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Tunable chitosan-alginate capsules for a controlled release of crystallisation inhibitors in mortars

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Abstract. Plasters and renders used in historic monuments are vulnerable to degradation caused by salt weathering. Crystallisation inhibitors (molecules/ions that alter salt crystallisation) mixed into mortars have shown promising results in mitigating salt damage by inhibiting salt crystallisation, promoting salt transport to the evaporating surface, and modifying crystal habit. However, past research suggests that inhibitors easily leach out from mortars, meaning their long-term positive effect is lost. Encapsulation of an inhibitor within a mortar is a potential solution to minimise leaching. Herein, capsules composed of a polyelectrolyte complex of calcium alginate coated in chitosan are investigated for the controlled diffusive release of sodium ferrocyanide, a known NaCl crystallisation inhibitor. Capsules with varying chitosan-calcium alginate ratios are prepared using the extrusion dripping technique. The release of the inhibitor from capsules in solutions of various pH values ranging from 7–13 is investigated. Results show that increasing the capsule's chitosan to calcium alginate ratio reduces the inhibitor release for all studied solution pH values compared to pure calcium-alginate capsules. Therefore, a controlled inhibitor release can be obtained by tuning the chitosan-alginate ratio. In future, additional tests will be performed to find suitable capsule compositions for optimising their performance when mixed in mortars.

1 Introduction

Materials used in the built cultural heritage are often susceptible to salt weathering. Salts, like sodium chloride (NaCl), are responsible for crystallisation-induced damage [1]. These salts (as ions) are either originally present in the building materials or find entry into the building materials through capillary transport from various sources (e.g., groundwater, salt spray etc.). Under super-saturated conditions in confined pore networks, salt crystallisation leads to crystallisation pressure in the porous matrix and progressive damage in the form of material loss [2,3]. Historic buildings are particularly prone to salt damage due to the limited strength of traditional materials they are made of, such as lime mortars, and the accumulation of salts and stresses over time. The costs associated with the repair and maintenance of these buildings are considerable. In particular, plaster and renders are often affected by salt decay and need replacement. The use of salt crystallisation inhibitors mixed in mortar is seen as a potential preventive solution that could reduce costs by improving the durability of repair works. Crystallisation inhibitors are chemical compounds that inhibit salt crystallisation by delaying crystal nucleation and/or modifying crystal habit by adsorbing on specific crystal surfaces, altering crystal growth [4].

Among inhibitors, alkali ferrocyanide (FeCN) is a well-known and an effective inhibitor of NaCl crystallisation, commonly used as an anti-caking agent in table salt [5]. FeCN suppresses NaCl nucleation by increasing the critical supersaturation [6]. Therefore, NaCl in solution in the presence of FeCN remains as ions (Na^+ and Cl^-) at higher supersaturations, allowing transport of the ions towards the evaporation surface. In porous building materials, this property has been exploited to promote harmless efflorescence (free crystallisation at the surface) against more severe subflorescence (confined subsurface crystallisation) [7,8]. Secondly, the presence of FeCN alters NaCl crystal habit, resulting in the NaCl crystals having disordered dendritic growth forms, as opposed to their equilibrium cubic form. FeCN ions preferentially sorb on the {100} face of NaCl crystals. A charge mismatch between FeCN and the NaCl cluster prevents crystal growth on the {100} faces of the NaCl crystals resulting in dendritic growth forms [9]. Gupta et al., have demonstrated that the increase in the crystal surface area due to the dendritic growth further increases the evaporation rate and promotes the advection of salt to the surface [10]. Crystallisation with high nucleation density (resulting in a high number of small crystals), as observed for NaCl in the presence of FeCN, is also thought to reduce pore clogging and limit crystallisation

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pressure [11]. Lower damage due to salt crystallisation has been reported in the presence of FeCN on different porous substrates [11–15].

FeCN, when mixed in fresh mortar during preparation, has effectively reduced salt decay [8] without significantly altering the mortar properties [16,17]. However, Granneman et al. [11], showed that after repeated crystallisation cycles, less than 1% of the initially added inhibitor was left in the mortar specimens; the rest of the inhibitor possibly leached out during moisture transport. Recent results from a case study, where plaster with mixed-in inhibitor was applied on a salt-contaminated wall, showed localised accumulation of FeCN in the outermost layer of the plaster, suggesting high mobility of FeCN ions and potential leaching [18]. If FeCN is leached out of renovation mortars, it will be depleted, reducing its effectiveness over time. Immobilisation and the controlled release of inhibitors from designer capsules could be an effective solution to this challenge.

Encapsulation and controlled release are common concepts that find many useful applications in drug delivery, fragrance release and corrosion treatments [19]. Even in cementitious materials, the use of capsules to protect and deliver self-healing agents has shown promising results [20–23]. Encapsulated crystallisation inhibitors prevent salt crystallisation and the progressive damage of the mortar. Therefore, a fracture based capsule trigger deployed in various self-healing cementitious materials would be too late to prevent the damage. In order to slow down and sustain the release of the inhibitor, a semi-permeable diffusion-based capsule shell is therefore more suitable than a rupture/dissolution-based trigger [24]. Naturally occurring semi-permeable hydrogels, like alginates, pectin, gelatine and chitosan, show interesting swelling behaviours that can be exploited for controlled release. Alginate-based hydrogels are easy to produce and have shown good survivability in construction materials [25]. However, alginates have one disadvantage in high-alkaline environments typically observed in cementitious systems: alginates are negatively charged (anionic) at pH >5.5 and swell due to electrostatic repulsion creating open structures [26]. These open structures result in high diffusion rates or even burst release of the core [27]. Several studies report improvements to the alginate stability by coating alginate capsules with cationic polymers like chitosan [28]. The positive charged chitosan forms an additional membrane with the negatively charged alginates. Moreover, chitosan shows the opposite swelling behaviour to alginates: chitosan shrinks in high pH solutions, thereby reducing its permeability. Studies with chitosan-coated alginate capsules have reported higher stability, lower leakage and improved controlled release of different encapsulated drugs compared to alginate-only capsules [29,30]. By using the above concepts, a superior technology with polyelectrolyte hydrogel capsules can be developed to engineer slow inhibitor release in building materials.

This study explores the feasibility of encapsulating FeCN in calcium-alginate (CA) capsules with a chitosan (Cs) coating. In addition, the release of encapsulated FeCN from capsules with different Cs:CA ratios under different pH conditions is investigated.

2 Materials and methods

Sodium alginate (SA) and calcium chloride dihydrate were purchased from Sigma Aldrich. Medium molecular weight chitosan (Cs) (190,000-310,000 Da) was obtained from Merck. Cs contained Fe impurities equivalent to ~0.18% by mass as measured using inductively-coupled plasma (ICP)-optical emission spectroscopy (OES. Acetic acid was bought from J.T.Baker. Lab grade sodium ferrocyanide decahydrate (NaFeCN) used as the crystallisation inhibitor was

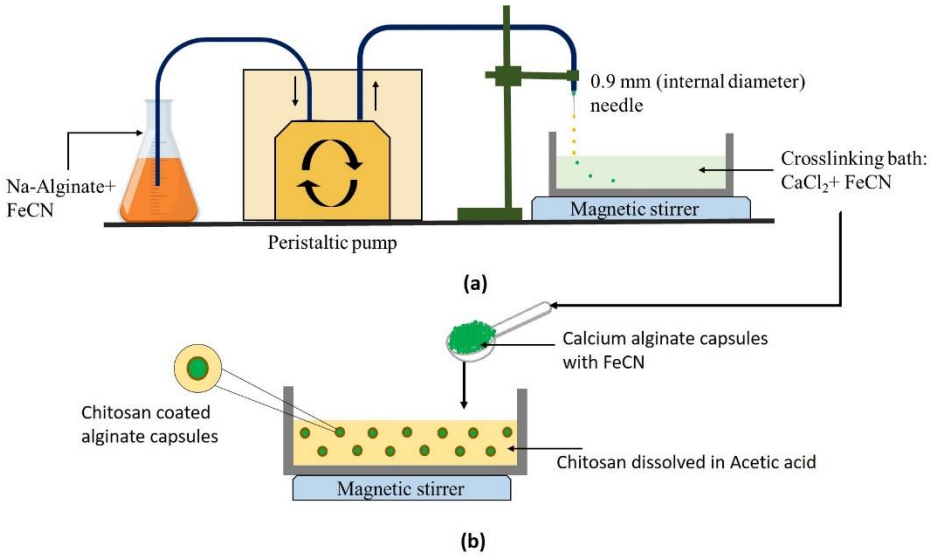

Fig. 1. Encapsulation of FeCN. **(a)** Preparation of calcium alginate (CA) capsules with FeCN where the solution containing sodium alginate (2% w/v) and FeCN(2% w/v) is added drop-by-drop into a crosslinking bath containing Ca^{2+} ions (3% w/v $CaCl_2$+ 2%w/v FeCN) at a constant rate using a peristaltic pump **(b)** Freshly prepared CA-FeCN capsules are coated with chitosan (Cs) by adding them to a gently stirring Cs solution (varying concentration) for a cross-linking time of 15 min.

purchased from Acros organic (Thermo Fischer Scientific).

2.1 Preparation of inhibitor loaded capsules

A schematic of the capsule preparation process is presented in Fig. 1

2.1.1 Production of calcium alginate capsules

Capsules were prepared by a simple extrusion dripping technique [31]. SA (2% w/v) ($w_{solute}/v_{solution}$) was first dissolved in demineralised water using vigorous stirring (1000 rpm) until SA was completely dissolved. Next NaFeCN was mixed in the alginate solution at a concentration of 2% (w/v) and stirred for 30 min. The obtained mixture was extruded drop-by-drop (under gravity) into a 3% (w/v) $CaCl_2$ bath using a peristaltic pump (Masterflex console drive, Cole palmer instruments) connected to a needle with a 0.9 mm internal diameter, forming calcium alginate droplets/capsules with encapsulated FeCN. NaFeCN was added to the $CaCl_2$ bath with the same concentration as in the SA solution to minimise FeCN diffusion from the capsules during production. The bath was continuously stirred using a magnetic stirrer at 300 rpm. The alginate beads were allowed to crosslink with Ca^{2+} ions from the bath overnight to form stable gel capsules.

The capsules were filtered out using a Büchner funnel (no paper/vacuum) and washed with demineralised water to remove excess unlinked Ca^{2+} ions. These capsules are denoted CA as they do not have any chitosan coating.

2.1.2 Production of calcium alginate capsules with a chitosan coating

Cs solutions were prepared by dissolving chitosan in 0.3 M acetic acid using a magnetic stirrer at 40°C for at least 6 h. Three different Cs baths were prepared containing 1%, 1.5% and 2% of Cs (w/v), respectively. The CA capsules, obtained as described in Section 2.1.1 (Fig. 1a), were added to the different Cs baths and cross-linked for 15 minutes. Subsequently, the capsules were filtered and washed with deionised water. At the end, Cs-coated CA capsules with Cs:CA ratios of 0.5, 0.75 and 1 by mass were obtained.

2.2 Procedure for testing the inhibitor release at different pH values

The release of FeCN from capsules containing different Cs:CA ratios was tested in bulk solutions with different pHs in the range of 7–13. Demineralised water was used for pH 7. Solutions with a pH of 13, 11 and 9 were prepared by adding potassium hydroxide (KOH) to demineralised water at concentrations of 10^{-1} M, 10^{-3} M, and 10^{-5} M, respectively. The pH of the solutions was measured using a pH meter (Metrohm).

5 g of freshly prepared capsules were added to 40 mL of each solution and placed separately in airtight plastic bottles. At day 7, eluates were sampled using a pipette and analysed using a UV-VIS spectrophotometer (Shimadzu UV2600) at 218 nm. The amount of FeCN released from the capsules was quantified using a calibration curve prepared with three FeCN solutions of known concentrations (6.25, 12.5 and 25 mg/L). When the absorption of the eluates was out of the calibration range, they were diluted 50x to stay within the calibration curve.

2.3 Visual observations of the capsules

Capsules with different Cs:CA ratios were imaged and their size measured using a digital light microscope (Keyence VHX-7000). 20 capsules were imaged and measured for each Cs:CA ratio, and the mean measured values with their coefficient of variation are reported.

2.4 Measuring Fe impurities in chitosan solutions

The Cs solution used for coating the CA capsules was analysed using ICP-OES for presence of Fe ions. The samples were first acidified with 1% (v/v) nitric acid (HNO_3) and passed through a filter before analysing using ICP. Sample was diluted 10 times.

3 Results and Discussion

The capsules were ellipsoids and uniformly sized as shown in Fig. 2. The mean size along the longer dimension and shorter dimension of the ellipsoid was 2.6 mm and 2.1 mm respectively. The coefficient of variation (C.V) was 0.11 along the longer dimension, higher compared to the shorter dimension (C.V = 0.06). The observed size was irrespective of the Cs:CA ratio.

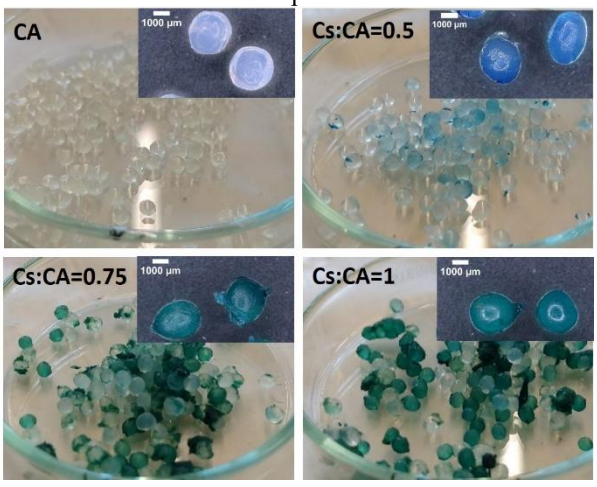

Fig. 2. FeCN loaded capsules with different chitosan (Cs): calcium alginate (CA) ratios. Inset: microscope image of capsules showing the ellipsoidal shape.

Increasing the amount of chitosan is shown to alter the colour of the capsules to a bluish-green hue as seen in Fig. 2. The blue colour might be due to formation of Prussian blue (Iron (III) hexacyanoferrate(II)) as summarised in Equation 1 [32].

$$4Fe^{3+} + 3[Fe^{III}(CN)_6]^{4-} \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 \text{ (blue)} \quad (1)$$

Trace amounts of Fe ion (<0.2%) were detected in the chitosan using ICP (data not shown). This Fe ion in the form of Iron (III) hexacyanoferrate(II) (Eq. 1) would be sufficient for the blue colouration of the chitosan beads (Fig. 2). Cs is positively charged at pH <6.5 and could possibly bind with the FeCN ion which has a net negative charge. Cs concentration is indicative of this interaction as we expect that with increased Cs concentration there are more positively charged functional groups on the Cs polymer for the FeCN to react with, thereby increasing the amount of bound or complexed FeCN. This could also contribute to a deeper blue colour (Fig.2). However, more research is needed to clarify Cs-FeCN interaction.

The release of FeCN obtained from UV-VIS spectroscopy is presented in Fig.3. The CA capsules (without Cs coating) are very permeable and release high amounts of FeCN in the whole pH range (7–13). In general, CA is anionic in nature, under alkaline conditions, the carboxyl group on the alginate (-COOH) is deprotonated to $–COO^-$. As the pH increases, the electrostatic repulsion due to the negative charge increases. The repulsion results in the alginate swelling, increasing the gel's open network structure and permeability. The increased permeability means that the release of encapsulated FeCN is very high.

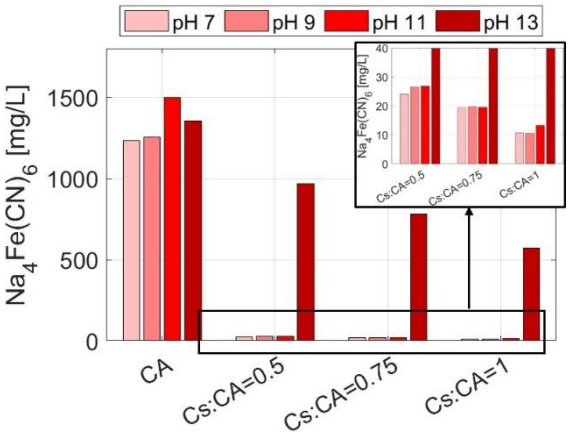

Fig. 3. Release of FeCN from the capsules in solutions with different pHs as a function of Cs:CA ratio. Inset: zoomed-in image of capsules with Cs:CA ratios for greater clarity.

Increasing the Cs:CA ratio dramatically moderates FeCN release at pH 7-11. Cs:CA capsules release almost 60 times less FeCN compared to CA, making Cs:CA capsules almost impermeable in this pH range. The reduced release is because the Cs coating creates an additional low permeable membrane reducing FeCN transport. In addition, the cationically charged Cs coating shrinks and potentially restricts the alginate from swelling, reducing the release.

At pH 13, the Cs:CA capsules show higher FeCN release compared to release at pH 7-11. However, the Cs coating is still able to reduce the rate of release significantly as compared to CA. It is possible that the Cs is no longer charged at high pH, and the Cs-CA bond is broken, leading to the degradation of the coating. Somewhere between pH 11 and 13, the Cs coating changes its response. Investigating the reason for the abrupt release is relevant for mortar application as the pH of the pore solution in cementitious materials (cement or lime mortar) lies between pH 11-13.

It is expected that the very fast release in high alkaline conditions (pH 13) can be controlled by adjusting the Cs:CA ratio. However, by increasing the Cs amount, complete immobilization of the inhibitor might arise at lower pH environments, such as those present in carbonated mortar. Therefore, a compromise should be found while designing the capsules.

4 Conclusions

In this study, the crystallisation inhibitor FeCN was successfully encapsulated in Cs-coated CA capsules. As expected, pure CA capsules demonstrated significant release in alkaline environments. However, coating of the CA capsules with Cs as a result of the ionic interaction between Cs and CA lowered the release FeCN due to the Cs-coating lowering the permeability of the capsules. In addition, the capsule can be designed to control FeCN release by optimising the Cs:CA ratio.

Furthermore, the presence of chitosan leads to colour alteration of the capsules. The colour change is attributed to the trace iron impurities present in chitosan, that react with the inhibitor. Coloured capsules could lead to unfavourable aesthetic effects like chromatic alteration to mortar. Further research needs to understand this reaction.

5 Outlook

This study shows promising results in designing of pH-controlled hydrogel capsules for controlling the release of encapsulated FeCN in bulk solutions. In the future, the effect of capsules will be studied in mortar, focussing on inhibitor leaching, capsule survivability during mixing and the effect of capsules on the performance of mortar against salt damage.

In addition to preventing leaching of FeCN, the application of such capsules can be relevant to other (self-healing, corrosion inhibitors) applications [33,34], especially those where pH plays an important role.

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References

1. A. E. Charola, J. Am. Inst. Conserv. **39**, 327 (2000)
2. G. W. Scherer, Cem. Concr. Res. **29**, 1347 (1999)
3. M. Steiger, J. Cryst. Growth **282**, 455 (2005)
4. M. P. Bracciale, S. Sammut, J. Cassar, M. L. Santarelli, and A. Marrocchi, Molecules **25**, 1873 (2020)
5. A. A. C. Bode, S. Jiang, J. A. M. Meijer, W. J. P. Van Enckevort, and E. Vlieg, Cryst. Growth Des. **12**, 5889 (2012)
6. A. Glasner and M. Zidon, J. Cryst. Growth **21**, 294 (1974)

7. C. Selwitz and E. Doehne, J. Cult. Herit. **3**, 205 (2002)
8. C. Rodriguez-Navarro, L. Linares-Fernandez, E. Doehne, and E. Sebastian, J. Cryst. Growth **243**, 503 (2002)
9. A. A. C. Bode, V. Vonk, F. J. Van Den Bruele, D. J. Kok, A. M. Kerkenaar, M. F. Mantilla, S. Jiang, J. A. M. Meijer, W. J. P. Van Enckevort, and E. Vlieg, Cryst. Growth Des. **12**, 1919 (2012)
10. S. Gupta, L. Pel, M. Steiger, and K. Kopinga, J. Cryst. Growth **410**, 7 (2015)
11. S. J. C. Granneman, B. Lubelli, and R. P. J. van Hees, Constr. Build. Mater. **194**, 62 (2019)
12. B. Lubelli and R. P. J. van Hees, J. Cult. Herit. **8**, 223 (2007)
13. T. Rivas, J. Feijoo, I. de Rosario, and J. Taboada, (2017)
14. T. Rivas, E. Alvarez, M. J. Mosquera, L. Alejano, and J. Taboada, Constr. Build. Mater. **24**, 766 (2010)
15. J. Feijoo, D. Ergenç, R. Fort, and M. Á. de Buergo, Mater. Struct. **54**, 14 (2021)
16. S. J. C. Granneman, B. Lubelli, and R. P. J. Van Hees, Int. J. Archit. Herit. **12**, 849 (2018)
17. A. Kamat, B. Lubelli, and E. Schlangen, AIMS Mater. Sci. **9**, 628 (2022)
18. B. Lubelli, E. des Bouvrie, T. G. Nijland, and A. Kamat, J. Cult. Herit. **59**, 10 (2023)
19. A. P. Esser-Kahn, S. A. Odom, N. R. Sottos, S. R. White, and J. S. Moore, Macromolecules **44**, 5539 (2011)
20. B. Dong, Y. Wang, G. Fang, N. Han, F. Xing, and Y. Lu, Cem. Concr. Compos. **56**, 46 (2015)
21. W. Xiong, J. Tang, G. Zhu, N. Han, E. Schlangen, B. Dong, X. Wang, and F. Xing, Sci. Rep. **5**, 1 (2015)
22. A. Al-Tabbaa, C. Litina, P. Giannaros, A. Kanellopoulos, and L. Souza, Constr. Build. Mater. **208**, 669 (2019)
23. C. Xue, W. Li, J. Li, V. W. Y. Tam, and G. Ye, Struct. Concr. **20**, 198 (2019)
24. M. Hu, J. Guo, Y. Yu, L. Cao, and Y. Xu, Materials (Basel). **10**, 369 (2017)
25. S. Xu, A. Tabaković, X. Liu, and E. Schlangen, Constr. Build. Mater. **169**, 379 (2018)
26. W. R. Gombotz and S. F. Wee, Adv. Drug Deliv. Rev. **31**, 267 (1998)
27. T. W. Wong, J. Pharm. Pharmacol. **63**, 1497 (2011)
28. M. George and T. E. Abraham, J. Control. Release **114**, 1 (2006)
29. M. L. Huguet and E. Dellacherie, Process Biochem. **31**, 745 (1996)
30. A. E. Polk, B. Amsden, D. J. Scarratt, A. Gonzal, A. O. Okhamafe, and M. F. A. Goosen, Aquac. Eng. **13**, 311 (1994)
31. E.-S. Chan, B.-B. Lee, P. Ravindra, and D. Poncelet, J. Colloid Interface Sci. **338**, 63 (2009)
32. H. J. Buser, D. Schwarzenbach, W. Petter, and A. Ludi, Inorg. Chem. **16**, 2704 (1977)
33. Y. Ç. Erşan, H. Verbruggen, I. De Graeve, W. Verstraete, N. De Belie, and N. Boon, Cem. Concr. Res. **83**, 19 (2016)
34. T. A. Söylev and M. G. Richardson, Constr. Build. Mater. **22**, 609 (2008)