Fundamental Characterisation of Surface and Internally Protected Concrete Pavement and Highways

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To

My Dad & Mom,

who always picked me up on time

and encouraged me to go on every adventure,

especially this one

Abstract

Despite excellent service history, concrete pavement faces accelerated deterioration due to water and chemical ingress through micro cracks and surface voids. Surface applied protective materials, especially silane, have been widely used to hinder the deterioration process of concrete structures. However, concrete pavements, in particular, are not protected at the moment due to the concerns over their frictional properties. The improper performance of silane when applied to wet surfaces and its inconvenient application method, especially if applied to concrete roadways and bridges, drove researchers to look for some new alternative materials. Accordingly, the internal incorporation of protective materials into fresh concrete mixtures and the application of some new alternative surface applied materials on concrete started to emerge. For the materials to be effectively benefited as protective treatments, some significant issues and impediments must be addressed by research: (I) The unsatisfactory mechanical properties emphasised in the literature as the main drawback of the internal integration method; (II) the affinity of the surface applied materials to moisture at the time of application, which is reflected on the rejection rate of concrete to the applied materials and, consequently, their efficacy in protecting concrete. In this research, the internal integration of crystalline material into fresh concrete and the application of new materials on the surface of matured concrete, namely; liquid crystalline material, fluoropolymer, silicate resin were used and compared with traditional silane. Standard and non-standard methodologies were utilised in this research to investigate the performance of the protective materials and to build an in-depth understanding of their mechanism of interaction with concrete pavement. Results demonstrated the enhancement of concrete's strength by more than 42% after optimising the added dosage of the integrated crystalline material and the water-to-cement ratio (w/c) of the concrete mix. Also, water absorption and chloride diffusion have been reduced by more than 65% and 90% respectively after the internal integration process. Applying the newly-developed surface applied materials to matured concrete with high moisture contents resulted in enhanced performance compared to silane when tested for water absorption and chloride penetration. Two standard and non-standard prolonged freeze-thaw investigations of all the materials, either internally integrated or surface applied, signified the adequate long-term performance of the treatments.

Overall, this research lays the foundations for using the proposed treatments in the construction industry.

Acknowledgements

Declaration

The work in this thesis is based on research carried out at Brunel University London, United Kingdom. I hereby declare that the research presented in this thesis is my own work except where otherwise stated, and has not been submitted for any other degree.

Publications emerged from this work

Journal articles:

1. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2019) 'Fundamental Interaction of Hydrophobic Materials in Concrete with Different Moisture Contents in Saline Environment', *Construction and Building Materials,* 207, pp. 122-135. https://doi.org/10.1016/j.conbuildmat.2019.02.119.

2. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2019) 'Moisture Evaluation of Concrete Pavement Treated with Hydrophobic Surface Impregnants', *International Journal of Pavement Engineering.* https://doi.org/10.1080/10298436.2019.1567917.

3. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2019) 'Optimum Mix Design for Internally Integrated Concrete with Crystallising Protective Material', *ASCE Journal of Materials in Civil Engineering,* 31(7), pp. 04019101-1- 04019101-8. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002694.

4. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2018) 'A Novel Approach of Introducing Crystalline Protection Material and Curing Agent in Fresh Concrete for Enhancing Hydrophobicity', *Construction and Building Materials,* 160, pp. 644-652. https://doi.org/10.1016/j.conbuildmat.2017.11.108

5. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2018) 'Development of Hydrophobic Concrete by Adding Dual-Crystalline Admixture at Mixing Stage', *Structural Concrete,* 19(5), pp. 1504-1511. https://doi.org/10.1002/suco.201700254

6. **Al-Kheetan, M.**, and Rahman, M. (2019) 'Integration of Anhydrous Sodium Acetate (ASAc) into Concrete Pavement for Protection against Harmful Impact of De-icing Salt', *JOM Journal of the Minerals, Metals & Materials Society* (Under review).

7. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2019) 'Extended Freeze-thaw Assessment of Internally Integrated Concrete Pavement with Sodium Acetate', *Cement and Concrete Research* (Under review).

8. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2019) 'Resistance of Hydrophobic Concrete Pavement with Different Moisture Contents to Advanced Freeze-thaw Cycles', *Cement and Concrete Composites* (Under preparation).

Conference papers:

9. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2017) 'Comparative Study of Different Hydrophobic Materials in Concrete Pavement Protection'. *The 8ᵗʰ International Conference on Water Repellent Treatment and Protective Surface Technology for Building Materials (Hydrophobe VIII).* Hong Kong, China, 7-9 December.

10. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2017) 'Influence of Crystalline Admixture on Fresh Concrete to Develop Hydrophobicity'. *Transportation Research Board 96ᵗʰ Annual Meeting,* Washington, D.C., United States, 8-12 January.

11. **Al-Kheetan, M.**, Rahman, M. and Chamberlain, D. (2017) 'Influence of Hydrophobic Admixture and Curing Agent on Water Resistant Concrete'. *Transportation Research Board 96ᵗʰ Annual Meeting,* Washington, D.C., United States, 8-12 January.

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List of Abbreviations

√t	Square root of time
°C	Celsius
μm	Micrometre
AASHTO	American Association of State Highway and Transportation Officials
ACI	American Concrete Institute
$AgNO_3$	Silver nitrate
ASTM	American Society for Testing and Materials
BS	British Standard
BS EN	British Standard European Norm
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C_4AF	Tetracalcium aluminoferrite
$C_9H_{20}O$	3,5,5-trimethylhexanol
$Ca(OH)_2$	Portlandite
$CaCO_3$	Aragonite
CH_3COOH	Acetic acid

CH$_3$COONa	Sodium acetate
C-S-H	Calcium silicate hydrated gel
EDX	Energy Dispersive X-ray
FT	Freeze-thaw
FTIR	Fourier-transform Infrared Spectroscopy
ATR-FTIR	Attenuated total reflectance-FTIR
gm	Grams
HNO$_3$	Nitric acid
ISAT	Initial Surface Absorption Test
Kg/m^3	Kilogram per cubic meter
Mg(OH)$_2$	Brucite
ml/m^2.s	Millilitre per square meters in second
MPa	Megapascal
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NH$_4$Fe(SO$_4$)$_2$	Ammonium ferric sulphate
NH$_4$SCN	Ammonium thiocyanate
PTV	Pendulum Test Value

SD   Standard Deviation

SEM   Scanning Electron Microscope

w/c   Water to cement ratio

XRD   X-ray Diffractometer

θ Contact angle

Chapter 1:   Introduction

1.1 Background

Concrete is a composite material made from mixing some compounds that are either found in nature or chemically formed; aggregates, cement, and some other admixtures in the presence of water will form this composite when they are mixed together in certain proportions.

Concrete, nowadays, forms the basic component of many structures that are used to serve people's needs and make their lives much easier, starting from buildings, roadways, bridges, highways infrastructures, airfields, marine ports, tunnels, embankments, and certainly not ending at drain systems.

Concrete pavement started to gain a special importance these days for being more capable to reduce energy consumption, where it consumes less fuel, its life is longer than other pavement types, and it needs less maintenance works (Taylor & Patten 2006). In the United Kingdom alone there are more than 61,000 highways and road bridges, most of them are made of reinforced concrete (Rahman & Chamberlain 2016). In the United States, there are more than 158,000 miles of highways and road networks, which are constructed from concrete (FHWA 2016). Although these structures were designed and built to withstand deterioration, they still need to be counted for some maintenance procedures, as they are affected by the surrounding environment (Perkins 2002). Concrete pavement serving taxiways, runways and aprons of airports are also under the impact of deterioration resulting from surrounding envrinoment and the impact of using de-icing salts for example (Shi 2008). From this regard, it is an important issue to do more research to enhance the quality of concrete, its durability, and its resistance to environmental impacts.

The cost of repairing and maintaining concrete pavements and bridges, for example, is highly expensive and needs high financial support from highway agencies. As a result and in order to decrease the expenses of repairing pavements and bridges and any other concrete structure, Purvis et al. (1994) believe that the most cost-effective solution will be through taking some actions at the construction level. Accordingly, protecting concrete by adding some safeguarding admixtures at the mixing stage may result in a cost-effective solution for concrete deterioration and distresses. However, the protection of concrete pavement has not performed yet due to some concerns that protection will affect its frictional properties. Furthermore, a thorough search in literature did not find any technical research that discusses the protection of concrete pavement, especially on the long term.

Major problems in any concrete structure that affect its durability were summarised by Dhir et al. (1990) in figure 1-1, where it shows that the main problems in concrete which causes most of its distresses originate from the design and construction phase, whereas the materials used in concrete construction have a little effect on its degradation. Adding to that, the exposure of concrete to harsh environments, either during or after the construction phase, will accelerate its deterioration process despite the quality of the used materials. Addition of admixtures, additives, and other materials that could replace part of the used cement like blast furnace slag, pulverized-fuel ash, and micro-silica would enhance concrete properties, increase its ability to resist deterioration and increase its service life. However, these materials still have some inconsistent performance where, sometimes, they improve certain properties in concrete and at the same time they have some negative effect on other properties (Dhir et al. 1990).
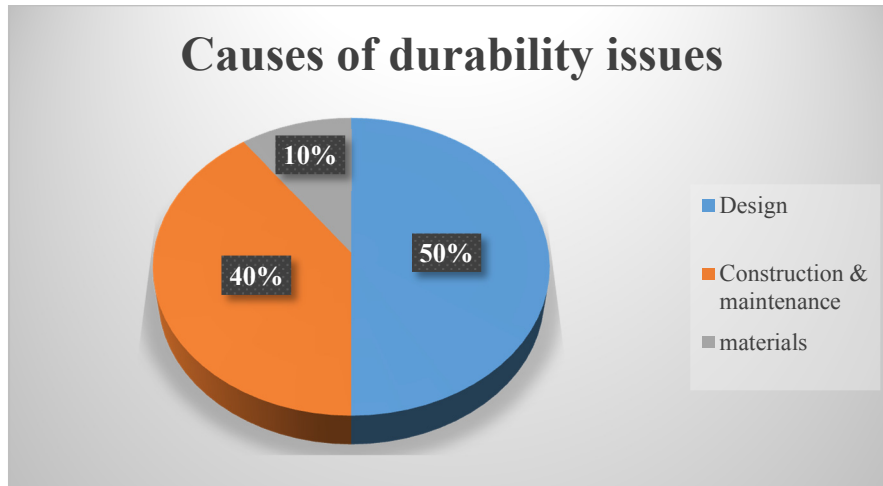
Figure 1-1- Main points for concrete durability problems (Dhir et al. 1990)

In the UK, for example, maintenance expenses of pavement and bridges have reached more than £4 billion in the period 2012-2013 (Comptroller and Auditor General 2014). They are subjected to a rainfall of 1420 mm, as recorded in the year 2012, and about 1120 mm in 2014 (The World Bank Group 2012; Rahman et al. 2016). The easy entrance of water into concrete can produce many disadvantages affecting its desired performance and durability, and could bring many problems into being; including corrosion of the embedded steel, and leakage. Also, water is linked to other deterioration causes like freezing and thawing which has the ability to produce cracks in concrete and eases the entrance of some harmful chemicals (Basheer et al. 2001).

The necessity to construct reliable and durable concrete infrastructures and highways has been acknowledged by existing standards and guildlines issued by many formal organisations like the BD 43/03 and the BS EN 1504-2 produced by the Transportation Research Laboratory and the British Standards Institution respectively (Highways agency 2003; British Standards Institution 2004). These standards encourage the application of protective materials to concrete to increase its service life and reduce its need for maintenance. Accordingly, this research

jumps from the need to protect concrete from moisture damages and to decrease its permeability without compromising its strength.

1.2 Research Motivations

Many researchers tried to investigate the effect of different environmental conditions on the properties of matured concrete (Ham & Oh 2013). However, these research have been performed with carefully restrained and well-structured laboratory conditions, so they did not reproduce the actual field conditions with different variables. Furthermore, there is no clear evidence for the unfavourable weather conditions on treated concrete.

Protective materials have been under investigation for a long time as a result to the need for an effective concrete protection against probable distresses that would develop in the future due to severe atmospheric and environmental conditions. The problem in this regard emerges from the disagreement between the laboratory conditions and the onsite environment when it comes to testing the performance of the protective materials. Moisture content values, as a major concern for protective materials, could be easily controlled under laboratory conditions, according to the standards, while in real life applications and in onsite works, moisture levels could become higher than desired which will affect the performance of protective materials.

Silane and siloxane materials were the most dominant options in protecting concrete, and since the 1980s, most of the research focused on testing these materials and enhancing their performance (Wong et al. 1983; Jones et al. 1995; Ibrahim et al. 1997; Basheer et al. 1998; Ibrahim et al. 1999). Conversely, some recent studies discussed the impact of those materials on the environment, and they proved their harmful effect on natural resources and environment as their main constituent is made from solvent and organic materials (Rahman et al. 2013; Bubalo et al. 2014). Adding to that, silane/siloxane materials were found to be less effective in the presence of moisture in concrete (Rahman et al. 2013).

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On the other hand, most of the researchers are trying to focus on the issue of deep penetration of protective materials in concrete, and the deficiency in achieving such goal is always prompted in the research, as Rahman, et al. (2016) suggest. Considering other issues related to these materials like applying them to fresh concrete is a vital thing and should be studied thoroughly.

The motivation for this research comes from the need to preserve concrete to resist chlorides and to have a good strength, durability and waterproofing. Also, the need to overcome the deficiency of some protective materials when applied to wet surfaces is another driving force for this resaerch. To achieve these goals, some protective agents will be used within the fresh mix, and other newly-developed materials that have high affinity to mositure will be applied to matured concrete to produce a good defence against water and chloride ingress. Most importantly, adding materials to the early production stage of concrete will give a new concept for concrete protection process while finishing work earlier onsite.

1.3   Research Aims and Objectives

This research focuses on developing a durable concrete by adding protection materials, mixed with fresh concrete in the mixing stage as well as applied on the surface of matured concrete, in order to enhance its reaction against chemical attacks and water absorption. Therefore, this research highlights the following objectives:

1. Investigate the influence of various concrete protective materials applied on matured concrete and added to fresh concrete.

2. Develop an optimum mix design for internally integrated concrete by optimising the w/c ratio and percentage of the protective material added in the mix.

3. Investigate the effect of the degree of saturation of concrete on the efficacy of surface applied materials.

4. Investigate the effect of the added dosage of protective materials and moisture content of fresh concrete on the level of concrete protection.

5. Investigate the long term performance of protective materials either when applied to the surface or when added to the mix.

6. Establish a better understanding of the interaction mechanism and behaviour of the used protective materials with concrete.

1.4 Scope of Work

Task 1:

Rationale: To gain an extensive understanding for the conducted work and to create a comprehensive database about the limitations of current treatments and the potentials of the proposed materials.

Activity: Producing a detailed comprehensive literature review that discusses up-to-date studies about concrete deterioration and concrete protection represented by surface treatments and internally integrated materials.

Task 2:

Rationale: Conducting an initial investigation about the protective materials that will be used in the research, by producing an initial trial mix design with different w/c ratios and different percentages of the internally integrated material and cured under different conditions. The mechanical properties of all the developed mixes will be investigated in order to shape the design of standard and non-standard mixtures (Standard mixtures: untreated concrete, and non-

standard mixtures: treated concrete). An optimum mix design will be produced following the results of this initial investigation.

Activity: This task will be divided into two parts. In the first part, a powder internal integrated material will be added to the fresh concrete mix with different percentages, and concrete will be tested for compressive and flexural strengths. In the second part of this task, a liquid form of the previous material followed by a water-based curing compound are applied to the surface of fresh concrete with a certain concentration. An attempt to test the compressive and flexural strengths of the treated mix under favourable and adverse curing regimes will be made. Based on the results obtained in the first part, an optimum mix design with different w/c ratios and different percentages of the internally integrated material will be developed. Mechanical properties such as compressive and flexural strengths will be tested.

Task3:

Rationale: Investigating the effect of moisture content on the efficacy of applied protective materials. This task springs from the need to develop a method to know the most appropriate moisture content at the time of treatment and the most appropriate dosage of material to be applied.

Activity: Concrete will be produced and treated with different surface treatments after conditioning concrete with different moisture contents. Water absorption of treated concrete will be tested and compared with untreated concrete.

Task 4:

Rationale: Investigating the chloride barrier performance of concrete produced in task 1 and 2. Chloride penetration of internally integrated concrete and concrete impregnated with surface

treatments will be evaluated, and results will be compared with standard concrete mixes (untreated).

Activity: Unidirectional salt ponding test will be carried out for treated and control specimens.

Task 5:

Rationale: Long-term performance of internally integrated concrete and concrete impregnated with surface treatments will be assessed, and results will be compared with standard concrete mixes (untreated).

Activity: Two methods will be used to evaluate the durability of concrete; a standard freeze-thaw test and a non-standard freeze-thaw test that was developed during this research. In both methods, testing has lasted for six months.

Task 6:

Rationale: The morphology of treatments, and the interaction mechanism of treatments with concrete will be investigated in this task. Outcomes of this investigation are intended to elucidate the mechanism for the development of concrete after treatment.

Activity: Concrete will be tested under the Scanning Electron Microscope (SEM), X-ray diffractometer (XRD), Energy Dispersive X-ray Analyser (EDX) and Fourier-transform infrared spectroscopy (ATR-FTIR).

The following chart shows the scope of work and the layout of the performed experimental work (Figure 1-2):
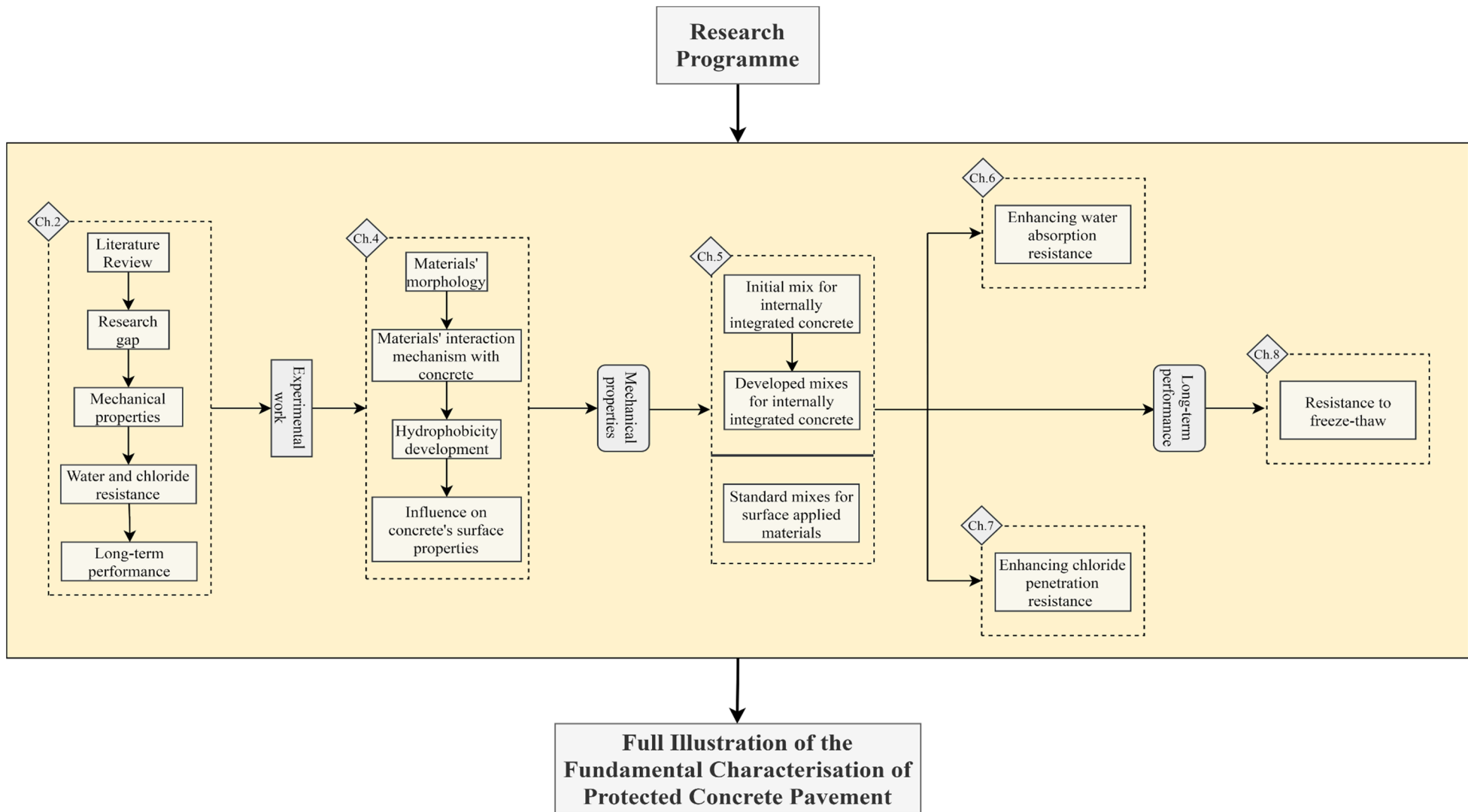
Figure 1-2 - Thesis layout

Chapter 2:   Literature review

2.1 Introduction

Concrete is one of the multipurpose materials used in the construction field as there is almost no structure being constructed around the world that does not use concrete or its main component, cement, in any respect (Pomeroy, 1990). This can be noticed in buildings, dams, bridges, and some highways. Even for steel structures and timber houses, concrete is usually involved in the foundation of these structures. Concrete has an edge over other construction materials; it has the needed properties to be shaped in any form and size so it can be easily controlled on site or even in precast works, and at different weather conditions and temperatures. Also, concrete has the ability to protect steel from corrosion when steel is embedded within the mix. Most importantly, concrete is considered as a cost-effective material, and it is cheaper than some of the materials used in constructions (Pomeroy 1990; Mehta & Monteiro 2006). Accordingly, concrete has been utilised in many life aspects and it forms the main element to start a lot of life-serving projects. Highway engineering field is one of these projects that could not be ignored when concrete is mentioned.

In recent years, concrete has regained importance in infrastructure and highways engineering for being more energy efficient material as it consumes less fuel, its life is longer than other materials, and it needs fewer maintenance works (Taylor & Patten 2006). Large-scale use of concrete in infrastructure engineering is to build bridges and concrete pavement for roads, airports, ports and in industrial ground floors. Concrete pavement, like other concrete structures, is susceptible to the impact of rainfall, freeze-thaw and chloride ions penetration, which affect the integrity and condition of concrete (Sutter et al. 2006; Bentz et al. 2001; Li et al. 2011a). In the United Kingdom, Maintenance and repair works of all forms of concrete structures, including concrete pavement, are responsible for 45% of the country's activity in

the construction industry (Van Breugel 2007). As a result, an urgent need to protect concrete from water and aggressive ions that water carries has emerged recently to reduce the expenses of concrete maintenance and to produce more durable concrete.

Therefore, this chapter will focus on the following objectives:

1. To analyse the current literature review on using protection materials to preserve concrete, in its early age and in its matured state, against deterioration.

2. To identify the proposed groundwork for the employed laboratory tests in evaluating the performance of protective materials.

This review covers all the deterioration issues associated with concrete pavement, and their influence and mechanisms on concrete's durability and serviceability. Also, it will discuss the classifications of protective materials, their role in extending the service life of concrete, and their interaction mechanism with concrete. Finally, the effect of adverse environment on concrete, and the main distresses developed in such environments will be studied in this literature, along with the methods used to assess some of the concrete properties that will be affected by treatment processes and materials.

2.2 Pavement

Thagesen (1996) defines Highway pavement as: "A structure whose primary aim is to support the traffic loads and transmit them to the basement soil after reducing the stresses to a level below the supporting capacity of the soil". He continues to explain more about this "structure" and divides it into three layers laid over each other and work as one body with a different essential role for each layer. The generated stresses from traffic and the influence of the surrounding environment will start to have less impact on the layers as going deeper from the surface reaching the base. On this base, the quality of materials used will be reduced too.

pavemnent is divided into six layers, considering an optional one to improve the performance of the pavement. These layers, shown in figure 2-1, are a subgrade layer, capping, sub-base, base, basecourse, and a wearing course layer (Thom 2014).
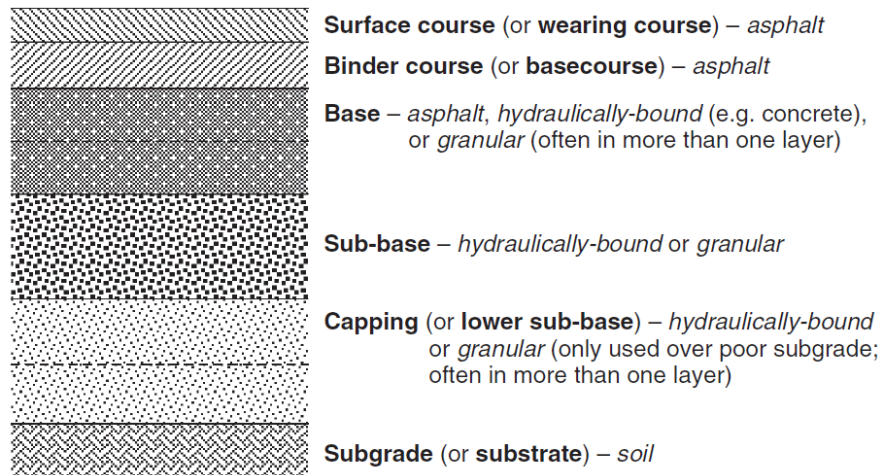
Figure 2-1- Typical pavement layers with an asphalt surface (Thom 2014)

The subgrade layer is an important unavoidable layer works as a foundation for the whole pavement structure. It consists of soil that originally exists in the place of work, or it could be obtained and transferred from other places and laid as fill. In the case of having a weak subgrade, a capping layer could be placed to strenghten the soil in the subgrade, and this layer is considered a cost-effective layer as it consists of locally found materials, or even the same existing subgrade treated by introducing some materials into the soil, such as portland cement or lime. Above the capping is the sub-base layer which is, typically, a 150 mm thick and formed from high-grade granular materials or a strong hydraulically bound ones that will support the resting base layer above it and protect it from deflection caused by heavy traffic. The base layer, which is usually 200 mm thick, is considered as the layer that contributes with the major strength that pavement needs. This layer could be formed from asphalt, concrete, or granular materials. On the top of this layer, a similar 50 - 80 mm layer called the basecourse is sitting with small size aggregates that serves as a "regulating layer" as Thom (2014) likes to describe

it. At the top of the all previously mentioned layers comes the wearing course or the surface course which is a shipshape tough layer consists of some excellent materials to resist the applied stresses as it is in a direct contact with the surrounding environment. In concrete pavement this layer does not exist as a distinct layer.

2.2.1 Pavement Types

Pavement could be divided into several broad categories with specific purpose for each (Mallick & El-Korchi 2013):

1. Pavement for roads: this type comes from the fact that there is a big range of roads with different designs and construction methods. Some of them have thicker pavement layers and others have thinner layers, this all depends on the purpose of the road and if it is to serve high volume traffic with heavy loads or to serve low volume traffic.

2. Pavement for airports: this kind of pavement intends to stand a considerably huge loads come from heavily weighted aircrafts. In addition to the special design of this type, other issues should be taken into consideration such as protection from fuel.

3. Pavement for parking lots: this type comes from the importance that parking lots form, where they are, nearly, found in all big cities and towns serving a lot of people attending different places for varying periods of times. This pavement could be found next to hospitals, offices, schools, companies and airports.

4. Loading and unloading areas: this type of pavement is intended to serve for heavyweight works in the ports. They are designed to stand heavy masses of different materials delivered by ships, railways, and trucks. This type of pavement may also need unusual protection from fuel.

On the other hand, pavement could also be classified, based on its properties and function, into two main types: Flexible pavement and rigid pavement, with different purpose and design for each type (Mallick & El-Korchi 2013). However, another classification divides pavement into three major groups; flexible pavement, concrete pavement and composite pavement (Thom 2014; Morse & Green 2009).

2.2.1.1 *Concrete Pavement (Rigid Pavement)*

This type of pavement is considered as a highly-tough and hard pavement, obtaining this feature from its essential constituent; the hydraulic cement concrete (Nikolaides 2015). Concrete forms the first and top layer of concrete pavement followed by a sub-base layer with the option of including steel in the concrete or not, as it could be constructed with control joints, movement joints, without joints, shrinkage and temperature reinforcemnt, or normal continuous reinforcement. Accordingly, Griffiths & Thom (2007) classify concrete pavement into: Unreinforced concrete (URC), jointed reinforced concrete (JRC), and continuously reinforced concrete (CRC). On the other hand, Nikolaides (2015) has included composite pavement as a fourth type of rigid pavement instead of considering it as a main pavement category; this type of pavement will be disscused later as a separate type. However, It is neseccery to point out that some authers in the literature, when discussing concrete pavement, may refer to the sub-base layer as the base course, and some of them they just call it sub-base and differentiate it from the base course, where they consider the latter as an optional additional layer found under the sub-base layer (Huang 2004).

Figure 2-2 a-c shows a typical concrete pavement structures with different construction styles.

(a)

(b)

(c)
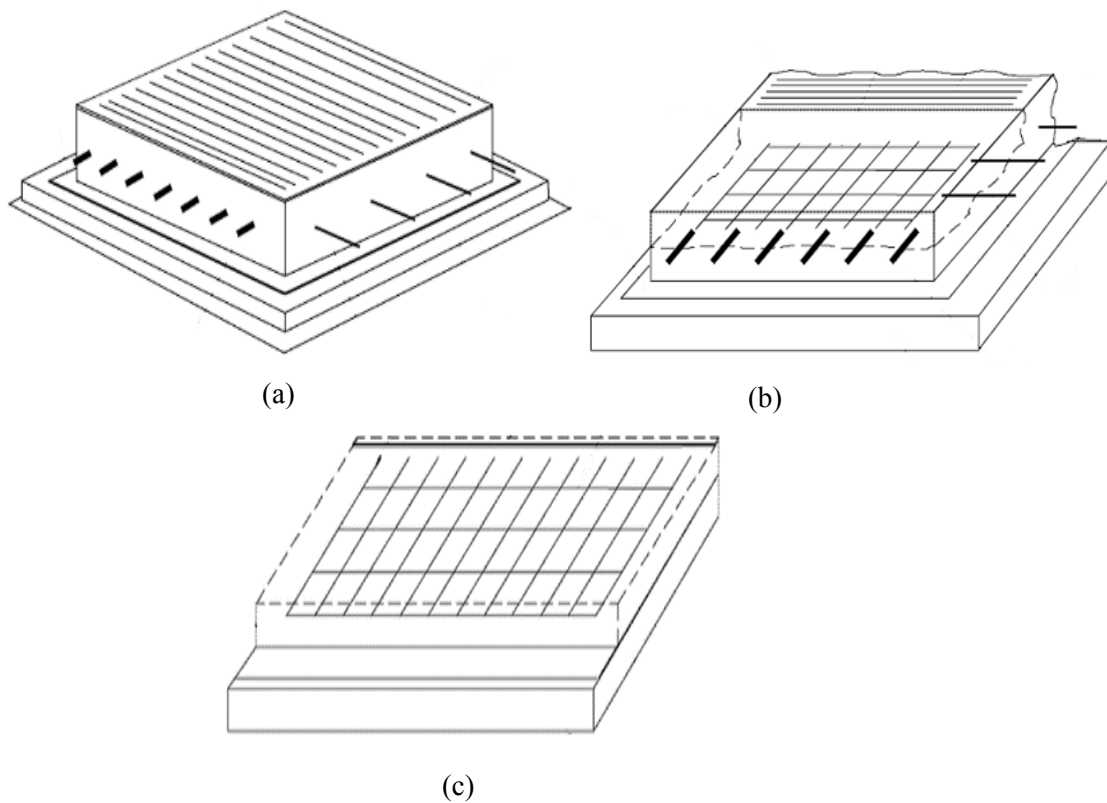
Figure 2-2- Typical concrete pavement sections with: (a) unreinforced concrete, (b) jointed reinforced concrete, and (c) countinuosly reinforced concrete (Griffiths & Thom 2007)

Unreinforced concrete pavement, as appears in figure 2-2 a, is made of a group of assembled concrete boards that are attached to each other by tie and dowel bars, and steel reinforcement is not used within the slab itself (Griffiths & Thom 2007). The importance of these dowels comes from the need to transfer applied stresses through transverse joints and give the joints the freedom to shift across the long direction of dowels. On the other hand, tie bars allow joints in the longitudinal direction to be embraced closely with each other (Mallick & El-Korchi 2013).

Next in order, jointed reinforced concrete pavement is similar to unreinforced concrete except for introducing reinforcement bars into the slab (Griffiths & Thom 2007). Figure 2-2 b

demonstrates the structure of this type. The significance of the provided reinforcement springs from the necessity to limit cracks within concrete and provide more toughness to it. Nowadays, this type of pavement is less commonly used (Delatte 2014).

The last type under this category is the continuosly reinforced concrete pavement, shown in figure 2-2 c. This type of concrete pavement, typically, consists of a reinforced concrete slabs with the absence of the joints that distinguish the previous two types. Griffiths & Thom (2007) think that this type of pavement has an economical advantage if garvel, sand, and water do exist in the working site in significant amounts. On this base, constructing continuously reinforced concrete pavement will be relatively cheaper than introducing thick asphalt pavement to serve the same intended purpose. However, Mallick & El-Korchi (2013) make a strong point when comparing this type of concrete pavement to the other two types in terms of cost. They claim that continuously reinforced concrete will cost more than the first two concrete pavements as heavy reinforcements have been used within its slab. Regardless of this, continuously reinforced concrete pavement may appear cost-effective if it is used to construct heavily trafficked roads because of their greater long-standing performance in comparison with the other two types.

On the other hand, using this type of pavement will reduce the cost of maintenance intended for joints, and it will grant a uniform movement for shear stresses, resulting from applied heavy weights, through its structure which will lead to develop fewer distresses (Delatte 2014).

Concrete pavement types have many construction purposes and they serve different applications depending on their structures and ability to overcome various distresses. Griffiths & Thom (2007) illustrate these applications and the proper type, of rigid pavement, to serve these applications. Unreinforced concrete for example could be used in aprons, taxiways, and runways of airports, and in constructing roads to withstand heavy traffic, especially in tropical

areas. On the other hand, parkings adjacent to industrial complexes, and roads constructed over weak subgrade are good applications for jointed reinforced concrete pavements. Finally, continuosly reinforced concrete pavement is usually used to build motorways in the areas that have the advantage of possessing large amounts of aggregates to be used in the mix.

2.2.1.2   Flexible Pavement

This type of pavement is composed of an asphalt surface with a layer of granular materials underneath it, followed by a layer of appropriate combiantion of fine and coarse aggregates (Garber & Hoel 2009). In this type of pavement, stresses move from the surface course down to following layers as a result of aggregate interlock, the friction results from the particles, and the effect of cohesion.

Flexible pavement is classified into three types: high, intermediate, and low types. High flexible pavement is constructed with a surface course that does not deform easily under applied loads, does not show any obvious disresses caused by fatigue, and resists bad weather conditions. The intermediate type has a course surface made from materials with a quality that vareis between treated materials and materials inferior to those used in the high type. Low type pavement has a wearing surface that consists of materials have a quality that is below the quality of these used in the other two types and they mainly range between loose materials and untreated ones (Garber & Hoel 2009).

2.2.1.3   Composite Pavement

This type of pavement is described, by Morse & Green (2009), as a rigid pavement dressed with an asphalt mix layer on the top. This construction type aims to reduce noise generated from concrete pavement (rigid pavement) surface that has a texture designed to provide an appropriate skid resistance. Mallick & El-Korchi (2013) agree strongly with Morse & Green

(2009) and both see that by introducing this asphalt dressing to concrete surface, both a proper friction and an adequate noise reduction can be achieved.

2.3 Concrete

Concrete is a composite substance that results from combining fine and coarse aggregates with a binding material, where the grains of aggregates are implanted inside it. In normal concrete, this binding material is made of cement and water, where the first interaction between cement and water results in changing the workable mixture into a hard and solid bulk in a process called "hydration" (American Society for Testing and Materials 2004; Powers & Brownyard 1946). The products of the hydration process are characterised by the ability of changing concrete from plastic state into solid state (Chadwick 1993). The properties of solid concrete are greatly influenced by the quality of the forming constituents, their mixing ratios, the process of mixing and the exposure of the constituents to the surrounding environment (Chadwick 1993).

One of the most important characteristics of concrete is its ability to resist water damage, to some extent, contrast to timber and traditional steel. This makes it more preferable and desirable, in industry, to be used in constructing different structures. In terms of maintenance, concrete requires less maintenance procedures and last longer than steel and timber without conducting maintenance. Also concrete is described as a fire resistant material and it resists excessive heat suffeciantly. However, some of structural components which are widely open to water all the time, like foundations, external slabs and beams, columns and pipes are usually constructed with reinforced concrete (Mehta & Monteiro 2006).

The improvement of concrete performance started at the mid of the 1800s by reinforcing concrete with steel (Hewlett 2003). Reinforced concrete, as briefly explained by Mehta & Monteiro (2006) "is a concrete usually containing steel bars, which is designed on the

assumption that the two materials act together in resisting tensile forces". The importance of reinforcing concrete comes from the fact that concrete is weak in tension and needs steel to cover this shortcoming, due to its high tensile strength, which leads to reduce cracks development in the structure (Pomeroy 1990). Tensile strength of concrete, usually, does not exceed 10 percent of its compressive strength due to its heterogeneous composition (Mehta & Monteiro 2006).

In some occasions, concrete needs more improvement to serve some purposes and fulfil the demands of the customers so there is a necessity to develop concrete properties to satisfy these demands (Pomeroy 1990). Adding some polymer based admixtures, crystallising materials, water-based emuslions, and some other chemical admixtures would give concrete a proof against damages caused by acids, unfriendly environments, and water damages. Also some of them have the ability to increae concrete strength. This subject will be discussed in more details in following sections.

2.3.1 Components of Concrete

2.3.1.1 Cement

Cement is a substance that works for bonding small fragments and convert them into a compact bulk due to its adhesive and cohesive properties. The cement that enters in concrete manufacturing is known as hydraulic cement since it reacts with water to produce a mortar that has the property of setting and hardening (Neville 2011).

Hydraulic cements are, first and foremost, made up of silicates and aluminates of lime, and can be divided into many types; natural cements, Portland cements, and high-alumina cements (Neville 2011). Portland cement, for example, consists of many raw materials such as, calcareous material like chalk or limestone, alumina and silica, and marl combined with some oxides like CaO, SiO_2, Al_2O_3 and Fe_2O_3 (Bye 1999). However, some chemical compounds

result from processing the previously mentioned oxides in the process of cement manufacturing (Bye 1999). These compounds are illustrated in table 2-1.

Table 2-1- Chemical compounds of Unhydrated Portland cement and their main functions (Hewlett 2003) (Bye 1999)

Compound's name	Oxide composition	Abbreviation	Ratio	Function
Tricalcium silicate	$3CaO.SiO_2$	C_3S	~ 65%	Early strength and initial setting
Dicalcium silicate	$2CaO.SiO_2$	C_2S	~ 14%	Late strength
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	~ 11%	Early strength and induce strength development
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	~ 6.5%	Decrease clinker temperature, and gives the grey colour to cement

High alumina cement, on the other hand, has different constituents and properties which distinguish it from Portland cement, and its application and usage is less than Portland cement. Going deep in its components; alumina and lime represent 40% of its components, 15% ferrous and ferric oxides, and 5% silica. Magnesia, TiO_2, and alkalis are also found in small proportions. In terms of raw materials, limestone and bauxite are the main materials that form this type of cement (Neville, 2011). The neccissity of high alumina cement originates from its

ability to resist sulphates and its instant and quick hardening properties (Rodger & Double 1984).

When it comes to natural cement, this type of cement results from calcining and grinding cement rocks. Cement rocks are muddy limestones that argillaceous material formes more than a quarter of its main components (Neville 2011). This type of cement falls between portland cement and lime in terms of properties and combination, only that C_3S is not a part of this type which makes it slow hardening.

When portland cement is mixed with water it starts an exothermic chemical reaction identified as hydration, where cement develops its adhesion characteristics (Neville 2011) (Mehta & Monteiro 2006). During the hydration process, all the chemical compounds of cement undergo an exothermic reaction illustrated as follows:

C_3S: $\quad\quad 2(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + Heat$

C_2S: $\quad\quad 2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 + Heat$

C_3A: $\quad\quad 3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + Heat$
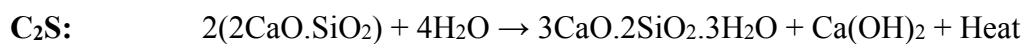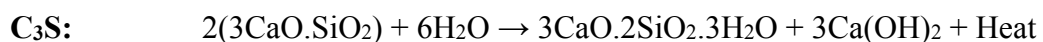
At the beginning of the hydration process, C_3A reacts with water to form the C_3AH_6 crystals ($3CaO.Al_2O_3.6H_2O$) that are responsible for early setting. However, the presence of gypsum works on slowing down this instant reaction and stops cement from flash setting. Moreover, this process will result in forming ettringite needle-shaped crystals ($3CaO.Al_2O_3.3CaSO_4.31H_2O$) that work on briefly inhibiting the hydration of C_3S, and ultimately, they will transform into monosulphate hydrate (Mehta & Monteiro 2006). In respect to calcium composite hydration, C-S-H (calcium silicate hydrated gel), $Ca(OH)_2$ (portlandite) and heat will be resulted. The C-S-H gel is responsible for the major of the expected compressive strength, while $Ca(OH)_2$ contributes less to the overall compressive strength

(Mehta & Monteiro 2006). The simplistic schematic diagram in Figure 2-3 illustrates the hydration process of cement and its resulting products.

Anhydrous clinker　　　　　　　　　　　　　**Hydration products**

C_3S — Fast ⎤
　　　　　　　⎥→ C-S-H gel
C_2S — Slow ⎦→ $Ca(OH)_2$ Portlandite

C_3A ⎤
　　　⎥ Fast but retarded by gypsum → Sulpho-ferri-aluminate hydrates
C_4AF ⎦

gypsum
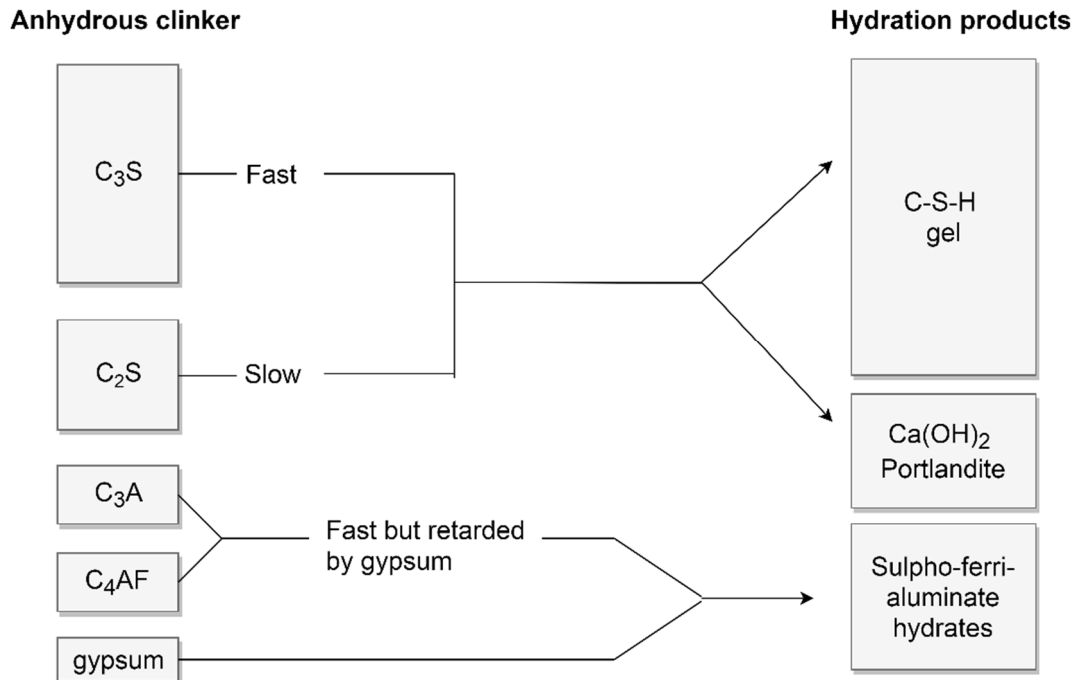
Figure 2-3- Schematic diagram of the hydration process and its products

As a result of hydration, the water used in the mix will have one of the following types: Capillary water, combined water, and gel water. Figure 2-4 shows volume portions for the components of the cement paste before and through out the hydration process.

The figure shows two vertical bars with labels. Bar (a) on the left has: V_w labeling the upper "Water" section, and V_c labeling the lower "Cement" section. Bar (b) on the right from top to bottom: V_{ec} for "Empty capillary", V_{cw} for "Capillary", V_{gw} for "Gel water", V_p for "Solids resulted from hydration", and V_{uc} for "Unhydrated cement". The right side is annotated with "Capillaries" (spanning empty capillary and capillary) and "Hydrated cement or cement gel" (spanning gel water, solids, and unhydrated cement).

(a)   (b)

Figure 2-4- volumetric ratios for the components of a typical cement paste: (a) before hydration process, and (b) throughout the hydration process

2.3.1.2 Aggregates

Aggregates are rough grains that are mixed with a cementitious material, in the presence of water, to generate concrete. Aggregates could be sand, gravel, crushed stones, or iron blast-furnace slag (American Society for Testing and Materials 2004).

Aggregates form nearly 75% of concrete volume, which makes their quality a major issue in concrete manufacturing, as it can touch concrete performance and affects its durability and strength. Aggregates are usually classified according to their particle size distribution, where they include a variety of sizes from tens of millimetres to smaller than one-tenth of millimetre (Neville 2011). According to American Society for Testing and Materials (2004), coarse aggregates would have sizes above 4.75 mm (retained on No. 4 sieve) and fine aggregates would have particle sizes that fall between 4.75 mm and 75 µm (Passing No. 4 sieve). On the other hand, British Standards Institution (2013) considers coarse agregates as those with sizes

above 5 mm, and fine aggregates with sizes less than 5 mm and larger than 75 μm. Gravel, for example, is basically coarse aggregate that is formed from rocks degradation under abrasion and weathering effects, and sands, as a typical fine aggregate example, result from weathering processes, just like gravel, or from stone crushing (Mehta & Monteiro 2006).

2.3.2 Concrete Quality Control

After considering the main components of concrete, it is important to look at some of the concrete properties that are affected by factors resulting in increasing or decreasing the quality of concrete either when it is fresh or hardened. Workability is the main feature of concrete, in its fresh condition, where it should be taken into consideration to meet the requirements. For matured concrete, strength and durability would be the main characteristics that their conditions have to be met (Delatte 2014).

2.3.2.1 *Workability*

American Concrete Institute (1980), in its ACI 116R report, defines workability as: "That property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, compacted, and finished."

According to the previous definition, workability is considered as a main characteristic for fresh concrete, since concrete has to own a suitable workability that offers a level of compaction to reach maximum density with an affordable effort (Neville 2011). As a result, compaction will have an influence on concrete strength, as the presence of voids inside the mix works on reducing its strength; 5 percent of voids content will reduce the strength by 30 percent.

The most famous, well known, and wide spread test method to measure workability is the slump test, which is conducted and arranged in the field. However, There are about 61 test methods for detremining workability and each test has its own usage and nesessity in industry (Koehler et al. 2003).

2.3.2.2 Strength

Strength is regarded as the most important characteristic of concrete since it reflects concrete's quality and its ability to resist transferred forces as it is concerned with the constitution of the cement paste (Neville 2011).

Since strength is linked with the hydration of the cement paste, Mehta & Monteiro (2006) indicate that the tests for concrete strength should be conducted after 28 days with suitable curing conditions, and this refers to the slow process of hydration, where concrete gains 99% of its strength after the 28 days curing period. For concrete pavement, it is believed that it will never fail in compression, but it is possible for thin concrete pavements that are exposed to excessive loads to fail under flexural or punching shear (Delatte 2014).

There are many factors affect the strength of concrete, and the most important one is the water to cement ratio (Neville 2011). Water to cement ratio is one of the main elements that is considered to affect the strength of concrete especially when it is completely compacted. When concrete is fully compacted, strength will have an inverse relationship with water to cement ratio, and this could be presented by a relation called Abrams' rule (Neville 2011):

$$f_c = \frac{K_1}{K_2^{w/c}}$$

Where f_c is the strength of concrete, K1 and K2 are empirical constants, and w/c is the water to cement ratio of the concrete mixture and it is taken by volume.

Abrams' rule is a special case of a more general formula put by René Féret where he links strength to both cement and water volumes (Neville & Brooks, 2010). Féret rule could be represented as follows:

$$f_c = K \left(\frac{V_c}{V_c + V_w + a} \right)^2$$

25

Where f_c is the compressive strength of concrete, V_c, V_w, and a are the volumetric quantities of cement, water, and entrapped air, respectively, and K is a constant.

Féret has included the volume of air in his equation since w/c ratio has a major effect on the porosity of cement paste during the hydration process, where both w/c ratio and compaction affect the volume of voids in concrete (Neville 2011).

Compressive strength and water to cement ratio relationship could be represented by the general curve shown in figure 2-5.
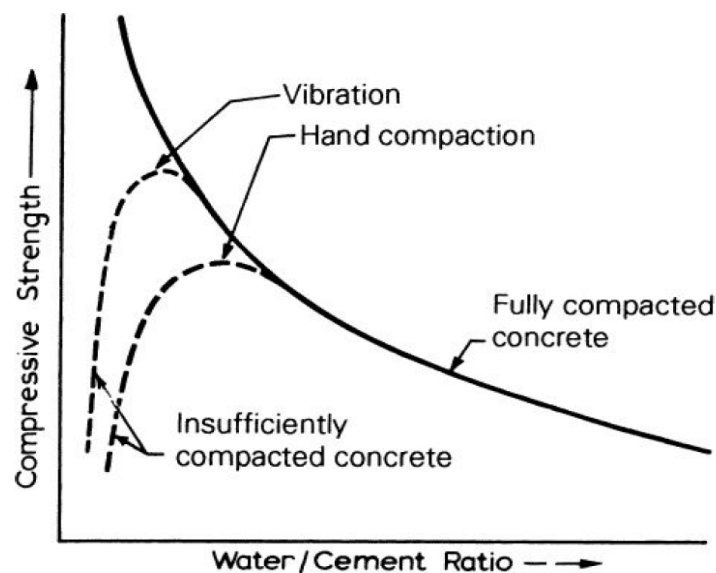
Figure 2-5- Strength and water to cement ratio general relationship (Neville, 2011)

The effect of compaction could be spotted obviously in the curve, where at low water to cement ratio levels the curve becomes very difficult to be followed when full compaction is unachievable any more (Neville 2011). Also, the method used to compact concrete will affect its strength; using vibrators would give a better compaction than hand compaction, which will be reflected on the strength of the mix.

Water to cement ratio controls porosity of hardened cement paste whatever the point of hydration it reached. Accordingly, water to cement ratio and the extent of compaction will shape the volume of voids in the mix (Neville 2011).

2.3.2.3 Durability

American Concrete Institute in their committee 201 (2001) defines concrete durability as "its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration". Accordingly, durable concrete keeps its primary structure, quality, and usefulness in accepted condition when subjected to the effects of the surrounding environment. However, concrete structure and properties will deteriorate in the course of time by means of different environmental impacts, and concrete deterioration will finally bring its service life to an end, as it will be unable to serve the purpose of its presence (Mehta & Monteiro 2006). Moreover, durable concrete does not have an unlimited lifetime, and it is not necessarily will endure any impact. What is more, maintenance and protection of concrete structures became a necessity to make their service life longer (Neville 2011).

Incompetent durability could be caused by surrounding environmental effects or by factors already exist inside concrete. These deterioration causes could be classified as mechanical, physical, and chemical (Neville & Brooks, 2010). Mechanical deterioraton could result from abrasion, erosion, and wearing actions. Physical deterioration is more related to frost actions and to the variations in thermal properties between aggregates and cement paste. Deterioration that results from chemical actions could result from either internal attacks like alkali-silica and alkali-carbonate reactions, or external attacks like chloride and sulfates ingress into concrete, beside other chemicals present in the surrounding environment (Neville & Brooks 2010; Neville 2011).

Mehta & Monteiro (2006) relate the physical and chemical deterioration processes to water ingress through concrete where they consider it as the main damaging factor. Water in its different states, like steam, ice, salt-water, rainwater, and ground-water is considered the richest fluid in the environment in terms of carrying other chemical ions and its high competency in dissolving other materials than fluids. Also, water particles are considered relatively small in size which give them the ability to penetrate easily through thin and small capillaries. Moreover, when water exists inside these capillary openings, it could lead to an out-of-control volume variations in concrete texture, like the changes caused by the freezing of water in the pores that increases their size and results in the formation of cracks.

When referring to concrete pavement, Sharp (1970) believes that highways are subjected to weather effects like other types of concrete structures but with an additional wearing forces result from vehicles, especially heavy loaded vehicles. For this reason, he sees that a minimum 4000-6000 lb/in^2 (27.5-41 MPa) concrete strength is required to establish concrete pavements. He also emphasise on producing this kind of concrete in a suitable manner by achieving a good compaction and reducing the presence of laitance on the surface.

2.3.2.4 *Permeability*

Permeability is the movement of fluids within concrete in an easy and smooth way, which makes it of importance regarding chemical attacks carried by water (Neville & Brooks, 2010).

According to Mehta & Monteiro (2006) water that presents in concrete pores and adheres to internal particles, when evaporates it will leave pores empty and unsaturated. After water leaves the capillaries, the chances of problems and damages associated with water, like freezing, become less possible to exist. However, succeeding exposures of concrete to ambient environment and weather conditions may lead to re-saturate the capillaries and increase damaging possibilities. From this regard, a concrete mix with low permeable aggregates and

high permeabile cement paste will have a low over all permeability, because aggregate fragments will block the pores of the cement paste and prevent water from passing through. This is from theory point of view, but when it comes to reality this is not what really happens. Mixing aggregates with cement paste will, significantly, increase the overall permeability, and the larger the dimensions of these aggregates, the higher the permeability of concrete (Mehta & Monteiro 2006). Accordingly, Neville (2011) suggests that water penetration depth could be used to assess concrete quality; concrete with penetration depth lower than 50 mm is impermeable, and lower than 30 mm is classified as impermeable under harsh conditions.

Water is not the only problem that threatens concrete integrity and cause it to deteriorate. Some other chemicals like chlorides, acids, and sulfates have the ability to penetrate into concrete and produce major effects on it. Chlorides, for example, could penetrate into concrete from ambient environment, as a result for the presence of de-icing salts or deposits of sea water touching concrete (Neville 1995). No matter what is the source of chlorides, water is the main carrier of chlorides and they enter concrete with water through the diffusion of their ions in water, and by absorption. This penetration of chloride ions if persisted for a long time could give rise to high levels of chloride ions that are in contact with steel embedded in concrete, leading to steel corrosion (Neville 1995).

2.4   Transport Mechanism in Concrete

Fluids, and its load of aggressive agents, when penetrate through concrete they react with its different ingredients causing some changes to its composition and leading concrete to start deteriorating. This ingress of fluids and chemicals takes place as a result of different water pressures, different air pressures, and different concentrations of solutions (Basheer et al. 2001). For instance, when concrete pores are saturated with moisture, pressure gradients will be the reason behind moisture transport, and when pores are unsaturated, capillary forces along

with pressure gradients will take place. The techniques by which liquids or gases could transport through concrete include many processes like diffusion, capillary absorption, and permeation (Basheer et al. 2001).

2.4.1 Diffusion

Neville (2011) describes this process as the driving force for fluid movement through concrete when different concentrations of fluids present. Oxygen, for example, when diffuses through concrete encourages the corrosion process of the reinforcement, and carbon dioxide, on the other hand, is the main reason for the carbonation of cement paste.

Fick's first law for diffusion expresses the mass transmission rate across unit area of a structure, concrete for example, in kg/m^2.s or moles/m^2.s and it is outlined in the following equation:

$$J = -D\frac{dc}{dL}$$

Where, D is the effective diffusion coefficient in m^2/s, dc/dL is the concentration gradient in kg/m^4 or moles/m^4, J is the mass transport rate in kg/m^2.s or moles/m^2.s, and L is the sample thickness in m.

Fick's first law correlates the diffusion of fluids to the concentration gradient assuming that ions are transported in a steady state process from areas of high concentration to those of low concentration (Poulsen & Mejlbro 2006). However, Fick's first law does not take into consideration the change of concentration of ions in repect to time. Accordingly, Fick's second law was introduced to deal with non-steady state conditions (Poulsen & Mejlbro 2006):

$$\frac{\partial C}{\partial t} = -\frac{\partial F}{\partial L}$$

The law suggests that the change in ions content per time ($\partial C/\partial t$) is equal to the change of flux per unit length ($\partial F/\partial L$).

Harmful chemical ions like chlorides and sulphates are transported through concrete by diffusion in the pore water where interactions between the hydrated cement and these chemicals occur leading to concrete deterioration and reinforcement corrosion. The diffusion of such ions is more active when concrete is saturated or even moderately saturated. It is noteworthy that diffusion is adversly proportional with w/c ratio, regardless the fact that the influence of w/c ratio on diffusion is less than its influence on permeability (Neville 2011).

Neville (2011) discusses some tests to determine the accessability of chlorides into concrete. One of these tests is proposed by ASTM C 1202-97 (American Society for Testing and Materials 1997), which checks the electrical conductance of concrete and its ability to resist chloride ions ingress, in terms of electrical charges that cross a concrete sample between sodium chloride and sodium hydroxide solutions. Another test, described in ASTM C 1543-02 (American Society for Testing and Materials 2002), is the ponding test where it measures chloride ions ingress into concrete from a sodium chloride mixture pond exists over a concrete surface.

2.4.2 Absorption

Absorption is defined by Basheer et al. (2001) as the movement of liquids in permeable solids that have a pore structure as a result of surface tension that takes effect in the capillaries. They also emphases that absorption is associated with the moisture condition in concrete as it is related to the pore structure. On the other hand, when water is absorbed through dry concrete it is affected by capillary rise and water amount that is needed to saturate concrete.

Many tests have been developed to measure concrete absorption and Basheer et al. (2001) put them in two general categories; surface absorption tests, and drilled hole absorptivity tests. First tests includes other minor tests like the Initial Surface Absorption test (ISAT), the

Autoclam Sorptivity test, and the Standpipe Absorptivity test. On the other hand, drilled hole absorptivity tests include the Figg water permeability test and the Covercrete Absorption test.

Initial Surface Absorption Test (ISAT) is a test proposed by the British Standards Institution (1996) in BS 1881-208:1996 to measure the absorption properties of the outer surface of concrete in terms of water flow rate per unit area, after a certain period of time, under a steady water loading and specified temperature (Neville & Brooks 2010). It measures the uniaxial water ingress under a pressure of 200 mm head of water, which represents the worst exposure of rainfall in the UK. Figure 2-6 shows a sketch for the ISAT apparatus.
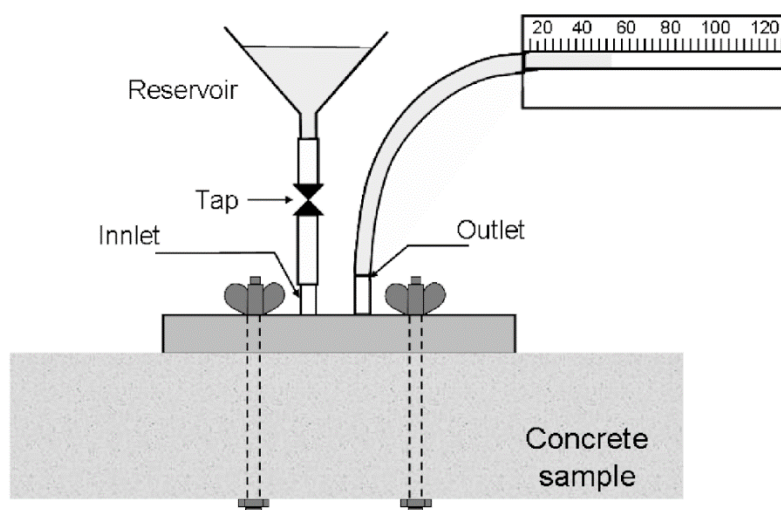
Figure 2-6 - Sketch for the ISAT apparatus (Basheer et al. 2007)

2.4.3 Permeability

The main concept and the general theory of permeability were discussed earlier in section 2.3.2.4 in terms of concrete integrity and how water penetrates through concrete. Other properties of water permeability and its tests are to be discussed in this section.

Permeability in concrete happens when fluids move through concrete under pressure differences and that is illustrated by the general form of Darcy's law (Basheer et al. 2001):

$$\upsilon = \frac{Q}{A} = -(K/\mu)(dP/dL)$$

Where υ is flow velocity, Q is the flow rate, A is the area of the section where fluid passes, K is the permeability coefficient of the porous medium, μ is the fluid's viscosity, and dP is the pressure loss along dL length of flow.

Testing concrete permeability and measuring its levels depends mainly on some laboratory tests that are described either in the British Standards (BS) or in the American Society for Testing and Materials standards (ASTM). For example, the depth of penetration of water under pressure testing method is a testing method prescribed by British Standards Institution (2009d) in BS EN 12390-8:2009, in which water ingress depth through hardened concrete is measured, in mm, after applying a water pressure of 0.5 MPa for 3 days.

2.5 Concrete Deterioration

Concrete deterioration was discussed briefly in a previous section in order to clarify the concept of durability and how it is affected by deterioration. However, it is important to explain some deterioration causes that are related to the on-going research and would affect highways more than other structures.

2.5.1 Carbonation

Concrete, in its nature, has the ability to protect reinforcement from corrosion, by itself, because of the high alkalinity of the concrete pore structure that forms a coating film over the steel surface. However, Carbon dioxide CO_2 can penetrate, by diffusion process, through concrete pores that are occupied by water, and reacts with this water to form carbonic acid, which in turn reacts with alkali hydroxide, calcium, potassium and sodium to produce carbonates (Saetta et al. 1993). Calcium hydroxide $Ca(OH)_2$ usually has higher concentrations in concrete than other hydration products, which makes the reaction of carbon dioxide with

calcium hydroxide the principal reaction to start carbonation, which can be illustrated in the following chemical reaction (Saetta et al. 1993):

$$CO_2 + Ca(OH)_2 \xrightarrow{H_2O} CaCO_3 + H_2O$$
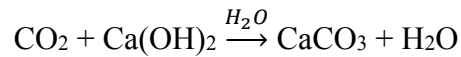
Following the formation of the calcium carbonate $CaCO_3$, the pH of pore water will decrease below 10, which will work on dissolving the passive layer of the steel surface and corrosion will take place (Steffens et al. 2002; Basheer et al. 2001). However, Zafeiropoulou et al. (2011) believe that the pH value must be below 9 to start a failure in the passivity which will lead reinforcement to develop corrosion.

On the other hand, carbon dioxide can react with the main product of hydration (C-S-H) and decompose it into calcium carbonate and silica gel. However, this reaction has insignificant effect on the alkalinity of concrete and could be ignored (Steffens et al. 2002). Nevertheless, Bier (1986) believes that the high decomposition rate of C-S-H into carbonate and silica gel will increase the size of the pore structure, which expedites more carbonation.

2.5.2 Chloride Penetration

Many concrete structures are subjected to chloride attacks, not only from seawater but from de-icing salts used in concrete pavement and from the soil surrounding pavement itself (raised marine soil) (Poulsen & Mejlbro 2006).When chloride penetrates into concrete it reacts with the hydration products resulting in destructive effects on concrete especially in winter due to frost damage (Basheer et al. 2001). Nevertheless, the main damage caused by chloride is not limited to frost damage, it has a primary impact in inducing steel corrosion due to its ability to reduce alkaline effectiveness in resisting corrosion. Moreover, corrosion caused by chloride penetration will be worse than that caused by carbonation, as it makes corrosion develops in

higher rates. For instance, chlordie ingress can cause corrosion in a rate of 5 mm per year whereas carbonation can cause corrosion in a rate of 0.05 mm per year (Basheer et al. 2001).

The deterioration process of reinforced concrete starts with the penetration of water that carries chloride ions through the pores of concrete which initiate rust in steel that in turn permeate in surrounding concrete. Finally and due to rust expansion, cracks start to appear in the structure which results in spalling and delamination of concrete (Suwito & Xi 2004). Accordingly, British and European standards concerns were aroused by the complications generated by the presence of chlorides in concrete composition, and they have put a threshold content of chloride that ranges between 0.2-0.4% in reinforced concrete and 0.1-0.2% in the case of prestressed concrete (Bertolini et al. 2013).

One of the main factors affecting the mechanism by which chloride passes through the pores of concrete is its moisture content, which results from the presence of concrete under various environmental circumstances. Complete diffusion is believed to take place in saturated concrete like those soaked under water, and sorption is preponderant in concrete subjected to sea and oceanic atmospheres, concrete pavement in contact with de-icing agents and dry concrete that is found in arid areas (Ma et al. 2001; de Vera et al. 2007). In the case of partially saturated concrete, capillary suction and diffusion of chloride ions are credited for the whole process of chloride transport (de Vera et al. 2007; Nielsen et al. 2003). In addition, it was proven by Conciatori et al. (2008) that environmental conditions and the quantity of de-icing agents are the major elements in the process of chloride transport, eliminating the importance of concrete cover when concrete is in direct contact with saline water.

2.5.3 Freeze-Thaw Action

This is one of the most significant causes of concrete deterioration especially in cold areas where concrete durability is highly affected with the cyclic freezing and thawing of the pore

solution (Cai & Liu 1998). Freezing and thawing of concrete depends mainly on the size of its pores, as the size of the pores and their distribution in concrete determine the frost degree of the pore solution and the quantity of ice created inside them. As a result, a very high internal pressure will be formed inside the pores with increasing the amount of frozen pore solution causing a serious frost damage (Cai & Liu 1998).

Basheer et al. (2001) sum up the main freeze-thaw actions in the following four points: (a) initiation of hydraulic pressure resulting from the frost in pores (b) freezing the penetrated gel water inside the pores (c) varying stresses caused by confined and focused shrinkage and swelling along with thermal stresses and (d) limited freezing of solutions in some pores with a modest salt concentration leading to an osmotic pressure.

According to Powers (1975) (as cited in Basheer et al. (2001)), the damaging stress inside concrete is created by the constrained movement of water outside the frosted zone. This will generate an internal pressure caused by the viscous reluctance to water movement across concrete texture.

In the case of concrete pavement, the effect of freeze-thaw actions is higher than other structures due to the presence of de-icing salts during frost seasons (Jiang et al. 2018). For instance, the presence of calcium chloride solution in the pores accelerates the deterioration process of concrete in higher rates than water (Hewlett 2003).

2.5.4 Sulphate Attacks

This deteriorating factor is common in concrete that is in contact with groundwater, lakes or soils (like concrete pavement) where sulphate ions are carried and have the ability to go through concrete texture and react with its constituents. Sulphates work on weakening the bond between the hydration products causing a reduction in the strength of the cement paste. This could

initiate cracks and increase the permeability of concrete which makes concrete suscpetible to other chemical attacks that would increase its deterioration (Aguirre & de Gutiérrez 2013).

2.6 Concrete Protection

Although concrete pavement is used where long serviceability is required, its performance could be greatly reduced when it is found in harsh environmental conditions. As discussed earlier, the easy entrance of water into concrete can produce many disadvantages affecting its desired performance and durability, and could bring many problems into being; including corrosion of the embedded steel and leakage. Also, some water associated issues like freezing and thawing could drag concrete into a series of deterioration stages (Basheer et al. 2001). Despite the fact that reinforcement in concrete is already protected by the high alkalinity of concrete, the environmental impacts and some severe conditions will bring down concrete's ability to protect its reinforcement by itself (Basheer et al. 1998). From this point, the need to use protective treatments has became a necessity to hold back concrete deterioration.

A suitable and high-quality concrete has the ability to withstand adverse and severe conditions that lead it to deteriorate. Using protective materials within the concrete mix or even after hardening, is meant to help improving concrete performance under these harsh and adverse conditions. Using concrete with modest permeability, sometimes, will not be enough to safeguard concrete against water and other harmful chemicals, which makes the application of some surface treatments and protective materials is a necessity, especially in severe environments (Kosmatka & Wilson, 2011). Those protective materials are either surface applied materials or internally integrated materials (mixed with concrete constituents).

Surface treatments, in general, work as a physical obstruction to prevent damaging substances from entering concrete from ambient environment and safeguard it from deterioration (Aguiar et al. 2008; Cabrera & Hassan 1990). According to Keer (1992), Dai et al. (2010) and

Christodoulou et al. (2012) surface treatments could be categorised into three types: (1) surface coatings, where different layers are applied on concrete surface, and they are found in many types like epoxy resins, polyurethane resins, acrylic resins and cementitious polymers (2) sealers or pore blockers, which react with some solvable parts in concrete to produce unsolvable materials, with large molecular size, that close the pores near concrete surface, and finally, (3) surface impregnants or pore liners, where the surface is treated with a water repellent material that has a small molecular size and has the ability to go through the capillaries of concrete and react with some concrete parts to initiate a water repellent pores. Figure 2-7 shows clarified drawings for the three main types of surface protection systems.
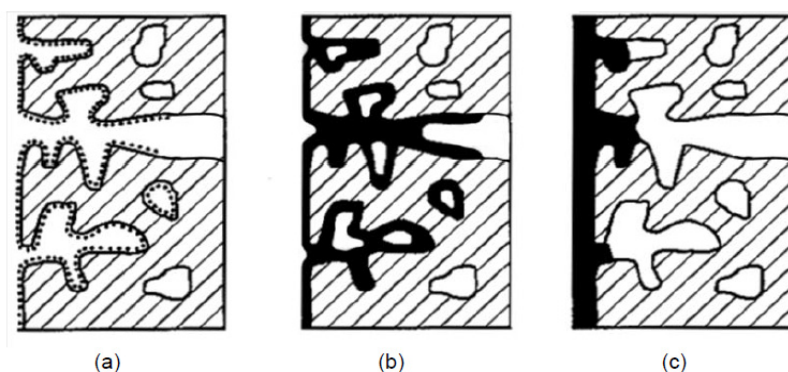
Figure 2-7 - Graphical illustration for concrete surface protection treatments: (a) hydrohobic (water repellent) impregnation (b) Sealing, and (c) coating (Meier & Wittmann 2011)

Another classification for surface treatments put them in two groups according to their chemical composition; organic and inorganic tretments (Pan et al. 2017). Organic treatments are more frequently used than inorganic treatments as they provide an acceptable degree of protection. Nevertheless, some doubts have arisen reagrding their efficacy in resisting fire and their ease to break and separate from the surafce. Some widely used organic treatments are epoxy resins, acrylic coatings and polyurethane coatings (Delucchi et al. 1997). On the other

hand, inorganic treatments have proven to possess better long-term performance than organic materials. However, few resaerch have studied their performance and their interaction with concrete. Sodium silicate, pottassium silicate, lithium silicate and fluosilicate are the most popular inorganic treatments that were studied by resaerchers (Franzoni at al. 2013; Franzoni at al. 2014; Pan et al. 2017).

On the other hand, the British Standards Institution BS EN 1504-2 (2004) divides surface treatments into four groups; coatings, hydrophobic impregnations, and impregnations. However, some recently-introduced protective materials are missed from this classification.

In a more recent classification, surface treatments have been calssified in four groups, including those missing in the BS EN 1504-2 classification; coatings, pore blockers, hydrophobic impregnation, and multifunctional treatments (Pan et al. 2017). However, this classification excludes some silane modified materials, which have hydrophobic characteristics, from being hydrophobic impregnation and classify them as multifunctional treatments.

In the late 1990s, Internal integration of concrete with protective materials has sprung as an alternative technique for surface treatments. Many materials have been integrated with the fresh mix of concrete, involving some of the materials that were used as surface treatments. However, few resaerch discussed this technique (Sommer 1998; Standke et al. 2004; Wittmann et al. 2006; Meier & Bäuml 2006; Zhang et al. 2009).

Internally integrated materials could be divided into three groups; natural hydrophobic materials, industrial hydrophobic materials and alternative chemical treatments (Justnes et al. 2004; Albayrak et al. 2005; Wittmann et al. 2011; Reiterman & Bäumelt 2014; Pazderka & Hájková 2016). Figure 2-8 shows a chart for the divisions of protective materials and their classifications as summerised from literature, and those highlighted by red colour are of the most interest in this research, and they will be discussed thoroughly.
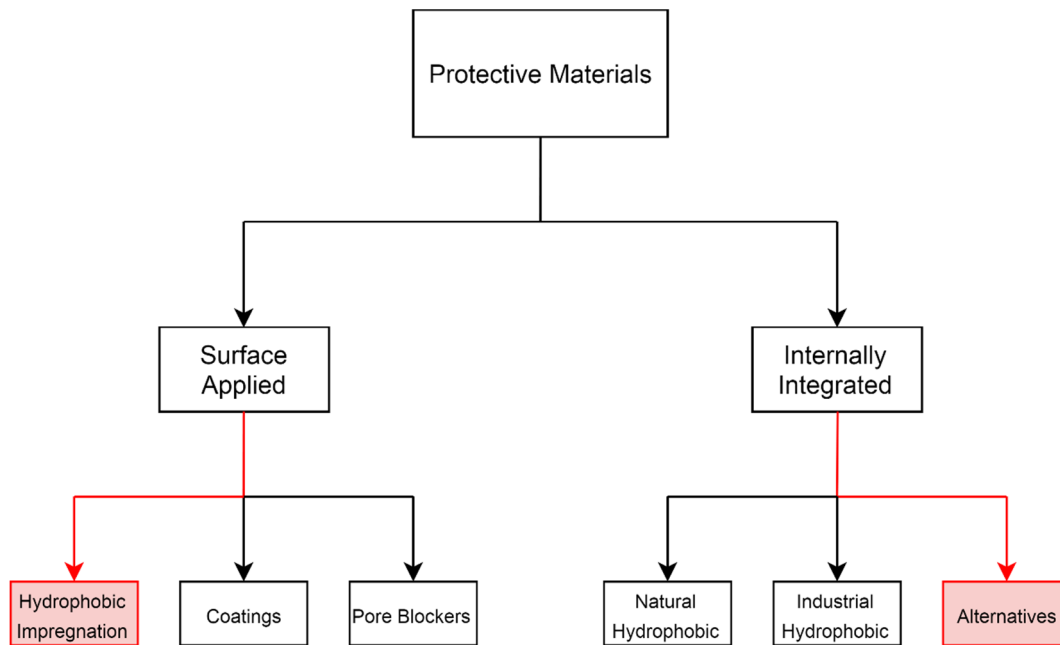
Figure 2-8 - Types and groups of concrete protective materials

2.6.1 Surface Applied Treatments

In order to increase the service life of concrete and reduce the cost of maintaining structures, more cost-effective solutions were followed which commence with the construction phase of these structures (Franzoni at al. 2013). In view of that, decision makers and research administrators started to promote the use of surface applied protective materials to control and incapacitate chloride ingress and water absorption into concrete structures (Brenna et al. 2013). In this chapter, surface applied treatments are divided into three groups; coatings, pore blockers, and hydrophobic impregnations (Pan et al. 2017).

2.6.1.1 *Hydrophobic Impregnations*

This type of materials passes through the surface of concrete, lines its pores and increases the pores' contact angle to more than 90°. Accordingly, they work on inhibiting the ingress of water and aquatic ions by repelling them outside the pores, and at the same time they allow concrete to breathe (they do not close the pores) (Medeiros & Helene 2008; Dai et al. 2010).

In general, most hydrophobic impregnations have silicon atoms in their chemical composition, where they represent the link between the applied hydrophobic material and concrete; they are chemically attached to concrete after application. Silane, siloxane and their derivatives are the most commonly employed hydrophobic impregnations in the concrete protection industry. They have a very small molecular size that ranges from 1.0×10^{-6} to 1.5×10^{-6} mm for silane and 1.5×10^{-6} to 7.5×10^{-6} for siloxane, which eases their penetration through the pores (Medeiros & Helene 2008). Regarding their molecular structure, silane is composed of one silicon atom bonded with an alkoxy group (carbon and hydrogen chain linked with oxygen), whereas siloxane contains multiple silicon atoms linked with an alkoxy group (De Vries & Polder 1997). Figure 2-9 a and b exemplifies the molecular structure of silane and siloxane.

(a)   (b)
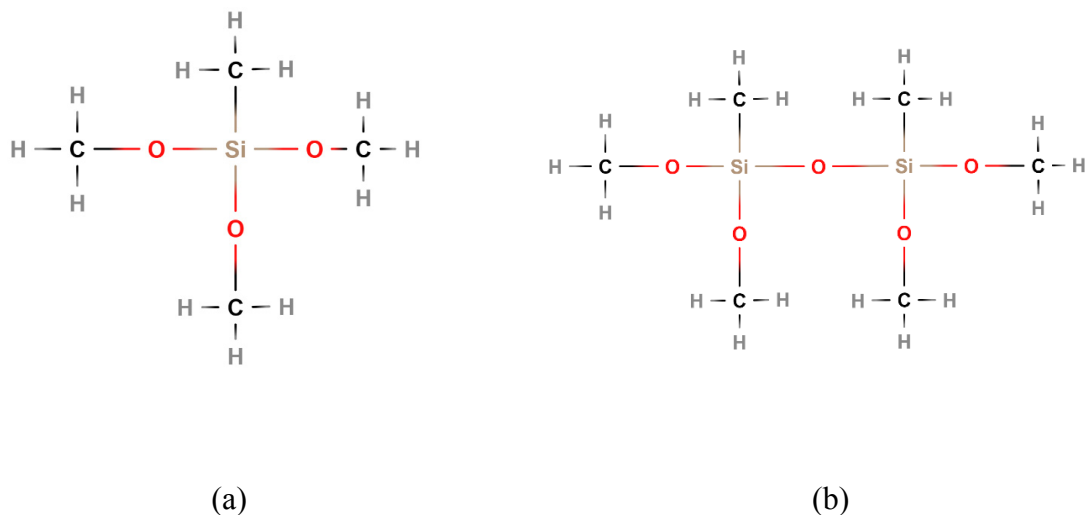
Figure 2-9 - Molecular structure and the distribution of atoms in: (a) Silane and (b) siloxane

(De Vries & Polder 1997)

The reaction between the alkoxy group and concrete will create a strong bond between silane/siloxane and concrete. Moreover, after this reaction and the penetration of silane/siloxane in the pores, the organic alkyl group (CH_3) will overhang from the pores and initiate a hydrophobic effect inside the pores because of their fatty properties (De Vries &

Polder 1997). Figure 2-10 shows a sketch for the reaction between silane/siloxane and concrete. More detailed, after the application of silane/siloxane to concrete surface, it will undergo a chemical reaction with moisture inside the pores, which results in the creation of a reactive silanol group (Si-O-H) through the hydrolysis of the alkoxy group. Silanol will then condensate inside the pores in low molecular weight polymers (oligomers), followed by a crosslinking between the hydroxyl group of silane and concrete (Woo et al. 2008).
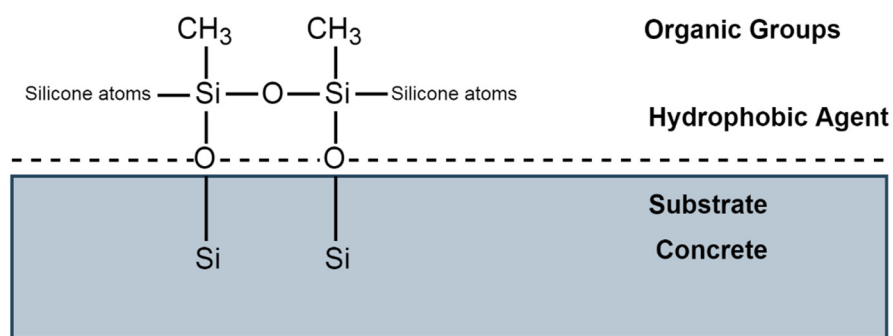
Figure 2-10 - Chemical reaction between silane/siloxane and concrete (De Vries & Polder 1997; Medeiros & Helene 2008)

When the alkyl group of the hydrophobic material contains many carbon atoms (for instance $(CH_3)_2CHCH_2$- or CH_3CH_2-), the hydrophobic material will offer a higher degree of hydrophobicity for the treated concrete. Even the distribution and the shape of the alkyl group within the chemical structure of the material have a major effect on the hydrophobicity of the material; a branched arrangement of alkyl group would offer higher hydrophobicity than a straight or cyclic structre. One more factor that affects the efficacy of the hydrophobic impregnation is the molecular weight of alkyl group. For instance, iso-butyl (($CH_3)_2CHCH_2$-) and n-octyl (C_8H_{17}-) groups that has higher molecular weight than other groups like methyl (CH_3-) and ethyl (CH_3CH_2-) are distinguished with their high efficacy and high hydrophobicity. However, higher molecular weight alkyl or even alkoxy groups could have a negative effect

on the efficacy of the treatment in general; it reduces the pentration depth of the material and restrains the size of the pores that could be penetrated (Attanayake et al. 2006).

It is believed that hydrophobic impregnation would have larger molecules in the course of hydrolysis and condensation which results in a restricted penetration depth (Attanayake et al. 2006). This deficiency brought a lot of questions regarding the performance of silane and siloxane in the presence of high moisture content in concrete.

Many researchers concentrated on treating mature concrete with silane and siloxane based materials as they have proven their efficacy in protecting concrete and enhancing its durability (Ibrahim et al. 1997; Basheer et al. 1998; Ibrahim et al. 1999; Zhan et al. 2003; Zhan et al. 2005; Wittmann et al. 2005; Dai, et al. 2007; Schueremans et al. 2007; Medeiros & Helene 2008; Dai et al. 2010; Leung et al. 2008; Hosoda et al. 2010; Johansson-Selander et al. 2010; Christodoulou et al. 2012; Balakrishna et al. 2013; Christodoulou, et al. 2013; Huang 2013; Huang & Dong 2013; Rahman et al. 2014; Christodoulou et al. 2014; Liu & Hansen 2016; Moradllo et al. 2016).

The efficacy of hydrophobic impregnations, mainly silane and siloxane, have been evaluated through running a range of systematic experiemntal work. This evaluation process involved many aspects that measure the durability of treated concrete. Amongst those aspects, the most important properties that were discussed in literature were water absorption, chloride ingress, freeze-thaw deterioration, carbonation, hydrophobic impregnation depth of penetration and resistance to weathering (Basheer et al. 1997).

In general, Concrete that was treated with silane/siloxane materials has shown a good performance in terms of reducing water absorption. Table 2-2 illustrates the performance of concrete treated with silane, siloxane and their derivatives in terms of water absorption and the testing methods that were used for each case.

Table 2-2 - Water absorption of concrete treated with hydrophobic impregnations

Reference	Testing method	Hydrophobic impregnation	Conclusion
Zhan et al. (2003)	Capillary suction following the RILEM test method CPC 11.2	- Liquid silane (100% active content) - Cream silane (80%) - Gel silane (85%)	Gel silane absorbed the least amount of water followed by cream silane then liquid silane
Zhan et al. (2005)	Capillary suction following the RILEM test method CPC 11.2	- Liquid silane - Cream silane - Gel silane	- w/c=0.4: cream, gel, then liquid - w/c=0.5: gel, cream, then liquid - w/c=0.6: gel, cream, then liquid - w/c=0.5(FA): gel, cream, then liquid
Dai, et al. (2007)	Immersion in sea water	- Liquid silane - Cream silane - Gel silane - Liquid silane/siloxane	- 17% pre-saturation: silane/siloxane, liquid silane, cream, then gel - 70% pre-saturation: gel, cream, then liquid silane - 100% pre-saturation: liquid silane, gel, then cream

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
Medeiros & Helene (2008)	- Immersion in water - Capillary absorption - Pipette absorption test	- Solvent-based silane/siloxane - Water-based silane/siloxane	- The solvent-based performed the best in the three test methods - In the immersion test, the water-based silane/siloxane showed similar performance to control
Woo et al. (2008)	Moisture permeability test	- Liquid silane - Modified silane-clay mixture (2 types: cloisite and octadecylamine)	Cloisite performed twice better than silane and octadecylamine
Gui-hong et al. (2008)	Capillary suction after contaminating concrete with NaCl	Liquid silane	- Water absorption of concrete with moderate contamination has been significantly reduced by treatment - More chloride ingress is reduced
Dai, et al. (2010)	Cyclic sea water shower	- Liquid silane - Cream silane - Gel silane	- Cylinders: liquid silane, gel, cream, then silane/siloxane - Prism (not cracked): gel, cream, silane/siloxane, then liquid

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
		- Liquid silane/siloxane	- Prism (before cracked): gel, cream, liquid silane, then silane/siloxane - Prism (after cracked): cream, gel, liquid, then silane/siloxane
Hosoda et al. (2010)	Immersion in water	- Gel silane/siloxane - Cream silane	Gel then cream
Johansson-Selander et al. (2010)	Capillary suction (Placing the treated side on a wet surface (towel))	Silane/siloxane	Major part of treatments after 10-15 years showed better performance than control
Mirza et al. (2011)	Immersion in water	- Silane - Siloxane	65% water absorption reduction for both impregnation with slightly better performance for silane
Zhu et al. (2011)	Capillary absorption	Silane	Significant reduction in concrete with recycled aggregate

Table Continues…

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Reference	Testing method	Hydrophobic impregnation	Conclusion
Basheer & Cleland (2011)	Autoclam water absorption test (under 0.02 bar pressure)	- 40% silane - 100% silane - Silane/siloxane	- All treatments reduced water absorption by 70-99% despite the initial mositure content - silane/siloxane applied to 0.45 w/c ratio with dry pores showed the least efficacy compared to all materials - All the applied materials showed higher efficacy with increasing the initial moisture content
Christodoulou et al. (2012)	- Capillary absorption - Capillary infiltration	Silane	Treatment still effective after 21 years of application
Christodoulou et al. (2013)	Capillary absorption	Silane	Treatment still effective after 20 years of application
Balakrishna et al. (2013)	- ISAT - Sorptivity test	- Solvent based silane - Water based silane	- C30 concrete: solvent based better than water based - C40 concrete: solvent based better than water based

Reference	Testing method	Hydrophobic impregnation	Conclusion
Rahman et al. (2013)	Sorptivity test	- Nanosilane - Aqueous silane	Both materials performed the same with better performance for nanosilane at the end of testing
Huang & Dong (2013)	Not stated	Silane	57.8% reduction for C30 and 58.6% for C40
Wang et al. (2014a)	Immersion in deionized water	- Long molecular chain silane and polysiloxane - Short molecular chain silane and polysiloxane	Long molecular chain silane performed better than the short molecular chain silane
Rahman et al. (2014)	Immersion in water	- Solvent-based silane - Water-based silane	50% redution for both impregnations
Christodoulou et al. (2014)	Capillary absorption	Silane	Treatment still effective after 20 years of application
Dang et al. (2014)	Capillary absorption	- Alkyltrialkoxy silane	Organic alkyltrialkoxy silane performed better than alkyltrialkoxy silane

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
		- Volatile Organic alkyltrialkoxy silane	
Zhang et al. (2017b)	Capillary absorption	- Liquid silane - Cream silane - Gel silane	All the three materials significantly reduced water absorption compared to control. However, gel silane performed the best
Xue et al. (2017)	- Immersion in water - Water penetrability (pressure head) - Penetration under hydraulic pressure	Silane	Significantly reduced water absorption compared to control
Ma et al. (2018)	Capillary absorption of concrete treated after freeze-thaw	Gel silane	Water absorption of treated concrete increases with increasing the number of freeze-thaw cycles

It is clear from Table 2-2 that silane, siloxane and their derivatives were highly efficient in reducing the water absorption of concrete. Even for existing structres that were treated with silane or siloxane, and tested after the application in 10 to 20 years, materials are still showing an acceptable performance regardless of the drop in their efficacy compared to newley treated structures (Christodoulou et al. 2012; Christodoulou et al. 2014). In addition, treatment has been effective in protecting concrete that suffers visible cracks, where the hydrophobic effect of such materials significantly reduced water permeability through concrete (Dai, et al. 2010). Figure 2-11 shows the effect of silane in protecting cracked concrete.

Figure 2-11 - The difference between untreated concrete and concrete treated with silane after the initiation of cracks (Jiesheng et al. 2018)

Majority of published work concentrated on testing the capillary absorption of treated structures and few considered testing water permeability due to pressure (either pressure head like ISAT or penetration under hydraulic pressure).

On the other hand, some uncertainties regarding the efficacy of silane and siloxane materials in the presence of high moisture content at the time of application started to emerge after the work of Dai et al. (2007). They found that the penetration depth of the materials has dramatically dropped with increasing the moisture content before application. Although water absorption has been reduced even when concrete was 100% saturated prior to treatment, some confirmations are still needed to evaluate their long-term performance. The same outcomes have been reported by Basheer & Cleland (2011), where the penetration depth of treatments

decreased with increasing the moisture content without a significant effect on water absorption. Those concerns have been discussed again by Calder & McKenzie (2008), Rahman et al. (2013) and Rahman et al. (2014), where a noticeable inconsistency between results obtained in the laboratory and the actual performance of such materials (on site) were noticed.

The protection of concrete against the harmful impact of chlorides using hydrophobic impregnations have been widely discussed in previous research. Many tests have been employed to measure chloride ingress through concrete. The most important tests were salt ponding test, immersion in salt solution, saltwater spray and diffusion test (Basheer et al. 1997). Table 2-3 discusses the efficacy of hydrophobic impregnations in protecting concrete against chloride penetration and its testing methods in previous research.

Table 2-3 - Summary of chloride penetration tests on concrete treated with hydrophobic impregnations

Reference	Testing method	Hydrophobic impregnation	Conclusion
Buenfeld & Zhang (1998)	Diffusion cell testing. One side was exposed to NaCl solution and the other side was exposed to NaOH solution	Alkylakoxysilane	Treatment significantly reduced chloride concentration compared to control
Ibrahim et al. (1999)	Unidirectional diffusion of chloride ions for 3 months (5% NaCl solution)	- Silane/siloxane - Silane/siloxane with an acrylic topcoat - Alkyl-alkoxy silane	- Silane/siloxane with an acrylic topcoat showed better performance than silane/siloxane and alkyl-alkoxy silane - Silane/siloxane and alkyl-alkoxy silane showed similar performance
Zhan et al. (2003)	Surface of concrete put into contact with sea water for 28 days	- Gel silane (3 coats, each 200 g/m^2) - Gel silane (1 coat, 600 g/m^2)	Both treatments significantly decreased chloride penetration with a better performance for the 3 coats
Zhan et al. (2005)	Surface of concrete put into contact with salt solution	- Liquid silane - Cream silane - Gel silane	- w/c=0.4: liquid, gel, then cream - w/c=0.5: similar performance for all - w/c=0.6: similar performance for all

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
Dai, et al. (2007)	Immersion in sea water for 5 months	- Liquid silane - Cream silane - Gel silane - Liquid silane/siloxane	17% pre-saturation: Liquid, cream, gel, then silane/siloxane
Medeiros & Helene (2008)	Accelerated chloride migration test	- Solvent-based silane/siloxane - Water-based silane/siloxane	The reduction in the chloride content for both materials was minimal compared to control
Woo et al. (2008)	Salty water spray resistance test	- Liquid silane - Modified silane-clay mixture	Liquid silane reduced chloride content by 92% and silane-clay mixture reduced chloride by 69%
Leung et al. (2008)	Salty water spray resistance test	- Liquid silane - Modified silane with 5% cloisite	Liquid silane performed better than the silane/cloisite material
Dai, et al. (2010)	Cyclic sea water shower	- Liquid silane - Cream silane - Gel silane	- Cylinders (not cracked): Liquid, cream, gel, then silane/siloxane.

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
		- Liquid silane/siloxane	- Prisms craked after impregnation with silane: silane only effective if the crack width is less than 0.08 mm
Basheer & Cleland (2011)	Salt ponding test in 15% NaCl solution	- 40% silane - 100% silane - Silane/siloxane	- 90% reduction in chloride content in the case of 0.55 and 0.65 w/c ratio - Chloride could not be detected in concrete with 0.45 w/c ratio (for both treated and untreated) - No considerable effect for moisture content at the time of application
Rahman et al. (2013)	- Salt ponding test (slabs) for 90-days - Salt ponding test (cubes) for 90-days	- Nanosilane - Aqueous silane	- Relatively similar performance for both materials - The differences by the two testing methods are within 20%
Rahman et al. (2014)	Immersing in a sodium chloride bath for 60-days	- Solvent-based silane - Water-based silane	- When materials are applied to dry surfaces, solvent-based silane performed the best

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
			- Pre-conditioning concrete before treatment negatively affected the performance of both materials (performance is worse with increasing the initial moisture content)
Zhang et al. (2017b)	Capillary absorption for 3% NaCl solution	- Liquid silane - Cream silane - Gel silane	- Chloride has migrated in control concrete up to depth of 30 mm, and in all treated concrete up to 13 mm - A significant reduction in the chloride content in treated concrete (similar performance for the three materials)
Xue et al. (2017)	One side of cylinder was exposed to sodium chloride solution, and the other side was exposed to sodium hydroxide solution. An electrical current was applied between the opposing sides	Silane	Treatment reduced chloride ion penetration by 63% in reference to control

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
Ma et al. (2018)	Concrete were placed in a sea tidal zone (concrete was treated after freeze-thaw)	Gel silane	- Chloride content in treated concrete increases with increasing freeze-thaw cycles - Increasing the applied amount of silane work on reducing chloride content of concrete with the same induced freeze-thaw damage

It is believed that diffusion is the dominant factor that controls chloride transport in the pore system of concrete, where moisture content inside the pores is around 60-70% (Climent et al. 2002; Pan et al. 2017). This is noticed from the test methods that most resaerchers have used in previous studies, where they concentrated on measuring chloride diffusion through concrete more than sorption and capillary suction (Table 2-3). On the other hand, silane and siloxane have shown a vacillating efficacy in reducing the chloride content from a study to another, where, for example, a modest reduction (11-17%) was observed in the work of Medeiros & Helene (2008) and a reduction of 92% in the work of Woo et al. (2008). Additionally, other research has revealed that siloxane was unsuccessful in retarding chloride diffusuion through the pores and only helped in delaying the initial time of diffusion (Pan et al.2017; Basheer et al. 1997).

On the other hand, Rahman et al. (2014) results (Table 2-3) showed that increasing the initial mosisture content reduces the efficacy of hydrophobic impregnations in protecting concrete from chloride ingress. Those important outcomes support previous claims about the deficiency of silane/siloxane in the presence of water (Calder & McKenzie 2008; Rahman et al. 2013).

Another durability aspect that was investigated by researchers is the effect of freeze-thaw action on the efficacy of hydrophobic impregnations. Concrete that exists in very cold regions suffers from substantial deterioration due to the effect of freeze-thaw, which led to the wide use of air-entrained concrete in those regions to decrease the risk of freeze-thaw actions (Figure 2-12). However, the use of air-entrained concrete only decelerates the rate of freeze-thaw deterioration rather than inhibiting it. Accordingly, hydrophobic imprregnations were used to to provide further protection for concrete, especially in the severe cold regions (Dang et al. 2014; Pan et al. 2017).
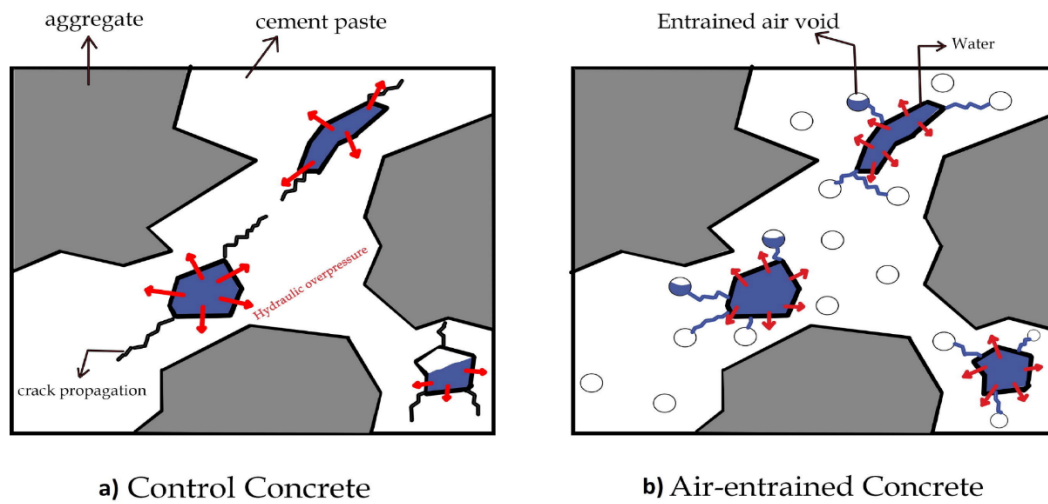
Figure 2-12- The effect of freeze-thaw action on: (a) normal concrete and (b) air-entrained concrete (Ebrahimi et al. 2018)

Table 2-4 illustrates the studies that have discussed the effect of freeze-thaw actions on the efficacy of hyrdophobic impregnations.

Table 2-4 - The effect of freeze-thaw action on concrete treated with hydrophobic impregnations

Reference	Testing method	Hydrophobic impregnation	Conclusion
Basheer & Cleland (2006)	- ASTM accelerated freeze-thaw test for 100 cycles (involves ponding the treated surface with fresh water) - RILEM fresh water test for 100 cycles (involves immersing treated sides in fresh water for one week) - RILEM salt scaling test for 97 cycles (involves immersing treated sides with 3% salt solution for one week)	- 100% alkyl (isobutyl) tri-alkoxy silane - 40% alkyl (isobutyl) tri-alkoxy silane - Undiluted siloxane	- All the conducted tests showed that treatments increased the freeze-thaw durability - Concrete with high w/c ratio resisted less number of freeze-thaw cycles compared to low w/c ratio concrete
Mamaghani et al. (2009)	- Salt scaling test for 100 cycles (potassium acetate solution) - Rapid freezing and thawing (300 cycles)	Isobutyl-trialkoxy silane	- Treated concrete did not show scaling until 100 cycles - Treatment after the rapid freeze-thaw action did not show significant improvement in protecting concrete

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
Basheer & Cleland (2011)	RILEM salt scaling test (100 cycles)	- 40% silane - 100% silane - Silane/siloxane	Applying the materials to low moisture content or dry concrete enhanced the resistance to freeze-thaw than saturated concrete
Dang et al. (2014)	Salt scaling test (3% NaCl solution)	- Alkyltrialkoxy silane - Volatile Organic alkyltrialkoxy silane	Alkyltrialkoxy silane performed better than the volatile organic silane and significantly increased the resistance to salt scaling
Liu & Hansen (2016)	- RILEM fresh water test - RILEM salt exposure test	- 100% silane - 40% silane	- Both treatments were effective in reducing 90% of the surface scaling - Water absorption during freeze-thaw test could not be stopped by treatment - Internal cracks were developed in treated concrete, especially in concrete with less air voids

Table Continues…

Reference	Testing method	Hydrophobic impregnation	Conclusion
Zhang et al. (2017a)	Freeze-thaw cycles following the chinese standard method (100 cycles)	Gel silane	- Compressive strength: 0.4 w/c ratio treated concrete was reduced by ~30%, and 0.6 w/c ratio treated concrete was reduced by ~45% - Chloride penetration: small amount of chloride penetrated 0.4 w/c ratio treated concrete. For 0.6 w/c ratio treated concrete, the water-repellent surface was damaged and chloride penetrated deep inside
Zhang et al. (2018)	Freeze-thaw cycles following the chinese standard method by placing one treated side under water (98 cycles)	Silane	- Treatment has reduced the mass loss of concrete - To accomplish suitable frost resistance, amount of silane should not be more than 5 m^2/kg

Concrete treated with hydrophobic impregnations, as illustrated in Table 2-4, have shown high resistance against frost damage. However, this resistance varies depending on some factors that affect the efficacy of treatment like the w/c ratio of treated concrete and the initial moisture content of concrete before applying the material. Results have demonstrated that efficacy of treatment is negatively affected with increasing the w/c ratio of concrete as increasing w/c ratio works on weaken the pore structure of concrete and facilitates mositure saturation during the freeze-thaw (Basheer & Cleland 2006; Basheer & Cleland 2011). In addition, applying silane/siloxane on dry concerte, which is reflected on a deeper material penetration, has resulted in more resistance against freeze-thaw actions than concrete with high initial moisture content. With the initiation of small scaling at the beginning of freeze-thaw, concrete with high moisture contnet and low penetration depth of silane/siloxane will act similarly to untreated concrete. However, drier concrete that has already guaranteed a deep penetration depth of silane/siloxane will delay moisture and chloride ingress during freeze-thaw, which slows down the scaling of concrete (Basheer & Cleland 2011).

The morphology and interaction of silane with concrete, before and after freeze-thaw test, has been investigated through Scanning Electron Microscope (SEM) (Zhang et al. 2018). As shown in Figure 2-13, silane material could be seen in the concrete texture as white small spots distributed over the hydration products of concrete, which resulted from the reaction of hydroxyl and polar groups of silane with the hydration products. Condensation of silane in concrete will form interconnected hydrophobic structure that is strongley fixed inside the pores, which works on enhancing the frost resistance of concrete. After the freeze-thaw action, ettringite crystals and calcium silicate gel could be seen in the SEM micrograph, with some moderate loss of hydration products and the silane itself. Despite the loss of some silane crystals from the pores, good presence of silane is still seen in concrete after freeze-thaw action, which indicates its good resistance to frost actions (Zhang et al. 2018).
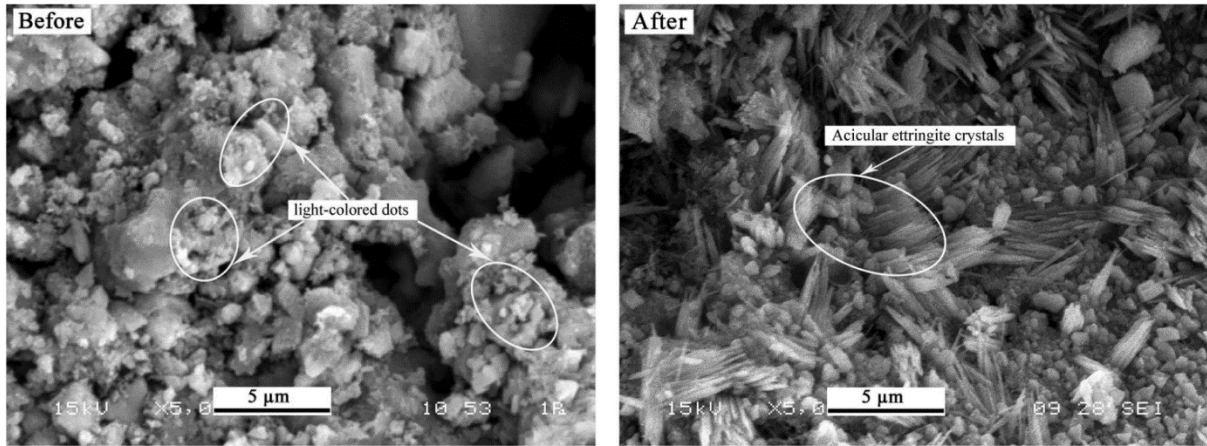
Figure 2-13 - SEM microfraphs of concrete treated with silane before and after the freeze-thaw action (Zhang et al. 2018)

To study the chemical composition of silane/siloxane products and their effect on concrete, Weisheit et al. (2016) performed an Infrared Spectroscopy (IR) assessment on untreated concrete, concrete treated with silane/siloxane matrial with 31% active content, and weathered treated concrete (Figure 2-14). The IR bands of untreated concrete show a distinctive peak at the range of 1409 to 1460 cm^{-1} which represents carbonate bonding. Treating concrete with the silane/siloxane has resulted in peaks at 1130, 1750 and 2900 cm^{-1}, which correspond to Si-O-Si, C=O and C-H bonds respectively, with a reduction to the carbonate C-O bond. The emerging of the Si-O-Si, C-H and C=O bonds refers to the reaction of silane/siloxane with hydration products and its bonding inside the pores. On the other hand, weathered concrete has decreased the intensity of C-H peak, which recognises the deterioration of the applied treatment (Weisheit et al. 2016).
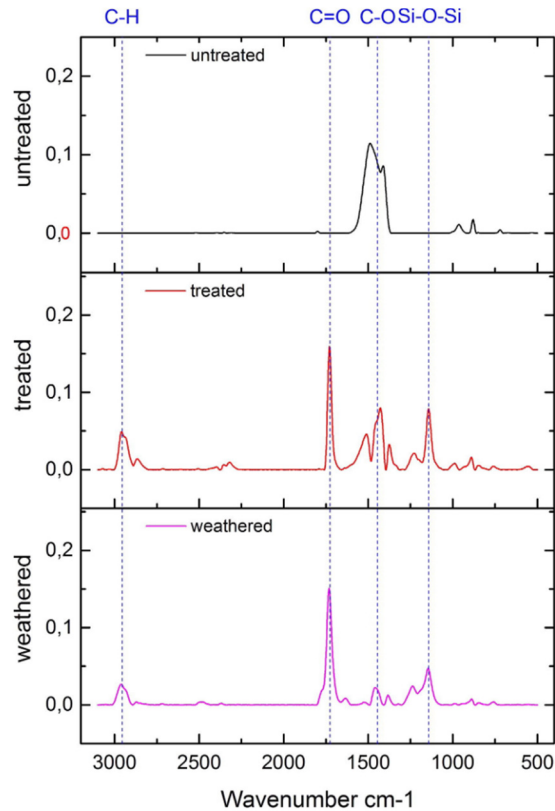
Figure 2-14 - IR spectroscopy of concrete before and after treatement and after weathering

(Weisheit et al. 2016)

Most of research about hydrophobic impregnations has focused on silane, siloxane and their derivatives. Some other hydrophobic materials were barely discussed in literature and their application in the construction industry is limited, like fluoropolymers and silicate resin (Krishnan et al. 2013; Pan et al. 2017).

Fluoropolymers, as explained by Gardiner (2015), are mainly formed from fluorine with a strong polar C-F bond in their composition. This gives fluorinated compounds a distinctive hydrophobic features and low surface tension making them water repellent and helpful in protecting concrete against weathering effects; the presence of fluorine in the chemical composition of fluoropolymer gives it the ability to resist chemical attacks and repel water (hydrophobicity). The amalgamation of fluorine in polymers provides the attached polymer with lower surface energy that increases its hydrophobicity and decreases its friction coefficient

and adhesion (Passaglia et al. 1994; Brady 2000; Li et al. 2002). When fluoropolymers are applied on concrete, the fluorine part of the polymer has the ability to form a well-organised structure on the surface of concrete that results in a sheet, which is combined of strongly, bundled –CF$_3$ groups (Li et al. 2002; Hayakawa et al. 2000). This gives the concrete the ability to repel water and reduces its water absorption, as it increases its hydrophobicity. Regardless of the role that fluoropolymers play in decreasing water absorption, some recent research found that fluoropolymers with long fluorinated side chains are hazardous to the environment and may cause cancer (Zaggia et al. 2009).

Polytetrafluoroethylene (PTFE) is one type of fluoropolymers that has been widely used as a waterproofing material for textiles, tiles and glass panels. However, its application in concrete has not been thoroughly discussed.

When fluoropolymer is applied to concrete, it forms an attached sheet that lines the interior pores without blocking them. Figure 2-15 shows SEM micrograph for cement mortar treated with fluoropolymer (Krishnan et al. 2013).
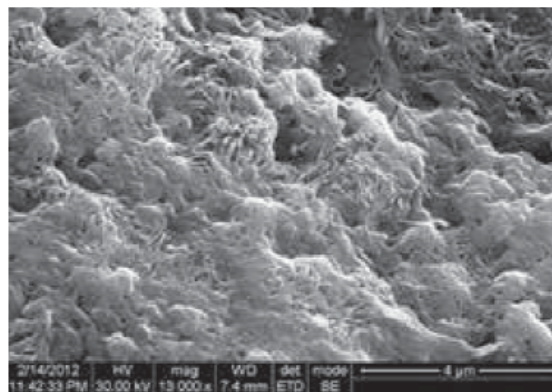
Figure 2-15 - SEM image for cement mortar treated with Fluoropolymer (Krishnan et al. 2013)

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Another hydrophobic impregnation is silicate resin. Silicate resin is a hydrophobic material that coats the internal walls of concrete pores with a hydrophobic film to repel water. Little research has studied this material, and for that reason, insufficient information about its performance against chloride or water penetration through concrete is known (Pan et al. 2017).

2.6.1.2 Coatings

Coatings usually produce a connected polymer layer on concrete surfaces that works on hindering the ingress of aggressive chemicals and water (Almusallam et al. 2003; Diamanti et al. 2013; Pan et al. 2017). They are divided into conventional polymer coatings, cementitious coatings and nanocomposite coatings. The nanocomposite and conventional polymer coatings are distinguished with their very small thickness that ranges between 0.1 to 1 mm, contrary to cementitious coatings that have large thickness reaches up to 10 mm (Pan et al. 2017).

Conventional polymer coatings have been utilised in concrete protection for many years and they are formed from epoxy resins, acrylics or polyurethane (Moloney et al. 1987; Chruściel et al. 2015; Carretti & Dei 2004; Pan et al. 2017). Despite the high efficacy of acrylics to resist weathering and oxidation they provide a lower bonding strength to concrete surfaces than epoxies. Polyurethane has shown a high level of protection against shrinkage and acid damages but when it is applied in alkaline environment it becomes unstable and weaker. Adding to that, the presence of isocyanates in its chemical composition has brought many questions regarding its safety to environment and human health (Pan et al. 2017).

Despite the limited number of research that discusses the utilisation of nanocomposite coating in concrete protection, this type of materials has shown a high level of protection against gas permeability, weathering and heat resistance (Woo et al. 2008; Pan et al. 2017). However, more investigation is still needed to evaluate its durability and performance in harsh environments.

Cementitious coatings are divided itno two types; polymer modified cementitious coatings and geopolymer coatings. Polymer modified cementitious coatings are formed from cement, fine aggregate and a polymer such as epoxy, acrylate or polyurethane. Former constituent is intended to provide the cementitious coating with strength, adhesion to concrete surfaces and the ability to resist chemical attacks (Pan et al. 2017). On the other hand, geopolymers are inorganic polymers that are stable and hard at elevated temperatures and formed from the reaction of aluminosilicates like metakaolin with alkaline solution (Zhang et al. 2012; Pacheco-Torgal et al. 2012). Geopolymers have proven their high efficacy in protecting marine structures and their durability for many years (Zhang et al. 2010; Pacheco-Torgal et al. 2012; Pan et al. 2017). However, geopolymers are believed to have some shortcomings when it comes to their resistance to shrinkage (Pan et al. 2017).

2.6.1.3 *Pore Blockers*

Pore blockers have been employed in protecting concrete for long time ago. These materials work on closing the pores of concrete and restrict the movement of moisture and chemicals through the pores (Dai et al. 2010; Pan et al. 2017). Many materials like calcium silicate and sodium silicate are classified under thio type of treatment where they have shown high efficacy in blocking the pores and reducing the permeability of concrete to very low levels (Bertolini et al. 2013).

Sodium silicate was the most widely discussed pore blocker in literature where it has proven to enhance the long-term performance of concrete (Moon et al. 2007; Pan et al. 2015; Jiang et al. 2015a). On the other, some results obtained in other studies contradicted the previous claims, where some microcracks have been observed on the surface of treated concrete and the improvement in reducing water absorption and chloride penetration was not significant (Ibrahim et al. 1999; Dai et al. 2010; Franzoni et al. 2013). Moreover, some concerns have

risen regarding the presence of NaOH inside the pores after the penetration of sodium silicate in the pores and its reaction with calcium hydroxide, as NaOH increases the alkali-silicate reaction (Dai et al. 2010; Pan et al. 2017). Figure 2-16 shows SEM images for the effect of treating concrete with sodium silicate, where some microcracks can be seen on the surface of concrete (Figure 2-16 b).
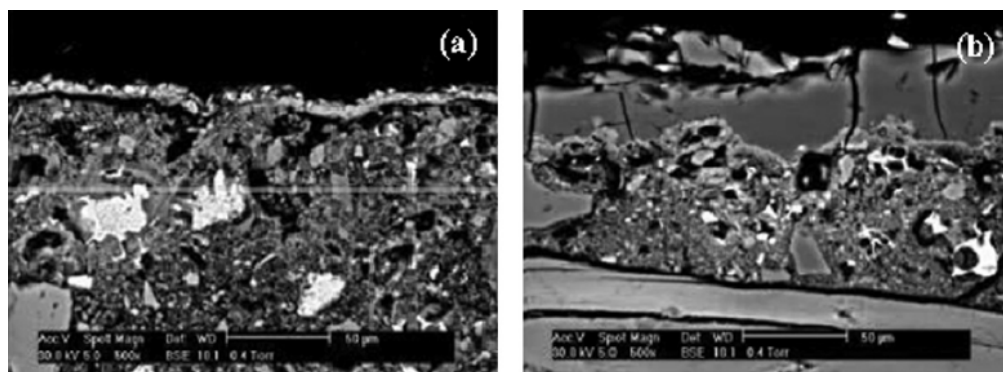
Figure 2-16 - The effect of sodium silicate on initiating microcracks in concrete: (a) before treatment and (b) after treatment (Franzoni et al. 2013; Pan et al. 2017)

Surface hydrophobic impregnants are believed to have a virtue over the other types of surface treatments as they encourage internal moisture content to vaporise out of concrete, contrary to coatings that confine water inside the pores and force it to accumulate there and prevent it from evaporation. This may lead water to form an increasing pressure beneath the protection layers causing some damages to concrete, especially when water freezes and expands (Christodoulou et al. 2012).

On the other hand and despite the good performance of surface hydrophobic impregnations, especially silane and siloxane, the presence of solvent-based materials in these treatments and their improper performance when applied to wet surfaces led researchers to look for other options that are environmentally friendly and tolerant to moisture at the time of application (Bubalo et al. 2014).

2.6.2 Internally Integrated Materials

Surface applied treatments were effective and helpful in protecting concrete from water ingress and the attacks of aggressive chemicals like chlorides. All previous research focused only on treating hardened and matured concrete with these materials without considering protecting fresh concrete, since the application of those materials requires dry concrete with minimum moisture content at the time of application. Also, treating fresh concrete will reduce the waiting-time needed for treatment to begin, reduce the effort of applying treatment to structures and bring down the expenses related to treatment (Standke et al. 2004). However, the number of studies and publications regarding fresh concrete protection by using hydrophobic materials were very few and limited (Zhang et al. 2009).

When it comes to highways, treating hardened concrete would involve some inconvenient procedures like closing the highway to traffic to allow concrete pavement to be impregnated (Sommer 1998). From this point, researchers started to look for new solutions to escape from such inconveniences which are also more cost-effective.

2.6.2.1 Natural hydrophobic integrated materials

Products from natural resources like oil, fats and animal blood have been used since the Roman Empire (27 BC) as protective treatments for mortars, clay and other construction materials (Pollio 1914; Wittmann et al. 2011; Nunes et al. 2018). Until recently, vegetable oils have been employed in protecting concrete from water ingress and aggressive ions attacks (Justnes et al. 2004; Nunes & Slížková 2014). It is believed that these natural oils participate in altering the pore structure of concrete after adding them to the mix resulting in a denser structure (Justnes et al. 2004).

Linseed oil, for instance, has proven its efficacy in increasing the durability of concrete by yielding a hydrophobic effect inside the pores of concrete (Čechová 2009; Nunes & Slížková

2014; Wang et al. 2014). Linseed oil includes some triglycerides that produce polymer chains when exposed to oxygen and start oxidising. When this oil is mixed with concrete, the glycerides react with the alkaline in cement and hydrolyse. Afterwards, carboxyl groups in the oil will react with calcium and create calcium salt of fatty acids that gives concrete hydrophobicity (Chandra & Ohama 1994; Nunes et al. 2018).

The hydrophobic behaviour of some vegetable oils like sunflower, peanuts, olives, corn, rapeseeds, linseeds and soya beans has been tested when added to cement mortar (Justnes et al. 2004). Oil has been dispersed in water by mixing it with lignosulphonate before adding it to the mortar to insure proper distribution of oil in the mix. Results showed that oils with higher percentages of monosaturated fatty acids performed better than other types of oils in terms of reducing water absorption and chloride penetration. However, when testing water absorption of the area near surface and compare it with that through the whole depth of a mortar sample, all types of oil did not provide any significant reduction in water absorption compared with untreated mortar. This proves that oil will be effective only on the skin of the mortar. On the other hand, treatment has negatively affected the compressive strength of mortar, especially when unsaturated oil is used, and the reduction was severe when linseed oil was used. This reduction in strength was attributed to dispersing oil in water, by using lingosulphonate, instead of adding it straight to the mix. Similar results have been reported by Albayrak et al. (2005), where unsaturated fatty oil decreased the compressive strength of treated concrete dramatically, which verifies, to some extent, the outcomes of Justnes et al. (2004). However, Albayrak et al. (2005) refer the reduction in the compressive strength to the reaction between the double bonds of the fatty acids with oxygen that dissolves in water causing some cracks in concrete and reduces the strength.

Internal integration of soybean oil within mortar mix has participated in reducing shrinkage of the treated mix compared to control. However, it did not improve the resistance of the mix against deicing salts penetration and it participated in reducing the compressive strength of the mix (Kevern 2010).

The effect of adding vegetable oils to fresh mortar on compressive strength was further investigated by Baghban et al. (2012), where rapeseed oil was mixed with mortar with different w/c ratios; 0.58, 0.44, and 0.36. Results revealed that compressive strength was significantly reduced when rapeseed oil were added to the mix. However, lower degree in strength reduction was observed in mortars with low w/c ratio. The reduction in compressive strength was attributed to the non-uniform distribution of the oil in the mix and its role in reducing the hydration degree of the mix (Baghban et al. 2012).

Wang et al. (2014) investigated the internal integration of linseed oil with concrete (w/c = 0.6) and its influence on water absorption, chloride penetration and compressive strength. Results showed that water absorption and chloride penetration decrease with increasing the amount of oil added to the mix. However, an adverse effect on compressive strength was noticed when linseed oil is added to the mix, and the reduction in strength increases with increasing the added amount of oil (28% strength loss with adding 4% linseed oil). Figure 2-17 illustrates the effect of adding linseed oil to compressive strength of concrete when added with different percentages.
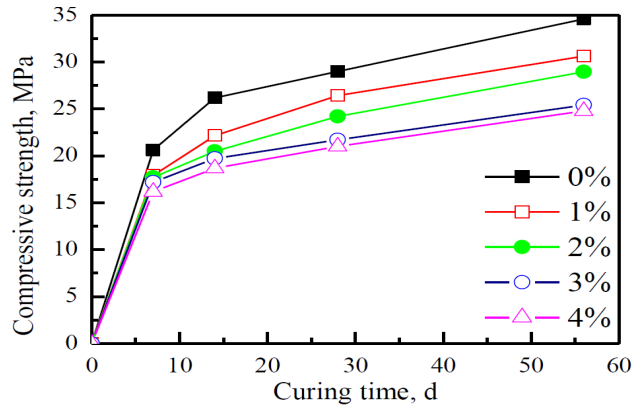
Figure 2-17 - Compressive strength development for untreated concrete and concrete

integrated with linseed oil (Wang et al. 2014)

Adding linseed oil to concrete was observed to produce large rounded pores inside the mix (Figure 2-18), which result from the saponification reaction of oil with alkaline materials in concrete (Nunes & Slížková 2014; Nunes et al. 2018). The reaction of oil with cement in the mix will create fatty acids with non-polar hydrocarbon chains attached to polar carboxyl groups that work on reducing the surface tension and developing air bubbles in the mix. The presence of air bubbles in the mix would work on weakening concrete structure and results in reducing its compressive strength, as reported by Wang et al. (2014).
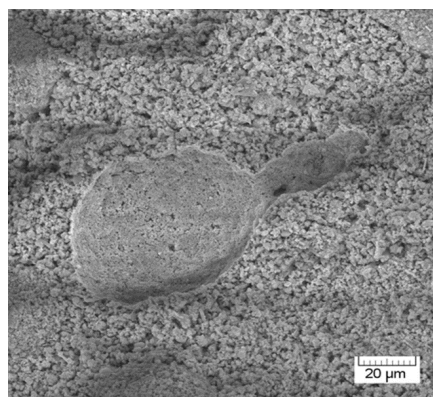
Figure 2-18 - SEM image for concrete treated with linseed oil (Nunes et al. 2018)

Linseed oil has been also tested by Wittmann et al. (2014) in similar procedures carried by Wang et al. (2014). Results were also in line with Wang et al. (2014) outcomes, where capillary

absorption of treated concrete was noticed to decrease gradually with time. Optimum performance for concrete treated with 4% of the oil was noticed, where water absorption was reduced by more than 50% from that of untreated concrete. However, compressive strength for this kind of treatment was noticed to decrease with increasing the amount of linseed oil added to the mix.

In a study where Ox blood was used as an internal integrated protective material, a significant reduction in water absorption and chloride penetration was noticed, especially with increasing the amount of added blood (Wittmann et al. 2011). Similar to other natural water-repellent products, ox blood has contributed in reducing the compressive strength of concrete to very low levels compared to untreated concrete (more than 40% reduction). Wittmann et al. (2011) attributed this reduction to the presence of a considerable amount of water within blood which increases the w/c ratio.

The dilemma of compressive strength reduction in concrete treated with natural materials has been also reported by many other researchers in literature (Čechová et al. 2010; Nunes & Slížková 2014; Centauro et al. 2017). Most of researchers attributed this reduction to the increased porosity in concrete and to the effect of oil in preventing the contact between aggregate and binder.

2.6.2.2 *Man-made Hydrophobic Integrated Materials*

Due to the high level of protection that surface applied hydrophobic impregnations had provided to concrete, and to overcome the problems associated with their application to hardened concrete, researchers tried to integrate such materials within the fresh mix (Sommer 1998; Standke et al. 2004; Wittmann et al. 2006; Meier & Bäuml 2006; Xian et al. 2007; Zhang et al. 2008). Silane and siloxane materials were the most used hydrophobic treatments to serve this purpose.

In an attempt to rehabilitate a parking garage in Basle, Switzerland, which was severely damaged by chloride penetration, concrete was removed and replaced by a new mix that was integrated with silane emulsion (Standke et al. 2004). Water absorption has shown a significant reduction by more than 80% due to treatment, and this reduction was maximum near the surface of concrete. This may refer to the accumulation of silane near the surface, which was confirmed by running FTIR analysis through the whole depth of the tested concrete samples. Silane concentration was found to be higher on the surface than other deeper areas, which might refer to the migration of the material to the surface during curing (Standke et al. 2004). On the other hand, authors claim that adding silane to the mix did not reduce the compressive strength, instead it maintained the compressive strength similar to control.

Alcyltrialkoxysilane emulsion when mixed with concrete has managed to reduce water absorption and chloride penetration by 85% and 95% respectively. However, when adding the same material to mortar, small cracks and modest debonding close to the edges were observed (Meier & Bäuml 2006). Wittmann et al. (2006) and Xian et al. (2007) results were in agreement with Meier & Bäuml (2006) outcomes, where a significant reduction in the capillary suction of concrete treated with silane emulsion were reported, especially with increasing the quantity of the added silane. However, modest quantities of silane (less than 2%) did not seem effective in reducing chloride penetration in concrete and even with adding 2% of silane, concrete did not act as a chloride barrier (Xian et al. 2007). Moreover, when comparing the efficacy of integrating silane into the fresh mix with applying the same amount of silane to the surface of dry concrete, Wittmann et al. (2008) and Wittmann et al. (2013) reported that surface impregnation was more effective in reducing chloride penetration than internal integration.

In order to check the effect of increasing the added amount of silane to concrete, Zhang et al. (2009) integrated 2%, 3%, 4% and 6% silane emulsion with concrete. Unlike the results

obtained by Standke et al. (2004), compressive strength was noticed to decrease with increasing the added amount of silane (Figure 2-19). Even with adding 2% silane, which is the minimum tested amount, compressive strength was noticed to drop down when compared to control. Same results were obtained by Zhao et al. (2011), Zhu et al. (2013) and Milenković et al. (2014), where significant reduction in compressive strength was reported in concrete integrated with silane with different percentages. This reduction in strength was refered to the retardation effect of silane on the hydaration process, which was proven by the calorimetric investigation run by Milenković et al. (2014). On the other hand, FTIR analysis showed that the highest concentration of the material is found near the surface, agreeing with the outcomes of previous research (Zhang et al. 2009).

Compressive strength of concrete after exposing to freeze-thaw action was found to decrease dramatically as well. Also, the amount of the protective material added to the mix was found to have a great effect on the strength as increasing its concentration leads to a considerable reduction in compressive strength (Ma et al. 2016)
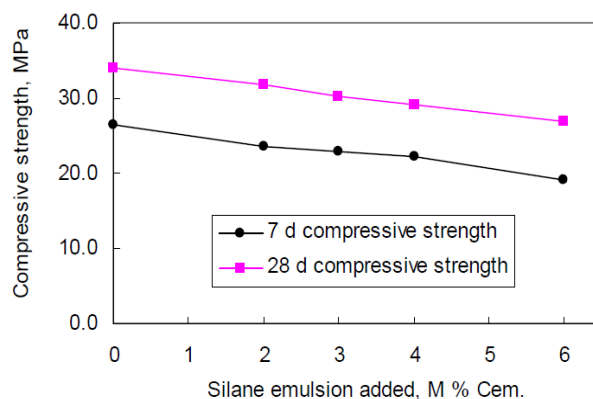
Figure 2-19 - The effect of integrating concrete with silane emulsion on compressive strength (Zhang et al. 2009)

Exposing mortar that was integrated with silane to aging conditions like UV emission along with temperature cycles that alternate between 40 °C and -20 °C and alternate cycles of sun

and rain, have shown a significant reduction to water absorption. However, when siloxane was used during aging process, water absorption of mortar has increased and the material did not provide protection against it. This was explained by a hypothesis put by researchers that siloxanes travel to the surface of the mortar where it worn out by rain which decreases its efficacy (Spaeth, Lecomte & Delplancke-Ogletree 2014).

2.6.2.3 Alternative Integrated materials (Newly Developed)

From previous sections it was clear that silane and siloxane based materials are the most widely used hydrophobic treatments for concrete in these days. Due to the existence of solvent agents in these materials the world started to avoid using such materials and trends toward using some environmentally friendly materials to drive down environment deterioration (Rahman et al. 2014). Adding to that, the negative effect of integrating silane, siloxane and natural products on compressive strength made researchers to look for some alternatives that have the ability to protect concrete and, at the same time, reserve its compressive strength. Crystalline materials are the most dominant materials under this category that researchers started to consider in their research in recent years.

Crystalline protective materials have shown some promising results in protecting concrete and enhancing its properties when implanted within the concrete ingredients. However, few research considered this type of protection (Gao et al. 2009; Weng & Cheng 2014; Reiterman & Bäumelt 2014; Pazderka 2016; Pazderka & Hájková 2016; Rahman & Chamberlain 2016).

The chemical composition of crystalline materials and their interaction mechanism are still vague and unknown (Roig-Flores et al. 2016). Some assume that the main reaction happens between tricalcium silicates (Ca_3SiO_5) in concrete and the crystalline material (American concrete Institute 2010). Other researchers believe that calcium hydroxide ($Ca(OH)_2$) is the main component in concrete that reacts with the crystalline material in the presence of water

(Sisomphon et al. 2012). According to the American Concrete Institute (2010), crystalline materials have an unknown promoter M_XR_X that reacts with tricalcium silicates in the presence of water and yields calcium silicate hydrates and a pore blocker compound, as described in the following reaction:

$$Ca_3SiO_5 + M_XR_X + H_2O \rightarrow Ca_XSi_XO_XR–(H_2O)_X + M_XCaR_X–(H_2O)_X$$

Where M_XR_X is the crystalline active content and $M_XCaR_X–(H_2O)_X$ is the pore blocker resultant product (Li et al. 2018). In line with former reaction, some researchers consider crystalline material as a hydrophilic material that uses water to form its crystals, which in turn work on blocking the pores (Sisomphon et al. 2012; Roig-Flores et al. 2016). On the other hand, some other researchers consider the crystalline material as a dual-action material that performs hydrophilic at the beginning (when first touches water) to form crystals that have hydrophobic properties. These crystals are believed to work on lining the pores of concrete instead of blocking them (Rahman & Chamberlain 2016; Hrbek et al. 2017).

When it comes to the chemical composition of the crystalline material, none of the research that discusses this kind of treatment has mentioned any of its compositions. However, Jiang et al. (2015b) have mentioned that it might contain sodium carbonate and talcum powder with other components. Moreover, Al-Otoom et al. (2007) revealed that this crystalline material might be formed mainly from sodium acetate that was produced by the reaction of sodium carbonate and acetic acid, which confirms with Jiang et al. (2015b) claim that crystalline material contains sodium carbonate.

The performance of crystalline materials that were considered in literature are illustrated in Table 2-5, where water absorption, chloride penetration and some long-term testing were considered.

Table 2-5- Performance of crystalline materials as reported in literature

Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
Gao et al. (2009)	Catalytic crystalline material (Integrated with 1%, 2%, and 3% amount)	0.7 and 0.5	Permeability under hydraulic pressure	Immersion in 5% NaCl	NA	NA	- Significantly reduced water absorption under all conditions. - Chloride penetration reduction in 0.5 concrete was more than 0.7 concrete
Bohus & Drochytka (2012)	Crystalline admixture	0.52	Permeability under hydraulic pressure	NA	NA	Aged in sulphur dioxide for 6, 12 and 18 months	- Increase in the water depth of penetration for all treated concrete under all conditions compared to control

Table Continues…

Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
Weng & Cheng (2014)	Crystalline admixture (Integrated with 3%, 5%, and 7% amount)	0.4	NA	NA	NA	- Compressive strength - Tensile strength	- Reduction in compressive strength when cured in air - Modest increase in compressive strength when cured in water - Modest increase in tensile strength for both curing conditions
Reiterman & Bäumelt (2014)	Crystalline admixture (Integrated with 0.5% and 1% amount)	0.78 (mortar)	Capillary absorption	NA	NA	Compressive strength	- Modest increase in compressive strength in both 0.5% and 1% treated concrete - Reduction in water absorption of 0.5% - 1% did not enhance impermeability

Table Continues…

Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
Pazderka & Hájková (2016)	Two types of crystalline admixtures (2%)	Not stated	Permeability under hydraulic pressure	NA	NA	Compressive strength	- Full protection from water starts on the 12th day of casting for both admixtures - Reduction in strength for both admixtures
Pazderka (2016)	Crystalline admixture (1%) compared with crystalline coating	Not stated	Permeability under hydraulic pressure	NA	NA	NA	- The integrated crystalline material absorbed more water than the coating
Žižková et al. (2016)	Crystalline additive (1%)	0.5 (mortar)	NA	NA	- Aging in sodium	- Compressive strength	- Small drop in bending and compressive strength when cured in water

Table Continues…

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Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
					sulphate solution - Aging in ammonium chloride solution	- Bending tensile strength	- Small drop in bending strength after 90 and 180 days aging in ammonium chloride, and modest increase when aged in sodium sulphate - modest increase in compressive strength after 90 and 180 days aging in sodium sulphate and ammonium chloride
Rahman & Chamberlain (2016)	Liquid crystalline material followed by wax based curing agent applied on	0.45	ISAT	NA	NA	Compressive strength	- Modest increase in strength of treated concrete when cured in water - Increase in strength of treated concrete when adversely cured

Table Continues…

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Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
	fresh concrete surface						- reduction in water absorption for both curing conditions, with better performance for water cured concrete
Pazderka (2017)	Crystalline admixture (2% with concrete and 1% with mortar)	Not stated	NA	NA	NA	Compressive strength	- Drop in compressive strength of concrete - Modest increase in compressive strength of mortar after 28 days when compared to control, and the increase continued at the age of 41 and 64 days (without making comparison with control)
Žižková et al. (2018a)	Crystalline Additive	0.5 (mortar)	NA	NA	- Freezing cycles (25 cycles)	- Compressive strength - Flexural strength	- Modest increase in compressive and flexural strength under normal conditions - Drop in compressive and flexural strength after carbonation

Table Continues…

Reference	Protective material	w/c ratio	Water absorption testing	Chloride penetration testing	Long-term testing	Strength testing	Conclusion
					- Carbonation		- Reserved strength after freezing cycles
Žižková et al. (2018b)	Crystalline additive	0.5 (mortar)	NA	NA	NA	- Compressive strength - Flexural strength	- Modest increase in compressive strength under all curing regimes - Drop in flexural strength when concrete cured under 95% humidity - Flexural strength was reserved when concrete cured in water

As illustrated in Table 2-5, crystalline material has shown different performance when tested for compressive and flexural strength and water permeability. In general, the crystalline material managed to reduce concrete's absorption for water to acceptable levels, and in some cases the material was able to reserve the strength of concrete or increase it to modest levels. However, the efficacy of the material was noticed to depend on the added dosage and the w/c ratio of concrete, which some researchers did not consider. Accordingly, some reduction in compressive strength was observed in some situations and under some curing conditions.

Figure 2-20 shows SEM micrographs for mortar treated with crystalline admixture from different studies in the literature. From all the presented micrographs, it could be seen that the material will exist in a needle-shaped crystals inside the pores (Drochytka & Bohus 2011; Žižková et al. 2018b). Those crystals are believed to grow within the texture of concrete in few days and their efficacy and growing rate depend on the presence of water inside the pores (Drochytka & Bohus 2011).
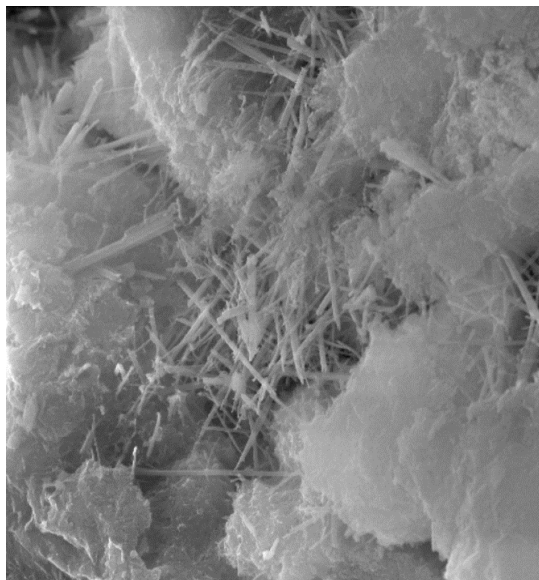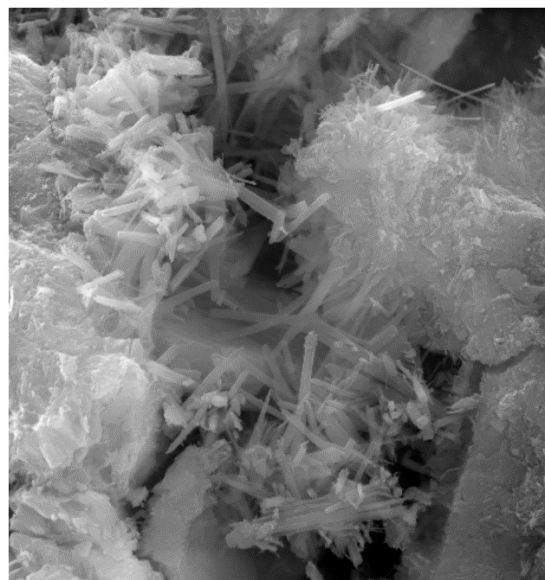
(a)   (b)

Figure Continues…
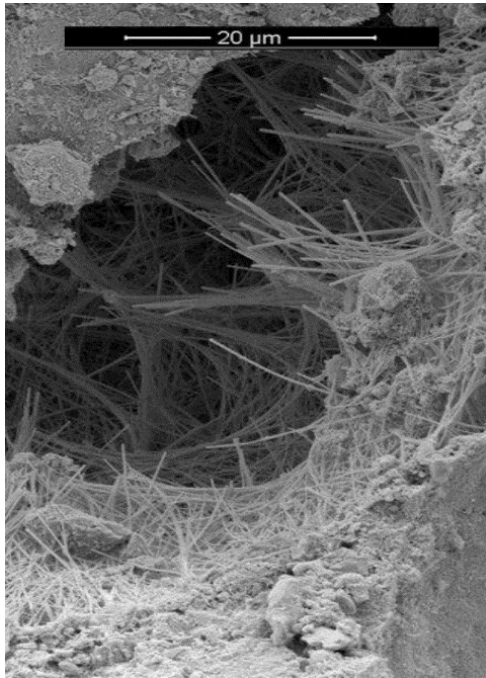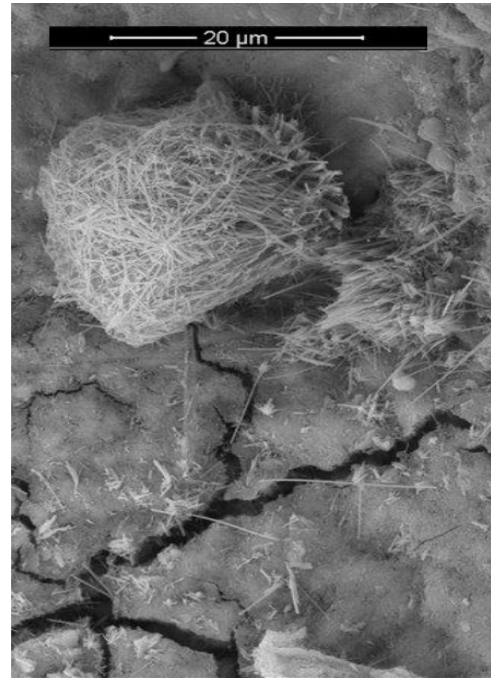
(c)   (d)

Figure 2-20 - SEM micrographs for the formation of crystals inside the pores of mortar as observed by: (a) Žižková et al. 2018b, (b) Žižková et al. 2018a, (c) Drochytka & Bohus 2011) and (d) Drochytka & Bohus 2011)

Another alternative integrated material that was used to produce hydrophobic concrete is the metal soap (Li et al. 2011b; Lanzón & García-Ruiz 2008). The incorporation of this material in concrete has shown a significant reduction in water absorption when added with different percentages. However, it was found that the maximum efficacy of metal soap presents near the surface of treated concrete, as water absorption starts to increase if the top layer of concrete was removed. This may refer to the migration of the material to the surface of concrete, following similar behaviour to silane (Li et al. 2011b). In contrast, metal soap has failed to reserve the compressive strength of treated concrete, where a severe reduction in strength has been observed, which might be caused by the retardation effect of the soap on the hydration process (Li et al. 2011b; Falchi et al. 2015).

2.7 Summary

From the research that were analysed in this literature, next observations are spotted:

- Water ingress is the main issue that affects concrete durability and causes it to deteriorate. Freeze-thaw action, frost damages, carbonation, aggressive chemicals penetration like chloride ions are all associated deteriorating factors that are linked with moisture.

- Means to improvement of concrete protection were either applied to matured concrete or fresh concrete with different application methods; brushing, spraying, and internal integration by mixing with concrete ingredients.

- Most of studies concentrated on treating existed matured concrete more than protecting fresh concrete. The greatest part of these studies adopted the surface impregnation method with hydrophobic materials like silane and siloxane despite their negative effect on the environment.

- Penetration depth of impregnation materials has been the main concern that researchers tried to enhance.

- Water absorption and chloride permeability were the most major issues investigated by researchers.

- Amount of silane and siloxane materials added to concrete, their penetration depths, and their effect in reducing chloride ingress are all issues related to the presence of moisture at application time; they need low moisture content to work sufficiently. On the other hand, crystalline materials would perform better and give their optimum with the presence of water.

- The chemical composition and the interaction mechanism of the crystalline material with concrete have not been studied or investigated in previous research.

- The protection of concrete pavement and highways, in particular, was not discussed in previous research.

- Most of internal integrated materials had a negative effect on the strength of treated concrete, especially materials from natural resources like vegetable oil.

- Most of researchers used a high w/c ratio for the concrete mix when testing for the protective materials. In their recommendations they mostly advise using lower w/c ratio so the materials they have added will perform better.

- When referring to concrete tested under extreme conditions, the value of w/c ratio has a significant effect on concrete resistance to these harsh conditions. Studies showed that lower w/c ratio helps untreated concrete to resist carbonation, chloride ingress, freeze-thaw actions, drying shrinkage, and water absorption.

Chapter 3: Materials and Methods

3.1 Introduction

In this chapter details of the used materials, their features and reasons behind their use will be discussed. The materials in this research are divided in two categories; those forming normal concrete and materials added to concrete to protect it and enhance its properties, either added to the fresh mix or applied to the surface of matured concrete. Methods for testing concrete and determining the efficacy of the used protective materials are discussed as well in this chapter.

3.2 Materials

All the materials used in this research are discussed in this section.

3.2.1 Cement

All the concrete samples in this research were made from Ordinary Portland Cement CEM II/32.5 N with Sulphates < 3.5%, Chlorides < 0.1%, and initial setting time of 1.25 hours. It was supplied by Crescent Building Supplies which satisfies the requirements of the British Standard BS EN 197-1 (British Standards Institution 2011). This type of cement is commercially available and used for normal concreting and suitable for constructing concrete pavement and highways.

3.2.2 Aggregates

Coarse and fine aggregates were supplied by Crescent Building Supplies where they conform to the requirements of the British Standard BS EN 12620 (British Standards Institution 2013c). Coarse aggregate of crushed stones with sharp edges and maximum size of 20 mm and specific gravity of 2650 Kg/m^3 were used. Finally, sharp silica sand with a specific gravity of 2620 Kg/m^3 was used with a uniform grain size distribution between 1 mm and 300 μm.

3.2.3 Protective materials

Two types of protective materials, in terms of application methods, were used in this work; internally integrated materials and surface applied materials. Table 3-1 outlines all the used materials, their categories and properties.

The main constituent of the used **crystalline material**, either in a powder form or in a liquid form, is sodium acetate (CH_3COONa), which is mixed with other proprietary materials. When first applying the **crystalline material** to concrete, it works on absorbing water that exists in the pores to form crystals. These crystals line the pores, without blocking them, allowing concrete to breathe and work on repelling penetrated water out of these pores. This material has an advantage over other commercially available and used materials, besides being environmentally-friendly that it can be applied on wet surfaces, when used as surface impregnation, and still works efficiently.

Fluorine is the main constituent of **fluoropolymer**, which gives it the ability to resist chemical attacks and repel water (hydrophobicity). The amalgamation of fluorine in polymers provides the attached polymer with lower surface energy that increases its hydrophobicity and decreases its friction coefficient and adhesion. In this research, an environmentally-friendly **fluoropolymer** material with short fluorinated side chains was used with a hydrocarbon link between the fluorinated side chain and acrylic.

Silicate resin is a hydrophobic material that coats the internal walls of concrete pores with a film to repel water. In this research, the used **silicate resin** has a 3-D polymeric structure with Si-O-Si backbone chains and organic R groups linking with silicon atoms, which provides a hydrophobic resistance against water, and high resistance to heat.

For comparison reasons, a solvent-based Monomeric alkyl (isobutyl) – trialkoxy **silane** with 100% active content was applied to concrete as well.

Table 3-1 - Details of the used protective materials

Type	Material	Main elements	Appearance	Colour	Application method	General information
Internally integrated	Crystalline	Sodium acetate with other proprietary materials	Powder	Grey	Mixed with concrete	Non-toxic and non-hazardous material and it does not block the pores and vapour permeable
Surface applied	Crystalline	Sodium acetate with other proprietary materials	Liquid – water based	Colourless	Applied to the surface	Non-toxic and non-hazardous material, it does not block the pores and vapour permeable
	Fluoropolymer	Fluorine, carbon and oxygen	Liquid – Water based	Colourless	Applied to the surface	Hydrophobic, resistance to high temperatures, chemicals and weathering
	Silicate Resin	Silicon, oxygen and carbon	Liquid – Water based	White/milky	Applied to the surface	Provides hydrophobic resistance against water, and has a high resistance to heat
	Silane	Silicon and hydrogen	Liquid – Solvent based	Colourless	Applied to the surface	Monomeric alkyl (isobutyl) – trialkoxy Silane with 100% active content. Provides hydrophobic resistance against water and chemicals

3.2.4 Chemical agents used for testing

Some chemical compounds were used throughout the testing procedures in this research and they are illustrated in Table 3-2.

Table 3-2 - Chemical compounds used for salt ponding testing

Chemical name	Chemical composition	Usage	Related chapters and sections
Sodium chloride	NaCl	Salt ponding test	Chapter 3, Section 3.4.5 & Chapter 7, Section 7.2 and Section 7.5
Nitric acid	HNO_3	Chemical analysis for salt ponding test	
Silver nitrate solution	$AgNO_3$		
Ammonium thiocyanate	NH_4SCN		
Ammonium ferric sulphate	$NH_4Fe(SO_4)_2$		
3,5,5-trimethylhexanol	$C_9H_{20}O$		

All chemicals mentioned in Table 3-2 were handled and used carefully according to safety rules and guidelines.

A liquid curing agent was sprayed on the surface of one mix (on a small scale) during one of the tests (Chapter 5, Section 5.2 & Chapter 6, Section 6.5).

3.3 Samples manufacturing

A standard concrete mixer with the size of 60 Litre was used to prepare all the used concrete mixtures at the temperature of 20 °C. All mixed concrete samples were cast in polystyrene

moulds with dimensions of 100mm x 100mm x 100mm. Plastic release films were fixed and glued to the internal surfaces of the polystyrene moulds to get smooth concrete surfaces and to ease the demoulding process. Also, some concrete mixtures were cast in steel moulds with the dimensions of 100mm x 100mm x 500mm, where their internal surfaces were painted with releasing oil to ease the demoulding process. Concrete was cast in accordance with the British standard BS 1881-125 (British Standards Institution 2013a), where moulds have been filled to their half and compacted by using an electrical vibrator, and in some cases, when concrete is hard, it was compacted manually by a compaction rod. Afterwards, moulds have been filled and compacted again via the previously mentioned techniques.

It is noteworthy that coarse and fine aggregates were dried in an electrical oven at a temperature of 110 °C following the British Standard BS EN 1097-6 (British Standards Institution 2013b). Aggregate were placed at room temperature to cool down before used in the mixing process.

Two groups of mix designs were cast to serve the objectives of this research; standard mix design without using any protective materials (with the mix) and a non-standard one by adding protective materials to the mix. Five mix designs were prepared for the standard mix and eleven mix designs for the non-standard mix that was integrated with the **crystalline material**. Table 3-3 shows the mixtures proportions for the standard mix designs and Table 3-4 outlines the mixtures proportions for the non-standard ones. More specifically:

- Mix 1 – Mix 4: used as control mixes.

- Mix 5: used as control + for surface treatments.

- Mix 6 – Mix 16: used for internal integration.

The **crystalline material** was incorporated within the fresh ingredients of the non-standard mixes by mixing it with cement before putting all the ingredients in the mixer. Moreover, the **crystalline material** was added to the mix in reference to the cement mass (certain percentage).

Table 3-3 - Adopted mix design for standard concrete mixtures (for control and surface applied materials)

	Quantity (kg/m³)				
Components	**Mix 1**	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**
Cement	480	513	491	450	457
Water	230	164	182	180	210
Fine aggregate	650	658	660	678	660
Coarse aggregate	1040	1068	1070	1092	1073
Total	2400	2403	2403	2400	2400
w/c ratio	0.48	0.32	0.37	0.40	0.46

Table 3-4 - Adopted mix design for non-standard concrete mixtures (for internal integration)

Components	Quantity (kg/m³)										
	Mix 6	Mix 7	Mix 8	Mix 9	Mix 10	Mix 11	Mix 12	Mix 13	Mix 14	Mix 15	Mix 16
Cement	474	469	440	503	492	481	471	441	432	448	439
Water	230	230	230	164	164	182	182	180	180	210	210
Fine aggregate	625	625	625	658	658	660	660	678	678	660	660
Coarse aggregate	1066	1066	1066	1068	1068	1070	1070	1092	1092	1073	1073
Crystalline material (%)	1%	2%	8%	2%	4%	2%	4%	2%	4%	2%	4%
Crystalline material	4.79	9.58	38.32	10.26	20.52	9.82	19.64	9.00	18.00	9.14	18.28
Total	2400	2400	2400	2403	2403	2403	2403	2400	2400	2400	2400
w/c ratio	0.48	0.48	0.48	0.32	0.32	0.37	0.37	0.40	0.40	0.46	0.46

Surface impregnations were applied to the surface of standard concrete mixes by brushing. All the sides of the concrete samples were brushed with the materials until refusal (until concrete starts to reject the applied materials). Figure 3-1 demonstrates the application process of surface applied impregnations on concrete.

Figure 3-1 - The process of treating concrete with surface impregnations

Concrete samples were cured under three different curing conditions: (i) in a water bath with a temperature of 21 °C (ii) in a curing room with a temperature of 20 °C and 60% humidity and (iii) under forced air generated by electric fans. Figure 3-2 shows the curing process of concrete under the forced air.

For surface applied materials, part of the concrete cubes were conditioned before applying the materials:

Condition 1: Cubes were assured to be fully dry.

Condition 2: Cubes were soaked in water until their moisture content (saturated surface dry) reached 2%.

Condition 3: Cubes were soaked in water until their moisture content (saturated surface dry) reached 4%.

Condition 4: Cubes were soaked in water until their moisture content (saturated surface dry) reached 6% (fully saturated).

Materials were applied to concrete surfaces when the required saturation level has been achieved. The application process continued until refusal (when concrete starts to reject any further applied material). Following the application of materials, part of the cubes in condition 4 was dried before testing, and the other part was tested without drying.

Figure 3-2 - Concrete curing under forced air

3.4 Testing methods

3.4.1 Fresh mix properties

The freshly cast concrete mixture was tested in terms of consistency by using the slump test and by following the British Standard BS EN 12350-2 (British Standards Institution 2009a). Slump test was carried out by filling the standard slump cone in three layers and compacting each layer with a compacting rod with 25 strokes. After filling the cone to the top and compact the concrete very well, the cone is removed and the difference between the height of the cone and the highest point of the slumped concrete is recorded. The recorded reading is the slump of the cast concrete. According to the BS EN 12350-2, slump values should range between 10 mm and 210 mm.

3.4.2 Mechanical properties

Mechanical properties of concrete were determined by running the compressive strength test and the flexural strength test. Compressive strength of cubic concrete samples (100mm x 100mm x 100mm) was determined by using the Autocon VJ technology machine and by following the British Standard BS EN 12390-3 (British Standards Institution 2009b). Flexural strength of beam samples (100mm x 100mm x 500mm) was determined by applying the two-point loading method and using the Instron 5584 machine following the British Standard BS EN 12390-5 (British Standards Institution 2009c). Figure 3-3 shows the compressive and flexural testing machines.

(a)   (b)

Figure 3-3 - Testing mechanical properties of concrete: (a) compressive strength and (b)

flexural strength

3.4.3 Water absorption

Initial Surface Absorption Test (ISAT) was used to measure the uniaxial water absorption of concrete cubes with dimensions of 100mm x 100mm x 100mm by following the guidelines of BS 1881-208 (British Standards Institution 1996). A pressure head of 200mm was applied to concrete samples, which represents a case that is worse than the severest rainfall in the UK. Figure 3-4 shows the used ISAT apparatus.

Figure 3-4 – Testing concrete for water absorption with the ISAT apparatus

Readings are taken after the beginning of the test in 10, 30 and 60 minutes intervals, and they are recorded in ml/m^2.s.

3.4.4 Capillary absorption

Water absorption by capillary action of concrete was determined by following the ASTM D 6489 guidelines (American Society for Testing and Materials 1999). One surface of concrete samples (100mm x 100mm x 100mm) is placed in contact with water in this test, and all other faces of the cubes were sealed using a waterproof sealer to prevent water ingress through them. Cubes were placed on steel wire mesh inside a container to allow water circulation under them, and then water was filled in the container until the level is about 70 mm from the top of the steel mesh. After 24 hours and 48 hours periods, concrete samples were removed from the container and weighed. Figure 3-5 shows concrete cubes during the capillary absorption testing.

Results were obtained as a percentage of the cubes' dry mass using the following equation, which is given in ASTM D 6489:

$$Percent\ Absorption\ (\%) = \frac{W_2 - W_1}{W_A} x100$$

 Where;

W$_A$: dry mass of concrete samples (g).

W$_1$: mass of the concrete samples after applying impregnant and sealer (g).

W$_2$: mass of concrete samples after immersing in water (g).
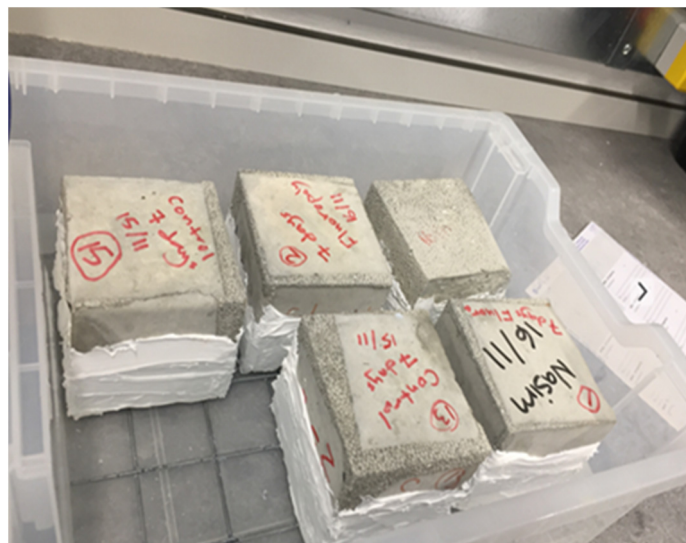
Figure 3-5 - Capillary absorption testing of concrete following the ASTM D 6489

3.4.5 Salt ponding

Concrete resistance to chloride penetration was evaluated by using the unidirectional salt-ponding test subjected to 100 mm cubes with an incorporated 15 mm deep recess above their top face for 90 days (American Association of State Highway and Transportation Officials 2002). A salt solution with 5% NaCl concentration was used to serve the purpose of the test. All external four sides of the cubes and the internal four sides of the 15 mm recess were sealed by a waterproof sealant to prevent water evaporation from concrete and water ingress from any other place except the upper face (Figure 3-6). After running the test for 90 days, powder samples were collected by drilling the cubes at different depths of 5 mm, 10 mm, 15 mm, 20 mm, and 50 mm. Finally, chloride content was evaluated by using Volhard's method following the recommendations of BS EN 14629 (British Standards Institution 2007).
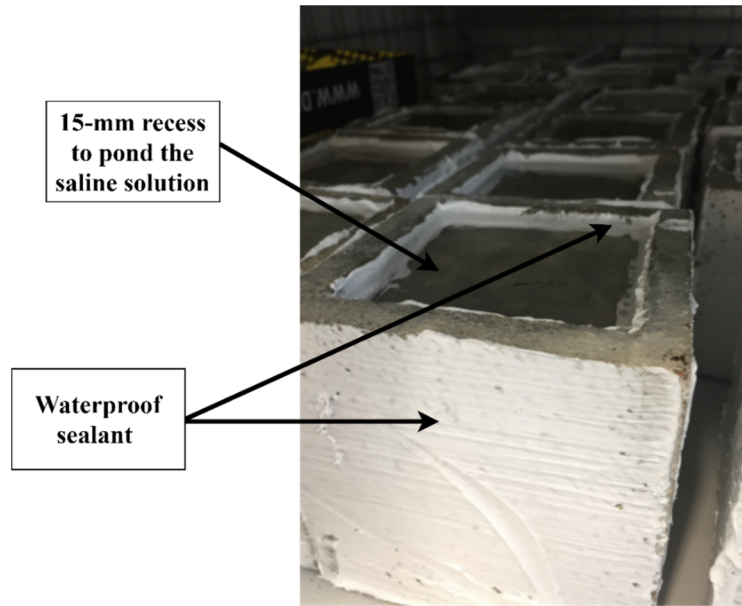
Figure 3-6 - Concrete cubes with a 15 mm recess on the top and sealed from the sides used for salt ponding test

All the collected powders were dried in an oven at a temperature of 105 °C to achieve a constant weight and then allowed to cool down in room temperature. Afterwards, 2 g of each sample is collected and placed in 250 ml beaker, moistened with 50 ml of water and 10 ml of 5 mol/L nitric acid, and finally 50 ml of hot water were added to the solution. The whole solution is then boiled for 3 minutes with continuous stirring. The same procedure should be carried out to prepare a blank solution without any concrete powder. From this point, Volhard's method will commence with adding 5 ml of silver nitrate solution by a pipette to the previous solution with strong stirring to precipitate the chloride. The indicator solution is then added to the solution with the amount of 5 drops, followed by the titration process by using thiocyanate solution (one drop at a time) until the solution's colour turns into pale reddish-brown. The used amount of thiocyanate solution is recorded, and the chloride content is calculated by using the following formula:

$$CC = 3.545 * f * (V2\text{-}V1) / m$$

Where;

CC: chloride content percent (%).

f: molarity of silver nitrate solution.

$V1$: volume of the ammonium thiocyanate solution used in the titration (ml).

$V2$: volume of the ammonium thiocyanate solution used in the blank titration (ml).

m: mass of concrete sample (g).

Figure 3-7 shows the titration process and the collection of powder from the cubes.

(a)   (b)
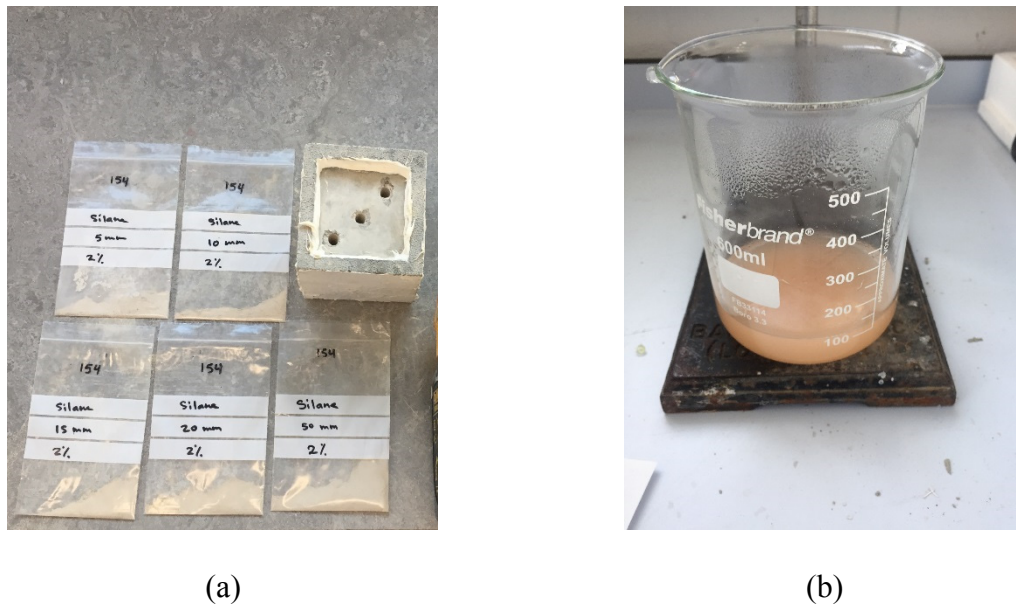
Figure 3-7 - The process of determining the chloride content of concrete: (a) collecting

powder samples from cubes and (b) titration process

3.4.6 Freeze-thaw

In this research two freeze-thaw testing methods were applied; freeze-thaw in water and in air. The freeze-thaw testing method in water has been widely used in literature (Wu & Wu 2014; Jianxun et al. 2014; Shang et al. 2014). However, the freeze-thaw testing in air has been proposed in this research as a new method. For both methods, concrete cubes with 100mm x

100mm x 100mm dimensions have been used, and the procedures followed in each method are explained in the following sections (3.4.6.1 and 3.4.6.2).

3.4.6.1 Freeze-thaw in air

In this proposed method, an environmental chamber that controls humidity and temperature was constructed. The chamber was constructed by utilising an existing industrial freezer as base for the freezing cycles and by introducing heating and humidity units inside the freezer to serve the thawing cycles. Furthermore, the heating and the humidity control units are additionally developed in order to complete the requirements for computer controlled scheduling of 24 hours cycles between -20 °C and 20 °C temperatures, and constant humidity that can go up to 90%. Figure 3-8 shows the constructed freeze-thaw chamber with an attached automatic unit for controlling the cycles.

Freeze-thaw chamber filled with concrete cubes

Automatic unit to control temperature and humidity

Figure 3-8 - Concrete inside a controlled freeze-thaw chamber

Cubes with the dimensions of 100mm x 100mm x 100mm were placed inside the chamber and it was programmed to run for 6 continuous months with a total of 180 freeze-thaw cycles. In the freezing process, temperature was set to reach -20 °C and in the thawing process temperature was set to reach 20 °C with 60% humidity. The internal temperature of concrete was measured by using embedded thermocouples and it ranged between 17 °C during the thawing process and -16 °C during the freezing process. Figure 3-9 shows the change in temperature during the air freeze-thaw test.
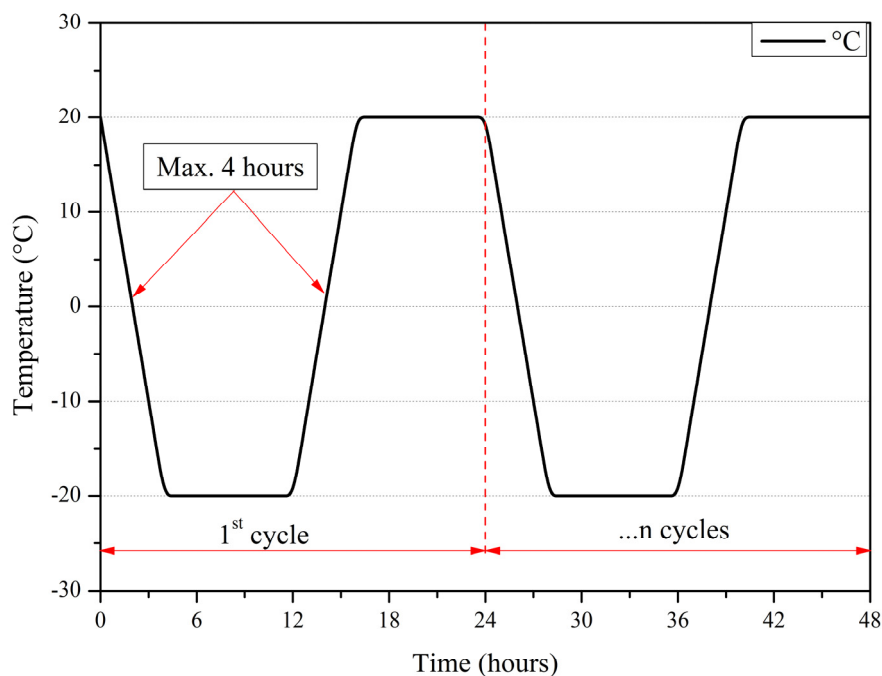
Figure 3-9 - Temperature alteration during the impact of the air freeze-thaw test

After completing the freeze-thaw test, the change in the mass of tested concrete in reference to their original mass before the test was recorded. Also, the cubes were tested for water absorption and compressive strength after finishing the test.

3.4.6.2 Freeze-thaw in water

In this method, cubes were immersed in water for 7 days to ensure they are saturated, and their final mass was recorded. Afterwards, they were placed in containers that are filled with water

(cubes are immersed in water), and all containers have been placed in Weiss-Voetsch Environmental Testing Chamber C340, shown in Figure 3-10. Temperature was set to alternate between -10 °C and 6 °C for a duration of 4 hours, representing a full rapid freeze-thaw cycle. The internal temperature of concrete cubes ranged between -6 °C and 4 °C during the freezing and thawing periods respectively. In total, 1080 freeze-thaw cycles during 6 months were carried out in this test. Figure 3-11 illustrates the temperature alteration during the freeze-thaw cycles.

After finishing the 1080 cycles, the mass of the tested concrete cubes was measured and the change in their masses was calculated. In addition, the freeze-thawed cubes were tested for water absorption and compressive strength.

Figure 3-10 - Freeze-thaw chamber for testing concrete under the effect of water
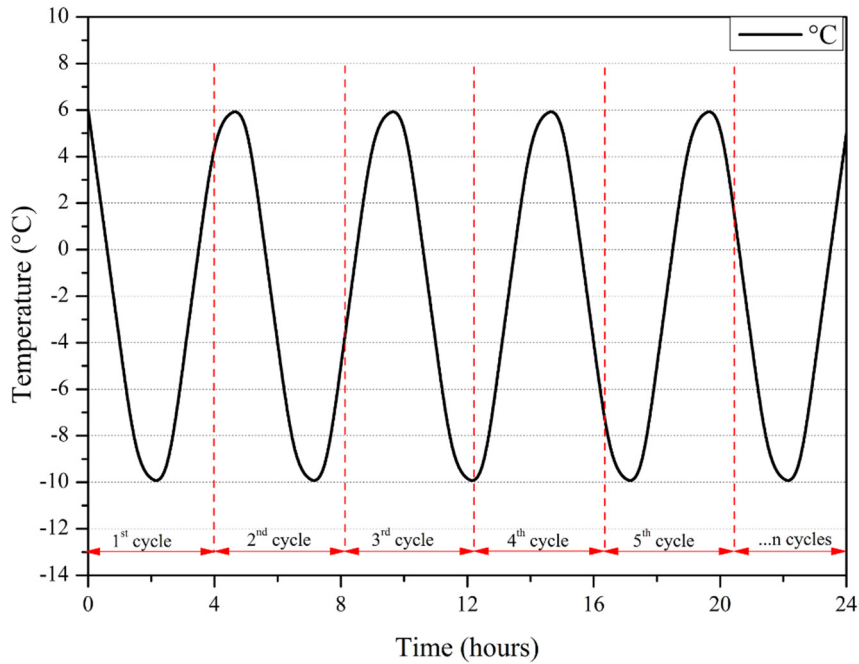
Figure 3-11 - Chnage in temperature during the water freeze-thaw test

3.4.7 Frictional properties

Concrete frictional properties were assessed by using the Pendulum test following the recommendations of the British Standard BS EN 13036-4 (British Standards Institution 2003). This test depends mainly on the energy loss when the base of the device's arm touches the tested surface (Ziari et al. 2017). Five measurements, on dry and wet surfaces, were taken for each concrete sample, and the Pendulum Test Value (PTV) was then calculated. All the surfaces of tested concrete had the same texture and roughness to make the comparison between samples more consistent.

3.4.8 Hydrophobicity

The degree of hydrophobicity of treated and untreated concrete was assessed by measuring the contact angle (θ) between a drop of water and the surface. A goniometer device was used for this purpose; it involves a video recording system, which is attached to a digital image-

processing program. Figure 3-12 shows the goniometer device that was used in this research to evaluate the degree of hydrophobicity of tested concrete.

Increasing the contact angle results in increasing the hydrophobicity of the surface; surfaces with contact angles higher than 90° are considered hydrophobic. However, if the contact angle has reached or exceeded 150°, then the material is considered super-hydrophobic (Anderson and Carroll 2011). Figure 3-13 illustrates the classifications of contact angles.
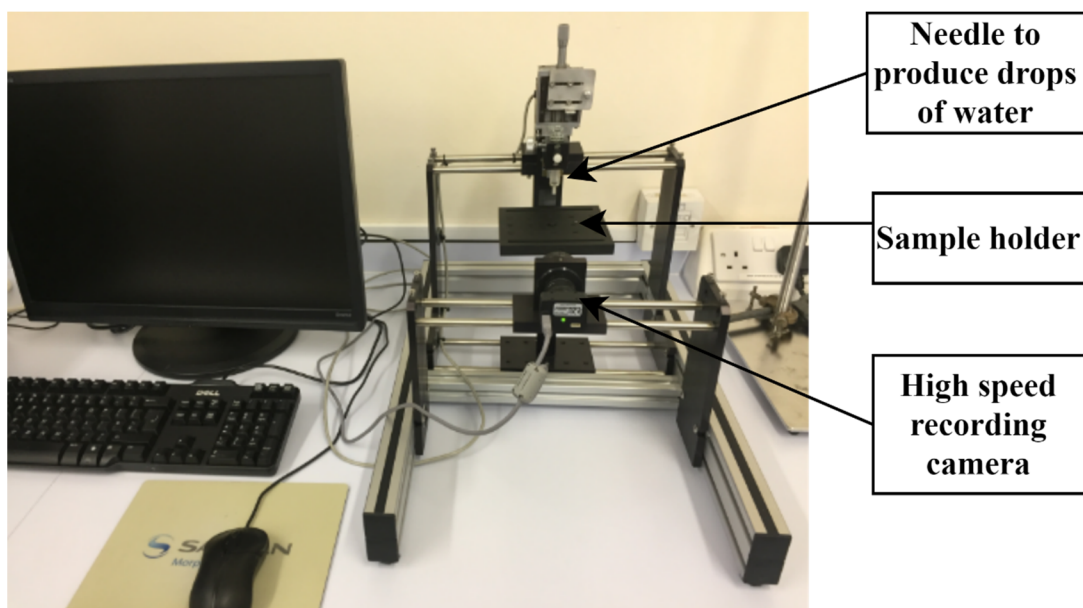
Figure 3-12 - The used goniometer device for measuring the hydrophobicity
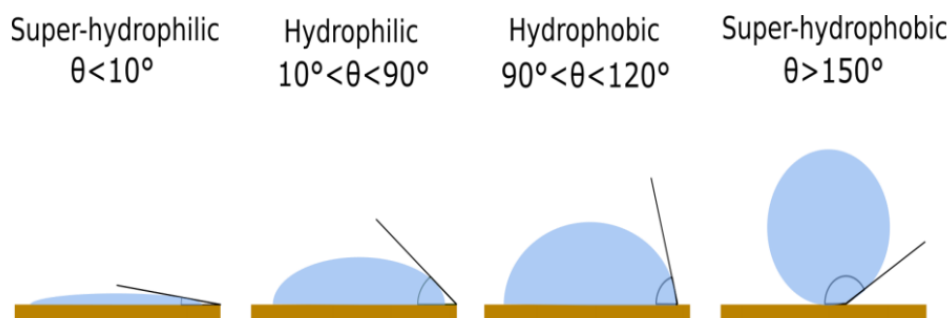
Figure 3-13 - Conact angle classification (Abo Madyan 2018)

3.4.9 Porosity

The porosity of all treated and untreated concrete was measured by using the vacuum saturation method (American Society for Testing and Materials 1997; Safiuddin & Hearn 2005). A vacuum saturation apparatus was used to measure the porosity; it involves a vacuum pump, desiccator and water source. Figure 3-14 shows the vacuum saturation apparatus that was used in this research to measure the porosity.
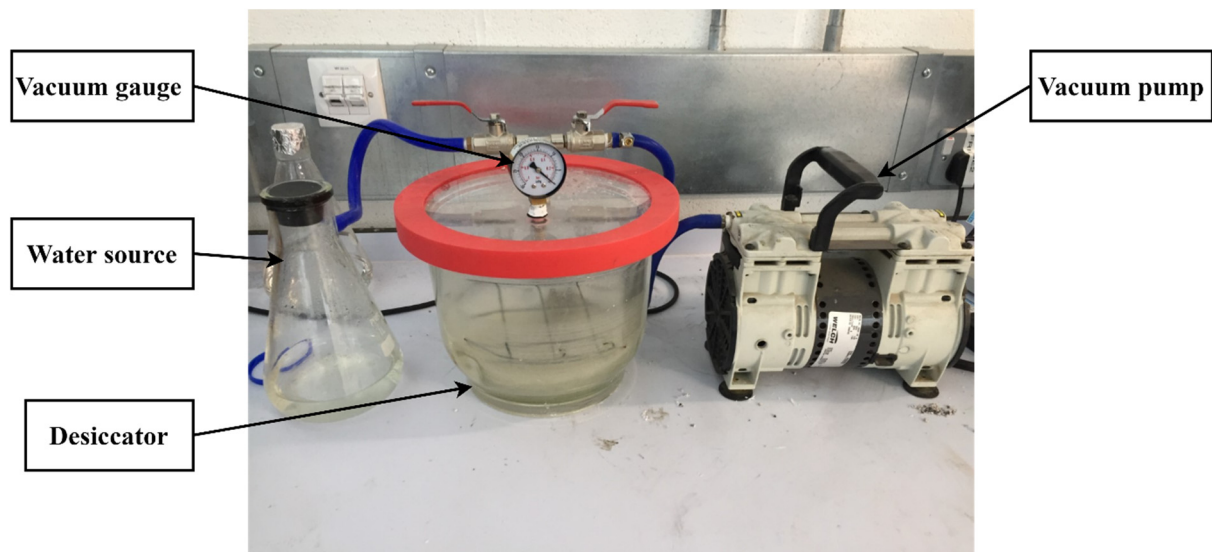
Figure 3-14 - Vacuum saturation apparatus

Concrete samples with sizes of 50mm x 50mm x 50mm were used in this experiment. All samples were dried in oven at a temperature of 105 °C until a constant mass is achieved. Samples were placed in the vacuum saturation apparatus and evacuated for 3 hours at a pressure of 90 kPa, and then they were soaked in water for 24 hours. At the end of the 24 hours period, samples were removed from the vacuum saturation apparatus and their saturated surface dry mass was measured. The porosity of all the samples was calculated by the following equation (Safiuddin & Hearn 2005):

$$Porosity\ (\%) = \frac{M_s - M_d}{M_s - M_b} x100\%$$

Where,

M_s: Saturated surface dry mass

M_d: Oven dry mass of the sample in air

M_b: Buoyant mass of the saturated sample in water

3.4.10 Analytical and microstructural techniques

3.4.10.1 Morphological assessment (SEM and EDX analysis)

Microstructural and morphological analyses of concrete and protective materials were run by using the Scanning Electron Microscope (SEM). A Zeiss Supra 35VP microscope with a high filed emission was employed to serve this purpose by producing micro images for the tested samples with range of magnifications between 1,000X and 50,000X. Moreover, the chemical composition of the tested samples was assessed by using an Energy Dispersive X-ray analysis (EDX), which is incorporated within the SEM instrument. Figure 3-15 shows the used Zeiss Supra 35VP SEM.
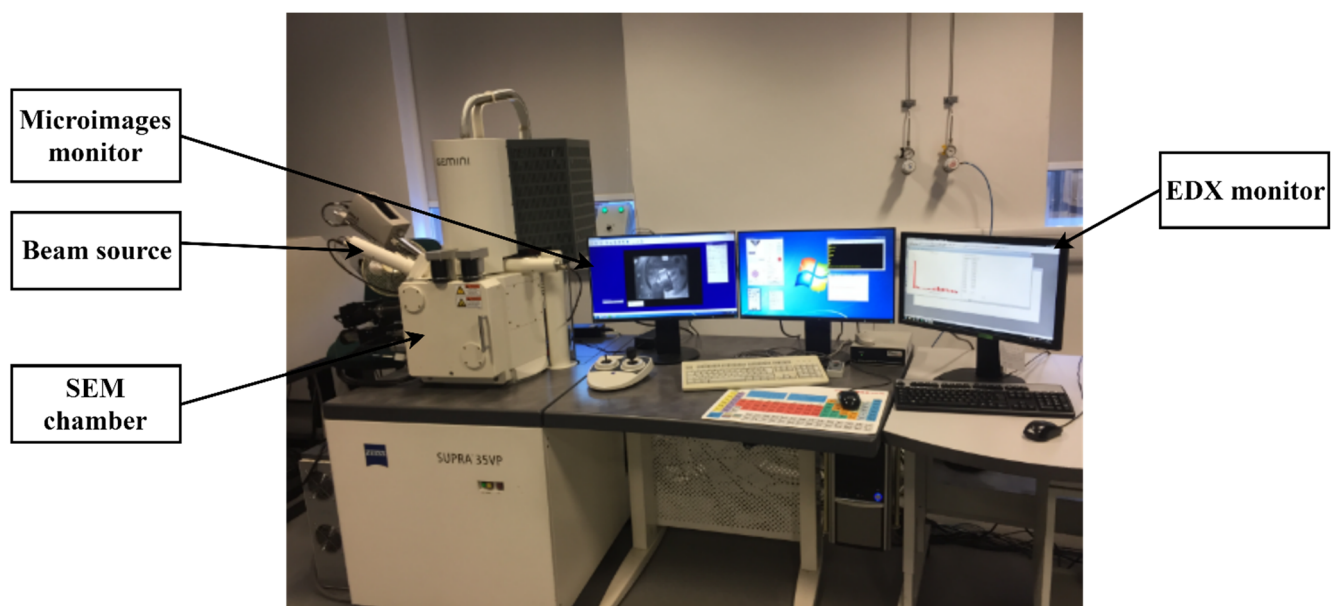
Figure 3-15 - The SEM instrument used for the microstructral investigation

To facilitate the testing process of liquid-form protective materials on the SEM, they were transformed into solid state by using a freeze-drying device. All liquid materials were subjected to cryodesiccation/lyophilisation (freeze-drying) by using Alpha 1-2 LD device with ice condensing ability of 2kg per 24 hours under a temperature of -55 °C (Figure 3-16). Before placing the samples inside the freeze-dryer, they were frozen by liquid nitrogen.

Figure 3-16 - Freeze-drying process of liquid protective materials

All tested materials were sputter-coated with a thin film of gold before analysing them under the SEM because of their non-conductive characteristics. The coating process was run for 120 seconds for each sample by using a Polaron-SC7640 device (Figure 3-17).
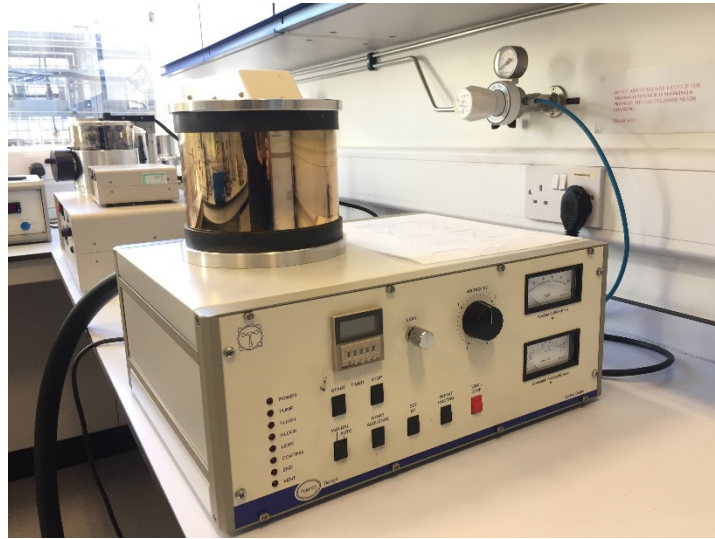
Figure 3-17 - The Polaron SC7640 coating device

3.4.10.2 *Fourier-transform Infrared Spectroscopy (ATR-FTIR)*

The chemical bonds inside the materials, their functional groups and their interaction mechanism with concrete were investigated through the Fourier-transform Infrared analysis (FTIR) using a Perkin Elmer Spectrum device, as shown in Figure 3-18. Samples are placed on Attenuated Total Reflection (ATR) stage that has a diamond detector, where the Infrared beam goes inside the sample and the resultant transmitted energy is measured. Afterwards, the Perkin Elmer device produces a spectrum with a wavenumber range of 600-4000 cm^{-1} over 14 scan for each sample. This technique is well known for its high sensitivity, accuracy, and reliability in quantifying and analysing materials (Hortling et al. 1997; Ghaffar & Fan 2013).

Figure 3-18 – ATR-FTIR device used for the analytical analysis of materials

3.4.10.3 X-ray Diffractometer (XRD)

This method was used to determine the size of the developed crystals of the used **crystalline material**. Solving Scherrer equation will identify the size of the crystals and check the development of crystals during time (Uvarov & Popov 2007);

$$D= K.\lambda/\beta Cos\theta$$

Where,

D: the crystal size

λ: X-ray wavelength

β: the width of the peak (radians)

θ: Bragg angle

K: Scherrer constant

The analysis was run using D8 advanced Bruker AXS diffractometer with a source of radiation of CuKα that has a wavelength of 0.1542 nm, a graphite monochromator and 2D-area detector

GADDS system. The diffracted intensity of the radiation was in the range of 5° to 100° (2θ). Figure 3-19 shows the used XRD machine.

Before starting the test, the material was grinded and then placed in a special holder inside the XRD device.
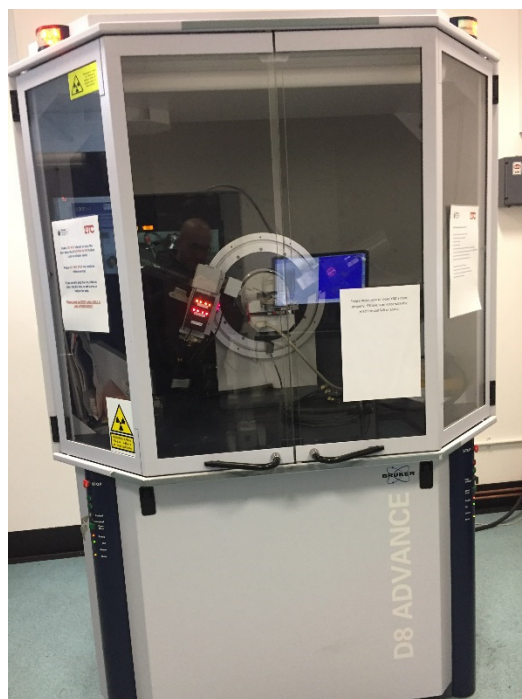
Figure 3-19 - The XRD device that was used for determining the size of crystals

3.5 Summary

All the materials, experiments and techniques that were used in this research have been explained in this chapter. The introduced methods of testing were used to obtain and analyse results in succeeding chapters to accomplish the objectives of this work.

Chapter 4: Microstructural Analysis and Interaction Mechanism of Protective Materials and Concrete

4.1 Introduction

Protective materials have been considered as valuable means for increasing the service life of concrete. Some solvent-based materials like **silane** and siloxane were the most used treatments in concrete because of their high availability and good performance (Cai et al. 2016). However, their inadequate performance and their high rejection rate by concrete when applied to wet surfaces made researchers to explore other options that have a high affinity for water at the time of application (Rahman et al. 2013). As discussed in Chapter 1 and 2, the proposed treatments like the **crystalline material**, **fluoropolymer** and **silicate resin** are intended to overcome the issues that accompany **silane**. Adding to that, the high curing time of **silane** when applied to concrete and its inconvenient application method for concrete pavement and bridges, which requires closing the roads in front of vehicles, drove researchers to look for new materials that are more effective when applied to pavement.

Most of the studies on protective materials are comparative investigations between different types of materials in terms of mechanical and physical performance without particulars of anatomical and interaction mechanism details (Pan et al. 2017).

The microstructure of the proposed materials is the most important characteristic for understanding their significance which will lead to their use in protecting concrete. A thorough analysis for the proposed materials and their interaction mechanism with concrete has been rarely discussed in literature. Many chemical and physical techniques could be used for understanding protective materials' structure that are either destructive or non-destructive. Fourier-transform Infrared Spectroscopy (FTIR) is a non-destructive technique that is

considered one of the most instructive methods for studying the interaction mechanism of protective materials with concrete. Furthermore, Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) and X-ray diffraction (XRD) analyses are other important techniques that are used to fully understand the chemical structure and morphology of protective materials. Accordingly, the morphological findings are correlated to the chemical characteristics of the examined anatomical parts (Ghaffar & Fan 2013).

This chapter outlines the used protective materials and investigates their morphology and interaction mechanism with concrete. Also, their frictional properties along with their hydrophobic characteristics are investigated to build up a deep understanding for their mechanical and physical performance in following chapters. Skid resistance is a very important measurement for the safety and condition of concrete pavement. Accordingly, the skid resistance and the wettability tests were employed to study the frictional properties and the hydrophobicity of the used materials respectively.

This chapter was divided into two main parts based on the protection method:

- **Part I: Internally Integrated Treatment**

- **Part II: Surface Applied Treatments**

Part I: Internally Integrated Treatment

4.2 Experimental programme

The experimental program in this part was divided into five sections: porosity measurement, surface wettability analysis, surface frictional properties, morphological analysis and interaction mechanism of the **crystalline material** and concrete. Different types of samples were prepared to serve each testing method. Table 4-1 illustrates the performed tests, the type and number of samples used in each test.

Table 4-1 - The tested properties, their testing methods and the types of tested samples

Tested properties	Testing method	Type of samples	Description of samples
Porosity	Vacuum saturation (Chapter 3, Section 3.4.9)	Concrete mixed with crystalline material and plain concrete (untreated)	Cubes with 50mm x 50mm x 50mm dimensions
Surface wettability (hydrophobicity)	Goniometer device (contact angle) (Chapter 3, Section 3.4.8)	Concrete mixed with crystalline material and plain concrete (untreated)	Prisms with 20mm x 20mm x 10mm dimensions
Surface friction (skid resistance)	Pendulum test (Chapter 3, Section 3.4.7)	Concrete mixed with crystalline material and plain concrete (untreated)	Cubes with 100mm x 100mm x 100mm dimensions
Morphology and chemical composition (microstructure analysis)	SEM, EDX and XRD (Chapter 3, Section 3.4.9.1 & Section 3.4.9.3)	Crystalline material	Powder
		Concrete mixed with crystalline material	Cross sectional slices cut from concrete cubes
Interaction mechanism	ATR-FTIR (Chapter 3, Section 3.4.9.2)	Untreated concrete	Powder
		Crystalline material	Powder
		Concrete mixed with crystalline material	Powder

For the preparation of samples for the surface wettability test, 36 small prisms with 20mm x 20mm x 10mm dimensions were cut from treated and untreated cubes. Afterwards, the contact angle of a sessile drop on the surface of concrete was measured by using the goniometer device to determine the hydrophobicity of samples. Measurements of contact angles were recorded at 0, 30, 60 and 120 seconds (Li & Neumann 1992; Anderson & Carroll 2011).

Frictional properties of 36 cubes with the dimensions of 100mm x 100mm x 100mm were investigated by using the pendulum test following the BS EN 13036-4 (British Standards Institution 2003). Five measurements on dry and wet surfaces were taken for each concrete

cube, and the Pendulum Test Value (PTV) was then calculated. All the surfaces of tested concrete had the same texture and roughness, to make the comparison between samples more consistent.

The porosity of 36 samples with dimensions of 50mm x 50mm x 50mm of treated and untreated concrete were evaluated after 28 days of curing. The vacuum saturation method was employed in this test following the procedure in Chapter 3, section 3.4.9.

The microstructural and morphological properties, the elemental composition and the size of the formed crystals of the **crystalline material** were analysed by using the SEM, EDX and XRD methods. The analyses were run on powdered **crystalline material** before its addition to concrete and on concrete treated with the **crystalline material**. Small samples of treated concrete were sliced from cubes with dimensions of 20mm x 20mm x 20mm. All the powder samples and the sliced samples were coated with thin film of gold, before their analysis under the SEM, to make their surfaces conductive. Powdered **crystalline material** was only analysed under the XRD technique to check the size of the crystals and compare it with results obtained from the SEM.

Finally, the interaction mechanism of the **crystalline material** and concrete and the functional groups of the **crystalline materials** were determined by using the FTIR method. Three types of samples were investigated to establish a relation between the **crystalline material** and concrete; plain concrete, **crystalline material** and concrete treated with the **crystalline material**. All samples were ground and transformed into powder to serve this test.

4.3   Results and discussion

4.3.1   Microstructural and elemental composition analyses

EDX analysis was run to fully understand the chemical composition of the used material. As expected, EDX showed that Sodium, Oxygen and Carbon are the main elements forming the **crystalline material**, with small percentages of Silicon and Calcium. The formation of crystals after mixing this material with concrete might refer to the presence of sodium acetate in the composition of this material; water activates their reaction with concrete to form crystals inside the pores (Al-Otoom et al. 2007). Also, it is believed that silicon and sodium, which present in this material, will react with calcium hydroxide that already exists in concrete, in the presence of water, to form silica gel that adheres to the walls of the pores (Teng et al. 2014; Cappellesso et al. 2016). This gel will develop into solid crystals after its hydration. Figure 4-1 shows a sketch for the activation process of the **crystalline material** by the available water, in fresh concrete, and the utilisation of water by conventional concrete (in the absence of the **crystalline material**).
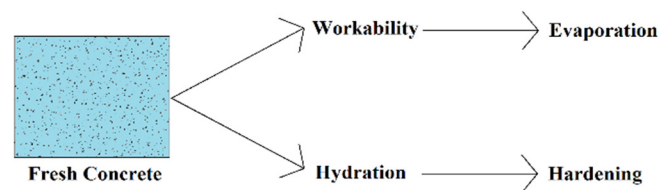
(a)
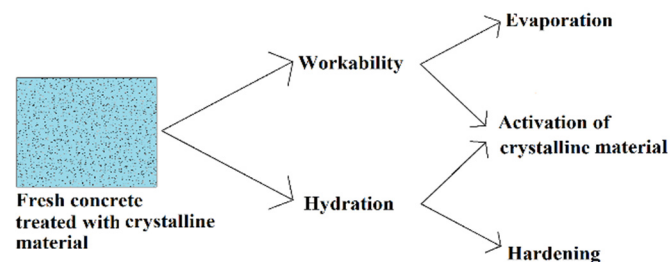
(b)

Figure 4-1 - Consumption of water in fresh (a) conventional concrete and (b) concrete treated with crystalline material

The structure of crystals formed from previously mentioned reactions could be recognised in the SEM micrographs shown in Figure 4-2, where they appear as needle-shaped crystals.

(a)

(b)

(c)

(d)
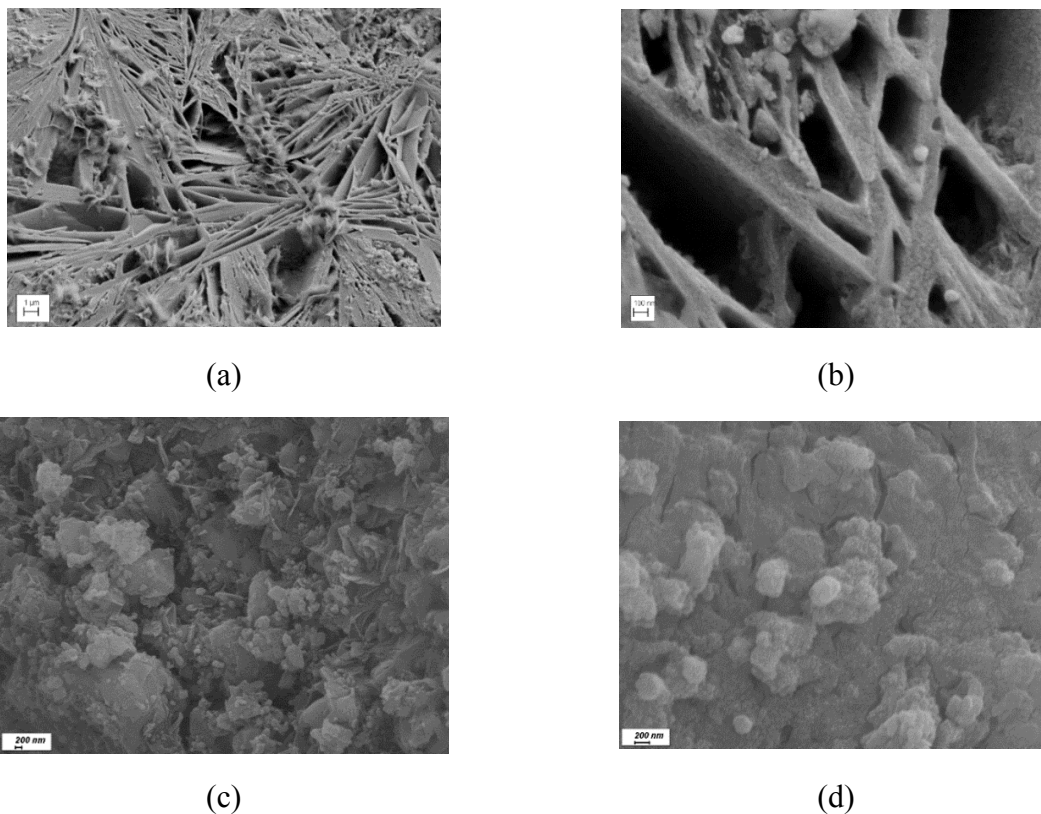
Figure 4-2 - SEM Micrographs for (a) Crsyatlline material before mixing with concrete (10,000X), (b) Crsyatlline material before mixing with concrete (100,000X), (c) the interaction between crystalline material and concrete (20,000X) and (d) the interaction between crystalline material and concrete (50,000X)

Micrographs were taken with different magnifications ranging between 10,000X and 100,000X to show the needed details. The formation of crystals in this shape might give the material the support to be integrated easily within the concrete mix, working on improving its density and reducing the size of pores and make them finer (Kumar et al. 2009; Teng et al. 2014). This could be spotted when referring to the interaction between the material and concrete in Figure 4-2 c and d, where they show graphs for the cross-sectional area of the internal parts of concrete. Crystals are noticed to be well distributed within the concrete mix, and they appear

in very small sizes (less than 200 nm) which ease their implantation inside the capillary pores (Chen at al. 2016). The presence of crystals within the concrete structure in such dense and well-distributed way would give treated concrete rigidity and strength, which is discussed later on in Chapter 5, section 5.3.2.2.

In order to investigate the development and distribution of the crystals with time, treated concrete specimens were investigated under the SEM at different magnifications, after day one and day seven of casting. Figure 4-3 illustrates the growth and distribution of crystals with time inside the concrete mix. It was witnessed that the **crystalline material** absorbs some of the water used in the concrete mix to form its crystals. These crystals grow and develop within the first 24 hours of casting concrete, and they integrate within the concrete ingredients at a very early age. This could be noticed from Figures 4-3 a-b, where the sequence of the micrographs taken from day 1 until day 7, shows that the size and distribution of the crystals maintained the same throughout the tested period.

(a)   (b)
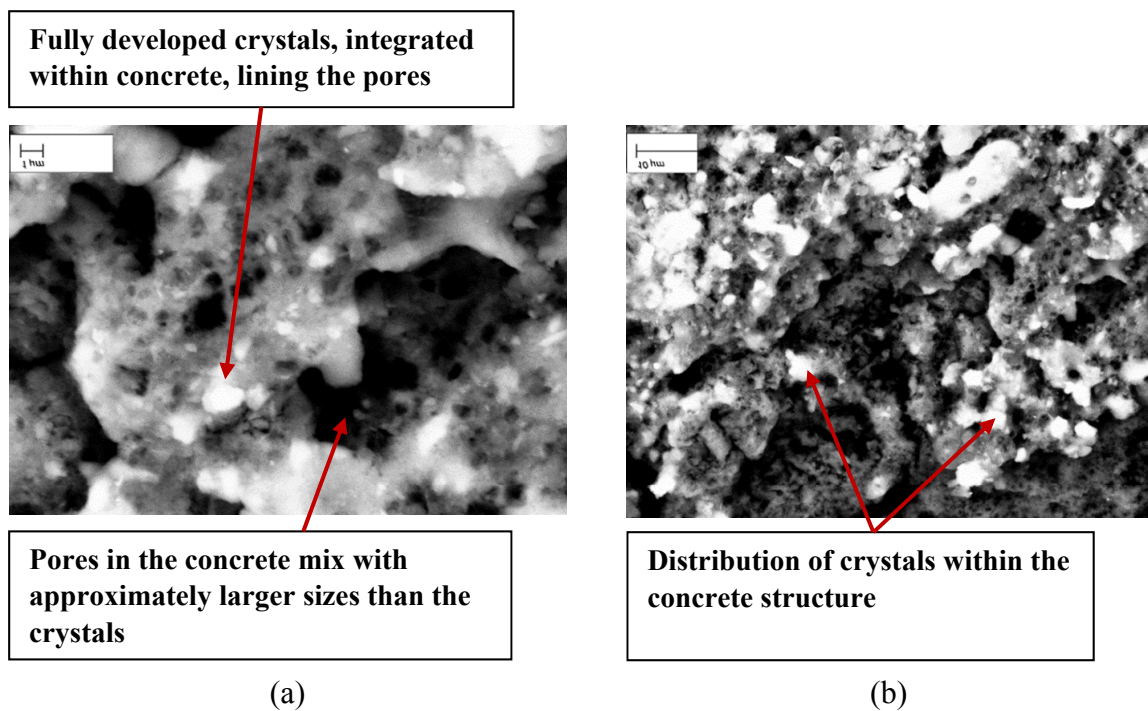
Figure 4-3 - The interaction of the crystalline material with concrete and its development

after: (a) 1 day of casting (5,000X) and (b) 7 days of casting (5,000X)

In parallel, treated concrete was tested under the X-Ray Diffractometer (XRD) instrument and analysed by using Scherrer equation to identify the size of the crystals, and to check if there is any change in the size during the time (Chapter 3, Section 3.4.9.3)

Testing was progressed for 28 days, and results showed that the growth of the crystals stops after the first 24 hours with a minimum size of 95 nm and maximum size of 200 nm, which confirms with the SEM results. This range of crystal sizes when compared with the pores of concrete, they were smaller than the macro-pores (>1000 nm), most of the capillary pores (100-1000 nm), most of the meso-pores (10-10000 nm), and some of the transitional pores (10-100 nm) (Kumar & Bhattacharjee 2003; Liu et al. 2014). It is witnessed that pores with sizes larger than 10 μm have the greatest effect on compressive strength (Li & Li 2014). This indicates that the **crystalline material** can merge easily within the concrete structure, attaches to the interiors of the pores and lines most of the existing voids, prevents the formation of more micro-cracks, and preserves concrete's compressive strength.

4.3.2 Functional groups of the crystalline material

FTIR spectra of the protective martial and its interaction with concrete are shown in Figure 4-4. The figure shows three spectra of concrete, **crystalline material** powder, and concrete integrated with **crystalline material** respectively.
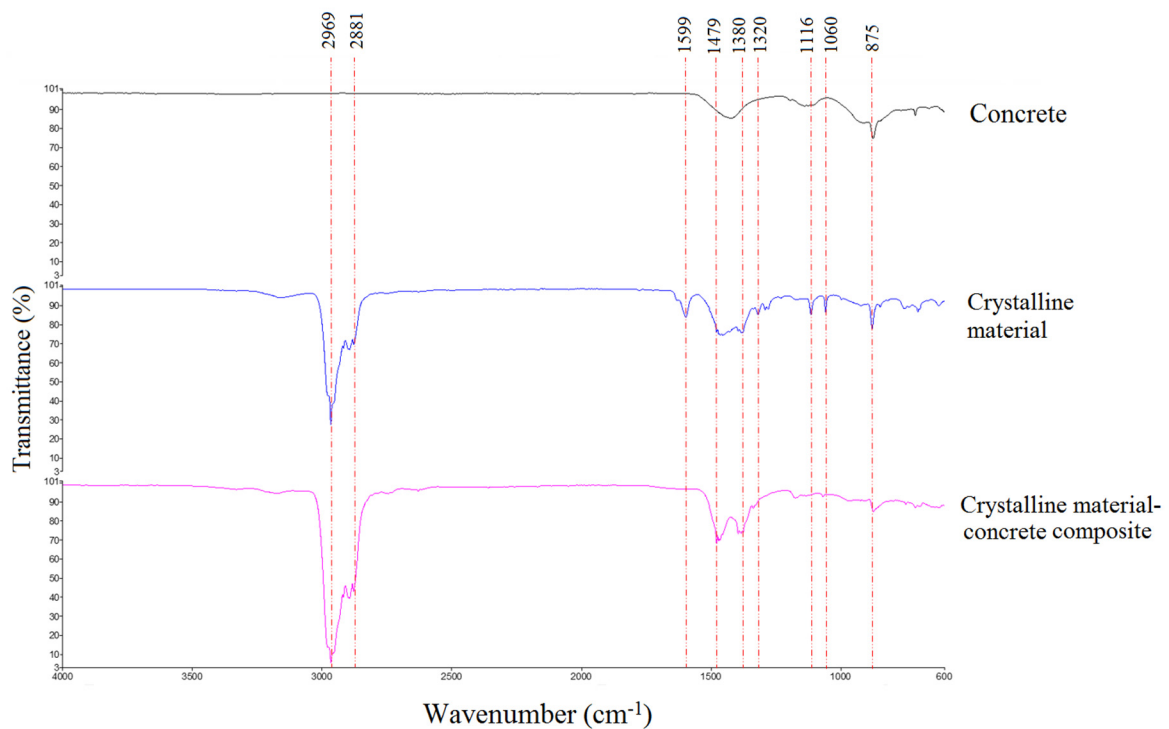
Figure 4-4 – ATR-FTIR analysis of the crystalline material and its interaction with cement

The characteristic peaks were almost steady and undeviating for the **crystalline material** powder and concrete mixed with the **crystalline material** at 2969, 2881, and 875 cm^{-1}. Within these peaks, the 875 cm^{-1} mostly corresponds to -CO$_3$ bond (Gadermann et al. 2007), the range of peaks 2969 until 2881 cm^{-1} is believed to correspond to –CH and –OH stretching vibrational bonds which result from anharmonic resonances of the –CH and –OH bonds in the crystal of the acetic acid chain (CH$_3$COOH) forming sodium acetate (Gadermann et al. 2007).

The most considerable variation in the transmittance of peaks could be noticed in 1599, 1479, 1380, 1320, 1116, and 1060 cm^{-1}. The 1599 cm^{-1} peak corresponds to –COO bond, the range of peaks 1479-1380 cm^{-1} may refer to the stretching vibrations of C-H bond (Ibrahim et al. 2005; Iacovita et al. 2015), and peak range 1060-1116 cm^{-1} corresponds to the stretching vibrational C-O bond in the –COOH carboxylic acid part. Finally, the peak at 1320 cm^{-1}

corresponds to C-O bond in the same –COOH part (Linstrom & Mallard 2014; Silverstein et al. 2014).

An increase in the peaks intensity is noticed within the 1479-1380 cm^{-1} and 2969-2881 cm^{-1} ranges (C-H and O-H) when the material is mixed with concrete (Figure 4-4). This increase in the hydrogen bond could be ascribed to the chemical reaction between sodium acetate and cement in the presence of water, where anhydrous sodium acetate dissociates in water forming CH_3COO^- and Na^+ ions (Sharma 1997; Chang 2005):

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
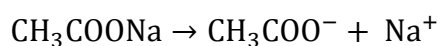
It is believed that CH_3COO^- ions will form a linkage with cement through their reaction with sodium, which already exists in cement, and form sodium acetate crystals all over again, which contributes in increasing the intensity of C-H bonds (Figure 4-4). In its turn, the dissociated Na^+ ions will react with free water forming Sodium hydroxide (NaOH) composite which increases the intensity of O-H bonds. Moreover, some of the free CH_3COO^- might react with water to form acetic acid (CH_3COOH) which also contributes in increasing the O-H bonds intensity. On the other hand, the reduction in the C-O (1320 cm^{-1}) and –COO (1599 cm^{-1}) bonds intensity could be referred to the ionic reaction between CH_3COO^- and H^+ ions forming small amounts of volatile CH_4 and CO_2 (Ferry 1992; Woodard 2001).

The presence of small quantities of acetic acid in the mix might work on delaying the hydration process and increase the workability of the concrete mixes, especially if high amount of the **crystalline material** has been added to the mix (Nguyen et al. 2016). In addition, the presence of sodium hydroxide (NaOH) in concrete mixes with reasonable amounts might further increase its workability, reduce segregation and accelerate C_3S hydration. However, high amounts of NaOH may contribute to decreasing the final strength of concrete, as a result of

forming metastable C-S-H with reduced bonding strength (Ramachandran 1996; Collins & Sanjayan 1999).

Another reason for increasing the C-H bonds is believed to be the replacement of –OH groups by –CH_3 groups, which in turn bond with silicon atoms in cement and result in forming a hydrophobic component integrated within the mix (organosilicon bonds) (Palomino et al. 2007; Wagh et al. 2010; Wagh et al. 2015).

4.3.3 Influence of internal integration on porosity

The average results of the porosity test are illustrated in Table 4-2.

Table 4-2 - Porosity of control and internally integrated concrete

w/c ratio	Crystalline material %	Average porosity %
0.32	0%	7.57%
	2%	7.32%
	4%	7.28%
0.37	0%	8.16%
	2%	8.02%
	4%	7.96%
0.40	0%	8.84%
	2%	9.17%
	4%	9.36%
0.46	0%	9.23%
	2%	9.83%
	4%	10.17%
0.48	0%	10.21%
	1%	10.56%
	2%	10.63%
	8%	10.89%

It is witnessed from the results that adding the **crystalline material** to the mix does not have a significant effect on the porosity of concrete. Adding the **crystalline material** to concrete with w/c ratios of 0.32 and 0.37 has slightly reduced the porosity of the mix, and adding the **crystalline material** to concrete with high w/c ratios of 0.40, 0.46 and 0.48 has contributed in a slight increase in the concrete's porosity. This insignificant increase/reduction in the porosity of treated concrete may refer to the small size of the formed crystals that work on lining the pores of concrete instead of entirely blocking them, which supports the outcomes of the morphological analysis in Section 4.3.1. On the other hand, the small increase in the porosity of concrete with high w/c ratios might indicate the formation of microcracks in the concrete mix due to treatment, contrary to concrete with low w/c ratios.

4.3.4 Hydrophobicity development

According to results obtained from the FTIR analysis in the previous section 4.3.2, a hydrophobic organosilicon bond will be formed within concrete after treatment. As a result, the hydrophobicity of concrete mixes 5 and 9 - 16 (Tables 3-3 and Table 3-4 in Chapter 3, Section 3.3) was measured by using the goniometer device and contact angle was determined. Table 4-3 shows the contact angle of all the tested concrete mixtures and its change along 120 seconds period.

Table 4-3 - Contact angle of standard (untreated) and non-standard (treated) concrete
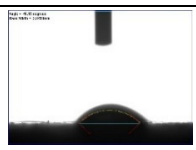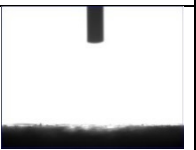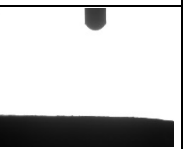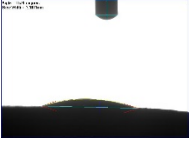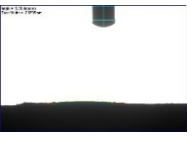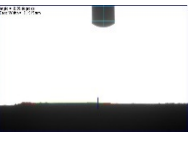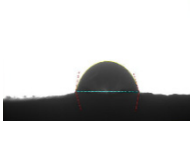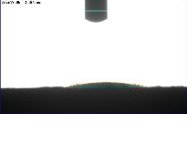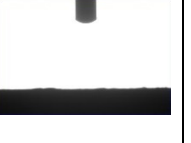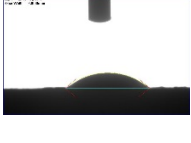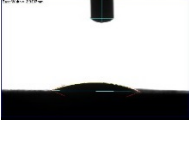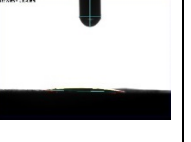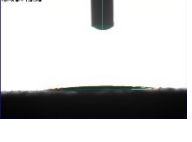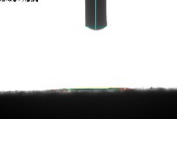
	T = 0 sec	T = 30 sec	T = 60 sec	T = 90 sec	T = 120 sec
Control	$\theta = 20.85°$	$\theta = 10.19°$	$\theta = 0°$	$\theta = 0°$	$\theta = 0°$

Table Continues…

	T = 0 sec	T = 30 sec	T = 60 sec	T = 90 sec	T = 120 sec
w/c = 0.32 material = 2%	$\theta = 34.89°$	$\theta = 16.20°$	$\theta = 5.95°$	$\theta = 2.35°$	$\theta = 0°$
w/c = 0.32 material = 4%	$\theta = 73.83°$	$\theta = 54.47°$	$\theta = 48.98°$	$\theta = 41.87°$	$\theta = 37.63°$
w/c = 0.37 material = 2%	$\theta = 34.77°$	$\theta = 20.77°$	$\theta = 14.41°$	$\theta = 11.66°$	$\theta = 0°$
w/c = 0.37 material = 4%	$\theta = 40.12°$	$\theta = 24.80°$	$\theta = 20.80°$	$\theta = 16.74°$	$\theta = 12.98°$
w/c = 0.40 material = 2%	$\theta = 34.76°$	$\theta = 20.82°$	$\theta = 15.97°$	$\theta = 11.95°$	$\theta = 7.15°$
w/c = 0.40 material = 4%	$\theta = 35.97°$	$\theta = 17.44°$	$\theta = 6.43°$	$\theta = 0°$	$\theta = 0°$
w/c = 0.46 material = 2%	$\theta = 21.55°$	$\theta = 10.76°$	$\theta = 7.71°$	$\theta = 3.54°$	$\theta = 0°$
w/c = 0.46 material = 4%	$\theta = 21.48°$	$\theta = 15.65°$	$\theta = 12.60°$	$\theta = 9.99°$	$\theta = 6.34°$

It is witnessed from Table 4-3 that hydrophobicity has developed in all the treated concrete samples, which is a result of the presence of the organosilicon bond in the pores. Regardless of the modest contact angle resulting from the treatment, a clear increase in the hydrophobicity was resulted from integrating the **crystalline material** in the mix, especially for concrete with w/c ratio of 0.32 and treated with 4% **crystalline material**, where the contact angle has increased more than three times that of control. Whereas, some of the mixes, especially those with high w/c ratio, have shown very poor hydrophobicity and this could be due to the relatively high water content of these mixes. Excess water might have contributed to decreasing the organosilicon bonds that are responsible for the modest hydrophobicity of the **'crystalline material-concrete'** composite (Section 4.3.2).

4.3.5 Frictional properties

The skid resistance of treated and untreated concrete mixtures was evaluated by using the pendulum tester. Table 4-4 illustrates the skid resistance of all concrete samples after applying the test on dry and wet surfaces. The Pendulum Test Value (PTV) for each case was evaluated by calculating the mean of five swings on every surface.

Table 4-4 - Frictional properties of tested concrete in terms of the pendulum test value

w/c ratio	Crystalline material %	Surface condition	Average PTV	Standard deviation (SD)
0.32	0%	Dry	33	0.89
		Wet	28	0.63
	2%	Dry	32	0.77
		Wet	27	0.77
	4%	Dry	33	0.77
		Wet	27	0.77
0.37	0%	Dry	32	0.89
		Wet	28	0.77
	2%	Dry	33	0.77
		Wet	28	0.63

Table Continues…

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w/c ratio	Crystalline material %	Surface condition	Average PTV	Standard deviation (SD)
	4%	Dry	32	0.77
		Wet	27	0.77
0.40	0%	Dry	33	0.63
		Wet	27	1.26
	2%	Dry	33	0.89
		Wet	28	0.89
	4%	Dry	32	0.63
		Wet	27	0.63
0.46	0%	Dry	32	0.89
		Wet	27	1.10
	2%	Dry	32	1.18
		Wet	28	0.77
	4%	Dry	32	0.77
		Wet	28	1.10

Results of skid resistance showed similar performance for all concrete samples, either treated or untreated. This indicates that the internally integrated **crystalline material** did not influence the surface properties of concrete. As explained in Section 4.3.2, the formed crystals have small sizes that enable them to be embedded in the pore structure of concrete. Furthermore, these crystals will be distributed all over the concrete matrix and will not be concentrated on the surface of concrete, e.g. the surface applied materials. Accordingly, treating concrete pavement with the **crystalline material** will not have a significant influence on the frictional properties of concrete's surface, which makes the addition of this material to concrete pavement safe in terms of skid resistance.

4.4   Summary of Part I

An analytical approach was built up to comprehensively investigate the morphology and chemical composition of the **crystalline material** and its interaction mechanism with concrete. The hydrophobic and frictional properties of the material was investigated as well to ensure its

suitability and compatibility with concrete pavement. Accordingly, these analyses will set up a database on the distinguished characteristics of the **crystalline material**.

The microstructure of the **crystalline material** before and after its integration with concrete was investigated by exploring its structure with SEM and EDX analyses respectively. The interaction mechanism of crystalline material with concrete, its effect on the frictional properties of concrete and its role in developing hydrophobicity in concrete were evaluated by running the FTIR and XRD analyses, skid resistance test and the contact angle test respectively.

The morphological analysis revealed the formation of the crystals inside the matrix within the first 24 hours of integration. The size and distribution of the formed crystals showed their well distribution inside the pores with sizes less than most of the pores, which eases their linkage to the walls of the pores.

The functional groups of the **crystalline material** and their interaction with concrete were quantified, revealing the formation of chemical bonds between the **crystalline material** and cement particles in the pores. FTIR analysis for the functional groups showed an increase in the intensity of hydrogen bonds due to the reaction between sodium acetate and cement in the presence of water. Also, replacement of $-OH$ groups by $-CH_3$ groups was noticed in the FTIR spectra, which corresponds to the bonding with silicon atoms that already exist in cement resulting in the formation of an organosilicon hydrophobic component integrated within the mix. Latter has worked on improving the hydrophobicity of treated concrete as revealed by the contact angle analysis.

The frictional properties of treated concrete showed that **crystalline material** did not change the surface integrity of concrete and retained its skid resistance similar to untreated concrete.

Results of this chapter form important factors for explaining the mechanical and physical behaviours of concrete treated with the **crystalline material**, which will be discussed in following chapters. Furthermore, the thorough analysis of this study shall provide researchers in this field with useful and fundamental information about this material and its influence on concrete.

Part II: Surface Applied Treatments

4.5   Experimental programme

In this part, four surface applied materials were analysed on the macro and micro scale; Liquid **crystalline material**, **fluoropolymer**, **silicate resin** and **silane**. An in-depth and fundamental analysis was run to understand the morphology, hydrophobicity, frictional properties and interaction mechanism of the materials with concrete. In addition, the influence of moisture content on protective materials was assessed. Table 4-5 outlines the fundamental investigations of the materials and the used testing methods.

Concrete mixture with w/c ratio of 0.46 was developed, as described in Section 3.3, to serve the experimental program of this chapter. Following the cast and curing of concrete, samples were conditioned with four moisture contents, before the application of materials, to check the affinity of materials to moisture (Chapter 3, Section 3.3). Accordingly, materials were applied to fully dry concrete, fully saturated concrete (6%), concrete with 2% moisture content and concrete with 4% moisture content. The rejection rate of concrete then was determined.

The hydrophobicity of the treated concrete was assessed by measuring the contact angle between a drop of water and treated surfaces of 15 concrete prisms with the dimensions of 20mm x 20mm x 10mm. Measurements of contact angles were recorded at 0, 30, 60 and 120 seconds (Li & Neumann 1992; Anderson & Carroll 2011).

The effect of the materials on the friction of concrete's surface was evaluated by using the pendulum test following the BS EN 13036-4 (British Standards Institution 2003). 15 cubes with the dimensions of 100mm x 100mm x 100mm were employed to serve the objectives of this test. It was made sure that all the surfaces of tested concrete had the same surface roughness for consistency reasons. Five measurements on dry and wet surfaces were taken for each concrete cube, and the Pendulum Test Value (PTV) was then calculated.

Table 4-5 - Fundamental analysis of surface applied protective materials

Tested properties	Testing method	Type of samples	Description of samples
Surface wettability (hydrophobicity)	Goniometer device (contact angle) (Chapter 3, Section 3.4.8)	Untreated concrete and concrete treated with liquid crystalline material, fluoropolymer, silicate resin and silane	Prisms with dimensions of 20mm x 20mm x 10mm
Surface friction (skid resistance)	Pendulum test (Chapter 3, Section 3.4.7)	Untreated concrete and concrete treated with liquid crystalline material, fluoropolymer, silicate resin and silane	Cubes with dimensions of 100mm x 100mm x 100mm
Morphology and chemical composition (microstructure analysis)	SEM and EDX (Chapter 3, Section 3.4.9.1)	Liquid crystalline material, fluoropolymer, silicate resin and silane	Powder (after cryodesiccation)
		Concrete treated with liquid crystalline material, fluoropolymer, silicate resin and silane	Cross sectional slices cut from concrete cubes
Interaction mechanism	ATR-FTIR (Chapter 3, Section 3.4.9.2)	Untreated concrete	Powder
		Liquid crystalline material, fluoropolymer, silicate resin and silane	Powder (after cryodesiccation)
		Concrete treated with liquid crystalline material, fluoropolymer, silicate resin and silane	Powder

SEM and EDX techniques were used to run an in-depth analysis for the microstructure and chemical composition of the applied materials and concrete treated with the materials. To achieve this purpose, materials were subjected to cryodesiccation (freeze-drying) to convert them into solid powder to facilitate their analysis procedure. Consequently, the resulting powder samples, and treated concrete samples, were coated with a thin film of gold to make them conductive, before imaging them with the scanning electron microscope at 20 kV.

The chemical properties and the functional groups of the surface applied materials and its interaction with concrete were analysed by using the FTIR method. The analysis involved samples of untreated concrete, different concrete samples treated with each material and the four surface applied materials. All the samples were converted into powder to facilitate the analysis; untreated concrete samples and concrete treated with the materials were ground and the protective materials were subjected to cryodesiccation.

4.6 Results and discussion

4.6.1 Impact of moisture on material dosage

The effect of moisture content on the dosage of protective materials was assessed by measuring the amount refused by concrete. Table 4-6 outlines the amount of material rejected by preconditioned concrete.

Table 4-6 - Percentage of material refusal corresponding to moisture content of concrete

Applied material	Rejection rate (%)			
	Fully dry	**2% moisture**	**4% moisture**	**Fully saturated**
Crystalline material	11.3%	17.2%	18.4%	24.5%
Fluoropolymer	11.2%	23.7%	25.6%	30.1%
Silicate resin	15.5%	21.6%	23.4%	28.2%
Silane	8.2%	20.3%	28.4%	40.5%

It is witnessed that the wasted amount of applied materials increases with increasing the moisture content of concrete. However, the **crystalline material** showed the least rejection rate, compared to other materials, when applied to concrete with high moisture content. This refers to its high affinity to water as it uses a certain amount of water to form its crystals. On the other hand, **silane** showed an increase in the rejection rate by increasing the moisture content of concrete, and it reached more than 40% when applied to fully saturated concrete. However, when applied to fully dry concrete the rejection rate was the least between all materials. Furthermore, rejection rate values of **fluoropolymer** and **silicate resin** were in between **crystalline material** and **silane.** It is believed that the low rejection rate of any material might contribute in increasing its efficacy in protecting concrete. This refers to the presence of high concentration of the material's active content in concrete when its rejection rate is very low.

4.6.2 Morphological and chemical analyses

The need for properly characterising the applied treatments will help in explaining the way these materials work and their interaction with concrete. It is obvious that the morphology of the three materials differs from each other, as seen from their microstructure in Figure 4-5. The utilisation of the tested materials for the purpose of concrete protection relies on the analysis of the materials themselves and the characteristics of their constituents.

Surface applied materials (before applying to concrete)   **Concrete treated with surface applied materials**
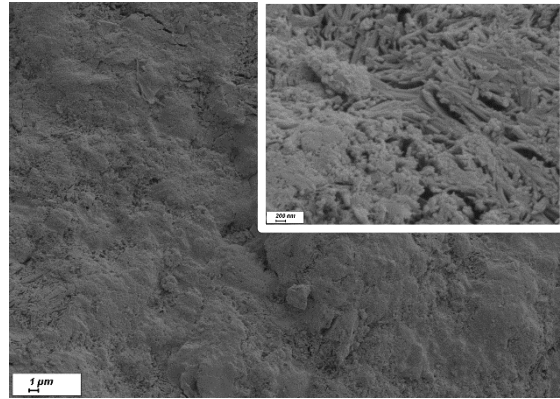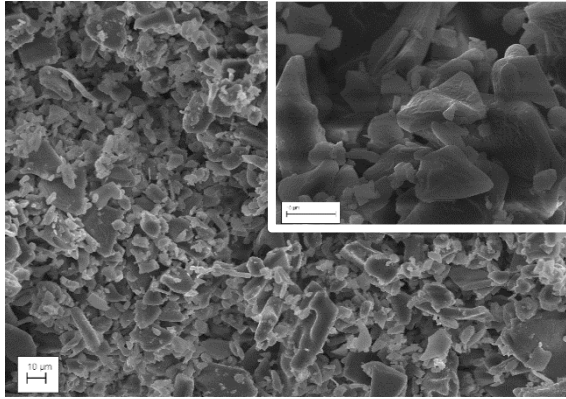
(a): Crystalline material
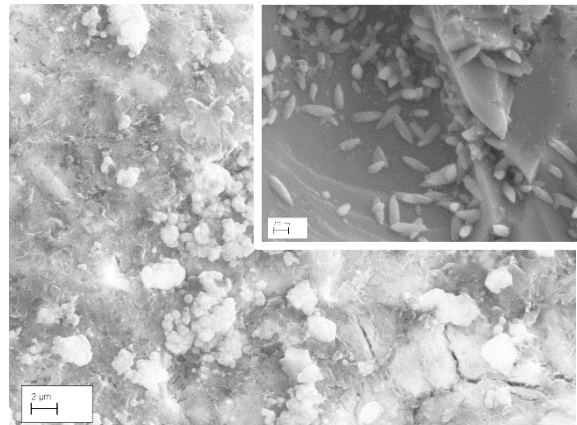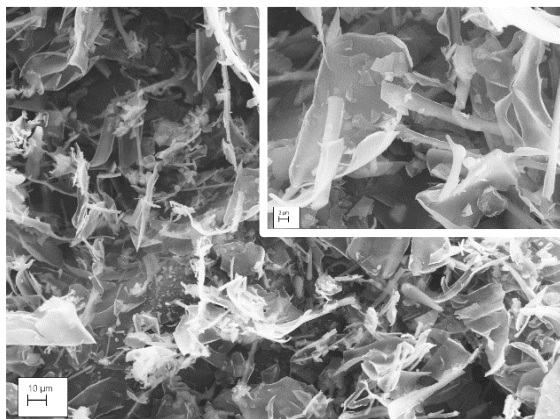
(b): Fluoropolymer
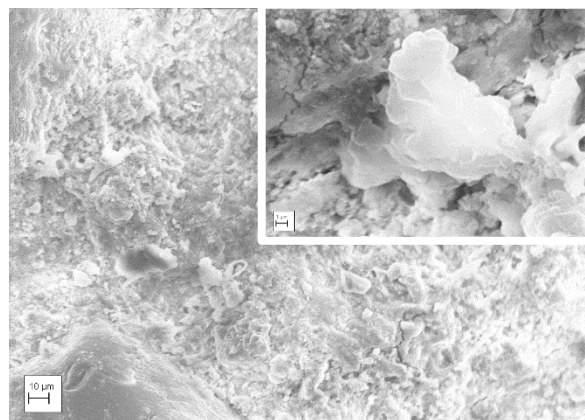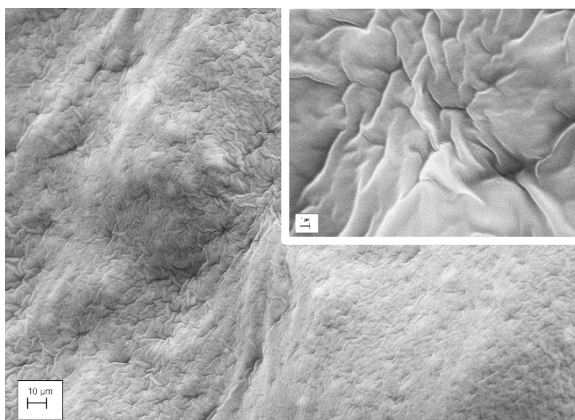
(c) : Silicate resin

Figure Continues…

Surface applied materials (before applying to concrete)	**Concrete treated with surface applied materials**
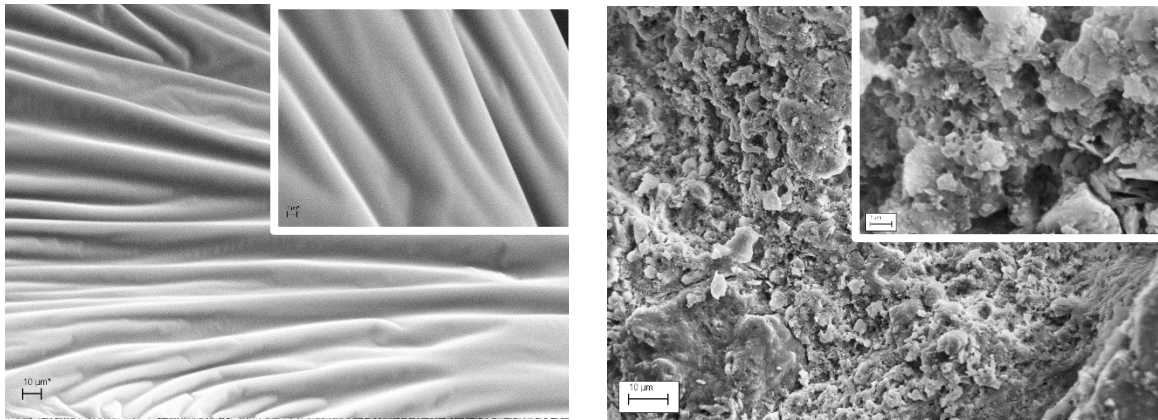
(d): Silane

Figure 4-5 - SEM micrographs for the applied protective materials and their integration with concrete: (a) crystalline material, (b) fluoropolymer (c) silicate Resin, and (d) silane

Results from EDX analysis showed that the main elements composing the **crystalline material** are Carbon, Oxygen, Sodium, and Silicon. These elements preliminary confirms that the active part of this compound is sodium acetate, which contains the former elements except Silicon (Al-Otoom et al. 2007). This compound is believed to diffuse through the pore structure of concrete, links to the walls of the pores and start forming its crystals in the presence of water. These crystals are characterised by being hygroscopic as they use water for their development; they trap water inside their crystalline structure and reduce its permeability (Al-Otoom et al. 2007). The presence of silicon in the elemental composition of this compound and the hydrophobic performance of the compound might indicate for the formation of another type of crystals. It is suggested that an organosilicon composite might present in the material, which is an organometallic compound with bonds of carbon and silicon (Abel et al. 1995; Pawlenko 2001).

The main characteristic of the organosilicon compounds is their high hydrophobicity, which gives them the advantage of being used for concrete protection. Furthermore, it is also believed that the presence of sodium and silicon in the composition of this compound will start a reaction with the calcium hydroxide, which is present in concrete, and generates some amounts of silica crystals (Xiao et al. 2014; Cappellesso et al. 2016). These silica crystals work on reducing the size of pores rather than blocking them allowing concrete to breathe and allowing for oxygen diffusion (Kumar et al. 2009; Qin et al. 2017). An anatomical analysis for the **crystalline material**, before applying to concrete, as shown in Figure 4-5 a on the left, revealed the presence of this material in dense and packed formation with amorphous and smooth surfaces, which contribute directly in increasing the material's hydrophobicity (Wenzel 1936; Barthlott & Neinhuis 1997; Inoue et al. 2000). This would be seen in treated concrete (Figure 4-5 a on the right), as the **crystalline material** has made the internal structure of concrete denser and more compact, which would be reflected on its strength and rigidity. This aspect is discussed in details in section 4.6.3.

Analysing the **fluoropolymer** material under the EDX has revealed that Fluorine, Carbon and Oxygen are the main constituents forming its elemental structure. As discussed previously in Chapter 2, Section 2.6.1.1, the presence of fluorine will provide the material with hydrophobic properties, which will contribute directly to concrete protection and waterproofing. A microstructural analysis for this material, as shown in Figure 4-5b (on the left), reveals that it forms fine, smooth and 'needle-shaped' polymers with sizes less than 200 nm. Their shape, size and characteristic are suggested to give enough support for the material to be integrated easily within the concrete pores and attached strongly to their walls (Kumar et al. 2009; Teng et al. 2014). The interaction between **fluoropolymer** and concrete (Figure 4-5b on the right) shows the integration of the material within the pores of the concrete and their dense distribution on the pores' walls. After the penetration of **fluoropolymer** through the pores, its

shape is recognised as 'rice-shaped' or 'pebble-shaped' clusters that are attached to the walls of pores and distributed over a wide area of them (Figure 4-5 b on the right). The small size of these clusters, their smooth surfaces and their high distribution within the pores allow them to act strongly against water and chemicals penetration.

EDX analysis of the **silicate resin** material has shown that carbon, oxygen and silicon are the main elements of its composition. The structural analysis of this material, described in Figure 4-5 c on the left, displays an attached sheet of resins that work together as one unit. The presence of the material in this state eases its connection to the pores as shown in Figure 4-5c (on the right). When applied to concrete, a silicate gel will develop and initiates strengthening points in the internal parts of the pores (Sandrolini et al. 2012; Franzoni et al. 2013). Hydroxyl groups, formed from the by-products of cement, will possibly react with the silicon in the **silicate resin**, in the presence of hydrogen bonds, allowing **silicate resin** to link strongly with the pores. This would possibly guarantee the development of some hydrophobic properties (Pan et al. 2017).

Comparing **crystalline material, fluoropolymer** and **silicate resin** with **silane** (Figure 4-5 d), the latter works on entirely blocking the pores, not allowing concrete to breathe, because of the alkoxy group that forms its molecular structure (Pan et al. 2017). This alkoxy group will generate a silanol group, after its reaction with water, and congregate inside the pores and block them (Pan et al. 2017). The aerogel microstructure of **silane**, as appears in Figure 4-5 d on the left, shows an obvious gel structure with multiple groves that increase the material's surface area. This gives the material the ability to extend its presence inside the pores and block them. Figure 4-5 d on the right reveals the presence of **silane** inside concrete in large-sized lumps, which are distributed all over the shown cross-section.

4.6.3 Functional groups of the surface applied materials

FTIR spectroscopy was chosen to run a quantitative analysis on the protective materials and their mechanism interaction with concrete. This technique is well known for its high sensitivity, accuracy, and reliability in quantifying and analysing materials (Hortling et al. 1997; Ghaffar & Fan 2013). The FTIR spectra of the protective materials and their interaction with concrete are shown in Figures 4-6, 4-7, 4-8 and 4-9.

The interaction between the liquid **crystalline material** and concrete is outlined in Figure 4-6.
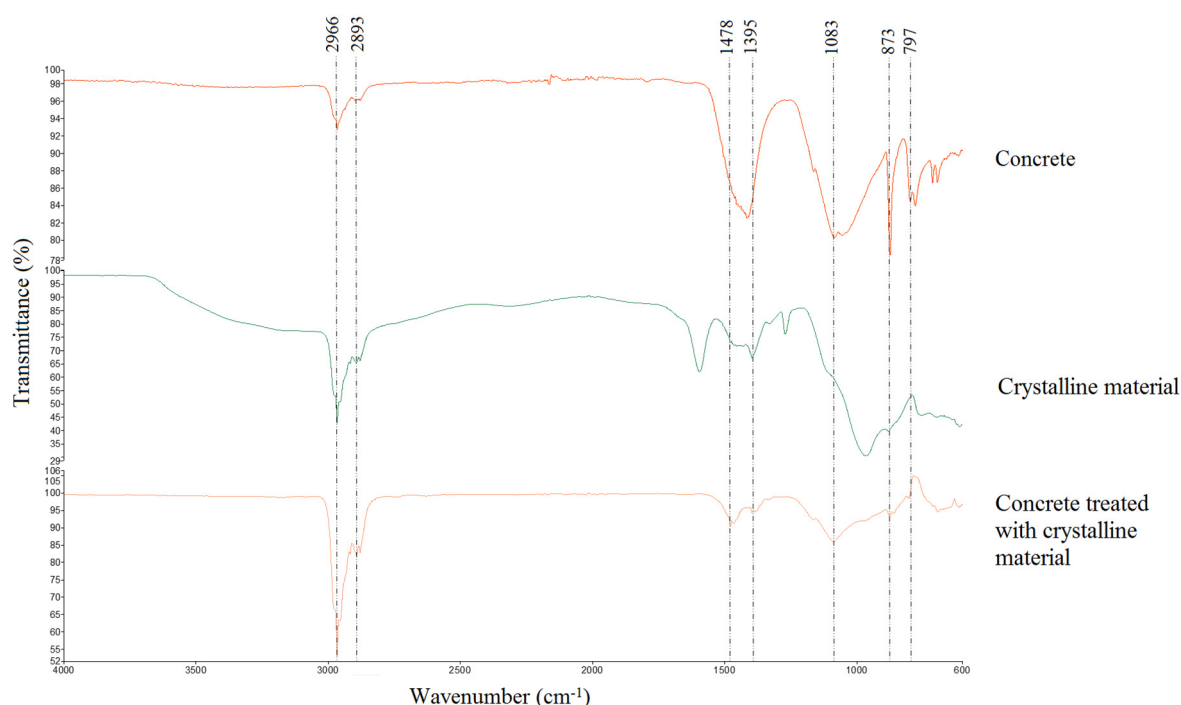
Figure 4-6 – ATR-FTIR analysis for the interaction between concrete and crystalline material

The analysis in Figure 4-6 is recognised with some characteristic peaks that range between 2966 to 2893 cm^{-1}, 1478 to 1395 cm^{-1}, 873 to 797 cm^{-1} and the peak at 1083 cm^{-1}. The sharpest band is found in 2966 to 2893 cm^{-1} range that may correspond to the –CH and –OH stretching vibrational bonds (Socrates 2004). These peaks are caused by the anharmonic resonances of the –CH and –OH bonds in the crystal of the acetic acid chain (CH$_3$COOH) forming sodium

acetate (Gadermann et al. 2007). The band range between 873 cm^{-1} to 797 cm^{-1} mostly refers to the –CO$_3$ bond (Rey et al. 1991) and the strong –CH$_2$ rocking vibrational bond in the Si-CH$_3$ fragment of the material's molecular structure (Socrates 2004). Also, it is believed that 1478 to 1395 cm^{-1} band may correspond to the stretching vibrations of the C-H bond (Ibrahim et al. 2005; Iacovita et al. 2015). Finally, the 1083 cm^{-1} refers to the stretching vibrational C-O bond in the –COOH carboxylic acid part (Socrates 2004).

After treating concrete with the **crystalline material** (Figure 4-6), an increase in the peaks' transmission (%) has been observed within the 2966 to 2893 cm^{-1} range (–CH and –OH). This increase in the intensity of the hydrogen bond could refer to the reaction between sodium acetate and concrete in the presence of moisture, where sodium acetate dissociates in water at the beginning to form CH$_3$COO$^-$ and Na$^+$ ions (Sharma 1997; Chang 2005). Afterwards, CH$_3$COO$^-$ is believed to connect with concrete pores by reacting with sodium that already exists in concrete to form another type of sodium acetate crystals, which link strongly with concrete pores. This process weighs strongly in increasing the intensity of the C-H bond (Figure 4-6). In addition, it is noticed that the peaks at 1478 and 1395 cm^{-1} had become sharper when concrete was treated with the **crystalline material**, regardless of the reduction in their transmission, which might reflect the increase in the strength of the C-H bond after treatment. On the other hand, the detached Na$^+$ ions are suggested to react with the available moisture to form a sodium hydroxide (NaOH) product, which in turn participates in increasing the intensity of –OH bonds.

The observed reduction in the intensity of the C-O and -CO$_3$ bonds could result from the ionic reaction between the unreacted CH$_3$COO$^-$ and H$^+$ ions that form small quantities of volatile CH$_4$ and CO$_2$ gases (Ferry 1992; Woodard 2001).

When it comes to the hydrophobicity of the **crystalline material**, it is believed that a substitution process for the –OH groups with CH_3 groups takes place, which results in increasing the intensity of the C-H peaks. With the presence of silicon in the used **crystalline material** (section 4.6.2), CH_3 will bond with silicon after its penetration in concrete to form an organosilicon bond with some hydrophobic effect (Palomino et al. 2007; Wagh et al. 2010; Wagh et al. 2015).

The FTIR analyses of the **fluoropolymer** material and concrete impregnated with **fluoropolymer** are shown in Figure 4-7.
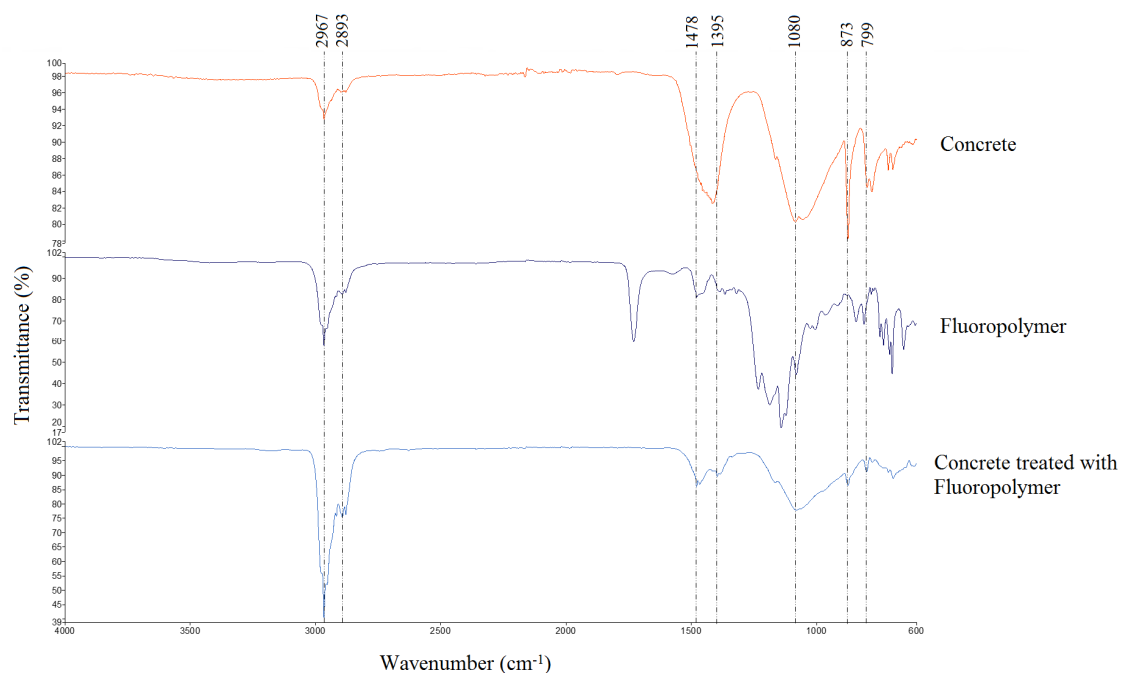
Figure 4-7 – ATR-FTIR analysis for the interaction between concrete and fluoropolymer

Fluoropolymer material has a number of distinctive bands; the sharpest band is found at 2967 cm^{-1} that refers to the C-H stretching vibrational bond (Pianca et al. 1999; Socrates 2004; Krishnan et al. 2013). Another distinctive small peak can be spotted at 2893 cm^{-1} that also refers to the C-H stretching vibrational bond (Pianca et al. 1999; Socrates 2004; Krishnan et al. 2013). Both bands are noticed to increase after treating concrete with **fluoropolymer**, which

might refer to the formation of strong carbon bonds between concrete and **fluoropolymer**, as **fluoropolymer** could strongly adhere to hydrated cement particles. Likewise, the 1478 and 1395 cm^{-1} bands are mostly associated with the C-H stretching vibrational bonds, which are observed to be distinguished with small peaks when concrete is treated with **fluoropolymer** (Ibrahim et al. 2005; Iacovita et al. 2015). The formation of these small peaks might also indicate the creation of carbon bonds between the applied **fluoropolymer** and concrete pores. Furthermore, the transmission (%) of the 1083 cm^{-1} peak, which might correspond to the strong stretching vibrational C-F bond (Socrates 2004; Krishnan et al. 2013), has been observed to increase by more than 4% when adding **fluoropolymer** to concrete. Accordingly, the increase in the intensity of this peak could be linked with the hydrophobic effect that **fluoropolymer** gives to concrete; fluorinated side chains are assembled together to form a tight $-CF_3$ groups that provide concrete with hydrophobicity (Li et al. 2002).

The functional groups of the silicate resin material and concrete treated with **silicate resin** are illustrated in Figure 4-8.
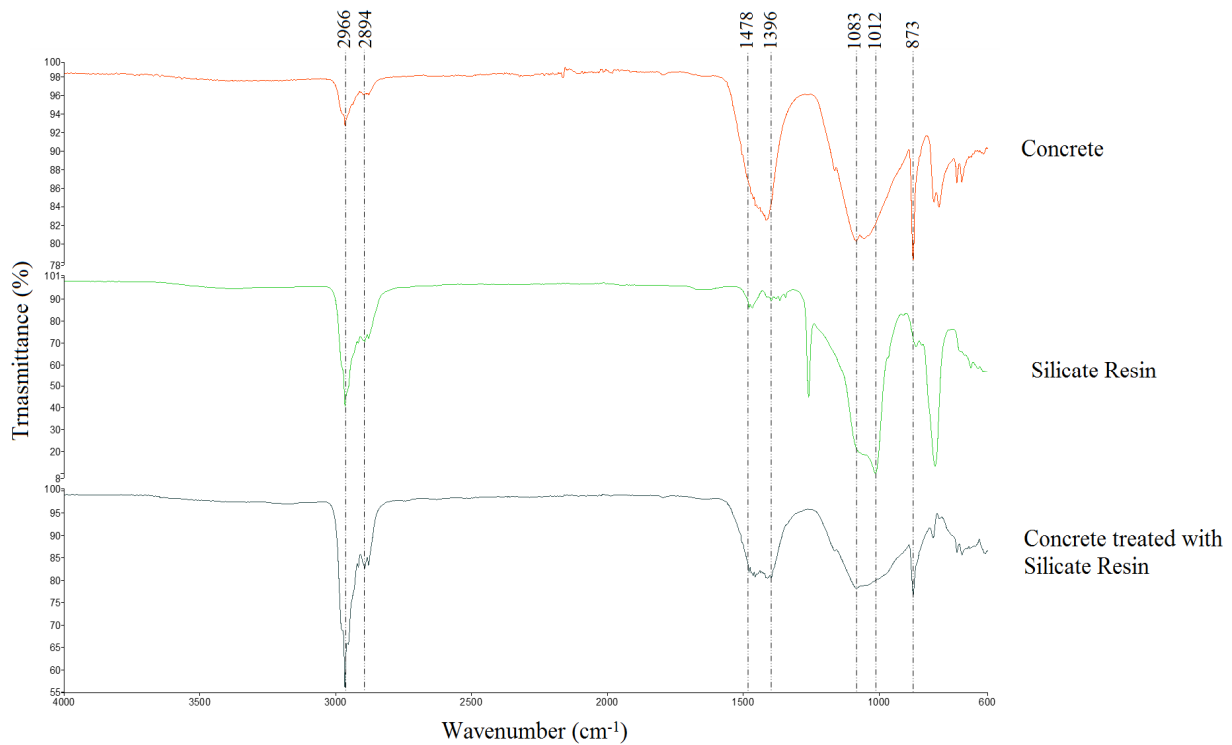
Figure 4-8 – ATR-FTIR analysis for the interaction between concrete and silicate resin

In the IR spectra of **silicate resin** and its interaction with concrete (Figure 4-8), two sharp distinctive peaks are noticed at 2966 cm^{-1} and 2893 cm^{-1} bands, and two broad peaks at 1478 cm^{-1} and 1395 cm^{-1}. All of them are believed to belong to the C-H stretching bonds, and they have shown an increase in their transmission (%) after treatment (Socrates 2004; Ibrahim et al. 2005; Huang et al. 2012; Iacovita et al. 2015; Pang et al. 2018). This increase in intensity was accompanied with an increase in the intensity of the 1083 to 1012 cm^{-1} bands (become broader) in treated concrete, which belong to the Si-O-Si absorption bond (Huang et al. 2012; Pang et al. 2018). The increase in the intensity of the C-H and Si-O-Si bands might refer to the high activity of **silicate resin**, which leads to the breaking of the hydrogen bonds in the material after impregnation into concrete and in the presence of moisture inside the pores. This will participate in consuming the calcium hydroxide that resulted from the hydration process, contributing towards the enhancement of the interfacial properties of the material and its

adhesion with concrete (Pang et al. 2018). In addition, it is believed that a methyl group (CH_3) will be formed after the contact of the material and concrete, which gives another reason for the increase in the C-H intensity. The presence of the methyl group inside the pores with a polarised Si-O-Si bonds will give concrete some hydrophobic properties (Tumiran et al. 2012; Syakur & Sutanto 2017).

Figure 4-9 shows the IR spectra of **silane** and its interaction with concrete. The 2966 cm^{-1} sharp peak presents the most distinctive band in the spectra, which corresponds to the –OH stretching vibrational bond (Socrates 2004). After applying **silane** to concrete, the band has shown an increase in its intensity going with another increase in the intensity of the 1079 to 1011 cm^{-1} bands, which belong to the Si-O-Si bonds (Socrates 2004; Huang et al. 2012; Pang et al. 2018). This increase in the transmission (%) of those bonds might refer to the reaction between **silane** and moisture inside the pores, which leads to the formation of silanol groups by the hydrolysis of alkoxy groups in **silane** (Woo et al. 2008). Finally, a linkage between silanol groups and the hydroxyl groups in concrete will take place after the drying of the pores, creating a strong water repellent bond between them (Basheer & Cleland 2006).
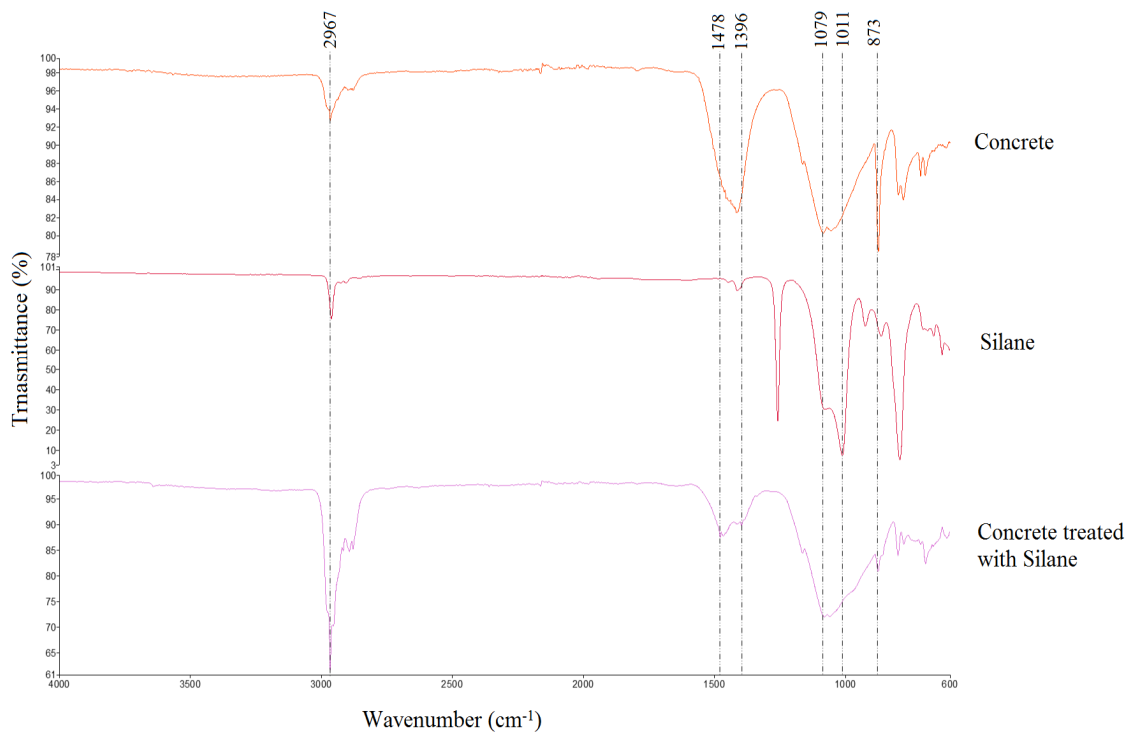
Figure 4-9 - FTIR analysis for the interaction between concrete and silane

4.6.4 Hydrophobic properties

The contact angle for treated and control concrete surfaces was measured, and readings from different locations on different samples were taken. Li & Neumann (1992) suggest taking three values for the contact angle with a 30 second interval between each measurement, for an overall period of 90 second. However, in this research, the test was run for a period of two minutes, and the contact angle was measured at 30 second intervals. Figure 4-10 shows the contact angle between a drop of water and the surfaces of concrete, at different time intervals, after one week of treatment with the four protective materials.

T = 0 sec	T = 30 sec	T = 60 sec	T = 120 sec

θ= 20°   θ= 10°   θ= 0°   θ= 0°

(a)

θ= 82°   θ= 56°   θ= 41°   θ= 29°

(b)

θ= 111°   θ= 111°   θ= 108°   θ= 95°

(c)

θ= 116°   θ= 112°   θ= 111°   θ= 107°

(d)

θ= 133°   θ= 129°   θ= 125°   θ= 122°

(e)
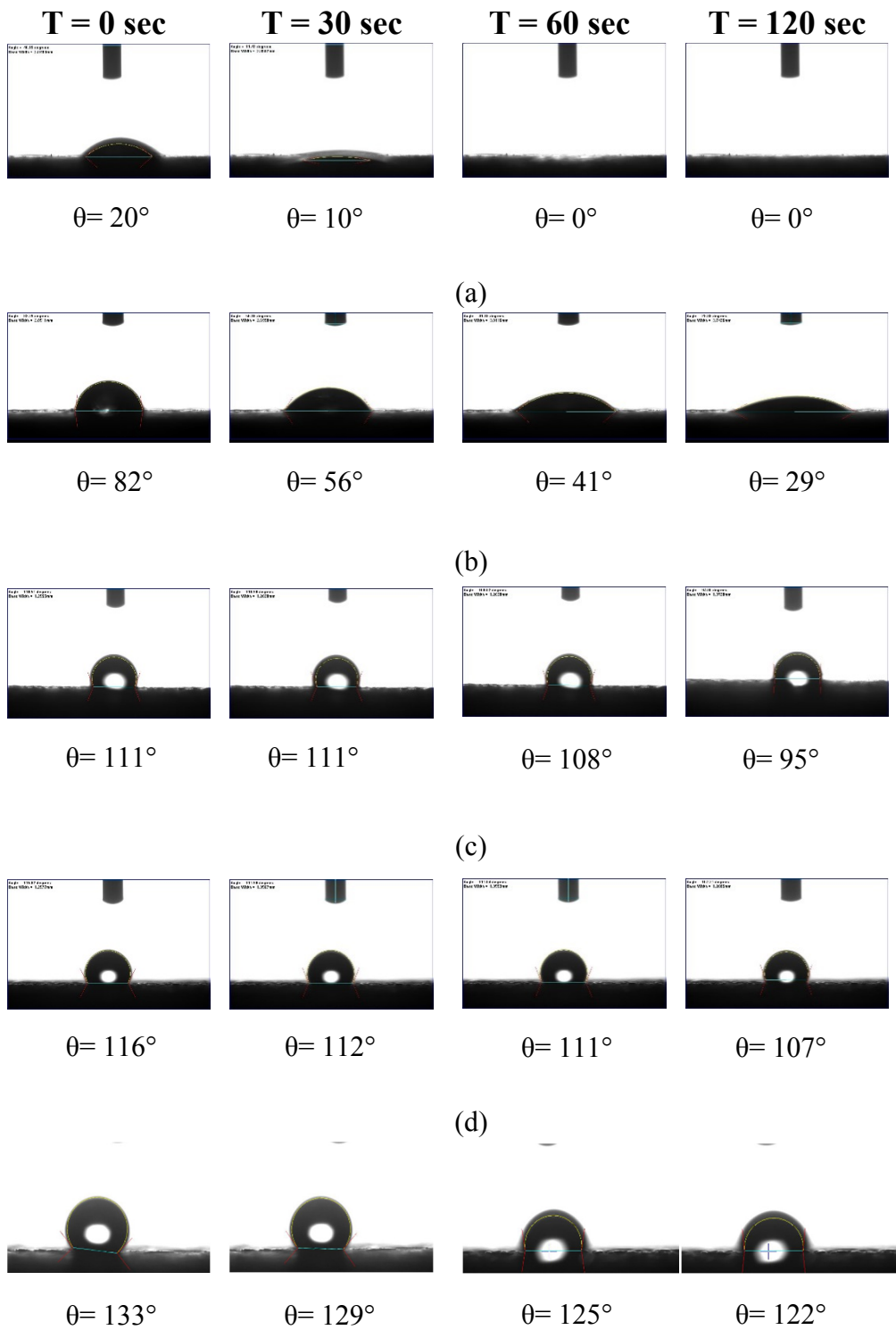
Figure 4-10 - Contact angle for concrete surfaces: (a) untreated, (b) treated with crystalline

material, (c) treated with Fluoropolymer, (d) treated with silicate resin and (e) treated with

silane

Results from this test support outcomes of the FTIR analysis obtained in the previous section 4.6.3, where high hydrophobicity levels have developed in all treated samples.

Concrete treated with **silane** has shown the highest hydrophobicity between all treating materials. Contact angle has reached 133°, which makes **silane** a superhydrophobic material (Superhydrophobic material has contact angles > 90°) (Law 2014). This refers to the formation of the silanol groups after the application of **silane** to concrete (Section 4.6.3).

Another superhydrophobic concrete surface was developed by the application of **silicate resin** (Figure 4-10 d). The application of this material to concrete has developed a contact angle started at 116° at the beginning of the test and decreased gradually to 107° after 120 second of testing. The presence of methyl groups and polarised Si-O-Si bonds, while linked with the pores, has significantly helped in creating this hydrophobic effect in concrete. However, the developed hydrophobicity is still less than that developed by **silane**.

Treating concrete with **fluoropolymer** has also developed a superhydrophobic effect in concrete during all the testing period (Figure 4-10 c). As explained in Section 4.6.3, the presence of $-CF_3$ groups in the material helps in forming the hydrophobic effect inside concrete. However, the hydrophobicity of concrete treated with **fluoropolymer** was less than that developed by **silane** and **silicate resin**. This refers to the short length of the $-CF_3$ chain of the **fluoropolymer** that was used in this research. Increasing the length of the fluorinated carbon chains would work on increasing the hydrophobicity of **fluoropolymer**, however it will become hazardous to environment (Zaggia et al. 2009; Honda et al. 2005).

The applied **crystalline material** has shown the least hydrophobicity (<90°) between all treatments when applied to the surface of matured concrete (Figure 4-10 b). Despite the formation of the organosilicon bond inside the pores, which has hydrophobic characteristics, the developed hydrophobicity was modest compared to other treatments. This refers to the high

penetration depth of the **crystalline material** inside the pores rather than the presence on the surface of concrete due to their small molecular size (Section 4.6.2). Adding to that, the presence of the organosilicon bonds in concrete was modest, as seen in the FTIR analysis, where small peaks of the –CH and –CH$_2$ bonds have developed after treatment (1478 to 1395 cm^{-1} band and 873 cm^{-1} to 797 cm^{-1} band), which form the Si-CH$_3$ fragment of the material.

Comparing all treatments with control, all the applied materials have managed to increase the hydrophobicity of concrete, where control samples showed the least hydrophobicity with maximum contact angle of 20° (Figure 4-10 a).

4.6.5 Skid resistance of concrete surfaces

Frictional properties of treated concrete are necessary to be evaluated to check the suitability of treatments on the safety of the road. The developed hydrophobicity in concrete after the application of treatments (Section 4.6.4) are believed to reduce the skid resistance of concrete. Accordingly, the pendulum test was carried out to check the reasonability of treating concrete pavement with those materials.

Table 4-7 outlines the skid resistance values of treated and untreated concrete surfaces. Concrete treated with **crystalline material** has shown the highest skid resistance after control concrete, which indicates its low influence on the properties of concrete's surface. This supports results from the hydrophobicity investigation in previous section, as **crystalline material** showed the least hydrophobicity between all treatments. The small size of the **crystalline material's** molecules and its ability to penetrate deeper in pores allows it to preserve the texture and properties of the surface without changing.

Table 4-7 - Skid resistance properties for all treated and untreated concrete in terms of the pendulum test values

Applied material	Surface condition	Average PTV	Standard deviation (SD)
Crystalline	Dry	30	0.77
	Wet	24	0.45
Fluoropolymer	Dry	29	0.63
	Wet	24	0.89
Silicate resin	Dry	22	0.63
	Wet	18	0.89
Silane	Dry	17	0.63
	Wet	14	1.10
Control	Dry	32	0.77
	Wet	26	0.63

Fluoropolymer treatment has shown similar skid resistance to **crystalline material**. This refers to the small size of its molecules that allows them to integrate easily within the surface texture of concrete without making significant changes to its roughness (Section 4.6.2).

On the other hand, concrete treated with **silane** has shown the least skid resistance between all treatments. The very low skid resistance value of this material, either when the surface is dry or wet, makes the application of this material to concrete pavement unsuitable and unsafe. Linking current results with the hydrophobicity of **silane** confirms that a very high concentration of the material will present on the surface (Section 4.6.4).

Silicate resin has shown better skid resistance than **silane** but less than that for the **crystalline material** and **fluoropolymer**. This could be attributed to its high hydrophobicity and its high concentration on the surface, like **silane**, which increases the skidding of the surface.

When referring to skid resistance values for the internally integrated **crystalline material** in Part I and compare them with those for the surface applied **crystalline martial**, it is clear that the internally integrated treatment had the same skid resistance as control. However, the surface applied **crystalline material** decreased the skid resistance by 6%. This could refer to the high distribution of the crystals in the concrete matrix in the case of internal integration, whereas surface applied **crystalline material** will stay near the surface area of concrete, despite its high penetration depth through the pores (compared with other surface applied treatments).

4.7   Summary of Part II

Liquid crystalline material, **fluoropolymer**, **silicate resin** and **silane** were applied to the surface of matured concrete. A systematic analysis was followed in this part to make a comprehensive investigation on the macro and micro scale for the used surface applied treatments. The morphology, chemical composition, frictional properties, hydrophobicity and the mechanism of interaction between the materials and concrete were investigated to establish a full understanding for the features of the materials and their performance.

The morphology and the chemical structure of the materials were explored by using the SEM and EDX analyses respectively. There were significant morphological alterations in the concrete matrix after the application of the materials. The changes involved the formation of crystals inside the pore structure of concrete, in the case of the **crystalline material**, and the formation of small rice-shaped polymers attached to the pores of concrete in the case of **fluoropolymer**. However, **silicate resin** has formed attached sheet of resins on the interior walls of the pores that work together as one unit to repel water. On the other hand, **silane** was found to close the pores with its large alkoxy group molecules.

Chemical functional groups of the materials and their interaction with concrete were analysed with the FTIR analysis. The results showed differences in the types of the formed functional

groups and bonds that each material develops with concrete. The different types of bonds were witnessed to have different hydrophobic effect on concrete. For instance, **silane** developed a very high hydrophobic effect in concrete due to its silanol groups that bond strongly with concrete. In the case of **silicate resin**, the presence of the methyl group inside the pores with a polarised Si-O-Si bonds will introduce some hydrophobic properties in concrete. On the other hand, fluorinated side chains of **fluoropolymer** are brought together to form a tight $-CF_3$ groups that provide concrete with hydrophobicity. However, **crystalline material** depends on the presence of water to form its crystals and develop some organosilicon bonds with concrete that have hydrophobic characteristics. The developed hydrophobicity of all materials were confirmed by running the contact angle test on concrete treated with the materials; obtained results have supported the analysis of the FTIR, where a clear hydrophobic effect has been shown.

The frictional properties of treated concrete were different depending on the used protective material. A general decrease in the skid resistance was noticed with increasing the hydrophobicity of the applied material.

Chapter 5:   Investigation of Strength Development of Concrete Mixes

5.1 Introduction

The internal integration of protective materials into the concrete mix, at the mixing stage, was the most appropriate solution for concrete pavement problems. This technique provided industry administrators and decision makers with a cost-effective solution to the dilemma of closing the roadway to traffic to allow concrete pavement to be impregnated (Sommer 1998). Many research were carried out on this discipline, and most of them focused on using silane and siloxane materials as internal impregnants but with different compositions (Wittmann at al. 2006; Meier & Bauml 2006; Xian et al. 2007; Zhang et al. 2009; Spaeth at al. 2014; Ma at al. 2016). However, most of these treatments negatively affected the compressive strength of the treated concrete regardless of their waterproofing effect. Adding to that, the environmental risks that this kind of materials imposes on environment due to the existence of solvent agents in their components (Bubalo et al. 2014). From this point, the world started to avoid using such materials and trends toward utilising some environmentally-friendly materials like the **crystalline material** to drive down environment deterioration (Pazderka & Hájková 2016; Rahman & Chamberlain 2016).

Even though most of the research conducted on the internal integration of fresh concrete reached a high level of waterproofing, compressive strength values were dropped down. Furthermore, all these research were performed only on high water to cement ratio mixes. Accordingly, the primary challenge of adding the **crystalline material** at the mixing stage is the uncontrolled hydration due to the utilisation of available water by both the crystalline powder and cement content, resulting in micro cracks and reduction in compressive strength.

In this chapter, the previous challenge has been tackled by producing an optimum formulation of **concrete-crystalline** mix design when integrating the material in fresh concrete to preserve the compressive strength of treated concrete. Adding to that, the effect of **liquid crystalline material** on the strength of concrete was investigated, when the material is applied to the surface of fresh concrete instead of matured concrete.

5.2 Experimental work

Two groups of concrete mixtures were prepared to serve the purpose of this chapter; standard concrete mixes (untreated) and non-standard concrete mixes (internally integrated). Standard concrete mixes were used for two purposes: (i) control specimens for comparing their strength with internally integrated concrete and (ii) to apply surface applied materials on their surfaces.

In total 276 concrete samples were used; 212 cubes with the dimensions of 100mm x 100mm x 100mm and 64 beams with the dimensions of 500mm x 100mm x 100mm. Cubes were used for the compressive strength test and beams were used for the flexural strength test. The compressive and flexural strength of all concrete mixes in Table 3-3 and Table 3-4 (Section 3.3, Chapter 3) were tested.

It is noteworthy to mention that liquid crystalline material has been applied to the surface of fresh concrete with w/c ratio of 0.48.

Figure 5-1 illustrates the testing procedure, the number and type of samples and the purpose of them.
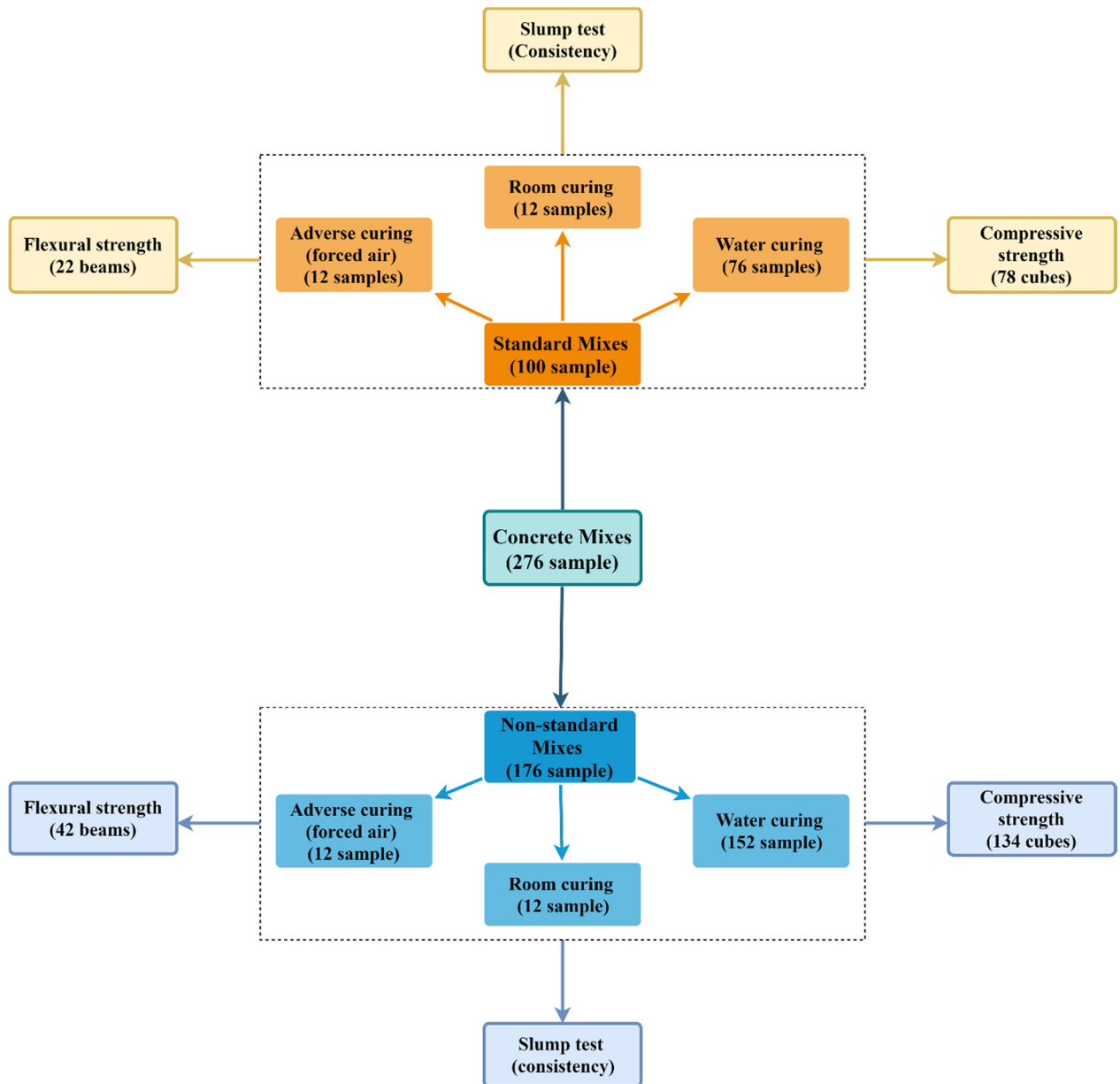
Figure 5-1 - Strength testing protocol for standard (untretaed) and non-standard (internally integrated) concrete samples

Concrete samples were conditioned under three curing regimes before testing: (a) part was cured in a water tank with a temperature of 21 °C, (b) part was cured in a curing room with 60% humidity and temperature of 20 °C, and (c) part was adversely cured under the effect of forced air. More specifically:

- Mix 1-16 were cured in a water bath (regime a).

- Part of mix 1 was treated, when it is fresh, with a **liquid crystalline material** with 2% dosage followed by the spraying of a water-based curing agent on the surface, and then cured in curing room and under forced air (regimes b and c).

The consistency of all mixes was evaluated by running the slump test (Chapter 3, Section 3.4.1). This test was carried out by using the standard slump cone.

5.3 Results and discussion

5.3.1 Mixtures consistency

Results from the slump test are outlined in Table 5-1 with some observations noted after 28 days of curing.

Table 5-1 - Slump values for all used concrete samples

Mixture	w/c ratio	Crystalline material %	Workability (mm)	Observations
Mix 1	0.48	0	40	No visible cracks
Mix 2	0.32	0	0	No visible cracks
Mix 3	0.37	0	0	No visible cracks
Mix 4	0.40	0	5	No visible cracks
Mix 5	0.46	0	25	No visible cracks
Mix 6	0.48	1	60	No visible cracks
Mix 7	0.48	2	190	No visible cracks
Mix 8	0.48	8	210	No visible cracks
Mix 9	0.32	2	0	No visible cracks
Mix 10	0.32	4	0	No visible cracks
Mix 11	0.37	2	5	No visible cracks
Mix 12	0.37	4	20	No visible cracks
Mix 13	0.40	2	15	No visible cracks
Mix 14	0.40	4	70	No visible cracks
Mix 15	0.46	2	50	No visible cracks
Mix 16	0.46	4	160	No visible cracks

It is witnessed that increasing the added amount of the **crystalline material** to concrete increases its consistency and flow properties. For instance, concrete with w/c ratio of 0.37 and 0% **crystalline material** has shown 0 mm slump value, however adding 2% and 4% **crystalline material** to the mix increased the slump to 5 mm and 20 mm respectively. Even in concrete with high w/c ratio, the slump value increased significantly with adding the **crystalline material**. Furthermore, the slump value of concrete with 0.48 w/c ratio and treated with 8% **crystalline material** has reached 210 mm, which is considered a very high slump though acceptable (British Standards Institution 2009a). Despite the high slump values, especially for treated concrete mixes that has a high w/c ratio, concrete did not show any sign of segregation in matured concrete after 28 days of curing. Figure 5-2 shows the interior of concrete with w/c ratio of 0.48 and treated with 8% **crystalline material**, which has the highest slump value between all mixtures (210 mm).

Figure 5-2 - Concrete with w/c ratio of 0.48 and treated with 8% crystalline material without

any visible cracks or segregation

5.3.2 Compressive strength

5.3.2.1 *Developed mix designs of internal integration*

More mix designs with different w/c ratios have been developed and integrated with different percentages of the **crystalline material** to overcome the dilemma of strength reduction that was observed in section 5.3.2.1. Accordingly, mixes 2 – 5 and mixes 9 - 16 were used to serve this purpose.

After 7, 14 and 28 days of curing, all treated and control mixes' compressive strength was determined. Outcomes from this test are illustrated in Table 5-2.

Table 5-2 - Average compressive strength results for control and treated concrete

		Compressive strength (MPa)											
	w/c ratio	**0.32**			**0.37**			**0.40**			**0.46**		
	Crystalline material (%)	**0**	**2**	**4**	**0**	**2**	**4**	**0**	**2**	**4**	**0**	**2**	**4**
Age	**7 days**	34.8	32.0	33.8	30.9	24.6	27.0	28.6	24.8	26.1	30.1	20.6	19.2
	_SD_	_1.97_	_1.15_	_1.68_	_0.94_	_1.67_	_1.90_	_3.77_	_1.79_	_0.70_	_0.51_	_0.56_	_0.64_
	14 days	39.2	32.8	31.4	35.2	25.9	25.7	38.2	27.5	27	32.8	26.1	20.4
	_SD_	_0.63_	_1.00_	_4.22_	_2.25_	_1.11_	_0.72_	_0.95_	_2.33_	_0.78_	_1.38_	_0.64_	_1.24_
	28 days	42.0	47.5	55.2	37.4	45.3	53.2	54.6	43.8	40.7	47.8	36.9	32.5
	_SD_	_2.15_	_1.68_	_3.00_	_1.03_	_1.89_	_4.12_	_3.63_	_1.49_	_3.93_	_1.68_	_4.66_	_2.48_
Change in compressive strength	**7 days**	-	-8.0%	-2.9%	-	-20.4%	-12.6%	-	-13.3%	-8.7%	-	-31.6%	-36.2%
	14 days	-	-16.3%	-19.9	-	-26.4%	-27.0%	-	-28.0%	-29.3%	-	-20.4%	-37.8%
	28 days	-	+13.1%	+31.4%	-	+21.1%	+42.2%	-	-19.8%	-25.5%	-	-22.8%	-32.0%

A remarkable damaging effect of adding the admixture to all the concrete mixes is noticed at early ages of 7 and 14 days (Table 5-2). At the age of 7 days, the strength of all mixes has dropped in the range of 3% to 36% with regard to their control mixes; the lowest drop was noticed for concrete with w/c of 0.32 and treated with 4% material, and the highest was for the 0.46 w/c ratio concrete and treated with 4% material. More reduction in strength of all treated mixes was seen at the age of 14 days when compared to their control; a drop of 16% to 38% in strength was noticed, with 0.32 w/c ratio concrete and treated with 2% material being the lowest and 0.46 w/c ratio concrete and treated with 4% material the highest. However, at the age of 28 days (Table 5-2), treatment has resulted in increasing the compressive strength of 0.32 and 0.37 w/c ratio mixes, ranging from 13% to 42%, with the maximum strength gain for concrete with w/c ratio of 0.37 and treated with 4% material. On the other hand, mixes with 0.40 and 0.46 w/c ratios and treated with either 2% or 4% admixture have continued to lose strength, and it reached 32% in the case of 0.46 w/c ratio concrete and treated with 4% material.

The reduction in strength noticed at the age of 7 and 14 days may refer to the high amount of water present at that time especially in the case of mixes with 0.40 and 0.46 w/c ratio. Adding the **crystalline material** to concrete has contributed in increasing the consistency of these mixes, which is noticed from Table 5-1. This increased level of workability alongside with the presence of activated hydrophobic crystals have teamed up to delay the hydration process which resulted in a reduced compressive strength at those early ages. Furthermore, at the age of 28 days, mixes with relatively low w/c ratios have managed to complete the hydration process and gain higher compressive strengths than their corresponding controls. These results prove that the **crystalline material** has participated in forming a denser concrete structure (Chapter 4, Section 4.3.1) with minimum micro-cracks, which resulted in higher compressive strength than control (in the case of 0.32 and 0.37 w/c ratio mixes). This could be seen from

the porosity outcomes (Table 4-2 in Chapter 4, Section 4.3.1), where porosity has decreased with adding the **crystalline material** to mixes with low w/c ratios. Moreover, concrete with high w/c ratio sustained its strength loss at the age of 28 days since the hydration process was inhibited by the dual effect of adding the admixture and increasing the w/c ratio. Adding to that, the presence of acetic acid in mixes with high w/c ratio would work on inhibiting the hydration process and reducing the compressive strength of concrete (Chapter 4, Section 4.3.2). Also, the slight increase in the porosity when treating concrete with high w/c ratios (Table 4-2 in Chapter 4, Section 4.3.1) confirms this reduction in strength.

According to the results illustrated in Table 5-2, an optimum mix design could be produced by adding 4% of the **crystalline material** to a mix with w/c ratio of 0.37. The next optimal mix would be prepared by adding 4% of the **crystalline material** to concrete with 0.32 w/c ratio.

5.3.2.2 *Surface impregnated fresh concrete*

2% **liquid crystalline material** followed by a water-based curing agent were applied to the surface of fresh concrete (before curing) of mix 1. All the treated and control samples were cured in a curing room and under forced air (Section 5.2).

Results for compressive strength testing after 7, 14 and 28 days, for treated and control concrete specimens, under favourable (room curing) and adverse (forced air) curing conditions are shown in Figure 5-3.

	Favorably cured - control concrete	Favorably cured - treated concrete	Adversely cured - control concrete	Adversely cured - treated concrete
7 days	27.3	21.2	16.1	12.8
14 days	31.6	21.8	18.0	16.9
28 days	35.5	24.3	22.0	18.4

Concrete condition
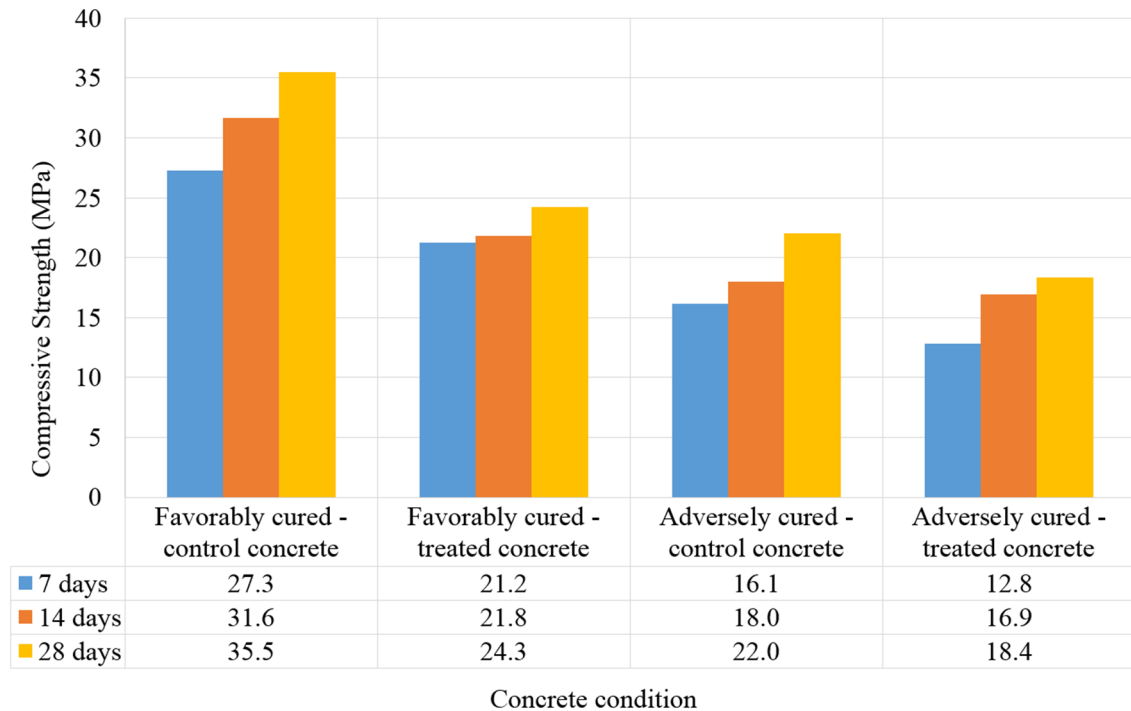
Figure 5-3 - Compressive strength values for adopted concrete mix under different curing conditions

Comparing each treated case with its corresponding control mix indicates a significant strength loss, especially in the case of favourable curing condition, where treated concrete experienced a 32% drop in strength compared to control mix (Figure 5-3). In the case of adverse curing condition, strength loss was, moderately, less severe than favourable curing condition. Treated and adversely cured specimens exhibited a loss in strength of 17% from their corresponding control specimens, which is about half the loss exhibited by concrete under normal curing regime (Figure 5-3). The applied **liquid crystalline material** uses water to form crystals inside concrete pores; this water is part of the water already used for hydration. Adverse conditions make the situation worse by accelerating the drying of water in concrete, which leaves less water for hydration and negatively affect the strength of concrete. This could be noticed in the higher compressive strength of favourable cured concrete than adverse cured concrete. On the other hand, it could be noticed that the **crystalline material** has the ability to increase the level

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of defence when conditions affecting concrete become worse than normal, which was shown in Figure 5-3; under harsh conditions, the presence of the material's crystals in treated concrete work on reducing the strength loss in concrete (compared to control) that results from the uncontrolled hydration. Moreover, early treatment with the **liquid crystalline material** followed by the water-based curing compound, achieved an increase in concrete strength of 43% for the period from day 7 to day 28, and this increase was about 36% in the case of its corresponding untreated mix.

5.3.3 Flexural strength

5.3.3.1 Developed mix designs of internal integration

Table 5-3 outlines the results of the 28 day flexural strength test on the developed concrete mixtures (Mixes 2 – 5 and Mixes 9 – 16).

Table 5-3 - Influence of internal integration on flexural strength of concrete

w/c ratio	Crystalline material (%)	28 days Flexural strength (MPa)	Change in flexural strength compared to control	Standard deviation	Coefficient of variance
	0	4.5	-	0.168	0.037
0.32	2	5.0	+11.1%	0.140	0.024
	4	5.8	+28.9%	0.129	0.026
	0	4.5	-	0.296	0.066
0.37	2	4.6	+2.2%	0.089	0.019
	4	5.3	+17.8%	0.199	0.037
0.40	0	3.5	-	0.226	0.048

Table Continues…

	2	3.0	-14.3%	0.155	0.042
	4	2.9	-17.1%	0.095	0.045
	0	4.7	-	0.191	0.055
0.46	2	3.7	-21.3%	0.217	0.075
	4	2.1	-55.3%	0.308	0.103

It is clear from Table 5-3 that treating a 0.46 and 0.40 w/c ratio mixes with any of the proposed concentrations of the **crystalline material** would result in losing the flexural strength of the mix without any enhancement or even preserving the original flexural strength. Concrete mixes with w/c ratios of 0.32 and 0.37 and treated with 4% **crystalline material** achieved the highest flexural strength values between all the mixtures with a total improvement of 29% and 18% respectively to their control mixes. The compatibility between the **crystalline material** and the amount of water in mixes with relatively low w/c ratios (0.32 and 0.37) has contributed in the thorough distribution of the crystals within the matrix. Adding to that, the amount of water in these two mixes were enough to complete the hydration process and, at the same time, activate the sodium acetate crystals in the mix without creating high amounts of acetic acid that work on delaying the hydration process. Also, the presence of low amount of water will keep the formed NaOH amounts in reasonable levels, which will work on reducing the segregation of concrete, accelerates the hydration of C_3S and increase the strength (Chapter 4, Section 4.3.2) (Ramachandran 1996; Collins & Sanjayan 1999). According to results from chapter 4, section 4.3.1, sodium acetate will work towards the formation of dense matrix with minimum micro-cracks, which will result in high flexural strength.

5.3.3.2 *Surface impregnated fresh concrete*

The effect of treating the surface of fresh concrete before curing (at early ages) with 2% **liquid crystalline material** on the flexural strength of concrete is shown in Table 5-4.

Table 5-4 - The effect of curing conditions and treatment on teh flexural strength of concrete

Curing condition	28 days Flexural strength	Change in flexural strength compared to control
Favourably cured - control concrete	2.9	-
Favourably cured - treated concrete	2.2	-24.1%
Adversely cured - control concrete	1.8	-
Adversely cured - treated concrete	1.5	-16.7%

Flexural strength of surface treated concrete has followed similar trend to compressive strength values of the same mixtures and treatments (Section 5.3.2.3). A general reduction in flexural strength has been observed in all mixes after the application of the **crystalline material**. A maximum reduction of 24% in strength was observed in favourably cured and treated concrete, and a minimum strength loss of 17% was observed in adversely cured and treated concrete. Favourable curing conditions allow concrete to keep its initial moisture content in high levels. The presence of water in such curing conditions will allow a proper progress in concrete's hydration and, at the same time, will work on activating the sodium acetate crystals. However, very high amount of water (w/c = 0.48) will have an adverse effect on concrete. The interaction between sodium acetate, which presents in the **crystalline material**, and concrete at early ages and in the presence of high amount of water will contribute in forming a hydrophobic organosilicon bond (Chapter 4, Section 4.3.2). Increasing the w/c ratio of the mix with the presence of the **crystalline material** will increase the rate of forming the hydrophobic content. Forming this hydrophobic content in large quantities, at early ages, will contribute in fending off excess water out of the concrete pores. Fighting off this water will result in lowering the quantity of water required to progress the hydration process, and finally reduce the strength of concrete.

Despite the reduction in the flexural strength of adversely cured and treated concrete, the strength loss was less than that in favourably cured concrete. Contrary to normally cured concrete, the conditions of adverse curing work on drying the high amount of existing water, which will not allow the formation of high quantity of hydrophobic organosilicon compound.

5.4 Summary

All the proposed mix designs in this research were evaluated in terms of mechanical properties; compressive and flexural strength, and an optimum formulation of **concrete-crystalline** mix design has been determined.

Testing procedures were divided into two parts: testing developed integrated concrete and testing surface protected concrete at early ages. In the two parts, the **crystalline material** was used as a protective material; internally integrated and externally applied. Furthermore, the **crystalline material** was only applied/integrated to concrete when concrete is fresh.

Concrete was cured under three different curing regimes: (i) in a water tank with a temperature of 21 °C, (ii) in a curing room with 6% humidity and temperature of 20 °C and (iii) in a harsh environment under the effect of forced air.

The developed mix designs with low w/c ratio (0.32 and 0.37) and treated with the **crystalline material** performed the best between all mixes. An optimum mix design could be obtained by treating the 0.32 and 0.37 w/c ratio mixes with 4% **crystalline material**; compressive strength increased by more than 31% and 42%, respectively, above the initially designed strength. Furthermore, an increase of 29% and 18%, respectively, in flexural strength was observed in both mixes.

The application of the **liquid crystalline material** to the surface of fresh concrete has shown an adverse effect on its compressive and flexural strength. This reduction in strength was

observed either when concrete was cured under normal conditions (curing room) or under harsh conditions (forced air).

Results from this chapter has not only met the set objectives of preserving the strength of internally integrated concrete but it has managed to increase the strength to high levels. However, more testing is still needed to confirm the ability of the **crystalline material** to waterproof the developed mixtures.

Chapter 6:   Water Absorption of Protected Concrete Pavement

6.1 Introduction

Concrete has been employed in the construction of roads and motorways that were designed to serve for more extended periods and reduced maintenance costs than flexible pavement (Delatte 2014). However, concrete pavement is still at the risk of deterioration generated from environmental impacts and climate changes like rainfall, snowfall, and freezing and thawing. Water is one of the main deterioration factors for reinforced concrete since all the mechanical and chemical degradation of concrete is initiated by the presence of water under any circumstances (Willway et al. 2008).

In this chapter the efficacy of treatments, either surface applied or internally integrated, was investigated in terms of their ability to reduce water absorption through concrete pavement. The main sources of water absorption through pavement is either from rainfall or groundwater, and two tests are designed to measure water absorption in these situations: Initial Surface Absorption Test (ISAT) and capillary action test (British Standards Institution 1996; American Society for Testing and Materials 1999). ISAT method represents the worst exposure of rainfall in the UK, and capillary action test is designed for testing protected concrete, by surface application, when it is exposed to groundwater.

This chapter will be divided into two main parts, in terms of treatment type:

- **Part I: Internally integrated treatment**

- **Part II: Surface applied treatments**

In the first part, a continuation for the set purpose, in chapter 5, of determining the optimum mix design for internally integrated concrete was validated in terms of water absorption after

the elimination of the preliminary mix design. This aims to support outcomes from the strength evaluation of internally integrated concrete (chapter 5). Accordingly, water absorption of concrete by ISAT has been evaluated and analysed.

In the second part, surface protected concrete by the **crystalline material**, **fluoropolymer**, **silicate resin** and **silane** was evaluated and analysed with regard to water absorption. The ability of treatments to protect concrete pavement from rainfall and groundwater was examined by the ISAT method and the capillary action method.

Part I: Internally Integrated Treatment

6.2 Experimental programme

In total 144 cubes with the dimensions of 100mm x 100mm x 100mm were cast and conventionally cured in a water tank at 20 °C temperature for 7, 14 and 28 days for serving the ISAT testing protocol (Chapter 3, Section 3.4.3). Specimens were cast with 4 different mix designs; 36 cubes with w/c ratio of 0.32, 36 cubes with w/c ratio of 0.37, 36 cubes with w/c ratio of 0.40 and 36 cubes with w/c ratio of 0.46 (Mixes 2-5 and Mixes 9-16). Part of the cubes were used as control and the other part was treated with 2% and 4% **crystalline material**. Figure 6-1 shows an illustrative diagram for the used mixtures and their testing procedure.
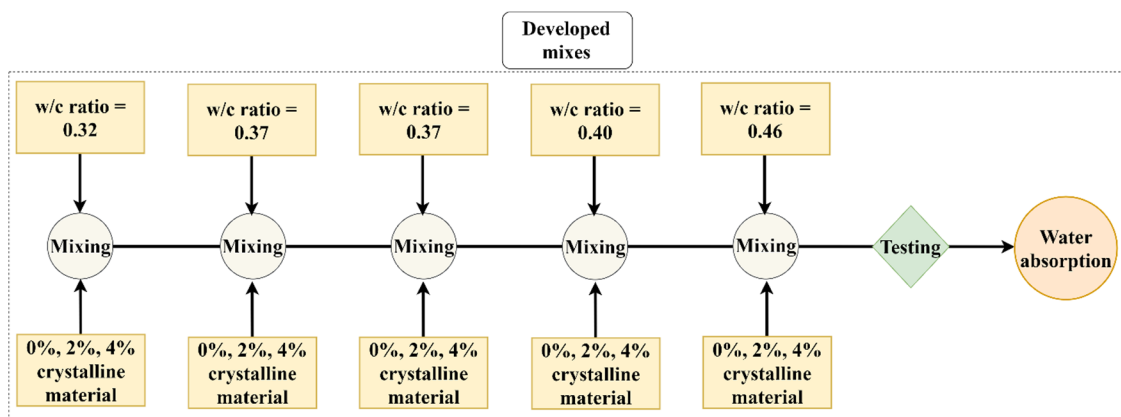
Figure 6-1 - Explanatory diagram of the mixing and testing stages to produce optimum

protection

6.3 Results and discussion

The efficacy of the **crystalline material** in reducing water absorption of the developed mixtures (Mixes 2 – 5 and Mixes 9 – 16) after 7, 14 and 28 days of curing was investigated and shown in Figure 6-2.

At 7 days, 0.32 w/c ratio mix achieved the least water absorption rate between all mixes, either when treated with 2% or 4% **crystalline material** (Figure 6-2 a). The same performance is observed at the age of 14 days where 0.32 w/c ratio mix, treated with 4% **crystalline material**, has absorbed the least amount of water (Figure 6-2 b). After 28 days of curing, concrete with w/c ratios of 0.32 and 0.37 and treated with 4% **crystalline material** achieved the best performance among all other mixes with water absorption close to zero and with efficacy of more than 50% and 60%, respectively, compared to their control (Figure 6-2 c).

Increasing the w/c ratio of the mixes above 0.37 is noted to have a negative effect on the performance of treated concrete. Treating mixes with relatively high w/c ratio (0.40 and 0.46) at the age of 7 days has shown a destructive effect which is recognised by their high water absorption rate that exceeded their corresponding control (Figure 6-2 a). With increasing the curing age to 14 days, the 0.40 w/c ratio concrete and treated with 4% material and the 0.46 w/c ratio concrete and treated with 2% material have managed to perform better than their controls. At the age of 28 days, concrete with w/c ratios of 0.40 and 0.46 and treated with 2% material had the best performance between all the 0.40 and 0.46 w/c ratio mixes, whereas the same mixes treated with 4% material showed worse performance than control.

7-days   **14-days**   **28-days**

w/c 0.32
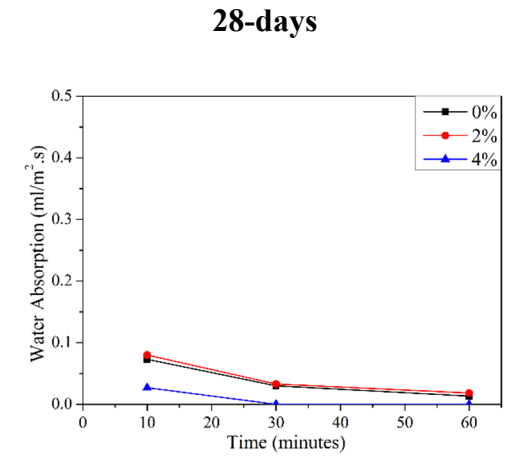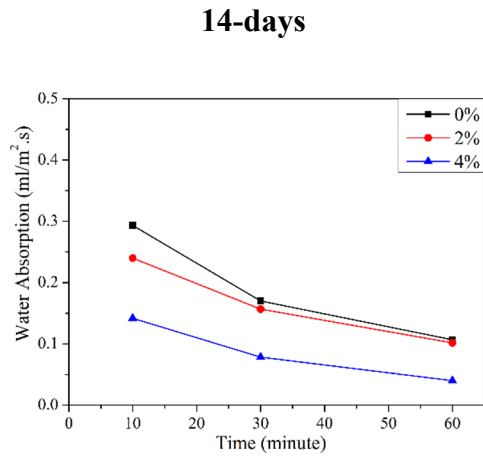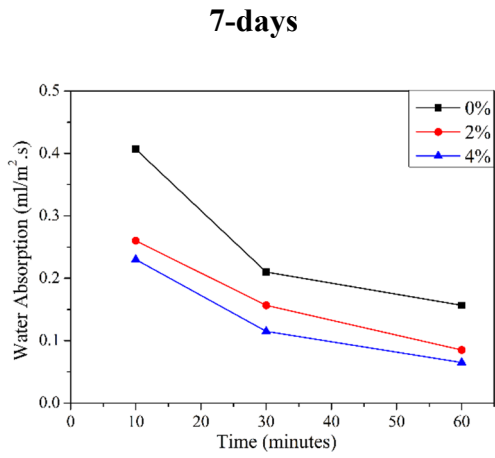
(a): w/c ratio of 0.32

w/c 0.37
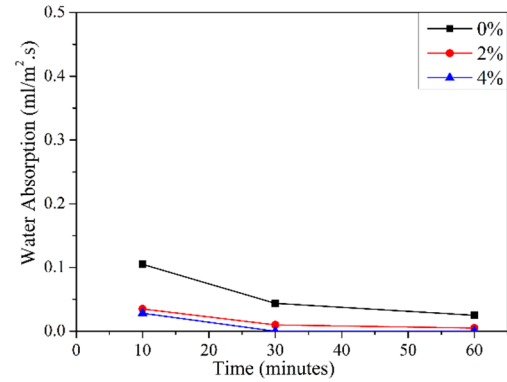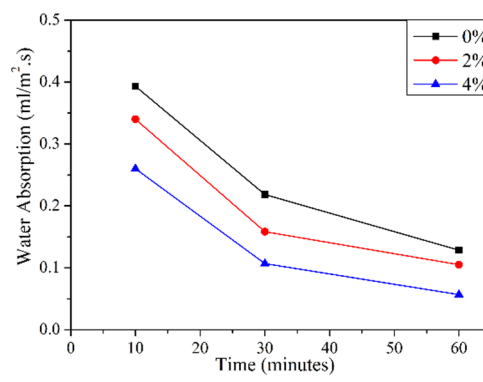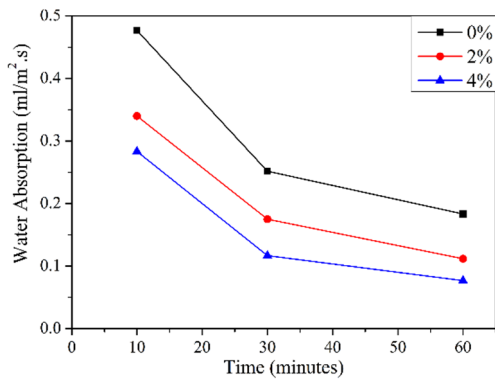
(b): w/c ratio of 0.37

Figure Continues…

7-days   **14-days**   **28-days**
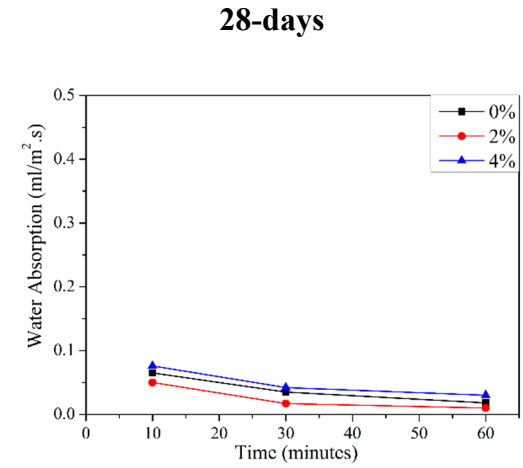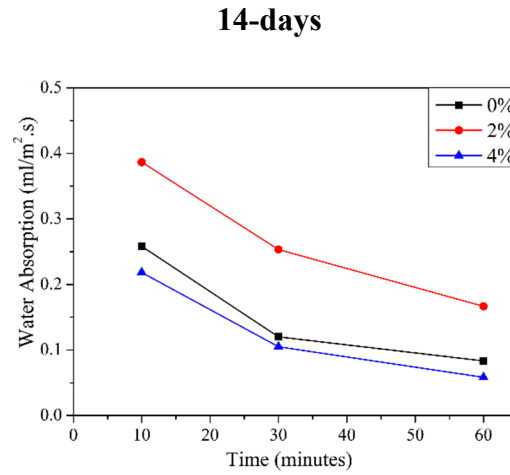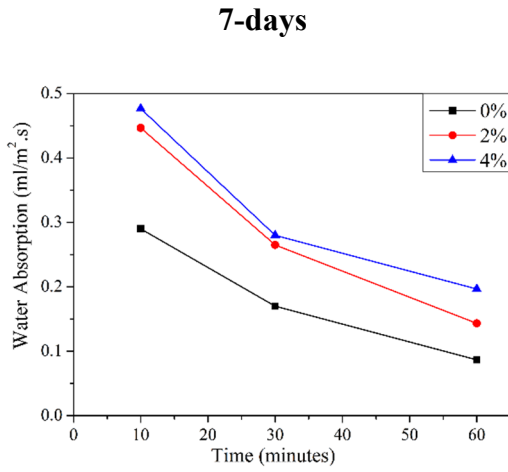
w/c 0.40

w/c 0.46
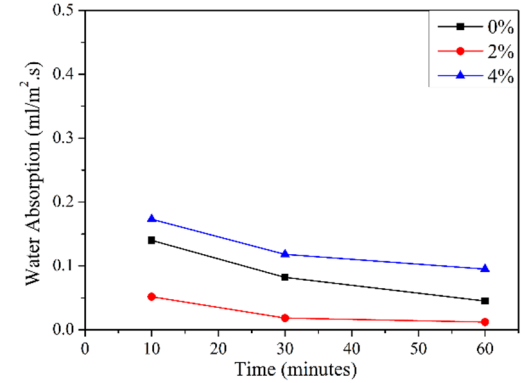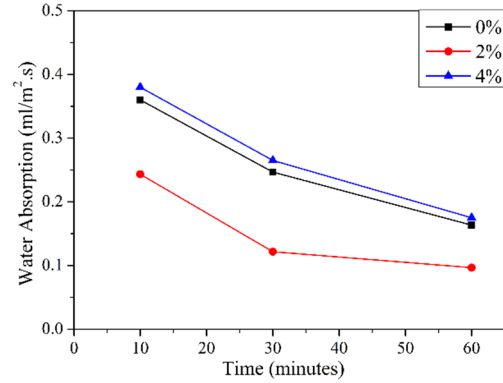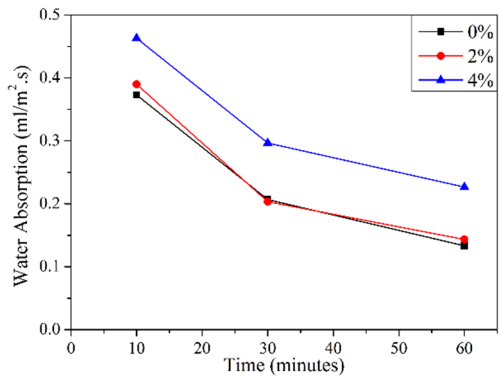
(c): w/c ratio of 0.40

(d): w/c ratio of 0.46

Figure 6-2 - Water absorption of concrete mixes at 7, 14 and 28 days treated with 0%, 2% and 4% crystalline material and with w/c ratio of:

(a)0.32, (b) 0.37, (c) 0.40 and (d) 0.46

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It is believed that the destructive effect of adding 4% **crystalline material** into the 0.46 and 0.40 w/c ratios mixes resulted from the higher amount of water used in these mixes, compared to concrete with 0.32 and 0.37 w/c ratios. Adding the 4% amount of the **crystalline material** to concrete with relatively high w/c ratios contributed to increasing the slump values and the consistency of these mixes due to the formation of high amounts of NaOH (Table 5-1 in Chapter 5), which in turn participated in increasing air voids and micro-cracks (Nguyen et al. 2016). This could be linked with the porosity outcomes in Table 4-2 (Section 4.3.1, Chapter 4), where an increase in the porosity was noticed when adding the **crystalline material** to concrete with high w/c ratios.

Another reason for this destructive effect is that the interaction between sodium acetate and cement in the presence of water most probably will contribute in forming a hydrophobic organosilicon bond (Chapter 4, Section 4.3.2). Increasing the added amount of water into the mix with a high dosage of **crystalline material** will increase the rate of forming the hydrophobic content. Forming this hydrophobic content in large quantities, at early ages, will contribute in repelling excess water out of the concrete pores. Forcing this water to leave the pores will result in reducing the needed quantity of water to continue the hydration process, which leads to form some micro-cracks within the concrete structure. As a result, more water will be absorbed in concrete, at later ages, with w/c ratios of 0.40 and 0.46 and treated with 4% **crystalline material**. In contrast, 0.32 and 0.37 w/c ratios concrete and treated with 4% **crystalline material**, or even 2% **crystalline material**, showed a very high ability to combat water absorption. This could be a result of using a compatible amount of water and **crystalline material**, where no excess water is present in the mix, and the amount of water was suitable to initiate the reaction between sodium acetate and cement, and at the same time enough to continue the hydration process.

6.4 Summary of Part I

The water absorption of the developed mix designs for internally integrated concrete and control concrete was examined by using the ISAT method.

Integrating the **crystalline material** into the fresh developed concrete mixes reduced water absorption significantly. A 2% dosage of the crystalline material relatively reduced water absorption of the 0.40 and 0.46 w/c ratio mixes. Also, a 4% dosage of the **crystalline material** in the 0.37 and 0.32 mixes dramatically decreased their water permeability. Accordingly, the 0.37 w/c ratio mix along with the 0.32 w/c ratio mix, both treated with 4% **crystalline material**, showed the best performance, regarding water absorption resistance, among all the mixes. They both prevented water ingress after 30 minutes and 60 minutes testing periods. Additionally, the 0.37 w/c ratio mix treated with 4% **crystalline material** showed a significant reduction in water absorption levels close to 65%, and the 0.32 w/c ratio mix treated with 4% **crystalline material** reduced water absorption levels by 55%.

Results from the 0.46 and 0.40 w/c ratios may suggest the impracticality of treating those mixes with 4% crystalline material. An increase in the water absorption of the aforementioned treated mixes has been observed, where, at some cases, it exceeded their corresponding control mixes. Adding to that, the reduction of strength values of these particular mixes, as seen in Chapter 5, confirms the unfeasibility of treating concrete with high w/c ratio with 4% **crystalline material**.

Based on the results obtained in this chapter and the previous chapter (Chapter 5), an optimum mix design could be obtained by treating the 0.32 and 0.37 w/c ratio mixes with 4% admixture.

Part II: Surface Applied Treatments

6.5 Experimental programme

To serve the purpose of this part, 199 concrete cubes with the size of 100mm x 100mm x 100mm were manufactured. The testing procedure of this part was divided into three sections:

- 61 cubes were manufactured with w/c ratio of 0.46 and cured in a curing room with 60% humidity and temperature of 20 °C. After finishing 28 days of curing, part of the cubes was treated with **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** by surface application (until refusal). The other part of the cubes was used as control (untreated). All the cubes were tested for water absorption by the capillary action test and the ISAT method (Chapter 3, Sections 3.4.3 and 3.4.4).

- 36 cubes were manufactured with w/c ratio of 0.48. All cubes were treated with 2% **liquid crystalline material** (surface application) followed by the spraying of a water-based curing agent, before starting the curing, and cured under two curing conditions:

    o 18 cubes were cured normally under 60% humidity and 20 °C temperature (referred to as favourable conditions).

    o 18 cubes were exposed to forced air generated by electric fans (referred to as adverse conditions).

- 102 cubes were manufactured with w/c ratio of 0.46 and cured in a water bath for 28 days. 90 cubes were used for treatment purposes and 12 cubes were used as control for comparison reasons. Once the curing period is finished, all concrete samples were dried in an oven at 105 °C until a constant mass was achieved (fully dry). The masses of cubes were measured after drying, and they were conditioned, before treatment, as follow (Chapter 3, Section 3.3):

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- o 20 cubes were assured to be fully dry.

- o 20 cubes were soaked in water until their moisture content (saturated surface dry) reached 2%.

- o 20 cubes were soaked in water until their moisture content (saturated surface dry) reached 4%.

- o 30 cubes were soaked in water until their moisture content (saturated surface dry) reached 6% (fully saturated).

- o 12 cubes were used as control and conditioned with all the previous conditions.

After finishing the conditioning process of the cubes, the **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** were applied to the surface of concrete (until refusal). Following the application of materials, part of the cubes in condition 4 was dried before testing, and the other part was tested without drying.

6.6 Results and discussion

6.6.1 Surface impregnated fresh concrete

Water absorption for treated and untreated concrete was examined at 7, 14 and 28 days by using the ISAT method, at favourably and adverse curing conditions. Results of this test are outlined in Figure 6-3.

All samples showed a declination in water absorption but with different performance. After 28 days of curing, adversely cured concrete and treated with the **crystalline material** has shown the highest absorption rate for water. Both treated and untreated specimens, under this regime, possessed similar performance after one hour of curing, with an absorption rate of 0.60 ml/m^2.s. However, favourably cured specimens showed better performance than all the adversely cured specimens. They absorbed less water during the first hour of the test, especially the control

mix. Treated concrete absorbed 0.37 ml/m^2.s and untreated concrete showed an optimum performance with absorption rate of 0.09 ml/m^2.s. Also, it is important to note that concrete under adverse curing conditions at all curing intervals, starting from day 7 and ending at day 28, had absorption rate values close to each other, ranging between 1.38 and 1.75 ml/m^2.s. These results confirm that adverse conditions are highly demanding and increase concrete permeability for water.
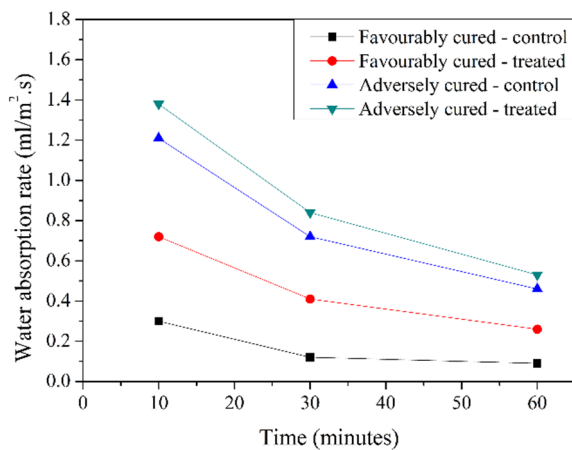
(a): 7 days curing
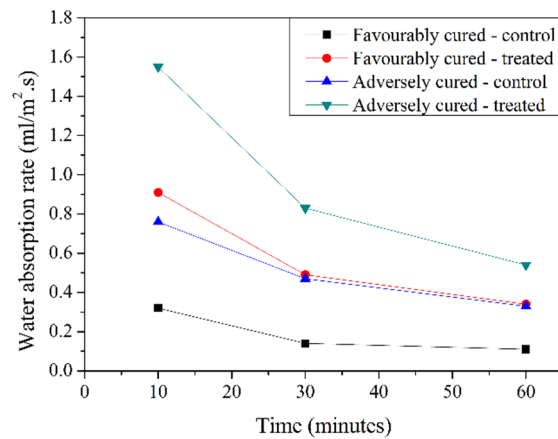
(b): 14 days curing
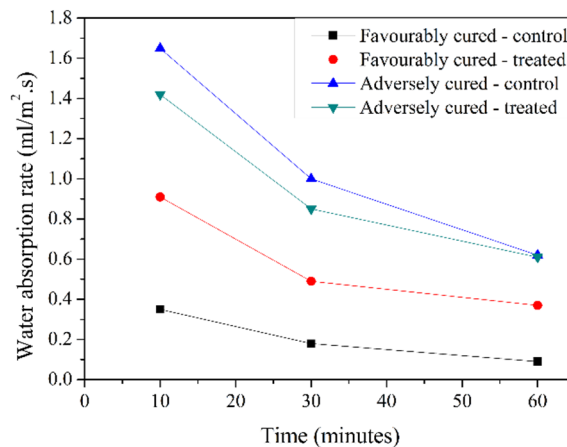
(c): 28 days curing

Figure 6-3 - Concrete sorptivity for treated and control concrete after curing ages of: (a) 7 days, (b) 14 days and (c) 28 days

Results demonstrate the inefficiency of conducting the treatment of **liquid crystalline material** on fresh concrete, either when concrete is present in friendly environment or in harsh

environment. This was demonstrated when concrete was tested for compressive and flexural strength as well (Chapter 5, Sections 5.3.2.3 and 5.3.3.3), where a significant strength loss was observed. For normal curing conditions, the formed organosilicon bonds will work on repelling water that is needed for the progress of the hydration process (Chapter 4, Section 4.3.2). This will create some micro-cracks in the matrix, which will work on increasing concrete's absorption for water. In the case of adverse curing conditions, harsh environment will work on drying the existing water that is needed for the hydration process and activating the sodium acetate crystals. Accordingly, the formation of the organosilicon bonds, which is responsible for the material's hydrophobicity, will not be sufficient to enhance concrete's impermeability. Adding to that, the remaining water in the mix will not be sufficient, as well, to progress an adequate hydration.

An anomaly in results obtained at 7 and 14 days curing periods for untreated concrete under adverse conditions could be spotted in Figure 6-3 a and b respectively. At the period between 7 and 14 days there would be a lot of water available, so hydration will be fast during that period. However, in the presence of harsh environment and lack of protection, the hydration process will be uncontrolled, which will create micro-cracks in the specimens. As a result, these aforementioned variations in ISAT outcomes are resulted from the uncontrolled hydration conditions. In addition, the BS EN 1881–208 mentions that ISAT should be performed on concrete when it has a constant mass (0.1% weight loss in 24 hours), which will be unavailable during the 7–14 days period, and this will bring some anomalies to the results in that period. It is noteworthy to mention that ISAT was performed on the same cubes and on the same sides of the specimens during the 7, 14 and 28 days period, and all the cubes were circulated regularly so all the sides will have the same conditions.

6.6.2 Influence of rainfall and groundwater on treatments

The efficacy of surface applied materials against the effect of rainfall was investigated by using the ISAT method. Concrete was cured in a curing room with 60% humidity and 20 °C temperature before its treatment with **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane**. Figure 6-4 shows the average water absorption rate for all treated and untreated concrete (the effect of rainfall).
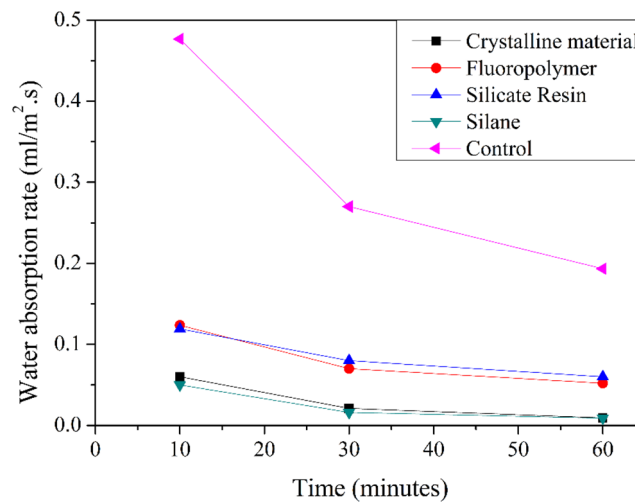
Figure 6-4 - Water absorption rates for control concrete and concrete treated with crystalline material, fluoropolymer, silicate resin and silane

A common feature between all treated and untreated concrete specimens, as shown in Figure 6-4, is the reduction of water absorption rates with time. However, treated concrete showed better performance than control concrete with a difference of 0.13 ml/m^2.s in the case of **silicate resin**, and 0.18 ml/ m^2.s in the case of the **crystalline material** after 60 minutes testing. Comparing treated concrete together; concrete treated with **silane** and **crystalline material** showed the least water absorption rate among all treated samples. Both, concrete treated with fluoropolymers and silicate resins, displayed similar performance to each other with a water absorption rate of nearly 0.06 ml/m^2.s at 60 minutes.

When comparing the four different treatments with each other, in reference to control concrete, concrete treated with **crystalline material** and **silane** showed a 95% efficacy with respect to control after 60 minutes. On the other hand, concrete treated either with **fluoropolymers** or **silicate resins** showed 69% efficacy compared to concrete. This, undoubtedly, proves the efficacy of the three impregnants, regardless of the difference in performance between them, and the high impact they provide in protecting concrete from water penetration.

Two factors had contributed in the reduction of water absorption in concrete treated with the four materials; their hydrophobic nature, outlined in Chapter 4, Section 4.6.4, and their distribution inside the pores (Chapter 4, Section 4.6.2). The **crystalline material**, **fluoropolymer** and **silicate resin** exhibit similar mechanism in protecting concrete, and they all depend on their hydrophobic nature and their ability in lining the pores and reducing their sizes (without blocking them) to reduce water penetration. However, **silane** works on completely closing the pores. The difference in performance between the four materials might come from their different interaction mechanism with concrete, discussed in Chapter 4, Section 4.6.3.

In parallel, the effect of groundwater on concrete pavement was investigated by testing the capillary rise in dry concrete after 24 and 48 hours from their partial immersion (Chapter 3, Section 3.4.4). The performance of each impregnant material after 24 and 48 hours of immersing in water is outlined in Figure 6-5.
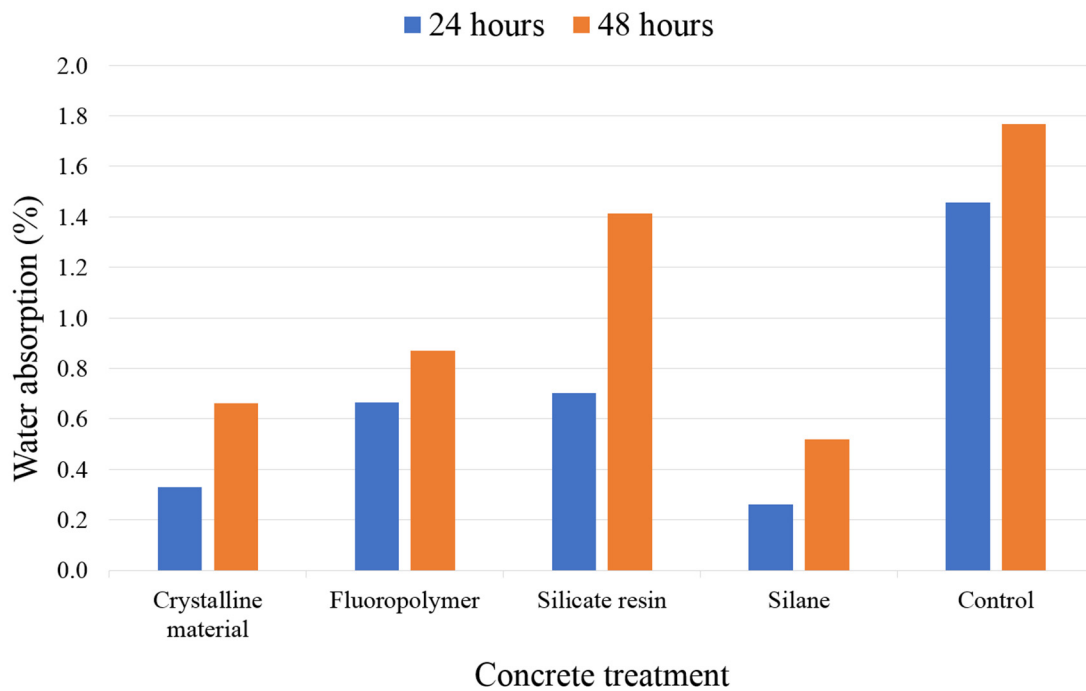
Figure 6-5 - Water absorption caused by capillary action for treated and untreated concrete after 24 and 48 hours of testing

Outcomes from this test show similar results to those obtained from the ISAT. Concrete treated with **silane** and **crystalline material** exhibited the least water absorption rate between all concrete samples, either after 24 hours or 48 hours of immersing. On the other hand, the performance of concrete treated with the **fluoropolymer** and the **silicate resin** materials was less efficient than the concrete treated with **silane** and **crystalline material**. After 24 hours of immersion, both **fluoropolymer** and **silicate resin** showed similar performance with water absorption of 0.7%. However, concrete treated with **silicate resin** started to absorb more water in the period between 24 and 48 hours of immersing with 1.4% after 48 hours, whereas concrete treated with **fluoropolymer** absorbed 0.87% after 48 hours. Control specimens consumed the highest amount of water among all the samples with 1.4% and 1.7% after 24 and 48 hours respectively.

The reduction in water absorption that **silane** achieved with reference to control was 82% and 71% at 24 and 48 hours respectively, whereas **crystalline material** achieved an efficacy of 77% and 63% at 24 hours and 48 hours respectively. On the other hand, after 48 hours of testing, **fluoropolymer** treated concrete achieved a reduction of 51% in water absorption, whereas concrete treated with **silicate resin** achieved a 20% reduction in water absorption. Moreover, after 24 hours of testing, both **fluoropolymer** and **silicate resin** treated concrete, absorbed 52% less water than untreated concrete.

In general, capillary action takes place in fine pores when the surface of concrete comes into contact with water and it starts to move up through these fine pores (Claisse 2014). It has been established in Chapter 4, Sections 4.6.2, 4.6.4 and 4.6.5 that **silane** may present on the surface of concrete after treatment and, at the same time, it goes inside the pores and block them. Covering **silane** the surface of concrete might work on establishing a barrier for the capillary suction to take place. Adding to that, the hydrophobic properties of **silane** will hinder the movement of water through the pores.

In order to combine the outcomes from both tests, ISAT and water intake by capillary, the rate of water absorption and the percentage of water intake were transferred into a water absorption quantity in millilitres. Figure 6-6 illustrates water absorption results for both tests starting from 10 minutes and ending at 48 hours.
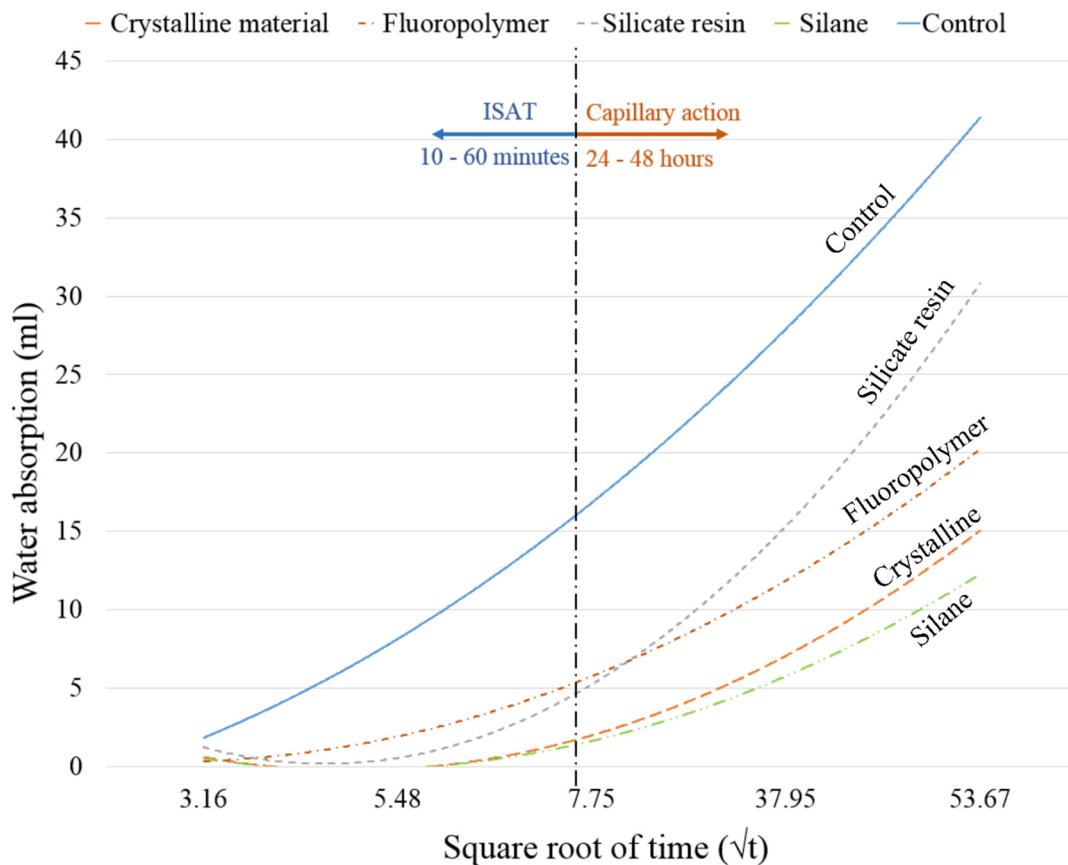
Figure 6-6 - Short-term and long-term water absorption of treated and control concrete over

48 hours period

Even though both tests operate in different ways, and they represent two different concepts for water absorption; water absorption by capillary suction and water absorption under pressure head, their outcomes could be linked together to have a full-scale measurement that covers more protracted periods of time (Figure 6-6). Also, combining results from both tests will give a close estimation to a real-life situation; water absorption through pavement is either from rainfall or groundwater, and both combined tests are designed to measure water absorption in these situations.

The continuity in water absorption, measured by both tests, could be spotted in Figure 6-6, as the behaviour of the materials persists on the same pattern in both phases of testing, with concrete treated with **silane** showing the least water absorption during the whole period,

followed by **crystalline material**. On the other hand, concrete treated with **fluoropolymer** performed similarly to that treated with **silicate resin** during the first 24 hours of testing. Nevertheless, **fluoropolymer** started to absorb less water and approaches a similar performance to **crystalline material** in the second 24 hours testing period. However, more confirmations are needed by performing a longer period. To the contrary, concrete treated with silicate resin continued to absorb water at higher rates after 24 hours of testing, getting closer to the behaviour of the control concrete.

6.6.3 Influence of moisture content on treatments

The effect of moisture content on surface applied materials has been investigated by conditioning concrete with different moisture contents; full drying, 2%, 4% and full saturation (6%). Figure 6-7 outlines water absorption of pre-conditioned treated and untreated concrete after testing them with the ISAT.

(a): fully dry   (b): 2% moisture content

Figure Continues…

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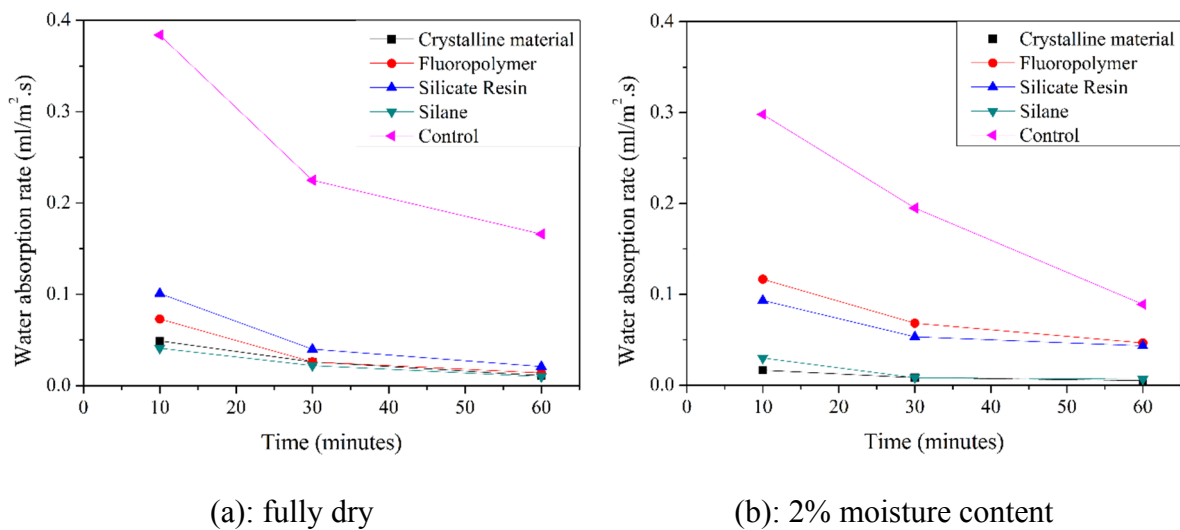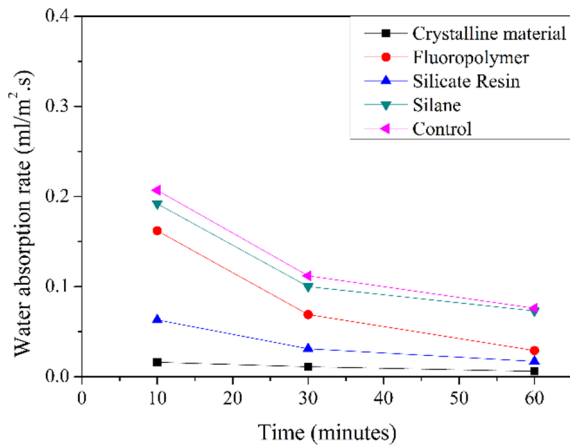
(c): 4% moisture content
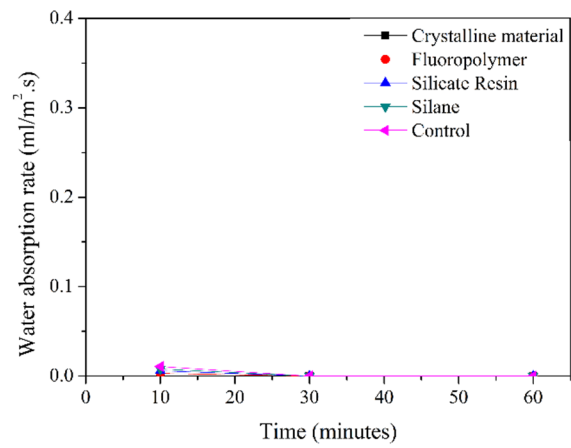
(d): fully saturated – before drying
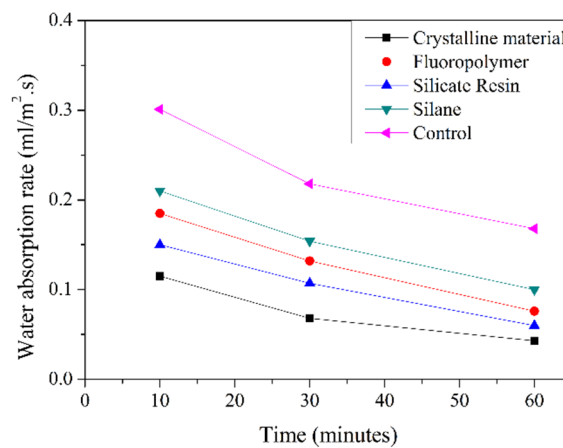
(e): fully saturated – after drying

Figure 6-7 - Water absorption rates for treated and untreated concrete after preconditions: (a) fully dry, (b) 2% moisture content, (c) 4% moisture content, (d) fully saturated (before drying), and (e) fully saturated (after drying)

As expected, fully saturated concrete showed the least water absorption rate when tested before drying (Figure 6-7 d). This is due to the presence of water that fully occupies the pores, not allowing more water to be absorbed, which shows a 'pseudo-performance' for the treatment. Accordingly, samples were dried after applying the materials to show the right performance of these materials when applied to fully saturated concrete. After drying, a high increase in water absorption can be noticed (Figure 6-7 e), which reflects the right performance of applied materials. **Crystalline material** has provided the optimal protection under all preconditions

except the fully dry condition, which might refer to its need for a certain amount of water to form its active crystals (Chapter4, Section 4.6.3). It is also noticed that **crystalline material** has shown better performance for saturated concrete after drying, which denotes its high affinity to water and its ability to work well in the presence of water. Moreover, reflecting the rejection rate of this material (Table 4-5 in Chapter 4, Section 4.6.1), once applied to saturated concrete, on water absorption outcomes, it shows that the presence of its high active content (around 75%) in concrete enhanced water impermeability, compared to other materials especially **silane**. The **crystalline material** uses a certain amount of water to create hydrogen bonds with concrete that allow the material to link properly in the pores, and at the same time, the material will create hydrophobic organosilicon crystals that work on fending off excess water (Sharma 1997; Woodard 2001; Chang 2005; Palomino et al. 2007; Wagh et al. 2010; Wagh et al. 2015).

Increasing moisture content above 2% showed an obvious negative effect on the performance of **silane**; exploring the sequence of water absorption for concrete treated with this material through Figure 6 a-e, shows the deficiency of this material to provide proper protection when the moisture content is higher than 2%. This refers to the activation process of **silane** inside the pores; it either needs to be applied on concrete with small amounts of water or on dry concrete surfaces to activate the silanol groups that provide the material with its hydrophobic properties (Woo et al. 2008). **Silane** mainly depends on the penetration depth it can achieve when applied to concrete, and this penetration depth is a fundamental requirement for an effective protection (Schueremans et al. 2007). In the presence of high amounts of water inside the pores (>2%), the penetration depth of **silane** would be nominal and insignificant which affects its efficacy in protecting concrete. Another reason for the reduction in **silane's** efficacy when applied to concrete with high moisture content (>2%), is the presence of Alkoxy groups that are attached to its silicon atoms and provide **silane** with its fatty nature. These Alkoxy fatty groups are

supposed to react with silicate in concrete to establish a stable bond with concrete. In the presence of high amount of water in concrete, and with the hydrophobic properties of the Alkoxy groups, the bonding between **silane** and concrete would be difficult (Bertolini et al. 2013). Most of concrete that exists near the sea are damp all the time due to their continuous contact with moisture, which makes their treatment with liquid **silane** an economic waste (matching results of Table 4-5 in Chapter 4, Section 4.6.1 with Figure 6-7 a-e).

Fluoropolymer and **silicate resin** have shown a converging performance with better efficacy for **silicate resin**. They both had an average performance between **crystalline material** and **silane** in reducing water absorption. However, **silicate resin** has shown a higher affinity to moisture than **fluoropolymer** due to its interaction mechanism with concrete that depends on the presence of certain amounts of moisture for better adhesion inside the pores, as discussed in chapter 4,section 4.6.3. In the presence of moisture in concrete, **silicate resin** works on breaking the hydrogen bonds, increase the rate of consuming calcium hydroxide and link its silicates on the walls of the pores with strong carbon and silicone bonds. On the other hand, **fluoropolymer** showed its optimum efficacy when applied to dry concrete, with a gradual reduction in its efficacy when moisture content increases inside the pores (Figure 6-7 a-e). This refers to the low surface energy of the fluorinated side chain of the material, which decreases its adhesion to applied surfaces in the presence of water (Passaglia et al. 1994; Brady 2000; Li et al. 2002; Chambers 2004).

6.7 Summary of Part II

Based on the performance evaluation of four surface applied protective materials; **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane**, their efficacy in reducing water absorption when applied to concrete has been investigated.

Applying the **liquid crystalline material** on the surface of fresh concrete demonstrated the impracticality of conducting such treatment to concrete, due to the increase of water absorption in treated concrete compared to control. Material was applied to concrete followed by a curing agent and cured under normal (friendly) conditions and adverse (harsh) conditions. Water absorption under both conditions has increased, which supports the outcomes of Chapter 5 where a significant strength loss was observed in treated concrete.

The suitability of treating concrete pavement by using the four protective materials was evaluated by using the ISAT method and the capillary action test. Both tests represent a real-life exposure for rainfall and groundwater. **Crystalline material** has shown promising results under both tests, where it absorbed the least amount of water in a converging performance to **silane**. **Fluoropolymer** and **silicate resin** have enhanced concrete impermeability as well, where both have reduced the absorbed amount of water, either due to head pressure (rainfall) or capillary action (groundwater). Both the ISAT and the capillary action test could be considered as a continuation and complementary to each other. This could be observed from the similar results that both tests imparted. For example, in the ISAT test, **silicate resin** and **fluoropolymer** treated concrete exhibited the same performance during 1 hour of testing. The same materials performed similarly during the first 24 hour in the capillary action test as well, reflecting the fact that the capillary action test is a prolonged test that continues the ISAT finding process.

The effect of moisture content on the efficacy of treatment has been investigated in terms of water absorption. Concrete was pre-conditioned with full drying, 2% and 4% moisture content and full saturation before applying the protective materials. **Liquid crystalline material** has provided the maximum protection when applied to fully saturated concrete followed by **silicate resin**. On the other hand, **silane** provided its maximum efficacy when applied to fully dry concrete followed by **fluoropolymer**.

Chapter 7: Protection against Harmful Impact of De-icing Salt

7.1 Introduction

Many concrete structures are subjected to chloride attacks, not only from seawater but from de-icing salts used in concrete pavement (Poulsen & Mejlbro 2006). The easy entrance and penetration of chlorides into concrete brings with it numerous problems to the concrete texture itself and the embedded steel inside it (Dai et al. 2010; Liu et al. 2017). The deterioration process of reinforced concrete starts with the penetration of water that carries chloride ions through the pores of concrete which initiate rust in steel that in turn permeate in surrounding concrete. Finally and due to rust expansion, cracks start to appear in the structure which results in spalling and delamination of concrete (Constantinou & Scrivener 1994; Suwito & Xi 2004).

One of the main factors affecting the mechanism by which chloride passes through the pores of concrete is its moisture content, which results from the exposure of concrete to different environmental circumstances. Complete diffusion is believed to take place in saturated concrete like those soaked under water, and sorption is preponderant in concrete subjected to sea and oceanic atmospheres, concrete pavement in contact with de-icing agents and dry concrete that is found in arid areas (MA et al. 2001; de vera et al. 2007). In the case of partially saturated concrete, capillary suction and diffusion of chloride ions are credited for the whole process of chloride transport (Nielsen & Geiker 2003; de vera et al. 2007). In addition, it was proven by Conciatori et al. (2008) that environmental conditions and the quantity of de-icing agents are the major elements in the process of chloride transport.

In order to increase the service life of concrete and reduce the cost of maintaining structures, more cost-effective solutions were followed, which commence with the construction phase of concrete (Franzoni et al. 2013).

In this chapter, the efficacy of internally integrated **crystalline material** in reducing chloride ingress through concrete pavement was evaluated. Also, the efficacy of four surface applied protective materials in reducing chloride penetration was evaluated under different conditions. **Liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** were applied to matured concrete with different moisture conditions; fully dry, 2%, 4% and fully saturated (6% moisture content). Accordingly, this chapter will be divided into two main parts, in terms of treatment type:

- **Part I: Internally integrated treatment**

- **Part II: Surface applied treatments**

Part I: Internally Integrated Treatment

7.2 Experimental programme

The developed mix designs Mixes 2-5 and Mixes 9-16 (Tables 3-3 and 3-4, Chapter3, Section 3.3) were investigated for their ability to resist chloride diffusion. A total of 48 cubes with the dimensions of 100mm x 100mm x 100mm were cast and cured for 28 days in a water bath with a temperature of 21 °C. Concrete was prepared with four different w/c ratios of 0.32, 0.37, 0.40 and 0.46, and it was mixed with 2% and 4% **crystalline material** at early stages. Part of the cubes were used as control for comparison reasons (0% **crystalline material**).

Concrete resistance to chloride penetration was evaluated by using the unidirectional salt-ponding test for a period of continuous 90 days (Chapter 3, Section 3.4.5). Also, some SEM micro-images were taken at a depth of 50mm inside concrete, after finishing the salt ponding

test, to check the presence and distribution of chloride in the matrix. Figure 7-1 illustrates the testing program in this chapter.
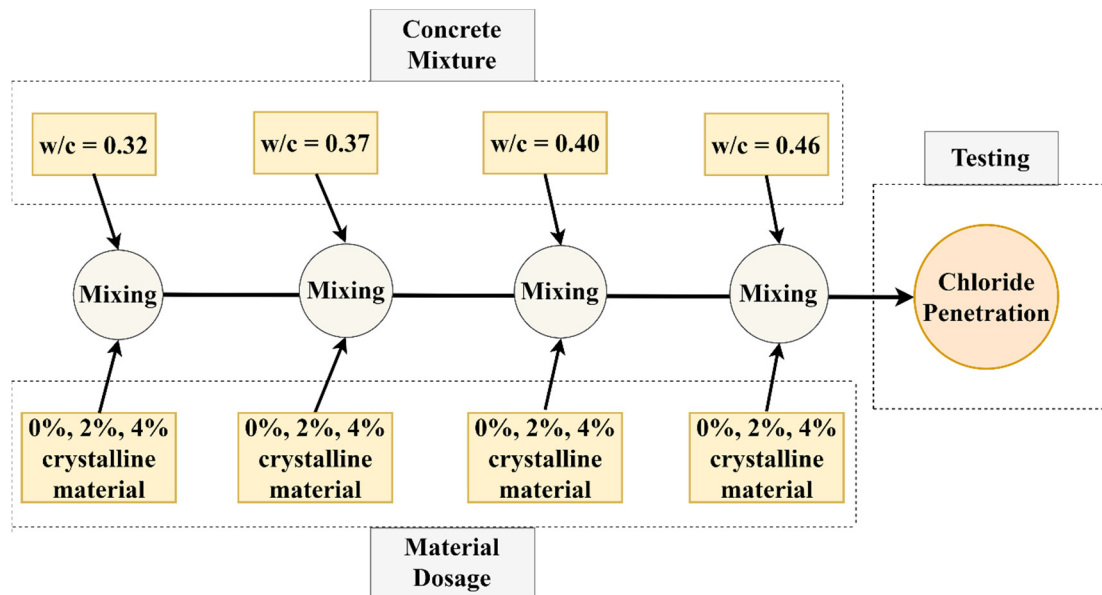
Figure 7-1 - Explanatory diagram of the mixing and testing stages for the salt ponding test

7.3   Results and analysis

Figure 7-2 illustrates the outcomes of testing the chloride diffusion through treated and untreated concrete with different w/c ratios. Chloride content was calculated based on the following equation (British Standards Institution 2007):

$$CC = 3.545 * f * (V2\text{-}V1) / m$$

Where;

CC: chloride content percent (%).

f: molarity of silver nitrate solution.

*V*1: volume of the ammonium thiocyanate solution used in the titration (ml).

*V*2: volume of the ammonium thiocyanate solution used in the blank titration (ml).

m: mass of concrete sample (g).
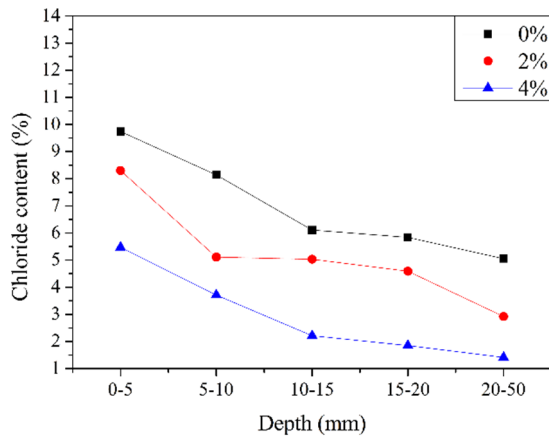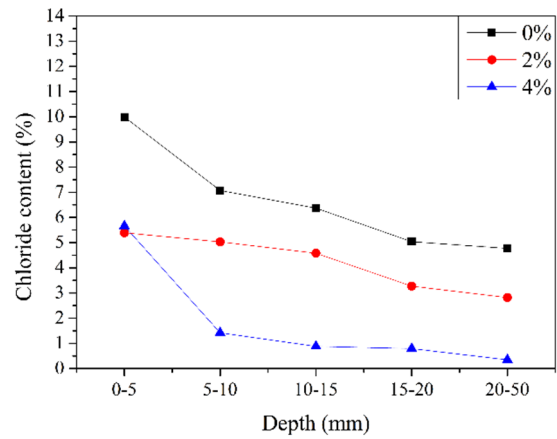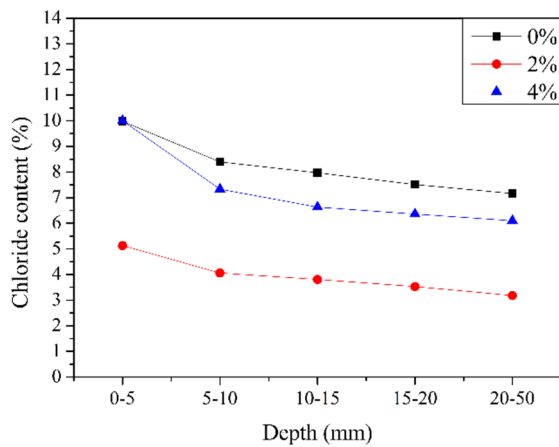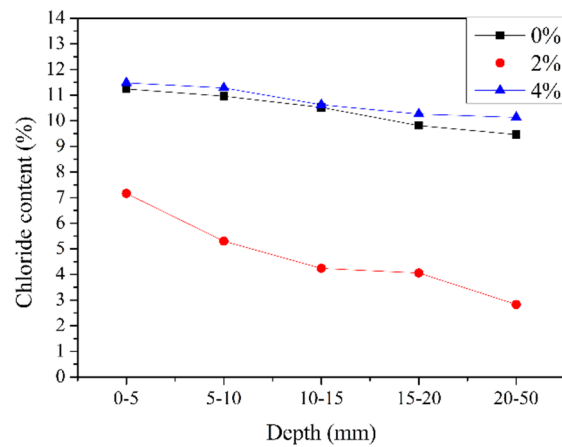
Figure 7-2 - Chloride content through internally integrated and control concrete mixes with w/c ratio of: (a) 0.32, (b) 0.37, (c) 0.40 and (d) 0.46

Results from the unidirectional chloride ponding test show a general reduction in chloride content with increasing depth.
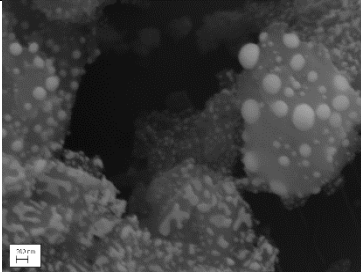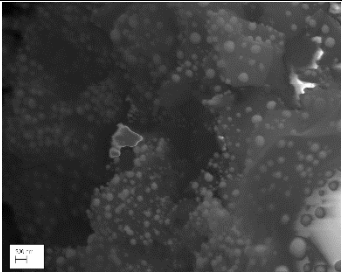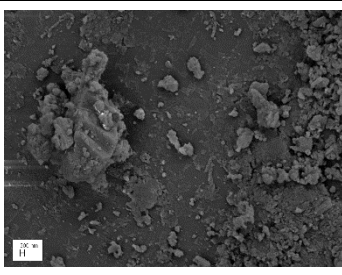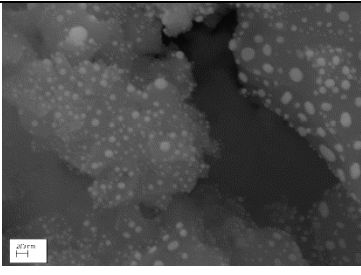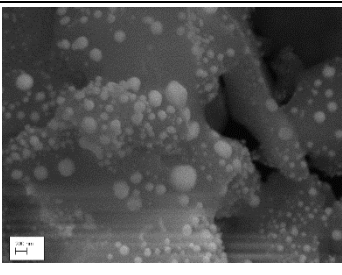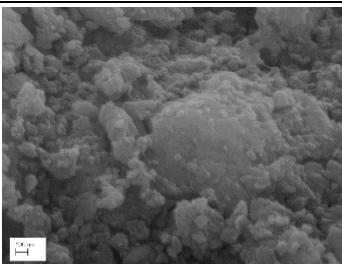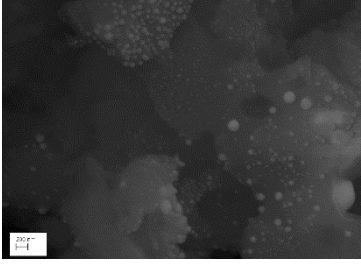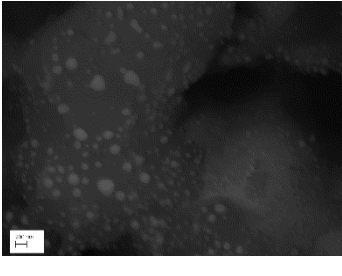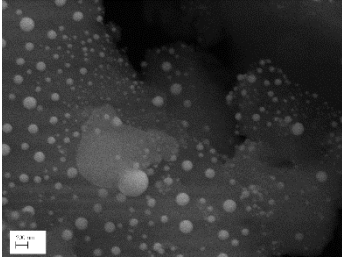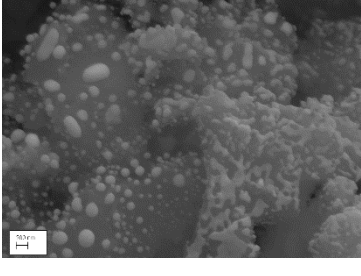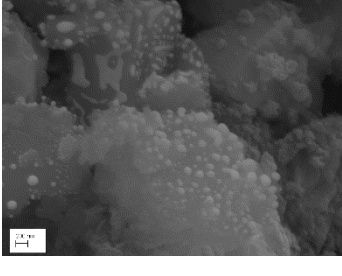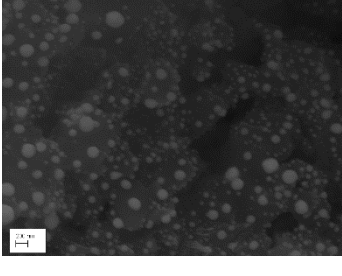
It is witnessed that concrete with w/c ratio of 0.37 and treated with 4% **crystalline material** (Figure 7-2 b) has reduced chloride diffusion the most between all the mixes and through the depth from 10 mm to 50 mm; chloride content at 20-50 mm depths was reduced by more than 90% with regard to the control mix. Concrete with w/c ratio of 0.32 and treated with 4% **crystalline material** (Figure 7-2 a) has shown a high resistance to chloride diffusion, however

less than that in the 0.37 w/c ratio concrete and treated with 4% **crystalline material** (Figure 7-2 b), with an efficacy above 70% at 20-50 mm depth range. On the other hand, adding 4% of admixture to concrete with w/c ratio of 0.46 (Figure 7-2 d) negatively affected the performance of concrete where an increase of chloride penetration was noticed when compared to the control; 7% increase at 20-50 mm depth range. The bad performance of this mix could also be correlated to the high workability of the mix (Chapter 4, Section 5.3.1).

Increasing w/c ratio has participated in increasing the voids and the size of the pore structure of concrete (Table 4-2 in Section 4.3.1, Chapter 4), which in turn increased the rate of capillary suction and permeation through the pores (Hilsdorf & Kropp 2014). Adding to that, at the beginning of chloride transport from the surface to concrete, chlorides from the saline solution will be amalgamated by the hydration outcomes until a balanced state between free and combined chlorides is reached. This should participate in decreasing the concentration of chloride with increasing depth (Hilsdorf & Kropp 2014). However, in the case of mixes with high w/c ratio and high amount of **crystalline material**, the crystalline material will reduce the hydration process prohibiting the balanced condition between free and combined chlorides to be reached. Moreover, the resistance of concrete for chloride diffusion followed similar trend noticed for water absorption (Chapter 6, Section 6.3), where the long-term testing revealed that it is possible to produce a durable concrete when low w/c ratios are used along with the **crystalline material**.

The investigation of the concrete's microstructure after running the salt ponding test was performed on all samples at 50 mm depth to check the presence of chloride in concrete texture, as shown in Table 7-1. The cross-sections of all the concrete mixes show the presence of chloride in all of them as white spots with different densities, which were confirmed to be chloride residuals by running an EDX point scan.

Table 7-1 - Chloride residues in concrete texture at 50-mm depth after testing for chloride

penetration (20, 000X - 50,000X)

W/C ratio	0%	2%	4%
0.32			
0.37			
0.40			
0.46			

Those white spots of chloride could be found adhered to some areas of concrete that have either minimum or no presence of the **crystalline material**. The micrographs, outlined in Table 7-1, show insignificant presence of chloride in the mixes with w/c ratios of 0.32 and 0.37 and treated with 4% **crystalline material**, which correspond to their high defiance against chlorides

ingress compared to other mixes. The presence of chloride in such low densities in those two mixes may refer to two factors; their low w/c ratio which contributes in reducing the size of the pore structure (Costa & Appleton 1999), and the presence of the **crystalline material** in compatible proportions with the w/c ratio, which does not negatively affect the hydration process (Chapter 4, Section 4.3.2). The first attack of waterborne chlorides to concrete, when water starts to permeate through the pores, results in combining hydration products with chloride until a steady state between free and combined chlorides is achieved (Hilsdorf, & Kropp 2014). This process in the case of mixes with low w/c ratios would help in reducing further chloride penetration, especially in the presence of compatible "w/c-crystalline material" amounts, in contrast to other mixes with high "w/c-crystalline material" proportions that work on reducing the hydration process, and decrease the hydration products amount necessary to achieve the previously mentioned stability.

7.4   Summary of part I

The developed mix designs with w/c ratios of 0.32, 0.37, 0.40 and 0.46 and integrated with 2% and 4% **crystalline material** along with their control mixes were evaluated in terms of chloride penetration. The unidirectional salt ponding test was employed to examine the chloride content of concrete at different depths of 5, 10, 15, 20 and 50 mm from the surface. Adding to that, SEM analysis was conducted to check the reliability of the salt ponding test and the presence and distribution of chloride in the concrete matrix.

Results revealed that chloride diffusion has been reduced by more than 90% at the depth range of 20-50 mm in the case of concrete with w/c ratio of 0.37 and integrated with 4% **crystalline material**. Also, more than 70% reduction in chloride content was observed at depth ranges of 20-50mm in the case of concrete with w/c ratio of 0.32 and integrated with 4% **crystalline material**. On the other hand, concrete with w/c ratio of 0.46 and integrated with 4% **crystalline**

material has exhibited the highest present of chloride in its mix, with more than 10% chloride content at 50mm depth.

Results of this chapter support the outcomes of previous chapters (Chapters 5 and 6) in terms of optimum protection. Concrete with low w/c ratios of 0.32 and 0.37 and integrated with 4% **crystalline material** would give the optimum performance among all mixes.

Part II: Surface Applied Treatments

7.5   Experimental programme

A total of 100 concrete cubes with the dimensions of 100mm x 100mm x 100mm were produced, cured in water for 28 days and conditioned with four different conditions of full drying, 2% moisture content, 4% moisture content, and full saturation (6% moisture content) (Chapter 3, Section 3.3). After the conditioning of concrete, the protective materials were applied to its surface; **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane.** 20 cubes out of 100 were used as control. Following the application of the materials to the surface, part of the fully saturated cubes were dried before testing and the other part was tested without drying.

Unidirectional salt ponding test was utilised to evaluate the chloride penetration through all treated and untreated cubes, followed by analysing the chloride content inside the concrete by Volhard's method (Chapter 3, Section 3.4.5). Figure 7-3 shows an explanatory diagram for the testing procedure of the internally integrated concrete in this chapter.
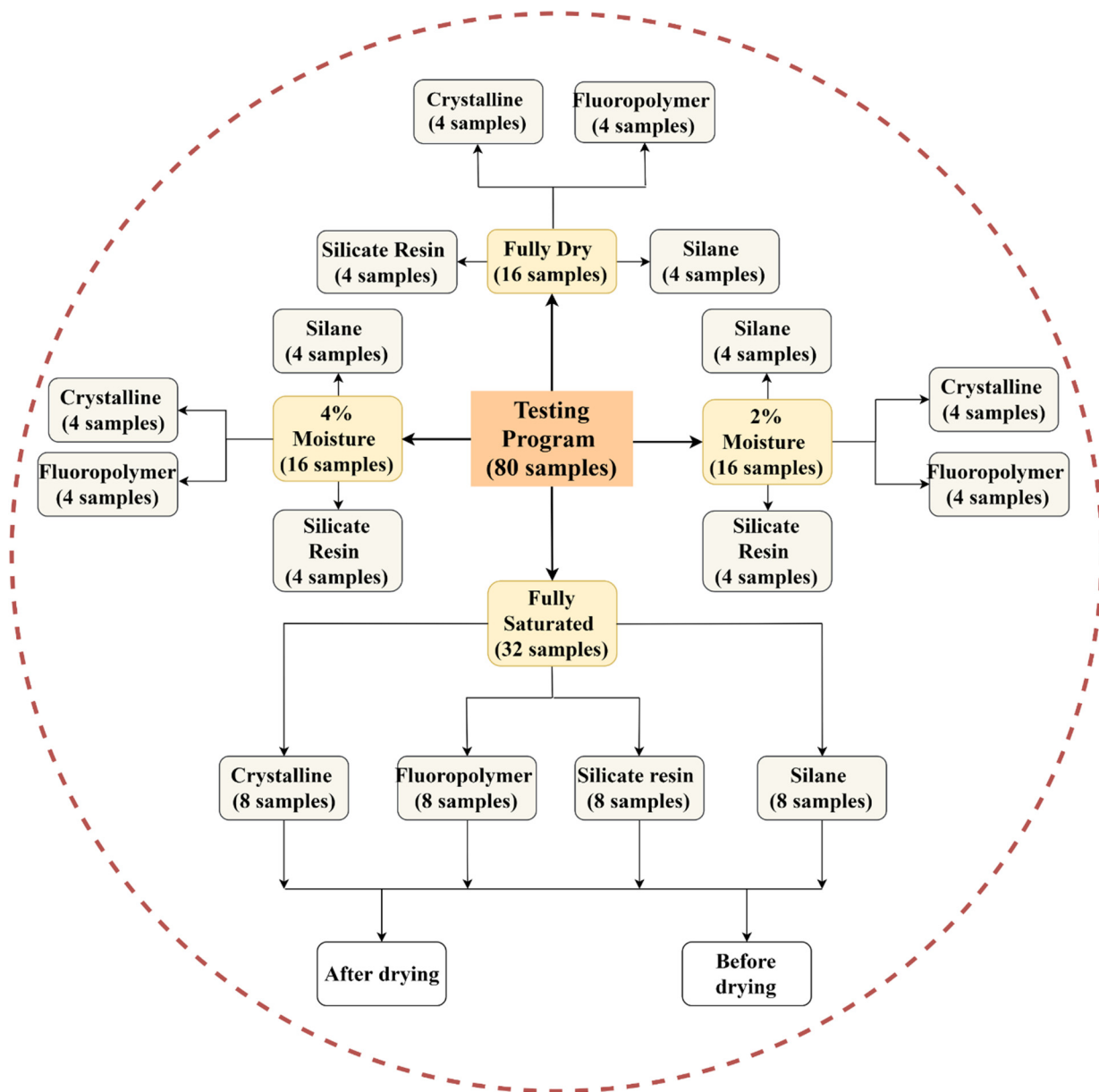
Figure 7-3 - Testing diagram of treated concrete samples and their saturation level

7.6 Results and analysis

The concentration of the free chloride in concrete at different depths and with different pre-conditions are shown in figure 7-4 a-e.
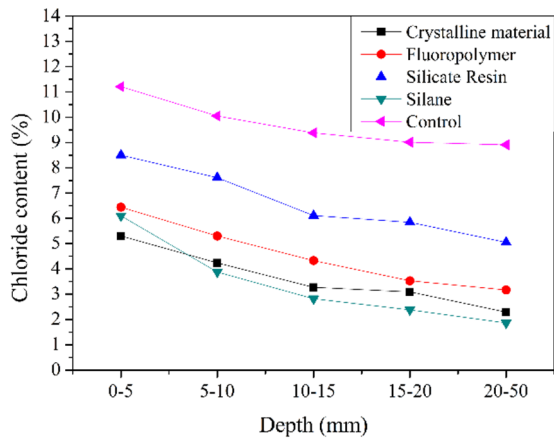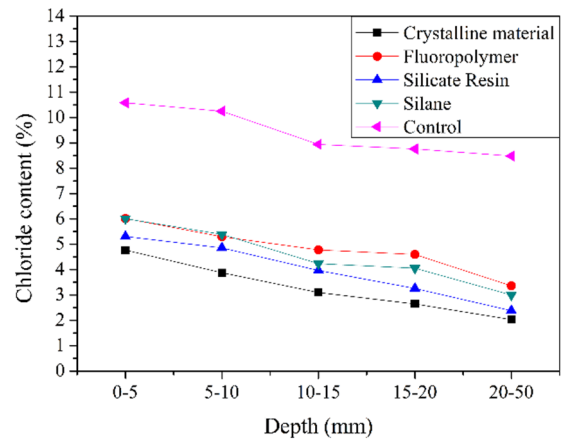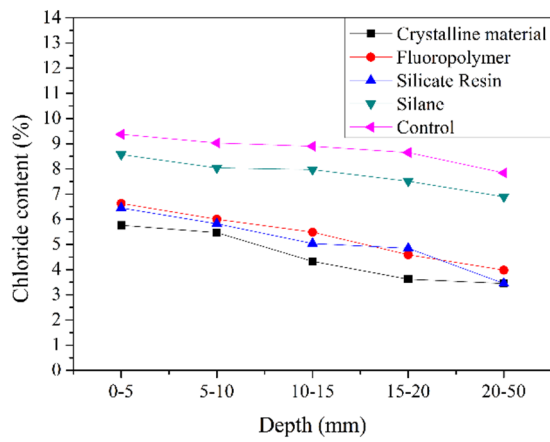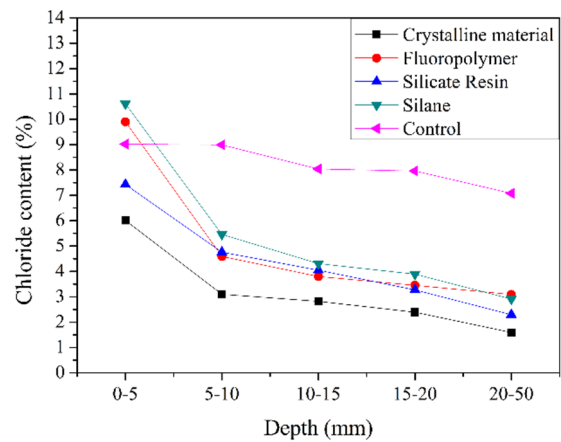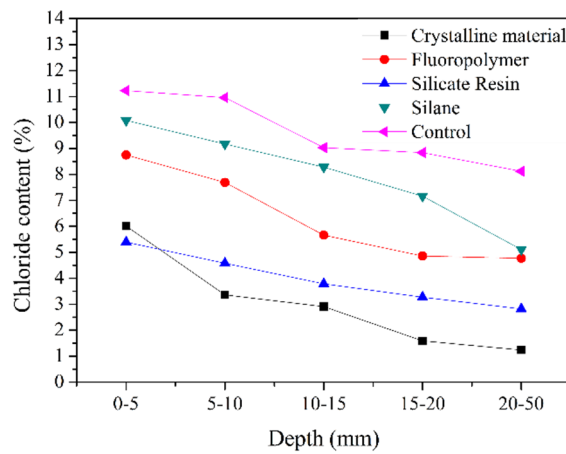
Figure 7-4 - Chloride profiles for treated and control preconditioned concrete: (a) fully dry, (b) 2% moisture content, (c) 4% moisture content, (d) fully saturated (tested before drying) and (e) fully saturated (tested after drying)

As expected, the chloride content was reduced with increasing the depth from the exposed surface for all the preconditioned samples. When observing the chloride content on the surface of all samples (0-5 mm), it is witnessed that their values show some anomaly for some of the exposure conditions, especially when concrete is treated with **silane**. This refers to the carbonation of some concrete surfaces that liberates some constrained chlorides (Costa & Appleton 1999). Adding to that, **silane** could contribute to accelerating the carbonation rate of concrete in laboratory conditions (Broomfield 2006).

Referring to the fully dry condition (Figure 7-4 a), **silane** has shown the least chloride content compared to other materials and control. This could be linked with the rejection rate of **silane** (Table 4-5 in Chapter 4, Section 4.6.1) as more than 91% of its active content has been integrated within the pores of the concrete. When **silane** is applied to dry surfaces, Alkoxy groups that are bonded with silicon atoms in **silane** will react with the silicate, which already exists in concrete, and adhere strongly in the pores (Bertolini et al. 2013). With increasing the moisture content of concrete before treatment, the protection efficacy of **silane** decreases until it reaches its minimum when applied to fully saturated concrete (the same reason discussed in Chapter 6, section 6.6.3). Adding to that, the continuous impact of aggressive chemicals over a long period will participate in breaking the hydrophobic Si-O-Si bonds of the applied **silane** and reduces its efficacy, especially when it is applied to wet surfaces (Costa & Appleton 1999; Moradllo et al. 2016). On the other hand, **crystalline material** and **silicate resin** where less efficient than **silane** when applied to dry concrete, due to their interaction mechanism with concrete that needs the presence of moisture inside the pores, as discussed previously in Chapter 4, sections 4.6.2 and 4.6.3. Furthermore, their efficacy starts to increase by increasing the moisture content in concrete (Figure 7-4 b-e). In contrast, **Fluoropolymer** has shown the best performance when applied to dry concrete, and its efficacy declined with increasing the moisture content of concrete. Water forms a barrier between concrete and the applied

fluoropolymer that weakens the adhesion of fluorine to concrete (Passaglia et al. 1994; Chambers 2004; Brady 2000; Li et al. 2002).

When referring to fully saturated concrete (before drying) (Figure 7-4 d), it could be seen that the chloride content for all samples is less than for fully dry, partially saturated and fully saturated (after drying) concrete. Chloride transport in fully saturated concrete depends mainly on ion diffusion, which is the same transport process that takes place in submerged marine structures. Accordingly, the low amount of chloride in saturated concrete is attributable to the formation of a protective layer on concrete surface that decreases chloride permeability. This occurs with increasing ions diffusion due to the reaction between the saline solution and concrete, resulting in coatings of $Mg(OH)_2$ (Brucite) and $CaCO_3$ (Aragonite) (Costa & Appleton 1999; Hilsdorf & Kropp 2014). After drying fully saturated concrete, the chloride content is witnessed to increase, as the penetration of chloride through the pores is backed by capillary absorption of the saline solution following its direct contact with concrete (Hilsdorf & Kropp 2014).

7.7 Summary of part II

Based on the performance evaluation of four surface applied protective materials; **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane**, their efficacy in reducing chloride ingress through concrete was investigated by using the salt ponding test. The effect of concrete moisture content on the efficacy of the treatment has been considered. Four pre-treatment conditions were counted; full drying, full saturation with 6% moisture content, 2% moisture content and 4% moisture content. In the case of full saturation condition, concrete was treated with the materials, and before testing part of it was fully dried and the other part remained without drying.

The increase in chloride penetration of treated concrete was associated with the rejection rate of the materials and their affinity to water, where **crystalline material** has provided the maximum protection when applied to fully saturated concrete followed by **silicate resin**. On the other hand, **silane** provided its maximum efficacy when applied to fully dry concrete followed by **fluoropolymer**.

Chapter 8:   Performance of Protected Concrete under Long-term Exposure to Extended Freeze-thaw Conditions

8.1 Introduction

Durability is the most important aspect to take into consideration when designing and constructing concrete pavement that exists in harsh environments. The alternating drop and increase in temperature during winter and summer seasons respectively can severely damage the concrete and initiate some cracks in its texture. Therefore, it is important to ensure that the used protective materials are increasing the durability of concrete under those harsh environments.

The performance of concrete throughout the process of freeze-thaw cycles depends on many factors like the moisture content of concrete, rate of freezing, surrounding temperature and the duration of freezing (Basheer & Cleland 2006). Accordingly, it is important to ensure that any protective material, mixed with fresh concrete or applied to its surface, has the ability to perform well under freeze-thaw environments, even when the previously mentioned factors present the worst conditions for concrete.

In this chapter, two freeze-thaw conditions will be applied to treated and untreated concrete, and the performance of the used protective materials, under these conditions, will be evaluated. In the first method, concrete was exposed to fast freeze-thaw cycles while it was immersed in water. This method has been widely used in previous studies but with less number of cycles than it is used in this research, where the number of cycles in this research is the highest until now. In the second freeze-thaw method, a new method is proposed where concrete is only in contact with air and under the effect of temperature change.

This chapter will be divided into two parts based on the types of treatment; internally integrated treatment and surface applied treatments.

Part I: Freeze-thaw of Internally Integrated Concrete

8.2 Experimental programme

72 concrete cubes with the dimensions of 100mm x 100mm x 100mm were cast and divided into two groups; 36 cubes were tested for freeze-thaw cycles in air and 36 cubes were tested for fast freeze-thaw cycles in water. From each group, 9 cubes were prepared with 0.32 w/c ratio, 9 cubes with 0.37 w/c ratio, 9 cubes with 0.40 w/c ratio and 9 cubes with 0.46 w/c ratio. For each w/c ratio, 3 cubes were integrated with 0% **crystalline material**, 3 cubes with 2% **crystalline material** and 3 cubes with 4% **crystalline material**. The mix design of these mixes are illustrated in Table 3-3 (mix 5) and Table 3-4 (mix 6 to mix 16) in Chapter 3, Section 3.3. After finishing the two freeze-thaw tests, the change in the mass of each cube was measured in reference to their original masses, followed by testing them for water absorption by ISAT and compressive strength. It is noteworthy to mention that all cubes were dried before testing them with the ISAT method. Figure 8-1 illustrates the main variables and the testing procedures for this experiment.

Freeze-thaw test in air (Chapter 3, Section 3.4.6.1) was run for 6 months with 180 cycles; each freeze-thaw cycle lasted for 24 hours. Temperature was set to alternate between -20 °C and 20 °C every 12 hours, with a constant humidity of 60% during the thawing phase. These conditions were chosen following the extreme weather measurements in the UK. On the other hand, the fast freeze-thaw test in water (Chapter 3, Section 3.4.6.2) was run for 6 months with 1080 cycles; each freeze-thaw cycle lasted for 4 hours. Temperature was set to alternate between -10 °C and 6 °C during each freeze-thaw cycle.
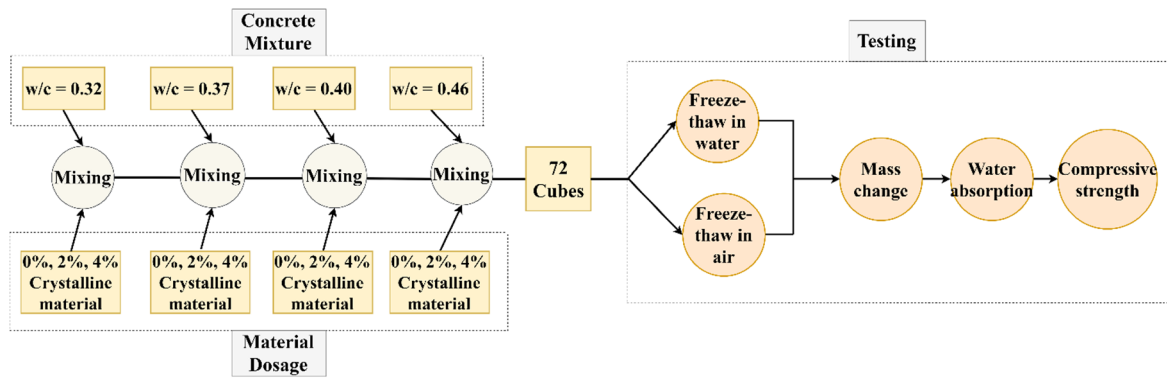
Figure 8-1 - Testing diagram for concrete integrated with crystalline material and exposed to freeze-thaw cycles

8.3 Results and discussion

8.3.1 Influence of freeze-thaw on mass change

The change in the concrete samples' mass is directly related to the degree of deterioration that developed from freeze-thaw cycles. In the freeze-thaw test in water, it is witnessed that concrete has suffered from mass loss during the applied 1080 cycles. Figure 8-2 illustrates the damage in all concrete samples in terms of mass loss percentage during the freeze-thaw water test.

In general, all concrete samples have shown a reduction in their masses during the test, and this reduction increases with increasing the number of applied cycles. The main reason for this trend could be attributed to the damage of the internal pores of concrete during the cyclic and fast freeze-thaw process, especially that pores were saturated with water before starting the test (Chapter 3, Section 3.4.2.6). This damage to the pore structure can cause surrounding water to move freely in and out concrete, which leads to the scaling of concrete surface (separation of paste from the surface) (Shang & Yi 2013). The scaling of concrete was visibly noticed in all concrete samples, either treated or control, as shown in Figure 8-3, where most of concrete samples showed similar appearance. The detected scaling in this test is believed to be more severe than what is observed in real life (naturally-occurring scaling) because of the fast alteration in temperature and because of the high number of applied cycles in this test.
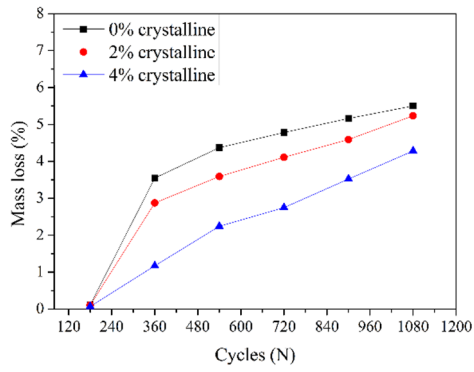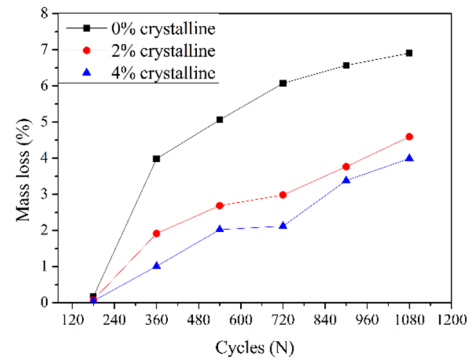
(a)   (b)
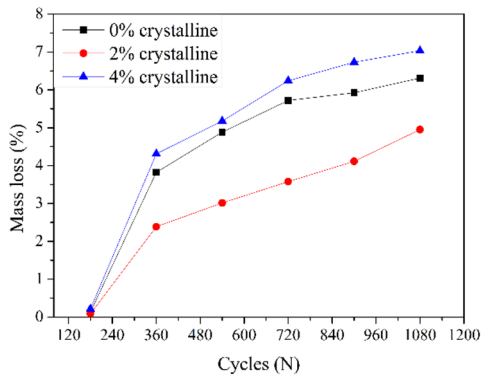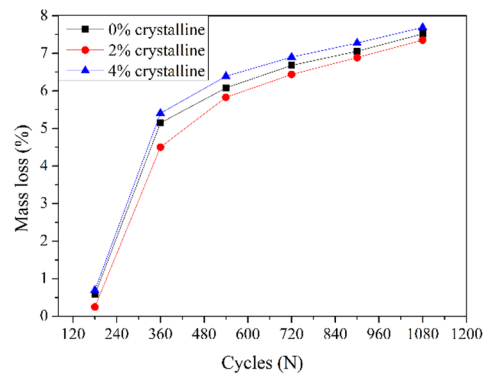
(c)   (d)

Figure 8-2 - Mass loss percentage during the water freeze-thaw test in treated and untreated concrete with w/c ratio of: (a) 0.32, (b) 0.37, (c) 0.40 and (d) 0.46
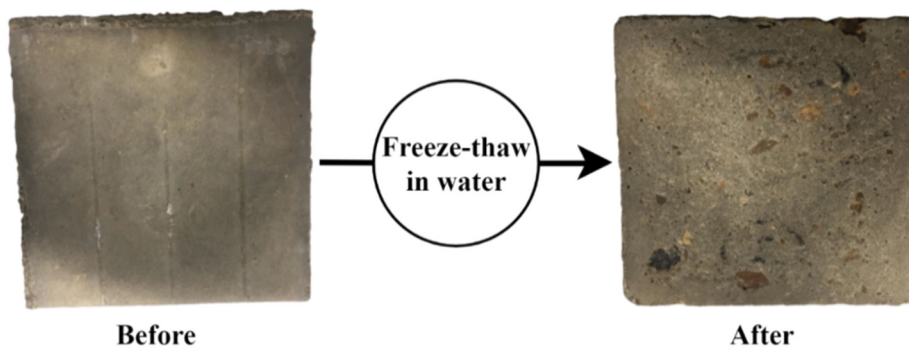
Figure 8-3 - Scaling of concrete due to the fast freeze-thaw cycles in water (after 1080 cycles)

It can be clearly observed, in Figure 8-2, that the development in the loss of mass in concrete with low w/c ratios was less than that in high w/c ratios' concrete. This could be spotted in the

gradient of the produced graphs, where concrete with w/c ratios of 0.32 and 0.37 (Figure 8-2 a and b) have shown a slow progress in the mass loss than concrete with w/c ratios of 0.40 and 0.46. More specifically, treatment of 0.32 and 0.37 concrete with 4% of the **crystalline material** has exhibited the least mass loss amongst all concrete mixtures, where the mass loss in both mixes was around 4%. On the other hand, adding 4% **crystalline material** to concrete with 0.40 and 0.46 w/c ratio increased the mass loss, where it reached 7% for 0.40 concrete and 7.7% for 0.46 concrete, which is even higher than untreated concrete.

Concrete with low w/c ratio would have lower porosity than concrete with high w/c ratio (Table 4-2 in Section 4.3.1, Chapter 4), which is reflected on the amount of capillary water exposed to frost action; less exposure in the case of low w/c ratio concrete as it has less capillary water. In addition, lowering the porosity would participate in reducing the movement of water to areas, like air bubbles, where water could be entrapped and initiates cracks due to its freezing and thawing inside these areas (Foy et al. 1988). Adding the 4% **crystalline material** to the low w/c ratio concrete participated in increasing its resistance to freeze-thaw, where mass loss decreased significantly compared to control. The presence of the **crystalline material** inside the pore structure of concrete would contribute in reducing the movement of water through the pores; either water that already exists inside the pores or the surrounding water. Adding to that and from the results obtained in Chapter 6, treating low w/c ratio concrete with 4% **crystalline material** has proven its ability to reduce water absorption of concrete, which could be reflected on the saturation process that was performed on concrete prior to starting the freeze-thaw test (Chapter 3, Section 3.4.6.2). In other words, low w/c ratio concrete and treated with 4% **crystalline material** was less saturated than other mixes, which reduces the amount of capillary water that is subjected to frost action.

On the other hand, adding 4% **crystalline material** to high w/c ratio concrete, like the 0.40 and 0.46 mixes, has increased the damage to concrete. This could be attributed to the presence of

high water content and high **crystalline material** content at the same time. Their presence in relatively large contents contributes in increasing the consistency of the mix due to the formation of high amounts of NaOH, which in turn takes part in increasing the air voids content and microcracks (Chapter 4, Section 4.3.2).

Contrary to the freeze-thaw test in water, concrete cubes were observed to increase their masses during the freeze-thaw test in air. Figure 8-4 illustrates the change in concrete's mass during the freeze-thaw test in air.

(a)   (b)

(c)   (d)
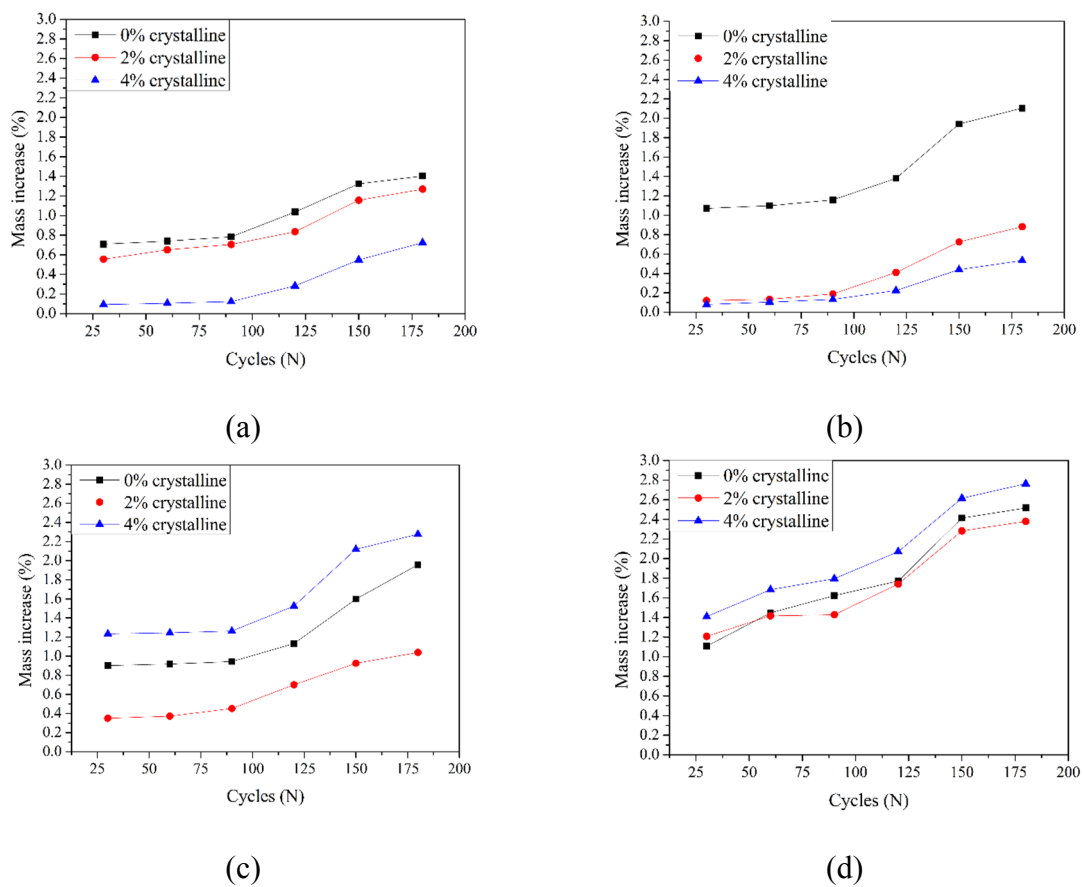
Figure 8-4 - Freeze-thaw in air effect on the mass of treated and untreated concrete with w/c ratio of: (a) 0.32, (b) 0.37, (c) 0.40 and (d) 0.46

All concrete cubes have shown a general trend of increasing their masses with increasing the applied number of cycles, with different performance for each mix. This increase in mass is attributed to the absorption of concrete to moisture from the surrounding environment due to

the applied humidity of 60% during the test (Chapter 3, Section 3.4.6.1). Water is believed to be absorbed through the pore structure of concrete during the thawing process. When the freezing phase starts, the absorbed water will freezes inside the pores and expands, which will create some microcracks inside the pore structure. These cracks will increase the absorption of concrete to moisture and participate in increasing the mass.

During all the cycles, concrete with low w/c ratio (0.32 and 0.37) has gained less weight than concrete with high w/c ratio (0.40 and 0.46). This could be attributed to the low porosity of concrete with the lower w/c ratio (Table 4-2 in Chapter 4, Section 4.3.3), which decreases their absorption to water during the thawing process. Accordingly, the amount of water that is exposed to frost action in the freezing process will be less, which will reduce the initiated microcracks inside concrete. Treating 0.32 and 0.37 concrete with 4% **crystalline material** has shown the least weight gain between all mixes, which is compatible with the results obtained from the freeze-thaw in water test. The 4% **crystalline material** when added to concrete with 0.32 and 0.37 w/c ratio may participate in forming enough organosilicon bonds inside the pores of concrete, which are capable of reducing the absorbed water during the thawing process (Chapter 4, Section 4.3.2). This will reduce the risk of frost action during the freezing phase.

On the other hand, treating concrete with w/c ratio of 0.32 with 2% **crystalline material** did not significantly enhance the performance of the mix when compared to control. This might refer to two reasons: the low amount of water needed to activate the **crystalline material** and the low amount of the used **crystalline material**. The presence of the **crystalline material** in such low quantity restricts the distribution of its active content all over the mix. Adding to that, the used water during mixing will not be enough to continue the hydration process and at the same time activates the crystals of the material. This was not observed in the case of concrete with w/c ratio of 0.37 and treated with 2% material due to the presence of relatively enough water for hydration process and activating the crystals.

Concrete with w/c ratio of 0.40 and 0.46 and treated with 4% **crystalline material** have shown the highest weight increase between all mixes, even higher than control. This may be a result of the high consistency of these mixtures (Table 5-1 in Chapter 5, Section 5.3.1), which contributed in forming some microcracks in concrete prior to the freeze-thaw test. Adding to that, the high porosity of these mixes will work with the previously mentioned microcracks on facilitating the absorption of moisture during the thawing process. After absorbing the moisture and with the start of the freezing process, water will expand inside the pores and creates more microcracks. These factors would ensure to increase the mass of such mixtures. On the other hand, adding 2% **crystalline material** to concrete with w/c ratio of 0.40 has, somehow, resisted the increase in the mixture mass when compared to its own control mix. However, its performance was less efficient than 0.32 and 0.37 mixes treated with 4% **crystalline material**.

One thing to be observed in the freeze-thaw in air testing method is the absence of scaling from concrete surfaces, unlike the freeze-thaw in water method where scaling forms an obvious characteristic. Regardless of the absence of scaling in the air method, some cracks have developed on the surface of concrete, which confirms with the mass increase during all the cycles. Table 8-1 shows some microscopic images (500X) for the developed cracks and their sizes on the surface of treated and untreated concrete after 180 cycles. It is clear from the images that the severest cracks have been developed in concrete mixes with w/c ratios of 0.40 and 0.46 and treated with 4% **crystalline material**. These micro-images support the previous claim about the formation of microcracks in these mixtures that caused them to absorb more moisture from the surrounding environment during the test. On the other hand, concrete mixes with w/c ratios of 0.32 and 0.37 and treated with 4% **crystalline material** have shown the least development for cracks. The developed cracks in these mixes were much less severe than those developed in concrete with w/c ratios of 0.40 and 0.46.

Table 8-1 - Development of cracks after 180 cycles of freeze-thaw in air
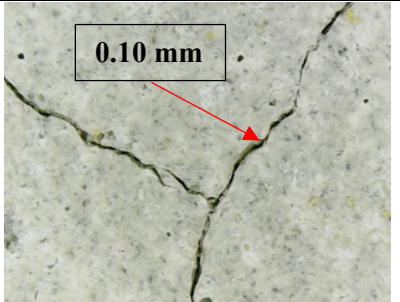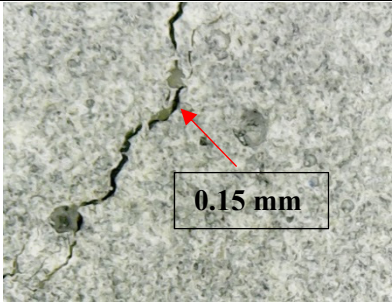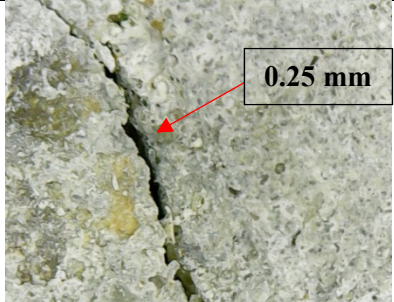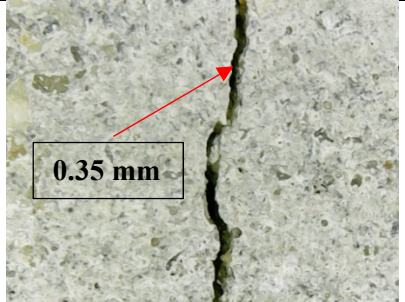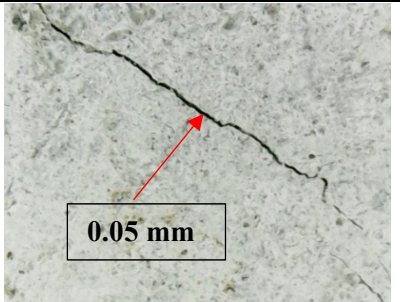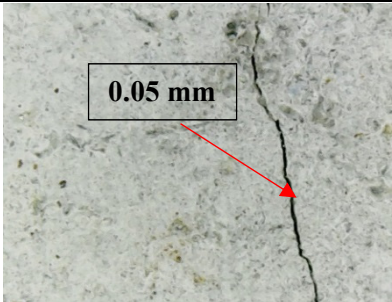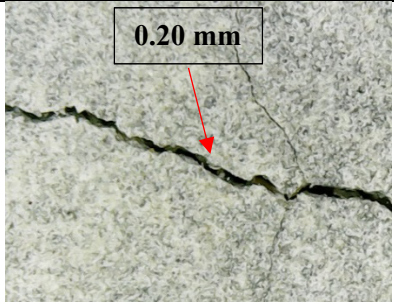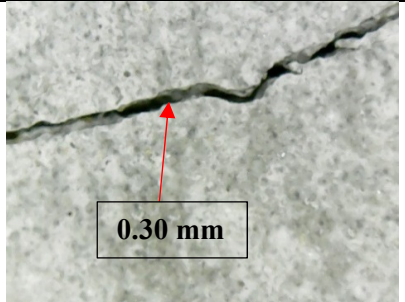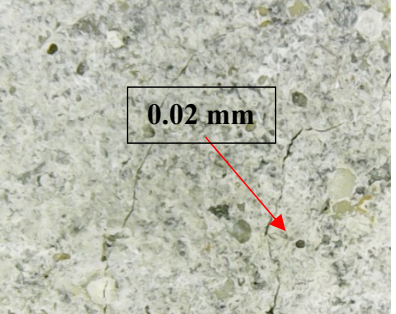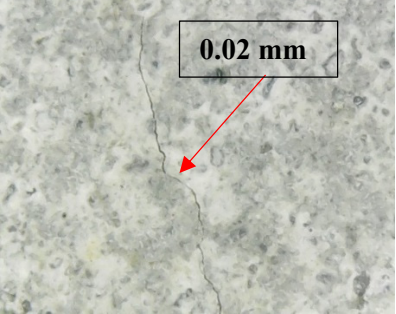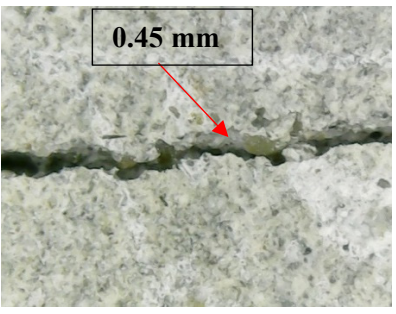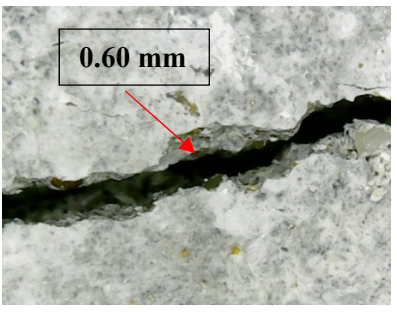
Crystalline material (%)	w/c ratio			
	0.32	0.37	0.40	0.46
0%	0.10 mm	0.15 mm	0.25 mm	0.35 mm
2%	0.05 mm	0.05 mm	0.20 mm	0.30 mm

Table Continues…

Crystalline material (%)	w/c ratio			
	0.32	0.37	0.40	0.46
4%	0.02 mm	0.02 mm	0.45 mm	0.60 mm

8.3.2 Water absorption

The ability of the **crystalline material** to preserve concrete from water ingress in harsh environments was assessed by running the ISAT test on the distressed samples. Concrete samples have shown a general increase in water absorption after the impact of freeze-thaw cycles in water compared to their performance before starting the test (Chapter 6, section 6.3). Figure 8-5 demonstrates the water absorption rate of concrete after the impact of 1080 cycles under the immersion effect.

(a)   (b)

(c)   (d)
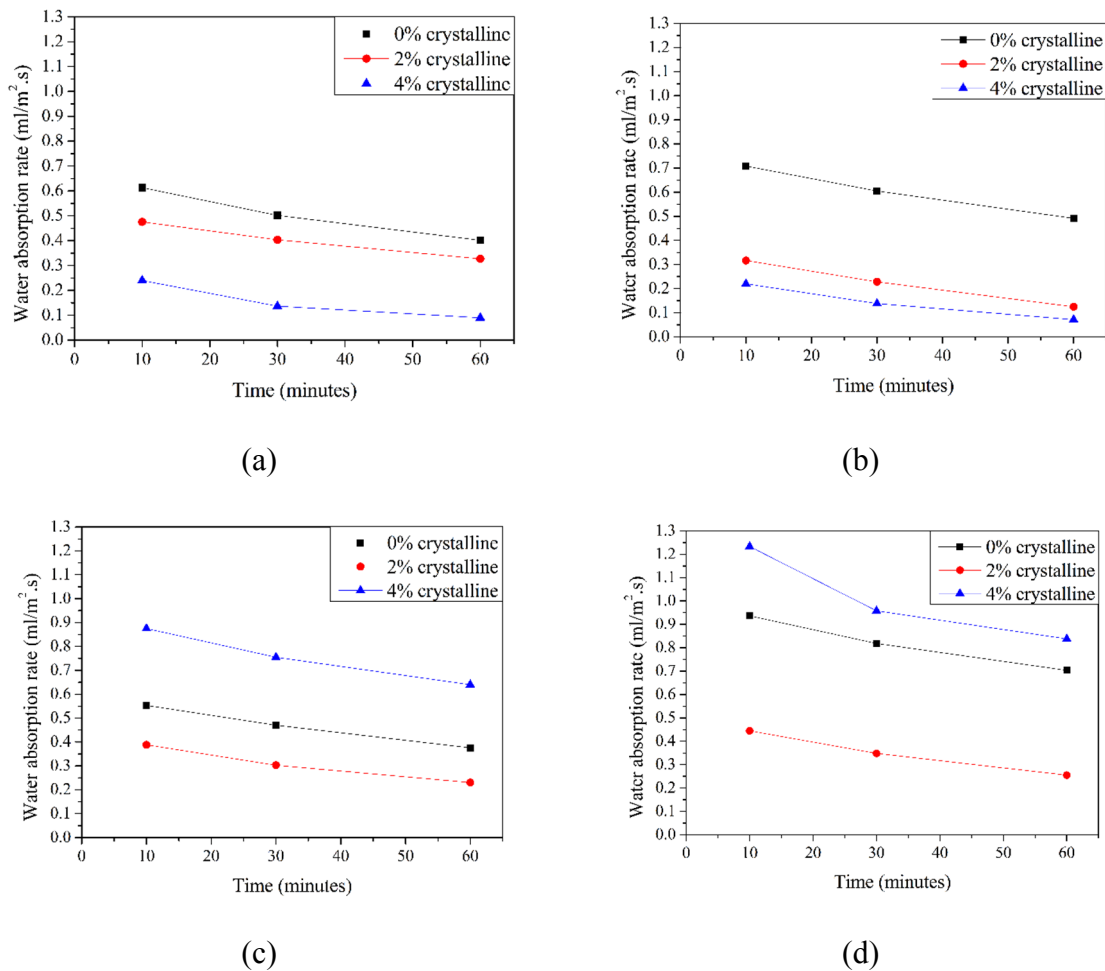
Figure 8-5 - Water absorption of concrete after the impact of 1080 freeze-thaw in water

cycles for concrete with w/c ratio of: (a) 0.32, (b) 0.37, (c) 0.40 and (d) 0.46

ISAT results were in line with the mass change outcomes of concrete after the impact of freeze-thaw tests; both the water and air tests. Concrete samples with w/c ratios of 0.32 and 0.37 and treated with 4% **crystalline material** have shown the least water absorption rates among all mixtures. This amount of treatment has helped water absorption rate to drop by 78% and 85% for mixtures with 0.32 and 0.37 w/c ratios respectively compared to their control mixtures (Figure 8-5 a and b). Even when both mixtures were treated with 2% **crystalline material** they have shown a high ability to reduce water absorption. This might be a result of using a compatible amount of water and **crystalline material**, where no excess water is present in the mix, and the amount of water was suitable to initiate the reaction between sodium acetate and cement, and at the same time water was enough to continue the hydration process (Chapter 6, Section 6.3). Despite the scaling effect that the freeze-thaw cycles has imposed on concrete (Figure 8-3), **crystalline material** has proven its efficacy against water absorption. This could give an indication that the protection and the presence of this material is not only near the surface of concrete but all over the structure.

In the case of concrete with w/c ratios of 0.40 and 0.46 and treated with 4% **crystalline material**, an obvious destructive effect could be seen from Figure 8-5 c and d. Water absorption of these two mixes has significantly increased compared to their control and to other mixtures after the impact of freeze-thaw. This might refer to their high porosity when they were first cast (Table 4-2 in Chapter 4, Section 4.3.3) and the formation of some microcracks in concrete after the impact of freeze-thaw cycles. Moreover, the high w/c ratio, especially in concrete with w/c ratio of 0.46, and the highly added dosage of the **crystalline material** will contribute in increasing the formation of the hydrophobic organosilicon content. The presence of this hydrophobic content in large amounts in concrete at early ages will probably work on reducing the needed amount for the hydration process by repelling water out from concrete. This will lead to the formation of some microcracks in concrete during its curing and before initiating

the freeze-thaw test. With the impact of the freeze-thaw test, these microcracks will develop into larger cracks, and concrete will absorb more quantities of water.

Referring to the results of water absorption of concrete under the impact of 180 freeze-thaw cycles in air, a clear increase in permeability can be noticed when compared to the results of water absorption before the impact of freeze-thaw in Chapter 6. Figure 8-6 illustrates the effect of freeze-thaw cycles in air on concrete's absorption of water.

Water absorption rates under the effect of air have followed a similar trend to those in water but with less absorbing rates. This is expected since the severity of the test in water is higher than that in air.

Similar to the freeze-thaw test in water, concrete with w/c ratios of 0.32 and 0.37 and treated with 4% protective material have shown the least absorption rate between all mixes, which refers to the compatibility between the used amount of water and the added percentage of the admixture. This could be linked with the micro-images in Table 8-1, where these mixtures have developed less cracks with small sizes

On the other hand, concrete with w/c ratios of 0.40 and 0.46 and treated with 4% admixture suffered from increasing the absorption rate of water. This issue could be explained by following the same reasons for their high absorption rates after the impact of freeze-thaw cycles in water. Also, their high tendency to absorb moisture during freeze-thaw in air, as noticed in section 8.3.1, confirms with current outcomes, because of the formation of large microcracks (Table 8-1) and the original high porosity of concrete (Table 4-2 in Chapter 4, Section 4.3.3).
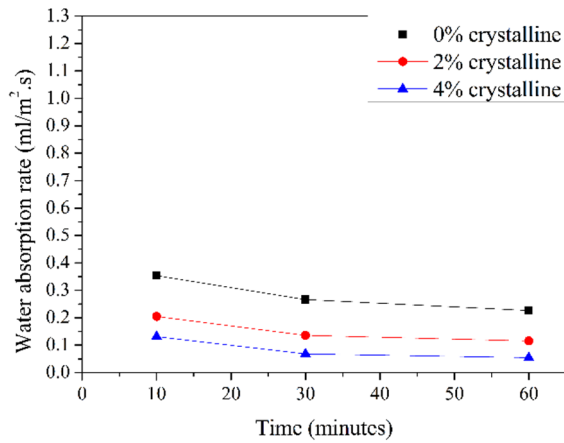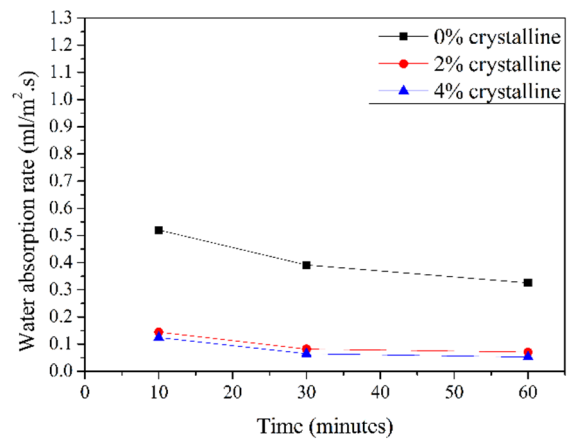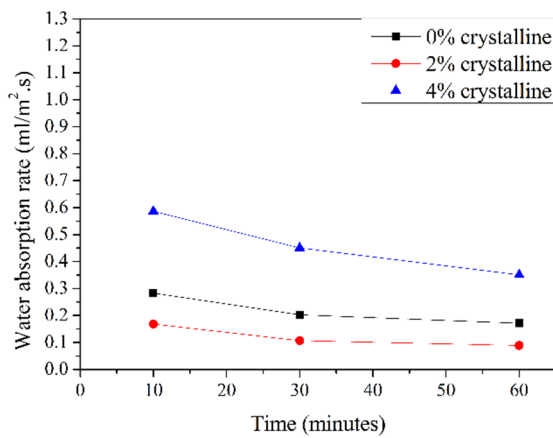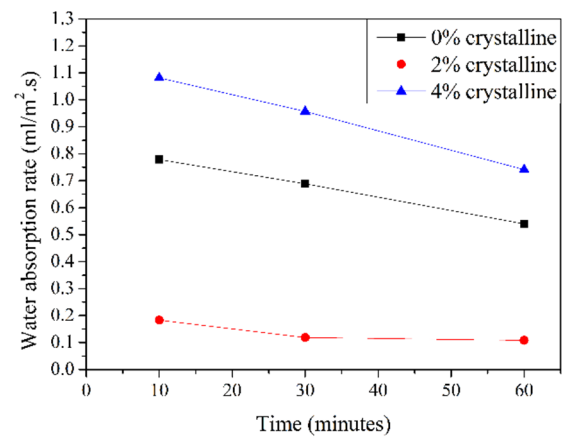
Figure 8-6 - The impact of freeze-thaw test in air on concrete with w/c ratio of: (a) 0.32, (b) 0.37, (c) 0.40 and (d) 0.46

8.3.3 Compressive strength

After finishing both freeze-thaw tests, in water and air, all samples have been tested for compressive strength to measure the ability of treatment to preserve the strength of concrete in harsh conditions. Table 8-2 shows the compressive strength and standard deviation values of concrete after their exposure to cyclic freeze-thaw in water and air.

Table 8-2 - Compressive strength of concrete after the impact of freeze-thaw cycles

Crystalline material %		Compressive strength (MPa)											
		Freeze-thaw in water						Freeze-thaw in air					
		0%	SD	2%	SD	4%	SD	0%	SD	2%	SD	4%	SD
w/c ratio	**0.32**	38.7	1.1	42.1	1.5	50.5	0.7	38.8	0.9	47.7	1.6	53.5	0.8
	0.37	31.2	0.9	39.2	1.3	46	2	34.8	2.8	45.2	2.3	50.5	1.3
	0.40	45.5	1.2	36.4	1.2	32.9	0.2	54.4	1.8	42.1	1.9	43.3	0.3
	0.46	36.1	0.8	29.1	1	21.2	0.4	45.1	2.3	37	1.6	30.3	1.6

It is witnessed that concrete under the impact of cyclic freeze-thaw in water has suffered from a drop in its compressive strength values when compared to concrete under freeze-thaw cycles in air. Once more, this refers to the severity of the applied conditions in the case of the freeze-thaw test in water. The frost action of the freeze-thaw test in water may damage the internal pores of concrete due to the presence of water inside the pores. The expansion of water inside the pores will damage the pore system and initiates cracks inside concrete, which in turn will weaken it and reduce its strength. Comparing these results with those obtained before the impact of freeze-thaw in water (Table 5-2 in Chapter 5, Section 5.3.2.1), a clear reduction in compressive strength could be noticed (Figure 8-7). Concrete with w/c ratio of 0.46 and treated with 4% **crystalline material** has suffered from 35% reduction in its strength, which shows that treatment with high w/c ratios will have a negative effect on the durability of concrete.
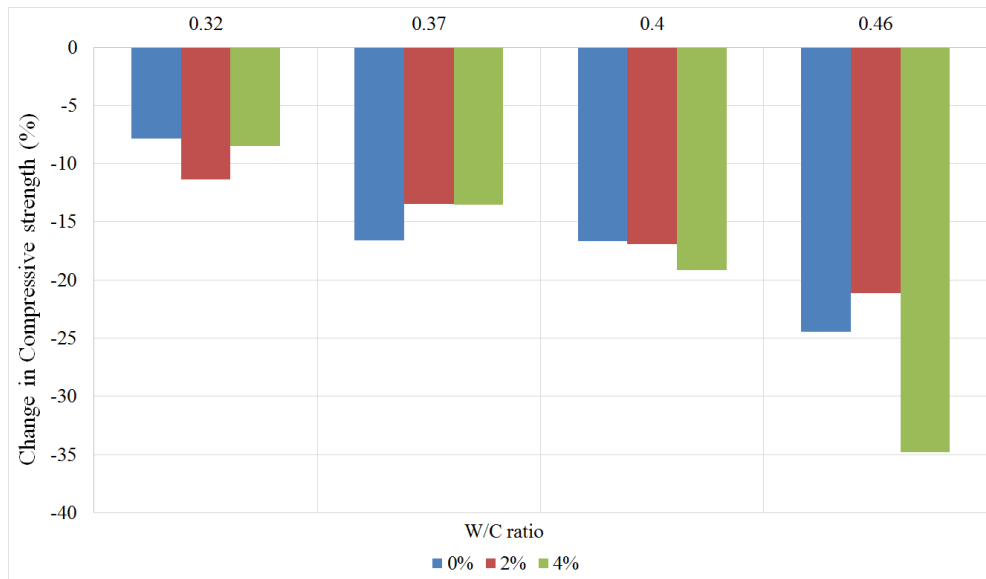
Figure 8-7 - The impact of freeze-thaw cycles in water on concrete's compressive strength compared to original strength

The reduction in compressive strength was less severe in the case of low w/c ratio concrete, especially concrete with w/c ratio of 0.32 and treated with 2% and 4% **crystalline material**. This reflect the high influence of treatment on low w/c ratio concrete, as it helps in making its structure denser and with minimum cracks even under harsh environments (Table 4-2 in Chapter 4, Section 4.3.3).

Compressive strength of concrete that was under the impact of freeze-thaw cycles in air did not show any reduction in compressive strength (Table 8-2 compared with Table 5-2 in Chapter 5, Section 5.3.2.1), which refers to the low severity of this freeze-thaw test. Also, the major impact of the freeze-thaw cycles in air might only affect the near-surface zone of the concrete, without affecting the internals of concrete, or they may have a minor effect on the interiors of concrete.

8.4 Summary of Part I

The long-term performance of concrete treated with 2% and 4% **crystalline material** has been tested through two freeze-thaw tests that operate differently; freeze-thaw under the effect of water and freeze-thaw under the effect of air. Both tests have run for 6 continuous months but

with different number of cycles and different speeds. In the freeze-thaw tests under the effect of water, saturated concrete was immersed in water and placed under the impact of fast 1080 freeze-thaw cycles during the 6 months. However, in the freeze-thaw test under the effect of air, concrete has been under the impact of slow temperature alteration with 180 cycles during the 6 months. Both tests have been destructive to concrete but with more severity in the case of freeze-thaw cycles in water.

Concrete with low w/c ratios of 0.32 and 0.37 have managed to resist deterioration more than concrete with high w/c ratios of 0.40 and 0.46. Treating the low w/c ratio concrete with the **crystalline material** has increased its resistance to deterioration unlike the high w/c ratio concrete. Treating high w/c ratio with **crystalline material** has increased its deterioration rate more than untreated concrete, and deterioration was noticed to increase with increasing the added dosage of treatment. The opposite was noticed in the low w/c ratio concrete, where increasing the dosage has improved concrete's resistance to deterioration.

After both freeze-thaw tests have finished, water absorption and compressive strength of the deteriorated concrete were evaluated. All concrete samples have shown an increase in water absorption when compared to their original state (before freeze-thaw). However, this increase was minimum in the case of concrete with low w/c ratio, especially when treated with 4% **crystalline material.** The maximum absorption rate was noticed in concrete with 0.46 w/c ratio and treated with 4% **crystalline material**. Similar results were noticed after testing the deteriorated concrete for compressive strength. However, in the case of concrete that suffered from the air cyclic freeze-thaw, its compressive strength values did not change and remained similar to original values of non-deteriorated concrete.

Part II: Freeze-thaw of Surface Treated Concrete

8.5 Experimental programme

In this part, 102 concrete samples with 100mm x 100mm x 100mm were cast to serve the testing methodology of this part. 96 cubes out of 102 were pre-conditioned with different moisture contents before treatment; full drying, full saturation, 2% and 4% moisture contents. After the pre-conditioning process, concrete was treated with **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane.** 6 cubes out of 102 cubes were used as control/reference for comparison reasons. Moreover, 48 cubes were assigned to serve the purpose of each freeze-thaw test. After finishing the two freeze-thaw tests, the change in the mass of each cube was measured in reference to their original masses, followed by testing them for water absorption by ISAT. Moreover, all the cubes were dried before testing them with the ISAT method. Figure 8-8 illustrates the explanatory diagram for the pre-conditions and the tests of treated concrete cubes. The used mix design for this testing program is mix 5, which is shown in Table 3-3 (Chapter 3, Section 3.3).
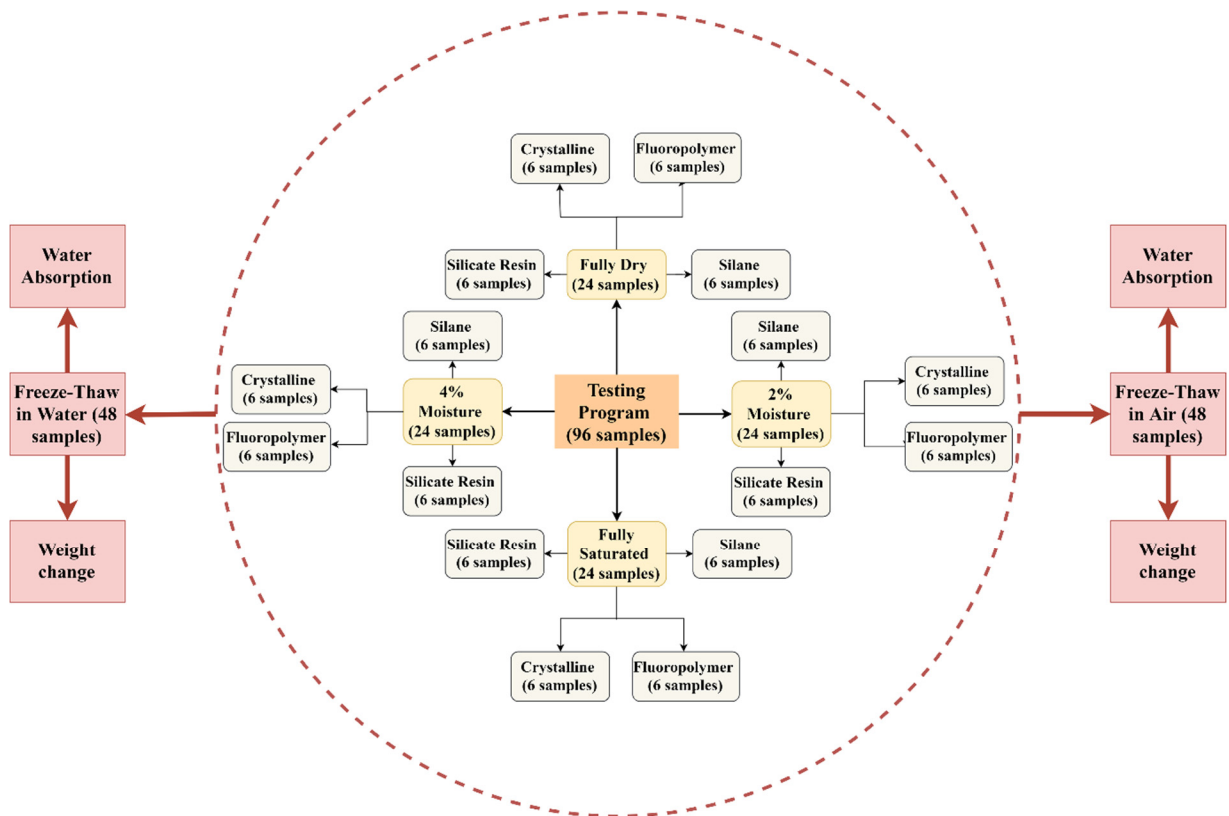
Figure 8-8 - Testing protocol of treated concrete and their saturation level before treatment

Similar to the procedures followed in Part I of this chapter, freeze-thaw in air was set to alternate between -20 °C and 20 °C during every freeze-thaw cycle (Chapter 3, Section 3.4.6.1). Around 180 cycles were run for a total duration of 6 months. On the other hand, 1080 cycles were operated during the freeze-thaw test in water, where concrete cubes have been saturated and then immersed in water before placing them in the testing machine (Chapter 3, Section 3.4.6.2). Every freeze-thaw cycle has lasted for 4 hours and temperature was set to alternate between -10 °C and 6 °C during every cycle.

8.6   Results and discussion

8.6.1   Influence of freeze-thaw on mass change

After the end of the 1080 freeze-thaw cycles in water, the change in the masses of all concrete samples was measured to evaluate the deterioration rate in concrete. Figure 8-9 shows the percentage of mass reduction in all pre-conditioned concrete after the 1080 cycles.
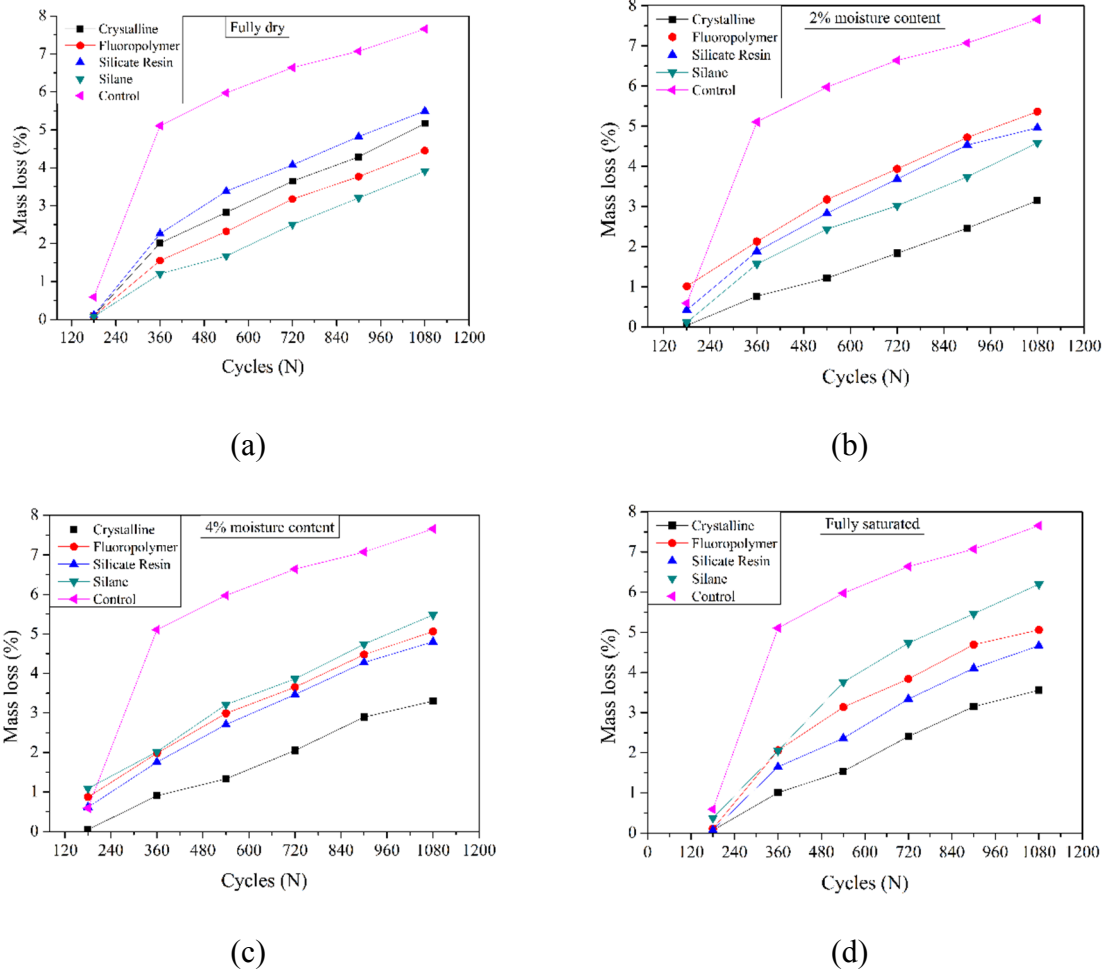
Figure 8-9 - The influence of 1080 freeze-thaw cycles in water on the mass reduction of pre-conditioned concrete: (a) fully dry, (b) 2% moisture content, (c) 4% moisture content and (d) fully saturated

The impact of the water freeze-thaw cycles was severe on all treated and untreated concrete samples regardless of their moisture content before treatment. However, the mass loss in control samples was the highest during the whole 6 months. When applying **silane** to the surface of dry concrete (Figure 8-9 a), minimum damage was exhibited compared to other treatments with a maximum loss in mass of 4%. Referring to Table 4-5 in chapter 4, the rejection rate of dry concrete to **silane** was minimal at the time of application, which allows **silane** to penetrate deeper in the pores and strengthen the pore structure. The formation of the **silane's** active content, silanol group, needs a very low moisture content or no moisture to be

activated and then create a strong link with the pores. This might explain the high resistance of **silane** to deterioration when applied to dry concrete.

Increasing the moisture content of concrete before the application of **silane** is noticed to reduce the efficacy of **silane** in protecting concrete against deterioration through the freeze-thaw cycles (Figure 8-9 a-d). When **silane** was applied to fully saturated concrete, the mass loss in concrete was maximum and close to control, which refers to the absence of the active content in the pores. The presence of Alkoxy groups in **silane**, which provide it with its hydrophobic nature, are expected to react with the silicates in the pores to establish a stable bond with concrete. In the presence of high amount of water in concrete, and with the hydrophobic properties of the Alkoxy groups, the bonding between **silane** and concrete would be difficult (Bertolini et al. 2013).

Crystalline material has managed to provide a high level of protection when applied to concrete with high moisture contents. The loss in the concrete's mass was less than 4% when the material was applied to concrete with 2% and 4% moisture contents and when it was applied to fully saturated concrete. However, the mass loss reached more than 5% when **crystalline material** was applied to fully dry concrete. This might refer to the need of its main component, sodium acetate, to a certain amount of water to form its active crystals (Chapter 4, Section 4.6.3).

Both **fluoropolymer** and **silicate resin** materials have followed similar trend at all saturation levels with an average performance between **crystalline material** and **silane**. However, deterioration in concrete treated with **fluoropolymer** was less in case of applying the material to dry concrete. This refers to the low surface energy of the fluorinated side chain of **fluoropolymer**, which reduces its adhesion to applied surfaces in the presence of water (Chapter 4, Section 4.6.3) (Passaglia et al. 1994; Brady 2000; Li et al. 2002; Chambers 2004).

On the other hand, **silicate resin** when applied to fully saturated concrete showed better performance than **fluoropolymer** due to its interaction mechanism with concrete that depends on the presence of moisture to adhere strongly to the pores (Chapter 4, Section 4.6.3).

The deterioration rate of concrete after its exposure to cyclic air freeze-thaw was less than that when exposed to water freeze-thaw. Figure 8-10 shows the mass increase in concrete after 180 cycles of air freeze-thaw.

(a)   (b)

(c)   (d)
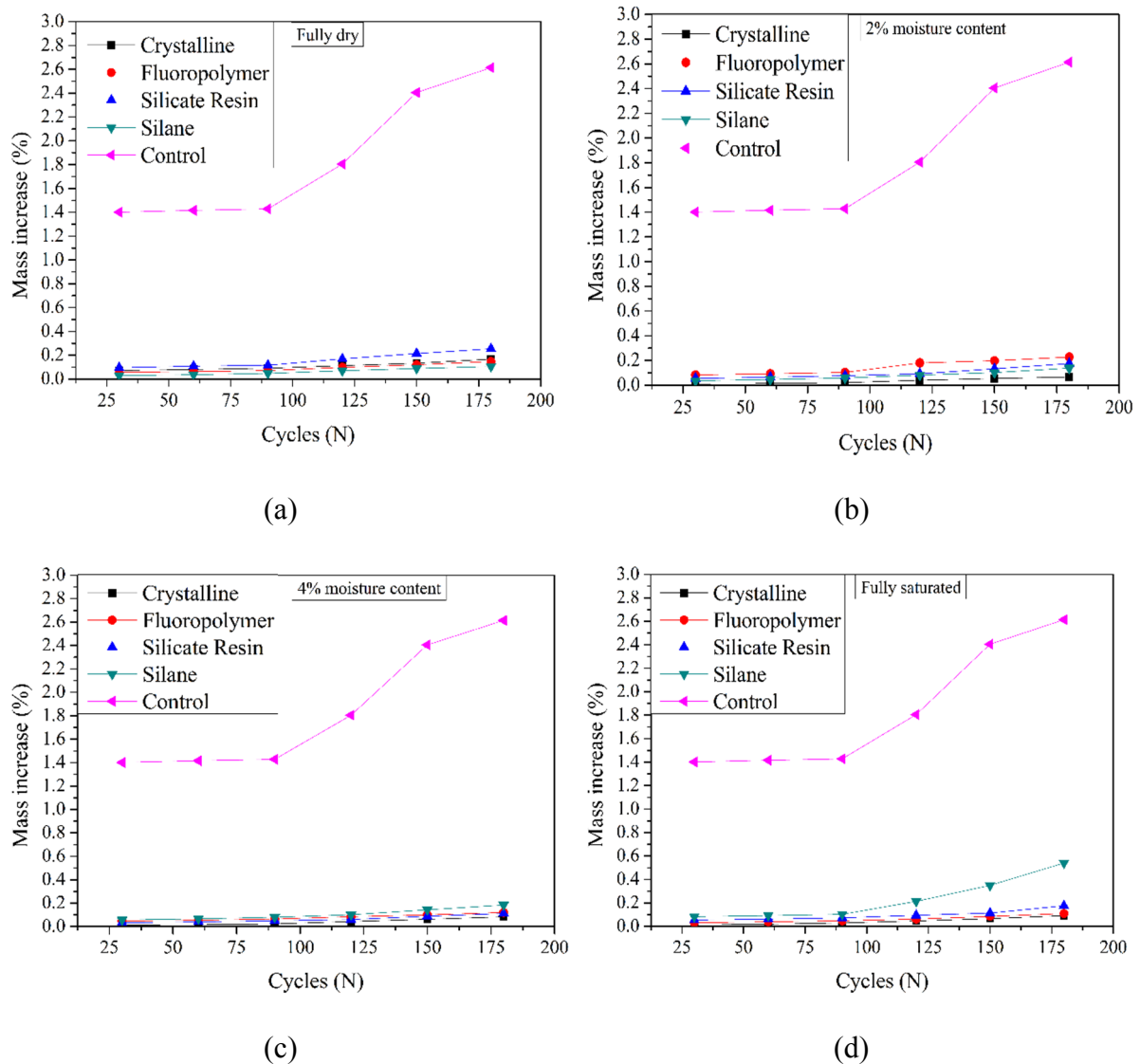
Figure 8-10 - The impact of air freeze-thaw on the mass change of concrete pre-conditioned with: (a) Full drying, (b) 2% moisture content, (c) 4% moisture content and (d) full saturation

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It is witnessed that the increase in the mass of all treated samples was minimal when compared to control with a maximum weight gain of 0.5% in the case of fully saturated concrete treated with **silane**. Other materials have shown similar performance to each other with very slight difference, even with changing the pre-application moisture content. The impact of the air freeze-thaw test on samples is much less than the water freeze-thaw test, which is reflected on the deterioration rate of concrete. The slow temperature variation of surrounding air, during the whole testing period, would have less impact on concrete than the fast temperature variation of surrounding water and water that already exists in the pores. Comparing treated concrete with control shows that the temperature alteration was much severer on control than treated concrete, which reflects the efficacy of protection during the freeze-thaw action. Even when the rejection rate of concrete to protective materials is very high, the remaining amount of material has managed to resist the impact of this type of freeze-thaw cycles (Table 4-5 in Chapter 4, Section 4.6.1). For instance, despite the waste of more than 40% of **silane** when applied to saturated concrete, the material has succeeded to reduce the damage that was induced by temperature alteration. However, some microcracks have developed at the end of the air freeze-thaw test, without showing any scaling on the surface of concrete. Table 8-3 shows the effect of the air freeze-thaw cycles on all concrete samples.

It is noticed from Table 8-3 that some microcracks have developed on the surface of deteriorated concrete (after finishing the freeze-thaw test). All the developed cracks in treated concrete appear to have small sizes when compared to their control, as the surface applied materials have contributed in protecting concrete from severe cracking. However, a difference in crack propagation is noticed with different materials and different pre-application conditions. For instance, applying **silane** to fully saturated concrete allowed the propagation of large cracks (0.10mm), in contrast to other protective materials with different pre-application conditions. This refers to the deficiency of **silane** to work well when applied to wet surfaces

due to the high refusal rate of wet surfaces to **silane** (Chapter 4, Section 4.6.1). On the other hand, some fine cracks (0.04mm) have developed when the **crystalline material** was applied to fully dry surfaces. This is maybe caused by the absence of water that is necessary for the development of the active crystals (Chapter 4, Section 4.6.3).

Comparing results from this part with results obtained in Part I, especially for concrete with w/c ratio of 0.46 as the same mix design is used in this part, crack propagation is noticed to be more severe in the case of internally integrated concrete and tested under the air freeze-thaw effect. The surface of concrete is the part of the sample that is in direct contact with the surrounding environment, which makes it the first element to start deteriorating. In the case of surface applied materials, the highest protection level will be near the surface, and decreases with increasing the depth. However, in the case of internal integration, the protective material will be distributed all over the concrete sample and will not be concentrated in one area. Accordingly, the concentration of protective materials when they are applied to the surface will be higher than the concentration when protective materials are internally integrated. Adding to that, the surface applied materials have been applied to matured concrete after a curing period of 28 days without affecting the hydration process of concrete (Chapter 8, Section 8.3.1).

Table 8-3 - Crack propagation in concrete after the impact of 180 air freeze-thaw cycles
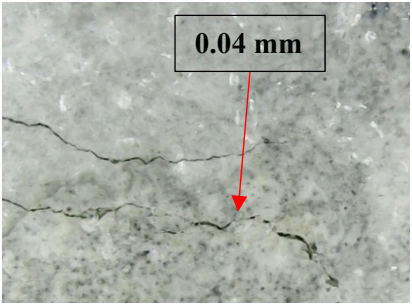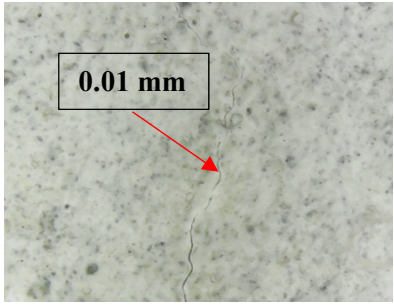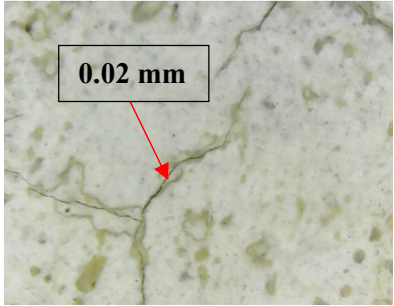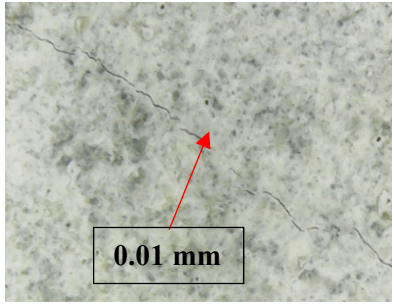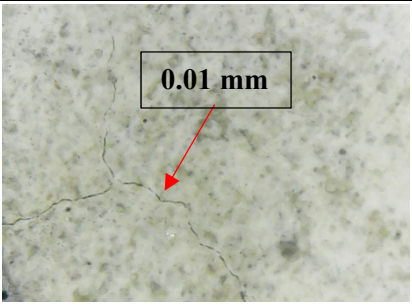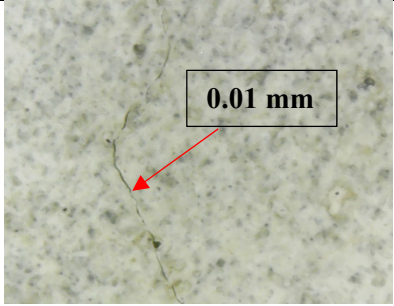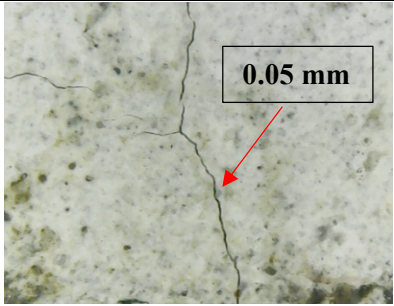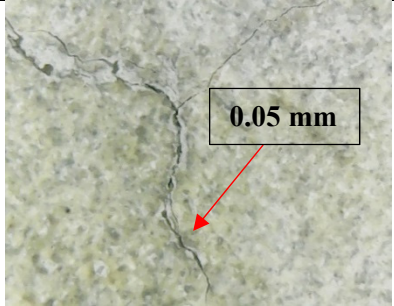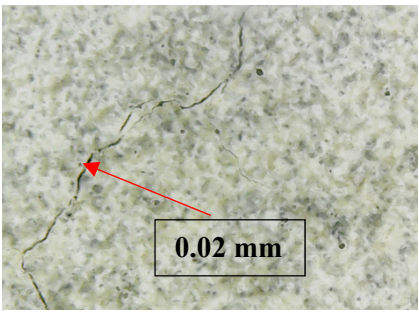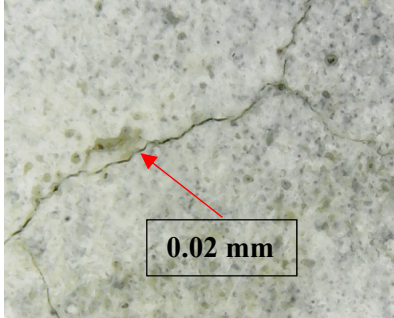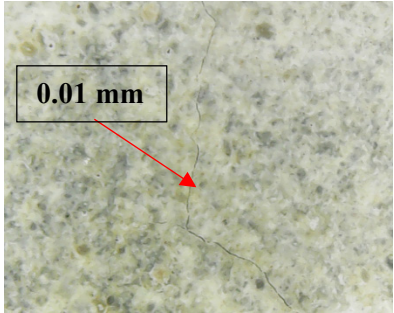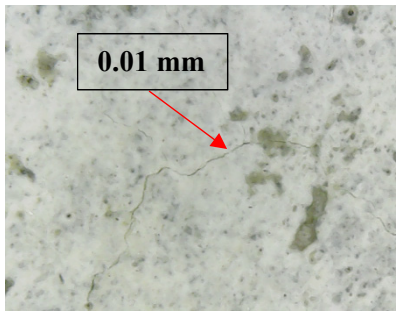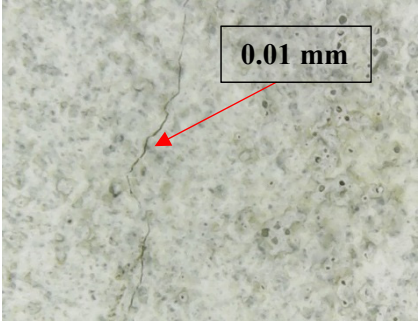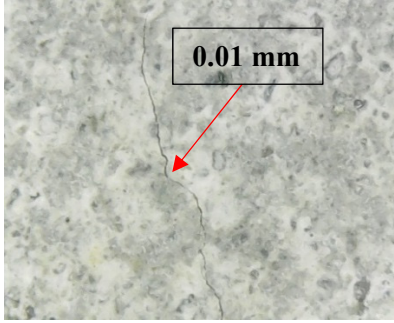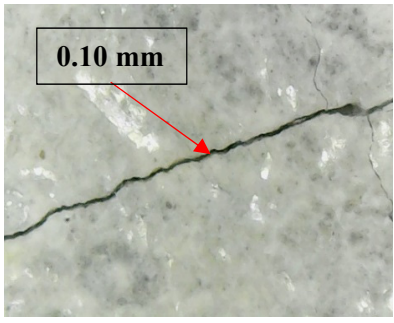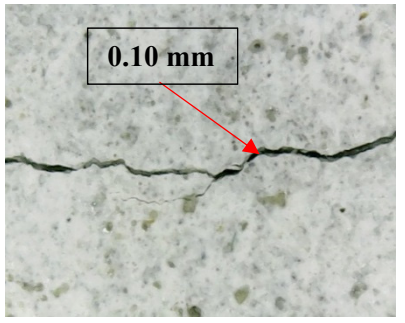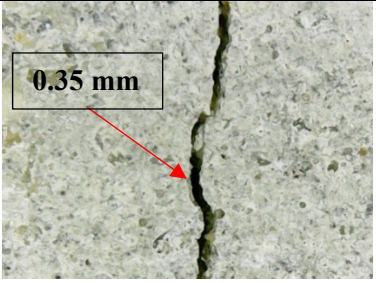
Protective material	Saturation level prior to application			
	Fully dry	**2%**	**4%**	**Fully saturated**
Crystalline	0.04 mm	0.01 mm	0.02 mm	0.01 mm
Fluoropolymer	0.01 mm	0.01 mm	0.05 mm	0.05 mm

Table Continues…

Protective material	Saturation level prior to application			
	Fully dry	**2%**	**4%**	**Fully saturated**
Silicate Resin	0.02 mm	0.02 mm	0.01 mm	0.01 mm
Silane	0.01 mm	0.01 mm	0.10 mm	0.10 mm
Control		0.35 mm		

8.6.2 Water absorption

After the completion of 1080 water freeze-thaw cycles, concrete cubes were tested for water absorption by using ISAT to assess the ability of surface applied treatments on protecting deteriorated concrete from water ingress under harsh environments. Figure 8-11 shows the water absorption rate of pre-conditioned concrete after the impact of water freeze-thaw cycles.

(a) (b)

(c) (d)
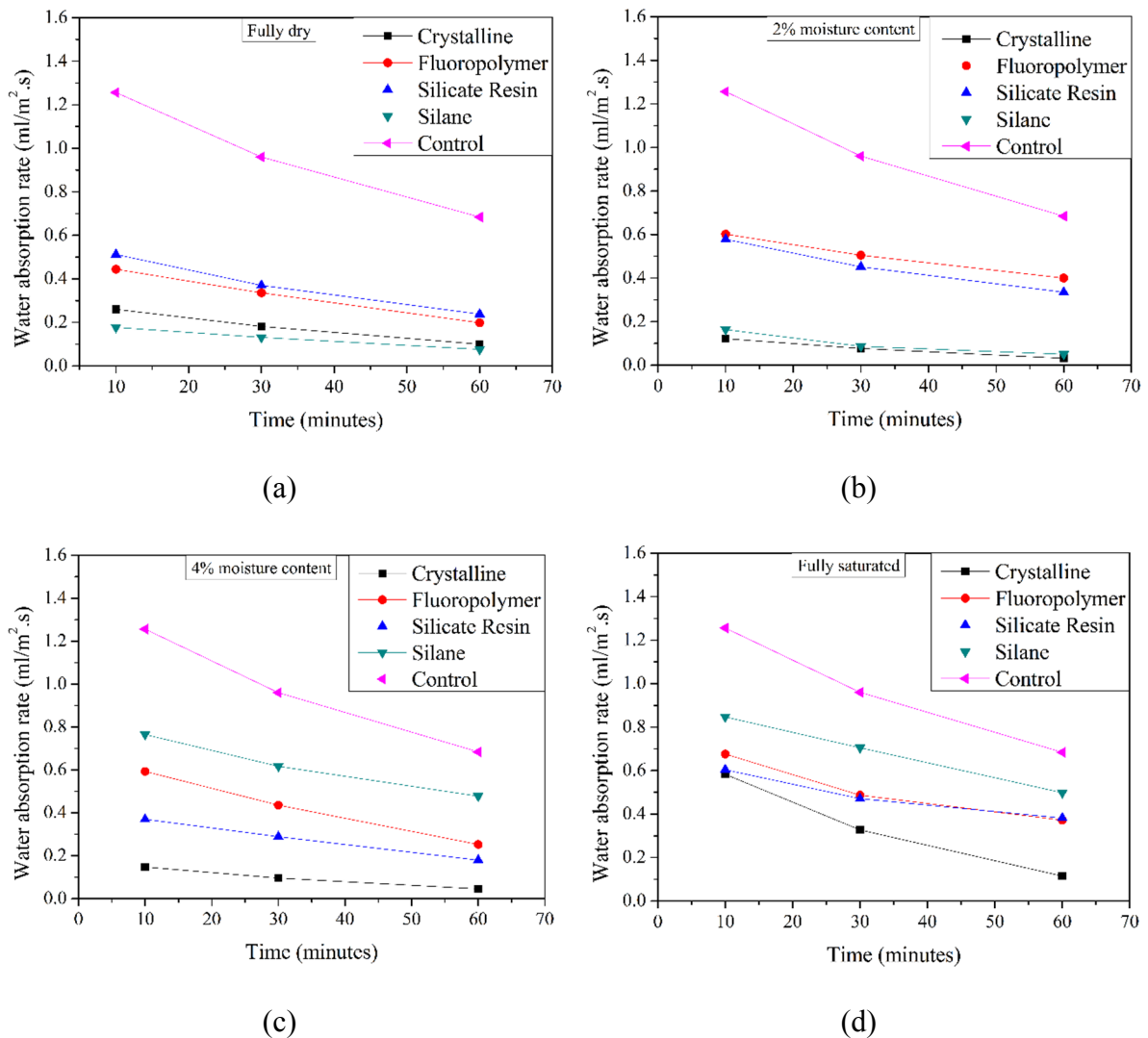
Figure 8-11 – Water absorption of concrete after the exposure to water freeze-thaw cycles and pre-conditioning with: (a) full drying, (b) 2% moisture content, (c) 4% moisture content and (d) full saruration

Comparing water absorption of concrete before the exposure to the water freeze-thaw cycles (Chapter 6, Section 6.6.3) and after the exposure to the freeze-thaw cycles (Figure 8-11), a clear increase in the water absorption rate is noticed after the exposure. Applying the materials to fully dry surfaces has shown different levels of protection depending on the properties of the applied material. **Silane** has managed to present the highest protection rate for concrete against water absorption after the impact of freeze-thaw, when applied to dry concrete. When **silane** applied to dry surfaces, Alkoxy groups that are bonded with silicone atoms in **silane** will react with the silicate, which already exists in concrete, and adhere strongly in the pores (Chapter 4, Section 4.6.3). Despite the scaling effect of this freeze-thaw test, **silane** managed to provide a good protection to concrete, as treatment increased the protection by more than 88% when compared to untreated concrete. This proves the high penetration depth of **silane** when applied to dry surfaces. On the other hand, increasing the moisture content of concrete over 2% before the application of **silane**, has shown a high deficiency in the protection level, where water absorption has increased significantly. When **silane** was applied to fully saturated concrete, the protection level was noticed to reach its minimum since the bonding between **silane** and concrete will be difficult to be achieved in the presence of water (Chapter 4, Section 4.6.3). Adding to that, the penetration depth of **silane** will be less if it was applied on saturated concrete; after scaling takes place, **silane** will be less effective in protecting concrete since it only presents near the surface.

Due to the high affinity of **crystalline material** to water, its application on saturated concrete or even partially saturated concrete (2% and 4% moisture content), has managed to significantly decrease the water absorption of deteriorated concrete, and provide high level of protection when compared with the other materials and control. The presence of sodium acetate in the **crystalline material** allows it to absorb the already existing moisture to form hydrogen bonds with concrete and link properly in the pores (Chapter 4, Section 4.6.3). However, the

absence of moisture from the fully dry concrete will cease the formation of such bonds and works on reducing the efficacy of **crystalline material** when applied to fully dry surfaces.

As discussed in Chapter 4, Section 4.6.3 **silicate resin** needs some moisture inside the pores to adhere properly to concrete. This could be noticed in Figure 8-11 as **silicate resin** has achieved better performance than **silane** and untreated concrete with increasing the moisture content above 2%. The presence of silicate resin inside the pores worked on enhancing the strength of the pores and decreased crack formation due to the expansion of water inside the pores (Chapter 4, Section 4.6.3).

Concrete treated with **fluoropolymer** has shown a convergent performance to **silicate resin** when applied to different saturation levels, but with a slight better performance when applied to dry surfaces. The low surface energy of the fluorinated side chain of **fluoropolymer** works on reducing the adhesion of the material to concrete in the presence of moisture (Chapter 4, Section 4.6.3).

The impact of 180 air freeze-thaw cycles on the efficacy of surface applied materials in reducing water absorption is shown in Figure 8-12. Water absorption rates of concrete exposed to this test are showing similar trend to those under the impact of water freeze-thaw test. However, the amount of water absorbed after the exposure to this test is less than that in the water freeze-thaw test.

The results clearly demonstrates that the alteration in the air temperature has accelerated the water absorption rate in concrete when compared to water absorption of concrete before the impact of these conditions (Chapter 6, Section 6.6.3). The formation of some microcracks in treated and untreated concrete, as shown in Table 8-3, has participated in increasing the water absorption rate despite the presence of protection within the concrete texture. However, the application of the protective materials has managed to reduce the deterioration rate of concrete.

This is seen in Figure 8-12 when comparing the water absorption of treated concrete with control (untreated concrete).

(a)

(b)

(c)

(d)
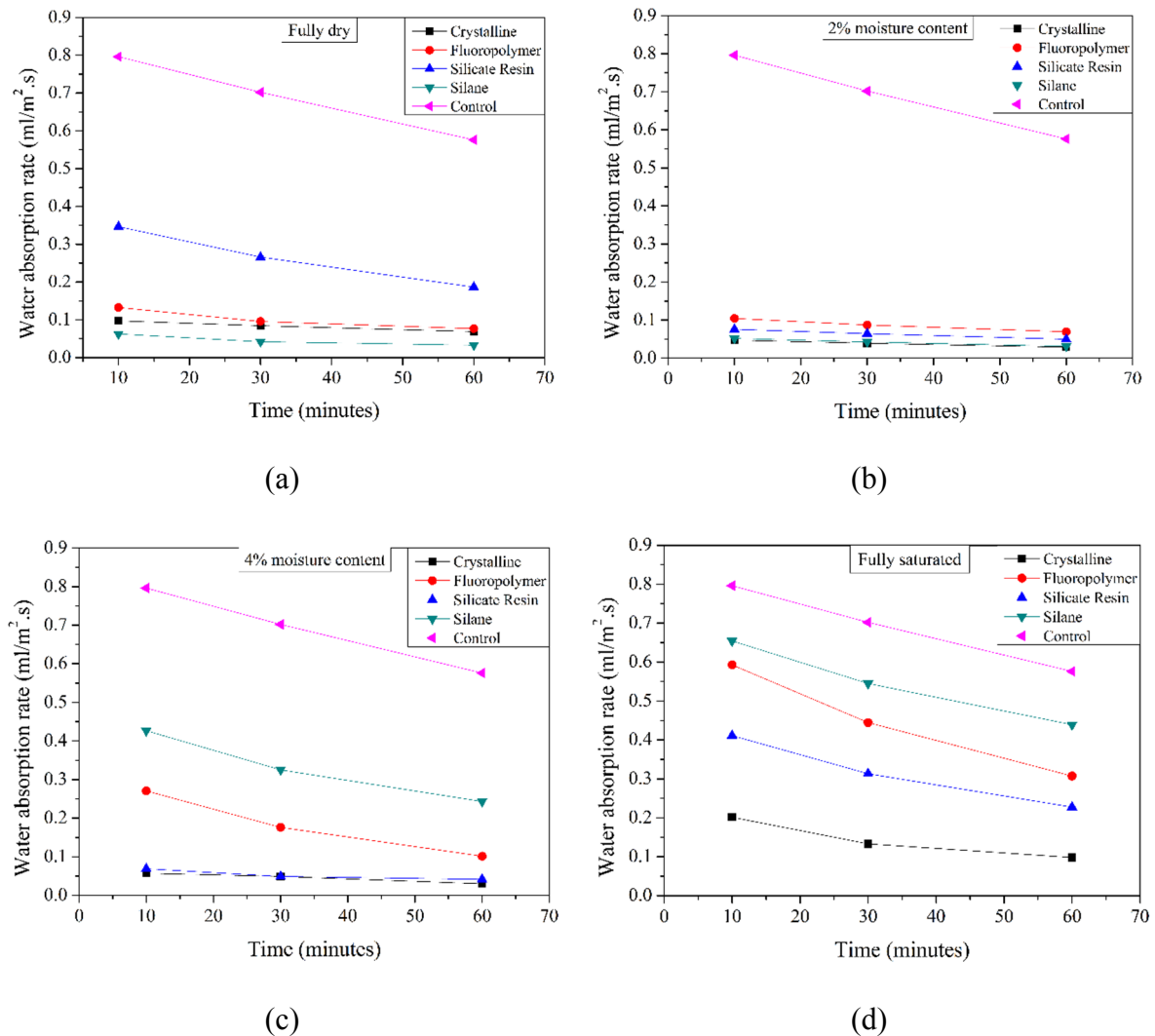
Figure 8-12 - The effect of air freeze-thaw cycles on the water absorption of concrete treated and pre-conditioned with: (a) full drying, (b) 2% moisture content, (c) 4% moisture content and (d) full saturation

The highest water absorption rate was recognised in concrete pre-conditioned with full saturation prior to the application of protective materials. This could be linked with the rejection rate of the applied materials shown in Table 4-5 (Chapter 4, Section 4.6.1), where less active content of the materials will be available in concrete after their application to fully saturated concrete. Also, the long-term temperature alteration has contributed in weakening the

adhesion of the protective materials to concrete, causing the applied materials to break down especially on the surface. However, the **crystalline material** has demonstrated the highest resistance to deterioration, when applied to fully saturated concrete, with the least water absorption rate amongst all other treated concrete. **Crystalline material** has shown the least rejection rate between all applied materials (Table 4-5, Chapter 4, Section 4.6.1), which increases the presence of its active content compared to other materials. On the other hand, concrete treated with **silane** absorbed the highest amount of water since its interaction mechanism with concrete depends mainly on the absence of water at the time of application or the presence of very small amount of water (Chapter 4, Section).

Concrete treated with **silicate resin** showed a modest protection against water absorption when applied to fully saturated surfaces but better than **fluoropolymer** and **silane**. The presence of more than 70% of the active content of **silicate resin** in concrete (Table 4-5, Chapter 4, Section 4.6.1) contributed in increasing the defiance of concrete to crack formation. Accordingly, this material will work on reducing the water absorption rate of deteriorated concrete. However, applying **silicate resin** to fully dry concrete showed less efficacy in reducing water absorption due to its need for moisture to its linkage with the pores (Chapter 4, Section 4.6.3).

Fluoropolymer has provided good protection to concrete during the freeze-thaw impact. However, this protection decreased with increasing the moisture content prior to its application to concrete. Still, **fluoropolymer** has offered better protection than **silane** when applied to surfaces with moisture contents higher than 2%.

8.7 Summary of Part II

The durability of four surface applied materials when applied to concrete with different moisture contents was evaluated by exposing concrete to harsh environmental impacts. Two sources of harsh conditions were utilised in this research; freeze-thaw under the effect of air

temperature alteration and freeze-thaw under the effect of water temperature alteration. Both conditions showed different impact on concrete with different severity. The impact of the water freeze-thaw cycles was more severe on concrete than the air freeze-thaw cycles.

Liquid crystalline material, **fluoropolymer**, **silicate resin** and **silane** were applied to concrete with four different moisture contents; fully dry concrete, 2% moisture content, 4% moisture content and fully saturated concrete. The damage induced by the two freeze-thaw tests on concrete was assessed by measuring the change in the concrete masses, and the change that appears on the surface of concrete. In the case of water freeze-thaw test, scaling was observed in all treated and untreated concrete. However, in the case of air freeze-thaw test, scaling was absent and some microcracks have been developed on the surface of concrete but with different sizes depending on the used protective material and the moisture content prior to treatment. Moreover, water absorption of deteriorated concrete was assessed as well to determine the level of protection provided by the applied materials.

Crystalline material has provided concrete with the highest level of protection when applied to saturated concrete. However, its performance when applied to dry concrete was less than other applied materials like **silane**. This refers to its interaction mechanism with concrete that depends on the presence of moisture at the time of application. On the other hand, **silane** showed the best performance when applied to dry surfaces, and the level of its protection started to degrade with increasing the moisture content of concrete prior to application.

Due to the need of **silicate resin** for moisture to form its linkage with concrete, it has shown good performance when applied to concrete with moisture content equal or higher to 2%. In contrast to **silicate resin**, **fluoropolymer** has shown the highest efficacy when applied to dry surfaces. However, it had higher affinity to water than **silane**.

Chapter 9: Conclusions and Future Work

9.1 Major conclusions

9.1.1 Summary

This research has contributed to the field of concrete protection by investigating different protective materials through concentrating on the details of their microstructure and interaction mechanism with concrete. The performance of the materials on the short-term and long-term was evaluated through comprehensive physical, chemical and mechanical characterisations. Five materials, with different chemistries, were investigated throughout the research, and they were divided into two categories: Internally integrated treatment and surface applied treatments. The internally integrated treatment involved a powder **crystalline material,** and the surface applied treatments involved **liquid crystalline material, fluoropolymer, silicate resin and silane.** In the internal integration process, the **crystalline material** was incorporated within the concrete mix at the mixing stage before casting, where an optimum mix design was developed by changing the added dosage of the material and the w/c ratio of concrete. However, in the surface application process materials were brushed on the surface of matured concrete (after concrete's curing).

9.1.2 Concluding remarks

- The internally integrated **crystalline material** forms a linkage with cement through its main component, sodium acetate, by bonding the acetate with the sodium that already exists in cement.

- Acetic acid and sodium hydroxide were formed during the reaction between the **crystalline material** and cement in the presence of water. Acetic acid and sodium hydroxide were noticed to increase the workability of concrete, and their presence in

high quantities worked on delaying the hydration process and reducing the final strength of concrete.

- The hydrophobicity of the **crystalline material** was established by the formation of organosilicon bonds between cement and the **crystalline material**.

- The interaction mechanism of surface applied materials with concrete depends mainly on the functional groups that the materials form with concrete:

  - ✓ **Liquid crystalline material** connects with concrete through acetate after its bonding with sodium that already presents in the mix. The formation of organosilicon bonds in the pores will create hydrophobic properties in the treated concrete.

  - ✓ **Fluoropolymer** was distinguished with its strong linkage with the pores (after treatment) due to the formation of carbon bonds between **fluoropolymer** and concrete. The fluorinated side chains are assembled together to form a tight – CF_3 groups that provide concrete with hydrophobicity.

  - ✓ **Silicate resin** was observed to work on consuming calcium hydroxide that resulted from the hydration process, contributing towards the enhancement of the interfacial properties of the material and its adhesion with concrete. The presence of the methyl group inside the pores with a polarised Si-O-Si bonds will give treated concrete its hydrophobic properties

  - ✓ **Silane** will react with moisture inside the pores to form a silanol groups by the hydrolysis of alkoxy groups that already exist in **silane**. A linkage between silanol groups and the hydroxyl groups in concrete will take place after the drying of the pores, creating a strong water repellent bond between them.

- The internal integration of **crystalline material** in concrete was observed to preserve the frictional properties of the road without changing along with a modest increase in

the hydrophobicity (<74°), which makes the addition of this material to concrete pavement safe in terms of skid resistance.

- Applying treatments on the surface of concrete pavement showed different levels of skid resistance depending on the type of the applied material.

- **Liquid crystalline material** displayed the highest skid resistance, **silane** showed the least skid resistance and **fluoropolymer** and **silicate resin** had skid resistance values that are between the **crystalline material** and **silane**.

- The hydrophobicity of **silane** was the highest between all treatments followed by **silicate resin**, **fluoropolymer** and then **crystalline material**. This indicated that treating concrete pavement with the **crystalline material** would be the safest choice in the case of surface application.

- The processing parameters that affect the efficacy of internally integrated concrete with **crystalline material** were inspected, namely the w/c ratio of the mix and the added dosage of the **crystalline material**.

- A significant reduction in the compressive and flexural strengths was observed in concrete with high w/c ratio and integrated with the **crystalline material.** The reduction was attributed to the formation of high amounts of acetic acid and NaOH that work on delaying the hydration process and increase the workability of the mix.

- An optimum mix design was produced to overcome the dilemma of strength reduction in internally integrated concrete with **crystalline material.** A remarkable improvement in the strength was noticed with reducing the w/c ratio of the mix.

- An optimum mix design could be obtained by integrating 4% **crystalline material** in mixes with w/c ratios of 0.32 and 0.37, where compressive strength has increased by more than 31% and 42% respectively. Mixes with relatively low w/c ratios have managed to complete the hydration process and gain higher compressive strengths,

compared to other mixes, due to the formation of modest amounts of acetic acid and NaOH in the mix.

- **Liquid crystalline material** was applied on the surface of fresh concrete (before curing) and cured in friendly and harsh conditions. This type of treatment has shown an adverse effect on the mechanical properties of concrete with a significant reduction in compressive and flexural strengths under all curing conditions.

- Adding 4% dosage of the **crystalline material** in concrete with w/c ratios of 0.37 and 0.32 mixes has significantly decreased their water permeability by more than 65% and 55% respectively.

- A small reduction in the water absorption of concrete with w/c ratios of 0.40 and 0.46 and treated with 2% **crystalline material** was noticed.

- Treating concrete with w/c ratios of 0.40 and 0.46 with 4% **crystalline material** may suggest the impracticality of treatment due to the negative effect of such treatment on concrete.

- Applying **liquid crystalline material** to the surface of fresh concrete at early ages (before curing) has revealed the inefficiency of conducting such treatment, either when concrete is present in friendly environment or in harsh environment. This back-up the outcomes of the strength testing.

- The differential performance of **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** was further explored under various pre-application conditions. The pre-application conditions of matured and cured concrete involved: a) full drying, (b) 2% moisture content, (c) 4% moisture content and (d) full saturation (6% moisture content).

- **Liquid crystalline material** has provided the maximum protection when applied to concrete with all the conditions except the fully dry one. This is due to the need of the

crystalline material for a certain amount of water to form hydrogen bonds with concrete that allow the material to link properly in the pores and create its active crystals.

- Increasing moisture content above 2% exhibited a negative effect on the performance of **silane** which is related to the activation process of **silane** inside the pores; it either needs to be applied on concrete with small amounts of water or on dry concrete surfaces to activate the silanol groups that provide the material with its hydrophobic properties.

- **Fluoropolymer** and **silicate resin** have shown a converging performance with better efficacy for **silicate resin**. In the presence of moisture in concrete, **silicate resin** works on breaking the hydrogen bonds, increase the rate of consuming calcium hydroxide and link its silicates on the walls of the pores with strong carbon and silicone bonds. On the other hand, the optimum performance of **fluoropolymer** when applied to dry surfaces refers to the low surface energy of the fluorinated side chain of the fluoropolymer, which decreases the **fluoropolymer's** adhesion to applied surfaces in the presence of water.

- The Practicality of applying **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** to the surface of matured concrete pavement was evaluated by reproducing a real-life exposure for rainfall and groundwater in the lab by two standard tests.

- **Crystalline material** has shown promising results under both tests, where it absorbed the least amount of water in a converging performance to **silane.**

- **Fluoropolymer** and **silicate resin** have enhanced concrete impermeability as well, where both have reduced the absorbed amount of water, either due to head pressure (rainfall) or capillary action (groundwater).

- Concrete with w/c ratio of 0.32 and integrated with 4% **crystalline material** has shown a high resistance to chloride diffusion with 70% efficacy. However, concrete with w/c

ratio of 0.37 and integrated with 4% **crystalline material** has shown a reduction of 90% in chloride diffusion.

- Adding 4% of the **crystalline material** to concrete with w/c ratio of 0.46 negatively affected the performance of concrete where an increase of chloride penetration was noticed when compared to control.

- Increasing the w/c ratio was noticed to participate in increasing the voids and the size of the pore structure of concrete, which in turn increase the rate of capillary suction and permeation through the pores. Adding to that, using high amount of the **crystalline material** will reduce the hydration process and works on introducing some microcracks in the mix.

- Chloride diffusion of concrete conditioned with full drying, 2% moisture content, 4% moisture content and full saturation and treated with **liquid crystalline material**, **fluoropolymer**, **silicate resin** and **silane** was investigated:

  ✓ **Crystalline material** has provided the maximum protection when applied to fully saturated concrete followed by **silicate resin**. Moreover, **silane** provided its maximum efficacy when applied to fully dry concrete followed by **fluoropolymer**.

  ✓ **Crystalline material** and **silicate resin** where less efficient than **silane** when applied to dry concrete, due to their interaction mechanism with concrete that needs the presence of moisture inside the pores.

  ✓ The efficacy of **fluoropolymer** declines with increasing the moisture content of concrete. Water forms a barrier between concrete and the applied **fluoropolymer** that weakens the adhesion of fluorine to concrete.

- Two freeze-thaw approaches were followed to achieve the purpose of long-term testing; freeze-thaw in water and a newly developed method of freeze-thaw in air. After both

freeze-thaw tests have finished, mass change, water absorption and compressive strength of the deteriorated concrete were evaluated.

- Integrating concrete with low w/c ratios with the **crystalline material** has shown a high resistance to deterioration more than concrete with high w/c ratios.

- Treating high w/c ratio with **crystalline material** has increased its deterioration rate more than untreated concrete, and deterioration was noticed to increase with increasing the added dosage of the **crystalline material**.

- Increasing the dosage of the crystalline material in concrete with low w/c ratios has improved concrete's resistance to deterioration.

- In surface applied treatments, the long-term performance of treatments when applied to pre-conditioned concrete with different moisture contents was evaluated:

  ✓ **Crystalline material** has provided concrete with the highest level of protection when applied to saturated concrete. However, its performance when applied to dry concrete was less than other applied materials like **silane**. This refers to its interaction mechanism with concrete that depends on the presence of moisture at the time of application.

  ✓ Due to the need of **silicate resin** for moisture to form its linkage with concrete, it has shown good performance when applied to concrete with moisture contents equal or higher to 2%.

  ✓ **Fluoropolymer** has shown the highest efficacy when applied to dry surfaces. However, it had higher affinity to water than **silane**.

9.2 Future work

This research has established significant contributions to the concrete pavement protection area. However, suggestions for expanding the scope of this research are listed following the findings of this project:

- The effect of treatments on the frictional properties of concrete pavement was carried out on trowelled and smooth surfaces. Therefore, treatment have to be integrated/applied to concrete pavement with different surface properties and roughness to study the influence of treatment on the friction of such surfaces. Adding to that, it is necessary to test the skid resistance of concrete pavement before and after adding water for long durations to assess how water absorption affects the performance. Other testing procedures and techniques, beside the Pendulum test, could be used to assess the effect of treatments on the surface properties of concrete like the sand patch test and multi-laser profiler.

- This thesis has demonstrated that surface applied treatments are highly influenced by the moisture content of concrete prior to their application to concrete's surfaces. Accordingly, some questions have emerged, after the completion of this work, which led to the validity of the recommendation of 4.0% moisture content, when applying the treatments, as specified in the Highways Agency Report BD 43/03 and the British Standard BS EN 1504-2. This moisture content is believed to be higher in the vicinity of the surface than what it is stated in the BD 43/03 and BS EN 1504-2. In other words, it is believed that the recommended 4.0% moisture content is not the true representation of the actual near-surface moisture, which significantly impacts the performance of protection materials. The near surface moisture content is likely to be considerably higher than 4.0%. It is therefore essential to understand how moisture content varies across the depth of the specimen and develop a relationship between the near-surface moisture and bulk moisture (suggested by the standard).

- A mathematical model could be produced to define the best time (in terms of moisture content) of applying the surface applied materials to concrete and the amount that

should be applied to gain optimum protection. This model could work as a guideline for the application of protective materials on-site.

- Life Cycle Assessment (LCA) could be performed to analyse the environmental impacts of the used protective materials along with all the phases of the materials' life from extracting the raw components, processing and producing the materials and using them. This will demonstrate the exact effect of the used materials on the environment.

- Unidirectional salt ponding test was carried out to determine the chloride diffusion through treated and untreated concrete. Based on the results obtained from this test, a prediction model could be produced to estimate the chloride diffusion of any structure, treated with the proposed materials, at any time of its life.

- The proposed freeze-thaw test in air has shown a less severe impact on concrete than the standard freeze-thaw test in water. The proposed freeze-thaw testing method could be improved by introducing a saline environment in the testing chamber, where salts could be put in contact with concrete during testing (through sprinkling).

- End -

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