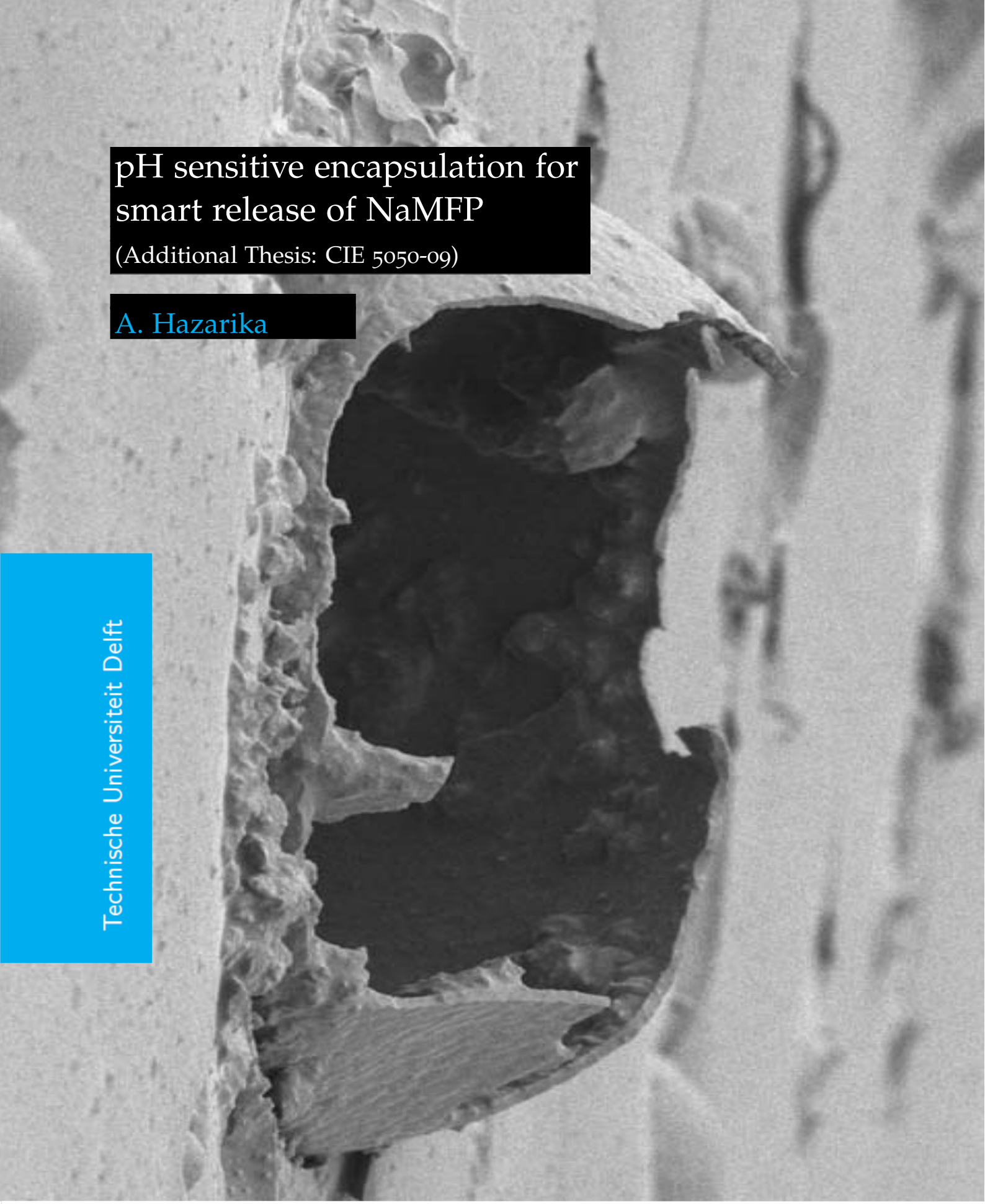

pH sensitive encapsulation for smart release of NaMFP

(Additional Thesis: CIE 5050-09)

A. Hazarika

Technische Universiteit Delft

TU Delft Delft University of Technology

Challenge the future

PH SENSITIVE ENCAPSULATION FOR SMART RELEASE OF NAMFP

An additional thesis submitted to the Delft University of Technology in partial fulfillment of the requirements for the degree of

Master of Science in Civil Engineering

by

Amrita Hazarika

Supervisor: Prof.dr. Oğuzhan Çopuroğlu (Lecturer, Materials & Environment)

Cover: An SEM image showing the fracture plane of a microcapsule. Photo credits - Michael Kessler, University of Illinois.

Preface

This thesis is an outcome of the work conducted as an Additional Thesis at the faculty of Civil Engineering and Geosciences, TU Delft. The basis of this work stem from my interest in durability and self-healing of cementitious materials. In this work, an investigation was carried out to assess the use of pH sensitive encapsulation for carbonation triggered release of Sodium Monofluorophosphate (NaMFP) - an inorganic healing agent. To do so, a state-of-the-art review of pH sensitive wall material and a technique to fabricate the same, to encapsulate NaMFP, was performed. The outcome of comparative analyses conducted on prospective shell materials and encapsulating techniques yielded three potential shell materials and two possible techniques. These findings can aid in future experimental investigations to scale up the use of such encapsulation technologies in the construction sector. This would contribute to the research in producing smart cementitious materials that can detect minute changes in their environment and perform targeted healing, without the need for human intervention.

I would like to express my gratitude towards Professor Oğuzhan Çopuroğlu, for conceiving the idea and showing me an opportunity to work in it. I also thank Yu Zhang for the fruitful discussions we have had on the topic.

Contents

List of Figures

List of Tables

1

Introduction

Concrete is undeniably the most popular and widely used construction material because of its high compressive strength, serviceability, availability of raw materials, and comparatively lower costs. However, its sensitivity to crack formation often manifests as a deterrent, as that paves way for ageing and degradation processes to occur. Penetration of chemicals such as chlorides and sulphates, and gases such as carbon-dioxide, through micro or macro cracks sabotages the durability and serviceability of concrete structures [72]. This necessitates frequent repairs which in turn is associated with substantial expenses. For instance, in Europe, in the past decade, a conservative cost estimate of replacing just highway structures alone, amounted to €600 billion whereas an additional €2 to 3 billion was spent annually on their upkeep [1]. At the same time in the US, annually about €18 billion was needed for repair and retrofitting of civic infrastructure, and €1.6 trillion was projected for repairing or replacing infrastructure in Asia [34, 70]. On the other hand, the available manual repair technologies that are used to restore durability, are often time consuming, and restricted by accessibility, location and environmental aspects [73], [82].

Besides the immense economic impact associated with repair and maintenance of constructions, the production of cement is also single handedly responsible for up to 8% of global anthropogenic CO_2 emissions. With escalating demand on new public constructions in fast growing economies like India and China, and the burgeoning repair activities in developed nations, the concerns related to socio-environmental costs have become equally alarming as of 21st century. All in all, this calls for an urgent intervention not only in the technology behind producing our built infrastructure, but also one that ensures their longevity.

1.1. Self-Healing Concrete

Rooij et al.[57] define self-healing materials as *man-made materials, which have the built-in capability to repair structural damage autogenously or with the minimal help of an external stimulus*. The numerous studies conducted on the topic of embedding this phenomena in cement based composites, demonstrate possibility of future civic infrastructure that, via a multitude of likely approaches, are smart enough to detect their own damage and un-

dergo healing or repair by themselves. This then would drastically reduce dependence on human intervention and the associated economic, social and environmental costs after damage initiation. This therefore has piqued an escalating research and development interest on the topic of self-healing concrete within the last 50 years. The drive to make our structures smarter and more resilient towards damage has led to an evolution of varying engineered approaches in the said technology, especially in the last decade. Figures 1.1 and 1.2 show the growing scientific interest in the field. These data have been collected from *Scopus* under the phrase 'self-healing concrete' for the years 2010-2021. The performance

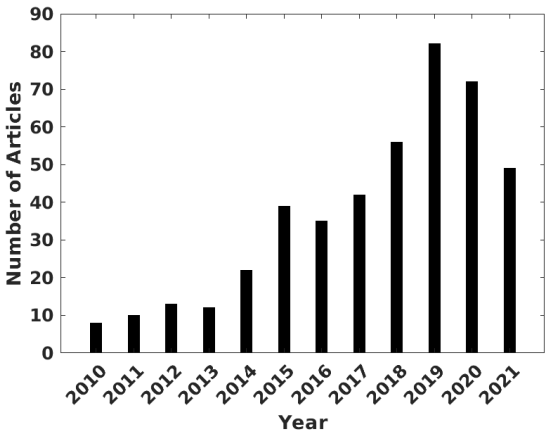

Figure 1.1: Publications on the topic of self-healing concrete

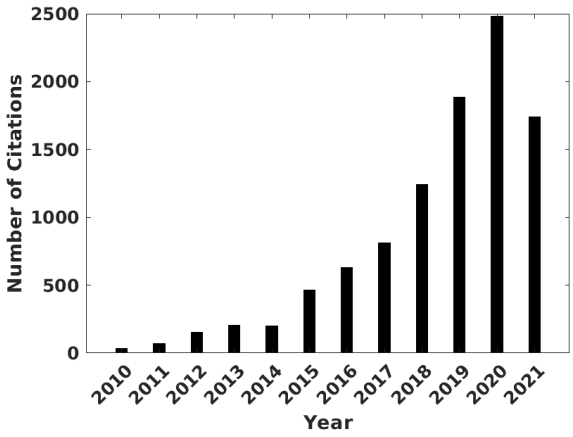

Figure 1.2: Citations garnered over the years on the topic.

comparison of a structure equipped with self-healing technologies versus a structure without it, can be better gauged with the curves demonstrated in figure 1.3 [71]. Over time, as cracks appear on concrete structures and degradation initiates, the first repair becomes necessary (shown in a) to maintain the required level of strength. Thereafter, depending on the quality and the subsequent durability of the repair work, a second repair is usually required within a span of 10-15 years. The total costs (shown in b) at the end of service life of the structure, rise progressively, depending on the frequency of the repair and maintenance activities needed over the years. Comparatively, in a self-healing concrete structure (shown in c and d), the occurrence of crack is followed by self-healing, which is why the total costs of such a structure can be projected to remain constant over the years. However, the initial costs of such a structure would be higher because of additional functionalities provided to it, compared to normal structures. Nevertheless, the elimination of frequent repair and maintenance demands would prove to be financially beneficial for the owners. Thus, self-healing of concrete holds significant promise towards sustainably and economically addressing the issues of damage associated with cracking and ageing.

1.1.1. Approaches to Self-Healing

The self-healing approaches studied and implemented so far, are varied. They range from traditional autogenous self-healing of concrete, wherein the concrete demonstrates an intrinsic healing ability, to introduction of stimulated autogenous healing via mineral addi-

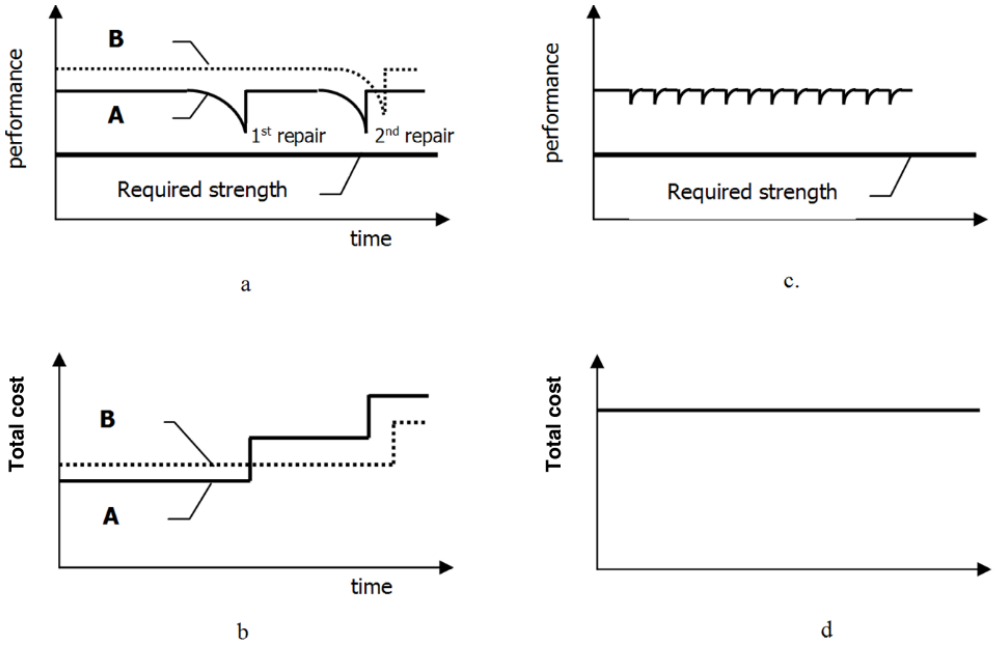

Figure 1.3: Performance (a) and costs (b) with elapse of time for normal (A) and high quality (B) structures. Direct costs of repair included. Performance (c) and cost (d) of a structure made with self-healing material (concrete) with elapse of time. Interest and inflation ignored. (Reproduced from [57])

tives, super absorbent polymers, and to autonomous healing via minerals and bacteria [13], [53]. The Rilem committee [57] proposes the following concise classification, using which the entire field of self-healing can be described:

1. **Autogenic:** intrinsic, where the the self-healing process uses materials components that could otherwise also be present when not specifically designed for self-healing (own generic materials). This property may be enhanced by the addition of fibres, shrinkable polymers like PET, and minerals such as supplementary cementitious materials and superabsorbent polymers.

2. **Autonomic:** engineered, where the self-healing process uses material components that would otherwise not be found in the parent material. This is often also termed as 'encapsulated' approach, wherein the healing agent is contained within a capsule or coating and are released upon encountering a certain physical or chemical trigger. This can comprise of microvascular and tubular capsules, microcapsules, coated pellets, and bacterial additions.

As previously mentioned, the research on the topic of self-healing concrete is still an evolving branch of study and the most optimal self-healing methodology has not been developed yet. Several researchers opine that the autogenous healing approach stands out as it is more efficient, cost effective, safer, and easier to implement in comparison with autonomous methods using capsules containing various types of healing agents [54]. However, from the point of view of the maximum crack width healed or sealed, autogenous

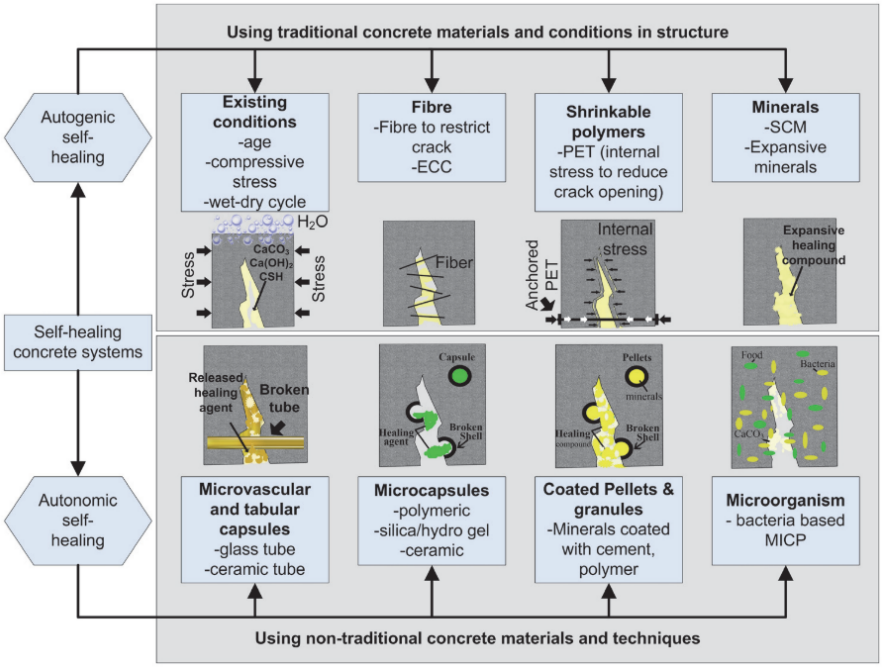

Figure 1.4: Self-Healing concrete systems [53]

healing are able to heal cracks of only upto 200μm whereas for efficient damage prevention, healing of crack widths larger than that is often crucial. Introduction of autonomous healing agents via encapsulation technologies on the other hand, has managed to heal wider cracks upto 0.9m and emerged as more promising from the laboratory scale studies conducted over the years. For enhanced durability and longer service-life of structures, autonomous healing strategies therefore appear as more optimistic.

1.1.2. Encapsulation of healing agents

The autonomous healing approach involves encapsulation of active healing agents. It has been the preferred technique to deliver the healing agents for effective in-situ repair [13]. The most widely investigated encapsulation systems are microcapsules and microvascular glass tube networks [53]. Typically, the capsules or tubular networks respond to a mechanical damage stimuli such as propagation of concrete cracks that induces fractures in the capsule shell walls, leading to release of healing agents into the crack. The following are the different types of encapsulation strategies, along with their pros and cons, that have been studied and applied so far:

1. **Microencapsulation:** This comprise of capsules with diameters below and upto 1mm, containing active healing agents. They are distributed throughout the matrix directly. A number of production methods, shell compositions, properties and cargo materials have been researched over the years, each aiming to resolve specific performance requirements of the cement composites [13].

    - Pros: They are easier to apply in bulk concrete production, compared to vas-

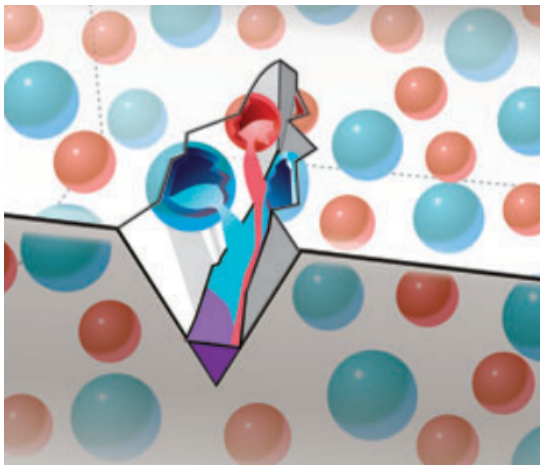

Figure 1.5: Micro capsule based healing [6]

cular or tubular encapsulation. They can be tailored to be responsive towards chemical triggers such as pH or chloride changes. Additionally, improved microencapsulation techniques such as microfluidics, offer even greater control over the production parameters than traditional techniques and enable a wide range selection of shell and cargo materials.

- Cons: The interlock or bonding between microcapsules and cementitious matrices is often incompatible which affects the efficiency of mechanical triggering in such a system. The production of microcapsules involves complexity compared to autogenous healing strategies.[54].

2. **Macroencapsulation:** This includes hollow polymeric or glass fibres or hollow glass concentric macrocapsules that could envelop a healing or repair agent. Fibres were proposed so as to additionally provide mechanical reinforcement besides healing. Other examples of macroencapsulated healing are CHT (Cementitious hollow tubes) and LWA (light weight aggregates).

    - Pros: It enables multiple healing and the added mechanical reinforcement.
    - Cons: Once ruptured, the presence of glass shells negatively affect the mechanical strength of the cementitious matrices. Besdies, long-term stability and repeatability have not been established yet.

3. **Vascular network:** This comprise of a network of glass or polymeric hollow tubes that resemble the human cardiovascular system that transports blood around the body [13]. There are 1D, 2D and 3D forms of vascular networks created to provide multiple alternative pathways for the healing agent to be transported and delivered at the damage sites in concrete matrices.

    - Pros: Healing agent can be continually supplied to reach the damage zones as appropriately as desired.

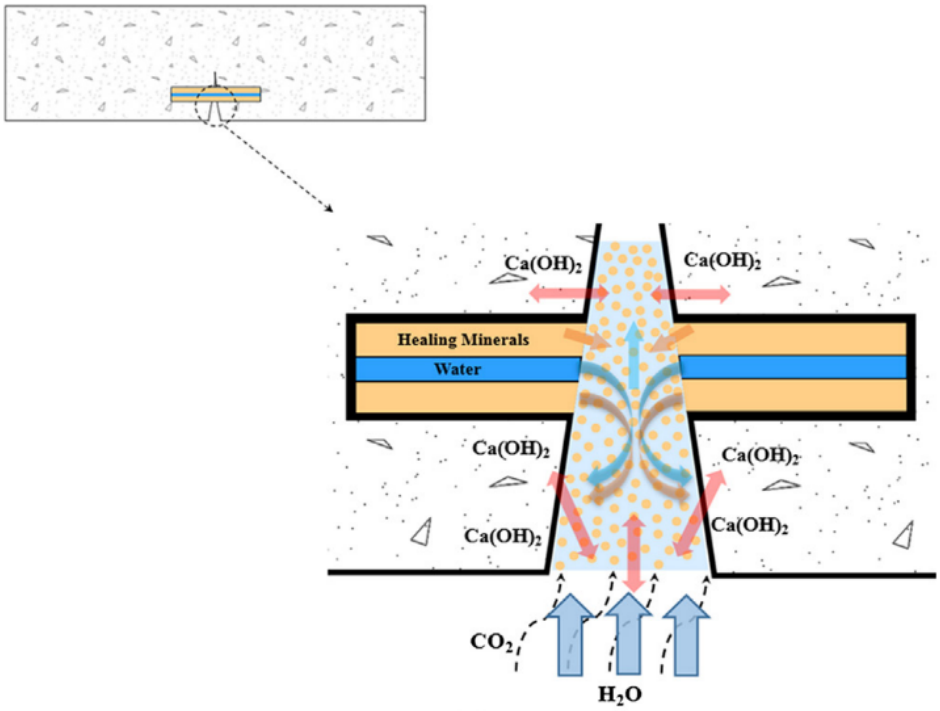

Figure 1.6: Basic concept of the concentric glass capsules in self-healing. The crack propagation triggers release of healing minerals. Consequent interaction of released healing agent with water and CO_2 results in the formation of different hydrated and carbonated products to seal and possibly heal the crack. [52]

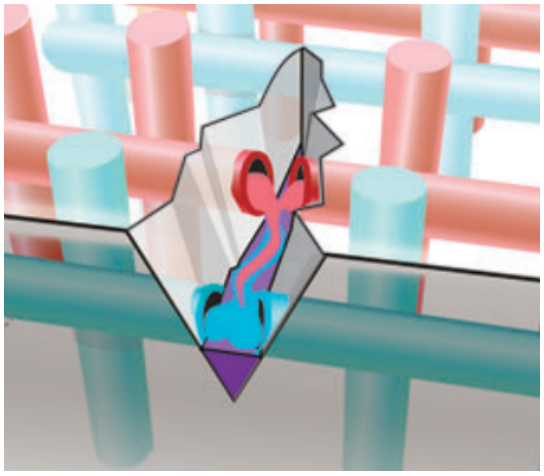

Figure 1.7: Vascular network based self-healing. [6]

- Cons: If the ends of the vascular network are left open to the atmosphere, it could provide a pathway for harmful gases and chemicals to enter the matrix and sabotage the durability. Challenges also persist to upscale this technology and to enable its remote activation.

Considering the pros and cons of the aforementioned encapsulation strategies, it can be

surmised that micro-encapsulation is a feasible approach as that eliminates the challenges relating to both macro and vascular encapsulation. Additionally, there have been successful field trials of using microcapsules in reinforced concrete panels [53]. This points to the feasibility of upscaling this technology for longer terms. However, many reports indicate the need for further research on microencapsulation, especially to address the bond interface problems leading to inefficient and unreliable mechanical triggering mechanisms [15]. It is also a challenge to ensure that all capsules will be broken or are responsive to mechanical stress trigger or crack propagation [81]. This essentially calls for a smarter encapsulation strategy to be fabricated which can respond to environmental or chemical stimulus such as a pH drop in the cementitious matrix, signifying damage initiation or depassivation of steel reinforcement. A few recent advances have therefore focused the discussion and investigation on alkaline sensitive or chloride binding shell materials to target carbonation or corrosion induced damage [15], [81], [85], [87], thereby modifying the efficacy of microencapsulating technology. This forms the broader subject of the current study.

1.2. Research question

The success of autonomic healing strategies rely on the efficiency of their encapsulation systems and their compatibility in the cementitious matrix. Factors such as response to trigger mechanisms, release rate and repeatability govern the feasibility of its application. Micro-encapsulation is an emerging and popular technology that has been successfully upscaled and applied on mass concreting on field. The surge in interest of the scientific community towards this technique is primarly because it eliminates the challenges otherwise associated with the tubular and vascular approaches. In that context, the current study investigates the formulation of an encapsulation system containing a synthethic healing mineral Sodium Monofluorophosphate (NaMFP), that is responsive to chemical triggers, or more precisely, a decrease in the pH of the cementitious environment. To that end the following research questions have been sought to be answered through the course of this study:

1. **What is a suitable shell material for encapsulating Na-MFP, such that it is stable at high pH environments and dissociates or ruptures at low pH environments?** Here high pH refers to the environment characterized by a normal, undamaged OP cementitious composite. A low pH environment is suggestive of initiation of degradation such as upon carbonation initiation and depassivation of the steel reinforcement.

2. **How to efficiently encapsulate the cargo material with the shell material?**

1.3. Research approach and outline of the thesis

To answer the above research questions, a study of existing literature on the techniques of microencapsulation, factors affecting its efficiency, responsiveness to chemical and environmental triggers are conducted to deduce a potentially compatible *shell material* for sodium monofluorophosphate as a healing agent, and a suitable *technique* for encapsulating it. The findings of this study could serve as a basis for laboratory experiments on

the topic of pH sensitive micro encapsulation for mineral healing agents like NaMFP. The outline of the study is as follows:

- Chapter 1 introduces the topic background, significance and research questions of the thesis.
- Chapter 2 provides an in-depth review on suggesting a suitable low pH sensitive shell material that can be used for encapsulating NaMFP.
- Chapter 3 provides a review on the techniques of microencapsulation, and the governing factors for checking efficiency and repeatability, to suggest an optimal or promising technique to encapsulate the findings of chapter 2.
- Chapter 4 incorporates the limitations of this study and concludes the findings. Additionally, it presents future scope of the study.

2

Encapsulation Material

The study of stimuli-responsive microcapsules have found considerable focus within a wide range of research domains such as pharmaceuticals, agriculture, printing, fragrance release, nutrient preservation, chemotherapy and concrete technology. The effectiveness of *environmentally triggerable* microcapsules lie on their ability to store their cargo (core material) until the shell material responds to a change in the environment, a stimuli, and undergoes disintegration. Thereupon, the cargo is released to the larger system or matrix and is aimed at responding to the specific stimuli [19], [7]. A variety of triggering phenomena have been investigated over the years in relation to encapsulation. The success of a triggering mechanism revolves around the application of the appropriate shell material that best responds to a particular trigger. In this chapter, the discussion is restricted to chemical triggering for cargo release and a compatible shell material that can facilitate this.

2.1. Cargo Material

The cargo material is an inorganic compound - Sodium Monofluorophosphate (Na_2PO_3F, MFP) or *NaMFP*. This compound has been reported to possess a multitude of benefits upon addition in cementitious composites. Na-MFP has been studied as an effective corrosion inhibiting agent [46],[3],[66], a surface treatment compound for carbonated blast furnace slag cements (BFSC) to resist frost-salt attack[11],[63],[61], a curing agent [62], and as a self-healing agent [30],[32].

It was found from the aforementioned studies that NaMFP protects the passive layer of steel reinforcement, which is vital for resistance against corrosion. It was found to be particularly beneficial for resisting carbonation induced corrosion. Additionally, when a Na-MFP solution was added as a surface post- or pre-treatment compound, the durability of BFSC against frost salt scaling of carbonated pastes was significantly enhanced [Figure 2.2], as the treatment modifies the minerological formation, leading to a more water-tight microstructure. After studying the E_H of pore solutions, [31] demonstrated that the application of Na-MFP as either a healing or corrosion inhibiting agent, can help reCover the pH of the carbonated cement paste to nearly 99% for CEMI (OPC) and 80% for CEMIII/B (BFSC) of untreated paste. It was also shown that if used as a curing agent, Na-MFP would

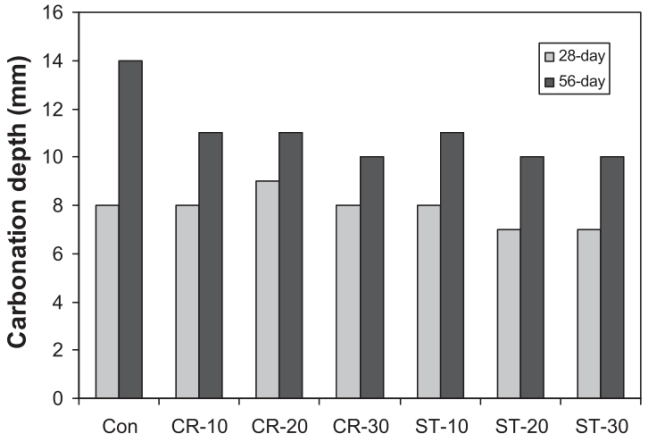

Figure 2.1: Carbonation depth observed on control (con), Na-MFP surface treated (ST), and NaMFP cured (CR) samples of BFSC. [62]

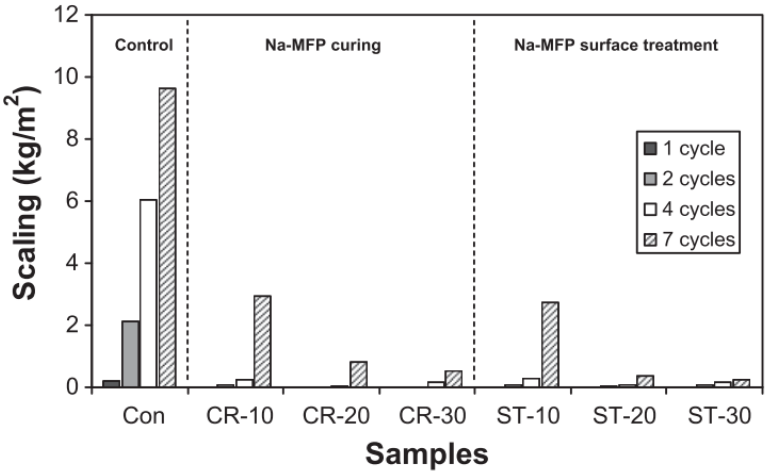

Figure 2.2: Frost scaling performance observed on control (con), Na-MFP surface treated (ST), and NaMFP cured (CR) samples of BFSC. [62]

further enable autogenous self-healing upon the initiation of carbonation on BFSC concrete. It does so by significantly recovering the pH of a carbonated paste, as it reacts with the latter to form secondary ettrigite, secondary portlandite, and amorphous apatite-like formations such as calcium phosphates (ACPs) [Figure 2.3]. These products assist in improving the mechanical properties and water-tightness of the carbonated microstructure, thereby *healing* the same.

2.1.1. Encapsulation of NaMFP by LWA

The direct addition of NaMFP as a healing agent proved disadvantageous. It was found to retard the setting time significantly, leading to further possibilities of bleeding and segregation in BFSC composites [62]. As such, encapsulation strategies of the compound were explored. The use of an expanded clay LWA (light weight aggregate) as an encapsulating ma-

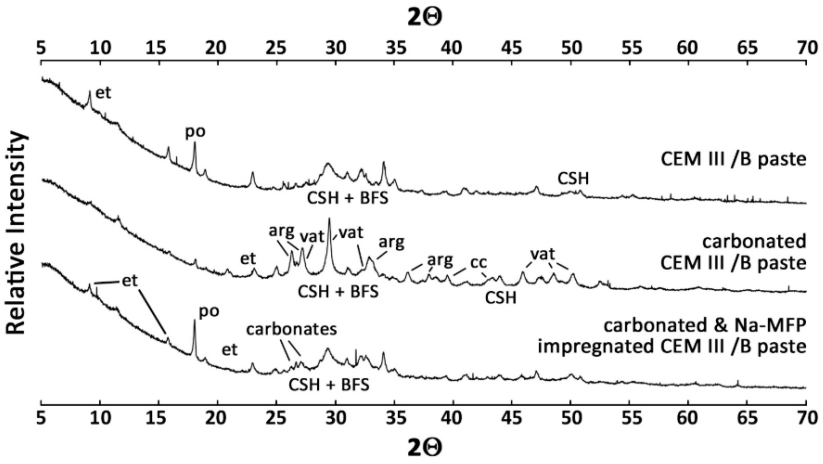

Figure 2.3: XRD data of formation of secondary cement phases upon reaction of Na-MFP with carbonated BFSC phases. [32]

terial, was checked accompanied by a coating of either OPC (ordinary portland cement) or BFSC on the surface of the LWA encapsulation. The LWA was first impregnated with NaMFP and was subsequently coated with a cement paste layer. Given that the aggregates are the major constituent of any concrete mix, they could be used to host self-healing agents as well [2]. LWA being porous, enables greater interstitial bond with the surrounding matrix, and has found much interest in research and application over the years. In case of being used as an encapsulating material, the addition of cement paste coating on the LWA is essential as it prevents the inner NaMFP to leach out into the matrix. EDS and ESEM data of the healing products indicated that the combination of treatment by NaMFP and portlandite from the cement paste coating, was potentially the healing mechanism.

2.1.1.1. Disadvantages of LWA based encapsulations

Although the studies well establish the efficiency of a carbonation triggered mechanism with the LWA - cement paste coating encapsulation system, yet it suffers from a couple of pitfalls. First, when an OPC cement paste layer is provided as a coating on the LWA, it has the tendency to densify upon carbonation. As CO_2 reacts with portlandite in OPC, it forms phases of $CaCO_3$, leading to a denser microstructure. As OPC is rich in CH, carbonation might yield a more compact coating over the LWA, thereby hindering the release of NaMFP.

Second, when a BFSC is added as a coating material, additional CH is provided in order to account for the lack of it in slag rich cements. The carbonation of CH would form calcite which would fill up the pore volume left by carbonation degradation. However, the authors indicate the formation of carbonate micro-crystals on the surface of CH which interferes with complete carbonation and poses restriction on the release of self-healing agent to the BFSC matrix.

In the light of these ambiguity and also on the data concerning the influence of the presence of LWA encapsulated systems in partial or full replacement of aggregates, it can be deduced that modifications on the encapsulation technique and an improvement of the response and release phenomenon of the same, are essential. Consequently, [31] and [30]

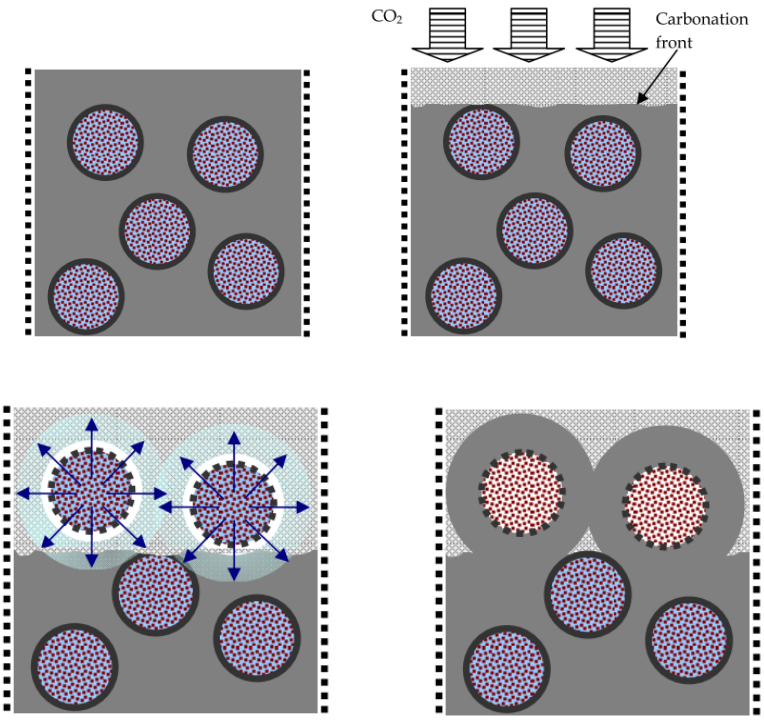

Figure 2.4: Encapsulated NaMFP in LWA reservoirs coated with cement paste, distributed in the metrix. When CO_2 enters the matrix, carbonation occurs and coarsens the porosity. As the front damages the coating layer, NaMFP is released to the matrix and healing takes place. [62]

suggest from their observations that a pH sensitive coating with affinity for carbonation would be desirable for encapsulating NaMFP in BFSC composites, as this would enable an autogenous healing mechanism. The requirement of this coating or shell material would be to be stable at high pH environments such as 13, characterizing an uncarbonated cementitious matrix. In the event of carbonation reaction with the hydration products of the matrix and the subsequent decrease of the pH in the pore solution, the shell material would require to destabilize and either dissolve, dissociate or rupture, releasing the healing agent into the matrix. The following section discusses the possible candidates that could fulfill these requirements.

2.2. Shell Material

From the previous discussion, for enabling a successful pH sensitive encapsulation mechanism for the healing agent NaMFP, the following are required of the shell material:

1. High chemical stability of microcapsules in high alkaline environment (pH > 12)
2. Successful encapsulation and protection of NaMFP in high alkaline environment
3. Chemical non-reactivity with the NaMFP.
4. The ability to disperse easily and stabilize in the cement matrix.

5. Rapid release of NaMFP after a pH drop on account of carbonation

A single core material is often unable to fulfill all requirements by itself. As a result, in practice either coating materials are employed in combinations or modifiers [49]. With particular focus on concrete applications, chemical responsive microcapsules have been used to encapsulate and deliver healing agents [15], corrosion inhibiting agents [85], [81], [87], self-immunizing agents [77], and phase change materials [59]. Of these, application of pH responsive microcapsules in concrete are limited. This is because, most pH sensitive materials that are otherwise used in alternate domains such as drug delivery systems, are designed to be unstable in high pH (> 7.5) surroundings, that are typical of disorders in human bodily requirements. For instance, BSA (Bovine Serum Albumin) was designed to possess reversible pH response as they become permeable below pH 4 (typical of stomach, colon, and lysosomes [80]) or those above pH 10 (typical of blood streams) [69] or polyamides that could respond to pH < 5 or pH > 7.5 [7]. In general however, pH sensitive micro-capsules research is a dominating field in pharmaceuticals arena, which offers a wholesome database on prospective materials that could be also potentially used in concrete applications with appropriate chemical modifications.

2.2.1. *Smart* Polymers

Stimuli responsive polymers have emerged as an attractive choice for micro encapsulation material due to their relatively inexpensive production compared to alternative materials and their highly tailorable chemical properties [48]. pH responsive polymers in particular, contain either acid or base segments or groups that either accept or release protons in response to a change in the environmental pH [56]. The physical properties of the polymer such as configuration, chain conformation, and solubility can be tailored by adjusting the pH or ionic strength [12]. The adjustment in pH alters the ionic interaction, hydrogen bonding, and hydrophobic interaction, resulting in a reversible micro phase separation or self-organization phenomenon. As such, the solubility, permeability and swelling of the pH sensitive polymer can be be manipulated [80]. This renders such polymeric systems as *smart* or *intelligent* as they can sense environmental changes and react autogenously. The pH range where the reversible phase transition can occur can be regulated by 2 ways [44]:

1. Selecting the ionizable moiety with a pK_a matching the desired pH range (selecting between polyacid or polybase), or incorporating a pH-responsive moiety to the polymer structure.

2. Incorporating hydrophobic moieties into the polymer backbone (selectively control their nature, amount and distribution)

Thus, by modulating the pH range by one of these methods, and selecting a pH responsive polymer that is compatible with the healing agent and which facilitates its rapid release, the shell material can be chosen for the current case.

2.2.2. pH responsive polymers in non-cementitious applications

In drug delivery systems, the following pH responsive polymers have been most widely used, as given in table 2.1. The purpose of studying these polymers is to explore potential

encapsulating material for self-healing applications in cement based composites. The research of the pharmaceuticals field is focused here for two reasons - first, it comprises of a vast body of existing research into the finer details of stimuli responsive encapsulation material. Secondly it is one field that deeply emphasizes timely, precision guided and targeted delivery of drugs into localized areas of infection - much like the requirement in degraded cementitious matrices.

In general, natural biodegradable polymers are often tailored to embed pH responsiveness at the desired pH range. Most of these polymers are combined to form hydrogels or super absorbent polymers (SAPs), both of which are comprised of hydrophilic polymer chains or networks, that can take up water and swell to several times their own weight. These are extensively used in drug delivery and has been found quite favorable for the purpose. They can also block cracks in concrete and aid in healing them [38].

#	pH Sensitve Polymer	Separation Mechanism	References
1	Poly(2-Diethylaminoethyl Methacrylate) or PDMAEMA	swells at low pH and ruptures	[9, 18, 45, 78, 79]
2	Poly(Acrylic Acid) (PAA)	dissociation at low pH	[25, 27, 28, 58]
3	Chitosan (CS) based hydrogels	swelling	[8, 29, 50, 51, 74, 76]
4	Alginate	swelling	[5, 21, 35, 38, 75]
5	Hyaluronic Acid (HA)	dissolves in low pH	[33, 42, 67, 80]
6	Ethyl Cellulose (EC)	dissociates in low pH	[47, 84, 86]

Table 2.1: pH sensitive polymers mostly used in drug-delivery systems.

Some other pH sensitive polymers that have found widespread applications in pharmaceuticals, nutrient preservation, fertilizers, and fragrance release industries are: polypeptides, poly(amidoamine), poly(aspartic acid), protamine, poly(l-lysine) (PLL), poly(Y-glutamic acid), poly(-amine ester)(PEA), dextran and derivatives, and other polymers containing phosphoric acid derivatives [80].

2.2.3. pH responsive polymers and other materials in cementitious applications

In literature of the recent past, some of the above mentioned polymeric materials were used for cementitious applications, either individually or in conjunction with each other. Table 2.2 provides an overview of the materials used for encapsulating healing or corrosion inhibiting agents, and their pros and cons. As mentioned earlier, the use of pH sensitive encapsulation for cementitious applications is relatively sparse compared to fields. This is because the concrete pore solution is complex and to modulate a "smart" environment responsive encapsulation in such a matrix requires in depth research into interdisciplinary fields such as polymer science, inorganic and organic chemistry, colloid chemistry, etc. Besides, research for successful applications in concrete involve large scale feasibility analyses which involves further complications. Nevertheless, some research on the topic of environmentally triggerable encapsulation for concrete application, have been reported from lab-

scale studies. Most are inspired from the research output of the pharmaceuticals branch. Out of this existing literature, the ones that closely fulfill the requirements of the current investigation are reported in table 2.2.

#	pH sensitive polymer	Core Material	Pros	Cons	Reference
1	Polystyrene resin (PS)	NaMFP	I. Shell thickness adjustable with dosage of material. II. Shell stable at pH 13, completely destroyed at pH 7	I. All capsules are not pH triggered. II. Capsule size determined by core content; higher amount of latter will imply bigger capsule size. III. Big microcapsule size (680-770 μm) IV. Unclear data about influence on concrete properties.	[14, 15, 89]
2	Ethyl Cellulose (EC)	Calcium Hydroxide	I. Successfully triggered by low pH and stable at high pH. II. Forms pinholes, crevices or peels off as pH decreases.	I. Presence of water causes local swell of EC II. Not all capsules could be pH triggered III. May promote negative influence due to big particle sizes of microcapsules (500μm) IV. Unclear data about influence on concrete properties	[16, 77]
3	SAPs based on acrylic acid, acrylamide, N,N' methylenebisacrylamide	-	I. Stable at pH 13 II. Swelling upto 450 times their original weight at pH 12. Reduction of swelling at lower pH. III. Assist in partial or full healing of cracks	I. Reduction of compressive strength upto 18% II. Reduction of bending strength upto 13% III. These polymers are prone to alkali induced hydrolysis	[37, 40]
4	Chitosan based hydrogel	Bacterial spores	I. Stable swelling capacity between pH 7-11. II. Good biocompatibility and cell entrapping property	I. Compressive strength still reduced by 5% with 1m% of hydrogel II. Only 32% of crack locations were completely bridged. III. Potentially better for bacterial healing than mineral based healing.	[75]
5	COCI (corrosion inhibitor)	BTA (Benzotriazole)	I. Shell was protected by Na-rich film at higher pH (>11), so limited core release. II. Rapid release of core material in low pH (<11).	I. Some release still occured at high pH (= 13) II.Investigations only simulated concrete pore solutions.	[88]
6	Poly(acrylic acid)–Acrylamide	corrosion inhibitors	I. Facilitates rapid release at pH 10 to 11. II. Successfully suppressed corrosion of rebar samples.	I. Limited study on further infleunces in concrete.	[20]
7	Silver Alginate hydrogel	-	I. Capsules collapse at 0.1wt% concentration of chloride ions. II. Can be modified for pH responsiveness	I. Big microcapsules (2.5mm) II.Unclear data about concrete applications	[81, 88]
8	PAM-*co*NaAlg hydrogel	-	I. Swelling degree higher at high pH. II. Improves compressive strength of concrete	I. Limited data about core release behavior at lower pH	[22]
9	Colophony	$NaNO_2$ corrosion inhibitors	I. High encapsulation efficiency of 83.2% II. Improved mechanical performance of concrete	I. Increased release of core with higher pH; unsuitable for acidic trigger based release.	[55]
10	Eudragit	Corrosion inhibitors	I. Controlled release at pH < 6 II. Possess self-healing potential III. Able to store high contents of inhibitor.	I. Limited release till pH reaches 6	[65]
11	Hybrid sol-gel	BTA	I. Facilitates local release at pH change.	I. Limited data on pH stability and sensitivity at pH 12-13. II. Limited data on concrete influences.	[60, 85]
12	Nanocapsules	TEA (Triethanolamine)	I. Facilitates local release at pH change from neutral.	I. Limited data on pH stability and sensitivity at pH 12-13. II. Limited data on concrete influences.	[10]

Table 2.2: Comparison of pH sensitive encapsulation materials used in cementitious applications

In particular, pH sensitive polymer based hydrogels and SAPs were extensively investigated at Universiteit Ghent [36–41, 75]. These hydrogels and SAPs take up water during mixing and release it during mortar hardening [36, 37, 40, 75] . If embedded with pH responsiveness mechansisms, they swell or shrink (thereby releasing water and core materials) with changes in the surrounding pH [39]. However, other than the SAP mentioned in point 3, and the hydrogels at points 7 and 8 in table, the other reported pH sensitive hydrophilic encapsulations have not been designed to release core contents at low alkaline environments. Moreover, the swelling of such encapsulations tend to leave behind pores that negatively affect the concrete properties. Larger the swelling, more the negative effect. Literature on this topic lack specific information on how the mechanical properties

are influenced by addition of SAPs and hydrogel based encapsulation.

Natural polymers on the other hand are more extensively available, economical and environmentally safe. Much research has been conducted at Shenzhen University on the topic of pH-triggerable polymer based microcapsules that encapsulate healing or corrosion inhibiting agents [14–16, 24, 77]. They indicate that polymers like PS and EC could effectively respond to a pH drop in a simulated cement pore solution and therefore possess significant potential for use in carbonation or corrosion detection. Surface damage at varying pH values by means of SEM, ESEM and texture element analysis microscopy, release mechanism after trigger, and recovery efficiency were checked for polymer based encapsulations. A significant limitation of these research that hinders large scale application, is the relatively big size of microcapsules that are being tested. Dosage of core material often determine the size of microcapsules. Presence of bigger capsules poses more challenges for the already weak capsule-cement matrix interface bond (Chapter1, section 1.1.2). This, followed by restriction of data about influence on concrete properties, presents some ambiguity on the topic. Nevertheless, out of the available material examined so far, polymers appear more favorable as their chemical properties are adaptable. In the light of the advantages offered by polymers, the following section presents recommendations that can be applied for encapsulating NaMFP for low-pH, trigger based release.

2.3. Recommended Material

From the preceding comparative review on the application of pH sensitive materials in cementitious and non-cementitious materials, one of the 3 following options are recommended. Some modifications are also suggested that can be employed to overcome the current limitations of these polymers in cementitious applications.

1. **Polystyrene (PS)**
2. **Ethyl Cellulose (EC)**
3. **COCI**

2.3.1. Limitations and potential modifications of suggested polymers

In general, the polystyrene and ethyl cellulose polymer based microcapsules examined in cementitious applications so far, suffer from a mutual restriction in pH sensitivity. Further, they would both benefit from a greater control on the capsule sizes. The pH sensitivity can be enhanced by coating these with thin polyelectrolyte films via electrostatic interactions through a layer-by-layer (LbL) method [80]. However, LbL method does have certain drawbacks of its own, which are further discussed in the following chapter. To produce more controlled microcapsule sizes, the solvent evaporation method or the upcoming and popular microfluidics technique can also be experimented to fabricate the microcapsules. More discussion on the feasibility of this follows in the next chapter.

3

Encapsulating Techniques

Based on the selection of core and shell materials, an appropriate encapsulating technique needs to be chosen for intended application. The choice of the most suitable method involves examining a variety of possible and widely documented techniques. This chapter contains a discussion and analysis of mostly used methods, their advantages or disadvantages, feasibility for application in the current context, and finally a recommendation of which one method is most likely well suited for encapsulating NaMFP with one of the three polymeric shell material choices presented in the previous chapter.

3.1. Encapsulation Techniques

A variety of techniques exist for microencapsulation, each with their specific field of applications, pros and cons. The choice of a strategy to encapsulate is governed by [4, 19]:

1. Required shell wall thickness
2. Chemical composition and mechanical integrity of the shell wall
3. Required capsule size and shape
4. Core characteristics such as acqueous, organic or inorganic
5. Expected application of the product

Broadly, the techniques are classified into three groups: Chemical processes, physico-chemical processes, and mechanical or physico-mechanical processes [26, 29]. Under chemical processes, interfacial polymerization (IFP) and in-situ polymerization are more popular. Under physico-chemical processes, the coacervation and phase separation, layer by layer adsorption and solvent evaporation techniques have been mostly applied for environment triggered release mechanisms. Under mechanical or physico-mechanical processes, spray-drying and congealing and fluidised bed coating are studied to be more advantageous [17],[29]. Table provides a comparative analysis of the different encapsulation methods, their pros and cons, materials on which the method has been investigated on . Out of the

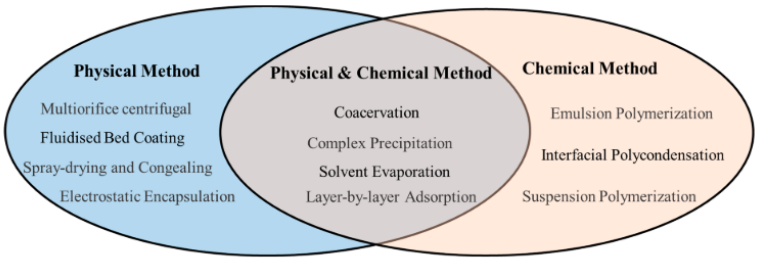

Figure 3.1: Some majorly used microencapsulation methods [26]. Note that solvent evaporation is sometimes categorised under *physico-mechanical* processes by different authors. In this study, the above classifications are adopted.

numerous methods currently available in literature pertaining to drug delivery, food technology, crop protection, energy, fragrance release, and concrete, the methods analysed in the table were chosen on the basis of: depth of research conducted, economical and their applicability in polymer or inorganic materials. As the topic of microencapsulation technology is a rapidly evolving branch of study, improvements to the disadvantages listed here are quite possibly already available or will be in the near-future, in most state-of-the-art research body. In this study, the attempt is to investigate the most widely used methods and to do that, a selection of recently conducted review literature have been consulted [4, 17, 19, 26, 29, 43, 49, 68, 83]. In addition to this, the flowchart presented in figure 3.2 provides a helpful and concise summary of the key features and potentials of the various microcapsule fabrication methods.

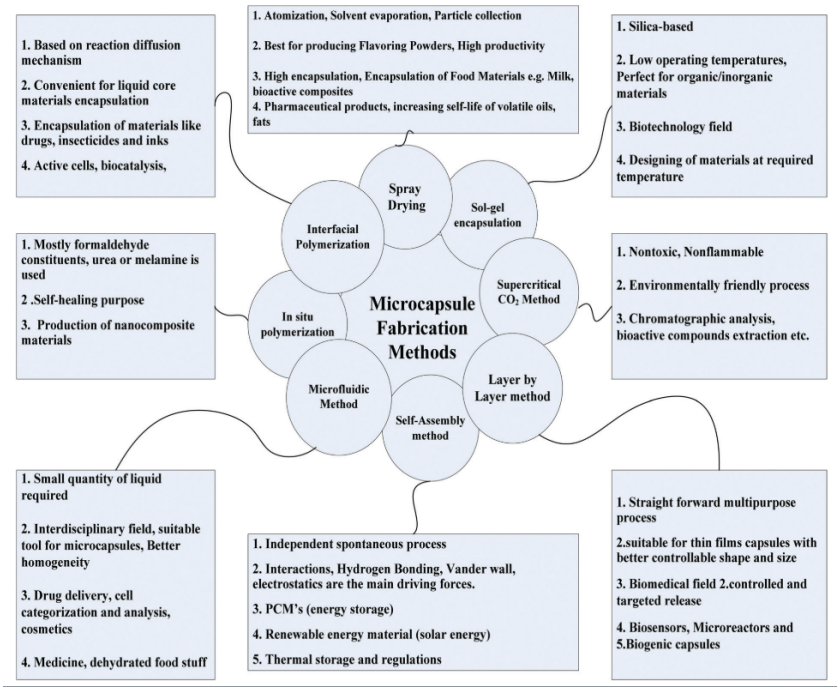

Figure 3.2: Key features and potential applications of the various methods [4]

#	Methods	Pros	Cons	Materials Invstigated
1	Emulsification Polymerization	I. High strength capsule shell walls II. Large scale synthesis III. Thick shell wall IV. Narrow size distribution	I. Difficult to encapsulate aqueous cores II. Can be loaded only once III. Surfactant and polymerization specific IV. Often large size distributions V. More suited for encapsulating lipophilic (insoluble or scarcely soluble in water) materials	Poly(alkyl acrylate)s
2	Interfacial polymerization	I. Suitable for oil and aqueous cores II. Fabrication processes are simple	I. Use of organic solvents required II. <Less than 100% release of active core ingredients III. Right wetting conditions critical for fabrication	Polyurea[insecticides, catalysts], Polyamide[oils], Polyurethane [insecticides], polyester[protein]
3	Layer by Layer Assembly	I. Compatible with aqueous and organic cores II. Easy trigger incorporation III. Post fabrication core loading IV. Narrow size distributions if particles are uniform V. Controllable shell thickness	I. Laborious fabrication procedures II. High flocculation tendencies III. Often poor structural integrity compared to other processes	Polyelectrolytes
4	Coarcevation	I. Ease of use in stimuli dependent application II. Simple fabrication	I. Often better for hydrophobic cores II. Low strength shell walls III. Can be loaded only once IV. Large size distribution	Protein, Polysaccharides, Ethyl cellulose, gelatin
5	Internal Phase separation	I. High strength shell walls II. Ideal for thermal triggers	I. Limited trigger capabilities II. Hydrophobic core required III. Limited core/shell polymer combination IV. Large size distribution	Polysaccharides
6	Spray drying and congealing	I. Low cost application II. Simple fabrication III. Could produce various sizes from 10 μm to 3mm. IV. Good encapsulation efficiency. V. Possibility of large scale production.	I. Difficult to control capsule size II. Inconvenient to remove solvents used during drying process.	Chitosan, Tripolyphosphate,Polystyrene, Ethyl Cellulose
7	In situ polymerization	I.Simple Fabricationn II. Good for ph sensitive shells III. Mainly used for production of microspheres	I. Incomplete release of core II. Not suited for liquid core encapsulation	Amonium phosphate, Urea,Melamine - Formaldehyde
8	Fluidised bed coating	I.Low cost II. Allows porosities into product III. Allows specific capsule size distribution	I. Degrdataion of highly temperature sensitive compounds	Emulsifiers, starches, gums
9	Solvent evaporation technique	I.Facilitates pH triggerable shells II. Allows porosities into product III. Allows easily scalable synthesis III. Economical	I. Difficulty in controlling evaporation and growth rate.	Colophony, Ethyl Cellulose,
10	Microfluidics	I.Allows huge range of shell materials for use II. Allows precise control over shell thickness III. Can manipulate small quantities of fluids to fabricate large number of desired microcapsules.	I. Requires expertise in inter-disciplinary fields II. Simplification of process yet to be made. III. pH sensitive release not yet studied in cement based applications	Polymers,glass.
11	Centrifugal extrusion	I. Facilitates good bonding of core and shell wall II. Relatively low temperature entrapping method	I. Difficult to fabricate if material is too viscous II. The capsule must be separated from the liquid bath and dried	Polyacrylonitrile
12	Liposome entrapment	I. Suits entrapment of liquid or lipid soluble material II. Facilitates good control of core delivery. Suitable to high water activity applications	I. Limited data of pH triggered release	Polymers

Table 3.1: Comparative analysis of the different fabrication methods.

3.2. Recommended Technique

From the preceding comparative analysis and taking into account the requirements of this study, the following two methods appear as best suited among the list: Spray-Drying and Solvent Evaporation.

1. **Spray-Drying:**

   - **Principle:** This process consists of spraying of an emulsion or dispersion in a stream of hot inert gas into a concentrated solution of wall material. The resultant emulsion is atomized into a spray of droplets by pumping the slurry through a rotating disc into the heated compartment of a spray drier. There the water portion of emulsion is evaporated, yielding dried capsules containing core material. This process mainly involves three steps: droplet production (atomization); droplet-to-particle conversion by drying (solvent vaporization); and particle collection (separation from the drying gas). Further, the operations

involved include homogenization, evaporation and coating. Due to the quick evaporation of water and the quick drying of particles, it has a high production ratio. This procedure is also used for putting a second or third wall layer around the capsules and thus for altering the wall permeability.[4, 17, 64]

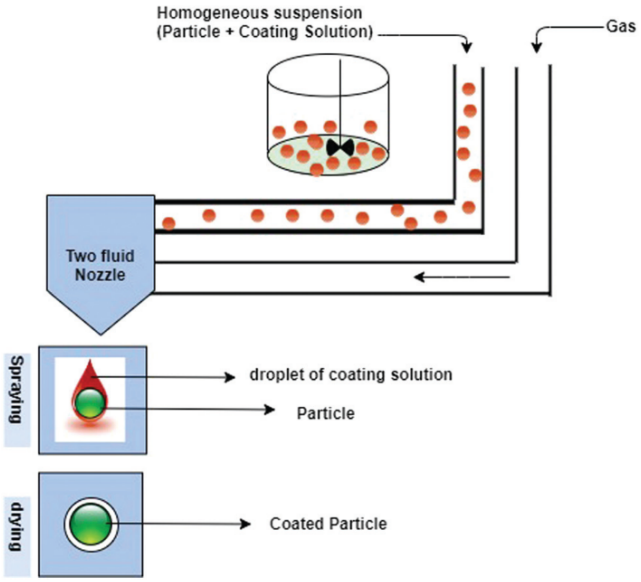

Figure 3.3: Schematic of spray-drying process [23]. Reproduced from [4]

- **Compatibility with shell material and cement matrix:** Spray drying method has been reported to be compatible with pH triggerable polystyrene capsules containing NaMFP [14, 15], for ethyl cellulose capsules containing CH [77] and finally for PLA based capsules containing NaMFP [90]. Considering the benefits offered by this fabrication method, such as low cost and possibility of large scale production of microcapsules, followed by its reported compatibility with the core material in this study and the recommended shell materials, it definitely manifests as a feasible method for the current study.

2. **Solvent Evaporation:**

- **Principle:** Solvent evaporation has been a promising alternative for microencapsulation. The polymer is dissolved in a water immiscible volatile organic solvent like dichloromethane or chloroform, into which the core material is also dissolved or dispersed. The resulting solution is added dropwise to a stirring aqueous solution having a suitable stabilizer to form small polymer droplets containing encapsulated material. The mixture is then dispersed in the liquid manufacturing vehicle (LMV) with continuous agitation to obtain tiny capsules with desired size. Solvent extraction produces microcapsules with higher porosities than those obtained by solvent evaporation [26, 29]. Figure 3.4 shows a schematic representation of microencapsulation by solvent evaporation technique.

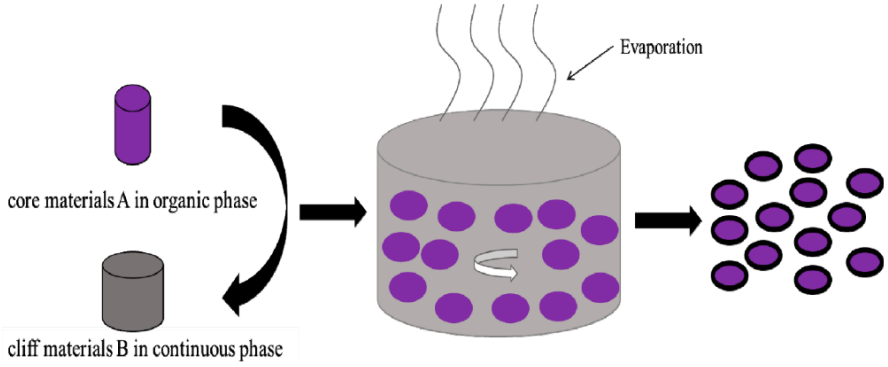

Figure 3.4: Schematic of solvent-evaporation method [26]

- **Compatibility with shell material and cement matrix:** It has been reported by [55] to be compatible with pH triggerable microcapsule containing colophony formation in cementitious environments, and for PS/NaMFP capsules by [89]. This method offers the advantage of producing capsules with adjustable sizes. Given the positive reports of compatibility of this method for use in NaMFP based core and polymer based shell materials, this is another method that can be adopted for the purpose of encapsulating NaMFP by polymeric shells for pH triggerable applications.

4

Limitations, Conclusion and Future Scope

This study investigates the use of a pH sensitive microcapsule material for encapsulating MaMFP, and the technique to fabricate the same. NaMFP has been widely reported to administer a multitude of benefits when applied in concrete. It has been studied as an effective corrosion inhibiting agent, a self-healing agent, a surface treatment compound for resisting frost-salt attack, and a curing agent. Since direct addition of the compound in cement based composites proved disadvantageous, encapsulation by clay LWA was studied in previous researches. However, despite the numerous benefits of this system, challenges with respect to response and release mechanisms of the encapsulations hindered feasibility of large scale applications. In the light of such challenges, it was deemed that a pH sensitive coating with affinity to carbonation would be a more suitable way to encapsulate NaMFP. To that end, the current study attempted to suggest a pH sensitive material for feasible microencapsulation along with a technique, by way of comparative analyses of existing research in the domains of cementitious and non-cementitious applications of microencapsulation. The following sections define the limitations of this study, a summary of the research output and future scope of the investigation.

4.1. Limitations:

The scope of this study was to study the possible material and strategies for encapsulating NaMFP, that could be responsive to pH sensitive triggers in cementitious systems. This involved reviewing, comparing and analysing the advances made in the field of environment-sensitive microencapsulations in the domains of pharmaceuticals, energy, food industry, agriculture and the relatively fewer applications in concrete science. The output of this study are the suggestion made in terms of shell material and technique that is deemed compatible for fabrication of such shells and the given core material. In that, this report could serve as a basis for potential laboratory-scale undertakings in the pursuit of effective encapsulation of NaMFP. The following limitations exist in the report:

1. The suggestions made in this report are hypothetical, based on the theoretical ideas collected from the past researches on the matter. Laboratory experimentation need to conducted in order to validate the feasibility.

2. This report does not detail the steps and procedures for applying the suggested materials, but only propose possible ways to modify the current drawbacks of the suggested materials, if any. For any lab experimentation of either materials or techniques, the steps defined in the cited literature need to be checked.

4.2. Conclusion

In conclusion, the study arrives at the following findings of the two research questions formulated:

1. **What is a suitable shell material for encapsulating Na-MFP, such that it is stable at high pH environments and dissociates or ruptures at low pH environments?**
    - The study proposed 3 possible and suitable candidates after analysing the compatibility, and pros and cons of several prospective materials. These are: Polystyrene (PS), Ethyl Cellulose (EC), and COCI.
2. **How to efficiently encapsulate the cargo material with the shell material?**
    - After a comparative analysis on several techniques, the study proposed 2 most suitable fabrication methods which are: Spray-Drying and Solvent Evaporation.

4.3. Future Scope

The study recognizes the following scope for a future evaluation of proposed materials and techniques:

1. The functional and mechanical behavior, and the durability of using the proposed materials in concrete made of varying cement types.
2. The influences in concrete made of varying water/cement ratios.
3. The economic and cradle-to-grave environmental life cycle assessments and costs of using the proposed material and techniques for fabrication.
4. Better understanding of the science involving enhancing pH sensitivity
5. Streamlining the fabrication methods for faster and more efficient use in large-scale applications for concrete.

Bibliography

[1] Procedures Required for the Assessment of Highway Structures (Final Report). 2004.

[2] R. Alghamri, A. Kanellopoulos, and A. Al-Tabbaa. Impregnation and encapsulation of lightweight aggregates for self-healing concrete. *Construction and Building Materials*, 124:910–921, 2016. ISSN 09500618. doi: 10.1016/j.conbuildmat.2016.07.143. URL http://dx.doi.org/10.1016/j.conbuildmat.2016.07.143.

[3] C. Alonso, C. Andrade, C. Argiz, and B. Malric. Na2PO3F as inhibitor of corroding reinforcement in carbonated concrete. *Cement and Concrete Research*, 26(3):405–415, 1996. ISSN 00088846. doi: 10.1016/S0008-8846(96)85028-9.

[4] Mohamed Gibril Bah, Hafiz Muhammad Bilal, and Jingtao Wang. Fabrication and application of complex microcapsules: A review. *Soft Matter*, 16(3):570–590, 2020. ISSN 17446848. doi: 10.1039/c9sm01634a.

[5] Subham Banerjee, Shivangi Singh, Shiv Sankar Bhattacharya, and Pronobesh Chattopadhyay. Trivalent ion cross-linked pH sensitive alginate-methyl cellulose blend hydrogel beads from aqueous template. *International Journal of Biological Macromolecules*, 57:297–307, 2013. ISSN 01418130. doi: 10.1016/j.ijbiomac.2013.03.039. URL http://dx.doi.org/10.1016/j.ijbiomac.2013.03.039.

[6] B. J. Blaiszik, S. L.B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White. Self-healing polymers and composites. *Annual Review of Materials Research*, 40:179–211, 2010. ISSN 15317331. doi: 10.1146/annurev-matsci-070909-104532.

[7] Kyle E. Broaders, Stefan J. Pastine, Sirisha Grandhe, and Jean M.J. Fréchet. Acid-degradable solid-walled microcapsules for pH-responsive burst-release drug delivery. *Chemical Communications*, 47(2):665–667, 2011. ISSN 1364548X. doi: 10.1039/c0cc04190d.

[8] A. S. Carreira, F. A.M.M. Gonçalves, P. V. Mendonça, M. H. Gil, and J. F.J. Coelho. Temperature and pH responsive polymers based on chitosan: Applications and new graft copolymerization strategies based on living radical polymerization. *Carbohydrate Polymers*, 80(3):618–630, 2010. ISSN 01448617. doi: 10.1016/j.carbpol.2009.12.047. URL http://dx.doi.org/10.1016/j.carbpol.2009.12.047.

[9] Bernardino Isaac Cerda-Cristerna, Sophie Cottin, Luca Flebus, Amaury Pozos-Guillén, Héctor Flores, Ernst Heinen, Olivier Jolois, Christiane Gérard, Gianni Maggipinto, Chantal Sevrin, and Christian Grandfils. Poly(2-dimethylamino ethylmethacrylate)-based polymers to camouflage red blood cell antigens. *Biomacromolecules*, 13(4):1172–1180, 2012. ISSN 15257797. doi: 10.1021/bm300127f.

[10] Hana Choi, Yon Kyun Song, Kyoo Young Kim, and Jong Myung Park. Encapsulation of triethanolamine as organic corrosion inhibitor into nanoparticles and its active corrosion protection for steel sheets. *Surface and Coatings Technology*, 206(8-9): 2354–2362, 2012. ISSN 02578972. doi: 10.1016/j.surfcoat.2011.10.030. URL http://dx.doi.org/10.1016/j.surfcoat.2011.10.030.

[11] O. Çopuroğlu, A. L.A. Fraaij, and J. M.J.M. Bijen. Effect of sodium monofluorophosphate treatment on microstructure and frost salt scaling durability of slag cement paste. *Cement and Concrete Research*, 36(8):1475–1482, 2006. ISSN 00088846. doi: 10.1016/j.cemconres.2006.02.003.

[12] Sheng Dai, Palaniswamy Ravi, and Kam Chiu Tam. pH-Responsive polymers: Synthesis, properties and applications. *Soft Matter*, 4(3):435–449, 2008. ISSN 1744683X. doi: 10.1039/b714741d.

[13] Nele De Belie, Elke Gruyaert, Abir Al-Tabbaa, Paola Antonaci, Cornelia Baera, Diana Bajare, Aveline Darquennes, Robert Davies, Liberato Ferrara, Tony Jefferson, Chrysoula Litina, Bojan Miljevic, Anna Otlewska, Jonjaua Ranogajec, Marta Roig-Flores, Kevin Paine, Pawel Lukowski, Pedro Serna, Jean Marc Tulliani, Snezana Vucetic, Jianyun Wang, and Henk M. Jonkers. A Review of Self-Healing Concrete for Damage Management of Structures. *Advanced Materials Interfaces*, 5(17):1–28, 2018. ISSN 21967350. doi: 10.1002/admi.201800074.

[14] B. Dong, Y. Wang, N. Han, and F. Xing. The smart releasing behavior of a microcapsule based on chemical self-healing system caused by chemical trigger activation. *4Th International Conference for Self-Healing Materials*, pages 25–28, 2013.

[15] Biqin Dong, Yanshuai Wang, Guohao Fang, Ningxu Han, Feng Xing, and Youyuan Lu. Smart releasing behavior of a chemical self-healing microcapsule in the stimulated concrete pore solution. *Cement and Concrete Composites*, 56:46–50, 2015. ISSN 09589465. doi: 10.1016/j.cemconcomp.2014.10.006. URL http://dx.doi.org/10.1016/j.cemconcomp.2014.10.006.

[16] Biqin Dong, Weijian Ding, Shaofeng Qin, Ningxu Han, Guohao Fang, Yuqing Liu, Feng Xing, and Shuxian Hong. Chemical self-healing system with novel microcapsules for corrosion inhibition of rebar in concrete. *Cement and Concrete Composites*, 85:83–91, 2018. ISSN 09589465. doi: 10.1016/j.cemconcomp.2017.09.012. URL https://doi.org/10.1016/j.cemconcomp.2017.09.012.

[17] Rama Dubey, T.C. Shami, and K.U. Bhasker Rao. Microencapsulation Technology and Applications. *Defence Science Journal*, 59(1):82–95, 2009.

[18] Ali Emileh, Ebrahim Vasheghani-Farahani, and Mohammad Imani. Swelling behavior, mechanical properties and network parameters of pH- and temperature-sensitive hydrogels of poly((2-dimethyl amino) ethyl methacrylate-co-butyl methacrylate). *European Polymer Journal*, 43(5):1986–1995, 2007. ISSN 00143057. doi: 10.1016/j.eurpolymj.2007.02.002.

[19] Aaron P. Esser-Kahn, Susan A. Odom, Nancy R. Sottos, Scott R. White, and Jeffrey S. Moore. Triggered release from polymer capsules. *Macromolecules*, 44(14):5539–5553, 2011. ISSN 00249297. doi: 10.1021/ma201014n.

[20] Lijuan Feng, Huaiyu Yang, Xiqing Dong, Haibo Lei, and Di Chen. pH-sensitive polymeric particles as smart carriers for rebar inhibitors delivery in alkaline condition. *Journal of Applied Polymer Science*, 135(8):1–9, 2018. ISSN 10974628. doi: 10.1002/app.45886.

[21] M. George and T. E. Abraham. pH sensitive alginate-guar gum hydrogel for the controlled delivery of protein drugs. *International Journal of Pharmaceutics*, 335(1-2): 123–129, 2007. ISSN 03785173. doi: 10.1016/j.ijpharm.2006.11.009.

[22] Mohamed Mohamady Ghobashy and Ghada Bassioni. pH stimuli-responsive poly(acrylamide-co-sodium alginate) hydrogels prepared by γ-radiation for improved compressive strength of concrete. *Advances in Polymer Technology*, 37(6):2123–2133, 2018. ISSN 10982329. doi: 10.1002/adv.21870.

[23] N. Hampel, E. Roydeva, A. Bück, and E. Tsotsas. Coating of finely dispersed particles by two-fluid nozzle. *Particuology*, 38:80–93, 2018. ISSN 22104291. doi: 10.1016/j.partic.2017.05.015. URL `https://doi.org/10.1016/j.partic.2017.05.015`.

[24] Ning Xu Han and Feng Xing. A comprehensive review of the study and development of microcapsule based self-resilience systems for concrete structures at Shenzhen University. *Materials*, 10(1), 2017. ISSN 19961944. doi: 10.3390/ma10010002.

[25] Huarong Hu, Haitao Wang, and Qiangguo Du. Preparation of pH-sensitive polyacrylic acid hollow microspheres and their release properties. *Soft Matter*, 8(25):6816–6822, 2012. ISSN 1744683X. doi: 10.1039/c2sm25135c.

[26] Miaomiao Hu, Jintang Guo, Yongjin Yu, Lei Cao, and Yang Xu. Research advances of microencapsulation and its prospects in the petroleum industry. *Materials*, 10(4):1–20, 2017. ISSN 19961944. doi: 10.3390/ma10040369.

[27] Yihong Huang, Huiqun Yu, and Chaobo Xiao. pH-sensitive cationic guar gum/poly (acrylic acid) polyelectrolyte hydrogels: Swelling and in vitro drug release. *Carbohydrate Polymers*, 69(4):774–783, 2007. ISSN 01448617. doi: 10.1016/j.carbpol.2007.02.016.

[28] Baptiste Jaquet, Dan Wei, Bernd Reck, Frank Reinhold, Xinya Zhang, Hua Wu, and Massimo Morbidelli. Stabilization of polymer colloid dispersions with pH-sensitive poly-acrylic acid brushes. *Colloid and Polymer Science*, 291(7):1659–1667, 2013. ISSN 0303402X. doi: 10.1007/s00396-013-2900-6.

[29] N. Venkata Naga Jyothi, P. Muthu Prasanna, Suhas Narayan Sakarkar, K. Surya Prabha, P. Seetha Ramaiah, and G. Y. Srawan. Microencapsulation techniques, factors influencing encapsulation efficiency. *Journal of Microencapsulation*, 27(3):187–197, 2010. ISSN 02652048. doi: 10.3109/02652040903131301.

[30] J. Kempl and O. Copuroglu. Sodium Monofluorophosphate - an inorganic self healing agent for blast furnace slag cement products. *Self healing materials- pioneering research in the Netherlands. IOS Press.*, pages 123–130, 2015. doi: 10.3233/978-1-61499-514-2-123.

[31] J. Kempl and O. Çopuroğlu. EH-pH- and main element analyses of Blast Furnace Slag Cement paste pore solutions activated with sodium monofluorophosphate - Implications for carbonation and self-healing. *Cement and Concrete Composites*, 71:63–76, 2016. ISSN 09589465. doi: 10.1016/j.cemconcomp.2016.05.004.

[32] Josepha Kempl and Oguzhan Copuroglu. Autogenous Self-Healing in Blast Furnace Slag Cement by Sodium Monofluorophosphate. *International Conference on Self-Healing Materials (ICSHM2015)*, pages 1–4, 2015.

[33] Soon Sik Kwon, Bong Ju Kong, and Soo Nam Park. Physicochemical properties of pH-sensitive hydrogels based on hydroxyethyl cellulose-hyaluronic acid and for applications as transdermal delivery systems for skin lesions. *European Journal of Pharmaceutics and Biopharmaceutics*, 92:146–154, 2015. ISSN 18733441. doi: 10.1016/j.ejpb.2015.02.025. URL `http://dx.doi.org/10.1016/j.ejpb.2015.02.025`.

[34] Victor C. Li and Emily Herbert. Robust self-healing concrete for sustainable infrastructure. *Journal of Advanced Concrete Technology*, 10(6):207–218, 2012. ISSN 13468014. doi: 10.3151/jact.10.207.

[35] Hsiang Fa Liang, Min Hao Hong, Rong Ming Ho, Ching Kuang Chung, Yu Hsin Lin, Chun Hung Chen, and Hsing Wen Sung. Novel method using a temperature-sensitive polymer (methylcellulose) to thermally gel aqueous alginate as a pH-sensitive hydrogel. *Biomacromolecules*, 5(5):1917–1925, 2004. ISSN 15257797. doi: 10.1021/bm049813w.

[36] Arn Mignon. *Effect of pH-Responsive Superabsorbent Polymers on the Self-Sealing and Self-Healing of Cracks in Concrete*. PhD thesis, 2017.

[37] Arn Mignon, Geert Jan Graulus, Didier Snoeck, José Martins, Nele De Belie, Peter Dubruel, and Sandra Van Vlierberghe. pH-sensitive superabsorbent polymers: a potential candidate material for self-healing concrete. *Journal of Materials Science*, 50 (2):970–979, 2014. ISSN 15734803. doi: 10.1007/s10853-014-8657-6.

[38] Arn Mignon, Dries Devisscher, Geert Jan Graulus, Birgit Stubbe, José Martins, Peter Dubruel, Nele De Belie, and Sandra Van Vlierberghe. Combinatory approach of methacrylated alginate and acid monomers for concrete applications. *Carbohydrate Polymers*, 155:448–455, 2017. ISSN 01448617. doi: 10.1016/j.carbpol.2016.08.102. URL `http://dx.doi.org/10.1016/j.carbpol.2016.08.102`.

[39] Arn Mignon, Didier Snoeck, Peter Dubruel, Sandra Van Vlierberghe, and Nele De Belie. Crack mitigation in concrete: Superabsorbent polymers as key to success? *Materials*, 10(3), 2017. ISSN 19961944. doi: 10.3390/ma10030237.

[40] Arn Mignon, Jolien Vermeulen, Didier Snoeck, Peter Dubruel, Sandra Van Vlierberghe, and Nele De Belie. Mechanical and self-healing properties of cementitious materials with pH-responsive semi-synthetic superabsorbent polymers. *Materials and Structures/Materiaux et Constructions*, 50(6):1–12, 2017. ISSN 13595997. doi: 10.1617/s11527-017-1109-4.

[41] Arn Mignon, Nele De Belie, Peter Dubruel, and Sandra Van Vlierberghe. Superabsorbent polymers: A review on the characteristics and applications of synthetic, polysaccharide-based, semi-synthetic and 'smart' derivatives. *European Polymer Journal*, 117(April):165–178, 2019. ISSN 00143057. doi: 10.1016/j.eurpolymj.2019.04.054. URL https://doi.org/10.1016/j.eurpolymj.2019.04.054.

[42] Maiko Miyazaki, Eiji Yuba, Hiroshi Hayashi, Atsushi Harada, and Kenji Kono. Hyaluronic Acid-Based pH-Sensitive Polymer-Modified Liposomes for Cell-Specific Intracellular Drug Delivery Systems. *Bioconjugate Chemistry*, 29(1):44–55, 2018. ISSN 15204812. doi: 10.1021/acs.bioconjchem.7b00551.

[43] Aude Munin and Florence Edwards-Lévy. *Encapsulation of natural polyphenolic compounds; a review*, volume 3. 2011. ISBN 3332691805. doi: 10.3390/pharmaceutics3040793.

[44] Kun Na, Kwang Hee Lee, and You Han Bae. pH-sensitivity and pH-dependent interior structural change of self-assembled hydrogel nanoparticles of pullulan acetate/oligosulfonamide conjugate. *Journal of Controlled Release*, 97(3):513–525, 2004. ISSN 01683659. doi: 10.1016/j.jconrel.2004.04.005.

[45] Kenichi Nagase, Jun Kobayashi, Akihiko Kikuchi, Yoshikatsu Akiyama, Hideko Kanazawa, and Teruo Okano. Preparation of thermoresponsive cationic copolymer brush surfaces and application of the surface to separation of biomolecules. *Biomacromolecules*, 9(4):1340–1347, 2008. ISSN 15257797. doi: 10.1021/bm701427m.

[46] V. T. Ngala, C. L. Page, and M. M. Page. Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 1: Calcium nitrite. *Corrosion Science*, 44(9):2073–2087, 2002. ISSN 0010938X. doi: 10.1016/S0010-938X(02)00012-4.

[47] J. Nunthanid, M. Luangtana-anan, P. Sriamornsak, S. Limmatvapirat, K. Huanbutta, and S. Puttipipatkhachorn. Use of spray-dried chitosan acetate and ethylcellulose as compression coats for colonic drug delivery: Effect of swelling on triggering in vitro drug release. *European Journal of Pharmaceutics and Biopharmaceutics*, 71(2):356–361, 2009. ISSN 09396411. doi: 10.1016/j.ejpb.2008.08.002. URL http://dx.doi.org/10.1016/j.ejpb.2008.08.002.

[48] David J. Peeler, Drew L. Sellers, and Suzie H. Pun. PH-Sensitive Polymers as Dynamic Mediators of Barriers to Nucleic Acid Delivery. *Bioconjugate Chemistry*, 30(2):350–365, 2019. ISSN 15204812. doi: 10.1021/acs.bioconjchem.8b00695.

[49] A. POSHADRI and APARNA KUNA. MICROENCAPSULATION TECHNOLOGY: A REVIEW. *Journal of Research ANGRAU*, 38(1):86–102, 2010.

[50] Qiaohua Qiu, Zhenzhen Quan, Hongnan Zhang, Xiaohong Qin, Rongwu Wang, and Jianyong Yu. pH-triggered sustained drug release of multilayer encapsulation system with hollow mesoporous silica nanoparticles/chitosan/polyacrylic acid. *Materials Letters*, 260:126907, 2020. ISSN 18734979. doi: 10.1016/j.matlet.2019.126907. URL https://doi.org/10.1016/j.matlet.2019.126907.

[51] X. Qu, A. Wirsén, and A. C. Albertsson. Novel pH-sensitive chitosan hydrogels: Swelling behavior and states of water. *Polymer*, 41(12):4589–4598, 2000. ISSN 00323861. doi: 10.1016/S0032-3861(99)00685-0.

[52] T. S. Qureshi, A. Kanellopoulos, and A. Al-Tabbaa. Encapsulation of expansive powder minerals within a concentric glass capsule system for self-healing concrete. *Construction and Building Materials*, 121(June):629–643, 2016. ISSN 09500618. doi: 10.1016/j.conbuildmat.2016.06.030. URL http://dx.doi.org/10.1016/j.conbuildmat.2016.06.030.

[53] Tanvir Qureshi and Abir Al-Tabbaa. Self-Healing Concrete and Cementitious Materials. *Advanced Functional Materials*, pages 1–24, 2020. doi: 10.5772/intechopen.92349.

[54] Magdalena Rajczakowska, Karin Habermehl-Cwirzen, Hans Hedlund, and Andrzej Cwirzen. Autogenous Self-Healing: A Better Solution for Concrete. *Journal of Materials in Civil Engineering*, 31(9):03119001, 2019. ISSN 0899-1561. doi: 10.1061/(asce)mt.1943-5533.0002764.

[55] Jacob Ress, Ulises Martin, Juan Bosch, and David M. Bastidas. pH-Triggered Release of NaNO2 Corrosion Inhibitors from Novel Colophony Microcapsules in Simulated Concrete Pore Solution. *ACS applied materials interfaces*, 12(41):46686–46700, 2020. ISSN 19448252. doi: 10.1021/acsami.0c13497.

[56] F. Reyes-Ortega. *pH-responsive polymers: Properties, synthesis and applications*. Number December 2014. Woodhead Publishing Limited, 2014. ISBN 9780857096951. doi: 10.1533/9780857097026.1.45. URL http://dx.doi.org/10.1533/9780857097026.1.45.

[57] M Rooij, K van Tittelboom, N Belie, and E Schlangen. *Self-Healing Phenomena in Cement-Based Materials: State-of-the-Art Report of RILEM Technical Committee*. 2013. ISBN 9400766246. URL http://www.worldcat.org/oclc/846968087.

[58] Seema Saroj and Sadhana J. Rajput. Tailor-made pH-sensitive polyacrylic acid functionalized mesoporous silica nanoparticles for efficient and controlled delivery of anti-cancer drug Etoposide. *Drug Development and Industrial Pharmacy*, 44(7):1198–1211, 2018. ISSN 15205762. doi: 10.1080/03639045.2018.1438467. URL https://doi.org/10.1080/03639045.2018.1438467.

[59] Branko Šavija. smart crack control in concrete through use of phase change materials (PCMs): A review. *Materials*, 11(5), 2018. ISSN 19961944. doi: 10.3390/ma11050654.

[60] Dmitry G. Shchukin, Mikhail Zheludkevich, and Helmuth Möhwald. Feedback active coatings based on incorporated nanocontainers. *Journal of Materials Chemistry*, 16 (47):4561–4566, 2006. ISSN 09599428. doi: 10.1039/b612547f.

[61] K. Sisomphon, O. Copuroglu, and A. L.A. Fraaij. Development of blast furnace slag mixtures against frost salt attack. *Cement and Concrete Composites*, 32(8):630–638, 2010. ISSN 09589465. doi: 10.1016/j.cemconcomp.2010.06.001. URL `http://dx.doi.org/10.1016/j.cemconcomp.2010.06.001`.

[62] K. Sisomphon, O. Copuroglu, and A. Fraaij. Application of encapsulated lightweight aggregate impregnated with sodium monofluorophosphate as a self-healing agent in blast furnace slag mortar. *Heron*, 56(1-2):17–36, 2011. ISSN 00467316.

[63] Kritsada Sisomphon, O. Çopuroğlu, and A. L.A. Fraaij. Properties of carbonated blast furnace slag mortars after Na 2FPO3 treatment. *ScienceAsia*, 36(3):223–230, 2010. ISSN 15131874. doi: 10.2306/scienceasia1513-1874.2010.36.223.

[64] By Wolfgang Sliwka. Microencapsulation. 14:539–550, 1975.

[65] Darya Snihirova, Sviatlana V. Lamaka, M. Margarida Cardoso, José A.D. Condeço, Humberto E.C.S. Ferreira, and Maria De Fatima Montemor. PH-sensitive polymeric particles with increased inhibitor-loading capacity as smart additives for corrosion protective coatings for AA2024. *Electrochimica Acta*, 145:123–131, 2014. ISSN 00134686. doi: 10.1016/j.electacta.2014.09.009. URL `http://dx.doi.org/10.1016/j.electacta.2014.09.009`.

[66] T. A. Söylev and M. G. Richardson. Corrosion inhibitors for steel in concrete: State-of-the-art report. *Construction and Building Materials*, 22(4):609–622, 2008. ISSN 09500618. doi: 10.1016/j.conbuildmat.2006.10.013.

[67] Robert Stern, Grigorij Kogan, Mark J. Jedrzejas, and Ladislav Šoltés. The many ways to cleave hyaluronan. *Biotechnology Advances*, 25(6):537–557, 2007. ISSN 07349750. doi: 10.1016/j.biotechadv.2007.07.001.

[68] V. Suganya and V. Anuradha. Microencapsulation and Nanoencapsulation: A Review. *International Journal of Pharmaceutical and Clinical Research*, 9(3):233–239, 2017. doi: 10.25258/ijpcr.v9i3.8324.

[69] Weijun Tong, Changyou Gao, and Helmuth Möhwald. pH-responsive protein microcapsules fabricated via glutaraldehyde mediated covalent layer-by-layer assembly. *Colloid and Polymer Science*, 286(10):1103–1109, 2008. ISSN 0303402X. doi: 10.1007/s00396-008-1885-z.

[70] K van Breugel. Is there a market for self-healing cement-based materials? *1St International Conference on Self-Healing Materials*, (April):1–9, 2007.

[71] Sybrand van der Zwaag. *Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*. 2007. ISBN 9781402062490.

[72] Kim Van Tittelboom and Nele De Belie. *Self-healing in cementitious materials-a review*, volume 6. 2013. ISBN 3292645522. doi: 10.3390/ma6062182.

[73] Kunamineni Vijay, Meena Murmu, and Shirish V. Deo. Bacteria based self healing concrete – A review. *Construction and Building Materials*, 152:1008–1014, 2017. ISSN 09500618. doi: 10.1016/j.conbuildmat.2017.07.040. URL http://dx.doi.org/10.1016/j.conbuildmat.2017.07.040.

[74] Chunyu Wang, Yuhuan Bu, Shenglai Guo, Yao Lu, Baojiang Sun, and Zhonghou Shen. Self-healing cement composite: Amine- and ammonium-based pH-sensitive superabsorbent polymers. *Cement and Concrete Composites*, 96(December 2018):154–162, 2019. ISSN 09589465. doi: 10.1016/j.cemconcomp.2018.11.023. URL https://doi.org/10.1016/j.cemconcomp.2018.11.023.

[75] Jianyun Wang, Arn Mignon, Gilles Trenson, Sandra Van Vlierberghe, Nico Boon, and Nele De Belie. A chitosan based pH-responsive hydrogel for encapsulation of bacteria for self-sealing concrete. *Cement and Concrete Composites*, 93:309–322, 2018. ISSN 09589465. doi: 10.1016/j.cemconcomp.2018.08.007. URL https://doi.org/10.1016/j.cemconcomp.2018.08.007.

[76] Tao Wang, Mahir Turhan, and Sundaram Gunasekaran. Selected properties of pH-sensitive, biodegradable chitosan-poly(vinyl alcohol) hydrogel. *Polymer International*, 53(7):911–918, 2004. ISSN 09598103. doi: 10.1002/pi.1461.

[77] Yanshuai Wang, Guohao Fang, Weijian Ding, Ningxu Han, Feng Xing, and Biqin Dong. Self-immunity microcapsules for corrosion protection of steel bar in reinforced concrete. *Scientific Reports*, 5(May):1–8, 2015. ISSN 20452322. doi: 10.1038/srep18484.

[78] Wei Wu, Jing Liu, Shuqin Cao, Hong Tan, Jianshu Li, Fujian Xu, and Xiao Zhang. Drug release behaviors of a pH sensitive semi-interpenetrating polymer network hydrogel composed of poly(vinyl alcohol) and star poly[2-(dimethylamino) ethyl methacrylate]. *International Journal of Pharmaceutics*, 416(1):104–109, 2011. ISSN 03785173. doi: 10.1016/j.ijpharm.2011.06.015. URL http://dx.doi.org/10.1016/j.ijpharm.2011.06.015.

[79] Wei Wu, Weigang Wang, and Jianshu Li. Star polymers: Advances in biomedical applications. *Progress in Polymer Science*, 46:55–85, 2015. ISSN 00796700. doi: 10.1016/j.progpolymsci.2015.02.002. URL http://dx.doi.org/10.1016/j.progpolymsci.2015.02.002.

[80] Jing Xie, Anqi Li, and Jianshu Li. Advances in pH-Sensitive Polymers for Smart Insulin Delivery. *Macromolecular Rapid Communications*, 38(23):1–14, 2017. ISSN 15213927. doi: 10.1002/marc.201700413.

[81] Wei Xiong, Jiaoning Tang, Guangming Zhu, Ningxu Han, Erik Schlangen, Biqin Dong, Xianfeng Wang, and Feng Xing. A novel capsule-based self-recovery system with a chloride ion trigger. *Scientific Reports*, 5:1–7, 2015. ISSN 20452322. doi: 10.1038/srep10866.

[82] Caihong Xue, Wengui Li, Jianchun Li, Vivian W.Y. Tam, and Guang Ye. A review study on encapsulation-based self-healing for cementitious materials. *Structural Concrete*, 20(1):198–212, 2019. ISSN 17517648. doi: 10.1002/suco.201800177.

[83] Huai Nyin Yow and Alexander F. Routh. Formation of liquid core-polymer shell microcapsules. *Soft Matter*, 2(11):940–949, 2006. ISSN 1744683X. doi: 10.1039/b606965g.

[84] Weizhong Yuan, Jinchun Zhang, Hui Zou, Tianxiang Shen, and Jie Ren. Amphiphilic ethyl cellulose brush polymers with mono and dual side chains: Facile synthesis, self-assembly, and tunable temperature-ph responsivities. *Polymer*, 53(4):956–966, 2012. ISSN 0032-3861. doi: https://doi.org/10.1016/j.polymer.2012.01.003. URL https://www.sciencedirect.com/science/article/pii/S003238611200016X.

[85] Mikhail L. Zheludkevich, Dmitry G. Shchukin, Kiryl A. Yasakau, Helmut Möhwald, and Mario G.S. Ferreira. Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor. *Chemistry of Materials*, 19(3):402–411, 2007. ISSN 08974756. doi: 10.1021/cm062066k.

[86] Qiang Zhu, Chang Liu, Zheng Sun, Xiaofei Zhang, Ning Liang, and Shirui Mao. Inner layer-embedded contact lenses for pH-triggered controlled ocular drug delivery. *European Journal of Pharmaceutics and Biopharmaceutics*, 128(September 2017):220–229, 2018. ISSN 18733441. doi: 10.1016/j.ejpb.2018.04.017. URL https://doi.org/10.1016/j.ejpb.2018.04.017.

[87] Yangyang Zhu, Yuwei Ma, Qijun Yu, Jiangxiong Wei, and Jie Hu. Preparation of pH-sensitive core-shell organic corrosion inhibitor and its release behavior in simulated concrete pore solutions. *Materials and Design*, 119:254–262, 2017. ISSN 18734197. doi: 10.1016/j.matdes.2017.01.063.

[88] Yangyang Zhu, Yuwei Ma, Qijun Yu, Jiangxiong Wei, and Jie Hu. Preparation of pH-sensitive core-shell organic corrosion inhibitor and its release behavior in simulated concrete pore solutions. *Materials and Design*, 119:254–262, 2017. ISSN 18734197. doi: 10.1016/j.matdes.2017.01.063. URL http://dx.doi.org/10.1016/j.matdes.2017.01.063.

[89] Jiandong Zuo, Biqin Dong, Feng Xing, Chaoyun Luo, and Dazhu Chen. Preparation of polystyrene/sodium monofluorophosphate microcapsules by W/O/W solvent evaporation method. *Advanced Powder Technology*, 27(4):1086–1092, 2016. ISSN 15685527. doi: 10.1016/j.apt.2016.03.017.

[90] Jiandong Zuo, Jia Zhan, Chaoyun Luo, Biqin Dong, Feng Xing, and Dazhu Chen. Characteristics and release property of polylactic acid/sodium monofluorophosphate microcapsules prepared by spray drying. *Advanced Powder Technology*, 28(11):2805–2811, 2017. ISSN 15685527. doi: 10.1016/j.apt.2017.08.006.