An investigation into marine biofouling and its influence on the durability of concrete sea defences

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Abstract: An investigation into marine biofouling and its influence on the durability of concrete sea defences.

This research has investigated marine biofouling and its influence on the durability of concrete sea defences using on-site and laboratory-based studies. The study was divided into three main phases namely: the surface analysis of armour concrete, the study of algal colonisation within the matrix and investigations into the presence of a bacterial biofilm within freshly hardened armour concrete. The effectiveness of photocatalytic coatings as a non-toxic anti-fouling strategy and cell attachment to synthetic fibres was also studied.

It was found that algal growth quickly developed at the interface of inclusions within the matrix and that power washing with the use of Dairy Hypochlorite to remove this accelerated wear, leading to significant mass loss. It was also observed that bacterial growth within local beach sand, which was used in the production of the revetment armour units, survived the concrete manufacturing process. Bacteria were cultured from the sand and were found to match the Actinomycete like growth in the freshly hardened matrix of armour concrete.

This thesis proposes a holistic model for biofouling of fibre reinforced marine concrete in which algal growth around inclusions facilitates a complex process of biodeterioration. Bacterial filamentous growth around and through synthetic fibres embedded in the new concrete mix, appears to be detrimental to the long term durability of synthetic fibres. Subsequent algal colonisation on the surface of newly placed units appeared to quickly penetrate the surface through exposed fibres and percolated interfaces of inclusions, subsequently weakening their bond. During the manufacture of the armour units, aggregate segregation in the 90° corners in the bottom of the form created a weaker matrix in the surface region most exposed to biodeterioration, the full force of wave action and power washing.

The main conclusions from this study are:

- Synthetic fibres used at the study site are inappropriate for marine concrete, particularly in algal rich waters, within the inter-tidal zone where beach sand is used in the concrete mix. Amendments to Concrete Society Technical Report No. 65: *Guidance on the use of Macro-synthetic-fibre-reinforced concrete* have been recommended.
- Bacterial loaded beach sand is detrimental to the durability of marine concrete in the inter-tidal zone and amendments are recommended to PD 6682-1:2013 Aggregates for concrete (BSI, 2013a) in order to highlight this concern. This UK guidance suggests limiting values for aggregate properties within the ranges permitted in BS EN 12620 (BSI, 2013) but does not place any limits on microorganisms present in beach sand. Further work is needed into the susceptibility of synthetic fibres to crystal growth. Alterations in the manufacture of armour units have been recommended by this author.

Table of Contents

Chapter 1..1

General introduction

Chapter 2..14

General review

The algal colonisation of concrete revetment armour

Copies of (ACI) competition papers.

Examples of conference papers presented during this research.

Examples of conference posters presented during this research.

Video of power washing at the study site.

Video of Photocatalytic coatings study site.

‘The Science Show’ audio recording.

Examples of oral and poster presentations in Japan (as part of a JSPS Fellowship).

Assignment undertaken after surface analysis course at Uppsala University, Sweden.

List of figures

Tables

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Glossary

Algae	Simple plants ranging from single cells to large plants.
Aspect ratio	The ratio of the length of a fibre to its equivalent diameter
Berm	A mound of earth formed to control the flow of surface water.
Biodegradable	Capable of being decomposed by bacteria or other living organisms.
Biodiversity	The diversity of plant and animal life in a particular habitat.
Breakwater	Structures constructed on the coastline as part of a coastal defence system or to protect beaches and/or harbours from the effects of wave action, coastal erosion or longshore drift. They can be constructed some distance from the coast, or with one end linked to the coast.
Capping layer	A layer of unbound aggregate of lower quality than sub-base that is used to improve the performance of the foundation soils before laying the sub-base and to protect the sub-grade from damage by construction traffic.
Cement	A binder, a substance that sets and hardens independently, and can bind other materials together. The most important use of cement is the production of mortar and concrete.
Concrete	A construction material that consists of cement (commonly Portland cement) as well as other cementitious materials such as fly ash and slag

	cement, aggregate (generally a coarse aggregate such as gravel, limestone or granite, plus a fine aggregate such as sand or manufactured sand) and water and chemical admixtures.
Durability	Ability to withstand wear and tear and decay, ability to endure.
Eddies	Circular motion of water or air.
Ecosystem	A biological community of interacting organisms and their physical environment.
Environment	Both the natural environment (air, land, water resources, plant, and animal life) and the habitats in which they live.
Erosion	The group of natural processes, including weathering, dissolution, abrasion, corrosion, and transportation, by which material is worn away from the earth's surface.
Ground granulated blast furnace slag	Material obtained by quenching molten iron slag (a by-product of iron and steel making) from a blast furnace in water or steam, to produce a glassy, granular product that is then dried and ground into a fine powder.
Hydrophilic	Having a tendency to mix with, dissolve in, or be wetted by water. The opposite of Hydrophobic.
Hydrophobic	Tending to repel or fail to mix with water. The opposite of Hydrophilic
Laitance	Over-wet surface, Scum
Marine environment	The natural and biological resources comprising any coastal, sea, seabed and subsoil ecosystem including

	both the living and nonliving components and the ecological patterns and processes that occur therein.
Maritime structures	Structures impacting on the marine environment.
Permeability	A measure of the ease with which a fluid can flow through a porous medium.
Portland cement	Portland cement is the most common type of cement in general usage in many parts of the world, as it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. It is a fine powder produced by fusing calcium and silicate sources (eg clay and limestone) in a kiln and grinding the resultant clinker. A limited amount of calcium sulphate is added that controls the set time.
Rebar	Steel reinforcing bar. (can be stainless steel, carbon and synthetic)
Reinforced concrete	This is concrete in which reinforcement bars (“rebars”) or fibres have been incorporated to strengthen concrete in tension, shear and flexure, as concrete (like rock) is strong in compression but weak in tension.
Revetment	Revetments are structures placed on banks or shorelines in such a way as to absorb the energy of incoming water. They are usually built to preserve the existing uses of the shoreline and to protect the slope against tide and wave action. They can be made from timber, rock armourstone or precast concrete. They prevent wave action reaching the base of the cliff and may be either watertight, covering the slope completely, or porous, to allow water to filter through after the wave energy has been dissipated.
Salinity	The saltiness or dissolved salt content of a body of water.
Scour	The removal of sediment and other material from around the base of a structure, caused by swiftly

	moving water, can scoop out scour holes, compromising the integrity of the structure.
Wear	The erosion of material from a solid surface by the action of another substance/surface/process.

Abbreviations and acronyms

ACI	American Concrete Institute
BDS	Biofouling Defence Strategy
BRE	Building Research Establishment
BSI	British Standards Institution
CPF	Controlled permeability formwork
CIRIA	Construction Industry Research and Information Association
DEFRA	Department for Environment, Food and Rural Affairs
EDAX	Energy dispersive X-ray analyser
EA	Environment Agency
GGBS	Ground granulated blastfurnace slag
ITZ	Interface Transition Zone
MPa	Megapascals
MSL	Mean sea level
OPC	Ordinary Portland cement
SEM	Scanning Electron Microscopy
SF	Silica fume
T	Design life
UCLAN	University of Central Lancashire
UPV	Ultrasonic pulse velocity

Chapter 1

General introduction

It is common to find growths such as algae, lichens, liverworts and moss growing on hard surfaces. Contrary to popular belief, they do not damage what they are growing on, but can cause patios, drives, paths and steps to become slippery.

Royal Horticultural Society (2014)

1.1 Rationale

This thesis describes an investigation into marine biofouling and its influence on the durability of concrete in seawater. As long ago as 400BC, the Greek Philosopher Aristotle referred to the slowing down of ships due to their hulls being covered by barnacles (Hellio and Yebra, 2009). Today, marine biofouling has implications for owners of a wide range of assets in seawater. Marine growth on concrete has generally been considered beneficial, as it keeps the concrete wet, thereby resisting diffusion of gases (Leeming, 1998), however, it can also make horizontal surfaces found on concrete sea defences slippery and unsafe. For many structures, biofouling is unwelcome and suitable control measures have to be found. Biofouling can lead to major economic costs when organisms settle on man-made surfaces such as stepped revetment armour incorporated into concrete sea defences at the study site (Figure 1.1), harbours, jetties, and desalination units. The accumulation of large amounts of biomass results in the creation of micro-environments that may encourage corrosion, physical obstructions and hazards. Each of these factors leads to extra cost with implications in relation to inspection, maintenance, health and safety issues and the repair of immersed surfaces. Control of biofouling on concrete and the effect of the measures on the durability of the concrete surface are, therefore, properties of universal interest. However, there is a lack of quality data, based on a controlled methodology and site experience, so that it is difficult to consider biofouling on concrete sea defences in fundamental terms. This research investigates marine biofouling of concrete sea defences and examines and quantifies the potential damage to surfaces by aggressive control measures used to remove it. The research has been structured to provide a rational explanation of the mechanisms controlling biofouling and its influence on the durability of marine concrete. The research also examines biofouling control technologies.

1.2 Concrete durability

Concrete mixes are designed for durability to resist attack by physical or chemical aggressive agents and to prevent premature corrosion of reinforcement. In the UK, new structures are governed by BS8500 (BSI, 2006) and are designed to achieve a target life of either 50 or 100 years. Legacy structures, built to superseded codes of practice, may fail to deliver predictable performance because of premature reinforcement corrosion (Robery, 2008), but the basic composition and therefore, the durability of cement and concrete in seawater has remained largely unchanged over recent years.

The known deterioration mechanisms of hydrated cement in seawater include: sulfate attack of the matrix, crystallisation pressure of salts drying in the concrete, frost action in cold climates and physical erosion due to wave action carrying sand and floating objects. Attack from any of the above mechanisms tends to increase the permeability; not only does this make the material progressively more susceptible to further action by the same destructive agent but also other types of attack. Thus a maze of interwoven chemical and physical causes of deterioration is at work when a concrete structure exposed to seawater is in an advanced stage of degradation (Mehta and Monteiro, 2006). Additional unplanned abrasion or chemical treatment of the surface, for example to control unexpected levels of biofouling, may place additional demands on the durability of the concrete structure. Currently little guidance exists on additional durability provisions needed to resist techniques such as high pressure water jetting or chemical treatments that may be used to remove biofouling.

1.3 The biofilm

Rocks, stones, beach sand and other natural and manufactured products are used as construction materials. In their natural state and when incorporated into a built structure, they are subject to the deteriorative and degradative action of the environment and microorganisms (Gaylarde and Morton, 2002). Biofilm formation is the beginning of the biofouling process and is investigated in Chapter 5. Biofilms were found to have a considerable bearing on all that was observed and measured throughout the project.

1.4 Marine biofouling

Biofouling is defined as the attachment and subsequent growth of a community of visible plants and animals on structures and vessels exposed to water (Fische *et al*. 1981). The surface pH has proved to be one of the most decisive parameters in determining the material bioreceptivity (Tran *et al*. 2012). A decrease in surface pH by carbonation can promote algal development significantly, with colonisation beginning much earlier and happening much faster (Tran *et al*. 2012). A precursor to visible macrofouling is microfouling caused by bacteria, fungi and other microscopic organisms (Harder and Yee, 2009). About 5000 biological species have been listed as involved in the fouling of structures exposed to or immersed in water. The composition and community assemblages of these species show wide variations from site to site. Once attached to a surface, bacteria rapidly divide and form a slime film. Mould and fungi communities develop along with a variety of single celled algae and multi-celled seaweeds that live as large filamentous or branching plants.

The concrete studied has four main constituents, limestone aggregate, fine aggregate, synthetic fibres and cement. Each of these separate elements will be individually investigated, recognising that the fouling of the concrete can be understood only in relation to the whole network of interactions in which that inclusion is embedded within the matrix.

By using the prefix *bio*, the author is knowingly focusing the scope of this thesis on the processes that lead to the accrual of a biological community at an interface. This excludes a considerable body of work on fouling in its broadest sense. Much of what is encompassed by this research concerns biofouling in a marine context and covers the processes of biofouling, its consequences and biofouling communities and introduces the term ‘bio-tenacious’ growth (Hughes, 2013a) and anti fouling strategies. It is important to understand the processes that influence settlement as this is the very point when fouling of structures and surfaces begins (Figure 1.1) although it is simply a transitional moment in the lifecycle of most species.

Figure 1.1 The study site for this research; Blackpool's Central Area Coast Protection Scheme (2010). Recently placed revetment armour units (pH 12 and historically considered not to be bioreceptive at this time) are colonised by *Ulva* (inside rectangle) within weeks.

1.5 Marine concrete surface analysis

Chapter 3 presents a study into the effect of daily power washing and the use of Dairy Hypochlorite on the revetment armour concrete. It focuses particularly on the development of surface roughness advancing, understanding how a particular concrete surface performs over three years exposure (Hughes, 2011) and how the innovative use of synthetic fibres (Rieder, 2007) within the concrete have influenced that performance.

1.6 Microbial colonisation

Chapter 4 describes an investigation into the colonisation of revetment armour at the study site and reports, microbial growth within synthetic fibre reinforced marine concrete (Hughes, 2012a). Firstly it presents a study into the colonisation of the revetment concrete surface leading to a better perception of biofouling and its effects on the durability of concrete sea defences. Secondly it investigates the porosity and surface energy of revetment concrete site specimens over time, creating a catalogue of data for the overall assessment of the performance and durability of the revetment units.

An algae survey of the Fylde coast was also undertaken to enable the identification of various species observed in concrete specimens (Details in appendix 1). The influence of marine concrete biofouling on the durability of concrete has been further studied using microscopy observations of epibiotic colonisation of site specimens over a period of time. Four elements within the cement matrix have been observed in specimens retrieved from the study site, including macro synthetic fibres leading to micro synthetic fibres, limestone coarse aggregate and fine aggregate (local beach sand). The effects of filamentous growth at the interface of these inclusions was investigated*.*

1.7 Anti-fouling marine concrete

Heterogeneous photocatalysis using titanium dioxide (TiO_2) is a rapidly developing field in concrete technology (Italcementi Group, 2006; Maury-Ramirez and De Belie, 2010; Maury-Ramirez *et al*. 2012). Self-cleaning concrete has already been used in several new buildings, including the *Dives in Misericordia in 2003*, a modern church in Rome (Italcementi Group, 2006). Such concrete combines self-cleaning photocatalytic and antibacterial properties (Fujishima *et al*. 2000). Product concepts for e.g. self-cleaning windows, hydrophobic ceramic tiles or antibacterial refrigerators have also been developed (Fujishima *et al.* 2000).

This research explores the potential of TiO_2 to reduce or prevent marine biofouling. This is achieved through trials with TiO_2 photoactive coatings, anticipating an anti-fouling surface that will limit marine biofilm development.

Extensive research into photocatalysts is being conducted worldwide (Fujishima *et al.* 2000; Maury-Ramirez *et al*. 2013; Zhang *et al*. 2013). However, before these materials can be widely used with confidence, long-term exposure tests of coatings in a marine environment are needed to determine the appropriate dosage rates and application techniques, compatibility with admixtures and fibres, the longevity of treatments, and the treatment's effect, on durability.

1.8 Degradation: A Holistic viewpoint

Chapter 8 presents two holistic models based on experiments and site observations described in earlier chapters, considering the effect of biofouling on the durability of marine concrete. Specifically, it illustrates the performance of synthetic fibres and limestone aggregate. The chapter also provides an example of the application of a holistic model developed by the author to study marine concrete durability, in the context of 'biodeterioration' (Hueck, 1965).

1.9 Purpose of the work

It is known within the concrete industry that chlorine-based chemicals can be detrimental to concrete (Hensey, 2008). However, these products are still used by some local authorities to control algal colonisation on marine concrete sea defences, ramps, stairs and other public access points. Another cleaning tactic is power washing, also known within the concrete industry to be detrimental to concrete and is actively discouraged by the American Concrete Institute (Hensey, 2008).

While local authorities try to keep beach access safe, by removing algae from horizontal surfaces to address any slip hazard, the techniques currently used, such as aggressive chemicals and power washing, can damage the surface of the concrete structure. At the study site, the sea defences at Blackpool, some revetment armour units have been in place for five years and appear to show signs of accelerated wear, partly due to power washing and biodeterioration.

1.10 Contribution from this work

Long-term strategies for the development of non-toxic, environmentally benign antifouling technologies require a greater understanding of the fundamental cellular and molecular processes by which biofouling organisms adhere to concrete. Knowledge of the mechanisms involved may then suggest novel approaches to intervene in the attachment process, reducing or possibly eliminating costly cleaning processes.

It is intended that the outcomes of this research will assist in the development of guidelines for the management of biofouling upon concrete sea defences. These guidelines will enable local authorities to make informed choices about reducing the cost of managing biofouling. This project has demonstrated the performance of photocatalytic concrete, by means of laboratory and site trials of anti fouling coatings, in an extremely hostile environment. This work investigated marine concrete degradation and explored the possible control of biofouling by surface engineering, discouraging spore settlement on the surface of the revetment armour.

1.11 Aims and objectives of the project

In recent times, there has been a growing awareness that not all concretes are durable as previously believed. The present study was undertaken with the objectives of advancing the understanding of how concrete surfaces and coatings respond in the marine environment, including analysis of the factors effecting the biofouling process, bioreceptivity, the manipulation of spore settlement, and attachment mechanisms of microorganisms within concrete.

There were four specific aims:

- To study the impact of existing, aggressive cleaning practises on the wear of concrete surfaces, and the use of topographical management as part of an anti-fouling strategy.
- To quantify the impact on biofilm development, of using TiO_2 photoactive coatings as antifouling surfaces.
- To produce a holistic model for durability analysis and prediction of marine concrete structures, taking colonisation, fracture mechanics and chemically-induced degradation processes into account.
- To propose solutions and progress towards a non-toxic, environmentally-benign, anti-fouling strategy for future industrial applications.

1.12 Outline of thesis

This thesis is divided into eight Chapters outlined in Figure 1.2. Chapter 2 reviews the general literature on concrete sea defence, durability and biofouling. The experimental work undertaken is described in the next five chapters and each contains a general introduction to the topic. Chapter 8 presents a holistic degradation model. Chapter 9 presents the overall conclusions from the investigation, followed by recommendations for future work. The appendices contain relevant experimental data, copies of papers and posters.

Chapter 1	•General Introduction
Chapter 2	•General Review
Chapter 3	•Phase 1 - Surface Analysis
Chapter 4	•Phase 2 - Algal colonisation
Chapter 5	•Phase 3 - The biofilm development
Chapter 6	•Photocatalytic anti-fouling coatings
Chapter 7	• Cell Attachment to Synthetic Fibres
Chapter 8	• The Holistic View
Chapter 9	•Overall Conclusions and Recommendations
Appendices	•Data and copies of published work

Figure 1.2 The thesis structure.

1.13 Original published journal papers included in this thesis

This thesis is supported by eight papers, published or pending publication in refereed journals, prepared during the research (Figures 1.3 and 1.4) and copies are contained in the appendices. A further nine articles have been published in learned society publications and other journals, also contained in the appendices.

Chapter 3 phase 1
Surface Analysis
published work

- The effects of power washing on concrete durability. *Maritime Engineering (ICE).*
- Innovative method used to evaluate the effect of power washing on marine concrete – a UK site study. *Insight – Journal of The British Institute of Non-Destructive Testing.*
- Innovative NDT method used in surface analysis. *Concrete.*
- Innovative method used to evaluate the effect of power washing on marine concrete – a UK site study. *Concrete Repair Bulletin; International Concrete Repair Institute.*

Chapter 4 phase 2
Algal colonisation
published work

- Microbial degradation of synthetic fibre-reinforced marine concrete. *International Biodeterioration & Biodegradation*.
- Microscopic study into biodeterioration of marine concrete. *International Biodeterioration & Biodegradation*.
- Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete.*Construction and Building Materials*.
- A new mechanism for accelerated degradation of synthetic-fibre-reinforced marine concrete. *Concrete*.
- Biodeterioration of marine fiber-reinforced concrete. *Concrete International.*

Chapter 5 phase 3
Biofilm Development
published work

- Bacterial filamentous growth in freshly hardened concrete. *The Indian Concrete Journal.*
- Microscopic study into biodeterioration of joint sealant.*Construction Material (ICE)*
- Bio-tenacious growth in subsea concrete. *World Tunnelling.*
- Microbial filamentous growth in marine concrete. *Concrete.*
- Bacterial growth with a new cement matrix. *Global Cement.*
- Microbial filamentous growth in subsea concrete. *Concrete.*

Figure 1.3 Supporting published material from the 3 main phases of this work.

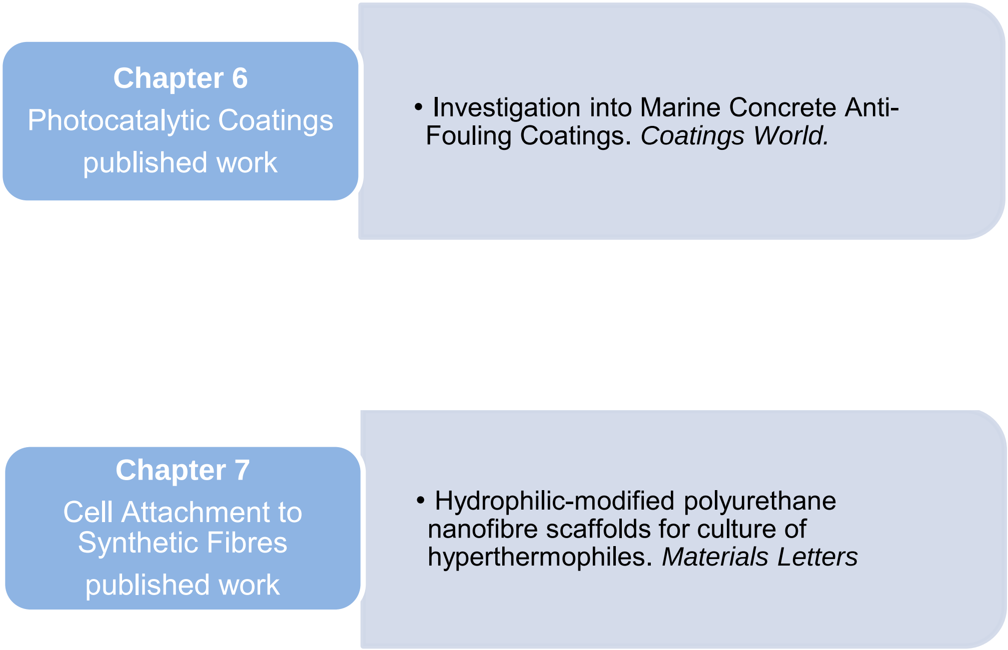


Figure 1.4 Additional supporting published work.

Chapter 2

General review

Think before you speak. Read before you think.

Fran Lebowitz (1996)

2.1 Introduction

This chapter will present a historical review of coastal defences using marine concrete, and associated issues concerning durability and marine biofouling. Specific reviews are featured in forthcoming chapters relevant to each phase of the research. In order to satisfy the needs of marine concrete durability, it is important to understand the deterioration mechanisms to which the concrete may be submitted. Among the different mechanisms of concrete deterioration, biodeterioration is one of the most recently observed in coastal concrete structures (Jayakumar and Saravanane, 2009). Its study is complex and has demanded a multidisciplinary approach which involved different disciplines.

2.2 Coastal defence

Corrosion of reinforced concrete is the most challenging durability problem that threatens reinforced marine concrete structures (Mohamed *et al*. 2013). Corrosion of reinforcing steel leads to cracking and spalling of the concrete cover and billions are spent every year on repairing such damaged structures (Mohamed *et al*. 2013). Over £800m is currently spent on coastal defences in the UK annually more than 15 per cent of which include concrete in various forms. The recent FORESIGHT project on flood and coastal defences (Evans *et al*. 2004) suggested that annual expenditure on flood and coastal defences will need to be doubled in real terms by the 2080s to take account of effects such as sea level rise and increased frequency of adverse weather conditions. Despite the recognised need for increasing levels of capital expenditure on concrete maritime structures, there is a limited number of technical guides on the design and maintenance of such structures that exist in the literature (Allen, 1998).

The British Standard Specification Code of Practice for Maritime Structures (BSI, 1984) was issued in seven parts progressively from 1984. The coverage was comprehensive in that most forms of coastal and harbour structures were considered. A past CIRIA (Construction Industry Research and Information Association) publication was offered on Seawall design (Thomas and Hall, 1992). Two useful technical notes were also issued (CIRIA, 1986a; CIRIA 1986b) which dealt with the maintenance of coastal revetments. It cites many maritime works, but does not name them, unlike previous guidance. However to its credit it discusses the environmental impact of revetments, and how, during the life of such units, adverse effects may include permanent change to the habitats of flora, fauna and marine life. Technical Note 124 (CIRIA, 1986b) comprised a survey of performance and design practice, it discussed the 1977/78 extensive flooding on the Fylde coast, caused by extreme conditions in the Irish Sea. TN 125 also discusses the sea defences at Fleetwood (part of the Fylde coast, north of the study site) in 1977 during the notorious storms. It summarises the design of sloping aprons in front of a low vertical wall, which perform well in normal conditions, but fail to prevent overtopping in extreme surge conditions with less wave action. Two further reports, numbers 119 (CIRIA, 1990) and 135 (CIRIA, 1990a) cover the use of groynes but still seem not to recognise the problems of biofouling.

From an international perspective, The Shore protection manual (Army Corps of Engineers, 1984), is a scientifically based work on coastal engineering, from which modern coastal management and structural design have developed and published manuals on the design of concrete structures (Army Corps of Engineers, 1985). Dutch publications, naturally, figure prominently on the subject of coastal defence, including Report 119 (The Dutch centre for Civil Engineering, 1989), a guide to concrete dyke revetments. The accent of the report is on the behaviour of concrete block revetment under the influence of hydraulic loads; and not on concrete as a material. Japan has also produced a general document compiling port and harbour engineering techniques in one volume: Technical standards for port and harbour facilities (Ins. of Japan, 1991) focusing on ports and breakwaters, rather than coastal structures. Important contributions at an international level have also been made by Germany (Committee for waterfront structures, 1992), Spain (Ministry of Public works Spain, 1993), and Hong Kong (Government civil engineering dept, 1992).

UK guidance (CIRIA, 2010) builds on limited past documents and combines material authored by contributors from within the maritime engineering industry. The work not only explores technical solutions, sometimes novel and always interesting, but also makes innovations and practices widely available. The guide presents principles, important issues and approaches for the use of concrete in the maritime and estuarine environment including advice on materials selection, design, construction, quality assurance and maintenance. It is material-focused but unfortunately does not cover in detail hydraulic, structural or geotechnical design, and more relevantly to this research; biofouling. Informative case studies are provided including work on the Fylde coast at the study site illustrating how particular aspects of management were carried out in practice.

2.3 Marine concrete durability

Marine structures have suffered from seawater attacks for decades (Ramli *et al*. 2013). Thus far, the best approach to minimize the deleterious effects on these structures is to use high-strength, high-performance concrete. However, this approach has its limitations. When a crack starts because of the expansion and shrinkage at splash zones and expansive products are formed because of sulfate attacks, the crack will grow and propagate uncontrollably. Ultimately, the durability of the structure is drastically reduced (Ramli *et al*. 2013). Marine concrete is subject to some of the harshest conditions in the engineering environment, often used in critical applications, where service life and structural reliability are crucial factors (Gjorv, 2009). Marine concrete is subject not only to attack from seawater but also from continuing wave loadings and the abrasive action of bed and suspended loads (Whittle, 2013). A wide range of loading scenarios may cause potential deterioration processes, which can then lead to a large number of different effects (Threlfall, 2013). Problems caused by the corrosion of reinforcement in deteriorating concrete structures are encountered across the globe and are recognised as a major limitation upon the durability of many such existing structures (CIRIA, 2010); however this mechanism is avoided at the study site by the innovative use of synthetic fibres (Rieder, 2007). Other forms of deterioration due to processes such as frost action (Neville, 2006), salt crystals (Sunagawa, 2005; Jafarzadeh and Burnham, 1992) and alkali-silica reaction (Neville,

2004) are less widespread in their occurrence, but can be no less significant in their effects upon some structures (Mehta and Gerwick, 1982). Important research into the mechanisms affecting fibre reinforced concrete, including thaumasite formation and thaumasite sulfate attack leading to the breakdown of the matrix; the most important deterioration mechanism was the composite bacterial and saline water attack (Hagelia, 2008).

As far back as 1924, workers (Atwood and Johnson, 1924) had assembled a list of approximately three thousand references, and today, the durability of concrete structures in the marine environment continues to be the subject of ongoing research and international conferences throughout the world. There is a general perception that concrete is a highly durable material. However the history of concrete in marine environments shows that no construction material is infallibly durable to seawater (Mehta and Haynes, 1975).

Inadequate durability manifests itself by deterioration which can be due either to external factors or to internal causes within the concrete itself (Whittle, 2013). The various actions can be physical, chemical or mechanical. Mechanical damage is caused by impact, abrasion, erosion or cavitation (Leeming, 1998). The chemical causes of deterioration include alkali-silica and alkali-carbonate reactions (Mehta and Monteiro, 2006). External chemical attack occurs through the action of aggressive ions, such as chlorides, sulphates, or of carbon dioxide, as well as many natural or industrial liquids used in cleaning, and gases (Gjorv, 2009). Physical causes include Freeze thaw damage (Ferreira, 2009), the use of de-icing salts (Mehta and Monteiro, 2006), the effects of high temperature (CIRIA, 2010) and thermal expansion of aggregate (Whittle, 2013), and the constant use of high powered water jet systems (Momber, 2005). Deterioration of concrete is rarely due to one isolated cause, therefore it is often difficult to assign deterioration to a particular factor, however with the exception of mechanical damage, all the adverse influences on durability involve the transport of fluids through the concrete (Hall and Hoff, 2002; Neville, 2006a). The provision of a static structure between the sea and the shore has, throughout history, been the dominant means of coastal defence (CIRIA, 2010). These structures have been located on the upper shore usually at or near high water mark since the construction of such defences is relatively easy here compared to the difficulties of establishing defences in the lower or near shore environments. Sea walls can either reflect or absorb wave energy (CIRIA, 1986). The relative roles of these two basic processes are determined by the type of construction. Guidance published in the UK (Ministry of Agriculture, Fisheries and Food, 1992) cast doubt over the durability of sea defences reporting that the maintenance of these structures is a major problem since they suffer considerable damage from waves and wave driven sediment blasting. It was boldly stated that most structures (90%) require maintenance within ten years of construction while 96% suffer damage over a 30 year period. High durability is essential for all concrete, but particularly for concrete in a maritime environment (Tsinker, 1995), these figures raise the question; is our concrete *fit for purpose*? The properties of the hardened concrete must be compatible with the environment, which will determine the choice of concrete constituent and their proportions. Today, structural Eurocodes are an international set of unified codes of practise that are comprehensively detailed elsewhere (Threlfall, 2013). Concrete is treated by many engineers as a sound homogeneous material but it has a very inhomogeneous complex structure (Neville, 2006). The pore structure has been extensively studied and is known to have voids of all sizes interconnected with capillary-sized micro-cracks (Mehta and Monteiro, 2006). These defects in the structure influence its durability and strength. It is inherent in its construction process that it cracks on setting due to shrinkage and differential temperature (Concrete Society, 2007). Many durability theories for concrete make the assumption that the concrete is sound and un-cracked. Research has shown that it is the presence of cracks, not their width that has the greatest influence on concrete durability (Leeming, 1989).

It was observed by other workers that the mortar phase of a concrete, when submitted to the *Cladosporium sphaerospermum* fungus colonisation, suffered aesthetic and microstructural changes and it was concluded that the development of this alteration could promote the destruction of the material (Pinheiro *et al*. 2005). The detrimental effect of the macro algae *Chaetomorpha antennina* was reported by other workers (Jayakumar and Saravanane, 2009). Concrete cubes were kept in a coastal area where abundant growth of *Chaetomorpha antennina* was studied and also laboratory simulation was carried out. The basic mechanism by which the algae deteriorates concrete structures was reported as a biosolubilization mechanism involving the production of metabolic acids by the algae.

2.4 Marine biofouling

Traditionally biofouling of structures in the sea has been divided into a number of major phases: the biofilm, a molecular fouling; primary film formation, slime layer by microorganisms such as bacteria, diatoms, blue green algae, fungi, actinomycetes, protozoa and algal spores. Secondary macro algae, barnacles, hydroids, serpulids; and tertiary mussels, ascidians and sponges. These are arbitrary sequences which can vary dramatically by season and with geographical location.

In 1952 the United States Naval Institute published the biofouling 'bible' 'Marine Fouling and its prevention' (Anon, 1952). This dealt with all aspects of marine fouling: fouling communities, seasonal sequence, geographical distribution, history of the prevention of fouling, to the effects of fouling on ships and other marine structures. In the chapter on marine fouling organisms it lists 37 bacteria, 14 fungi, 111 diatoms, 452 seaweeds (algae), 33 sponges, 120 barnacles, 116 holothuroidea, to list but a few, giving a total of 1964 marine fouling organisms. This emphasizes the problem facing those in the many industries affected by biofouling and charged with counteracting this rich biodiversity.

Biofouling is widespread as marine organisms produce prolific spores, or larvae, that ensure their survival on any intertidal and subtidal substrata (Callow and Callow, 2002; Jayakumar and Saravanane, 2009). Aquatic environments offer ideal conditions for their growth, such as hydration of the organisms, and water movement that brings a constant supply of nutrients and carries away metabolic wastes (Crisp, 1973; Callow and Callow, 2002). Many industries are affected by biofouling; many examples include shipping (Hellio and Yebra, 2009), sea defence/marinas, seawater cooling systems, underwater monitoring instruments and underwater cables (Callow and Callow, 2002). It has also had important implications in the off shore industry, in particular oil and gas platforms (Grey, 1978; Gjorv, 2009).

Marine growth on concrete has in some quarters been considered beneficial. It has been argued that it kept the concrete wet, thereby resisting diffusion of gases (Leeming, 1998). Microorganisms do not live as pure cultures of dispersed single cells but instead accumulate at interfaces to form polymicrobial aggregates such as films, mats, flocs, sludge or 'biofilms' (Flemming, 1998). The surface of concrete is readily colonized by micro-organisms and the decay of the surface is dependent on the production of corrosive metabolites. Several authors have reported examples of disfigurement and possible damage to stone monuments in tropical regions due to presence of algae (Fusey and Hynert, 1964; Wee and Lee, 1980; Lee and Wee, 1982; Gaylarde and Morton, 1999). However, evidence for algal contribution to the decay process of stone has been conflicting (Kumar and Kumar, 1999). Since the introduction of Portland cement, concrete has become one of the most widely used synthetic materials within the construction industry. The factors, which promote deterioration of the material, are a result of transportation of fluids and gas into the concrete and their magnitude is controlled by the greater or smaller facility of deleterious agents to penetrate the material (Pinheiro *et al*. 2005; Whittle, 2013). When transported into the concrete, these agents are able to react with the calcium hydrates of cement pastes (calcium silicates, hydroxides and aluminates) and enhances solubility of the bonding compounds of the concrete, modifying its mineralogical composition and its microstructure, thus altering the material (Pinheiro *et al.* 2005).

The first effect of the growth of photosynthetic micro organisms is disfigurement or discolouration of the surface (Gaylarde and Morton, 2002) often mistaken by the public at large as common dirt. Wood, plastic, coated surfaces, natural stonework and concrete can all be affected (Callow and Callow, 2002). Growth is rarely uniform; frequently there are streaks of growth, green, grey and brown, indicating areas of dampness or water run-off. Once established, growths may form a slippery film, for example on steps and paths, which can constitute a danger to pedestrians. More direct damage can be caused to the structure itself by the acids and other metabolites produced by the organisms, which, together with the ability of some species to penetrate the surface of the substrate, leading to degradation, increased porosity and serious implications on durability of the structure.

Based on their relationship with concrete, algae can be divided into two groups: epilithic algae, which grow on the exposed surface; and endolithic algae, which colonize the interior of the substratum (Kumar and Kumar, 1999). Endolithic algae may be further classified as chasmoendolithic algae, which live inside preformed fissures and cavities open to the surface of the concrete; cryptoendolithic algae, which colonize structural cavities within porous substratum; and euendolithic algae, which actively penetrate into the material (Caneva *et al.* 1991). Although direct damage by algae may not always be significant, they indirectly damage stone by supporting growth of more corrosive biodeteriogens (lichens, mosses, liverworts, and higher plants) (Kumar and Kumar, 1999). This is a natural successional sequence, but unless there is a complete lack of maintenance, a final stage does not develop (Wee and Lee, 1980). Algae may also cause biochemical deterioration. They produce a variety of metabolites, predominantly organic acids (Jain *et al.* 1993). These acids either actively dissolve stone constituents or increase their solubility in water and stimulate migration of salts in stone, causing powdering of its surface (Kumar and Kumar, 1999). The change in solubility of stone constituents alters properties of the stone, such as its coefficient of thermal expansion, which can increase the sensitivity of stone to physical processes of deterioration. Algae also secrete other products of metabolism, such as proteins, which are chelating agents contributing to the dissolution of stone (Jain *et al.* 1993), and sugars, which promote the growth of heterotrophic epilithic bacteria (Bell *et al*. 1974). Algal growth, together with the dissolutive effect of water, may also result in microcavities, or pitting of the stone. It is also possible that endolithic algae may widen pre-existing fissures in stone through increased volume and mass resulting from their growth and water-binding capacity. However, in many such reported cases of actual biophysical deterioration of the stone surface, the algae were growing together with fungi (Garg *et al.* 1988).

At present there is little information of the diversity and ecology of these communities within marine concrete. Most studies have been focused much more on the biodeterioration inflicted by these organisms on natural surfaces than on their biology and prevention in the context of sea defence structures. A detailed list of research carried out in various regions is given by Samad and Adhikary (2009).

2.5 Biodeterioration

Biodeterioration can be classified into three categories: physical or mechanical, aesthetic, and chemical (Allsopp *et al*. 2004). However, due to the great diversity of microorganisms, materials, and environmental conditions, these mechanisms have been observed to occur separately or simultaneously (Allsopp *et al*. 2004; Kumar and Kumar, 1999). The physical or mechanical biodeterioration is the cracking of the material resulting from the tension promoted by the organism during its growth or locomotion (Morton, 2003).

Concrete is considered a bioreceptive material, particularly due to its roughness, porosity, humidity, and chemical composition. These properties, combined with environmental conditions such as the presence of water, temperature, and luminosity can promote the biodeterioration of the material (Guillitte and Dreeson, 1995). Microorganisms can destroy the concrete matrix (cement paste) and its aggregates, thus reducing their durability (Guillitte and Dreeson, 1995). The intensity of concrete deterioration depends on the interaction of several factors, which can interfere on the aesthetic aspect or promote the deterioration of the material (Pinheiro *et al*. 2005).

The biodeterioration of the concrete matrix, the most sensitive phase to microbial attack, is mainly caused by the solubilisation of the calcium products, through the release of alkalis, the oxidation of iron and magnesium, and the extraction of silica (Ribas Silva, 1995). The cement paste is very sensitive to acid solutions, which promote the progressive dissolution of its hydrates, such as portlandite, calcium silicates, and calcium aluminates. Among the biologically produced acids there are organic acids (lactic and oxalic) and inorganic acids (nitric and sulphuric) which react with the cement paste constituents and can also form expansive minerals (such as ettringite) and non-cohesive compounds (such as gypsum) (Biczok, 1972). Aggregates of concrete are normally originated from natural rocks and siliceous sand, both composed of minerals such as quartz, mica, clay-minerals, carbonates (calcite and dolomite), sulfates (pyrite and marcassite), and sulphides (Mehta and Monteiro, 2006). The minerals from aggregates that are more commonly attacked by microorganisms are mica, feldspars, and siliceous minerals. Their solubilisation acts on the properties of the aggregate by reducing its resistance. The effects of bacterial erosion of both limestone and concrete, situated 1mm beneath the surface was reported by other workers, 3D image analysis indicated that no internal pore changes occurred after bacterial weathering (De Graef *et al.* 2005).

2.6 The use of Synthetic fibres in marine concrete

Fibre inclusions in cement have been used in a large variety of applications in civil engineering (Concrete Society, 2007). Fibre cement surfaces can create suitable microhabitats for fungal growth and the fibres could supply nutrients, in addition to carbon sources available in dust or rainwater run-off (Tanaca *et al.* 2011). Fibre content can change the porosity of the material (Bentur and Mindess, 1990) and this could play a fundamental role in microbial growth. For crack control synthetic fibres were used in the revetment armour concrete at the study site (Rieder, 2007; Cunningham *et al.* 2012) and current guidance was followed offered by TR65 (Concrete Society, 2007). The design methods being used were outlined, although it states that in many cases the approaches were still being developed. The expansion of the use of macro synthetic fibres at the time was by individual manufacturers, supported by a limited amount of published work. The report aims to provide some independent guidance on the use of macro synthetic fibres and review their use in construction, even though funded by fibre manufacturers. Given the stage of development at the time of publication and the relatively restricted experience of their use in service, the guidance is necessarily circumspect in some areas such as marine applications require updating. Design methods were in their infancy but where possible the approaches being used were outlined. The report clearly states the perceived notable benefits arising from the inclusion of fibres in hardened concrete for bulk field applications relating to the post-cracking state. However this claim is not backed up by marine site trials. It states in the cracked composite, fibres bridging the crack may contribute to an increase in tensile or flexural strength, failure strain and energy absorption capacity. The use of macro fibres in the revetment armour, featured as a case study, utilize the potential improved energy absorption capacity and toughness of the fibre composite, which, according to the guidance, may also be of use in high strain rate applications such as impact. The concrete mix should be designed so that there is sufficient cement paste to ensure full coating of the fibre for complete bond, as well as the compressive and flexural requirements of the concrete. The guidance specifies how care should be taken not to allow segregation of fibres, which would float to the surface. The production of the revetment armour units, upside-down does not facilitate the avoidance of surface fibres. The presence of surface fibres observed at the study site (Section 3.3.3) plays a significant role in the degradation of the surface concrete. Workmanship has a key role to play, finishing by float or trowel should not be excessive but sufficient to produce the required finish without the production of excessive surface laitance or surface exposed fibres. The report states it is expected that small numbers of fibres may be visible on the worked surface; such an occurrence is not detrimental and there should be no need to use a dry shake topping as a fibre suppressant. The occurrence of large numbers of fibres floating through the concrete matrix to the surface and observed at the study site is indicative of poor mixing, with insufficient fines and/or excess water in the concrete.

The bond between fibre and cement is paramount (Mehta and Monteiro, 2006). In outlining the properties of macro fibres, the report notes that historically all prismatic fibres suffered from relatively poor bond, the property on which composite behaviour depends. However, in polymer fibre reinforcement manufacturing processes enable fibres to be produced with a variety of anchorage mechanisms to enhance bonding.

From a durability viewpoint, the report highlights the fibre's resistance to acidic and alkaline environments, stating they do not require concrete cover as protection against corrosion. The concrete surface zone in marine concrete is its defence against the elements and the lack of such will be investigated. It states surprisingly that fibres will not be significantly affected by moisture and will not be attacked by chlorides when used in a marine environment.

Polypropylene micro fibres were also used in the revetment armour to improve the properties of the fresh concrete, making the mix more cohesive and reduce the risk of blockages during pumping. During compaction, the micro fibres help to control the movement of bleed water and reduce the risk of segregation. This can lead to a reduction in the risk of plastic settlement cracking and early plastic shrinkage cracking.

2.7 Conclusions

Despite the recognised need for increasing levels of capital expenditure on concrete maritime structures, few comprehensive technical guides on the design and maintenance of such structures exist in the literature. Guidance recently published fails to recognise marine biofouling and its implications on the durability of marine concrete. Given the stage of development of synthetic fibres at the time of the publication of TR65 and the relatively restricted experience of their use in service, the guidance is necessarily circumspect and requires updating.

Chapter 3

The surface analysis of concrete revetment armour– phase 1

Power washing is artificially eroding and abrading the concrete surface. Quite literally adding 'wear and tear' starting a devastating vicious cycle.

Portland Cement Association (2012)

3.1 Introduction

This chapter reports on an investigation into the effects of power washing on a concrete surface. Surface roughness, surface hardness, consolidation and uniformity were studied over three years at a site in the North West of England. Segregation analysis was also used to evaluate the concrete surface.

The expensive, time consuming cleaning of concrete is often undertaken on health and safety grounds. In a marine environment control of algal biofouling on stepped sea defences may be required. The action of concrete cleaning methods, both physical and chemical, on concrete sea defences can alter their properties and may alter the susceptibility of the concrete surface to algal colonisation (Hughes, 2013). Bioreceptivity, for a material such as concrete, involves the surface roughness, moisture content, pH, structure and texture of the material. A High pH of concrete can affect the materials bioreceptivity. Variation in pH can affect algal growth in a number of ways. It can change the distribution of carbon dioxide species and carbon availability, alter the availability of trace metals and essential nutrients, and at extreme pH levels potentially cause direct physiological effects. Materials that have a high surface roughness and high macroporosity such as concrete, show high bioreceptivity (Guillitte and Dreeson, 1995).

Current practises employed by the local authority in biofouling management at the study site include power washing, initially with hand held apparatus (Figure 3.1) the use of dairy hypochlorite (Figure 3.1. inset), and more recently specially adapted vehicles (Figure 3.2).

3.1.1 Aims and objectives

The aim of this phase of study was to advance the understanding of how a concrete surface responds in a marine environment. The main objective was to measure the impact of existing cleaning practices at the study site, and discuss its implications on the durability of the concrete armour surface.

Figure 3.1 Operative with hand held water jet controlling biofouling with power washing at the study site; inset, dairy hypochlorite (chlorine-based disinfectant) used at the site, video on CD in appendix.

Figure 3.2 Specially adapted motorised vehicle at the study site, cleaning algae from the revetment armour steps.

3.2 Review

3.2.1 The effects of power washing on concrete

Water jet cleaning can be classified according to the level of the applied operational pressure. Power washing can be defined as the use of pressurised water, with or without the addition of other liquids or solid particles, to remove unwanted matter from various surfaces, and where the pump pressure is below 340 bar (34 MPa) (W.J.T.A., 1999). It is this category of pressure that is applied to clean many marine structures, jetties and steps to combat biofouling, reducing slip hazard, and used at the study site. Further guidance concerning high-pressure water jet cleaning and maintenance management, incorporates hot water and a 15° fan nozzle at an appropriate distance (at least 150 mm) from the surface and appropriate pressure (C.M.A.A., 2000). In general, the higher the water pressure, the more effective the cleaning and the greater the potential damage to the surface. Power washing can start a destructive cycle (Portland Cement Association, 2012). The frequency of cleaning and the cleaning-method used (especially high-pressure cleaning) can have an influence on concrete deterioration (De Belie, 1997). While good quality concrete shows excellent resistance to the steady flow of clear water, nonlinear flow at velocities exceeding 12 $m.s^{-1}$ (7 $m.s^{-1}$ in closed conduits) may cause severe damage to concrete (Mehta and Monteiro, 2006). During cleaning, the water exits the nozzle at both a high pressure and a high velocity (Figure 3.1). The resulting momentum is great enough to dislodge not only dirt and debris, but also to create flakes, popouts, and even concrete spalls (Portland Cement Association, 2012). Early industrial cleaning using water jet technology began in the 1920s in the steel industry. In the late 1950s as reliable high pressure pumps were developed, the water jet revolutionised sewer and pipe cleaning. Reviews about early cases of water jet utilisation for material removal, namely for soil removal and hydraulic mining are available (Wilson, 1918; Jeremic, 1981; Summers, 1991). Today, commercialised water jetting covers many cleaning applications; concrete, stone and masonry, cement kiln and autoclave vessels, chemical pipes, sewers, and ships hulls (Wood, 1996; Momber, 1997; Lenz and Wielenberg, 1998; Lee *et al*. 1999; Momber, 2003).

Dated published guidance (Higgins, 1983) tackles the removal of algae from concrete recommending power washing at velocities of between 50 – 150 bar (5 – 15 MPa). Research (Campbel and Fairfield, 2006) quantified the erosion of concrete focusing on British civil engineering practice, a range of pressures and flow rates covering that used in the routine cleaning and maintenance of drains and sewers. Damage from jetting tests was measured. Volumetric erosion rates at 4000 psi (27.6 MPa) on concrete were found to be in the order of 6.90 mm^3 s^{-1}. Concrete showed more volumetric erosion than clay because of its greater surface roughness (Campbel and Fairfield, 2006). The asperities and pits making up the surface profile were more prominent in the concrete and as such were more exposed to attack by the jet. The particle size, or effective grain diameter, was greater in the concrete pipe, when material was removed by brittle fracture it tended to be in larger pieces than were removed in the finer grained clay pipe. Given the similarities in water absorption and initial porosity, these parameters cannot be held accountable for the difference in erosion rates under high pressure water jetting. A further exploration of the effects of surface roughness upon erosion rate is needed.

3.2.2 Surface roughness

A recent paper presented a review on roughness quantification methods for concrete surfaces, describing their main characteristics and highlighting the advantages and drawbacks of each method (Santos and Julio, 2013). There are several methods for describing surface roughness (Silfwerbrand, 1986; Sherrington and Smith, 1988). In this research, the surface roughness geometry of the concrete surface was measured in 3 dimensions by white light interferometry (Zecchino, 2002). For the surface of revetment armour, the advantage of a 3 dimensional technique is that it offers an overall view of texture, direction, material/void volume, pits and troughs invisible from a 2 dimensional view, (Stout, 1994). No standard method for measuring surface roughness of concrete has been adopted. A range of methods are available and are in use for measuring the surface texture of concrete floors, but no method is accepted as standard and different organisations use different methods. Depending on conventions in for example different countries, industries, applications, the units used to express surface roughness will vary. Holt and Musgrove (1982) carried out a review of the main methods. The interest in measuring surface texture of floors stems from its effect on skid resistance. Research by Wambold (1982) used the mean texture depth to characterise surface roughness. Silfwerbrand (1986) suggested other parameters for quantifying the surface roughness in his study on the effect of roughness on bond of repair materials. A more recent method (Abu-Tair *et al*. 2000) referred to as the roughness gradient method, examined the surface of cut concrete, and was defined in a series of irregular waves, the roughness parameter being dependent on the peak-to-trough depth and the respective wavelength. After careful consideration white light interferometry was preferred by the authors, over 2 dimensional analysis, for its combination of non-contact measurement, accuracy, repeatability, speed and resolution.

Individual test results should not be used in isolation to assess a given durability parameter. A test should therefore be considered within the context of a programme of experiments, requiring data to be assessed from a variety of tests and other sources. Surface hardness, Ultrasonic pulse velocity (UPV) and segregation analysis was also used in this phase of the study to compliment the surface roughness measurements.

3.2.3 Surface hardness

To further understand how the armour surface performs in its marine environment, it was considered prudent to examine the quality of the material over time. One of the many factors connected with the quality of concrete is its hardness. *In-situ* testing methods for surface hardness used in this research have followed guidance from (Bungey *et al*. 2006). Surface hardness testing of concrete is a long established non destructive test (NDT) method for *in situ* strength estimation. The rebound hammer is the surface hardness testing device for concrete most widely used. Suitability for site work was an advantage in this project. A recent, comprehensive literature review of the instrument used is given by Szilágyi *et al*. (2011).

3.2.4 Ultrasonic pulse velocity

Ultrasonic pulse velocity, an NDT procedure was also used to evaluate the quality and the characteristics of concrete armour on site. It consists of measuring the transit time of an ultrasonic pulse through the material. According to the theory of sound propagation in solids, the sound transmission velocity is a function of the density and the elastic modulus of the material (Bungey *et al*. 2006). The method has become widely accepted around the world and the commercially produced, robust, lightweight equipment was very suitable for site work, further details Section 3.3.10. The influence of the amount of aggregate, size, type and shape of aggregate, environmental temperature, and w/c ratio on the strength–velocity relationship was studied by (Trtnik *et al*. 2009). It was shown that the influence of aggregate is very important and cannot be neglected for accurate concrete-based Ultrasonic pulse velocity.

3.2.5 Segregation

Segregation can be defined as a separation of the constituents of a heterogeneous mixture so that their distribution is no longer uniform (Neville, 1995). Water is the lightest component in a concrete mix, therefore bleeding is a form of segregation because solids within the mix tend to move downward under the force of gravity. It is important to reduce the tendency for segregation in a mix because full compaction, which is essential for achieving maximum strength, is not possible in a segregated mixture. It is possible that not all the bleed water reaches the surface, a large amount of it gets trapped within the concrete, bleed water pockets occurring under coarse aggregate and fibres can be responsible for weakening these areas (Mehta and Monteiro, 2006). Coarse aggregate separating from the mix is not only a problem related to the concrete mix, but may be the result of poor construction practices (ACI, 2005). There are few tests for measuring segregation, however visual observation and inspection of samples of hardened concrete has been used to determine whether segregation has occurred during the manufacture of the revetment armour units in this study. Other workers presented a means of evaluating the segregation via an image processing based technique (Barbosa *et al*. 2011). Recent research concluded that concrete cast with high quality materials and mix proportions in accordance with current guidelines may still be vulnerable to poor segregation resistance which can result in adverse effects on surface transport properties and durability performance (Panesar and Shindman, 2012). Segregation resistance means that the distribution of aggregate particles in the concrete is similar in all locations and at all levels. Segregation resistance (SR) plays an important role because poor SR can cause poor deformability, high drying shrinkage as well as non-uniform compressive strength of concrete. Therefore, it is important to have an appropriate method to assess segregation. However, there are few publications devoted to testing methods for segregation resistance. The test results of the testing methods for deformability, blocking behaviour and segregation resistance in vertical direction were partially reported elsewhere (Bui *et al.* 1998).

3.2.6 $CaCO_3$ crystals at the surface zone of armour concrete samples

Fine cracks in fractured armour concrete, if allowed to close without tangential displacement, will heal completely under moist conditions (Neville, 2006). This is known as autogenous healing, and is due primarily to the hydration of the hitherto unhydrated cement which becomes exposed to water upon the opening of the cracks (Neville, 1995). Healing is also aided by the formation of insoluble calcium carbonate from calcium hydroxide in hydrated cement if carbonation takes place. While undergoing surface analysis, unexpected observations were made of $CaCO_3$ crystals at the surface zone of armour concrete samples retrieved from the study site. Autogenous healing is the natural process of crack repair that can occur in concrete in the presence of moisture, and the absence of tensile stress (Mehta and Monteiro, 2006). The repair is by a combination of mechanical blocking by particles carried into the crack with the water and the deposition of calcium carbonate from the cementitious material. Autogenous healing has practical applications for closing dormant cracks in a moist environment, such as may be found in mass structures and in water retaining or watertight structures. Both BS EN 1992–3 (BSI, 2006a), and the water Services Association’s Specification imply that cracks up to 0.2 mm wide will autogenously seal within 28 days; cracks up to 0.1 mm will seal within 14 days. However, this crystal growth would appear to have implications for the durability on synthetic fibres within concrete and will be featured in the discussion section of this chapter.

3.3 Methodology

3.3.1 Revetment armour units

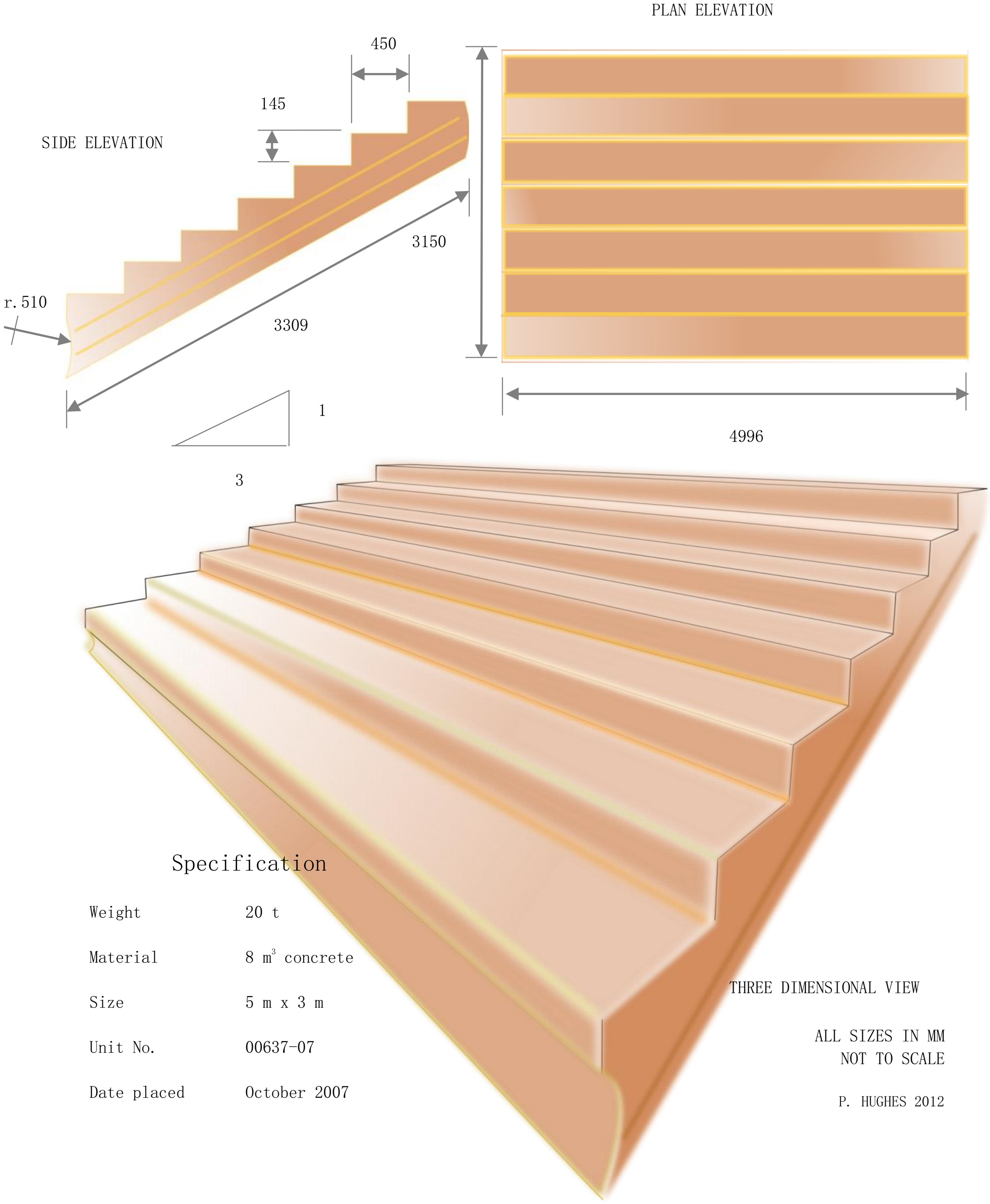
The 10 Revetment armour units tested are located at 53°46’37”N, 3°03’27”W, 2.8 m above Irish sea level, and have been monitored from casting in August 2007 (Figure 3.3) to placement six weeks later (Map reference, Figure 6.5). The precast units are produced in four-step sections, 2,791 of which are needed over the 3.3 km stretch of beach between the toe beam and the promenade level.

Figure 3.3 Four point lifting revetment armour at the casting yard. Cast unit number 00367-07 (arrowed) membrane cured, for 28 days at the casting yard (north west England) in 2007.

The units are 5 m by 3.5 m, weigh 20 tonnes and contain 8 m^3 of macro and micro synthetic fibre reinforced concrete. It is probably the first time in the world, that this technology has been employed for major precast concrete elements in marine coastal defences (Rieder, 2007). Further details on manufacture and mixing within the concrete are reported elsewhere (NCE., 2006; Perry, 2006) The current ‘flagship’ project (Figure 3.4) has involved the placing of 65,000 m^3 of ready mix concrete with 44,000 m^3 of precast concrete elements (Figure 3.5). The ‘as struck’ units are steel cast in a horizontal, ‘upside down’ position. The revetment is formed from fill material, placed at a slope of 1:3, and capped with a concrete blinding layer (Perry, 2006). Behind this stepped apron is a flat, cast *in situ* berm and precast wave wall. The fully exposed units face westwards, into the prevailing wind. The climate in the region has been recorded between mild and moist. The temperature at the study site varied between -7° and 26° over the three years of study (own data).

Figure 3.4 One (of ten studied) of the revetment armour units (arrowed) number 00367-07 set at the study site (Blackpool, north west coast, England) in October 2007.

3.3.2 Revetment armour unit dimensions



Specification

Weight	20 t
Material	8 m^3 concrete
Size	5 m x 3 m
Unit No.	00637-07
Date placed	October 2007

Figure 3.5 Dimensions of revetment armour unit (as seen at site in Figure 3.4). Video of transportation and placing at site are in the appendix.

3.3.3 Exposure conditions and test site

The test site has been surveyed and monitored by the author for 8 years which includes 4 years outside the scope of this project (Figure 3.6). The original casting of armour was monitored and the same units have been examined over the years *in situ*. The seawall and revetment armour is subject to cyclic wetting and drying conditions, with a six hour tidal window within which measurements were conducted.

Figure 3.6 Position (St. Chads Headland) of a monitored unit at the study site (arrowed). Hammer and UPV test on other units were also undertaken at Waterloo Headland. The red line indicates the area of the study site for this phase of work. Video of site on disc in Appendix.

The exposure is very harsh due to wave action, which is exacerbated by sand and occasionally shingle/debris from the beach. This attrition meant that, in the design stage, cover loss during service was anticipated. This occurred at many locations; particularly inter-tidal regions, where an early exposed aggregate appearance was noted, and patch repairs have been carried out. The revetment's primary role is coastal protection and as such is subject to the wear associated with tidal and wave action, hence the design team and client expect a degree of surface deterioration.

The position of the concrete in relation to seawater level is a crucial factor, as both agents and deterioration processes vary in nature and intensity depending on the level of moisture in the environment. Also, the position of the pre-cast units in relation to the sea will dictate the constraints on design/construction/maintenance. The following zones are standard terminology:

- the wave wall (featured in Chapter 6) is located in the spray zone above the water, which is not exposed to wave action but is exposed to seawater spray.

- splash zones, which are exposed to wave action.

- the revetment armour units studied at the study site (Figure 3.5) are subjected to daily high tides, in the the inter-tidal zone, which is alternately located above/below water due to tidal water level variation, and is exposed to wave action and currents.

- the submerged zone, which is permanently below water.

- the buried zone, which is below the seabed.

Note that several agents can lead to the same deterioration process, e.g. both chloride ingress and carbonation can lead to corrosion of reinforcement but because of different mechanisms and at different rates. The distribution and intensity of agents and associated effects may vary depending on whether the structure presents a sloping or vertical face.

3.3.4 Site surveys

Visual inspections, which are an essential precursor to any intended experimental programme, have been carried out extensively throughout this research over the construction period of the project. Meetings throughout the construction period with the resident engineer have been extremely informative. Interviews and informal discussions with contractors and operatives have also been found to be very useful.

3.3.5 White light Interferometry

An Omniscan Microxam 5000B, 3D ADE Phase Shift Interface Contrast Optical Profiler was used (Figure 3.7). In this system light from a common monochromatic source is reflected by a beam-splitting device from the observed surface and from a standard plane reference surface, The combination of these two beams gives rise to a pattern of interference fringes, which are in effect contour lines that indicate the relative height of the surface (Veeco Instruments Inc., 2004). One limitation of this technique is that it only allows viewing of a small, and perhaps unrepresentative, sample of the surface. Vertical resolution is 0.1 nm, minimum lateral resolution is 0.11 μm.

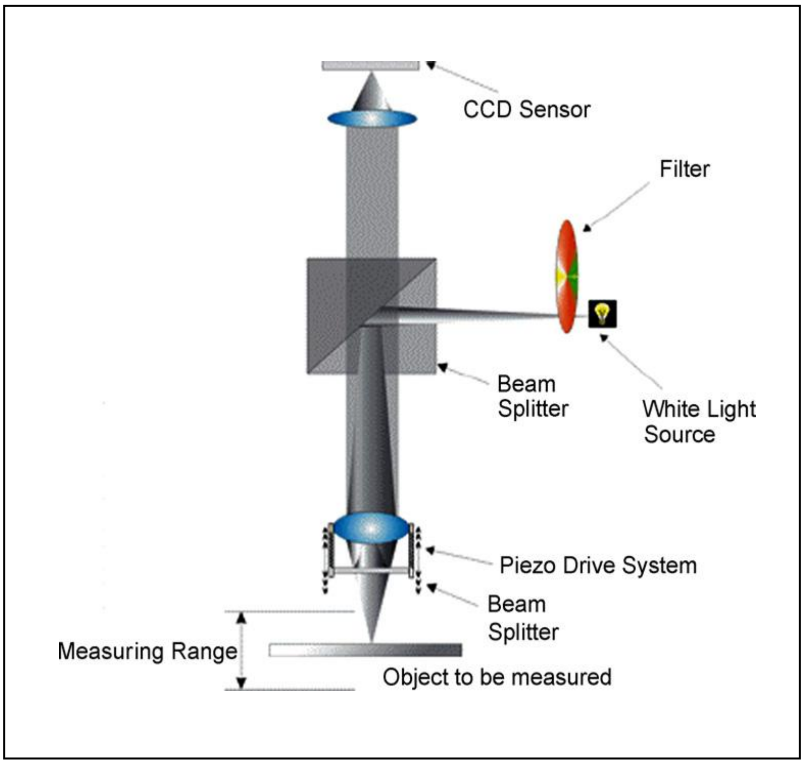


Figure 3.7 Schematic of white light Interferometry used for measuring surface roughness in this project.

3.3.6 Surface roughness analysis

To investigate the surface of the armour units, and to determine any change in topography, surface roughness was used to quantitatively record any change in cleaned areas compared to uncleaned ones. In this work the surface topography of the concrete was defined using the three dimensional average surface roughness parameter (S_a). The change in surface roughness parameters with surface wear over a three year period was observed. This qualitative approach had the advantage of avoiding profilometry relocation techniques, as representative samples from approximately the same area were assessed during the experiment using replicas.

3.3.7 Replication techniques

The replica technique originally used in the aerospace industry, produces a copy of the surface which can be peeled away and examined microscopically in the laboratory.

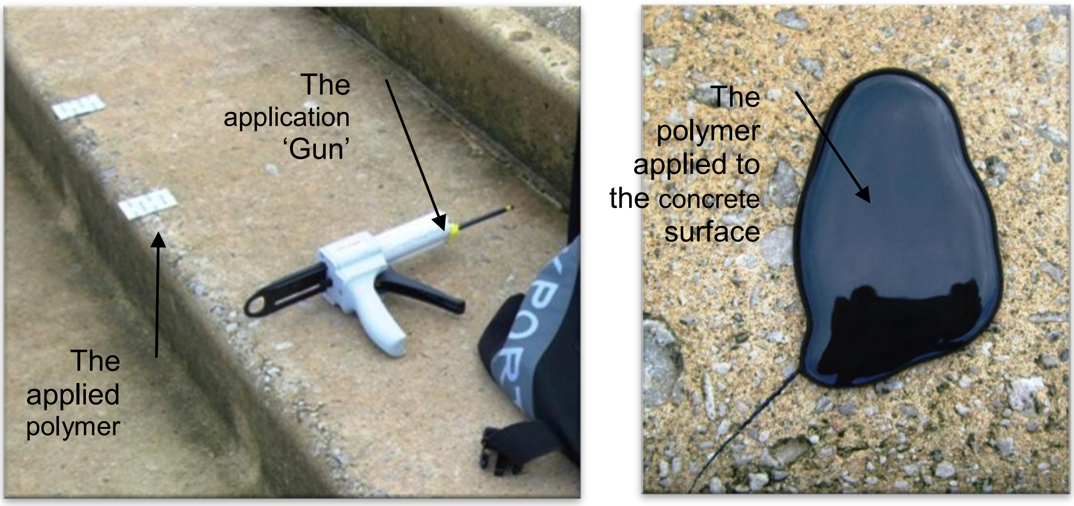


Figure 3.8 Equipment used for the surface replication technique at the study site.

High-resolution, silicone-based replicating polymers (Microset Ltd), have been used for the quantitative, non-destructive evaluation of surface defects in this project (Figure 3.8). It is suggested in BS EN12504-2 (BSI, 2001) if taking rebound numbers, that where the total number of readings (*n*) taken at a location is not less than ten, the accuracy of the reading is likely to be within ±15/√*n*% with 95% confidence. As there is no set guidance for polymer replication of concrete, this idea was also applied to S_a measurement in this study.

3.3.8 Surface Measurement Parameters

The S_a parameter, is the 3 dimension average roughness i.e. the arithmetic mean of the absolute values of the surface departure from the mean plane.

The S_a parameter is defined by:

$$\frac{1}{A} \int_A |z(x,y)| dxdy \qquad \text{Equation1}$$

where A is the sample area and IZ(x,y) is the modulas of the surface height relative to the reference plane.

Other 3 dimensional parameters are defined for parameterising three dimensional arrays, such as those generated by an optical profiler to characterise roughness, spatial and hybrid information. The parameters provide three dimensional equivalents to the standard 2D R parameters (R_a, S_{sk} for R_{sk}, etc.), in additional to information such as directionality relevant to three dimensional surfaces only.

3.3.9 Surface hardness

One of the many factors connected with the quality of concrete is its hardness. This study used data from rebound hardness and pulse velocity to assess durability-related properties. At the present time, the most widespread method for surface hardness testing of concrete is the rebound hammer method. The method used in this project measures the modulus of elasticity of the near surface concrete and has followed the guidance of BS EN 12504-2 (BSI, 2001). The principle is based on the absorption of part of the stored elastic energy of the spring through plastic deformation of the surface and the mechanical waves propagating through the sample while the remaining elastic energy causes the actual rebound of the hammer. The distance travelled by the mass, expressed as a percentage of the initial extension of the spring, is called the *Rebound number.*

A 100 mm x 100 mm template with ten points established was used to guide the instrument (Proceq. Type N-34). All locations and surfaces were dry and free from biofouling. Comparisons to a laboratory Ordinary Portland cement (OPC) and Ground granulated blastfurnes slag (GGBS) mix's were made for the evaluation of any general similarities and differences.

3.3.10 Ultra sonic pulse velocity

For the measurement of concrete uniformity in this research Ultrasonic pulse velocity (UPV) testing is a valuable and reliable application of the method in the field of non-destructive testing.

The Pulse Velocity is recorded by the formula:

$$\textbf{Pulse Velocity (km/s)} = \frac{\text{Path Length (km)}}{\text{Transit Time (s)}} \qquad \text{Equation 2}$$

where the path length being pulse length through the concrete.

The test generates an ultrasonic pulse that is transmitted through the concrete from a transmitter to a receiver and has followed the guidance of BS EN 1250-4 (BSI, 2004). The time taken (kms^{-1}) for the pulse to pass through the concrete is recorded. By measuring the distance between the transmitter and receiver the (UPV) may be calculated (Equation 2). The instrument used (Pundit. CNS Electronics, London.) consisted of a transmitter and a receiver (two probes). The time of travel for the wave to pass from the transmitter to the receiver in a semi-direct path (adjacent faces of the step) was recorded. The probes were set back from the nose of the step 100mm, one along the step (the horizontal plane), the other down the riser (vertical plane). The distance between the two probes (path length) therefore was 141 mm. A comprehensive evaluation of this UPV method is provided by Bungey *et al.* (2006).

3.3.11 Segregation analysis

The importance and effect of segregation on durability has been discussed by Panesar and Shindman (2012). To understand the development of ‘blackspot’ a blemish caused by exposed aggregate particles at the surface, segregation was investigated. Segregation is difficult to measure quantitatively. However indices may be used and have been outlined elsewhere (ACI, 2003). The method does not always reflect actual conditions and may present difficulties locating concentrations of aggregate, which would demand weighing and comparing several samples. A simple test used in this project suggested by Neville (2006) was to vibrate a concrete cube and then strip it and observe the distribution of coarse aggregate: any segregation will be easily seen. Six, steel cast 150 mm x 150 mm sample cubes, were taken at the casting yard, table vibrated (Triton Engineering Ltd), for 5 minutes to simulate actual armour units. They were cured in the laboratory for 28 days, 20°C, and 60% humidity. They were dry diamond cut into 150 mm x 150 mm x 25 mm pieces, (Norton, Clipper brick and tile cutter) to expose a new face, washed and examined.

3.4 Results

Surface roughness measurements from the study site, along with surface hardness, U.P.V., segregation analysis and an armour unit 00367-07 time lapse digital photographic record are presented in this section.

3.4.1 Surface roughness data

Surface roughness measurements were taken at 28 days, 56 days, 1 year, 2 year and 3 year concrete samples (Figure 3.9). Replicas were cast on site on 1, 2, and 3 year placed revetment armour units. When compared with original surfaces the replication techniques had a 25% accuracy level, higher than reported in previous research (Nilsson and Ohlsson, 2001).

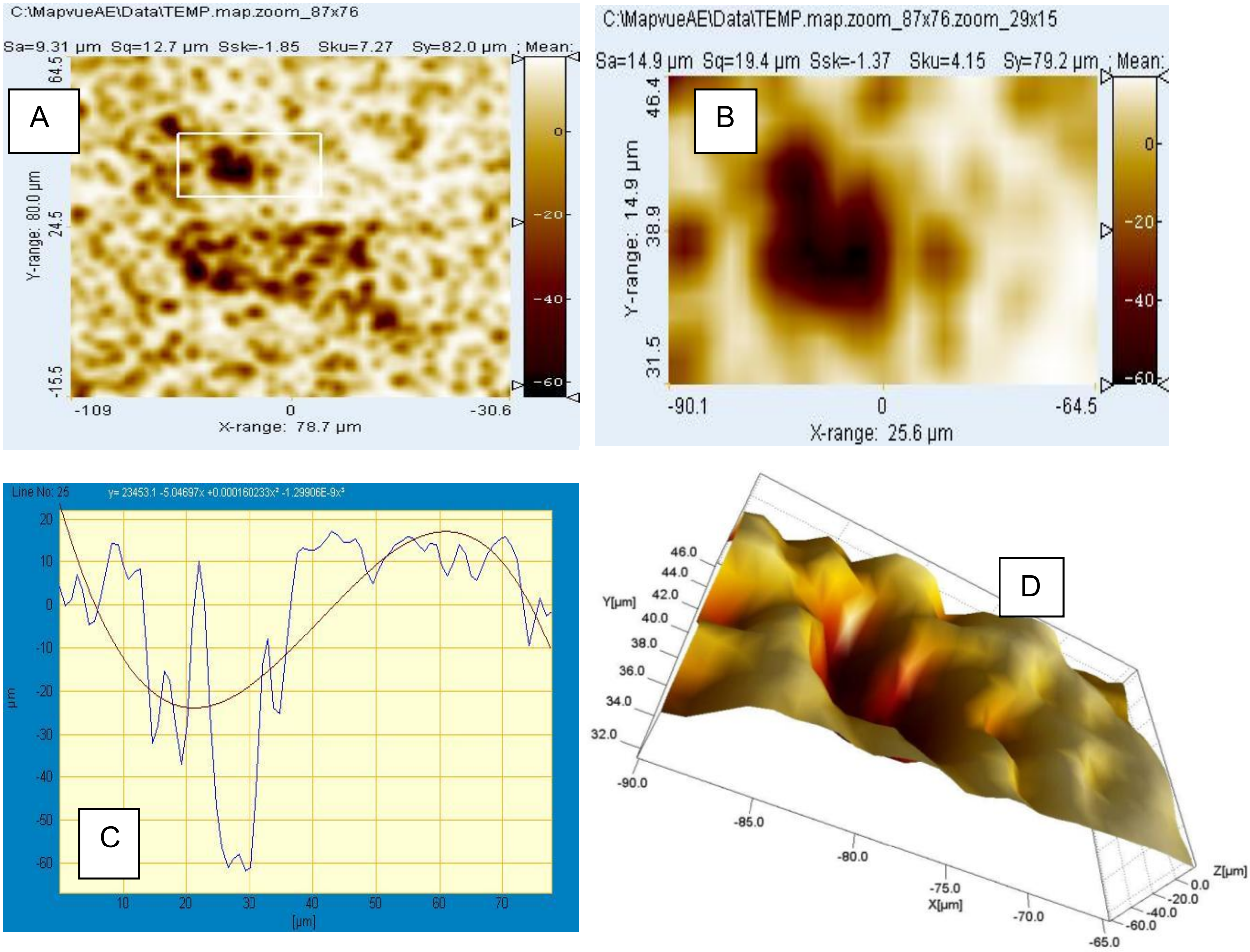
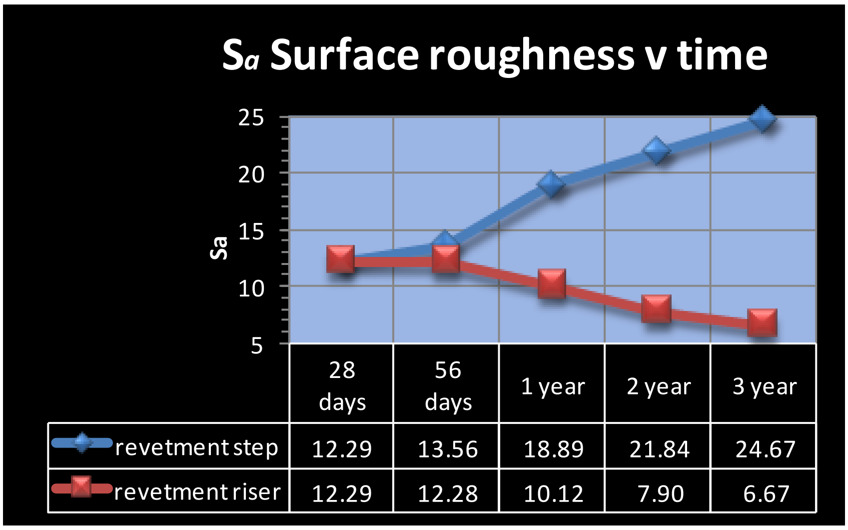


Figure 3.9 Typical Interferometry data on the concrete surface. **A & B**-False colour representation of revetment armour concrete at 28 days. **C**-Profile extraction of revetment armour concrete at 28 days, wavy line refers to the mean. **D**-3D Profile of revetment armour concrete at 28 days, the area measured shows an average roughness of S_a14.9 µm and a total height variation of 80 µm over a 1200 $µm^2$ area

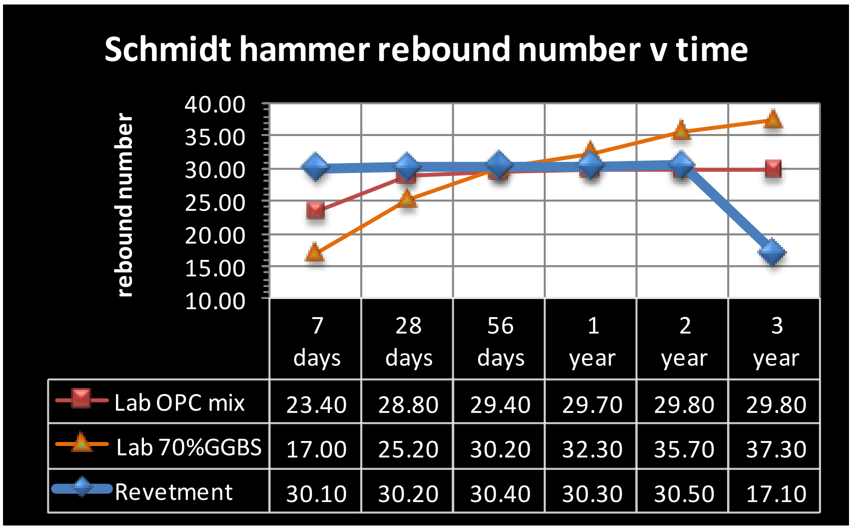


Variability in S_a data	
mean of 10	12.29
standard deviation	*σ 4.61*
variation	21.27
confidence limit	95%±2.85

Figure 3.10 Surface roughness data from armour units over 3 years.

3.4.2 Surface hardness data

Hammer readings from casting to two years remain at approximately 30*r* (correlating to 30 Nmm^{-2} (concrete strength) Figure 3.11) (Bungey *et al.* 2006) but in year three a large reduction to 17*r* was recorded correlating to under 10 Nmm^{-2} (Figure 3.12).



Variability in rebound data	
mean of 10	30.10
standard deviation	*σ*1.71
variation	2.93
confidence limit	95%±1.05

Figure 3.11 Rebound hammer number data from armour units over 3 years.

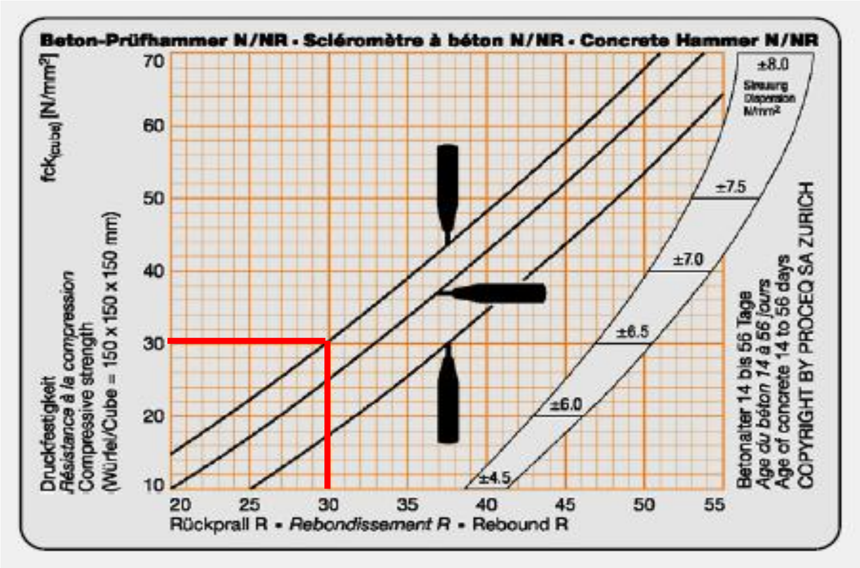
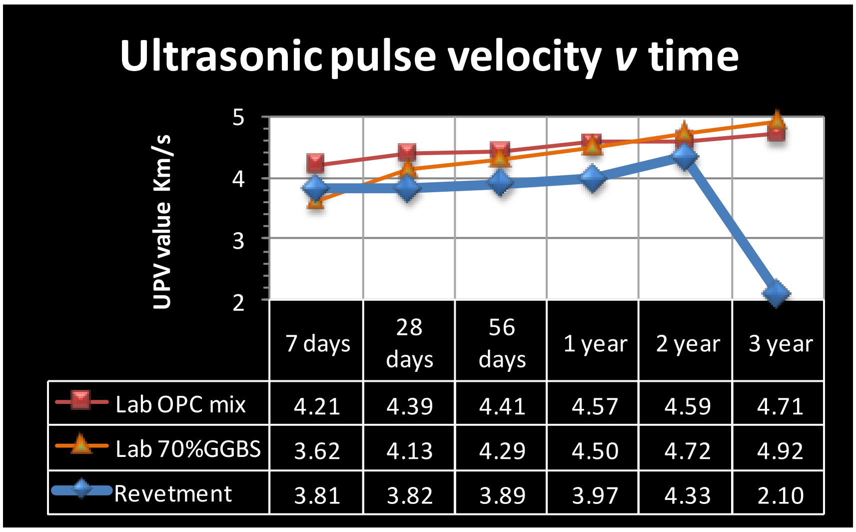


Figure 3.12 Manufacturers conversion curve, which will enable the average rebound value to be converted to an estimated concrete strength in N/mm2 (red line), 30 being the reading for the first two years (Fig. 3.11), a reading of 17 in the final year is off the scale. Source: SA ZURICH (Manufacturers) graph on the instrument.

The influence of aggregate type and proportions can be considerable, and the rebound number will be influenced more by hardened paste. Limestone, as used at the test site, is expected to yield a lower number (Bungey *et al*. 2006). At three years the poor condition of the surface made the further use of the instrument inappropriate because of possible damage to the armour surface. The hardness of the revetment surface is lower when wet than when dry, and the rebound/strength relationship will be influenced accordingly.

3.4.3 Ultrasonic pulse velocity data

High pulse velocity readings are generally indicative of good quality concrete. As the revetment units are subject to a 6 hour tidal window consideration must be made to account for seawater within the units, as moisture, normally present in concrete will encourage a reading up to 5% higher. A plot of pulse velocity contours has given a clear picture of variations (Figure 3.13).



	7 days	28 days	56 days	1 year	2 year	3 year
Lab OPC mix	4.21	4.39	4.41	4.57	4.59	4.71
Lab 70%GGBS	3.62	4.13	4.29	4.50	4.72	4.92
Revetment	3.81	3.82	3.89	3.97	4.33	2.10

Variability in UPV 7 days	
mean of 10	3.81
standard deviation	σ 0.43
variation	0.18
confidence limit	95%±0.26

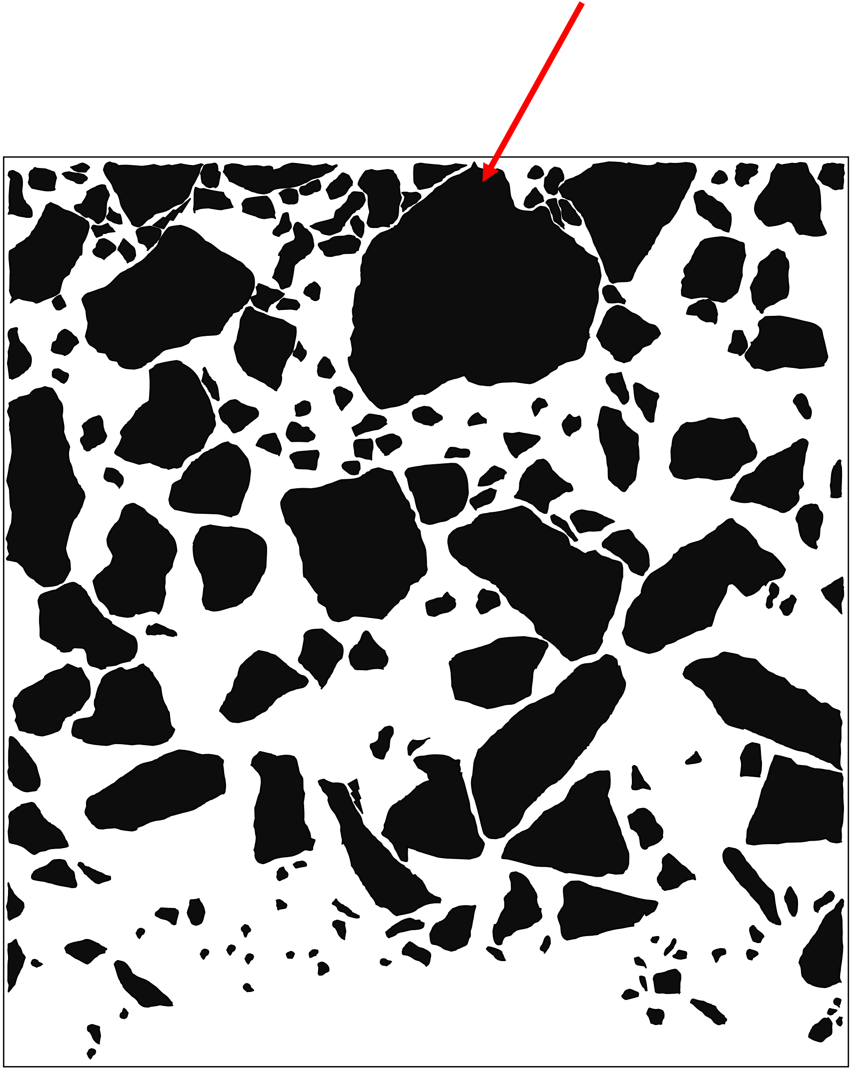
Figure 3.13 UPV data from revetment armour readings over 3 years.

Ordinary Portland cement (OPC) and ground granulated blastfurness slag (GGBS) control samples were not subject to marine site exposure, therefore direct comparisons are not made, but an indication of degradation is apparent. Semi-direct paths were chosen, giving a satisfactory angle of 45° and a modest length for accuracy. Readings were taken on 10 surface dry units, at an ambient temperature of 21°C. At three years, the poor condition of the surface at the nose of the steps (on the ten units being monitored) made the further use of the instrument inappropriate because of liberating aggregate from the revetments.

3.4.4 Site concrete segregation analysis

Figure 3.14 illustrates a typical example of a concrete sample, indicating how larger aggregate tends to settle towards the bottom of the mix. Figure 3.15, a graphical representation of the segregation, shows how the bottom of the cast specimen now becomes the surface. Segregation of aggregate, in the manufacture of the revetment armour units, occurs towards the bottom of the form during compaction, which then becomes the exposure surface, reducing the thickness of cement matrix over the aggregate and increasing the risk of its removal by hydrodynamic forces.

Figure 3.14 Cut cube specimens of site concrete, showing larger aggregate tending to drift to the bottom of the mix. Consequences of aggregate near to the surface were observed at the study site (Figure 3.16).



The revetment units are cast upside down, what was originally the bottom of the form (cube) now becomes the surface of the unit with 1mm protection/surface zone.

Figure 3.15 Binary representation of inverted specimen detailed in Fig. 3.14 The tightly packed and overlapping limestone aggregate now at the exposed surface of the unit. Figure 3.16F is a typical example of aggregate tightly packed at the surface of the armour unit at the study site, particularly at the nose of the step.

3.4.5 Armour unit 00367-07 time lapse digital photographic record

Six digital images of the same unit at the study site over a period of five years.

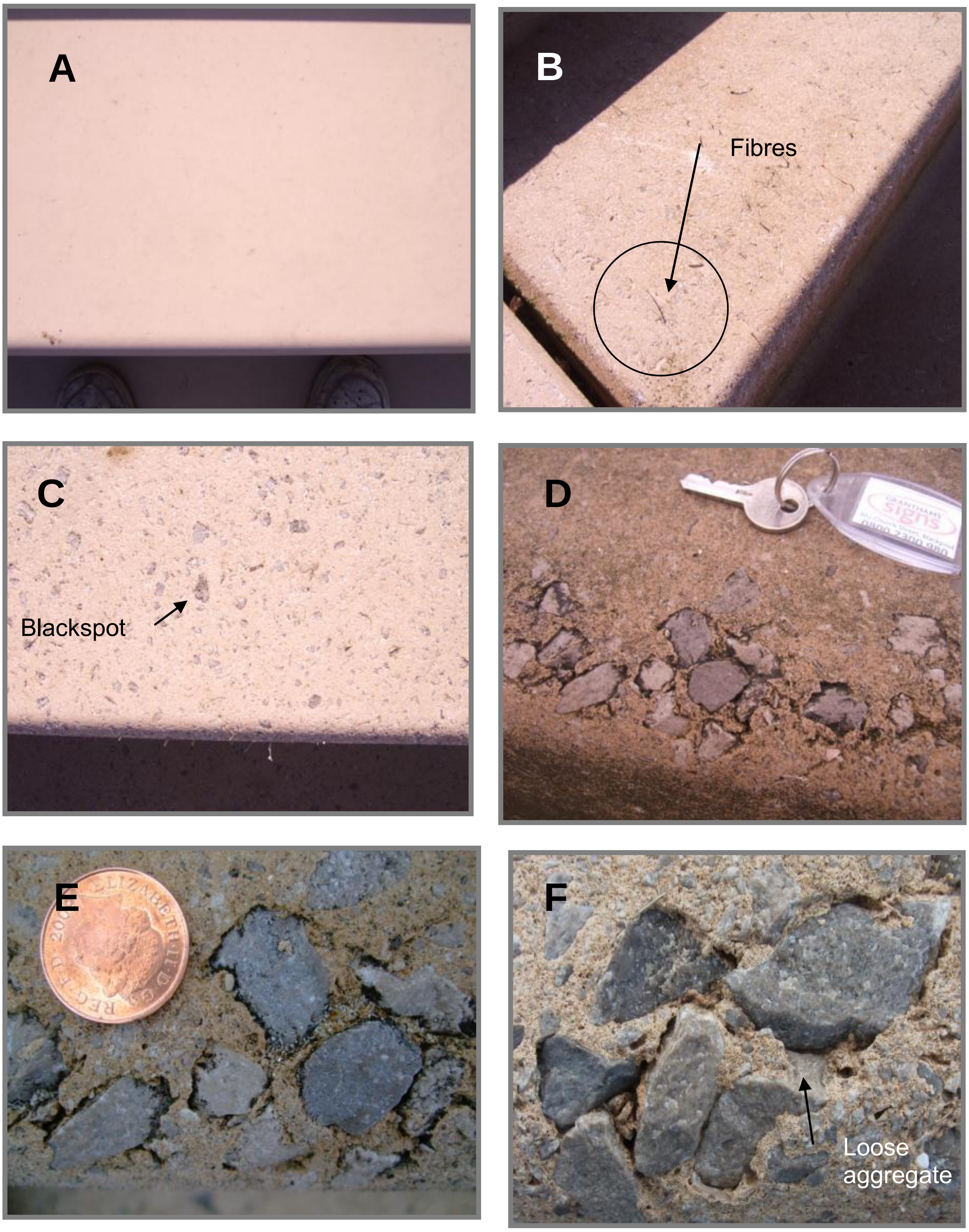


Figure 3.16 Armour unit 00367-07 over 5 years marine exposure. **A**-shows a new armour unit surface. **B**-1yr showing many fibres at the surface. **C**- 2yrs. shows ‘Blackspot’. **D**- 3yrs. Aggregate appears at the surface. **E**- 4yrs loss of fines around aggregate (Two pence coin). **F**- Aggregate tightly packed at the nose of the step due to segregation (Fig 3.14/3.15) leading to material loss and large aggregate liberation.

3.5 Discussion

From the measurements and observations, it is clear that many of the physical and chemical causes of concrete deterioration are present on, or within the concrete examined. Classification of the causes of concrete deterioration observed at the study site into several categories probably has a limited value so failure analysis of the concrete, which was found in some revetment armour units to be in an advanced state of degradation (Figure 3.16). This has demonstrated a number of interrelated chemical and physical phenomena, of a synergistic nature. For example, fibres protruding from the surface of the armour at various orientations has encouraged micro-cracking at the entry points (Figure 3.16-B). As these exposed fibres move under tidal loading and deteriorate, the concrete surface around the fibres breaks allowing loss of water-tightness leading to the increase of permeability, further paving the way for deleterious chemical interactions between seawater and cement hydration products. Additionally this fractured area will allow the penetration of micro-organisms into the material, something that will be studied and discussed in chapter four.

From Figures 3.14 and 3.15 it is apparent the manufacturing process used in the pre-cast armour units has resulted in large aggregate lying very close to the surface, in some cases less than 1mm (Figure 3.15). The lack of a protective surface zone exposes the material surface to the detrimental physical effects of water from wave impact and power washing. However, categorisation of the processes of the concrete deterioration studied at the site, into physical and chemical as shown in the results, does have merit. It makes it easier to look at the various phenomena involved, one at a time, in order to understand the causes and consequently, the control of the causes. It seems that the physical and chemical processes of seawater attack manifest themselves either as cracking of concrete (Figure 3.16-B) or as loss of material mass (Figure 3.16-F). Although there are several phenomena capable of causing cracks in concrete, they are not equally important. At the study site, cycles of wetting and drying, heating and cooling were observed which will contribute to the concrete armour deterioration due to a combination of stresses generated by these processes. Thermal expansion and contraction will also encourage surface cracking around exposed fibres. Modern marine structures, such as concrete platforms in the North Sea, are built with concrete mixtures that are relatively impermeable and, therefore, less vulnerable to chemical attack. Such concrete is very expensive and can not be viable to all construction projects.

The results from the experiments undertaken and described earlier in this chapter will now be briefly discussed, however the results from the whole project, will also be discussed collectively in chapter eight. An understanding of the causes of deterioration observed throughout this research will provide a logical background for their control.

3.5.1 Surface roughness

Surface roughness (S_a) doubled from 12.29 μm to 24.67 μm in three years on the revetment steps. These steps had been power washed on approximately 150 occasions at 1200 psi (Figures 3.1 and 3.2). The risers of the steps are not power washed and obviously are subject to the same tidal impacts, but showed a smooth erosion pattern; reducing in S_a from 12.29 μm to 6.67 μm (Figure 3.10). Laboratory tests by other workers confirmed the implication of roughness on the biofouling rate (Tran *et al*. 2012). When numerous anchorage points are offered, the adherence of algae is promoted (Tran *et al*. 2012). Thus the latency time is shortened and the rate of colonization is increased. Particular attention has to be paid to a surface finish: a slight increase in roughness might abruptly increase the susceptibility to colonization by microorganisms (Tran *et al*. 2012). The replication techniques, not usually associated with concrete surfaces have proved to be extremely useful and adaptable (Figure 3.8). The ability of polymers to provide a visual microscopic picture of 3 dimensional surfaces whilst at the same time, yielding accurate dimensional data, has been useful as a permanent record for subsequent reference or monitoring purposes and lays the foundation for the development of a new non-destructive testing method for concrete surface analysis (Hughes, 2011). Replicating compounds used have a resolution better than 0.1 microns (Rollins, 2001). One of the main concerns when working with replicas has been accuracy. However, a comprehensive study of three different materials used for surface roughness replication on five different types of machined surfaces was offered by Nilsson and Ohlsson (2001). Measurements on site from the ‘step’ and ‘riser’ (Figure 3.10) were taken to distinguish between cleaned and uncleaned areas. All areas were exposed to the tide. The scatter also suggested that a considerable variation of S_a would be obtained from ‘identical’ concrete.

3.5.2 Surface hardness

Surface hardness values remained steady for two years and then reduced substantially in the third year. In general one would expect a relatively higher rebound number of 30*r* for a C40/50 mix with a pre-cast steel formed finish for two years. Segregation analysis and the appearance of ‘Black spot’ (Simpson, 2008) indicates the surface zone is shallow with little or no protection over the aggregate and this may be a factor in low readings for the initial two years (Figure 3.11), calculated from manufacturers graph on the instrument (Figure 3.12). This lower reading may result from the fact that the synthetic fibres exposed at the surface are acting as impulse absorbers. This is an enhancement in the design stage of coastal structures subject to cyclic impacts and is seen as a useful property provided the fibres are fully embedded in the cement surface. At three years, a rebound number of 17*r* correlating to under 10 Nmm^{-2} represents a significant reduction in surface hardness and would tentatively indicate a large reduction in compressive strength. An area or band of liberated aggregate 100 mm wide from the leading edge of the step made this area unsuitable due to the fact that the hammer would further damage the surface. Abrasion resistance is generally affected by the same influences as surface hardness, and research by Chaplin (1980) has suggested that the rebound number may be used to classify this property. It is also reasonable to suppose that other durability characteristics that are related to a dense, well cured, outer surface zone may be similarly classified. However, the substantial reduction recorded in the third year indicates further investigations are required.

There are several factors other than concrete strength that influence rebound hammer test results, including surface roughness and finish, moisture content, coarse aggregate type, and the presence of carbonation. Surface roughness has been shown to have doubled in some areas and this may have affected the rebound number. Variations in compaction, uniformity of the concrete mix will also affect the rebound number. However, a considerable 50% reduction in compressive strength was detected. Although compressive strength directly is not an important criterion for the revetment concrete, the author notes that marine concretes with low permeability and a high stability, normally possess greater than 60MPa strength and therefore, the compressive strength of the armour unit concrete can be used as a basis for proportioning and quality control. Thus after only three years exposure, the concrete has deteriorated and from a long term durability viewpoint, an expected design life of 100 years appears ambitious.

3.5.3 Ultrasonic pulse velocity

Ultrasonic pulse velocity information has enabled the variations in concrete quality to be assessed, and areas of poorer quality concrete to be identified. The measurement of UPV over three years (Figure 3.13) has shown that more detailed examination is necessary. Since the pulse cannot travel through air, the presence of a crack or void on the path will increase the path length, as it goes around the flaw, and increase attenuation so that a longer transit time will be recorded. The pulse velocity obtained is lower than that of the control. Consideration must be made to the influence of seawater inside the units, as the presence of moisture, normally in concrete will give a higher reading (Bungey *et al*. 2006). Since compression waves will travel through water, it follows that this philosophy will apply only to cracks or voids which are not water filled. Similar research (Tomsett, 1980) has examined this in detail and concluded that although water-filled cracks cannot be detected, water-filled voids will show a lower reading than the surrounding concrete. Experience from site, indicates that poor quality concrete in general becomes dirtier, encourages more biofouling and develops more colonisation than dense concrete, furthermore these phenomena provoke and encourage each other. UPV values have remained steady for the first two years at 3.81 – 4.33 $\mathrm{kms^{-1}}$ and have reduced substantially in the third year to 2.1 $\mathrm{kms^{-1}}$. High pulse velocity readings are generally indicative of good quality concrete and a general relation between concrete quality and pulse velocity has been shown (Leslie and Cheeseman, 1949). The results of this investigation indicate the concrete initially showed a good quality but reduced to a very poor one. Variability in UPV recorded at 7 days (from a mean of 10 readings) was 3.81 $\mathrm{kms^{-1}}$, the standard deviation (σ) 0.43 gave a variation 0.18, hence a confidence limit at 95% ± 0.26 in agreement with the literature.

The difference in UPV compared with the OPC of the control mix may be due to the fact that the density in the revetment mix has been altered by the presence of the fibres, the velocity changing as it encounters each fibre. The reduction in UPV is particularly significant suggesting the core of the concrete may be affected by the weakening process.

3.5.4 Segregation of aggregate

The revetment units when set down at site were in pristine condition (Figure 3.16-A). The surface 'as struck' seemed to portray a durable, quality finish. However, after only months of exposure the surface layer was eroded, exposing the aggregate (Figure 3.16). This surface blemish is normally considered as a function of coarse aggregate particles at, or near, the surface is referred to as 'black spots' (Simpson, 2008) (Figure 3.16-C). There are a number of other blemishes believed to be related to aggregate particles situated close to the surface of concrete (Figures 3.14 and 3.15). One such blemish is considered to be caused by the loss of cement over the aggregate particles. When 'black spots' occur the thin layer of cement over the coarse aggregate particle may be worn away or mechanically removed, leaving a shallow depression exposing the aggregate particle. This effect which has been observed at the study site, is more likely to occur where flatter pieces of limestone aggregate are orientated parallel to the armour surface. Shrinkage of the cement layer may show as a star pattern above the coarse aggregate particle, which can be worn away. Coalescence of a number of these blemishes, where loss of the surface occurs, may appear as a delamination. The placing, compaction and finishing operations should produce a continuous uniform layer of cement of adequate thickness at the surface (Simpson, 2008), covering the coarse limestone aggregate particles. There are a number of potential factors causing a high concentration of aggregate at the surface, for example, congestion around the nose of the step when cast, caused by the aggregate travelling to this area under vibration.

3.5.5 $CaCO_3$ crystal formation and potential impairment of synthetic fibre bond

The Scanning Electron Microscope micrographs reported here confirmed the formation of crystals and are representative images of growth within the concrete matrix examined (Figure 3.17). Methodology for the scanning electron microscope (SEM) and energy dispersive X-ray analyser (EDAX) is detailed in Chapter 4, Section 4.2.5. Structures observed on direct examination were small clusters of $CaCO_3$ crystals attached to micro synthetic fibres within the matrix of the cement to a depth of 20mm from the surface (Figure 3.18). The individual crystals often formed uniform collections, in some places several μm thick, localised at the surface of the concrete armour. Figure 3.19 shows the typical robust attachment of $CaCO_3$ to the micro fibres within the surface of armour concrete.

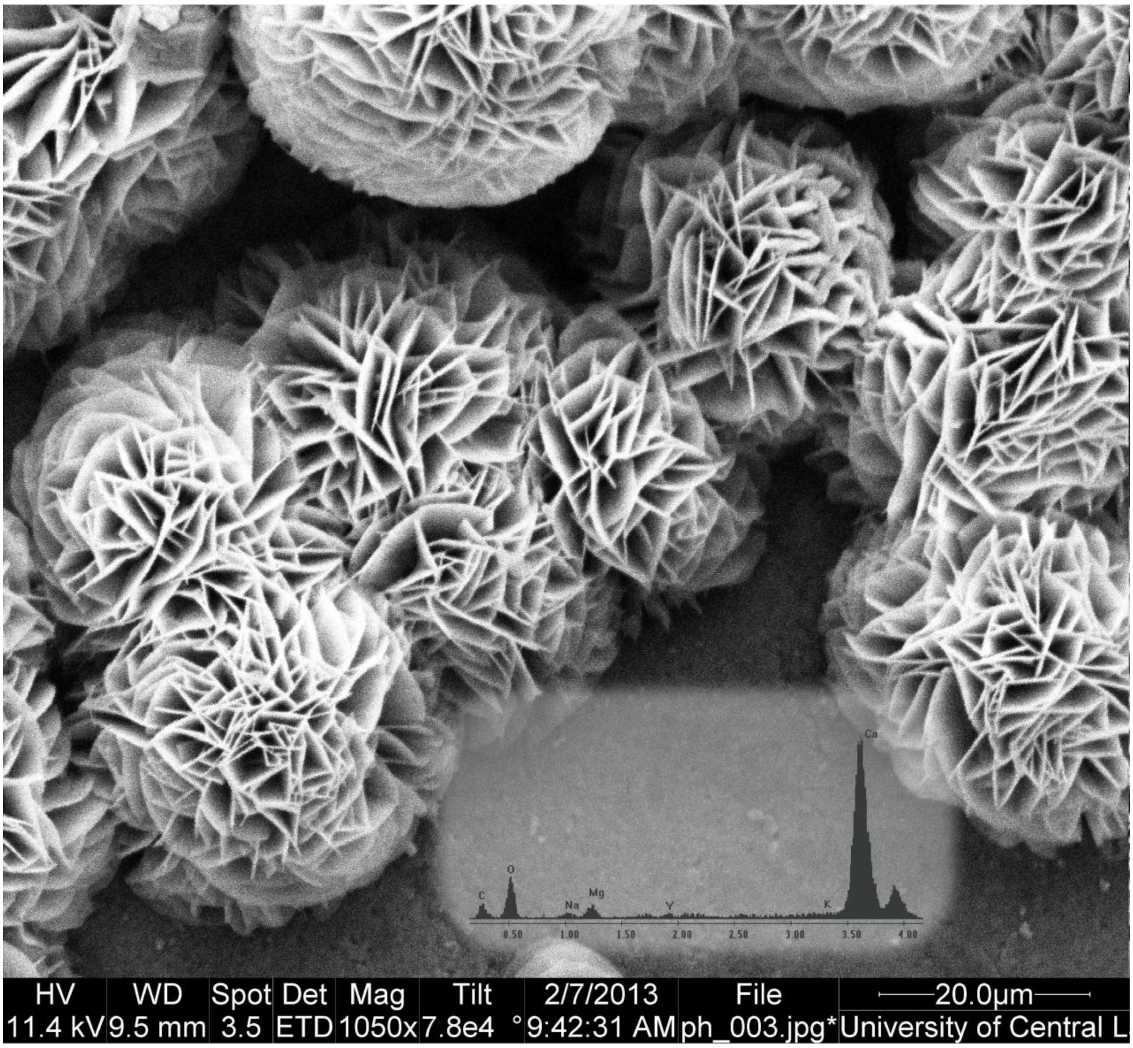


Figure 3.17 Scanning Electron Microscope Micrograph: Clusters of fully formed $CaCO_3$ crystals of 'rosette' habit within the cement matrix. Energy dispersive X-ray analyser data (inset) indicates that the 30.22% Ca. (weight), 13.35% C., 48.96% O. and 3.53% Mg. were consistent with $CaCO_3$

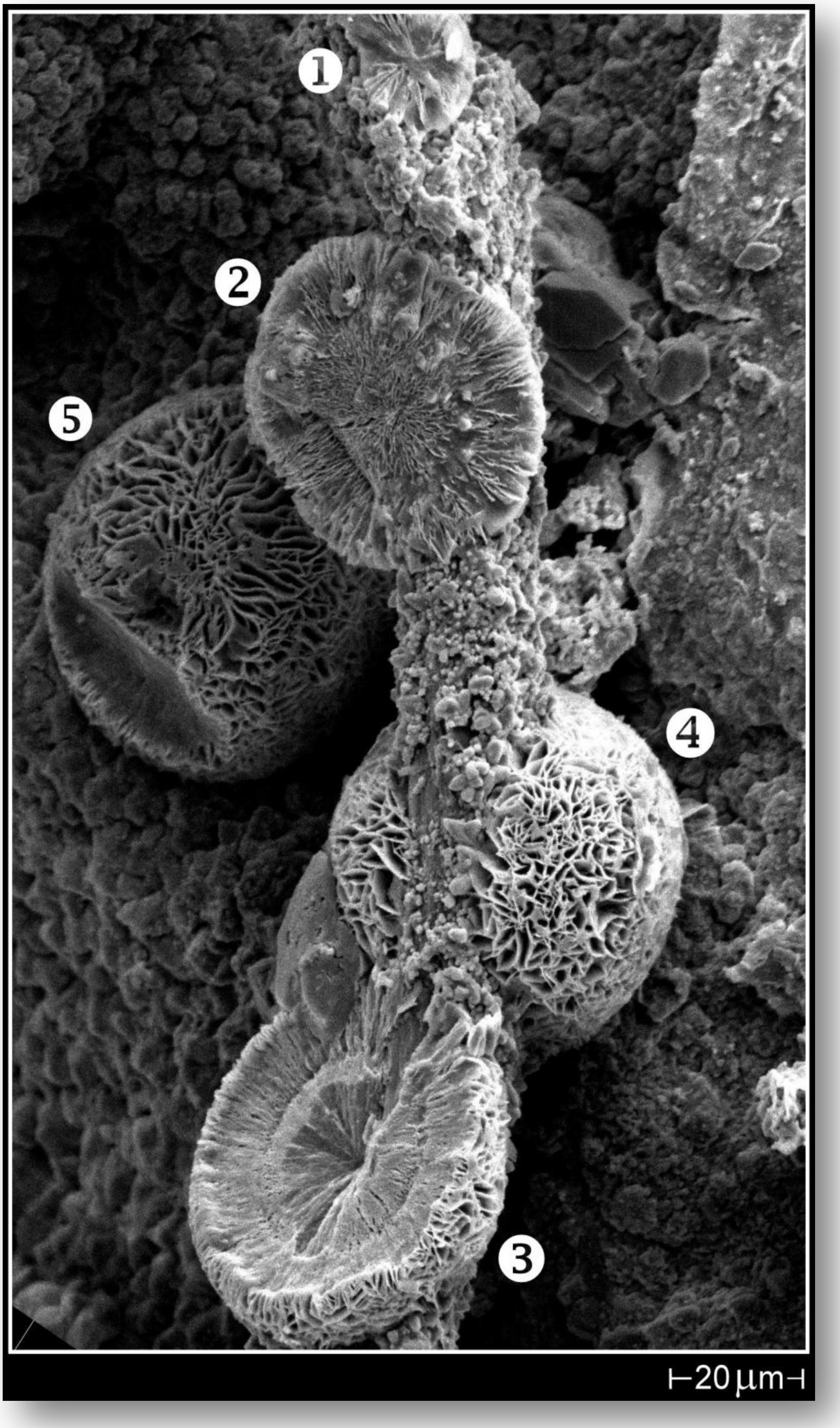
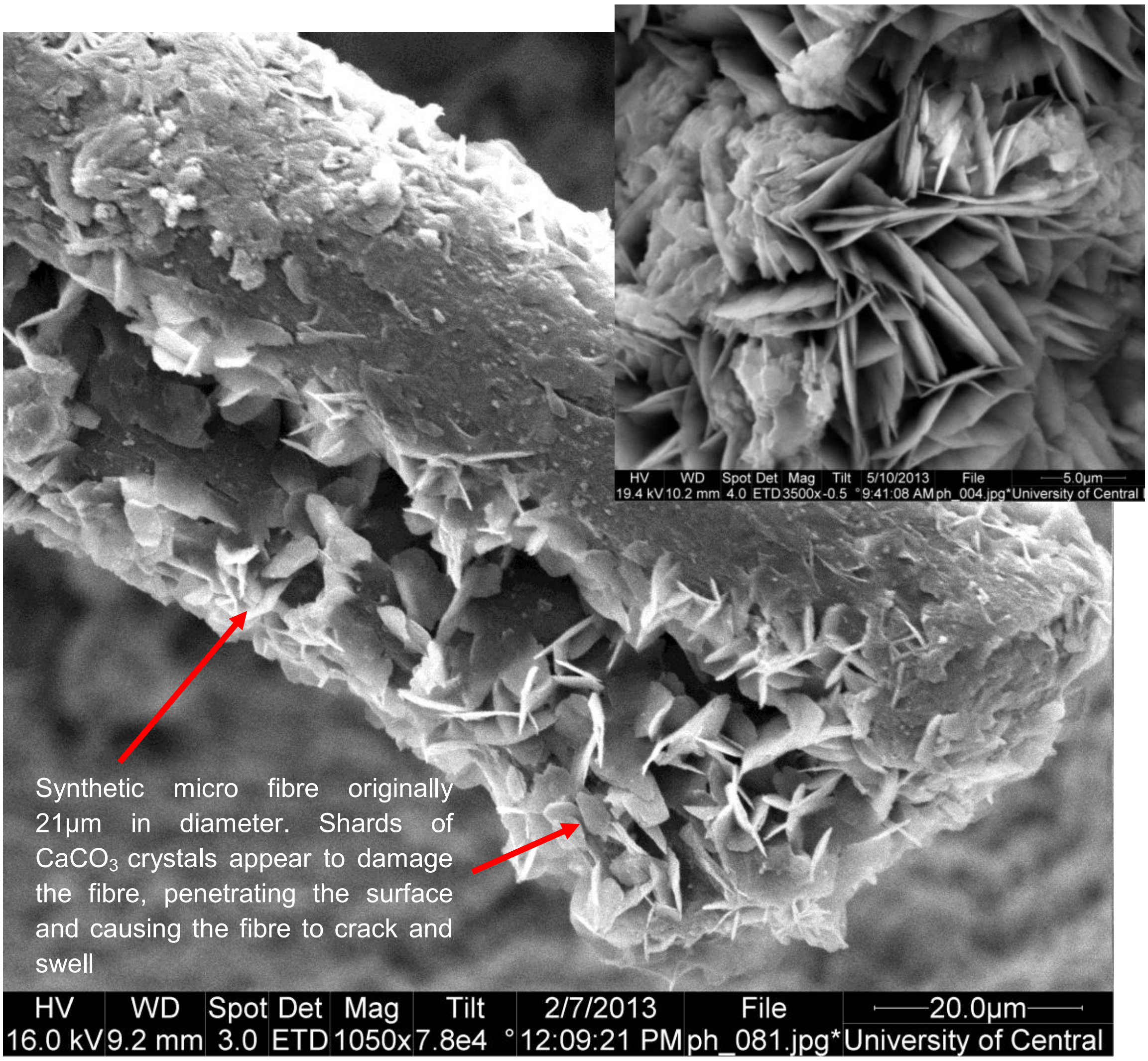


Figure 3.18. SEM micrograph showing several stages of growth of crystals attached to a micro fibre (fibre diameter 22 µm). **1**. Illustrates initial growth. **2**. Depicts established, early formation. **3**. Shows central attachment to the fibre. **4**. Shows deformed crystal pushing against cement matrix. **5**. Depicts a fully formed crystal detached from the fibre.



Synthetic micro fibre originally 21µm in diameter. Shards of $CaCO_3$ crystals appear to damage the fibre, penetrating the surface and causing the fibre to crack and swell

Figure 3.19. $CaCO_3$ crystal attachment within micro fibre, original size of 21 µm. Due to splitting and subsequent attachment the fibre has increased in diameter by approximately 50%. Inset: Clusters of fully formed $CaCO_3$ crystals at the base of the micro fibre shown in the main image.

Recent research has proposed findings that crystallisation plays an aggravating role in the failure of concrete (Liu *et al*. 2010). The crystals observed initially appeared to assemble in an unorganised manner. Closer evaluation, however revealed that the crystal arrays are actually organised, periodically repeating themselves three dimensionally, as one would expect in crystals. Figure 3.17 shows the flower-like structure, similar to that of desert rose structures occurring among gypsum and barite crystals in arid areas (Jafarzadeh and Burnham 1992). The SEM micrograph shows an interesting spherical morphology, which consists of a rosette-like microstructure of irregular-shaped columnar pores with crystalline walls interconnected to each other. The crystal samples studied were uniform in appearance with an average size of about

50 μm in diameter. EDAX analysis indicated that the 30.22% Ca (weight), 13.35% C and 48.96% O were consistent with $CaCO_3$.

The exposure of polymers with crystal attachment and growth may lead to a weakening of the bond between materials. SEM analysis into fibre performance and the change in their physicochemical properties has been observed (Artham *et al*. 2009). Associated with marine sports, the washing of equipment after use is mandatory due to the potential damage from crystals. Recent research in this area investigated polypropylene fibres within sports rope, SEM examinations revealed that salt crystals were the main contributors to fibre damage (Koohgilani, 1998).

Figure 3.7 shows crystals in a plate like (flaky) habit in several stages of development that grew in a layer-by-layer fashion. The occurrence of crystalline formations, particularly attached to fibres (Figure 3.18) accelerates the debonding of the polymer fibre, making it more susceptible to tidal impact or power washing. Due to the non-polar nature of the polypropylene fibres, and their lower surface free energy, compared to cement paste, a gap is generated between the fibre and the cement matrix (Faran, 1996). In this void, moisture could permeate around the fibres, thereafter, following submersion; drying will facilitate disruptive crystals growing at the fibre/cement Interface Transition Zone (ITZ).

Figure 3.19 illustrates crystal growth, of plate like $CaCO_3$ crystals similar to observations elsewhere (Sunagawa, 2005). The formation of insoluble calcium carbonate from calcium hydroxide in hydrated cement creates an expansive force when carbonation takes place. Other workers studying gypsum in the ITZ also found deposits of gypsum up to 50μm wide. The crystallization pressure produced tensile stresses causing disruptive expansion (Bonen and Sarkar 1993). Previous research by Winkler (1975) lists a number of salts that are known to cause a cracking and spalling type of damage to rocks and stone monuments, which includes gypsum. This phenomenon was also attributed to the large pressures produced by crystallisation of salts from their supersaturated solutions. SEM has enabled observations of several stages of attachment and growth.

3.6 Conclusions

Various techniques were used to investigate how the surface of the units performed, and to build a more complete picture of their performance over three years. The surface of the precast elements have been investigated, examined and monitored for seven years at a marine test site. Power washing appears to accelerate the degradation of the concrete which is brought about by a combination of biotic and abiotic factors.

The armour units have been affected by regular power washing indicated by the surface roughness of the (horizontal) steps having doubled over a three year, while the risers have become smoother over the same period. The significant reduction in the rebound number implies a 50% fall in compressive strength. The reduction in UPV indicates the units are in a very poor condition and is particularly significant suggesting the core of the concrete may be affected by the weakening process. Segregation towards the bottom of the form during compaction, which then becomes the exposure surface, reduces the thickness of a cement surface zone over the aggregate and increases the risk of its removal by high pressure cleaning. From a long term durability viewpoint, the collected data suggests an expected design life of the armour units of 100 years appears to be extremely ambitious.

This research has generated new insights into surface degradation and opens up the prospect of more detailed surface analysis on the performance of fibre reinforced marine concrete. This phase of the research has measured the reduction in the quality of the concrete surface and indicates how aggressive management of biofouling on marine concrete sea defences at a study site may actually accelerate wear and encouraged further colonisation, with long term implications for the concrete durability. Surface analysis has also laid the foundation for the next phase of the research which will investigate algal colonisation.

Potential influences of crystals as reported here for the first time, on synthetic fibres within marine concrete could have an effect on the long term durability of concrete sea defences and clearly warrants further investigation.

3.6.1 Research constraints

The author recognises that the site-specific differences in biofouling management and the type and number of species that grow on concrete structures can be important, and also to the design and materials used in the construction of the structures themselves influence this process. Consequently this case study is limited in that it involves only a single site and, therefore, is not representative of marine environments in general, but the conclusions relating to the mechanisms of material loss remain generic.

Chapter 4

The algal colonisation of concrete revetment armour – phase 2

The tubular fronds of Ulva are bright green, and the gas
they contain makes them swell out in water,
but when dry they deflate and flatten.

I.O. Evans
The Observers Book of the Seashore 1962

4.1 Introduction

This chapter reports on an investigation into the effects of algal colonisation on a concrete surface. Microscopy, surface energy determination and porosity testing were undertaken to assess the effects of colonisation on the concrete. A survey of algae at the study site was undertaken (Appendix 1) to enable the identification of the dominant algal genus observed in concrete specimens, in order to interpret the analysis of microscopic observations, leading to a further understanding of a large diverse marine community at the site.

Bioreceptivity, which refers to the susceptibility of a material such as concrete to colonisation by living organisms relates to the surface energy, moisture content, structure and texture of the material. Materials that have a high surface roughness and high macroporosity such as concrete, show high bioreceptivity.

4.1.1 Aim and objectives

The aim of this phase of the study, was to observe marine biofouling, specifically algal colonisation at the fibre and aggregate-cement matrix interface, and to see how its presence may affect performance in respect to the durability of the structure. This examination of the bond between fibre/aggregate, cement and microorganism enables the further understanding of this interaction. To achieve this aim specimens from precast elements were examined microscopically and monitored for seven years at a marine test site. The environmental performance of the fibres and aggregate was observed before and after tidal impact, power washing and colonisation.

Current algal fouling at the study site (Figure. 4.1), is the focus of this chapter, there now follows a review, specific to this phase of the study.

Figure 4.1 *Ulva* firmly attached to armour surface (after 2 years exposure) in the splash zone (Two pence coin).

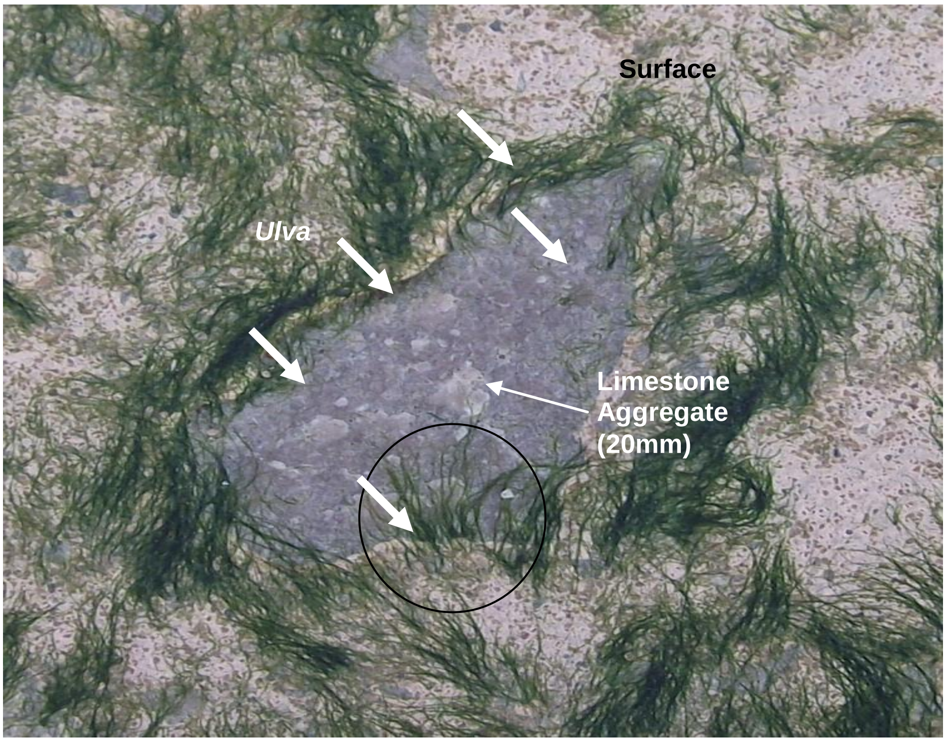


Figure 4.2 Armour surface as seen in Figure 4.1 after power washing. Hair-like filaments of *Ulva* often remain attached. Arrows depict filaments growing ‘from’ the substratum, out from the interface of the aggregate and cement matrix.

4.1.2 Colonisation

The low installation costs, maintenance, flexibility, durability and high quality finish of precast concrete-stepped units used as revetment armour in a marine environment, make them increasingly more popular in the construction of sea defences. This proliferation of concrete coastal protection has transformed sections of naturally dynamic coastlines into artificially static material. These are colonised by epibiotic organisms such as algae (Figure 4.1), that are commonly found on natural rocky habitats (Blomster *et al.* 1998; Brodie *et al*. 2007). The colonising marine epibiota of concrete coastal defence structures, and their effect on concrete durability has received limited attention in academic literature.

Microbial endoliths occupy distinct ecological niches inside rocks in terrestrial, freshwater and marine environments (Hellio and Yebra 2009; Khattar *et al*. 2009; Durr and Thompson, 2010). Cryptoendoliths inhabit existing spaces inside porous rocks, whereas euendoliths penetrate calcareous substrates actively and leave microscopic boring traces (Golubic, 1981). The fouling of concrete surfaces by microorganisms can have detrimental effects, accelerating deterioration (Gaylarde and Morton, 1997). Microorganisms such as bacteria, fungi, algae and lichens have been widely reported to be involved in the deterioration of concrete (Gaylarde and Morton, 1997; Lisci *et al*. 2003; Giannantonio *et al.* 2009; Jayakumar and Saravanane, 2009). Important biological interactions include competition for resources such as food, nutrients, light and space, grazing and predation (Hawkins and Hartnol, 1983). Once established on concrete revetment armour steps, growths form a slippery surface and constitute a danger to the public. Growth of green ephemeral algae has been a major problem for local beach tourism; these algae can be partly removed by power washing (Figure 4.2), as described in Chapter 3 and washed up the shore, adversely affecting the amenity value of the beach from where they needed to be periodically removed. More direct damage can be caused to the concrete itself by the acids and other metabolites produced by the organisms, which together with the ability of some species to tunnel into surfaces; (Figure 4.3), leads to degradation, increased porosity and decreased durability (Allsopp *et al*. 2004).

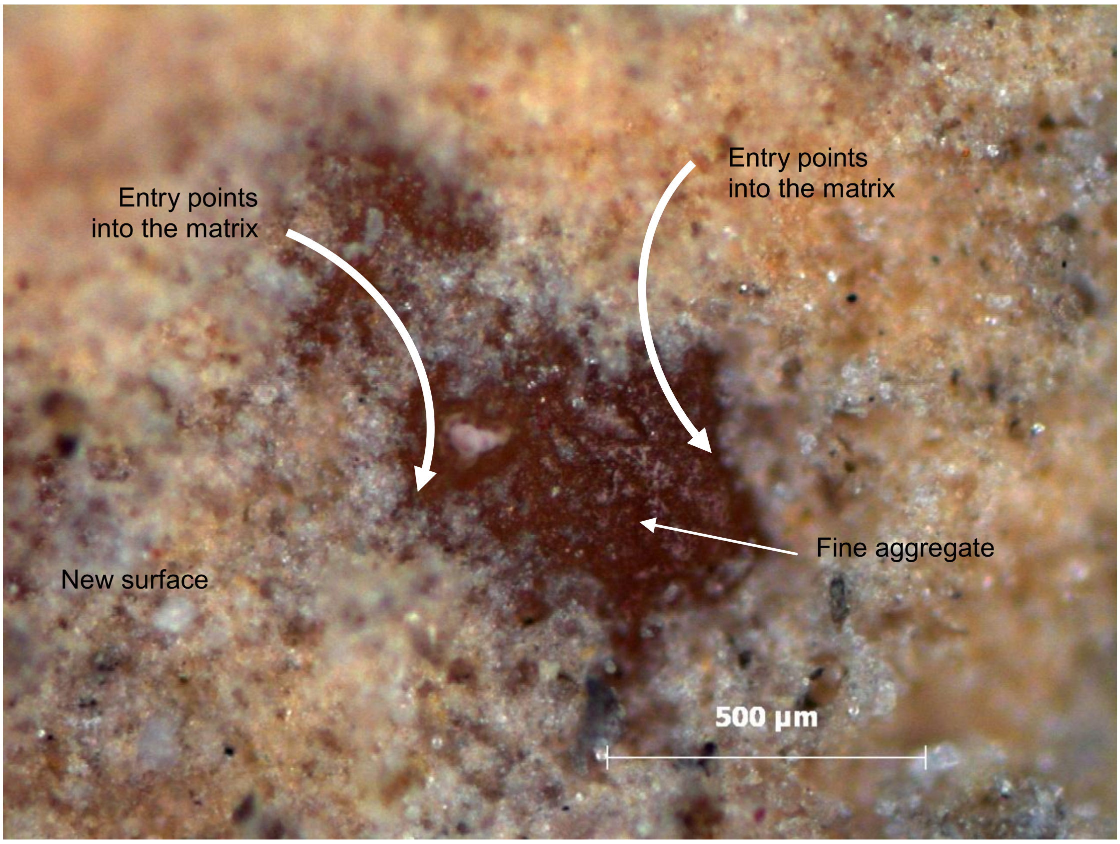


Figure 4.3 Typical representation of a new surface of the revetment armour. The white arrows depict possible entry points for microorganisms into the matrix.

Experimental evidence indicates that porous concrete creates a favourable environment for microbial colonisation, indicating that aquatic organisms including algae adhere to both the inner and outer surfaces of this material (Tamai *et al*. 1992). The mechanism observed and presented in this study occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth (Morton, 2003). As part of an E.U. funded project (DELOS, 2002), several coastal defence schemes were investigated in the UK and throughout Europe, targeted studies were carried out on the bioerosion of concrete structures. A survey of 80 (UK) coastal defence structures was undertaken, and surprisingly no sign of bioerosion was detected; possibly due to the poor selection of study sites.

4.1.3 Fibre reinforced concretes

Well compacted and cured reinforced concretes, seem to possess excellent durability as long as the fibres remain protected by the cement paste (Mehta and Monteiro, 2006). Deterioration of concrete structures usually starts at the surface and progresses into the structure. It is therefore, the skin of the concrete that is the major factor influencing the longevity of the material. Synthetic fibre-reinforced concrete was used only recently in the manufacture of the revetment armour in a marine environment (Rieder, 2007). Therefore, there is little information on how the physical properties of synthetic fibres change with time or how long-term mechanical performance of fibre-reinforced marine concrete may be affected.

Synthetic fibres, used at the test site during this research, have become more attractive in recent times as reinforcements for cementitious materials. Research by Al-Tayyib and Al-Zahrani (1990) has suggested they may retard the deterioration process at the surface of concrete. Synthetic fibre-reinforced concrete utilises fibres derived from organic polymers which are available in a variety of formulations and in two basic size ranges, namely macro and micro (Further details of fibres used at the study site are in Table 1, appendix 4). Synthetic fibre of types used in cement-based matrices includes acrylic, aramid, carbon, nylon, polyester, polyethylene and polypropylene. Macro synthetic polymer fibres have the potential to improve the post-cracking properties of hardened concrete, as set out in the sector guidance (Concrete Society, 2007). Their use at the test site as an alternative to nominal bar or fabric reinforcement is a relatively recent development (Rieder, 2007). Micro synthetic fibres, also used at the site, can be used in ground-supported slabs to reduce plastic shrinkage cracking and plastic settlement cracking.

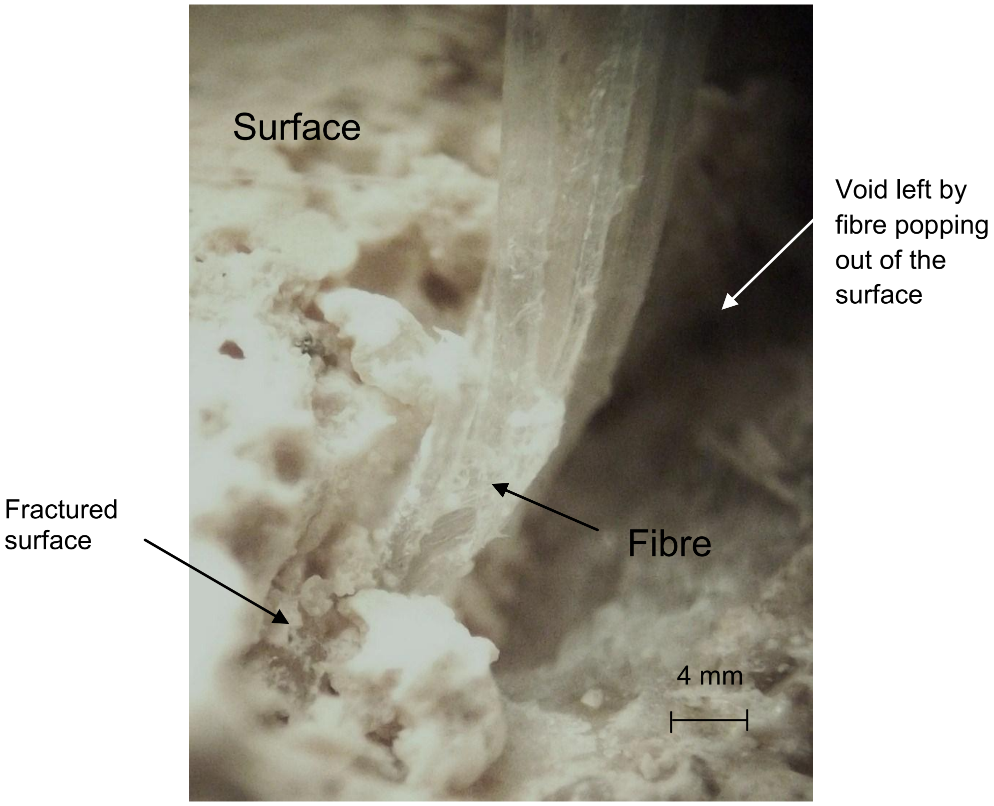


Figure 4.4 Macro synthetic fibre at the surface of new concrete in vertical orientation. Many fibres at the study site were observed to be exposed at the surface of the armour. (Digital image).

Polypropylene fibres have some unique properties that make them suitable for incorporation into the concrete matrix (Figure 4.4). They are chemically inert and very stable in the alkaline environment of concrete. The polymer has a hydrophobic surface so that it does not absorb water, which may reduce the bond between fibre and cement. Disadvantages include: sensitivity to sunlight and oxygen, a low modulus of elasticity, and a poor bond with the concrete matrix (Zheng and Feldman, 1995). These disadvantages are not necessarily critical, as embedment within the matrix provides a protective cover, helping to minimise susceptibility to environmental effects.

One of the benefits of polyethylene fibre, is that it can be produced with a relatively high modulus of elasticity, due to the intrinsic strength of the carbon backbone of the polymer chain which gives desirable strength retention properties under long-term exposure to aggressive environments, such as seawater. These fibres also have reasonable thermal stability, and when used with cement paste, are highly effective at improving plastic properties and impact resistance (Concrete Society, 2007). However, outdoor applications are also limited by the polymer’s susceptibility to ultra-violet light (Horrocks and Anand, 2000). Figure 4.4 shows how fibres create a fractured surface around their anchor point. Relatively recent research into fibre-reinforced cement roof tiles confirmed the growth of the Cyanobacterium *Scytonema* (a blue green alga) within cementitious elements, causing cohesive failure (Murphy, 2002). Recent SEM investigations (Suseela and Toppo, 2007) of degradation due to algal colonisation of cracks within polymers revealed that polythene acts as a substratum. Recent research by the author (Hughes *et al.* 2012) investigated the colonisation of various polymers, reporting the successful attachment of bacterial cells to synthetic fibres.

4.1.4 Algae

Algae are a diverse group of photosynthetic organisms ranging from microscopic single-cell micro-organisms to very large organisms such as seaweeds, there are thousands of species and many can live on either acid or alkaline surfaces (Brodie *et al.* 2007; Newman, 2003). Many commonly occurring fouling algae belong to the macroalgal group Chlorophyta (green algae). The Chlorophytes comprise a number of genera and species that actively bore into carbonate substrates (Khattar *et al.* 2009). They produce branching networks of filaments varying greatly in size. Some may be as little as 2 μm in diameter. In some species such fine filaments may collect together forming a biomass as wide as 25 μm (Golubic *et al*. 1975). Concrete structures in tropical and sub-tropical seas have been shown to be subject to the same bioerosive forces as carbonate substrates.

Figure 4.5 *Ulva* filaments (un-branched, fresh-from the study site) in a flattened, deflated condition. Arrows depicts a large healthy mature filament in a deflated state, approximately 280mm in length and 2 mm in diameter, suspended in a saline solution.

Many of the genera implicated in calcium carbonate disintegration have been demonstrated to be capable of bioeroding concrete (Scott *et al*. 1988). Attached macro-algae obtain different elements for their metabolism from the concrete. When algae colonise concrete structures they start to absorb calcium, silica and magnesium (Javaherdashti *et al.* 2009). Research into the degradation of marine concrete (Jayakumar and Saravanane, 2009) showed that marine algae had utilized crystals such as Yeelimite, Gismondine and Portlandite (calcium hydroxide) as a source of minerals.

4.1.5 Settlement and adhesion of *Ulva*

Algae absorb water, carbon dioxide and other nutrients through their filaments in order to respire, photosynthesise and grow (Hawkins and Jones, 1992); they are essential for the healthy condition of our coastal waters. The dominant algal genus at the test site is *Ulva*, (Figure 4.5), conspicuous bright grass-green seaweed, consisting of inflated irregularly constricted, tubular fronds that grow from a small discoid base and it is a common, green macroalga (larger genus, seen without use of a microscope) found throughout the world. Filaments from the study site ranged from 10cm to over 20cm in length. Their dispersal, colonisation and adhesion have been investigated elsewhere (Callow and Callow, 2002). Settlement cues for motile spores range from features connected with the substratum to biological and chemical conditions (Maggs and Callow, 2003). Much research has been conducted on settlement cues for *Ulva* zoospores (Callow *et al*. 2000; Finlay *et al*. 2002) showing that zoospores prefer to settle on organically conditioned hydrophobic, rough surfaces and actively seek the angle between a ridge and valley to settle in as the increased contact area reduces the amount of energy required for adhesion (Callow *et al.* 2005). Rough surfaces provide a greater surface area so that the spore is protected from desiccation and wave action (Maggs and Callow, 2003). Hydrophobic surfaces repel water, aiding adhesion by allowing closer contact between the adhesive and surface. Spores are, however, more easily removed from hydrophobic than hydrophilic surfaces due to a weak strength of attachment (Callow *et al.* 2000). Environmental scanning electron microscope studies have shown that as the wettability of a surface increases, the adhesion spreads further and there is, therefore, a higher surface area of contact between the spore and a hydrophilic surface (Callow *et al*. 2005), which may explain why a spore shows stronger attachment strength. Zoospores are negatively phototactic (Joint *et al*. 2000) and tend to settle gregariously which is thought to be of adaptive value due to the reduced turbulence that zoospores experience when they are settled in a group (Finlay *et al*. 2002). Attachment of zoospores is enhanced by the presence of a bacterial biofilm with greater numbers settling on surfaces with a higher bacterial cover (Joint *et al*. 2000)

It is thought that the presence of bacteria gives either a topographic and/or physicochemical cue for settlement. Settlement of the zoospores may depend on a signal produced by bacteria (Joint *et al*. 2000). ‘Quorum sensing’ involves the use of diffusible chemical signal molecules by bacteria that upon reaching a threshold level activate target genes that are used by the bacteria to regulate population growth. *Ulva* zoospores have been shown to exploit this bacterial system with enhanced settlement in the presence of quorum sensing *N*-acylhomoserine lactone (AHL) signals from bacteria (Joint *et al*. 2000).

4.1.6 Transition zone

It is now accepted and well documented, that in cement composites, whether with fibre or aggregate inclusion, the matrix in the vicinity of the inclusion, i.e. in the transition zone, can be quite different in its microstructure to that of the bulk cement matrix. This modified matrix can be as great as 50 to 100μm in area (Bentur *et al.* 1995). In contrast, research by (Diamond and Huang, 2001) proposed the existence of the interfacial transition zone around aggregates can have only marginal effects. The higher porosity at this interface, together with a well rounded texture of some types of aggregate, favour the appearance and development of bioerosive forces in the form of chasmolithic (Kleemann, 2001) microbial growth. The presence of a transition zone between fibres and bulk matrix has been confirmed by SEM (Bentur, 1991), micro-hardness measurements (Stang, 1995) and fluorescence microscopy (Kawamura and Igarashi, 1995). Another study of the transition zone evolution in cement composites, with cellulose fibres, registered an increase in porosity (Bentur and Akers, 1989).

At sufficiently high aggregate volumetric percentage in the armour concrete (Figures 3.14, 3.15 and 3.16) the interfaces will start to overlap to form a continuous connected path of high porosity through the material allowing microbial growth. Such a state can be called the state of percolated interfaces and may influence the transport properties so as to reduce the overall durability of the concrete. The percolation problem of interfaces in a composite has been considered in the past using analytical and computational methods (Bentz and Garboczi, 1991).

4.2 Materials and methods

4.2.1 Concrete specimens

The study site for this research is part of a coastal protection scheme, which involved the placing of 65,000 m^3 of ready mix concrete and 44,000 m^3 of precast concrete revetment armour. The precast concrete units, measure 5m by 3.5 m, weigh 20 tonnes and contain 8 m^3 of synthetic fibre reinforced concrete (Table A3.2 Appendix 3). Casting of units was monitored and the same units have been regularly examined over the years *in situ*. The 'as struck' concrete surface exposed to the sea was cast in a horizontal, 'upside down' position against a steel mould. The compressive strength class was C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4 and water/cement ratio of 0.45. The minimum cement content was 340 kg/m^3, CEMIIIA, with 50% ground granulated blast furnace slag and a chloride class of 0.2, maximum chloride content of the concrete, 0.20% by mass of cement. Concrete prisms (150 mm x 150 mm x 500 mm long) were also supplied by the manufacturer, some were dry diamond cut into 25 mm lengths, (using a Norton, Clipper brick and tile cutter) then washed and examined. Six specimens (cut as above) were fastened in test locations at the study site, in the splash zone strapped to a pipe. At various timed intervals the specimens were retrieved, microscopically examined, and then returned to the site. Colonised surface fragments breaking away from the revetment armour units were also obtained for inspection from the study site.

4.2.2 Details of the study site aggregate

Marine dredged sand was extracted from the beach, 5 km south from the study site, and blended with crushed limestone for use as fine aggregate by the precast concrete manufacturer. The fluvio-glacial deposits on the floor of the eastern Irish Sea adjacent to the study site are the dominant source of sediments. Whole-rock mineralogical analysis of a range of intertidal sediment samples has shown that they are predominantly quartz with associated plagioclase, orthoclase, calcite, dolomite, chlorite/kaolinite and mica (Bryant *et al.* 1996). Locally sourced 20 mm coarse limestone aggregate (Older Palaeozoic) was also utilized in the production of the armour concrete. Sedimentary in origin, limestone is primarily composed of calcium carbonate, $CaCO_3$. Dolostone (commonly called dolomite) is calcium magnesium carbonate, $CaMg(CO3)_2$. An informative review of aggregate has been offered by Fookes (1995).

4.2.3 Study site and exposure conditions

The study site is located in a temperate climate, and provides a compact and diverse ecosystem. The concrete stepped revetment armour allows public open access to the beach and is constantly colonised by *Ulva* and microorganisms, creating a slip hazard to the public. The local authority had utilised high pressure water (1200 psi), dispensed from motorised units with multi oscillating jets, to remove the microorganisms. The fully exposed units face westwards and were subject to cyclic wetting and drying conditions. The concrete is exposed to very harsh wave action, which was exacerbated by sand and occasionally shingle and debris content. Spring tidal ranges reach up to 10 m and the area from which concrete samples were examined was 2 km long x 15 m high and was completely submerged at high tide. Erosion has occurred at many locations, particularly at inter-tidal regions, where an exposed aggregate appearance has been noted and patch repairs had been carried out. The primary role of the revetment armour was coastal protection and as such is subject to the wear associated with tidal and wave action, both the design team and client view a degree of surface deterioration as normal.

4.2.4 Sample analysis - Microscopy

Observations of concrete were made in a step-by-step progression from large to small scale allowing selection of samples that represented the concrete surface zone. Concrete samples were initially observed with a Leica Strata Lab, monocular light microscope, and then with a Meiji MT4000 Biological and a Zeiss Axiovert 40 MAT inverted microscope which had a large specimen stage, ideal for the examination of heavy and bulky concrete specimens. Individual samples of limestone aggregate and microbial specimens from the study site were also observed on standard glass slides with a cover slip. The Axiovert was fitted with a 5 megapixel, high-resolution digital camera. These images were measured with the AxioVison AC software (Zeiss, 2001). This software allowed accurate measurement, image processing and analysis of microbial filaments and limestone aggregate on a captured image. Visual examination of samples revealed large-scale features such as the nature of the external concrete and aggregate surfaces, and the presence of aggregate within the matrix.

4.2.5 Scanning Electron Microscopy (SEM) - Energy Dispersive X-ray Analyser (EDAX)

Microbial morphological characteristics, concrete topography and, aggregate distribution were observed using a FEI Quanta 200 scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser, (EDAX). Genesis software was used for the elemental analysis of synthetic fibres within the cement matrix and of microbial filaments. Sample preparation is an absolute prerequisite and followed guidance from Echlin (2010). Specimens were attached on a 12 mm (diameter) x 3mm (deep) aluminium stub, fixed by a 10 mm (diameter) carbon mount with double sided organic adhesive (Agar). Initially specimens were viewed uncoated under low vacuum to observe general characteristics. All specimens were cleaned with a jet of air, to remove unattached microbial growth, before gold sputtering (Emitech K550X) at 25 milliamps for 2 minutes (thickness 20 nm) to improve image clarity. Specimens were examined using a 2.5–4.5 µm spot size and a working distance of 15 mm (Goldstein *et al*. 2003), by secondary electron (SE) emission (to observe morphology), backscattered electrons (BS) (to examine differences in atomic number), and with a low accelerating voltage of between 8-12 Kv to reduce specimen damage from the beam. The chamber could accommodate samples up to 5 cm x 5 cm x 2 cm in size.

4.2.6 Contact angle analysis

It is generally agreed (Zisman, 1964) and adopted in this research that the measurement of a contact angle on a given solid surface is the most practical way to obtain surface energy values. The theory of the contact angle of pure liquids on a solid was developed nearly 200 years ago in terms of the Young equation. Several contact angle measurements were taken on revetment armour concrete specimens retrieved from the study site; a drop of liquid was placed upon the surface of the concrete (Figure 4.6). It was assumed that the liquid did not react with the concrete surface and that the solid surface was relatively smooth and rigid. The drop was allowed to flow and equilibrate with the surface. The measurement of the contact angle, θ(theta), is usually made with a goniometer which is simply a protractor mounted inside a telescope. However this machine was not available, so a digital camera (Fujifilm Finepix JX) secured on a tripod was used with a spirit level.

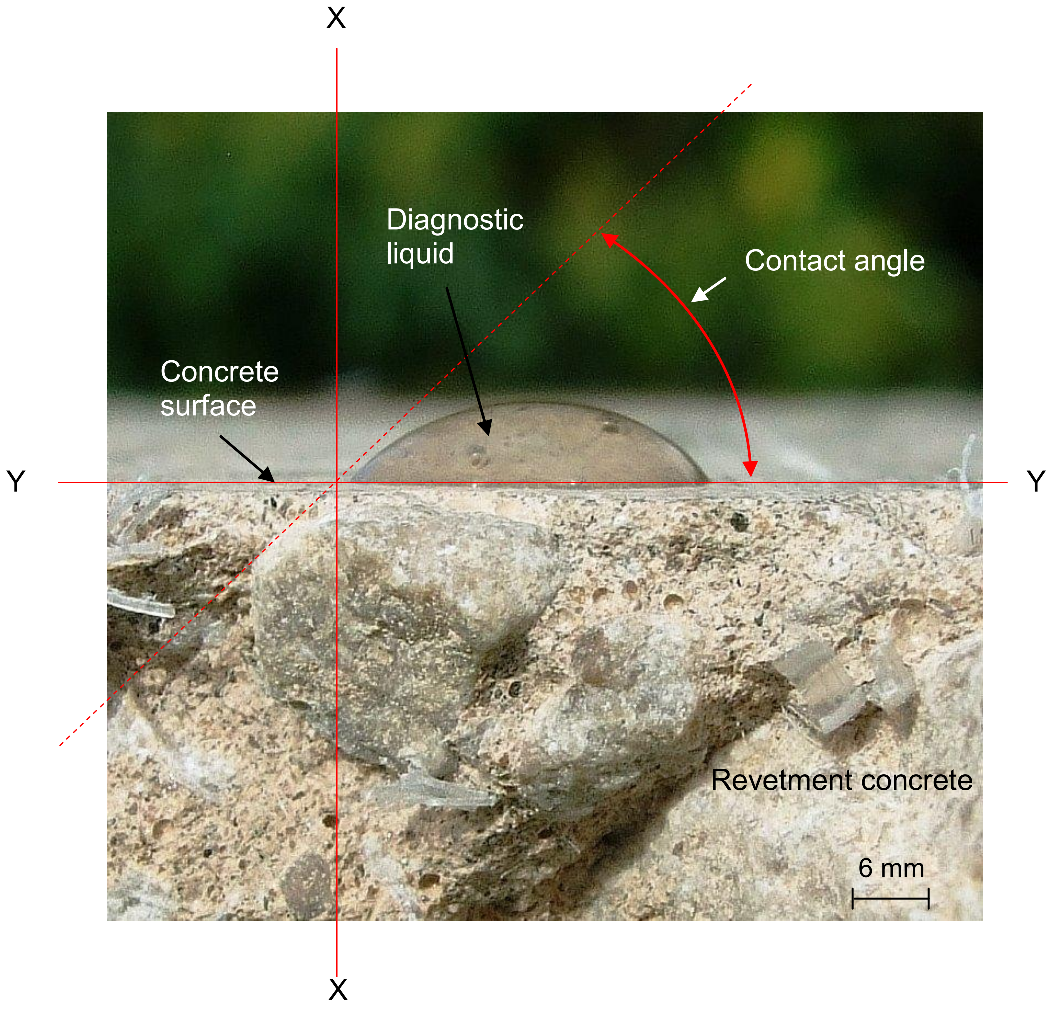


Figure 4.6 contact angle measurement methodology.

A rather simple method of estimating the surface energy of solids was developed by Zisman (1964). Zisman proposed that a critical surface tension, γc, can be estimated by measuring the contact angle of a series of liquids with known surface tensions on the surface of interest. These contact angles are plotted as a function of the γ_{LV} of the test liquid (Table A4.3 in appendix 4). The critical surface tension is defined as the intercept of the horizontal line, cos θ = 1, with the extrapolated straight-line plot of cos θ against γ_{LV} (Table A4.2 in appendix 4). This intersection is the point where the contact angle is 0 degrees. A hypothetical test liquid having this γ_{LV} would just spread over the substrate.

4.2.7 Porosity

Porosity relates to the total voids within the concrete; it can be defined as:

$$\frac{\text{Volume of pores in a given sample}}{\text{bulk volume of sample}} \times 100 \qquad \text{Equation 3}$$

The water cement : ratio of the mix mainly determines the porosity of the concrete. The solid products of hydration occupy a volume which is less than the sum of the absolute volumes of the original dry cement and of the combined water; hence, there is a residual space within the gross volume of the paste. For fully hydrated cement this residual space represents about 18.5% of the original volume of dry cement. This space takes the form of voids or capillary pores. There is a corresponding relationship between porosity and strength. The volume of pore space in the revetment concrete, as distinct from the ease with which a fluid could penetrate it, was measured by absorption. Ten samples from the study site were measured by drying to a constant mass, immersing them in water, and measuring the increase in mass as a percentage of dry mass.

4.2.8 Algal identification

The sea defence study site presents hard concrete armour in areas that are otherwise largely sedimentary, thus providing discrete new habitats for opportunistic colonising species. The revetment armour has been found to support a varied plant and animal community characteristic of a rocky shore, tending to be dominated by encrusting mussels, barnacles and a variety of algal species. *Ulva* was identified to the genus level on the basis of morphological characteristics (observed using a Meiji MT4000 Biological microscope). These characteristics included thallus and cell arrangement (Blomster *et al*. 1998). Filaments of algae are able to grow from 0.15 cm to 0.25 cm per day (Parchevskij and Rabinovich, 1991) and specimens from the study site ranged from 10 cm to over 20 cm in length; however a mature plant can grow to 1 m in length. Their dispersal, colonisation and adhesion have been described in detail elsewhere (Callow and Callow, 2002).

Fresh algal samples were also taken from site, cleaned, (using Decon 90), and ground to powder. DNA was extracted from specimens, using (DNeasy) Blood and tissue kit, (from Qiagen), according to the manufacturer's protocol. New barcodes (sequences) were aligned with published sequences, (following the guidelines of BOLD) (The Consortium for the barcode of life, 2009).

4.2.9 Health and Safety

When working alone on site or in a laboratory with hazardous materials, care at all times for the safety of everybody is governed by the University of Central Lancashire Faculty of Science and Technology Health and Safety Plan for Laboratory Work. A copy of this document can be found on the CD at the back of this thesis.

4.2.10 Summary

The experiments in the UCLAN laboratory and on site allowed data to be collected in two ways, those from non-destructive and destructive techniques. The focus of these experiments has been on durability, in order to fulfil the aims and objectives of this work. Scientific and technical advances rely heavily on the support that a critical experiment, or a series of experiments can give, putting new and old theories to test. The fact that macro synthetic fibres have not been used before in a marine environment, point to the need for carefully performed experiments which may reveal new effects that require existing explanations to be modified.

4.3 Results

4.3.1 Microscopy results

The sampling of limestone aggregate was centred on the inter-tidal zone and was not intended to determine the distribution of the genus over the whole sea defence structure. The inverted microscope image, (Figure 4.7), demonstrates the presence of algal filaments at the interface of the cement and aggregate. Figure 4.8 shows the epilithic growth of coiled filaments of algae, growing on the limestone aggregate. When one considers that algal assemblages may be composed of a number of species, a complex system for investigation may be present. The results from the algae survey can be found in the appendix.

When observing filamentous growth using the SEM, EDAX the method was also used to enable elemental analysis to differentiate between transparent synthetic micro fibres (22 µm in diameter) and microbial filaments, of similar size. Additionally light microscopy showed that some algal genera produced empty, transparent filaments. SEM micrographs, were from (winter) samples retrieved from site, showing abundant growth within the fibre cement interface. Figure 4.12 shows a sample that was not sputter coated, to show the filament in its natural condition. Coatings gave the algae an artificial, smooth surface, but allowed for higher resolution and clarity. The following micrographs illustrate how inclusions were colonised within the matrix (Figures 4.9 to 4.16) and are discussed in section 4.4.

4.3.2 Algal colonisation of limestone aggregate

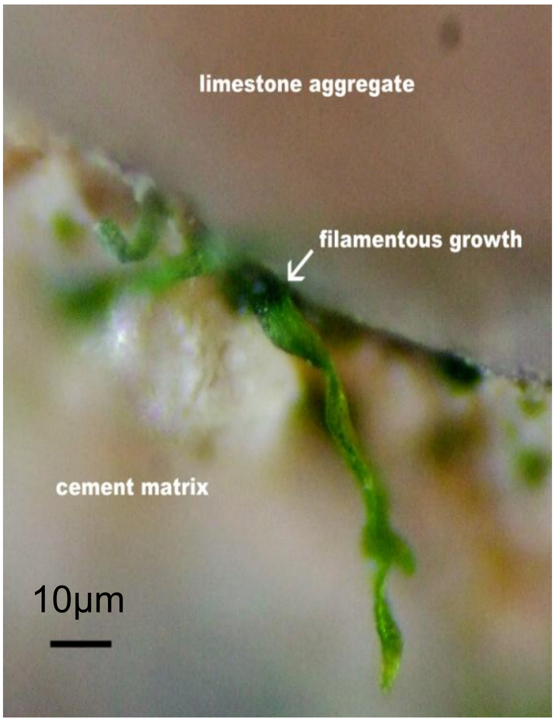


Figure 4.7 Growth at the aggregate interface

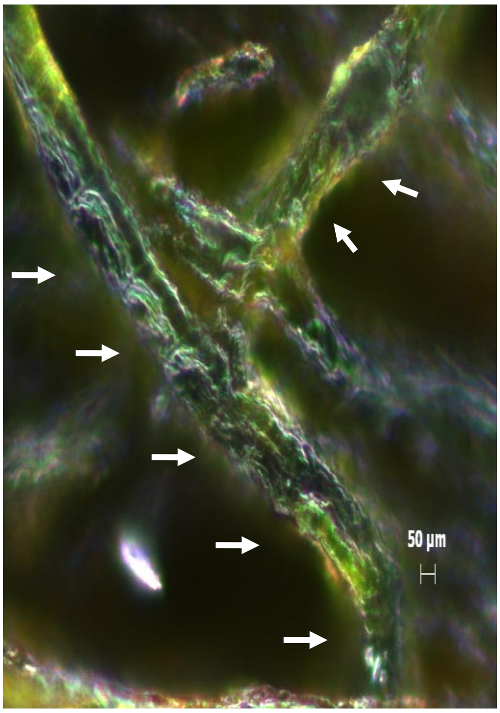


Figure 4.8 Copious growth on limestone, epilithic growth of coiled filaments of algae (arrowed).

Figure 4.9 Network of algal filamentous growth intertwine over the limestone aggregate within the matrix to a depth of approximately 25 mm. Filaments appear to cut into the surface of the aggregate surface (circled).

4.3.3 Algal colonisation of fine aggregate

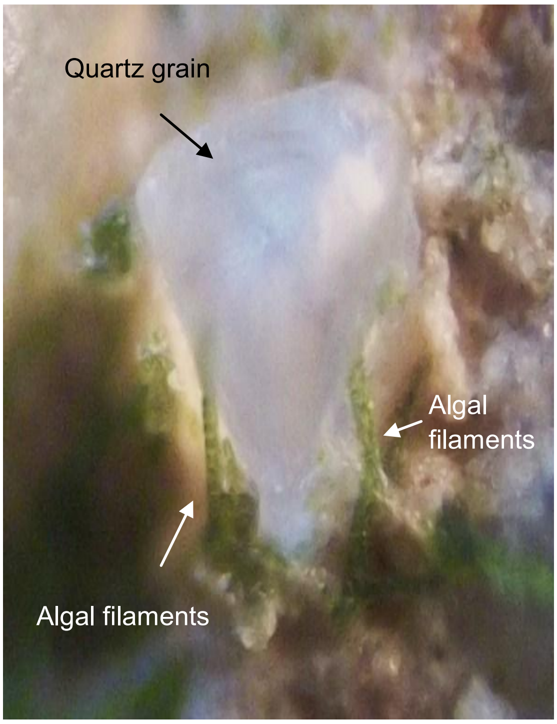


Figure 4.10 Filamentous algal growth around a quartz grain (constituent of fine aggregate used in the armour concrete mix) appearing to wrap around the grain.

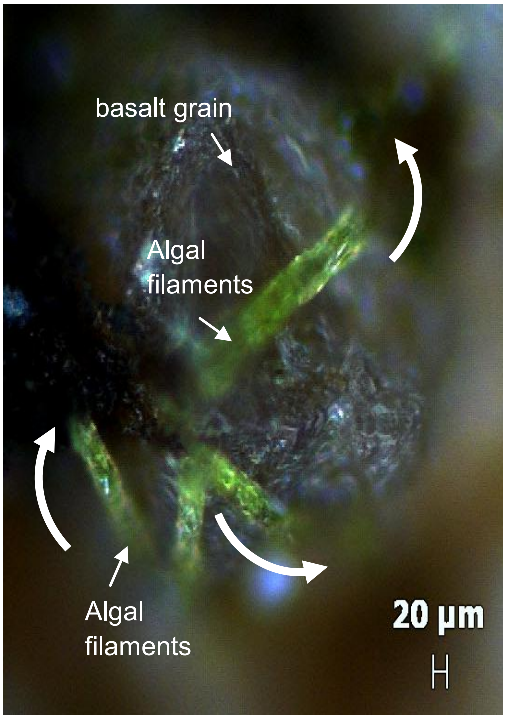


Figure 4.11 Filamentous algal growth around basalt grain (constituent of fine aggregate used in the armour concrete mix) appearing to wrap around the grain.

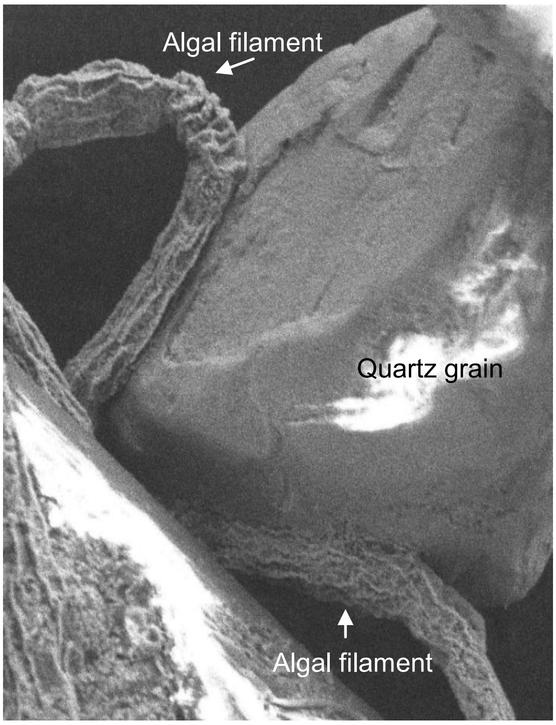


Figure 4.12 Filamentous algal growth at a depth of 20 mm within a sample of revetment armour concrete under a quartz grain appearing to wrap under and around the grain.

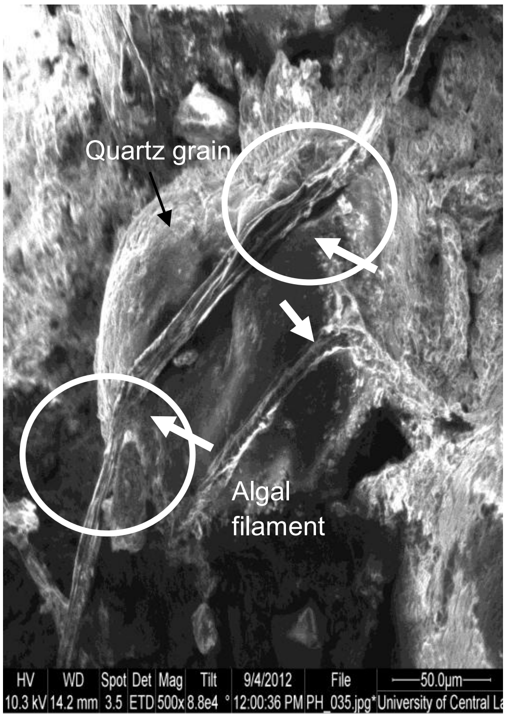


Figure 4.13 Filamentous algal growth around quartz grain appearing to cut into the surface of the grain (circled).

4.3.4 Algal colonisation of synthetic fibre

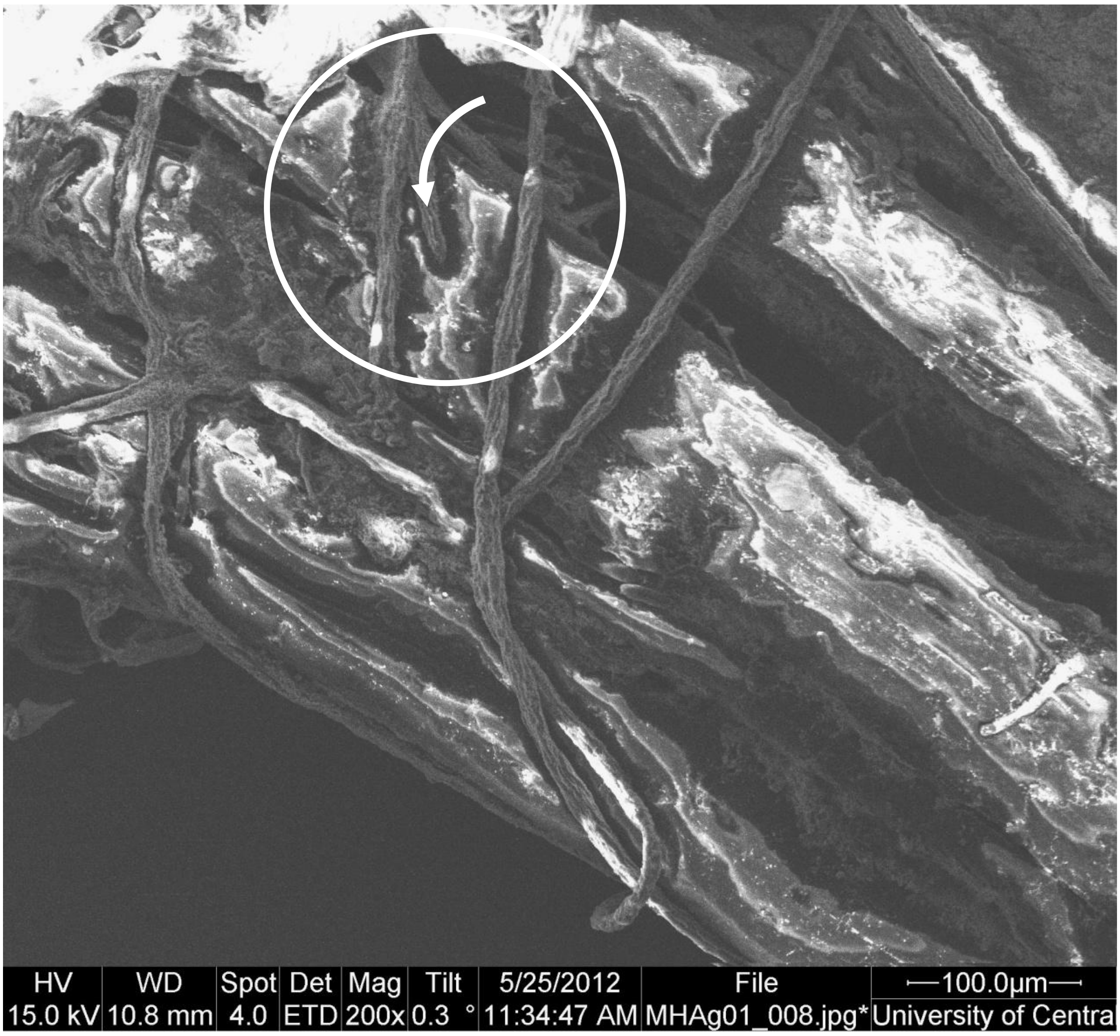


Figure 4.14 Filamentous growth around fibres, arrow depicts penetration of a filament of algae.

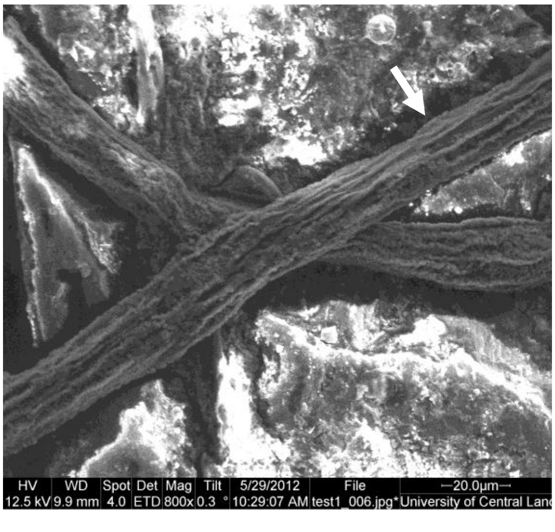


Figure 4.15 Growth cutting into fibre

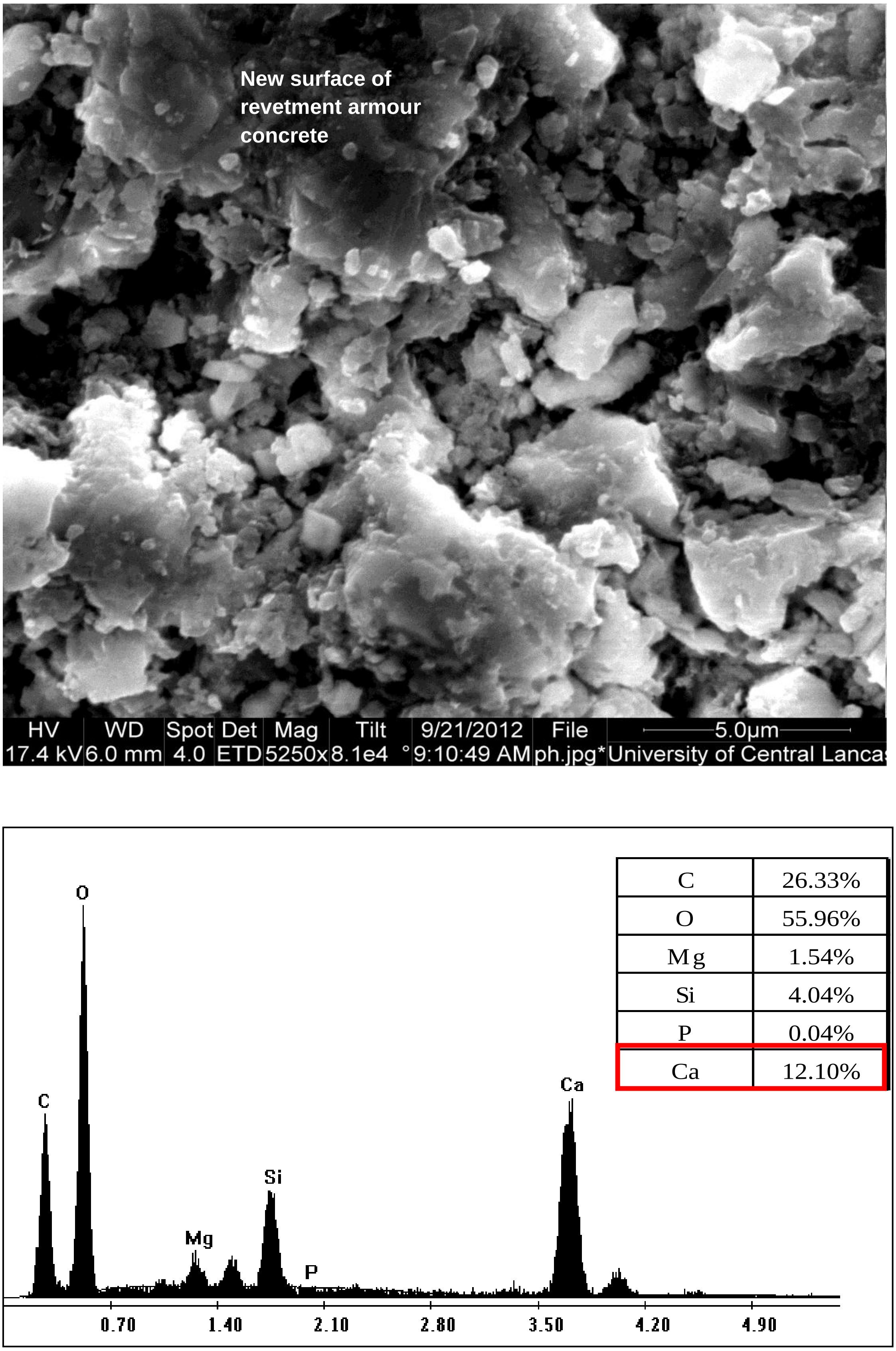
Figure 4.16 Bio-tenacious algal growth

The effects of algal colonisation of cement are seen in SEM micrograph shown in Figure 4.17 which shows a new concrete surface, prior being placed at the study site, illustrating a composite substratum where cement particles can be clearly seen, whilst Figure 4.18 shows the revetment surface after 3 years exposure, showing a layer of microorganisms or biomass covering the surface. Voids can be seen left from liberated aggregate. The results of EDAX analysis show the calcium element has reduced over time from 12.10% by atom to 1.74%, an 86% decrease. Algae are able to obtain several elements for their metabolism such as calcium and potassium (Keller, 1957; De Belie, 1997)

Surface energy results of the revetment armour concrete surface are shown in Figure 4-19. New concrete revetment armour demonstrates a surface energy of 21 MJm^{-2} (SI $10^{-3}kg.s^{-2}$). This decreases to 11 MJm^{-2} at 3 years. The surface energy measurement has reduced by half in three years. The nature of the substratum, being of a composite nature, has to be considered when analysing these data.

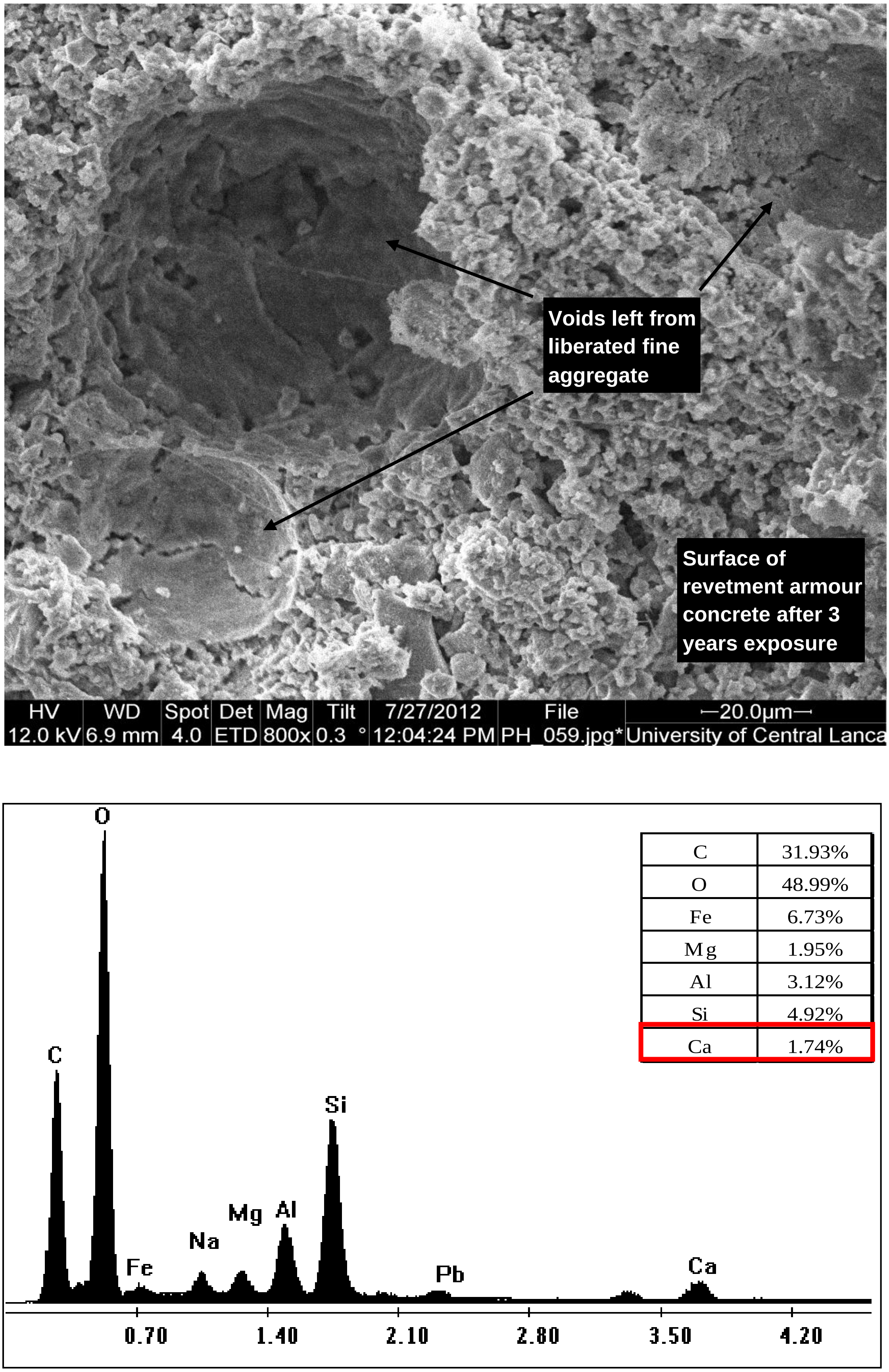
The results of the porosity of concrete armour surface can be seen in Figure 4.20. Porosity has increased by volume from 7.7% at 7 days to 26.89% at 3 years. This equates to a 250% increase. Further Porosity data can be found in Table A4.3 Appendix 4. A comparison can be made to an OPC mix which was not exposed to a marine environment.

4.3.5 Algal colonisation of cement surface of armour unit



C	26.33%
O	55.96%
Mg	1.54%
Si	4.04%
P	0.04%
Ca	12.10%

Figure 4.17 SEM micrograph and EDAX spectrum analysis of new concrete surface.



C	31.93%
O	48.99%
Fe	6.73%
Mg	1.95%
Al	3.12%
Si	4.92%
Ca	1.74%

Figure 4.18 SEM micrograph and EDAX spectrum analysis of 3yr. concrete surface.

4.3.6 Surface energy of the revetment armour concrete surface

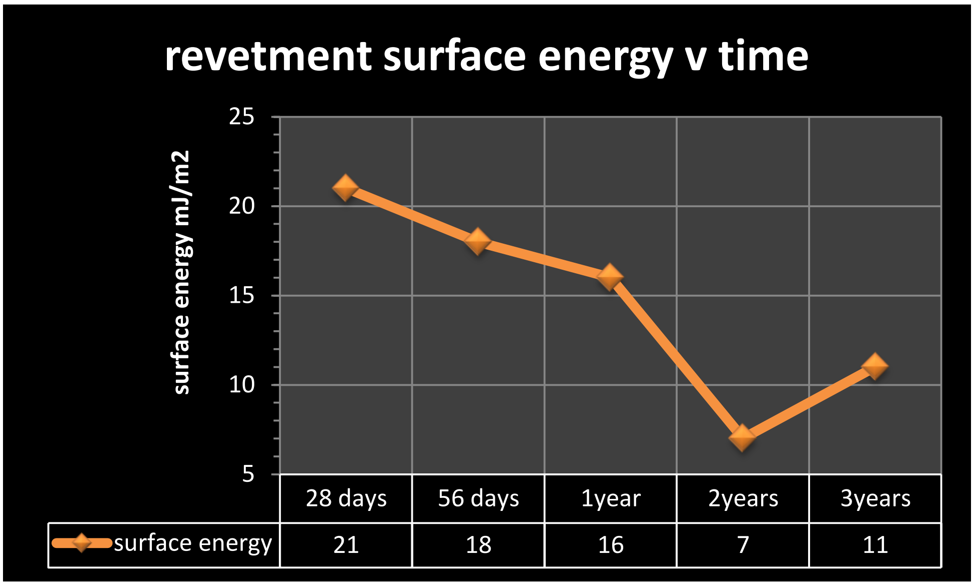


Figure 4.19 Revetment surface energy versus time over 3 years.

4.3.7 Porosity of concrete armour surface

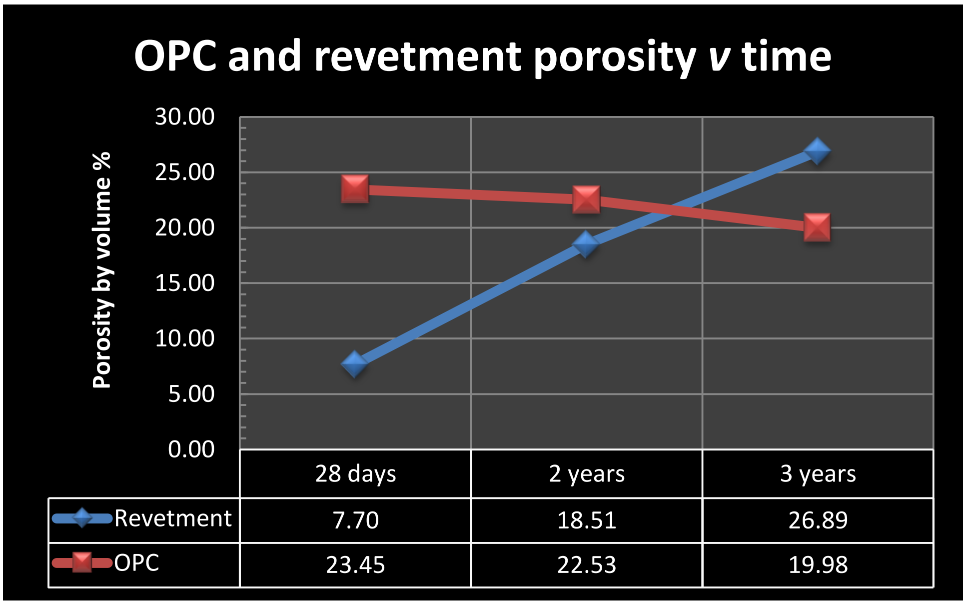


Figure 4.20 OPC control specimens and revetment armour surface specimens porosity by volume.

4.4 Discussion

4.4.1 Microscopy; Limestone aggregate

Limestone is a bedded rock, having planes and joints along which the sea can penetrate. It is slightly soluble, and the brine slowly dissolves its surface (Evans, 1962). It is also tunnelled with caverns and crevices formed by water, which the sea or microorganisms can enter and enlarge. It appears that filamentous microorganisms at the study site can grow readily between limestone aggregate and the cement matrix of the concrete revetment armour. The images, Figures 4.7, 4.8, & 4.9, demonstrate the existence of a microbial presence around the surface of the aggregate, within the armour concrete. This destructive presence of algal growth will lead to the eventual release of the aggregate. This physical degradation, by endolithic cells penetrating concrete through micro-cracks, absorbing water, causes growth of their molecular mass generating tensile stresses leading to an increment in the size of cracks (Gaylarde, 2003). It is not suggested that this mechanical degradation mechanism, resulting from the growth of microorganisms is solely responsible for the erosion observed at the study site, but it is suggested that it should be considered as a factor along with tidal action, power washing and bio-fouling control, such as treatment with a chlorine-based disinfectant. The observations in this study, particularly the attachment of filamentous organisms, cohesion between particles, the penetration and growth are comparable to those observed by Ortega-Calvo *et al*. (1991) on boring activity within the concrete of historic buildings. Biological activity was sometimes observed at the study site even though filaments had detached from the concrete. Figure 4.7 shows the upward and outward epilithic growth of coiled algal filaments, exiting the substratum between aggregate particles. Figure 4.8 shows a compressed, branched filament with epilithic characteristics of microbial growth on aggregate within the matrix. As a result of this research, it is proposed that filamentous growth between aggregate and the matrix can weaken the bond between aggregate and cement, accelerating material loss and concrete surface degradation. Examples of algal growth at the aggregate cement interface within armour concrete after 2 years exposure at the study site show copious growth to a depth of 20mm (Figure 4.21).

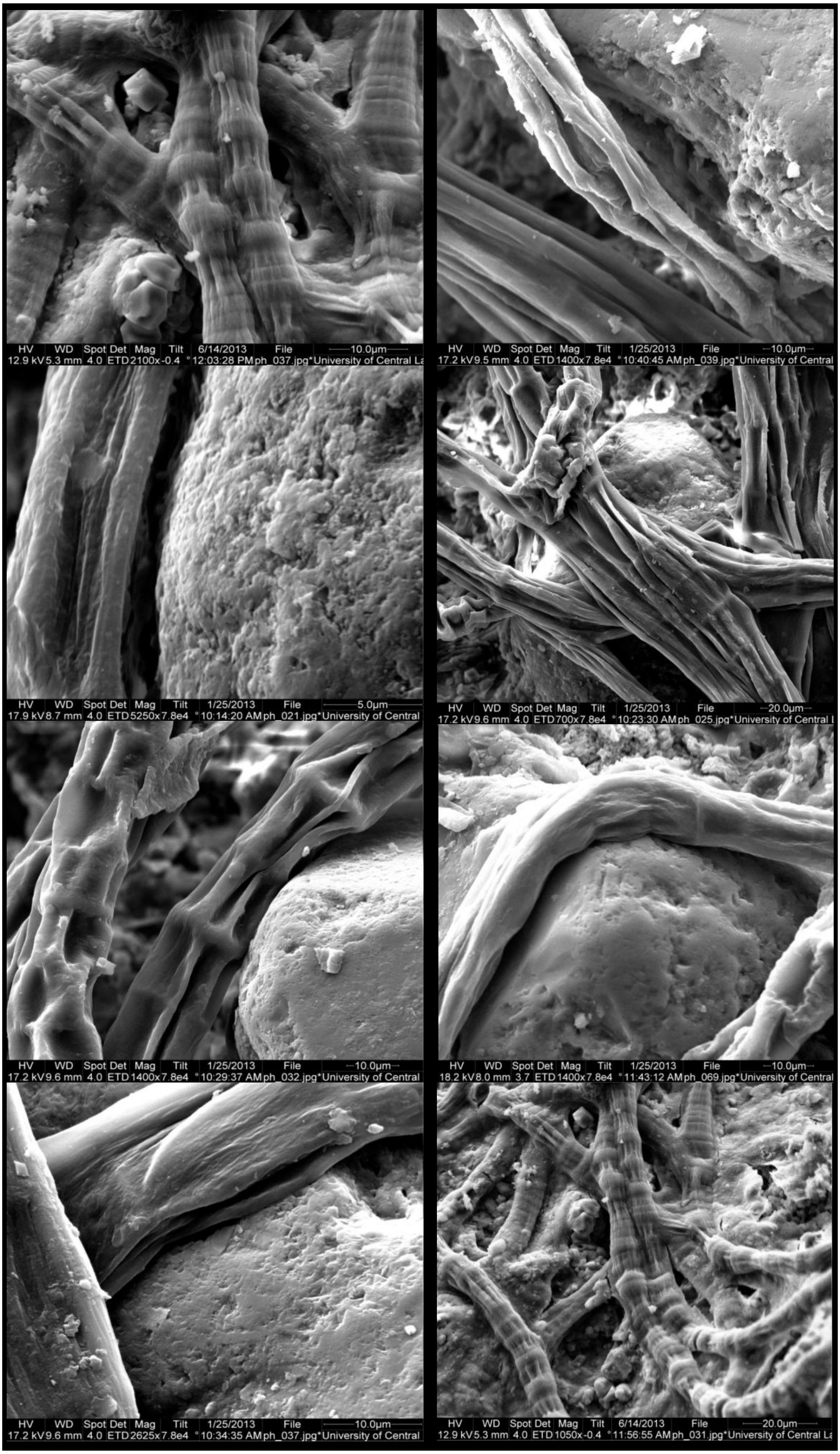


Figure 4.21 Examples of algal growth at the interface of aggregate.

4.4.2 Microscopy; fine aggregate

Little is known about the algal communities that live on sand (Round, 1965). His report was followed by a number of studies describing problems of algal attachment, production and burial in marine sands (Cadee and Hegeman, 1974). Since then, more has been learnt about species composition (Edlund *et al*. 1996), life cycles (Jewson and Lowry, 1993) and aspects of colonisation. However, relatively little is known about the ecology of individual species and their specialized adaptations for living on sand. The light-inverted microscope images, (Figures 4.10 and 4.11) are typical representations of filamentous growth commonly observed, and demonstrate the existence of algal growth around the surface of the fine aggregate, within the armour concrete. Figure 4.12 indicates the destructive presence of growth which will lead to the eventual release of the fine aggregate. Figure 4.13 shows the upward and outward growth of coiled algal filaments, exiting the substratum between fine aggregate particles.

4.4.3 Microscopy; synthetic Fibres

Surface microorganisms are often cleared by power washing; as investigated in Chapter 3, however penetration into the surface, particularly under fibres, offers refuge from hydraulic forces. Their presence at the cement interface (Figure 4.14), disrupts or distorts the fibre by growth. Fibres having just been cleaned at the surface starts the process of breaking away. This gives microorganisms the opportunity to penetrate under the fibre and quicken the degradation. This colonisation is observed in Figure A4.1 Appendix 4), where the majority of growth is on the surface, however filamentous growth from the underside of the fibre in contact with the concrete. It is also important to note that algae can act as the focus for other biofouling organisms such as fungi, bacteria and diatoms (Figure A4.2 Appendix 4) so that the deterioration process may gain momentum after the structure’s condition has become suitable for the survival of one or more such organisms. The filaments shown in Figure 4.15 absorb and store seawater and associated nutrients during periods of submersion and from moisture found within the concrete. Figure 4.15 shows the filamentous growth cutting the actual fibre depicted by the arrows. If the conditions (nutrients, UV, temperature, and seawater) are favourable, the filaments will grow, and extend over larger and deeper areas of the concrete (Figure 4.16). The effects of shrinking and swelling of the hydrophilic filaments during dry conditions and periods of moisture intake, will accelerate the mechanical biodeterioration process of the fibre bond and cement. Figure 4.22 shows a proposed schematic of sequence of behaviour of fibre at the study site, based on 8 years experience at the study site.

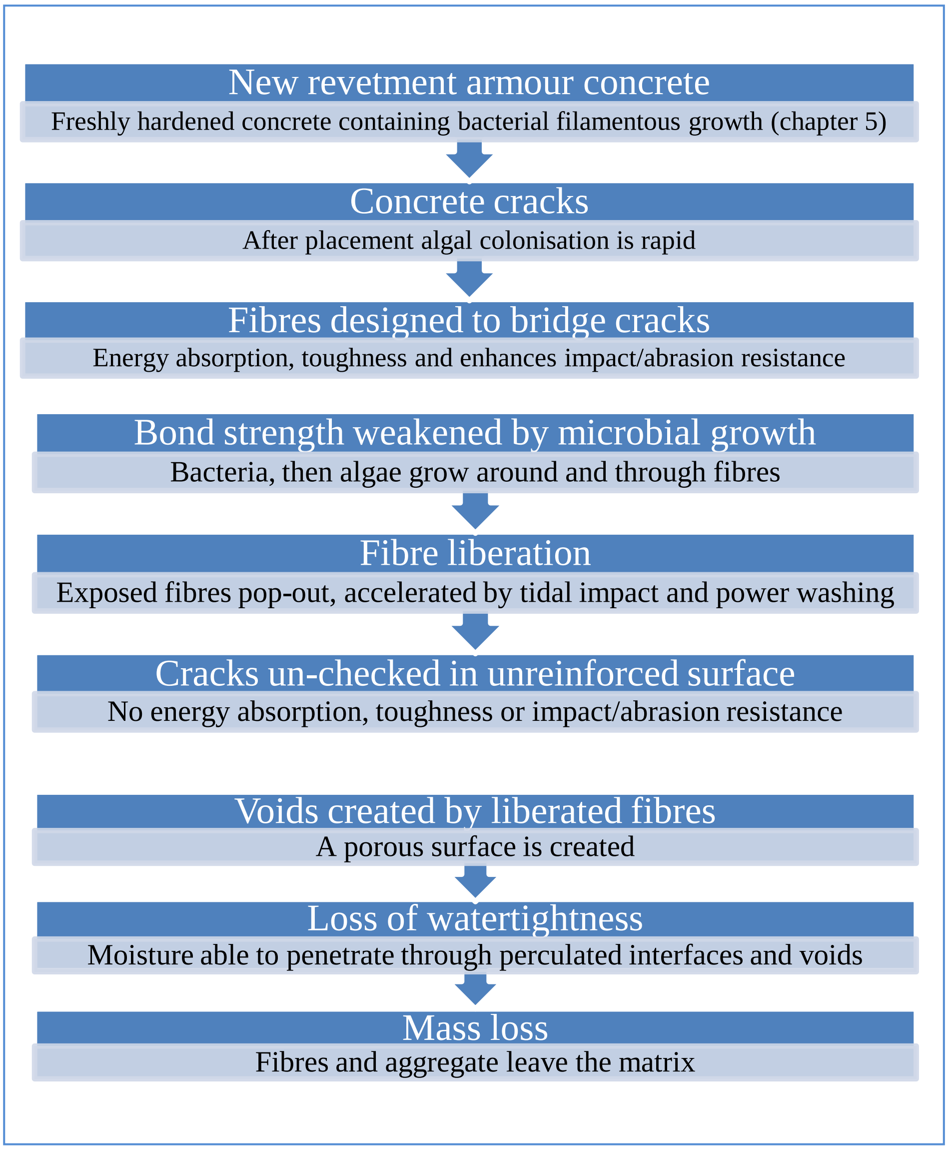


Figure 4.22 Schematic of fibre performance at the study site.

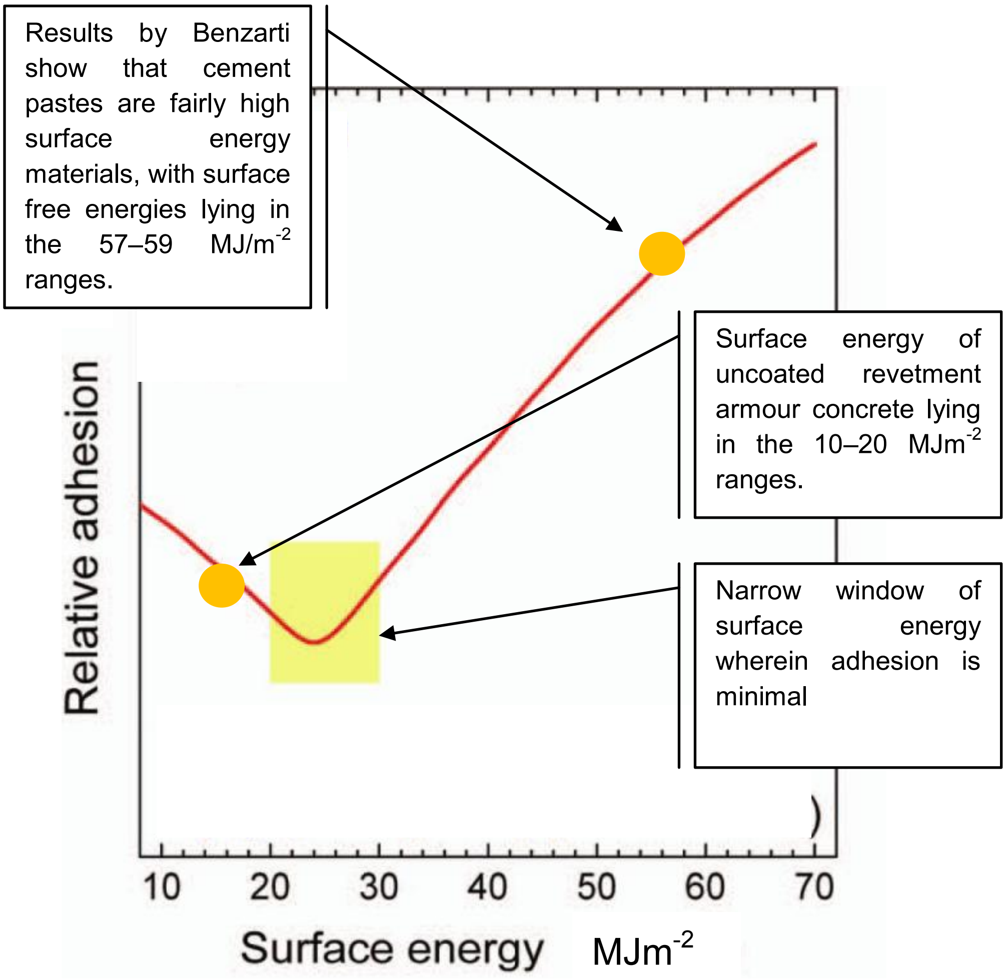
It was observed that filaments grow freely in between fibrillated and monofilament fibres. It was at this stage in the research it was found that filaments could be mistaken for micro fibres. Initial observations of site specimens were made using light microscopy. This knowledge of the topography and colonisation aided the identification at the SEM analysis (monochrome) stage of the research. The micro-fibres could easily be mistaken for juvenile *Ulva* filaments; therefore EDAX was used to confirm the specimen under investigation was a filament along with a visual reference from earlier light microscopy (being in colour). Figure 4.4 shows a macro fibre leaving the surface and creating a void for possible moisture transportation into the concrete. Microbial cell attachment is tentatively observed on the fibres and will be further investigated in Chapter 5. Unused fibres were fixed and monitored in an exposed, non-marine environment, after 1 year they became hard and brittle.

4.4.4 Revetment armour surface EDAX elemental analysis (cement)

Elemental analysis in conjunction with SEM observations showed calcium depletion over a period of two years, as seen in Figures 4.17 & 4.18. Attached macro-algae obtain different elements for their metabolism from the substratum. This observation is in agreement with research reported by Javaherdashti *et al.* (2009).

4.4.5 Revetment concrete surface energy data

Figure 4.19 depicts the revetment surface energy versus time demonstrating how the concrete surface energy decreased by 48% over 3 years. Experimental results by Benzarti (Chehimi *et al*. 2006), show that cement pastes are fairly high surface energy materials, with surface free energies lying in the 57–59 MJm^{-2} ranges. A generalised relationship between surface tension and the relative amount of bioadhesion has been established, and is shown in Figure 4.23. This is commonly known as the Baier curve (Baier and De Palma, 1971), and shows the relationship between the Critical Surface Free Energy and Relative adhesion. The key feature of this curve is that the minimum in relative adhesion, at 22/24 MJm^{-2} does not occur at the lowest surface energy. A variety of explanations have been given to account for this including the effects of elastic modulus (E), thickness and surface chemistry.



Results by Benzarti show that cement pastes are fairly high surface energy materials, with surface free energies lying in the 57–59 MJ/m^{-2} ranges.

Surface energy of uncoated revetment armour concrete lying in the 10–20 MJm^{-2} ranges.

Narrow window of surface energy wherein adhesion is minimal

Figure 4.23 Surface energy results from this research plotted against the Baier curve.

The calculation of surface free energy from contact angle measurements has been the subject of much discussion. The revetment concrete is a complex material, and its wettability depends on many factors: e.g. mix design, type of cement and aggregates, additives of synthetic fibres, membrane curing and water cement ratio. Environmental conditions such as exposure to salt water, weathering or biological attack and surface roughness are important factors to consider. Moreover, the concrete as a complex composite material has a heterogeneous, rough and even porous surface. Therefore, contact angle hysteresis, a difference between advancing contact angle (i.e. contact angle of the liquid advancing across a dry solid surface) and receding contact angle (i.e. contact angle of the liquid receding from a solid surface) has to be expected. The major causes for contact angle hysteresis include roughness and chemical heterogeneity of the surface but also other reasons are stated in the literature. The study of the contact angle on a rough surface is difficult, because the problem of defining roughness is a complex one. Another major constraint with this method is the complex composite nature of the substratum. Several images presented within this project show a number of different materials at the surface. Particularly synthetic fibres, limestone, sand, shells and voids occupied with filamentous growth. This information was not apparent at the planning stage of the project and the amount of degradation observed on the revetment units was not anticipated. It could be argued that these measurements are too varied to be relevant.

4.4.6 Revetment concrete Porosity data

It has been previously reported that fibre inclusions can change the porosity of the material (Bentur and Mindess, 1990). One would expect the porosity to only increase over a long period of time. Twenty eight day revetment cubes recorded a porosity of 7.70%; 3 year site samples recorded a much higher porosity of 26.89%, (Figure 4.20). Higher porosity facilitates a microorganism's attachment or material fouling (De Muynck *et al*. 2009). It has been observed through experiments in phase one, that fibres are extremely close to the surface of the revetment armour. They quickly 'pop out', become brittle and fall away, as a result of colonisation and power washing. The many voids left by the departed fibres affect the matrix; increasing porosity far sooner than expected.

4.4.7 Interface zone

Microscopy illustrates how filamentous growth can thrive at the interface of inclusions. Research into failure-paths in the interface zone of aggregate-paste, suggests three explanations for failure: (i) the hydrated cement paste in the interface zone is weaker than the bulk paste; (ii) there are discontinuities in the contact between the paste and the substrate aggregate; and (iii) the local stresses in the interface zone are higher than elsewhere (Maso, 1969). It is known that the interface zone has a different microstructure from the bulk of the hardened cement paste; the interface zone is the locus of early microcracking, known as bond microcracking (Neville, 2003). The first explanation of Maso, that is, the weakness of the interface zone, was studied in depth and confirmed elsewhere (Larbi, 1993). The difference in the compound composition of the paste in the interface zone, the orientation of the crystals of Ca $(OH)_2$, and the lower strength of this paste are now universally accepted.

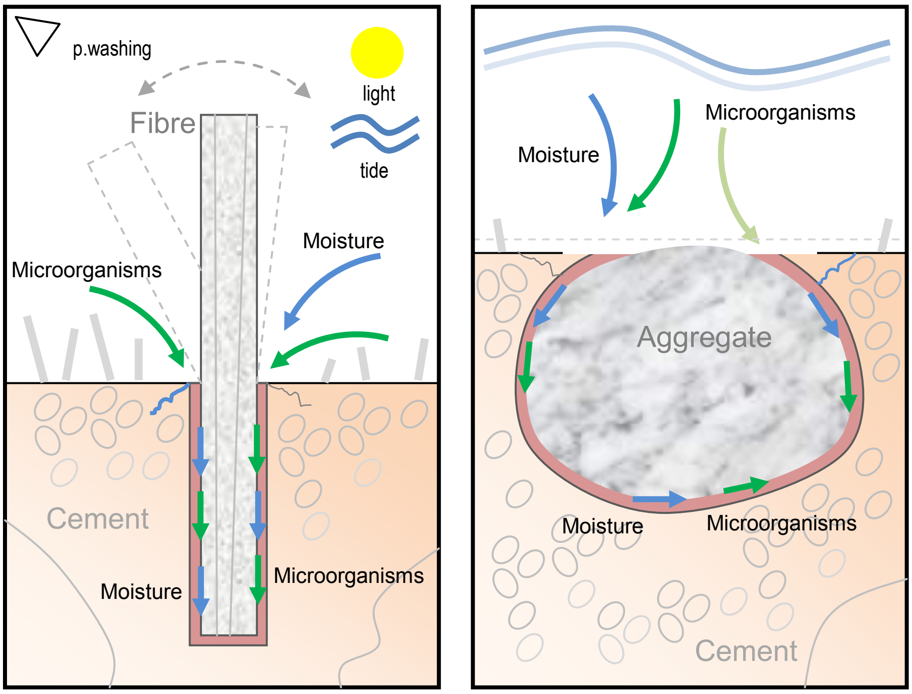


Figure 4.24 Schematic representation of interface around inclusions.

This area lays open the opportunity for growth and is illustrated in Figure 4.24, the second explanation of failure at the interface is the presence of discontinuities.

These may be the consequence of air voids on the surface of aggregate particles or bleed voids (Neville, 2006b). Both types of void are the consequence of the treatment of concrete during compaction (consolidation), covered in the Chapter 3, and are not intrinsic properties of the material. This is illustrated in Figure 4.24, the third explanation, namely the elevated local stresses, is related to the difference between the values of the modulus of elasticity of the hydrated cement paste and that of the aggregate particle. It has been found that this difference has a considerable influence on the bond between cement paste: the smaller the difference the smaller the local stress concentration. Furthermore, since it is the elastic properties of the concrete which affect pulse velocity, measured in the Chapter 3, which indicated a 45% reduction, further indicating a weakening process.

To understand the processes of subsurface microbial transport (Figures 4.24 and 4.25), one must recognize the important role of spatial structures in heterogeneous porous media, which affect microbial movement and population dynamics (Li *et al.* 1996). Percolation theory is one of the best developed of these techniques (Bentz and Garboczi, 1991; Li *et al.* 1996). Invasion percolation, considered an extension of ordinary percolation theory (Maier and Laidlaw, 1993), can also be used to describe microbial percolation through a subsurface (Figure 4.25). On the basis of this model, one can estimate and simulate an invasion threshold of microbes when considering the biodeterioration of the matrix and inclusions by subsurface microbiota. The invasion threshold lies between a watertight concrete surface and a surface with protruding fibres and aggregate. Once this transition takes place microorganisms can penetrate the matrix.

Algal filaments observed were able to grow at a rate from 0.10 cm to 0.25 cm per day which agrees with (Parchevskij and Rabinovich, 1991) and specimens from the study site ranged from 10 cm to over 20 cm in length; however mature plants can grow to 1 m in length.

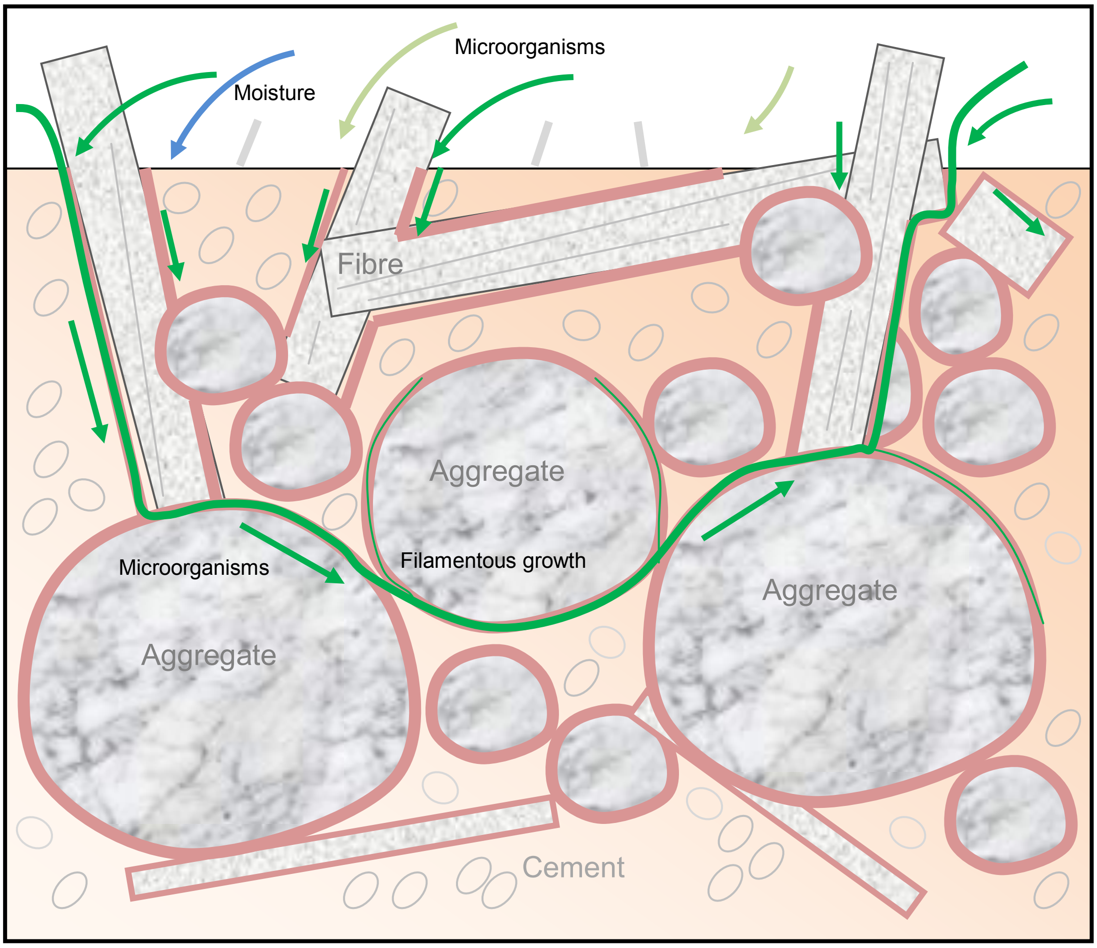


Figure 4.25 Percolated interfaces leading to the development of an integrated pathway for microorganisms. This schematic depicts inclusions within the concrete, illustrating how an integrated pathway could have facilitated the transportation of waterborne microorganisms.

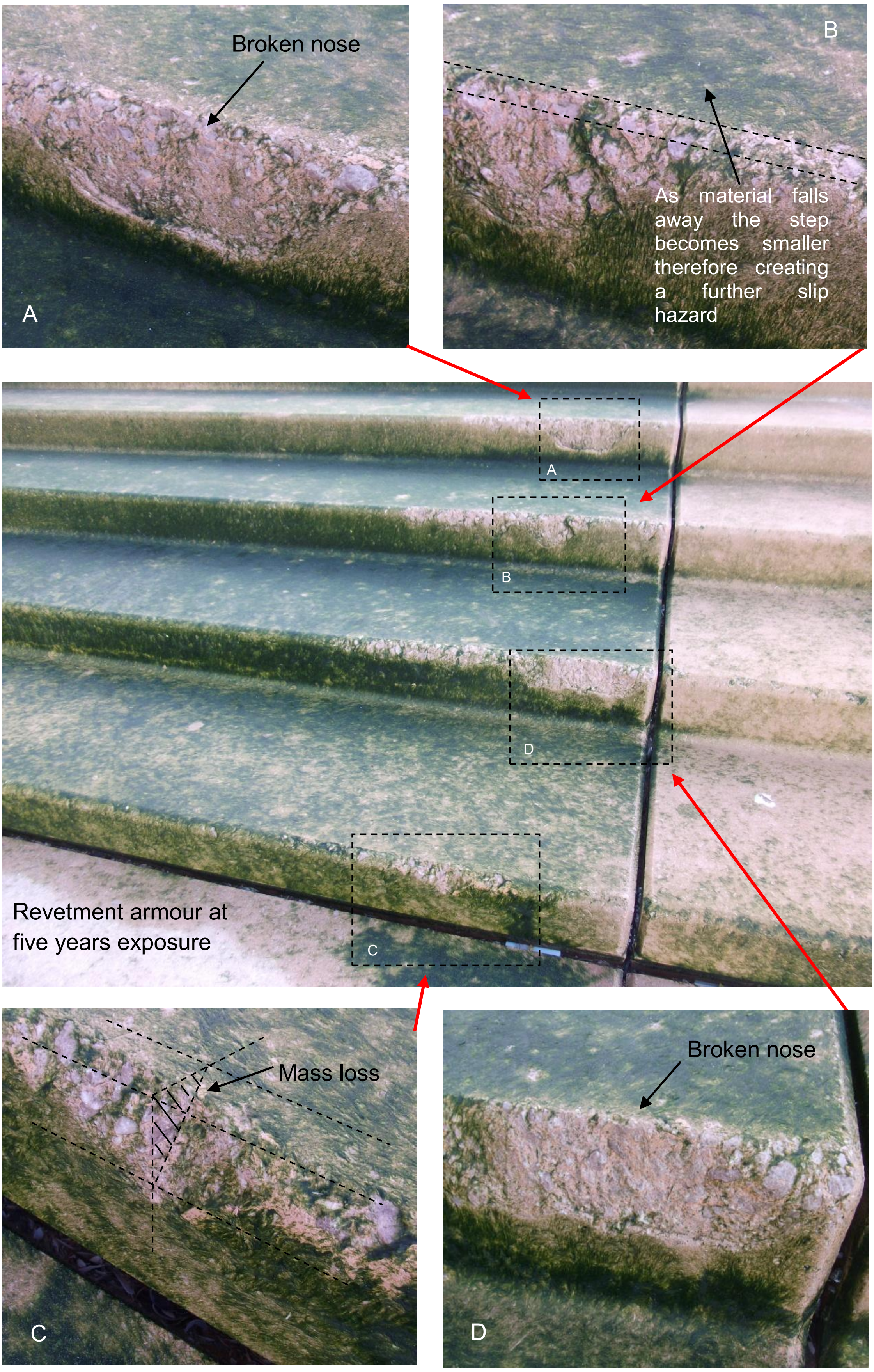


Figure 4.26 Material loss from revetment armour.

4.5 Preliminary conclusions

The aim of this chapter was to investigate the effects of algal colonisation upon a concrete surface and to discuss how its presence may affect the durability of the concrete. Figure 4.26 shows material loss at the nose of the step of several units at the study site. Microscopy revealed algal filamentous growth had penetrated the concrete surface and grew at the interface of inclusions. Filamentous algae tunnelling into the aggregate/fibre cement interface, appears to occur. This growth inflating with tidal submersion or power washing, deflating and flattening under drying, weakens the bond within the concrete, making the aggregate and fibres more susceptible to tidal impact and power washing. Figures 4.27 and 4.28 depict examples of the condition of 100 revetment armour units at the study site after five years exposure. It is accepted that tidal impact is partly responsible, but a combination of other factors outlined in this thesis has significantly impacted on the condition of the units.

EDAX analysis showed the algae may have reduced the calcium content within the cement by 86%. Carbonation will be a factor to consider which has been recognized for many years to be a commonly identified result of the attack of carbon dioxide upon exposed concrete surfaces. Although carbonation has been considered to be a cause of surface defects, it can also contribute to deeper distress in concrete at cracks and at joints when calcium hydroxide is replaced by calcium carbonate. The occurrence of $CaCO_3$ crystals on the concrete armour at the study site has been studied in Chapter 3. Surface energy results, were treated with caution, however they demonstrated a 48% reduction from 21 to 11 MJm^{-2}. A generalised relationship between surface tension and the relative amount of bioadhesion has been established, where the minimum in relative adhesion, at 22/24 MJm^{-2} does not occur at the lowest surface energy. This indicates the substratum continues to offer adhesion to microorganisms, thus to be bio-receptive. Liberated fibres and fine aggregate, along with loosened large aggregate has led to a surface porosity increase by 250%. This significant value, along with microscopy results confirms the lack of water tightness. A survey of algae at the study site identified the current dominant genus as *Ulva* and various other species observed in concrete specimens, leading to a further understanding of a large diverse community.

The discussion highlighted the relevance of the interface zone within the matrix and its susceptibility to microorganisms. A schematic illustration was presented based on this phase of work. The presence of algal filamentous growth was detrimental to the concrete, having implications for long term durability. Potential influences of marine organisms on the durability of concrete sea defences clearly warrants further investigation.

4.5.1 Constraints

Due to the composite nature of the substratum, the contact angle analysis of the revetment armour surface is treated with caution. Experimental work carried out in phase one revealed how aggregate and fibres were extremely close to the surface, thus a variety of materials will influence the results. Also the use of digital photography would not have been as accurate as the use of a special instrument e.g. an optical goniometer, therefore these limitations outlined suggests the results can only be regarded as indicative.

SEM investigations as part of this research have been generally regarded with a degree of caution (Neville, 2006). Artefacts by way of specimen changes or cracks caused by the method preparation and the effects of high vacuum in the sample chamber can occur (Zelic *et al*. 2000). Sample geometry and its relationship to the incident angle of the electron beam and the take off angle of the detector can result in misinterpretation of the morphology. Consequently a limitation to this case study is that it involves only a single site and therefore may not be representative of marine environments in general, but the conclusions relating to the mechanisms of material loss remain valid.

Figure 4.27 Noticeably imperfect after five years exposure

Figure 4.28 Material loss after five years exposure

Chapter 5

The Biofilm – phase 3

*Slime on surfaces is the usual manifestation of a phenomenon called “biofouling”.
It occurs in a wide range of industrial processes and in all of them it is a nuisance,
sometimes a very expensive one. It is fought against in each industrial area
individually and there are many “re-inventions of the wheel” and many
common mistakes – although the underlying problem
is always the same: microbial biofilms.*

Hans-Curt Flemming (1998)

5.1 Introduction

Biofilms represent the oldest form of life on this planet and can be found in an extreme range of environments (Schopf *et al*. 1983). Biofilms can be destructive, and coccoid-shaped cyanobacterial cells like *Gloeocapsa* have been shown to be involved in degradation and boring into limestone (Gaylarde and Englert, 2006). Early biofilm formation, composed of bacteria and organic matter on the concrete revetment armour are the key drivers for subsequent attachment of fouling organisms such as algae. Initial site observations of precast concrete units being put in place, revealed unusually rapid algal biofouling at the surface of the units, within days of positioning. After detailed inspection of the new cement matrix, used in the production of the units, the early and unexpected presence of a bacterial biofilm within freshly hardened armour concrete was observed (Hughes, 2013).

Durability of polymer sealant used at the study site was investigated. In light of the early degradation and failure of a polymer sealant used at the study site, designers and managers of coastal and marine structures should appreciate the importance of selecting sealants suitable for use within a hostile environment (Hughes *et al*. 2012b).

5.1.1 Objectives

The objectives were: To evaluate the development of a bacterial biofilm, the beginning of the biofouling process as based on observations by microscopy and the culture of cells. To study and record biodeterioration of a polymer silicon sealant samples from the study site with various microscopy techniques.

5.1.2 The biofilm

Microbial biofilms are extremely complex microbial ecosystems that are difficult to study by conventional microbiological techniques (Flemming, 1998). They consist of complex consortia of bacteria, algae, and grazing protozoa which may display morphological features not usually associated with the organisms when grown as a pure culture. It is therefore acknowledged to be difficult to produce a biofilm which is truly representative of that found in a particular environment (Morton and Surman, 1994). The diversity of the biofilm, microflora and microfauna and their interspatial relationships are extremely difficult to reproduce (Morton and Surman, 1994), this motivated a site study.

Previous workers have reported on the biofilm matrix, its composition and architecture, as well as the numerous intra- and intercellular processes within the matrix (Givskov and Kjelleberg, 2007; Stoodley *et al*. 2002; Sutherland, 2001). Whereas adhesion determines the initial rate of accumulation of cells on the surface, the main processes leading to a biofilm are usually maturation of attached cells and their production of an extracellular, hydrated matrix (Flemming, 1998). From a marine biofouling perspective, this additional production and secretion of extracellular polymers that embeds and glues the cells more firmly to a concrete surface, is potentially of significance.

The phases of a ‘classic’ biofilm development are illustrated in Figure 5.1 and were described by Hamilton and Characklis (1989) as follows:

- The transport of organic molecules and cells to the surface.
- The adsorption of organic molecules to give a 'conditioned' surface.
- The adsorption of cells to the conditioned surface.
- The growth of adsorbed cells with associated synthesis of expolymeric substances (EPS).

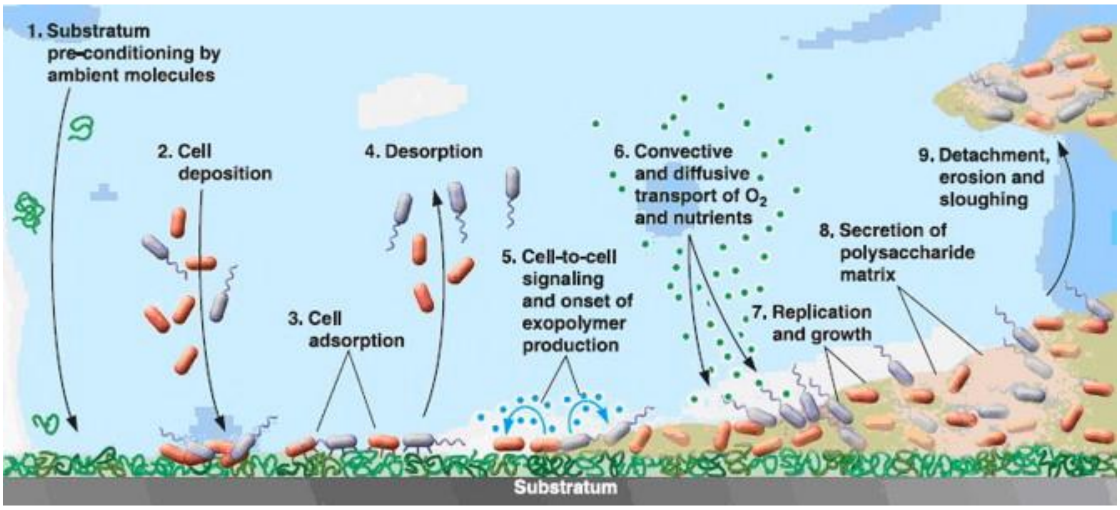


Figure 5.1 A schematic: 'Classical' biofilm formation, (Breyers and Ratner, 2004)

Several techniques for microscopic examination of biofilms *in situ* on the substrata supporting their growth have been documented (Surman *et al.* 1996), in this informative study a comparison of the advantages of several individual techniques to visualise biofilms was discussed. Light microscopy techniques, although unable to reproduce the high magnification, are still of importance in the examination of intact biofilms.

The high pH of cement, within a new concrete matrix, which ranges from 11 to 13, has traditionally been considered, within the concrete industry to prevent the initial biofilm formation and subsequent growth of microorganisms in fresh concrete. This study is the first to report observations of filamentous bacterial growth within new, unplaced marine concrete. Microorganisms such as bacteria have been widely reported to be involved in the deterioration of concrete (Gaylarde and Morton, 1999; Giannantonio *et al*. 2009). However, relatively few direct relationships have been established between the activities of microorganisms and fibre-reinforced concrete, in marine environments. Active biofilms are found in any location where microorganisms and moisture are present (Gaylarde and Morton, 1999). Algae and fungi are often involved in biofilm formation; however, it is the important role of bacteria within the biofilm upon which this review will now focus.

5.1.3 Sequential steps of bacterial adhesion and growth

Bacterial adhesion to a substratum is generally described as a multi-stage process comprising the transportation of cells to the material surface, initial adhesion of cells, followed by irreversible attachment and surface colonisation (Marshall, 1985). Unlike multicellular organisms, increases in the size of bacteria (cell growth) and their reproduction by cell division are tightly linked in unicellular organisms. Bacteria grow to a fixed size and then reproduce through binary fission, a form of asexual reproduction. Under optimal conditions, bacteria can grow and divide extremely rapidly, and bacterial populations can double every 9.8 min (Siddique and Kaur Chaha, 2011). The magnitude of bacterial adhesion varies greatly among species (Fletcher and Pringle, 1985). This is mainly due to the fact that different bacterial strains differ with respect to their surface properties, for example, hydrophobicity and surface charge, and hence attachment abilities. Bacteria can be generally classified on the basis of their cell envelope structure and composition. The Gram-negative cell envelope contains proteins, lipids, peptidoglycan and on the outer surface, lipopolysaccharides (Harder *et al.* 2002). The chain length of these extracellular polymers varies considerably and largely determines the degree of hydrophobicity on the cell surface. The Gram-positive cell envelope is simpler and contains primarily peptidoglycan with small amounts of teichoic and teicuronic acids, polysaccharides and proteins (Harder *et al.* 2002). Not only are bacterial envelopes chemically complex and structurally diverse, the cell surface properties of a given bacterium can change with respect to environmental or growth conditions, thus providing bacteria with a dynamic range of attachment options (Fletcher and Pringle, 1985). The mechanisms of bacterial and diatom adhesion to hard substratum have been reviewed in several publications (Cooksey and Wigglesworth-Cooksey, 1995; Flemming *et al*. 2001). Adhesion of bacteria and microalgae to surfaces is mediated by secretion of a slimy, glue-like substance of extracellular polymers (EPS), which contain polysaccharides, lipopolysaccharides, proteins and nucleic acids (Flemming *et al*. 2001). As such, bacterial biofilms are informative signposts and often a prerequisite for attachment and metamorphosis of many fouling organisms (Harder *et al.* 2002). Given the pivotal role of the organic conditioning films and bacteria as main constituents of early marine biofilms and modulators of subsequent fouling, this chapter will focus on the mechanisms of bacterial adhesion, in order to further understand this process.

5.1.4 Biodegradation of polymer silicon sealants

Sealants are used to seal joints between two or more components, and are important for buildings and infrastructures such as sea defences, bridges, highways and retaining walls. The main purpose of sealants is to prevent water and environmental elements from entering between components while permitting limited thermal and shrinkage movement, particularly important in ground-bearing and soil-retention applications (Figure A5.2 Appendix 5). The regular replacement of sealant is time consuming and expensive. Common sealants include silicone, acrylic, urethane, butyl and other polymeric types. Silicon is one of the most abundant elements of the earth's crust (about 28%) and is an important part of rock mineral structure, present in most of the materials that comprise the crust. In view of the prevalence of silicon in the natural world, it is not surprising that there exist microorganisms capable of both degrading silicon minerals and absorbing silicon. Hueck (1965) defined biodeterioration as any undesirable change in the properties of a material caused by the vital activities of organisms. Silicon is a structural element in diatoms, the cell walls of which consist of up to 95% hydrated amorphous silica. They take up the element in the form of orthosilicate (H_4SiO_4) (Lewin, 1965). Less well studied has been the take up of silicon by bacteria, but this has been shown to occur from silica gel, quartz, or sodium silicate (Heinen, 1968). All these processes are linked to the biodeterioration of silicon minerals, with an informative overview offered by Gaylarde and Morton (2002). Previous research into the durability of construction sealants (Wolf, 1999) examined environmental exposure and case studies. A review and study into sealant life and performance was presented by Odum-Ewuakye and Attoh-Okine (2006) but this did not include biodeterioration. Research into refined and processed materials (Allsopp *et al.* 2004) recognised and detailed the biodeterioration of polymeric materials, however little attention has been given to site-specific concrete sealants and their performance in algal-rich environments.

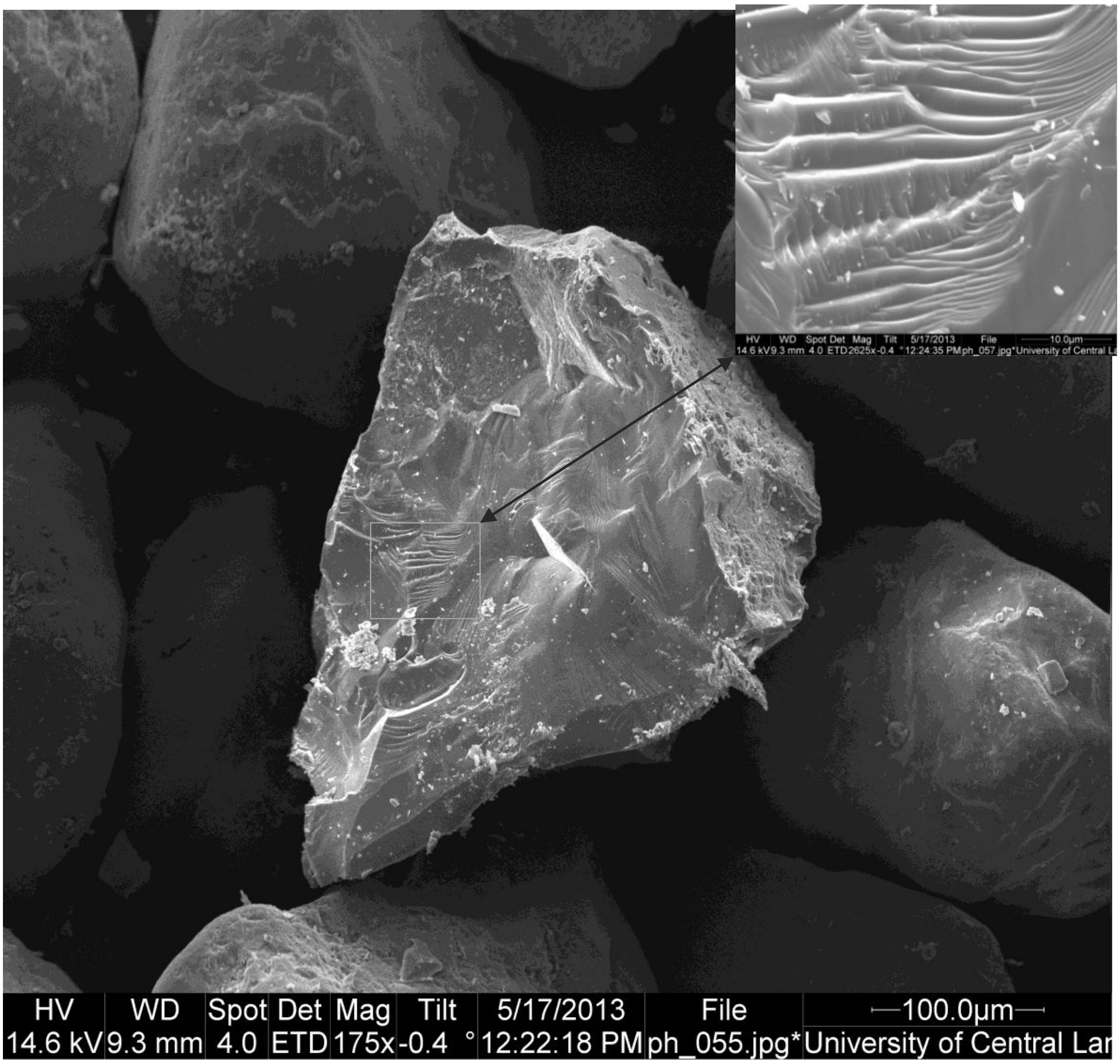


Figure 5.2 Quartz sand particle. EDAX confirmed the primary component was silica (SiO_2). Beach sand used in the production of concrete can harbour bacteria. This specimen was collected from the dredging area used for the manufacture of the armour concrete, cracked in half to show its compressed, rippled core structure (inset).

5.1.5 The use of Beach sand in concrete manufacture

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades, however; no provision is made in the current UK standard for the control of microbial growth within or on the surface of beach sand. Local beach sand (Figure 5.2) was used in the production of the revetment armour. Research by Steele *et al.* (1970) found viable cells buried to a depth of 0.2m below the sand surface in a Scottish sea loch. A similar finding occurred 200km from the source of the marine aggregate used in the study mix, in Lough Neagh

(Northern Ireland), where high concentrations of living cells were found attached to sand grains down to 0.5m below the sand surface (Jewson and Briggs, 1993).

5.2 Methodology

5.2.1 Concrete

Six 150 mm x 150 mm cubes were made in accordance with BS EN 12390-2, *Testing hardened concrete. Making and curing specimens for strength tests*. They were produced at the casting yard, at an ambient air temperature of 20°C, 55% relative humidity, the mix being supplied by the concrete manufacturer (Tarmac), with a slump value of 100 mm, mix design (A3.3 Appendix 3). The steel moulds were cleaned and lightly oiled with the same release agent as used by the casting yard (Grace Construction). They were filled in 50 mm layers and compacted, with a cleaned steel tamping bar, with a minimum of 35 tamps per layer for a 150 mm mould. After tamping each layer, the mould was lifted slightly and dropped and the sides tapped, to close the top surface of each layer. The final layer was slightly overfilled above the mould. Finally the top layer was trowelled off, level with the top of the mould. The cubes were also vibrated for 3 minutes, as was the case with the revetment armour units. The fresh cubes were kept away from the open air, to avoid air borne spores, and extremes of heat and cold. They were covered to prevent surface evaporation and stored as close to 20°C as possible until the moulds were stripped after 24 hours. They were stored within a university laboratory for an air curing period of 28 days. Over a period of six months 100 samples, suitably sized for microscopy, were carefully broken into pieces with the use of a rubber mallet. Samples from throughout the cubes, including from the near surface and from the inner mass, were chosen to achieve a representative study. Cracked or damaged specimens were avoided and at no time were the samples taken outdoors, they were kept in a secure cupboard.

5.2.2 Sampling of bacteria for culture

After careful observations of concrete specimens, samples were catalogued and prepared for the isolation of bacterial cells. Cell capture using the cellotape method

(Morton, 2003) proved unsuccessful. Small plugs were taken from agar using a sterile 8 mm cork borer, they were pressed against the surface of the concrete samples in the vicinity of previously observed colonies. These plugs were placed in a Petri dish and incubated at 35°C for 48 hours. One gram of beach sand was serially diluted with ¼-strength ringer's solution, plated out and incubated.

5.2.3 Light microscopy

Observations of concrete and bacteria were made in a step-by-step progression from large to small scale allowing for the selection of specimens that represented the concrete matrix. Light microscopy methodology was described in Chapter 4, Section 4.2.4.

5.2.4 Scanning Electron Microscopy

Concrete topography and cell distribution were also observed using a FEI Quanta 200 scanning electron microscope (SEM) as described in Chapter 4, Section 4.2.5. Broken concrete samples may have had micro cracks, however observations were of voids and chambers, hence cracking was not relevant in this part of the study.

5.2.5 Study site sealant specimens

Performance of sealants was surveyed and monitored over the full length of the construction period. Location and exposure details at the study site can be found in Section 5.1.8. The concrete pavement joint sealant studied (Geocel, UK) has been formulated to accommodate repeated and pronounced cyclic movement has been applied to both *in-situ* and pre-cast elements, such as floor slabs and wave walls; as part of the coastal protection scheme. The sealant used at the study site is a one part, high strength, flexible, sealant specifically developed for structural marine applications. It is non hazardous (Isocyanate and solvent free), offering long term performance with resistance to staining, UV and salt water degradation. However, vandalism and damage from cleaning vehicles was observed in the field.

5.3 Results

This section presents the results of the experimental work described in Section 5.2. In line with objectives previously set out, representative observations are offered. Petrographic examination revealed filamentous bacterial growth in new concrete (Figures 5.3 to 5.8). SEM photomicrographs, along with light and inverted microscopy have enabled the observation of the early formation of a bacterial biofilm, the start of the biofouling process. Light microscope images of bacteria cultured from beach sand samples are presented (Figures 5.9 and 5.10) allowing comparisons to bacterial filamentous growth within freshly hardened revetment armour concrete.

Photomicrographs show biodeterioration of hybrid polymer silicone sealant samples from the study site, electron microscopy showed evidence of microbial growth at the surface and within the matrix of the sealant (Figures 5.11 to 5.15).

Examination of the freshly hardened concrete revealed many small voids within the matrix, especially under aggregate. Approximately 100 voids were examined by SEM, 50 of which showed a symmetrical smooth interior, indicating an air void. The remaining 50 observed were often irregular shaped with rippled walls, (Figure 5.3). The rippled effect, on the wall of the cavity indicates that this void may have contained water at some time, probably during and after the mixing process. This effect is often seen on beaches after the tide has receded. This moisture may have been available for bacteria growth. Even though moisture was not present at the time of examination, filamentous bacterial growth was observed, Figure 5.4 is a typical example.

5.3.1 Bacterial filamentous growth in new concrete

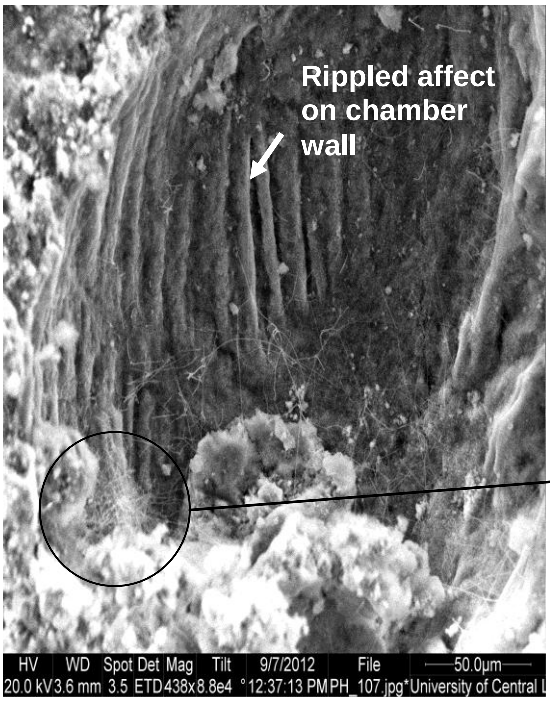


Figure 5.3 Possible water void in new concrete.

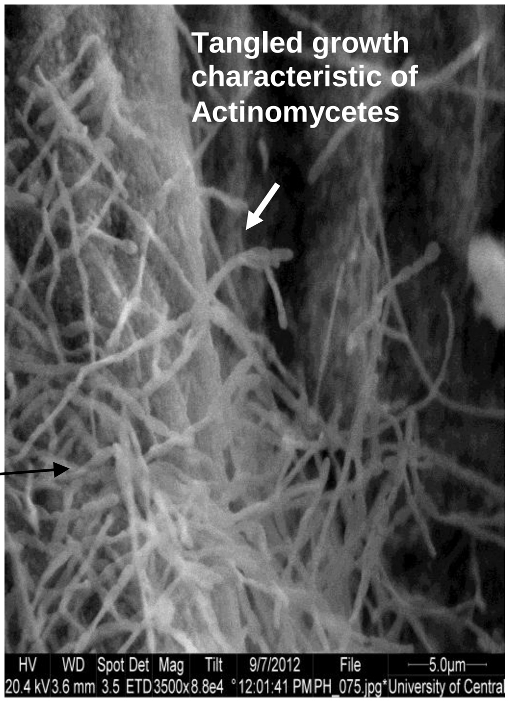


Figure 5.4 Biofilm formation in the void.

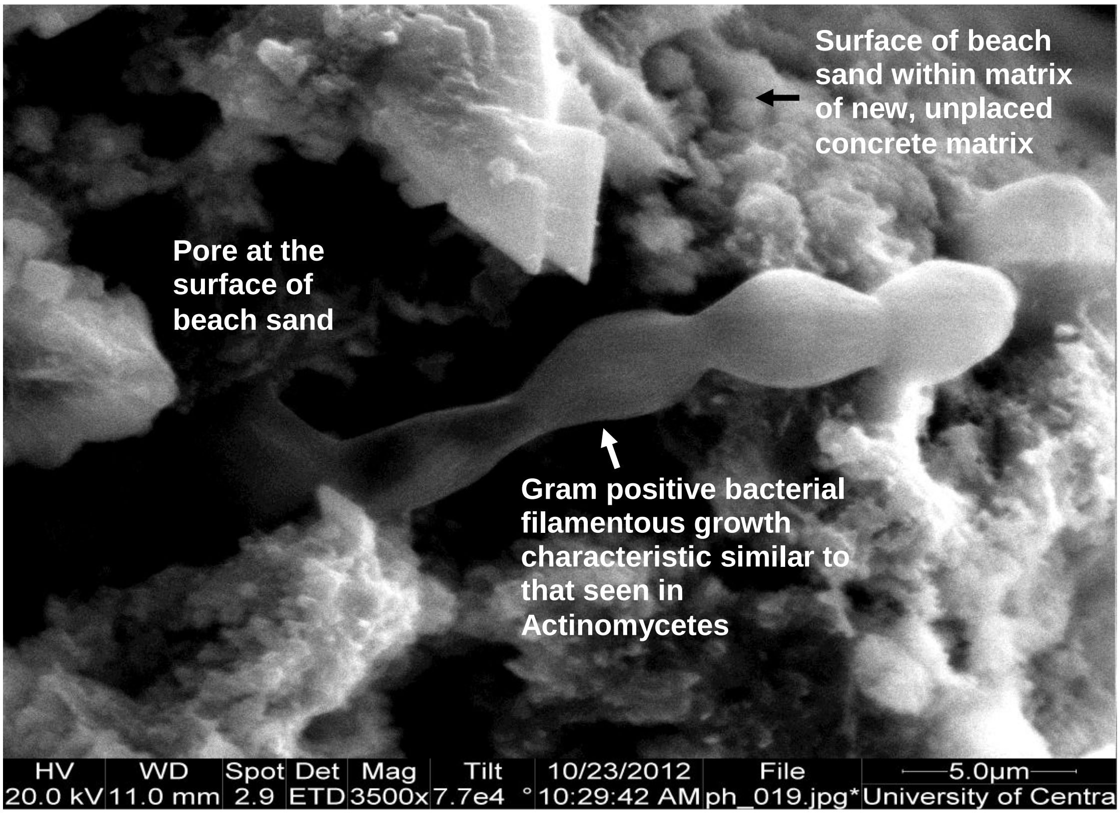


Figure 5.5 Filamentous bacterial growth out of the pore of fine aggregate.

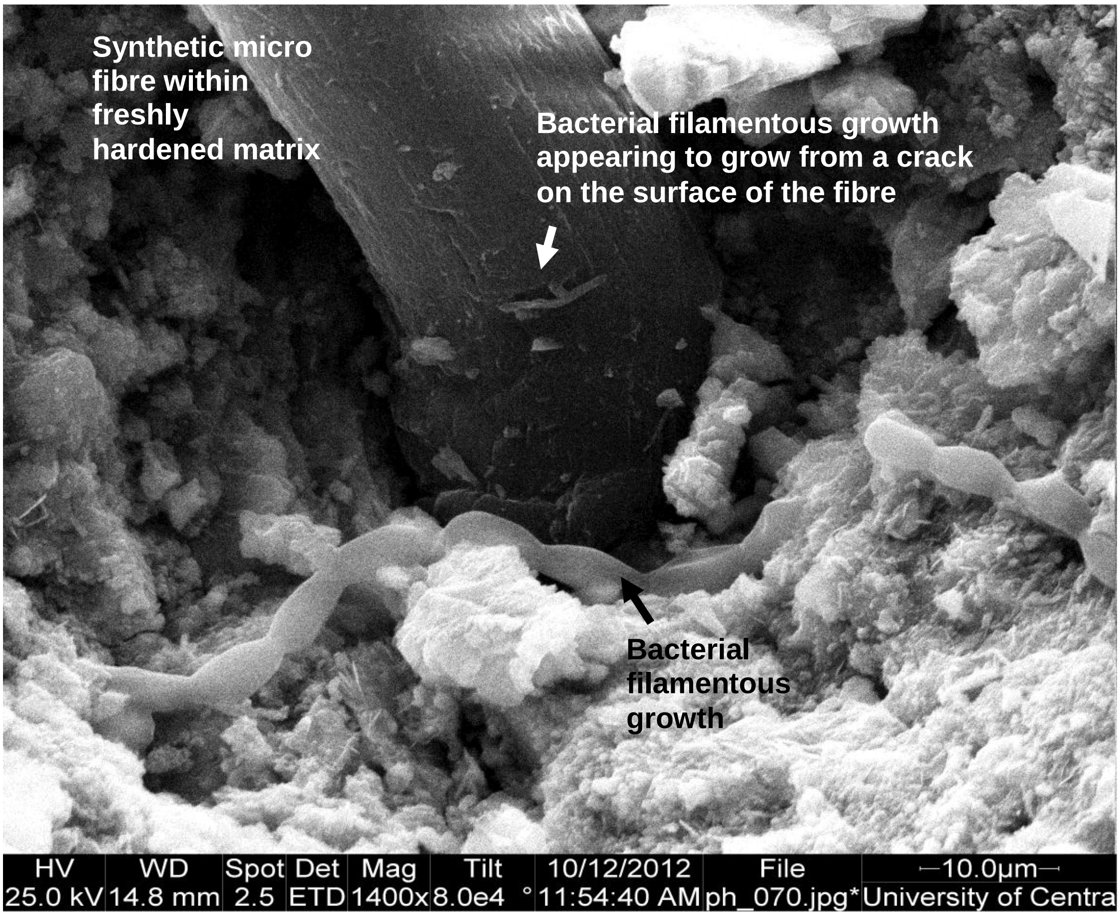
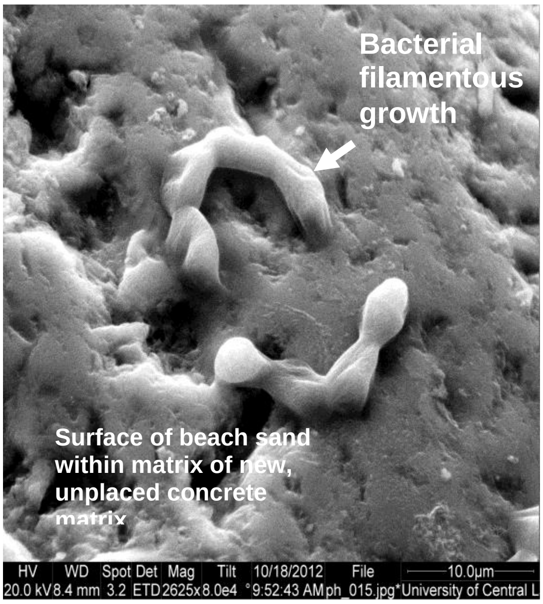


Figure 5.6 Filamentous bacterial growths at the base of a micro fibre.



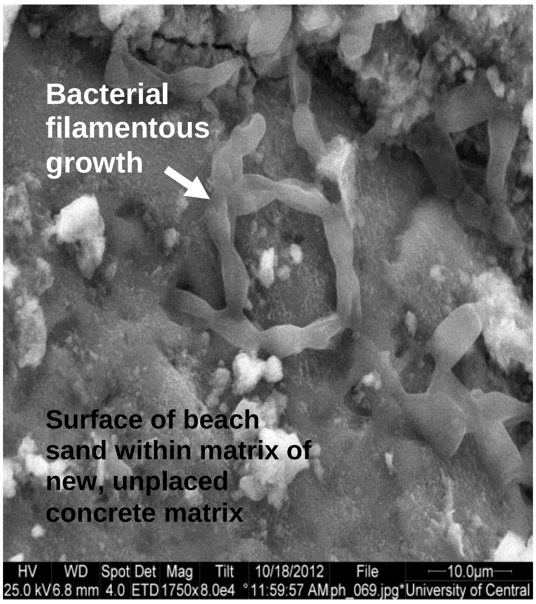


Figure 5.7 Filamentous bacterial growth.

Figure 5.8 Early bacterial growth

5.3.2 Bacteria culture from beach sand

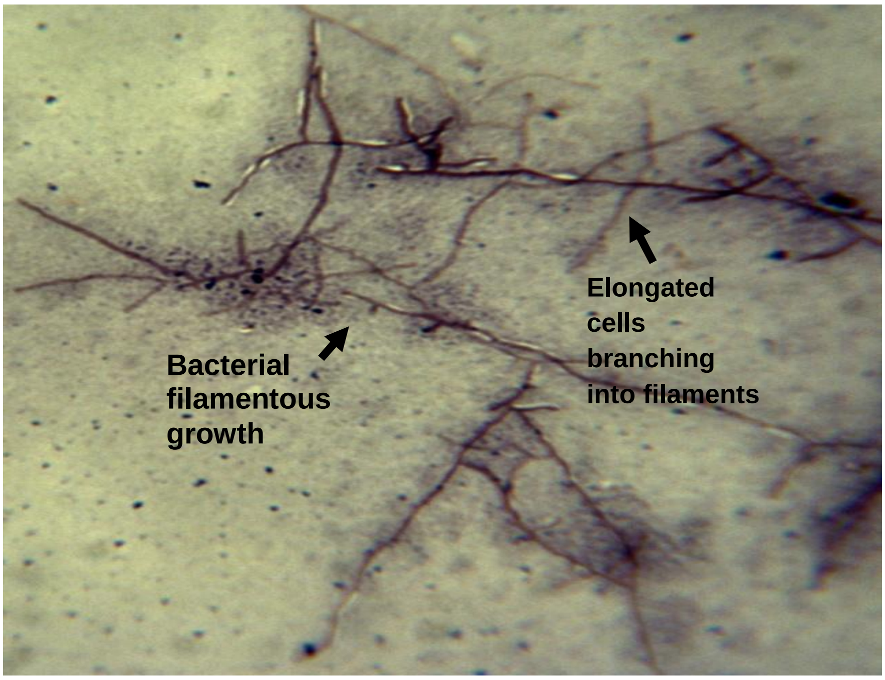


Figure 5.9 Filamentous bacteria from sand sampled from beach site (x400 magnification).

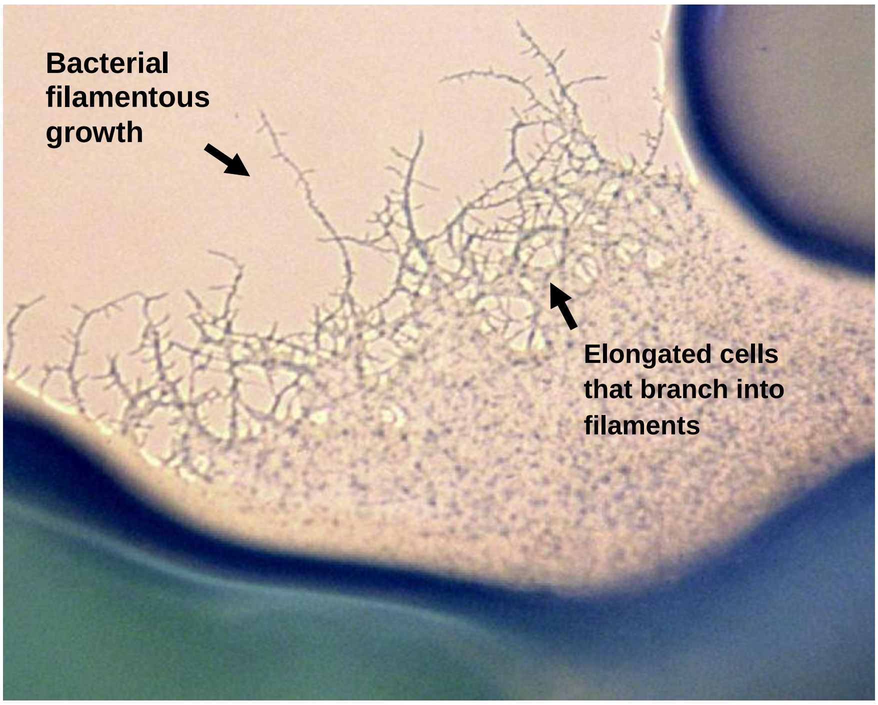


Figure 5.10 Filamentous growth characteristic of *Actinomycetes* cultured from beach sand (x100 magnification).

5.3.3 Biodeterioration of a hybrid polymer silicone sealant

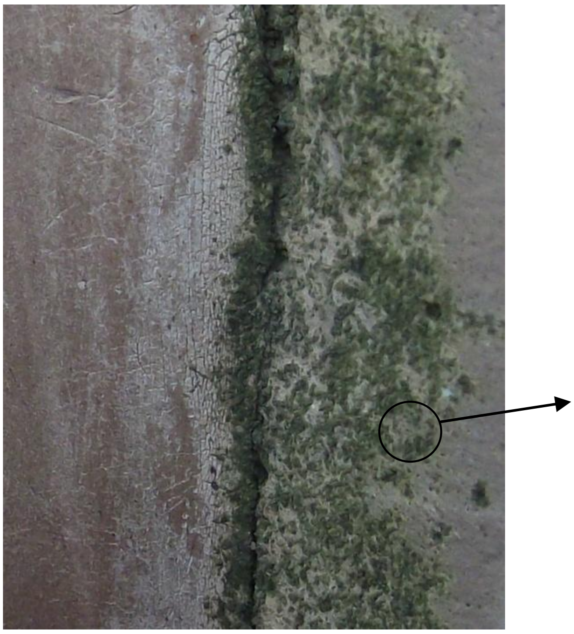


Figure 5.11 Concrete sealant interface

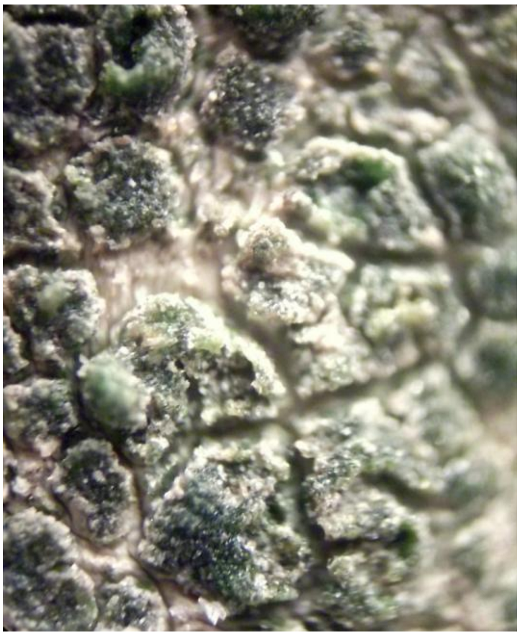


Figure 5.12 Surface of sealant at 2yrs exposure.

Figure 5.13 Algal colonisation on the surface of the sealant after 2 years exposure.

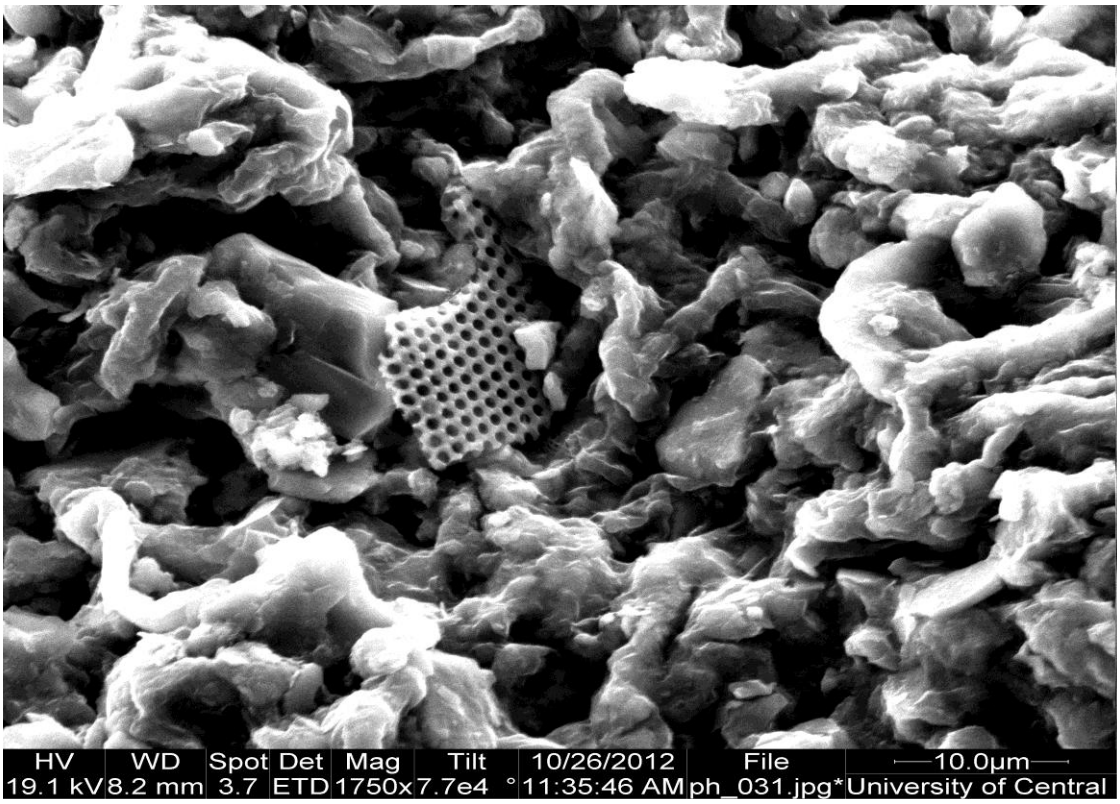


Figure 5.14 Biomass and frustule on the surface of the sealant.

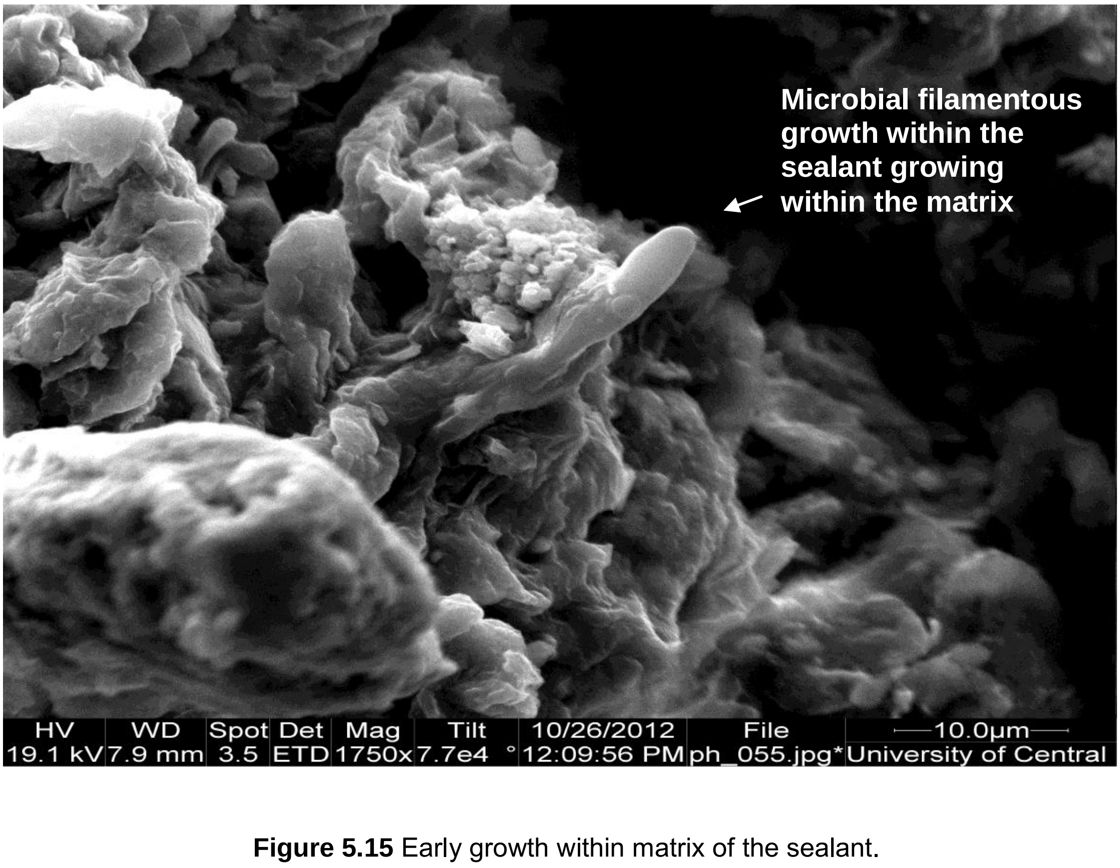

Microbial filamentous growth within the sealant growing within the matrix

Figure 5.15 Early growth within matrix of the sealant.

5.4 Discussion

During this phase of work, cells were cultured and examined from the early formation of a biofilm within freshly hardened concrete (Hughes, 2013). The effect of the formation of a conditioning layer and the subsequent colonisation and biofouling of polymer silicone sealant samples taken from the study site were studied (Hughes *et al* 2013). The laboratory investigations undertaken do not, and are not intended to reflect the complexities of the study site. In the marine environment, organisms interact with each other and there are seasonal influences along with environmental factors.

5.4.1 Bacterial filamentous growth in freshly hardened fibre reinforced concrete

Fragments of test cubes of freshly hardened revetment concrete were examined under SEM. The observation of filamentous bacterial growth within fresh, cured concrete was unforeseen and unanticipated. This concrete already had a detectable bacterial population before being placed on site. Site observations, discussed in Chapter 4 have shown that this concrete is colonised almost immediately after placing, confirming the bacteria were already established within the concrete samples. This new phenomenon has a bearing throughout this research and will influence the perception of marine concrete biofouling in general.

Figure 5.6 shows a micro synthetic fibre (22 μm in diameter) within the cement matrix. Interestingly, filamentous growth has started at the base and on the surface of the fibre (arrowed). This demonstrates the ability of the bacteria to attach to this ‘inert’ material in a natural environment and has been further studied in laboratory based experiments, (Chapter 7) attaching bacterial cells to polymers.

SEM of individual sand grains within the matrix were examined, filamentous bacterial growth was observed from within the pores of the material, (Figure 5.7 and 5.8). A chain-like structure of cells approximately 350 nm in diameter growing within the sand can be clearly observed. Considering the constant mixing of sediment at a beach surface, it may follow that microbial endoliths could occupy some of the sand used in the production of the concrete examined.

MPA-Cement (formally The British Cement Association) warns that washed beach sand is generally unsuitable by itself for good quality concrete, because of its single-sized grading. However, this can be overcome by the blending of aggregates. While aggregates for unreinforced concrete can be washed with sea water, as was the case in this study, for reinforced concrete, the aggregates must be carefully washed with potable water to remove excess chloride from sea water, despite this they will still retain shell fragments and organic matter that can affect the water demand of the mix. The organic content refers only to water-soluble organic compounds derived from decaying vegetation, tests for which no longer appear within (UK) standards.

The observations suggest that the blanket use of marine-sourced aggregates should be reconsidered for concrete that is to remain in contact with sea water, particularly mass (unreinforced) concrete. Washing in water may only partly remove some of the epilithic biomass present on the surface of the aggregate, possibly leaving endolithic microorganisms, to exist and thrive (Figures 5.8). It has been reported (Cardon *et al*. 2008) that some microorganisms have resting stages (spores and zygotes) that allow cells to lay dormant in unfavourable environments, even freezing conditions or to survive in ephemeral pools. Previous research found that even after soils had air-dried for 35 years, cells could be cultured from them. Therefore the microbial content may need to be controlled in structures subject to permanent wetting by sea water, to control growth on and inside the matrix. BS EN 12620 (BSI, 2013) is the predominant specification concerning the use of aggregates for concrete supported by UK national guidance document PD 6682-1 (BSI, 2013a). This guidance should consider undesirable elements such as microorganisms more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach-sourced fine aggregate, leading to increased colonisation of higher plants such as algae, and the further biodeterioration of concrete.

The use of beach sand in many European countries is to be avoided. In some countries e.g. China, its illegal, yet in the UK about 20% of natural gravel and sand is dredged from the sea. Samples of beach sand from the vicinity of the dredging site (the source of fine aggregate used in the concrete production) were examined microscopically and found to be colonised by filamentous microbial growth. Figures 5.9 and 5.10 show cultured bacterial filamentous growth from beach sand. The existence of microbial populations that live on or within sand is well documented and has been discussed. However, the bacterial growth observed earlier in the freshly hardened matrix may have originated from the beach sand. This material, washed only in seawater before use needs further investigation. This practice and its consequences will be further discussed in Chapter 8, however, the fact that these cells have survived the concrete manufacture, found a food source, grown and been successfully cultured, may affect the durability of marine concrete studied in this research. Bacteria with the ability to form biofilms are the forerunners of marine biofouling observed in this project.

Although bacteria, and particularly acid-producing bacteria, have been traditionally considered as harmful organisms for concrete, an alternative perspective is that the growth of microorganisms may afford some level of protection from weathering and erosion. Interesting research by De Belie and De Muynck (2009) showing the ability of certain bacteria to promote the precipitation of calcium carbonate, has been used advantageously for consolidation of concrete and stone. Biomineralisation is defined as a biologically-induced precipitation in which an organism creates a local micro-environment with conditions that allow optimal extracellular chemical precipitation of mineral phases (Hamilton, 2003). Numerous diverse microbial species participate in the precipitation of mineral carbonates in various natural environments including soils, biofilms, and oceans. Figure 5.16 depicts filamentous growth (arrowed) from sodium chloride (NaCl) crystals within the matrix of armour concrete after 3 years exposure at the study site. The excessive amounts of potassium or sodium ions could have originated from beach sand which had been washed in sea water and used in the concrete armour manufacture.

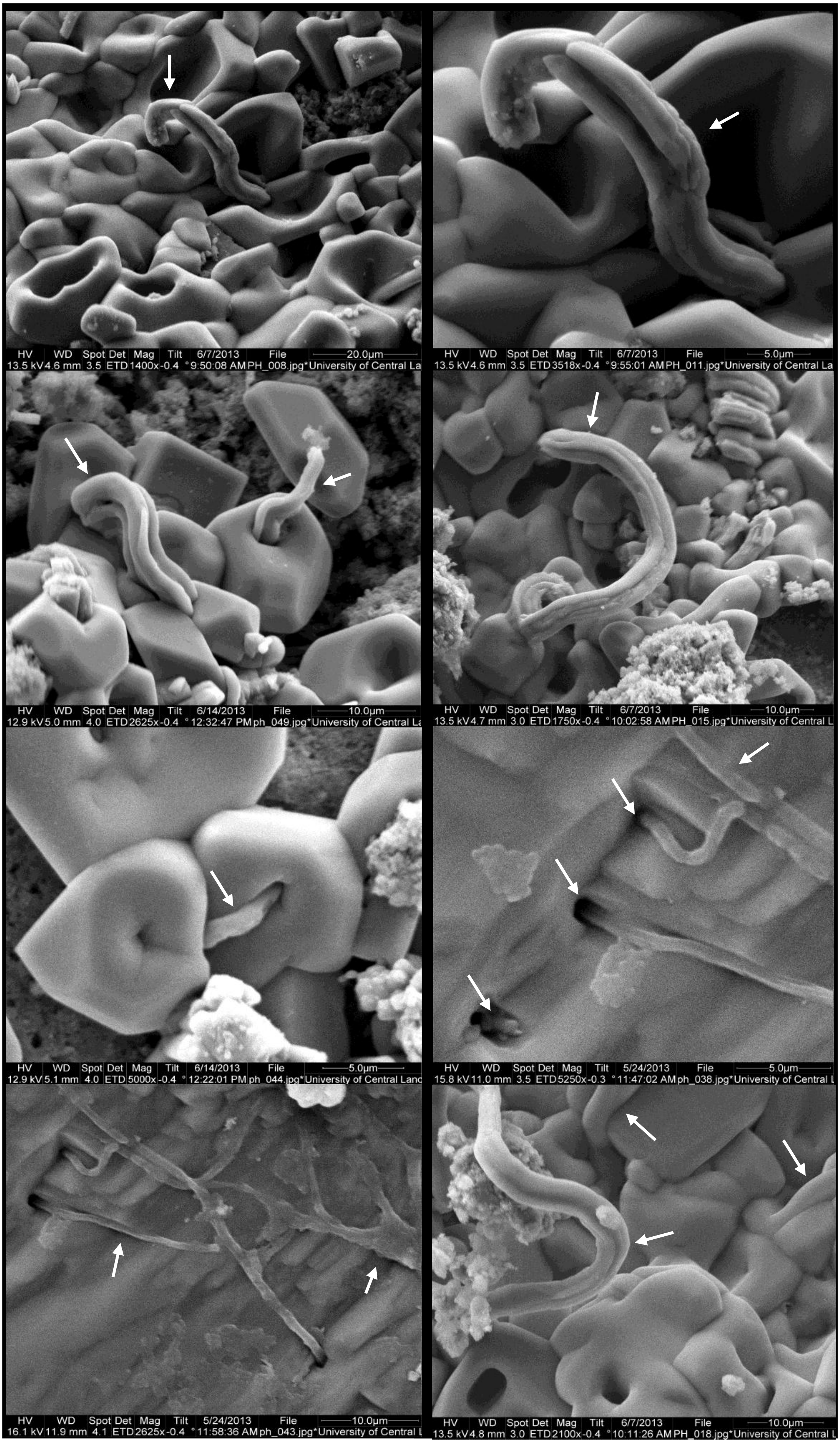


Figure 5.16 Filamentous growth (arrowed) from sodium chloride (NaCl) crystals

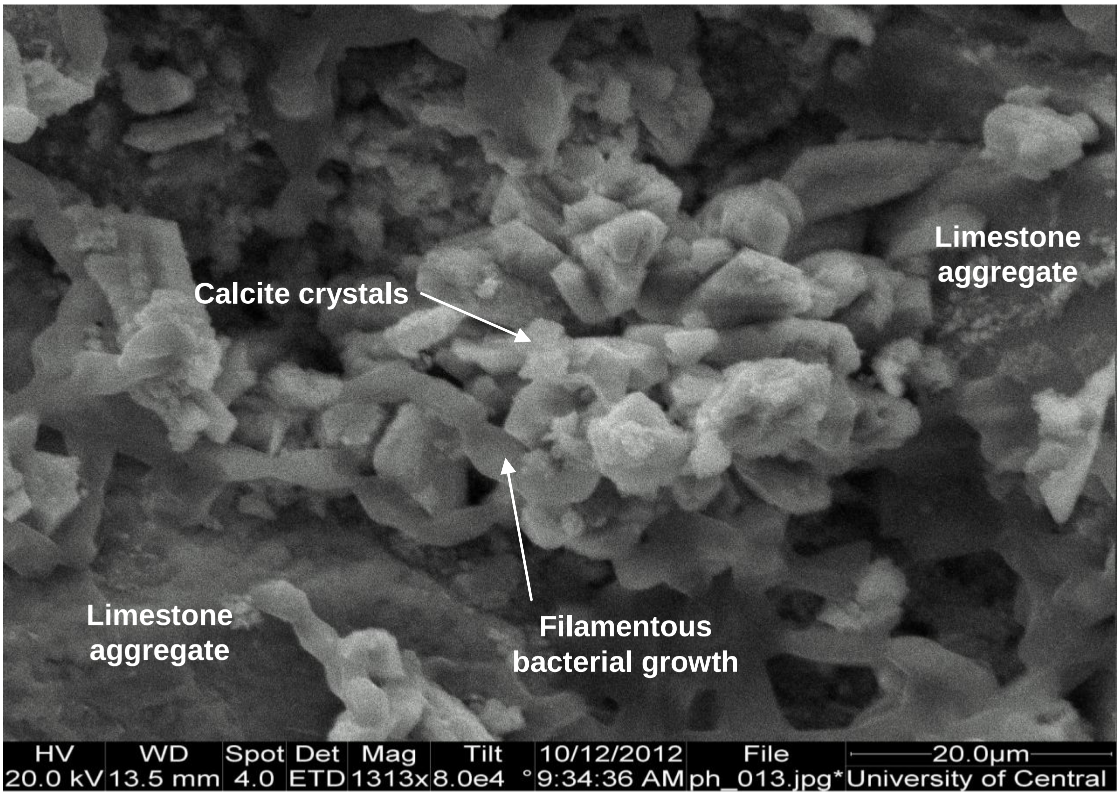


Figure 5.17 Precipitation of calcium carbonate in fresh concrete, filamentous bacterial growth and calcite crystals at the cement limestone interface.

The precise role of microbes in the carbonate precipitation process is still not clear, however, almost all bacteria have been shown to be capable of calcium carbonate precipitation (Boquet *et al*. 1973). Figure 5.17 shows precipitation of calcium carbonate in fresh concrete. A novel technique for the remediation of damaged structural formations has been developed by employing a selective microbial sealing process, in which metabolic activities promote precipitation of calcium carbonate in the form of calcite. A recent and informative review was offered by De Muynck *et al.* (2010). Biomineralisation of calcium carbonate is one of the strategies to remediate cracks in building materials. Recently, microbial mineral precipitation resulting from metabolic activities of some specific microorganisms in concrete to improve the overall performance of concrete has become an important area of research. It has been hypothesized that almost all bacteria are capable of calcium carbonate ($CaCO_3$) production because precipitation occurs as a by-product of common metabolic processes such as photosynthesis, sulfate reduction, and urea hydrolysis (Hammes *et al*. 2003).

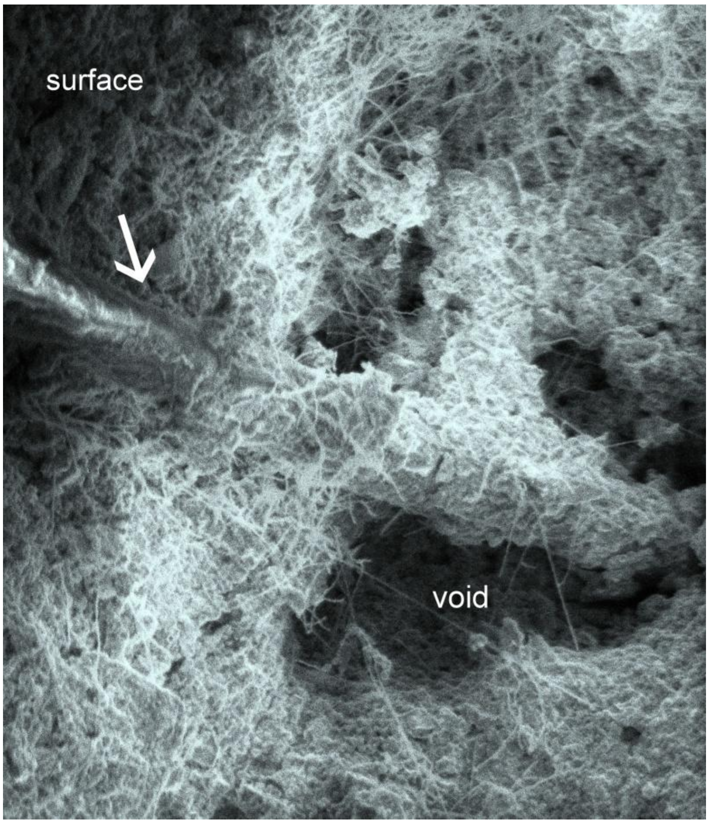


Figure 5.18 A micro-fibre within revetment cement matrix (22 μm in diameter) with bacterial biotenacious growth (350 nm in diameter).

The biotenacious growth on and around the micro-fibres in Figure 5.18 can be likened to the natural process of retting where micro-organisms have been used for many years, in the extraction of fibres from plant materials. Retting employs the action of bacteria to dissolve and degrade the surrounding tissue of bast-fibre, thus separating the fibres (Rosemberg, 1965). This is essentially an assimilative process, during which organic residues are washed away, leaving the fibres intact. Degradation of fibre reinforced concrete however, is essentially a dissimilative process, but with a similar result.

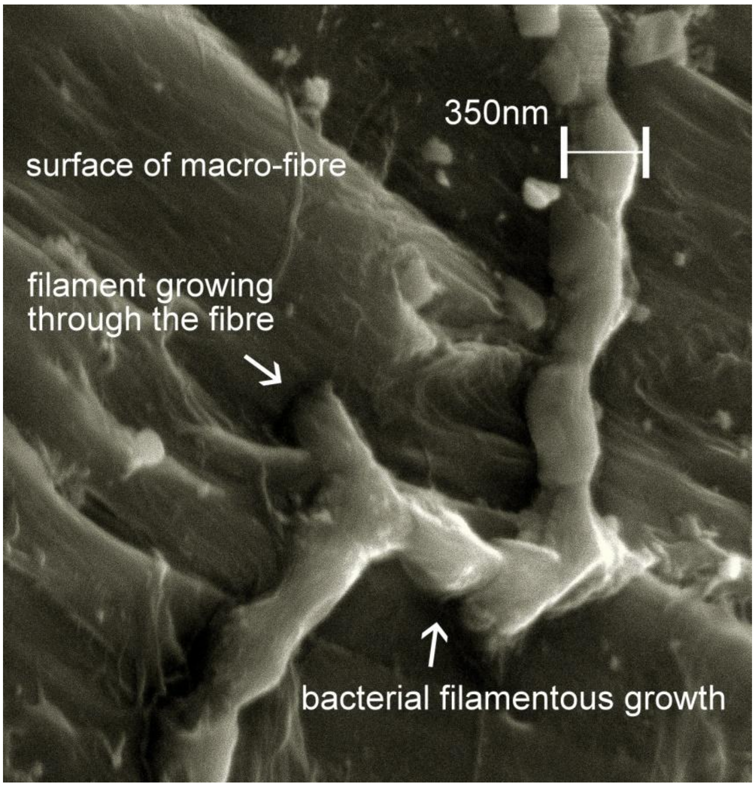


Figure 5.19 A macro-fibre within revetment cement matrix with filamentous growth through the polymer.

Figure 5.19 shows bacterial filamentous growth at the surface of a macro fibre within the matrix penetrating the polymer. This image is representative of fibre degradation within freshly hardened revetment concrete. This type of biodeterioration has also been reported in subsea tunnels in Norway (Hagelia, 2008), where steel fibre reinforced concrete used for rock support was attacked by saline ground waters along the concrete/rock interfaces as well as the outer rough and more reactive concrete surfaces. The process had frequently led to the total disintegration of the cement paste matrix and steel fibre after less than five years exposure and was reported as closely related to the growth of biofilms (Hagelia, 2008). Examples of bacterial filamentous growth on synthetic fibres from freshly hardened armour concrete appear to firmly attach and penetrate the polymer (Figure 5.20).

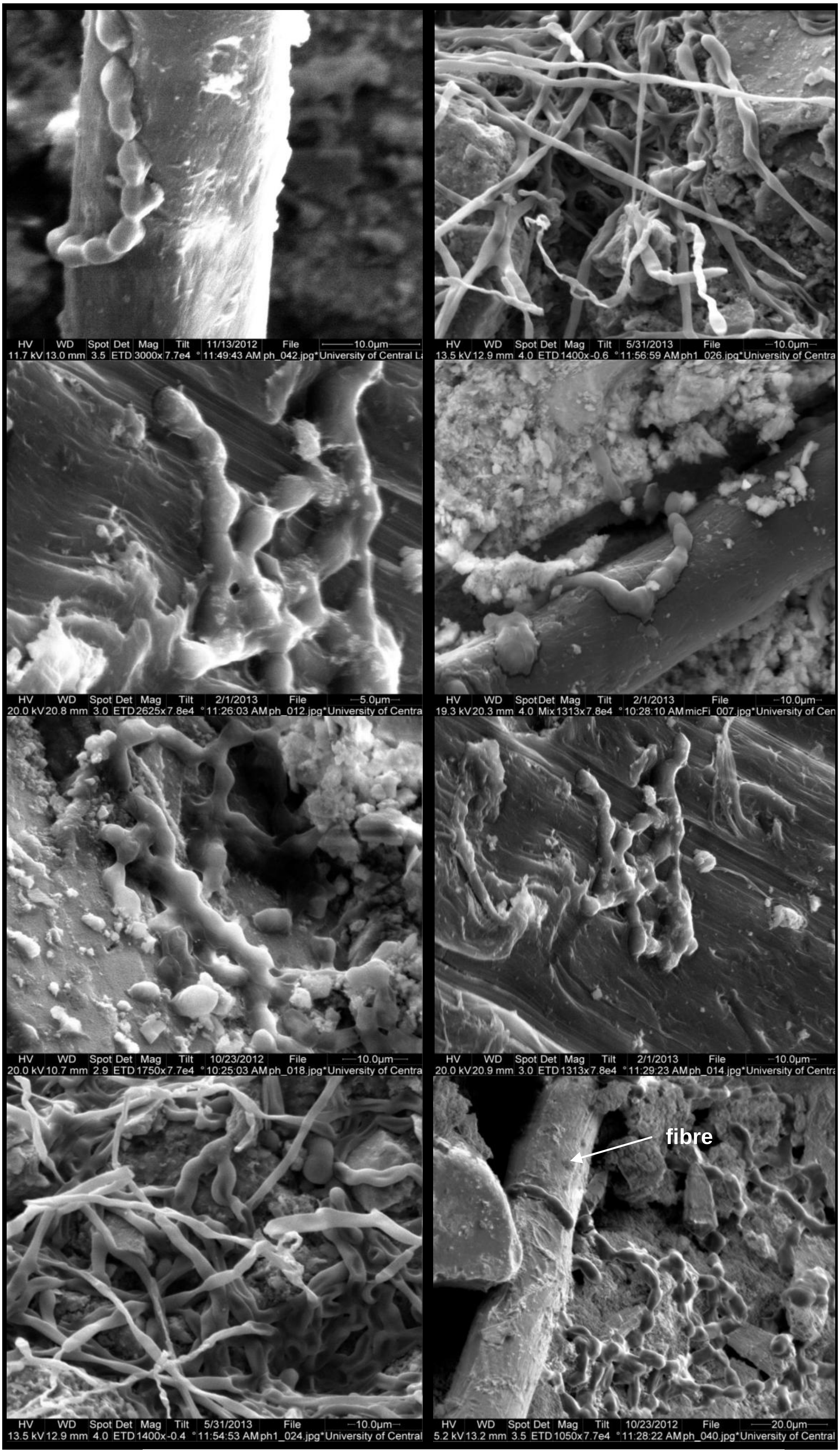


Figure 5.20 Examples of bacterial filamentous growth on synthetic fibres

5.4.2 Biodeterioration of a hybrid polymer silicone sealant

When these materials were introduced for practical applications during the 1930s, they were believed to be completely inert to the action of microorganisms. It is now well known that microorganisms can interfere severely with the function and stability of synthetic polymers (Flemming, 1998). There are different ways in which microorganisms can hamper the structure and function of synthetic polymers. The undesired effects range from the mere presence of accumulated biomass as represented by biofilms, via the degradation of leaching components, to direct attack and penetration (Flemming, 1998). Polymers used as additives in concrete can be microbially attacked as well. In the case of high concentrations of additives, they are degraded resulting in microbial contamination and mass development of biomass, as observed in drinking water reservoirs (Morgenstern, 1982). Concrete additives in lower concentrations still can be used by microorganisms as soon as other corrosion mechanisms have made them bioavailable (Herb and Flemming, 1996). In this case, the microorganisms multiplied on the interior walls of drinking water reservoirs, formed pigments and led to an unhygienic appearance on the reservoir, giving rise to expensive sanitation measures (Herb and Flemming, 1996).

Surveying the study site over several years has enabled the materials used to be monitored. It has been shown that algal filaments at the study site can tunnel within the sealant matrix. The SEM micrograph (Figure 5.15) demonstrates the existence of microbial filamentous growth, from within the sealant matrix. Figures 5.13 indicate the destructive presence of surface growth which will lead to the eventual failure of the sealant. When algae colonise concrete structures they start to absorb calcium, silica and magnesium (Javaherdashti *et al*. 2009). Sealants are polymers that commonly contain silicon together with carbon, hydrogen, oxygen and may offer food sources for microbial growth. This could partly explain the abundant colonisation (Figure 5.12). It is not implied that this mechanism is solely responsible for the biodeterioration observed at the study site, but it is suggested that it should be considered with associated environmental conditions, for example tidal impact, power washing and vandalism, to be a factor in the durability and performance of polymer sealants.

The Biomass shown in Figures 5.12 will be capable of absorbing and storing water and associated nutrients during periods of submersion. If the conditions are favourable for growth, the filaments will grow and extend over larger and deeper areas of the sealant, pioneering filaments are shown in Figure 5.15. The effects of shrinking and swelling of the hydrophilic filaments during dry conditions and periods of moisture intake, will accelerate the mechanical biodeterioration process of the sealant.

Sealants, once in place, are exposed to harsh environmental degradation which eventually affect their performance, and ultimately cause them to fail (Figure Appendix 5.1). Civil Engineers, therefore need to know the predicted service life of a marine sealant in order to estimate the overall costs associated with a marine structure. This phase of the research highlights a potential durability issue, and will enable a more accurate material service life prediction. The correct application of a marine sealant involves not only choosing a material with appropriate physical and chemical properties, but also having a good understanding of joint design, substrates to be sealed, performance needed, and biodeterioration which can profoundly influence the service life of the installed sealant. Rather than rely on manufacturers literature, independent guidance should be available to Civil Engineers on such matters. Changes in sealant that repel the colonisation and growth of algae, and other microorganisms, using forms of biocide, may offer ways of reducing biodeterioration and extending sealant life to first maintenance.

5.5 Conclusions

Bacterial biofilms are informative signposts and a prerequisite for attachment of macrofoulers. New fresh concrete was examined and filamentous bacterial growth was observed. Cultured bacterial cells from the concrete were also examined, indicating the cells have survived the concrete manufacture process. The origin of these cells is probably from beach sand, the source of fine aggregate for the production of the concrete. It follows that these cells have survived, have resourced moisture from within the cement matrix and grown. This chapter has observed the biofilm development and examined its progression. Bacteria present in fresh concrete, designed for a marine environment, have a significant impact on the material, its growth within the matrix is the start of the fouling process. It will have to be considered when testing the material, in this project and throughout the marine concrete industry.

All potential biodeterioration mechanisms of marine joint systems need to be better understood in order to select a suitable sealant for use in a joint system. This phase of study observed marine microbial colonisation within a polymer silicone sealant, and discussed how microorganisms may affect the performance of the sealant matrix in a marine environment. Polymer sealant samples from within precast elements have been examined microscopically and the results presented. The environmental performance of the sealant has been observed at a study site under ‘real life’ conditions. Biodeterioration of the sealant, by way of algal filaments tunnelling into the polymer has been observed. Filamentous growth within the matrix of the sealant will weaken the material, making it more susceptible to other hostile elements.

5.5.1 Constraints

A limitation to this chapter is that it involves only a particular concrete mix design and therefore may not be representative of marine concrete generally. The observations of bacteria within fresh concrete were made in a small number of cubes and it could be argued that a diminutive sample is not comparable to the total amount of concrete used overall at the study site.

Chapter 6

Photocatalytic anti-fouling coatings

In the future, we will be striving to create additional
new technologies and industries that can
be disseminated to the world.
For that purpose, it is essential that
our research and development be
advanced in tandem with the
exchange of ideas among
ourselves and the rest of the world.

Akira Fujishima (2011)
President, University of Tokyo

6.1 Introduction

Civil engineers involved in the construction or maintenance of marine structures are faced with the problem of preventing unwelcome microbial growth in an environmentally friendly way. A long term ecologically sound answer to organic growth remains unsolved, however the use of titanium dioxide (TiO_2) particles within coatings for concrete pavements has received considerable attention in recent years as these particles can trap and decompose organic and inorganic air pollutants by a photocatalytic process (Fujishima *et al*. 2000). In spite of these promising benefits, the durability and resistance to wear of TiO_2 surface coatings upon fibre reinforced marine concrete has not been evaluated. In this chapter, the development of fundamental research on the application of TiO_2-based photocatalysis in a marine environment will be examined. The problems restricting a larger scale application of the technology and some future developments are also discussed.

Evaluation of zinc and titanium nano-oxide silan/siloxane emulsions and their resistance to biofouling by algal colonisation has recently been reported (Zhang *et al.* 2013). Three TiO_2 containing white cements and a TiO_2 coating applied on autoclaved aerated concrete have been evaluated as strategies to avoid algal fouling on new and existing buildings (Maury-Ramirez *et al.* 2012). The TiO_2 based coating showed a significant reduction of the algal coverage rate. Among the different treatments investigated by De Muynck *et al*. (2009), the application of a biocide, once proved to be the best method to prevent algal fouling on autoclaved aerated concrete. The performance of the surface treatment was shown to be dependent on the bioreceptivity of the concrete, which was examined in Chapter 4. Combinations of water repellents and biocides appeared to be the most effective treatments for the prevention of algal fouling on concrete with a high bioreceptivity.

Current remediation methods used at the study site affect the revetment armour concrete durability, as discussed in previous chapters, therefore alternative strategies need to be investigated. Photocatalytic coatings are successfully used on many other building materials and have shown to retard algal growth on concrete (Peller *et al*.

(2007). In spite of these promising benefits, applications of this technology are currently limited. The durability of this technology in a marine application needs to be established before large-scale practical implementation is undertaken.

6.1.1 Titanium dioxide

Titanium dioxide (TiO_2) is a white inorganic substance that is thermally stable, non-flammable, and insoluble. TiO_2, is an oxide of the metal titanium which is the ninth most abundant element in the earth's crust. TiO_2 is present widely and cheaply in many rocks and mineral sands, the most common forms being ilmenite and rutile deposits. TiO_2 can be found in a variety of crystallographic structures such as rutile or anatase. Rutile is the most common, most stable, chemically inert, and can be excited by both visible and ultraviolet (UV) light (Austin and Lim, 2008). Anatase is only excited by UV light and can be transformed into rutile at high temperatures. Both rutile and anatase have a tetragonal ditetragonal dipyramidal crystal system but have different space group lattices. Figure 6.1 shows ball and stick models of the different tetragonal lattice systems for rutile and anatase (Austin and Lim, 2008). Ultra-fine (nano-scale) titanium dioxide (anatase) was used in this phase of work for surface treatments (Supplied by Cristal Global - http://www.cristal.com).

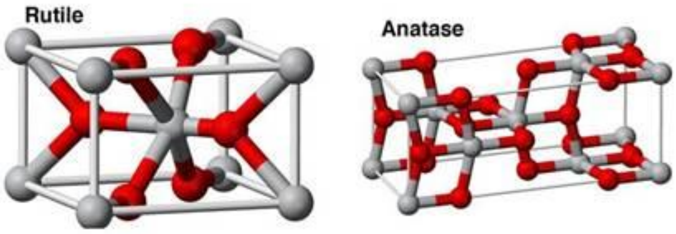


Figure 6.1 Crystal structures of rutile and anatase titanium dioxide (Austin, 2008.). The titanium atoms are grey and the oxygen atoms are red.

The potential of titanium dioxide as a photocatalyst was discovered by Fujishima and Honda (1972). This process, which is similar to plant photosynthesis, allows the decomposition of water into oxygen and hydrogen in the presence of light, by means of a TiO_2-anode (Fujishima *et al*. 2000). Based on this heterogeneous photocatalytic oxidation process, nitrogen oxides are oxidized into water-soluble nitrates while sulphur dioxide is oxidized into water-soluble sulfates; these substances can be washed away by moisture in the form of rainfall or seawater.

Titanium dioxide photocatalysis has shown to improve the durability and aesthetical properties of cementitious materials (Maury-Ramirez and De Belie, 2010); e.g. maintaining original colours (Maury-Ramirez and De Belie, 2010). Thus TiO_2 could be used as an anti-fouling agent to increase the longevity of marine concrete. TiO_2-based coatings recently investigated by other workers (Maury-Ramirez *et al.* 2012a) showed a significant reduction in algal fouling and these authors concluded that the coatings had the potential to reduce cleaning and maintenance activities; thus contributed to the sustainability of concrete. The basic reaction mechanisms on photocatalyst surface under the irradiation of ultraviolet and their corresponding applications in building and construction materials are reviewed by Chen and Poon (2009). Previous research into the use of titanium dioxide (TiO_2) ultrafine particles as coating for concrete pavement has been reported by Hassan *et al*. (2010) highlighting the considerable attention in recent years to TiO_2 particles' ability to trap and decompose organic and inorganic air pollutants by a photocatalytic process.

6.1.2 The aim of this phase of work

The aim of this phase of study was to determine the durability properties of TiO_2 coating and potential anti-fouling capabilities. To achieve this objective, samples of revetment armour concrete were placed on a sea wall (study site 3, see section 6.2.4) for three months (Figure 6.8). The coating was observed before and after exposure. The resistance to wear and the presence of microorganisms on the coating surface were observed using Scanning Electron Microscopy (SEM). Results of the experimental programme allowed to estimate the wear properties of TiO_2 coating and its resistance to delamination and adhesion failure through the occurrence of microorganisms.

The overall aim of this chapter, is to advance the understanding of photocatalytic coatings in a marine environment. This phase of work will progress towards a non-toxic, environmentally-benign strategy for future industrial applications.

6.2 Methodology

6.2.1 Concrete specimens

The compressive strength class of the samples used in the experiments was C35/45 and a water/cement ratio of 0.45. The minimum cement content was 340 kgm^{-3}. More details of the mix design may be found in Chapter 3 and Appendix 3.

6.2.2 The 'Development' TiO_2 Coating used in this research

Mixed distribution of 10 nm to 60 nm particles of ultrafine TiO_2 uniformally dispersed in the coating was used not only as existing discreet primary particles but within aggregates, with secondary particle sizes typically >100 nm. The coating trialled in this research was a stable aqueous dispersion (sol) of ultrafine TiO_2 particles. Key features included an anatase crystal form with a 10 wt% of TiO_2 content. The coating had a neutral to moderately alkaline pH of 8.5, with a high surface dry area of 300 gm^{-2}, it dried clear, and was UV light activated. The coating has now become commercially available and is marketed for Architectural applications.

6.2.3 TiO_2 Coating application in this study

The coating procedure, consisted of a three stage process of independently applied layers either brushed (for the concrete tiles at study site 3) or roller recommended by the manufacturer (at study site 1 & 2) onto the surface of concrete. Both applications produced a satisfactory and resilient finish (Figure 6.2). A first primer layer was applied to the porous surface to help further levels adhere and to achieve uniformity of the coating. This assisted in creating a good seal filling cracks and blowholes in the concrete surface. The primer formed a dry film thickness of 10 µm. The second layer, an undercoat was applied after a drying time of 24hr. Finally, three separate topcoats were applied, each 10 µm and a further 24hr. drying time between applications, thus, bringing the overall thickness of the photocatalytic coating to 50µm. Although the coating was composed of several layers, the comparatively short time between applications ensured that the finished complete layer did not show any distinct separate layers. Neither, interferometer, optical or electron microscopic examination showed any significant boundary between layers. Glass slides were dip-coated, immersed for five minutes, dried for 24hr and repeated a further twice, to confirm a coating thickness of 50 µm. After 4 months, monitoring of TiO_2-based strategies was conducted by other workers using visual inspections, to determine the algal coverage (%) and human perception of the colour changes (Maury-Ramirez, 2012).

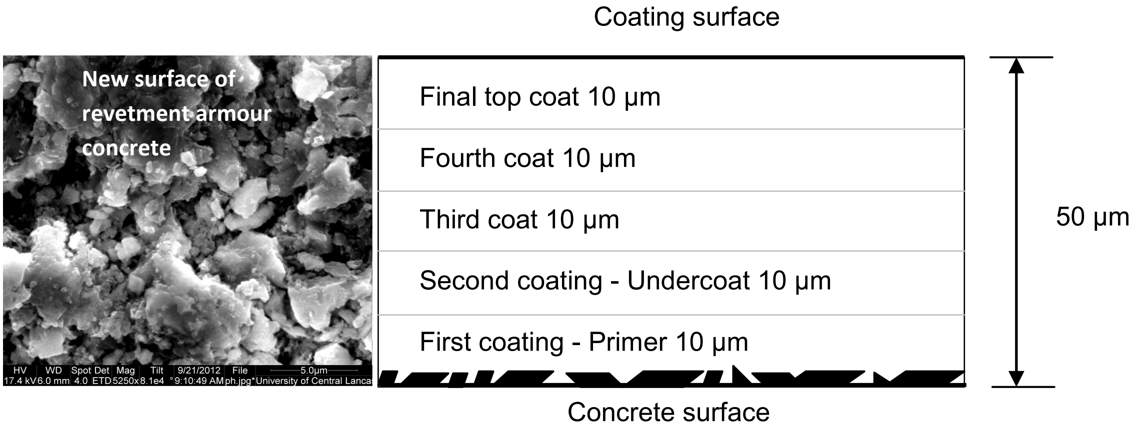


Figure 6.2 TiO_2 50 µm coating layer formation, primer coat bond was vital because of the nature of the surface of the concrete (inset).

Criteria for the evaluation of performance followed four points:

1 Good; after three months site trials, the coating remained intact and appeared to have anti-fouling capabilities.

2 Fair; after three months, the coating showed signs of wear but remained intact.

3 Poor; partial areas cracked and debonding started to occur.

4 Failure; coating had broken away from the surface.

6.2.4 Study sites in this research

The seashore at the study site is characterised by a plain and flat surface covered with sand and with a small amount of rocks in a marine environment characteristic of a temperate climate (Evans, 1962) (Figures 6.3, 6.4 and 6.8).

Figure 6.3 Study site 1 (Stargate steps). Lat. 53° 46’ 37.13” N – Long. 3° 3’27.64”W before the application of the coating (Figure 6.7), video in Appendix.

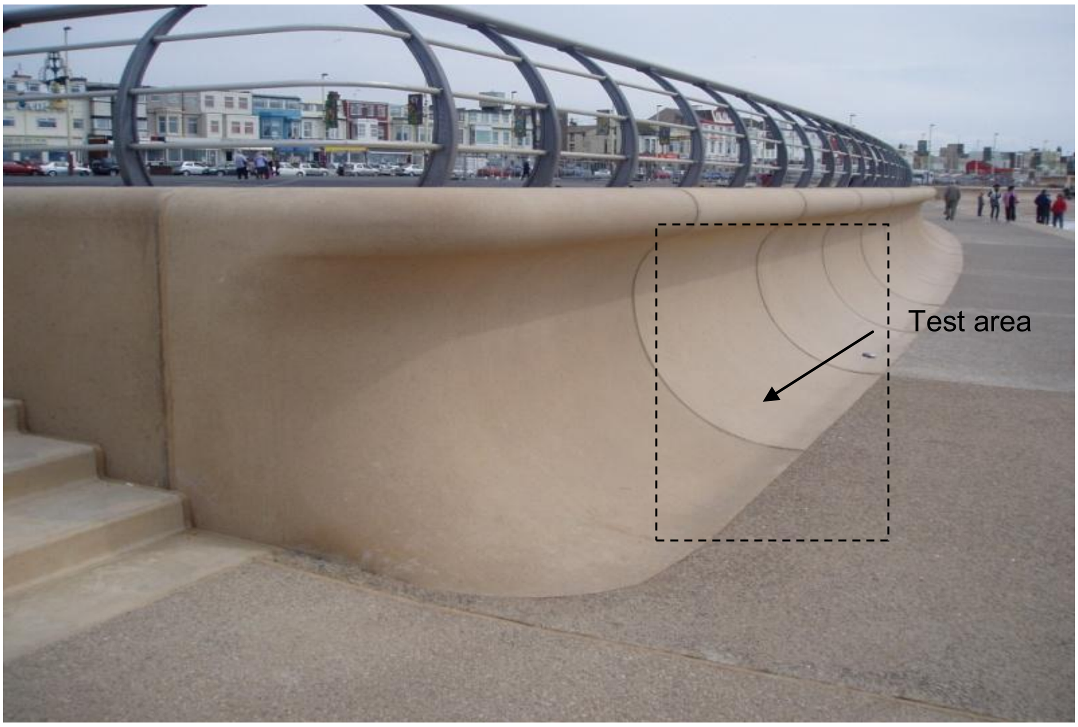


Figure 6.4 Study site 2. (Wave wall) Lat. 53° 46’52.41”N – Long. 3° 3’30.22”W

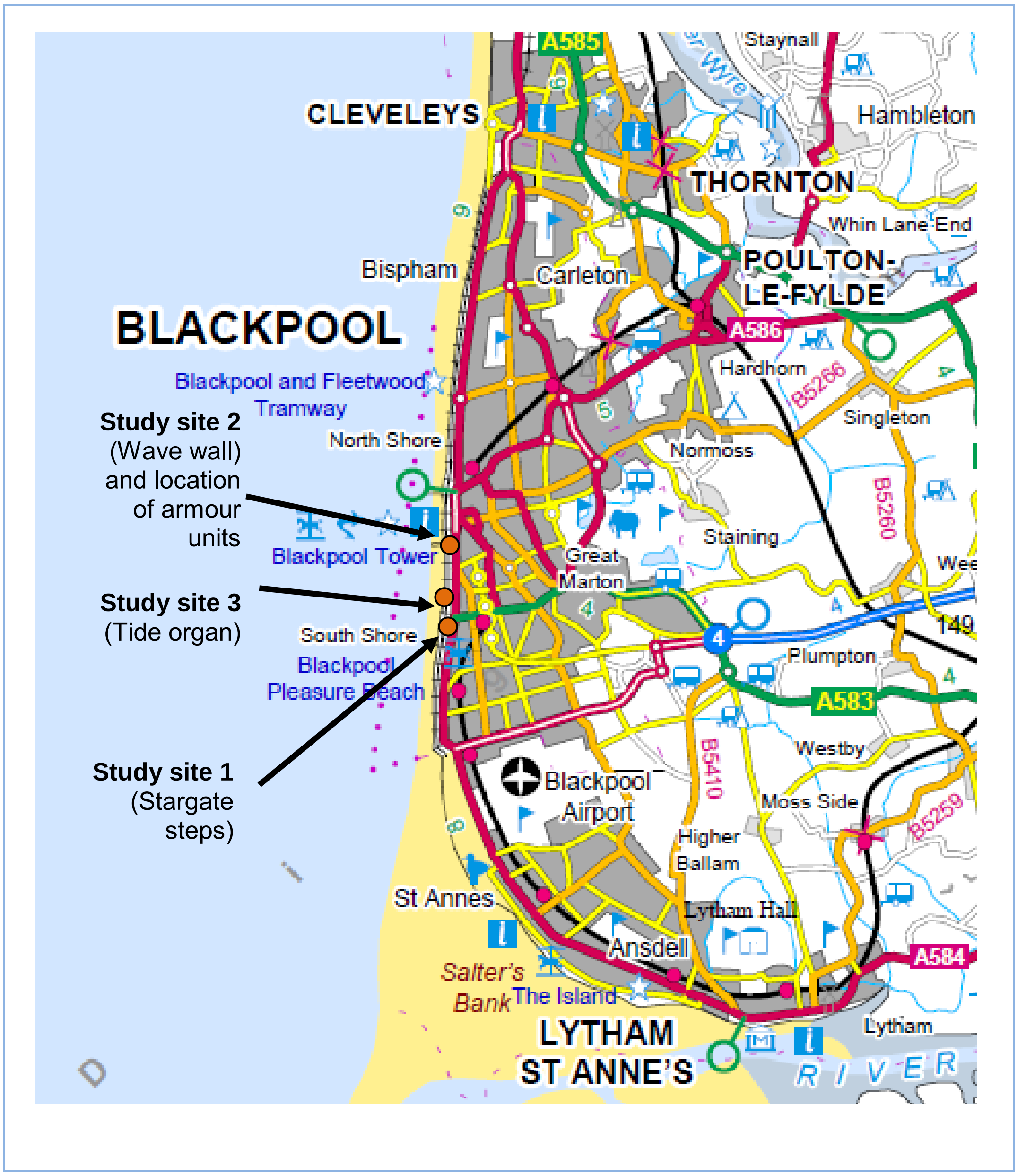
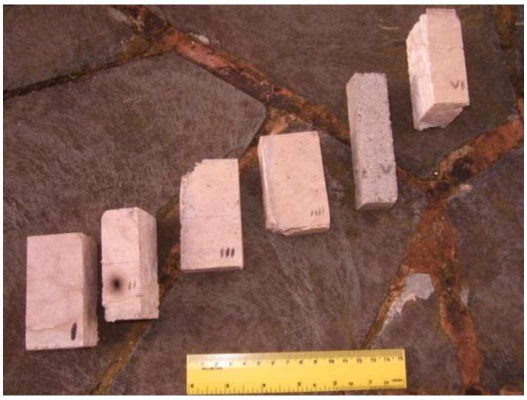


Figure 6.5 Fylde coast coating study site locations, video in Appendix.



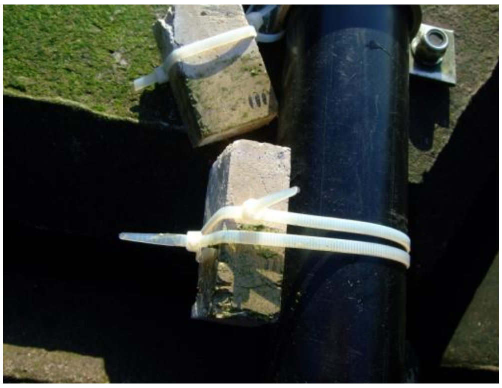


Figure 6.6 Revetment concrete tiles

Figure 6.7 Revetment tiles secured to pipe

Figure 6.8 Study study site 3. (Tide organ) – revetment armour concrete and OPC cement (control) coupons Lat. 53° 47’30.85”N – Long. 3° 3’31.16”W. This location was difficult to access however, and vandalism was avoided, video in Appendix.

6.3 Results

According to the objective of this phase of work, observations are presented of coating performance over three months at the study sites. The UV intensity of direct sunlight in summer is 20-30 Wm^{-2}, compared to 1 Wm^{-2} on a cloudy winter day (Defra, 2013). The testing period from March to the end of May was reported to be mild and moist (Coastal Observatory, 2013). Therefore the UV was estimated between 10-15 Wm^{-2}. Samples of data collected are in Appendix 6.

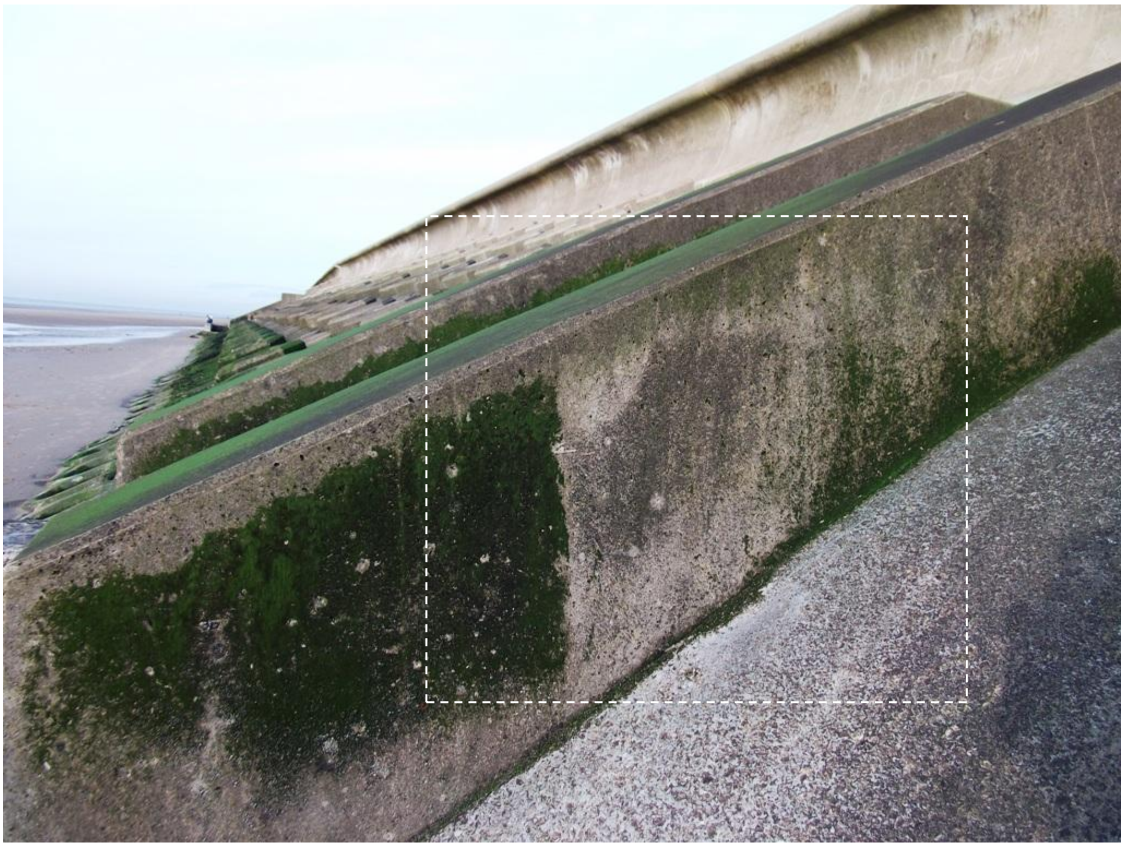


Figure 6.9 TiO_2 coated area at study site 1 shows anti-fouling capabilities, image taken April 2011.

Stargate site (Figure 6.9): 1 metre square trial of photcatalytic coating applied March 2010. Test site Location: 53° 46’37”N, 3° 03’27”W, 2.8 m above sea level. Biofouling intensity and surface coverage was reduced through the use of the coating as reported by other workers (Zhang *et al.* 2013; Maury-Ramirez *et al.* 2013).

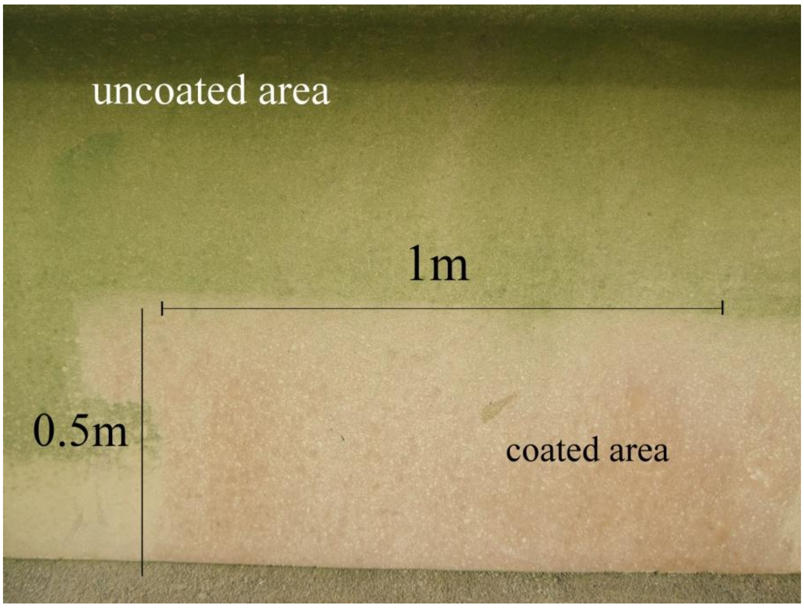


Figure 6.10 TiO_2 coated area study site 2 shows anti-fouling capabilities.

Note: The Wavewall was in the splash zone. This particular design of precast unit did not contain synthetic fibre reinforcement.

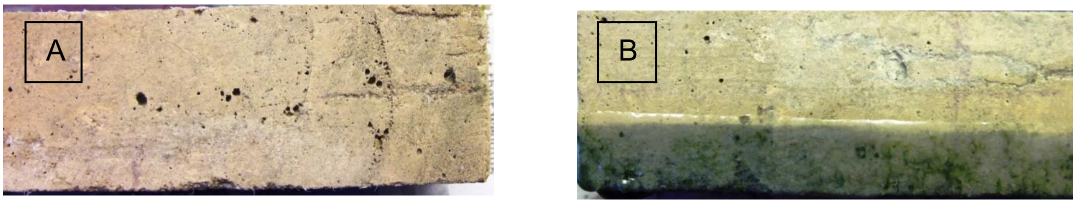


Figure 6.11 A.Coating performance from site 3 at 1 week B. Coating at 1 month's exposure

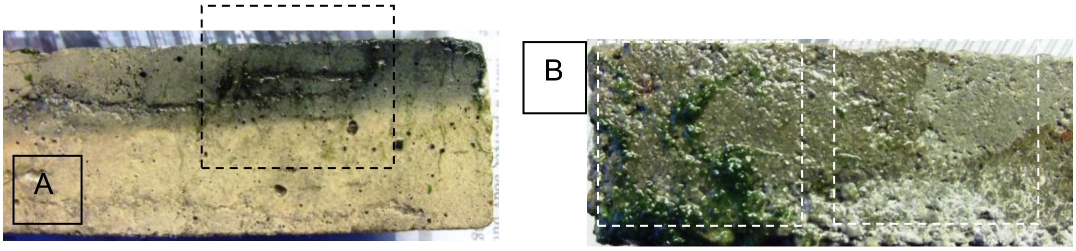


Figure 6.12 A. Shows revetment tiles after three months exposure, from site 3, box indicates fouling. B. Shows OPC tiles after 3 months exposure, boxes indicate coated areas.

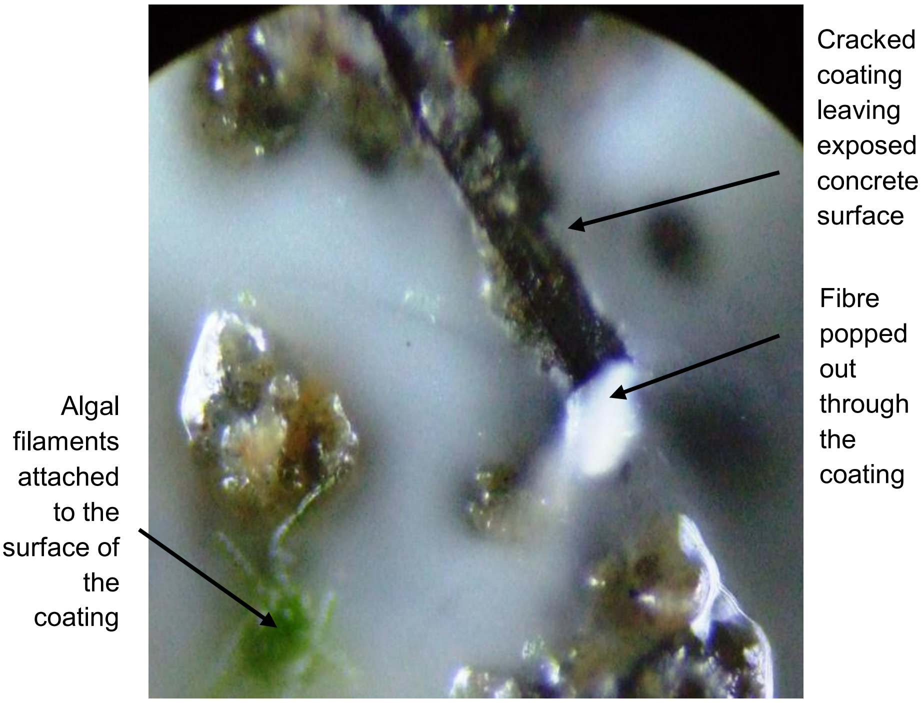


Figure 6.13 Light microscopic digital image of revetment concrete tile, site 3. Note a lifting macro-fibre has broken through the coating (arrowed).

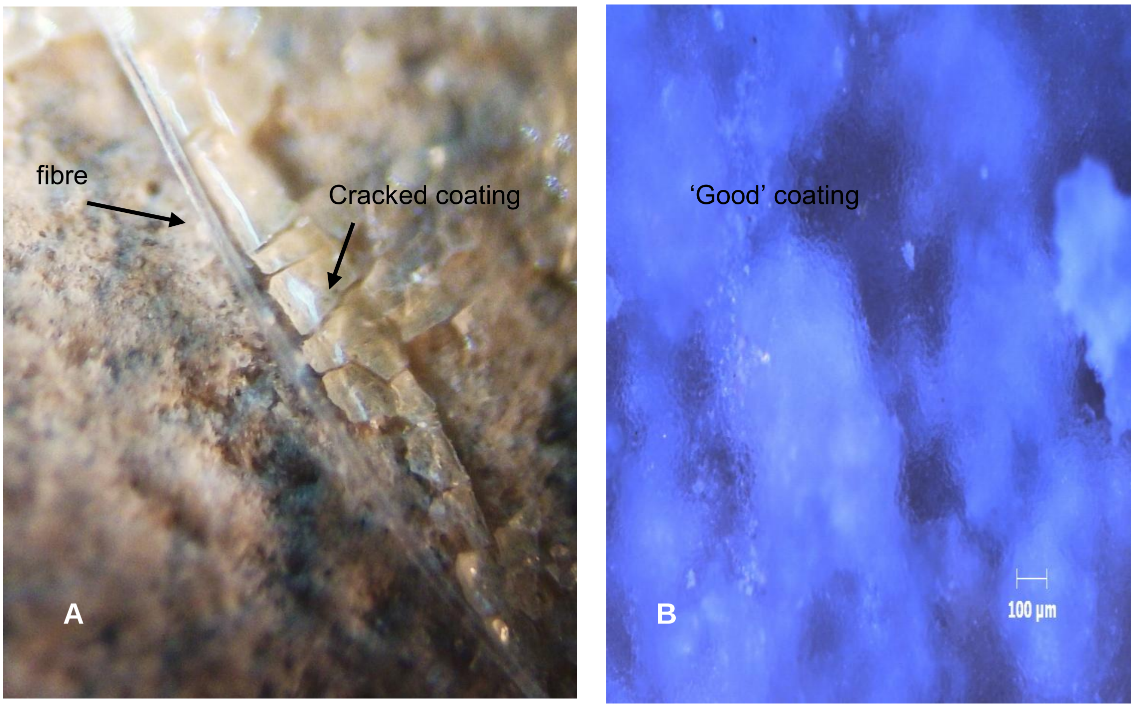


Figure 6.14 A: Light microscopic digital image of a micro-fibre (21 µm diameter) at the surface of revetment tile, site 3, under the coating (arrowed). B: Durable coating on fibre free concrete surface from site 2, classed as 'No. 1' in criteria set for these trials.

Figure 6.15 TiO$_2$ coating after 1 month, site 3.

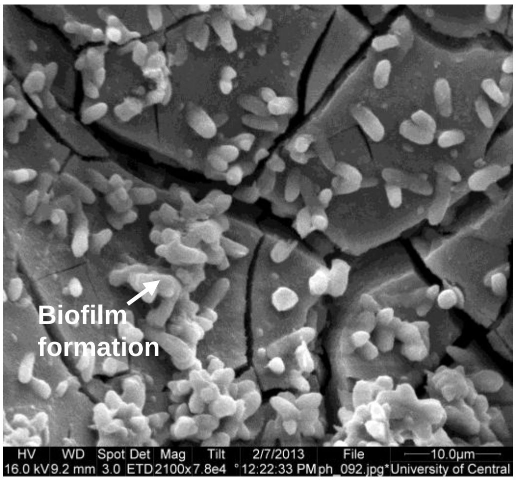


Figure 6.16 Coating after 2 months, site 3.

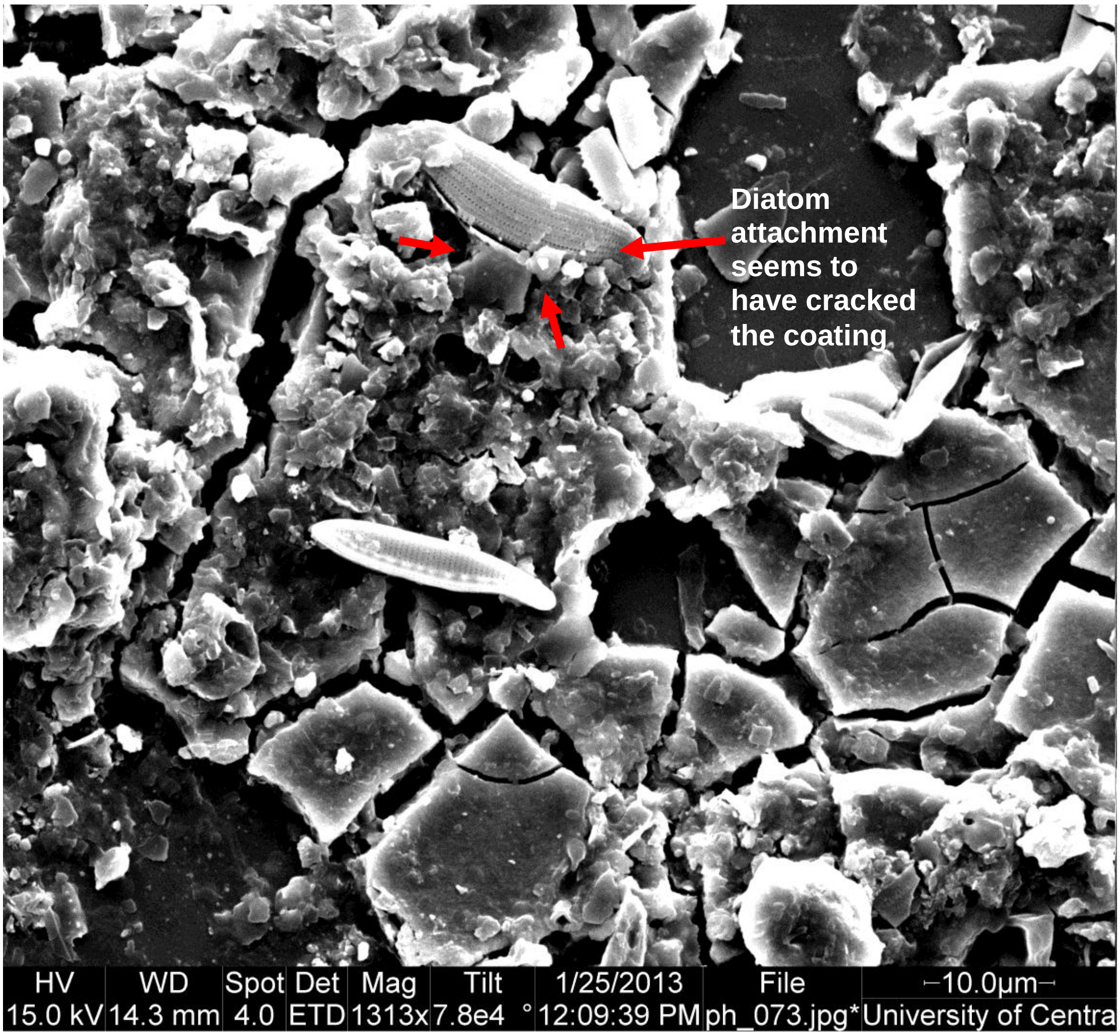


Figure 6.17 TiO$_2$ coating on revetment concrete tile, site 3, after 3 months exposure.

Figure 6.18 Coating of revetment tile after 2 months exposure at site 3. Algal filament (arrowed) is shown attached to the surface of the coating.

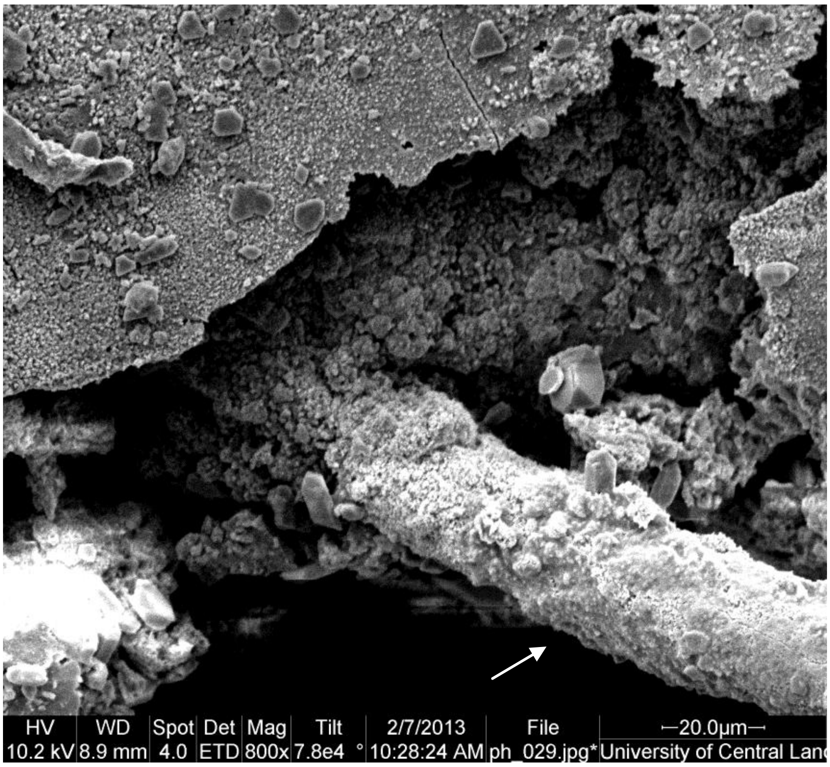


Figure 6.19 Micro-fibre (22 µm in diameter) is shown (arrowed) lifting out of the cracked coating surface of a revetment concrete tile, site 3, after 3 months exposure.

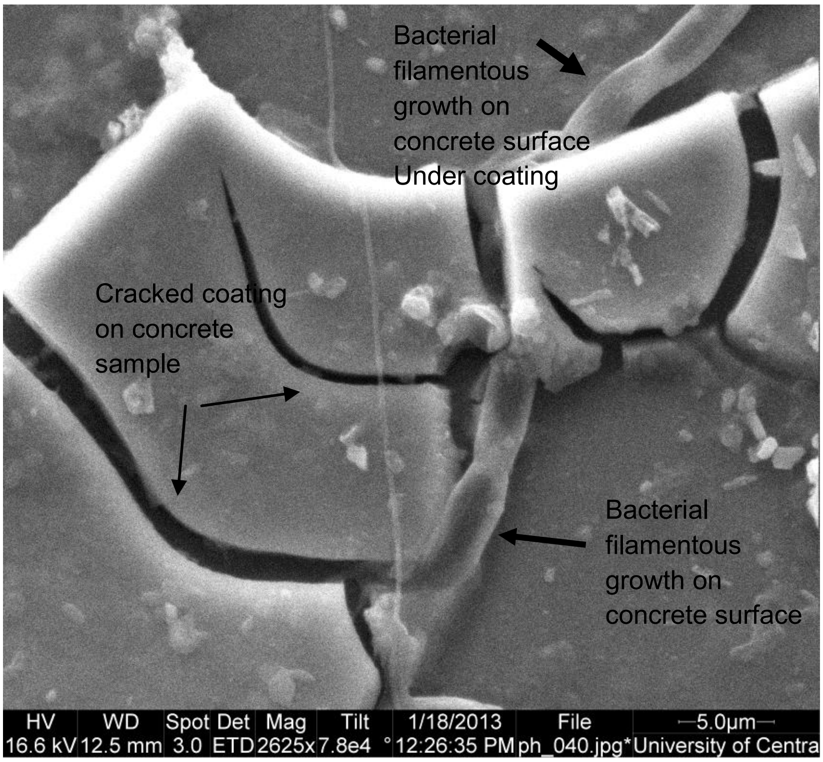


Figure 6.20 Bacterial filamentous growths (arrowed) beneath the coating, site 3.

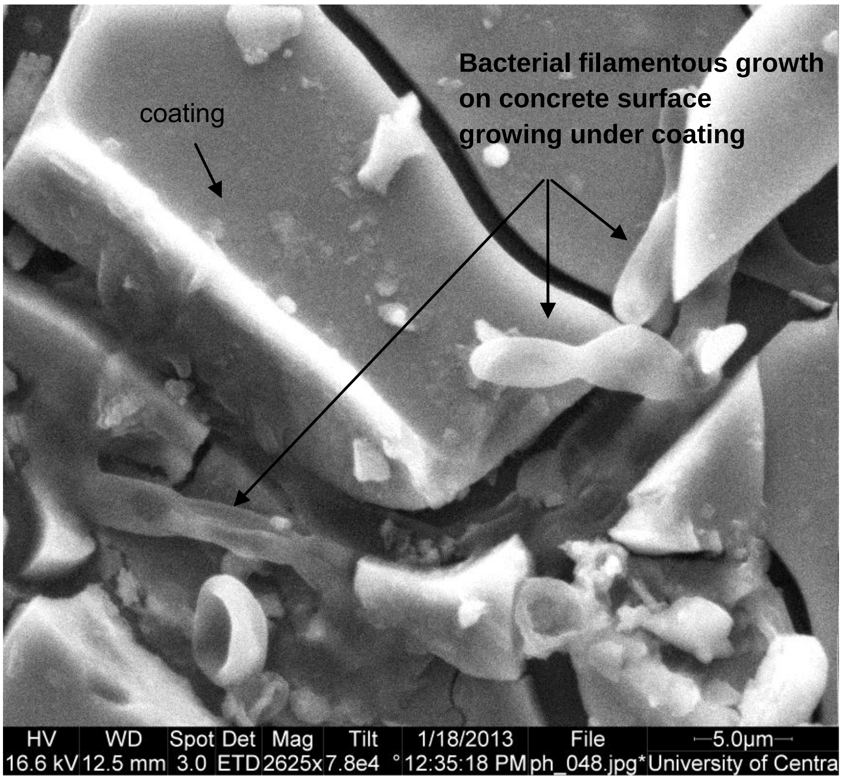


Figure 6.21 Bacterial filamentous growth (arrowed) from within the matrix of a revetment concrete tile, site 3.

Analogously, within each of the three study sites, two complementary tests were preformed in order to complete the durability and anti-fouling assessment of the coating. Figure 6.9 showed a promising antifouling effect, although the concrete mix design differs from that of the revetment armour mix. Figure 6.10 (wave wall) also demonstrates an antifouling capability but the mix design, was the same as the revetment armour, and does not contain synthetic fibres. Figure 6.11 and 6.12 depicts the tiles used at study site 3 to evaluate durability and anti-fouling performance of the revetment concrete. Figure 6.13 shows a modest antifouling quality on the OPC (non-fibre) mix design.

6.4 Discussion

From the results of the trials, TiO_2 coatings have been shown to be capable of controlling algal growth on a fibre-free concrete surface in agreement with other workers (Zhang *et al.* 2013). There are however several aspects to be considered before titanium dioxide photocatalyst technology can be adopted in the control of marine biofouling. Including the fact that the applicability of this technology is limited considerably because the catalyst works only where there is light, and the fact that application of a coating to composite materials, such as the revetment armour concrete has limitations. Fibres protruding from the surface of the new armour (Figure 6.14A), as discussed in Chapter 3, their movement and degradation, do not allow for a satisfactory bond between coating and substratum (Figure 6.14B). The attachment of filamentous algae to the surface of the coating (Figure 6.18) was seen to be detrimental to its long term durability. Filamentous bacterial growth from within the matrix of the new revetment concrete, as observed and reported in Chapter 5, also played its part in the eventual cracking and de-lamination of the coating from the concrete surface.

Coatings for marine concrete structures are subject to harsh environments, including dynamic loads, continuous expansion and contraction by heat, rain/seawater splash, impacts from debris, erosion and micro-organisms. In this condition, coatings may deteriorate in a short period of time in the form of cracking, disbonding or microbial attack (Figure 6.22).

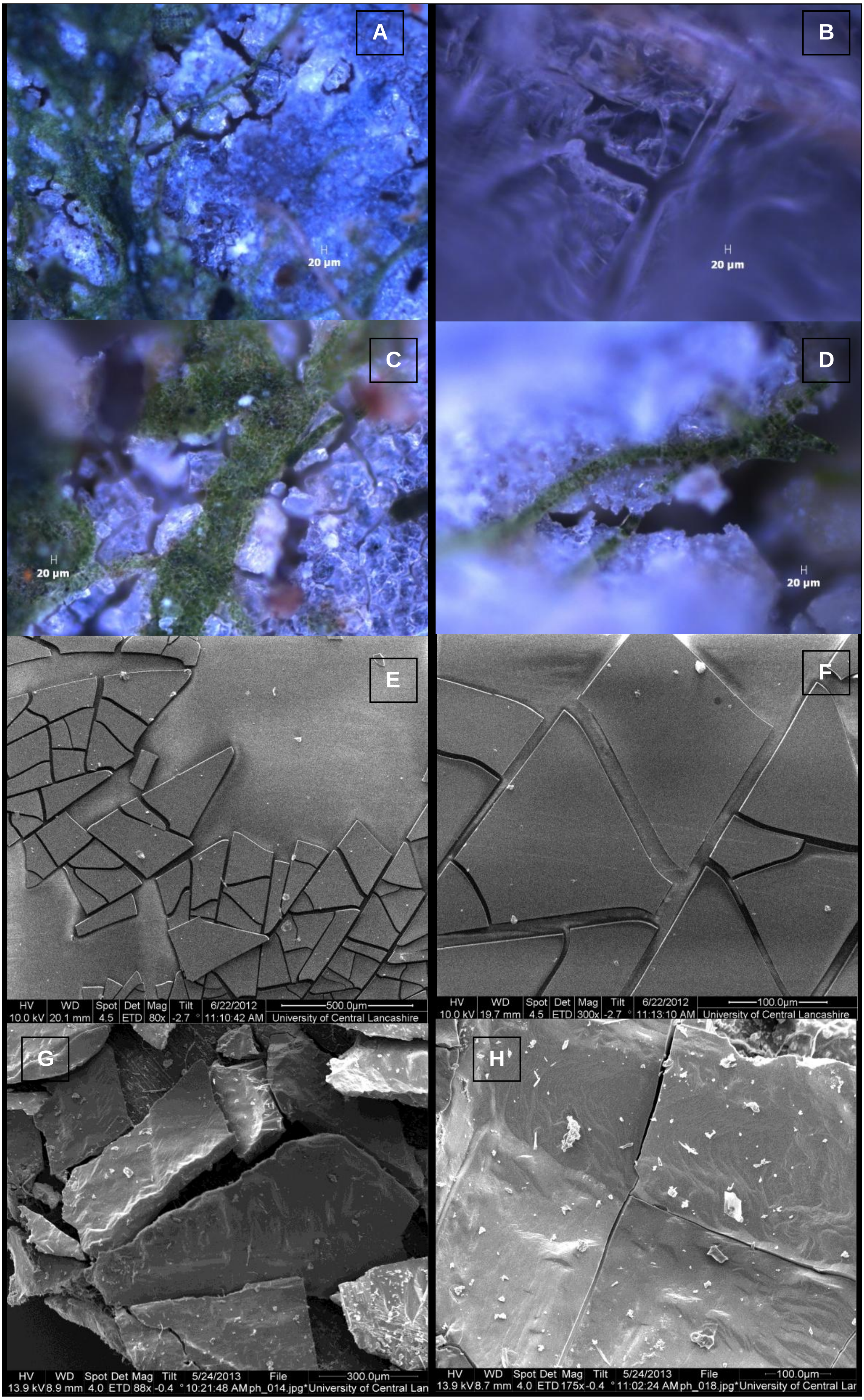


Figure 6.22 Coating modes of failure. A, C & D are examples of algal attack, B, C, E, F & H are examples of cracking, G & H are the effects of three months site exposure.

The application of the (development) TiO_2-based coating trialled in this phase of work was not designed to defend microbial growth from within the concrete, effectively a living substratum (Figure 6.21).

The study site performance of coatings on actual marine structures (study site 1 & 2) was quite different from the test results obtained from the small concrete tiles at the study site 3. The coatings applied to the tiles in the laboratory were applied in optimum conditions. Therefore, long-term study site observations from sites 1 & 2 recorded the actual anti-fouling performance and durability of TiO_2 marine coatings. Information from more than one testing site was used during this study as a means of assessing the coating anti-fouling performance in different locations. Long term durability of the coating is one of the most important factors for photocatalytic self-cleaning coatings for marine structures. For other applications of TiO_2, e.g. ceramic tiles and glass, because of the high temperature treatment in the application process thermal-spray coatings available for coastal Infrastructure (Holcomb *et al.* 2000), the photocatalyst layer would be stronger and more permanent. Thermal expansion and movement, instigated 'fibre pop out', discussed in Chapter 4, of exposed fibres causing the cracking of the coating, (Figure 6.13), resulting in not only reduced photocatalytic activity but also structural and strength degradation, (Figure 6.14A). Coatings on fibre-free concrete were more durable (Figure 6.14A) The use of nano (below 100 nm diameter) or micro particles of TiO_2 have been reported to degrade polymeric surfaces, and so to prevent this, it is necessary to apply an inorganic barrier between the anatase layer and the polymeric layer, separating the surfaces (Gaylarde *et al*. 2011).

At each weekly inspection, the potential presence of mechanical defects such as, discolouration, whitening, blistering and cracking was evaluated using criteria set out earlier (6.2.3). Figure 6.15 illustrates a coating after 1 month exposure; the coating shows a more homogeneous surface without defects. However, the self cleaning effect would be limited due to the physical anchoring of the microorganisms in large cracks and pores

(Figure 6.16). Loss of TiO_2 coating due to wearing, as seen in Figures 6.16, is comparable to observations by Marwa *et al*. (2010).

The performance of the coating was observed to be dependent on the underlying composite material. First of all, due to differences in intrinsic properties discussed above on the surface treatments. Furthermore, diatoms (Figure 6.17) observed throughout the whole study, which form another component of marine biofilms and act as a settlement mediator for larger fouling, secrete large amounts of EPS from a slit (raphe) or apical pore in the frustule. This attachment process, specifically its strength of attachment on macroalgae, is discussed in Chapter 3, (Figure 6.17). The diatom attachment to coatings examined, showed that this single algal cell actually accelerated coating degradation.

Algal filamentous growth attached to the surface of the coating, (Figure 6.16) and applied pressure to the integrity of the coating. This may explain why loss of the photocatlytic effect occurred due to the cracking of the coating and similar to observations made by De Muynck *et al*. (2009). As a result, the durability of some of the coatings became impaired in such a dynamic environment. Figure 6.19 shows a microfibre breaking through the coating after 2 months exposure. In general, a typical life of coatings for marine concrete structures is about 10 to 15 years depending on the coating quality and the all important application technique. Using an accelerated test set-up simulating a weathering period of about 25 years the effects of intensive weathering on TiO_2 coatings applied on autoclaved aerated concrete were systematically investigated by other workers. Two different coating techniques were studied: dip-coating and a novel vacuum saturation method (Maury-Ramirez *et al*. 2012b). However the innovative use of synthetic fibres within marine coated concrete needs further evaluation.

Figure 6.20 shows bacterial filamentous growth from within the matrix. This previously un-reported phenomenon is discussed in Chapter 5. The occurrence of a bacterial biofilm formation under the coating has significantly affected the performance of the coating. A study into the addition of TiO_2 powder with an average size 21 nm

(30% rutile and 70% anatase) into a bacterial colony, was reported, and the results showed that 60–120 min were sufficient to destroy all the bacteria (Saito, 1992). Those authors stated that using bigger TiO_2 particles reduces the bactericidal capacity and that the best results are obtained for a TiO_2 concentration of 0.01 and 10 mg/ml. Other workers also confirmed that using lower dimension TiO_2 particles leads to a faster bacterial destruction (Huang *et al*. 2000). Those authors notice that bacteria destruction begins after 20 min of UV radiation exposition, and that after 60 min all of them have been destroyed. They also reported that after the destruction has been initiated the fact that UV radiation is stopped does not reduce the bactericidal effect. The effect of bacterial growth observed in this research and highlighted in Figure 6.21 is in disagreement with the literature and requires further investigation.

6.5 Conclusions

In spite of its promising benefits elsewhere (Zhang *et al*. 2013), the durability and resistance to wear of TiO_2 surface self-cleaning coatings for fibre-reinforced marine concrete had not been previously evaluated. The objective of this phase of work was to monitor the anti-fouling capabilities and durability properties of TiO_2 coatings at a marine study site and microscopically observe its effect on the coatings' environmental performance. Based on the analysis conducted, the following conclusions may be drawn:

- Macro and micro synthetic fibres at the surface of the revetment armour inhibit a strong and durable bond between the coating and the substratum, accelerating cracking and the eventual breakdown of the coating.

- Algal filamentous growth including diatoms attached to the surface of the coatings, applied further pressure on the integrity of the coating.

- Bacterial filamentous growth from within the matrix of the concrete, grew at the coating and concrete interface. This growth disrupted and weakened the bond between coating and substratum, leading to the de-lamination of the coating.

Chapter 7

Cell attachment to synthetic fibres under laboratory conditions

The outcome of any serious research can only be to make
two questions grow where only one grew before.

Thorstein Veblen (1908)

7.1 Introduction

Commercially produced plastics, including polyethylene, polypropylene, polystyrene, polyvinyl chloride and the polyamides (nylons) have generally been considered to be inert (Morton, 2003), however, many are susceptible to microbial attack under certain conditions. Polyethylene and polypropylene are the main constituents of the fibres within the matrix of the test concrete examined in this research. Rubbers and plastics contain a wide variety of additives that are susceptible to damage by microbes. These include plasticizing compounds such as adipates, ricinolates and sebacates which are used to confer flexibility to rigid plastics such as PVC. The effects are often severe and in some cases unexpected, however microorganisms have been shown to be involved in the deterioration and degradation of both synthetic and natural polymers (Gu *et al*. 2003), and very little is known about the biodeterioration of synthetic polymeric materials. The reason is partly due to the recent development and manufacture of this class of material and the incorrect assumption of a relatively slow rate of degradation in natural environments. Since chemically synthesized polymeric materials have become an important element of concrete technology (Rieder, 2007), (fibre reinforced concrete) issues related to polymer deterioration and protection, especially in the marine environment will receive increased attention in the future.

Microbial degradation of polymers depends on their molecular compositions, molecular weights and the presence of specific microorganisms on the surfaces of materials. A review of microbial deterioration of synthetic materials was offered by Gu (2003). Polyethylenes of high and low density are primarily used in product packaging as sheets and thin films. Their degradability in landfill sites poses serious environmental concerns due to their assumed slow degradation rates under natural conditions, and the hazard they may present to freshwater and marine animals. However, degradation is assumed very slow, estimated in decades (Gu, 2003). Biodeterioration of polyethylenes has been studied extensively by Imam and Gould (1990). Polypropylenes are also widely utilised as engineering pipes and containers.

Degradation of polypropylenes results in a decrease of their tensile strength and molecular weight. The mechanism may involve the formation of hydroperoxides which destabilise the polymeric carbon chain to form a carbonyl group (Severini *et al.* 1988). The adhesion of *Staphylococcus aureus* and *Escherichia coli* to polypropylene was evaluated elsewhere (Pompermayer and Gaylarde, 2000). Degradability of pure and high molecular weight polypropylene is still an open question.

7.1.1 Objectives

The objectives were: To evaluate cell attachment to synthetic fibres, the beginning of the biofouling process. To characterise bacterial attachment under laboratory conditions and compare results with observations from study site specimens.

7.2 Methodology

7.2.1 Culture conditions for the microbial attachment to synthetic fibres

Achaeans are single-celled microorganisms that join bacteria to make up a category of life called the prokaryotes. Prokaryotes' genetic material, or DNA, is not enclosed in a central cellular compartment called the nucleus. Bacteria and archaea are the only prokaryotes, all other life forms are Eukaryotes, organisms whose cells have nuclei.

The thermoacidophilic archaeon *Sulfolobus solfataricus* P1 (JCM11322) was obtained from the Japan Collection of Microorganisms (Saitama, Japan). It was cultured aerobically in medium containing casamino acids (1 g/L), yeast extract (1 g/L) and the following trace minerals; $(NH_4)_2SO_4$ (4.9×10^{-2} M), KH_2PO_4 (2.1×10^{-3} M), $MgSO_4$ (1.0×10^{-3} M), $CaCl_2$ (4.8×10^{-4} M), $FeCl_3$ (7.1×10^{-5} M), $MnCl_2$ (9.1×10^{-6} M), $Na_2B_4O_7$ (1.2×10^{-5} M), $ZnSO_4$ (7.7×10^{-7} M), $CuCl_2$ (2.9×10^{-7} M), Na_2MoO_4 (1.2×10^{-7} M), $VOSO_4$ (1.5×10^{-7} M), $CoSO_4$ (6.5×10^{-8} M), adjusted pH 3.0 with 10N H_2SO_4. One mL of the seed culture was inoculated onto nanofibres scaffold in a 35-mm polystyrene suspension culture dish (Corning, NY, USA) with 3 ml of medium. The dish was taped firmly and incubated at 80 °C for 1 week.

7.2.2 Fluorescent microscopy

Cultures were washed twice in phosphate buffered saline (PBS) to remove non-adherent cells then fixed with 4% paraformaldehyde (PFA) for 30 min. After the fixed cells were washed with PBS twice, they were stained with Hoechst 33342 (diluted 1:2000; Dojindo Laboratories, Kumamoto, Japan) for 30 min, being left in darkness, and finally washed twice in PBS. The adherent cells on each nanofibre were observed on a fluorescence microscope (BX51; Olympus, Tokyo, Japan).

7.2.3 SEM

Cultures were fixed with PFA as described above, dehydrated through a graded series of ethanol (50, 60, 70, 80, 90, 95, 99 and 100%), replaced into 2-methyl-2-propanol (Wako), frozen at 4°C, and then lyophilized with a vacuum evaporator. Dried samples were sputter-coated with Au/Pt, and observed by a scanning electron microscope (S-2600; Hitachi, Tokyo, Japan).

7.2.4 Fabrication of fibre scaffolds by electrospinning

Electrospinning is a process in which a charged polymer jet is collected on an earthed collector; a rapidly rotating collector results in aligned nanofibres while stationary collectors result in randomly oriented fibre mats. The polymer jet is formed when an applied electrostatic charge overcomes the surface tension of the solution. There is a minimum concentration for a given polymer, termed the critical entanglement concentration, below which a stable jet cannot be achieved and no nanofibres will form. It was originally planned to use manufactured fibres for the colonisation experiments. However, lengthy discussions with a supplier, and the early experience of obtaining materials with a confidentiality agreement discouraged this approach.

A stable jet has two domains, a streaming segment and a whipping segment. While the whipping jet is usually invisible to the naked eye, the streaming segment is often visible under appropriate lighting conditions. Observing the length, thickness, consistency and movement of the stream is useful to predict the alignment and morphology of the nanofibres being formed. A short, non-uniform, inconsistent, and/or oscillating stream is indicative of a variety of problems, including poor fibre alignment, beading, splattering, and curlicue or wavy patterns. The stream can be optimized by adjusting the composition of the solution and the configuration of the electrospinning apparatus, thus optimizing the alignment and morphology of the fibres being produced. In this experiment, a procedure for setting up a basic electrospinning apparatus, empirically approximating the critical entanglement concentration of a polymer solution and optimizing the electrospinning process.

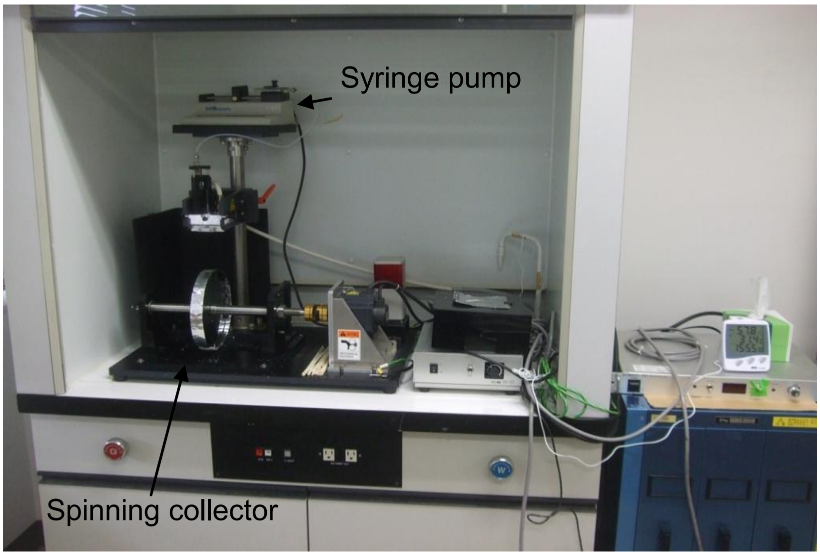


Figure 7.1 Electrospinning apparatus.

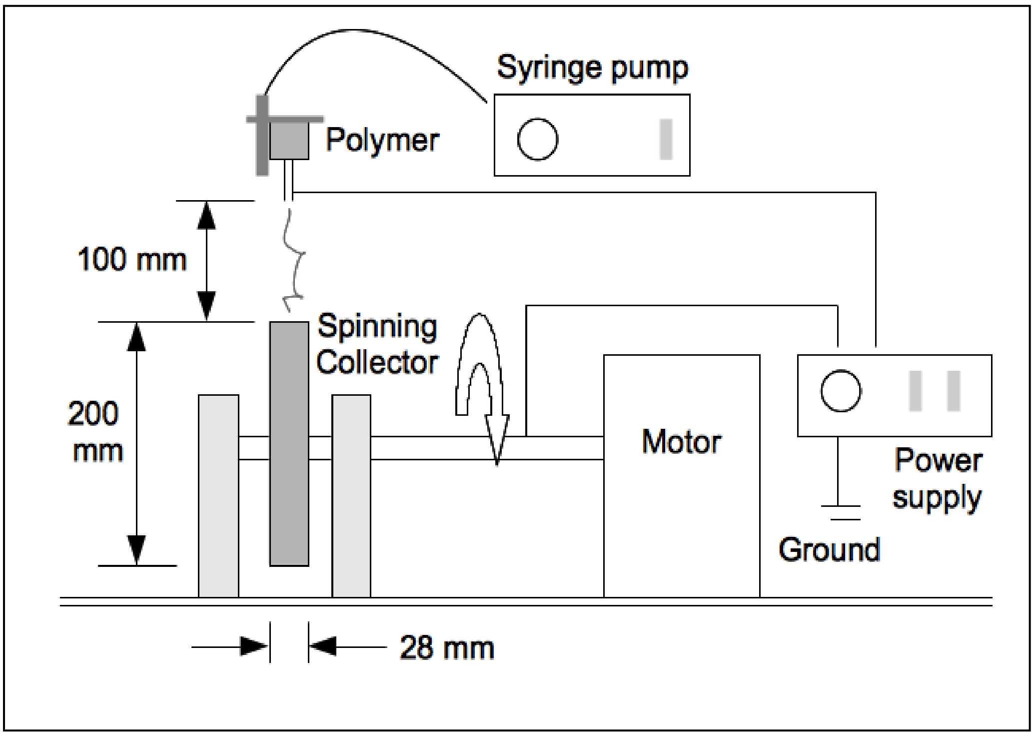


Figure 7.2 Electrospinning schematic of major components.

Synthetic fibres of varying polymers, detailed in Table 7.1, were fabricated by electrospinning. The sizes of the fibres were manufactured to a similar diameter than that of site specimens. The micro fibres used at the study site were 22 μm in diameter and of a monolithic design, which meant they kept their original dimensions. The macro synthetic fibres used at the study site however, where of a fibrillated design, meaning they separated into much smaller strands of material, taking their dimensions into the nano-scale. This can also be observed in Chapter 8.

Polymer solutions chosen are shown in Table 7.1. Polyurethane (PU; P22SRNAT, JIS hardness; 82A) was purchased from Nippon Polyurethane Industry (Tokyo, Japan), polystyrene (PS; Mw 20,000) from Sigma-Aldrich (MO, USA), tetrahydrofuran (THF) and dimethylformamyde (DMF) from Wako Pure Chemical Industries (Osaka, Japan).

#	Polymer	Solvent	Conc., w/v%	Voltage, kW	Infusion rate, ml/hour	Collector rotation, rpm
1	PU	95% THF / 5% DMF	15	25	0.8	1,200
2	PS	THF	20	25	0.7	900
3	PS	THF	30	25	1.0	900

Table 7.1 Polymer solutions used.

The electrospinning set-up (MECC Co., Ltd., Fukuoka, Japan) is detailed in Figure 7.3. A polymer solution was loaded into a syringe and driven through a metallic needle at a constant feed rate by a syringe pump, forming a droplet at the tip of the needle. A high voltage was applied between the tip and the rotating collector. The electrospinning parameters tested are listed in Table 7.1.

To enhance colonisation of the fibres, each polymer was electrospun over a unique 'bridging' system (Hughes *et al*. 2012), lifting the fibres from the cover slip, exposing fibres between rubber mounts, allowing more surface area to be colonised (Figure 7.3).

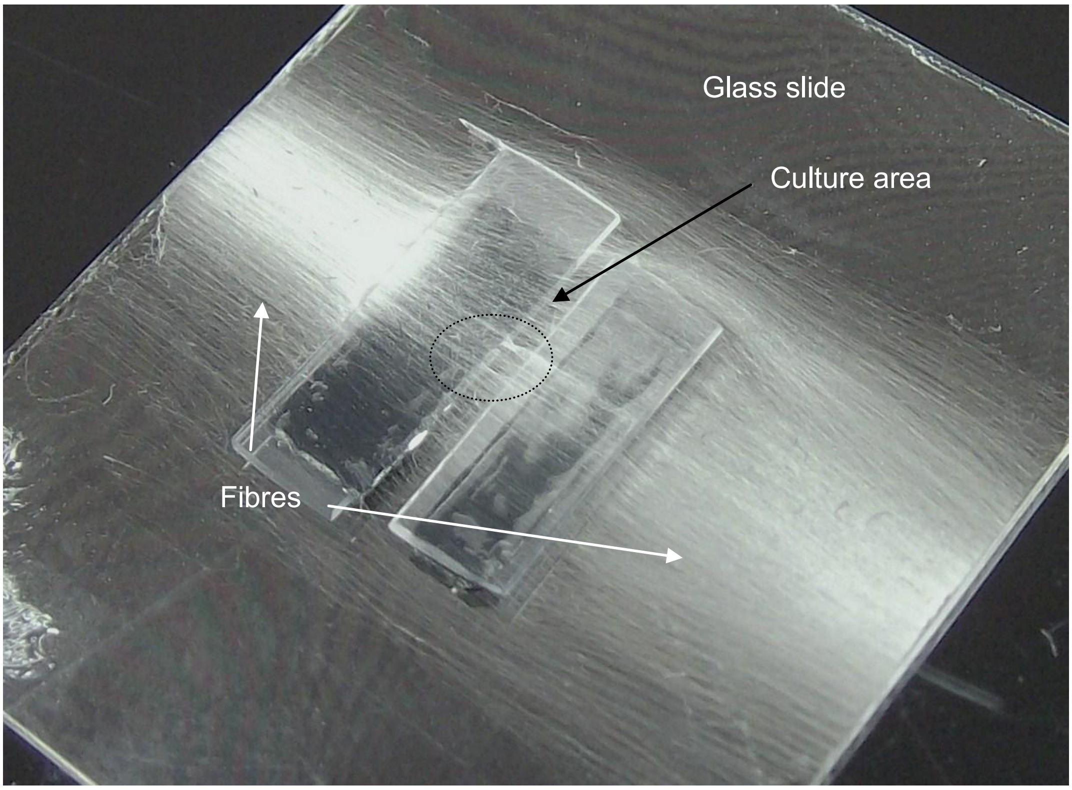


Figure 7.3 Glass slide with unique ‘bridging’ technique. This technique allowed the fibres to lift off the glass slide, over the two sections of silicon, creating a larger surface area for the eventual attachment of cells.

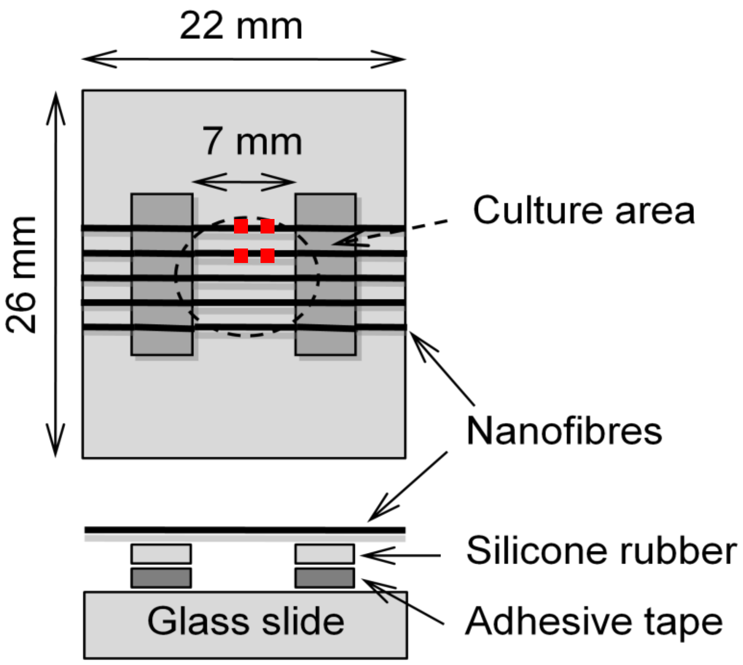


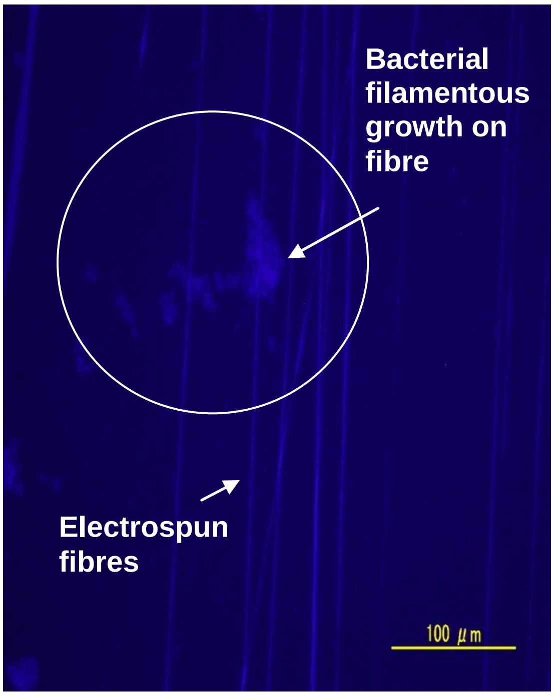
Figure 7.4 Schematic of ‘bridging’ technique.

Glass slides (with cover slip, 22 mm x 26 mm, thickness no. 5; Matsunami, Osaka, Japan), were used as a base, upon which two pieces of conductive double adhesive tape (thickness 0.2 mm) were applied (Figure 7.4). Silicone rubber 0.3 mm thickness was then placed on the tape. This arrangement lifted the fibres 0.5 mm up and away from the surface of the glass slide. The optimum distance of rubber mounts was 7mm between lifts. To improve surface hydrophilicity of PU and PS nanofibres, an oxygen plasma treatment (100 W, 30 s, 0.1 MPa) was carried out using a plasma reactor (PR300; Yamato Scientific, Tokyo, Japan), increasing bioreceptivity.

7.3 Results

7.3.1 Cell attachment to synthetic fibres

SEM photomicrographs, along with light and inverted microscopy have enabled the observation of bacterial colonisation to synthetic fibres in laboratory conditions.



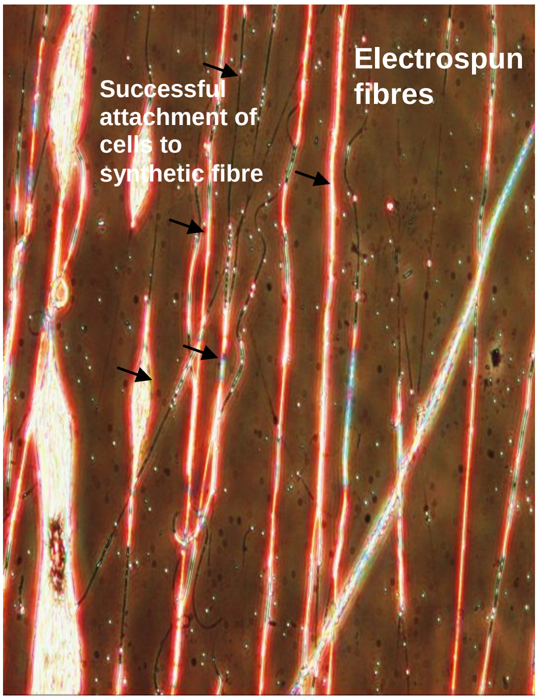


Figure 7.5 Florescent image of cell

Figure 7.6 Cell attachment to fibres

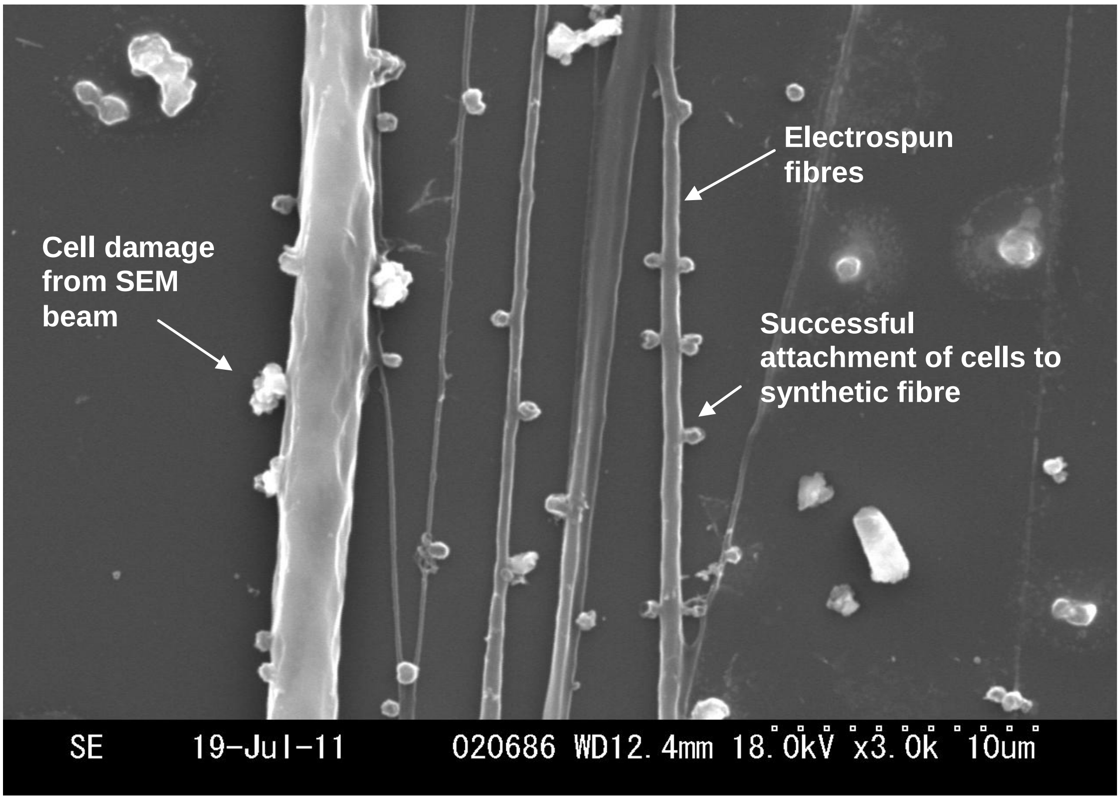


Figure 7.7 Thermophiles on PU fibres

7.4 Discussion

7.4.1 Cell attachment to synthetic fibres

Microorganisms such as bacteria and algae have been widely reported to be involved in the deterioration of concrete (Gaylarde and Morton, 1997; Jayakumar and Saravanane, 2009). However, relatively few direct relationships have been established between the activities of microorganisms and synthetic fibres within concrete, in harsh environments such as bridges. It has been reported that steel fibres within sprayed concrete were severely attacked by bacteria (Hagelia, 2008). This phase of work focused on the application of a culture of hyperthemophiles *S. solfataricus* to electrospun nanofibres. Polyurethrane (PU), polyethylene (PE) and polystyrene (PS) were used, because they offered the ability to produce a wider range of mechanical properties and polyethylene is a component of the synthetic fibres used at the study site. After the fibres were electrospun (Figure 7.3) a method of encouraging the fibres to uniformly cross a bridging device, or scaffold, in a firm alignment was developed and is shown in Figure 7.4. Oxygen Plasma Treatment was used to weather the surface of the polymers, roughening the surface there making the polymer more bioreceptive. More details of the synthetic fibres used at the study site are offered in Chapters 5 and 6. However the fibres at the study site are exposed at the surface of the concrete to the harsh environment, making them susceptible to the elements. It is known that plasmas can be used to alter material surfaces by removing surface layers to activate the surface hydrophilicity. Hydrophobic surfaces have been found to favour the formation of biofilms, and hydrophilic surfaces have therefore been investigated for their antifouling potential. Plasma treatment aged the new material to alter the wetability and bioreceptivity of the electrospun fibres. A simplified definition of plasma is the reference to a gas, which contains a small amount of charged particles: the atoms/molecules are ionized, i.e. they have lost or gained one or more electron. A more extensive overview of the use of plasma treatments is offered by Shishoo (2007). As plasma is generated by placing a gas within an electric field, which then ionizes the gas, or breaks it down, this can also be referred to as discharge. It is known that plasmas can be used to alter material surfaces by removing surface layers, to activate the surface to become polar, to passivate surfaces making them less polar and to deposit thin films (Tomasino, 1997). Advances in plasma technology have led to the development of coatings which increase surface hardness and lower the coefficient of friction of metals. Removing surface matter, such as fibre finishes, size, contaminants from fibre surfaces; also the etching of fibre surfaces to reduce fibre diameters. Activating surfaces to change their polarity (Shishoo, 2007). Polar surfaces can be made more non-polar to render them repellent to liquids and reduce adhesion of soil particles, non-polar surfaces can be made more polar to improve water wetting and soil release properties. The culture of *S.* s*olfataricus* on various nanofibres was undertaken for a period of 1 week. As a result, cell attachment was not observed on a PS scaffold, while attachment was observed by fluorescent microscopy on a PU fibre (Figure 7.5). Cell attachment to PE fibres was initially observed under light microscopy (Figure 7.6). Consistent with the observations by SEM (Figure 7.7) *S. solfataricus* attached and colonised onto the PU nanofibres, while they showed no attachment and colonisation onto the same-sized PS fibres. It was considered that this result was due to the difference of surface chemistry of the polymers. When the polymer fibres were exposed to the culture medium, proteins in the medium are rapidly adsorbed onto their surface before the cells can adhere. The adsorbed proteins determine the subsequent cell attachment behaviours.

7.5 Conclusions

This phase of work investigated the bioreceptivity of an electrospun polymer fibre scaffolds, which showed hydrophilicity, enhanced by oxygen plasma treatment, and the successful colonisation of hyperthermophiles was observed by SEM. Successful attachment of bacterial cells to inert polymer fibres in laboratory conditions demonstrates a developing sequence in the formation of a biofilms, leading to the biofouling process. In Chapter 5, observations were made of bacteria cells attached to micro synthetic fibres within the matrix of fresh concrete. This phase has shown attachment in a controlled regime. The potential for bacterial cell attachment to polymer fibres and marine study site observations will enable a more informed choice of materials within marine concrete suitable for such a hostile environment.

Chapter 8

The Holistic view

Systems thinking is process thinking; form becomes associated with process, interrelation with interaction, and opposites are unified through oscillation.

Fritjof Capra (1991)

8.1 Introduction

This chapter presents two holistic models of biodeterioration. These illustrate the algal colonisation of synthetic fibres (Hughes *et al.* 2012a), and limestone aggregate (Hughes *et al*. 2013c), within their marine environment. By adopting the holistic approach, two new models offer an alternative explanation of the damage caused by biodeterioration. The first model, a study of synthetic fibre performance, is based on six elements: including the new surface, colonisation, fibre pop out and material loss (Figure 7.8). The second model (Figures 8.11 – 8.13) illustrates the resilience of limestone aggregate and has three elements: the new surface, surface loss and the penetration of filamentous growth. Each element, in turn, can be related to numerous causes. For instance, the loss of material could be promoted by tidal impact, power washing, filamentous growth or other causes, such as water and aggregate quality. Theoretically the biodeterioration can be reduced or prevented by controlling at least one of the above elements.

The models presented will give designers of future concrete sea defences a new understanding as to how a marine concrete structure can fail when subjected to loading and harsh environmental conditions. Furthermore such a model can be used to assess existing structures, assist in the explanation of accelerated degradation of fibre-reinforced marine concrete, or in the design of a new structure.

The constituents of matter and the basic phenomena involving them, are all interconnected; that they cannot be understood as isolated entities but only as integral parts of a unified whole (Capra, 1991). Knowledge of the cellular and molecular aspects of biological structures will continue to be important, however a more complete understanding of biofouling, proposed in this chapter, can be achieved by developing a 'systems biology,' a biology that sees fouling as a living system rather than a single mechanism. It is the development of this concept that forms the philosophy of this phase of the work.

The term holistic refers to an understanding of a phenomenon or structure in terms of an integrated whole, whose properties cannot be deduced from the sum of the properties of the constituent parts. To further understand the biofouling of marine concrete in accordance with the holistic approach, the integration of experimental data and observations recorded earlier in this research with available scientific knowledge discussed in literature reviews throughout this thesis will be considered as an integrated whole. When addressing a complex problem, the whole system can be decomposed and organized into hierarchical subsystems. But those subsystems, e.g. fibres or aggregate, are not independent; they must be integrated into a whole; the concrete matrix.

Too often in the past, marine concrete durability has been treated on a component reductionist basis, instead of the holistic approach. There now follows a brief outline of these two approaches and their differences.

Reductionism consists of the belief that everything can be reduced, or disassembled to simple elements, phases or conditions. Analysis consists firstly of taking apart what is to be explained; disassembling it, to the independent parts; second, of explaining the behaviour of these parts; and finally, of compiling these partial explanations into the explanation of a whole. For example, the analysis of concrete degradation consists of breaking it down into a set of simple problems, such as the extent of the damaged area, materials and method of a potential repair, longevity of the affected area. Solving each, and assembling their solutions into a solution as a whole. If an engineer succeeds in decomposing a problem into simpler problems that are independent of each other, then combining the partial solutions is not required, because the solution to the whole is the sum of the solutions to its independent parts. Therefore, the effect of degradation on the whole structure and its overall durability is ignored.

In a systematic approach, something to be explained is viewed as part of a larger system and is explained in terms of its role in that larger system. The system concept is more interested in analysing things together rather than in taking them apart. The systematic mode of thought, when applied to marine concrete durability, is called the systems approach. It is based on awareness of the essential interrelatedness and interdependence of all phenomena – physical, biological, psychological, social and cultural (Capra, 1982).

Other workers in concrete durability research, are reporting an increasing appreciation of the value of a holistic approach to concrete technology, research and site practice (Basheer *et al*. 1996; Mehta, 1999). The prevailing reductionist approach is, in fact, responsible for many wasteful practices in concrete technology today (Mehta, 1999; Swamy, 2005). As a result specifications and test methods for concrete durability have failed to consider that durability is not an intrinsic property dependent on concrete making materials and mixture proportions alone (Mehta, 1999). It is a holistic performance criterion that is determined by several other factors, including environmental exposure conditions, structural design, concrete materials and processing, along with technology, workmanship and maintenance.

According to the holistic model proposed by Mehta and Monteiro (2006), a well-constituted, properly consolidated, and cured concrete continues to be substantially watertight and durable as long as the capillary pores and microcracks in the interior do not become interconnected pathways leading to the surface of the concrete. In his model the influence of environmental factors results in the propagation of these microcracks until they become continuous. Degradation and material loss caused by the biodeterioration at the study site is as rapid (as reported in earlier chapters) as Mehta's (1999) model.

A holistic model of the damage process of reinforced concrete structures exposed to a marine environment was offered by Collepardi (2005). One relevant recommendation in that research was a measure to protect against corrosion of metallic reinforcements with the increase in thickness of concrete cover. The revetment armour concrete surface was 1mm above the aggregate; this has had a bearing on the early degradation of the surface studied, as reported in previous chapters. A holistic model similar to Mehta's was proposed by Basheer *et al*. (1996), for predicting the deterioration of concrete structures. The interaction models presented in that work, between deterioration mechanisms and the microstructure of concrete was established to form a series of holistic models. The qualitative predictive capabilities of the macro-model, using *in situ* investigations was successfully demonstrated by Basheer *el al*. (1996) and has been developed in this current research. A holistic approach based on the principle that strength through durability, rather than durability through strength was offered by Swamy (2005), underlining the need for holistic design, with a global approach to all aspects of concrete technology. The *in situ* performance of synthetic fibres at the study site, are key elements in the durability of the marine concrete investigated in this research.

8.1.1 Objective

The objective of this phase of work was to develop and offer two holistic models using data obtained and presented earlier. This was to enable a further understanding of biofouling and its effect on synthetic fibres and limestone aggregate within marine concrete.

8.1.2 Constraints

It is appreciated that the data obtained is from one site with specific environmental conditions and materials, such as poor water quality and algal rich waters and these are not representative of marine sites in general.

8.2 Methodology

8.2.1 Holistic model of fibre degradation

The first and second elements are graphic representations (produced in Microsoft Word 2007) of the new surface of the revetment armour concrete (Figures 8.1 & 8.2). The third element represents the colonisation process, and has been observed in previous chapters and site observations (Figure 8.3). The fourth element illustrates the pop out of the synthetic fibres from the surface, a process studied and commonly observed at the study site (Figure 8.4). The fifth element details the fracture process; this degradation has been observed and monitored for the entire construction period at the study site (Figure 8.5). Finally the sixth element of the model illustrates material loss, which typifies many armour units at the study site (Figure 8.6).

8.2.2 Holistic model of Limestone Aggregate liberation

Information regarding the colonisation of aggregate studied in Chapter 6 has been used to illustrate the second holistic model of limestone aggregate liberation. A new surface with epilithic microorganisms is initially shown. The next stage details aggregate appearing at the surface of the concrete unit. Finally, material loss by way of aggregate liberation is accelerated due to the filamentous growth weakening and displacing the material.

8.3 Holistic model of fibre degradation

Based on site study experience over seven years, surveys and microscopic investigations, a holistic model is presented here for predicting the biodeterioration of synthetic fibres within marine concrete, (Chapter 3, Figure 3.6).

The salient elements of the model can be explained as follows (Figure 8.7)

1. A new surface with horizontal orientated fibres is initially shown. In agreement with Mehta’s (1999) holistic model this model features the penetration of corrosive species, and indicates the opportunities for water and microbial incursion. The new surface of the revetment armour contains many protruding fibres. Immediately these exposed fibres are subject to tidal action, as well as power washing and treatment with a chlorine-based disinfectant (5% or over but less than 15% bleaching agent).

2. The second phase of the model also depicts a new surface; however fibres are shown in a vertical orientation. The entry point of fibre into the matrix, not present in a horizontal fibre, becomes damaged as the exposed part of the fibre reacts to environmental conditions such as submersion in seawater, rich in algae.

3. Colonisation is shown in the next stage of the model. The ingress of moisture through cracks and damaged areas around exposed fibres, allows micro-organisms to penetrate the surface under the fibres and to attach, this leading to colonisation.

4. Fibre 'Pop out'. The presence of growth at the fibre cement interface accelerates bond weakening, causing fibres to 'pop out' from the surface and eventually falling away. This leaves voids at the surface, allowing spores to enter and more algal attachment to take place.

5. Fracture. Algal fronds grow abundantly between fibrillated and monofilament fibres.

6. Material loss is accelerated due to algal filaments weakening and displacing the material. As degradation progresses, more fibres are lost, resulting in a more permeable cement matrix. This entire process continues and phase one of the model now repeats in sequence. Due to variations in the fibre orientation, environmental conditions and fibre positions within the revetment armour (splash/submerged zones); a precise determination of the length of each stage is not possible.

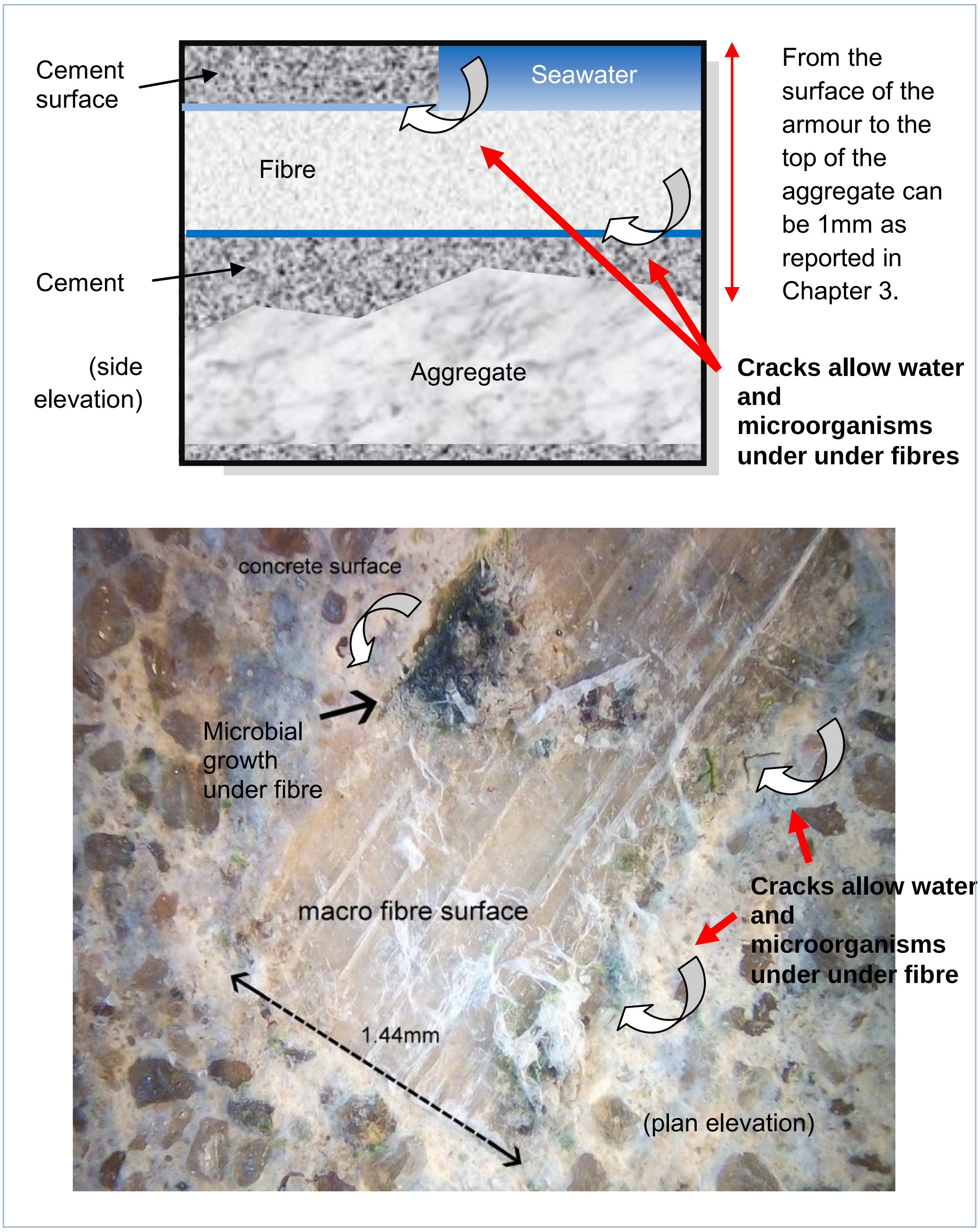


Figure 8.1 First element of the holistic model; schematic and digital image showing the new surface of the revetment armour concrete.

1 – NEW SURFACE WITH FIBRES IN HORIZONTAL FORM

Side elevation of a new surface is shown in the schematic with a horizontal orientated fibre partly exposed which will allow moisture ingress and microorganisms through cracks (shown in the digital image). The surface zone of aggregate can be as little as 1mm.

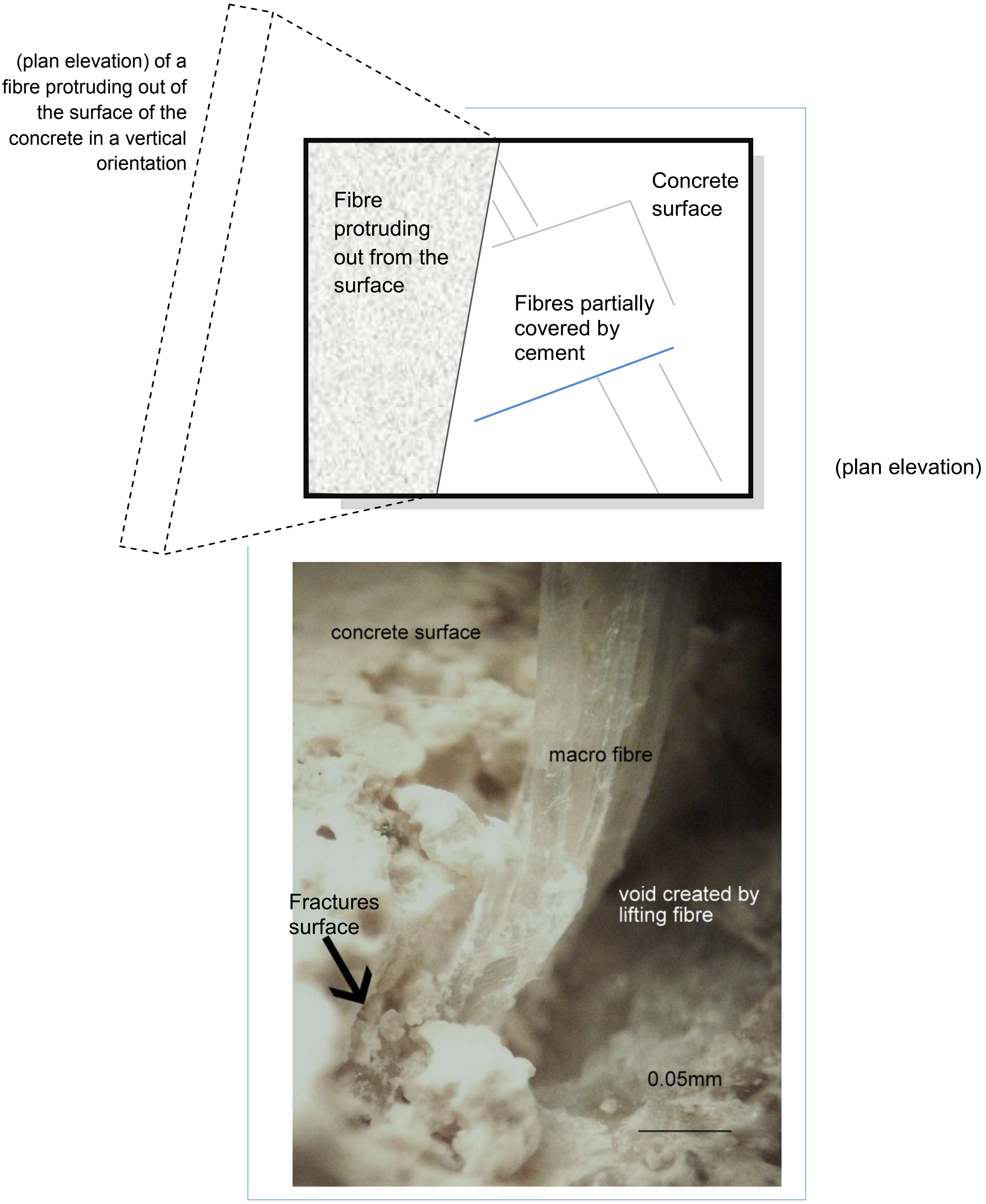


Figure 8.2 Second element of the holistic model; schematic and digital image showing fibres protruding from the surface of the revetment armour concrete.

2 – NEW SURFACE WITH FIBRES IN VERTICAL FORMATION

The schematic shows a new armour surface with a vertical orientated fibre protruding from the concrete, dotted line indicates the complete fibre. Once water tightness is lost, more water carrying microorganisms can be transported into the interior of the armour unit.

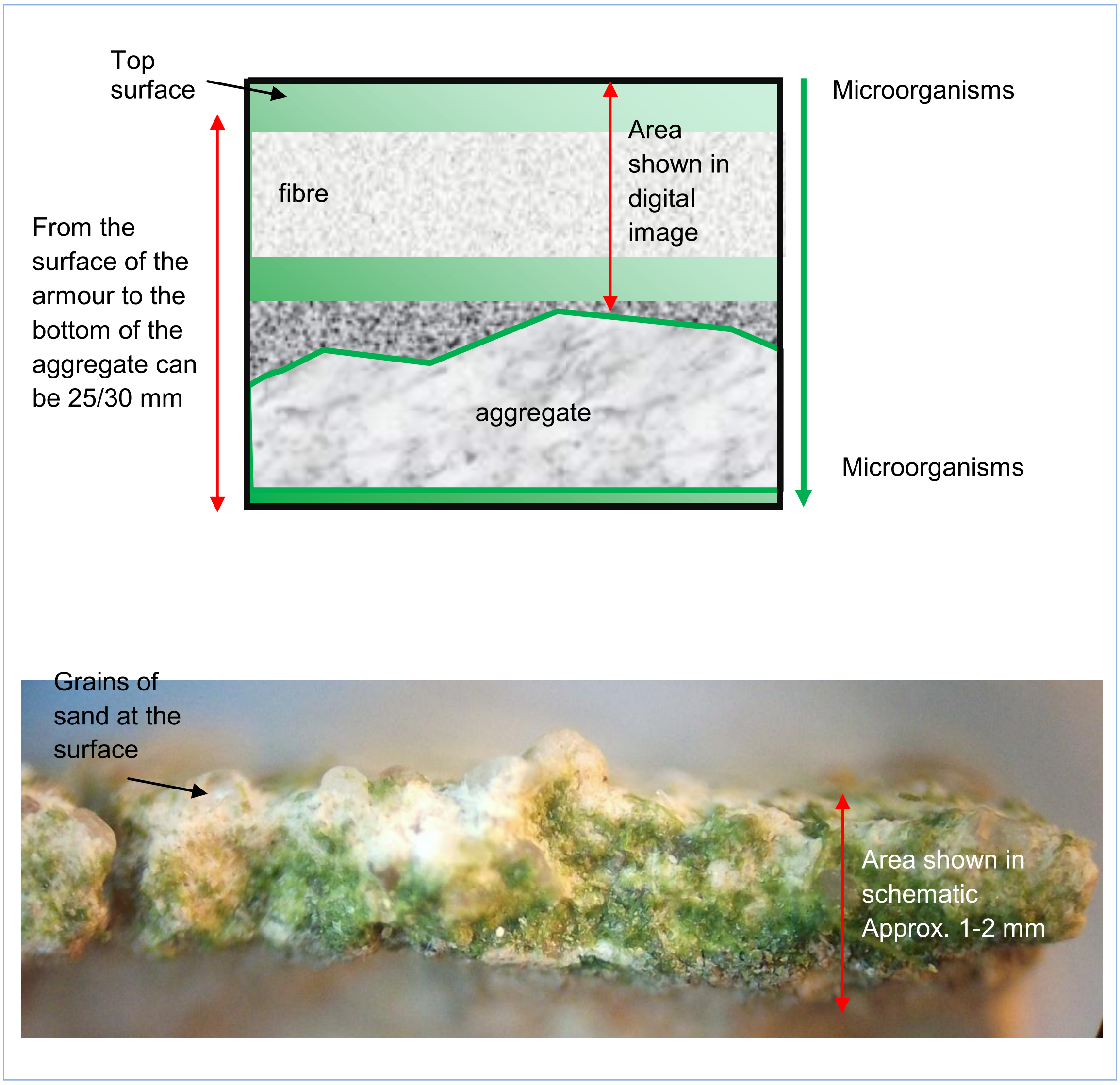
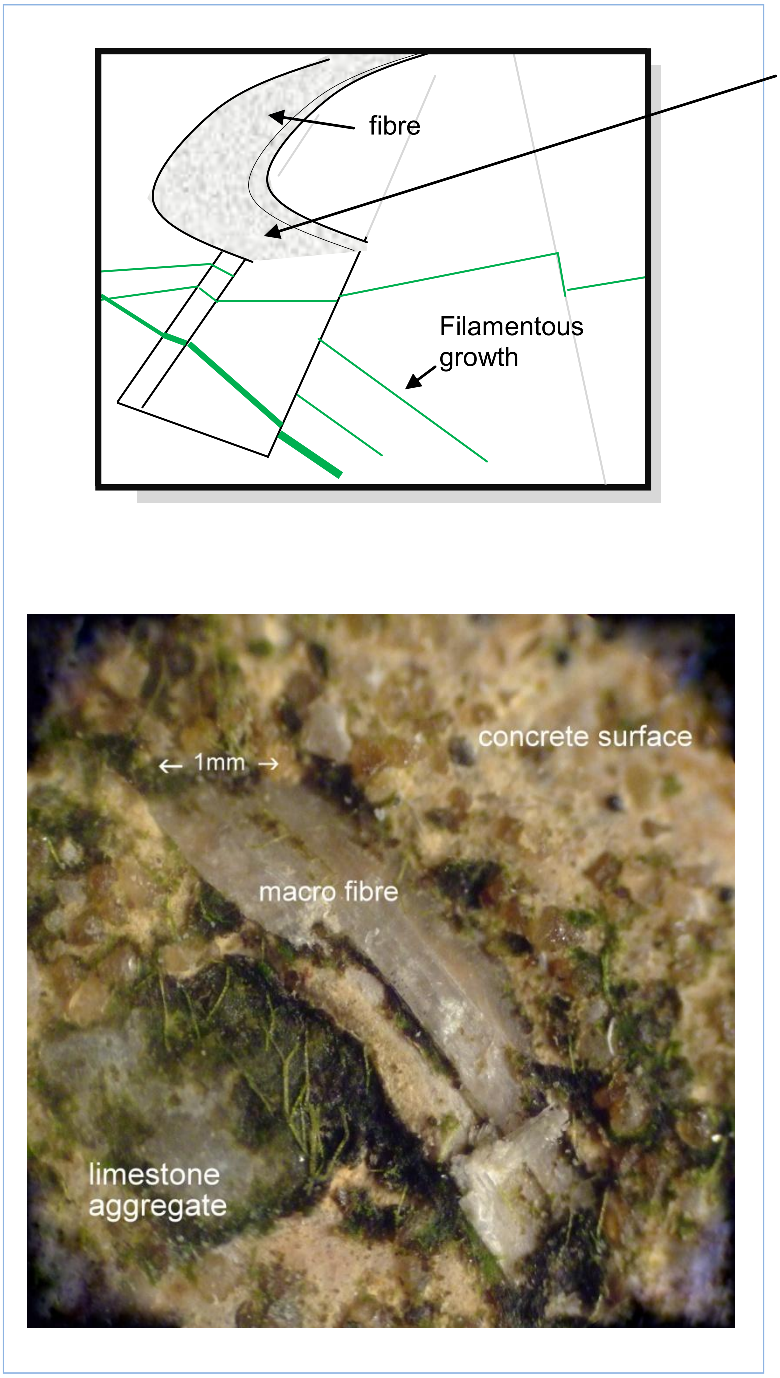


Figure 8.3 Third element of the holistic model; schematic of the surface (side elevation) and digital image showing a detached colonised surface zone sample of revetment armour concrete.

3 – COLONISATION OF THE SURFACE ZONE

The schematic shows a side elevation of a horizontal orientated fibre within its reducing cover through expected erosion and colonised above and below the fibre. Digital image of typical 1 mm original surface zone colonized by *Ulva*.



As fibres peel away the underside of the fibres are colonized by *Ulva* and the newly exposed concrete surface also has attached *Ulva* growing up from the matrix.

Figure 8.4 Fourth element of the holistic model; schematic and digital image showing filaments of algae growing under fibres.

4 – FIBRE POP-OUT

Plan elevation of an armour unit with a horizontal orientated fibre lifting out from the surface. Digital image shows filaments growing under the fibre.

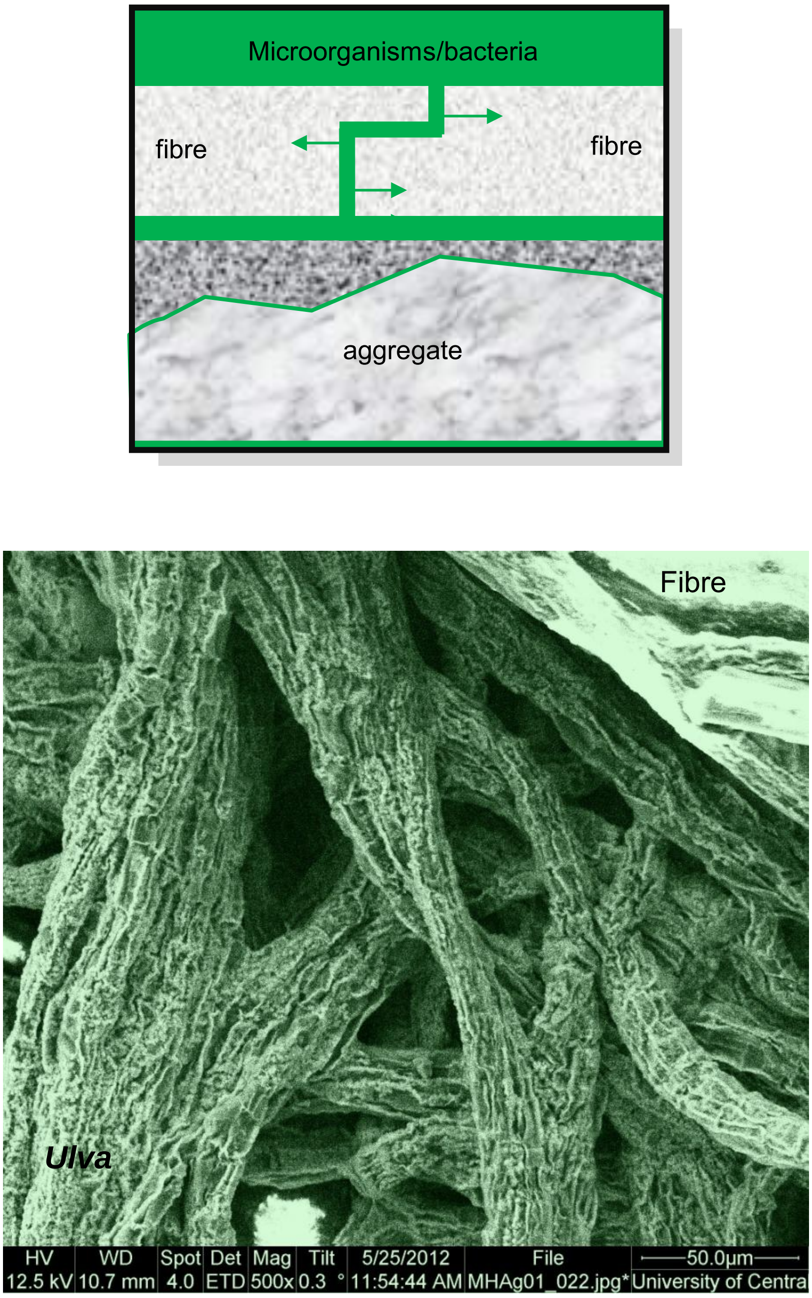


Figure 8.5 Fifth element of the holistic model; schematic and digital image showing showing algal colonisation under synthetic fibres.

5 – FIBRE FRACTURE

Side elevation of a substratum with a horizontal orientated fibre partly begins to fracture allowing algal filaments to grow around and through fibres. Micrograph depicts algae under fibres.

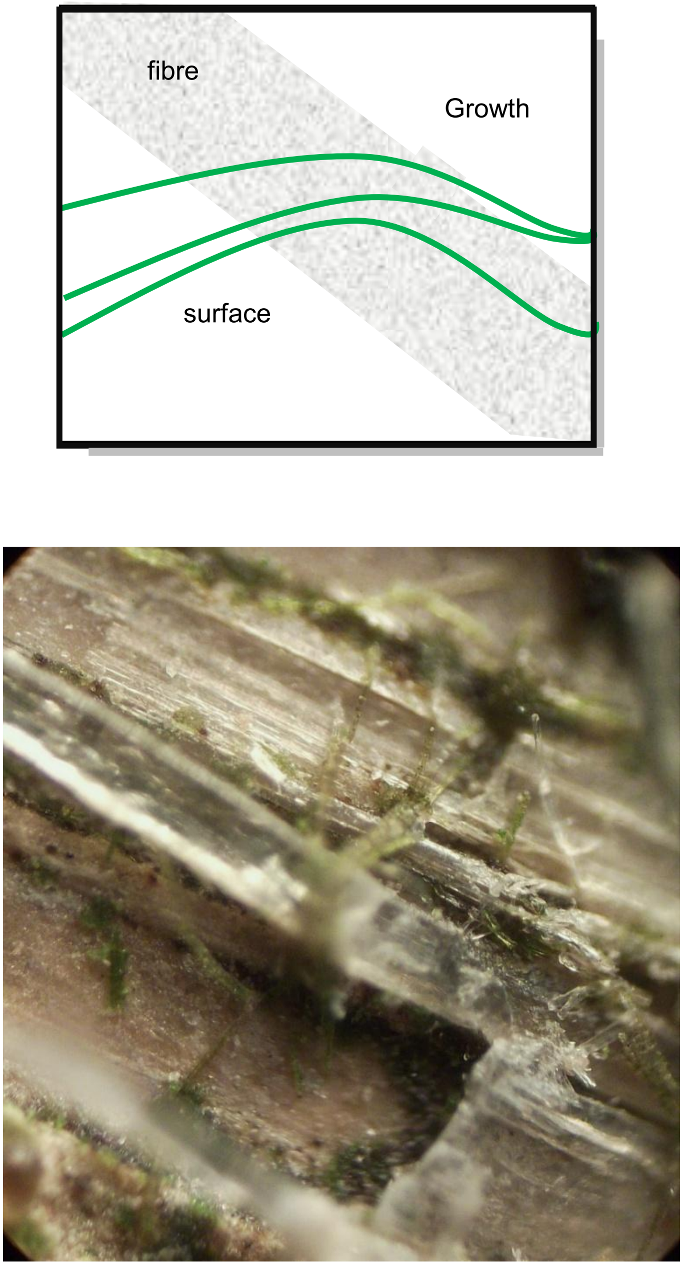
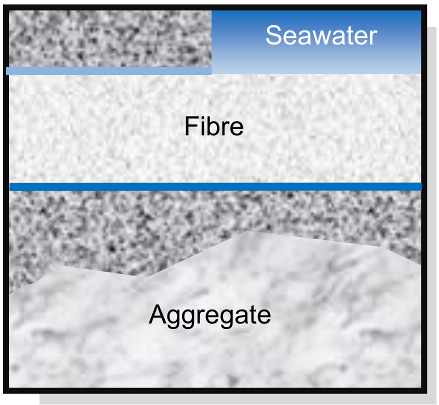


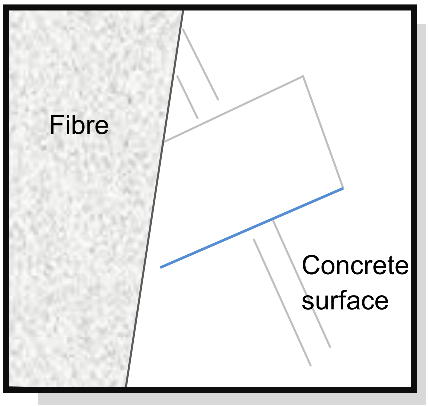
Figure 8.6 Sixth element of the holistic model; schematic and digital image showing how filaments can grow within the surface zone of the revetment armour concrete.

6 – MATERIAL LOSS

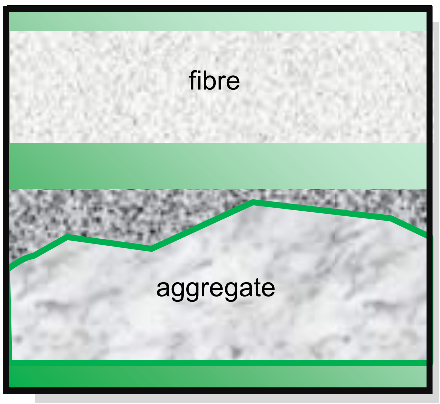
Plan elevation with remnants of a horizontal orientated fibre. Filaments freely growing within remaining fibre.



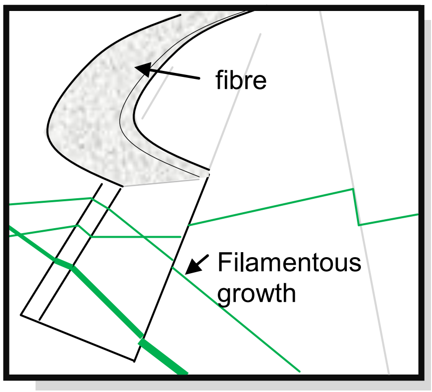
1. New armour surface



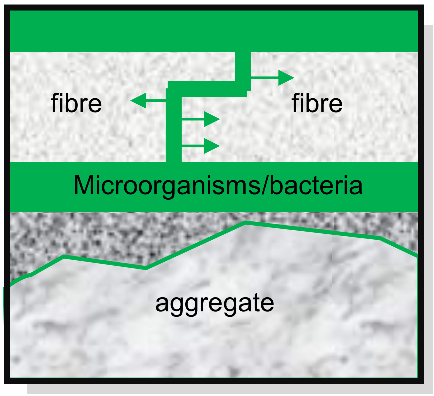
2. New surface



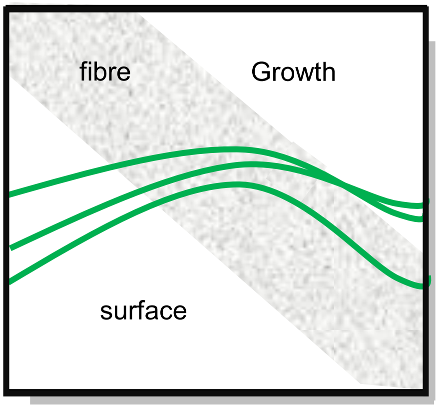
3. Colonisation



4. Fibre pop out



5. Fibre fracture



6. Material loss

Figure 8.7 The 6 individual elements of the holistic model of fibre degradation.

The Holistic Model (sequential)

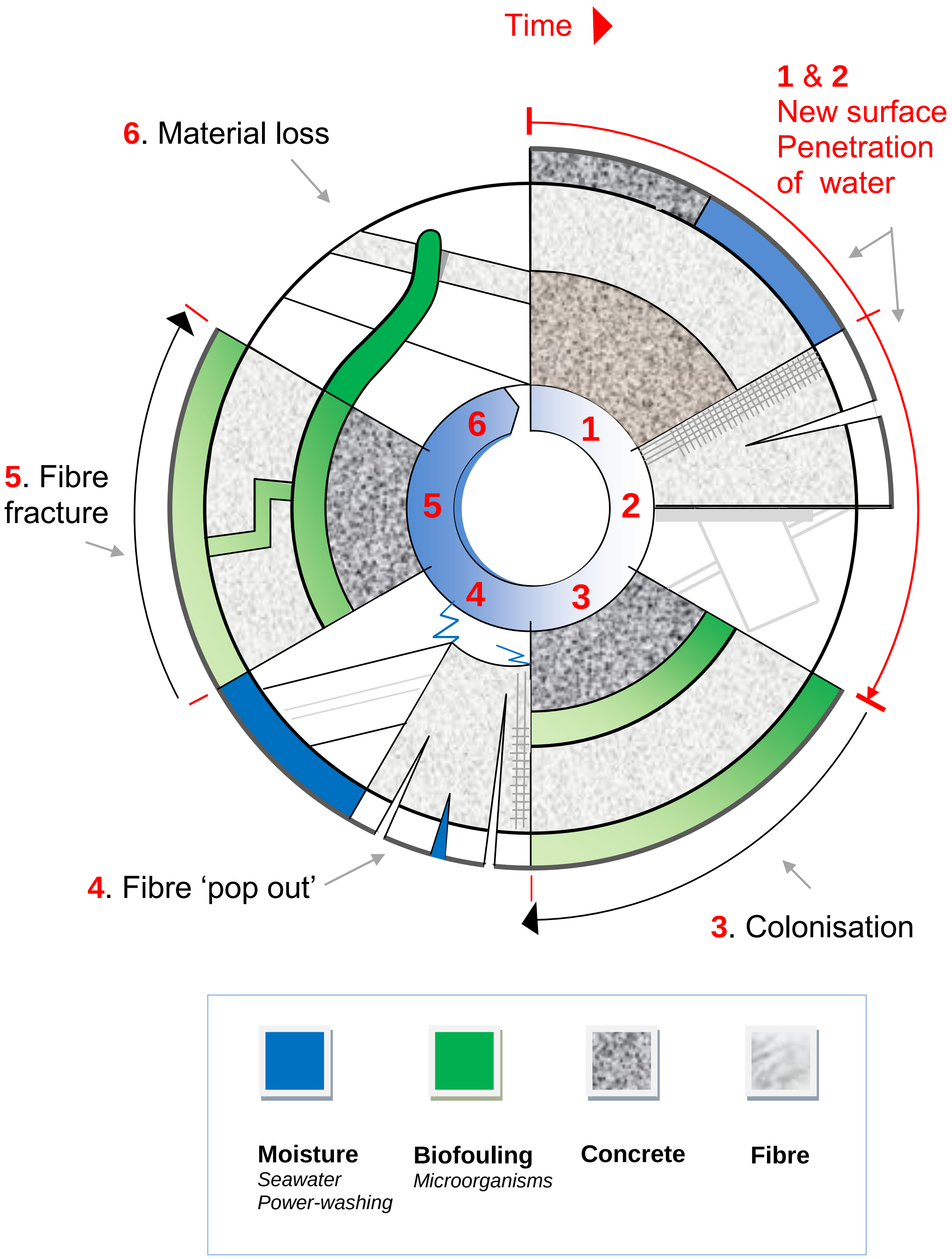


Figure 8.8 A Holistic Model of fibre degradation, combining elements (of Figure 8.7).

8.4 Holistic model (number 2) of limestone aggregate liberation

Based on site study experience over seven years, surveys and microscopic investigations, a second holistic model is proposed here for predicting the liberation of limestone aggregate from marine concrete.

Figure 8.9 Algal colonisation around large aggregate

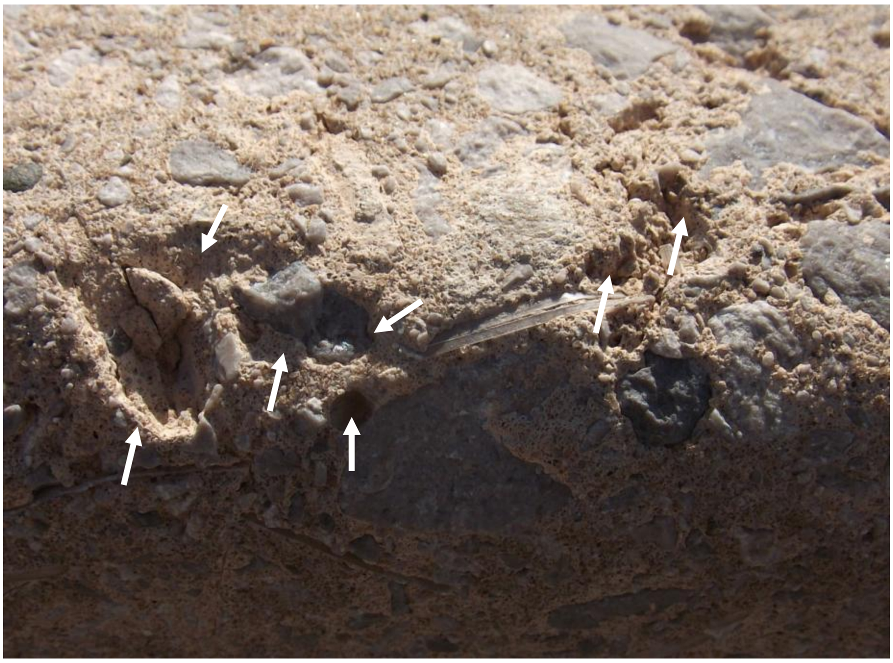


Figure 8.10 Recently cleaned surface of armour with aggregate liberation (arrowed)

The salient elements of the second model can be explained as follows (Figures 8.11, 8.12 and 8.13)

A. A surface with epilithic microorganisms is initially shown (Figure 8.9 & 8.11). The new surface of the revetment armour contains many protruding synthetic fibres. Immediately these exposed fibres are subject to tidal action, as well as biofouling control, where the surface is power washed and treated with a chlorine-based disinfectant. The entry point of fibre into the matrix, not present in a horizontal fibre, becomes damaged as the exposed part of the fibre reacts to environmental conditions such as submersion in seawater, rich in microorganisms.

B. Aggregate appearing at the surface of the concrete unit is shown in the next stage of the model (Figure 8.12). The ingress of moisture around exposed aggregate, allows microorganisms to penetrate the surface under the aggregate and to attach, this leading to colonisation, therefore allowing more microorganisms to enter leading to more attachment to take place.

C. Material loss is accelerated due to the filamentous growth weakening and displacing the material (Figure 8.10 & 8.13). As degradation progresses, more aggregate is lost, resulting in a more permeable cement matrix. This process continues and phase one of the model now repeats in sequence. Due to variations environmental conditions and aggregate positions a precise determination of the length of each stage is not possible.

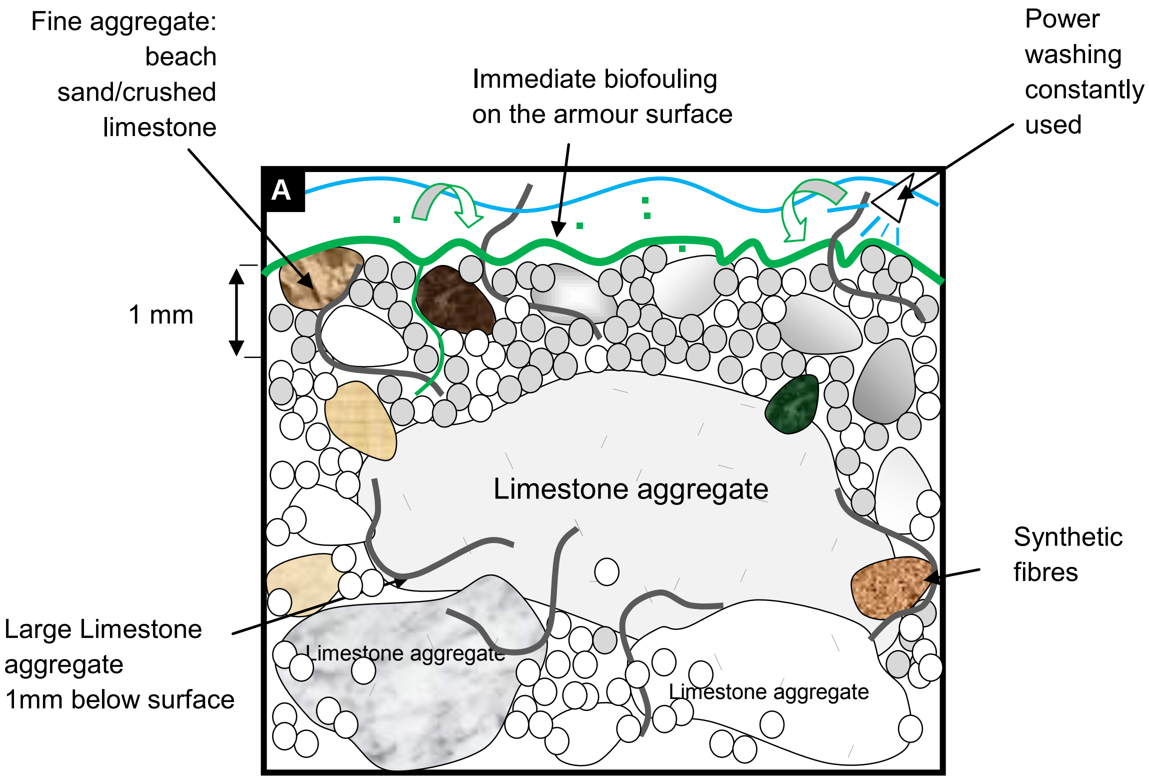
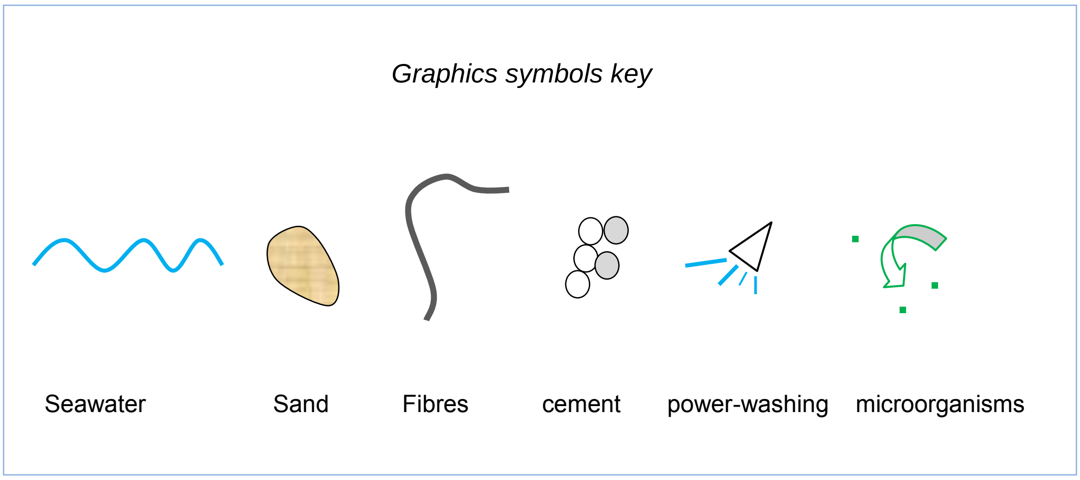
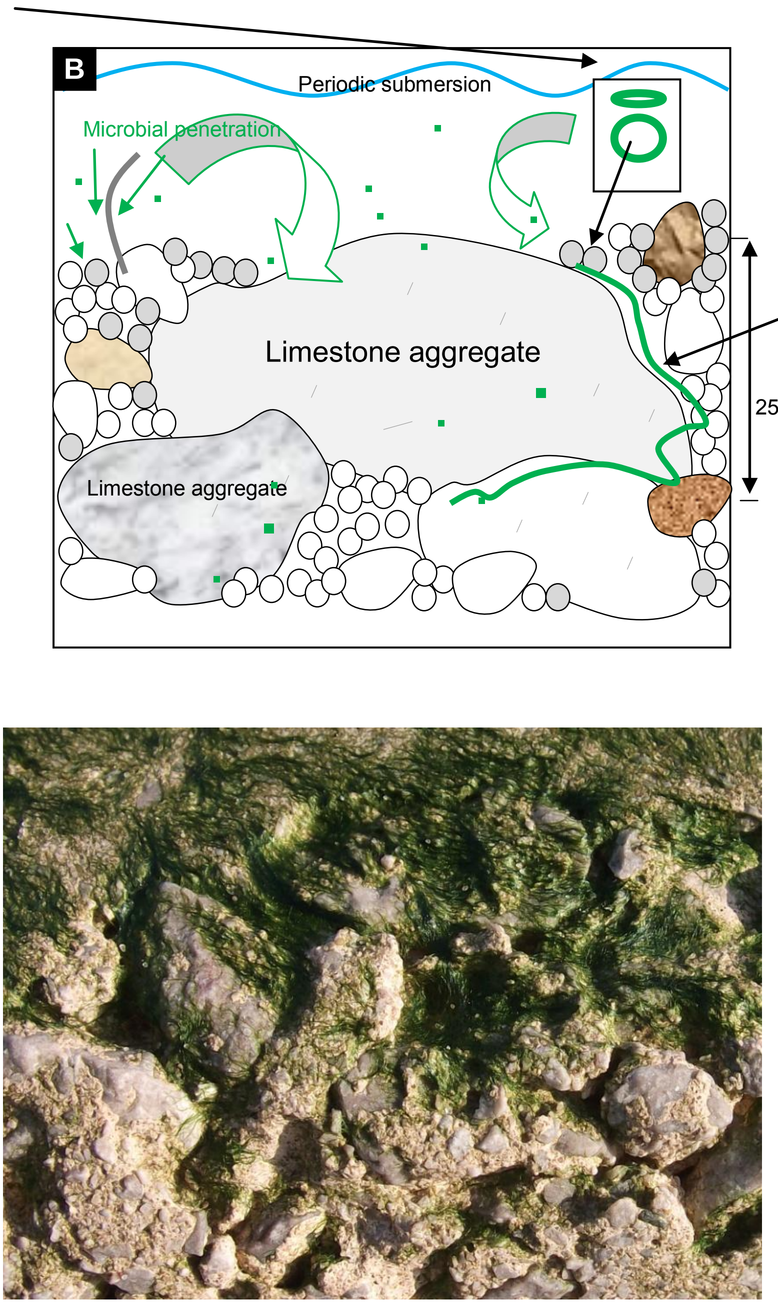


Figure 8.11 A new surface with epilithic microorganisms. Large aggregate packed together at the nose of the armour unit as discussed in Chapter 4.

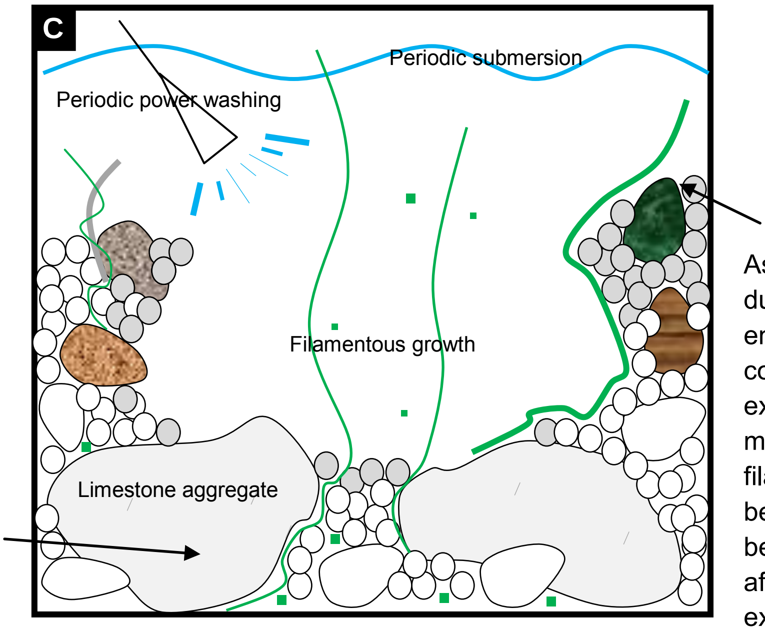




Filament sectional view. The more open being hydrated and closed being dehydrated.

Filament growth within aggregate cement interface, see SEM micrographs in Chapter 6.

Figure 8.12 The initial surface has now eroded. Aggregate appearing at the surface of the concrete unit.



Newly formed macro voids create settlement opportunities for marine life such as limpets and barnacles

As material is lost due to environmental conditions exacerbated by microorganisms, filament growth can be observed 25 mm below the surface, after 3 years exposure.

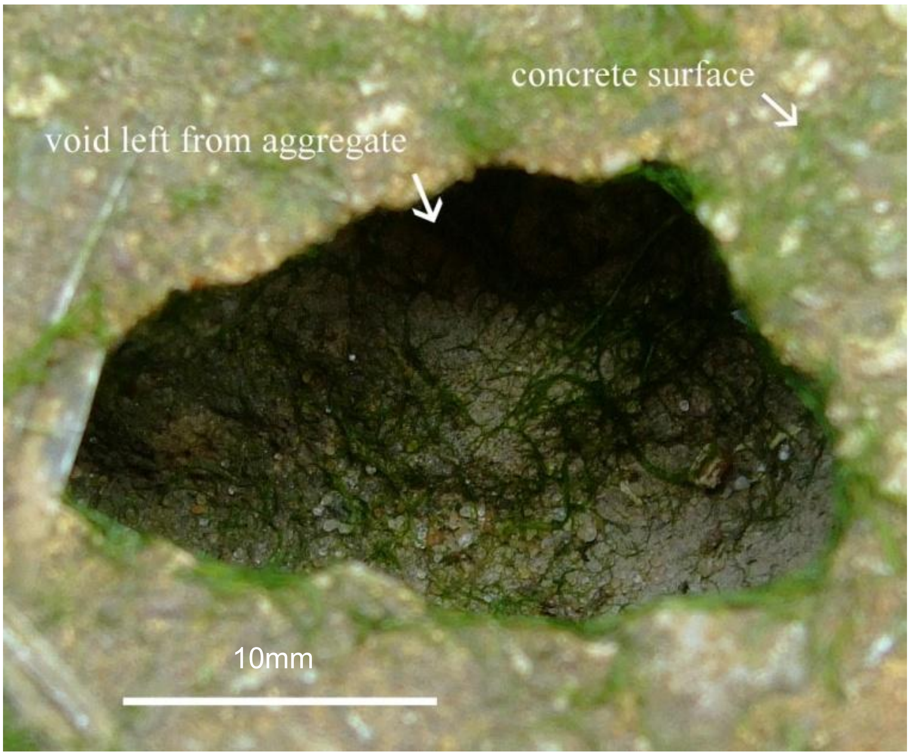


Figure 8.13 Material loss. Large aggregate particles having left the material leave voids of approximately 25 mm in depth. Note the filaments of algae are still in place although the aggregate has gone.

8.5 Discussion

Historically, the general approach has been to relate concrete durability directly to the strength of concrete (Mehta and Monteiro, 2006). A generally accepted argument is that low strength, more permeable concrete is less durable. However, in the marine concrete structure featured in this research, durability issues are far more complex, and consideration of the strength alone is inadequate.

The approach adopted by Mehta in his holistic model of concrete degradation, focused on the soundness of concrete under service conditions as a fundamental measure of concrete durability rather than on the strength of concrete. According to this model, concrete manufactured to high quality standards and guidance is initially considered to be an impermeable structure. This condition exists so long as interior pores and microcracks do not form interconnected paths extending to the exterior surfaces. This condition is depicted in phase 4 of the holistic model of fibre degradation, featuring fibre pop out, followed by phase 5, fibre fracture and phase 6, material loss (Figure 8.2). Under environmental exposure and loading, the revetment armour concretes watertightness gradually decreases, one mechanism being fibre loss, another being aggregate loss, as the network of defects becomes more interconnected over time. It is then that water and microorganisms can enter the armour concrete and produce detrimental effects.

This phase of work has compiled all the information and data on the degradation mechanisms observed and measured earlier, and formed a holistic model of degradation. The first model, a study of synthetic fibre performance (Figure 8.2). The second model, (Figures 8.3 – 8.5), has featured the durability of limestone aggregate. The biodeterioration mechanisms involved are discussed in more detail in previous sections. In turn, these internal stresses lead to degradation and material loss. Extensive surface damage produced in this manner is shown in Chapters 5 and 6. It is clear that the damage inflicted by filamentous growth (and other effects) reduces the soundness of concrete and facilitates further deterioration at an increasing rate. In the light of the importance that Mehta’s model of environmental concrete degradation attaches to defects such as the penetration of corrosive species (Mehta and Monteiro, 2006), the reliance on the high strength of concrete alone for satisfactory service life becomes questionable. High strength levels in concrete alone certainly do not guarantee a high degree of durability and longevity.

Every organism from the smallest bacterium through the wide range of plants and animals to humans is an integrated whole and thus a living system (Capra, 1982). The unexpected observations of bacterial filamentous growth within fresh, cured concrete discussed in Chapter 4 shows the need for a systematic viewpoint. This concrete has been affected by the biofouling process before being placed in the natural environment. This new phenomenon has a bearing throughout this research and will influence the perception of marine concrete biofouling in general. Concrete testing methods used in this research and in general have to avoid a reductionist approach, favouring a holistic performance criterion. The presence of bacterial filamentous growth within fresh concrete has a significant effect upon the materials durability and on testing methodology. Research investigating the effect of biomass concentration on the compressive strength of porous Portland cement mortar cubes was offered by Ramachandran *et al*. (2001). Bacteria were mixed with cement and sand, and set into 5cm cube moulds. After 24 hours, the cubes were de-moulded and placed into a urea/calcium solution for 28 days. The bacterially-treated cubes showed a 24% improvement in compressive strength. When testing concrete or assessing durability at a study site one must take a holistic view of an integrated whole and thus a living system. The knowledge of bacteria present, affecting the material, enables a more accurate quantification of the biodeterioration of marine concrete. When the revetment armour prematurely fails and no longer serves its purpose, it will be classified as ineffectual, regardless of what caused the failure, biodeterioration, poor design, unsuitable materials, poor workmanship, or a combination of these. The entire system failed. For the marine concrete industry, which includes design engineers, stakeholders, material manufacturers, and contractors; in order to successfully meet the needs of our future marine structures, the entire process of concrete degradation should be considered and a systems concept adopted.

8.6 Conclusions

A systematic approach to marine concrete performance, long term durability, design and choice of materials is necessary. Selection of design values and design decisions should be more rational and choices should consider long term rather than short term performance.

Concrete testing methods used in this research and in general, have to avoid a reductionist approach, favouring a holistic performance criterion. The presence of bacterial filamentous growth within fresh concrete has a significant effect upon the materials durability and on testing methodology.

A holistic approach to concrete durability ensures that no part of the system is overlooked and takes into account the concurrent interaction of many factors and the consequent changes occurring in marine concrete. A shift in the science of concrete durability from a reductionist to holistic approach is also necessary before one can develop more accurate systematic test methods, specifications and relevant codes that are truly applicable to the durability of our marine structures. Absence of the holistic system concept in designing, implementing and manufacture of marine concrete sea defences is clearly demonstrated in the current examples of early degradation featured in this research.

Chapter 9

Overall conclusions and discussion

Discovery consists of seeing what everybody has
seen and thinking what nobody has thought.

Albert Szent-Gyorgyi (1962)

9.1 General

This chapter provides a summary of the main conclusions from earlier Chapters and discusses the implications for marine concrete engineering in the inter-tidal range, particularly where algal build-up can be an issue. Finally, recommendations for further investigation and research are discussed.

9.2 Aims and objectives achieved

This research has advanced the understanding of how synthetic fibre reinforced concrete responds to biofouling in the marine environment. The analysis of the factors affecting the biofouling process, bioreceptivity, filamentous growth, and attachment mechanisms of microorganisms reported in this thesis has brought new insights into this process. A durable, efficient and effective sea defence structure is implicit through compliance with current codes and standards. The evidence gathered in this research highlight that material degradation and damage can occur in service, implying that the revetment armour units at this location are affected after only five years exposure.

Objectives achieved during the investigation include:

- Chapter 3 described the impact of existing, aggressive cleaning practises on the wear of concrete surfaces.
- Chapter 4 quantified the impact of cleaning on algal colonisation and biofouling development.
- Chapter 5 reported the bacterial filamentous growth in freshly hardened fibre reinforced marine concrete, including previously unreported observations.
- Chapter 6 investigated TiO_2 photocatalytic coatings at the study site, but this met with limited success due to bacterial growth damaging the coating. Trials on some areas showed promise, and further studies will progress towards a non-toxic, environmentally-benign, anti-fouling strategy for future industrial applications.

- Chapter 7 reported on successful cell attachment to synthetic fibres.
- Chapter 8 introduced a holistic model for durability analysis and prediction of marine concrete structures, taking a combination of colonisation, fracture mechanics, maintenance procedures and chemically-induced degradation processes into account.

This research advocates an holistic philosophy; an integrated material, structural, design and maintenance strategy. A holistic view envisages a global approach to all aspects of marine concrete and construction technology, embracing material selection, project design, to construction techniques and maintenance over the service life, integrating material characteristics with *in-situ* performance.

9.3 Main findings of the research

9.3.1 Surface analysis

This research has explored the degradation and durability of concrete revetment armour units in the inter-tidal range at the study site. The regular immersion cycles provide ideal damp conditions for algal growth, but the horizontal surfaces of the revetments also provide tempting walking surfaces for the public between the tides, which has created slip hazard issues. The Council's battle to keep the revetments free from algae has also increased the rate of algal re-population, by affecting the concrete surface, as explained below.

9.3.2 Colonisation

Algal attack has been found to be progressive and traditional measures at removal such as high pressure water jetting serve simply to roughen the surface and weaken it, providing more opportunities for microbial attachment. Parts of the as-cast surfaces of the revetment armour units have been significantly affected by daily power washing and the use of Dairy Hypochlorite.

9.3.3 Surface roughness

Surface roughness and topography are important elements for the settlement of many organisms; it has long been known that rough surfaces are preferred by algae to smooth surfaces. Surface roughness of the (horizontal) steps at the study site has doubled over a three year period following regular high pressure washing, while the risers have become smoother over the same period.

9.3.4 Surface zone

The significant reduction in the rebound number implies a diminution in the density of the surface layer, suggesting a 50% decrease in compressive strength. There is a significant reduction in UPV in the near-surface zone of the units, indicating the concrete is weakened at depth and suggests the core of the unit may also be affected.

9.3.5 Segregation

Segregation occurred at the 90° corners in the bottom of the moulds during placing and compaction, producing a high aggregate concentration. When inverted, these corners are a weak zone that is prone to erosion by high pressure cleaning and tidal impact.

9.3.6 Algal colonisation

A survey of algae on the Fylde coast identified the current dominant genus as *Ulva* and various other species in concrete specimens, forming a diverse community. Observations and examination of retrieved samples show that rough surfaces offer algal spores protection against wave action; in particular the reduced water flow in voids, depressions and crevices that are opened-up by cleaning offer refuges for settling spores and juveniles, protecting them against removal by hydrodynamic forces and high powered water jet cleaning systems.

9.3.7 The interface

Concrete in the tidal range, which is subjected to wave impact, should be relatively strong and watertight to provide a durable surface resistant to salt crystallisation and freeze-thaw cycles. Observations revealed algal filamentous growth had penetrated the concrete surface and grew at the interface between materials. The interface between hardened cement paste, aggregate and fibres is slightly weaker than the cement matrix itself and this plays an important role, as filamentous algae can tunnel into the interface and reach a depth of up to 30mm. This filamentous growth will inflate or swell with tidal submersion and power washing, and deflate and flatten under drying, so weakening the bond between the components of the concrete. The reduction in bond will make the aggregate and fibres more prone to erosion under tidal impact and power washing. A schematic illustration was presented based on this phase of work (Figure 4.24).

9.3.8 Surface energy

Surface free energy significantly influences the propensity for biofouling of the concrete surface and results showed a 48% reduction from $21MJm^{-2}$ (SI $10^{-3}kgs^{-2}$) to $11MJm^{-2}$ in the worst-affected units over three years. A generalised relationship between surface tension and the relative amount of bioadhesion has been established, indicating the revetment armour concrete continues to offer adhesion to microorganisms and is thus bio-receptive.

9.3.9 Calcium depletion

EDAX analysis of site specimens showed the algae may have partly been responsible for the reduction of the calcium element content within the cement matrix of the surface zone by 86%. This was contrary to other workers findings (Jayakumar and Saravanane, 2009) and may be explained by site specific details, location of samples and length of sample exposure.

9.3.10 Fibres

The fibres were widely observed at the surface of the new concrete, exposed by hydrodynamic action (whether tidal impact or power washing) and microbial forces and then liberated from the surface to leave behind voids, creating a more porous and algae-susceptible surface. In this situation synthetic fibres do not increase the toughness of the armour as intended (Mehta and Monteiro, 2006).

9.3.11 Porosity

Liberated fibres and fine aggregate, along with loosened large aggregate has led to a surface porosity increase by 250%. This result suggests a lack of water tightness which can allow microorganisms to enter the substratum.

9.3.12 The use of beach sand as fine aggregate

Bacteria from local beach sand, used in the production of the concrete units, survived the manufacturing process and grew within the freshly hardened matrix. When the bacterially-loaded concrete was placed in a marine environment, algal colonisation occurred and the biofouling process continued over a five year period, and penetrated into the interfaces within the matrix. This microbial interaction appeared to weaken the interface bond, leading to mass loss accelerated by power washing. Bacterial biofilms are informative signposts and a prerequisite for attachment of macrofoulers, such as algae. Concrete cubes from the casting yard and the concreting beach sand were examined and cultured cells grown, showing bacterial filamentous growth similar in size and morphology to Actinomycetes.

9.3.13 Bacterial cell attachment to synthetic fibres

Bioreceptivity of electrospun polymer fibre scaffolds, which showed hydrophilicity, enhanced by Oxygen Plasma treatment, and the successful colonisation of hyperthermophiles was observed by SEM. Successful attachment of bacterial cells to ‘inert’ polymer fibres in laboratory conditions demonstrated the possibility for a fundamental sequence in the fouling process, consistent with the observations that bacteria cells attached to micro synthetic fibres within the matrix of fresh concrete. This work has shown attachment is possible in a controlled regime and that bacteria and other microorganisms do attach and colonise on synthetic fibres in the concrete at the study site.

9.3.14 Biodeterioration of polymer sealants

All potential biodegradation mechanisms of marine joint systems need to be better understood to select a suitable sealant for use in a joint system. Observations of microbial colonisation within the polymer silicone sealant currently used at the study site showed how microorganisms affect the performance of the sealant matrix in a marine environment. Polymer sealant samples from within precast elements were examined microscopically and biodeterioration was observed, where algal filaments tunnelled into the polymer. It is expected that filamentous growth within the matrix of the sealant will weaken the material, making it more susceptible to other hostile elements.

9.3.15 TiO_2 photocatalytic anti-fouling coatings

From the results of the trials, TiO_2 coatings were capable of controlling algal growth on a fibre free concrete surface. There are however several obstacles to be cleared before this technology can be adopted in the control of marine biofouling. The application of a coating to composite materials, such as the revetment armour concrete has constraints. Fibres protruding from the surface of the new armour do not allow for a satisfactory bond between coating and substratum. Filamentous bacterial growth from within the matrix of the new revetment concrete, as observed and reported in Chapter 5, leads to the eventual cracking and de-lamination of the coating from the concrete surface. The application of the TiO_2-based coating trialled was not designed to defend from microbial growth from within the concrete, effectively a living substratum.

9.4 Conclusions

9.4.1 Revetment armour concrete

The armour units studied in this research should be regularly monitored for further development of degradation, and other sites, utilising this design should be included. The reasons for this are twofold:

- Biofouling and its effect on the durability of fibre-reinforced concrete sea defences has not been investigated previously. It remains uncertain as to whether both weakening and loss of the surface concrete skin and apparent weakening in the core of the units, is progressive or has now stopped.
- Bacterially-loaded beach sand has been shown in this work to be detrimental to the durability of the concrete and should be avoided in future, especially when used in conjunction with synthetic fibre reinforcement.

Particular care and attention is required in selecting mix constituents and practises, as some parameters clearly contribute to algal attack, for example by reducing the resistance of the surface to high pressure cleaning.

Guidelines for the design of concrete units for use in seawater that reduce the incidence of biofouling are needed as amendments to current standards. Advice is also needed on the methods for effective management of biofouling on concrete in seawater, particularly where such build-up can weaken the surface or give cause for concern about making walking surfaces more slippery, so giving rise to aggressive cleaning methods. These guidelines will enable local authorities to make informed choices about design and reducing the cost of managing biofouling.

Based on the findings of this research, frequent power washing and the use of Dairy Hypochlorite on the revetment armour steps should be avoided. Lessons could be learnt from other authorities who do not use such practises. The neighbouring Wyre council does not use power washing, but uses periodic application of an environmentally friendly sprayed biocide treatment on revetment steps.

Training should be considered for the operatives of cleaning machines considering alternative procedures which consider the consequences of current practises.

As described in this research, the current manufacture process of the revetment armour, where the units are cast up-side down, does not appear to produce the intended dense and impervious concrete surface.

- Synthetic fibres are quickly exposed on the surface and as bacteria and then algae grow around and through the fibres, it is the view of the author that the fibres in their current form are inappropriate for marine concrete, particularly where beach sand is used in the mix. Amendment to Concrete Society Technical Report No. 65: *Guidance on the use of Macro-synthetic-fibre-reinforced concrete* are required, and the Concrete Society have received and are considering an amendment proposed by the author as a result of this work for the next re-print, enclosed in Appendix A6-3.

- Aggregate segregating out in the 90° corners in the bottom of the form is another unintended problem, creating a weaker matrix in the region most exposed to the full force of wave action and impact. A more robust surface may be realised with bevelled corners to the form to help prevent segregation, or providing a lining to the formwork to improve the surface strength and density: porous formwork liners or permanent formwork made from glass-reinforced cement, may offer ways of providing a surface that is substantially stronger and more resistant to algal growth.

- Beach sand should be avoided for concrete structures in the tidal range where rapid algal build-up is of concern. This is particularly the case where synthetic fibres are also to be used in the concrete for plastic shrinkage crack control. Bacterial loading of the beach sand may be detrimental to the durability of marine concrete in the tidal range and amendments may be required to PD 6682-1:2009 *Aggregates for concrete* (BSI, 2013a) to highlight this concern. This UK guidance recommends limiting values for aggregate properties within the ranges permitted in BS EN 12620 (BSI, 2013) but does not place any limits on microorganisms present in beach sand.

Designated pedestrian access steps, with barriers to prevent access onto the flat revetment areas by the public, could be used as part of the design to the sea defences to control access by the public onto the slippery surfaces.

The self cleaning concrete jetty at Staffa, discussed in Chapter 2, is a unique example of coastal engineering sustainability in practice and could be adopted in similar situations. The remarkable and innovative project is still working today. Surfaces which are largely free of algae tend to be less slippery and dangerous and could be partly achieved at the study site. Since construction 20 years ago, circa 1 million visitors have used the Staffa jetty and it is still functioning as intended.

9.5 Future work

Alternatives to the use of Dairy Hypochlorite and power washing are required at the study site, regarded as a flagship project. Alternatives are used by other authorities and this information and these practises should be shared. Research is required into why local authorities do not communicate with one another regarding cleaning and maintenance. Designated access incorporated into design needs to be investigated. Effective biofouling management requires international cooperation between governments, industry and researchers.

The use of fibres for the first time in a marine environment has brought to light some problems. Anti-bacterial coated fibres, now available on the open market, may be beneficial and should be investigated. Fibres within concrete prisms could be placed at secure marine test sites over time to assess their performance. The effect of microbial growth could be observed with the use an interesting technique for the visualisation of bacterial weathering within the matrix with computerised X-ray microtomography (De Graef *et al*. 2005).

The use of beach sand (in the UK) as fine aggregate is not appropriate for marine structures. Observations of bacteria from beach sand within new unplaced concrete are a significant discovery which merits further research. DNA investigation is required into the species observed in this research enabling further understanding. Eliminating bacterial growth from within new concrete would enhance the performance of photocatalytic coatings. Application techniques needs further research for marine applications and further site trials would be beneficial.

Salt weathering of synthetic fibres needs further study. Crystal growth on synthetic fibres may be detrimental to their long term performance and may not have been anticipated at the design stage when used in a hostile environment.

The manufacture of the revetment armour units featured in this research requires more study into their long term durability. Further monitoring of these units, on a national level is needed, investigating their long term performance. A study on mortar components centered on maintaining a high pH by preventing carbonation should be considered.

Biological control, as used at Staffa (Appendix 2) has shown great promise and requires research to appreciate this opportunity. The biological control concept has a future role to play in biofouling management, but is constrained by the great variation of fouling microorganisms. However, herbivores with a broad dietary range, may be successful control agents on stepped revetment armour. It is clear to those who have studied biofouling and its management, that new societal paradigms are needed if environmentally responsible, holistic strategies are to be developed and implemented.

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Appendices

Table of Contents

Appendix 1
Additional documentation to Chapter 1

Introduction

A1-1 Results of Algae survey undertaken on the Fylde coast:

A1.1 *Ulva* (formally *Ulva* intestinalis)

A1.2 *Ulva lactuca*

A1.3 *Chorda filum*

A1.4 *Laminaria saccharina*

A1.5 *Halidrys siliquosa*

A1.6 *Fucus spiralus*

A1.7 *Ascophyllum nodosum*

A1.8 *Fucus vesiculosus Linnaeus*

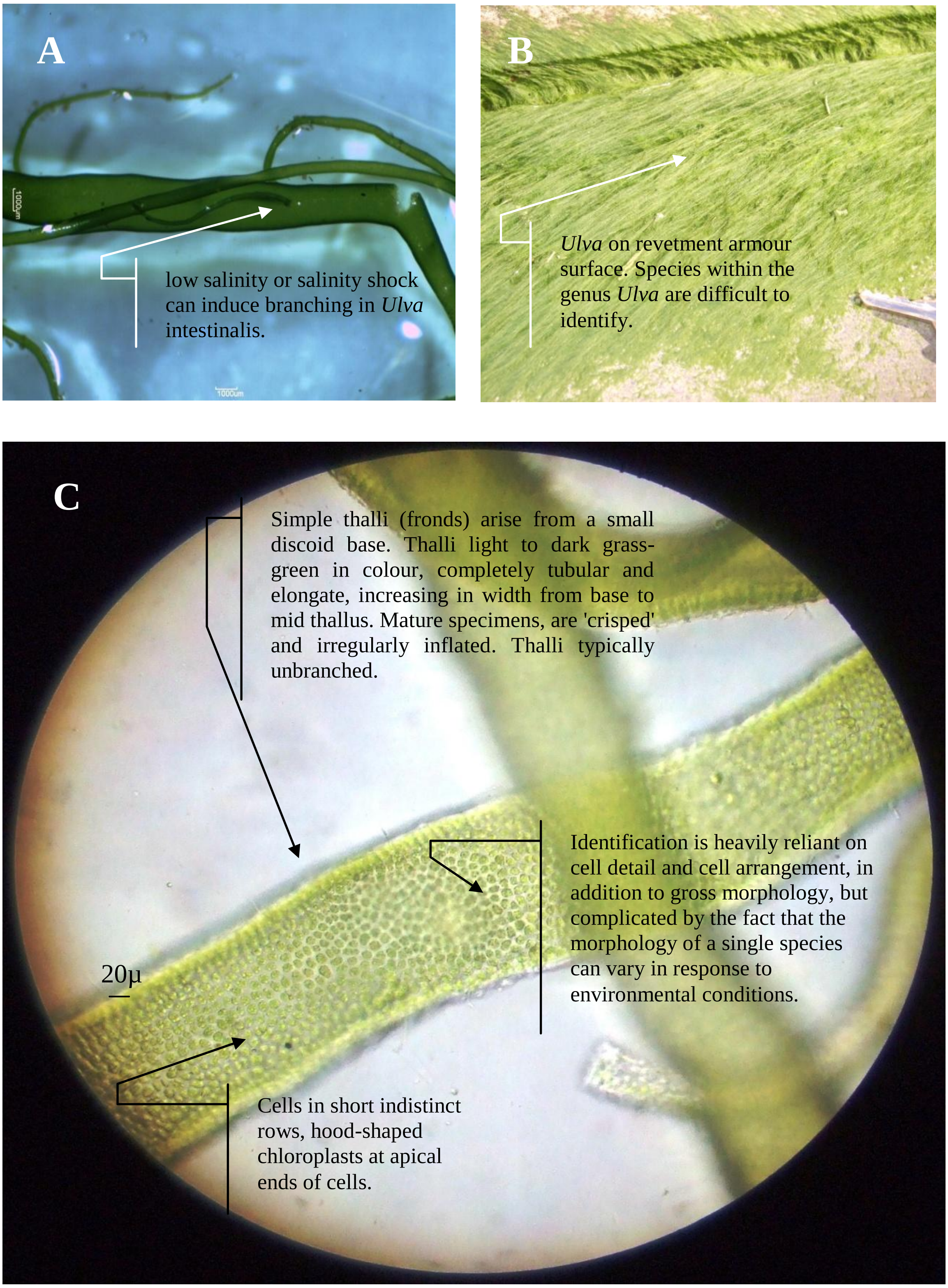
A1.9 *Porphyra umbilicalis*

A1.10 *Dictyota dichotoma*

A1.11 *Gracilaria verrucosa*

A1.12 *Ptilota plumose*

A1.1 *Ulva* – Fylde Coast resident



low salinity or salinity shock can induce branching in *Ulva* intestinalis.

Ulva on revetment armour surface. Species within the genus *Ulva* are difficult to identify.

Simple thalli (fronds) arise from a small discoid base. Thalli light to dark grass-green in colour, completely tubular and elongate, increasing in width from base to mid thallus. Mature specimens, are 'crisped' and irregularly inflated. Thalli typically unbranched.

Identification is heavily reliant on cell detail and cell arrangement, in addition to gross morphology, but complicated by the fact that the morphology of a single species can vary in response to environmental conditions.

Cells in short indistinct rows, hood-shaped chloroplasts at apical ends of cells.

Figure A1.1 *Ulva* common name; Gut weed, sample taken from Blackpool revetment armour May 24th 2010 A. Branched specimen from 53°46’37”N 3°03’27”W 2.8 m above sea level. B. Dense population of typical inflated tubular thalli on Blackpool revetment armour. C. Cells in short indistinct rows, hood-shaped chloroplasts at apical ends of cells.

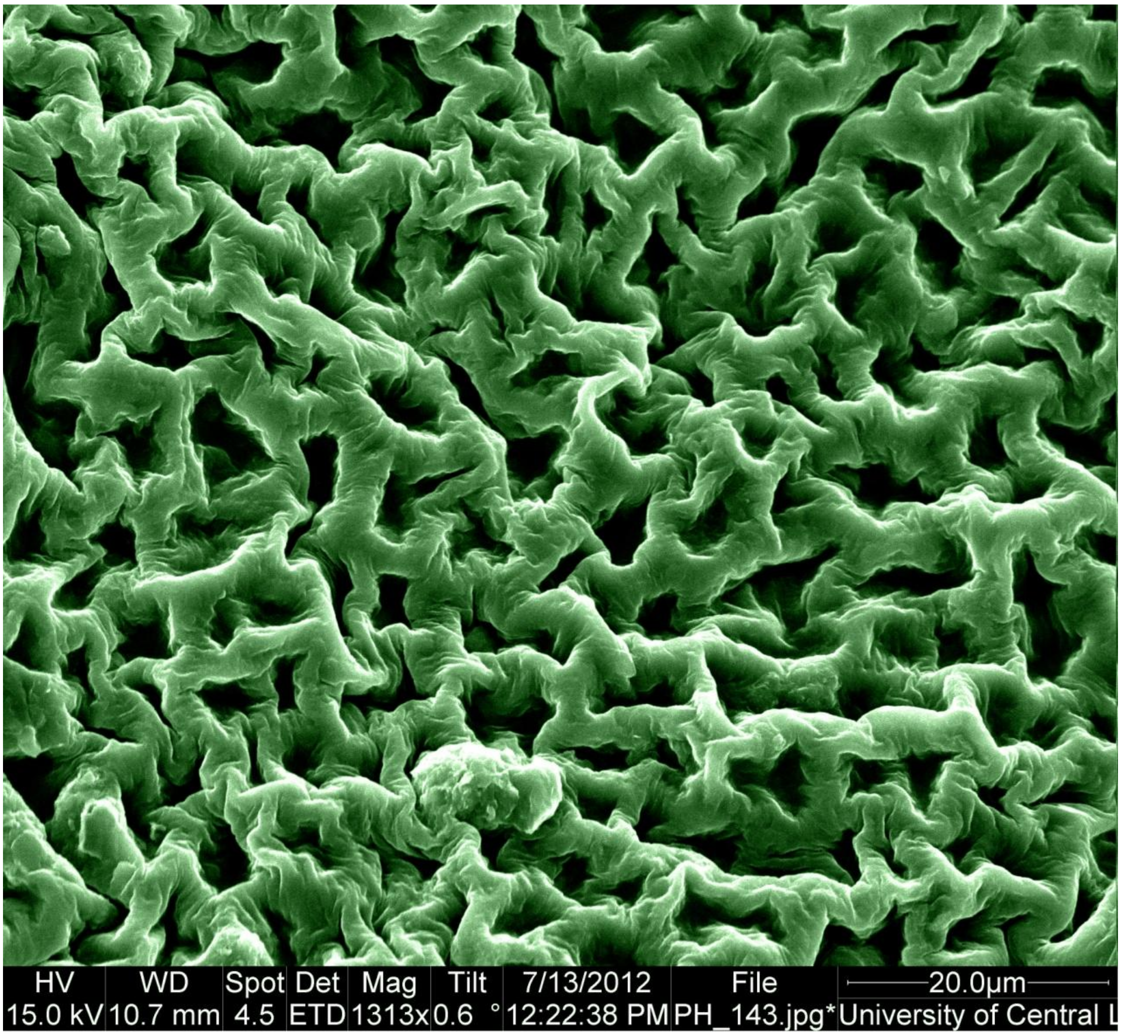


Figure A1.2 SEM (coloured) micrograph showing structured surface of *Ulva* (site sample)

Species within the genus *Ulva* are difficult to identify, see Figure A1.1. Identification is heavily reliant on cell detail and cell arrangement, in addition to gross morphology, see Figure A1.2, but complicated by the fact that the morphology of a single species can vary in response to environmental conditions. The presence or absence of branching fronds of site specimens was useful, see Figure 3.2A, for gross morphological characteristics, distinguishing species. But ambiguity exists because low salinity or salinity shock can induce branching in *Ulva*. However, if environmental factors, such

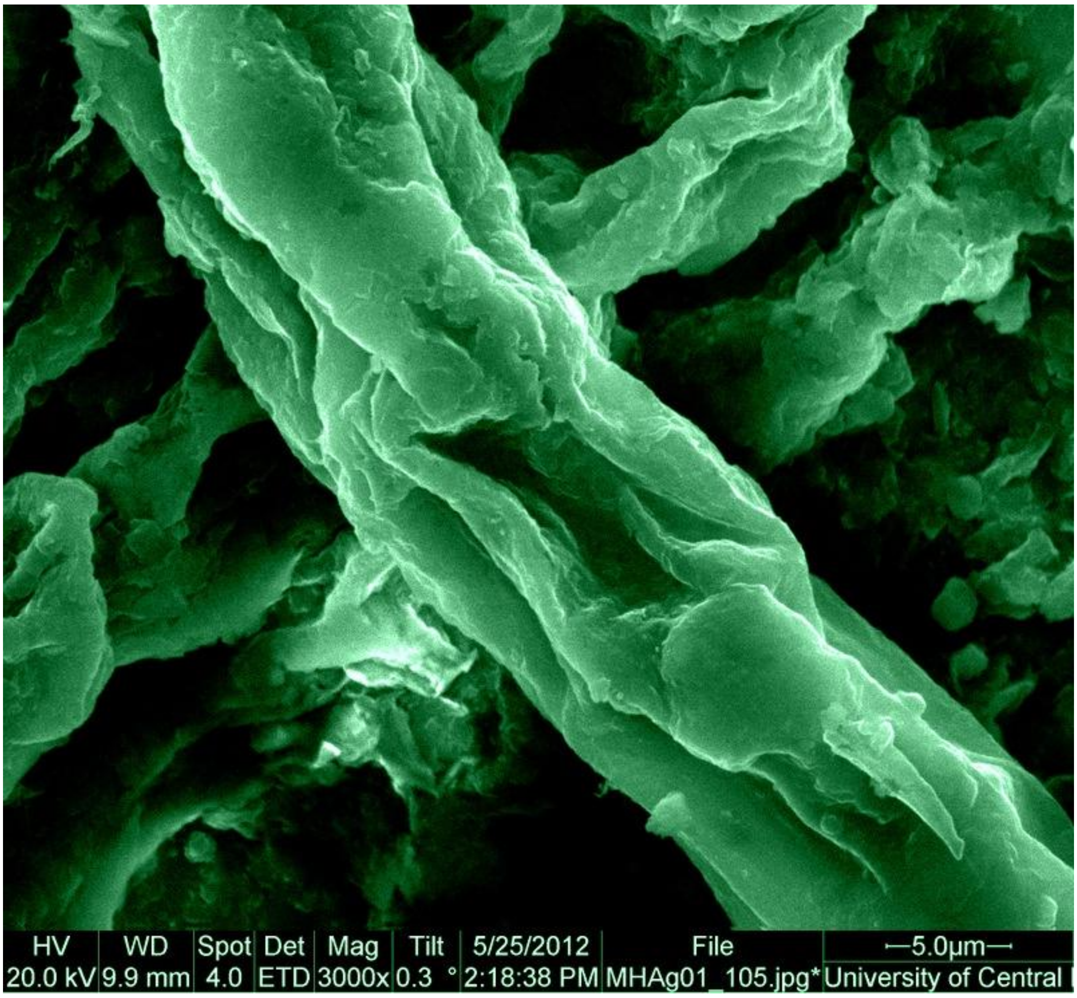


Figure A1.3 SEM (coloured) micrograph showing filament of *Ulva* (site sample)

as salinity is taken into account, branching can be used to identify the great majority of thalli correctly, see Figure A1.3. Thallus typically tubular and inflated, sometimes compressed, unbranched or with few branches towards base, 10-30 cm long and 0.5-6 cm wide, light to dark green, typically rather soft and fragile; cells unordered, or arranged in short longitudinal rows, rounded, 8-20 m in diameter, containing single hood-shaped chloroplast, usually at the apical end of the cell, and one pyrenoid per cell, see figure 3.1C. Reproduction by anisogamous biflagellate gametes, males 6 x 2 m, females 7 x 4 m, and quadriflagellate zoospores 10 x 5 m; male and female gametes can develop without fertilisation into males and females respectively (Brodie, 2007). *Ulva* is generally distributed and very abundant throughout Britain. Widespread in Europe and globally. Plants can be found in reproductive state at all times of the year. Maximum development and reproduction is during the summer months especially towards the northern end of the species distribution. The tubes of this species can open out to form monostromatic sheets in the Baltic Sea, but this morphology has not been noted in Britain, (Brodie, 2007).

A1.2 *Ulva lactuca* – Fylde Coast resident

Figure A1.4 *Ulva lactuca* (Marlin, 2010) common name; sea lettuce. Small green alga up to 30 cm across with a broad, crumpled frond that is tough, translucent and membranous.

A ubiquitous plant, see figure A1.4, found on all but the most exposed rocky shores, and commonly found at the study site. The sea lettuce was found at all levels of the intertidal zone, although in more northerly latitudes and in brackish habitats it is found in the shallow sub littoral zones. It has been observed at the study site that in very sheltered conditions, plants that have become detached from the substrate can continue to grow, forming extensive floating communities. The plant tolerates brackish conditions and can be found on suitable substrata in estuaries (Marlin, 2010). A small green alga (up to 30 cm across) with a broad, crumpled frond that is tough, translucent and membranous. It has been observed attached to the revetment armour concrete, and rocks via a small hold-fast.

- Up to 30 cm across.
- Frond broad and crumpled, that is tough, translucent and membranous.
- Disc like holdfast.
- Green to dark green in colour.

A1.3 *Chorda filum* – Fylde Coast transient

Figure A1.5 *Chorda filum* Brown seaweed with long cord-like fronds, only 5mm thick in diameter.

A transient species at the study site, see figure A1.5, and seen on all coasts of Britain and Ireland, but rarer in south east England. Found in rock pools on the low shore and in the sublittoral down to 5 m. It is most commonly found in sheltered bays attached to stones and shells, often with the holdfast buried in sand. *Chorda filum* is a brown seaweed with long cord-like fronds, only 5 mm thick in diameter. The fronds are hollow, slippery, unbranched and can grow up to 8 m long. The species attaches to the substratum using a small discoid holdfast. It is an annual species, disappearing in winter (Marlin, 2010).

- Frond round in section, cord-like and unbranched.
- Attached by a tiny disc-like holdfast.
- Slimy texture.
- Colourless short hairs on frond in summer.

Other common names include mermaid's tresses and cat gut.

A1.4 ***Laminaria saccharina* –** Fylde Coast resident

Figure A1.6 Study site specimen of *Laminaria saccharina*

Can grow up to 2 or 3 meters long at the study site, growing at the low tides level *Laminaria saccharina* is a brown algae which has the characteristic of emerging only at spring tides, see figure A1.6. Its name of "saccharina" stems from the sugars which crystallize on the surface of the algae as it dries up. *Laminaria saccharina* has nutritional properties close to that of *Laminaria digitata* but it differs by its thicker structure and by its organoleptic characteristics (slightly sweet taste). Up to 2 or 3 meters long it grows at the low tides level and is collected from March to June. Thallus up to 4 m long, attached to the revetment armour concrete and rock by strong terete stipe and haptera. Long leathery blade, unbranched and without a midrib about 15 cms wide, flat but wrinkly with wavy margins (Marlin, 2010). Common name: Sea belt.

A1.5 *Halidrys siliquosa* – Fylde Coast transient

Figure A1.7 *Halidrys siliquosa*; common name, sea oak A large sturdy brown algae 0.3 -1 m in length at the study site (occasionally up to 2 m) rising from a strong, flattened cone shaped holdfast

Widely distributed and fairly common at the study site and in Britain and Ireland, see figure A1.7. A distinctive and common rock pool seaweed from the middle to lower shore (may be found in upper eulittoral but only in rock pools). It may also form a zone in the sublittoral below the lower limit of *Laminaria digitata*. It often supports a range of invertebrate epifauna such as bryozoans, hydroids and ascidians and epiflora such as small red algae, *Ulva sp*. and other fucoids. A large sturdy brown alga 0.3 -1 m in length (occasionally up to 2 m) rising from a strong, flattened cone shaped holdfast. The main stem is flattened and branches alternately to give a distinctly zigzag appearance. The stem bears a few, flattened ribbon-like 'leafy' fronds. The ends of some branches bear characteristic pod-shaped air bladders (about 0.5 cm wide by 1-4 cm long) that are divided by transverse septa into 10 or 12 compartments. The branches also bear reproductive bodies that appear similar to the bladders but lack the septa. Young plants are olive-green in colour while older specimens are dark brown and leathery. This species is perennial, (Marlin, 2010).

- Flattened cone shaped holdfast.
- Regularly alternately branched.
- Main stem 'zigzag' in appearance.
- Presence of terminal pod-shaped air bladders, resembling seed pods, divided by septa into 10 or 12 compartments.

A1.6 *Fucus spiralus* – Fylde Coast resident

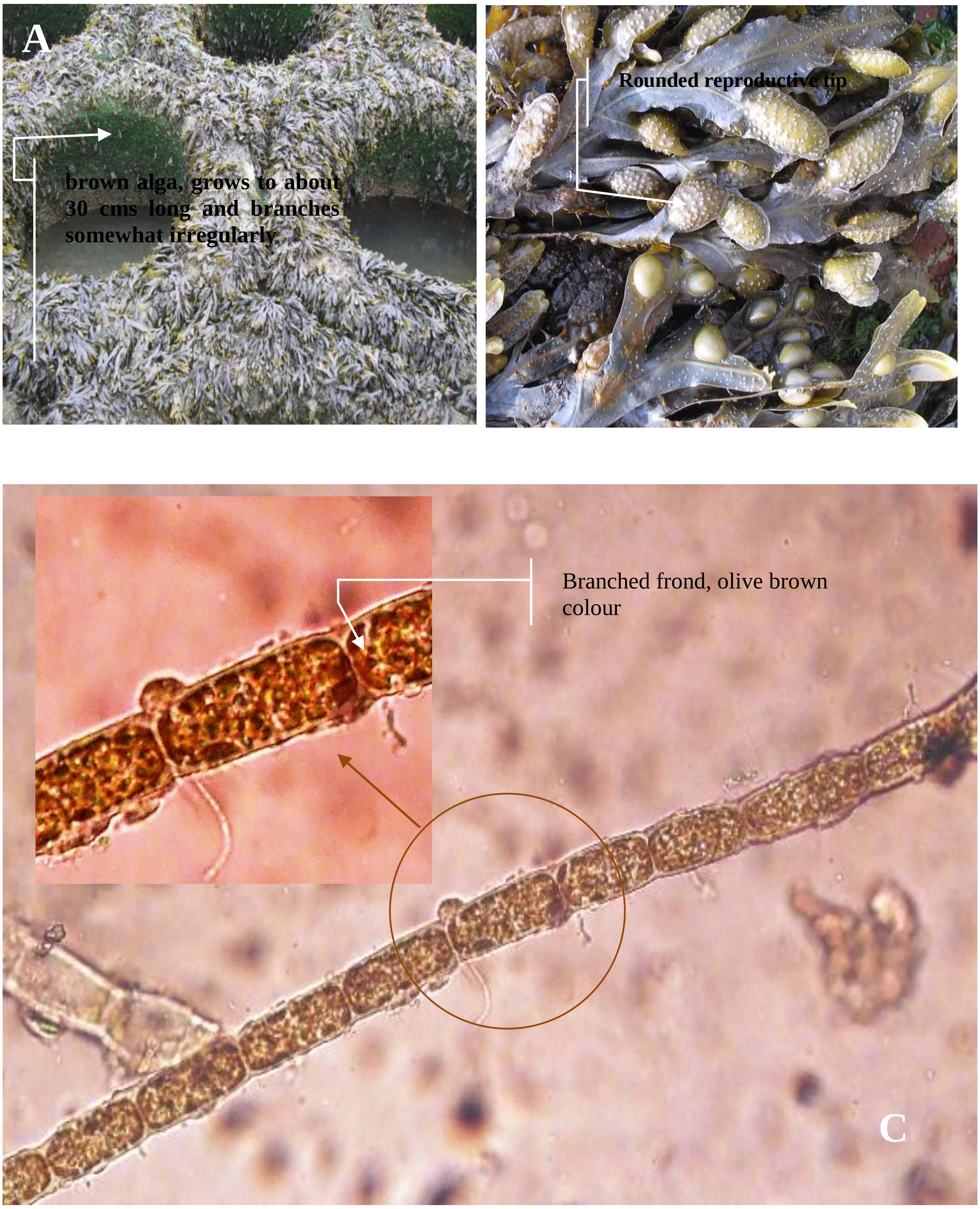


Figure A1.8 *Fucus spiralus* Common name Spiral Wrack, In-situ specimen from Blackpool seabee sea wall, south shore, 53°46’37”N 3°03’27”W 1.8m above sea level. Dense population of typical inflated tubular thalli specimen from Blackpool (May 2010).

Fucus spiralus is a brown alga, a primary resident of the Fylde coast, growing to about 30 cms long and branches somewhat irregularly, dichotomous and is attached, generally to the revetment armour concrete and rock, by a discoid holdfast, see figure 3.9. The flattened blade has a distinct mid-rib and is usually spirally twisted without a serrated edge. In lacking bladders or serrations, Flat Wrack is one of the more tricky wracks to identify. The tendency of its fronds to twist is a useful clue, but this characteristic is far from constant, and its reproductive bodies will have to be examined to confirm identification. A key feature is the prominent midrib on the flat, spiralling frond (Gibson, 2008). A perennial which favours sheltered to moderately exposed rocky shore habitats, at mid–to upper–shore levels; it may also penetrate estuaries. It may grow to 40cm in length, with a reproduction period from July to September. Similar species include *Fucus ceranoides*, which does not spiral and has more regular branching, with often rather pointed reproductive bodies. Also *Fucus virsoides*, which has fan-like branching, more spherical reproductive bodies and is restricted to the Mediterranean (Gibson, 2008).

A1.7 *Ascophyllum nodosum* –Fylde Coast resident

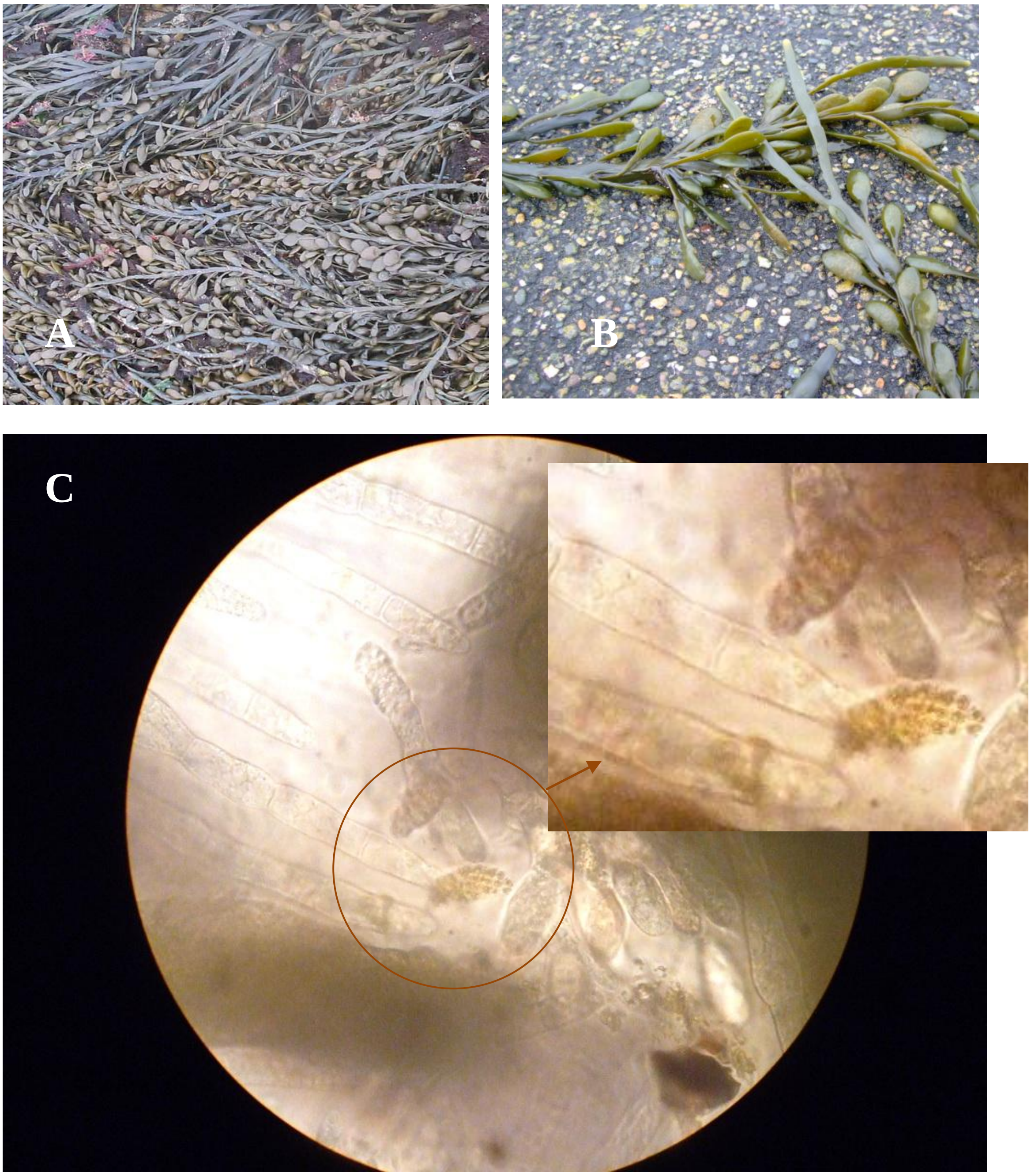


Figure A1.9 *Ascophyllum nodosum* A. Site specimens from Blackpool seabee sea wall, south shore, 53°46’37”N 3°03’27”W 1.8m above sea level. B. Dense population of typical inflated tubular thalli at Blackpool (May 2010). C. Cells in short indistinct rows, hood-shaped chloroplasts at apical ends of cells; specimen taken from Langstone Harbour June 2010.

The species attaches to rocks and boulders on the middle shore in a range of habitats, from estuaries to relatively exposed coasts, see figure A1.9. It occupies a similar shore height as *Fucus vesiculosus*. Subtidal populations have been reported, for example in the very clear waters of Rhode Island, USA. However, an intertidal habit is more usual. A common large brown seaweed, dominant on sheltered rocky shores. The species has long strap like fronds with large egg-shaped air bladders at regular intervals. The fronds of *Ascophyllum nodosum* are typically between 0.5 m and 2 m in length. The species often bears tufts of the small reddish-brown filamentous epiphytic algae *Polysiphonia lanosa*. *Ascophyllum nodosum* occurs on the middle of the shore, often with *Fucus vesiculosus*. The species grows slowly and plants can live to be several decades old. Individual fronds can become up to 15 years old before breakage (Marlin, 2010).

- Frond narrow without midrib.
- Large swollen egg shaped air bladders at intervals along middle of the frond.
- Reproductive bodies rounded on short stalks.
- Dichotomously branched.

Ascophyllum nodosum is found on very sheltered shores, in sea lochs and is sometimes common on the west coasts of Ireland and Scotland. The frond has extensive dichotomous branching and bears few air bladders. The plants drift in large, spherical masses in sheltered waters. *Ascophyllum nodosum*, which is abundant in New Hampshire (U.S.A.), is often associated with the marsh grass *Spartina alterniflora*. If branching is both 'apical and lateral' the algae would be designated as mackaii while if it is 'almost entirely lateral' it would be designated as scorpioides. Unattached forms arise when detached fragments of *Ascophyllum nodosum* are deposited onto the shore where they continue to multiply and branch independently of the original fragment (Marlin, 2010).

A1.8 *Fucus vesiculosus Linnaeus* – Fylde Coast resident

Figure A1.10 *Fucus vesiculosus* Linnaeus Branched specimen from 53°46’37”N 3°03’27”W 2.8m above sea level.

A mid-shore wrack easily recognised by its paired bladders occurring on either side of a prominent midrib, see Figure A1.11. The frond is generally not strongly spiralled and the receptacles do not have a sterile rim as *(Fucus spiralis)*, and the frond does not have a serrated margin as *(Fucus serratus)*. *Fucus vesiculosus* is attached by a small, strongly attached disc which gives rise to a short stipe. The reproductive receptacles are swollen area at the tips of fronds that have many flask-shaped cavities called conceptacles. These house the male and female reproductive structures known as antheridia (borne on antheridiophores) and oogonia (containing 8 eggs). The eggs and sperm are liberated onto the surface of the receptacles and a pheromone (sex-attracting substance) is released by the eggs that attracts the sperm. Fertilization results in a zygote that forms a new Fucus adult (Guiry, 2008).

A1.9 *Porphyra umbilicalis* – Fylde Coast resident

Figure A1.12 *Porphyra umbilicalis* A. small red alga (up to 20 cm across) with an irregularly shaped, broad frond that is membranous but tough.

Also known as Purple laver, Figure 2.12 is highly adaptable to conditions on different parts of the rocky shore and able to withstand prolonged periods of exposure to the air as well as tolerating a greater degree of wave action than most other red algae. It occurs singly or in dense colonies throughout the intertidal but most frequently at upper levels.

A small red alga (up to 20 cm across) with an irregularly shaped, broad frond that is membranous but tough. The plant attaches to rock via a minute discoid hold-fast, is greenish when young becoming purplish-red and has a polythene-like texture (Marlin, 2010).

- A small red seaweed, up to 20 cm across
- Tough irregularly shaped broad frond.
- Small disc-like holdfast.
- Greenish when young becoming purplish-red.
- Has a polythene-like texture

Also known as sloke, the plant is boiled and eaten as a jelly in South Wales. Used to make laver bread a famous dish in south Wales and reportedly eaten cold with vinegar in Cornwall.

A1.10 Dictyota dichotoma – Fylde Coast transient

Figure A1.13 *Dictyota dichotoma* Habitat: pools from mid-tide and below. Distribution: Widely distributed and common. Dense population key characteristics**:** Absence of midrib, ± regular branching, and reproductive structures scattered, sample from Fleetwood 2010.

This is very common on beaches at the study site, Figure A1.13, a brown algae, thallus flat with fairly regular dichotomous branches with parallel sides to 30 cms long, the tips usually bifid. Outer layer of small cells enclosing a single layer of large cells no more than one cell thick even near the base. Branches 3 to 12 mm wide, membranous without a mid-rib. Thallus flat and leaf-like, to 300 mm long (usually 100-150 mm) and 5-30 mm broad; fronds thin and translucent, olive to yellow-brown, occasionally with a bluish iridescent, and ± regularly dichotomously forked, but lacking a midrib, and the reproductive structures are scattered over the fronds. Very variable, with narrow spirally twisted plants being found in mid-tidal pools, broader less twisted and more regularly branched plants being found in lower tidal pools, and broader very regularly branched, less twisted plants in the subtidal. Often growing epiphytically (Guiry, 2008). It is likely that more than one species is represented in Britain and Ireland.

A1.11 ***Gracilaria verrucosa* –** Fylde Coast transient

Figure A1.14 *Gracilaria verrucosa* Specimen branches 0.5-2 mm diameter, repeatedly dividing.

The plants, seen in Figure A1.14, are often bushy, with age often becoming free, texture firmly fleshy, colour dull purplish, greyish or greenish translucent, branches 0.5-2 mm diameter, repeatedly dividing, alternately or occasionally dichotomously branched with numerous lateral proliferations, terete throughout, tapering to the ultimate branchlets, cells of the medulla 300-450 micron diameter, with thin walls (Marlin, 2010).

A1.12 ***Ptilota plumose* –** Fylde Coast transient

Figure A1.15 *Ptilota plumose* Red Algae, *flat thallus*.

These red Algae, seen in Figure A1.15, showing a flat thallus, narrow-linear, bushy, bright red, densely pinnately branched in one plane. Litophyte and sublittoral down to 25m depth, in exposed localities, often among Laminariales.

Appendix 2

Additional documentation to Chapter 2

Review

A2-1 Background information on a self cleaning concrete jetty at Staffa Island, Inner Hebrides, Scotland, United Kingdom.

A2.1 Self-cleaning concrete; naturally

The self cleaning concrete jetty at Staffa is a unique example of coastal engineering sustainability in practice (Figure A2.1). The remarkable and innovative research (Clokie, 2008) using nature for self cleaning concrete, still working today (Figure A2.2) will be briefly summarised. When the landing jetty at Staffa (West Scotland, U.K.) was replaced the opportunity was taken to seek to mimic on it the mature overgrazed, in part sessile animal dominated, facies in the locality. In such facies, algal settlement and production is equalled or exceeded by consumption by herbivores, mainly limpets. Surfaces which are largely free of algae tend to be less slippery and dangerous. Since construction 20 years ago, circa 1 million visitors have used the jetty and it is functioning as was intended. Design features were added at emplacement and post emplacement phases within the whole tide range, e.g. roosting areas for limpets (small trenches), the structure being of unreinforced concrete cast within permanent steel facing. The aim was to obtain the best compromise between maintaining the integrity of the concrete and having the sought after effect on algal communities. Different levels of the shore presented different problems within the complicated micro-structured series of ecotones and gradients within the tide range. In the early years some biological interventions and transplanting of herbivores was performed. On the smallest scale, littorinid activity in older communities seems relatively more important than the literature suggests in augmenting patellid activity. Maintaining overgrazed facies relied on the boatmen users not using biocides when algal production was temporarily ahead of removal. They also took a great deal of care with the surface. This approach may have wider application wherever intertidal slipperyness is a problem whether of structures or armouring. Each situation will necessitate design for its own habitat.

Figure A2.1 Staffa jetty June 1992, colonised path.

Figure A2.2 Staffa October 1993, hazard free walkway.

Appendix 3

Additional documentation to Chapter 3

Surface Analysis

A3-1 Copies of original published papers (2) specific to this Chapter:

1 - Hughes, P. 2013. The effects of power washing on concrete durability. *Maritime Engineering (ICE).* Accepted manuscript no. MAEN-2011-45.

2 – Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton, LHG., Robery, P., Cunningham, L. 2013A. Innovative method used to evaluate the effect of power washing on marine concrete – a UK site study. *Insight – Journal of The British Institute of Non-Destructive Testing.* Accepted manuscript no. ID INSI-03-2013-OA-0033.

A3-2 Original published articles (2) specific to this Chapter:

1 - Hughes, P. 2011. Innovative NDT method used in surface analysis.
Concrete, inc. Concrete Engineering International. 08, Vol. 45, 42 - 44.

2 - Hughes, P. 2013E. Innovative method used to evaluate the effect of power washing on marine concrete – a UK site study.
Concrete Repair Bulletin; International Concrete Repair Institute.
July/August, accepted manuscript.

A3-3 Concrete mix design.

A3-4 Surface roughness data.

A3-5 Interferomter data.

Maritime Engineering
Volume 000 Issue MA000

Briefing: The effects of power washing on concrete durability
Hughes

ice | proceedings

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Briefing: The effects of power washing on concrete durability

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The cleaning of concrete is often undertaken on health and safety grounds, especially in a marine environment when controlling algal biofouling on stepped sea defences. Despite the fact that more local authorities are doing this, there is no published research or guidance on possible durability issues when exposing a marine concrete to regular power washing regimes. Surface analysis of concrete revetment armour at a UK study site was undertaken in order to investigate the effects of power washing over 3 years on durability. Revetment armour units were monitored from casting to placing on site and surface roughness was found to have doubled. Surface hardness and uniformity have also been measured indicating degradation. When casting revetment units upside down, vibration may encourage the larger aggregate to migrate downwards towards the exposed surface once inverted at the site. Large aggregate particles at the surface leave no surface zone giving no erosion protection. It is at the top surface where the strongest, most impermeable and most wear-resistant concrete is needed. Continual water jet cleaning practices lead to a higher surface roughness, thereby increasing the surface area offering a bioreceptive surface for further, quicker and denser colonisation; these phenomena provoke and encourage each other.

1. Introduction

The cleaning of concrete is often undertaken on health and safety grounds, especially in a marine environment in order to control algal biofouling on stepped sea defences. The action of the concrete cleaning methods, both physical (water jet) and chemical (chlorine-based disinfectant), on concrete sea defences can alter their properties and may alter the susceptibility of the concrete surface to algal colonisation. The communities of algae at the study site often form uniform green microbial lawns extending over large areas, several 1 metres wide and 3/4 mm thick in some places, and localised at the surface of the concrete.

Bioreceptivity, which refers to the susceptibility of a material to be colonised by living organisms, for a material such as concrete, relates to the surface roughness, moisture content, structure and texture of the material. Materials such as concrete, which have high surface roughness and high macroporosity, show high bioreceptivity (Guillitte *et al.*, 1995). Concrete can be modelled to consist of cement paste, pore water, aggregate particles and reinforcements such as fibres. Interfaces between these phases largely affect the mechanical properties and the behaviour of concrete under load. Generally, the interface between cement and aggregate is the weak link in the concrete, and these interfaces may determine the response of the material to water jet impingement.

2. Method

In the present study the removal of algae from the surface of concrete revetment armour units at a study site was investigated in terms of how the units are influenced by certain physical parameters of the concrete, including surface roughness, surface hardness, consolidation and uniformity. The aim of the study was to investigate the quality of the concrete in the structure and how the management of biofouling on marine concrete sea defences may accelerate wear and encourage further colonisation by algae, thus having long-term implications on the concrete durability.

Whereas good quality concrete shows excellent resistance to a steady flow of clear water, nonlinear flow at velocities exceeding 12 m/s (7 m/s in closed conduits) may cause severe damage to the concrete (Mehta and Monteiro, 2006) Early industrial 2 cleaning using water jet technology goes back to the 1920s in the steel industry. In the late 1950s, as reliable high-pressure pumps were developed, the water jet revolutionised sewer and pipe cleaning. Reviews about early cases of water jet utilisation for material removal, namely for soil removal and hydraulic mining, are provided by Summers (1991). Today, commercialised water jetting is used in many applications including the cleaning of concrete, stone and masonry, cement kilns and autoclave vessels, chemical pipes, sewers and ships hulls.

Published guidance (Higgins, 1983) recommends the removal of algae from concrete by power washing at velocities of

3 between 50 and 150 bar (5 to 15 MPa) (Figure 1) Water jet applications can be distinguished (WJTA, 1999) according to the level of the applied operational pressure. Pressure cleaning is defined as the use of pressurised water, with or without the addition of other liquids or solid particles, to remove unwanted matter from various surfaces, where the pump pressure is below 340 bar (34 MPa). This is the category of pressure that is applied to clean many marine structures including jetties and steps to combat biofouling and to reduce slip hazard, and it was used at the study site. Further guidance (Concrete Masonry Association of Australia, 2000) concerning high-pressure water jet cleaning and maintenance management advises the incorporation of hot water and a 15° fan nozzle at an appropriate distance (at least 150 mm) from the surface and at an appropriate pressure. In general, the higher the water pressure, the more effective the cleaning and the greater the potential damage to the surface. Research by Campbell and
4 Fairfield (2008) quantified the erosion of concrete, focusing on British civil engineering practice and a range of pressures and flow rates covering those used in the routine cleaning and maintenance of drains and sewers. Damage from jetting tests was measured. Volumetric erosion rates at 4000 psi (27·6 MPa) on concrete were 6·90 mm^3/s. The concrete showed more volumetric erosion than clay because of its greater surface roughness. The asperities and pits making up the surface profile were more prominent in the concrete, and as such were more exposed to attack by the jet. The particle size, or effective grain diameter, was greater in the concrete pipe. When material was removed by brittle fracture it tended to be in bigger pieces than those removed in the finer grained clay pipe. Given the similarities in water absorption and initial porosity these parameters cannot be held accountable for the difference in erosion rates under high-pressure water jetting. Further exploration of the effects of surface roughness upon erosion rate is needed.

Figure 1. Revetment armour surface after 2 years exposure (Fujifilm Finepix JX). As the surface zone is eroded, fibres at the surface 'pop out', dry, crack, and are washed away exposing new voids for micro-organisms

The properties of the concrete in the surface zone are strongly affected by the finishing operations, and are greatly influenced by curing (Neville, 2006). Up to now, little is known of the extent of the damage caused by water pressure used for the cleaning of concrete surfaces, despite extensive research and guidance on marine concrete surfaces (CIRIA, 2010. Deterioration of concrete structures usually starts at the surface and progresses into the structure; therefore the skin of the concrete is an important factor in the longevity of the material.

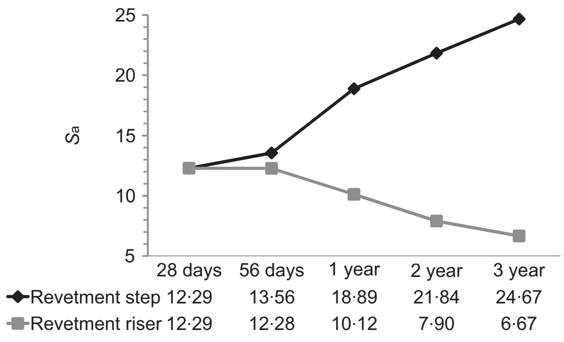
The use of vibration in the production of the precast units may allow separation of coarse aggregate towards the bottom of the form. Such concrete may be susceptible to erosion from water jet cleaning practices. As the revetment units are cast upside down, this phenomenon is of particular relevance.

Extensive studies addressing wear mechanisms are presented by Momber (1997), who observed the general behaviour of concrete during failure and investigated the influence of water velocity and exposure time. The results show that the interface between hardened cement paste and aggregate grains plays the main role in the fracture process. This range is also defined as a micro-crack region (Schneider and Herbst, 1989) and describes the influence of the interfaces between the cement paste and aggregate grains. As Morin (2011) has shown, this zone is characterised by a high degree of micro-porosity and reduced strength properties, and can be described as the 'weakest link' in concrete with respect to strength. It is expected that these interfacial zones play important roles during water flow from power washing, thereby accelerating concrete surface erosion.

3. Results

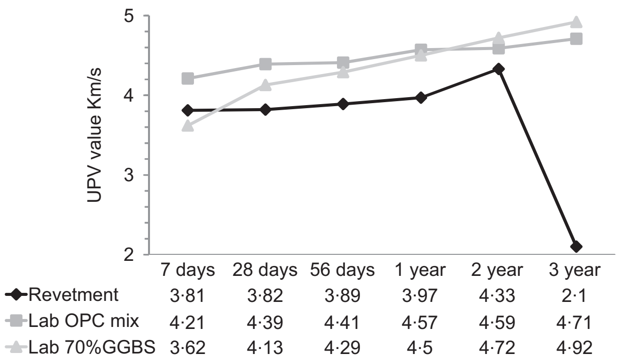
Experience from the site has shown that more cleaning leads to a rougher surface, in turn leading to more rapid colonisation. The primary role of the revetment armour is coastal protection and as such it is subject to the wear associated with tidal and wave action; hence the design team and client expect a degree of surface deterioration.

To analyse the surface of the revetment units and to determine
any change in topography surface roughness provides a means 5
of qualitatively recording any change in the cleaned areas as 6
opposed to the uncleaned (Figure 2) The horizontal steps were 7
cleaned and the vertical risers were not. The surface roughness
on the revetment steps doubled from S_{a} 12·29 to S_{a} 24·67 in 8
3 years. These steps were power washed on approximately



	28 days	56 days	1 year	2 year	3 year
◆ Revetment step	12·29	13·56	18·89	21·84	24·67
■ Revetment riser	12·29	12·28	10·12	7·90	6·67

Figure 2. Surface roughness of revetment armour step, which is power washed and the revetment unit riser which is not power washed



	7 days	28 days	56 days	1 year	2 year	3 year
◆ Revetment	3·81	3·82	3·89	3·97	4·33	2·1
■ Lab OPC mix	4·21	4·39	4·41	4·57	4·59	4·71
▲ Lab 70%GGBS	3·62	4·13	4·29	4·5	4·72	4·92

Figure 3. Ultrasonic pulse velocity results over study period

150 occasions at 1200 psi. The risers of the steps were not power washed and obviously were subject to the same tidal impacts, but showed a smooth erosion pattern with values from S_a 12·29 reducing to S_a 6·67.

3.1 Surface hardness

Hammer readings from casting to 2 years remain at approxi-
9 mately 30*r* [correlating to 30 N/mm^2 (concrete strength)] but in
year three a large reduction to 17*r* was recorded.

3.2 Ultrasonic pulse velocity

Readings were taken on 10 surface dry units, with ambient temperatures from 7 to 21℃. Semi-direct paths were chosen, giving a satisfactory angle of 45°. Ultrasonic pulse velocity (UPV) values remained steady for 2 years at 3·81–4·33 km/s
and then reduced substantially in the third year to 2·1 km/s
10 (Figure 3) These results indicate the concrete had initially
shown a good quality but it was reduced to a very poor quality. The difference in UPV compared with the ordinary Portland cement control mix may be due to the fact that the density in the revetment armour mix has been altered by the presence of fibres, the velocity changing as it encounters each fibre. Variability in UPV at 7 days from a mean of 10 readings gave 3·81 km/s, the standard deviation (σ) 0·43 gave a variation of 0·18, and hence a confidence limit at 95 ± 0·26% in agreement with the literature.

4. Discussion

As concrete stepped revetment armour designs that allow beach access become more common, the need to keep such surfaces free of marine biofouling by way of water jet cleaning practices, adds to the long list of degradation mechanisms. The risers of the steps, which were not power washed, were subject to the same tidal impacts, but showed a smooth erosion pattern. The different wave absorption and reflection characteristics of a vertical plane (the riser of the step) and the horizontal plane may cause differential wear and should be considered.

In these conditions it is essential that the concrete should be durable with the lowest practicable permeability. The surface of the concrete is the front line in the defence from such an aggressive environment, whether natural or man-made. Information about pulse velocities in the revetment armour has enabled the variations in concrete quality to be assessed, and areas of poorer quality concrete to be identified. As the revetment units are subject to a 6 h tidal window consideration must be given to seawater within the units, as moisture, which is normally present in the concrete will encourage a 5% higher reading. The plot of pulse velocity contours (Figure 3) has given a clear picture of variations and the measurement of UPV over 3 years has shown that a more detailed examination is necessary.

5. Conclusions

- The concrete revetment unit surface has been affected by regular power washing. The surface roughness of the horizontal steps doubled over a 3 year period following regular high-pressure washing, whereas the vertical risers became smoother over the same period.
- The quality of the precast concrete surface has altered. The surface hardness (*r*) values remained steady for 2 years and then reduced substantially in the third year of the study.
- The reduction in UPV is significant suggesting that the core of the concrete may have been affected by the weakening process.

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Innovative method used to evaluate the effect of power washing on marine concrete – a UK site study

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At a study site on the north west coast of England, concrete revetment armour that has been power washed on a regular basis has been monitored for surface changes over three years. Three tests have been utilised. Replication was employed as a means of measuring surface roughness of the concrete surfaces and lays the foundation for the development of a new non-destructive testing (NDT) method for concrete surface analysis. Surface roughness doubled from S_a *12.29 µm, increasing to* S_a *24.67 µm in three years. A Schmidt/rebound hammer test has also been used throughout the research to evaluate the surface hardness of the concrete, and has demonstrated a significant deterioration in the concrete surface after three years. Ultrasonic pulse velocity (UPV) testing, used to measure the sound velocity of the concrete, has also implied degradation.*

1. Introduction

This paper reports early findings from an on-going study into the effects of power washing on concrete. At a study site on the north west coast of England, concrete revetment armour has been monitored for any surface changes over three years. Power washing is becoming more commonly used by maintenance teams throughout the world. However, the often inappropriate use at high pressures can have a damaging effect on many material surfaces, leading to a reduction in long-term durability[1].

Visual inspections, which are an essential precursor to any intended non-destructive tests, have been extensively adopted throughout this research over the lifetime of the project, some seven years. Deterioration to concrete structures usually starts at the surface and progresses into the structure. In order to study the effect of aggressive cleaning practices and its implications, the surface roughness of revetment armour needed to be measured over time. Replication was employed as a means of inspecting the concrete surfaces and lays the foundation for the development of a new NDT method for concrete surface analysis. The technique produces an exact copy on site of the surface, which is peeled away after curing and examined microscopically in the laboratory. Schmidt/rebound hammer tests have also been used throughout to evaluate the surface hardness of the concrete and UPV testing was used to measure the sound velocity.

Water jet applications can be distinguished according to the level of the applied operational pressure. Power washing can be defined as the use of pressurised water, with or without the addition of other liquids or solid particles, to remove unwanted matter from various surfaces, where the pump pressure is below 5000 psi[2]. It is this category of pressure that is applied to clean many marine structures, jetties and steps to combat biofouling, reducing the slip hazard. A modest 1200 psi is used at the UK study site. Further guidance concerning high-pressure water jet cleaning and maintenance management incorporates using hot water and a 15° fan nozzle at an appropriate distance (at least 150 mm) from the surface and at an appropriate pressure[3]. In general, the higher the water pressure, the more effective the cleaning and the greater the potential damage to the concrete surface.

Annual power washing can start a devastating vicious cycle[4]. The frequency of cleaning and the cleaning method used (especially high-pressure cleaning) could have an influence on concrete deterioration[5]. While good quality concrete shows excellent resistance to a steady flow of clear water, a non-linear flow at velocities exceeding 12 m/s (7 m/s in closed conduits) may cause severe damage to concrete[6]. The water exits the nozzle at both a high pressure and a high velocity. The resulting momentum is great enough to dislodge not only dirt and debris but also to create flakes, popouts and even concrete spalls[4]. Early industrial cleaning using water jet technology dates back to the 1920s in the steel industry. In the late 1950s, as reliable high-pressure pumps were developed, the water jet revolutionised sewer and pipe cleaning. Reviews about early cases of water jet utilisation for material removal, namely for soil removal and hydraulic mining, are provided elsewhere[7]. Today, commercialised water jetting covers many cleaning applications: concrete, stone and masonry, cement kiln and autoclave vessels, chemical pipes, sewers and ships' hulls. Dated UK published guidance tackles the removal of algae from concrete, recommending power washing at velocities of between 725-2175 psi[8]. Research has quantified the erosion of concrete, focusing on British civil engineering practice, with a range of pressures and flow rates covering that used in the routine cleaning and maintenance of drains and sewers[9]. Damage from jetting tests was measured and volumetric erosion rates reported at 4000 psi on concrete were 6.90 $mm^3\ s^{-1}$.

The expensive, time-consuming cleaning of concrete is often undertaken on health and safety grounds, especially in a marine environment, controlling algal biofouling on stepped sea defences. The action of concrete cleaning methods, both physical and chemical, on concrete sea defences can alter their properties and may alter the susceptibility of the concrete surface to algal colonisation[10].

No standard method for measuring surface roughness of concrete has been adopted. A range of NDT methods are available and are in use for measuring the surface texture of concrete floors, but no method is accepted as standard and different organisations use different methods. Holt[11] carried out a review of the main methods. The interest in measuring the surface texture of floors stems from its effect on skid resistance. Wambold[12] used the mean texture depth as a measure of surface roughness. Silfwerbrand[13] suggested a

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different method of quantifying the surface roughness in his study on the effect of roughness on the bonds of repair materials.

The aim of this study was to investigate the effects of daily power washing on concrete and to discuss its implications. To achieve this aim, surface roughness, hardness and uniformity were measured over three years.

Consequently, a limitation to this case study is that it involves only a single site and, therefore, may not be representative of marine environments in general, and also to the design and materials used in the construction of the structures themselves may influence this process.

2. Methodology

Revetment armour concrete

The armour units contain micro and macro synthetic fibres. The compressive strength class was C35/45, BS8500-1 exposure class was XS3, XF4, XC3, XC4 and the water/cement ratio was 0.45. The minimum cement content was 340 kg/m^3, CEMIIIA, with 50% ground granulated blast furnace slag and a chloride class of 0.2, the maximum chloride content of the concrete, 0.20% by mass of cement. 10 pre-cast revetment armour units were monitored from casting to placing on site, and consequently five years' exposure, and comparisons were made to the rear of sheltered 'wave-wall' elements.

Exposure conditions

The fully-exposed concrete pre-cast units face westwards into the prevailing wind and were subject to cyclic wetting and drying conditions. The concrete is exposed to harsh wave action, which was exacerbated by sand and occasionally shingle and debris from the beach. The stepped revetment armour is constantly colonised by algae, Ulva, creating a slip hazard to the public.

Surface roughness

To analyse the surface of the revetment armour units, and to determine any change in topography, surface roughness was a means of quantitatively recording any change in cleaned areas as opposed to uncleaned. In this research, the surface roughness geometry of concrete is described with profilometry analysis. The three-dimensional (S_a) surface roughness parameter used for characterisation is a measurement of surface finish; it is topography at a scale that might be considered 'texture' on the surface. The qualitative approach has the advantage of avoiding profilometry relocation techniques.

It is suggested[14], if taking rebound numbers, that where the total number of readings (n) taken at a location is not less than ten, the accuracy of the reading is likely to be within ±15/√n% with 95% confidence. This theory has been applied to the S_a measurement.

White light interferometry

Light from a common monochromatic source is reflected by a beam-splitting device from the observed surface and from a standard plane reference surface (Omniscan MicroXAM 5000B, 3D ADE phase shift interface contrast optical profiler). The combination of these two beams gives rise to a pattern of interference fringes, which are in effect contour lines that indicate the profile of the surface[15]. Such instruments give a good representation of the surface texture and are self-calibrating, since it is known that the vertical distance between adjacent fringes represents one-half of the wavelength of the light used, approximately 0.25 µm; however, this technique only allows one to view a very small, and perhaps unrepresentative, sample of the surface.

Replication materials

The technique originally used in the aerospace industry produces an exact copy of the surface, which can be peeled away and examined microscopically in the laboratory. Replication was employed as a means of inspecting concrete surfaces at the study site. A total of three suppliers with different options have been used. High-resolution silicone-based replicating polymers, which have been developed and extensively tested, have been used for the qualitative, quantitative and chemical non-destructive evaluation of surface defects. One product being used is a replication technique known as Microset, which uses liquid polymers to replicate large surface areas in remote locations quickly and easily in a single operation. It offers a method of non-destructive surface inspection capable of providing greater detail than other methods currently available. Given the nature of the substrate, a scatter of results was considerable and expected. The scatter also suggested that a considerable variation of S_a would be obtained from 'identical' concrete.

Rebound and UPV tests

The proposed study involves the combined method of rebound hardness and pulse velocity, which can provide versatile information other than strength and possibly predict durability-related properties. Nowadays, the most widespread method for surface hardness testing of concrete is the rebound hammer method. The method measures the modulus of elasticity of the near-surface concrete and has followed the guidance of[16]. The principle is based on the absorption of part of the stored elastic energy of the spring through plastic deformation of the surface and the mechanical waves propagating through the sample while the remaining elastic energy causes the actual rebound of the hammer. The distance travelled by the mass, expressed as a percentage of the initial extension of the spring, is called the rebound number. A 100 mm × 100 mm template with ten points established was used to guide the instrument (Proceq type N-34). All locations and surfaces were dry and free from biofouling.

For the measurement of concrete uniformity in this research, UPV testing is probably the most valuable and reliable application of the method in the field of non-destructive testing.

The pulse velocity is recorded by the formula:

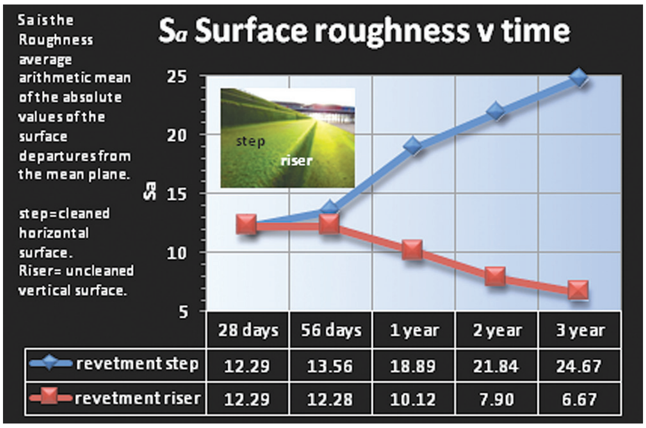
$$\text{Pulse velocity (km/s)} = \frac{\text{Path length (km)}}{\text{Transit time (s)}} \quad \text{....................(1)}$$

The test equipment used generates an ultrasonic pulse that is transmitted through the concrete from a transmitter to a receiver and has followed the guidance of[17]. The time taken for the pulse to pass through the concrete is recorded. By measuring the distance between the transmitter and receiver, the UPV may be calculated using Equation (1). The instrument (Pundit, CNS Electronics, London) consists of a transmitter and a receiver (two probes).

The time of travel for the wave to pass from the transmitter to the receiver in a semi-direct path (adjacent faces of the step) is recorded. The probes were set back from the nose of the step 100 mm, one along the step (the horizontal plane) and the other down the riser (vertical plane). The distance between the two probes (path length) therefore was 141.42 mm. Comprehensive evaluation of this UPV method can be found in[18].

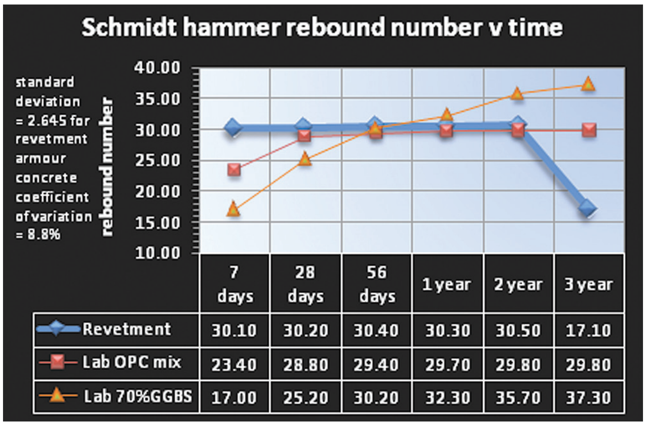
3. Results

Figure 1 depicts surface roughness measurements taken on the interferometer on 28-day, 56-day, 1-year, 2-year and 3-year concrete samples. Replicas were cast on site on 1-, 2- and 3-year placed revetment armour units. Semi-direct paths were chosen, giving a satisfactory angle of 45° and a modest path. Readings were taken on ten surface-dry units, with ambient temperatures at 21°. At three years the poor condition of the surface at the nose of the steps (on the ten units being monitored) made further use of the instrument inappropriate because of liberating aggregate from the revetments. On comparison with the original surfaces, the replication techniques had a 25% accuracy level. Surface roughness doubled from S_a 12.29 µm to S_a 24.67 µm in three years on the revetment steps; these steps have been power washed approximately 150 times at 1200 psi over the three years. The risers of the steps are not power washed and are obviously subject to the same tidal impacts but showed a smooth erosion pattern, from S_a 12.29 µm to S_a 6.67 µm. Figures 2 and 3 show that the rebound and UPV readings from the surface of the armour units consistently remained at around 30 *r* and 4 km/s for two years. At three years, a significant reduction was recorded of nearly 50%. Weekly site surveys have enabled a comprehensive photographic archive to be catalogued. Figure 4 shows the new unit tested at site. Figure 5 demonstrates the condition after 2.5 years' exposure and Figure 6 demonstrates its current condition after 5 years' exposure.



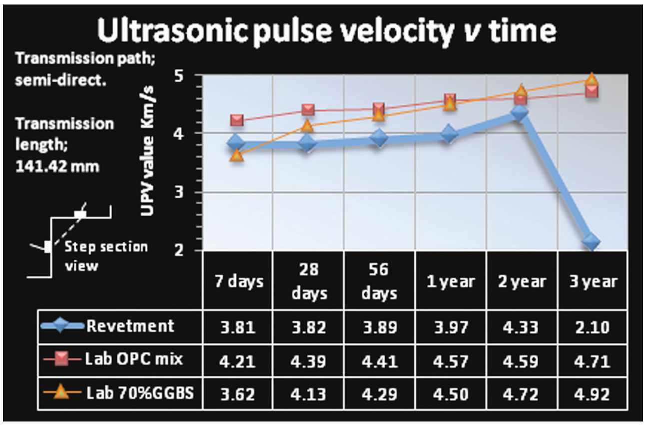
	28 days	56 days	1 year	2 year	3 year
revetment step	12.29	13.56	18.89	21.84	24.67
revetment riser	12.29	12.28	10.12	7.90	6.67

Figure 1. Revetment armour surface roughness measurements over three years



	7 days	28 days	56 days	1 year	2 year	3 year
Revetment	30.10	30.20	30.40	30.30	30.50	17.10
Lab OPC mix	23.40	28.80	29.40	29.70	29.80	29.80
Lab 70%GGBS	17.00	25.20	30.20	32.30	35.70	37.30

Figure 2. Revetment armour surface hardness measurements over three years. For comparison, two laboratory controls were used: an Ordinary Portland Cement (OPC) mix and a 70% ground granulated blast furnace slag (GGBS) mix, neither of which contained synthetic fibres



	7 days	28 days	56 days	1 year	2 year	3 year
Revetment	3.81	3.82	3.89	3.97	4.33	2.10
Lab OPC mix	4.21	4.39	4.41	4.57	4.59	4.71
Lab 70%GGBS	3.62	4.13	4.29	4.50	4.72	4.92

Figure 3. UPV readings taken from revetment armour over three years


Peter Hughes | Revetment armour unit no. PH1. | 19th October, 2007. | Fujifilm Finepix JX | I-----100 mm-----I

Figure 4. Digital photograph of the step of the newly-placed (in 2007) revetment armour unit tested in this research


Peter Hughes | Revetment unit PH1 | 5th August 2010 | Fujifilm Finepix JX |------25 mm-----

Figure 5. Digital photograph showing the nose of the step of the unit, tested in this research after 2.5 years' exposure (2010)


Peter Hughes | Revetment armour unit PH1 | 23rd February, 2013. | Fujifilm Finepix JX | I---------- 25 mm----------I

Figure 6. Digital photograph showing the nose of the step of the unit, tested in this research after 5 years' exposure (2013)

4. Discussion

Roughness and surface topography are important features for the settlement of many organisms. It has long been known that rough surfaces are preferred by algae to smooth surfaces. In addition to surface roughness, other factors including surface free energy significantly influence biofouling. It has been suggested that rough surfaces protect algal spores from wave action and water currents. In particular, reduced water flow in depressions and crevices may offer a refuge for settling spores and juveniles from the strong hydrodynamic forces present in the wave-swept zone and high-powered water jet cleaning systems. Surface roughness measurements seen in Figure 1 were taken on the step (horizontal) and the riser (vertical). Areas of testing were focused away from the nose of the step. The surface roughness increase on the step, rather than the riser, indicates that power washing the step has altered the surface. It is noted that the marine environment in which this surface exists would have partly been responsible. However, the riser that was not power washed became smoother. Replication techniques, not usually associated with concrete surfaces, have proved to be extremely useful and adaptable. The ability of polymers to provide a visual microscopic picture of 3D surfaces, whilst at the same time yielding accurate dimensional data, was useful as a permanent record for subsequent reference or monitoring purposes and lays the foundation for the development of a new non-destructive testing method for concrete surface analysis[19]. The replicating compounds used have a resolution better than 0.1 microns[20]. One of the main concerns when working with replicas has been the accuracy. However, a comprehensive study of three different materials used for surface roughness replication on five different types of machined surfaces was reported[21].

A previous paper from this research has reported micro and macro fibres, commonly observed at the surface of the concrete, in many orientations[22]. As these fibres are liberated due to hydrodynamic forces, whether tidal impact or power washing, they leave behind voids. Such voids at the surface have been responsible for creating a porous, fractured surface; this is portrayed in the rebound numbers in Figure 2. In general, you would expect a relatively higher value of 30 r for a C40/50 mix with a pre-cast steel-formed finish for two years. The appearance of 'black spot'[23] indicated that the surface zone was shallow, with little or no surface zone over the aggregate, and may be a factor in low readings for the initial two years. This lower reading may also be a result of the fact that the synthetic fibres exposed on the surface are acting as impulse absorbers. This is an enhancement utilised in the design stage and is seen as a useful property (if the fibres are embedded in the cement surface) on coastal structures subject to cyclic impacts. At two years, a common pattern of degradation appeared on the units rather than the wave walls. An area or band of liberated aggregate 100 mm wide from the leading edge of the step made this area unapproachable due to the fact the hammer would further damage the surface, see Figure 6. Abrasion resistance is generally affected by the same influences as surface hardness and research[24] has suggested that the rebound number may be used to classify this property. It is also reasonable to suppose that other durability characteristics that are related to a dense, well-cured outer surface zone may be similarly classified. However, the substantial reduction in the third year indicates that further investigations are required.

UPV information has enabled the variations in concrete quality to be assessed and areas of poorer quality concrete to be identified. High UPV readings are generally indicative of good quality concrete. UPV values have remained steady for two years at 3.81-4.33 km/s and have then reduced substantially in the third year to 2.1 km/s. High pulse velocity readings are generally indicative of good quality concrete, and a general relationship between concrete quality and pulse velocity was shown by[25]. These results indicate that the concrete has initially shown a good quality but reduced to a very poor quality; this change has been illustrated in Figures 4, 5 and 6. Since the pulse cannot travel through air, the presence of a crack or void on the path will increase the path length, as it goes around the flaw, and increase attenuation so that a longer transit time will be recorded. The pulse velocity obtained is lower than that of the control. Consideration must be made to sea water within the units, as moisture, normally present in concrete, may encourage a higher reading[18]. Since compression waves will travel through water, it follows that this philosophy will apply only to cracks or voids that are not water filled. Similar research[26] has examined this in detail and concluded that although water-filled cracks cannot be detected, water-filled voids will show a lower velocity than the surrounding concrete. Experience from site indicates that, in general, poor quality concrete becomes dirtier, encourages more biofouling and suffers more colonisation than dense concrete, and these phenomena provoke and encourage each other. Hence, the further and more frequent use of power washing at the study site. A variability in UPV at seven days from a mean of 10 readings gave 3.81 km/s, the standard deviation (σ) 0.43 gave a variation of 0.18, hence a confidence limit at 95% ±0.26, in agreement with the literature. The difference in UPV compared with the OPC control mix may be due to the fact that the density in the revetment mix has been altered by the presence of the fibres, the velocity changing as it encounters each fibre. The reduction in UPV is particularly significant, suggesting the core of the concrete may be affected by the weakening process. The measurement of UPV over three years has shown that more detailed examination is necessary.

Observations of filamentous bacteria in the unplaced revetment concrete have been previously reported[27]. It was observed by other workers that with the addition of bacteria, the compressive strength of concrete showed a significant increase by 15% at 28 days[28]. Thus, the revetment concrete may have shown an initial increase in readings reported here, meaning the data could be interpreted as munificent.

5. Conclusion

Various techniques were used to investigate how the surface of the units performed to build a more complete picture showing their performance over three years. The surfaces of the precast elements have been investigated, examined and monitored. The results reveal how the steps became rougher and the risers became smoother. Degradation, through power washing, may not be the primary cause, but accelerates the condition. The units have a design life of 100 years; after 5 years' exposure, this design life seems unlikely. This research has generated new insights into surface degradation and opens up the prospect of more detailed surface analysis on the performance of fibre-reinforced marine concrete. The reduction in UPV is particularly significant, suggesting the core of the concrete may be affected by the weakening process. Also, there is a lack of expert guidance for the safe and prolonged use of power wash systems on concrete in the UK.

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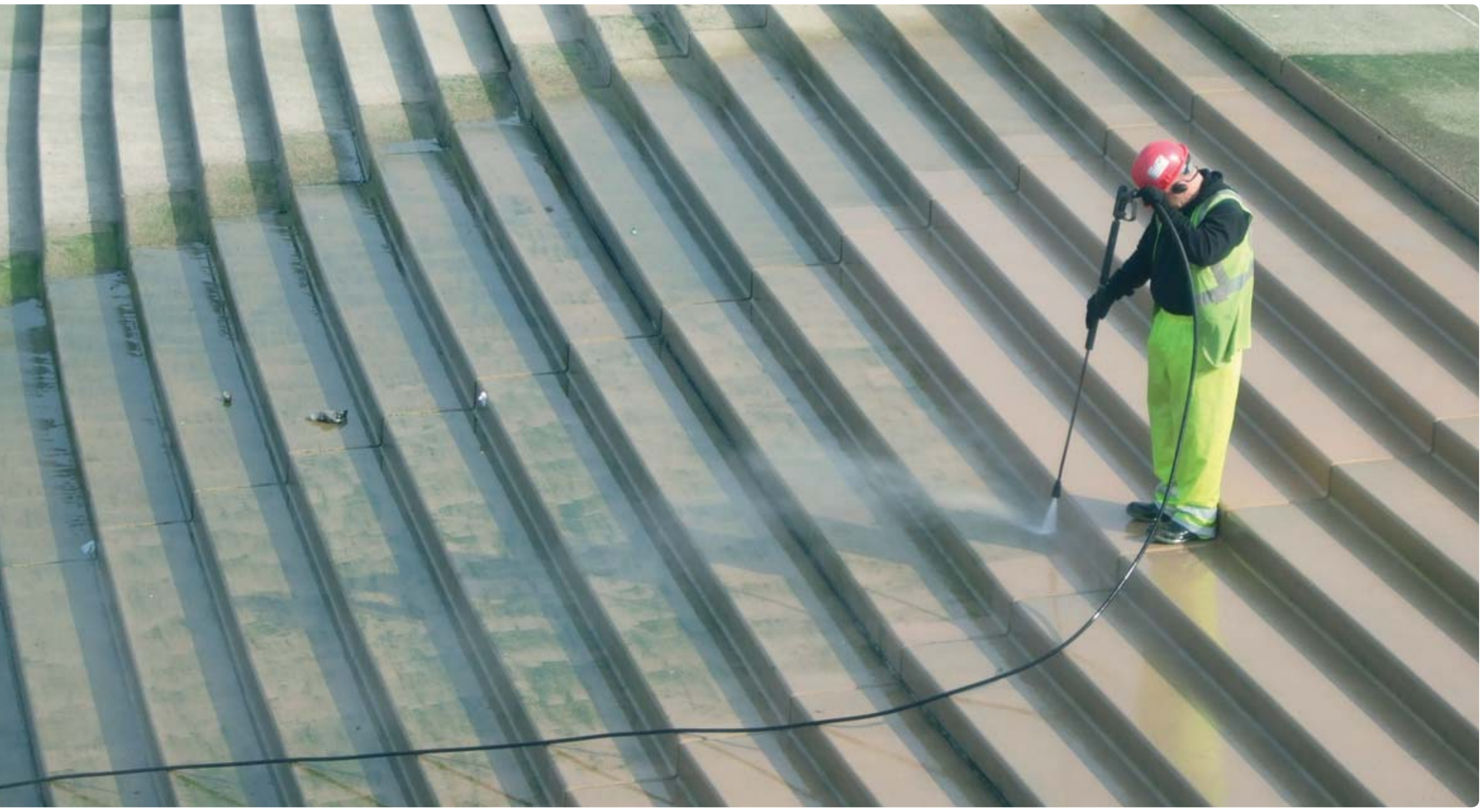
Rough and tough?

Durability of marine concrete

Special Concretes
Formwork and Falsework



Innovative NDT method used in surface analysis

> **A range of NDT methods are available and are in use for measuring the surface texture of concrete floors, but no method is accepted as standard and different organisations use different methods.**

Peter Hughes is a PhD student at the University of Central Lancashire investigating marine biofouling and its implications for the durability of marine concrete.

This original, innovative research uses a non-destructive testing (NDT) method to investigate surface damage of the concrete at Blackpool sea defences, due to aggressive cleaning practices, and also measures surface roughness of concrete revetment armour. It determines wear rate, records surface roughness increase and predicts long-term damage due to aggressive cleaning practices. Visual inspections, which are an essential precursor to any intended non-destructive tests, have been extensively adopted throughout this research over the lifetime of the project – some five years. Replication has been used as a means of inspecting concrete surfaces and lays the foundation for the development of a new NDT method for concrete surface analysis.

The technique produces an exact copy of the surface, which is peeled away and examined microscopically in the laboratory.

In order to study the effect of aggressive cleaning practices and their implications, surface roughness of revetment armour at Blackpool needed to be measured over time. No standard method for measuring surface roughness of concrete has been adopted. A range of NDT methods are available and are in use for measuring the surface texture of concrete floors, but no method is accepted as standard and different organisations use different methods. Holt and Musgrove(1) has carried out a review of the main methods. The interest in measuring surface texture of floors stems from its effect on skid resistance. Wambold *et al*(2) used the mean texture depth as a measure of surface roughness. Silfwerbrand(3) suggested a different method of quantifying the surface roughness, with the sand area method, in his study of the effect of roughness on bond of repair materials.

Revetment armour units

The precast units come in four-step sections, 2791 of which are needed to cover the 3.3km stretch of beach between the toe beam and the promenade. Each unit measures 5 × 3.5m, weighs 20 tonnes and contains 8m^3 of macro-synthetic-fibre-reinforced concrete. The revetment is formed from fill material, placed at a slope of 1:3, and capped with a concrete blinding layer. Behind this stepped apron is a flat, cast-in-situ berm and precast wave wall.

Exposure conditions and test locations

The stepped revetment armour is constantly colonised by algae – predominantly *Ulva intestinalis* – creating a slip hazard. The seawall and revetment armour is subject to cyclic wetting and drying conditions. The exposure is very harsh due to wave action, exacerbated by sand and occasionally shingle from the beach. This aggression meant that cover loss during service was anticipated in the design stage. This has occurred at many locations, particularly inter-tidal regions, where an early exposed aggregate appearance was noted, and patch repairs have been carried out. The revetment's primary role is coastal protection and as such is subject to the wear associated with tidal and wave action, so the design team and client expect a degree of surface deterioration.

Surface roughness

S_a surface roughness is a measurement of surface finish; it is topography at a scale that might be considered 'texture' on the surface. Surface roughness is a quantitative calculation of the relative roughness of a linear profile or area, expressed as a single numeric parameter. Roughness and surface topography are important features for the settlement of many organisms; it has long been known that rough surfaces are preferred by algae to smooth surfaces. In addition to surface roughness, other factors including surface free energy significantly influence biofouling.

It has been suggested that rough surfaces protect algal spores from wave action and tidal currents. In particular, reduced water flow in depressions and crevices may offer a refuge for settling spores and juveniles from the strong hydrodynamic forces present in the wave-swept zone and high-powered water jet cleaning systems.

White light interferometry

Light from a common monochromatic source is reflected by a beam-splitting device from the observed surface and from a standard plane reference surface. The combination of these two beams gives rise to a pattern of interference fringes, which are in effect contour lines that indicate the profile of the surface.

Replication materials

Replication is being used as a means of inspecting concrete surfaces at Blackpool sea defences. A total of three suppliers with different options have been used. The technique produces an exact copy of the surface, which can be peeled away and examined microscopically in the laboratory.

High-resolution, silicone-based replicating polymers, which have been developed and extensively tested, have been used for the qualitative, quantitative and chemical non-destructive evaluation of surface defects.

One product being used is a replication technique known as Microset, which uses liquid polymers to replicate large surface areas in remote locations quickly and easily in a single operation. It offers a method of non-destructive surface inspection capable of providing greater detail than other methods currently available. The ability of polymers to provide a visual microscopic picture of 3D surfaces, while at the same time yielding accurate dimensional data, is highly useful as a permanent record for subsequent reference or monitoring purposes. Replicating compounds have a resolution better than 0.1 microns.

Measurements from the 'step' and 'rise' were taken to distinguish between cleaned and uncleaned areas. All areas were exposed to the tide. These replicas have been taken back to the interferometer where measurements were recorded. Given the nature of the substrate, a scatter of results was expected. The scatter also suggested that a considerable variation of S_a would be obtained from 'identical' concrete.

Top: Revetment armour steps at Blackpool colonised with* Ulva intestinalis*.

Centre: : Power washing by Blackpool Council to avoid slip hazard.

Left: Replica of revetment surface at three years. Curing time of polymer was ten minutes.

Results

Surface roughness measurements were taken on the interferometer on 28-day, 56-day, one- , two- and three-year concrete samples. Replicas were cast on-site on one-, two- and three-year placed revetment armour units. On comparison with original surfaces the replication techniques had a 25% accuracy level. Surface roughness doubled from S_a 12.29 to S_a 24.67 in three years on the revetment steps; these steps have been power washed approximately 100 times at 1200psi over three years. The risers of the steps are not power washed and are subject to the same tidal impacts but showed a smooth erosion pattern – from S_a 12.29 to S_a 6.67.

Discussion

The majority of NDT on various properties of concrete, including the tests contained in this research, were developed in the days when the material and what was expected of it were sometimes quite different. Water:cement/binder ratios of 0.45 and higher was fairly typical.

Today, for many reasons, we use somewhat lower values of w/c. Moreover, to make high-performance concrete, we use w/c ratios in the range 0.22–0.30 and at these values the behaviour of cement may be quite different. Of particular importance is the behaviour of concrete in the presence of fibres.

Non-destructive testing of concrete in the UK needs to be rediscovered and brought into the 21st Century. There is no doubt that research leading to new knowledge and better understanding of the behaviour of concrete must continue. However, as the material itself evolves and improves, along with higher expectations, the future development of NDT of concrete is vital. ●

Further information:

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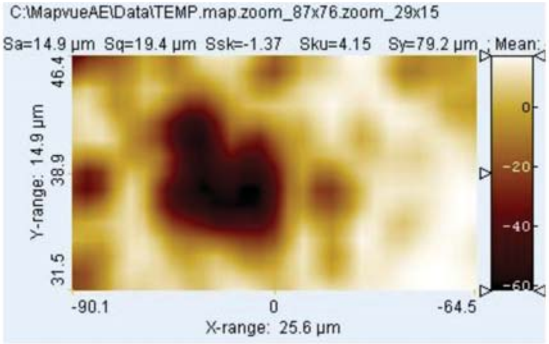
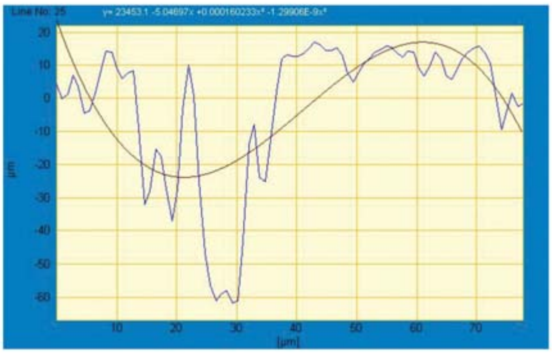
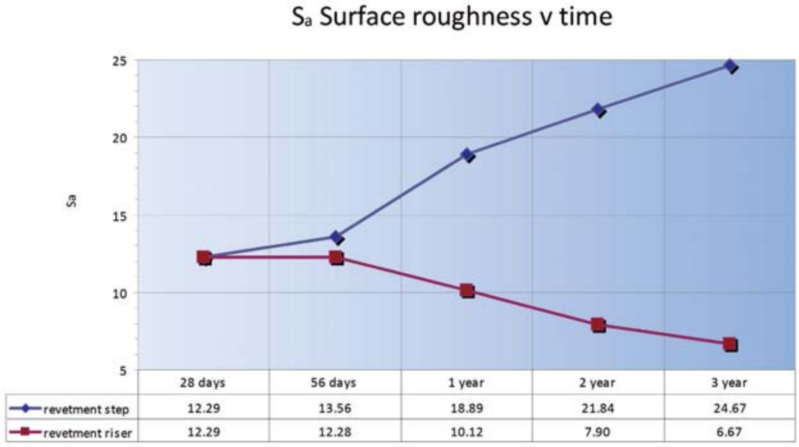
Right: Replica of revetment surface at three years. Exposed aggregate detail can be seen.

Far right: Revetment surface data from interferometer.

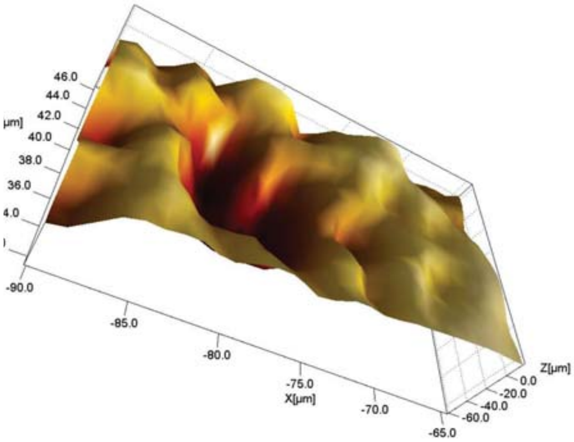
Below: Linear relationship between surface roughness of the step (horizontal plane), which is power washed, and the riser (vertical plane), which is unwashed but subject to wave action only







	28 days	56 days	1 year	2 year	3 year
revetment step	12.29	13.56	18.89	21.84	24.67
revetment riser	12.29	12.28	10.12	7.90	6.67



INNOVATIVE METHOD USED TO EVALUATE THE EFFECT OF POWER WASHING ON MARINE CONCRETE

A UK SITE STUDY

BY PETER HUGHES

Power washing is becoming more commonly used by maintenance teams throughout the world but the inappropriate use of high-pressure washing may have a devastating effect on the long-term durability of many material surfaces.[1] This article reports early findings from an ongoing study into the effects of power washing concrete. The study was conducted at a site on the northwest coast of England (Fig. 1), where concrete revetment armor with a design life of 100 years has been monitored for surface changes over a period of 3 years (Fig. 2).

Fig. 1: Equipment used to manage biofouling at the study site

Fig. 2: Revetment armor steps colonized with algae

HISTORY OF POWER WASHING

Early industrial cleaning using water-jet technology reaches back to the 1920s in the steel industry. In the late 1950s, as reliable high-pressure pumps were developed, the water jet revolutionized sewer and pipe cleaning. Reviews about early cases of water-jet use for material removal—namely, for soil removal and hydraulic mining—are provided elsewhere.[2] Today, commercialized water jetting covers many cleaning applications: concrete, stone and masonry, cement kiln and autoclave vessels, chemical pipes, sewers, and ship hulls.

CHARACTERISTICS OF POWER WASHING

Water-jet applications can be distinguished according to the level of the applied operational pressure. Power washing can be defined as the use of pressurized water applied below 5000 psi (34.5 MPa),[3] with or without the addition of other liquids or solid particles, to remove unwanted matter from various surfaces. Dated UK published guidance tackles the removal of algae from concrete recommending power washing at velocities between 725 to 2175 psi (5 to 15 MPa).[4] This type of pressure is applied to clean marine structures, jetties, and steps to combat biofouling and reduce slip hazard. A modest 1200 psi (8.2 MPa) was used at the UK study site.

Further advances in high-pressure water-jet cleaning and maintenance management incorporate hot water and a 15-degree fan nozzle at an appropriate distance (at least 6 in. [150 mm]) from the surface, and with appropriate pressure.[5] In general, the higher the water pressure, the more effective the cleaning and the greater the potential damage to the concrete surface.

DAMAGE FROM POWER WASHING

Research has quantified the erosion of concrete, focusing on a range of pressures and flow rates used in the routine cleaning and maintenance of drains and sewers.[6] Damage from jetting tests was measured, and volumetric erosion rates reported at 4000 psi (27.6 MPa) on concrete were 240 ft^3/s (6.90 mm^3/s).

Power washing can start a devastating vicious cycle.[7] The frequency of cleaning and the cleaning method used (especially high-pressure cleaning) could have an influence on concrete deterioration.[8] While good-quality concrete shows excellent resistance to the steady flow of clear water, nonlinear flow at velocities exceeding 39.4 ft/s (12 m/s) (23 ft/s [7 m/s] in closed conduits) may cause severe damage to concrete.[9] The water exits the nozzle at both a high pressure and a high velocity. The resulting momentum is great enough to dislodge not only dirt and debris but also creates flakes, popouts, and even concrete spalls.[7]

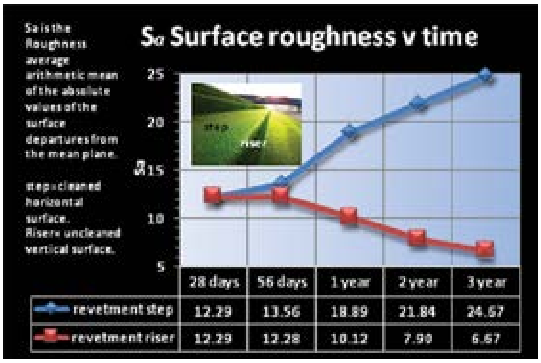
METHODS OF MEASURING DETERIORATION

Deterioration of concrete structures usually starts at the surface and progresses into the structure. To study the effect of aggressive cleaning practices and its implications, a number of testing methods were used.

The surface roughness of the revetment armor was measured over time (Fig. 3). While no standard method for measuring surface roughness of concrete has currently been adopted, a range of nondestructive testing (NDT) methods are available. These methods are in use for measuring the surface texture of concrete floors, but no method is accepted as a standard and different organizations use different methods.

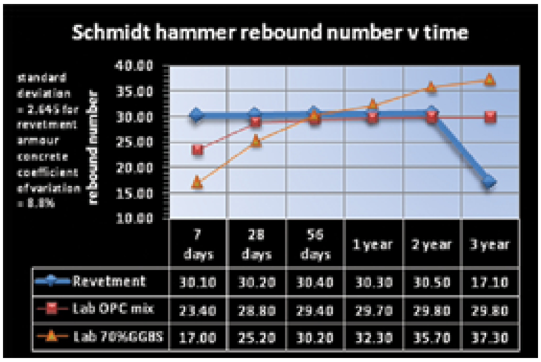
Holt and Musgrove[10] carried out a review of the main methods of surface texture classifications that are summarized in an ASTM International special technical publication. The interest in measuring the surface texture of floors stems from its effect on skid resistance. Wambold et al.[11] used the mean texture depth as a measure of surface roughness. Silfwerbrand[12] suggested a different method of quantifying the surface roughness in his study on the effect of roughness on bond of repair materials.

Surface roughness measurements were taken with an interferometer on 28-day; 56-day; and 1-, 2-, and 3-year concrete samples. Semi-direct paths for interferometric readings were chosen using an angle of 45 degrees and a modest path. Readings were taken on 10 surface-dry units with ambient



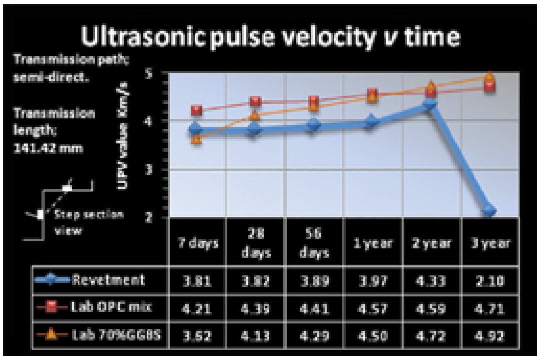
	28 days	56 days	1 year	2 year	3 year
revetment step	12.29	13.56	18.89	21.84	24.67
revetment riser	12.29	12.28	10.12	7.90	6.67

Fig. 3: Revetment armor surface roughness measurements



	7 days	28 days	56 days	1 year	2 year	3 year
Revetment	30.10	30.20	30.40	30.30	30.50	17.10
Lab OPC mix	23.40	28.80	29.40	29.70	29.80	29.80
Lab 70%GGBS	17.00	25.20	30.20	32.30	35.70	37.30

Fig. 4: Revetment armor surface hardness measurements



	7 days	28 days	56 days	1 year	2 year	3 year
Revetment	3.81	3.82	3.89	3.97	4.33	2.10
Lab OPC mix	4.21	4.39	4.41	4.57	4.59	4.71
Lab 70%GGBS	3.62	4.13	4.29	4.50	4.72	4.92

Fig. 5: UPV readings taken from revetment armor

temperatures at 70°F (21°C). At 3 years, the poor condition of the surface at the nose of the units being monitored made further use of the instrument inappropriate because of liberating aggregate from the revetments.

Schmidt/rebound hammer tests were used to evaluate the surface hardness of the concrete (Fig. 4). Tests were performed on site on 1-, 2-, and 3-year placed revetment armor units. For hardness comparisons, replicas were cast and tested in the laboratory. Two laboratory control mixtures were used: an ordinary portland cement (OPC) mixture and a 70% ground-granulated blast-furnace slag (GGBS) mixture—neither of which containing synthetic fibers.

Ultrasonic pulse velocity (UPV) testing was used to appraise the quality of the concrete (Fig. 5). UPV information allows the variations in concrete quality to be assessed and areas of poorer quality

Fig. 6: Newly placed concrete tested in this research

Fig. 7: Nose of the step of the unit shown in Fig. 6 after 5 years' exposure

concrete to be identified. High UPV readings are generally indicative of good-quality concrete. A general relation between concrete quality and pulse velocity is well-accepted.[13] Because the pulse cannot travel through air, the presence of a crack or void on the path increases the path length. As the pulse goes around the flaw, an increase in the transit time will be recorded. Consideration was given for seawater within the units, as moisture normally present in concrete may encourage a higher reading.[14]

Weekly site surveys yielded a comprehensive photographic archive so visual evidence could also be observed. Figure 6 shows a photo of the new unit at the test site and Fig. 7 shows the condition after 5 years of exposure.

Replication was used as a means of performing a comparative surface analysis. This technique uses silicone-based replicating polymers and produces an exact copy of the surface (Fig. 8). After curing, the sample is removed and examined microscopically in the laboratory.

DISCUSSION OF RESULTS

Surface roughness measurements were taken on the step (horizontal) and the riser (vertical). Areas of testing were focused away from the nose of the step. The surface roughness increase on the step, rather than the riser, indicates that power washing the step has altered the surface. The marine environment in which this surface exists should have partly been responsible; however, over time, the riser that was not power washed became smoother. Results showed that in 3 years the surface roughness on the steps doubled from $S_a12.29$ to $S_a24.67$. The steps were power washed approximately 150 times at 1200 psi (8.2 MPa) over the course of the 3 years. The risers of the steps were not power washed and were subject to the same tidal impacts, but they showed a smooth erosion pattern—from $S_a12.29$ to $S_a6.67$.

Schmidt/rebound hammer readings from the surface of the armor units remained consistent at around 30*r*. After 2 years, a common pattern of degradation appeared on the units. An area or band of liberated aggregate approximately 3.9 in. (100 mm) wide occurred on the leading edge of the step and the impact hammer could no longer be used because the hammer would have further damaged the surface.

Abrasion resistance was also evaluated and is generally affected by the same influences as surface hardness. Research on this subject[15] has suggested that the rebound number may be used to classify this property.

UPV readings from the surface of the armor remained steady for 2 years at 2.4 to 2.7 miles/s (3.81 to 4.33 km/s) and then reduced substantially in the third year to 1.3 miles/s (2.1 km/s). These results initially indicated good-quality concrete; however, the decline in UPV values showed the deterioration of the concrete. The substantial reduction in the third year of the study indicates a correlated reduction in compressive strength of more than 50%. The reduction in UPV is particularly significant, suggesting the core of the concrete may be affected by the weakening process.

Replication techniques proved to be extremely useful and adaptable. The ability of the polymers used for replication to provide a visual microscopic picture of three-dimensional surfaces while, at the same time, yielding accurate dimensional data, was useful as a permanent record for subsequent reference or monitoring purposes and could lay the foundation for the development of a new NDT method for concrete surface analysis.[16]

The replicating compounds used had a resolution better than 0.1 microns[17] and were able to accurately recreate the surfaces being studied. Confirmation of this accuracy can be found in a comprehensive study of three different materials used for surface roughness replication on five different types of machined surfaces. The results were reported in Reference 18.

POSSIBLE EFFECTS ON LONG-TERM LIFE OF CONCRETE

Various techniques were used to investigate how the surface of the units performed to build a more complete picture of their performance over 3 years. The surface of the precast elements were investigated, examined, and monitored. The results revealed that the steps became rougher with power washer use and the risers became smoother, even though they were exposed to the same tidal conditions. Early degradation of these units from power washing was observed and the expected design life of 100 years for the concrete could be compromised by the power-washing activities.

ACKNOWLEDGMENTS

The author thanks his PhD supervisors for their endless patience: D. Fairhurst, I. Sherrington, N. Renevier, L. H. G. Morton, P. C. Robery, and L. Cunningham.

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Fig. 8: Surface that was copied using silicone-based replicating polymers

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__Peter Hughes__ is a final-year PhD Candidate at the University of Central Lancashire, UK. His current work involves investigating marine biofouling and its influence on the durability of concrete sea defenses. He has presented his work at the ACI fall conventions in St. Louis, MO, in 2008 (PhD proposal), and New Orleans, LA, in 2009. Hughes was recently awarded a Japanese Society for the Promotion of Science Fellowship to study photocatalytic coatings for concrete at Fukui University in Japan (2012). He has several journal papers published from his current work and articles printed around the world.

A3.3 Concrete mix design

Armour concrete mix design	
Type of mix	Designed
Compressive strength class or designation	C35/45
Intended working life of structure	100 years
BS8500-1 exposure classes	XS3, XF4, XC3, XC4
Maximum w/c ratio	0.45
Minimum cement content (kg/m3)	340
Cement or combination types	CEM111/A
	(maximum 50% ggbs)
Chloride class	0.2
Maximum aggregate size (mm)	20
Minimum air content (%)	not applicable
Additives	3.5kg/m3 Grace Strux 90/40
	0.91kg/m3 Fibrin XT Polypropylene micro fibres
Colour	Fylde buff
Target slump (mm) & slump range (mm)1	100
	Range +25 to -25

Table A3.1 Site concrete mix design.

Armour concrete fibre details		
	A - *Macro*	**B** - *Micro*
Polymer	Polypropylene & Polyethylene	Polypropylene
Design	–	Monofilament
Length	40mm	Blended
cross section	rectangular	circular
Dosage	3.5kg/m^3	0.91kg/m^3
Diameter	–	22 micron
Average width	1.4mm	–
Av. thickness	0.105mm	–
Applications	Sea DefenceWork	Sea DefenceWork
Alkali resistance	High	100%
Acid resistance	High	High
Salt resistance	High	–
Alternative to Air Entraining Agent	–	Yes

Table A3.2 Site fibre details.

Fibres

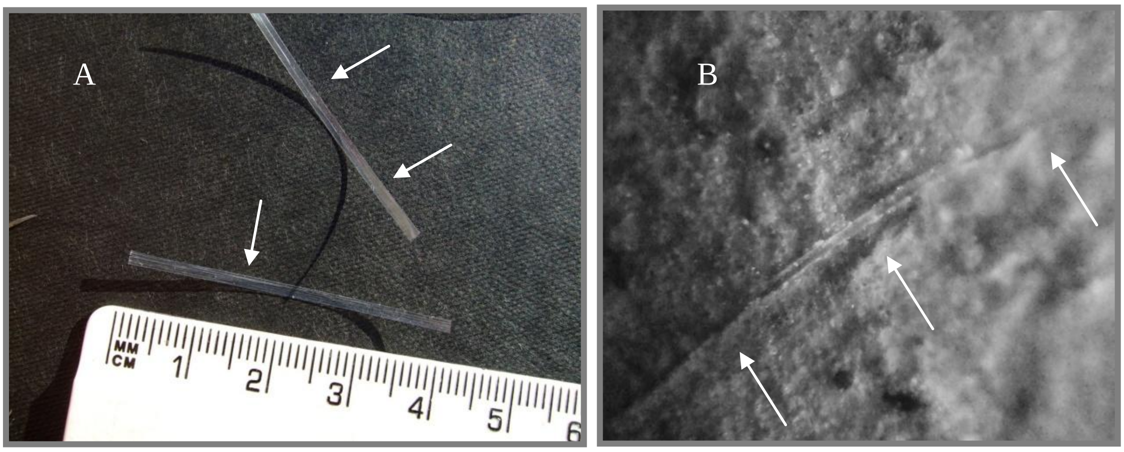

Figure A3.1 A-Macro synthetic fibre. B-Micro synthetic fibre.

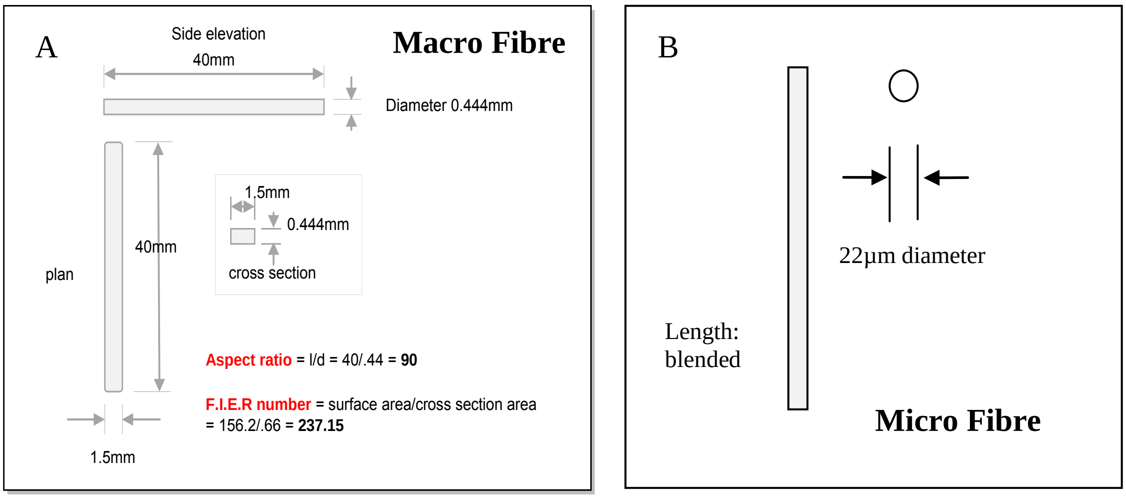

Figure A3.2 -Macro fibre dimensions. B-Micro fibre dimensions.

Surface parameters of new revetment concrete					
	Sa	*Sq*	*Ssk*	*Sku*	*Sy*
1	13.70	17.50	0.88	3.36	104.00
2	12.20	15.80	1.06	4.00	85.70
3	17.70	20.60	0.02	1.95	87.30
4	6.08	7.58	0.51	3.12	46.80
5	6.81	8.51	0.26	2.88	53.70
6	6.56	8.10	0.24	2.86	51.10
7	15.80	18.80	0.15	2.14	83.30
8	18.80	22.10	0.73	2.31	84.50
9	14.00	17.00	0.48	2.54	80.40
10	11.20	13.80	0.36	2.60	68.40
M	**12.29**	**14.98**	**0.47**	**2.78**	**74.52**

Table A3.2 Data of surface roughness measurements from new revetment concrete; taken from actual concrete specimens from the site.

Surface parameters of replica of new revetment concrete					
	Sa	*Sq*	*Ssk*	*Sku*	*Sy*
1	8.20	10.40	0.89	4.35	66.47
2	8.34	10.60	1.04	4.02	68.30
3	9.31	12.70	1.85	7.27	82.00
4	6.29	8.03	1.16	4.82	58.30
5	14.00	16.80	0.39	2.36	79.30
6	6.66	8.29	0.51	3.09	52.70
7	6.57	8.25	0.43	3.31	57.20
8	6.81	8.46	0.50	3.09	56.00
9	9.95	12.50	0.96	3.70	72.90
10	6.70	8.47	1.04	4.01	54.10
M	**8.28**	**10.45**	**0.88**	**4.00**	**66.47**

Table A3.3 Data of surface roughness measurements from new revetment concrete; taken from replicas.

Surface parameters of revetment concrete at 3 years					
	Sa	*Sq*	*Ssk*	*Sku*	*Sy*
1	7.78	11.10	2.08	10.70	85.40
2	6.25	7.92	0.64	3.60	59.10
3	14.20	16.70	0.59	2.25	65.80
4	15.70	18.40	0.17	1.96	69.80
5	21.90	24.90	0.53	1.84	80.50
6	24.70	27.00	0.07	1.44	83.70
7	19.90	22.10	0.18	1.54	70.90
8	21.20	24.90	0.84	2.20	83.70
9	20.80	24.20	6.56	2.06	84.30
10	16.00	20.40	1.14	3.20	81.50
M	**16.84**	**19.76**	**1.28**	**3.08**	**76.47**

Table A3.4 Data of surface roughness measurements from three year exposure revetment concrete; taken from replicas.

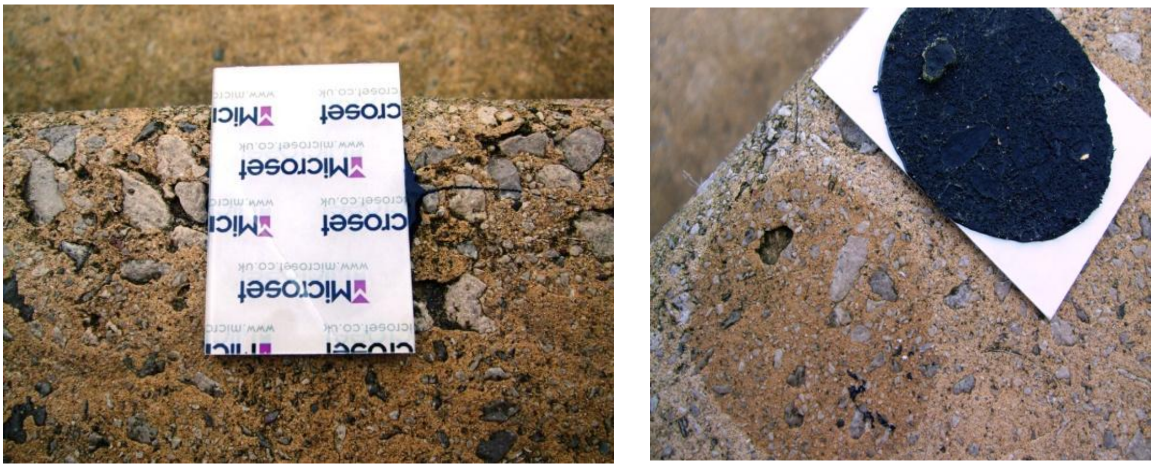

Figure A3.3 Curing replication polymer at the study site.

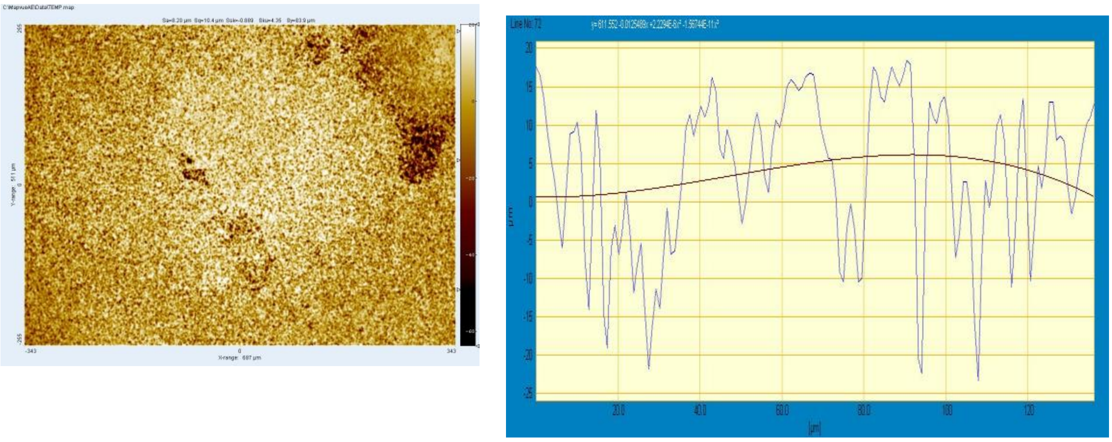

Figure A3.4 Interferometer data of a new surface

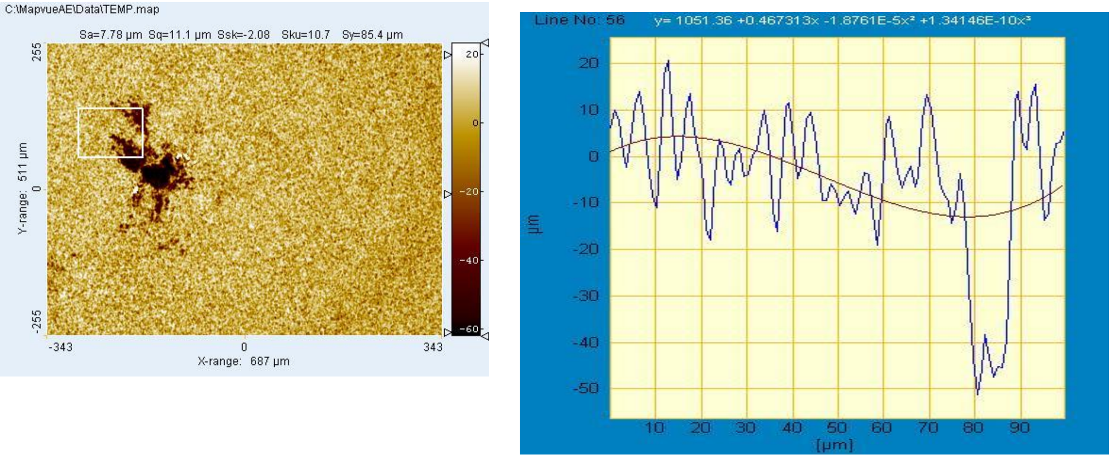

Figure A3.5 Interferometer data of replica of 3 years exposed surface

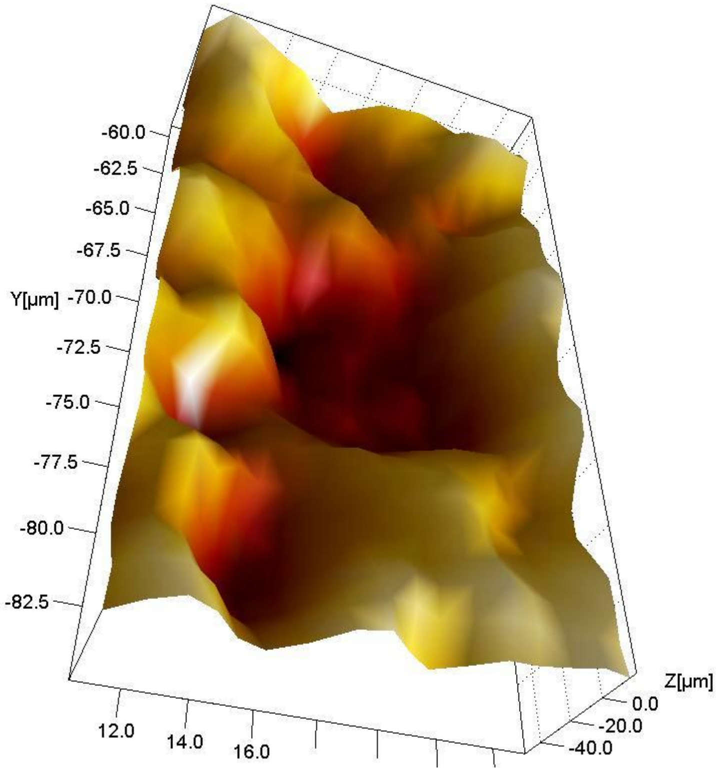

Figure A3.6 Three dimensional image of Figure 3.

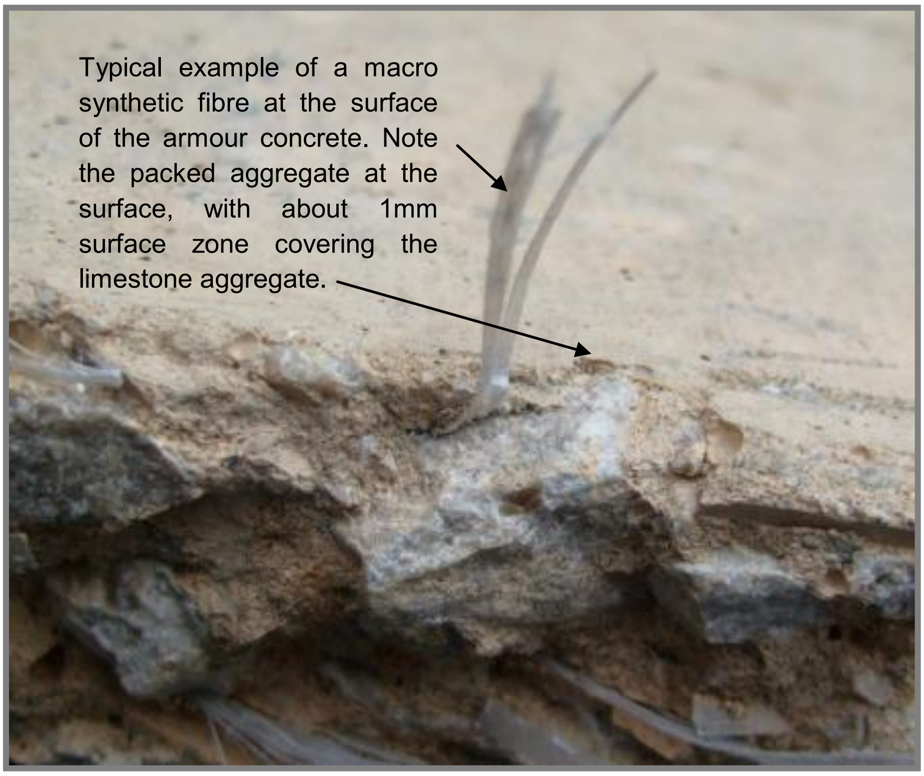

Figure A3.7 Macro synthetic fibre protruding in vertical orientation on a new armour sample.

Figure A3.8 Typical surface zone to revetment armour (after 1 yrs exposure).

Appendix 4

Additional documentation to Chapter 4

Colonisation

A4-1 Copies of original published papers (3) specific to this Chapter:

1 - Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robery, P., Cunningham, L. 2013. Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete.
Construction and Building Materials. 41, 498-504.

2 - Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robery, P., Cunningham, L. 2013. Microscopic study into biodeterioration of marine concrete. International Biodeterioration & Biodegradation. 79, 14-19.

3 - Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robery, P., Cunningham, L. 2013F. Microbial degradation of synthetic fibre-reinforced marine concrete. International Biodeterioration & Biodegradation. Article in Press.

A4-2 Copies of original published articles (2) specific to this Chapter:

1 - Hughes, P. 2012. A new mechanism for accelerated degradation of synthetic-fibre-reinforced marine concrete. Concrete. 9, Vol. 46, 18-20.

2 - Hughes, P. 2012. Biodeterioration of marine fiber-reinforced concrete.
Concrete International. 11, 2012, Vol. 34, 42-44.

A4-3 Porosity data

A4-4 Surface energy calculations

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Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete

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HIGHLIGHTS

- ▶ Algal fronds have been observed growing between fibre and cement.
- ▶ Colonisation has been observed, entangled with, and adhered to fibres.
- ▶ A holistic model is presented, detailing the degradation process of macro and microsynthetic fibres.

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ABSTRACT

This research presents an exploratory study into the mechanical biodeterioration of synthetic fibre reinforced marine concrete. Light and inverted microscopy, scanning electron microscopy (SEM) with energy dispersive X-ray analyser (EDX) of site specimens were used to observe colonisation at the fibre cement interface, enabling the further understanding of this interaction. Algal fronds have been observed growing between fibre and cement. Colonisation has been observed, entangled with, and adhered to fibres. This new mechanism occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its growth. Loss of surface material, either through biodeterioration or through other mechanical means, such as power washing, is not the primary cause of degradation, but may exacerbate the condition. A holistic model is presented, detailing the degradation process of macro and microsynthetic fibres. Microscopic investigation of site concrete revetment armour units was used to validate the model. This multidisciplinary study is the first to report the composition of microbial assemblages fouling and degrading synthetic fibres within marine concrete in the United Kingdom, laying the foundation for more study into this new phenomenon.

1. Introduction

The algal colonisation of concrete sea defences is a well known global phenomenon. Once established, growths form a slippery surface and may constitute a danger to the public. More direct damage can be caused to the concrete itself by the acids and other metabolites produced by the organisms, which together with the ability of some species to tunnel into surfaces, leads to degradation, increased porosity and decreased durability [1]. Fibre reinforced concretes, well compacted and cured, seem to possess excellent durability as long as the fibres remain protected by the cement paste [2]. Deterioration of concrete structures, usually, starts at the surface and progresses into the structure; it is therefore, the skin of the concrete that is the major factor in the longevity of the material. This research presents an exploratory study into the mechanical biodeterioration of synthetic fibre reinforced marine concrete. Microscopic examination of the bond between fibre, cement and algae, enables the further understanding of this interaction. This new mechanism, observed and presented in this study occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth [3]. The revetment forms a coastal defence scheme where some parts have been in service for 7 years; the armour units protect the structure against erosion. Synthetic fibre reinforced concrete

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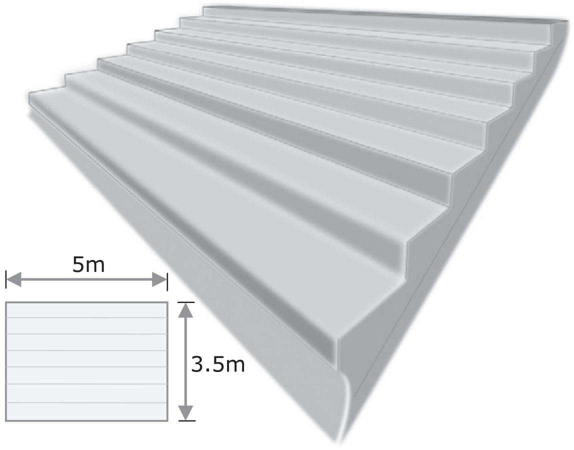


Fig. 1. Precast revetment armour unit, designed to protect the revetment.

used in the manufacture of the revetment armour (Fig. 1) was used in a marine environment for the first time. Therefore, there is little information on how the physical properties of synthetic fibres change with time and how long-term mechanical performance of fibre-reinforced marine concrete may be affected.

Synthetic fibres, used at the test site during this research, have become more attractive in recent times as reinforcements for cementitious materials and research [4] has suggested they may retard the deterioration process at the surface of concrete. Synthetic fibre reinforced concrete utilises fibres derived from organic polymers which are available in a variety of formulations and in two basic size ranges, namely macro and micro (Table 1). Synthetic fibre types used in cement-based matrices include acrylic, aramid, carbon, nylon, polyester, polyethylene and polypropylene. Macro-synthetic polymer fibres have the potential to improve the post-cracking properties of hardened concrete, as set out in the sector guidance [5]. Their use at the test site as an alternative to nominal bar or fabric reinforcement is a relatively recent development. Microsynthetic fibres, also used at the site, can be used in ground-supported slabs to reduce plastic shrinkage cracking and plastic settlement cracking. The properties of the fibres used at the test site are detailed (Table 1). Polypropylene fibres have some unique properties that make them suitable for incorporation into the concrete matrix. They are chemically inert and very stable in the alkaline environment of concrete. The polymer has a hydrophobic surface so that it does not absorb water, which may reduce the bond between fibre and cement. Disadvantages include: sensitivity to sunlight and oxygen, a low modulus of elasticity, and a poor bond with the concrete matrix [6]. These disadvantages are not necessarily critical, as embedment within the matrix provides a protective cover, helping to minimise susceptibility to environmental effects. One of the benefits of polyethylene fibre is that it can be produced with a relatively high modulus of elasticity, due to the intrinsic strength of the carbon backbone of the polymer chain giving desirable strength retention properties under long-term exposure to aggressive environments, such as seawater. These fibres also have reasonable thermal stability, and when used with cement paste, are highly effective in improving plastic properties and impact resistance [5]. However, outdoor applications are also limited by the polymer's susceptibility to ultra-violet light [7].

Table 1
Test site fibre details.

	A – Macro	B – Micro
Polymer	Polypropylene and polyethylene	Polypropylene
Design	–	Monofilament
Length	40 mm	Blended
Cross section	Rectangular	Circular
Dosage	3.5 kg/m^3	0.91 kg/m^3
Diameter	–	22 µ
Average width	1.4 mm	–
Av. thickness	0.105 mm	–
Applications	Sea defence work	Sea defence work
Alkali resistance	High	100%
Acid resistance	High	High
Salt resistance	High	–
Alternative to air entraining agent	–	Yes

It is now well accepted and well documented, that in cement composites, whether with fibre or aggregate inclusion, the matrix in the vicinity of the inclusion, i.e. in the transition zone, can be quite different in its microstructure to that of the bulk cement matrix. This modified matrix is characterised by a width that can be as great as 50–100 µm [8]. The presence of a transition zone between fibres and bulk matrix has been confirmed by SEM [9], microhardness measurement [10] and fluorescence microscopy [11]. Another study of the transition zone evolution in cement composites, with cellulose fibres, registered an increase in porosity [12]. Experimental evidence indicates that porous concrete creates a new environment, because aquatic organisms including algae adhere to the insides and surfaces of porous concrete [13].

The local authority responsible for the coastal protection scheme (the test site) have utilised high pressure water (1200 psi), dispensed from motorised units with multioscillating jets to remove algae from the surface of the revetment armour. The stepped design allows access to the beach by the public, but algae create a slip hazard. The fully exposed armour units face westwards and are subject to cyclic wetting and drying conditions. The exposure is very harsh due to wave action, which is exacerbated by sand and occasionally pebbles and debris. These conditions meant that, in the design stage, surface loss during service was anticipated. Algae must absorb water, carbon dioxide and other nutrients through their fronds to respire, photosynthesis and grow [14]; they are vital for the health of our coastal waters. The dominant algal genus at the test site is *Ulva*, a conspicuous bright grass-green seaweed, consisting of inflated irregularly constricted, tubular fronds that grow from a small discoid base and it is a common, green macroalga (larger genus, seen without a microscope) found throughout the world. Fronds from the test site ranged from 10 cm to over 20 cm in length. Their dispersal, colonisation and adhesion have been investigated elsewhere [15]. Recent research into fibre reinforced cement roof tiles confirmed the growth of the *Cyanobacterium Scytonema* (a blue green alga) within cementitious elements, causing cohesive failure [16]. Recent SEM investigations [17] of degradation due to algal colonisation of cracks within polymers revealed that polythene acts as a substratum. Previous research by the author [18] investigated the colonisation of various polymers. The aim of this study was to observe marine algal colonisation at the fibre-cement matrix interface, and to see how its presence may affect synthetic fibre performance in the environment. To achieve this aim synthetic fibres within precast elements have been microscopically examined and monitored for 7 years at a marine test site. The environmental performance of the fibres has been observed before and after tidal impact, power washing and colonisation. A limitation to this case study is that it involves only a single site and therefore may not be representative of marine environments in general.

2. Materials and methods

2.1. Concrete specimens

The test site, on the North West coast of England, has been surveyed and monitored over the full length of the construction period, approximately 7 years. The synthetic macro and microfibre reinforced concrete has been used in the manufacture of revetment armour as part of a coastal protection scheme. The precast units, see Fig. 1, are 5 m by 3.5 m, weigh 20 t and contain 8 m^3 of fibre reinforced concrete. Original casting of units was monitored and the same units have been regularly examined over the years in situ. The 'as struck' concrete units were cast in a horizontal, 'upside down' position in steel moulds. The compressive strength class was C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4. Water cement ratio of 0.45%. Minimum cement content 340 kg/m^3, CEMIIIA, with 50% ground granulated blast furnace slag and a chloride class of 0.2. (maximum chloride content of the concrete, 0.20% by mass of cement). Fresh concrete was supplied by the manufacturer, formed into cubes, cured, then dry diamond cut into 150 mm × 150 mm × 25 mm pieces, (Norton, Clipper brick and tile cutter) washed and examined. Some specimens were secured on site and on occasion retrieved, microscopically examined, and then returned to the site. Subsequently, colonised surface specimens, affected to a depth of 10 mm, from the armour units in situ were obtained.

2.2. Microscopy

Concrete samples were initially observed with a Leica Strata Lab, monocular light microscope, Meiji MT4000 Biological and a Zeiss Axiovert 40 MAT inverted microscope with a large specimen stage, ideal for the examination of heavy and bulky concrete specimens. Individual fibres and algae were also observed on glass slides with a cover slip. The Axiovert was fitted with a 5 megapixel, high-resolution digital camera. These images were measured with the AxioVison AC software [19]. This software allowed accurate measurement, image processing and analysis of algal fronds and remnant synthetic fibres on a captured image. Visual examination of samples revealed large-scale features such as, the nature of the external concrete and fibre surfaces, the presence and position of both types of fibre reinforcement within the matrix, and the fibre shape and diameter under stress.

2.3. SEM–EDX

Algal morphological characteristics, concrete topography, fibre phases, distribution and orientation, were observed using a scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser, (EDX) using Genesis software. The FEI Quanta 200 used in this research is capable of producing high resolution digital images at over 100,000× magnification, allowing objects as close as 3.5 nm to be resolved. Specimens were cleaned with a jet of air before gold sputtering, (Emitech K550X), at 25 milliamps for 2 min. Specimens were examined by secondary electron (SE) signal with a low accelerating voltage of 10–12 kv to reduce beam damage. The chamber can accommodate samples up to 5 × 5 × 2 cm in size.

2.4. Fibre details

New (unused) macrosynthetic fibres have been secured and monitored in a outdoor, non-marine, controlled environment, to observe the fibres susceptibility to UV irradiation.

2.5. Algal identification

Ulva was identified to the genus level on the basis of morphological characteristics observed (Meiji MT4000 Biological) such as thallus and cell arrangement [20]. Fresh algal samples were also taken from the site, cleaned, (Decon 90), and ground to powder. DNA was extracted from specimens, using (DNeasy) Blood and tissue kit, (Qiagen), according to manufacturer's protocol. New barcodes (sequences) were aligned with published sequences, (BOLD) [21].

3. Results

3.1. Microscopical analysis

The majority of concrete specimens examined, were from an area of the revetment armour which was only submerged by high tide. Fig. 2 depicts a macrofibre, within a relatively new armour surface, appearing to be free of algae, but on close inspection algae was present. Fig. 3 is a typical representation of macrofibres at the surface of the concrete from the test site. Figs. 4–7 Light microscope images enable colour observations of algal fronds, as the microfibres (clear and 22 μm in diameter) used in the concrete matrix could be easily mistaken for algae. SEM micrographs, Figs. 8–11 are from (winter) samples retrieved from site, showing abundant growth within the fibre cement interface. Fig. 8 shows a sample that was not sputter coated, to show the frond in its natural condition. Coatings gave the algae an artificial, smooth surface. Confirmation between algae or microfibre was obtained by EDX analysis.

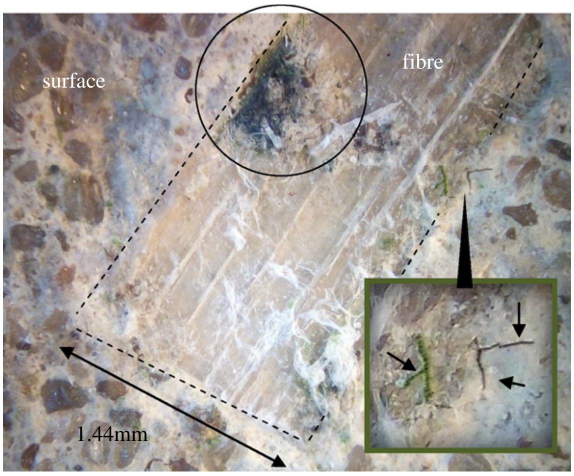


Fig. 2. Light microscope, surface view after 1 year's exposure, of a horizontal fibre specimen. Growth can be seen underneath the fibre. Insert; depicts a crack at fibre cement interface and a frond growing out and then back into the fibre. Refer to phase 1 of the model, Fig. 12.

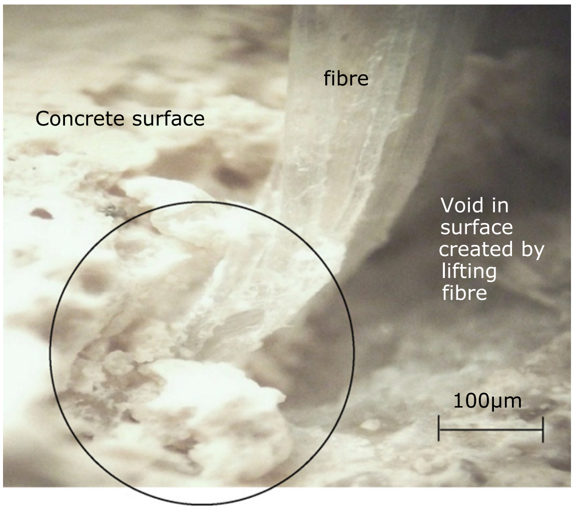


Fig. 3. Light microscope, surface view of vertically orientated fibre. This fibre specimen was from a new piece of concrete (not used at site). In some cases, a fibre may move from horizontal to a vertical orientation, leaving a void at the surface, see model phase 4. Fibre entry into a fractured surface (circled) can be observed.

4. Discussion

There is a growing interest within the field of concrete durability research in the holistic approach. According to this approach, all aspects of a complex system, an integrated whole, can be fully understood and controlled by reducing it to parts and by considering one part at a time. Based on field experience, surveys and microscopic investigation, a holistic model is proposed here for predicting the degradation of synthetic fibres within marine concrete (Fig. 12).

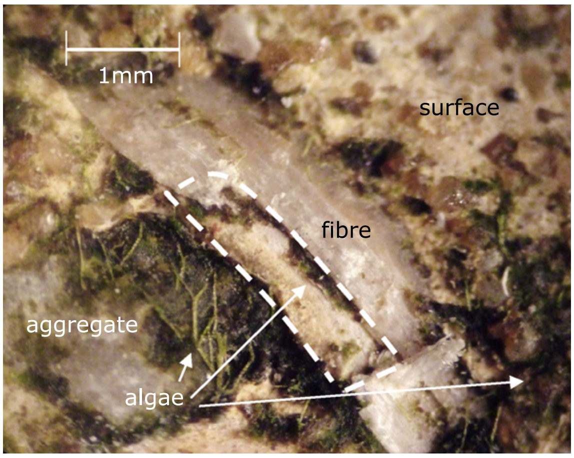


Fig. 4. Light microscope, surface view of concrete specimen retrieved from site after 3 years exposure. Macrosynthetic fibre partly exposed and fractured. Lost fibre material has been indicated by broken white line. Colonisation indicated by white arrows can be observed at the surface, under the remaining fibre and across the limestone aggregate. See phase 3 of model (Fig. 12).

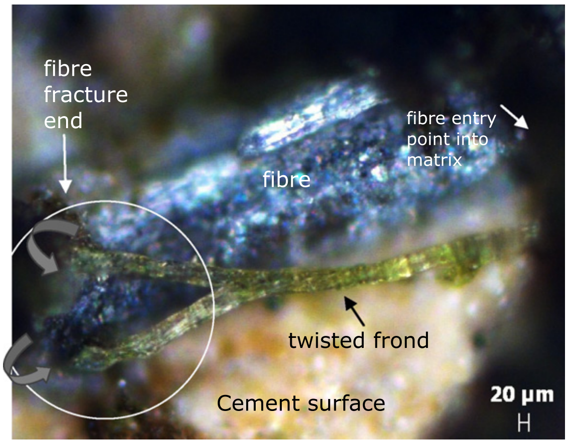


Fig. 5. Light, inverted microscope, surface view of concrete specimen retrieved from site after 3 years, showing remnant of macrosynthetic fibre protruding from the cement surface. A hydrated frond has created a loop and anchored around the end of the fibre.

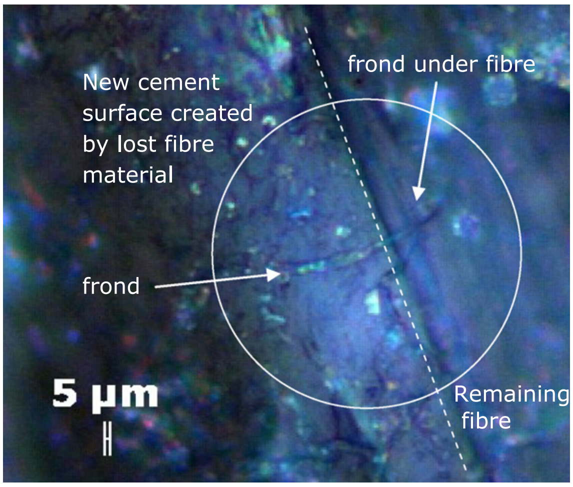


Fig. 6. Light, inverted microscope, surface view of concrete specimen retrieved from site after 2 years, showing a macrosynthetic fibre partly removed creating a new surface. White line indicates fibre fracture. A juvenile frond can be seen attached to this newly exposed surface extending through the interface of the remaining fibre and cement matrix.

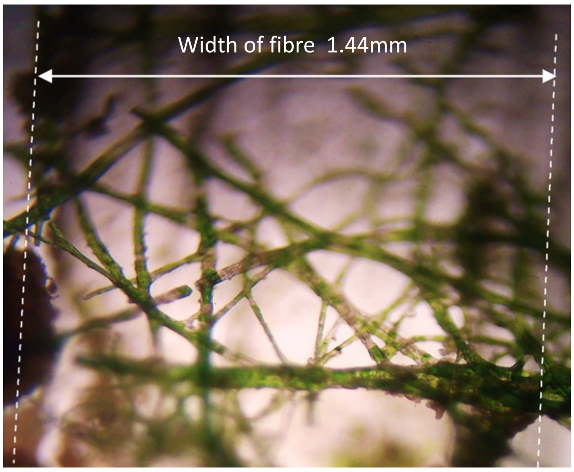


Fig. 7. Light microscope, surface view of the underside of a macrosynthetic fibre collected from site, after 4 years exposure. Interconnected, hydrated fronds are able to grow at the interface of fibre and cement across the width of the fibre.

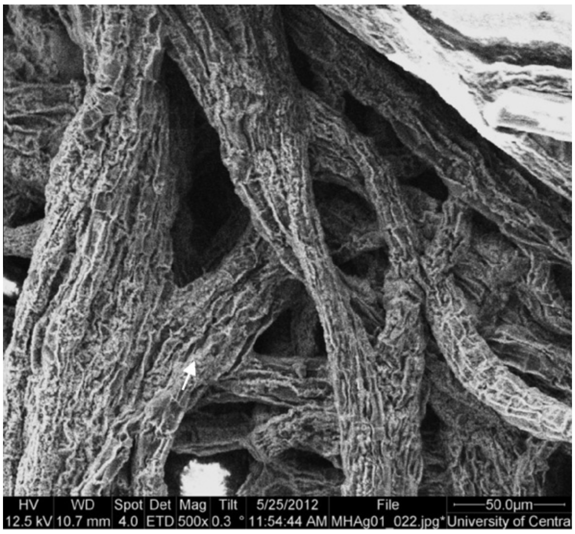


Fig. 8. SEM micrograph, side view of algal colonisation under a fibre specimen, after 4 years exposure.

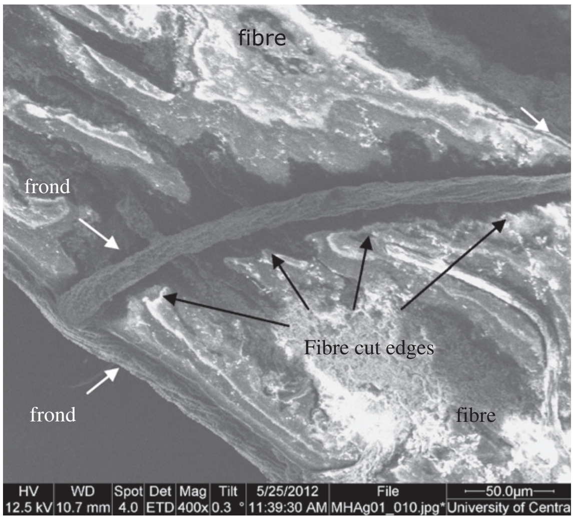


Fig. 9. SEM micrograph, surface view of frond which has cut across the face, through the fibre.

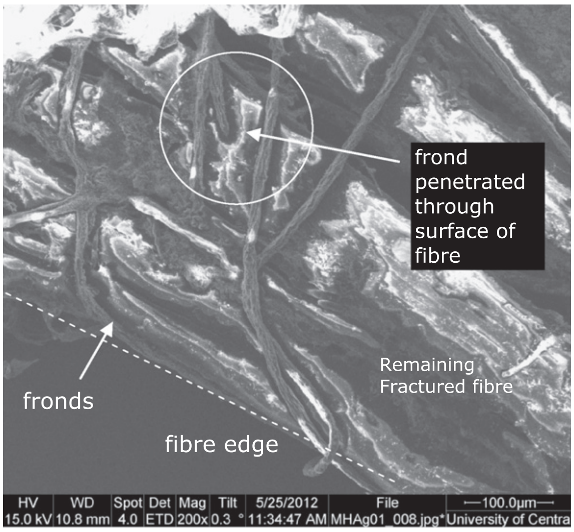


Fig. 10. SEM micrograph, surface view of specimen retrieved from site, after 4 years exposure. White line indicates the edge of the fibre. Note a frond that has penetrated the surface of the fibre (circled).

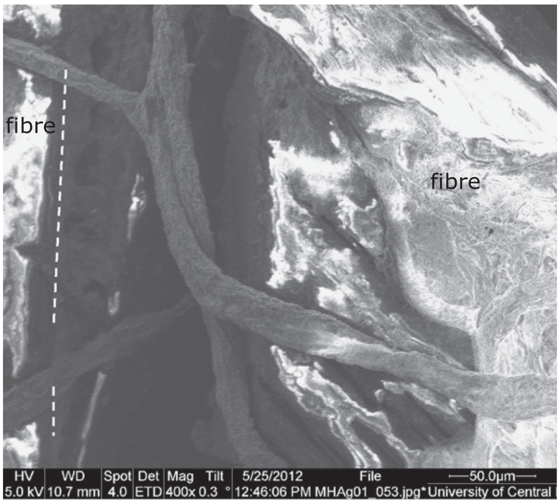


Fig. 11. SEM micrograph, surface view of frond firmly anchored and able to grow freely between fibre and surface of cement.

The salient elements of the model can be explained as follows:

1. A new surface with horizontal orientated fibres is initially shown. As with [2] this model starts with the presence of cracks. The new surface of the revetment armour contains many protruding fibres. Immediately these exposed fibres are subject to tidal action, as well as biofouling control, where the surface is power washed and treated with a chlorine-based disinfectant.
2. The second phase of the model also depicts a new surface, however fibres are shown in a vertical orientation. The entry point of fibre into the matrix, not present in a horizontal fibre, becomes damaged as the exposed part of the fibre reacts to environmental conditions such as submersion in seawater, rich in algae.
3. Colonisation is shown in the next stage of the model. The ingress of moisture through cracks and damaged areas around exposed fibres, allows microorganisms to penetrate the surface under the fibres and to attach, this leading to colonisation.
4. Fibre 'Pop out'. The presence of growth at the fibre cement interface accelerates bond weakening, causing fibres to 'pop out' from the surface and eventually falling away. This leaves voids at the surface, allowing spores to enter and more algal attachment to take place.
5. Fracture. Algal fronds grow abundantly between fibrillated and monofilament fibres.
6. Material loss is accelerated due to the fronds weakening and displacing the material. As degradation progresses, more fibres are lost, resulting in a more permeable cement matrix. This entire process continues and phase one of the model now repeats in sequence. Due to variations in the fibre orientation, environmental conditions and fibre positions within the revetment armour (splash/submerged zones), a precise determination of the length of each stage is not possible.

In the production of the concrete armour units, industry recommendations and fibre manufacturer's guidelines require surface finishing by float or trowel to produce a finish without surface exposed fibres [5]. Such finishing techniques, however, cannot be used as the units at the test site are cast upside down. From site observations, many fibres can be seen of varying orientations at the surface of new units; with many protruding from the surface. For an example of a fibre of horizontal orientation taken from site, see Fig. 2. For an example of a vertical orientated fibre, see Fig. 3. The macrofibres can be seen with the naked eye, however the microfibres are just as abundant when viewed by microscope. This 'hairy' substratum offers more surface area for algal attachment and possible entry points into the interior of the concrete. Figs. 2 and 3 shows clear features of entry points into the cement matrix interface for water-borne microorganisms. This is the starting point for the holistic degradation model, (Fig. 12; phase 1 and 2), highlighted in red. Tidal impact, power washing and the use of chlorine-based disinfectant also start at this point see Fig. 13.

The next element of the model, phase 3, depicts colonisation. Surface algae are often cleared with power washing, however penetration into the surface, particularly under fibres, offers refuge from hydraulic forces. There presence at the cement interface disrupts or distorts the fibre by growth, not using it as a food source. When algae colonise concrete structures they start to absorb calcium, silica and magnesium [22]. This colonisation is observed in Fig. 4, where the majority of growth is on the underside of the fibre in contact with the concrete, however growth is also noted on the fibre surface. It is also important to note that algae can act as the focus for other biofouling organisms such as fungi and bacteria, so that the deterioration process may gain momentum after the structure's condition has become suitable for the survival of one or more such organisms. The observations made in this research, compliments a study of algal growth on fibre cement [16] confirming biodeterioration of the cementitious components. The fronds (Fig. 5) absorb and store seawater and associated nutrients during periods of submersion and from moisture found within the concrete. If the conditions (nutrients, UV, temperature, and seawater) are favourable, the fronds will grow, and extend over larger and deeper areas of the concrete. The effects of shrinking and swelling of the hydrophilic fronds during dry conditions and periods of moisture intake, will accelerate the mechanical biodeterioration process of the fibre bond and cement.

Phase 4 of the model represents fibre 'pop out'. Fig. 6, shows the track left by part of the fibre having left the substratum; the circle depicts the growing juvenile frond under the remaining fibre. The presence of this growth at the fibre cement interface, which can be 0.15–0.25 cm/day [23] accelerates bond weakening, making the fibre more susceptible to environmental conditions and encouraging fibres to 'pop out' from the surface of the cement. Algal fronds grow freely in between fibrillated and monofilament fibres leading to phase 5 of the model. (Figs. 9 and 10) highlight the opportunity for growth, enabling the fronds to cut through the fibres. It was at

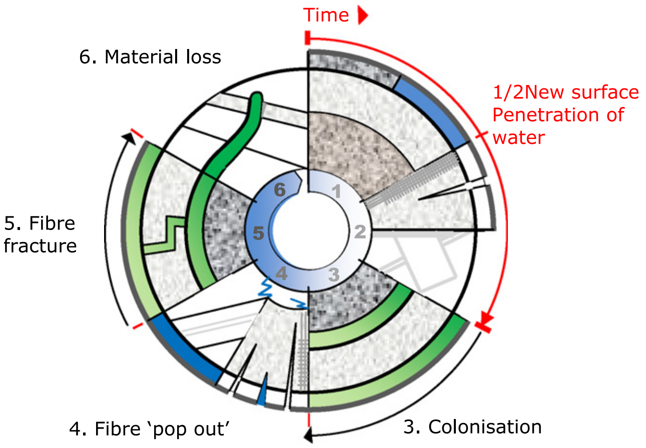
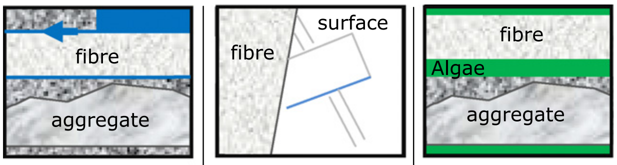


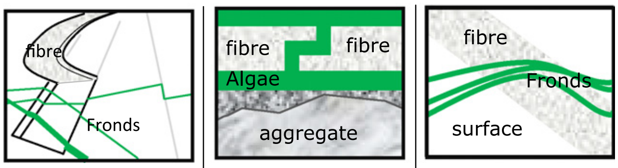
Fig. 12. Holistic fibre degradation model.



1–NEW SURFACE side elevation of a new substratum with a horizontal orientated fibre partly exposed which will allows moisture ingress. Cover from surface to large aggregate can be as little as 1mm. See figure 4 for site example.

2–NEW SURFACE plan view of a new substratum with a vertical orientated fibre protruding from the surface. See figure 5 for site example, once water tightness is lost (circled) water carrying microorganisms can be transported into the interior.

3-COLONISATION side elevation of a horizontal orientated fibre having lost its initial cover through expected erosion and colonized above and below the fibre. See figure 6 for example.



4–POP-OUT plan elevation of a substratum with a horizontal orientated fibre lifting out from the surface. Figure 8 shows frond growing under fibre

5-FRACTURE side elevation of a substratum with a horizontal orientated fibre partly begins to fracture allowing fronds to grow. See figure 12.

6–MATERIAL LOSS plan elevation with remnants of a horizontal orientated fibre. Figure 13 shows fronds freely growing within remaing fibres.

Fig. 13. Six, phases of the holistic degradation model.

this stage in the research it was found that fronds could be mistaken for fibres. Initial observations of site specimens were made using light microscopy. This knowledge of the topography and colonisation was helpful in the identification at the SEM analysis (monochrome) stage of the research. The microfibres could easily be mistaken for juvenile *Ulva* fronds, therefore EDX was used to confirm the specimen under investigation was a frond along with a visual reference from earlier light microscopy (being in colour). Finally phase 6 of the model depicts the material loss, and demonstrates how the algae grow. Unused fibres were monitored in an exposed, non-marine environment, after 1 year they became hard and brittle.

The addition of excess nutrients from land run-offs of phosphates and nitrates from chemical fertilizers and sewage disposal, encourage algae to grow abundantly on site. By adopting the holistic approach, poor water quality leading to an algal rich environment and the use of chlorine must be considered as valid parts of the model of degradation.

5. Conclusions

This study is the first to report the composition of *Ulva* assemblages fouling and degrading synthetic fibres within marine concrete in the UK. Various established microscopic techniques were used to investigate the colonisation of synthetic fibres. These techniques complemented each other in the structural analysis of colonisation, to build a new and more complete picture showing their opportunistic growth. The aim of this study was to observe marine algal colonisation at the fibre cement matrix interface, and how it affected synthetic fibre performance. Synthetic fibres within precast elements have been investigated, examined and monitored for 7 years at a marine test site. The present observations reveal algal growth in between fibre and cement. The mechanism described is detrimental to the long term performance of the fibres and has a significant effect on the durability of the concrete surface.

Degradation, either through the algal attack or through other mechanical means (e.g., power washing), is not the primary cause of degradation, but exacerbates the condition. Exposed fibres on new concrete units and eroded surfaces offer opportunities for further algal attachment. This research has generated new insights into algal colonisation and opens up the prospect of more detailed studies on the mechanical biodeterioration of fibre reinforced marine concrete.

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Microscopic study into biodeterioration of marine concrete

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ABSTRACT

This research presents an exploratory study into the biodeterioration of marine concrete. Monocular and inverted light microscopy, scanning electron microscopy (SEM) with energy dispersive X-ray analyser (EDX) were used to observe colonisation of site specimens at the fine aggregate cement interface, enabling the further understanding of this interaction. Algal filaments have been observed growing between fine aggregate and cement. Colonisation has been observed, entangled around, and adhered to fine aggregate. This degradation mechanism occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its growth. Loss of surface material, either through biodeterioration or through other mechanical means, such as power washing, is not the primary cause of degradation, but may exacerbate the condition.

1. Introduction

The fouling of concrete surfaces by microorganisms can have detrimental effects, accelerating deterioration of the structure (Gaylarde and Morton, 1999). Once established on concrete revetment armour steps, as observed at the Fylde coast, UK study site, growths form a slippery surface and may constitute a danger to the public. More direct damage can be caused to the concrete itself by the acids and other metabolites produced by the organisms, which together with the ability of some species to tunnel into surfaces, leads to degradation, increased porosity and decreased durability (Allsopp et al., 2004). Durability of marine concrete, the essence of this study, is arguably its principal property; it is important that concrete should be capable of withstanding the harsh conditions throughout the expected life of the structure.

In cement composites with aggregate inclusions the matrix in the vicinity of the inclusion can be quite different in its microstructure to that of the bulk cement matrix. This modified matrix can be as great as 50–100 μm in area (Bentur et al., 1995). The higher porosity at this interface, together with a smooth, well rounded texture of some types fine aggregate (beach sand), favour the appearance and development of biodeterioration. Experimental evidence indicates that porous concrete creates a favourable environment for microbial colonisation, because aquatic organisms including algae adhere to both the inner and outer surfaces (Tamai et al., 1992).

Algae are a diverse group of photosynthetic organisms ranging from microscopic single-cell micro-organisms to very large organisms such as seaweed. Many commonly occurring fouling algae belong to the macroalgal group Chlorophyta (green algae). The Chlorophytes comprise a number of genera and species that actively bore in carbonate substrates. They produce branching networks of tunnels varying greatly in size. Some may be as little as 2 μm in diameter. In some species such fine filaments may collect together in main canals as wide as 25 μm (Golubic et al., 1975). Concrete structures in tropical and sub-tropical seas have been shown to be subject to the same biodeterioration forces as carbonate substrates. Many of the species implicated in calcium carbonate disintegration have been demonstrated to be capable of the biodeterioration of concrete (Scott et al., 1988). Attached macroalgae obtain different elements for their metabolism from the substratum. When algae colonise concrete structures they start to absorb calcium, silica and magnesium (Javaherdashti et al., 2009). Research into the degradation of marine concrete (Jayakumar and

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Saravanane, 2009) showed that marine algae had utilized crystals like Yeelimite, Gismondine and Portlandite (calcium hydroxide) as a source of minerals. This study looks at a site where *Ulva* is the dominant algal genus, a conspicuous bright grass-green seaweed, consisting of inflated irregularly constricted, tubular filaments that grow from a small discoid base, it is a common, green macroalga found throughout the world. Filaments from the site ranged from 10 cm to over 20 cm in length. Their dispersal, colonisation and adhesion have been described elsewhere (Callow and Callow, 2002).

The aim of this study was to observe marine algal colonisation at the fine aggregate-cement matrix interface, and to see how its presence may affect fine aggregate performance within the cement matrix. To achieve this aim fine aggregate (sometimes referred to as sand) within precast concrete elements has been microscopically examined and monitored for seven years at the marine study site.

This research presents an exploratory site study into the biodeterioration of marine concrete. Microscopic examination of the bond between fine aggregate, cement and algae enables the further understanding of this interaction. The mechanism observed and presented in this study occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth (Morton, 2003).

2. Materials and methods

2.1. Concrete specimens

The study site for this research is part of a coastal protection scheme, which involved the placing of 65,000 m^3 of ready mix concrete and 44,000 m^3 of precast concrete revetment armour. The project has been surveyed and monitored over the full length of the construction period, approximately 7 years. The fine aggregate studied was used in the manufacture of the revetment armour. The precast concrete units, measure 5 m by 3.5 m, weigh 20t and contain 8 m^3 of synthetic fibre reinforced concrete. Original casting of units was monitored and the same units have been regularly examined over the years *in situ*. The 'as struck' concrete surface exposed to the sea was cast in a horizontal, 'upside down' position against a steel mould. The compressive strength class is C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4 and water/cement ratio of 0.45. The minimum cement content of 340 kg/m^3, CEMIIIA, with 50% ggbs, chloride class 0,2. Concrete prisms (150 mm × 150 mm × 500 mm long) were also supplied by the manufacturer, some were dry diamond cut into 25 mm lengths, (Norton, Clipper brick and tile cutter) washed and examined. Some specimens (cut as above) were placed at the site, in the splash zone strapped to a pipe. At intervals the specimens were retrieved, microscopically examined, and returned to the site. Subsequently, colonised surface fragments breaking from the revetment armour units were obtained.

2.2. Study site fine aggregate details

Marine dredged sand was extracted from the beach, 5 km from site, and blended with crushed limestone for use as fine aggregate by the precast concrete manufacturer. The sand was washed with sea water to reduce silt content and then screened to remove any significant debris such as litter and driftwood. The chloride content of the sand was monitored weekly. The fluvio-glacial deposits on the floor of the eastern Irish Sea adjacent to the study site are the dominant source of sediments. Whole-rock mineralogical analysis of a range of intertidal sediment samples has shown that they are predominantly quartz with associate plagioclase, orthoclase, calcite, dolomite, chlorite/kaolinite and mica (Bryant et al., 1996). Beach sand samples were collected by hand 1 km seaward from the sea defence site, adjacent the dredging area.

2.3. Study site and exposure conditions

The concrete stepped revetment armour allowing open access to the beach is constantly colonised by algae, predominantly *Ulva*, creating a slip hazard to the public. The colonisation of newly placed pre-cast elements on site-was noted; some became covered with algae after only a few weeks of exposure. The local authority have utilised high pressure water (1200 psi), dispensed from motorised units with multi oscillating jets, to remove the algae. The fully exposed units face westwards and are subject to cyclic wetting and drying conditions. The exposure is very harsh due to wave action, which is exacerbated by sand and occasionally shingle and debris. Because of this, surface erosion during service was anticipated in the design stage. This erosion has occurred at many locations, particularly at inter-tidal regions, where an exposed aggregate appearance was noted and patch repairs have been carried out. The primary role of the revetment armour is coastal protection and as such is subject to the wear associated with tidal and wave action, hence the design team and client expected a degree of surface deterioration.

2.4. Sample analysis – microscopy

Approximately 25 Concrete samples (50 mm × 25 mm × 10 mm) retrieved from site over a five year period were initially observed with a Leica Strata Lab, monocular light microscope, and then with a Meiji MT4000 Biological and a Zeiss Axiovert 40 MAT inverted microscope with a large specimen stage, ideal for the examination of heavy and bulky concrete specimens. All samples had filamentous growth. Individual sand grains collected from the beach and algal specimens from the study site were also observed on glass slides with a cover slip. The Axiovert was fitted with a 5 megapixel, high-resolution digital camera. These images were measured with the AxioVison AC software (Zeiss, 2001). This software allowed accurate measurement, image processing and analysis of algal filaments, diatoms and sand grains on a captured image. Visual examination of samples revealed large-scale features such as the nature of the external concrete and sand surfaces, and the presence of fine aggregate within the matrix.

2.5. SEM – EDX

Algal morphological characteristics, concrete topography and, fine aggregate distribution were observed using a FEI Quanta 200 scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser, (EDX) using Genesis software. EDX was used for the elemental analysis of synthetic fibres within the cement matrix and of algal filaments. 10 site specimens were cleaned with a jet of air, to remove unattached algae, before gold sputtering (Emitech K550X) at 25 milliamps for 2 min. Specimens were examined by secondary electron (SE) signal to show morphology, backscattered electrons (BS) to reflect differences in atomic number, with a low accelerating voltage of 10–12 kv to reduce beam damage. The chamber can accommodate samples up to 5 cm × 5cm × 2 cm in size.

2.6. Algal identification

The sea defence site offers hard substrata in areas that are largely sedimentary, thus providing discrete new habitats for opportunistic colonising species. The revetment supports a plant and animal community characteristic of a rocky shore, tending to be dominated by encrusting mussels, barnacles and a variety of algal species. Resident algae include: *Ascophylum nodosum*, *Fucus vesiculosus*, *Fucus spiralis*, *Porphyra umbilicalis and Halidrys siliquosa*. *Ulva* was identified to the genus level on the basis of morphological characteristics observed (Meiji MT4000 Biological) such as thallus and cell arrangement (Blomster et al., 1998). Fresh algal samples were also taken from site, cleaned, (Decon 90), and ground to powder. DNA was successfully extracted from one specimen, using (DNeasy) Blood and tissue kit, (Qiagen), according to manufacturer's protocol. New barcodes (sequences) were aligned with published sequences, (The Consortium for the barcode of life, 2009).

3. Results and discussion

It has been shown that algal filaments at the study site can grow freely between fine aggregate and the cement matrix of the concrete revetment armour. The light-inverted microscope images, Figs. 1–4., demonstrate the existence of complex microbial populations around the surface of the fine aggregate, within the armour concrete. This complexity is increased when one considers that algal assemblages are composed of a large number of species, providing an incredibly complex system for investigation. Fig. 1 indicates the destructive presence of growth which will lead to the eventual release of the fine aggregate. It is not suggested that this mechanical degradation mechanism, by algal growth is solely responsible for the erosion observed at the site, but it is suggested that it should be considered as a factor along with tidal action, power washing and biofouling control, such as treatment with a chlorine-based disinfectant.

Fig. 5 shows the upward and outward epilithic growth of coiled algal filaments, exiting the substratum between fine aggregate particles. Fig. 6 shows a compressed, branched filament with epilithic characteristics of algal growth on fine aggregate within the matrix. EDX was used throughout the investigation, enabling element analysis to distinguish between synthetic micro fibres (22 μm in diameter) and algal filaments, often of similar size. Micro fibres showed 86% (Wt.) carbon and 14% oxygen, where algal filaments showed 24% carbon and 66% oxygen. EDX analysis of the colonised cement matrix compared to new concrete at the test site indicated the loss of calcium over two years and is the subject of further work.

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades (Newman, 1968). Marine aggregates are an important source of sand for the construction market in the UK and continental Europe; however, no provision is made in the current standards for the control of algae growing within or on the surface of beach sand.

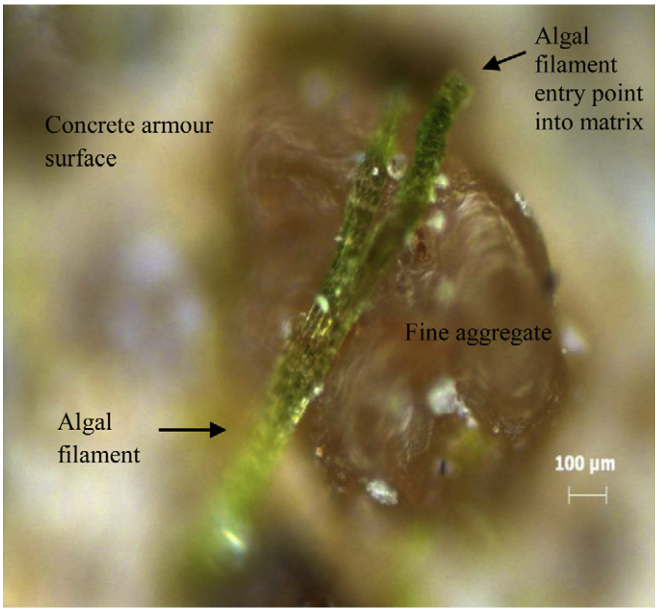

Fig. 2. Light inverted microscope surface view of revetment armour concrete sample, after 2 years exposure. Boring, mature algal filaments can be seen wrapping around the partly exposed fine aggregate, eventually penetrating the cement matrix.

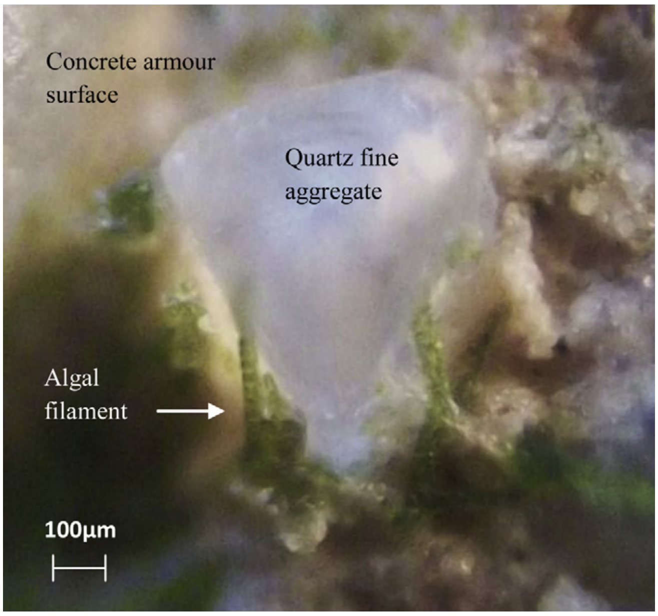

Fig. 1. Light microscope surface view of revetment armour concrete sample, after 2 years exposure. Algal filaments can be seen growing from the surface of the matrix, up and around the contour of the almost fully exposed quartz fine aggregate.

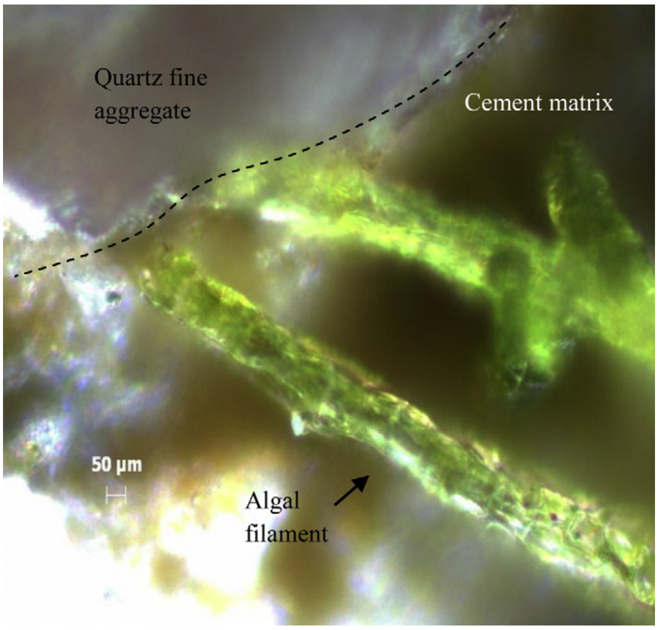

Fig. 3. Light inverted microscope surface view of revetment armour concrete sample, after 3 years exposure. Mature algal filaments are growing out of the aggregate cement interface (indicated by the dotted line).

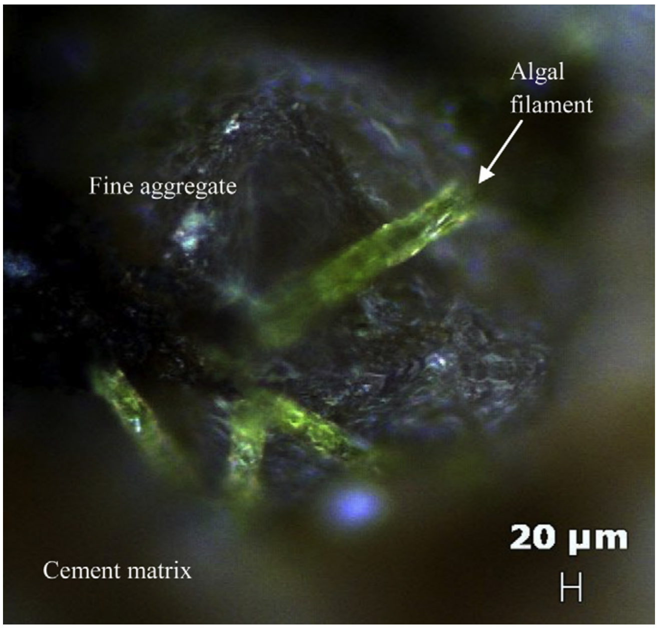

Fig. 4. Light inverted microscope surface view of revetment armour concrete sample, after 2 years exposure. Boring, mature algal filament seen wrapping around partly exposed fine aggregate, eventually penetrating the cement matrix.

Fig. 6. SEM, secondary electron micrograph, surface view of revetment armour concrete surface, after 3 years exposure. This sample was not sputter coated, showing the filament in its natural condition. A branched mature filament can be seen growing over the exposed fine aggregate.

Research by Round (1965) pointed out how little was known about the algal communities that live on sand, (see Figs. 7 and 8). His report was followed by a number of studies describing problems of algal attachment, production and burial in marine sands (Cadee and Hegeman, 1974). Since then, more has been learnt about species composition (Edlund et al., 1996), life cycles (Jewson and Lowry, 1993) and aspects of colonization, however, we still know relatively little about the ecology of individual species and their specialized adaptations for living on sand. Steele et al. (1970) found viable cells buried to a depth of 0.2 m below the sand surface in a Scottish sea loch. A similar finding occurred 200 km from the source of the marine aggregate used at the study site, in Lough Neagh, where high concentrations of living cells were found attached to sand grains down to 0.5 m below the sand surface (Jewson and Briggs, 1993). Considering the constant mixing of sediment at a beach surface, it may follow that microbial endoliths could occupy some of the beach extraction of fine aggregate used at the study site.

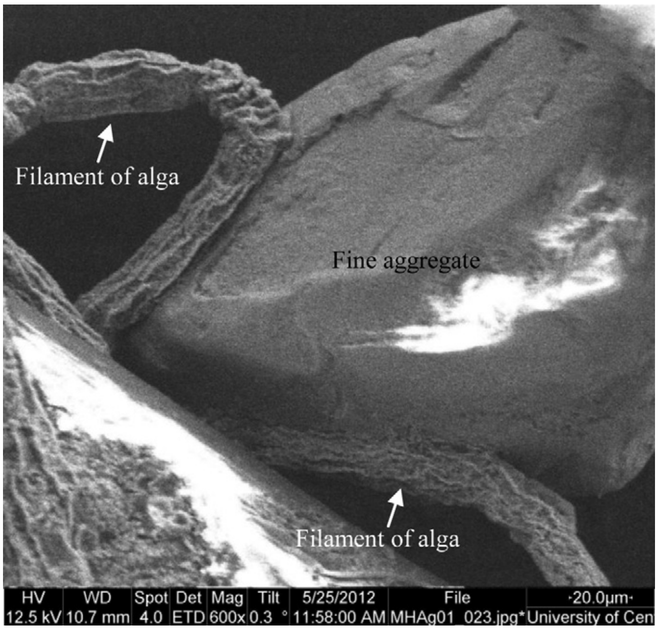

Fig. 5. SEM, secondary electron micrograph, side view of revetment armour concrete surface, after 3 years exposure. This sample was not sputter coated, showing the algae filament in its natural condition. The filament can be clearly observed growing freely around the almost fully exposed fine aggregate.

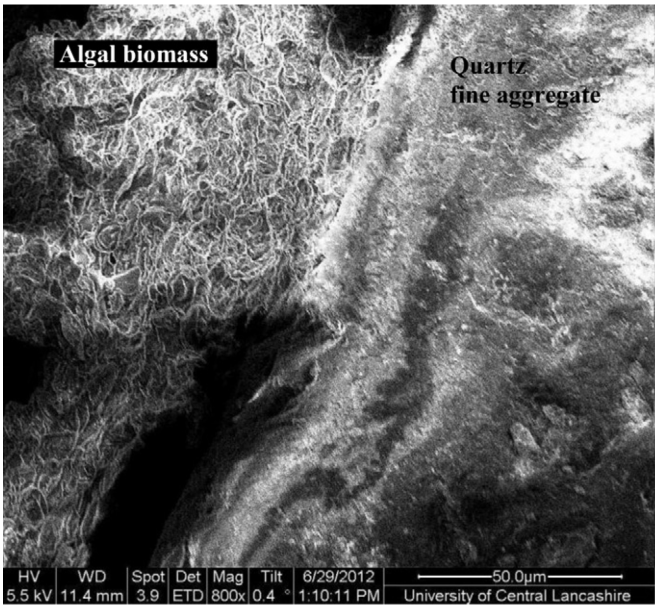

Fig. 7. SEM, secondary electron, low voltage micrograph, surface view of revetment armour concrete surface, after 3 years exposure. The algal biomass can be clearly seen attached and growing on the partly exposed quartz fine aggregate particle.

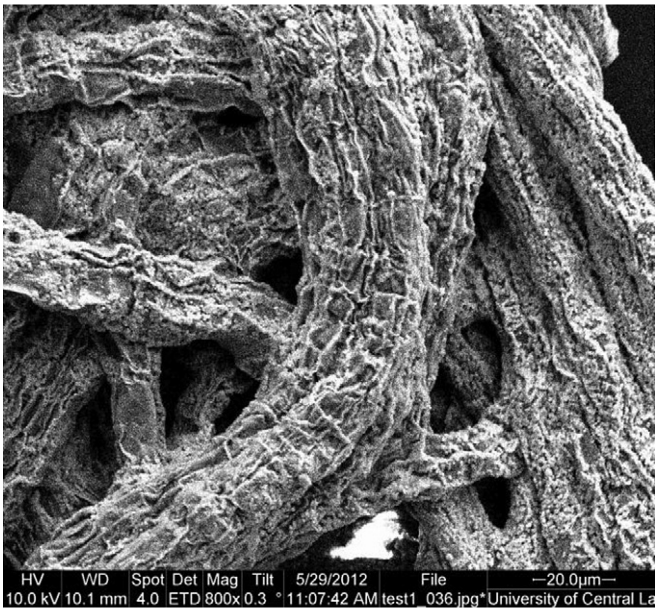

Fig. 8. SEM, secondary electron micrograph, side view of void within revetment armour concrete matrix, after 2 years exposure. The dehydrated, branched algal filaments can be clearly seen.

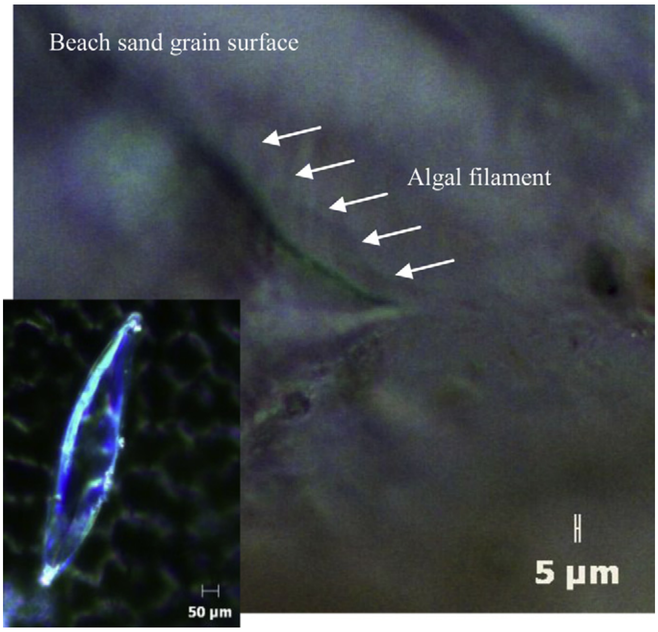

Fig. 10. Light inverted microscope, surface view of beach sand specimen from site. An algal filament can be seen attached to the surface (indicated by arrows). Insert: Diatom from beach sand sample.

Beach sand samples from the vicinity of the study site (the source of fine aggregate used in the concrete production) were examined under the microscope and found to be colonised by algal filaments and diatoms, see Figs. 9 and 10. The existence of microbial populations that live on or within sand is well documented (Miller et al., 1987) investigated the role of micro-topography of sand grains and its influence on distribution of diatoms demonstrating habitat partitioning. The work of Krejci and Lowe (1986) documented the role of sand grain mineralogy on colonisation using SEM for sand grain elemental analysis. Further examples were presented by Greenwood et al. (1999) who also used SEM to examine the distribution and behaviour of diatoms moving through sediments. The work of Huang and Boney (1984) showed that interactions take place between juvenile macroalgae and littoral diatoms. Young plants of *Ulva* grown in the presence of diatoms showed growth enhancement. It is hypothesized that such interactions may take place at the fine aggregate cement interface, between pioneering algal spores and original resident sand dwellers. If the growth of young *Ulva* plants is enhanced in the presence of a diatom population then a more rapid onset of reproductive phases of the green alga will occur, with production of more young plants, in turn interacting with the diatom populations. Certain diatom-green algae synergistic combinations may thus favour a more rapid colonization process by green algae, as seen at the study site, as early colonisation of new precast concrete elements and are in themselves highly resistant to strong alkaline conditions found in concrete.

Large quantities of aggregates are obtained from marine deposits, and are widely and satisfactorily used for making concrete including prestigious structures within hostile environments, such as the second Severn Crossing, Canary Wharf development and the Channel Tunnel Rail Link (BRE, 2008). The aggregate has to be used with care: The British Cement Association warns that washed beach sand is generally unsuitable by itself for good quality concrete, due to the single-sized grading, but this can be overcome by blending aggregates. While aggregates for unreinforced concrete can be washed with sea water, as was the case for the study site, for reinforced concrete the aggregates must be carefully washed with potable water to remove excess chloride from sea salt, but they will still retain shell and organic matter that can affect the water demand of the mix; the organic matter refers only to water-soluble organic compounds derived from decaying vegetation, tests for which no longer appear within standards. The results of this study suggest that blanket use of marine sourced aggregates should be reconsidered for concrete that is to remain in contact with sea water, particularly mass (unreinforced) concrete. Washing in water may only partly remove some of the epilithic biomass present on the surface

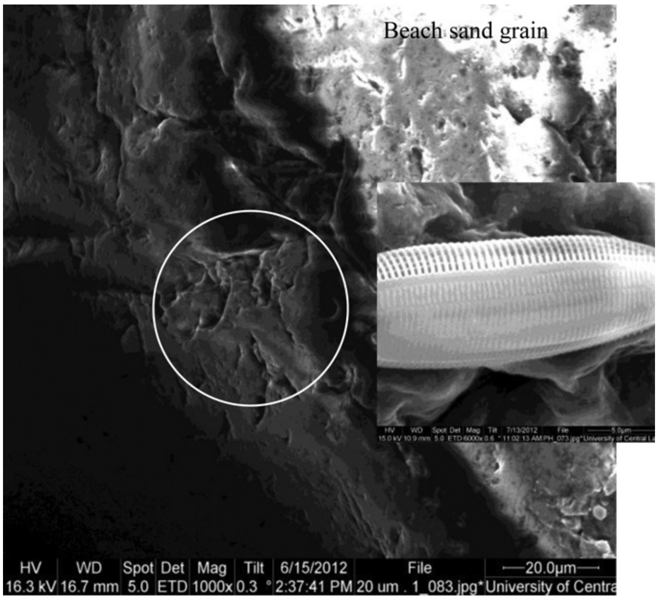

Fig. 9. SEM, secondary electron micrograph, side view of beach sand specimen. This sample was not sputter coated, showing the sand grain in its natural condition. Juvenile algal filaments can be observed growing on the surface of the sand grain (circled). Insert: Diatom from site.

of the aggregate, possibly leaving endolithic algae to continue and thrive. Concrete needs to age in the ocean for at least 6 months before the pH in the surface region approaches the pH of sea water (Guilbeau et al., 2003) hence making a substratum bioreceptive. It has been reported by Cardon et al. (2008) that green algae have resting stages (spores and zygotes) that allow cells to lay dormant in unfavourable environments, even freezing conditions or to survive in ephemeral pools. (Trainor and Gladych, 1995) found that even after soils had air-dried for 35 years, green algae could be cultured.

Therefore the algal content may need to be controlled in structures subject to permanent wetting by sea water to control growth on and inside the surface. BS EN 12620 is the predominant specification concerning the use of aggregates for concrete supported by UK national guidance document PD 6682-1. This guidance should consider undesirable elements such as colonising algae more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that algae will remain on or within the beach fine aggregate, leading to increased colonisation and the biodeterioration of concrete.

4. Conclusions

The aim of this work was to study marine algal colonisation at the fine aggregate-cement matrix interface, and to discuss how its presence may affect fine aggregate performance within the cement matrix. Fine aggregate samples from within precast elements have been examined microscopically and the results presented. The environmental performance of the fine aggregate has been observed before and after tidal impact, colonization and power washing. Biodeterioration of the concrete, by way of coiled algal filaments tunnelling into the fine aggregate cement interface, has been observed. As a result of this research it is proposed that algal presence and growth within the matrix under immersed and tidal conditions must weaken the bond between fine aggregate and cement, accelerating material loss and concrete surface degradation.

Standards and guidance on the use of beach sand ought to define undesirable elements such as colonising algae more closely and place precise limits on their presence. This multidisciplinary study graphically illustrates the potential for biodeterioration of marine concrete, providing a new insight into the destructive habitat of concrete biofouling. A limitation to this case study however, is that it involves only a single site and therefore may not be representative of marine environments in general.

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Microbial degradation of synthetic fibre-reinforced marine concrete

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ABSTRACT

This investigation looked at the microbial degradation of synthetic fibre-reinforced marine concrete. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) of site specimens were used to observe colonisation at the fibre/cement interface. Algal filaments were observed growing between fibre and cement. Microbial filaments were observed entangled with, and adhered to, synthetic fibres. This degradation mechanism occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its growth. This multidisciplinary study, the first to report the composition of microbial assemblages fouling and degrading synthetic fibres within marine concrete in the United Kingdom, lays the foundation for more study into this new phenomenon.

1. Introduction

Microbial degradation of synthetic fibre-reinforced marine concrete observed in this research has implications for the integrity and long-term durability of concrete sea defences. The microbes that influence degradation of concrete are ubiquitous in the environment; they produce either organic or inorganic acids that can dissolve and disintegrate the concrete matrix (Rogers et al., 1993), and physically penetrate into the substrate (Gaylarde and Morton, 1999). Microorganisms such as bacteria, fungi, algae, and lichens have all been widely reported to be involved in the deterioration of concrete (Gaylarde and Morton, 1997; Lisci et al., 2003; Giannantonio et al., 2009; Jayakumar and Saravanane, 2009).

The reported low installation costs, low maintenance, durability, and high-quality finish of precast concrete units used as revetment armour in a marine environment are making this material ever more popular in the construction of sea defences. This proliferation of concrete coastal protection has transformed sections of naturally dynamic coastlines into artificially static, hard substrata. These structures are colonised by epibiotic organisms such as algae that are commonly found in natural rocky habitats. The durability of marine concrete is arguably its principal property; it is important therefore that the concrete should be capable of withstanding the harsh conditions throughout the expected 100-yr life of the structure. It is also important to know and understand the stability of polymer additions within the cement matrix exposed to natural marine environments.

The study site for this research is part of a sea wall, a revetment that forms a coastal defence scheme, concrete armour units protecting the structure against erosion; some parts have been in service for 7 yr. The synthetic fibre-reinforced concrete used in the manufacture of this revetment armour has been used in a marine environment for the first time (Rieder, 2007). Thus there is little information on how the physical properties of the synthetic fibres change with time and how long-term mechanical performance may be affected.

Deterioration of concrete structures usually starts at the surface and progresses into the structure; it is, therefore, the skin of the precast concrete units that is the major factor in the longevity of the concrete. Here we report the results of an investigation on the presence of algal filamentous growth leading to microbial degradation of synthetic fibre-reinforced marine concrete used at this study site, which is on the northwest coast of England.

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2. Materials and methods

2.1. Concrete specimens

The precast concrete units measure 5 m by 3.5 m, weigh 20 tonnes, and contain 8 m^3 of synthetic fibre-reinforced concrete. The “as struck” concrete surface exposed to the sea was cast in a horizontal, “upside-down” position against a steel mould. The compressive strength class was C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4 and water/cement ratio 0.45. Minimum cement content was 340 kg/m^3, CEMIIIA, with 50% ground granulated blast-furnace slag and a chloride class of 0.2; maximum chloride content of the concrete was 0.20% by mass of cement. Concrete prisms (150 × 150 × 500 mm long) were also supplied by the manufacturer; some were dry diamond cut into 25-mm lengths (using a Norton Clipper brick and tile cutter), then washed and examined. Six specimens (cut as above) were fastened in test locations at the study site, in the splash zone, strapped to a pipe. At various timed intervals the specimens were retrieved, microscopically examined, and then returned to the site. Subsequently, surface specimens colonised to a depth of 10 mm were obtained from the armour units in situ.

2.2. Synthetic fibres

Synthetic fibre types used in the revetment concrete include polyethylene and polypropylene macro-fibres, 40 mm in length, 1.4 mm wide, 0.105 mm in depth, rectangular in section, and are dosed into the cement at 3.5 kg/m^3. The micro-fibres are polypropylene, monofilaments, circular in section, 22 µm in diameter, and used at a recommended dosage rate of 0.91 kg/m^3.

2.3. Study site and exposure conditions

The concrete stepped revetment armour allows public open access to the beach and is constantly colonised by microorganisms, creating a slip hazard. The local municipality has utilised high-pressure water (1200 psi), dispensed from motorised units with multi-oscillating jets, to remove the microorganisms. The fully exposed units face westward and are subject to cyclic wetting and drying conditions. The concrete is exposed to harsh wave action, which is exacerbated by sand and occasionally shingle and debris from the beach.

2.4. Sample analysis – SEM – EDX

Microbial morphological characteristics, concrete topography, and fibre distribution were observed using an FEI Quanta 200 scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser (EDX). Genesis software was used for the elemental analysis of synthetic fibres within the cement matrix and of microbial filaments. Sample preparation followed guidance from Echlin (2010). Specimens were attached on a 12-mm (diameter) × 3-mm (deep) aluminium stub, fixed by a 10-mm (diameter) carbon mount with double-sided organic adhesive (agar). Initially specimens were viewed uncoated under low vacuum to observe their general characteristics. Twenty-five specimens were cleaned with a jet of air, to remove unattached microbial growth, before gold sputtering (Emitech K550X) at 25 ma for 2 min (thickness 20 nm) to improve image clarity. Specimens were examined using a 2.5–4.5-µm spot size and a working distance of 15 mm (Goldstein et al., 2003). Secondary electron (SE) emission was used to observe morphology; backscattered electrons (BS) were also used to examine differences in atomic number. A low accelerating voltage (between 8 kV and 12 kV) was utilised to reduce specimen damage from the beam.

2.5. Algal identification

Ulva was identified to the genus level on the basis of morphological characteristics observed using a Meiji MT4000 biological microscope. These characteristics included thallus and cell arrangement (Blomster et al., 1998). Fresh algal samples were also taken from the site, cleaned (Decon 90), and ground to powder. DNA was extracted from specimens using DNeasy blood and tissue kit (Qiagen), according to the manufacturer’s protocol. New barcodes (sequences) were aligned with published sequences (The Consortium for the Barcode of Life, 2009).

3. Results

Microorganisms observed on direct examination of samples were filamentous algae within synthetic fibres and cement matrix to a depth of 20 mm from the surface. The communities of microorganisms often formed green uniform microbial lawns, in some places several millimetres thick, localised at the surface of the concrete armour. Sampling was concentrated at the splash zone and was not intended to categorise species distribution over the whole sea defence structure. Fig. 1 shows the typical robust colonisation of the fibres, where the filaments of algae grow between sections of fibre. *X* indicates growth penetrating the polymer. The observations in this study, particularly the attachment of filamentous organisms, the cohesion between particles, and the penetration and growth, are comparable to those observed by Ortega-Calvo et al. (1991) on boring activity within the concrete of historic buildings. Fig. 2 shows abundant growth on the underside of a fibre, dislodging the material. Biological activity was sometimes observed at the study site even though filaments had detached from the substratum. Fig. 3 shows the disruptive presence of filamentous growth, cutting into the polymer material. Filaments observed and measured were able to grow 0.15–0.25 cm/day, a finding in agreement with Parchevskij and Rabinovich (1991), and specimens from the study site ranged from 10 cm to over 20 cm in length; however, mature plants can grow to 1 m long. Their dispersal, colonisation, and adhesion have been described elsewhere (Callow and Callow, 2002).

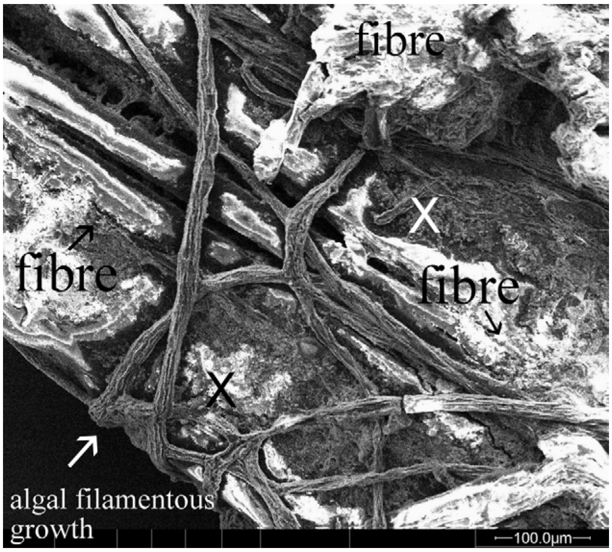

Fig. 1. SEM micrograph of synthetic fibre within the matrix after 2 yr exposure.

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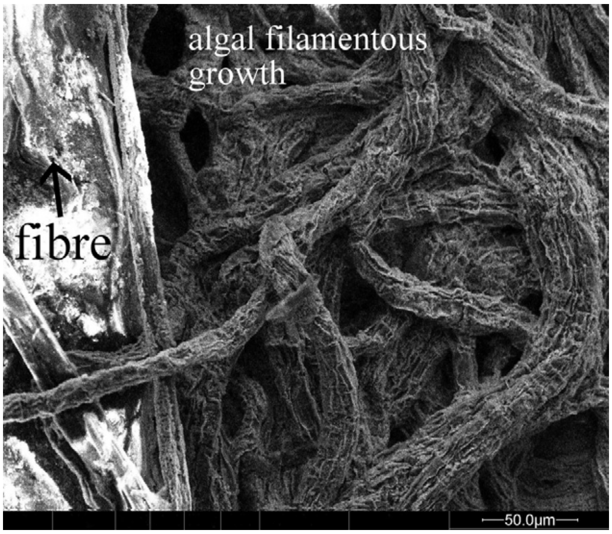

Fig. 2. SEM micrograph of synthetic fibre within the matrix after 3 yr exposure.

EDX was used to differentiate between transparent synthetic micro-fibres (22 µm in diameter) and microbial filaments, which were often of similar size. Additionally, light microscopy showed that some algal genera produced empty, transparent filaments.

4. Discussion

Fibre-reinforced concretes that are well compacted and cured seem to possess excellent durability as long as the fibres remain protected by the cement paste (Mehta and Monteiro, 2006). The macro synthetic fibres at the site have been used successfully in concrete aprons at a recycling plant (Cunningham and Conroy, 2006), but their use in a marine context is still unproven. Such fibres have become more attractive in recent times as reinforcements for cementitious materials, and Al-Tayyib and Al-Zahrani (1990) suggested they may retard the deterioration process at the surface of (non-marine) concrete. When manufacturing the concrete units, industry recommendations and fibre manufacturer's guidelines require surface finishing by float or trowel to produce a smooth finish without surface exposed fibres (Concrete Society, 2007). Such finishing techniques, however, could not be used at the study site, as the units were cast upside down. Visual inspections at the site over time showed many fibres protruding from the surface of the concrete, before breaking away. The exposure of polymers to seawater and microorganisms observed at this site led to degradation, as shown in the SEM micrographs. Artham et al. (2009) observed similar changes in physicochemical properties of polymers in seawater. However, Pegram and Andrady (1989), studying the durability of fibres in a marine environment, measured 12% and 26% reduction in tensile properties of polyethylene and polypropylene, respectively, when these were exposed to seawater for a period of 1 yr.

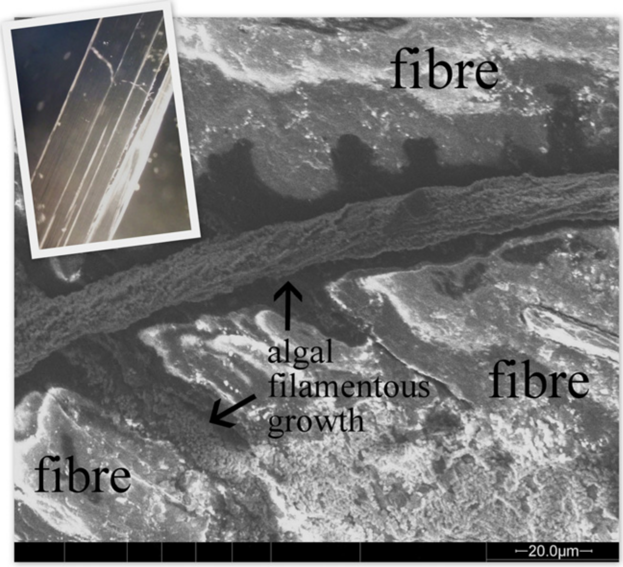

Fig. 3. SEM micrograph of filamentous growth apparently cutting into synthetic fibre within the matrix after 2 yr exposure. Insert: New, unused, macro fibre (40 mm [L] × 1.44 mm [W]).

The penetration of algae into the concrete surface, particularly under and through fibres, as seen in Fig. 1, accelerates the degradation of the polymer and also offers algae refuge from hydraulic forces, whether these are tidal impacts or power washing. The presence of algae at the fibre/cement interface disrupts or distorts the fibre by its very growth; the organisms do not use the materials as nutrients, but weaken the mechanical bond. This colonisation is observed in Fig. 2, where the majority of algal growth is on the underside of the fibre in contact with the concrete; however, growth is also noted on the fibre surface (Fig. 3). It is also important to note that algae can act as the focus for other biofouling organisms such as fungi and bacteria, so that the deterioration process may gain momentum after the structure's condition has become suitable for the survival of one or more such organisms. The algal filaments absorb and store seawater and associated nutrients during periods of submersion and from moisture found within the concrete. If the conditions (nutrients, UV, temperature, and seawater) are favourable, the filaments will grow, and extend over larger and deeper areas of the concrete. The effects of shrinking and swelling of the hydrophilic filaments during dry and wet conditions will accelerate the mechanical biodeterioration of the fibre bond and cement.

Such exposure to a hostile environment leads to material liberation and increased porosity.

As a result of this research it is proposed that algal filamentous growth between synthetic fibre and the cement matrix can weaken the bond between fibre and cement, accelerating material loss and concrete surface degradation.

5. Conclusions

This study is the first to report the composition of *Ulva* assemblages fouling and degrading synthetic fibres within marine concrete in the UK. The aim of this study was to observe marine algal colonization at the fibre/cement matrix interface, and show how it affects synthetic fibre performance. Synthetic fibres within precast elements were investigated, examined, and monitored for 7 yr at a marine study site. The observations reveal algal growth in between fibre and cement. The mechanism described is detrimental to the long-term performance of the fibres and has a significant effect on the durability of the concrete surface.

Degradation, either through algal attack or by other mechanical means (e.g., tidal impact and power washing), is not the primary cause of degradation, but exacerbates the condition. Exposed fibres on new concrete units and eroded surfaces offer opportunities for further algal attachment. This research has generated new insights into algal colonisation and opens up the prospect of more detailed studies on the microbial degradation of synthetic fibre reinforced marine concrete.

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Volume 46 September 2012 Issue 09

concrete

Incorporating CONCRETE ENGINEERING *International*

Floors and Screeds
Formwork and Falsework

Fibres and algae

Improving durability of marine concrete

A new mechanism for accelerated degradation of synthetic-fibre-reinforced marine concrete

Peter Hughes is a final year PhD student at the University of Central Lancashire investigating marine biofouling and its implications for the durability of marine concrete.

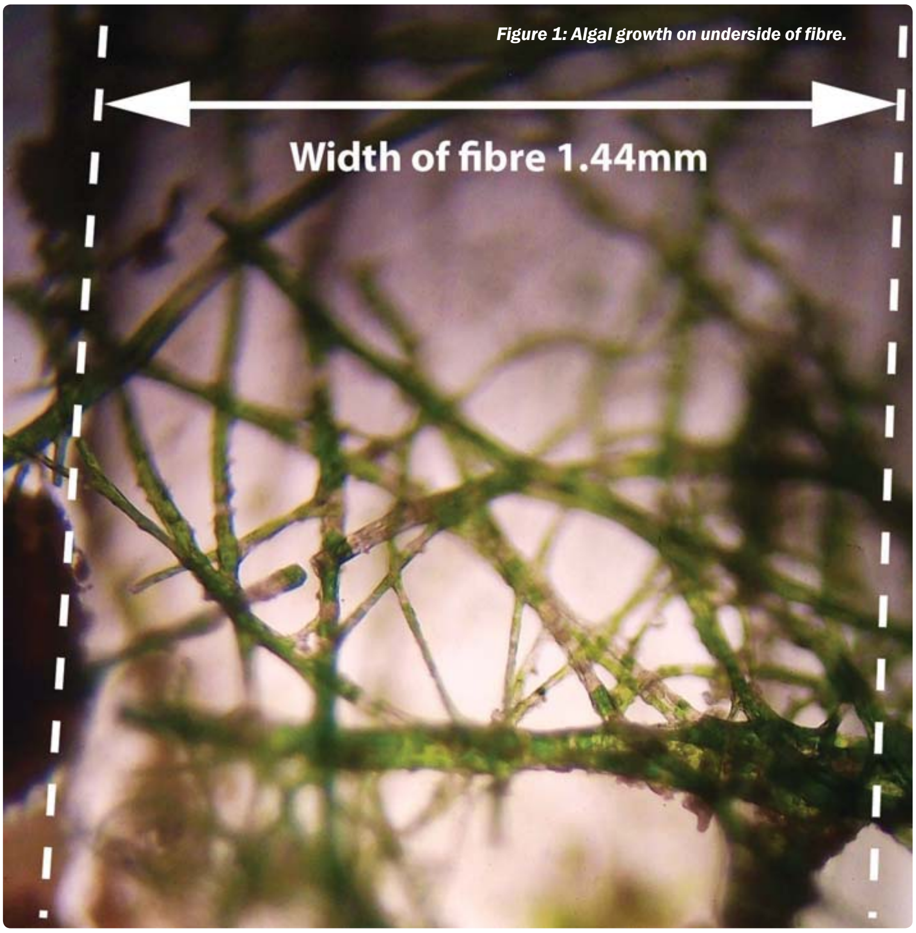


Figure 1: Algal growth on underside of fibre.

Fibre-reinforced concretes, well-compacted and cured, seem to possess excellent durability as long as the fibres remain protected by the cement paste. Usually, deterioration of concrete structures starts at the surface and progresses into the structure; therefore, it is the skin of the concrete that is the major factor in the longevity of the material. The author's research presents an exploratory site-study into the mechanical biodeterioration of synthetic-fibre-reinforced marine concrete.

Microscopic examination of the bond between fibre, cement and algae enables the further understanding of this interaction. This observed mechanism occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth. Synthetic-fibre-reinforced concrete has been used in a marine environment for several years. There is little information available on how the physical properties of synthetic fibres change with time and how long-term mechanical performance of fibre-reinforced marine concrete may be affected.

Synthetic fibres, used at the test site for this research, have become more attractive in recent times as reinforcements for cementitious materials and previous studies(1) have suggested they may retard the deterioration process at the surface of concrete. Synthetic-fibre-reinforced concrete uses fibres derived from organic polymers, which are available in a variety of formulations. Fibre types used in cement-based matrices are: acrylic, aramid, carbon, nylon, polyester, polyethylene and polypropylene. For many of these fibres there is little reported research from site experience, of their use in a marine environment.

Macro-synthetic polymer fibres have the potential to improve the post-cracking properties of hardened concrete. Their use at the test site as an alternative to nominal bar or fabric reinforcement is a relatively recent development. Micro-synthetic fibres, also used at the site, are used extensively in ground-supported slabs for the purpose of reducing plastic shrinkage cracking and plastic settlement cracking.

Methodology

Microscopy

Concrete samples were observed with a Meiji MT4000 Biological microscope and a Zeiss Axiovert 40 MAT inverted microscope fitted with a 5 megapixel, digital camera. These images were measured with the AxioVison AC software from Carl Zeiss.

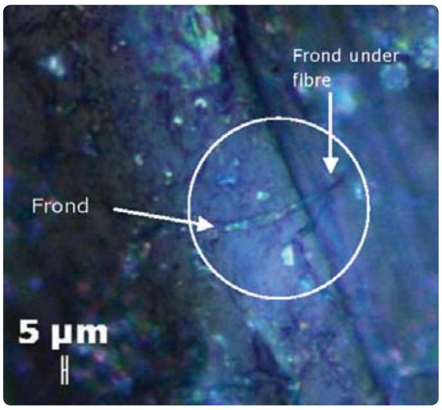
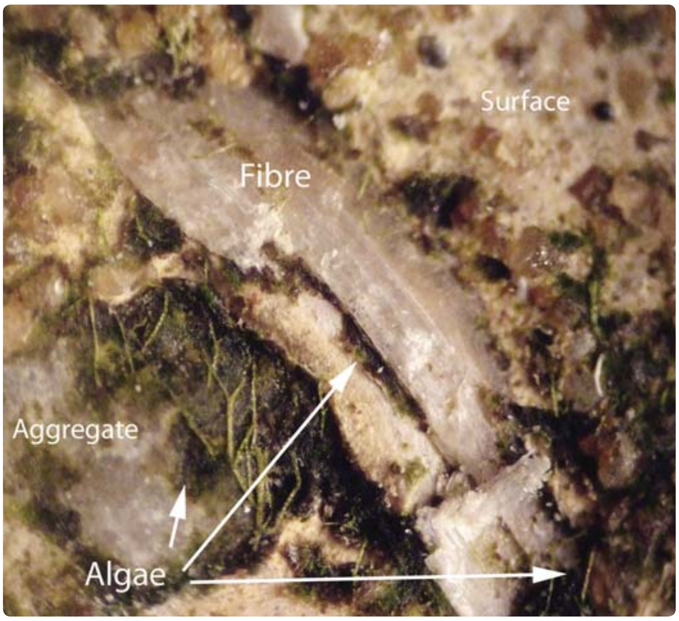
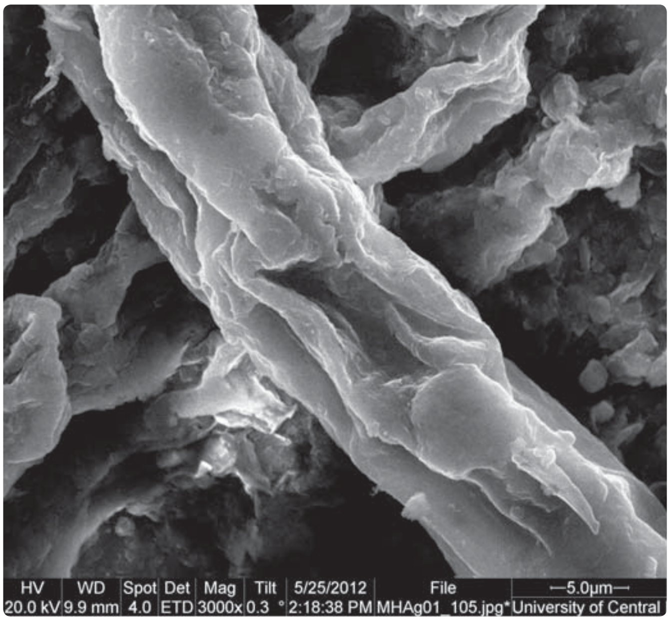


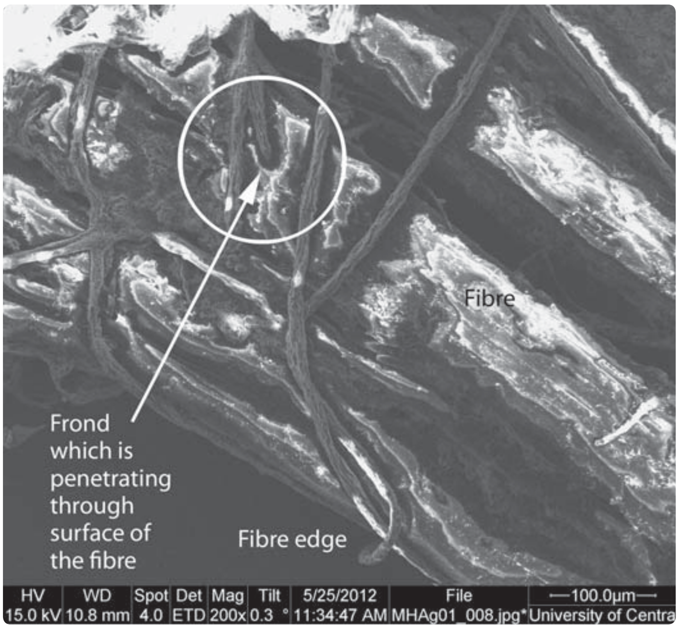
Figure 2 (above): Algal frond growing under fibre.

SEM

Algal morphological characteristics, together with concrete topography, fibre phases, distribution and orientation, were observed using an FEI Quanta 200 scanning electron microscope (SEM). Specimens were gold sputtered (using Emitech K550X sputter coater) and examined with a low accelerating voltage of 10–15kV to reduce beam damage.







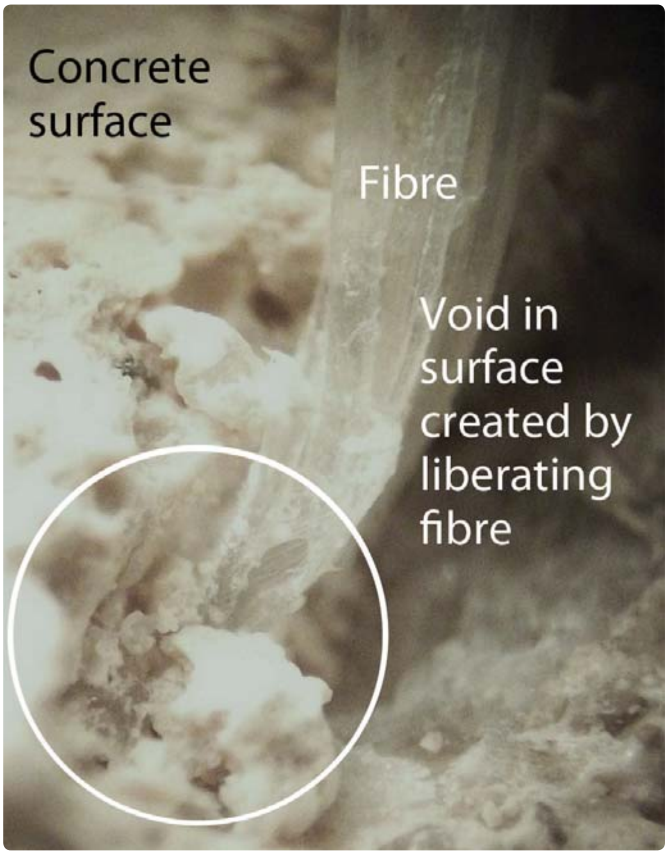


Figure 3 (top left): Extensive microbial surface fouling – algae growth can be seen on concrete surface, fibre cement interface and underside of fibre.

Figure 4 (top right): SEM of algal frond.

Figure 5 (above): Fronds growing through and across the fibre.

Figure 6 (right): Vertically orientated fibre; note entry point into fractured surface (circled).

Concrete specimens

The fibre-reinforced concrete discussed here has been used in the manufacture of revetment armour as part of a coastal protection scheme. The precast units are 5 × 3.5m, weigh 20 tonnes and contain 8m^3 of macro- and micro-fibre-reinforced concrete. Original casting of units was monitored and the same units have been regularly examined over the years in-situ. The as-struck concrete units are steel cast in a horizontal, 'upside down' position. The compressive strength class is C35/45, BS 8500-1$^{(2)}$ exposure class XS3, XF4, XC3/4 with a water:cement ratio of 0.44, minimum cement content 340kg/m^3, CEM III/A, CEM IIIA, with 50% GGBS, chloride class 0,2.

Test site and exposure conditions

The revetment armour is constantly colonised by algae, predominantly *Ulva*, creating a slip hazard to the public. The local authority has used high-pressure water (8MPa), dispensed from motorised units with multi-oscillating jets, and used chlorine-based chemicals to remove algae. The fully exposed units face westwards and are subject to cyclic wetting and drying conditions. The exposure is very harsh due to wave action, which is exacerbated by sand and occasionally shingle and debris.

Results and discussion

In the production of the concrete units, industry recommendations$^{(3)}$ and the fibre manufacturer's guidelines require the surface finishing by float or trowel to produce a finish without surface exposed fibres. However, such finishing techniques cannot be used as the units at the test site are cast upside down. From site observations there are many fibres of varying orientations, at the surface of new

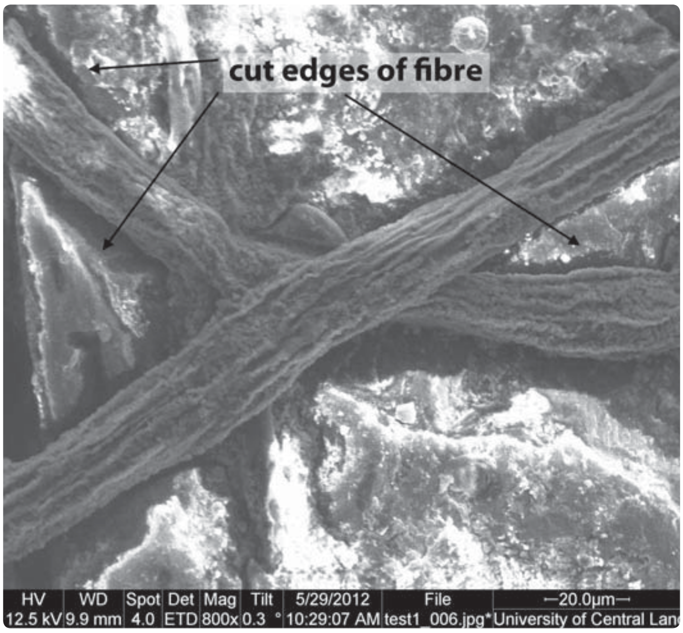


Figure 7: Algae growth on fibre cutting through fibre.

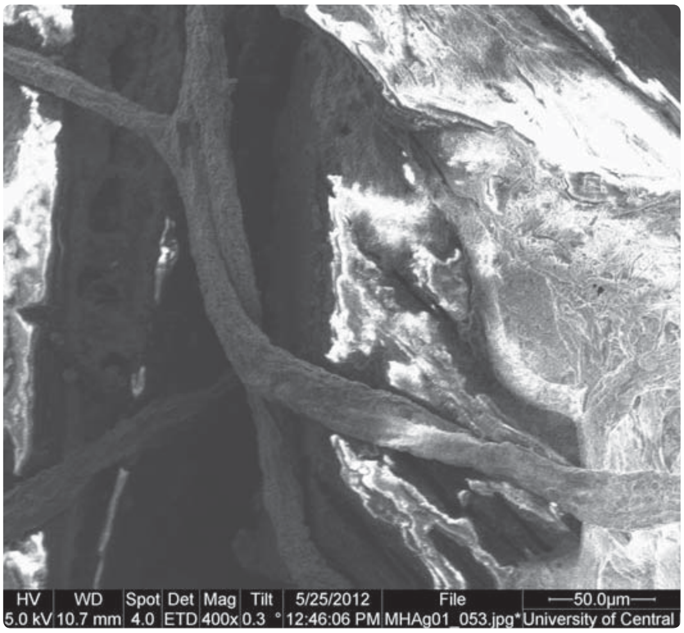


Figure 8: Algae growth on underside of fibre.

units, many protruding from the surface. An example of a horizontal orientated fibre is shown in Figure 3 and an example of a vertical orientated fibre in Figure 6.

The macro-fibres can be seen with the naked eye; however, the micro-fibres are just as abundant when viewed by microscope. This ‘hairy’ substratum offers more surface area to the algae and more possible entry points into the interior of the concrete. Surface algae are often cleared with power washing; however, spore penetration into the surface, particularly under fibres, offers refuge from hydraulic forces. Their presence disrupts or distorts the fibre by growth, rather than by using it as a food source. When algae colonise concrete structures they start to absorb calcium, silica and magnesium. The result of this is observed in Figure 1, where the majority of growth is on the underside of the fibre; however, growth was also observed on the fibre surface.

It is also important to note that algae can act as the focus for other biofouling organisms, such as fungi and bacteria, so that the deterioration process may gain momentum after the structure’s condition has become suitable for the survival of one or more such organisms. The observations made in this research complement a study of algal growth on fibre cement roof tiles(4) confirming biodeterioration of the cementitious components. The fronds (Figure 4) absorb and store seawater and associated nutrients during periods of submersion and from moisture found within the concrete. If the conditions (nutrients, UV light, temperature, and seawater) are favourable, the fronds will grow, and extend over larger and deeper areas of the concrete. The effects of shrinking and swelling of the hydrophilic fronds during dry conditions and periods of moisture intake will accelerate the mechanical biodeterioration process of the fibre bond and cement.

The presence of this growth at the fibre–cement interface, which can be 0.15–0.25cm/day, accelerates bond weakening, making the fibre more susceptible to environmental conditions, encouraging fibres to ‘pop out’ from the surface of the cement.

Concluding remarks

This study is the first to report the composition of microbial assemblages fouling and degrading synthetic fibres within marine concrete in the UK.

Various established microscopic techniques were used to investigate the colonisation of synthetic fibres. These techniques complemented each other in the structural analysis of colonisation to build a new and more complete picture showing their opportunistic growth.

The aim of this study was to observe marine algae colonisation at the fibre–cement matrix interface and how it affected synthetic-fibre performance. The present observations reveal algal growth between fibre and cement. Degradation, either through the algal attack or through other mechanical means (eg, power washing), is not the primary cause of degradation but exacerbates the condition. Exposed fibres on new concrete units and eroded surfaces offer opportunities for further algal attachment.

This research has generated new insights into algal colonisation and opens up the prospect of more detailed studies on the mechanical biodeterioration of fibre-reinforced marine concrete. ●

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Biodeterioration of Marine Fiber-Reinforced Concrete

Examination of a potential mechanism for accelerated degradation

by Peter Hughes

Synthetic fibers are used extensively in concrete slabs-on-ground for the purpose of reducing plastic shrinkage and plastic settlement cracking. Studies[1] have suggested that synthetic fibers may also retard deterioration processes at the surface of concrete, but there is little information available on how the physical properties of synthetic fibers change with time. If the concrete is well-compacted and cured, however, the fibers seem to possess excellent durability as long as they remain protected by the cement paste.[2]

Recently, synthetic fibers have been used as an alternative to nominal reinforcing bars in a concrete marine structure at the Fylde coast of England. This structure provides an excellent platform for studying the effects of a marine environment on the long-term mechanical performance of synthetic fibers and the durability of the surrounding concrete.

It's well-known that green algae and other species can cause significant deterioration of concrete through biosolubilization.[3,4] Biodeterioration of cementitious components has also been observed on fiber-cement roof tiles[5] produced with cellulose fibers. I'm aware of no previous studies of similar effects in concrete with synthetic fibers, but my exploratory study of the marine structure indicates that biological activity can lead to weakening of the bond between fibers and the concrete matrix.

Precast Units

The fiber-reinforced concrete mixture discussed herein has been used in the manufacture of precast units, which are part of a coastal protection system. Each unit measures 5 x 3.5 m (16.4 x 11.5 ft), weighs 20 tonnes (22 tons), and contains 8 m^3 (10.5 yd^3) of macro- and microsynthetic fiber-reinforced concrete.

The concrete units were fabricated in a horizontal, "upside-down" position in steel forms. The concrete mixtures were designed for a BS 8500-1:2006[6] exposure class designation of XS3, XF4, XC3, and XC4. The concrete has a compressive strength class of C35/45 (35 MPa [5000 psi] cylinder strength); a water-cementitious material ratio (*w/cm*) of 0.44; and a minimum cementitious material content of 340 kg/m^3 (575 lb/yd^3), comprising 50% portland cement and 50% slag cement.

Each precast unit has seven steps. In this location, 2791 units are needed to cover a 3.3 km (2 mile) stretch of beach. The revetment on which the units are installed is formed from fill material, placed at a slope of 1:3, and capped with a concrete blinding layer. Behind this stepped apron is a flat, cast-in-place berm and precast wave wall.

Exposure Conditions

The fully exposed units face westward and are subject to cyclic wetting and drying conditions. The exposure is very harsh due to wave action, which is exacerbated by sand and, occasionally, gravel and debris.

The units are constantly colonized by algae, predominantly *ulva intestinalis*. This creates a slip hazard to the public (Fig. 1), so local authorities use 8 MPa (1200 psi) pressure washers with multiple oscillating jets to clean the surfaces with water and chlorine-based chemicals (Fig. 2).

Evaluation Techniques

Concrete samples obtained from the precast units were examined with a Meiji MT4000 biological microscope and a Zeiss Axiovert 40 MAT inverted microscope fitted with a 5 megapixel digital camera. The images were measured with the AxioVison AC software from Carl Zeiss.[7]

Algal morphological characteristics, together with concrete topography, fiber phases, distribution, and orientation, were studied using a FEI Quanta 200 scanning electron microscope (SEM). Specimens were gold-sputtered using the Emitech K550X system and examined with a low accelerating voltage of 10 to 15 kV to reduce beam damage.

Findings

Industry recommendations and fiber manufacturers' guidelines indicate that float or trowel finishing should be used to produce a surface without exposed fibers.[8] The studied precast units were cast upside down, however, so the exposed surfaces have many fibers at or protruding from the surface. In fact, on newly cast units, macrofibers can be seen with the naked eye, and an equal number of microfibers can be seen under the microscope. This "hairy" substrate offers more surface area to the algae and more possible entry points into the interior of the concrete. Also, although fibers don't provide a food source, algae spore penetrations can be observed around and in fibers (Fig. 3). The fibers, therefore, are probably providing channels for the spores and refuge from hydraulic forces.

When algae colonize concrete structures, they absorb calcium, silica, and magnesium.[9] This process accelerates

Fig. 1: Precast steps at the Fylde coast of England. The steps have been colonized by algae

Fig. 2: Power-washing of the precast steps to remove biological growth and minimize slipping hazards

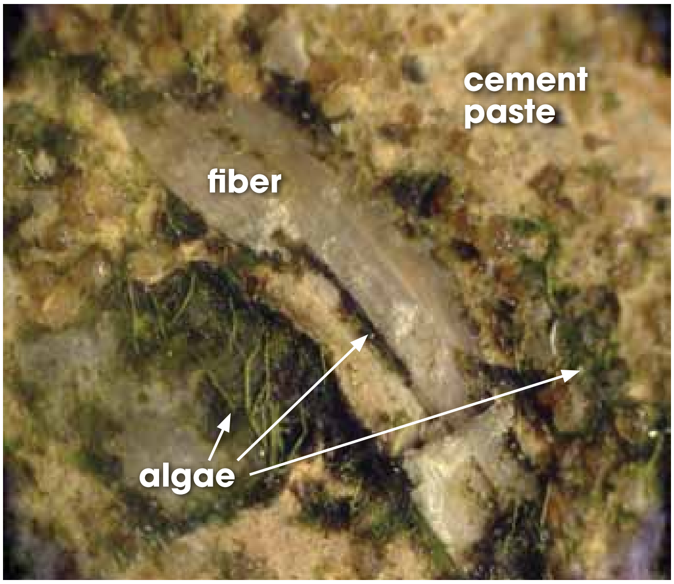

Fig. 3: Algae growth on underside of fiber within cement paste matrix and fiber-cement paste interface

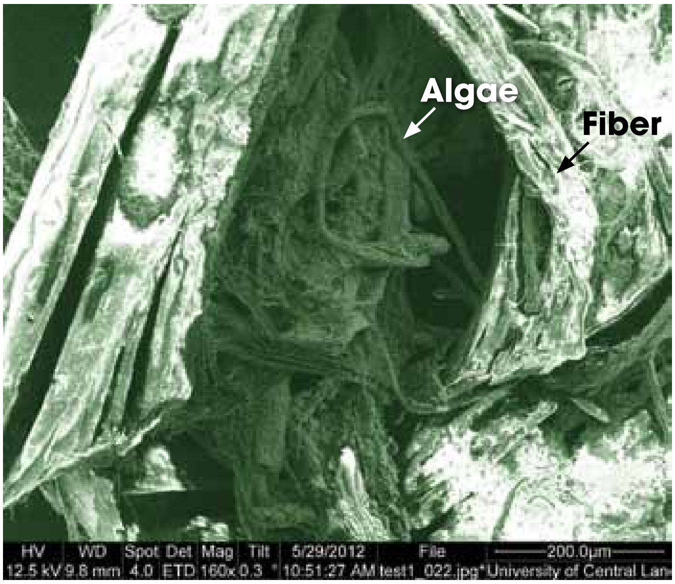

Fig. 4: SEM view of algal fronds growing through and around the fiber embedded in concrete

the microbiological degradation of concrete and results in the formation of small "cavities" in cement paste, which may lead to possible cracks. Also, algae fronds, such as those seen in Fig. 4, tend to swell as they absorb and store seawater and associated nutrients during periods of submersion. As observed in Reference 7, this swelling will accelerate the mechanical biodeterioration process as the structure undergoes cyclic drying and wetting. If the conditions are favorable (nutrients, sunlight, temperature, and seawater), the fronds will grow and extend over larger and deeper areas of the concrete (Fig. 4). The presence of this growth at the fiber-cement paste interface, which can be 0.15 to 0.25 cm/day (0.06 to 0.1 in./day),[10] accelerates bond weakening, making the fiber more susceptible to environmental conditions and allowing additional growth to occur.

Summary

The aim of this exploratory study was to observe marine algae colonization and its effect on synthetic fiber-reinforced concrete exposed to a marine environment. Observations of precast concrete units reveal that algal growth occurs in the cement paste around and through the fibers. It appears that the algae growth is promoted by the presence of exposed fibers on the concrete surface. This growth and erosion due to tides and cleaning procedures results in significant deterioration of the concrete surface.

Acknowledgments

The author thanks his supervisors, D. Fairhurst, I. Sherrington, N. Renevier, L.H.G. Morton, P. C. Robery, and L. Cunningham, for their endless patience.

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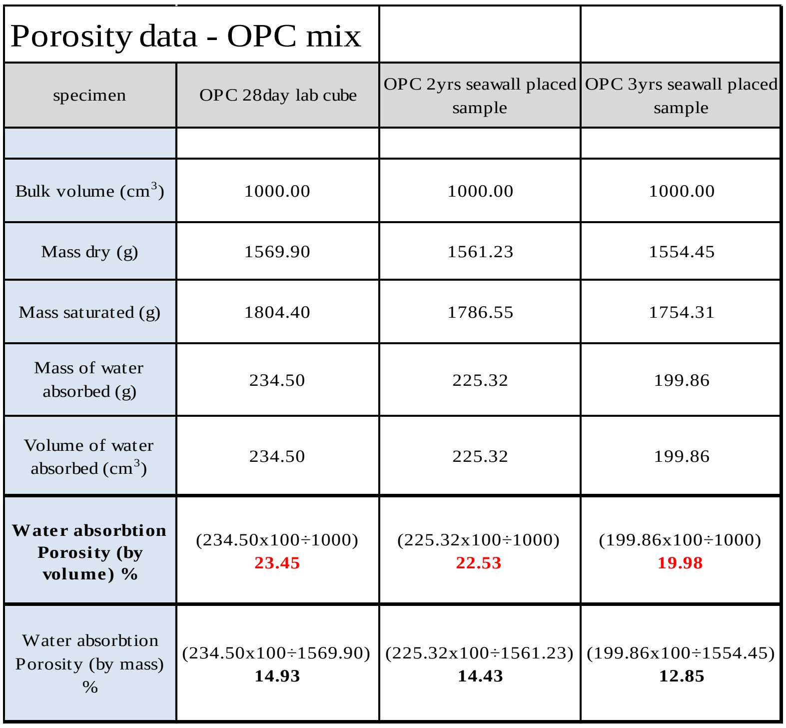
Selected for reader interest by the editors.

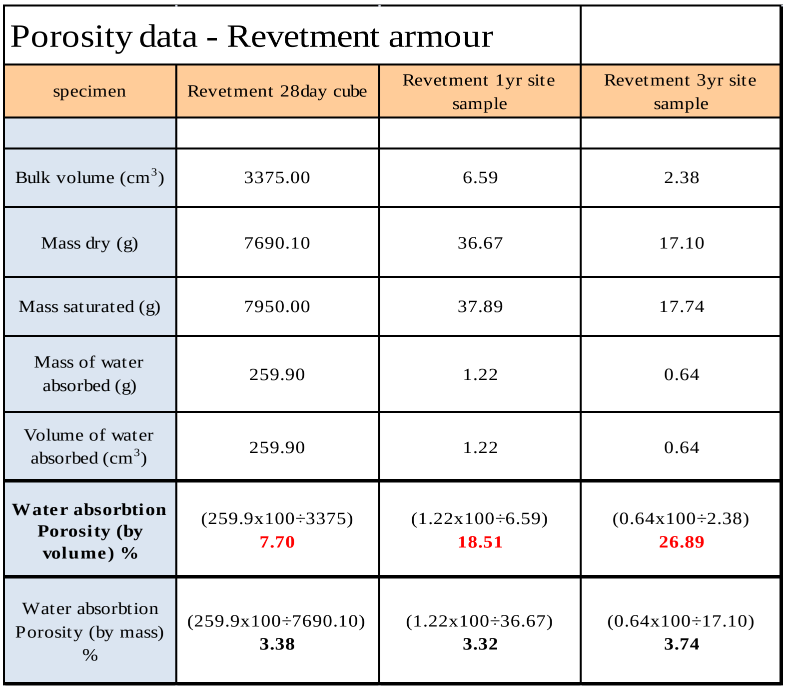
Peter Hughes is a PhD Candidate at the University of Central Lancashire in the United Kingdom. He has presented his work at the ACI fall conventions in St. Louis, MO, in 2008, and New Orleans, LA, in 2009. Hughes was recently awarded a Japanese Society for the Promotion of Science Fellowship to study photocatalytic coatings for concrete at Fukui University in Japan.

A4-3 Additional Porosity data



Porosity data - OPC mix			
specimen	OPC 28day lab cube	OPC 2yrs seawall placed sample	OPC 3yrs seawall placed sample
Bulk volume (cm^3)	1000.00	1000.00	1000.00
Mass dry (g)	1569.90	1561.23	1554.45
Mass saturated (g)	1804.40	1786.55	1754.31
Mass of water absorbed (g)	234.50	225.32	199.86
Volume of water absorbed (cm^3)	234.50	225.32	199.86
Water absorbtion Porosity (by volume) %	(234.50x100÷1000) **23.45**	(225.32x100÷1000) **22.53**	(199.86x100÷1000) **19.98**
Water absorbtion Porosity (by mass) %	(234.50x100÷1569.90) **14.93**	(225.32x100÷1561.23) **14.43**	(199.86x100÷1554.45) **12.85**

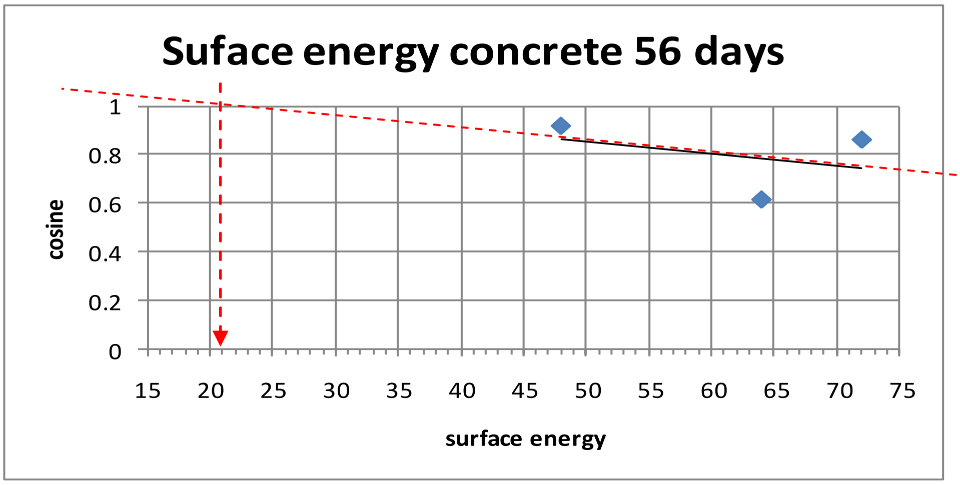
Table A4-1 Porosity measurements from OPC concrete control.

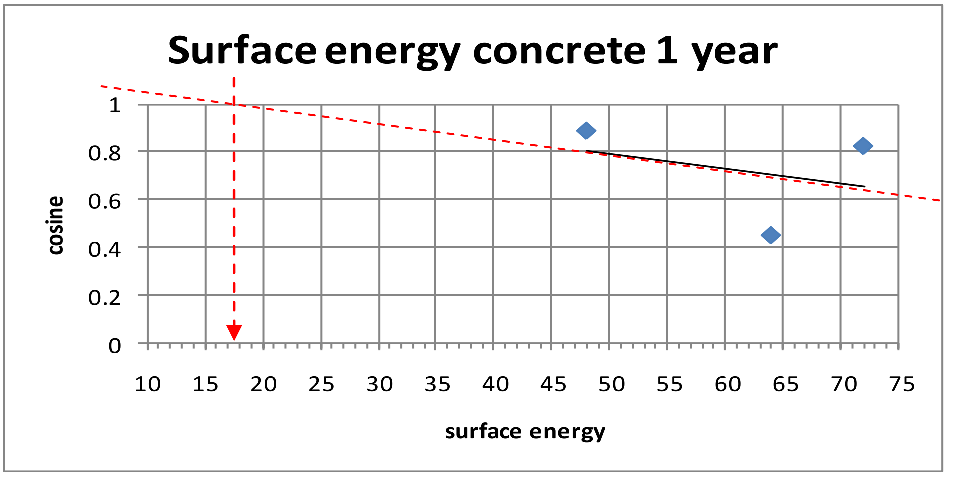


Porosity data - Revetment armour			
specimen	Revetment 28day cube	Revetment 1yr site sample	Revetment 3yr site sample
Bulk volume (cm^3)	3375.00	6.59	2.38
Mass dry (g)	7690.10	36.67	17.10
Mass saturated (g)	7950.00	37.89	17.74
Mass of water absorbed (g)	259.90	1.22	0.64
Volume of water absorbed (cm^3)	259.90	1.22	0.64
Water absorbtion Porosity (by volume) %	(259.9x100÷3375) **7.70**	(1.22x100÷6.59) **18.51**	(0.64x100÷2.38) **26.89**
Water absorbtion Porosity (by mass) %	(259.9x100÷7690.10) **3.38**	(1.22x100÷36.67) **3.32**	(0.64x100÷17.10) **3.74**

Table A4.1a Porosity measurements from revetment concrete. In the case of the revetment armour with a fairly low porosity of 7.70 at 28 days the equation indicates that the percentage difference between the bulk density and the solid density is equal to its percentage porosity. The bulk density of the 28 day, 150 mm cube being 2278kg/m^3 and porosity of 7.70% would have a solid density of 1.077 times 2278kg/m3 = 2453kg/m^3

A4-4 Surface energy calculations





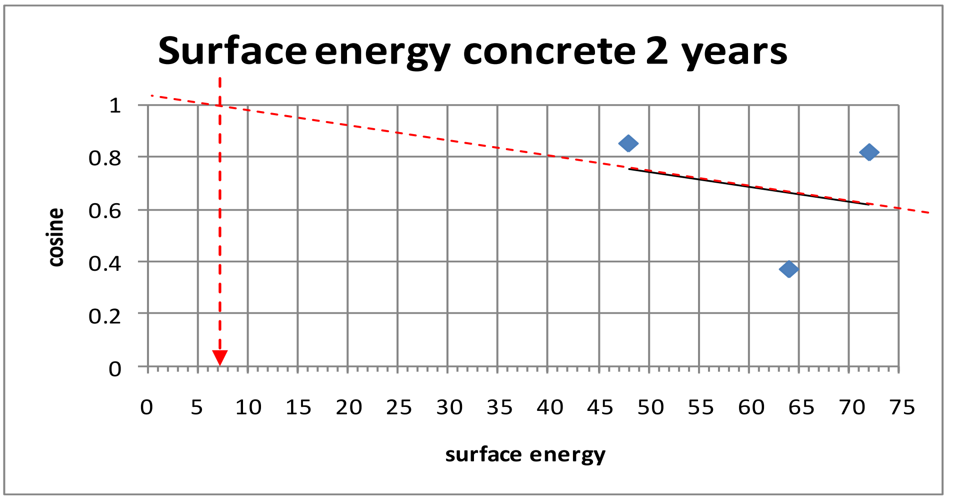


Figure A4.2 Plotting as a function of surface tension of known diagnostic liquids.These contact angles are plotted as a function of the (γ_{LV}) the surface tension of the test liquid (see table 3). The critical surface tension is defined as the intercept of the horizontal line, cos θ = 1, with the extrapolated straight-line plot of cos θ against γ_{LV} as shown in Figure 2. This intersection is the point where the contact angle is 0 degrees. A hypothetical test liquid having this γ_{LV} would just spread over the substrate.

Contact Angle data for uncoated revetment concrete at 28 day, 56 day, 1 year, 2 year and 3 year.						
Diagnostic liquid	liquid surface tension	contact angle 28d	contact angle 56d	contact angle 1year	contact angle 2year	contact angle 3year
H2O	72	33	34	38	39	43
Monoethylene Glycol	48	25	26	30	35	36
Glycerine Glycerol	64	56	58	70	76	79
						(mean of ten)

Table A4.3 Diagnostic liquid surface tension values required for plotting surface energy.

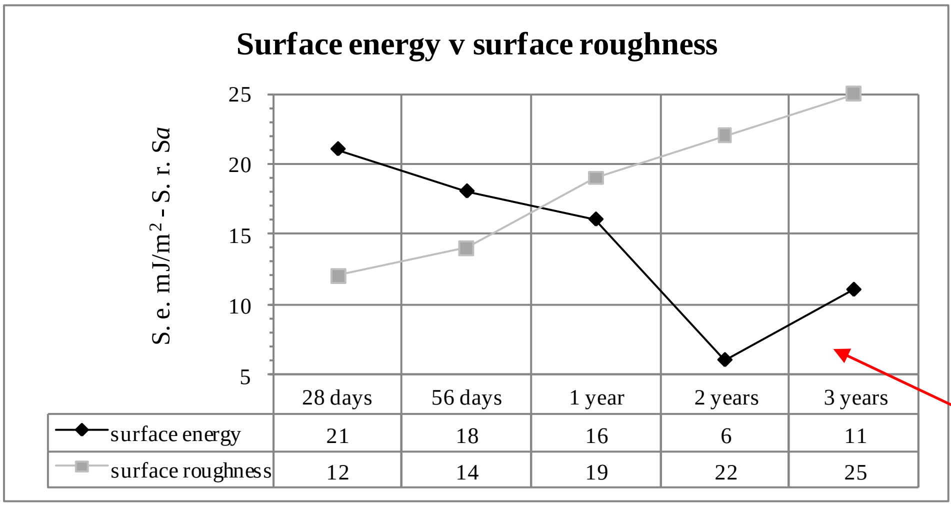


Table A4.4 correlation between surface energy and surface roughness.

Variability in H2o contact angle data 3yrs	
mean of 10	43°
standard deviation	σ 1.63
variation	2.66
confidence limit	95%±1.01

Variability in MEG contact angle data 3yrs	
mean of 10	36°
standard deviation	σ 1.96
variation	3.87
confidence limit	95%±1.21

Variability in GG contact angle data 3yrs	
mean of 10	79°
standard deviation	σ 1.93
variation	3.73
confidence limit	95%±1.19

Surface roughness increases over time which is known to increase bioadhesion. The surface energy decreases and moves away from the window of low adhesion expressed in Braier's work.

Table A4.5 Example of contact angle data variability

Additional example of synthetic fibre colonisation

Figure A4.1 Biotanacious algal growth around and within fibres.

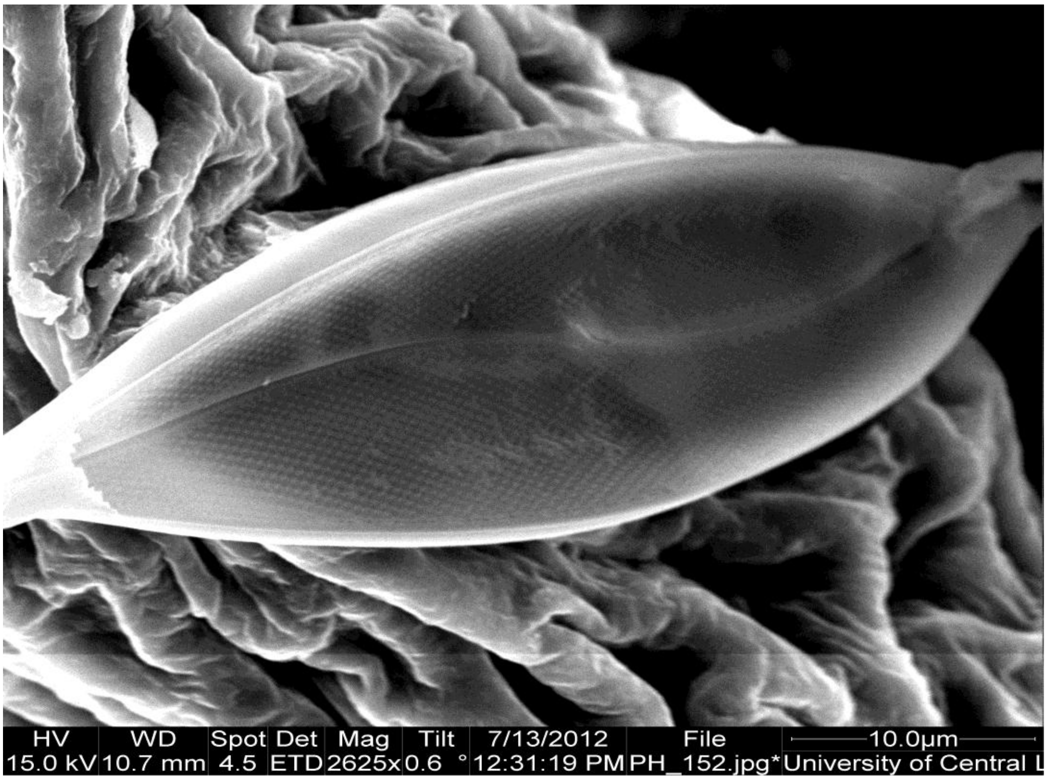


Figure A4.2 Diatom attached to *Ulva*.

Appendix 5
Additional documentation to Chapter 5

Biofilm

A5-1 Copies of original published papers (2) supporting this Chapter:

1 - Hughes, P. 2013F. Bacterial filamentous growth in freshly hardened concrete. *The Indian Concrete Journal.* July, Accepted manuscript.

2 - Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton, L.H.G., Robery, P., Cunningham, L. 2013. Microscopic study into biodeterioration of joint sealant. *Construction Material.*, Article in press.

A5-2 Copies of original published articles (4) supporting this Chapter:

1 - Hughes, P. 2013. A study into the microbial growth within new marine concrete. *Concrete.* 1, Vol. 47, 34-36.

2 - Hughes, P. 2013C. Bio-tenacious growth in subsea concrete. *World Tunnelling.* April, 30-32.

3 - Hughes, P. 2013. Bacterial growth with a new cement matrix. *Global Cement.* April, 2013, 28-30.

4 - Hughes, P. 2013. Microbial filamentous growth in subsea concrete. *Concrete.* 2, Vol. 47, 53-54.

Bacterial filamentous growth in freshly hardened concrete

Peter Hughes

This short communication presents preliminary observations from an on-going investigation into the effects of biofouling on the durability of sea defences, and specifically the occurrence of bacteria within unplaced synthetic fibre reinforced marine concrete. Scanning electron microscopy (SEM) of freshly hardened concrete was used to observe colonisation at the cement interface. Gram positive bacterial filamentous growth has been observed growing from sand within the new cement, colonising and adhering to the fine aggregate. This multidisciplinary study is the first to report the composition of microbial assemblages fouling within fresh marine concrete in the United Kingdom, laying the foundation for continued study and the further reporting of this new phenomenon.

Keywords: *Bacteria; concrete; fine aggregate; durability.*

The proliferation of concrete coastal protection has transformed sections of our naturally dynamic, coastline into artificially static, hard-substrata. The colonising marine epibiota of concrete coastal defence structures, and their effect on durability has received limited attention in academic literature. Initial site observations of precast concrete units being placed, as part of a coastal protection scheme, in the United Kingdom, revealed unusually prompt algal biofouling to the unit's surface, within only days of positioning. After detailed inspection of the new cement matrix, used in the production of the units, the early and unexpected formation of a biofilm within freshly hardened concrete was discovered.

The high pH of cement, within a new concrete matrix, which ranges from 11 to 13, has traditionally been considered, within the concrete industry to prevent the initial biofilm formation and subsequent growth of microorganisms in fresh concrete. This study is the first to report observations of filamentous bacterial growth within new, unplaced marine concrete. The durability of marine concrete, part of a larger study, is arguably its principal property; it is important therefore that concrete should be capable of withstanding the harsh conditions throughout the expected 100 years life of a marine structure.[1]

Microorganisms such as bacteria have been widely reported to be involved in the deterioration of concrete.[2] However, relatively few direct relationships have been established between the activities of microorganisms and concrete, in marine environments. Previous experimental evidence by other workers indicates that porous, exposed concrete creates a favourable environment for microbial colonisation, because aquatic organisms including bacteria adhere to its inner and outer surfaces.[3] New research in this field has even reported on the addition of bacteria into the matrix as a self healing addition, or the study of microorganisms within the matrix following environmental exposure.[4]

The aim of this on-going study was to report filamentous bacterial growth within a new, unexposed cement matrix and to discuss its origins. To achieve this aim new test cube specimens of fibre reinforced concrete were examined using scanning electron microscopy.

Methodology

Concrete specimens examined

The compressive strength class was C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4 and a water/cement ratio of 0.45. The minimum cement content was 340kg/m^3, CEMIIIA, with 50% ground granulated blast-furness slag, with a chloride class 0.2. Twelve test cubes (150 mm x 150 mm) were made with concrete supplied by the manufacturer, at the casting yard, air cured at 20°C inside the laboratory for 28 days. Some cubes were dry diamond cut into 25 mm lengths, (using a good brick and tile cutter) and examined. Some cubes were broken into smaller pieces, with a cleaned light hammer, approximately 10 mm^3, suitable for microscopic examination.

Aggregate details within the study mix

Marine dredged sand was extracted from a beach on the North West coast of England, and blended with crushed limestone for use as fine aggregate by the concrete manufacturer. The sand was washed with sea water to reduce silt content and then screened to remove any significant debris such as litter and driftwood. Beach sand samples were collected by the author, by hand, 1 km landward from the dredging area for microscopic comparisons. The fluvio-glacial deposits on the floor of the eastern Irish Sea adjacent to the dredging site are the dominant source of sediments. Whole-rock mineralogical analysis of a range of intertidal sediment samples has shown that they are predominantly quartz with associate plagioclase, orthoclase, calcite, dolomite, chlorite/kaolinite and mica.[5] Locally sourced 20 mm coarse limestone aggregate (Older Palaeozoic) was also utilized in the production of the concrete.

Scanning electron microscopy

Microbial morphological characteristics, concrete topography and, aggregate distribution were observed using a FEI Quanta 200 scanning electron microscope (SEM). Specimens were attached on a 12 mm (diameter) x 3 mm (deep) aluminium stub, fixed by a 10 mm (diameter) carbon mount with double sided organic adhesive (Agar). Initially specimens were viewed uncoated under low vacuum to observe general characteristics. All specimens were cleaned with a jet of air, to remove unattached microbial growth, before gold sputtering (Emitech K550X) at 25 milliamps for 2 minutes (thickness 20 nm) to improve image clarity. Specimens were examined using a 2.5–4.5 µm spot size and a working distance of 10 mm, by secondary electron (SE) emission (to observe morphology), backscattered electrons (BS) (to examine differences in atomic number), and with a low accelerating voltage of between 8-12 Kv to reduce specimen damage from the beam. The chamber could accommodate samples up to 5 cm x 5 cm x 2 cm in size.[6]

Results and discussion

The SEM micrographs confirmed the formation of the biofilm and are representative images of microbial growth

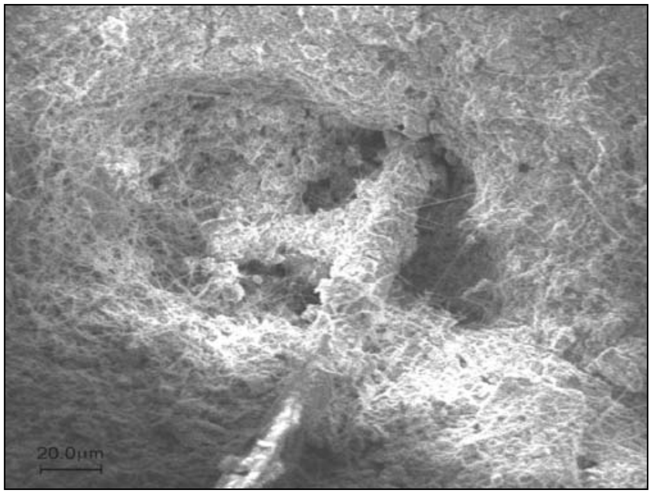


Figure 1. SEM: Gram positive filamentous bacterial colonisation of a micro fibre (22µm diameter)

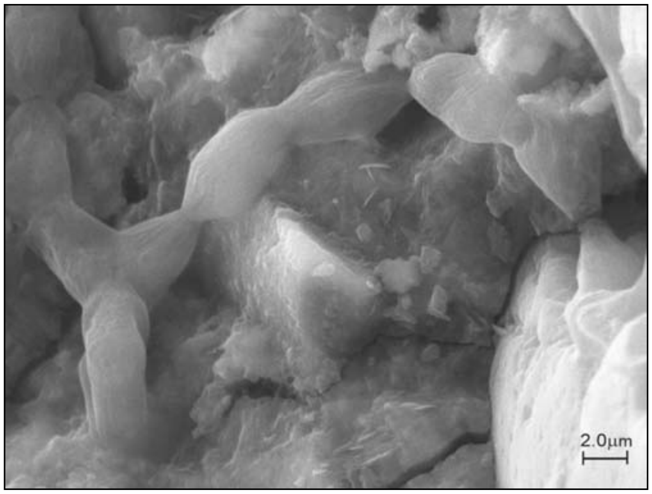


Figure 2. SEM: Initial biofilm formation on limestone aggregate within the new matrix

within the new concrete matrix examined (Figure 1). Bacterial filamentous growth at the aggregate/cement interface (Figure 2) shows biotenacious growth on the limestone aggregate within the mix. Empty water voids were often observed within the matrix, forming rippled effect chambers, these pockets of water within the matrix may have been utilized by the microorganism.

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades however; no provision is made in the current standard (UK) for the control of microbial growth within or on the surface of beach sand, (Figure 3). Research by J Steele *et al* has found viable cells buried to a depth of 0.2 m below the sand surface in a Scottish sea loch.[7] A similar finding occurred 200 km from the source of the marine aggregate used in the study mix, in Lough Neagh (Northern Ireland), where high concentrations of living cells were found attached to sand grains down to 0.5m below the sand surface.[8] Considering the constant mixing of sediment at a beach surface, it may follow that microbial endoliths could occupy some of the beach extraction used in the production of the concrete examined in the current investigation. Beach sand samples from the vicinity of the dredging site (the source of fine aggregate used in the concrete production) were examined under the microscope and found to be colonised by filamentous microbial growth. The existence of microbial population that live on or within sand is well documented.

Biotenacious growth, (Figure 4) illustrates a chain-like structure of cells approximately 350 nm in diameter growing within the new cement matrix. Attached filaments can be clearly observed growing out from pores on the surface of sand within new concrete (Figure 5).

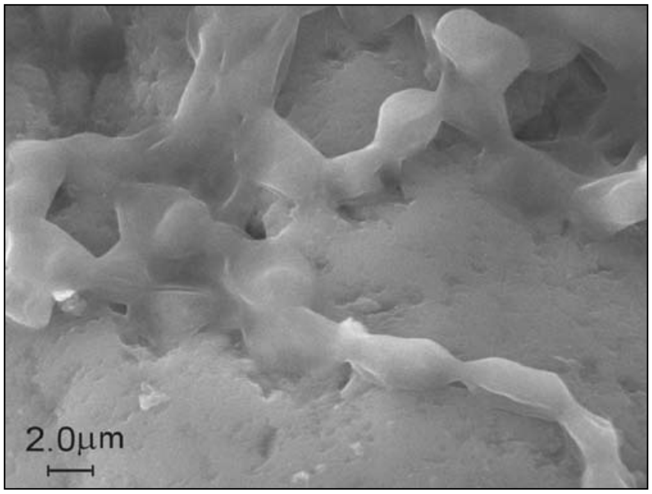


Figure 4. SEM: Biotenacious, chain like growth

The British Cement Association warns that washed beach sand is generally unsuitable by itself for good quality concrete, due to the single-sized grading, but this can be overcome by blending aggregates. While aggregates for unreinforced concrete can be washed with sea water, as was the case in this study, for reinforced concrete the aggregates must be carefully washed with potable water to remove excess chloride from sea salt, however they will still retain shell fragments and organic matter that can affect the water demand of the mix. The organic content refers only to water-soluble organic

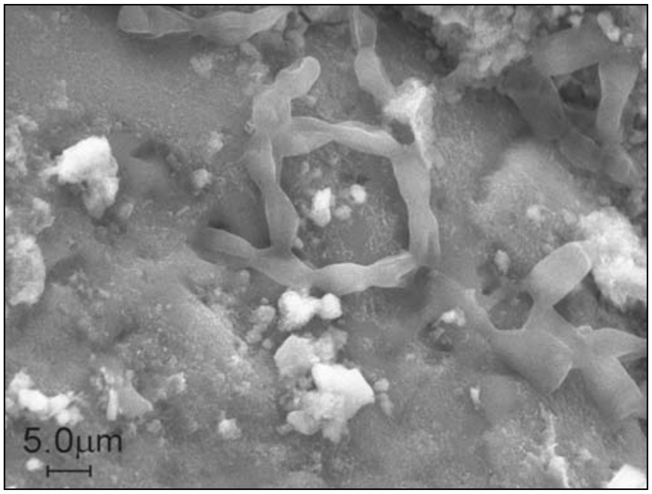


Figure 3. SEM: Bacterial growth from a pore on the surface of sand within the fresh matrix

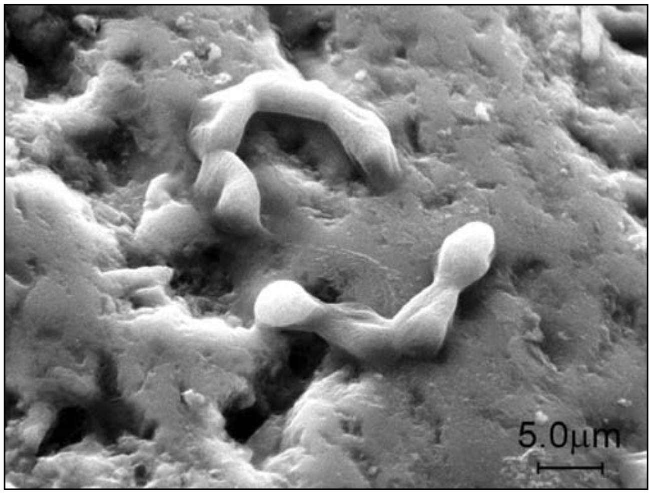


Figure 5. SEM: Pioneering filamentous growth on the surface of sand within new concrete

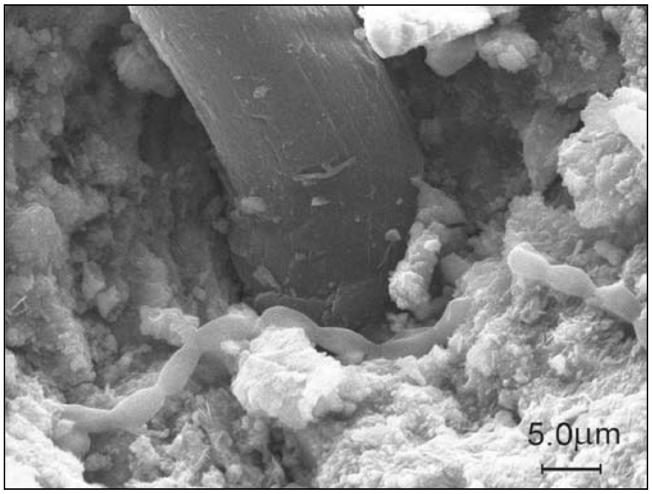


Figure 6. SEM: Early occurrence of filamentous growth around the base of a micro fibre within freshly hardened concrete matrix

compounds derived from decaying vegetation, tests for which no longer appear within (UK) standards.

Although bacteria, and particularly acid-producing bacteria, have been traditionally considered as harmful organisms for concrete, an alternative perspective is that the growth of microorganisms may afford some level of protection from weathering and erosion. As discussed by the ability of certain bacteria to promote the precipitation of calcium carbonate, has been used advantageously for consolidation of concrete and stone.[9] Previous research has illustrated a reduction of the capillary permeable porosity and an increased resistance to damage processes such as chloride ingress and carbonation by this biodeposition procedure.

The formation of the biofilm reported here is the start of the biofouling process. When the concrete is placed at the study site, algae colonise the pre-cast units, these higher plants now dominate and there effect on durability is covered in a previous paper.[1] Work continues by the author on DNA analysis and cultured specimens from retrieved beach sand shows promise. The preliminary results suggest that the blanket use of marine sourced aggregates should be reconsidered for concrete that is to remain in contact with sea water, particularly mass (unreinforced) concrete. Washing in water may only partly remove some of the epilithic biomass present on the surface of the aggregate, possibly leaving endolithic microorganisms, (Figure 6) to continue and thrive. It has been reported some microorganisms have resting stages (spores and zygotes) that allow cells to lay dormant in unfavourable environments, even freezing conditions or to survive in ephemeral pools.[10] Previous research found that even after soils had air-dried for 35 years, cells could be cultured. Therefore the microbial content may need to be controlled in structures subject to permanent wetting by sea water to control growth on and inside the matrix. BS EN 12620 is the predominant specification concerning the use of aggregates for concrete supported by UK national guidance document PD 6682-1. This guidance should consider undesirable elements such as microorganisms more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach sourced fine aggregate, leading to increased colonisation of higher plants such as algae, and the further biodeterioration of concrete.

Conclusion

Based on the analysis so far conducted, it can concluded that microbial content within sand used in concrete manufacturing needs to be controlled particularly when used in structures subject to permanent wetting by sea water. The bacterial biofilm formation is the starting point of the fouling process even before the precast unit is placed on site. Current (UK) guidance should consider undesirable elements such as microorganisms more closely and place precise limits on their presence within marine dredged aggregates. Furthermore, research in this field, needs to be developed to determine a more complete, long term strategy against marine concrete biofouling.

Acknowledgement

The author thanks his supervisors: Don Fairhurst, Senior Lecturer, School of Built and Natural Environment, University of Central Lancashire (UCLAN), Preston, UK; Professor Ian Sherrington, Director, Jost Institute for Tribotechnology, UCLAN; Dr. Nathalie Renevier, Senior Lecturer, Jost Institute for Tribotechnology, UCLAN; Professor Glyn Morton, Emeritus Professor of Microbiology, School of Forensic and Investigative Science, UCLAN; Professor Dr. Peter Robery, Halcrow Group Limited, Birmingham, UK; Dr. Lee Cunningham, Lecturer of Structural Engineering, University of Manchester, UK, for their endless patience.

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Construction Materials

Briefing: Microscopic study into biodeterioration of joint sealant
Hughes, Fairhurst, Sherrington *et al.*

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Briefing: Microscopic study into biodeterioration of joint sealant

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This research presents an exploratory study into the biodeterioration of joint sealants used in concrete coastal structures. Monocular, inverted-light microscopy and scanning electron microscopy with an energy dispersive X-ray analyser were used to observe colonisation of site specimens, enabling the further understanding of this interaction. Algal filaments have been observed growing within the matrix of a polymer sealant. Growth has been observed tunnelling within and adhered to the surface of the sealant. This degradation mechanism will weaken the material bond as a direct result of the physical activity of an organism, resulting from its growth. Loss of material, either through biodeterioration or through other mechanical means, such as tidal action, is not the primary cause of degradation, but it should be considered with associated environmental conditions, to exacerbate the condition.

1. Introduction

As part of a larger site study (Hughes, 2011) into marine biofouling and its effects on the durability of concrete, this research presents an exploratory study into the biodeterioration of a marine concrete joint sealant. Hueck (1965) defined biodeterioration as any undesirable change in the properties of a material caused by the vital activities of organisms. The bioreceptivity of the hybrid polymer silicone sealant has been observed over 4 years. Specimens have been collected from the Fylde coast (UK) study site and microscopically examined with a view to further understanding of this interaction. The growth of marine algae is abundant at the study site and surfaces of sealants are often quickly colonised, see Figure 1.

Sealants are used to seal joints between two or more components, and are important for buildings and infrastructures such as sea defences, bridges, highways and retaining walls. The main purpose of sealants is to prevent water and environmental elements from entering between components while permitting limited thermal and shrinkage movement, particularly important in ground-bearing and soil-retention applications. The regular replacement of sealant is time-consuming and expensive. Common sealants include silicone, acrylic, urethane, butyl and other polymeric types. Previous research into the durability of construction sealants (Wolf, 1999) examined environmental exposure and case studies. A review and study into sealant life and performance was presented by (Odum-Ewuakye and Attoh-Okine, 2006) but this did not include biodeterioration. Research into refined and processed materials (Allsopp *et al.*, 2004) recognises and details the biodeterioration of polymeric materials; however, little attention has been given to site-specific concrete sealants and their performance in algal-rich environments.

Algae form a diverse group of photosynthetic organisms ranging from microscopic single-cell microorganisms to very large organisms such as seaweed. Commonly occurring at the study site, the fouling algae are derived from the macroalgal group Chlorophyta (green algae). The Chlorophytes comprise a number of genera and species that actively bore in carbonate substrates. They produce branching networks of tunnels varying greatly in size. Some may be as little as 2 μm in diameter. In some species fine filaments may connect together in main canals as wide as 25 μm, (Golubic *et al.*, 1975).

Algae must absorb oxygen, water, carbon dioxide and other nutrients through their filaments to respire, photosynthesise and grow (Hawkins and Jones, 1992); they are important for

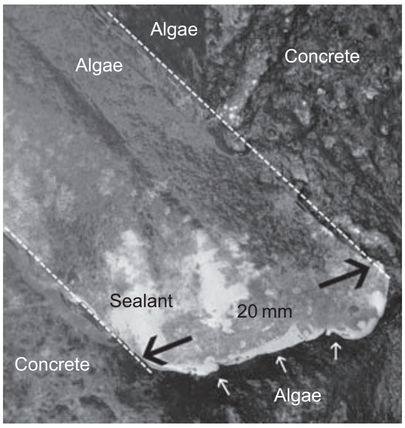

Figure 1. Digital surface view of polymer silicone sealant sample, after 2 years of exposure. Algae can be seen growing from the surface of the material, beneath, up and around the contour of the debonding sealant

the health of our coastal waters. Macroalgae, when attached to a surface, are able to obtain different elements for their metabolism from the substratum. The dominant algal genus at the study site is *Ulva*, a conspicuous, bright grass-green seaweed, consisting of inflated, irregularly constricted, tubular filaments that grow from a small discoid base; it is a common, green macroalga found throughout the world. Thalli from the site ranged from 10 cm to over 20 cm long. Their dispersal, colonisation and adhesion have been investigated elsewhere (Callow and Callow, 2002).

The aim of this study was to observe and report on the biodeterioration and performance of a polymer silicone sealer at a marine concrete study site. The observations will be useful to designers and managers of coastal and maritime structures, regarding the importance of the selection of materials within the hostile habitat of marine biofouling, in order to combat the potential degradation mechanism for marine sealants. A limitation to this case study, however, is that it involves only a single study site and therefore may not be representative of marine environments generally.

2. Materials and methods

2.1 Microscopy

Sealant samples were initially observed with a Leica Strata Lab monocular light microscope, and then with a Meiji MT4000 Biological and a Zeiss Axiovert 40 MAT inverted microscope with a large specimen stage, ideal for the examination of bulky specimens. Individual algae specimens were also observed on glass slides with a cover slip. The Axiovert was fitted with a 5 megapixel, high-resolution digital camera. These images were measured with the AxioVison AC software (Zeiss, 2001). This software allowed accurate measurement, image processing and analysis of algal filaments and sealant specimens on a captured colour image. Visual examination of samples revealed large-scale features, including the nature of the external sealant surfaces and the presence of algal filaments within the matrix.

2.2 Scanning electron microscopy–energy dispersive X-ray analysis

Algal morphological characteristics and sealant topography were observed using a scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser (EDX) using Genesis software. The EDX was used for the elemental analysis of algal filaments within the sealant matrix. The FEI Quanta 200 used in this research is capable of producing high-resolution digital images at over ×100 000 magnification, allowing objects as small as 3·5 nm to be resolved. Specimens were cleaned with a jet of air, to remove unattached algae, and examined by secondary electron (SE) signal, to show morphology and backscattered electrons (BS) to reflect differences in atomic numbers, with a low accelerating voltage of 8–12 kV to reduce specimen beam damage. The chamber can accommodate samples up to 5 cm × 5 cm × 2 cm in size.

2.3 Sealant specimens

The study site has been surveyed and monitored over the full length of the construction period, approximately 7 years. The concrete pavement joint sealant studied has been formulated to accommodate repeated and pronounced cyclic movement, which has been applied to both in situ and pre-cast elements, such as floor slabs and wave walls, as part of a coastal protection scheme. The sealant used at the study site is a one-part, high-strength, flexible sealant specifically developed for structural marine applications. It is non-hazardous (isocyanate and solvent free) and offers long-term performance with resistance to staining, ultraviolet light and salt water degradation.

2.4 Test site and exposure conditions

The fully exposed elements face westwards and are subject to cyclic wetting and drying conditions. The exposure is very harsh, and is exacerbated by sand and occasionally shingle and debris.

2.5 Algal identification

Ulva were identified to the genus level on the basis of the morphological characteristics observed (Meiji MT4000 Biological), such as thallus and cell arrangement (Blomster *et al.*, 1998).

3. Results

Figure 1 is a digital image (FujiFilm Finepix JX) which shows a typical application of a sealant at the study site. Figure 2 is

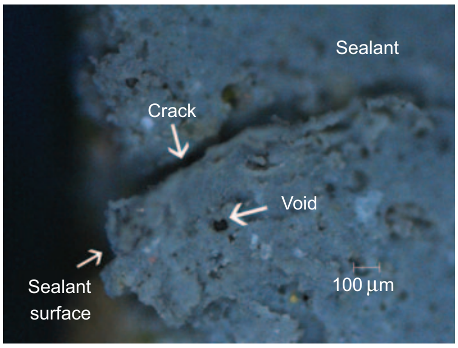

Figure 2. Light inverted microscope side view (section) of polymer silicone sealant sample, after 2 years of exposure. Boring, mature algal filaments penetrate the cracked material

an inverted microscope view of the sealant surface showing how algal filaments can grow into the material. Figure 3 is a SEM micrograph demonstrating the ability for algal filaments to penetrate the sealant surface.

4. Discussion

It has been shown that algal filaments at the study site can tunnel within the sealant matrix. The digital and light-inverted microscope images, Figures 1 and 2, demonstrate the existence of microbial populations around the surface and within the sealant. This complexity is increased because of the large number of algal species in the assemblages, providing an incredibly complex system for investigation. Figure 3 indicates the destructive presence of growth, which may lead to the eventual failure of the sealant. When algae colonise concrete structures they start to absorb calcium, silica and magnesium (Javaherdashti *et al.*, 2009). Sealants are polymers that commonly contain silicone, together with carbon, hydrogen and oxygen, and may offer food sources for algal growth. This could partly explain the abundant colonisation. It is not implied that this mechanism is solely responsible for the biodeterioration observed at the study site, but it is suggested that this should be considered, along with associated environmental conditions such as tidal impact and power washing, to be a factor in the durability and performance of polymer sealants.

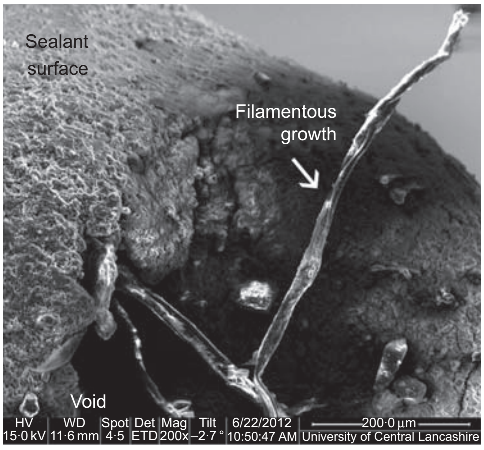

Figure 3. Scanning electron microscopy, secondary electron micrograph: side view of sealant specimen from site. Mature algal filaments can be seen growing within the matrix of the sealant and up to the surface of the sealant

The filaments (Figure 3) absorb and store water and associated nutrients during periods of submersion. If the conditions are favourable for growth, the filaments will grow and extend over larger and deeper areas of the sealant. The effects of shrinking and swelling of the hydrophilic filaments during dry conditions and periods of moisture intake will accelerate the mechanical biodeterioration process of the sealant.

Figure 3 shows the upward and outward growth of algal filaments, exiting the sealant. It has been observed that algal filaments are able to grow on, around and within the sealant and up through its surface. EDX was used throughout the SEM investigation to confirm the presence of microbial filaments, rather than liberated microfibres from the concrete or a sealant fibre additive.

Sealants, once in place, are exposed to harsh environmental degradation which eventually affects their performance, and will ultimately cause them to fail. Civil engineers, therefore, need to know the predicted service life of a marine sealant in order to estimate the overall costs associated with a marine structure. This research highlights a potential durability factor, enabling a more accurate material service life prediction, which has been previously unreported. The correct application of a marine sealant involves not only choosing a material with appropriate physical and chemical properties, but also having a good understanding of joint design, the substrates to be sealed, the performance needed, and the biodeterioration, which can profoundly influence the service life of the installed sealant. Rather than rely on manufacturers, independent guidance should be available to civil engineers on such matters. Changes in sealant formulation to tackle the colonisation and growth of algae, and other site-specific microorganisms, using forms of biocide, may offer ways of reducing biodeterioration and extending sealant life to first maintenance.

5. Conclusions

All potential biodegradation mechanisms of marine joint systems need to be better understood in order to select a suitable sealant for use in a joint system. The aim of this study was to observe marine algal colonisation of a polymer silicone sealant, and to discuss how algal filaments may affect the performance of the sealant matrix in a marine environment. Polymer sealant samples from within pre-cast elements have been examined microscopically and the results presented. The environmental performance of the sealant has been observed at a study site under 'real life' conditions. Biodeterioration of the sealant, by way of algal filaments tunnelling into the polymer, has been observed. Filamentous growth within the matrix of the sealant will weaken the material, making it more susceptible to other hostile elements.

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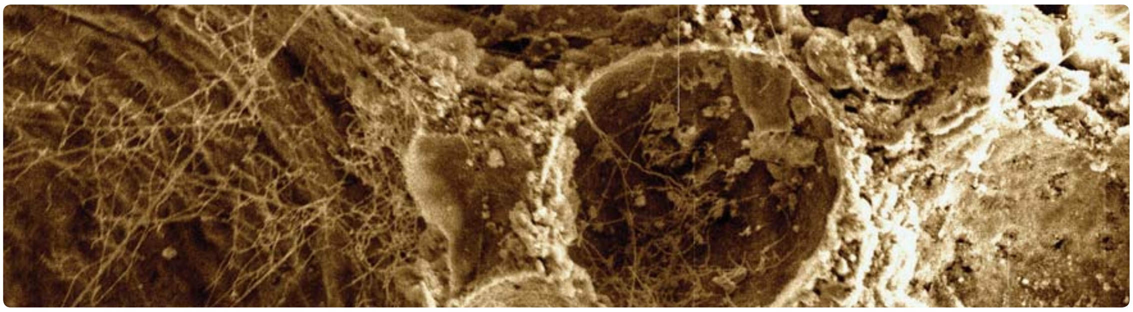


A study into microbial growth within new marine concrete

Peter Hughes is a final-year PhD student at the **University of Central Lancashire** investigating marine biofouling and its implications for the durability of marine concrete.

Microbial growth and the ability of some species to tunnel into concrete surfaces leads to degradation, increased porosity and decreased durability. However, recent research into the use of certain micro-organisms for the improvement of durability has drawn the attention of research groups all over the world and an informative review has been given by De Muynck *et al*(1).

Most research in this field has reported on the addition of bacteria into the matrix as a self-healing addition(2), or has involved the study of micro-organisms within the matrix following environmental exposure; however, this study is the first to report observations of filamentous bacterial growth within new, unplaced synthetic-fibre-reinforced marine concrete (see Figure 1). Durability of marine concrete – part of a larger study(3) – is arguably its principal property; it is important that concrete should be capable of withstanding the harsh conditions throughout the expected life of a structure.

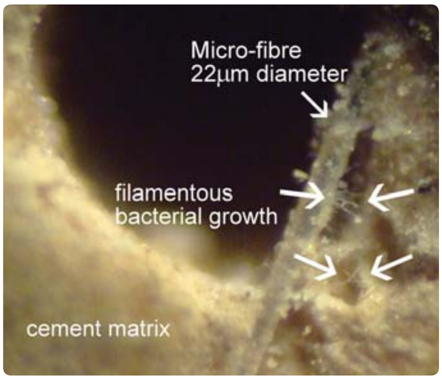


Figure 1: Filamentous bacterial growth on underside of fibre (arrowed) within new concrete.

Previous experimental evidence indicates that porous, exposed concrete creates a favourable environment for microbial colonisation because aquatic organisms including algae and bacteria adhere to its inner and outer surfaces. They produce branching networks that vary greatly in size, from as little as 350µm in diameter (see Figure 2). In some species (eg, *Ulva*), such fine filaments may collect together to form tubular thalli up to 25µm in diameter. Concrete structures exposed in tropical and subtropical seas have been shown to be subject to the same bioerosive forces as carbonate substrates. Many of the species implicated in calcium carbonate breakdown have been demonstrated to be capable of bioeroding concrete. The aim of this study was to observe and report filamentous bacterial growth within a new, unexposed cement matrix and to discuss its origins and how its presence may affect future performance. To achieve this aim, new test cube specimens of concrete destined for use at a coastal protection scheme in the UK were examined using light microscopy and scanning electron microscopes (SEM).

Concrete specimens

The compressive strength class was C35/45, BS 8500-1(4) exposure class XS3, XF4, XC3, XC4 and a water/cement ratio of 0.45. The minimum cement content was 340kg/m^3, CEM IIIA, with 50% GGBS and a chloride class 0.2. Cubes (150 × 150 × 150mm) were made with concrete supplied by the manufacturer and air cured at 20°C inside the laboratory for 28 days. Some cubes were dry diamond cut into 25mm lengths, then washed and examined. Some cubes were broken into smaller pieces, approximately 10mm^3, suitable for microscopic examination. Locally sourced 20mm coarse limestone aggregate (older Palaeozoic) was used in the production of the concrete. Marine dredged sand was extracted from a beach on the north-west coast of England, and blended with crushed limestone for use as fine aggregate by the concrete manufacturer. The sand was washed by the concrete manufacturer with sea water to reduce silt content and then screened to remove any significant debris such as litter and driftwood. Beach sand samples were collected by hand 1km landward from the dredging area for comparisons.

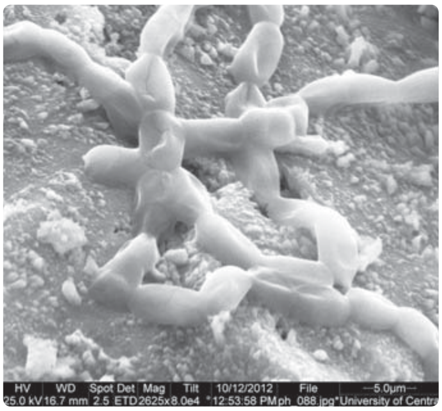


Figure 2: Extensive microbial surface fouling; filamentous bacterial growth can be seen on the surface of sand from within new concrete.

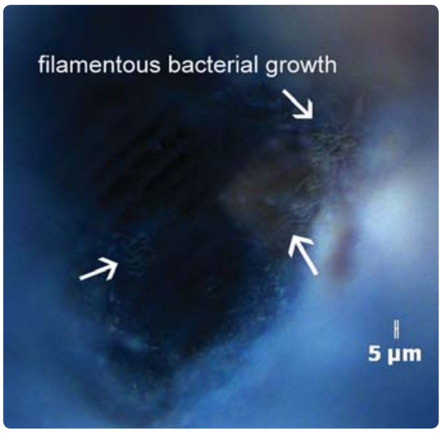
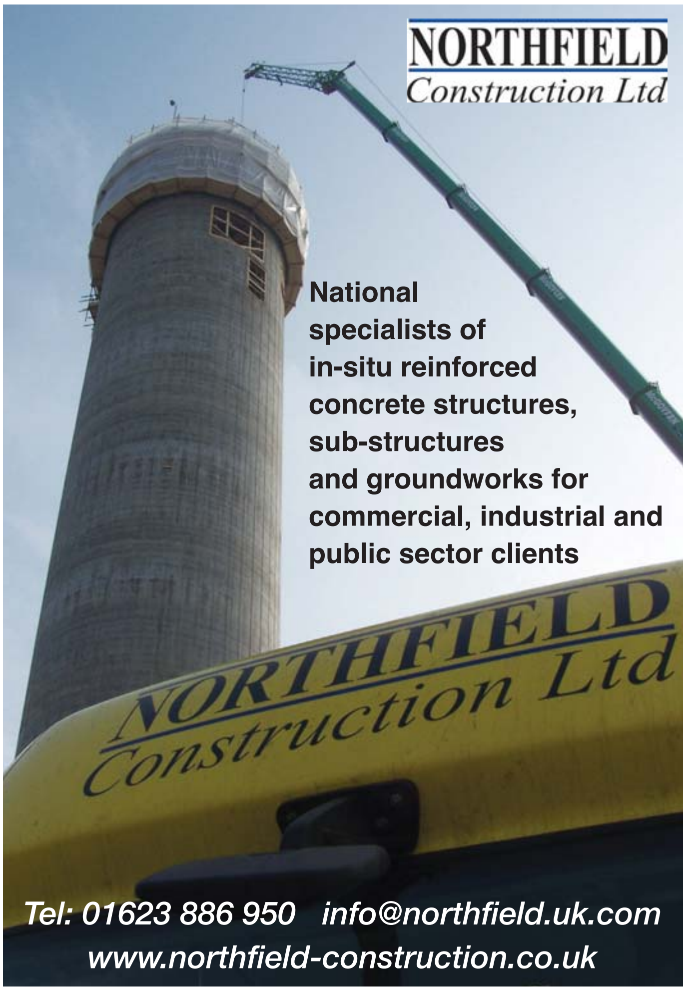


Figure 3: Filamentous growth in a void from within new concrete.



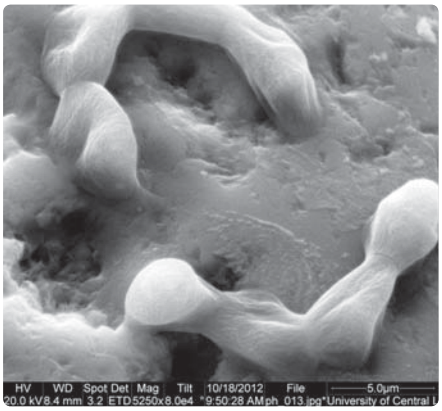


Figure 4: Filamentous bacterial growth on the surface of sand within unplaced concrete.

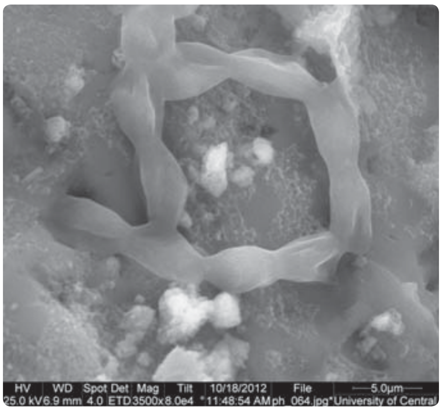


Figure 5: Filamentous bacterial growth out of the surface of sand within new concrete.

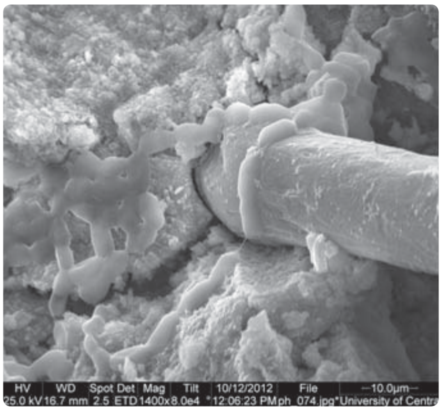


Figure 6: Filamentous bacterial growth on the surface of a micro-fibre within unplaced concrete.

Observations

The SEM micrographs illustrate microbial growth within the concrete. Figure 3 shows a water void with filamentous growth on the rippled walls of the chamber. EDX analysis distinguished between remnants of synthetic fibres within the matrix and micro-organisms; fibre results differed from micro-organism, showing 86% carbon and 14% oxygen. Figure 4 shows attached filaments on the surface of new sand. Figure 5 illustrates a chain-like structure of cells approximately 350µm in diameter climbing the surface of the fine aggregate.

Discussion

Although bacteria, and particularly acid-producing bacteria, have been traditionally considered as harmful organisms for concrete, an alternative perspective is that the growth of micro-organisms may afford some level of protection from weathering and erosion. As discussed by De Belie and De Muynck(5), the ability of certain bacteria to promote the precipitation of calcium carbonate has been used advantageously for consolidation of concrete and stone. Previous research has illustrated a reduction of the capillary permeable porosity and an increased resistance to damage processes such as chloride ingress and carbonation by this biodeposition procedure.

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades. However, no provision is made in the current Standards for the control of microbial growth within or on the surface of beach sand (see Figures 4 and 5).

Research by Steele *et al*(6) found viable algal cells buried to a depth of 0.2m below the sand surface in a Scottish sea loch. A similar finding occurred 200km from the source of the marine aggregate used in the study mix, in Lough Neagh, where high concentrations of living algal cells were found attached to sand grains down to 0.5m below the sand surface.

Considering the constant mixing of sediment at a beach surface, it may follow that microbial endoliths could occupy some of the beach extraction used in the production of the concrete examined in the current work.

Beach sand samples from the vicinity of the dredging site (the source of fine aggregate used in the concrete production) were examined under the microscope and found to be colonised by filamentous microbial growth. The existence of microbial populations that live on or within sand is well documented.

MPA–Cement warns that washed beach sand is generally unsuitable by itself for good-quality concrete, due to the single-sized grading, but this can be overcome by blending aggregates.

While aggregates for unreinforced concrete can be washed with sea water, as was the case in this study, for reinforced concrete the aggregates must be carefully washed with potable water to remove excess chloride from sea salt; however, they will still retain shell fragments and organic matter that can affect the water demand of the mix. The organic content refers only to water-soluble organic compounds derived from decaying vegetation, tests for which no longer appear within Standards.

Preliminary results

The preliminary results of this on-going study suggest that the blanket use of marine-sourced aggregates should be reconsidered for concrete that is to remain in contact with sea water, particularly mass (unreinforced) concrete. Washing in water may only partly remove some of the epilithic biomass present on the surface of the aggregate, possibly leaving endolithic micro-organisms (see Figure 6) to continue and thrive.

It has been reported that some micro-organisms such as algae have resting stages (spores and zygotes) that allow cells to lay dormant in unfavourable environments, even freezing conditions, or to survive in ephemeral pools. Previous research found that even after soils had air-dried for 35 years, green algae could be cultured.

Therefore the microbial content may need to be controlled in structures subject to permanent wetting by sea water to control growth on and inside the matrix. BS EN 12620(7) is the predominant specification concerning the use of aggregates for concrete supported by UK national guidance document PD 6682-1(8). This guidance should consider undesirable elements such as micro-organisms more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach fine aggregate, leading to increased colonisation and the bioerosion of concrete. ●

● **Acknowledgements**
The author thanks his supervisors for their endless patience: D Fairhurst, Professor I Sherrington, Dr N Renevier, Professor LHG Morton, Professor PC Robery and Dr L Cunningham. Further discussion, e-mail: PHughes1@uclan.ac.uk

The Editor welcomes comments from readers – is bioerosion of concrete a serious issue? Should PD 6682-1 place limits on microbes on aggregates? E-mail: editorial@concrete.org.uk

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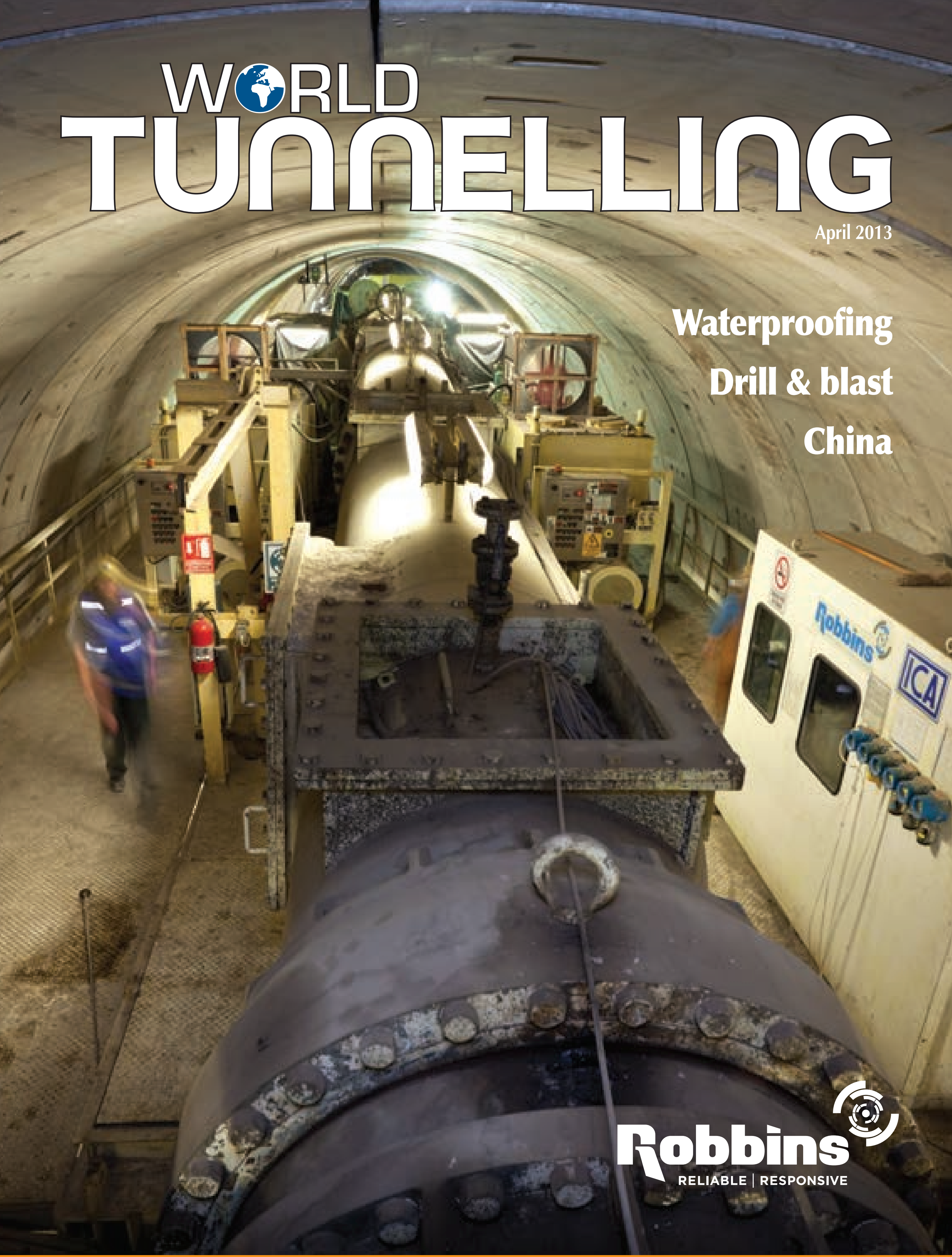

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Bio-tenacious growth in subsea concrete

Researcher Peter Hughes suggests that marine bio-fouling has implications for the durability of undersea SNFRC and therefore on the safety of tunnels, postulating how micro-organisms might play a significant role in the deterioration of this type of concrete

Figure 1: a micro-fibre (22μm-diameter) with bacterial bio-tenacious growth (350nm-diameter) around the cement interface

SAFETY is of the utmost importance in the tunnelling and mining industries. Concrete durability in tunnels is essential, as failures in the past have led to the loss of life. There is a tendency for biological cells and debris to accumulate on the outer and inner surfaces of sprayed concrete, whether used in tunnel works or in open-air applications. This further attracts moisture, which may facilitate chemical reactions and promote the growth of bacteria(1).

Micro-organisms such as bacteria and algae have been widely reported to be involved in the deterioration of concrete(2, 3). However, relatively few direct relationships have been established between the activities of micro-organisms and the synthetic fibres within concrete, in harsh environments such as tunnels. It has been reported that steel fibres within sprayed concrete were severely attacked by bacteria(1), and synthetic fibres have also been observed in a marine environment to be susceptible to microbial colonisation(4,5).

> “Micro-organisms such as bacteria and algae have been widely reported to be involved in the deterioration of concrete”

It is claimed by other researchers that some species of bacteria may enhance the durability of concrete. However, it is the view of the author that filamentous growth is detrimental to the durability of synthetic fibre-reinforced concrete in harsh environments. In related studies by the author, the degradation of synthetic fibres has been observed in a marine environment over the eight-year lifetime of a sea defence scheme in the UK(4).

It is usually accepted that watertight concrete is durable. However, once water tightness is lost, the interior of the concrete may become saturated, allowing micro-organisms carried in water to play a greater active role in deterioration. As the micro-organisms are transported into the matrix of the material, they will contribute to successive cycles of expansion, further cracking, fibre de-bonding and liberation, leading to increased permeability.

The occurrence of bacteria in concrete tunnels was reported in 1934(6), highlighting an interesting and serious problem, by the appearance of crenothrix, a type of bacterium found growing in ground water in the Hetch Hetchy Valley of Yosemite National Park, California, US.

This seepage water, having a high mineral content and containing the crenothrix organism, flowed through the tunnel and carried the micro-organism into several lines of conveying water. After intensive study, the organism was controlled with a chlorine-ammonia treatment. Algae have also been commonly observed within subsea tunnels, causing the clogging of drains(7).

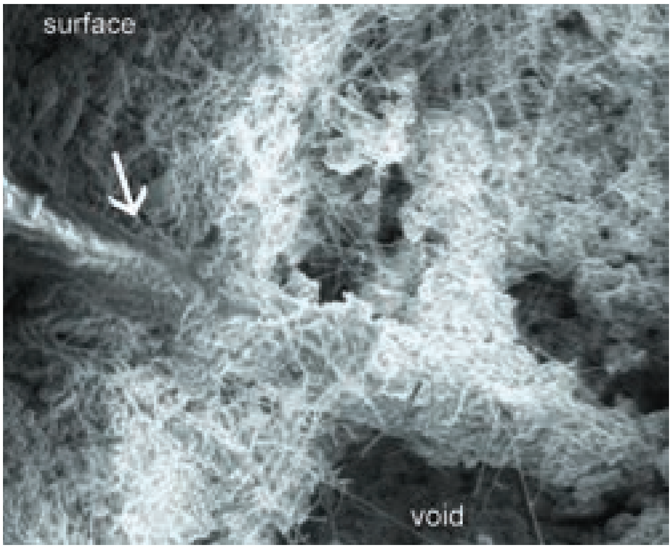

Figure 2: a micro-fibre protruding from the surface (arrowed) of the concrete; note the bacterial colonisation within the void beneath the surface

DISCUSSION

The bio-tenacious growth on and around the micro-fibres in Figures 1 & 2 can be likened to the natural process of retting, where micro-organisms have been used for many years, in the extraction of fibres from plant materials. Retting employs the action of bacteria to dissolve and

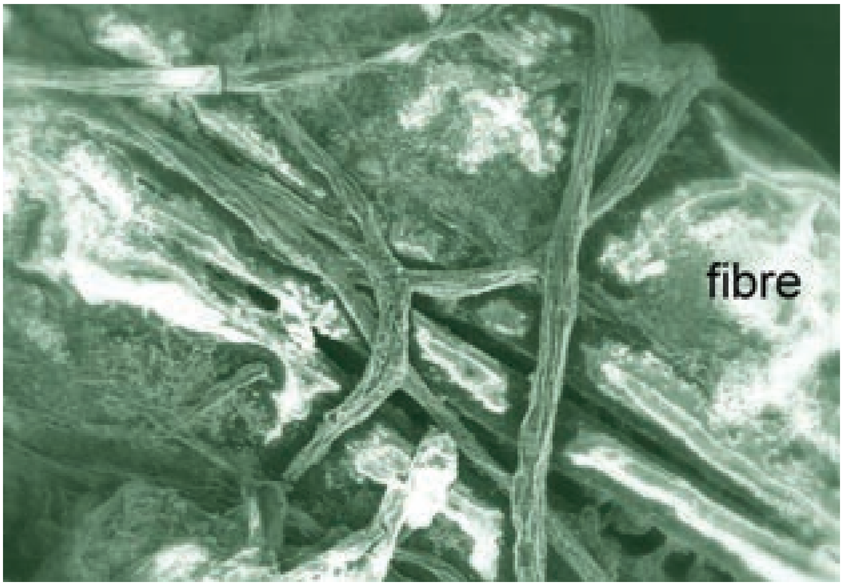

Figure 3: algal filamentous growth wrapping around synthetic fibre within the cement matrix of marine concrete

degrade the surrounding tissue of bast-fibre, thus separating the fibres. This is essentially an assimilative process, during which organic residues are washed away, leaving the fibres intact. Degradation of fibre-reinforced concrete, however, is essentially a dissimilative process, but with a similar result.

Filamentous bacterial growth (Figure 2), which can occur at very low nutrient levels, not only wraps around the fibres, weakening the fibre/concrete matrix bond, but conditions the surface of the fibre, making it more amenable to colonisation by other micro-organisms such as algae (Figure 3). The mechanisms observed and presented in Figures 1 & 2 occur when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth(8).

In cement composites with fibre inclusions, the matrix in the vicinity of the inclusion can be quite different in its microstructure from that of the bulk cement matrix. This modified matrix can be as great as 50-100μm(9). The higher porosity at this interface favours the appearance and development of bio-erosive forces in the form of microbial filamentous growth.

Experimental evidence from other researchers indicates that porous concrete creates a favourable environment for microbial colonisation, because water-borne organisms including algae adhere to both its inner and outer surfaces(10). The observations reported in this study, particularly the attachment of filamentous organisms, the cohesion between particles, and the penetration and growth (seen in figure 4), are comparable to those observed in previous work on boring activity within the concrete of historic buildings(11).

This type of deterioration has also been reported in subsea tunnels in Norway(1), where steel-fibre-reinforced concrete used for rock

➔

support was attacked by saline ground waters along the concrete/rock interfaces, as well as the outer rough and more reactive concrete surfaces. The process had frequently led to the total disintegration of the cement paste matrix and steel fibre after less than five years' exposure and was reported as being closely related to the growth of biofilms(1).

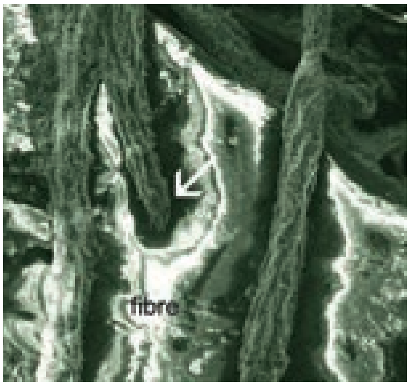

Figure 4: algal filamentous growth (30μm-diameter) penetrating through the synthetic fibre (arrowed)

CONCLUSION

It is the author's understanding that early bacterial biofilm formation within the matrix is the start of the marine fouling process, leading to further colonisation of algae and other micro-organisms. This continual growth at the fibre/cement interface weakens the bond between fibre and cement.

Filamentous microbial growth around fibrillated polymer and the penetration of microbial filaments through the material is detrimental to the overall durability of the concrete itself. Potential influences of marine organisms on the durability of synthetic fibres in concrete used in harsh environments clearly warrant further detailed investigation.

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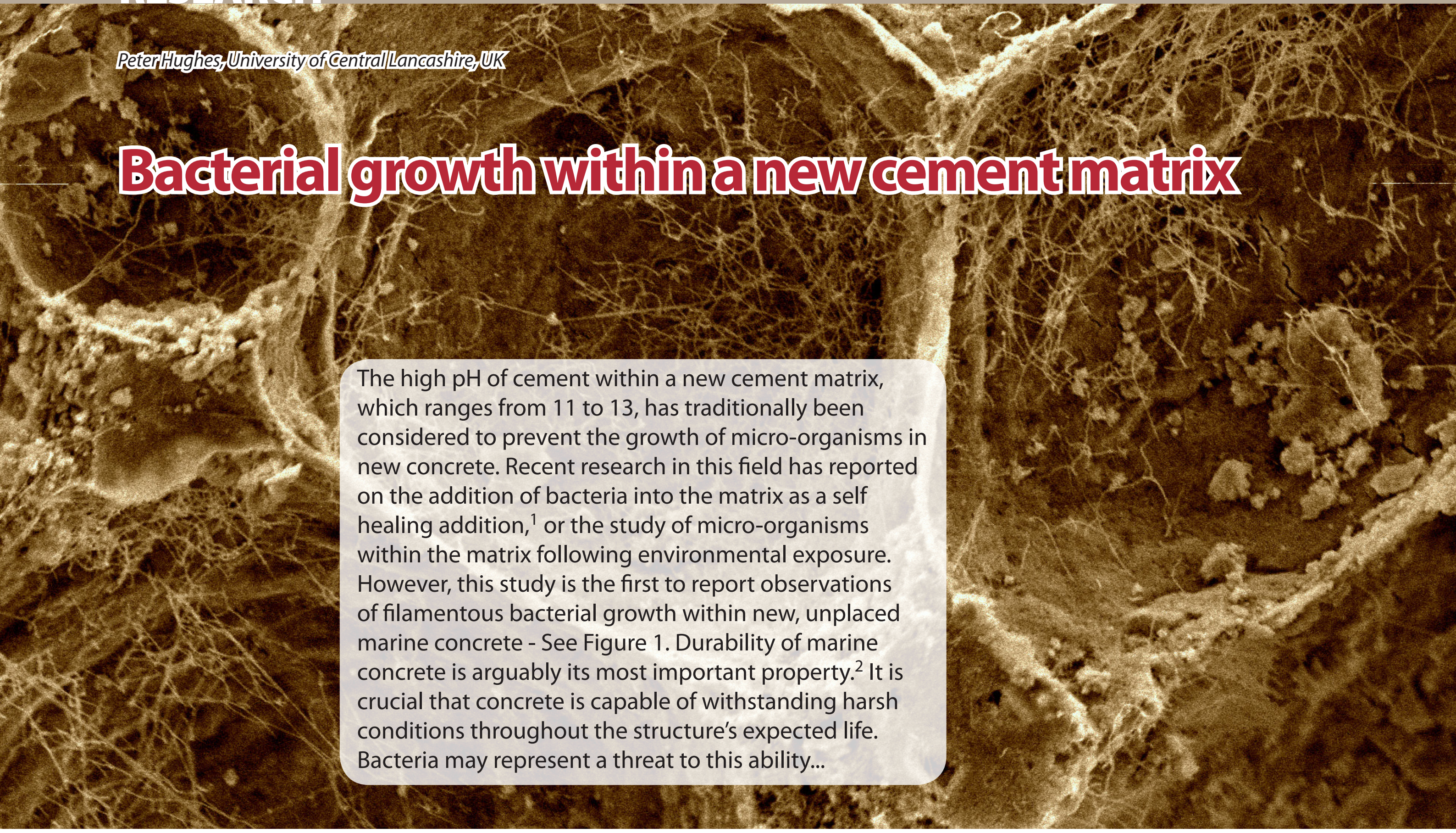
Peter Hughes is a final-year PhD student at the University of Central Lancashire, UK, investigating marine bio-fouling and its implications for the durability of marine concrete. The author would like to thank his supervisors for their endless guidance: D Fairhurst, Prof I Sherrington, Dr N Renevier, Prof LHG Morton, Prof PC Robery and Dr L Cunningham. Further discussion is invited – contact phughes1@uclan.ac.uk

Peter Hughes, University of Central Lancashire, UK

Bacterial growth within a new cement matrix

The high pH of cement within a new cement matrix, which ranges from 11 to 13, has traditionally been considered to prevent the growth of micro-organisms in new concrete. Recent research in this field has reported on the addition of bacteria into the matrix as a self healing addition,[1] or the study of micro-organisms within the matrix following environmental exposure. However, this study is the first to report observations of filamentous bacterial growth within new, unplaced marine concrete - See Figure 1. Durability of marine concrete is arguably its most important property.[2] It is crucial that concrete is capable of withstanding harsh conditions throughout the structure's expected life. Bacteria may represent a threat to this ability...

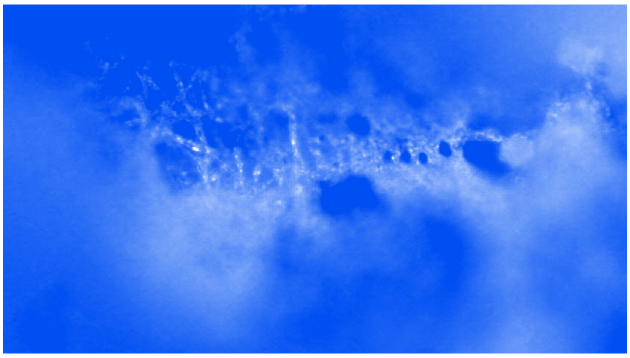


Above: Bacteria in fresh cement.

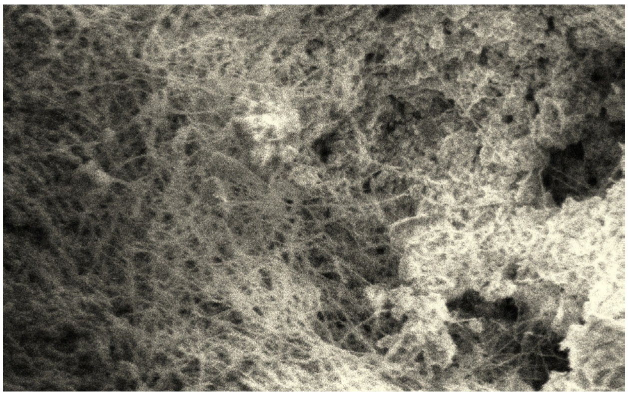
Microbial growth and the ability of some species to tunnel into concrete surfaces, leads to degradation, increased porosity and decreased durability in concrete structures. Micro-organisms such as bacteria,[3] fungi[4] and algae[5] have been widely reported to be involved in the deterioration of concrete.

Previous experimental evidence indicates that porous, exposed concrete creates a favourable environment for microbial colonisation, because aquatic organisms including algae and bacteria adhere to its inner and outer surfaces.[7] They produce branching networks that vary greatly in size from as little as 350nm in diameter - See Figure 2. In some species such as Ulva, such fine filaments may collect together to form tubular thalli up to 25µm in diameter.[8]

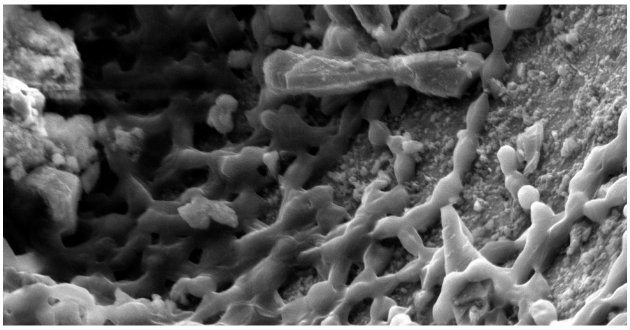
Concrete structures exposed in tropical and sub-tropical seas have been shown to be subject to the same bioerosive forces as carbonate substrates. Many of the species implicated in calcium carbonate breakdown have been demonstrated to be capable of bioeroding concrete. The aim of this phase of the study was to observe and report filamentous bacterial growth within a new, unexposed cement matrix and to discuss its origins. To achieve this aim new test cube specimens of concrete destined for use at a coastal protection scheme in the UK were examined using light microscopy and scanning electron microscopy (SEM).



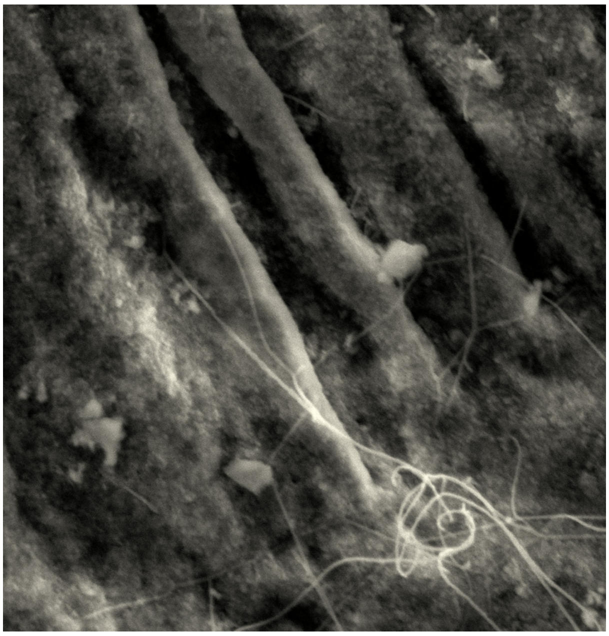
Right - Figure 1: Light microscopy image of filamentous bacterial growth within matrix of new, unplaced marine concrete.



Right - Figure 2: Scanning electron microscopy (SEM) image of bacteria within an empty water void, within the fresh, hardened concrete matrix.



Right - Figure 3: SEM Bacterial biofilm formation at the fine aggregate/cement interface within unplaced concrete.



Left - Figure 4: SEM of a water void within the matrix. The chamber had 'rippled' effect walls, similar to tide marks on a beach. This cavity probably held water utilised by the micro-organism.

Concrete specimens examined

The study site for this research is part of a coastal protection scheme, which involved the placing of 65,000m^3 of ready mix concrete and 44,000m^3 of precast concrete revetment armour. The compressive strength class was C35/45, BS8500-1 exposure class XS3, XF4, XC3, XC4 and a water/cement ratio of 0.45.

The minimum cement content was 340kg/m^3, CEM IIIA, with 50% ground granulated blast-furnace slag, with a chloride class 0.2. Cubes (150mm x 150mm) were made with concrete supplied by the manufacturer, air cured at 20°C inside the laboratory for 28 days. Some cubes were dry diamond cut into 25mm lengths, washed and examined. Some cubes were broken into smaller pieces, approximately 10mm^3, suitable for microscopic examination.

Aggregate details

Marine dredged sand was extracted from a beach on the north west coast of England and blended with crushed limestone for use as fine aggregate by the concrete manufacturer. The sand was washed with sea water to reduce silt content and then screened to remove any significant debris such as litter and/or driftwood.

Beach sand samples were collected by hand 1km landward from the dredging area for comparison. The fluvio-glacial deposits on the floor of the eastern Irish Sea adjacent to the dredging site are the dominant source of sediments. Whole-rock mineralogical analysis of a range of intertidal sediment samples has shown that they are predominantly quartz with associate plagioclase, orthoclase, calcite, dolomite, chlorite/kaolinite and mica.[9]

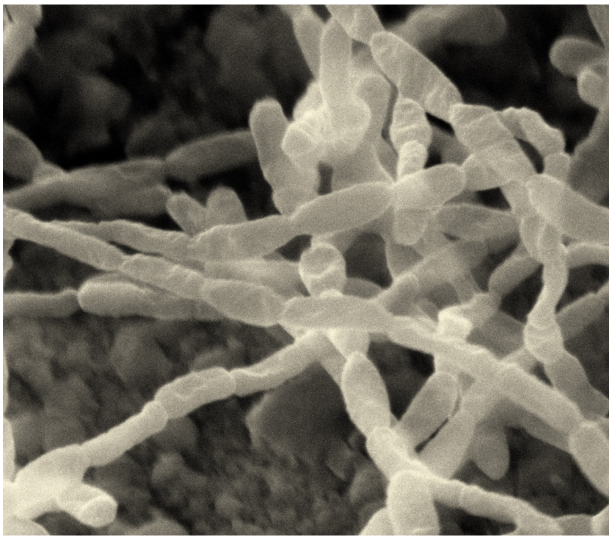
Locally-sourced 20mm coarse limestone aggregate (older palaeozoic) was utilised in the production of the concrete.

Results

The SEM micrographs illustrate microbial growth within the new concrete. Figure 3 shows bacterial filamentous growth at the aggregate/cement interface. Figure 4 shows a water void with filamentous growth on the rippled walls of the chamber. Figure 5 illustrates a chain-like structure of cells approximately 350nm in diameter growing within the cement matrix. Figure 6 shows attached filaments growing out from pores on the surface of new sand.

Discussion

Material from marine deposits around the coast of UK has been used in concrete production for several decades. However, no provision is made in the current standard (UK) for the control of microbial growth within or on the surface of beach sand.

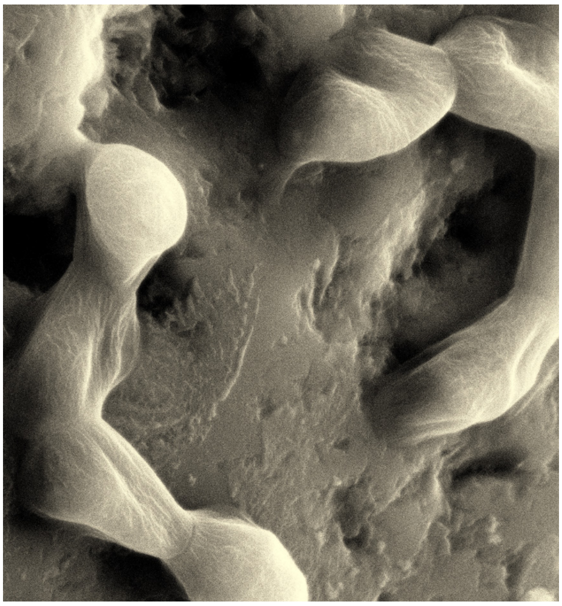


Left - Figure 5: Early bacterial biofilm formation in the cement matrix.

Research by Steele[10] found that viable algal cells buried to a depth of 0.2m below the sand surface in a Scottish sea loch. A similar finding occurred 200km from the source of the marine aggregate used in the study mix, in Lough Neagh (Northern Ireland), where high concentrations of living algal cells were found attached to sand grains down to 0.5m below the sand surface.[11]

Considering the constant mixing of sediment at a beach surface, it may follow that microbial endoliths could occupy some of the beach extraction used in the production of the concrete examined in the current work. Beach sand samples from the vicinity of the dredging site (the source of fine aggregate used in the concrete production) were examined under the microscope and found to be colonised by filamentous microbial growth. The existence of microbial populations that live on or within sand is well documented.

The British Cement Association warns that washed beach sand is generally unsuitable by itself for good quality concrete, due to the single-sized grading, but this can be overcome by blending aggregates. While aggregates for un-reinforced concrete can be washed



Right - Figure 6: Bacteria growing from the surface of sand, at the cement interface of new concrete.

with sea water, as was the case in this study, for reinforced concrete the aggregates must be carefully washed with potable water to remove excess chloride from sea salt. However they will still retain shell fragments and organic matter that can affect the water demand of the mix. The organic content refers only to water-soluble organic compounds derived from decaying vegetation, tests for which no longer appear within standards.

Although bacteria, and particularly acid-producing bacteria, have been traditionally considered as harmful organisms for concrete, an alternative perspective is that the growth of micro-organisms may afford some level of protection from weathering and erosion.

It has been reported[12] that certain bacteria have the ability to promote the precipitation of calcium carbonate, has been used advantageously for consolidation of concrete and stone. Previous research has illustrated a reduction of the capillary permeable porosity and an increased resistance to damage processes such as chloride ingress and carbonation by this biodeposition procedure.

The preliminary results of this on-going study suggest that the blanket use of marine sourced aggregates should be reconsidered for concrete that is to remain in contact with sea water, particularly mass (unreinforced) concrete. Washing in water may only partly remove some of the epilithic biomass present on the surface of the aggregate, possibly leaving endolithic micro-organisms to continue to thrive.

It has been reported some micro-organisms such as algae[13] have resting stages (spores and zygotes) that allow cells to lay dormant in unfavourable environments, even freezing conditions or to survive in ephemeral pools. Previous research found that even after soils had air-dried for 35 years, green algae could be cultured. Therefore the microbial content may need to be controlled in structures subject to permanent wetting by sea water to control growth on and inside the matrix.

BS EN 12620 is the predominant specification concerning the use of aggregates for concrete supported by UK national guidance document PD 6682-1. This guidance should consider undesirable elements such as micro-organisms more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach fine aggregate, leading to increased colonisation and the bio-deterioration of the concrete.

Acknowledgement

The author thanks his supervisors for their endless patience. D. Fairhurst, Professor I. Sherrington, Dr. N. Renevier, Professor L.H.G. Morton, Professor P. C. Robery and Dr. L. Cunningham.

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Microbial filamentous growth in subsea concrete

Following on from his article in *Concrete* February(1), Peter Hughes, a final year PhD student at the University of Central Lancashire, discusses issues of concrete durability for tunnels in a marine environment.

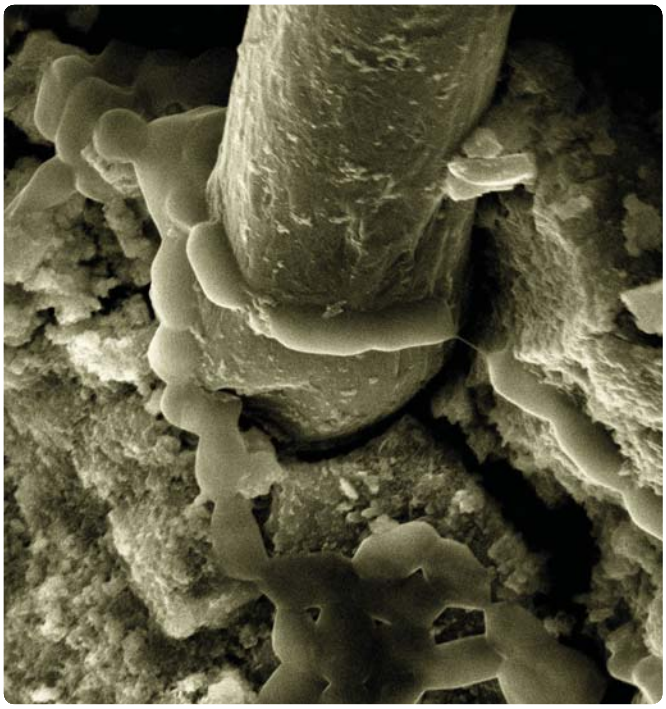


Figure 1 right: A micro-fibre (22µm in diameter) with bacterial biotenacious growth (350µm in diameter) around the cement interface.

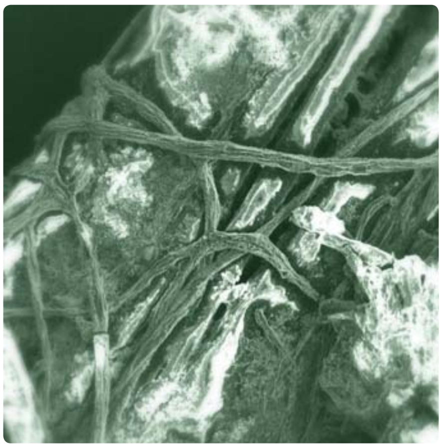
It is obvious that safety is critically important in the mining industry. Concrete durability in tunnels is vital as failures in the past have led to the loss of life. As in the case of sprayed concrete used in tunnel works, as well as in the open air, particles and sometimes biological material tend to accumulate on the outer surfaces of concrete. This formation further attracts moisture, which may facilitate chemical reactions and even the growth of bacteria.

Micro-organisms such as bacteria and algae have been widely reported to be involved in the deterioration of concrete(2,3). However, relatively few direct relationships have been established between the activities of micro-organisms and synthetic fibres within concrete, in harsh environments such as tunnels. It has been reported that steel fibres within sprayed concrete were severely attacked by bacteria(4) and synthetic fibres have also been observed in a marine environment to be susceptible to micro-organisms(5,6).

Even though it is claimed by other researchers that some species of bacteria may enhance the durability of concrete, it is the view of the author that filamentous growth is detrimental to the durability of synthetic-fibre-reinforced concrete in harsh environments. In related studies by the author, synthetic fibres have been observed in a marine environment over the lifetime of a sea defence scheme, some eight years.

It is usually accepted that a watertight concrete is durable. However, if the concrete is permeable, the interior may become saturated, allowing water-carrying micro-organisms to play a more active role in deterioration. They can be transported into the matrix, helping to create successive cycles of expansion, further cracking, fibre de-bonding and liberation leading to increased permeability.

Among all the microbial groups, bacteria stand out in their ability to grow at low oxygen concentration. The problem of bacteria in concrete tunnels has previously been reported(7), highlighting an interesting and serious problem as far back as 1934, by the appearance of crenothrix, a type of bacteria found growing in the ground water



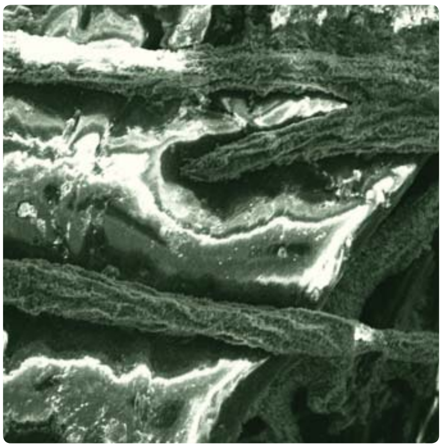


Figure 2 above: A micro-fibre protruding from the surface of concrete. Note the bacterial colonisation within the void beneath the surface.

Figure 3 middle: Algal filamentous growth around synthetic fibre within the cement matrix of marine concrete.

Figure 4 top right: Algal filamentous growth (30µm in diameter) through the synthetic fibre.

that leaked into the tunnel. This seepage water, having a high mineral content and containing the crenothrix organism, suspended in the Hetch Hetchy water (USA), flowed through the tunnel and carried the micro-organism into several lines of conveying water. After intensive study, control of the organism with a chlorine-ammonia treatment was used. Algae have been commonly observed within subsea tunnels, causing the clogging of drains.

Discussion

Bacteria are ubiquitous and the biotenacious growth around the micro-fibre in Figure 1 can be further understood by relating it to a natural process where the micro-organism has been used for many years, in the production of fibre extraction from plant materials. Retting employs the action (as seen in Figure 2) of bacteria to dissolve and degrade the surrounding tissue of bast fibre, separating the fibre. The bacteria found in seawater attack the plant tissues surrounding the fibres, softening them so they can be washed away, leaving the fibres intact. Timing is important in obtaining good-quality fibre: if the plant (or the bark of a tree) is under-retted it will be difficult to remove; over-retting will allow the bacteria to not only remove the surrounding material but to also attack the fibres themselves.

Filamentous bacterial growth (Figure 2), which can grow at very low nutrient levels, not only wraps around the fibres, weakening the bond, but also conditions the polymer surface, making it more amenable to colonisation by other damaging micro-organisms such as algae (Figure 3). The mechanism observed and presented in this study occurs when the material bond is weakened as a direct result of the physical activity of an organism, such as its movement or growth and is reported elsewhere(8).

In cement composites with fibre inclusions, the matrix in the vicinity of the inclusion can be quite different in its microstructure to that of the bulk cement matrix. This modified matrix can be as great as 50–100µm in area. The higher porosity at this interface favours the appearance and development of bioerosive forces in the form of microbial filamentous growth, as reported here. Experimental evidence from other researchers indicates that porous concrete creates a favourable environment for microbial colonisation, because aquatic organisms including algae adhere to both the inner and outer surfaces(9). The observations in this study, particularly the attachment of filamentous organisms, cohesion between particles, the penetration (seen in Figure 4) and growth are comparable to those observed by previous work(10) on boring activity within the concrete of historic buildings. This deterioration has also been reported in subsea tunnels in Norway. Steel-fibre-reinforced concrete used for rock support was attacked by saline ground waters along the concrete/rock interfaces as well as the outer very rough and reactive concrete surfaces. The process had frequently led to the total disintegration of the cement paste matrix and steel fibre after less than five years' exposure and was reported as closely related to the growth of biofilms.

Concluding remarks

It is the author's understanding that early biofilm formation (bacteria) within the matrix is the start of the marine fouling process, leading to further colonisation of algae. This continual growth at the fibre–cement interface weakens the bond between fibre and cement. Filamentous growth around fibrillated polymer and the penetration of microbial filaments through the material presented here is detrimental to the overall durability of the concrete itself. Potential influences of marine organisms on the durability of synthetic fibres in concrete used in harsh environments clearly warrant further detailed investigation. ●

● **Acknowledgements:**
The author thanks his supervisors for their endless patience: D Fairhurst, Professor I Sherrington, Dr N Renevier, Professor LHG Morton, Professor PC Robery and Dr L Cunningham. Further discussions are invited at: PHughes1@uclan.ac.uk

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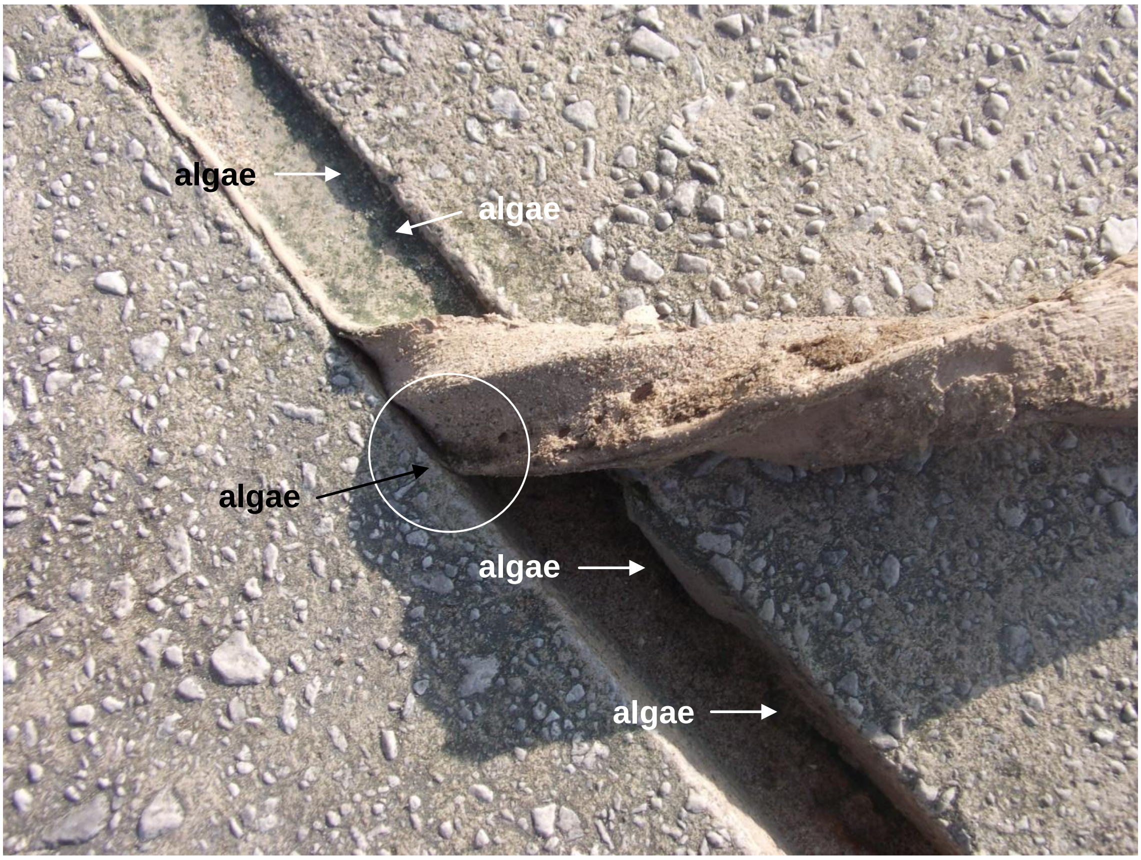

Figure A5-1 Sealant at the study site. Algae growing under the sealant (arrowed), eventually causing the material to de-bond. Other degradation mechanisms such as cleaning and tidal impact will also play a role.

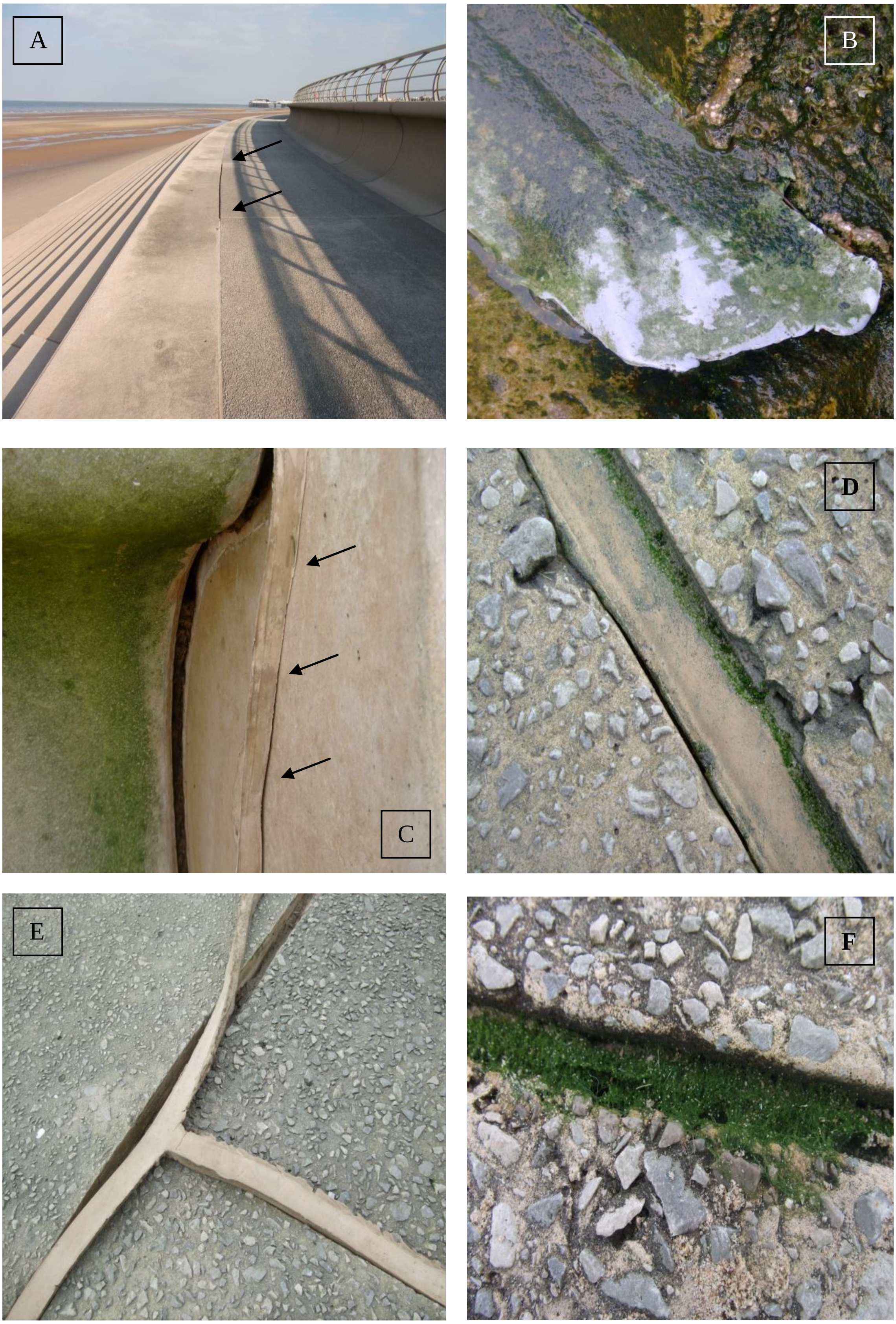

Figure A5.2 Sealants used at the study site. **A**. Section of sealant missing. **B**. *Ulva* growing on and underneath. **C**. A section of wave wall with sealant fallen away. **D**. *Ulva* at the surface of sealant. **E**. Illustrates a serious trip hazard to the public. **F**. *Ulva* growing under sealant before being removed.

Appendix 6
Additional documentation to Chapter 6

Coatings

A6-1 Copy of original published article supporting this Chapter:

1 - Hughes, P. 2013B. Investigation into Marine Concrete Anti-Fouling Coatings. *Coatings World.* 4, Vol. 18, 40-43.

COATINGS WORLD

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ECS 2013 REVIEW

PLUS:

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Investigation Into Marine Concrete Anti-Fouling Coatings

Peter Hughes, *Contributing Writer*

Our civil engineers involved in the construction or maintenance of marine concrete structures are faced with the problem of preventing unwelcome microbial growth in an environmentally friendly way. A long term ecologically sound answer to organic growth remains unsolved, however the use of titanium dioxide (TiO_2) particles within coatings for concrete pavements have received considerable attention in recent years as these particles can trap and decompose organic and inorganic air pollutants by a photocatalytic process (1). In spite of these promising benefits, the durability and resistance to wear of TiO_2 surface coatings upon fibre reinforced marine concrete has not been evaluated. In this article, the development of fundamental research on the application of TiO2-based photocatalysis in a marine environment will be introduced. The problems encountered at a UK study site restricting a larger scale application of the technology are discussed.

Photocatalytic coatings are successfully used with many other building materials and have been shown to retard algal growth on concrete (2). In spite of these promising benefits, applications of this technology are currently limited. The durability of this technology in a marine application needs to be established before large-scale practical implementation is undertaken. Titanium dioxide (TiO_2) is a white inorganic substance that is thermally stable, non-flammable and insoluble. TiO_2, the oxide of the metal titanium, which is the ninth most abundant element in the earth's crust, occurs in many rocks and mineral sands, the most economically important being ilmenite and rutile deposits. Ultra-fine (nano-scale) titanium dioxide (Anatase) was used in this research for surface treatments. The potential of titanium dioxide as a photocatalyst was discovered by (3). This process, which is similar to plant photosynthesis, allows the decomposition of water into oxygen and hydrogen in the presence of light, by means of a TiO_2-anode (1). Based on this heterogeneous photocatalytic oxidation process, nitrogen oxides are oxidized into water-soluble nitrates while sulfur dioxide is oxidized into water-soluble sulfates; these substances can be washed away by moisture in the form of rainfall or seawater. The overall aim of this research, is to advance the understanding of how a photocatalytic (TiO_2) coatings responds in a marine environment. This phase of work, carried out in the northwest of England, has recorded anti-fouling performance and intends to progress towards a non-toxic, environmentally-benign strategy for future industrial applications.

The 'Development' Tio_2 Coating Used In This Research

Primary particles of ultrafine TiO_2 within the development coating used was typically in the range of size from 10 to 60 nm, not only as existing discreet primary particles but as aggregates, with secondary particle sizes typically >100 nm. The coating was a stable aqueous dispersion (sol) of ultrafine TiO_2 particles. Key features included an anatase crystal form with a 10 wt% of TiO_2 content. The coating had a neutral pH of 8.5, with a high surface area (dry) of 300 m²/g, it dried clear, and was UV light activated with limited fluorescent light activity. It is marketed for architectural applications.

Tio_2 Coating Application In This Study

The coating procedure consisted of three independently applied layers brushed (concrete tiles) or roller applied (static site) onto the surface of concrete specimens, as per the manufacturer's recommendation. The primer layer was applied to lower the viscosity of the material. This assisted in generating a good seal in the priming process through the filling of cracks and blowholes in the concrete surface. The primer formed a coating layer with a dry film thickness of 10μm. On top of the dried primer, an undercoat was applied after a drying time of 24h. Then, three separate topcoats were applied, each 10µm and a further 24h drying time, thus, bringing the overall thickness of the photocatalytic coating to 50µm. Although the coating was composed of a number of different layers, the comparatively short time between applications ensured that the finished complete layer did not show any distinct separate layers, but can be treated for all intents and purposes in this research as a single layer, see figure 1.

Results And Discussion

The biological complexity of the phenomenon, part of a larger study (4), referred to as marine biofouling, is enormous. It has been shown here and in previous research (5) that it is an ecological community with entities originating from all that we call life. Also, each organism has its own solution for how to find and attach on a surface, evolved during millions of years. It is the author's view, it is impossible to invent new antifouling coatings without restricting the problem, meaning that several antifouling strategies have to be part of a holistic approach, leading to a bigger solution.

There are however several obstacles to be cleared before titanium dioxide photocatalyst technology can be adopted in the control of marine biofouling. Not only the fact that the applicability of this technology is limited considerably because the catalyst works only where there is light, but the application of a coating to composite materials such as concrete has limitations, as shown in figure 2.

The performance of the coating was observed to be heavily dependent on the underlying composite material. First of all, due to differences in intrinsic properties the synthetic fibres, in abundance at the surface of the concrete samples, inhibited a satisfactory bond between coating and substrate. The thermal coefficients of the coating were different from that of the concrete and its constituents. Thermal expansion and movement, referred to as 'fibre pop out', of exposed fibres instigated a cracking of the coating, as seen in figure 3, resulting in not only reduced photocatalytic activity but also structure and strength destructions.

Furthermore, the attachment of filamentous algae to the surface of the coating, seen in figure 4, was also observed to be detrimental to its long term durability. Diatoms, illustrated in figure 5, form another component of marine biofilms and act a settlement mediator for larger fouling. The diatom attachment to coatings examined showed that this single algae cell accelerated coating degradation.

Filamentous bacterial growth from within the matrix of the new concrete, as observed in figure 6, also played its part in the eventual cracking and delamination of the coating from its foundation. This previously unreported phenomena is discussed in more detail elsewhere (6). Coatings for marine concrete structures

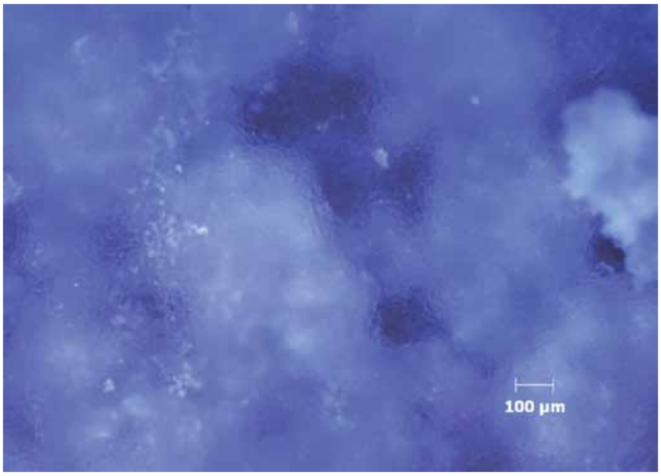

Figure 1. Homogeneous coating surface without defects (3 months exposure).

Figure 3. Fibre 'pop out' through the coating.

are subject to harsh environments, dynamic loads, continuous expansion and contraction by heat, rain/seawater splash, impacts from debris, erosion, micro-organisms etc. In this condition, most coatings deteriorate in a short period of time in the form of cracking, blistering, disbanding or chalking. The application of the TiO_2 based coating tested in this research was not designed to defend from microbial growth from 'within' the concrete, effectively a living substratum, observed in figure 7. The occurrence of a bacterial biofilm formation under the coating has significantly effected the performance of the coating. A study into the addition of TiO_2 powder with an average size 21 nm (30% rutile and 70% anatase) into a bacterial colony, showed that 60–120 min were sufficient to destroy all the bacteria (7). Other workers also confirm that using lower dimension TiO_2 particles leads to a faster bacterial destruction (8). These new observations of bacterial growth seen in figure 6 are detrimental to the long term durability of the coating and requires further investigation. This newly observed degradation mechanism, see figure 8, reported here, of a coating has implications for not only the construction sector.

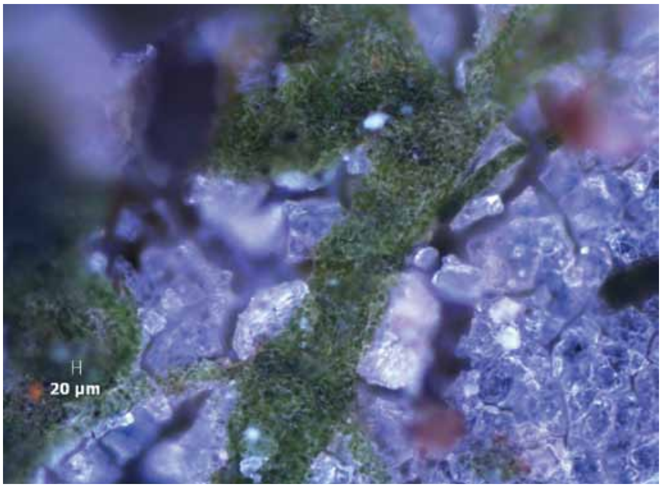

Figure 2. Algal colonisation on the coating (also at 3 months exposure).

Conclusions

Based on the analysis conducted, the following conclusions may be drawn that macro and micro synthetic fibres at the surface of concrete inhibit a strong and durable bond between the coating and the substratum, accelerating cracking and the eventual breakdown of the coating. Algal filamentous growth including diatoms attached to the surface of the coatings, applies further pressure on the integrity of the coating. Bacterial filamentous growth from within the matrix of the concrete, grows at the coating/concrete interface. This growth disrupts the bond between coating and substratum, leading to the de-lamination of the coating. Based on the results presented, further research is recommended to consider factors such as microbial growth under a coating, application methods and variation, coating composition, and long term durability. Furthermore, research in this field, needs to be developed to determine if any coatings have the potential to be effective in the long term strategy against marine biofouling. ***CW***

Peter Hughes is a final year PhD student at the University of Central Lancashire, UK, investigating marine biofouling and its implications for the durability of marine concrete.

Acknowledgement

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Further discussions are invited at: PHughes1@uclan.ac.uk

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Figure 4. Attachment of filamentous algae to the surface of the coating.

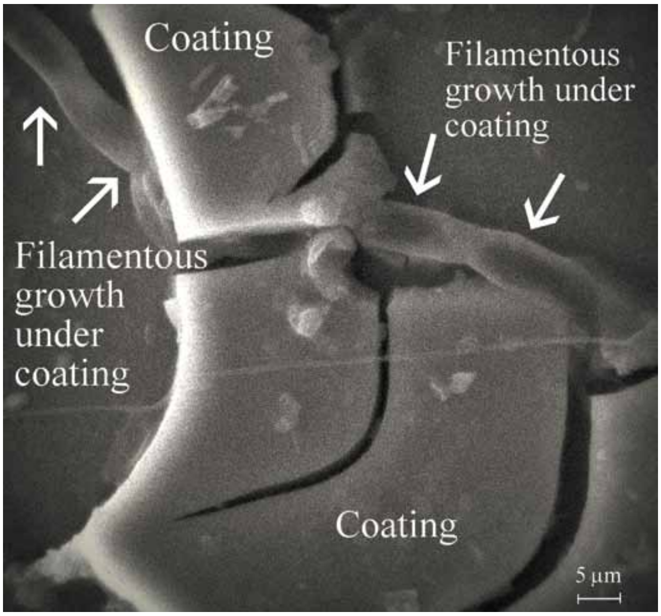

Figure 6. Bacterial filamentous growth from within the new concrete matrix. after 1 months exposure.

Figure 8. Algae penetrating through the coating (arrowed).

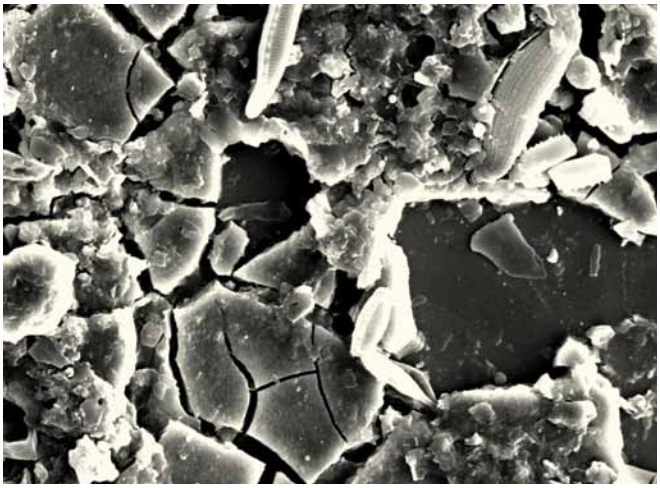

Figure 5. Microorganisms on the surface of the coating including Diatoms, after 1 months exposure.

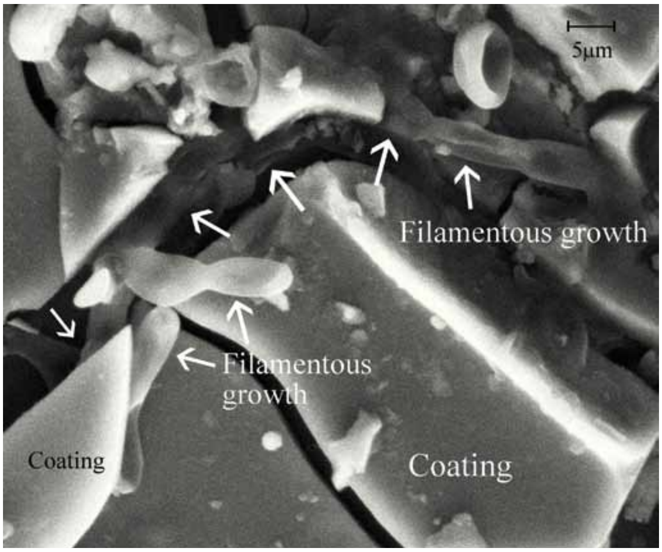

Figure 7. Bacterial filamentous growth from within the concrete matrix.

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4. Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robbery, P., Cunningham, L. Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete. Construction and Building Materials. 41, 2013, 498-504.

5. Hughes, P. A new mechanism for accelerated degradation of synthetic-fibre-reinforced marine concrete. Concrete. 9, 2012, Vol. 46, 18-20.

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Appendix 7

Additional documentation to Chapter 7

Japan

A7-1 Copy of original published paper supporting this Chapter:

1 - Hughes, P, Fujita S, Satomura T, Suye S. 2012. Hydrophilic-modified polyurethane nanofibre scaffolds for culture of hyperthermophiles. *Materials Letters*, Vol. 72, 88-91.

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Hydrophilic-modified polyurethane nanofibre scaffolds for culture of hyperthermophiles

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ABSTRACT

Hyperthermophiles are expected as the source of thermostable enzymes, but agarose-gel culture is unavailable for isolating them because of the high temperature culture condition. In this paper, we proposed the scaffold suitable for long-term culture of hyperthermophiles, which is applicable for an extremely high-temperature. We have investigated the dynamics of the attachment and colonisation of *Sulfolobus solfataricus*, onto electrospun nanofiber scaffold. Observation by fluorescent microscopy and SEM demonstrated adhered and colonised onto the polyurethane nanofibres the hydrophilicity of which was enhanced by oxygen plasma treatment. This research is a first step towards developing a new approach to successful solid-culture of hyperthermophiles under extreme conditions.

1. Introduction

Hyperthermophiles, isolated from continental and marine volcanic environments, grow at near 100 °C [1]. They have different metabolic pathways and enzymes from those of bacteria and eukarya [2,3] that they are expected as the source of novel enzymes stable in extreme conditions; high temperature, high pH, low pH, and high concentration of organic solvent. Therefore, they are not only biological concerns for the advancement of research, but also the concern with their industrial application has been growing [4].

To isolate and culture hyperthermophiles, the liquid medium has been conventionally employed instead of the solid agarose-gel medium for common bacteria and other cell types [4–6]. Liquid medium burdens the isolation of colony because picking up a single colony from liquid medium is difficult. The main reason why the solid medium has not been used in their culture is due to the long cultivation time. Their proliferation is slow and, therefore, it was difficult to keep the medium volume at high temperature preventing vaporisation. Thus, the improvements are needed in the recovery of these 'unculturable' microorganisms [7,8]. Furthermore, it is difficult to prepare agarose gel at high temperature, which hyperthermophiles favour. To address these problems, the culture scaffold is highly desired instead of solid-gel medium. But, the main hindrance to cultivation is the prevailing lack of knowledge on the initial attachment and colonisation of the scaffold [9–11]. This research is a first step in the culture scaffold of *Sulfolobus solfataricus*, hyperthermophiles living at high temperature and low pH. To prepare the nanofiber scaffolds, we employed electrospinning. This process is widely used in the culture scaffold for mammalian cell and medical devices, [12,13] because it is convenient and inexpensive to fabricate scaffolds, applicable to use various polymers and easy-to-control dimensions of scaffolds.

2. Materials and methods

2.1. Fabrication of nanofiber scaffolds by electrospinning

Polymer solutions chosen were shown in Table 1. Polyurethane (PU; P22SRNAT, JIS hardness; 82A) was purchased from Nippon Polyurethane Industry (Tokyo, Japan), polystyrene (PS; Mw 20,000) from Sigma-Aldrich (MO, USA), tetrahydrofuran (THF) and dimethylformamide (DMF) from Wako Pure Chemical Industries (Osaka, Japan).

The electrospinning set-up (MECC Co., Ltd., Fukuoka, Japan) is detailed in Scheme 1A. A polymer solution is loaded into a syringe and driven through a metallic needle at a constant feed rate by a syringe pump, forming a droplet at the tip of the needle. A high voltage is applied between the tip and the rotating collector grounded. Electrospinning parameters tested are listed in Table 1.

To enhance colonisation nanofibers, each polymer was electrospun over a unique 'bridging' system, lifting the nanofibres from the cover slip, allowing more surface area to be colonised, see Scheme. 1B. Glass slides (cover slip, 22 mm × 26 mm, thickness no. 5; Matsunami, Osaka, Japan), were used as a base, upon which two pieces of conductive double adhesive tape (thickness 0.2 mm) were applied. Silicone rubber

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Table 1
Polymer solutions and the condition of electrospinning.

#	Polymer	Solvent	Conc., w/v%	Voltage, kV	Infusion rate, mL/h	Collector rotation, rpm
1	PU	95% THF/ 5% DMF	15	25	0.8	1200
2	PS	THF	20	25	0.7	900
3	PS	THF	30	25	1.0	900

(thickness 0.3 mm) was then placed on the tape. This arrangement lifted the fibres 0.5 mm up and away from the surface of the glass slide. The optimum distance was 7 mm between lifts. To improve surface hydrophilicity of PU and PS nanofibres, oxygen plasma treatment (100 W, 30 s, 0.1 MPa, chamber size, diameter 64 mm × depth 160 mm) was carried out using a plasma reactor (PR300; Yamato Scientific, Tokyo, Japan).

2.2. Culture conditions

The thermoacidophilic archaeon *S. solfataricus* P1 (JCM11322) obtained from Japan Collection of Microorganisms (Saitama, Japan). It was cultured aerobically in medium containing casamino acids (1 g/L), yeast extract (1 g/L) and the following trace minerals; $(NH_4)_2SO_4$ (4.9×10^{-2} M), KH_2PO_4 (2.1×10^{-3} M), $MgSO_4$ (1.0×10^{-3} M), $CaCl_2$ (4.8×10^{-4} M), $FeCl_3$ (7.1×10^{-5} M), $MnCl_2$ (9.1×10^{-6} M), $Na_2B_4O_7$ (1.2×10^{-5} M), $ZnSO_4$ (7.7×10^{-7} M), $CuCl_2$ (2.9×10^{-7} M), Na_2MoO_4 (1.2×10^{-7} M), $VOSO_4$ (1.5×10^{-7} M), $CoSO_4$ (6.5×10^{-8} M), adjusted pH 3.0 with 10 N H_2SO_4 [14]. One millilitre of the seed culture was inoculated onto nanofibres scaffold in a 35-mm polystyrene suspension culture dish (Corning, NY, USA) with 3 mL of medium. The dish was taped firmly and incubated at 80 °C for 1 week.

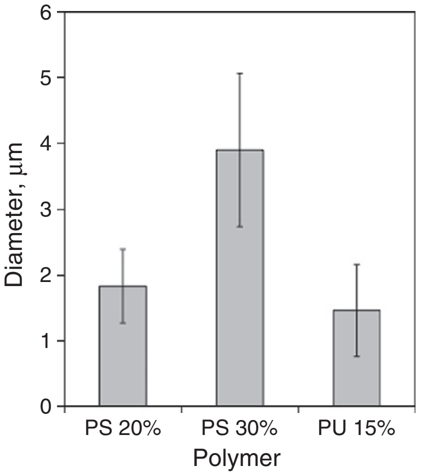
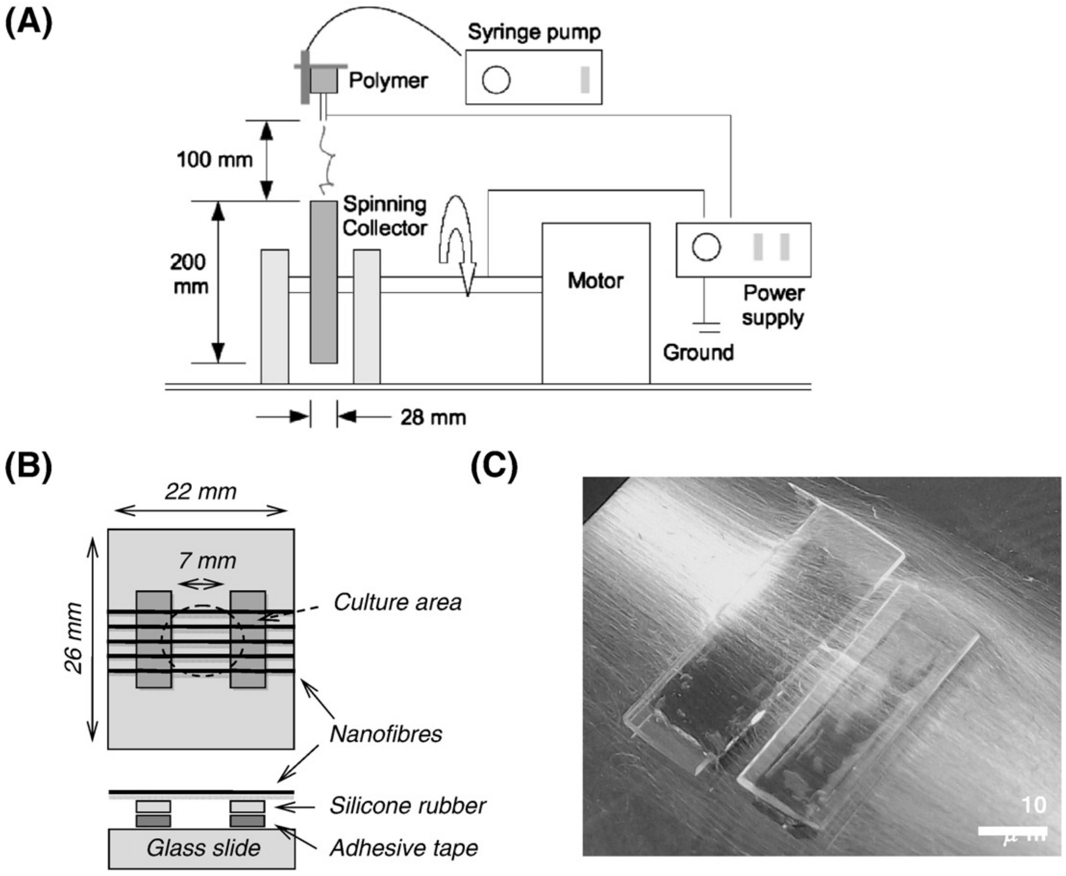


Fig. 1. Diameters of fabricated nanofibres. Means ± SD.

2.3. Fluorescent microscopy

Cultures were washed twice in phosphate buffered saline (PBS) to remove non-adherent cells then fixed with 4% paraformaldehyde (PFA) for 30 min. After the fixed cells were washed with PBS twice, they were stained with Hoechst 33342 (diluted 1:2000; Dojindo Laboratories, Kumamoto, Japan) for 30 min, being left in the dark,



Scheme 1. Schematic illustration of (A) electrospinning set-up and (B) the 'bridging' system, designed to lift and separate individual nanofibers from the glass. Cells are inoculated and cultured onto the bridged fibres between lifts. (C) Digital photograph of the 'bridging' system. Good alignment of PU nanofibres has bridged the 7-mm gap between the two pieces of silicone rubber. Bar = 10 µm.

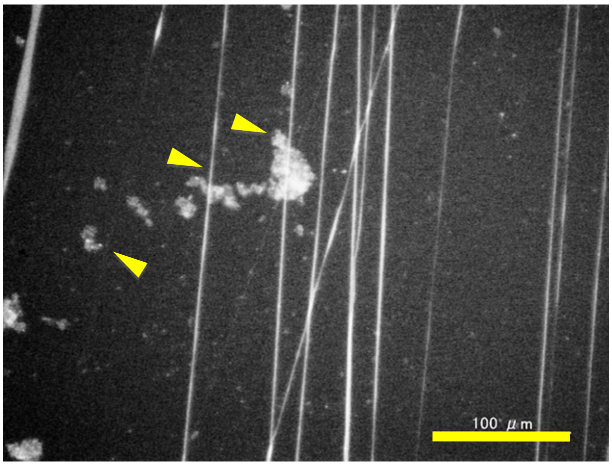


Fig. 2. Fluorescent microscopic observation of *S. solfataricus* which adhered and spread well onto the PU nanofibers after 1-week culture. Arrowheads indicate colonies. Cell nuclei were stained with Hoechst 33342. Fibres showed intrinsic fluorescence. Bar = 100 μm.

and finally washed twice in PBS. The adherent cells on each nanofibre were observed on a fluorescence microscope (BX51; Olympus, Tokyo, Japan).

2.4. Scanning electron microscopy

Cultures were fixed with PFA as described above, dehydrated through a graded series of ethanol (50, 60, 70, 80, 90, 95, 99 and 100%), replaced into 2-methyl-2-propanol (Wako), frozen at 4 °C, and then lyophilised with a vacuum evaporator. Dried samples were sputter-coated with Au/Pt (thickness 20 nm), and observed by a scanning electron microscope (S-2600; Hitachi, Tokyo, Japan) [15].

3. Results and discussion

We focused on the wide application and availability of electrospun nanofibres and applied to the culture scaffold for *S. solfataricus*, hyperthermophiles. In this study, PU and PS were chosen, because they offered many advantages over natural, mainly the ability to produce a wider range of mechanical properties [16]. The fibres uniformly crossing the bridge in a firm alignment were shown in Scheme. 1C. In the preliminary experiment, polylactic-co-glycolic acid (75:25; Mw 20,000; Wako) has been examined, but it has not kept without dissolution for 1 week at culture conditions (80 °C, pH 3.0). In the preparation of PU fibres, DMF was added to the solvent THF to slow the evaporation of the solvent. The concentration of each polymer was determined on the basis of the viscosity. The collector was rotated to align fibres. The collector speed was adjusted for each polymer. The diameters of fabricated fibres were measured by scanning electron microscopy (SEM) and shown in Fig. 1. The diameters of 15% PU, 20% PS and 30% PS were 1.46 ± 0.70, 1.83 ± 0.56 and 3.90 ± 1.17 μm, respectively (mean ± standard deviation). This result shows that PU and PS fibres in the wide range of micron to sub-micron have been made. We have tried to fabricate 12% PU fibre, but it was too thick to make a bridging substrate.

Then, we tried to culture *S. solfataricus* on nanofiber for 1 week. As a result, cell attachment was not observed on PS scaffold, while attachment was observed on PU fibre (Fig. 2). Consistent with the observations by SEM (Fig. 3), *S. solfataricus* attached and colonised onto the 15% PU nanofibers, while they showed no attachment and colonisation onto the same-sized 20% PS fibres. The number of attached cells was 0.95 cells/μm, which was counted by SEM images (the number of counted fibre: n = 57; the total length of counted fibre: 855 μm). We considered that this result is due to the difference of surface chemistry. When the polymer fibres were exposed to the culture medium, proteins in the medium are rapidly adsorbed onto their surface before the cells can adhere. The adsorbed proteins determine the subsequent cell attachment behaviours [17]. In addition, both of the non-plasma treated-PU fibre and non-plasma treated-PS

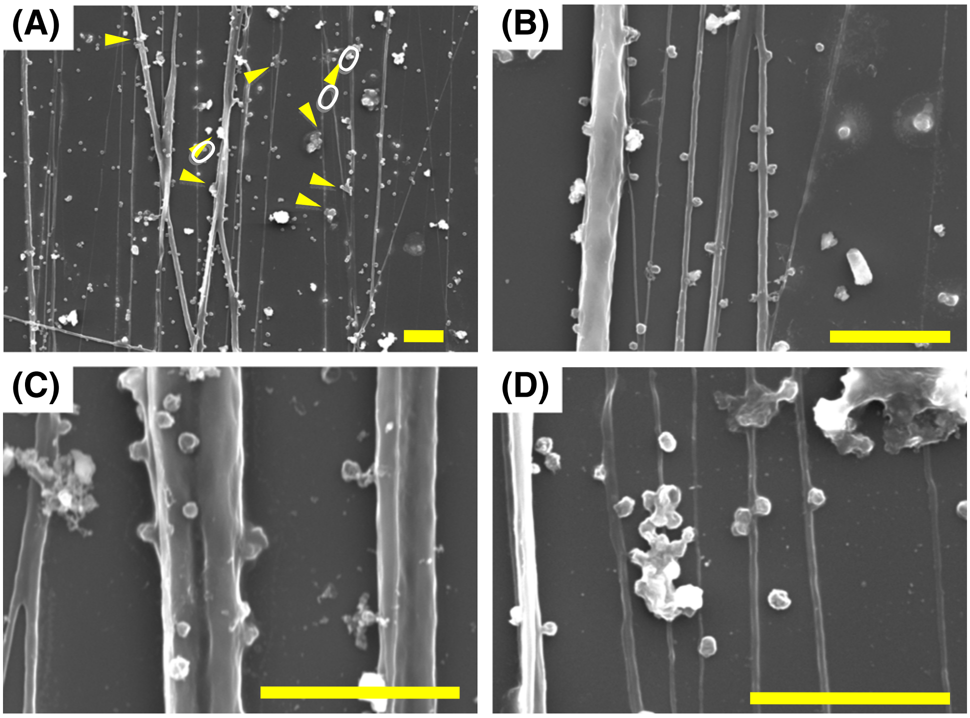


Fig. 3. SEM observation of *S. solfataricus* cultured on PU nanofibers for 1 week. (A) Low magnification image. Arrowheads indicate colonies. (B, C) High magnification images of a single cell attached on a thin (B) or thick (C) fibre. (D) High magnification image of a clump of proliferated cells. Bar = 10 μm.

fibre showed no attachment. It is known that plasmas can be used to alter material surfaces by removing surface layers, to activate the surface hydrophilicity [18]. The water drop contact angles of the cast film of PU and PS by after plasma treatment have been reduced from 94.6° ± 10.2° to 67.9° ± 1.5° and 109.5° ± 3.9° to 20.2° ± 2.9°. We considered that the optimal surface for the adsorption of the adhesion protein was moderately hydrophilic surface, as seen in the plasma-treated PU.

4. Conclusions

We have investigated the availability of electrospun scaffold, which showed hydrophilicity by O_2 plasma treatment, and the successful colonisation of hyperthermophiles was observed by SEM. This research is a first step towards developing the scaffolds for cell attachment and colonisation at extreme condition, which leads to the application of extremophiles to environmental materials and industrial usage.

Acknowledgements

This work was supported by the Japanese Society for the Promotion of Science, Summer Program 2011.

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Appendix 8

Additional documentation to Chapter 8

Holistic model

A8-1 Copy of original published paper supporting this Chapter:

As seen in appendix 4.1 - Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robery, P., Cunningham, L. 2013. Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete. Construction and Building Materials. 41, 498-504.

Appendix 9

Additional documentation to Chapter 9

Conclusions/Future work

A9-3 Proposed amendment to TR65.

A9-4 Local press feature.

A9–5 ABC Radio, ‘The Science Show’ (Manuscript).

A9-6 Published letter to Editor featured in ‘Concrete’.

A9-3 Proposed amendment to TR65

Amends to Technical Report No. 65: Guidance on the use of Macro-synthetic-fibre-reinforced concrete. The Concrete Society is considering the following amendment proposed by the author as a result of this work for the next re-print:

3.5 Long-term properties *(original TR65 section on page 24)*

3.5.1 Durability

Proposed addition to TR65 text

Hughes *et al* (1), studied the mechanical biodeterioration of macro and micro synthetic fibres at a marine study site over six years. Algal filamentous growth was observed interacting with synthetic fibres, weakening the bond between fibre and cement (2). Bacterial filamentous growth was also observed growing through synthetic fibres in fresh concrete (3).

Proposed additional references to TR65

References

1. Hughes, P., Fairhurst, D., Sherrington, I., Renevier, N., Morton., L.H.G., Robery, P., Cunningham, L. Microscopic examination of a new mechanism for accelerated degradation of synthetic fibre reinforced marine concrete. Construction and Building Materials. 41, 2013, 498-504.

2. Hughes, P. A new mechanism for accelerated degradation of synthetic-fibre-reinforced marine concrete. Concrete. 9, 2012, Vol. 46, 18-20.

3. Hughes, P. A study into the microbial growth within new marine concrete. Concrete. 1, 2013, Vol. 47, 34-36.

Transcript
ABC Radio - The Science Show
Broadcast 19th April 2013

The use of beach sand in concrete

My name is Peter Hughes, I'm a final year PhD candidate at the University of Central Lancashire in the UK, investigating marine biofouling and its implications for the durability of marine concrete.

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades, even though other countries throughout Europe avoid this practice However no provision is made in the current UK standards for the control of microbial growth within, or on the surface of beach sand. In the UK about 20% of natural gravel and sand requirements are sea dredged, there are over 2000 quarries operating around Australia that produce 150 million tones of rock, limestone, gravel and sand. Recent research into the use of certain microorganisms for the improvement of durability has recently drawn the attention of research groups all over the world. Most research in this field has reported on the addition of bacteria into the matrix as a self healing addition, but this study is the first to report observations of filamentous bacterial growth within new, unplaced marine concrete. Durability of marine concrete, is arguably its principal property; it is important that concrete should be capable of withstanding the harsh conditions throughout the expected life of the structure.

Beach sand samples from the vicinity of the dredging site (the source of fine aggregate used in the concrete production at the study site) were examined under a scanning electron microscope and found to be colonised by filamentous microbial growth. Bacterium was then cultured in the laboratory from these sand samples and matched to bacteria found in new concrete. Freshly hardened concrete containing the sand was examined by SEM, confirming the formation of the bacterial biofilm within the new concrete matrix. Bacteria had survived the concrete making process.

I note production on some projects in southern China have been recently suspended following reports that the concrete contained marine dredged sand (illegal sea sand), rather than river sand. The Shenzhen Housing and Construction Bureau held a news conference recently stating that it had launched an inquiry into this inferior practice. The use of concrete made from marine sand is believed to be widespread throughout the Pearl River Delta area of Guangdong province, one of the major hubs of industry and commerce in China. The UK Mineral Products Association warns that washed beach sand is generally unsuitable by itself for good quality concrete, due to the single-sized grading, but this can be overcome by blending aggregates. While aggregates for unreinforced concrete can be washed with sea water, as was the case in this study, for reinforced concrete the aggregates must be carefully washed with potable water to remove excess chloride from sea salt, however they will still retain shell fragments and organic matter that can affect the water demand of the mix. The preliminary results of this on-going study suggest that the blanket use of marine sourced aggregates in the UK should be reconsidered for concrete that is to remain in contact with sea water. Washing in water may only partly remove some of the epilithic biomass present on the surface of the aggregate, possibly leaving endolithic microorganisms, to continue and thrive.

After only five years monitoring at the study site several pre-cast units units are in a very poor condition, these units have a design life of 100 years, it is doubtful if a large number of the units will last 10 years. Microbial content needs to be controlled, particularly in structures subject to permanent wetting by sea water to control growth on and inside the matrix. Guidance should consider undesirable elements such as microorganisms more closely and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach fine aggregate, leading to increased colonisation and the biodeterioration of concrete.

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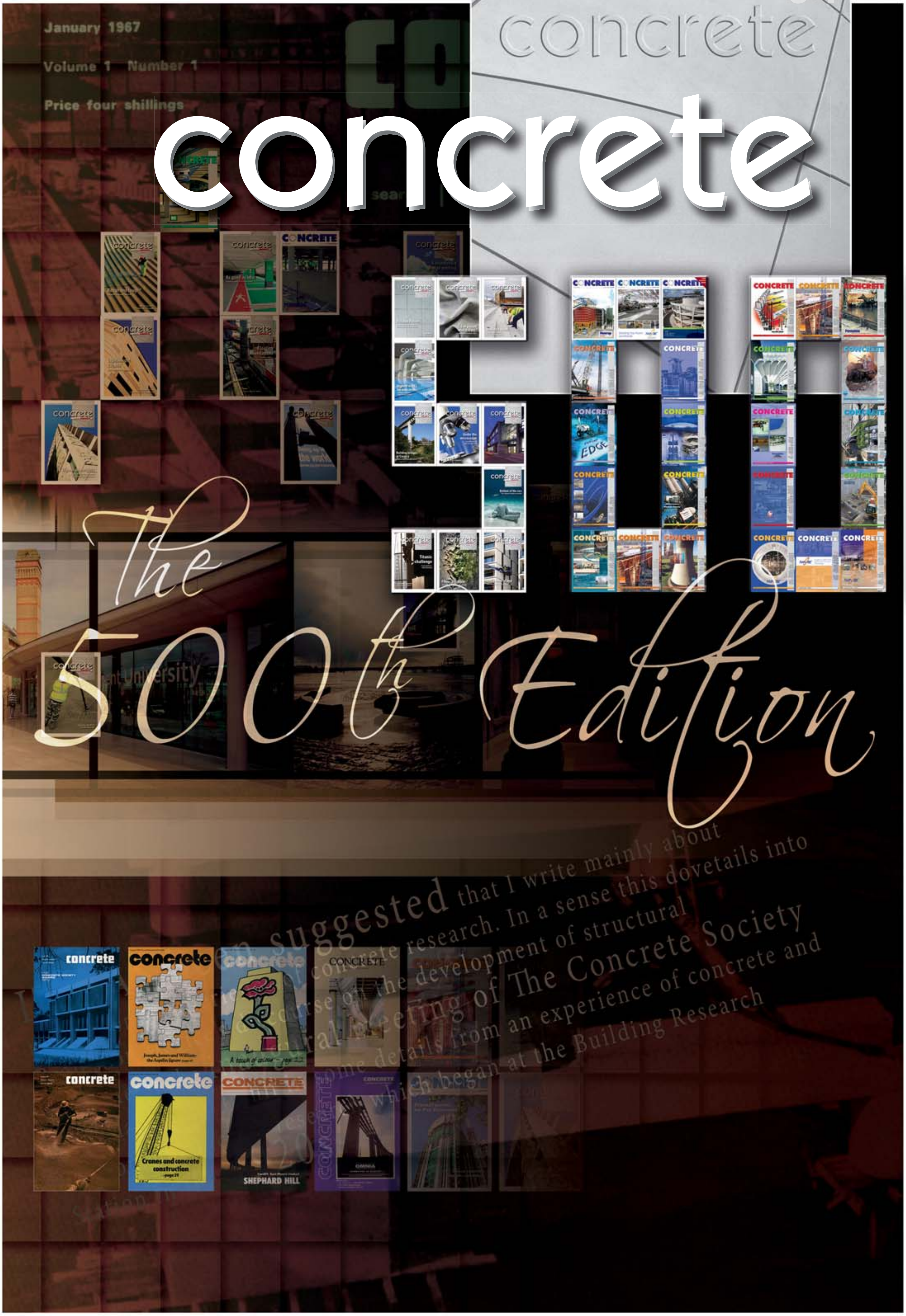

Microbial attack on synthetic fibres

Dear Sir,

In recent issues of *Concrete* some cases of microbial attack on synthetic fibres have been reported, which I found very interesting. In my opinion the role of microbes on concrete durability is underestimated, at least in certain environments.

Some years ago a RILEM group was focusing on the role of microbes, as summarised by Gaylarde *et al*(1). It was stated that there is a need for a cross-disciplinary look at the problem. Another important research field, which has had a significant impact in environmental sciences, is geomicrobiology. During the past couple of decades it has become increasingly apparent that the interaction of microbes, minerals and water is in fact important and very complex.

The role of microbes in relation to concrete durability is, in my opinion, two-fold: 1) direct interaction with the concrete material itself; and 2) indirect interaction due to the impact of microbes on ground water chemistry.

In Norway, this correspondent has found evidence of acid generation within biofilms carrying Mn and Fe oxidising bacteria, which results in surface deterioration of steel-fibre sprayed concrete used for rock support in subsea road tunnels. Another example is the impact of sulfide oxidising bacteria in black shale, causing acidification and sulfate enrichment in ambient groundwaters, hence triggering sulfuric acid attack.

Engineers and their collaborating material scientists are mostly dealing with the physical world and inorganic chemistry. Thus, despite all the good work being done, there is a risk that certain concrete deterioration phenomena remain under-characterised.

Only when taking a fresh look by using state-of-the-art analytical techniques and a forensic approach can we be sure to understand the role of microbial activity on concrete. Indeed, mitigation sometimes depends heavily on a fundamental understanding of the reaction mechanisms. Likewise, concrete researchers are now testing out bacteria as a way to promote self-healing of concrete. The nature of all these problems is intrinsically cross-disciplinary.

Per Hagelia
Norwegian Public Roads Administration,
Oslo, Norway

Reference

1. GAYLARDE, C., RIBAS SILVA, R. and WARSCHIED, T.H. Miocrobial impact on building materials: an overview. *Materials and Structures*, Vol.36, pp.342–352, June 2003.

Concrete made with marine sand

Dear Sir,

Material from marine deposits around the coast of Great Britain has been used in concrete production for several decades however; no provision is made in the current Standards for the control of microbial growth within, or on the surface of, beach sand.

I note production on some projects in the southern Chinese metropolis of Shenzhen has been recently suspended following reports that the concrete contained marine-dredged sand (illegal sea sand), rather than legal river sand. The Shenzhen Housing and Construction Bureau held a news conference on 15 March 2013 stating that it had launched an inquiry into this inferior practice. Their investigations have reported that several concrete producers in Shenzhen used marine sand. The use of concrete made from marine sand is believed to be widespread throughout the Pearl River Delta area of Guangdong province, one of the major hubs of industry and commerce in China.

Some concrete companies have already been named and shamed by the central Government's media outlets as having engaged in the illegal practice. Microbial growth and the ability of some species to tunnel into concrete, leads to degradation, increased porosity and decreased durability. While Chinese officials have not made the public aware of the precise number of projects containing the concrete, it is believed to have affected work on some of the most high-profile projects in Shenzhen. Most renowned is the Pingfan Financial Centre, set to be the tallest building in Guangdong province.

Microbial content needs to be controlled, particularly in structures subject to permanent wetting by sea water to control growth on and inside the matrix. BS EN 12620(1) is the predominant specification concerning the use of aggregates for concrete, supported by UK national guidance document PD 6682-1(2). This guidance should consider more closely undesirable elements such as micro-organisms and place precise limits on their presence. For marine concrete structures there is a tangible risk that microbial growth will remain on or within the beach fine aggregate, leading to increased colonisation and the biodeterioration of concrete.

Peter Hughes
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References

1 BRITISH STANDARDS INSTITUTION, BS EN 12620. *Aggregates for concrete*. BSI, London, 2002+A1:2008.
2. BRITISH STANDARDS INSTITUTION, PD 6682-1. *Aggregates. Aggregates for concrete. Guidance on the use of BS EN 12620*. BSI, London, 2009.

Appendix 10
Additional documentation on CD
Competition winning papers
Conference papers and posters

(CD attached to the inside back cover)

ACI International Students Paper Competition St. Louis.

ACI International Students Paper Competition New Orleans.

ICE Paper competition.

Conference Papers.

Selected examples of Posters presented during this research.

Selected examples of oral presentations made during this research.

Recording of contribution made to ‘The Science Show’ – ABC Radio.

Video of study site.

Health and Safety publication.