50°C	2.21-2.64	1.83-1.94
S1	20°C 55% RH	2.03-2.41	2.2-2.51
	50°C	2.36-3.12	2.12-2.29

(a)



(b)

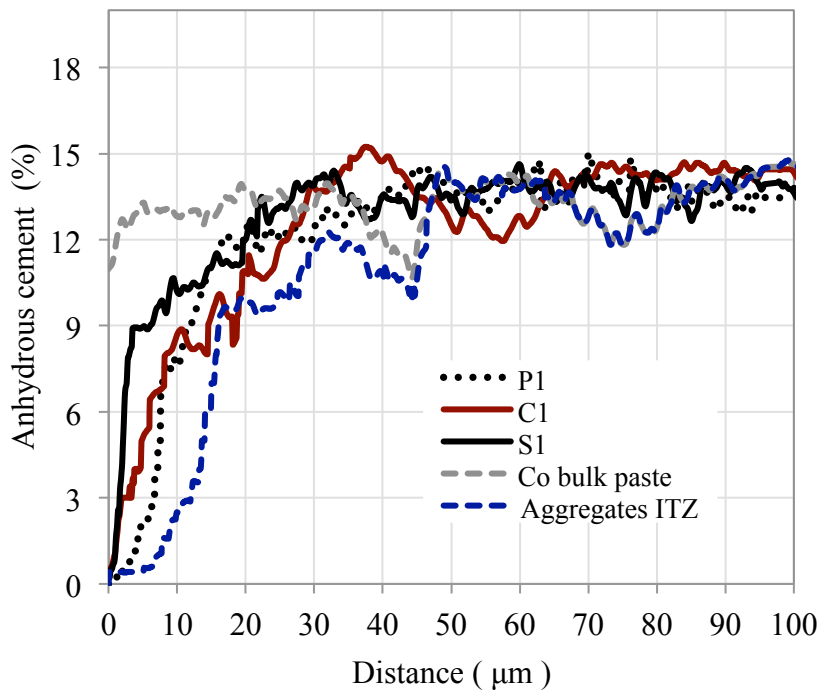
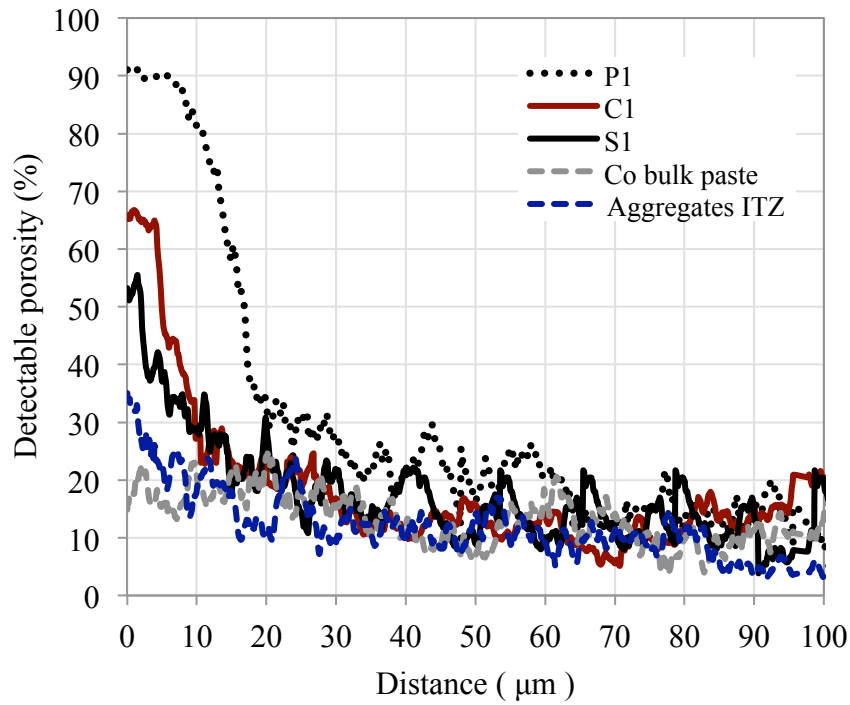


Figure 5.11 Effect of spacer type on the average distribution of porosity (a) and anhydrous cement (b) from the spacer-paste interface. Results are compared to the observed gradients at the aggregate-paste interface (ITZ) and bulk paste of the control sample. Values are the average of 50 frames. Samples were cured for 28 days and conditioned at 20°C, 55%RH.

(a)



(b)

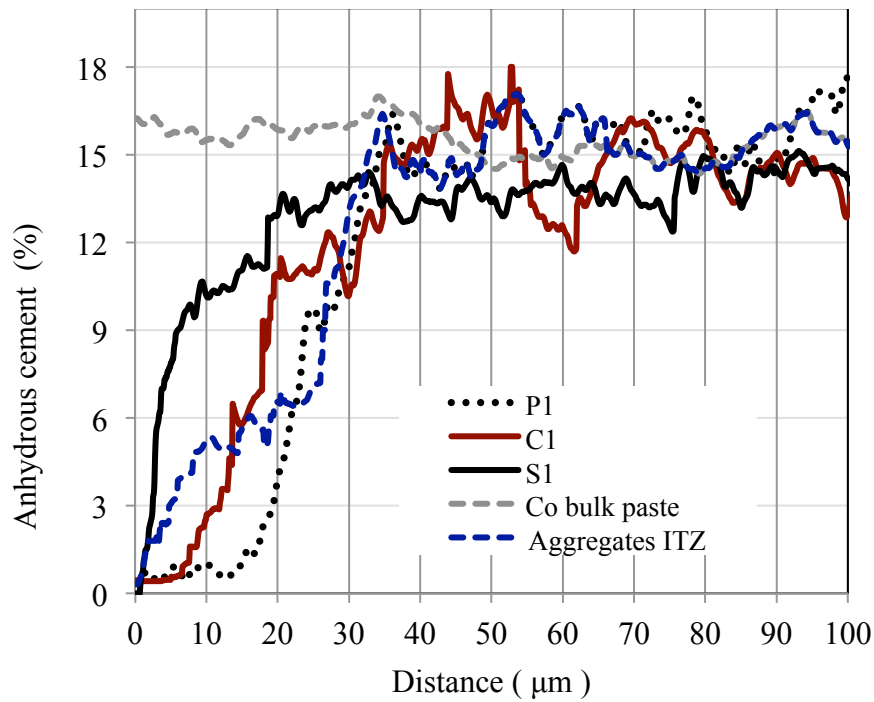


Figure 5.12 Effect of spacer type on the average distribution of porosity (a) and anhydrous cement (b) from the spacer-paste interface. Results are compared to the observed gradients at the aggregate-paste interface (ITZ) or bulk paste of the control sample. Values are the average of 50 frames. Samples were cured for 28 days and conditioned at 50°C.

For samples containing plastic spacer, the microstructure of the concrete located on the “inside” zone (i.e. nestled within the legs of the spacer) was analysed and compared to that of the “outside” zone. Different porosity and anhydrous cement gradients were observed. The zone within the plastic spacer showed higher porosity gradient compared to that outside of the spacer as presented in Figures 5.13 and 5.14. At 100 μm from plastic spacer boundary, the porosity of the paste inside the zone of plastic spacer was four times that of the bulk paste of the outside zone as shown in Figure 5.14 (a). The anhydrous cement fraction increased steadily from 0% at the boundary to around 9% at 100 μm , which is significantly lower than that of bulk paste in the “outside” zone. A similar trend was noted in the epoxy impregnation results (Section 4.6.2) for samples with different thickness and condition regimes. Furthermore, the samples appear to be adequately compacted as discussed in Section 3.2.4.

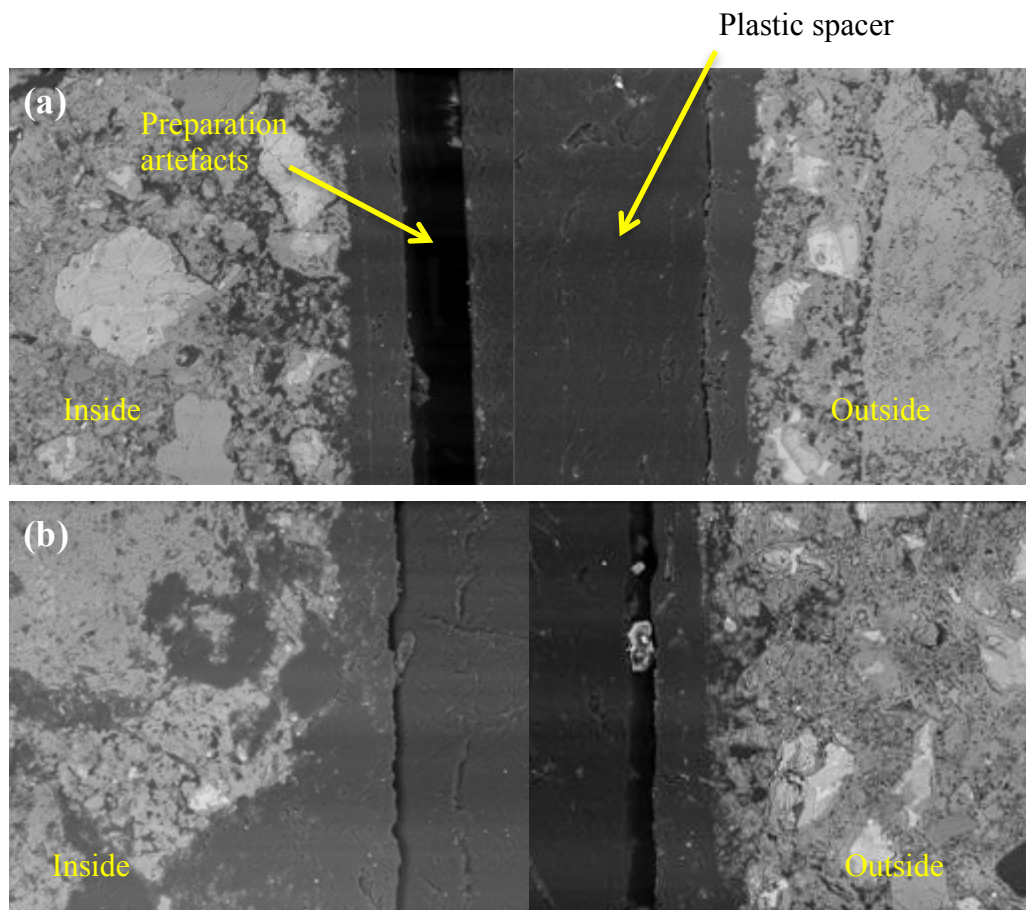
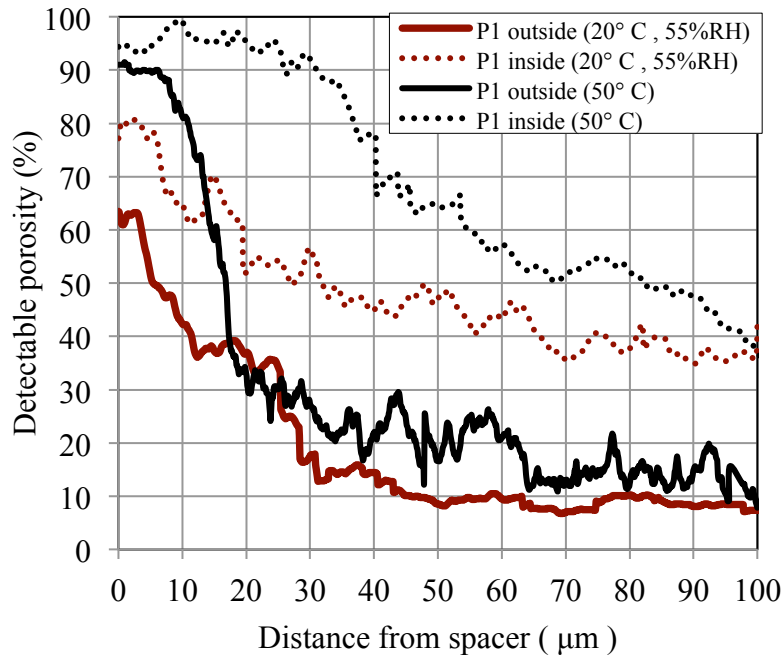


Figure 5.13 Montage images showing the paste microstructure on the inside and outside zone of the plastic spacer. Sample is (a) C10- 28d- 20°C,55% RH - 50:P1, and (b) C10- 28d- 50°C - 50:P1. (Images captured at 500x, field of view is 480 x 192 μm).

(a)



(b)

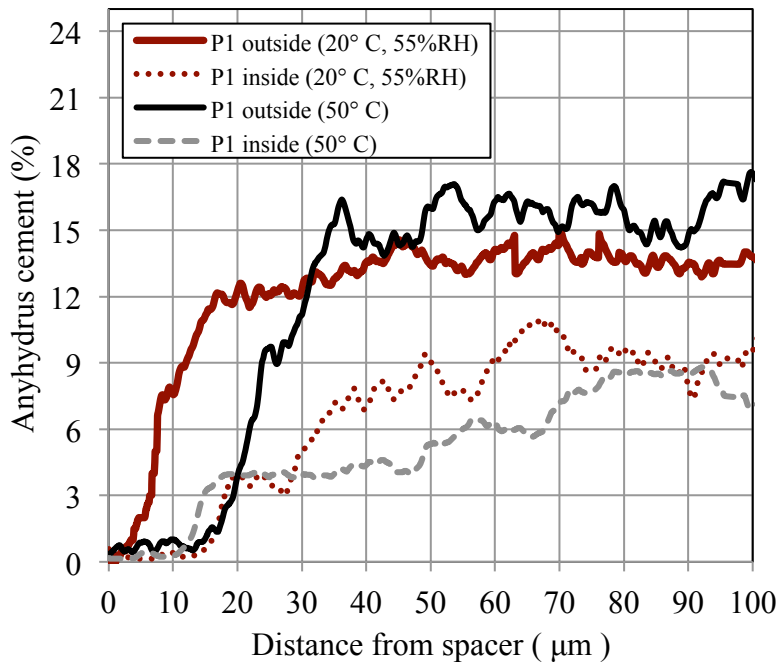


Figure 5.14 Distribution of detectable porosity (a) and anhydrous cement (b) up to 100 μm from plastic spacer-paste interface on the inside and outside zone of the plastic spacer. Values are averages of 30 frames. Samples were cured for 28 days and conditioned at 50°C.

5.3.2 Heterogeneity of the spacer-concrete interface

When all of the acquired images of the spacer-concrete interface and their individual porosity gradients were compared, it can be seen that the microstructure is indeed heterogeneous. Several types of interface characteristics were observed and examples of these are shown in Figures 5.15 to 5.22. Despite the fact that the averaged results for porosity and unreacted cement display clear trends, the individual result from each location is quite variable. For example, Figure 5.15 shows a low-magnification montage of a sample containing plastic spacer that was preconditioned at 50°C. The image shows different localised interface characteristics within a 3600 μm wide region: zones A and C showing high porosity gradient at the interface of different widths, while zone B showing a relatively dense interface next to spacer boundary followed by a high porosity gradient.

The visible bond cracks between the plastic spacer and the surrounding cement paste were formed at two stages. The first crack (adjacent to cement paste) formed during curing and conditioning periods, and occurred due to drying induce-shrinkage. This crack is impregnated with fluorescent epoxy and so is considered as part of the original pore structure that would contribute to transport processes. The second bond crack (adjacent to spacer) is not filled with epoxy and appears darker in the BSE images. This crack occurred after the epoxy impregnation stage due to relative movements between the spacer and concrete, possibly during the grinding and polishing stages. Therefore the second crack is a preparation artefact and is not as considered part of the original microstructure. The width of the first epoxy-filled cracks was highly variable as seen in Figure 5.15 and Figure 5.16, ranging from 4 μm to 58 μm . The second crack (due to preparation artefacts) is narrower, ranging from 2 μm to 33 μm . A more detailed analysis of the local porosity gradients are presented in Figure 5.16 and Figure 5.17. Figure 5.16A shows a very porous interface up to 40 μm thick that is almost five times that of the bulk paste. However, there is a drop in porosity within the first 10 μm from the spacer boundary and this is because of a thin strip of cement paste that is bonded to the spacer. Figure 5.16 B and C shows similarly porous interface, but occurring only within the first 20 μm . When conditioned at 20°C, 55%RH, a similar heterogeneous microstructure can be observed (Figure 5.17). Here, the porosity at interface is around 4 - 4.5 times of the bulk paste.

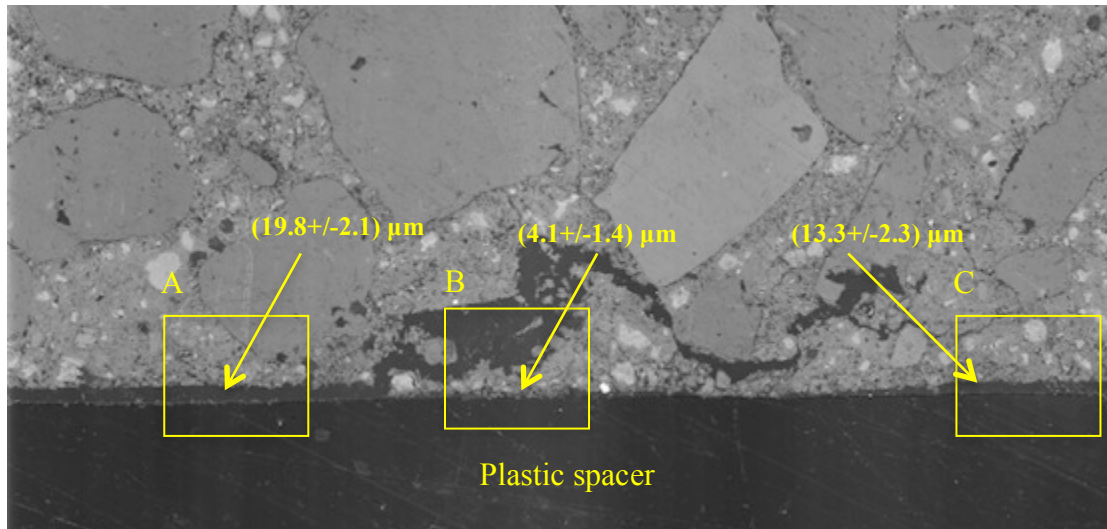


Figure 5.15 Montage image of sample with plastic spacer showing heterogeneous microstructure at the spacer-paste interface. Sample is C10-28d-50°C-50:P1. (Images captured at 100x, field of view is 3600 x 960 μ m).

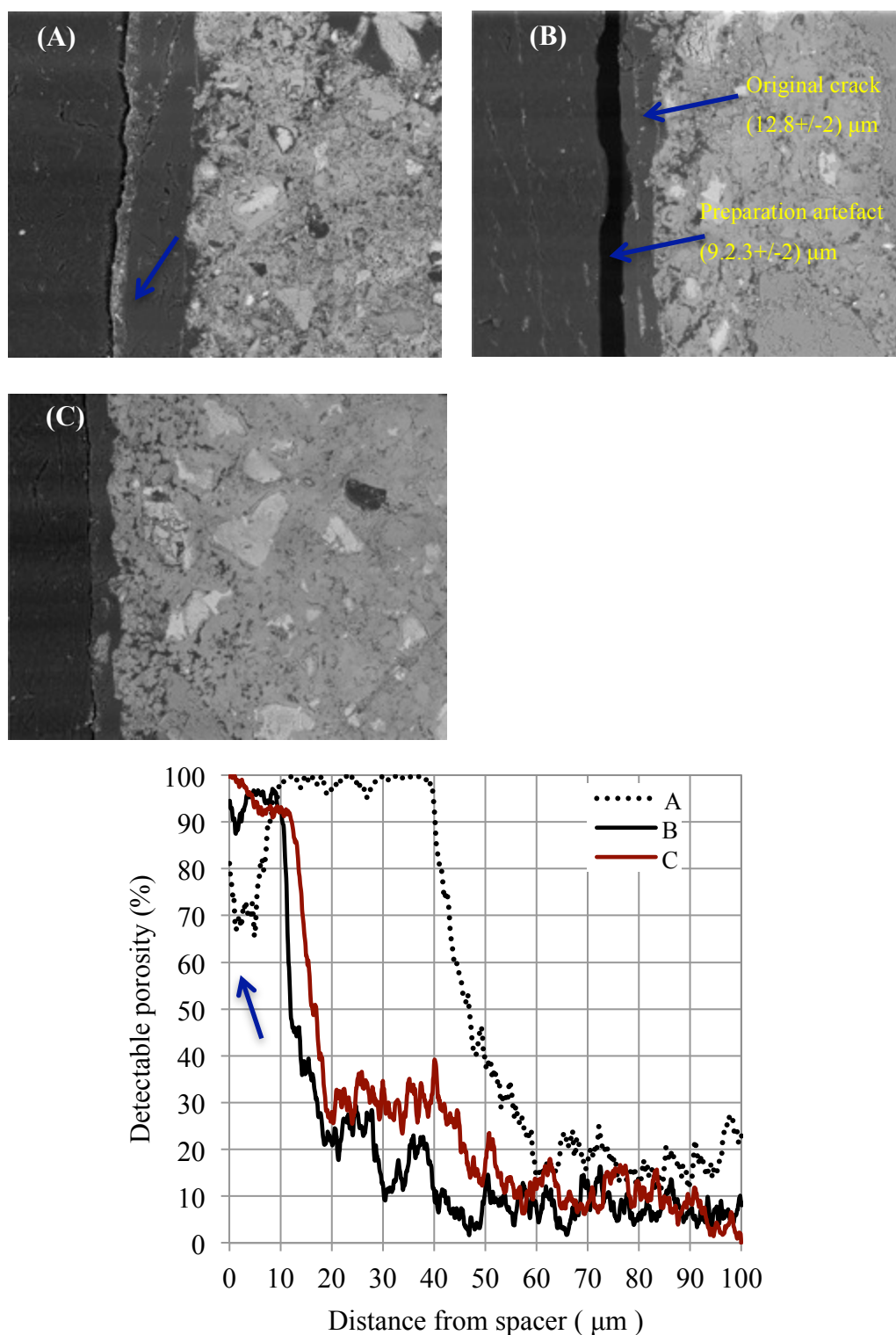


Figure 5.16 Detectable porosity distribution plots of three locations showing different interface characteristics. Sample is C10-28d-50°C-50:P1. Arrow in image (A) shows a thin strip of cement paste bonded to the spacer surface causing a drop in porosity within the first 10 μm . (Images captured at 500x, field of view is 240 x 192 μm).

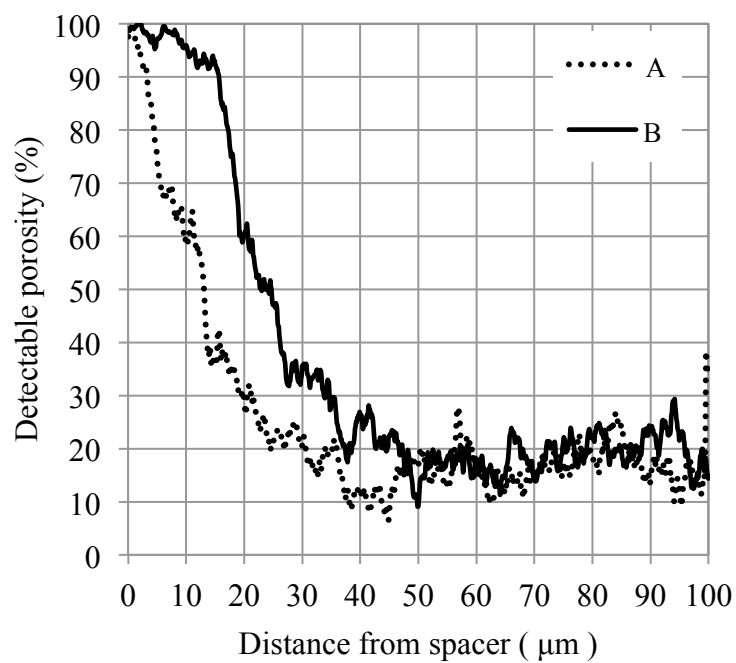
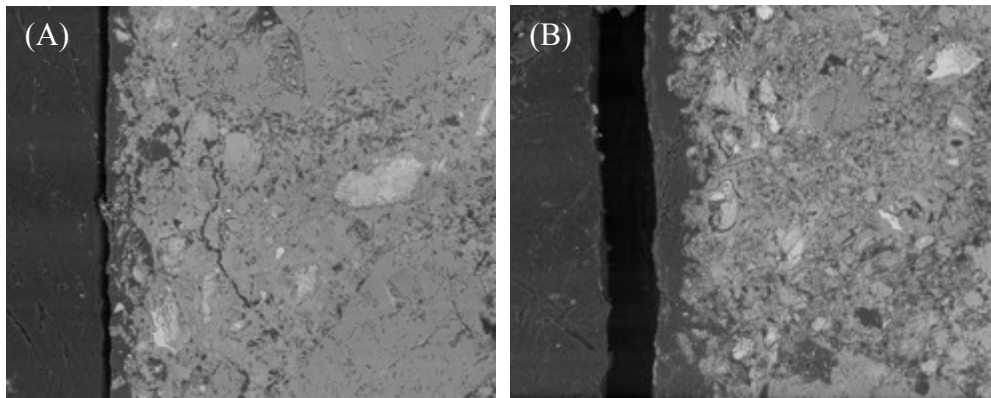


Figure 5.17 Detectable porosity distribution plots of two locations showing different interface characteristics. Sample is C10-28d-20°C, 55%RH-50:P1. (Images captured at 500x, field of view is 240 x 192μm).

Samples containing with steel wire spacers also showed variable spacer-concrete interface characteristics for each conditioning method. Some locations appear dense and contain no or insignificant amount of bond cracking at the spacer-concrete interface. These locations, for example Figure 5.18 (B, D) show a very weak porosity gradient. However, other locations such as in Figure 5.18 (A, C) show a very porous interface with a strong porosity gradient within the first 100 μm from the spacer boundary. There appears to be no significant difference between porosity gradient at top or underside of steel wire as shown in Figure 5.19.

Figures 5.20 to 5.22 show some examples of interface microstructure in samples with cementitious spacers. In these examples, the variation in the microstructure from one location to another within a short separating distance is again evident. Some locations (e.g. Figures 5.21B and 5.22B) show very dense interface with porosity of only 1.1 to 1.5 times that of the bulk paste and weak porosity gradient. Other locations are very porous and display strong gradients (e.g. Figures 5.21A and 5.22C). In some locations, a mixture of porous and dense interface can as seen such as in Figures 5.20C and 5.22A. It should be noted that Figure 5.21 (c) was at the location of a groove on the spacer surface and a similar trend of higher porosity gradient was also noted at other locations adjacent to grooves. This seems to contradict the manufacturer's assumption that the grooves would enhance spacer bond and adhesion with surrounding concrete by increasing surface area.

Figure 5.23 and Figure 5.24 show the coefficient of variation of the average porosity and anhydrous cement content plotted against distance from the spacer interface for samples conditioned at 50°C and 20°C, 55%RH. The coefficient of variation is equal to the standard deviation divided by the mean, and expressed as a percentage. This is used as an indication of the spatial variability of the measured porosity and anhydrous cement. In all cases, the coefficient of variation ranged between 50% and 150% for anhydrous cement and between 10% and 80% for detectable porosity. Higher variation was noted near the interface for some cases (e.g. Figure 5.23 b and c), but this trend was not consistent throughout. Samples with steel spacers showed relatively lower coefficient of variation compared to samples with cementitious or plastic spacers. It is also evident that conditioning regime had no significant effect on the coefficient of variation.

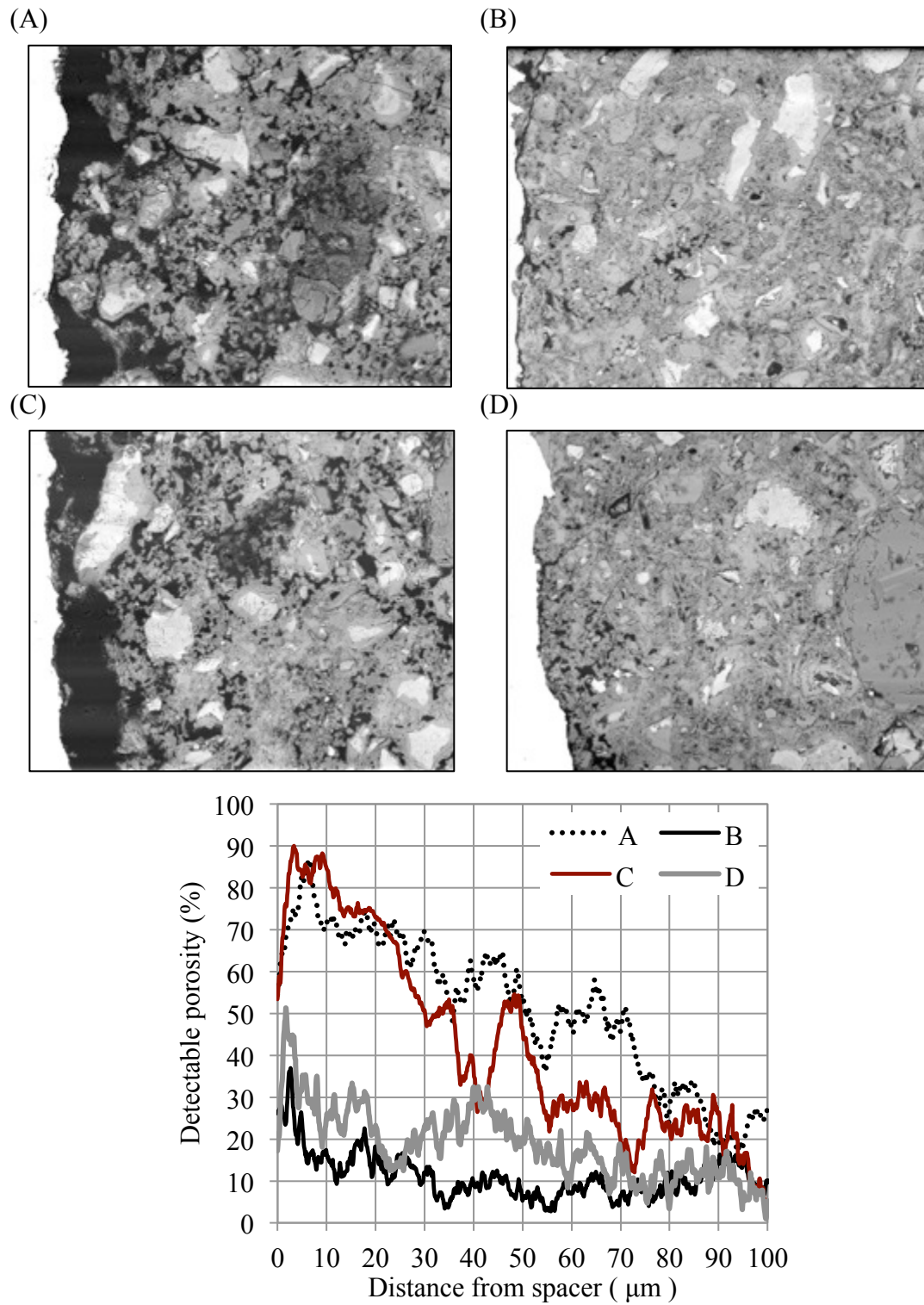


Figure 5.18 Detectable porosity distribution plots showing different interface characteristics in sample with steel spacer. Sample is C10-28d-20°C, 55%RH-50:S1 (A, B) and C10-28d-50°C-50:S1 (C, D). (Images captured at 500x, field of view is 240 x 192 μm).

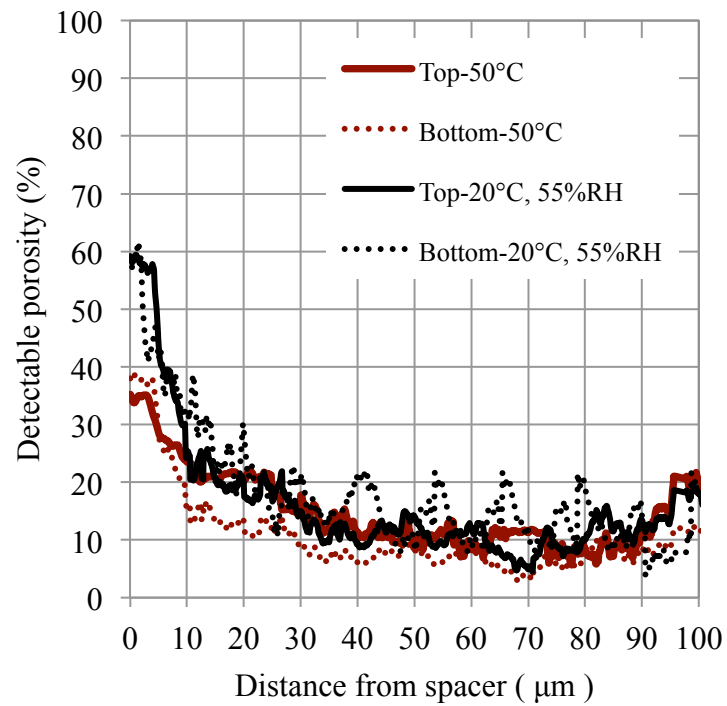


Figure 5.19 Distribution of detectable porosity up to 100 μm from steel spacer-paste interface on the top and bottom zones of the steel wire.

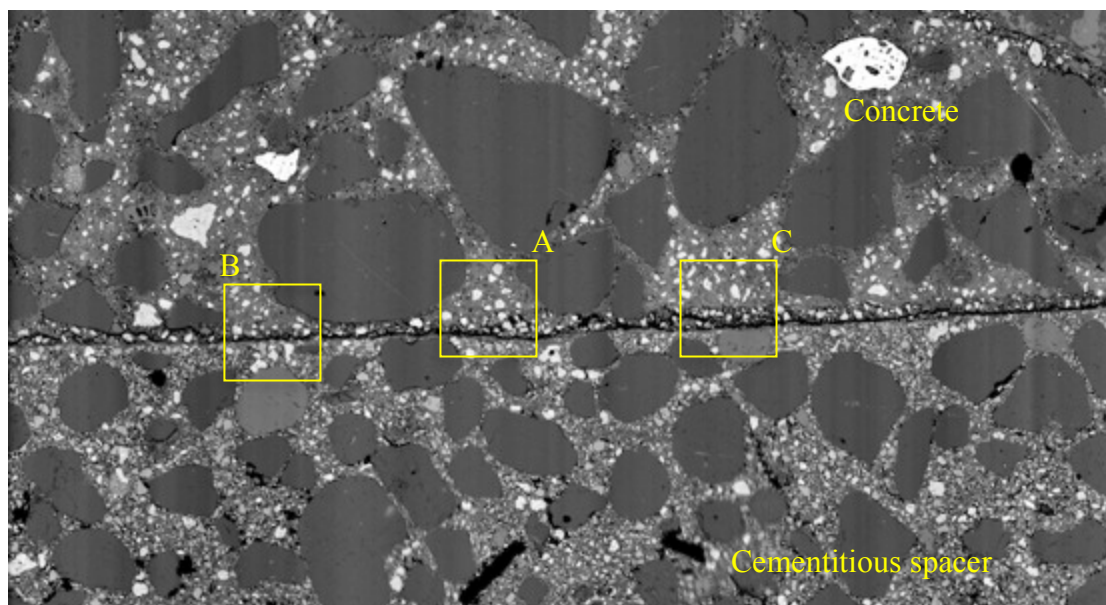
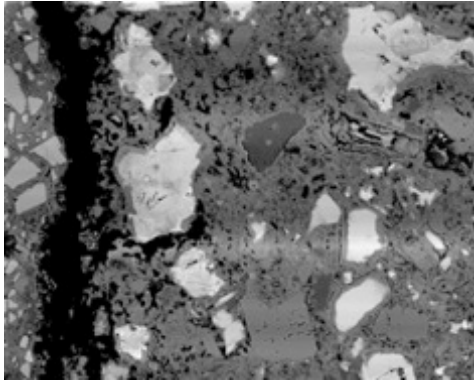
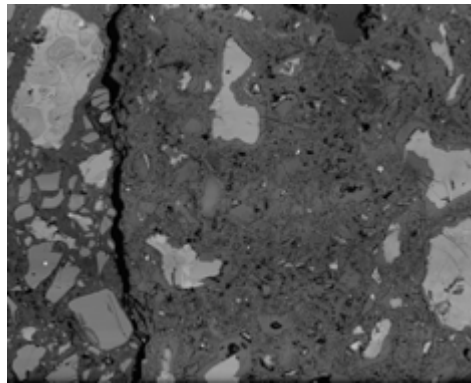


Figure 5.20 Montage image of sample with cementitious spacer showing heterogeneous microstructure at the spacer-paste interface. Sample is C10-28d- 50°C-50:C1. (Images captured at 100x, field of view is 3600 x 960 μm).

(A)



(B)



(C)

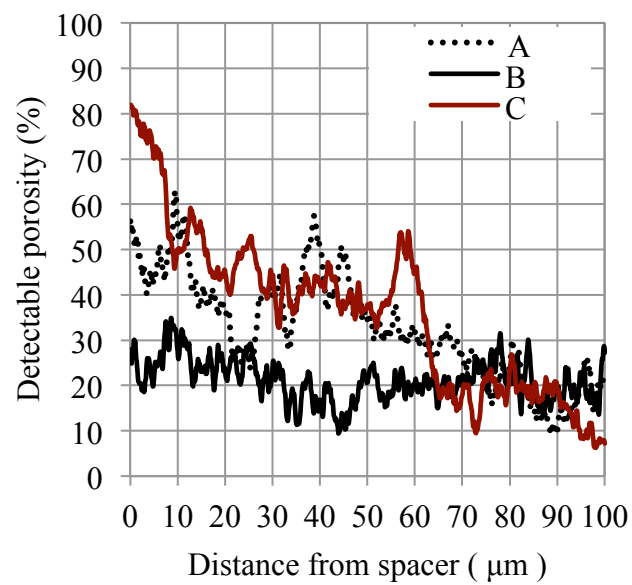
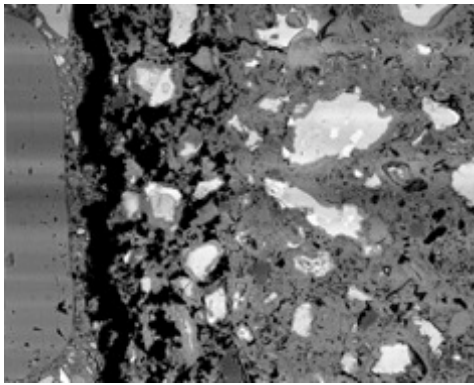
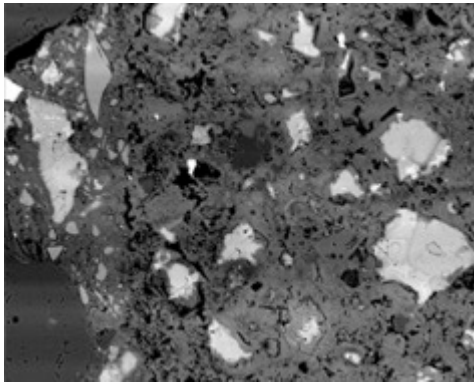
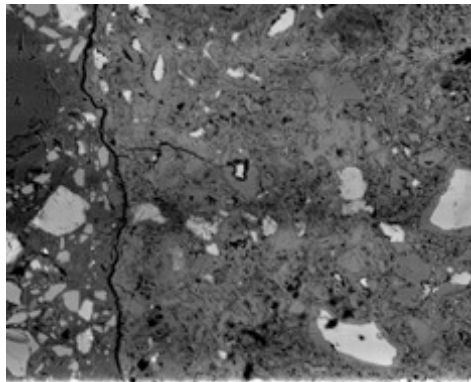


Figure 5.21 Detectable porosity distribution plots showing different interface characteristics in sample with cementitious spacer (C10-28d-50°C-50:C1). (Images captured at 500x, field of view is 240 x 192 μm).

(A)



(B)



(C)

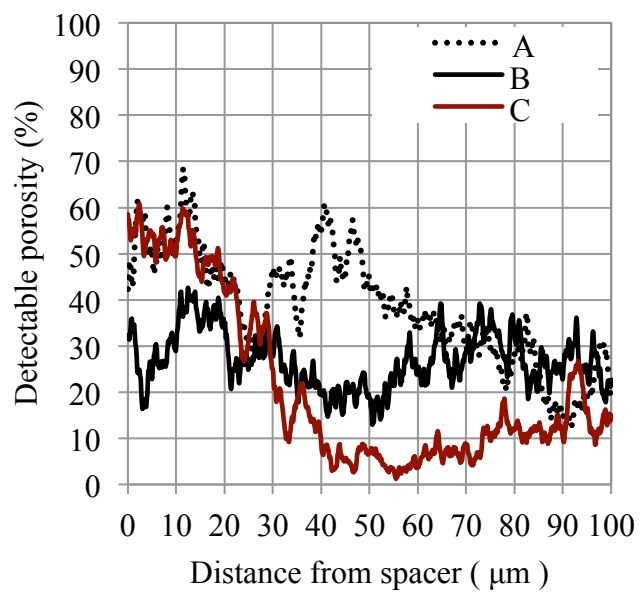
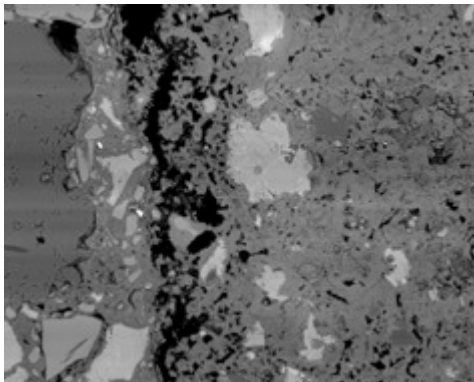


Figure 5.22 Detectable porosity distribution plots showing different interface characteristics in sample with cementitious spacer (C10-28d-20°C, 55%RH-50:C1). (Images captured at 500x, field of view is 240 x 192 μm).

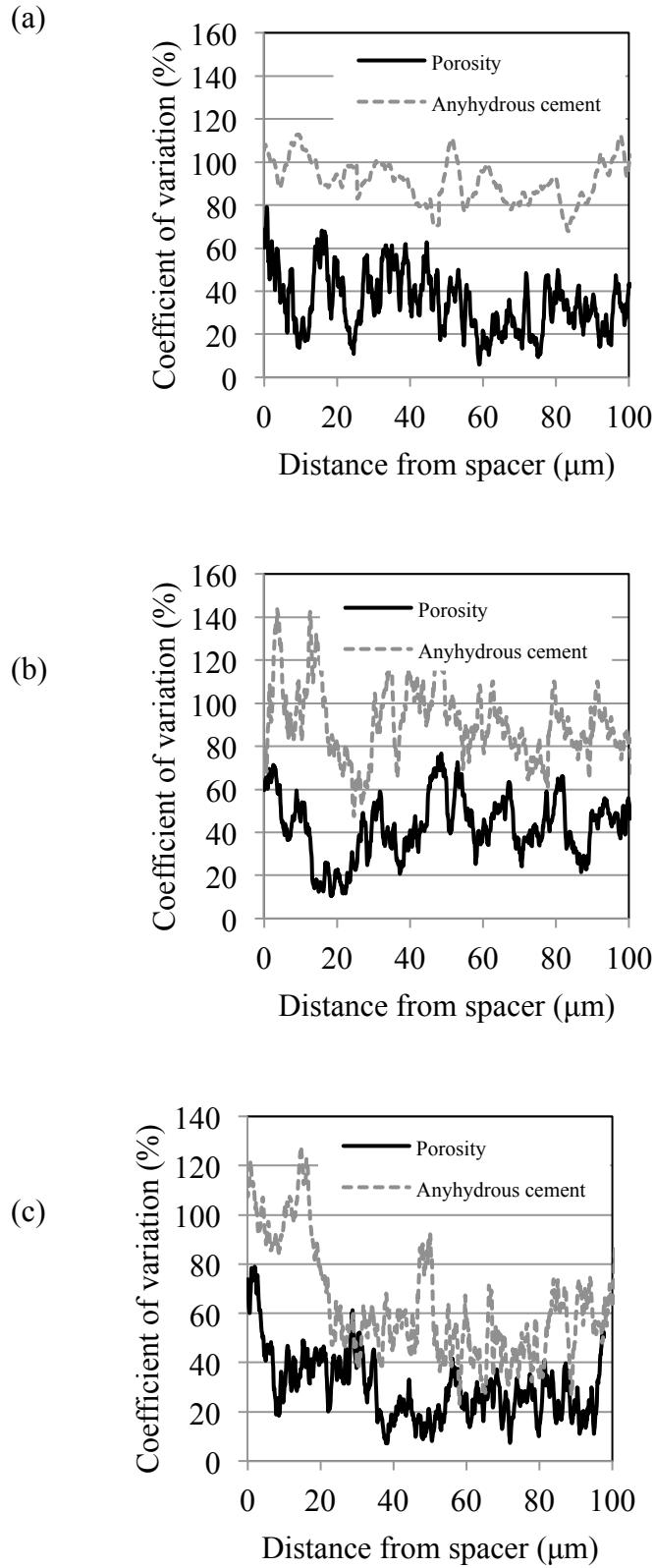


Figure 5.23 Coefficients of variation for the average detectable porosity and unreacted cement plotted against distance from spacer surface for (a) C10-28d-50°C-50:P1; (b) C10-28d-50°C-50:C1 and (c) C10-28d-50°C-50:S1.

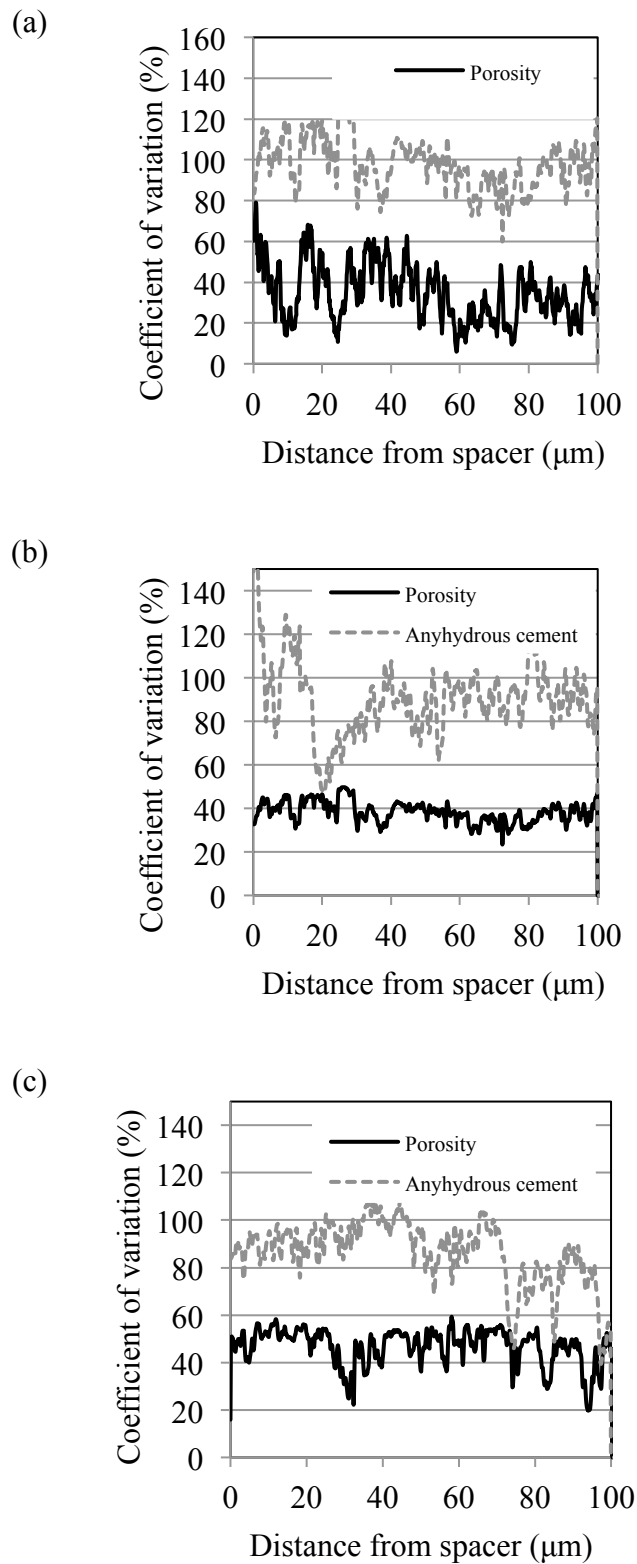


Figure 5.24 Coefficients of variation for the average detectable porosity and unreacted cement plotted against distance from spacer surface for (a) C10-28d-20°C, 55%RH-50:P1; (b) C10-28d-20°C, 55%RH-50:C1 and (c) C10-28d-20°C, 55%RH-50:S1.

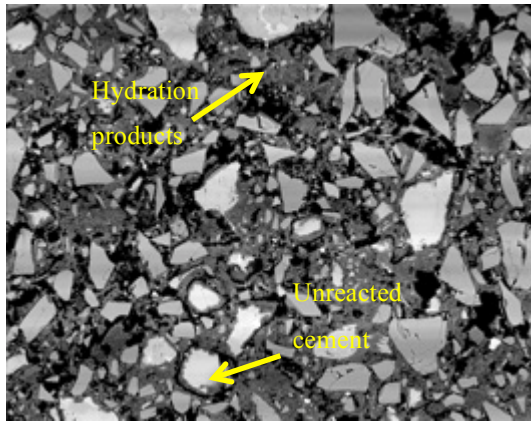
5.3.3 Microstructure of cementitious spacer

Figure 5.23 presents BSE images showing the microstructure of the cementitious spacer used in this study. The main features that can be seen include unreacted slag, unreacted cement, sand particles, polypropylene fibres, hydration products and pores. The sand particles are typically smaller than 2 mm, while the polypropylene fibres are typically 100-150 μm in length. These observations are in line with the composition reported by the cementitious spacer manufacturer as given in Table 3.2.

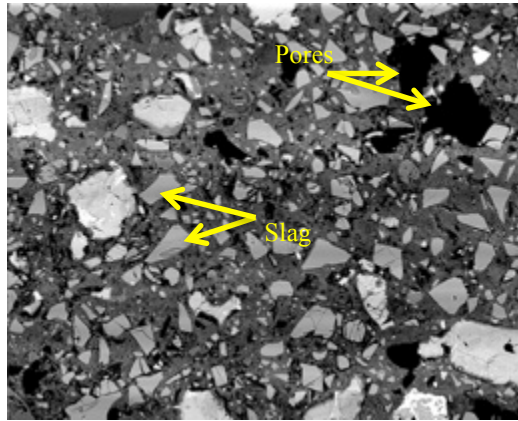
Image analysis was carried out to measure the porosity of the cementitious spacer after conditioning at 20°C, 55%RH and 50°C. The results were compared against the bulk cement paste porosity of the respective control sample (C10-28d). Thirty BSE images were captured within the cementitious spacer and the bulk cement paste. The porosity was then segmented according to the procedure described in Chapter 5.2.4 and expressed as percentage of the cement paste. The average detectable porosity is presented in Figure 5.24 where the variation is presented as the standard error ($S.E = \sigma / \sqrt{n}$), where σ is the standard deviation and n is the number of frames. It is noted that the variation within the frames (standard error) is relatively small compared to the difference in porosity between the bulk paste and cementitious spacers.

The results show that the porosity of the cementitious spacer is lower than bulk cement paste of the control sample by about 20% regardless of the conditioning method. This shows that the cementitious spacer is denser than the surrounding concrete. This is not surprising considering that the water/cement (w/c) ratio of the cementitious spacer (0.35) was lower than that of the concrete prepared in this study (0.4). Furthermore, the cementitious spacer contained a large amount of ground granulated blastfurnace slag, which would promote densification of the pore structure via its hydration and pozzolanic reaction.

(a)



(b)



(c)

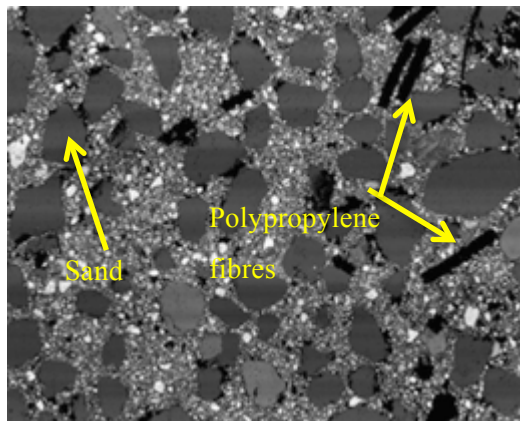


Figure 5.25 Microstructure of the cementitious spacer showing unreacted slag, unreacted cement, sand, polypropylene fibre, hydration products and pores. (Images (a,b) captured at 500x, field of view is 240 x 192 μ m. Image (c) captured at 100x, field of view is 1200 x 960 μ m).

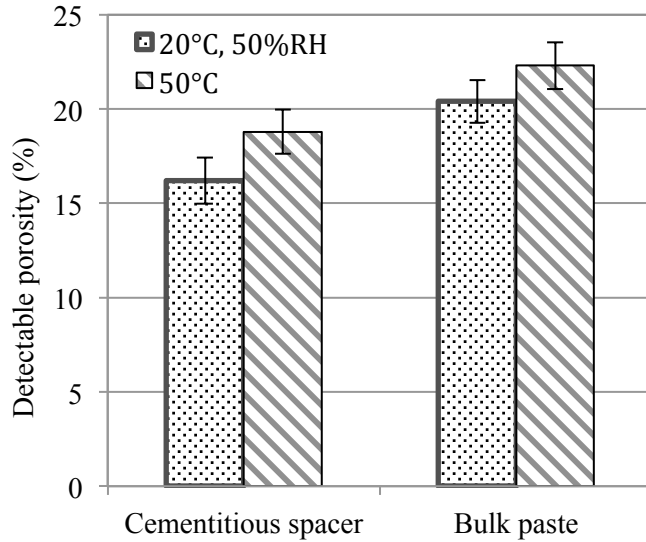


Figure 5.26 Average detectable porosity of the cementitious spacer compared to the bulk cement paste of the control samples. Sample is C10-28d-20°C, 55%RH-50:C1 and C10-28d-50°C-50:C1.

5.4 Discussion

5.4.1 Spacer interface and microstructure

The results presented in this chapter clearly show that the inclusion of spacer disturbs the concrete microstructure at the vicinity of the spacer. Samples containing plastic spacers consistently had the highest porosity gradient along its interface followed by samples with cementitious spacers, and then steel spacers. The porosity gradient was also influenced by the conditioning method, a more severe drying produced higher porosity and stronger gradients at the interface. The anhydrous cement distribution showed a similar characteristic of low cement content at the spacer-concrete interface, increasing steadily to the bulk paste value at about 50 μm away regardless of spacer type and conditioning regime.

The increased porosity near the spacer-concrete interface can be explained by a higher initial water content due to micro bleeding along spacer surface. Furthermore, debonding occurs at the interface when the sample is subjected to drying and this increase in severity with the level of drying. The deficiency in cement content at the spacer-concrete interface is due to difficulties in packing of the cement particles close to the spacer surface. These particle

packing and bleeding effects are similar to those causing the microstructural gradients observed in the aggregate-paste ITZ [Ollivier et al., 1995; Scrivener et al., 1988; Wong and Buenfeld, 2006a; Wong et al., 2011].

The zone around the spacer with affected microstructure extends to around 50 μm away from the spacer boundary, with respect to both anhydrous cement and detectable porosity gradients. This value is similar to the typical range of 20–50 μm reported for the aggregate-cement paste interface [Lutz et al., 1997]. It should be noted that there have been no previous studies on the effect of spacers on the microstructure of concrete. However, the findings of this study bear similarities to the well-researched effects aggregates, embedded steel reinforcing bars and air voids on the microstructure of concrete.

For example, the measured porosity and anhydrous cement gradients from the steel spacer boundary are within the range reported by [Horne et al., 2007] for embedded steel reinforcement. However, [Horne et al., 2007] reported higher porosity under horizontal bar than above due to micro bleeding on bar surface, which have not been observed in this study. This could be attributed to the fact that the spacer wire was inclined and its diameter was much smaller than that of the ribbed steel bar.

The trend of very porous ITZ, with a strong porosity gradient and detectable porosity at the interface that is two to five times that of the bulk paste, is consistent to the results from other studies reported for aggregate ITZ [Scrivener et al., 2004; Wong and Buenfeld, 2006a; Wong et al., 2013; Wong et al., 2011]. Also the microstructural gradient are similar to those of air voids interface with cement paste reported by [Rashed and Williamson, 1991; Wong et al., 2011] except for lack of calcium hydroxide deposits at the void interface with cement paste, probably because more bleed water is trapped along spacer surface compared to air voids or aggregates. It should be pointed out that no investigation was carried out to quantify bleed water along spacer surface as it was out of the scope of this study.

The increased porosity of concrete enclosed within plastic spacer compared to concrete far from the spacer might be caused by bleeding, segregation or poor compaction due to restrictions caused by the openings of the plastic spacer. However, the workability of the fresh concrete should be sufficiently high to ease the flow of concrete inside spacer and the size of opening was checked to be larger than the aggregate MSA. Furthermore, no significant segregation was observed and the measured concrete density was in accordance with theoretical concrete density. The poor packing of cement grains within the enclosed four sides of plastic spacer might possibly explain this behaviour.

The increased porosity at the grooves of cementitious spacer might be caused by the accumulation of bleed water trapped beneath horizontal surface of the groove leading to higher w/c ratio at interface. The observed drop in porosity at less than 10 μm from the spacer boundary for different spacers was due to the presence of a thin layer of hydration products bonded along surface of spacer. A similar effect on the porosity gradient of aggregate ITZ was also reported by [Diamond and Huang, 2001; Wong and Buenfeld, 2006a].

5.4.2 Role of spacer interface on transport properties

Studies by [Abyaneh et al., 2013; Buenfeld and Okundi, 1998; Wong et al., 2009] have reported that increasing the aggregate-paste ITZ fraction beyond its percolation limit should cause an increase in the bulk transport properties of concrete. However, this is balanced by the reduction in the cement paste content and increase in cement paste tortuosity and bulk paste impenetrability. The overall effect of increasing the aggregate-paste ITZ, as shown in experimental and numerical studies, is a reduction in the bulk transport properties of concrete. However, this effect of the ITZ is clearly different to that of the spacer-concrete interface despite both having similar microstructure characteristics in terms of porosity and unreacted cement gradients.

Spacers are either impermeable (plastic and steel spacers) or have lower porosity (cementitious spacers) than the cement paste around it. As such, the inclusion of spacers should act as obstacles to transport by reducing the cross-sectional area available for flow, i.e. the cement paste content. Therefore, the substantial increase in transport properties recorded for samples with spacers can be attributed to the porous interface zone between the spacer and concrete. This effect is different to that of the aggregate-paste ITZ because the spacer interface forms a continuous porous link that spans the entire depth of the sample, providing an easy path for mass/ionic transport to occur through the sample. The porosity along spacer interface was significantly higher than that of the bulk cement paste by a factor of 1.5 to 5 depending on the spacer type and conditioning method. The effect of spacer type on transport properties was matched by its porosity gradient, i.e. samples with plastic spacer had the highest transport coefficients and the highest porosity gradient from interface; followed by cementitious and steel spacers.

5.5 Conclusions

Scanning electron microscopy in the backscattered electron mode (BSE) and image analysis using Euclidean Distance Mapping [Edmond] was applied to investigate microstructural

gradients at the interface of plastic, cementitious and steel spacers with surrounding concrete. The microstructure of the spacer-paste interface indicated significantly lower cement content and higher porosity compared to the 'bulk paste' farther away from the interface. This characteristic of the microstructure is similar to other interfaces such as the aggregate-paste interfacial transition zone. The porosity near the spacer interface and within the plastic spacer is about 1.5 to 5 times that of the bulk paste, and the width of the zone of disturbed microstructure is around 50 μm from the spacer boundary. Spacers disrupt the packing of cement grains and increase the local w/c ratio and heterogeneity of the paste microstructure. Although the spacer-concrete interface can be characterised by a strong average gradient in anhydrous cement and detectable porosity, it is highly variable from location to location. The substantial increase in transport properties for samples with spacers is attributed to the porous interface zone between the spacer and concrete

Chapter 6 Influence of spacers on chloride-induced corrosion

This chapter investigates the influence of different types of spacers on the transport of chloride ions through concrete and the initiation of chloride-induced reinforcement corrosion. Furthermore, the influence of spacer on the service-life of reinforced concrete structures will be investigated on the basis of estimating the time to corrosion initiation. Cylindrical concrete samples and reinforced concrete beams were prepared with 50 mm high plastic and cementitious spacers, and maximum aggregate size (MSA) of 10 and 20 mm. Samples were cured for 28 days in a fog room, then conditioned to designated periods at 20°C 55% RH or 40°C oven drying prior to exposure to chloride solution for various periods of time. The ingress of chloride, particularly near the interface between spacer and concrete matrix was studied using micro X-ray fluorescence spectrometer (μ XRF). Concrete samples containing plastic spacers consistently gave the least resistance to chloride transport, followed by samples with cementitious spacers. The control samples (without spacers) had the highest resistance to chloride transport in all cases. Modelling suggests that the inclusion of spacer accelerates the time to reach the chloride threshold level for corrosion initiation and therefore reduces the residual service life of concrete structures.

6.1 Introduction

It is well known that chloride ion penetration plays a major role in causing premature deterioration of concrete structures in the form of chloride-induced corrosion. Volumes have been written on the effect of chloride ingress on reinforcement corrosion, durability and service life of concrete structures. Hence, measuring the rate of chloride ion ingress into concrete and understanding the factors that influence it are of great interest.

Corrosion of embedded reinforcing steel is one of the most common forms of damage in reinforced concrete costing billions of dollars a year for repair and rehabilitation [Smith and Virmani, 2000]. Corrosion of steel causes two major types of damage in structures. First, the products of corrosion (i.e., the rust) occupy a volume several times larger than the original steel. The resulting expansive stresses from corrosion cause cracking and eventual spalling or delamination of the concrete cover. Second, the progress of corrosion reduces the effective cross-sectional area of reinforcing steel, which results in a dramatic reduction in load-carrying capacity of the structural system. There are two common causes of reinforcement

corrosion in concrete, carbonation-induced and chloride-induced. Chloride-induced corrosion will be investigated in this study.

Chloride ion transport occurs through pores, cracks and other large voids that are orientated such to produce a continuous network through the concrete. The rate of any transport processes will depend on the volume fraction, tortuosity and connectivity of the pore structure [Glass and Buenfeld, 2000]. The concrete cover to embedded reinforcement provides protection against corrosion in two ways. Firstly, the concrete alkalinity provides an environment that promotes passivity and non-corroding condition of the iron oxide layer on the reinforcing steel surface. Secondly, the cover provides a physical outer shield separating the reinforcement from exterior agents that causes corrosion.

The effectiveness of the concrete cover to protect against corrosion is dependent on its thickness and concrete quality. The presence of spacers may also be an important factor because it disrupts the microstructure (Chapter 5) and facilitates ingress of aggressive species. This can potentially accelerate corrosion because spacers provide a direct access to embedded reinforcement. However, the significance of this has not been investigated before.

6.2 Sample preparation

Table 6.1 summarises the overall sample preparation programme. A brief description of the materials, mix proportions, sample conditioning, chloride exposure, chloride penetration analysis and imaging technique is presented below.

6.2.1 Samples

Two concrete mixes with w/c 0.4 and total aggregate volume fraction of 70% were prepared according to the proportions given in Table 3.5. The main variable in the mix design was the maximum size of aggregate (MSA) of 10 and 20 mm. Properties of the spacers; cement and aggregates are available in Sections 3.1 and 3.2.

Cylindrical samples (Series I, II & III) with 100 mm diameter and thickness of 50 mm were prepared for chloride penetrating testing. Full description of the sample preparation and setup are given in Section 3.2.3. The samples were then cured in a fog room (20°C, 100% RH) for 28 days. Two replicates were prepared for each sample.

Reinforced concrete beams (Series IV & V) of 100×100×200 mm were prepared for chloride-induced corrosion testing. Each beam contained a single 10 mm diameter high yield reinforcing steel bar placed on either a 50 mm cementitious or plastic spacer at mid-length. Ends of the rebar were coated to prevent corrosion. Details of the beam preparation and end coating are given in Section 3.2.3. Control beam samples were also be prepared with the same cover depth, but without spacer. The samples were then cured in a fog room (20°C, 100% RH) for 28 days. Two replicates were prepared for each sample.

The chloride exposure time selected for series II and III were 40, 60 and 90 days, which are similar to those used in previous studies [Hong and Hooton, 1999;Hooton et al., 1997;Stanish et al., 2001]. Series I samples were exposed for 1 day to investigate the effect of chloride penetration by absorption only. Exposure time is similar to the time required for full saturation of sorptivity testing samples in Section 4.3.3. Once samples reach saturation; chlorides penetrate concrete sample by diffusion mechanism.

Table 6.1 Experimental programme

Series	Sample	MSA (mm)	Test	Conditioning	Chloride exposure (day)
I	100Φ x 50 mm cylinder	10	Chloride penetration	20°C 55%RH – 120 days 40°C - 90 days	1
II	100Φ x 50 mm cylinder	10*, 20	Chloride penetration	20°C 55%RH - 120 days 40°C - 90 days	40, 90
III	100Φ x 50 mm cylinder	10*, 20	Chloride penetration	20°C 55%RH - 28 days 40°C - 28 days	60, 90
IV**	100 x 100 x 200 mm RC beam	10, 20	Corrosion via capillary rise	40°C - 90 days	190, 800
V**	100 x 100 x 200 mm RC beam	10, 20	Corrosion via cyclic wetting and drying	-	200, 740

*Samples marked with * will be used for service life modelling, samples marked with ** will*

be used for chloride-induced corrosion.

6.2.2 Conditioning regimes

For the cylindrical samples (Series I, II & III), two conditioning regimes were used to produce samples with different moisture states prior to chloride exposure so that the influence of spacers can be examined under different environmental conditions. The first regime is a gentle technique of drying at 20°C, 55% RH for designated periods. Saturated $\text{Mg}(\text{NO}_3)_2$ solution was used to produce the targeted RH. The second regime is drying at a higher temperature of 40°C for designated periods to replicate hot weather condition. Beam samples for capillary rise (Series IV) were dried in an oven at 40°C until a constant weight is achieved prior to chloride exposure. Beam samples were also exposed to wetting/drying cycles in chloride solution (Series V) immediately after curing without any pre-conditioning. Drying was carried out either in an enclosed chamber at room temperature (20°C) or in a 40°C oven. Both contained fans to generate circulating air and soda lime to minimise carbonation. Samples were assumed to have reached equilibrium when the mass loss was no more than 0.01% per day. Samples dried at 40 °C were cooled to room temperature in a vacuum desiccator for 24 h prior to chloride exposure to prevent moisture from re-entering the samples during cooling. Checks by weighing found negligible mass increase.

Samples in series III were dried for 28 days, similar to salt ponding test AASHTO T259 described by [Stanish et al., 2001]. Series I and II samples were conditioned for longer period (i.e. to equilibrium) to investigate the effect of extended drying on chloride penetration. The longer drying method replicates the time of which newly built concrete structures are naturally drying prior to use and exposure to chlorides.

6.3 Chloride penetration and inducing corrosion

Capillary rise and wetting and drying cycles induced chlorides into concrete beams.

6.3.1 Chloride penetration

Transport of chloride in concrete occurs via a number of mechanisms. These include diffusion under a concentration gradient, absorption, permeation and wick action. [Nilsson and Ollivier, 1995a]. In this chapter chloride transport via absorption and diffusion will be

investigated. When non-saturated concrete is exposed to salt solution, chloride ions rapidly ingress concrete due to transport with water through capillary suction [Nilsson and Ollivier, 1995b]. However, binding of chloride ions delays the penetration of chloride relative to water [Volkwein, 1993]. Chloride ions can be chemically and physically bound in concrete. Chemically, chlorides bind with the products of cement hydration while physical binding generally takes place at the pore walls.

The test setup for chloride penetration is illustrated in Figure 6.1. After predetermined curing and conditioning, two layers of adhesive tape were used to seal the curved side of samples to generate unidirectional chloride penetration. Samples were then placed in a shallow tray containing sodium chloride (3% by mass) solution for designated time. The solution level was about 5 mm above the lower surface of the sample. The tray was covered all time to minimize evaporation. At the end of the exposure period, the samples were sectioned and analysed with μ XRF (Section 6.5.2) to determine the concentration distribution of chlorides.

Chlorides in this setup penetrate concrete via two main mechanisms. The first is absorption since the samples were pre-conditioned prior to chloride solution exposure (Refer to Table 6.1 for drying methods and duration). Once the sample is saturated which occurs within a day, chlorides will penetrate concrete by a diffusion mechanism. This occurs due to concentration gradient and chlorides are driven from the zone of higher concentration toward the zone of lower concentration. Fick's second law of diffusion describes this process and allows the calculation of the non-steady state diffusion coefficient according to Equation 6-1.

$$\frac{C(x,t)}{C_s} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{4D_{\text{eff}}t}}\right) \quad \text{Eq. (6-1)}$$

Where:

$C(x, t)$ = Concentration of chlorides at a distance x from the concrete surface at time t

C_s = Initial concentration of chlorides at the surface

erf = Error function

x = Depth (mm)

D_{eff} = Non-steady state diffusion coefficient (m^2/s)

t = Time (s)

The chloride concentration gradient measured from μ XRF was fitted to Eq. 6.1. A Microsoft

Excel Solver function was then used to find the best-fit values for C_s and D_{eff} that minimises the sum of the squares of the residuals.

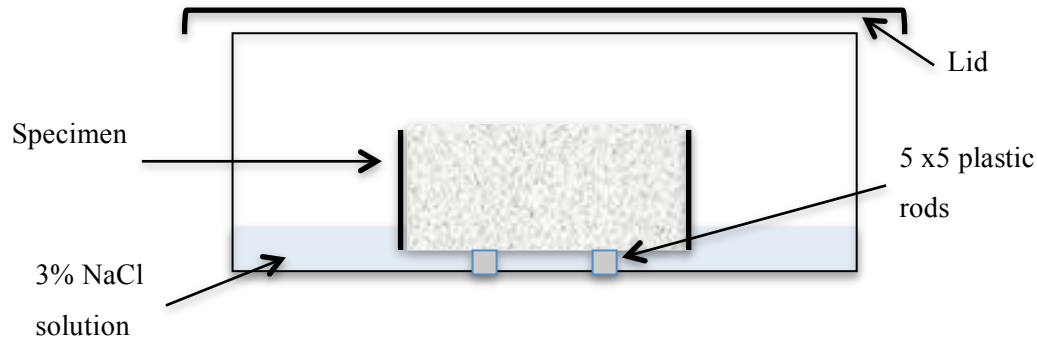


Figure 6.1 Chloride penetration test setup.

6.3.2 Inducing corrosion by exposure to capillary rise

Beam samples from Series IV were placed in a tray containing shallow sodium chloride (3% by mass NaCl) solution for up to 800 days to induce reinforcement corrosion. The solution level is about 5 mm above the lower surface of the sample. The tray was covered to minimise evaporation. Samples were sealed from all sides excluding the side immersed in water to generate unidirectional flow of chloride, which is a more realistic approximation to the way chloride ions penetrate structures in service. Two layers of waterproof adhesive tape were used to seal the samples. Tape strips were overlapped to prevent leakage along the sides. The test setup is shown in Figure 6.2. At the end of the exposure period, the beam samples were split in half to expose reinforcing bar and spacer for visual inspection of corrosion products.

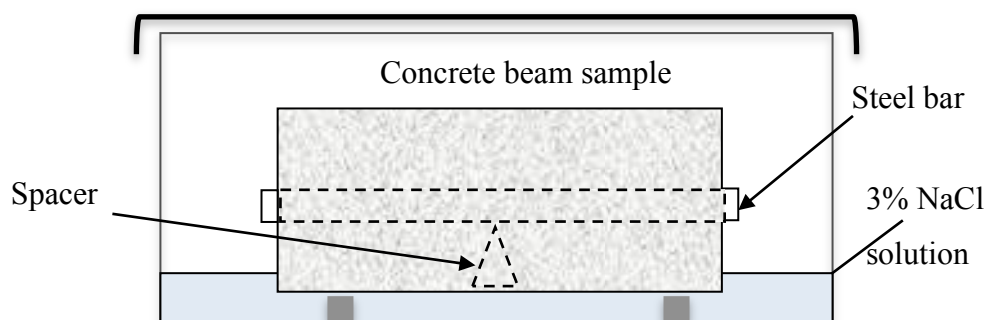


Figure 6.2 Capillary rise test setup for inducing corrosion on beam samples.

6.3.3 Inducing corrosion by exposure to wetting/drying cycles

It is common that reinforced concrete structures exposed to chlorides experience cyclic wetting and drying. Examples include marine structures, particularly in the splash and tidal zones, parking garages and highway structures exposed to deicing salts. Cyclic wetting and drying can speed the rate of chloride penetration because drying increases the concentration of chloride ions due to water evaporation. Subsequently during the wetting phase, chlorides are rapidly absorbed into the partially saturated concrete via capillary suction. Once the chloride concentration at the depth of the embedded reinforcement reaches a critical threshold level, corrosion initiates and continues as long as there is availability of oxygen and water.

After 28 days of curing, the concrete beam samples from Series V were immersed in a 3% by mass sodium chloride solution to about 5 mm above the top surface of the sample for 4 days. The tray was covered to minimise evaporation. Subsequently, the samples were dried for 3 days in ambient air (20°C, 45% RH) as shown in the schematic setup in Figure 6.2. This wetting and drying cycle was repeated until corrosion-induced cracking occurs. Details of the beam sample preparation and end coating are provided in Section 3.2.3.

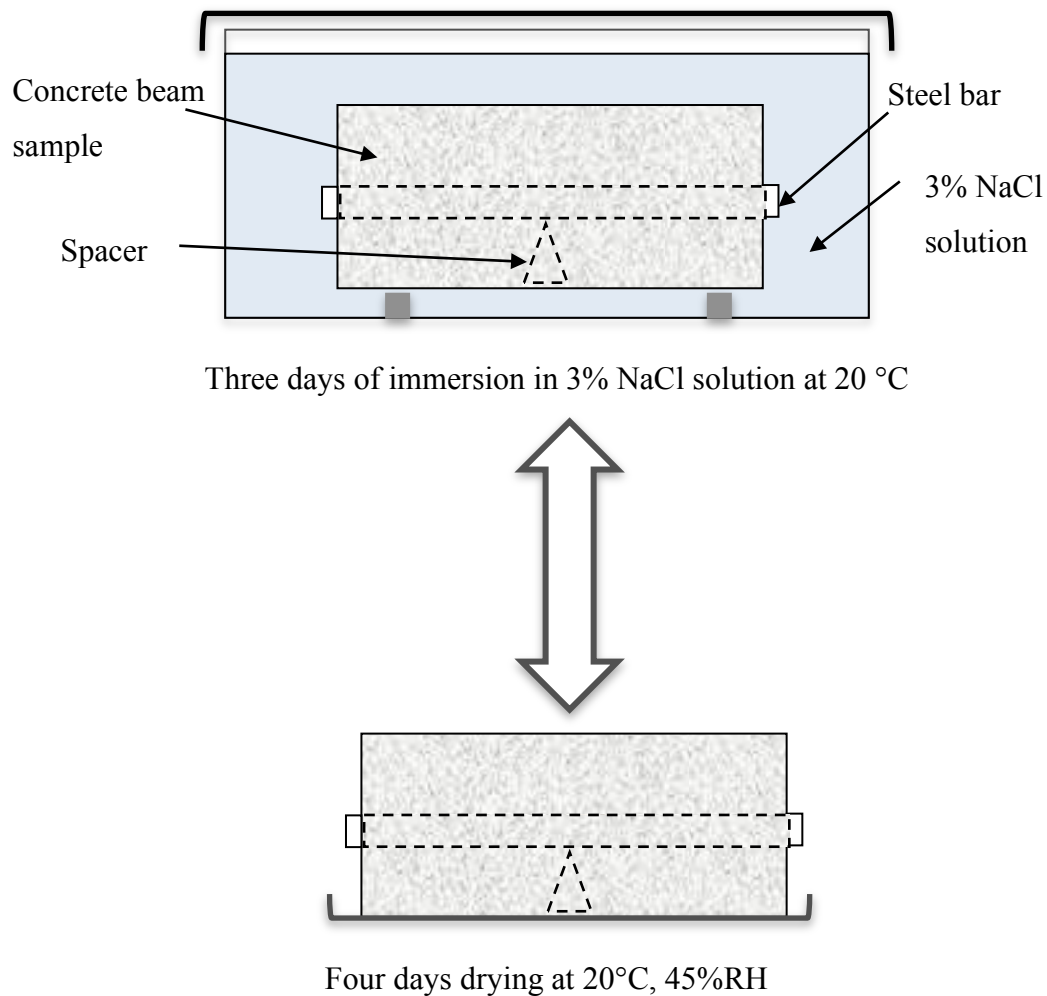


Figure 6.3 Cyclic wetting and drying setup for inducing corrosion on beam samples.

6.4 Characterising chloride ingress and corrosion

6.4.1 Visual inspection

Samples from Series IV and V were carefully inspected using a magnifying lens to detect initial cover cracking. Beams were inspected every other week of the first year of exposure then every week after. However, none of the samples reached initial cracking even after 800 days of exposure. This is due to the relatively dense (w/c 0.4) and well-cured (28 day) concrete, and the thick cover of 50 mm that was used. Nevertheless, replicate beams were split in half to expose reinforcing bar and spacer after 190 and 800 days of exposure via capillary rise and after 200 and 740 days of exposure via wetting and drying cycles for visual

inspection of corrosion initiation.

6.4.2 Micro X-ray fluorescence (μ XRF) spectroscopy

μ XRF is a technique for determining elemental composition. It uses an X-ray beam to excite the sample and then measures the emitted fluorescence signals from the excitation. The energy spectrum of the emitted fluorescence signal depends on the elements that are present and the quantity of photons detected (counts per second) is related to the quantity of each element present in the sample. The main advantage of μ XRF is its ability to map large and irregular samples, under ambient pressure environment, without requiring potentially destructive and time-consuming sample preparation.

The ORBIS PC micro X-ray fluorescence (μ XRF) bench top analyser from EDAX equipped with the ORBIS Vision (v.2.0) software was used throughout this thesis to obtain chloride profiles for different samples. The Orbis is used for analysing elements from Na (Z=11) to U (Z=92), which covers a wide range of elements found in concrete. The ORBIS PC is equipped with 30 μ m poly-capillary optics and 1 mm and 2 mm automated brass collimators.

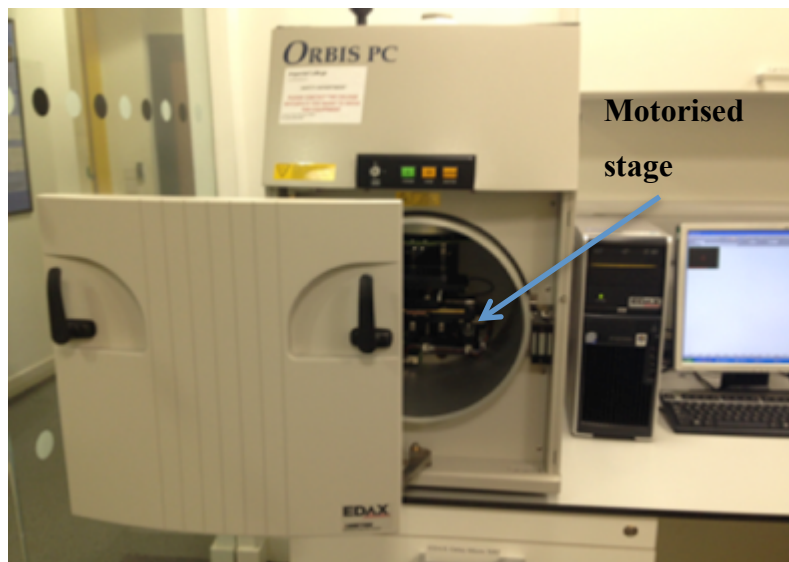


Figure 6.1 ORBIS PC μ -XRF analyser.

The sample was mounted and secured on the motorised stage in the μ -XRF' s chamber.

Stage was then moved by altering the X,Y and Z coordinates to bring the sample into a clear focused view on the low magnification camera (10x) and high magnification (75x) camera directly perpendicular to the sample. A primary beam of X-ray photon is generated from the X-ray tube that uses a Rhodium (Rh) anode target layer. The X-ray photons exiting the tube window are then guided by the optics to produce a focused beam on to the sample. Next, the characteristics fluorescent X-rays emitted from the sample are detected by a Si(Li) detector and analysed with the ORBIS Vision software. The results can be presented in the form of an element map, spot analysis or line scan.

Optimising operating conditions

A parametric study was conducted in order to determine the optimal operating conditions of the μ XRF for detecting and measuring chloride. The parametric study was conducted on the same spot of control concrete sample and samples with different types of spacers throughout. The main parameters investigated are the effects of beam spot size, beam voltage, amplifier time and dwell time. The optimised operating conditions used for this study are listed in Table 6.2.

The μ XRF analyser is capable of producing three beam spot sizes of 30 μ m, 1mm and 2mm. The beam spot size affects the intensity of the characteristic radiation received. It was observed that a 30 μ m spot size gives the highest intensity and also spatial resolution. The amplifier time constant is length of time in microseconds each emitted photon is processed by the detector. Hence, a shorter amplifier time results in a higher count rate of photons which is good for element identification via mapping, but the processed signal is of poorer accuracy and resolution. The amplifier time constants available are 1.6 μ s, 3.2 μ s, 6.4 μ s, 12.8 μ s, 25.6 μ s, 51.2 μ s and 102.4 μ s. The parametric study found that 12.8 μ s was optimal because it achieves an acceptable dead time of 40% which is in the range of 30-50% recommended by manufacturer. Dead time is the percentage of time that the detector rejects an incoming photon because it is still processing the one that has arrived earlier.

Dwell time is the amount of time the X-ray beam spends at a particular point and it is expressed in terms of milliseconds (ms). Dwell time options in the ORBIS PC μ XRF are 30 ms, 50 ms, and 100 ms up to a value of 5000 ms. A higher dwell time increases the chance of

detecting trace elements, but it also increases the total amount of time required to analyse each sample. The beam voltage controls the acceleration of electrons towards the anode of the X-ray tube. A higher beam voltage increases the energy of the X-ray beam, allowing heavy elements to be excited and detected. It was found that a beam voltage of 30 kV is sufficient to excite and detect all the elements present in the concrete. Finally, a 25- μ m thick aluminum (Al) foil filter was used to eliminate Rayleigh scatter causing an Rh peak from the measured spectrum to allow for a better detection of chloride. The measured chloride intensity is presented as counts per second (cps).

Table 6.2 Optimal operating conditions of the μ XRF for chloride analysis.

Parameter	Optimal condition
Chamber	Vacuum
Beam spot size	30 μ m
Time constant	12.8 μ s
Dwell time	500 ms
Dtm (dead time)	40%
Shutter filter	25 μ m Al

Qualitative element mapping

Element mapping was initially trialled to analyse the distribution of chloride. Examples of the obtained maps for samples containing cementitious and plastic spacers are shown in Figure 6.6. However, it was found that this method was very time consuming and the obtained sensitivity was poor. For instance, around 44 hours of imaging time was required to map 50 x 50 mm using 30 μ m beam. Hence, this was deemed impractical and element mapping was replaced by another more efficient and sensitive method of a matrix spot analysis.

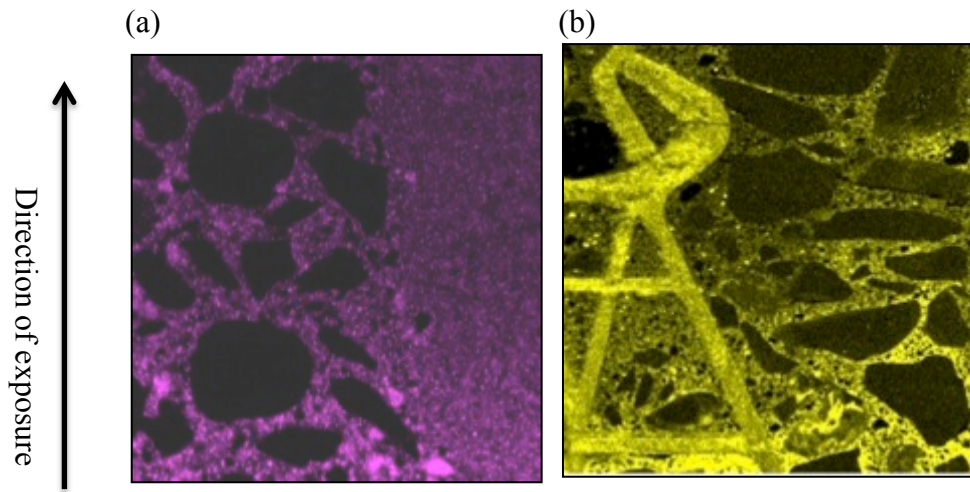


Figure 6.2 μ XRF element maps of chlorine for samples from Series III with (a) cementitious spacer and (b) plastic spacer. Samples were conditioned at 20°C 55%RH for 28 days and then submerged in 3% NaCl for 40 days. Higher intensity indicates higher concentration of chlorine.

The second method involves the collection of a large matrix of spot analyses at points spaced at 2.5 mm horizontally and 2.5 mm depth increments. The spot analyses are then used to produce a contour chloride profile as shown in Figure 6.6. Chloride profiles are expressed as %wt. of cement, and details of converting count per second into weight percentage of cement is detailed below. The issues with this time consuming analysis is to ensure avoidance of the interference from aggregate or voids that cause discontinuities or gaps in the generated profiles. Also, this method considers areas that are not within the areas of interest (mainly spacer interface). Furthermore, the contour map assume linear interpolation between the spot analysis points which is not correct specifically at areas close to aggregates or voids.

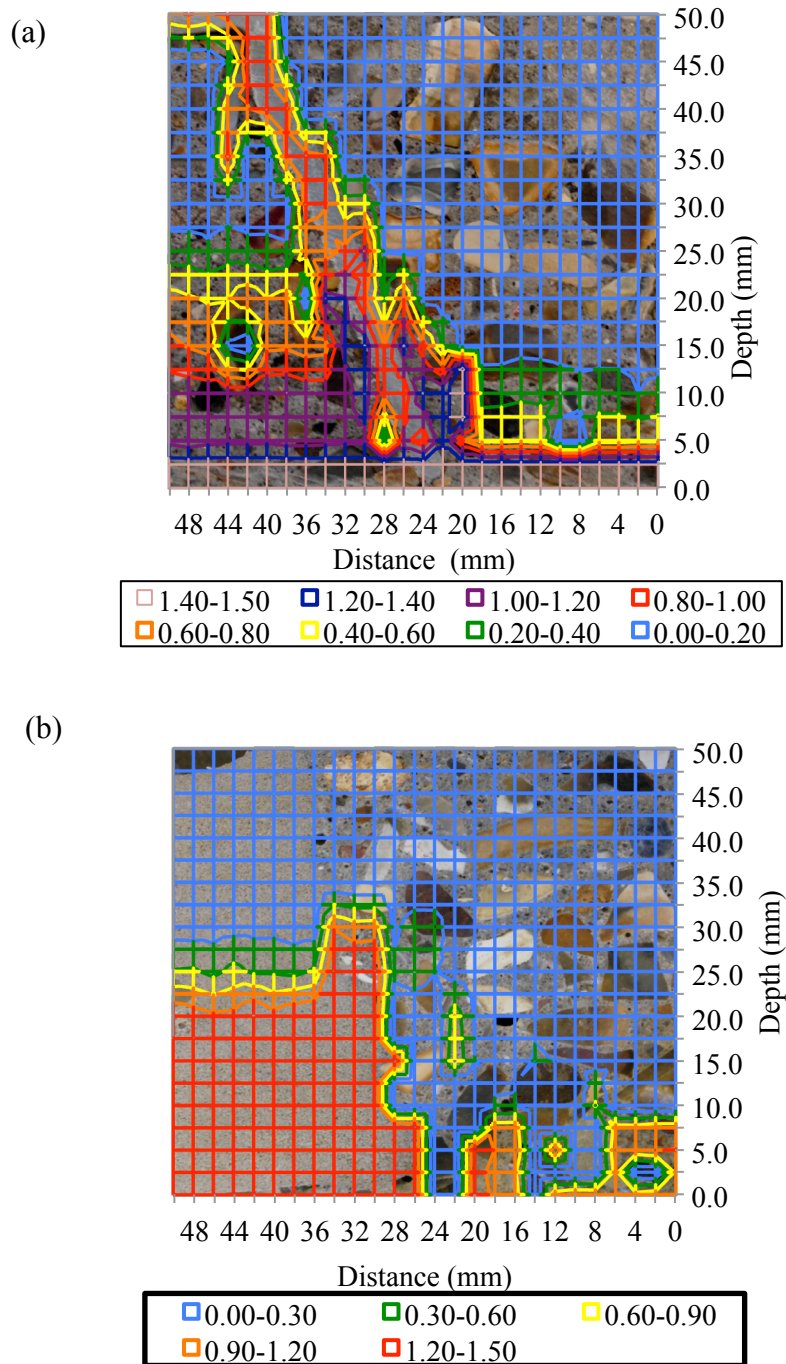


Figure 6.3 Contour map from matrix spot analysis showing the distribution of chlorine in samples from Series III with (a) plastic spacer and (b) cementitious spacer. The samples were conditioned at 40°C for 28 days and then submerged in 3% NaCl solution for 40 days. Values in box represent chloride concentration expressed as %wt of cement

Line scans

The method adopted to obtain quantitative concentration gradient of chloride is by conducting line scans. Each line scan consists of 50 spot analyses equally spaced at a distance of 1mm to produce a detailed chloride profile, as shown in Figure 6.7. Chloride profiles were measured at the spacer-concrete interface, within the cementitious spacer and along the edge of the sample farthest away from the spacer. The stage was programmed to stop at equally spaced y-coordinates, but the x-coordinates were changed to avoid aggregate particles or large voids that would otherwise cause discontinuities in the generated chloride profiles.

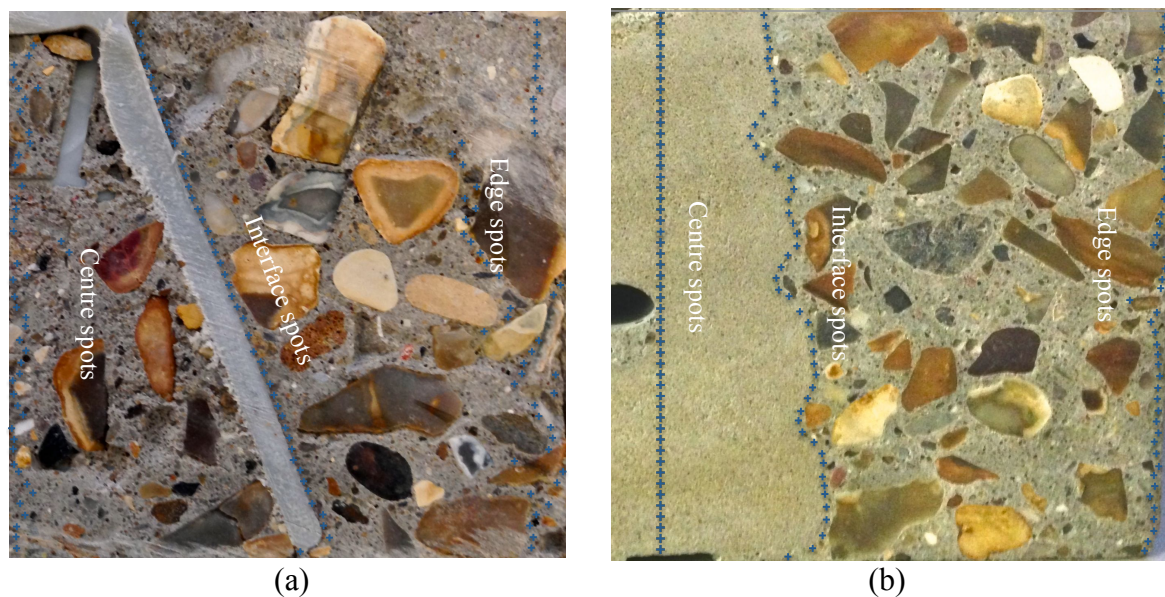


Figure 6.4 Images of samples with (a) plastic spacer and (b) cementitious spacer showing the locations of spot analysis (crosses) for producing line scans of chloride profile at the spacer-concrete interface, within the cementitious spacer and at the sample edge farthest away from the spacer.

The outline of the methodology is shown in Figure 6.8. First, the sample was secured on the stage and brought to a suitable position by altering the X, Y and Z coordinates of the stage to obtain clear view from both the low and high magnification camera. Secondly, a spot analysis is carried out using the optimal operating conditions in Table 6.2 to obtain the spectrum at the spot where the X-ray beam impinges to identify all the elements that are present in the concrete sample.

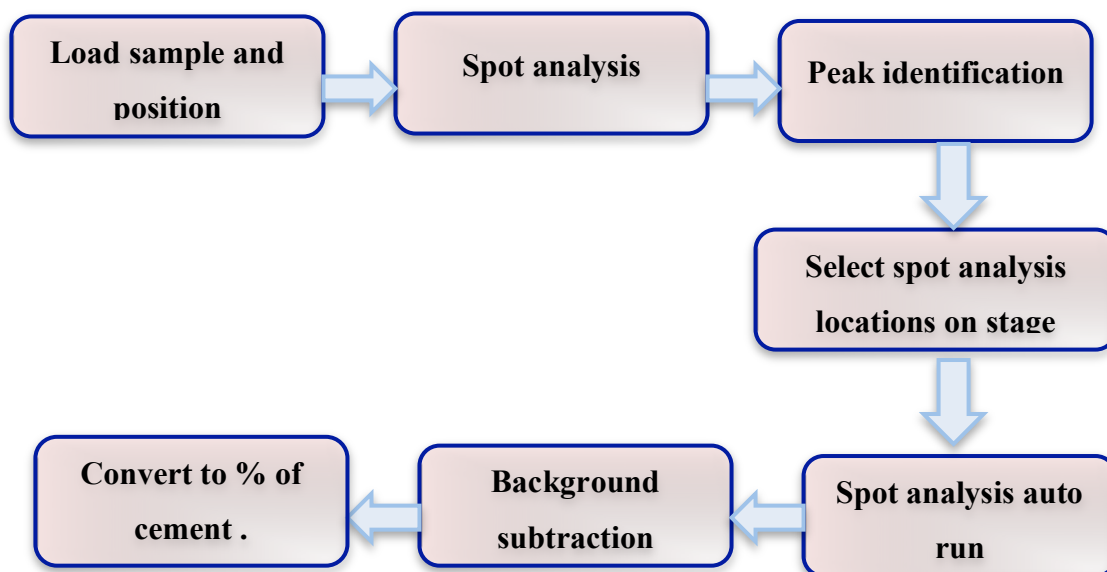


Figure 6.5 Outline of μ XRF methodology for measuring chloride.

A typical spectrum of a concrete sample obtained from μ XRF spot analysis is shown in Figure 6.9. Note that the y-axis represents the number of detected characteristic X-ray photons. Subsequently, a peak identification process is carried out whereby the element corresponding to each peak is detected by a curve-fitting procedure using the ORBIS Vision (v.2.0) software fitted with the μ XRF system. However, there are two types of false peaks that might exist in the spectrum: sum and escape peaks that must be accounted for. Sum peaks are produced when two X-ray photons arrive in the detector simultaneously resulting in a signal pile-up in the spectrum. Escape peaks occur during the photoelectric process whereby part of the energy supplied causes the silicon atom in the detector to be ionised which then produces Si-K α photons and reduce peak energy by 1.74 keV. Using the ORBIS Vision software, the escape peaks are subtracted from the spectrum while sum peaks are labelled in the spectrum.

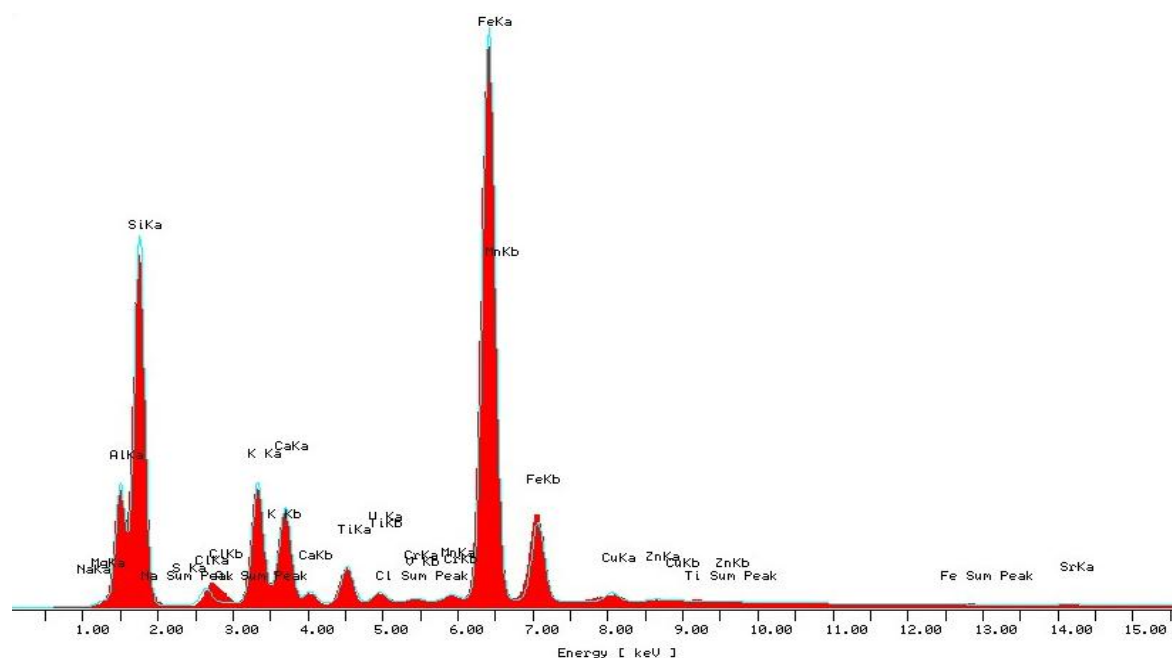


Figure 6.6 Typical spectrum from μ XRF spot analysis showing the main elements present in concrete.

Locations for spot analysis were then carefully selected and saved to ensure that each spot is located within the cement paste. Dead time (Dtm) was checked for each spot analysis to ensure that the targeted value of around 40% was achieved. If a particular spot hits an aggregate particle or a void, then the dead time will be reduced significantly. This gives a convenient means to check the accuracy of the spot locations. Once all the spot locations are checked and saved, an auto spot analysis run is carried out. However, the resulted spectrum contains several peaks obscured by the background and so are not well-resolved. Therefore, the signal-to-noise ratio (SNRs) of spectral peaks method [Ernst et al., 2014] was used to subtract the background. The background counts were computed by multiplying the number of channels in the peak by the average of the pre-peak and post-peak values. Subsequently, the signal was obtained by subtracting the background counts from the sum of counts within the peak range, and the noise was calculated as the square root of background counts under the peak of interest. A peak with signal-to-noise ratio larger than 3 indicates that the element is present at significantly greater concentration than the background [Ernst et al., 2014].

The final stage is to convert the collected data in terms of counts per second to percentage of chlorides by mass of cement. This is done by referring to an appropriate calibration curve.

The calibration curve was obtained by doing the same spot analysis on a series of cement paste samples at w/c of 0.40 that contained known amounts of chlorides (0%, 0.05%, 0.15%, 0.5% and 2% by weight of cement. Samples were provided by [Wahid, 2015]. The cement paste samples were cured for 28 days and dried to equilibrium following the conditioning regimes similar to the samples used in this study. Specimens were then analysed in ORBIS PC μ -XRF analyser using the same operating conditions in Table 6.2. Twenty spot analyses were performed for each paste. The measured X-ray counts for chlorine was corrected for background and then plotted against the known chloride concentration as shown in Figure 6.10. Note that each data point is an average of twenty spot analysis and variation is presented as the standard error ($S.E = \sigma / \sqrt{n}$), where σ is the standard deviation and n is the number of replicates.

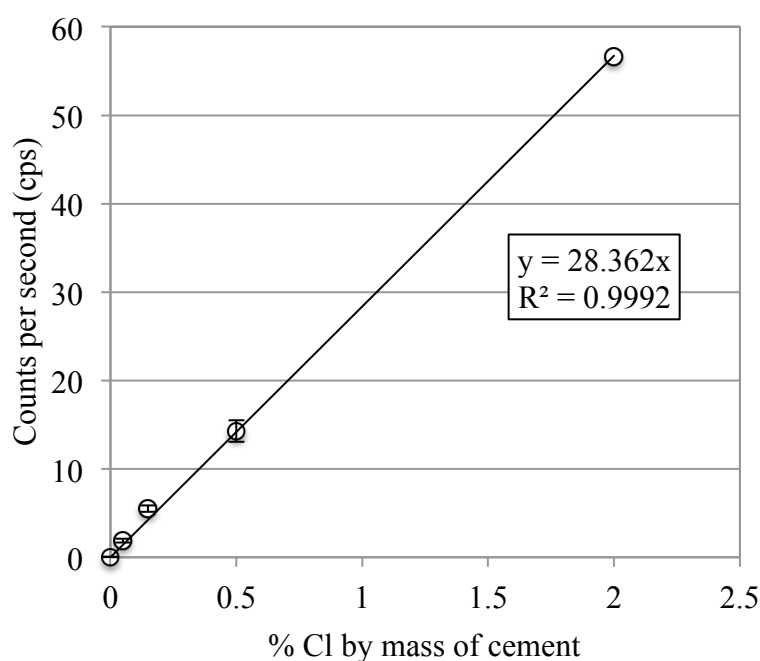


Figure 6.7 Calibration curve to convert chloride intensity from counts per second to %Cl by mass of cement.

6.5 Estimating time to corrosion initiation

The development of concrete deterioration can be approximated to a two-phase process of initiation and propagation as suggested by Tuutti [Tuutti, 1982]. This model is illustrated in Figure 6.8. During the initiation phase, ingress of aggressive species (such as chlorides) occur, but the structure experiences no substantial weakening or loss of functionality [Rostam, 1996]. When the amount of aggressive species reaches a critical level, degradation initiates and this marks the beginning of the propagation phase. The structure then continues to deteriorate until ultimate failure if no intervention is provided. Many service-life models have been developed to estimate the length of time to which reinforced concrete structures maintain an accepted level of functionality. In the majority of cases, the critical limit state is taken as the initiation of corrosion. In some cases, the propagation phase is also considered as part of the service life [Pease et al., 2010]. The latter gives a more realistic estimate of service life, but it is harder to implement accurately.

In this study, the chloride profiles measured from μ XRF will be used to model the penetration of chloride to predict the time required to reach the reinforcement level and achieve sufficient amount to destroy the passive layer and initiate corrosion. This known as the chloride threshold level and it is usually presented as a ratio of the total chloride to cement content (expressed as a weight percentage). Typical values of the chloride threshold level reported in the literature range from 0.2 to 2.5% by weight of cement [Glass and Buenfeld, 1997]. For this study, the chloride threshold level is assumed to be 0.4% by mass of cement as recommended by EN1992-EC2 [Euro code 2, 2004]. It should be noted again that the predicted time to reach the chloride threshold level is a conservative estimate of service life. Furthermore, values of D_{eff} and C_s obtained from fitting experimental data to Fick's second law (Equation 6.1) are assumed to be constant over time for the sake of simplicity. This assumption leads to an underestimation of the time to corrosion initiation.

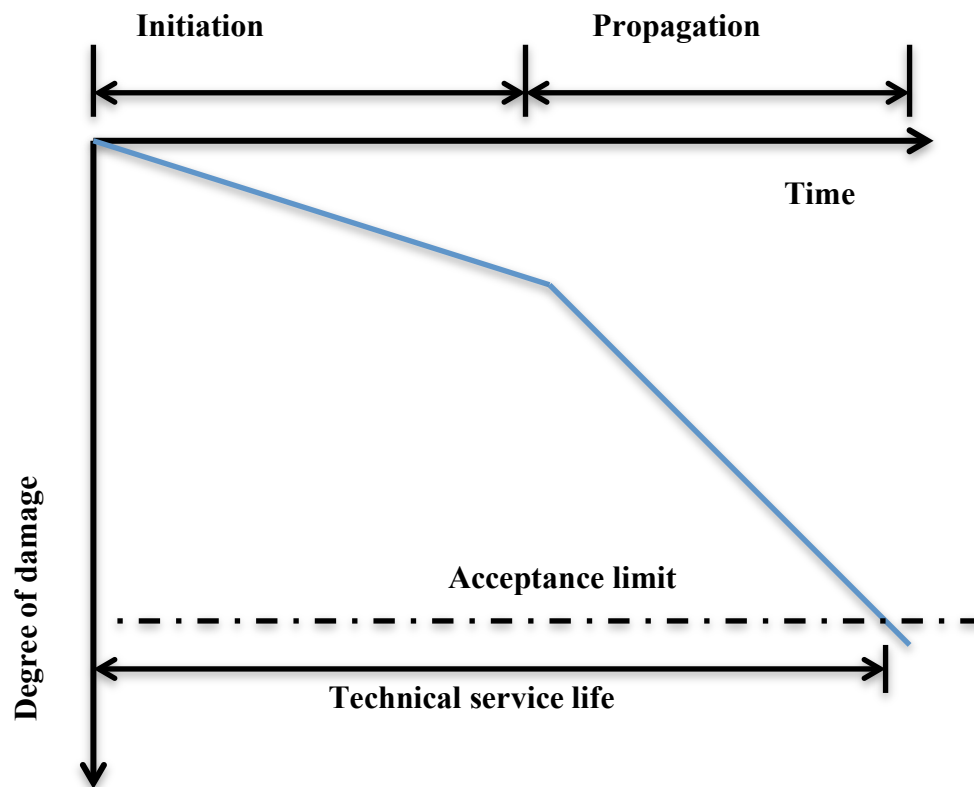


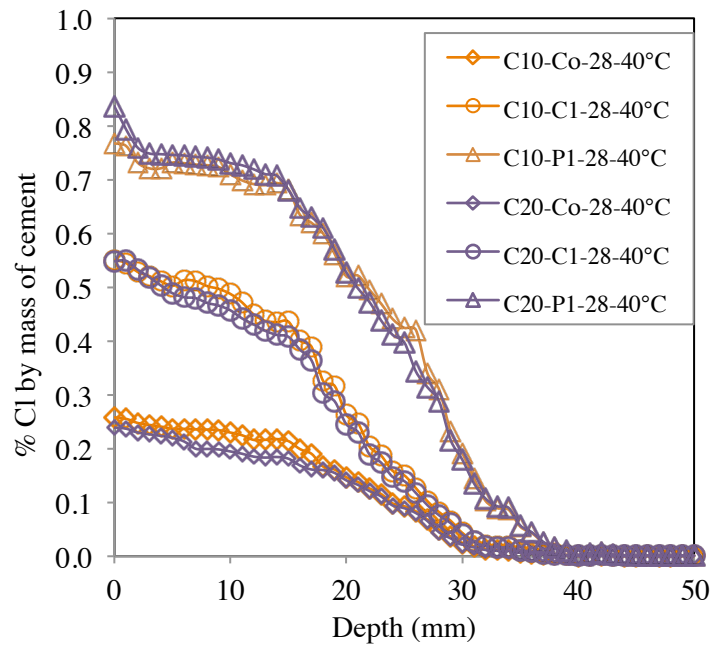
Figure 6.8 Service-life model for reinforced concrete structure [Tuutti, 1982].

6.6 Results

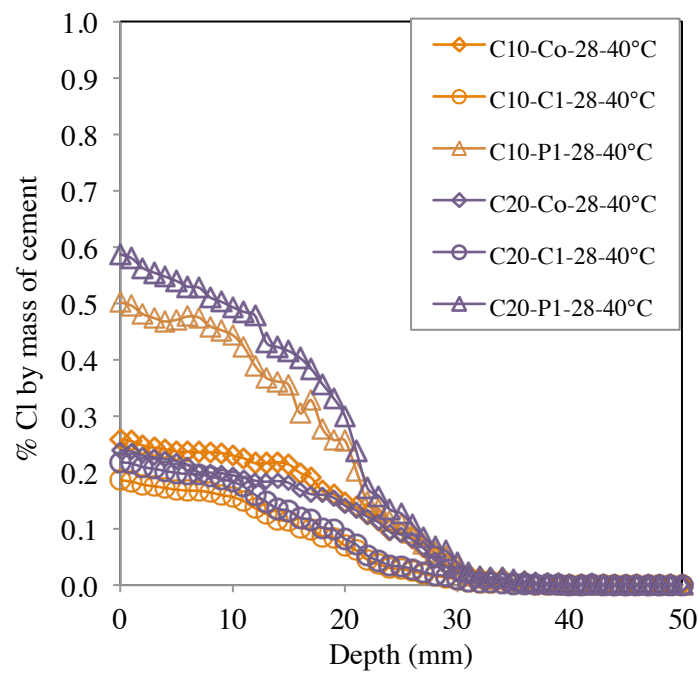
6.6.1 Influence of spacers on chloride penetration

The chloride profiles measured at the interface of the spacer with concrete, at the centre and edge of the sample are shown in Figure 6.9. It is evident that the concentration and depth of chloride penetration were the highest at the spacer-concrete interface and for samples containing plastic spacer, followed by samples with cementitious spacer (Figure 6.9a). The control sample had the lowest chloride concentration in all cases. Concentration of chlorides within the plastic spacer was higher than the concentration of chloride within the cementitious spacer (Figure 6.9b). However, it is interesting to note that the concentration of chloride within the cementitious spacer was slightly lower than that of the control sample.

(a)



(b)



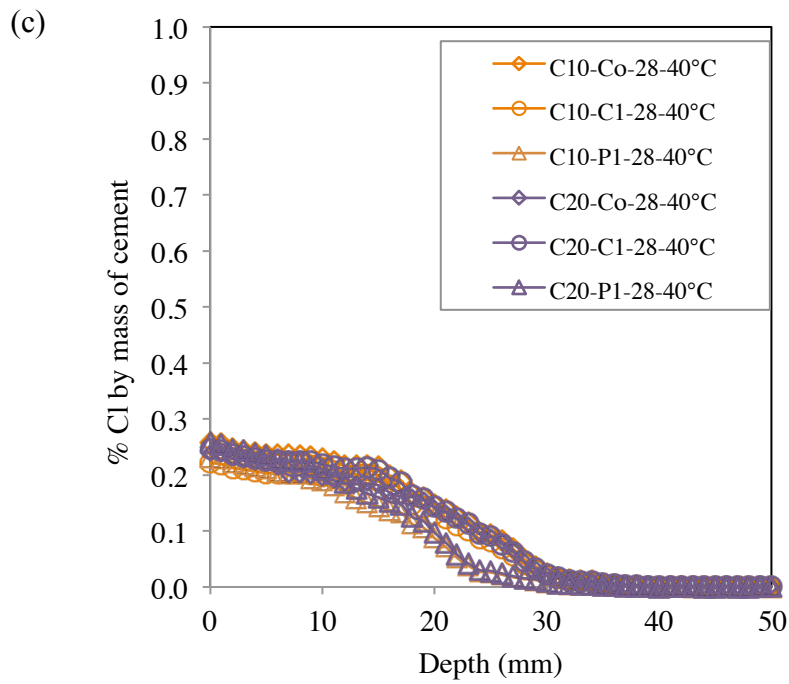


Figure 6.9 Typical chloride profiles at (a) spacer-concrete interface, (b) centre of spacer and (c) edge of sample. Results are compared to chloride profiles from the control with no spacers. Samples are from Series III conditioned at 40°C for 28 days and then exposed to 3% NaCl solution for 60 days.

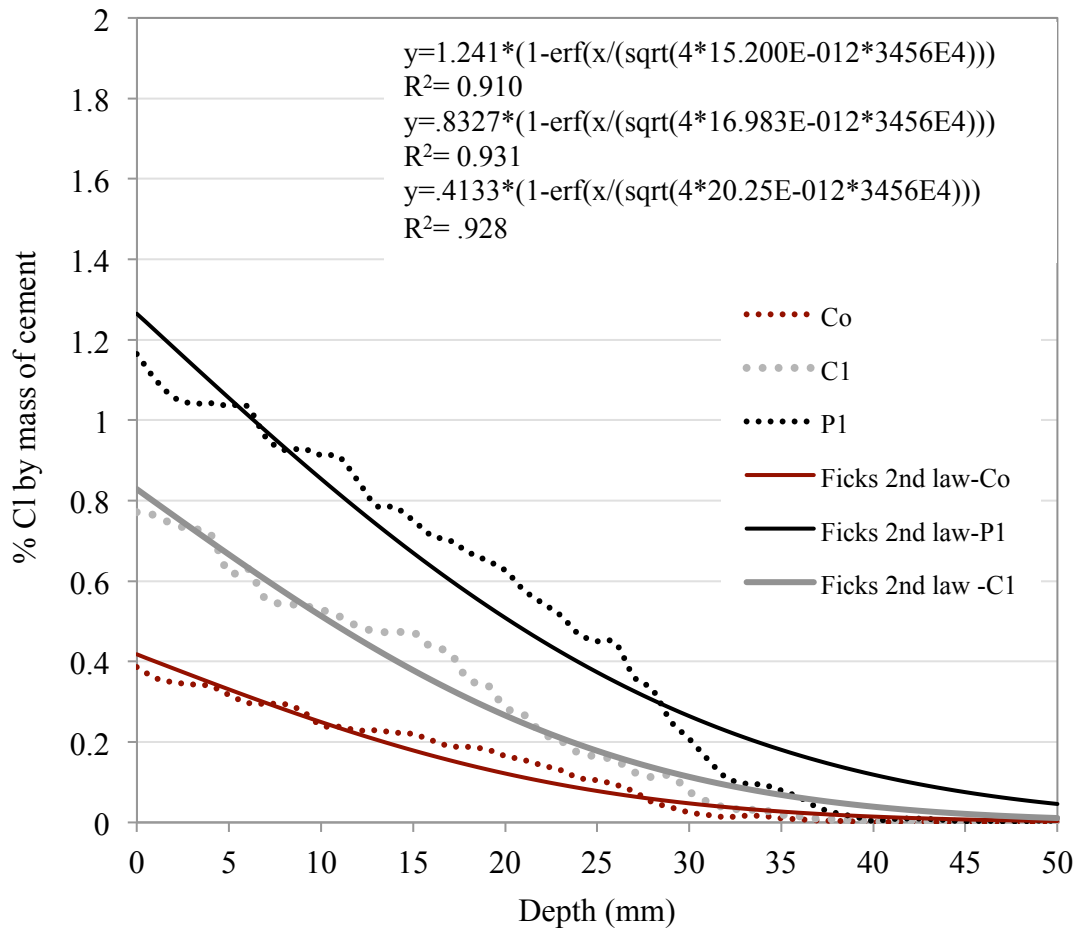


Figure 6.10 Example showing the fitting of chloride profiles at the spacer-concrete interface to Fick's 2nd Law to obtain D_{eff} and C_s . Samples are from Series II conditioned at 40°C for 90 days and then exposed to salt solution for 40 days.

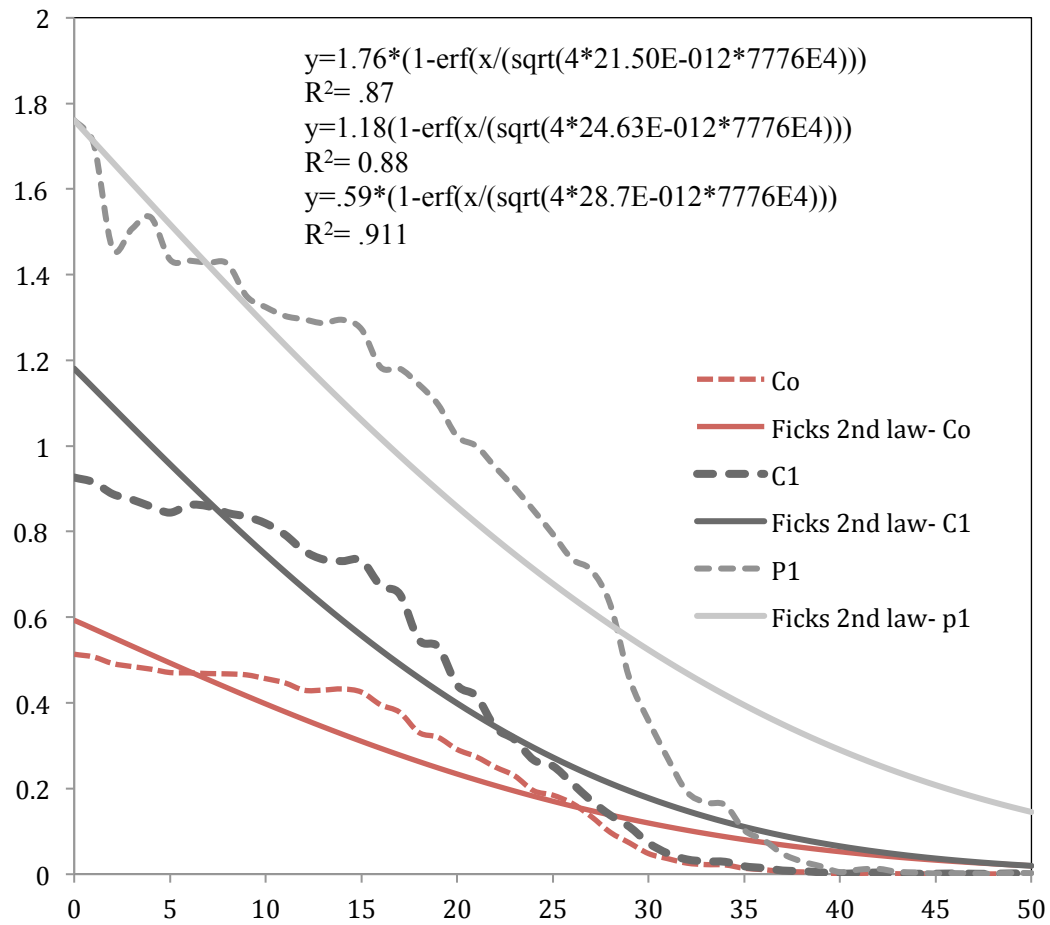


Figure 6.11 Example showing the fitting of chloride profiles at the spacer-concrete interface to Fick's 2nd Law to obtain D_{eff} and C_s . Samples are from Series II conditioned at 40°C for 90 days and then exposed to salt solution for 90 days.

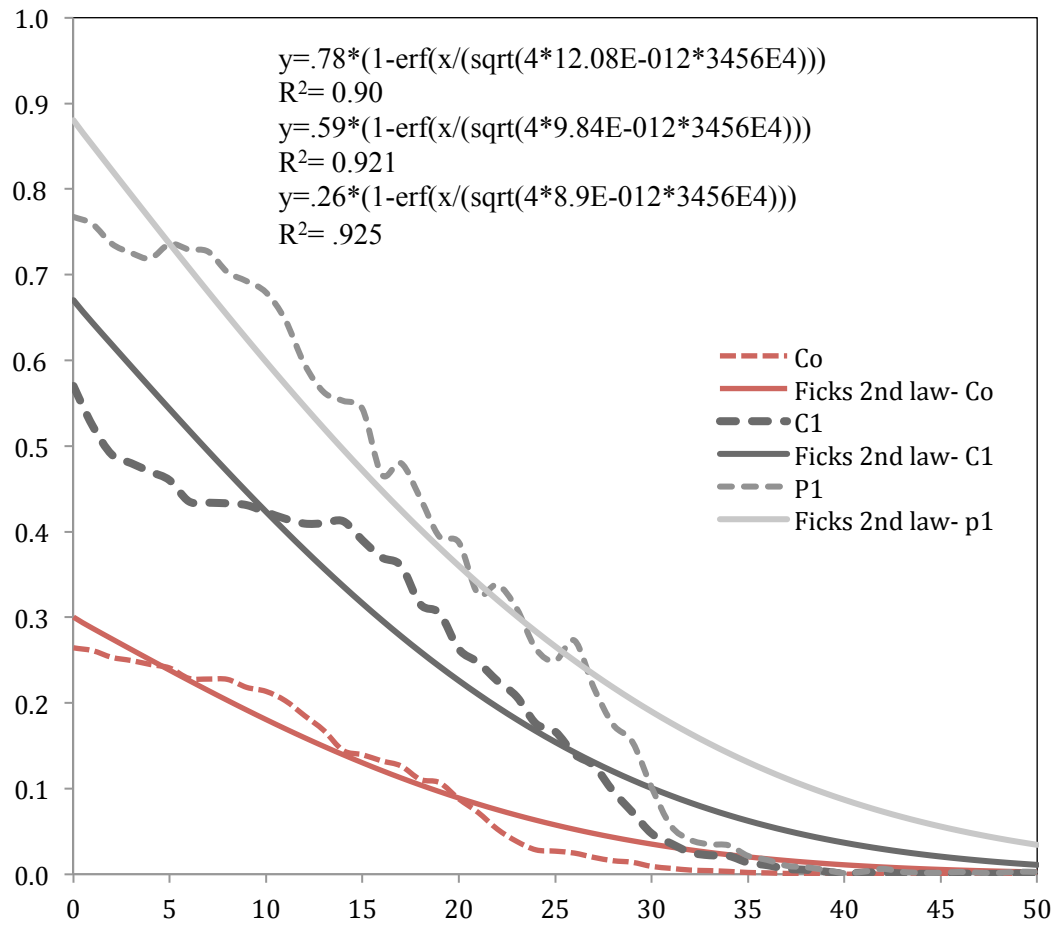


Figure 6.12 Example showing the fitting of chloride profiles at the spacer-concrete interface to Fick's 2nd Law to obtain D_{eff} and C_s . Samples are from Series II conditioned at 20°C 50% RH for 90 days and then exposed to salt solution for 40 days.

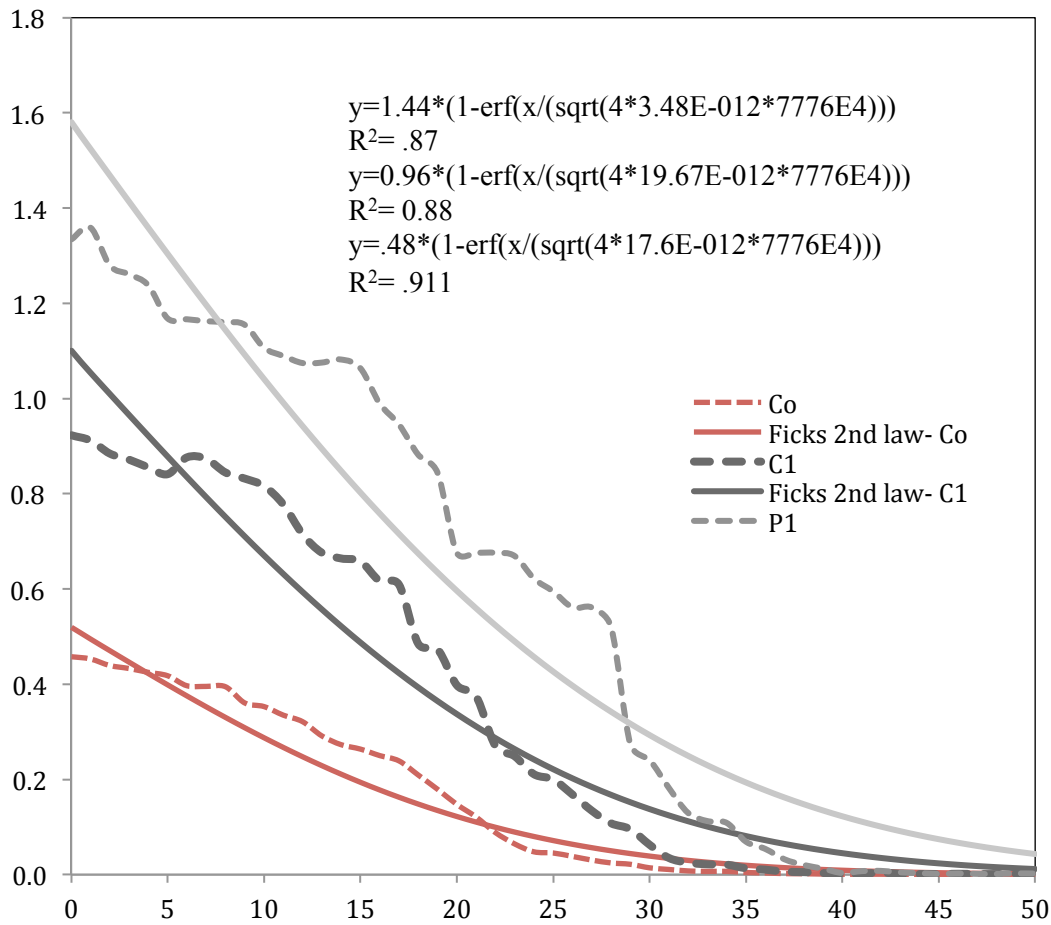


Figure 6.13 Example showing the fitting of chloride profiles at the spacer-concrete interface to Fick's 2nd Law to obtain D_{eff} and C_s . Samples are from Series II conditioned at 20°C 50% RH for 90 days and then exposed to salt solution for 90 days.

The non-steady state diffusion coefficient D_{eff} and surface chloride concentration C_s are presented in Tables 6.3 to 6.9. The coefficients were calculated by best fitting the acquired chloride profiles to Fick's second law of diffusion as shown in Figure 6.10-6.13. It is noted that the coefficient of regressions of the best-fit lines (R^2) was always above 0.87 for all cases.

In general, the chloride diffusion coefficient D_{eff} and surface chloride concentration C_s for samples with spacers were higher than that of the control samples (without spacers). At the edge of sample away from spacer, the measured diffusion coefficients and surface chloride concentrations were almost similar to those of the control samples in all cases, as shown in

Figure 6.9(c) and in Tables 6.3-6.6.

Factors influencing the measured diffusion coefficients and surface chloride concentrations other than spacer inclusion are conditioning regime, length of conditioning, exposure duration and MSA as shown in Tables 6.3-6.6. As expected, conditioning regime prior to chloride exposure has a major influence on the measured diffusion coefficients and surface chloride concentrations. Generally samples dried at 40°C (Table 6.3 and 6.5) produced higher chloride diffusion coefficients and surface concentrations compared to those conditioned at 20°C, 55%RH (Table 6.4,6.6) when conditioning time, exposure time and max size of aggregates remained constant.

It is evident that the length of conditioning period affects the measured diffusion coefficients and surface chloride concentrations. For example, Series II samples that were dried between 90 and 120 days had higher diffusion coefficients and surface concentrations compared to Series III samples which were dried for 28 days, but had the same MSA, conditioning regime and period of chloride exposure of 90 days. When exposure time to chloride increased, the measured diffusion coefficients and surface chloride concentrations increased, when comparing samples of the same MSA, conditioning regime and time. Max size of aggregates had no influence on the measured diffusion coefficients and surface chloride concentrations.

The measured diffusion coefficients and surface chloride concentrations along the interface of spacer with surrounding concrete are presented in Figures 6.12 and 6.13. In general, samples with plastic spacer had the highest diffusion coefficients and surface chloride concentrations along its interface followed by the interface of the cementitious spacer. Control sample had the lowest diffusion coefficients and surface chloride concentrations.

Samples with plastic spacer had higher chloride diffusion coefficients than the control by a factor of 1.05 when dried at 40°C for 28 days and 1.4 when dried at 40°C for 90 days. Conditioning at 20°C, 55%RH resulted in higher diffusion coefficient along plastic spacer interface by a factor of 1.2 to 1.4 depending on length of drying regime and exposure. The trend of surface chloride concentration is similar to that of diffusion coefficient.

Concrete within the inside of the plastic spacer (P-centre) as shown in Tables 6.3-6.6 consistently had higher diffusion coefficients and surface chloride concentrations than the

control sample by a factor of 1.1-1.3 depending on conditioning regime and length, and chloride exposure period.

The measured chloride diffusion coefficients and surface concentrations of the cementitious spacer interface with concrete were higher than the control sample regardless of conditioning regime, length of conditioning and exposure period. However, the chloride diffusivity coefficients and surface concentrations of the cementitious spacer were relatively lower than control sample in all cases.

Chloride profiles for Series I samples exposed to chlorides by capillary absorption are shown in Figure 6.14. The trend is similar to that of Series II and III. Chloride concentration was the highest at plastic spacer interface followed by cementitious spacer interface then within plastic spacer then control sample. The lowest chloride concentrations were within the cementitious spacer.

The increase in Series II measured chloride coefficients and surface concentrations compared to Series III when dried in similar regime and exposed to chloride for 90 days, was assumed to be due to absorption effects. Hence, chloride profile of Series I was subtracted from Series II sample profiles and then fitted to Fick's 2nd law to calculate the modified diffusion coefficient and surface concentration. The results are presented in Table 6.7. The results are higher than Series III samples by around 10-15%.

Table 6.3 Chloride diffusion coefficient D_{eff} and surface chloride concentration C_s from fitting to Fick's 2nd Law for samples from Series II & III (MSA = 10 mm, samples were conditioned at 40°C prior to chloride exposure). P-center represents concrete nestled within the plastic spacers.

Spacer/ location	Series II				Series III			
	Exposure							
	40 days		90 days		60 days		90 days	
	C _s (%)	D _{eff} ⁻¹² x 10 ¹⁰ (m ² /s)	C _s (%)	D _{eff} ⁻¹² x 10 ¹⁰ (m ² /s))	C _s (%)	D _{eff} ⁻¹² x 10 ¹⁰ (m ² /s)	C _s (%)	D _{eff} ⁻¹² x 10 ¹⁰ (m ² /s)
Co	0.32	10.96	0.59	21.54	0.28	9.62	0.42	15.39
C-interface	0.65	12.03	1.18	24.06	0.57	10.55	0.84	17.19
C-centre	0.28	10.06	0.50	19.89	0.22	9.09	0.35	14.29
C-edge	0.30	11.19	0.56	21.70	0.27	9.82	0.40	15.50
P-interface	1.24	15.28	1.76	28.70	0.84	12.97	1.26	20.50
P-centre	0.72	12.58	1.31	24.72	0.63	11.03	0.93	17.65
P-edge	0.33	11.19	0.60	21.73	0.29	9.82	0.43	15.52

Table 6.4 Chloride diffusion coefficient D_{eff} and surface chloride concentration C_s from fitting to Fick's 2nd Law for samples from Series II & III (MSA = 10 mm, samples were conditioned at 20°C, 55%RH prior to chloride exposure). P-center represents concrete nestled within the plastic spacers.

Spacer/ location	Series II				Series III			
	Exposure							
	40 days		90 days		60 days		90 days	
	C _s (%)	D ₋₁₂ ^{eff} _{x 10} (m ² /s)	C _s (%)	D ₋₁₂ ^{eff} _{x 10} (m ² /s))	C _s (%)	D ₋₁₂ ^{eff} _{x 10} (m ² /s)	C _s (%)	D ₋₁₂ ^{eff} _{x 10} (m ² /s))
Co	0.26	8.96	0.48	17.61	0.23	7.87	0.34	12.58
C-interface	0.53	9.84	0.96	19.67	0.47	8.63	0.69	14.05
C-centre	0.23	8.22	0.41	16.26	0.18	7.43	0.29	11.68
C-edge	0.25	9.15	0.46	17.74	0.22	8.03	0.33	12.67
P-interface	0.78	12.08	1.44	23.46	0.69	10.60	1.03	16.76
P-centre	0.59	10.29	1.07	20.21	0.52	9.02	0.76	14.43
P-edge	0.27	9.15	0.49	17.77	0.24	8.03	0.35	12.69

Table 6.5 Chloride diffusion coefficient D_{eff} and surface chloride concentration C_s from fitting to Fick's 2nd Law for samples from Series II & III (MSA = 20mm, samples were conditioned at 40°C prior to chloride exposure). P-center represents concrete nestled within the plastic spacers.

Spacer/ location	Series II				Series III			
	Exposure							
	40 days		90 days		60 days		90 days	
	C _s (%)	D ₋₁₂ ^{eff} x 10 ⁻¹² (m ² /s)	C _s (%)	D ₋₁₂ ^{eff} x 10 ⁻¹² (m ² /s))	C _s (%)	D ₋₁₂ ^{eff} x 10 ⁻¹² (m ² /s)	C _s (%)	D ₋₁₂ ^{eff} x 10 ⁻¹² (m ² /s))
Co	0.29	10.06	0.54	19.76	0.26	8.83	0.39	13.99
C-interface	0.60	11.04	1.08	22.08	0.52	9.68	0.77	15.63
C-centre	0.20	9.23	0.46	18.25	0.20	8.34	0.32	12.92
C-edge	0.28	10.27	0.51	19.91	0.25	9.01	0.37	14.10
P-interface	0.88	13.56	1.61	26.33	0.77	11.90	1.16	18.64
P-centre	0.66	11.54	1.20	22.68	0.58	10.12	0.85	16.06
P-edge	0.30	10.27	0.55	19.94	0.27	9.01	0.39	14.12

Table 6.6 Chloride diffusion coefficient D_{eff} and surface chloride concentration C_s from fitting to Fick's 2nd Law for samples from Series II & III (MSA = 20 mm, samples were conditioned at 20°C, 55%RH prior to chloride exposure). P-center represents concrete nestled within the plastic spacers.

Spacer/ location	Series II				Series III			
	Exposure							
	40 days		90 days		60 days		90 days	
	C _s (%)	D _{eff} ⁻¹² x 10 ⁻¹² (m ² /s)	C _s (%)	D _{eff} ⁻¹² x 10 ⁻¹² (m ² /s))	C _s (%)	D _{eff} ⁻¹² x 10 ⁻¹² (m ² /s)	C _s (%)	D _{eff} ⁻¹² x 10 ⁻¹² (m ² /s))
Co	0.24	8.22	0.44	16.16	0.21	7.22	0.31	11.54
C-interface	0.49	9.03	0.88	18.05	0.43	7.92	0.63	12.89
C-centre	0.20	7.54	0.38	14.92	0.17	6.82	0.27	10.72
C-edge	0.23	8.40	0.42	16.28	0.20	7.37	0.30	11.63
P-interface	0.72	11.08	1.32	21.53	0.63	9.73	0.95	15.38
P-centre	0.54	9.44	0.98	18.54	0.48	8.28	0.70	13.24
P-edge	0.25	8.40	0.45	16.31	0.22	7.37	0.32	11.64

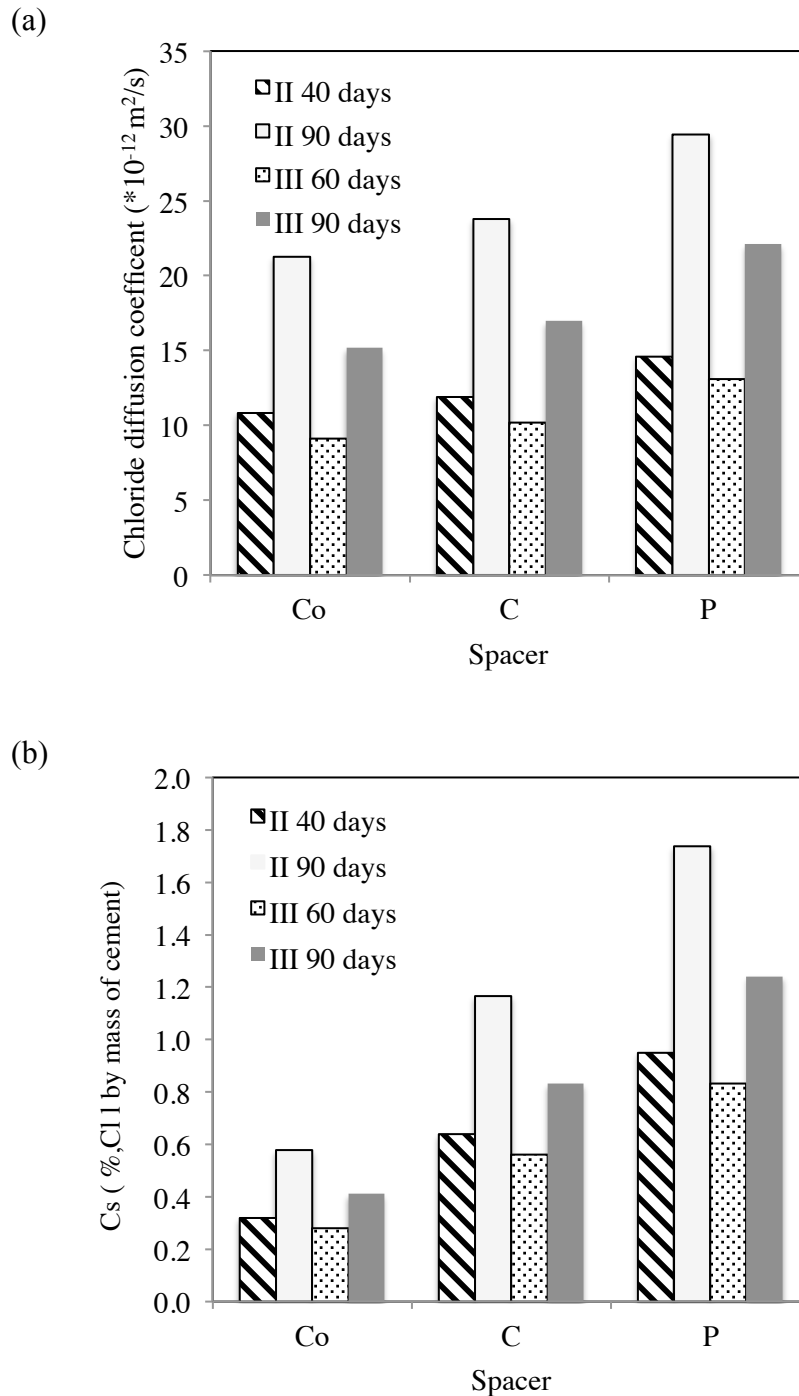


Figure 6.14 Effect of spacers on a) chloride diffusion coefficient D_{eff} and b) chloride concentration on the surface C_s , measured at the spacer-concrete interface. Samples were cured for 28 days, then conditioned at 40°C prior to chloride exposure (MSA = 10 mm).

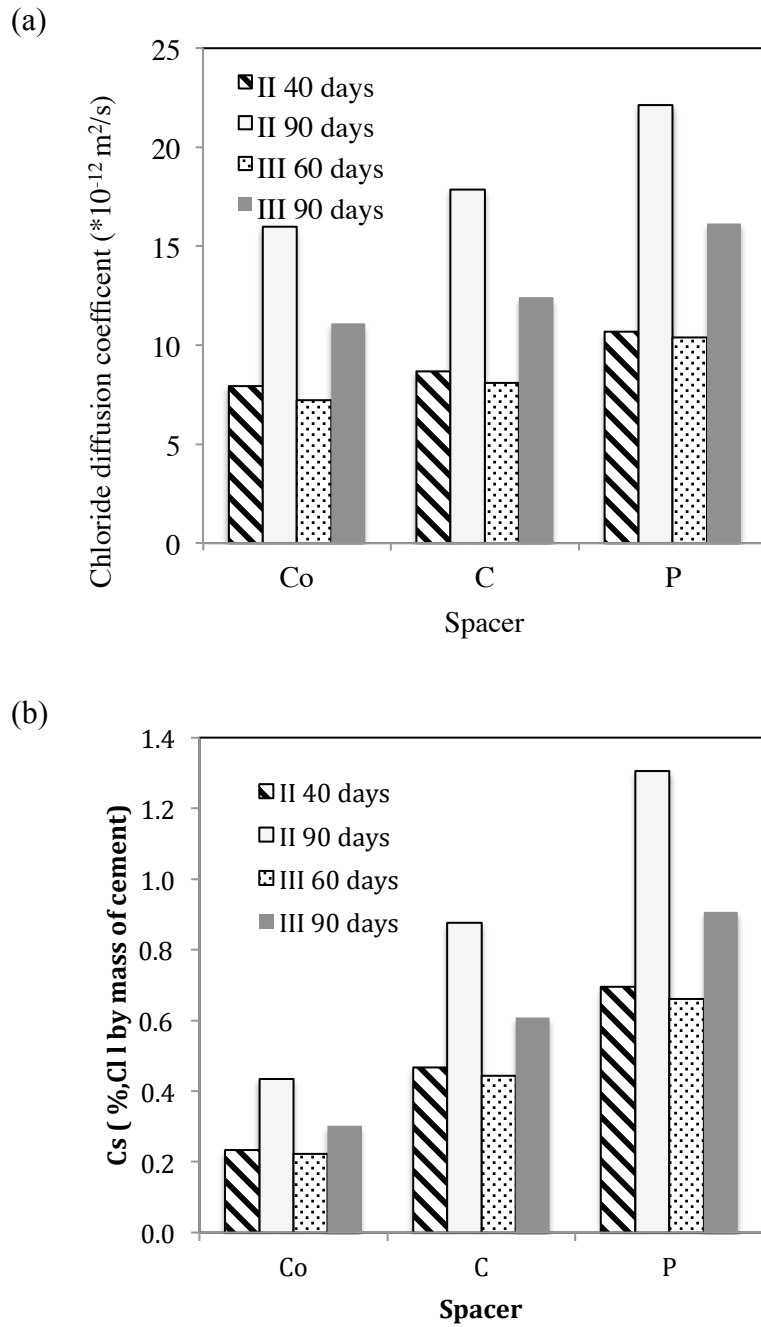


Figure 6.15 Effect of spacers on a) chloride diffusion coefficient D_{eff} and b) chloride concentration on the surface C_s , measured at the spacer-concrete interface. Samples were cured for 28 days, then conditioned at 20°C, 55% RH prior to chloride exposure (MSA = 10 mm).

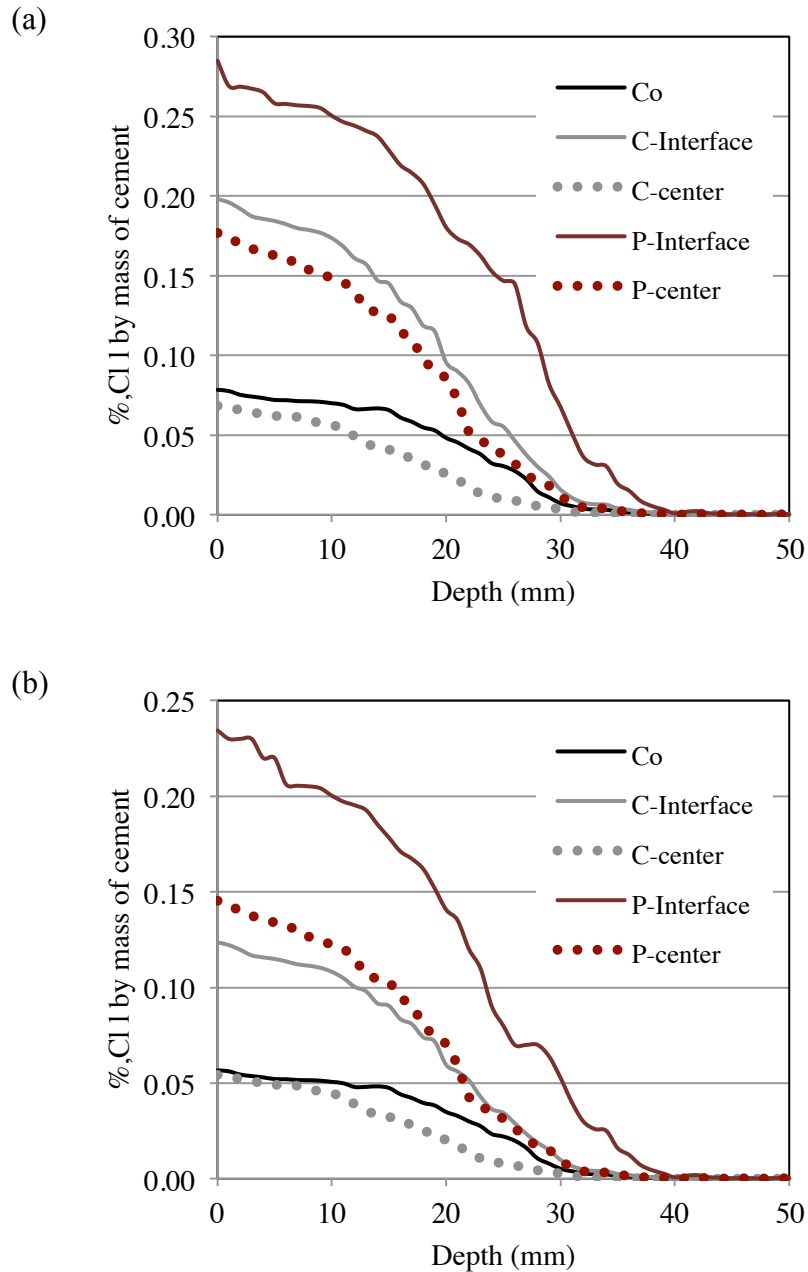


Figure 6.16 Effect of spacers on chloride absorption profiles for samples from Series I that were conditioned at (a) 40°C, and (b) 20°C, 55% RH. Samples were cured for 28 days (MSA = 10 mm).

Table 6.7 Chloride diffusion coefficient D_{eff} and surface chloride concentration C_s from fitting the modified profiles from Series II to Fick's 2nd Law (MSA = 10mm)

Spacer/ location	Series II (modified)			
	Exposure 90 days			
	40°C		20°C, 55% RH	
	C_s (%)	$D_{\text{eff}} \times 10^{-12}$ (m ² /s))	C_s (%)	$D_{\text{eff}} \times 10^{-12}$ (m ² /s))
Co	0.45	16.31	0.36	13.33
C-interface	0.89	18.22	0.73	14.89
C-centre	0.37	15.15	0.31	12.38
C-edge	0.42	16.43	0.35	13.43
P-interface	1.34	21.73	1.09	17.77
P-centre	0.99	18.71	0.81	15.30
P-edge	0.46	16.45	0.37	13.45

6.6.2 Influence of spacers on reinforcement corrosion initiation

None of the prepared beams from Series IV and V reached the stage of cover cracking. Therefore, at the end of this study samples were split in half and checked for any visual signs of corrosion products. Seven samples (four with cementitious spacer, three with plastic spacer) showed limited amount of corrosion products (rust) on the reinforcing bar at the location of spacer as shown in Figures 6.17 and 6.18. Reinforcing bar at locations far from spacer showed no indication of corrosion. However, nine beams out of twenty four were excluded (two control, four with plastic spacer, three with cementitious spacer) because of insufficient sealing at the ends of the beam resulting large rust deposits along the edges of reinforcing bar. Reinforcing bar in the remaining eight beams including all control samples showed no signs of corrosion.

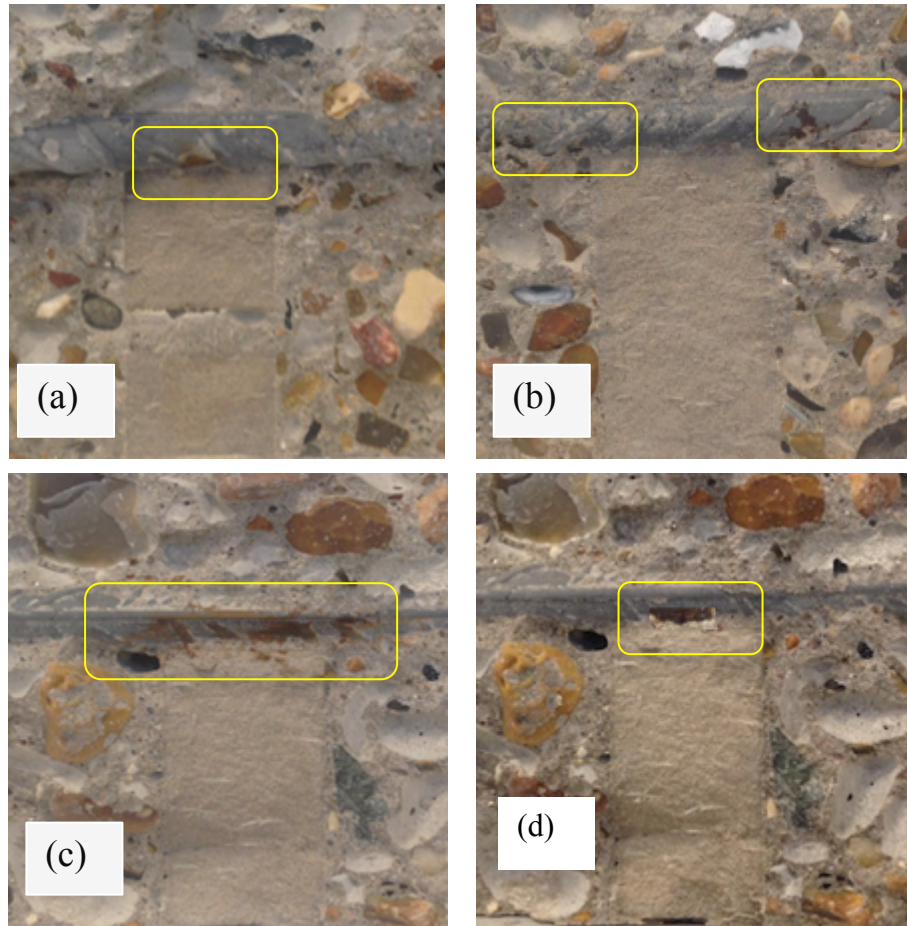


Figure 6.17 Corrosion initiation at cementitious spacer location; (a) capillary rise for 800 days, MSA=10mm, (b) wetting and drying cycles for 740 days, MSA=10mm, (c) capillary rise for 800 days, MSA=20mm, (d) wetting and drying cycles for 740 days, MSA=20mm.

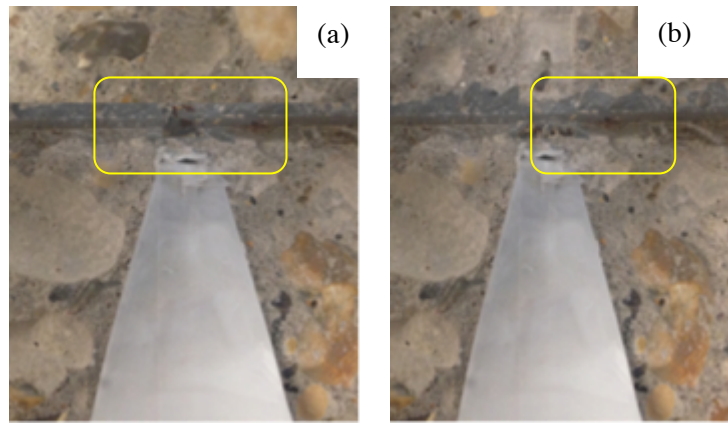


Figure 6.18 Corrosion initiation at plastic spacer location; (a) capillary rise for 800 days, MSA=20mm, (b) wetting and drying cycles for 740 days, MSA=20mm.

6.6.3 Influence of spacers on time to corrosion initiation

Figure 6.19 show typical measured and predicted chloride profile at plastic spacer interface with concrete. It is predicted that chloride concentration will reach the assumed chloride threshold level of 0.4% wt. of cement e at 50 mm cover depth after 21 years of exposure. The modelled time to corrosion initiation for different samples is listed in Table 6.8.

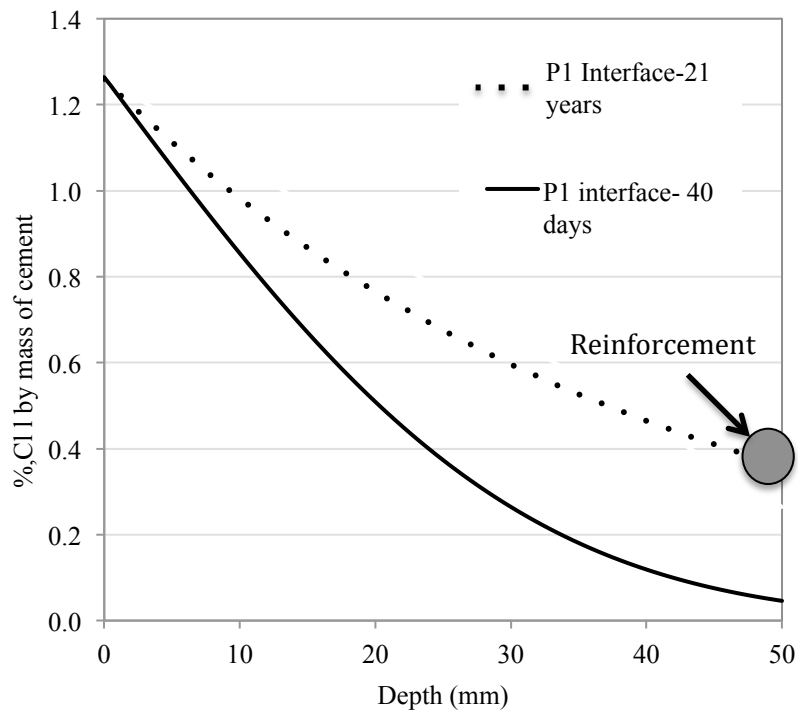


Figure 6.19 Measured and predicted chloride profiles at spacer interface with concrete.
Series II sample dried at 40°C for 90 days and exposed to salt solution for 90 days.

Table 6.8 Predicted time to corrosion initiation (years).

Spacer/ location	Series II		Series III	
	Exposure			
	40 days	90 days	60 days	90 days
Co	49	48	47	43
C-interface	39	37	38	35
P-interface	25	21	24	27

It is very clear that the inclusion of spacer accelerates the time to corrosion initiation and therefore reduces the expected service life. The effect is most significant in the case of plastic spacer where the predicted service life is almost half that of the control sample. The expected service life for samples with cementitious spacer is around 70% of the control. However, these predicted time to corrosion initiation appear to contradict with the actual corrosion initiation results shown in Section 6.6.2. It was observed that in some samples, corrosion had initiated near the spacer after only 2 years of exposure rather than the predicted period of

more than 21 years.

6.7 Discussion

The results presented in this chapter shows that the inclusion of spacers increases chloride ions transport in concrete, initiates local corrosion and reduce the predicted service life. The net effect depends on the type of spacer, the conditioning method prior to chloride exposure, the length and the mechanism of the exposure. The results clearly show that spacers facilitate chloride transport where the aggregate fractions, MSA, curing, w/c ratio, conditioning regime exposure condition and duration were held constant. Concrete samples containing plastic spacers consistently gave the highest chloride diffusion coefficients and chloride surface concentration along its interface, followed by samples with cementitious spacers. The control samples had the lowest coefficients and concentration in all cases excluding the case of chloride penetration through cementitious spacer.

There have been no previous studies on the effect of spacers on transport properties. However, the control sample results can be compared to those available in literature presented in Table 6.9. The chloride diffusion coefficient and surface chloride concentration increased over time. Bentz et al. [1996] reported similar trend while [Hooton et al., 1997;Nokken et al., 2006] reported a decrease in diffusion coefficient over time. The surface concentration was not influenced by exposure time [Nokken et al., 2006].

The measured diffusion coefficient and surface concentration for Series II samples (Table 6.4) and modified Series III (Table 6.7) dried at 20°C, 55%RH prior to chloride exposure were relatively higher than those reported by [Hooton et al., 1997;Liu et al., 2011;Nokken et al., 2006;Yang, 2005;Yang et al., 2006]. This could be due the background chloride concentration in the original mix ingredients, which was not subtracted from the measured total chloride concentrations.

The similarity between results of Series II samples (Table 6.4) and modified Series III (Table 6.7) is due to elimination of absorption effect resulting from initial drying of samples. The slight increase might be due to the 1-day exposure of Series I. It should be noted that the 1-day exposure was chosen based on sorptivity results to reach full saturation of samples (Section 4.3.3). However, it seems likely that this initial exposure should be for a longer

period to ensure full saturation of samples, beyond which chloride penetration occurs due to diffusion only. Other factors include the effect of other mechanisms of chloride penetration such as chloride binding and wicking which were not investigated in this thesis.

Table 6.9 Reported values of the diffusion coefficients and surface chloride contents of specimens exposed to chloride solution.

Study	Diffusion coefficient (10^{-12} m ² /s)	C _s (%)	w/c ratio	Exposure (days)	Notes
[Liu et al., 2011]	6	10.4	0.4	90	Modified salt ponding test. To eliminated absorption and 7 days moist curing with 21 days drying
[Yang, 2005]	8.09	.38	.35	90	Salt ponding
	16.5	.38	.45		
[Yang et al., 2006]	1.672	-	.40	90	Salt ponding
[Nokken et al., 2006]	19.08	.33	.40	28	Bulk diffusion
	11.75	.34		90	
[Hooton et al., 1997]	7	-	.40	90	Salt ponding
	3.3	-		365	
[Bentz et al., 1996]	12	2.93	.40	1year	Submerged specimen
	20	4.72		4years	

The effect of spacers can be compared to the influence of aggregates presence in concrete. Penetration of chlorides into concrete depends on the chloride ion diffusion coefficient of the cement paste, aggregates, aggregate-paste ITZ and cracks [Hobbs, 1999]. The presence of aggregates can vary the the concrete chloride diffusion coefficient by a factor of 10 because increasing aggregate content will cause a reduction in cement content. This might increase or decrease the concrete chloride diffusion coefficient depending on the diffusivity of the aggregate relative to the cement paste. Diffusion coefficient also varies depending on the ITZ volume content and tortuosity [Caré, 2003]. The substantial increase in chloride ions transport for samples with spacers can be attributed to the porous interface zone between the spacer and concrete which forms a continuous link that provide an easy path for mass/ionic transport as indicted in Chapter 5.

Estimating the time to corrosion initiation was based on a simplified analytical method without considering time dependency of the diffusion coefficient and surface concentration. Diffusion coefficients show clear time dependence and the surface chloride concentration increases considerably over time [Costa and Appleton, 1999]. Hence, service-life modelling should account for this variation. It should be pointed that this simplified method also did not consider the effects of concrete cracking, curing and conditioning regimes, and other chloride transport mechanisms. The influence of service load-induced cracking on corrosion initiation should be taken into account when dealing with corrosion in reinforced concrete structures [Arya and Wood, 1995]. As the measured diffusion coefficients are higher than that reported in literature, this explains the much-reduced estimated time to corrosion.

The estimated time to corrosion appear to contradict the visual observation reported Section 6.6.2 whereby corrosion was observed in seven samples at the location of the spacers. However, the remaining beams showed no corrosion products after 2 years of exposure. The seven samples showed corrosion at the location of spacer only with no corrosion products noted elsewhere.

6.8 Conclusions

The influence of plastic and cementitious spacers on the transport of chloride ions through concrete, and the initiation of chloride-induced reinforcement corrosion was investigated. Cylindrical concrete samples and small reinforced concrete beams with concrete cover of 50 mm and maximum aggregate size (MSA) of 10 and 20 mm were prepared. Samples were cured for 28 days in fog room, then conditioned to designated periods at 20°C 55% RH or 40°C oven prior to exposing specimens to 3% NaCl solutions for various periods of time. The distribution of chloride ingress, particularly near the interface between spacers and concrete matrix was studied using μ XRF. Subsequently, chloride diffusion coefficient and surface concentrations were calculated from best-fit to Fick's 2nd law. Concrete samples containing plastic spacers consistently gave the least resistance to chloride transport, followed by samples with cementitious spacers. The control samples (without spacers) had the highest resistance to chloride transport in all cases. It is evident that spacer-concrete interface is the preferential path for penetration of chlorides. Hence, the presence of spacer can accelerate time to corrosion initiation and potentially reduce the service-life of reinforced concrete structures significantly.

Chapter 7 Conclusions, implications and recommendations

7.1 Main conclusions

Limited studies have investigated the effect of spacers on the durability of concrete structures. There is also a lack of research on understanding the effect of spacers on mass transport properties and the microstructure of concrete in the cover zone. Therefore, the aim of this thesis was to establish the effect of spacers on the transport properties, chloride-induced reinforcement corrosion and microstructure of concrete. A better understanding of the effect of reinforcement spacers on these properties can assist in improving the durability of concrete structures and developing more accurate service-life modeling.

This thesis clearly confirms that the inclusion of spacers increases the transport properties of concrete. The substantial increase in transport is attributed to the porous interface zone between the spacer and concrete, which forms a continuous link that span the entire depth of the sample providing an easy path for ingress of aggressive species to reach embedded steel reinforcement.

The main conclusions arising from this thesis are as follows:

- Spacers increase oxygen diffusivity, oxygen permeability, water sorptivity and chloride diffusivity. The extent of the effect of spacers on transport properties depends on the spacer type, curing age, MSA and drying method. Overall, spacers increase oxygen diffusivity, permeability and water sorptivity by a factor of 1.3 to 3.4 relative to the control. Spacers increase chloride diffusivity by a factor of 1.1 to 1.4 relative to the control.
- The microstructure of the spacer-concrete interface indicated significantly lower cement content and higher porosity compared to the 'bulk paste' farther away from the interface. The porosity near the spacer-concrete interface is about 1.5 to 5 times that of the bulk paste, depending on the spacer type and conditioning regime. The width of the disturbed microstructure is around 50 μm from the spacer. Spacers disrupt the packing of cement grains and increase the local w/c ratio and heterogeneity of the paste microstructure.

- Concrete samples containing plastic spacers consistently gave the least resistance to transport and highest porosity gradient at the spacer-concrete interface. This is followed by samples with cementitious and steel spacers. The control samples (without spacers) showed the highest resistance to transport in all cases.
- Increasing the surface roughness of plastic spacer in order to improve its bond to concrete matrix resulted in a reduction of transport properties by a factor of 1.1 - 1.2 compared to samples containing unmodified spacer
- It is evident that the spacer-concrete interface provides a preferential path for ingress of aggressive species such as chloride. Fluorescent epoxy penetration occurred mainly along the spacer-concrete interface and also within the concrete inside plastic spacers. μ XRF showed that the spacer-concrete interface facilitates chloride penetration.
- Modeling suggests that the inclusion of spacer accelerates the time required to reach chloride threshold level for corrosion initiation and therefore it can reduce the service life of concrete structures.
- Increasing the severity of drying prior to transport testing increases the severity of the effect of spacers on mass transport and microstructure. This is due to the difference in thermal coefficient of expansion and drying shrinkage characteristics between the spacer and the surrounding concrete, in particular for the case of plastic spacers.
- Current standards of practice provide little guidance on spacer material, manufacture and shape. There is also no guidance on performance testing of the durability of spacers or concrete containing spacers.

7.2 Implications

It is well known that low quality and inadequate concrete cover is a major factor for premature degradation of concrete structures all over the world resulting into huge replacement or repair costs. Spacers seem small and inconsequential. However, they are left permanently in the structure and their presence provides easy access of moisture, oxygen and aggressive agents like chlorides through spacer or its interface with concrete. Spacers initiate early corrosion and may reduce the service-life of

reinforced concrete structures. Hence, this will compromise the durability and long-term performance of concrete structures

The findings of this thesis suggest that the assumed protection afforded by a targeted concrete cover depth will not be achieved at the location of spacer as the transport coefficients and porosity gradients at the spacer-concrete interface are significantly higher than elsewhere. For instance the effect of using plastic spacer is similar to reducing the cover by almost half. It should be noted that the conditioning regimes used in this thesis (50°C, 20°C, 55%RH or 20°C, 75%RH) are within the range of natural exposure environments experienced in real structures. Without available standards advising designers on specifying spacer's material according to the durability requirements of particular structural member might result with specifying a spacer that can compromise the long-term performance of the structure.

Contractors would follow design engineers drawings and specification and would refer to current standard for spacer choice and instillation. However, if these guideline and instruction are not provided then contractors will base their decision mainly on cost purposes. The quality of the used spacers can be questioned if there are no standards conspiring the shape or material specifications of the spacers neither testing its bond with surrounding concrete.

It should also be noted that single cover spacers were used in this study for the sake of convenience because it allowed testing to be carried out on relatively small samples. However, continuous spacers are used in some structures for example in bridge decks and large slabs. These continuous spacers will create a spacer-concrete interface area that is substantially larger compared to that of single cover spacers. Therefore, the findings from this study suggest that the use of such continuous spacers would be more problematic in terms of the effect on transport of aggressive species and long-term durability.

Furthermore, the samples in this study were tested under non-loaded conditions. In real concrete structures, parts of certain elements will be subjected to tensile stresses from working loads, for example at the bottom of beam or slab. It is expected that tensile stresses will increase the likelihood of cracking and debonding at the spacer-concrete interface. Thus the porous spacer-concrete interface is likely to widen and

propagate, and potentially accelerate the transport of aggressive species and degradation.

7.3 Recommendations

Many factors influence the use of spacers in reinforced concrete structures. Therefore, several recommendations are provided for spacer specifications in standards of practice and for improving spacer design. Finally, recommendations for further research are presented.

Current standards need to provide further guidance on spacer material; manufacture and shape to ensure that the properties of the spacer-concrete interface are equal to or better than that of the concrete cover. Standards should require testing of the durability of concrete with spacers and of cementitious spacers, similar to the performance-based testing required for load capacity. It is also suggested that the British Standards should follow the approach by ACI 315-99, CRSI's Manual of Standard Practice and DIN EN 13670:2011-03 to provide guidance on specifying spacers according to exposure condition and to require the inclusion of spacers specifications on contract documentations or drawings.

To minimise the global effect of spacers on concrete structure and reduce the number of spacers used per structural member; current codes can work towards increasing the spacing of spacers in structural elements. This can be achieved by improving the load capacity of spacers to carry the additional loading of reinforcement and construction work due to increase in spacing.

All of the testing carried out in this study show that the interface of spacer with concrete is the preferential path for transport because of its higher porosity. Thus, the main challenge is to improve the microstructure of the spacer-concrete interface. In this thesis, a small study was carried study to increase the surface roughness of plastic spacers and this appeared to produce a slight decrease in transport properties. Further modifications to the surface roughness of plastic and cementitious spacers can be carried out by sand blasting for example.

The use of supplementary cementitious materials such as microsilica, fly ash and GGBFS in concrete is known to densify the microstructure of the aggregate-paste interfacial transition zone. This is because their particle size distribution is much

smaller than that of Portland cement and this promotes a more efficient packing of cementitious materials at the aggregate-paste ITZ [Ollivier et al., 1995]. Therefore, it would be interesting to carry out a study to establish whether the use of such supplementary cementitious materials has a similar effect on the microstructure of spacer-concrete interface and to what extent does it influence mass transport properties.

The spacers tested in this thesis cover a range of spacer types and sizes, but they were by no means exhaustive. Future work could investigate a wider range of spacers for example circular plastic spacers and continuous spacers of varying depths. In addition a wider range of concrete types should be tested (e.g. self-compacting concrete, high-performance concrete) for a more comprehensive understanding of the influence of spacers on concrete microstructure and durability. The effect of supplementary cementitious materials such as silica fume, fly ash and GGBFS on the spacer-concrete interface and overall performance of concrete would be of interest.

Further work could be carried out to investigate the effect of spacers on carbonation-induced corrosion and transport of other aggressive species such as sulfates. As mentioned earlier, the results presented in this study were obtained from sound and unloaded concrete samples. Real concrete under loading will crack and this can lead to additional weakening of the spacer-concrete interface. The effect of structural loading on spacers and properties of the spacer-concrete interface should be investigated by future studies.

An aspect of this thesis that can be improved concerns the use of simple analytical method to estimate the time to corrosion initiation and residual service-life (Chapter 7). More advanced and sophisticated models are available that considers for example the variation in diffusion coefficient and surface concentration over time and space, and takes account of effects such as transport under non-saturated conditions, chloride binding and wick action. Furthermore, the time to corrosion initiation is a conservative estimate of service life. A more accurate and rigorous approach that considers the propagation phase and damage induced by reinforcement corrosion is required. Clearly, more studies are required to quantify the extent of the effect of spacers on long-term durability and service-life of concrete structures.

Reference

- Abyaneh, S. D., Wong, H. S. & Buenfeld, N. R. 2013. Modelling the Diffusivity of Mortar and Concrete Using a Three-Dimensional Mesostructure with Several Aggregate Shapes. *Computational Materials Science*, 78, 63-73.
- ACI 2004. *Sp-66(04): Aci Detailing Manual*, American Concrete Institute.
- American Concrete Institute 2004. *Sp-66(04): Aci Detailing Manual*, American Concrete Institute.
- American Concrete Institute 2011. Aci 318-11. Building Code Requirements for Structural Concrete and Commentary. ACI.
- Arya, C. & Wood, L. A. 1995. *The Relevance of Cracking in Concrete to Corrosion of Reinforcement*, Concrete Society.
- Bentz, E. C., Thomas, M. D. A. & Evans, C. M. 1996. Chloride Diffusion Modelling for Marine Exposed Concretes. *Special Publication-Royal Society of Chemistry*, 183, 136-145.
- British Standard Institution 2010. Bs En 13670: Execution of Concrete Structures. British standard institution.
- British Standards Institution 2001a. Bs 7973-1. Spacers and Chairs for Steel Reinforcement and Their Specification. *Product performance requirements*. London: BSI.
- British Standards Institution 2001b. Bs 7973-2. Spacers and Chairs for Steel Reinforcement and Their Specification. *Fixing and application of spacers and chairs and tying of reinforcement* London: British Standards Institution.
- British Standards Institution 2009. Bs En 12390-7. Testing Hardened Concrete. *Density of hardened concrete*. London: BSI.
- Buenfeld, N. R. 1995. Measuring and Modelling Transport Phenomena in Concrete for Life Prediction of Structures. *Prediction of Concrete Durability*, 77-90.
- Buenfeld, N. R. & Okundi, E. 1998. Effect of Cement Content on Transport in Concrete. *Magazine of Concrete Research*, 50.
- Cabrera, J. G. & Lynsdale, C. J. 1988. A New Gas Permeameter for Measuring the Permeability of Mortar and Concrete. *Magazine of Concrete Research*, 40, 177-182.
- Caré, S. 2003. Influence of Aggregates on Chloride Diffusion Coefficient into Mortar. *Cement and Concrete Research*, 33, 1021-1028.
- Chemrouk, M. Influence of Poor Workmanship and Construction Defects on the Durability and Strength of Concrete. Concrete Durability:- achievement and enhancement, 2008 Dundee, Scotland. IHS BRE Press, 153-164.
- Cheng, H.-D. & Sun, Y. 2000. A Hierarchical Approach to Color Image Segmentation Using Homogeneity. *Image Processing, IEEE Transactions on*, 9, 2071-2082.
- Claisse, P. A. 2014. *Transport Properties of Concrete: Measurements and Applications*, Elsevier.
- Clark, L. A., Shammass-Toma, M. G. K., Seymour, D. E., Pallet, P. F. & Marsh, B. K. 1997. How Can We Get the Cover We Need? *Structural Engineer*, 75.
- Concrete Reinforcing Steel Institute 2009. *Manual of Standard Practice*, CRSI.

- Concrete Reinforcing Steel Institute 2011. *Placing Reinforcing Bars*, Concrete Reinforcing Steel Institute.
- Concrete Society 1981. Choosing the Right Bar Support in Aggressive Environments. *Concrete Technology Today*.
- Concrete society 1989. Spacers for Reinforced Concrete. London.
- Costa, A. & Appleton, J. 1999. Chloride Penetration into Concrete in Marine Environment—Part I: Main Parameters Affecting Chloride Penetration. *Materials and Structures*, 32, 252-259.
- Deutscher Beton-Und Bautechnik-Verein E.V. (DBV) 2011. Leaflet - Spacers According to Eurocode 2. DBV.
- Deutsches Institut für Normung (DIN) 2011. Din En 13670:2011-03:Execution of Concrete Structures ; En 13670:2009. Deutsches Institut für Normung (DIN).
- Diamond, S. & Huang, J. 2001. The Itz in Concrete—a Different View Based on Image Analysis and Sem Observations. *Cement and concrete composites*, 23, 179-188.
- Echlin, P. 2011. *Handbook of Sample Preparation for Scanning Electron Microscopy and X-Ray Microanalysis*, Springer Science & Business Media.
- Edmond, C. B. 2001. A New Paradigm for Practice Education. *Nurse Educ Today*, 21, 251-9.
- Ernst, T., Berman, T., Buscaglia, J., Eckert - Lumsdon, T., Hanlon, C., Olsson, K., Palenik, C., Ryland, S., Trejos, T. & Valadez, M. 2014. Signal - to - Noise Ratios in Forensic Glass Analysis by Micro X - Ray Fluorescence Spectrometry. *X - Ray Spectrometry*, 43, 13-21.
- Euro code 2 2004. Design of Concrete Structures-Part 1-1: General Rules and Rules for Buildings, Bs En 1992-1-1: 2004. *British Standards (BSi)*.
- European Concrete Societies, N. 2001. *Concrete Best Practice: Guidance from a European Perspective*, Concrete Society.
- Frost, A. 2005. The Material World. *New civil engineer*, Concrete engineering supplement, 24.
- Garbacz, A., Courard, L. & Kostana, K. 2006. Characterization of Concrete Surface Roughness and Its Relation to Adhesion in Repair Systems. *Materials characterization*, 56, 281-289.
- Gjorv, O. E. 2011. Durability of Concrete Structures. *Arabian Journal for Science and Engineering*, 36, 151-172.
- Glass, G. K. & Buenfeld, N. R. 1997. The Presentation of the Chloride Threshold Level for Corrosion of Steel in Concrete. *Corrosion Science*, 39, 1001-1013.
- Glass, G. K. & Buenfeld, N. R. 2000. Chloride - Induced Corrosion of Steel in Concrete. *Progress in Structural Engineering and Materials*, 2, 448-458.
- Hall, C. 1977. Water Movement in Porous Building Materials—I. Unsaturated Flow Theory and Its Applications. *Building and Environment*, 12, 117-125.
- Hobbs, D. W. 1999. Aggregate Influence on Chloride Ion Diffusion into Concrete. *Cement and Concrete Research*, 29, 1995-1998.
- Hong, K. & Hooton, R. D. 1999. Effects of Cyclic Chloride Exposure on Penetration of Concrete Cover. *Cement and Concrete Research*, 29, 1379-1386.
- Hooton, R. D., Pun, P., Kojundic, T. & Fidjestol, P. Influence of Silica Fume on Chloride Resistance of Concrete. Proceeding International Symposium of High Performance Concrete, Chicago, (P. Johal, Precast Prestressed Concrete

- Institute) pp, 1997. 245-249.
- Horne, A. T., Richardson, I. G. & Brydson, R. M. D. 2007. Quantitative Analysis of the Microstructure of Interfaces in Steel Reinforced Concrete. *Cement and Concrete Research*, 37, 1613-1623.
- Jahren, P. 1994. Carat - a Development Programme for New Reinforcement Chairs, . Oslo: BETONG- industrien 2/94.
- Julio, E. N. B. S., Branco, F. A. B. & Silva, V. t. D. 2004. Concrete-to-Concrete Bond Strength. Influence of the Roughness of the Substrate Surface. *Construction and Building Materials*, 18, 675-681.
- Kawahigashi, T., Kuzume, K. & Miyagawa, T. Deterioration Process and Estimation of Durability of Reinforced Concrete Beams in Long-Term Exposure to Marine Environment. Proceedings-japan society of civil engineers, 1999. DOTOKU GAKKAI, 71-84.
- Kenai, S. & Bahar, R. 2003. Evaluation and Repair of Algiers New Airport Building. *Cement and concrete composites*, 25, 633-641.
- King, E. S. & Dakin, J. M. 2001. *Specifying, Detailing and Achieving Cover to Reinforcement*, CIRIA.
- King, E. S., Dakin, J. M., Construction Industry, R., Information, A. & Concrete, S. 2001. *Specifying, Detailing and Achieving Cover to Reinforcement*, CIRIA.
- Klinkenberg, L. J. The Permeability of Porous Media to Liquids and Gases. Drilling and production practice, 1941. American Petroleum Institute.
- Lawrence, C. D. Transport of Oxygen through Concrete. In: Glasser, F. P., ed. The chemistry and Chemically-Related Properties of Cement, British Ceramic Society Proceedings, 1984. 277-293.
- Levitt, M. & Herbert, M. R. M. 1970. Performance of Spacers in Reinforced Concrete. *Civil Engineering*, 1-5.
- Liu, X., Chia, K. S. & Zhang, M.-H. 2011. Water Absorption, Permeability, and Resistance to Chloride-Ion Penetration of Lightweight Aggregate Concrete. *Construction and Building Materials*, 25, 335-343.
- Lutz, M. P., Monteiro, P. J. M. & Zimmerman, R. W. 1997. Inhomogeneous Interfacial Transition Zone Model for the Bulk Modulus of Mortar. *Cement and Concrete Research*, 27, 1113-1122.
- Mackey, G. & Januszek, R. 1995. Influence of Bar Chairs, Spacers and Blocks on Concrete Structures.
- Max Frank 2015. Frank: Spacer Technology. Germany: Max frank.
- Mehta, P. K. & Monteiro, P. J. M. 2013. *Concrete: Microstructure, Properties, and Materials*, McGraw-Hill Education.
- Neville, A. M. 2011a. Properties of Concrete.
- Neville, A. M. 2011b. *Properties of Concrete*, Harlow, England ; New York, Pearson.
- Nilsson, L. O. & Ollivier, J. P. 1995a. Chloride Transport Due to Wick Action in Concrete. *RILEM International workshop on chloride penetration into concrete*, 315-324.
- Nilsson, L. O. & Ollivier, J. P. Chloride Transport Due to Wick Action in Concrete. RILEM International workshop on chloride penetration into concrete, 1995b. RILEM Publications SARL, 315-324.
- Nokken, M., Boddy, A., Hooton, R. D. & Thomas, M. D. A. 2006. Time Dependent Diffusion in Concrete—Three Laboratory Studies. *Cement and Concrete Research*, 36, 200-207.

- Ollivier, J. P., Maso, J. C. & Bourdette, B. 1995. Interfacial Transition Zone in Concrete. *Advanced Cement Based Materials*, 2, 30-38.
- Omer, T. Y., Suliman, W. A., Thomas, L. & Joseph, J. 2013. Perception of Nursing Students to Two Models of Preceptorship in Clinical Training. *Nurse Educ Pract*, 13, 155-60.
- Pease, B. J., Geiker, M. R., Stang, H. & Weiss, J. 2010. *Influence of Concrete Cracking on Ingress and Reinforcement Corrosion*. Purdue UniversityPurdue University.
- Poulsen, E. & Mejlbro, L. 2010. *Diffusion of Chloride in Concrete: Theory and Application*, Taylor & Francis.
- Rashed, A. I. & Williamson, R. B. 1991. Microstructure of Entrained Air Voids in Concrete, Part I. *Journal of materials research*, 6, 2004-2012.
- Rayner, R. 2005. Concrete Spacers. *Concrete*, 39, 31-31.
- Rostam, S. 1996. High Performance Concrete Cover—Why It Is Needed, and How to Achieve It in Practice. *Construction and Building Materials*, 10, 407-421.
- Rostam, S. 2005. Service Life Design of Concrete Structures-a Challenge to Designers as Well as to Owners. *Asian Journal of Civil Engineering (Building and Housing)*, 6, 423-445.
- Russ, J. C. 2002. *The Image Processing Handbook, Fourth Edition*, CRC Press.
- Santos, P. M. D. & Julio, E. N. B. S. 2007. Correlation between Concrete-to-Concrete Bond Strength and the Roughness of the Substrate Surface. *Construction and Building Materials*, 21, 1688-1695.
- Scrivener, K. L., Bentur, A. & Pratt, P. L. 1988. Quantitative Characterization of the Transition Zone in High Strength Concretes. *Advances in Cement Research*, 1, 230-237.
- Scrivener, K. L., Crumie, A. K. & Laugesen, P. 2004. The Interfacial Transition Zone (Itz) between Cement Paste and Aggregate in Concrete. *Interface Science*, 12, 411-421.
- Seymour, D., Shammas - Toma, M. & Clark, L. 1997. Limitations of the Use of Tolerances for Communicating Design Requirements to Site. *Engineering Construction and Architectural Management*, 4, 3-22.
- Shaw, C. 2007. Cover to Reinforcement-Getting It Right. *Structural Engineer*.
- Shaw, C. Long Term Durability of Plastics Spacers in Reinforced Concrete: A Case Study. Concrete Durability:- achievement and enhancement, 2008 Dundee, Scotland,UK. IHS BRE Press, 259-269.
- Shaw, P., Materialrontgen, A. & Kutti, T. 2003. Field Measurement and Experience of Chloride Induced of Reinforcement in Submerged Structures. Goteborg, Sweden: AB Fardig Betong,.
- Smith, J. L. & Virmani, Y. P. 2000. Materials and Methods for Corrosion Control of Reinforced and Prestressed Concrete Structures in New Construction.
- Stanish, K. D., Hooton, R. D. & Thomas, M. D. 2001. Testing the Chloride Penetration Resistance of Concrete: A Literature Review. 2001.
- Struble, L. 1987. Microstructure and Fracture at the Cement Paste-Aggregate Interface. *MRS Online Proceedings Library*, 114, null-null.
- Stutzman, P. E. & Clifton, J. R. Specimen Preparation for Scanning Electron Microscopy. Proceedings of the international conference on cement microscopy, 1999. Citeseer, 10-22.
- Tang, L. & Utgenannt, P. 2009. A Field Study of Critical Chloride Content in

- Reinforced Concrete with Blended Binder. *Materials and Corrosion*, 60, 617-622.
- Tuutti, K. 1982. Corrosion of Steel in Concrete.
- Vik, O. T. K. 2002. The Role of Bar Supports in Combatting Corrosion in Reinforced Concrete. In: Engineering, C. S. f. C. (ed.) *The sixth International Conference on Short and Medium Span Bridges*,. Vancouver, Canada.
- Volkwein, A. 1993. The Capillary Suction of Water into Concrete and the Abnormal Viscosity of the Porewater. *Cement and Concrete Research*, 23, 843-852.
- Wahid, F. A. 2015. *Characterising Concrete Using Micro X-Ray Fluorescence*, Imperial College London, Phd Thesis (in Progress).
- Wong, H. S. 2006. *Quantifying the Pore Structure of Cement-Based Materials Using Backscattered Electron Microscopy*. Imperial College London (University of London).
- Wong, H. S. & Buenfeld, N. R. 2006a. Euclidean Distance Mapping for Computing Microstructural Gradients at Interfaces in Composite Materials. *Cement and Concrete Research*, 36, 1091-1097.
- Wong, H. S. & Buenfeld, N. R. 2006b. Patch Microstructure in Cement-Based Materials: Fact or Artefact? *Cement and Concrete Research*, 36, 990-997.
- Wong, H. S., Head, M. K. & Buenfeld, N. R. 2006. Pore Segmentation of Cement-Based Materials from Backscattered Electron Images. *Cement and Concrete Research*, 36, 1083-1090.
- Wong, H. S., Matter, K. & Buenfeld, N. R. 2013. Estimating the Original Cement Content and Water-Cement Ratio of Portland Cement Concrete and Mortar Using Backscattered Electron Microscopy. *Magazine of Concrete Research*, 65, 693-706.
- Wong, H. S., Pappas, A. M., Zimmerman, R. W. & Buenfeld, N. R. 2011. Effect of Entrained Air Voids on the Microstructure and Mass Transport Properties of Concrete. *Cement and Concrete Research*, 41, 1067-1077.
- Wong, H. S., Zobel, M., Buenfeld, N. R. & Zimmerman, R. W. 2009. Influence of the Interfacial Transition Zone and Microcracking on the Diffusivity, Permeability and Sorptivity of Cement-Based Materials after Drying. *Magazine of Concrete Research*, 61, 571-589.
- Wu, Z., Wong, H. S. & Buenfeld, N. R. 2015. Influence of Drying-Induced Microcracking and Related Size Effects on Mass Transport Properties of Concrete. *Cement and Concrete Research*, 68, 35-48.
- Yang, C. C. 2005. A Comparison of Transport Properties for Concrete Using the Ponding Test and the Accelerated Chloride Migration Test. *Materials and Structures*, 38, 313-320.
- Yang, C. C., Cho, S. W. & Wang, L. C. 2006. The Relationship between Pore Structure and Chloride Diffusivity from Ponding Test in Cement-Based Materials. *Materials chemistry and physics*, 100, 203-210.

Appendix 1 Technical drawings

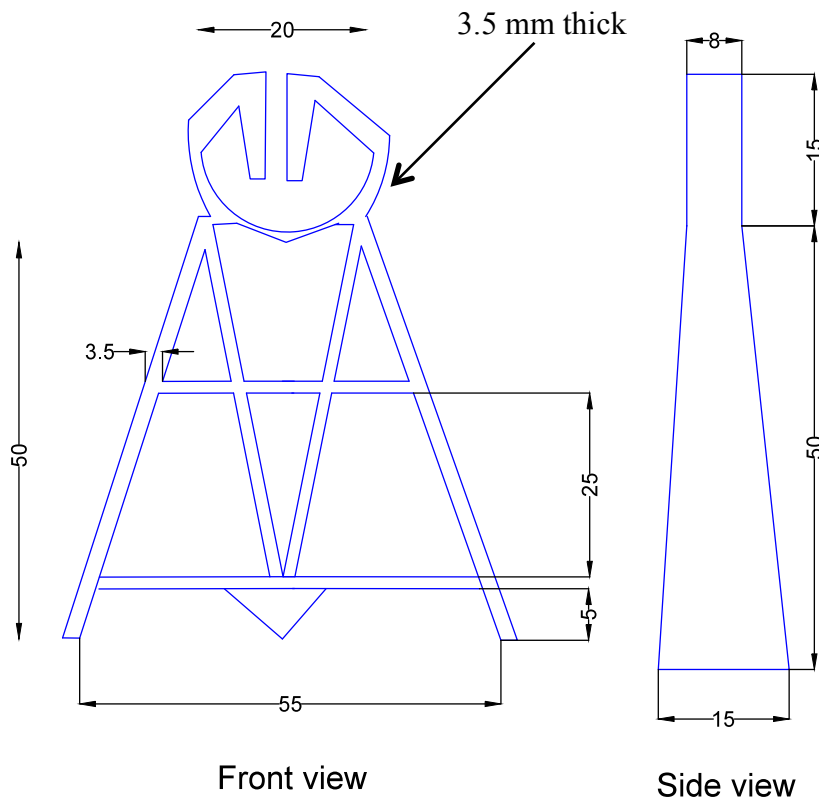


Figure 1. Dimensioned technical drawing of plastic spacer used in this study.

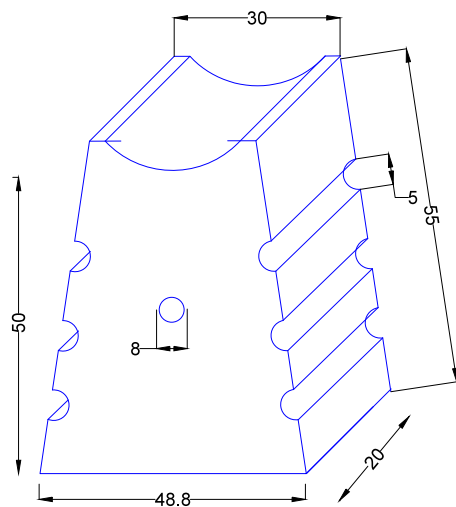


Figure 2. Dimensioned technical drawing of cementitious spacer used in this study.

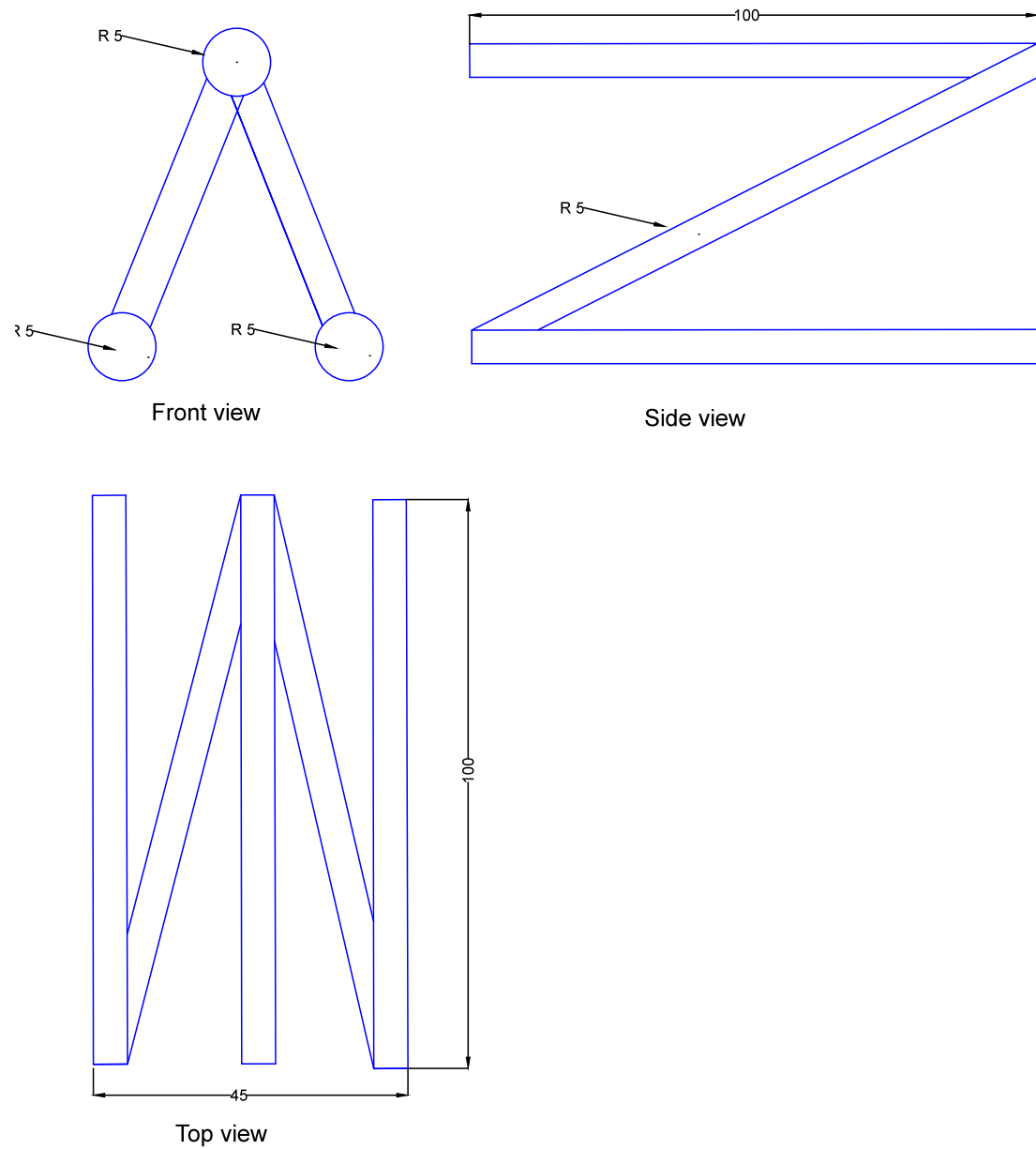


Figure 3. Dimensioned technical drawing of sectioned steel wire chair used in this study

Appendix 2 Mass transport results

Table 1. Results O₂ diffusivity, O₂ permeability, and sorptivity. Standard errors are shown in italic.

Series	Spacer	Depth (mm)	O ₂ diffusivity ($\times 10^{-8} \text{ m}^2/\text{s}$)				O ₂ permeability ($\times 10^{-17} \text{ m}^2$)				Sorptivity ($\text{g}/\text{m}^2 \cdot \text{min}^{0.5}$)			
			20°C, 50%RH		50°C	20°C, 75%RH	20°C, 50%RH		50°C	20°C, 75%RH	20°C, 50%RH		50°C	20°C, 75% RH
			3d	28d	28d	28d	3d	28d	28d	28d	3d	28d	28d	28d
C10	Co	25	3.78	2.56	-	-	6.98	4.37	-	-	59.51	51.8	-	-
			<i>0.24</i>	<i>0.05</i>	-	-	<i>0.02</i>	<i>0.03</i>	-	-	<i>0.83</i>	<i>1.47</i>	-	-
		50	3.73	2.74	5.85	2.04	3.78	2.01	5.11	1.52	71.77	60	73	57
			<i>0.23</i>	<i>0.27</i>	<i>0.37</i>	<i>0.05</i>	<i>0.02</i>	<i>0.09</i>	<i>0.09</i>	<i>0.1</i>	<i>1.28</i>	<i>1.04</i>	<i>1.58</i>	<i>0.7</i>
	C1	25	4.7	3.26	-	-	12.7	9.4	-	-	68.24	60.29	-	-
			<i>0.2</i>	<i>0.17</i>	-	-	<i>0.02</i>	<i>0.02</i>	-	-	<i>1.44</i>	<i>1.51</i>	-	-
		50	4.64	3.25	10.53	2.62	7.01	6.01	9.46	4.35	76.00	69	86	65
			<i>0.26</i>	<i>0.01</i>	<i>0.81</i>	<i>0.23</i>	<i>0.04</i>	<i>0.2</i>	<i>0.27</i>	<i>0.18</i>	<i>1.20</i>	<i>2.04</i>	<i>1.02</i>	<i>1.71</i>
	P1	25	6.62	4.52	-	-	17.4	14	-	-	82.68	72.95	-	-
			<i>0.19</i>	<i>0.2</i>	-	-	<i>0.03</i>	<i>0.13</i>	-	-	<i>1.55</i>	<i>1.84</i>	-	-
		50	5.67	4.16	6.93	3.2	10.8	7.18	12	5.73	89.63	85	106	79
			<i>0.24</i>	<i>0.02</i>	<i>0.4</i>	<i>0.13</i>	<i>0.08</i>	<i>0.14</i>	<i>0.34</i>	<i>0.11</i>	<i>0.78</i>	<i>0.17</i>	<i>1.02</i>	<i>1.51</i>
	P2	50		4.32	14.47	2.85	-	6.69	7.51	4.64	-	81	97	69
			-	<i>0.02</i>	<i>0.36</i>	<i>0.11</i>	-	<i>0.13</i>	<i>0.19</i>	<i>0.09</i>	-	<i>0.16</i>	<i>1.68</i>	<i>1.33</i>

	P3	50	-	4.23	13.66	2.94	-	6.32	7.8	5.1	-	79	92	72
			-	0.18	0.34	0.12	-	0.12	0.14	0.1	-	0.17	1.6	1.38
	S1	50	3.87	2.96	6.26	2.7	3.92	3.6	6.2	1.7	64.94	65	79	63
			0.13	0.03	0.21	0.22	0.03	0.19	0.25	0.11	1.77	0.68	0.83	1.33
C20	Co	50	-	3.03	5.85	2.19	-	3.29	5.36	3	-	63.74	76.3	58.01
			-	0.13	0.37	0.12	-	0.16	0.09	0.15	-	1.11	1.66	1.01
	C1	50	-	3.61	11.31	2.92	-	7.48	11.1	6.9	-	77.4	100.74	68.82
			-	0.13	0.93	0.1	-	0.12	0.61	0.11	-	0.99	1.19	0.88
	P1	50	-	5.02	17.01	3.63	-	11.7	14.8	10.6	-	104.81	130.49	91.09
			-	0.5	0.48	0.42	-	0.26	0.54	0.24	-	2.24	2.81	1.94
	S1	50	-	3.99	7.19	2.89	-	4.57	6.6	4.22	-	69.76	84.22	62.16
			-	0.12	0.22	0.11	-	0.21	0.27	0.2	-	0.8	0.88	0.71

Appendix 3 Epoxy impregnated samples images

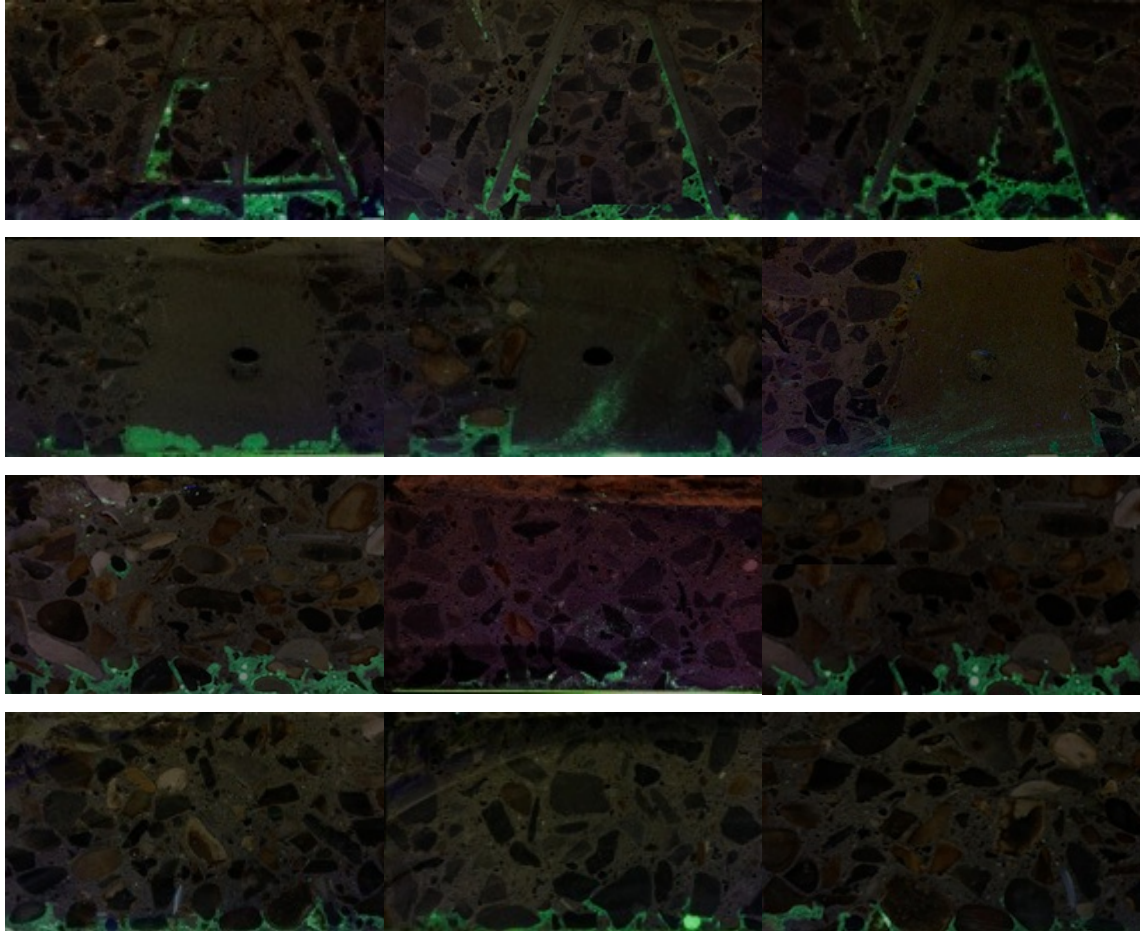


Figure 1. Cross-sections of the epoxy impregnated samples imaged under UV light and. Samples are C10-28d-50°C-50:C1, C10-28d-50°C-50:P1, C10-28d-50°C-50:S1 and C10-28d-50°C-50:Co (top to bottom). (Replicates 1-3)

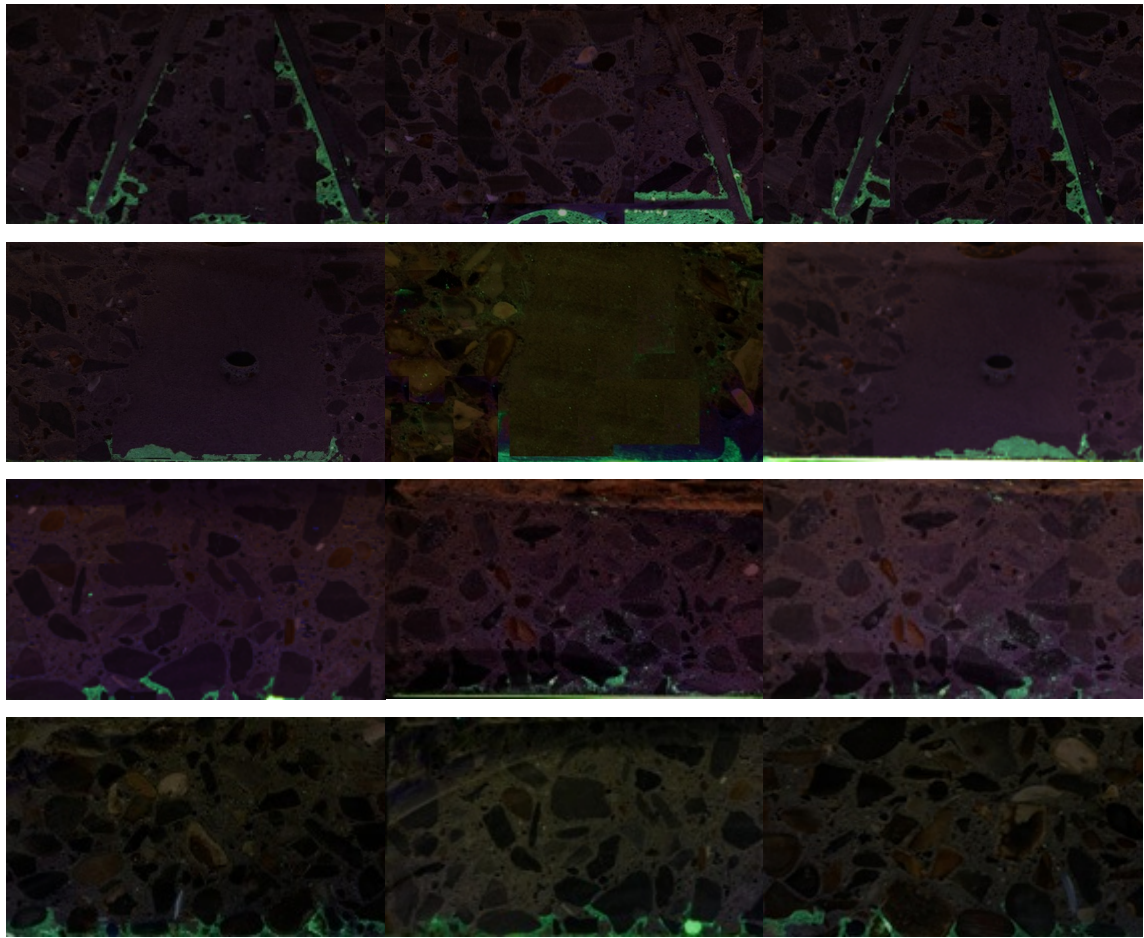


Figure 1. Cross-sections of the epoxy impregnated samples imaged under UV light and. Samples are C10-28d-20°C 55%RH -50:C1, C10-28d-20°C 55%RH -50:P1, C10-28d-20°C 55%RH -50:S1 and C10-28d-20°C 55%RH -50:Co (top to bottom). (Replicates 1-3)

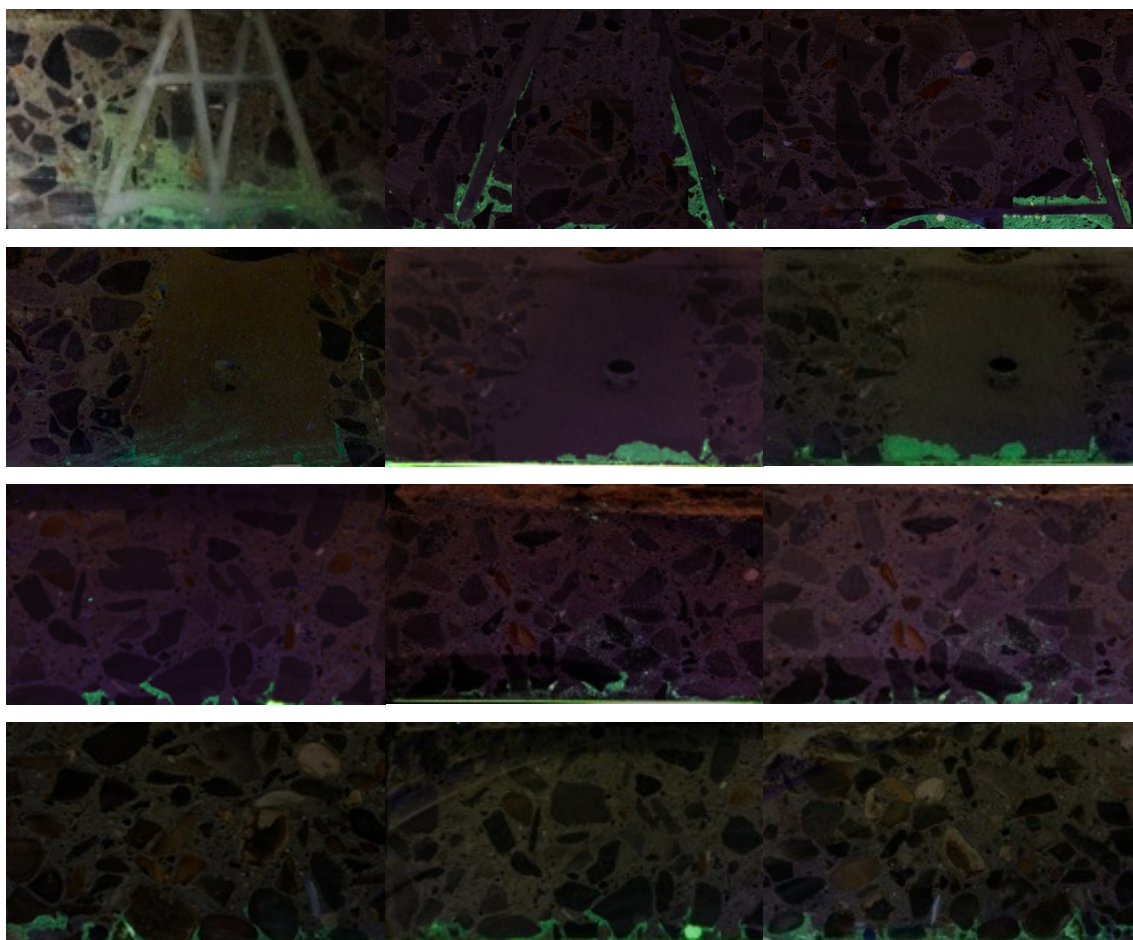


Figure 1. Cross-sections of the epoxy impregnated samples imaged under UV light and. Samples are C10-28d-20°C 70%RH-50:C1, C10-28d-20°C 70%RH -50:P1, C10-28d-20°C 70%RH -50:S1 and C10-28d-20°C 70%RH -50:Co (top to bottom). (Replicates 1-3)