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Concepts for construction materials inspired by self-healing and self-assembly in nature

by

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2014/2015

I hereby declare that, except where specifically indicated, the work submitted herein is my own original work.

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Technical Abstract

The durability of current construction materials limits the typical design life of most civil engineering structures to around 50 years. During this time, essential repair and maintenance works must be carried out regularly in order to mitigate the effects of inevitable material degradation. The annual cost of these works is around £37 billion in the UK (35% of the annual total output of the UK construction industry), and approximately $2.2 trillion in the USA. In addition, the manufacture and transport of construction materials accounts for 10% of the UK's carbon emissions and 24% of the UK's total waste. The demand exerted on the manufacture of these materials by the construction industry, compounded by their lack of durability, suggests that they are not sustainable.

The use of self-healing and self-assembling construction materials, more durable and adaptable than the materials currently used, would reduce annual maintenance costs and lessen the adverse impact on the environment. Studying nature can provide insight into efficient mechanisms that may deliver more adaptable, effective and sustainable solutions to scientific design problems. In this project, these natural mechanisms are studied and current developments in self-healing and self-assembling construction materials are investigated and assessed. Two novel concepts for construction materials, inspired by natural self-healing and self-assembly mechanisms, are then proposed. Lastly, the experimental work conducted is presented.

The first concept is inspired by the function and form of the periosteum layer around bone, which is mimicked with a calcium alginate gel coating applied to concrete. The experiment involved observing the effects of this calcium alginate gel coating on the healing of cracked cement paste specimens. The presence of calcium alginate gel appeared to seal the cracks to a greater extent, and induced more calcite and calcium hydroxide production in the cracks than the control specimens after 28 days in a water bath. However, three-point bending tests showed that none of the specimens regained their initial mechanical properties. These results are promising as

they suggest that a calcium alginate gel coating would improve the durability of concrete.

The second concept introduces a new paradigm for the manufacture of construction materials, in which they self-assemble by harnessing natural resources and processes. It is proposed to use a freeze-drying technique to form a collagen and chitin scaffold upon which calcium carbonate nucleates to form a structural composite material similar to bone. It is predicted that manufacturing construction materials based on such natural processes will improve their versatility, adaptability, ability to self-heal and self-assemble, and enable the sustainable integration of the built environment into the natural environment.

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1 Introduction

1.1 Motivation

The Construction Industry

The durability of current construction materials limits the typical design life of most civil engineering structures to around 50 years. During this time, essential repair and maintenance works must be carried out to mitigate the effects of inevitable material degradation and in turn, preserving structural performance, function and aesthetics.

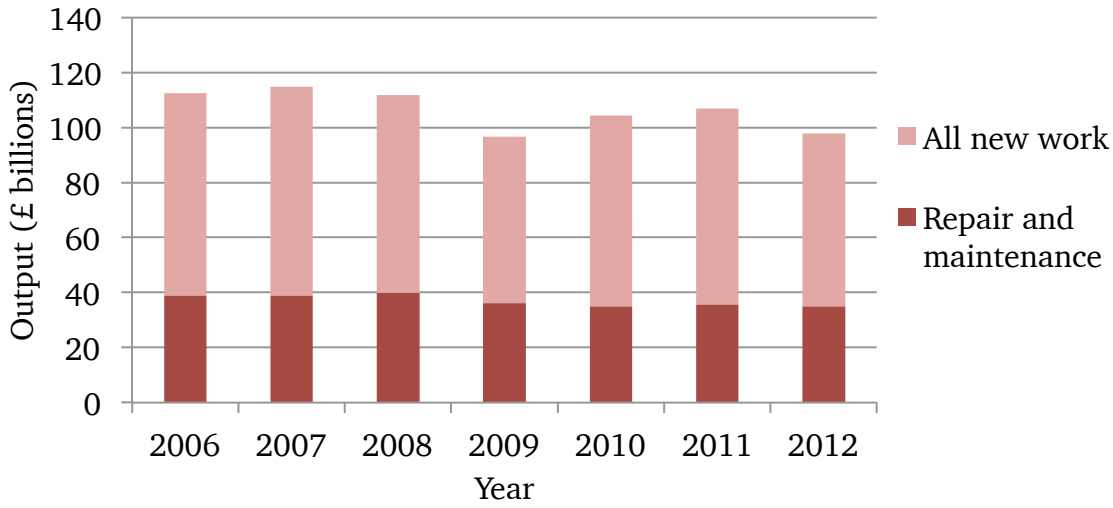

Figure 1 - Annual UK construction output (constant (2005) prices, seasonally adjusted). Source: ONS - 'Output in the construction industry summary, December and Q4 2012'

The construction industry is very important to the UK economy as it accounts for a significant portion of UK gross domestic product (6% in 2013 [1]). Figure 1 shows that a substantial portion (35% between 2006-2012) of the total annual output of the UK construction industry is spent on the maintenance and repair of buildings and infrastructure. These annual costs are around £37 billion in the UK, and are estimated to be $2.2 trillion in the USA [2]. Although the costs are high, it is imperative to design and maintain structures to adhere to strict safety regulations, with most countries investing to prevent degradation of infrastructure. However, poor

countries with weak economies often don't have the finances for maintenance and repair, which results in buildings degrading at the risk of lives and even higher costs.

Cementitious materials, structural steel, or a combination of the two, are the most commonly used construction materials worldwide, all of which are susceptible to environmental degradation. Their impact on the environment is also a large cause for concern. The manufacture and transport of construction materials accounts for 10% of the UK's carbon emissions, and constitutes 24% of the UK's total waste [3]. Globally, the manufacturing process used to produce cement alone accounts for approximately 7% of the total anthropogenic atmospheric CO_2 emissions [4]. The demand exerted on the manufacture of these materials by the construction industry, compounded by their lack of durability and adaptability, suggests that they are not sustainable.

Natural self-healing materials

Studying nature can provide insight into efficient mechanisms that harness chemical, geometric and electrostatic molecular interactions, which may deliver more adaptable, effective and sustainable solutions to scientific design problems. Natural materials that have the ability to efficiently and effectively repair and assemble hierarchical structures have attracted great scientific interest and inspired the development of biomimetic man-made self-healing materials.

1.2 Summary

The use of self-healing and self-assembling construction materials that are more durable and adaptable would revolutionise the construction industry. Annual maintenance costs would reduce as the frequency of required repair works decreased, and the adverse impact on the environment would lessen, increasing sustainability.

This report draws inspiration from natural self-healing mechanisms in order to propose novel concepts for self-healing and self-assembling construction materials. The current developments in self-healing materials are also considered with a focus on those applicable for use in the construction industry.

1.3 Aims

- To understand the self-healing and self-assembly processes in nature
- To understand how nature has inspired the development of construction materials to improve their durability and sustainability
- To develop novel concepts for self-healing and self-assembling construction materials that are more durable and sustainable than current practice

2 Self-healing and self-assembly in nature

In light of the heightened scientific interest in self-healing materials, it seems appropriate to investigate nature's solutions to inspire new materials for the construction industry.

2.1 Self-healing in nature

Nature is an example of on-going experimentation and development, as fauna and flora adapt to their changing environments and co-habiting species. Some species have developed the ability to heal damaged soft and/or structural elements of their skeleton and organs.

2.1.1 Tissue regeneration

Different animals have the ability to regenerate body tissue to different extents, depending on numerous physical and chemical factors, through signalling and genetic make-up at the cellular level. One of the main components that affect an animal's ability to regenerate tissue is the extracellular matrix (ECM).

Extracellular matrix (ECM)

All animal cells locally secrete a variety of proteins (mainly collagen) and polysaccharides, water and minerals that are assembled into an organised network, known as the ECM [5]. It constitutes a substantial proportion of the tissues' volume and controls cells' (and hence the tissues') behaviour, form and function. The ECM is also a dynamic part of the tissues that accommodate cell communication, motility and gene expression required for cell development [5]. The interaction between its constituents and surrounding cells modulates growth factor (proteins that stimulate growth of specific tissues) sequestration, permits angiogenesis (the growth of new capillary blood vessels in the body), and dictates the inflammatory response to damage through leukocyte (white blood cell) signalling and protein control [5].

Highly regenerative organisms: Axolotls and Zebrafish

The Axolotl, also known as the Mexican Salamander, has been recognised as a master of regeneration, with the ability to completely regenerate lost limbs (see Figure 2), damaged lungs, sliced spinal cord, and even bits of damaged brain [6]. The Zebrafish has also attracted scientific interest with its impressive ability to re-grow its heart and bony structures in its fins when amputated [7]. Such 'superpowers' have fuelled investigation into the reasons why these animals have such superior healing abilities compared to humans.

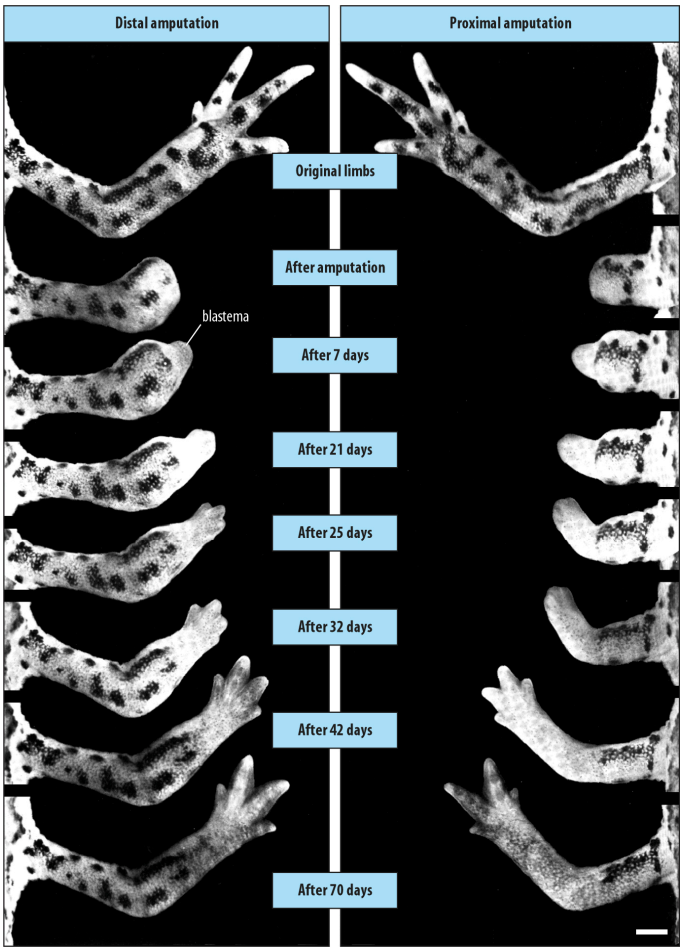

Figure 2 - Natural regeneration of a salamander limb. Source: evolvefresno.blogspot.co.uk

When a tissue is damaged, blood is released from the wound, activating a biochemical-signalling cascade resulting in the formation of a fibrin clot to prevent haemorrhaging [8]. Epithelial cells and fibroblasts (tissue generating cells) then flow over the clot forming a sheet, underneath which presents the ideal conditions for blastema accumulation and growth factor deployment [5]. Blastema are pools of

proliferative, dedifferentiated (unspecialised) mature cells of a particular cell lineage, called progenitor cells (bone cells, for example) [7]. The area becomes inflamed due to blood vessel dilation [7], attracting leukocytes that release proteases (enzymes that break down peptide bonds of proteins) to degrade the clot, and temporary ECM components to release stored growth factors [10]. These growth factors cause the progenitor cells in the blastema to proliferate and differentiate (specialise) into the appropriate cells designed for the regeneration of nervous, muscular and bone tissues [7]. Generally, a temporary proteinaceous matrix is formed under the wound by differentiated progenitor cells, which is remodelled and cross-linked at the very late stages of the repair process [5].

This mechanism facilitates the regrowth of any type of tissue (of any part of the body) in Zebrafish and Axolotls, replicating the form and function it had before injury [11]. Cells use a self-assembling system based on positional information inherited from progenitor cells to achieve this [12].

Mammalian wound healing

In mammals, wound healing is dictated by cytokines (small proteins important for cell signalling) and growth factors, controlled by activity of the extracellular matrix and leukocytes. Classically, there are three distinct stages of wound healing: Inflammation, proliferation and remodelling [13].

Initially, a fibrin clot is formed at the damage site to prevent haemorrhaging and achieve homeostasis, followed by a flow of epithelial cells and fibroblasts under the clot (instead of over it as in regenerative organisms) [5]. During the inflammatory stage, blood vessels dilate to permit sufficient flow of leukocytes and minerals to the damage site [14]. The Leukocytes enzymatically digest necrotised cells, releasing sequestered growth factors [14]. During the proliferation phase, a temporary matrix is built in the wound by fibroblasts that produce an extracellular matrix and collagens, which allow angiogenesis. Dedifferentiation does not occur alongside cell proliferation in mammalian wound healing, hence there is no blastema accumulation under the epithelial cell layer [5]. The remodelling phase involves the transformation of fibroblasts to myofibroblasts, that pull the edges of the wound together, and collagen

type III to type I, resulting in a highly cross-linked acellular scar [5]. This occurs once the wound has closed, corresponds to a reduction in cell activity and blood flow around the wound, and can last for months or years [14].

Human bone regeneration

Bones in humans are not only used for structural and mechanical purposes, but also to regulate minerals in the body's tissues [15]. When there is a deficiency or excess of calcium in these tissues, it is taken away from or deposited in bone tissue, respectively, by transportation through the blood [16]. Therefore, bones in the human body are constantly being regenerated. This process is carried out by osteoclasts, cells that dissolve the collagen and calcium of old or damaged bone and release it into the bloodstream, and osteoblasts, cells that deposit lamellae of collagen fibres, which are mineralised to form bone. The regeneration of bone is a very sensitive and highly regulated process, coordinated by sets of growth factors, cytokines and genes that respond to internal or external stimuli [15]. For example, osteoclasts are stimulated by hormones and formed by the fusion of macrophages, hence are controlled by the immune system.

Directly in contact with the bone surface on the cavity face is a thin layer of cell-rich connective tissue called the endosteum, and on the external face is a dense layer of connective tissue called the periosteum (see Figure 3). They both possess osteoprogenitor cells (progenitor cells of bone), which differentiate into osteoblasts following injury or for mineral homeostasis. Osteoblasts deposit collagen I (95%) fibres, other protein fibres, polysaccharides, and growth factors that form an adhesive isotropic woven network – the organic bone matrix [15]. Tri-calcium phosphate crystals are then deposited onto the organic matrix, and undergo a mineralisation reaction to form hydroxyapatite (calcium phosphate) [17], creating an almost entirely extracellular substance. The organic matrix gives bone its tensile strength, elasticity and flexibility, whereas the minerals (that make up 50% of the dry weight of bone) give its compressive strength and rigidity, rivalling the properties of reinforced concrete.

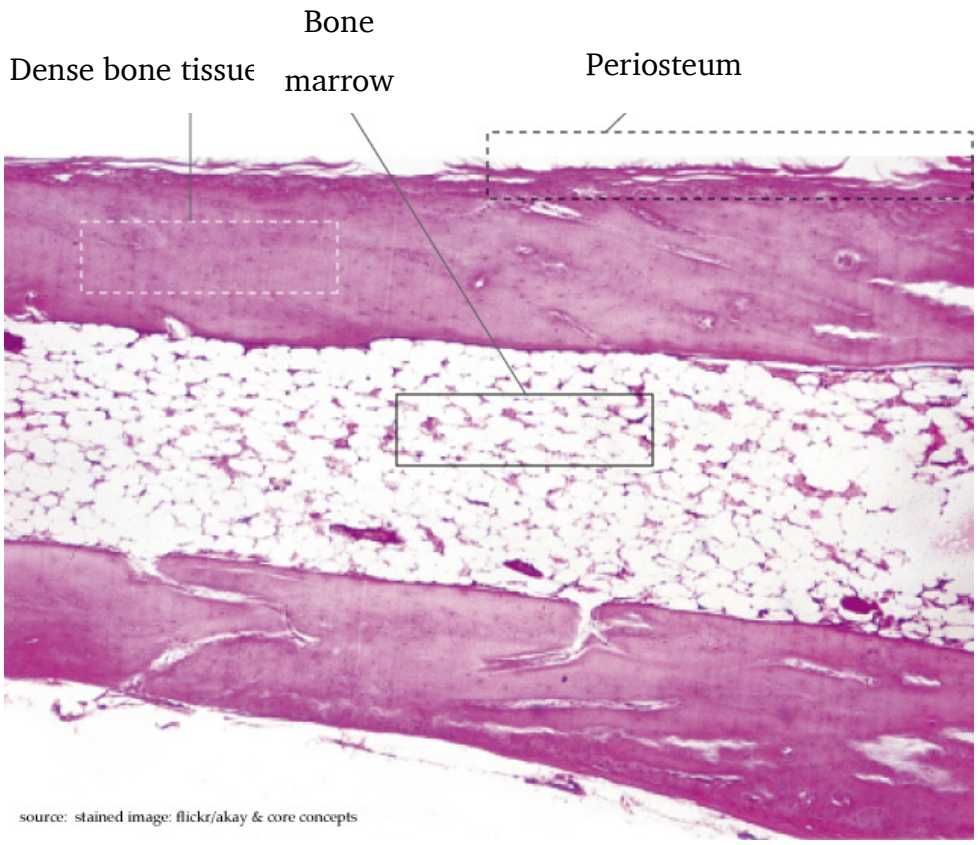

Figure 3 - Cross-section through a human bone, highlighting the location of the periosteum. Source hlss-bodysystems.wikispaces.com/Bones

The ability of bone to constantly regenerate allows it to repair small damages without scarring, but it cannot fully regenerate in the event of amputation due to the lack of dedifferentiation.

Key factors of tissue regeneration

A comparison between the regeneration ability of mammalian and regenerative organisms can highlight the factors that make it an effective process, as follows:

1. *The ability to dedifferentiate and proliferate mature cells*

The formation of the blastema through proliferation, migration and dedifferentiation is a process that facilitates the continuous regeneration of cells and growth of body parts that have been lost in injury [7]. To be effective at regeneration, the material needs to allow adhesion, migration, proliferation and differentiation of progenitor cells.

2. *The cytokine environment*

During the inflammatory stage, the cytokine environment is thought to be critical for the initiation and completion of wound healing and regeneration as it dictates the rate of leukocyte infiltration, cellular proliferation, angiogenesis, and collagen remodelling of damaged tissues through fibroblast activation and ECM breakdown [5]. Macrophages, identified as an important leukocyte in the regeneration process [18], are the source of both the inflammatory and anti-inflammatory signals. Although Mammals and Axolotls share many of the same features of cytokine signalling, Axolotls deploy them more dynamically, with simultaneous induction of the inflammatory and anti-inflammatory stages over the first 24 hours after injury [6]. Mammals deploy them separately over the first 48-96 hours of regeneration, so it is suspected that their early arrival and simultaneous induction promotes the efficient regeneration of limbs [18].

3. *An energy source*

All cellular activity requires oxygen, and is fuelled by the energy stored in the food consumed by the animal.

4. *Cellular self-assembly*

Positional information stored in cells, and chemical communication, allows them to regenerate the appropriate tissues in the correct arrangement where needed.

2.1.2 Intrinsic healing: mussel byssal threads

In contrast to tissue regeneration, which is dependent on cell activity, intrinsic healing relies on re-assembly of microstructural components that have been disrupted by external factors. It does not encompass the regeneration of severed or lost material, but involves the time-dependent recovery of elastic modulus and initial strength after plastic deformation [19].

Mussels use byssal threads to anchor themselves to solid objects when in intertidal zones to prevent being washed away under the force of moving water [20]. The threads are made up of protein chains arranged in a stiff crystalline formation cross-linked by metal cations, embedded in a network of amorphous protein chains [22]. Under an increasing tensile load, the crystalline regions (being the stiffest

component in the microstructure) yield by breaking the metallic cross-linking bonds, thus transferring the load to the soft matrix [20]. The crystalline regions uncoil and extend, allowing large plastic strains to occur. Elastic recoil after loading returns the metal ions back to their original positions, allowing the reversible cross-linking bonds to reform, rebuilding the crystalline regions and hence regaining mechanical properties [21].

Experiments have shown that mussel byssal threads exclusively undergo intrinsic healing when submerged in seawater, suggesting that pH conditions through interaction with chelators and disulphides affect their intrinsic healing ability [22]. In addition, cyclic loading tests conducted on the threads imply the extent of intrinsic healing is time-dependent (see Figure) [20].

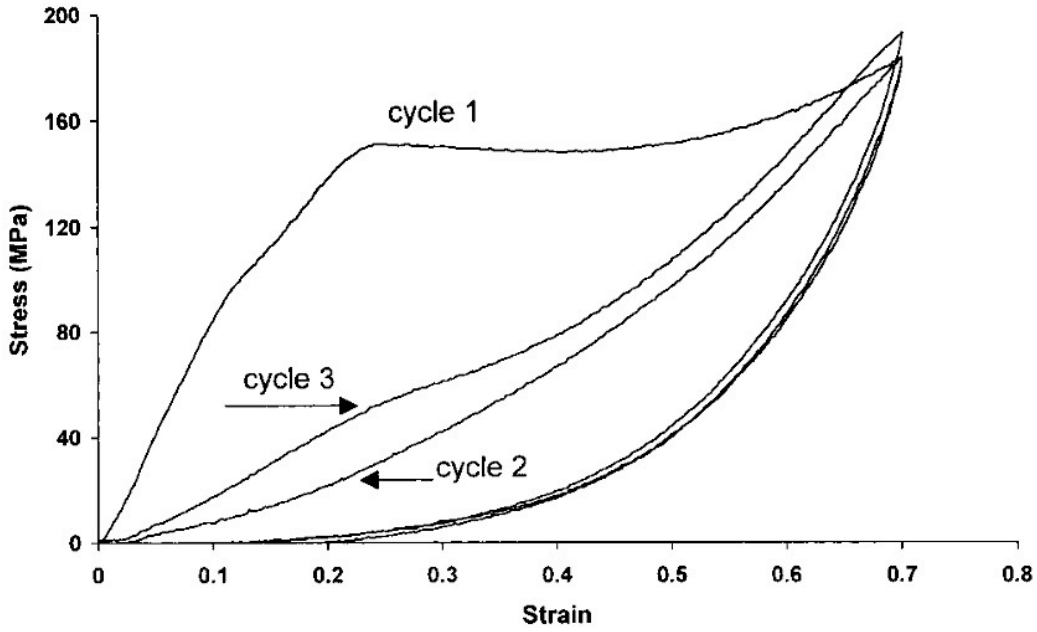

Figure 4 - Cyclic loading of a mussel byssal thread. Cycle 1 was followed by cycle 2, showing 17% retainage of the initial modulus due to stress softening. Loading cycle 3 was performed 1 hour after cycle 2 and showed 30% retainage of the initial modulus [20].

2.2 Self-assembly and mineralisation in nature

Hierarchical self-assembly is ubiquitous in natural materials, exhibiting a bottom-up approach to macromolecular design wherein a desirable structure forms spontaneously through covalent and non-covalent interactions. An example of nature

exploiting this to form materials with impressive mechanical properties is biomineralisation.

2.2.1 Biomineralisation

Biomineralisation is the process by which natural materials are stiffened, hardened or stabilised by formation of calcite and silica via catalysed chemical reactions. Bones manage to strike a balance between brittleness and ductility due to the high organic matrix content, but other organisms, such as nacre, adopt extreme properties of hardness and stiffness [17].

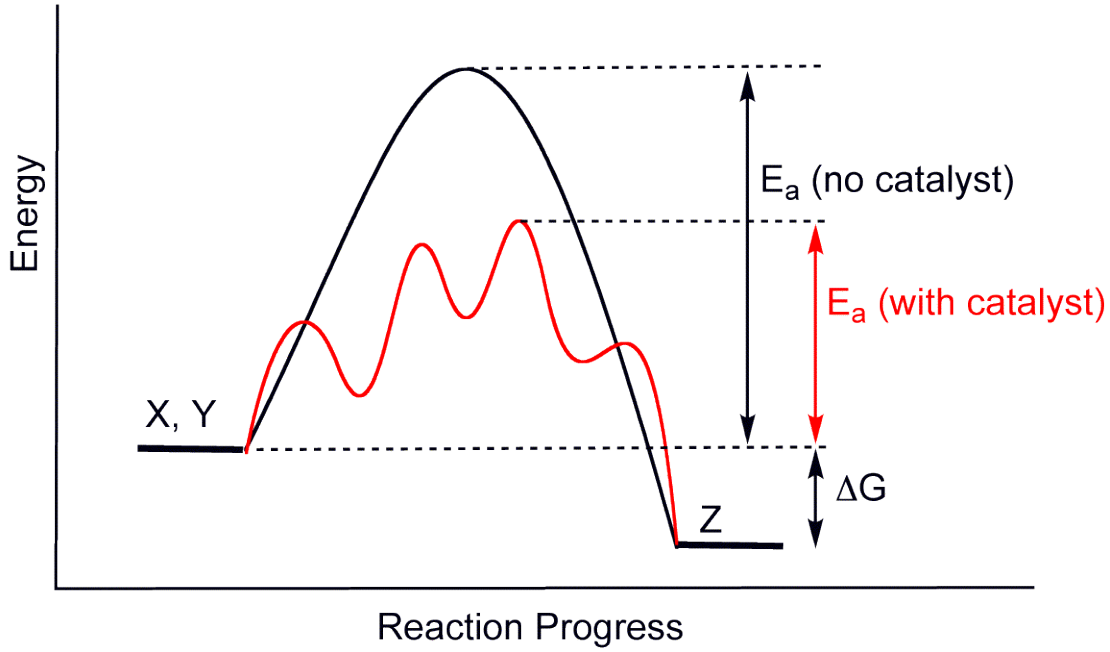

Figure 5 - The difference between activation energies in the presence (red line) and absence (black line) of a catalyst. Source: en.wikibooks.org/wiki/Biochemistry/Enzymes

It is an efficient process in which enzymes reduce activation energies of reactions (see Figure), allowing them to proceed at ambient conditions. For example, the reversible hydration of carbon dioxide to bicarbonate, in the presence of calcium ions, to form calcium carbonate, is catalysed by the enzyme carbonic anhydrase (CA) [23]. The process is induced by mineral deposition and crystallisation on a protein substrate, which acts as a template for further crystallisation of mineral phases [17]. A group of glycoproteins rich in aspartic acid (an amino acid) are unique to many

mineralised tissues and are thought to help the control of mineral crystallisation [24]. In biomineralisation processes it is common for crystals to be grown from a transient unstable solid amorphous phase, almost devoid of water, that subsequently transforms into a more energetically stable mature phase, rather than nucleating from a supersaturated solution [24]. Molluscs employ this technique to transform amorphous calcite to aragonite in nacre, as amorphous phases are easier to transport and mould than crystalline phases. This also avoids the logistical problem of excreting volumes of water from the site of mineral formation [24].

Some animals obtain ions for mineralisation from their food, but marine organisms utilise the resources in the surrounding seawater. The concentration of calcium ions (Ca^{2+}) is an order of magnitude higher than bicarbonate ions (CO_3^{2-}) in seawater, making CO_3^{2-} the limiting factor in the formation of calcium carbonate ($CaCO_3$) for marine creatures [25]. The precipitation of $CaCO_3$ in seawater causes the pH of the local environment to fall, resulting in a reduction in CO_3^{2-} concentration, and hence a reduction of the rate of $CaCO_3$ formation [25]. However, marine creatures have the ability control the local pH environment, and so increase the pH of the surrounding seawater to replenish CO_3^{2-} concentrations to manage crystallisation rates [24]. The calcium carbonate forms in aqueous environments due to the following set of equations, where reaction (1) is catalysed by carbonic anhydrase:

$$H_2O + CO_2(dissolved) \rightleftharpoons H_2CO_3 \quad (1)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (3)$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \quad (4)$$

2.2.2 Protein scaffold self-assembly

Evidently, a key factor in the formation of a protein-mineral composite is the control of the nucleation and growth of mineral phase by the proteinaceous matrix [26].

Proteins are also assembled by a hierarchical self-assembly process [27]. At the fundamental level, they are made up of nitrogen, carbon, oxygen, and hydrogen atoms that link with covalent bonds to form organic compounds called amino acids (a

natural monomer). Directed by genetics, amino acids covalently link together with peptide bonds (rejecting a water molecule) in repeating sequences to form polypeptide chains (natural polymers). One or more polypeptide chains make up a protein, which is defined by its unique amino acid residue sequence and the arrangement of polypeptide chains [28]. The nucleation of hydroxyapatite crystals on collagen fibrils in bone is dependent on fibril orientation and the amino acid sequences of the polypeptide chains within them [26]. The position of the oxygen in the hydroxyl groups of hydroxyapatite crystals have epitaxial relationships with those in the carboxylate groups of collagen fibrils, implying that natural geometric and chemical composition programming of the protein scaffold guides mineralisation [26].

Conditions of pH, water loss and external forces can cause multiple polypeptide chains to fold into stiff crystalline regions called beta sheets, and cross-link, or twist into helical structures called alpha helices. These helices form amorphous regions, stabilising the structure thermally, geometrically and mechanically [29] with non-covalent hydrogen bonds [30]. Nature compensates for the relative weakness of hydrogen bonds compared to covalent bonds by employing high densities of non-covalent bonds, resulting in strong and robust yet biodegradable materials, such as mussel byssal threads and collagen fibrils [30].

2.2.3 An example of hierarchical assembly: Nacre

Nacre, commonly known as mother of pearl, is the iridescent inner layer of mollusc and snail shells. It is very stiff, strong and tough [31] due to its unique hierarchical composite structure of polysaccharide, proteins, and mineral phases [32]. The genetics of the organism and the chemical species present in the local environment dictate the self-assembly of nacre, which occurs extracellularly [32].

The microstructure of nacre is analogous to a brick and mortar structure where the mortar is deposited first and the brick is grown into it [32]. Each brick of the microstructure is composed of aragonite (a crystalline calcium carbonate polymorph) and the mortar is a composite of chitin (a polysaccharide) embedded in a proteinaceous matrix [32]. Although the chitin and protein together form less than 5% of the structure by both mass and volume [31], their inclusion is extremely

important. They provide the initial template for crystallisation of calcite in the mineralisation process [33], and they increase the fracture toughness to 3000 times what it would be in their absence.

Initially, the animal secretes liquid crystal chitin from small pores, which crystallise by inter-chain hydrogen bonding on exit form the core [32]. This is coated by glycoproteins that stabilise the crystallites to form a self-assembled, strong, porous composite material called the interlamellar membrane (the mortar). The glycoproteins are delivered by the extrapallial liquid, an aqueous substance that surrounds the membranes and contains all the constituents of nacre [32]. Once the interlamellar membranes have formed, calcite (an amorphous calcium carbonate morphology) is transported to fill the space between them, transforming to c-axis-oriented aragonite on deposition onto the protein membrane [34]. It is believed that the polyanionic proteins in the membranes and inorganic ions in the extrapallial fluid control the phase and location of mineral deposition, requiring no change in temperature or pressure for crystallisation [35]. Aragonite crystals then become the template for future calcite crystallisation, allowing continuous mineral growth through the membrane structure (brick formation) (see Figures 6 and 7) [34]. This creates mineral bridges between mineral bricks, whose growth rate, crystal orientation and mechanical properties are influenced by the interlamellar membrane pore size and density [32].

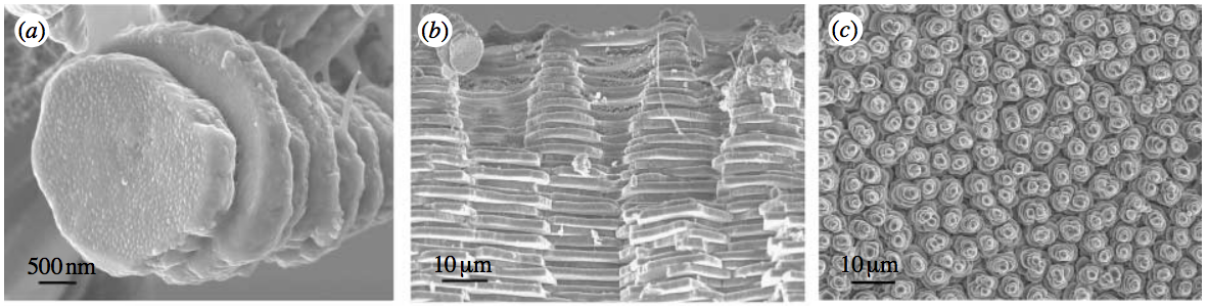

Figure 6 - SEM (Scanning Electron Microscope) images of gastropod nacre. This shows the formation of aragonite tablets grown through the interlamellar membrane to form towers, from (a) above, (b) side-on, (c) zoomed-out view from above [32].

2.2.4 Key factors of natural self-assembly

Self-assembly is a fascinating process that is still largely a mystery to scientists, but the key factors of the processes associated with it can be identified as the following:

1. *Genetic make up*

The genetics are determined by the amino acid sequences of polypeptide chains, which characterise the protein [28].

2. *Substrate characteristics*

The geometry and the chemical composition of the substrate determines the orientation, morphology and type of minerals that crystallise on contact with it [36].

3. *Surrounding environment*

The ions present in the surrounding environment, which dictate the pH, can affect interactions between molecules, and thus influence molecular bonding and reaction rates [36].

4. *Reaction activation energies: enzymes*

Enzymes facilitate the procedure of reactions or changes of phase at non-saturating, ambient conditions, unlike modern manufacturing methods, by reducing the activation energies required to achieve a lower, and hence more stable, energy state. They are not consumed in the process, but simply catalyse it [17].

2.3 Learning from nature

The dynamics of the natural self-healing and self-assembly processes discussed are exceptionally complex, highly regulated and occur largely on the micro and nano-scale. The key factors contributing to these processes involve sets of cells, chemical interactions, and intricate nano-scale geometries whose behaviour is still not completely understood by scientists. However, the potential to learn from these natural mechanisms, in order to develop more efficient and adaptable materials for human use, is becoming more apparent and appreciated in the scientific community. This has led to increased interest in biomimetics with the development of self-healing materials and self-assembling structures inspired by nature.

3 Materials science development

The field of self-healing materials has been gaining interest since the start of the twenty-first century, with the first conference held in 2007. The University of Illinois (USA), TU Delft (Netherlands), and the Universities of Cardiff, Bath and Cambridge (UK), have been pioneering research in this field across different classes of materials.

3.1 Self-healing materials

As the field of self-healing materials has progressed, it has become convenient to distinguish between self-healing mechanisms that are 'autonomous' and 'autogenic'. Autonomous self-healing materials have been 'manufactured' to exhibit self-healing after cracking by implementing alien objects such as capsules into the material, whereas autogenic self-healing materials have the 'natural' ability to heal due to the characteristics of their microstructure.

Autonomous self-healing

One of the first advancements in self-healing materials research was the development of self-healing polymers by White et al. at the University of Illinois in 2001 [37]. They conceived an autonomous mechanism in which microcapsules containing an adhesive monomer resin are embedded in a polymer matrix. When broken on crack propagation through the material, the microcapsules release the resin into the crack. A catalyst in the matrix induces cross-linking of the resin monomers, causing it to harden at ambient conditions, filling the crack and preventing further propagation [38]. The catalyst mimics the role of enzymes in biomineralisation of nacre and bone by reducing the activation energy needed for polymer cross-linking. This mechanism has also been applied to asphalt [39], anticorrosion coatings on metals and cementitious materials. The latter uses an urea-formaldehyde capsule filled with epoxy resin or an alkali-silica agent [40]. Although it has been shown to restore a polymer's mechanical properties by up to 90% [41], it is limited to healing a

particular location only once. After the resin has been released from the microcapsule it is no longer available to heal future cracks [37].

An improvement on the microencapsulation design that allows repeated crack healing in a particular location is the use of vascular networks of micro-capillaries. They facilitate the flow of healing agents to the damage site once they have been severed [38], mimicking the role of blood vessels in the human body. This mechanism has also been applied to cementitious materials [40], woven composites [42] and polymers [37].

Another approach to healing concrete, developed by Jonkers et al. [4], is to induce calcium carbonate precipitation by mixing bacteria from the genus *Bacillus* into the concrete mixture. The bacteria cause the enzymatic hydrolysis of urea to ammonia and carbon dioxide on contact with water, increasing the pH within the concrete, and in turn encouraging the precipitation of calcium carbonate, significantly reducing pore size. This supplements the autogenic healing ability of concrete through hydration of unhydrated cement particles.

Autogenic self-healing

Autogenic self-healing materials are effective at regaining mechanical properties through molecular re-assembly after loading or damage. Just like the intrinsic self-healing of mussel byssal threads (see section 2.1.2), the re-formation of energetically favourable reversible bonds between molecules through genetic programming enables microstructural re-assembly. Ying et al. [43] have achieved this by developing a self-healing polymer that can re-assemble with urea bonds at ambient conditions by polymer chain inter-diffusion without the need for a catalyst. However, some autogenic self-healing materials require an external stimulus such as heat, pH or UV light to induce molecular re-arrangement. For example, UV light has been employed to heal scratched polyurethane paints and coatings by cross-linking chitosan, regaining initial aesthetics [44].

3.2 Self-assembly

A recent project called '4D printing', developed by the Self-assembly Lab at MIT (Massachusetts Institute for Technology), involves the 'programming' of human-scale objects to self-assemble into complex structural arrangements under the influence of a stimulus or random energy [45]. They have developed objects that are 3D-printed in a simple geometry but transform into more complex shapes when stimulated, as well as objects that self-assemble into a structure defined by their individual geometry through random motion [46]. These are tangible, man-made, representations of self-assembly processes that occur on the micro-scale in nature.

Advances are also being made in the programmed assembly of molecules to form designed microstructures using DNA [47]. The polymer length and monomer sequence within DNA can be designed to dictate the interactions between specific macromolecules, through the selectivity of the receptor sites, arranging them into the desired form. It is these DNA characteristics that also dictate the self-assembly of natural materials to give them their form and function. The understanding of how to genetically control the architecture and behaviour of macromolecules such as DNA is being improved by developing models that can simulate molecular interactions. These techniques can be used to direct the self-assembly of proteins into appropriate configurations with desirable chemical and geometric characteristics.

Modelling self-assembly

There are different modelling techniques that can approximate the atomic behaviour and interaction of proteins. Quantum mechanics methods are the most accurate [48], but also the most computationally expensive. Therefore, different 'force fields' (potential energy landscapes created by considering bonded and non-bonded interactions between atoms) are developed to best represent certain macromolecular interactions. The accuracy of these 'force fields' is crucial to the successful modelling of self-assembly and to the accuracy of the simulation methods.

However, due to the extremely complex nature of a 'force field' with 3N degrees of freedom (3 degrees of freedom for each atom), it is not possible to obtain analytical solutions to the atomic equations of motion. Different simulation techniques

have varying ways to deal with this complexity. Molecular Dynamics (MD) simulations use numerical integration algorithms which are used to solve the equations of motion [49], whereas Monte Carlo (MC) simulations are based on statistical sampling of outcomes generated by perturbing the EOMs [50]. Spatial perturbations of a molecule's degrees of freedom are randomly generated, with the simulation adopting the configuration of the perturbation with the lowest energy. This process repeats and results in a distribution of accepted perturbations that have converged to a stable state. The Self-assembly Lab are working in collaboration with AutoDesk to develop a software called 'Project Cyborg' that enables the simulation of self-assembly behaviour from the nano-scale to the human-scale [51].

Guided self-assembly

Although progress is being made in the design and fabrication of nanostructures using computational simulation techniques, it is not yet possible to self-assemble microstructures on a larger scale. Methods of guiding self-assembly with external stimuli and particular macromolecular design can be applied to synthetic collagen fibres to mimic the self-assembly of hierarchical composite structures in nature such as bone and nacre [52].

Freeze-drying, technically known as 'lyophilisation', is a process in which collagen slurry (collagen dissolved in water) is frozen, forcing the collagen to gather at the edges of the ice crystals on crystallisation. The pressure around the frozen slurry is then reduced until the ice converts directly to vapour, leaving a 3D collagen matrix scaffold behind [53]. The freezing process and latent heat removal from the slurry on freezing can enable close control over the scaffold microstructure [54]–[57]. A process that has a similar effect on the collagen fibrils is 'emulsion templating' whereby polypeptide chains cross-link around emulsion droplets in the presence of a crosslinking agent, which is then cured in a manner that leaves just the organic porous matrix [58].

Rather than using mechanical stimuli to form the scaffolds, dielectrophoresis, electrospinning and electrospraying apply electrostatic forces via electric fields to guide polymer chain cross-linking and self-assembly. In dielectrophoresis, electrodes

create an AC field to polarise dipolar polypeptide chains, pulling them to the point of maximum potential to trigger self-assembly [52]. Electrospinning and electrospraying instead use a DC voltage between capillary tubes containing a solution at high potential and a grounded collector plate to shoot the solution out of the tube, causing polypeptides to cross-link or beaded particles to form, depending on the solvent used [59]. Different microstructure morphologies can be achieved by varying the electric fields spatially and temporally.

3.3 Application to the construction industry

Self-healing cementitious materials present one of the most exciting prospects for the construction industry. Their implementation would increase longevity of infrastructure in the built environment through improved durability and preservation of mechanical properties. The mechanisms for developing self-healing cementitious materials are threefold; encapsulated healing agents, vascularised networks that allow flow of healing agent towards the crack location, and the use of bacterial spores to stimulate calcium carbonate precipitation. They have the potential to be used for any structure in the built environment, but may be particularly useful for those difficult to maintain and repair due to access or visual restrictions.

Although the majority of the literature on self-assembly focuses on its applications for nano composites and micro-scale devices in medical implants and devices [33], biomimetic hierarchical self-assembly processes also have exciting prospects for the construction industry. They could enable the rapid assembly of construction materials and structures without mistakes (and with higher energy efficiency than in current practice), minimising waste and eliminating certain design limitations from construction methods. In addition, biomimetic self-assembling materials could vastly improve the sustainability of material manufacture through reducing the energy input needed for fabrication.

3.4 Future developments

Despite the promise of self-healing materials, there are limitations to current designs, thus a set of future developments for self-healing and self-assembling construction materials are postulated:

1. *Quantification of healing behaviour as a function of healing mechanism and damage characteristics*

These factors will be important when performing structural design calculations based on expected loading scenarios, considering the timings of maintenance checks, environmental degradation mechanisms, and the design life of the structure. Until this is known and the mechanisms are proved to be reliable, they cannot be used in design.

2. *Manufacturing the materials*

Due to the delicate nature of microcapsules and vascular networks it may be difficult to mass-produce concrete without breaking the vessels and releasing the resin before it is needed. Techniques of gently distributing the microcapsules or vascular networks into concrete would need to be developed.

3. *Application to current structures*

Applying self-healing mechanisms to current infrastructure would increase their longevity by decreasing aesthetic and structural deterioration, reducing the current demand for maintenance and repair.

4. *Infinite healing capacity*

Materials and structures that have the ability to re-assemble or repeatedly heal using resources in the environment around them could mitigate the need for maintenance and repair, increasing the industry's sustainability. Natural materials, such as bone and nacre, become part of the natural systems around them to facilitate assembly and healing to great effect. However, materials used in the construction industry are manufactured in extreme conditions that could not be replicated using environmental resources at ambient conditions. In order to obtain an infinite healing and re-assembling capacity, construction materials must be re-designed to allow a symbiotic relationship with the environmental systems surrounding them.

4 Concepts for novel construction materials

Inspired by the natural self-healing and self-assembly processes investigated and the developments in materials science, two concepts for novel construction materials were conceived. The conceptual designs and ways to develop the concept further are discussed in each case.

4.1 Concept 1: 'Concrete's periosteum'

The periosteum, a dense layer of connective tissue that covers human bones, is responsible for regenerating bone tissue as a result of injury or ageing. It contains blood vessels to permit diffusional flow of minerals to the regeneration site, and provides osteoblasts that deposit the organic matrix required to regenerate the bone. The initial concept was to coat concrete with a material that enables self-healing, mimicking periosteum form and function.

4.1.1 Design considerations

The following key design components were considered in order to develop and evaluate the concept:

1. *The crack filling material and its function*
2. *The concrete damage detection mechanism*
3. *The chemical reactions required for the precipitation of the crack-filling material*
4. *Diffusional flow of the reactants to the damage site*
5. *Adhesion to the surface of the concrete*

4.1.2 Conceptual Design

It is proposed to cover concrete with a layer of calcium alginate gel to encourage the precipitation of calcium carbonate ($CaCO_3$) within cracks, filling them to reduce degradation and regain mechanical properties.

Calcium carbonate formation

The precipitation of calcium carbonate requires the presence of bicarbonate (CO_3^{2-}) ions and calcium ions (Ca^{2+}), which can be delivered to the crack site by ingress water and by the gel, respectively. The precipitation reaction of calcium carbonate in an aqueous solution is considered (see equations 1-4, section 2.2.1) Carbonic anhydrase, an enzyme employed by nacre to catalyse Reaction (1), would be mixed into the gel and surface layer of the concrete to speed up the reaction [17]. However, the delivery of reactants for the precipitation reaction is dependent on the diffusivity of the gel.

Calcium alginate gel

Calcium alginate gel is made up of alginate polysaccharide chains (extracted from seaweed) ionically cross-linked by calcium ions. It was selected for this concept because of its permeable microstructure and ability to store calcium ions. In a study by Klein et al. [60], the pore sizes of calcium alginate gels were found to be in the range of 6-17nm for 3-7wt% alginate. This is two orders of magnitude greater than the diameters of the reactants needed for calcium carbonate precipitation (the approximate diameters of calcium ions, water molecules, and bicarbonate ions are 0.2nm, 0.275nm, and 0.36nm, respectively), implying diffusion can occur.

The properties of the gel are controllable via the amount and arrangement of G-block (guluronic acid) amino acid sequences and the degree of cross-linking with calcium ions. An increase in both the amount of G-block sequences and amount of cross-lining with calcium ions results in a stiffer and more stable gel with smaller pore size [61]. This suggests the need to experimentally vary these parameters to optimise the rigidity of the gel as well as the diffusion speed of reactants in order to achieve the most effective solution.

The healing mechanism

Figure 7 shows a schematic representation of the postulated healing mechanism.

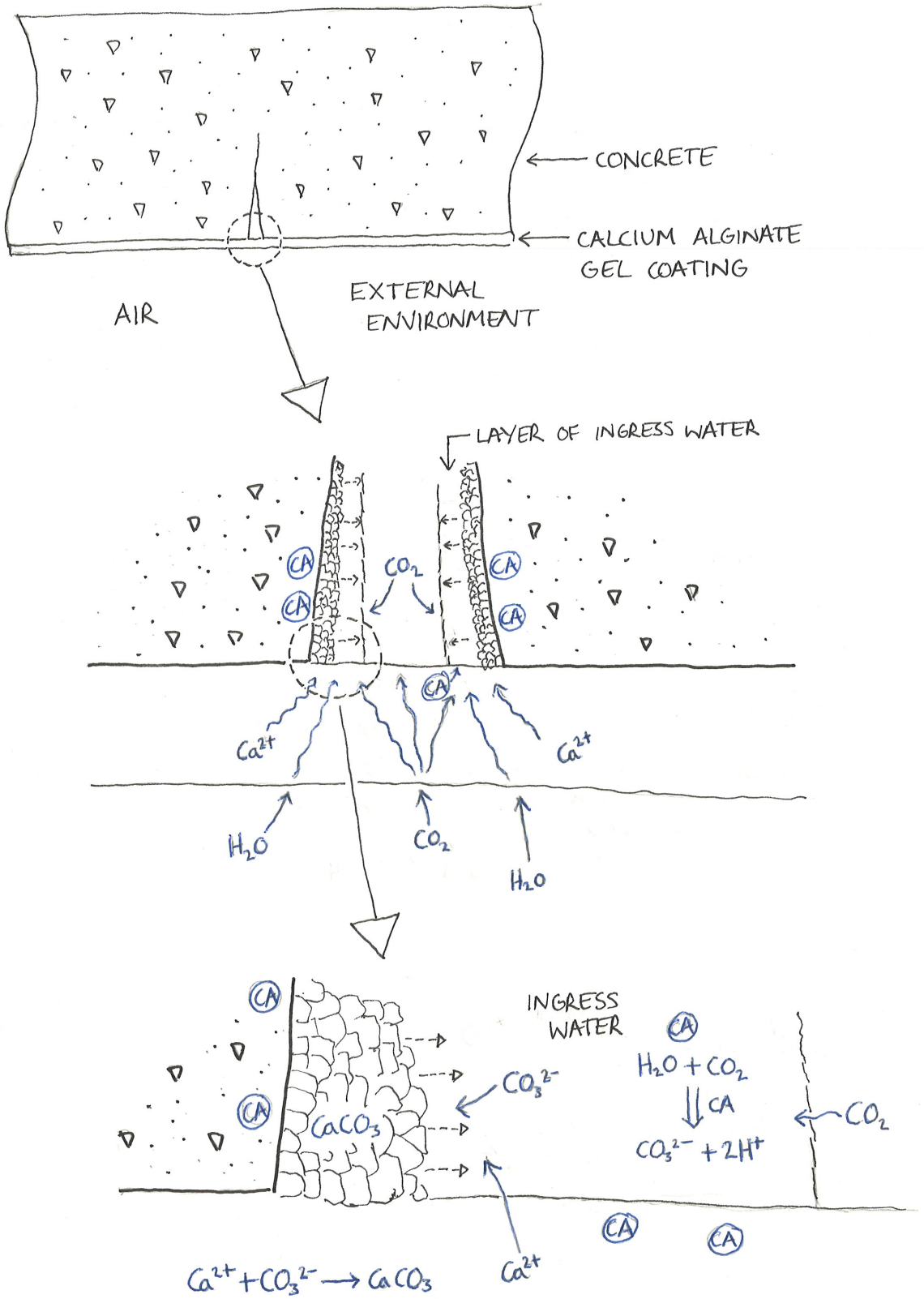

Figure 7 – Conceptual design schematic

The porous gel allows water molecules and carbon dioxide molecules (dissolved or not) to pass through to the crack site, which produce bicarbonate ions in the presence of the carbonic anhydrase. Calcium ions released from the calcium alginate gel then react with the bicarbonate ions resulting in the precipitation of calcium carbonate within the crack. The formation of calcium carbonate would hinder the ingress of water, decreasing the diffusion of dissolved carbon dioxide and chlorine salts that cause corrosion of steel reinforcement within the concrete, and reducing the chance of surface spalling due to freeze-thaw.

Although further experimental analysis of this self-healing concept is required to assess it's potential for use in the construction industry, it has been shown that calcium alginate increases the production of calcite (an amorphous polymorph of calcium carbonate) and calcium hydroxide (see section 5.1).

4.1.3 Further concept developments

It is not yet clear how damage detection will be implemented, enabling the reaction to occur exclusively at the time and location of crack formation, and inhibited elsewhere. An initial idea is to develop a mechanism of damage signalling through gel strain, stimulating the release of calcium ions from their ionic cross-links with alginate. This is a key aspect of the design that needs to be resolved in future work.

Another important requirement of the coating layer is that it remains passive in to the environment around it, and is more durable than the material it's protecting to ensure effective healing throughout the lifetime of the material. On exposure to the environment, calcium alginate gels are susceptible to oxidation and chelation (loss of divalent cations such as calcium ions to bacteria), causing them to degrade in an uncontrollable manner [61]. Therefore, the calcium alginate gel composition would need to be modified with anti-degradation agents or microbial preservatives [61] to permit its effective use in concrete construction.

Another barrier to overcome when considering the built environment could be its aesthetic impact. The gel could be mixed into the outside layer of a concrete structure, rather than applying it externally, achieving the same healing benefits and

reducing exposure to the environment whilst maintaining the same outward appearance.

4.1.4 Comparison to current self-healing mechanisms for concrete

The advantages of this concept over the mechanisms developed to self-heal concrete discussed in section 3.1 are:

- It will ensure reliable healing of any surface crack, as the mechanism doesn't rely on the crack passing through a certain point in the cross-section to release the healing agent.
- It would be more versatile, and could be applied to cracked concrete in current infrastructure.
- Minimal interference with the concrete mixture means that concrete properties and manufacturing processes would not be altered, allowing for easier implementation into concrete design for construction.

Conversely, the disadvantages are:

- The healing agent is exposed to the environment, making it susceptible to degradation.
- It may not be aesthetically pleasing to have a gel coating on the external face of a building.

4.2 Concept 2: Self-assembled construction materials

Inspired by the biomineralisation processes of bone and nacre, the initial concept was to create a self-assembling structural organic-inorganic composite material that can be repaired via further self-assembly using local natural resources. This outlines a new paradigm for the manufacture of construction materials to create a more sustainable construction industry.

4.2.1 Design considerations

The following key design components were considered in order to develop and evaluate the concept:

1. *The energetic stability of molecules*
2. *The self-assembly stimulus*
3. *Scaffold reactivity: The degree of polypeptide chain cross-linking*
4. *Scaffold pore size and porosity*
5. *The mechanical properties: organic matrix content*
6. *The reliability of mechanical properties*

4.2.2 Conceptual design

It is proposed to create a collagen scaffold using the lyophilisation technique (see section 3.2) upon which minerals such as calcium and phosphate crystallise to form a composite material that has mechanical properties suitable for structural design, and can be manufactured and repaired by molecular self-assembly.

The organic phase

Synthetic collagen fibres made from collagen-mimetic amino acid sequences that replicate the triple-helix structure and functional properties of collagen, will form the organic matrix scaffold [62]. This could be combined with chitosan, a polysaccharide produced abundantly in nature, to enhance its anti-corrosion, anti-bacterial and mechanical properties, as occurs in nacre [59]. The collagen polypeptide crosslinking will be controlled using the local environmental pH conditions and hyaluronic acid (an amino acid sequence that has been observed to augment the degree of crosslinking of a collagen matrix [57]) to dictate protein scaffold stiffness and mineral receptor site availability.

Bone, a material whose mechanical properties can be compared to those of reinforced concrete, has organic matrix content of 30-50% by volume. Therefore, the collagen concentration of the slurry to be freeze-dried should result in a matrix voids ratio of approximately 0.6. The desired mechanical properties for members in

different locations of a structure can be achieved by varying the organic matrix content and hence pore size.

Organic scaffold assembly

Lyophilisation is to be used to form the collagen scaffold due to its versatility, low cost and potential to be scaled up for use in the construction industry. This method can be used to precisely regulate the collagen matrix microstructure by controlling the ice crystallisation process [63]. The following can provide this regulation:

- Enforcing certain temperature time histories
- Temporally and spatially controlling the absorption of latent heat by the mould
- Incorporating particulates to stimulate heterogeneous nucleation

The scaffold pores must be large enough to provide sufficient space for mineral transport, nucleation and growth, but they must also be small enough to provide adequate ion receptor site density for mineral nucleation [54]. Therefore, a designed network of larger pore sizes could be produced to act as a vascular network to ensure all parts of the member section are mineralised. This will ensure confidence in reliable mechanical properties of the material, which dictates whether it can be used in structural design.

The mineral phase

The scaffold is to be mineralised with calcium phosphate (mimicking bone) or calcium carbonates (mimicking nacre), depending on the material's local mineral resources and mechanical properties to be achieved. This biomineralisation process stiffens and hardens the elastic, ductile collagen matrix [64]. If calcium carbonate is the crystal to be formed on the scaffold, it will follow the same precipitation reaction that occurs in nacre (see section 2.2.1).

The self-assembly mechanism

Synthetic collagen-mimetic polypeptides are produced, and then assembled in controlled conditions guided by lyophilisation to produce a scaffold with the desired

micro-scale geometry. The scaffold is then submerged into a mineral-rich aqueous solution and biomineralisation of the scaffold initiates due to the abundance of carboxyl receptor sites, matrix geometry and balance between hyaluronic acid and pH conditions of the solution. The pH of these underwater 'assembly sites' could be regulated by controlling ionic concentrations around the scaffold to dictate the rate of crystal growth, as molluscs do in nacre formation.

If the composite is being applied in a mineral-rich aqueous environment (such as offshore wind turbine structures), any damage incurred could instigate the re-assembly of the proteins into their states of energetic stability, and the re-mineralisation of the organic scaffold. If the composite is used on land, electrospinning and electrospraying could be employed to spray on new proteins and minerals, respectively. This allows self-assembly into the initial composite microstructure, replenishing any damaged or lost material.

Due to the composite's potential intrinsic self-healing capabilities in a mineral-rich aqueous environment, applying it in offshore uses such as wind turbine masts and foundations, bridge columns, oilrigs, quaysides, submarine armour, or dams seems most appropriate.

4.2.3 Further concept developments

A crucial consideration for the viability of this concept is whether lyophilisation and synthetic protein production can be scaled up to industrial production levels. Furthermore, various processes and material parameters such as amino acid sequence, slurry cooling conditions, slurry mould geometries, and amount of chitosan could be experimentally modulated to achieve protein assembly in the desired configuration. The extent to which agents or coatings to reduce environmental degradation and maintain passivation would be needed could also be determined by experimental investigations. These suggested experiments were not executed in this work, as they would have been challenging within the time constraints.

Alternatively, the assembly of the collagen scaffold could be guided with electrospinning for better control over the microstructure geometry. It is seen as a promising technique for the simultaneous deposition of collagen and hydroxyapatite

onto implant surfaces [65], which would avoid depriving parts of the matrix from mineral deposition. However, this process would also need to be optimised for large-scale protein scaffold formation.

Ideally, the protein scaffold would be formed from genetically programmed amino acids whose self-assembled configuration has been modelled with Quantum Mechanics or a very realistic 'force field' and accurately simulated. This would enable the precise design of a synthetic protein that 1) self-assembles into a designed configuration, 2) optimises the spatial and temporal control over mineral deposition and 3) is specialised to the function of the material.

4.2.4 Comparison to current construction materials

The advantages of this concept over current construction materials are as follows:

- Structural properties can be precisely controlled with matrix pore size and collagen content implying it would be more versatile and adaptable to specific needs.
- Manufacture would generate no waste and the processes require less energy, making it more sustainable.
- The materials can integrate into and be adapted to their local environment.
- There is a reduced need for human interference in manufacture, construction, maintenance and repair due to self-assembly and self-healing properties, eliminating structural imperfections and mistakes made during construction.
- Efficient structural designs that would distribute loads according to controlled microstructural and section geometries can be achieved.

Conversely, the disadvantages are as follows:

- The current processes proposed are not yet available on the scale required to manufacture construction materials

5 Experimental work

5.1 Concept 1 Experiment

It was decided to investigate whether concept 1 (see section 4.1) would be viable by applying calcium alginate gel to the crack face of cement paste specimens, monitoring the progression of crack healing over 28 days, analysing precipitates extracted from the crack face after 28 days, and comparing the results to a set of control specimens. The objectives of the experiment were to:

- Observe whether calcium alginate gel adheres to concrete.
- Monitor the progression of crack healing of a set of control and Ca-Alg specimens over of 28 days.
- Investigate whether the specimens regained their load capacity having been cracked then left in a water bath for 28 days.
- Investigate the composition of precipitate accumulated in the crack.
- Deduce whether the Ca-Alg coating has encouraged a greater degree of crack healing than the control specimens and hence whether the concept has the potential to be developed further with a view to using it in the construction industry.

5.1.1 Materials

Cement paste of 40wt% distilled water made with Ordinary Portland cement (OPC) was used for all specimens (480g OPC and 192g distilled water per specimen). A 2wt% sodium alginate solution, (4g sodium alginate powder ($NaC_6H_7O_6$) and 200g distilled water) was mixed with calcium chloride ($CaCl_2$) to make calcium alginate gel ($C_{12}H_{14}CaO_{12}$).

5.1.2 Experimental procedure

1. *Preparation of specimens*

Two steel mould sets, each with three 160 x 40 x 40 mm prismatic moulds, were used to cast six cement paste specimens. The mould was brushed with a lubrication oil to ensure the easy release of the prisms from the mould after they had set. The prismatic moulds all had a small hole at either end, covered with duct tape to prevent moisture or cement paste escaping whilst setting. A 3.5mm diameter zinc-plated steel was passed through the holes (and duct tape) at either end, such that it occupied the middle horizontal axis of the prism. This prevented the specimens undergoing brittle failure in 3-point bending later in the experimental procedure. Once the moulds had been prepared, cement powder and distilled water were mixed together using a planetary-type mixer producing cement paste that was poured into the moulds in two layers. Each layer was followed by adequate compaction to remove trapped air resulting in a more homogenous and dense matrix. The moulds were then covered with acetate film to prevent moisture escaping during setting and were left to set and harden for 24 hours at ambient conditions (21°C ±1°C). They were then released from their moulds and placed in a water bath at ambient conditions (21°C ±1°C) to cure for one week.

2. *Cracking the specimens*

After one week, all specimens were taken out of the water bath and cracked in 3-point bending using an Instron machine. The specimens were supported over a span of 125mm and loaded in the centre of the specimen (see Figure 8A). Load vs. extension data at a ramp speed of 0.1mm per minute was recorded for each specimen. Before removing the specimen from the machine, it was ensured that the crack widths were approximately 500µm by allowing the load cell to extend further. This safeguarded against the control specimens healing completely through cement particle hydration after 28 days (see Figure 8B). The maximum crack width that concrete can autogenically self-heal is 150µm. This enabled differences in crack healing between the control and Ca-Alg-coated specimens to be observed.

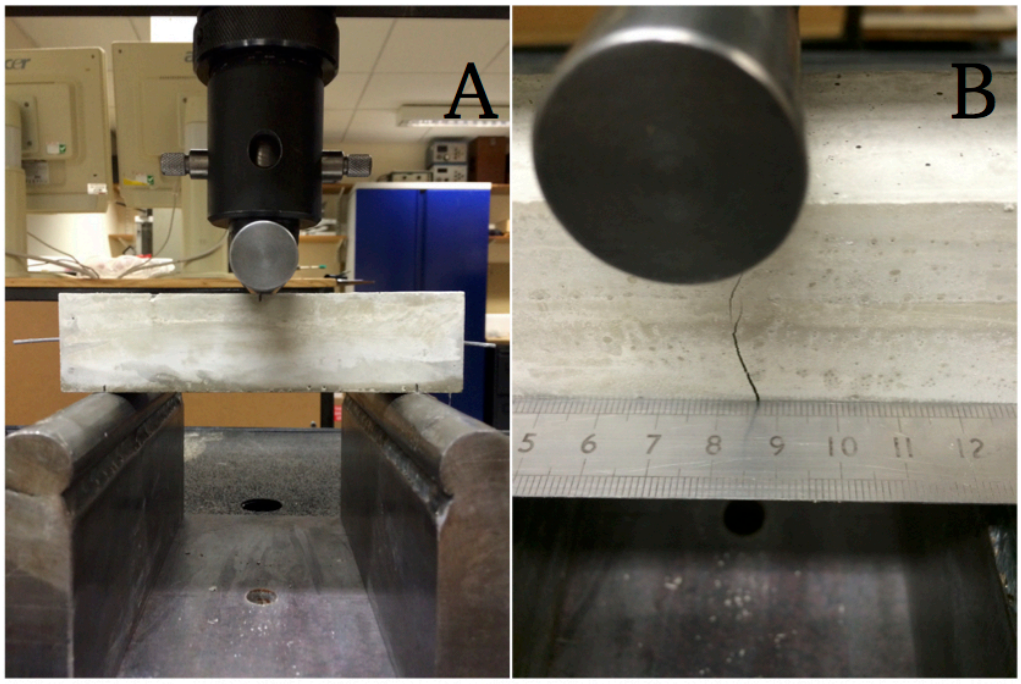

Figure 8 - Cracking the specimens. A) Three-point bending test set-up, B) Ensuring the crack width is greater than 0.5mm

3. *Applying calcium alginate gel*

The sodium alginate solution was prepared by mixing sodium alginate powder with water using an 'IKA T18 Ultraspeed Homogeniser' for approximately two minutes at a speed of 18,000 rpm (see Figure 9A). The solution was painted onto the cracks of three specimens using a brush (Figure 9B), and then sprayed with calcium chloride solution from a spray bottle (Figure 9C). Sufficient calcium chloride was sprayed onto the sodium alginate to ensure the degree of ionic cross-linking between the calcium ions and alginate polysaccharide chains was such that the resulting gel had enough structural rigidity to adhere to the concrete. Figure 9D shows the appearance of the Ca-Alg specimens. The remaining three specimens that were not coated with Ca-Alg gel are referred to as the control specimens. All specimens were then placed upright in a water bath.

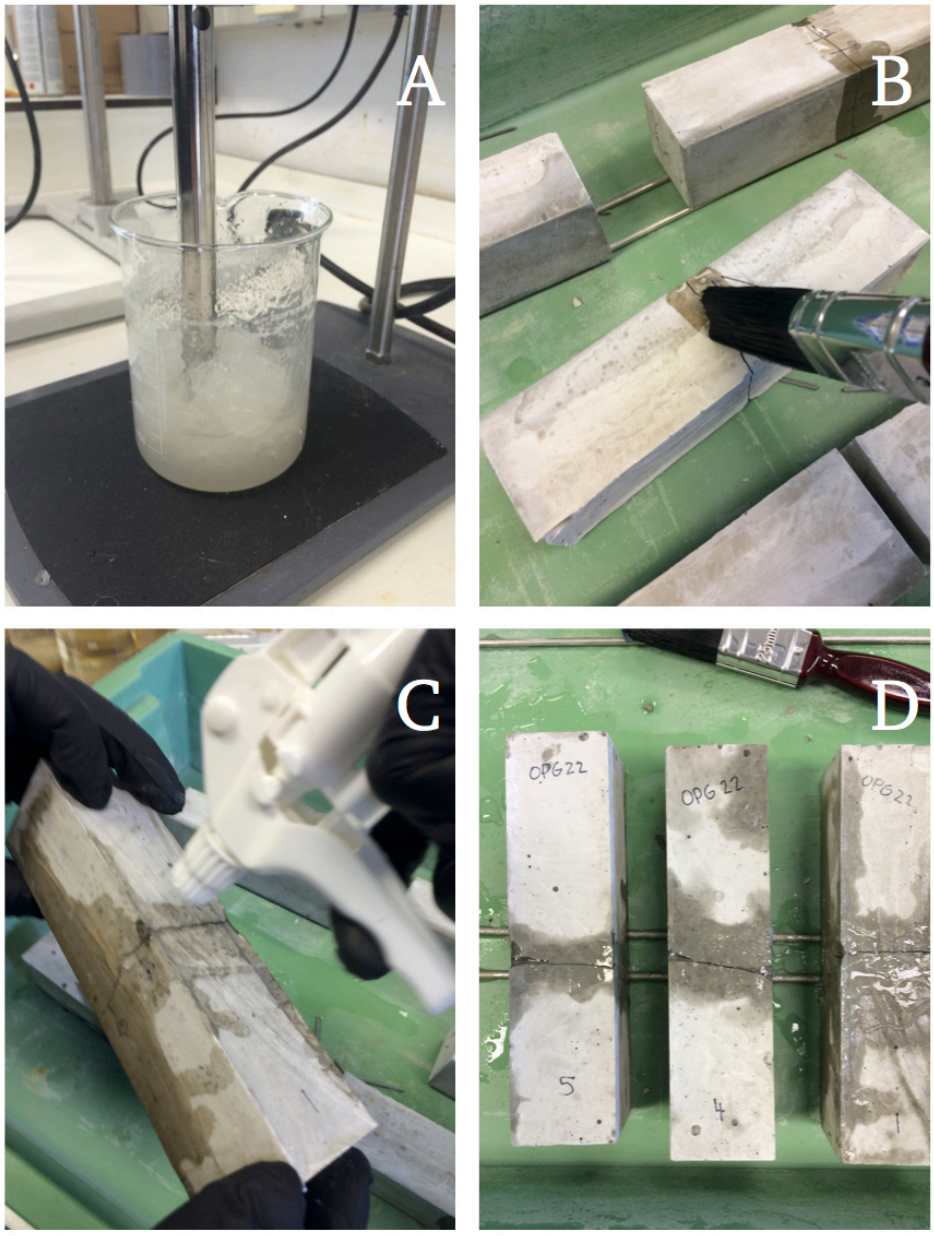

Figure 9 - Applying Ca-Alg to three of the specimens. A) Homogenising the sodium alginate solution, B) Painting the sodium alginate solution onto the crack, C) Spraying calcium chloride on to the sodium alginate, D) The Ca-Alg-coated specimens.

4. *Monitoring crack widths*

A stereomicroscope was used to measure the initial crack widths at marked locations on all specimens immediately after cracking. Then every week, at days 7, 14 and 28, all six specimens were taken out of their water baths and photographs were taken at the same marked locations on the specimens, to observe growth of precipitates and record changes in crack width. All specimens were permanently taken out of their water bath on day 28 (see Figures 10A and 10B). It was very difficult to monitor crack

widths of the Ca-Alg samples because the gel obscured the view of the crack in most cases. Furthermore, the cracks extended across the entire cross-section of the specimens due to their brittleness in the absence of aggregates, so the two halves of each specimen were loosely fixed. This made it impossible to transfer the specimens from the water bath to the stereomicroscope without altering crack widths. Therefore, the crack monitoring conducted was qualitative rather than quantitative. Methods to prevent this would have been considered but this problem was not anticipated before cracking the specimens.

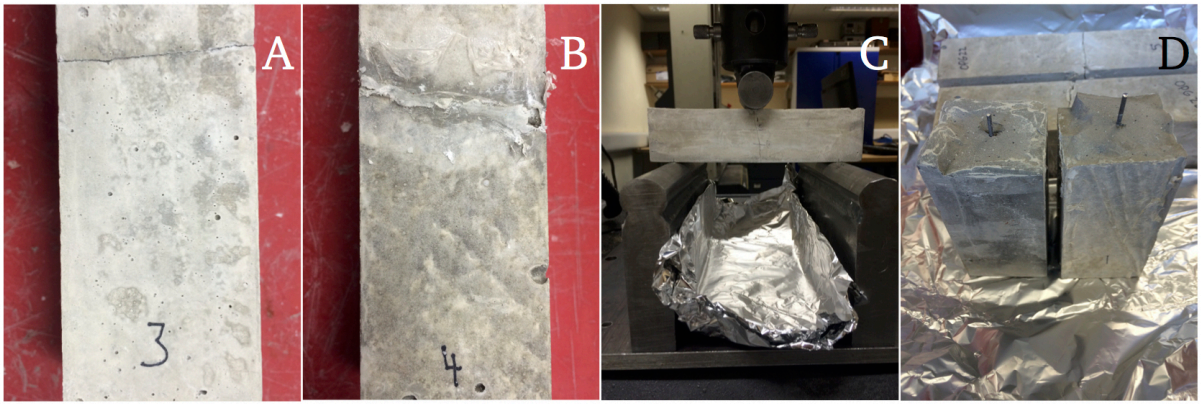

Figure 10 - A) Control specimen typical crack appearance, B) Ca-Alg typical crack appearance, C) Catching loosened precipitates with an aluminium foil sheet, D) Broken specimens with a filed crack face

5. *Re-cracking the specimens*

On day 28, the three-point bending tests were repeated on all specimens after being removed from the water bath and allowed to dry. An aluminium foil sheet was placed underneath the specimens during loading (one sheet for the control specimens and a separate one for the Ca-Alg specimens) to catch broken off pieces or crack face precipitate material that fell from the specimens during loading (see Figure 10C).

6. *Crack precipitation phase analysis*

A Panalytical X'Pert with X'Celerator detector (Powder X-ray Diffractor (PXRD)) was used to identify the phases present in the crack precipitate material of each specimen, to investigate any difference in composition. To do this, the specimens were broken apart at their crack face into two sections (see Figure 10D). The material caught by the aluminium foil sheet during three-point bending of the control specimens, and

material filed from their crack surface, was pulverised into a fine powder and stored in a pot. The same procedure was repeated for the Ca-Alg specimens. The file and pestle and mortar, used for filing and pulverising, respectively, were cleaned with ethanol before each use to avoid contamination of the powder sample. The two powder samples obtained (one containing powder from the Ca-Alg specimen and the other from the control specimen) were analysed by the powder X-ray diffractor separately, and a diffractogram showing X-ray intensity vs. angle subtended (2θ) was produced for each sample.

5.1.3 Results

Three-point bending tests

The key results from the three-point bending tests are shown in Table 1, which were extracted from the load vs. extension data for each specimen.

Table 1 – Key results from the three-point bending tests of the specimens.

Specimen		Maximum load capacity [N]		% Load capacity regained
		Uncracked	Cracked	
Control Specimens	Specimen 2	629	200	32%
	Specimen 3	572	115	20%
	Specimen 6	856	10	1%
Calcium Alginate Specimens	Specimen 1	516	140	27%
	Specimen 4	868	100	12%
	Specimen 5	962	180	19%

The ‘cracked’ specimens’ maximum load capacity represents the load reached when compressive creep in the concrete is initiated, identified by a region of dramatically alternating positive-negative gradient on the load vs. extension graphs (see Figure 11). These results show a large variation in both uncracked and cracked load capacities. The latter observation is reflected in the values of ‘percentage load

capacity regained' across control specimens. The loading of the cracked specimens was characterised by a shallow graph gradient implying very low bulk stiffness and ductile behaviour of the steel reinforcing wire as in Figure 11. Yielding of the steel wire may have been induced on initial cracking where the extension was increased to open the crack to 500µm.

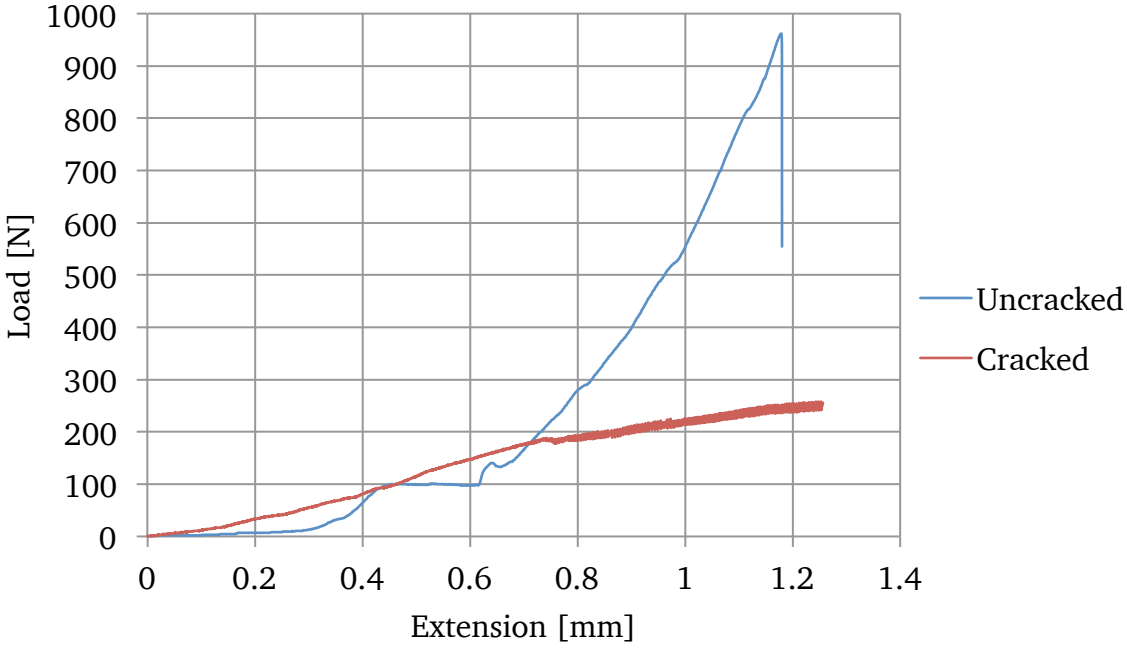

Figure 11 - Specimen 5 load vs. extension results from three-point bending tests

Powder X-ray diffraction tests

The observations of phases present in the samples from the PXRD diffractograms (see Figure 12) are based on the diffractograms for cement components computed by Jadhav and Debnath [66]. Alite, C_3S (tricalcium silicate), was identified at $2\theta=29.5°$ and 51.7° in its monoclinic polymorph, with the control and Ca-Alg samples showing very similar intensity. Belite, C_2S (dicalcium silicate), in its β-C_2S polymorph, C_4AF, gypsum and C_3A were found to be absent from the mixture as their characteristic peaks are not present on the diffractogram. The amount of unhydrated silicates present in the samples was shown to be very similar for both samples.

PXRD diffractograms of calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) by Taglieri et al. [67] were used to identify these phases in the samples. $Ca(OH)_2$ was identified in both samples, but the Ca-Alg sample showed a consistently higher intensity of it (see peaks at 18°, 28.8° and 34.2° in Figure 12). The intensity of

calcite (a polymorph of calcium carbonate) in the Ca-Alg samples was also consistently greater than in the control samples (see peaks at 23°, 29.5°, and 39.5° in Figure 12). However, Aragonite, a crystal polymorph of $CaCO_3$, was not identified in either sample.

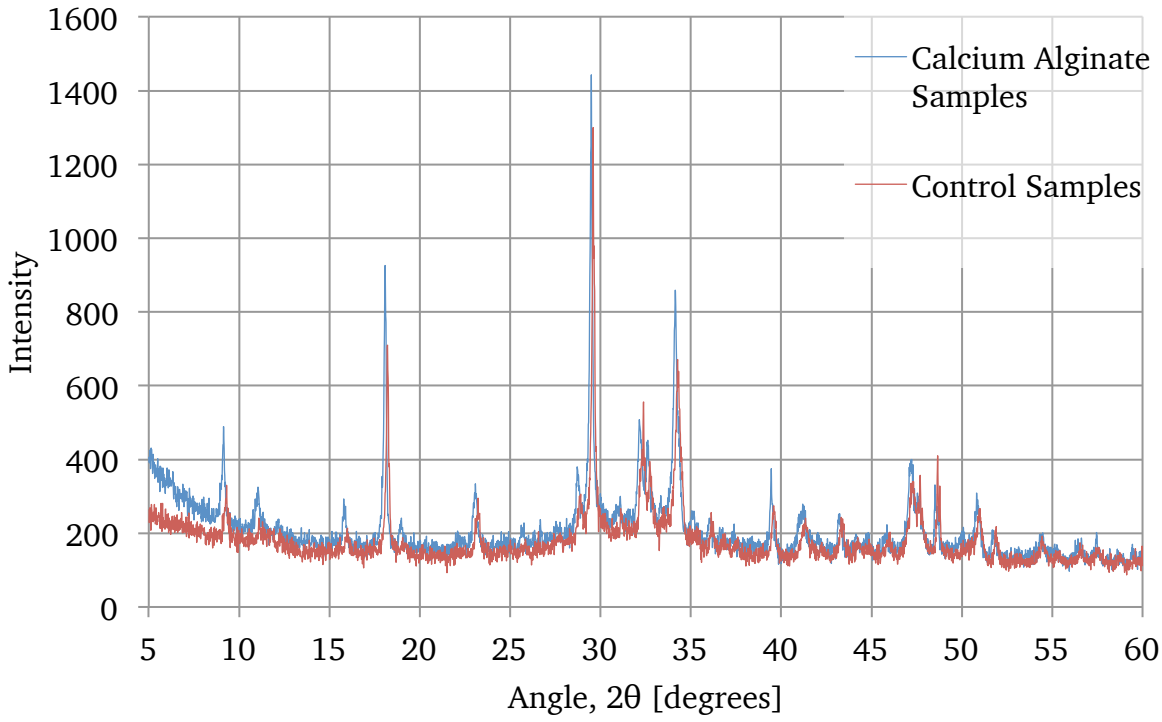

Figure 12 - Powder X-ray diffraction results for the specimens coated with calcium alginate and the control specimens

Stereomicroscope observations

Figures 7 and 8 show a selection of photographs taken with the stereomicroscope of cracks in the Ca-Alg specimens and control specimens, respectively. Only the photographs from the day of cracking (day 0) and from day 28 are shown for each specimen (at the same crack site). The stereomicroscope photos taken (see Figures 13 and 14) imply that the cracks of the Ca-Alg specimens were filled to a greater extent than those of the control samples after 28 days.

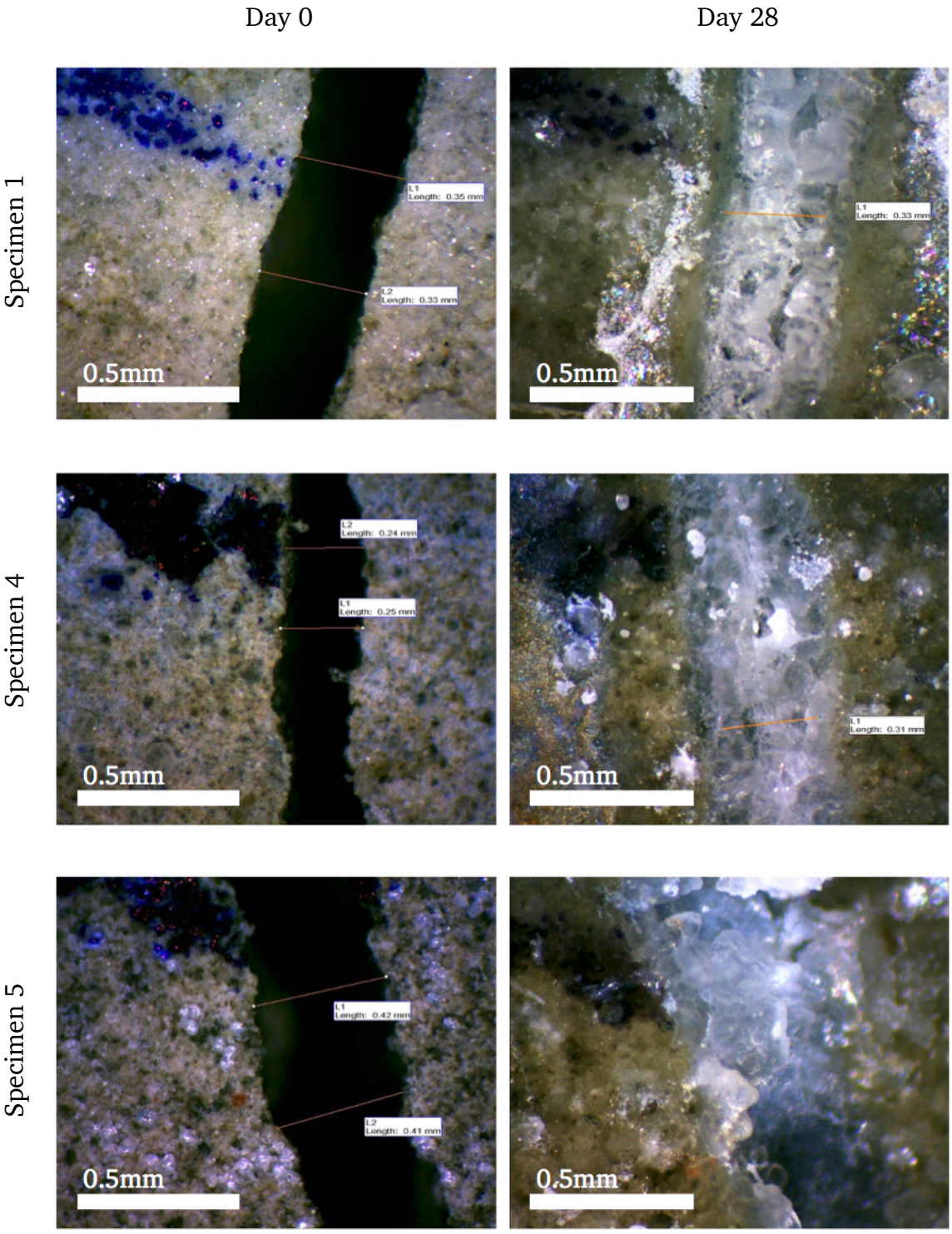

Figure 13 - Stereomicroscope photographs representative of the general appearance of cracks of the Ca-Alg specimens directly after initial cracking in three-point bending, and after 28 days in a water bath.

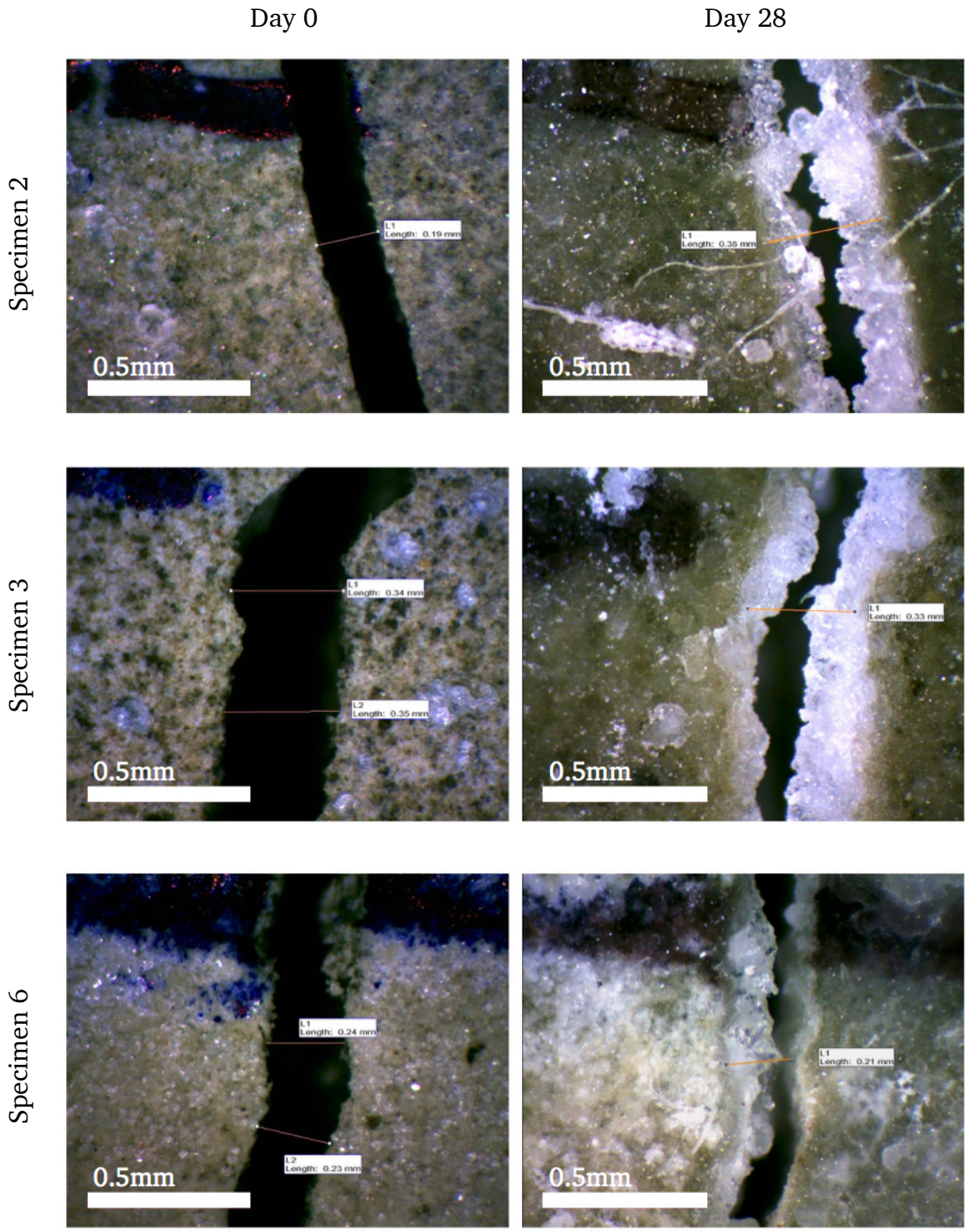

Figure 14 - Stereomicroscope photographs representative of the general appearance of cracks of the control specimens directly after initial cracking in three-point bending, and after 28 days in a water bath.

5.1.4 Discussion

The results from the three-point bending tests imply that the material precipitated within the all cracks (of calcium alginate and control specimens) did not regenerate any of the specimens' mechanical properties. The observations made of the control sample cracks with the microscope show that the cracks in the control specimens had not sealed after 28 days. Conversely, the stereomicroscope photos of the cracks in the calcium alginate specimens showed they had sealed. Sealing of cracks greatly improves the durability of the concrete as it decreases permeability to ingress water, suggesting it a promising result. However, it also suggests that the material that did seal the calcium alginate specimen cracks have very poor mechanical properties.

The PXRD analysis of the powder samples shows that the presence of calcium alginate gel increased the formation of calcite and calcium hydroxide compared to the control samples. This suggests that calcium ions ionically bound to the alginate chains were released over the 28 days. It follows that calcium alginate has the ability to improve the healing behaviour of concrete if the gel is modified to release more calcium ions to provoke more calcium carbonate precipitation. However, it is unknown whether the calcium-based phases had precipitated on the crack face of the concrete or within the calcium alginate gel matrix that got mixed into the powder sample analysed by the PXRD. Perhaps an analysis of the specimens with an SEM (scanning electron microscope) would have given clarification.

However, due to the small sample sizes (3 control specimens and 3 calcium alginate-coated specimens), only broad conclusions can be drawn from the results. Therefore, same experiments should be repeated with a larger sample size to verify these results. The experimental procedure could also be adapted by modulating numerous variables to thoroughly test the impact of calcium alginate gel on the self-healing of concrete. Further experimenting could include: varying the concentration of the sodium alginate solution at discrete intervals; monitoring and varying the amount of calcium chloride sprayed onto the sodium alginate solution at discrete intervals; removing visually obscuring calcium alginate gel from specimens before each stereomicroscope viewing to observe changes in crack width more accurately; re-

applying calcium alginate after each week; incorporating aggregates into the cement paste mixture.

5.1.5 Conclusions

From the discussion and results, it can be concluded that:

- Calcium alginate gel adhered to concrete and remained attached to it for the duration of the experiment
- The presence of calcium alginate appeared to be seal the cracks to a greater extent and induced more calcite and calcium hydroxide production in the cracks than the control specimens. This implies that there is potential for further development into an effective self-healing mechanism for concrete.
- There was no observable difference in regeneration of mechanical behaviour between specimens, and neither set of specimens regained mechanical properties after 28 days in a water bath.
- Due to the small sample size, only broad conclusions can be drawn from the results.

6 Conclusions

Having investigated natural self-healing mechanisms, it was found that the following are key to effective tissue regeneration in fauna:

- The extracellular matrix
- Damage signalling through the dynamics of the cytokine environment
- The migration, proliferation and dedifferentiation of cells
- The ability of cells to self-assemble

This provoked research into the natural self-assembly mechanisms that underpin these dynamic processes. It was found that molecular characteristics, and stimuli from the surrounding environment, dictate interactions between molecules, which in turn define the self-assembly, resulting microstructure, and function of a material by achieving energetic stability.

Two novel concepts were developed in response to the investigations into self-healing and self-assembling materials in nature. The first concept was to mimic the function and form of the periosteum layer around bone with a calcium alginate gel coating on concrete. The results of an experiment observing the effect of a calcium alginate gel coating on the healing of cracked cement paste specimens implied that the gel had a positive impact on healing, suggesting the concept has potential. However, further experimenting is required to verify the results and assess the full healing ability of this mechanism.

The second concept introduced a new paradigm for the manufacture of construction materials in which they self-assemble using natural resources and harnessing natural processes, as natural organisms do. It was proposed to use a freeze-drying technique to form a collagen and chitin scaffold upon which calcium carbonate nucleates (stimulated by the amino acid sequencing, scaffold matrix geometry, and environmental conditions) to form a structural composite material similar to bone. This concept needs to be experimentally investigated to assess its potential, with its main barrier to implementation being manufacturing scalability. It is predicted that this paradigm would revolutionise the construction industry if implemented, by greatly reducing the energy demand and excessive waste in manufacturing, eliminating errors made in construction, and creating adaptable structures that would be degradable when redundant or old.

From the initial investigation of natural self-healing processes, it was evident that the ability of molecular re-assembly is a prerequisite for effective self-healing at ambient conditions. Due to the extreme conditions in which construction materials such as steel and concrete are manufactured, molecular re-assembly after perturbation by mechanical loading or degradation is not possible at ambient conditions. Therefore, current construction materials will not be able to self-heal unless autonomous self-healing mechanisms are integrated within them. Thus it is believed that manufacturing construction materials based on natural processes, such as those described in concept 2, will improve their versatility, adaptability, ability to self-heal and self-assemble, and enable the sustainable integration of the built environment into the natural environment.

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8 Appendix

8.1 Risk assessment retrospective

The risk assessment submitted at the start of Michaelmas Term 2014 reflected the hazards encountered during the project perfectly. If starting the project again, I would go about assessing the risks in exactly the same way.