MICROBIALLY MEDIATED CARBONATION OF MARINE ALKALINE MINERALS: POTENTIAL FOR CONCRETE CRACK HEALING

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ABSTRACT

Concrete constructions in the marine environment suffer from chemical attack of sea salts which can induce damage to both the concrete matrix and embedded steel reinforcement. For example, ingress of sulfate and chloride ions can respectively result in detrimental ettringite formation and enhanced corrosion of the steel rebars. The first degradation mechanism is due to development of expansive minerals within the concrete matrix, a process where increased internal pressure can result in crack formation. Cracking dramatically increases matrix porosity further enhancing the ingress rate of detrimental chemicals. However, with controlled mineral expansion comes the possibility of an employable mechanism for autonomous sealing of cracks. In this research project our aim is to study the potential for carbon dioxide-producing bacteria to act as an agent to control expansive carbonation reactions following serpentinization (hydration reactions) of alkaline precursor minerals in marine concrete. Early experimental results showed that seawater derived magnesium ions and carbon dioxide molecules show high potential for self-healing due to the formation of crack-filling expansive minerals. Environmental scanning electron microscopy combined with X-ray element analysis revealed that dolomite $(CaMg(CO_3)_2)$ formation via intermediate conversion of brucite $(Mg(OH)_2)$ is the mechanism underlying this process. Several previously documented studies have reported that dolomite formation, analogous to delayed ettringite formation, can be detrimental to concrete as it can in fact induce crack formation due to increased internal stresses. In this project our aim is to control expansive mineral formation by bacterial CO₂ production channelling the process for healing- but not for causing cracks in concrete constructions in the marine environment.

1. INTRODUCTION

Autonogenous crack-healing in concrete has certain limitations as was e.g. observed in an early study by Edvardsen [1] and appears commonly limited to crack widths of maximally up to 0.2mm. In order to enhance crack-healing several mechanisms have been tested in a number of studies, varying from increased cement content, mineral (expansive) additives, organic polymers and limestone-producing bacteria [2]. In these systems autonomous crack-healing up to 0.5mm crack width has been observed [3]. As most documented studies focussed on crack-healing of concrete specimens and structures in freshwater environments, limited information is available of crack-healing in marine environments. Due to the presence of much higher concentrations of (interfering) sea salt compounds such as sulphate molecules and magnesium ions, processes as secondary cement particle hydration and calcium carbonate mineral formation may differ substantially in fresh- and seawater. The objective of this study therefore was to investigate if and how the presence of typical seawater salts influence inorganic mineral formation on the surface of concrete specimens and furthermore if the presence of metabolically active bacteria might influence this process. While both mineral formation on the surface of both Portland cement and blast furnace slag cement was investigated, only results of Portland cement based specimens are presented in this study.

2. MATERIALS AND METHODS

Mineral formation on mortar specimens surface as well as autogenous crack-healing was compared between freshwater and sea water incubated specimens. Mineral formation was assessed by Environmental Scanning Electron Microscopy (ESEM) combined with X-ray element (EDAX) analysis. Crack-healing was guantified observing surface crack closure using light microscopy. Mortar specimens were prepared according to the following recipe: 294g sand (0.125-0.25mm), 154g sand (0.25-0.5mm), 392g sand (0.5-1mm), 560g sand (1-2mm), 850g CEMI 42.5N and 360ml tapwater, thus with a water cement ratio of 0.42. Small 1.5cm cubes were cut out of larger specimens after 10 days curing. Sets of these small cubes were subsequently cured for 7 and 21 days by submersion in respectively tapwater and artificial seawater at room temperature. Artificial seawater was prepared by amending 1L tapwater with KCI (0.8g), CaCl₂.2H₂O (1.5g), NaCl (27.35g), MgSO₄.7H₂O (6.9g) and MgCl₂.6H₂O (5.1g). Mineral formation on surfaces of these specimens were compared to those who were not water cured (kept in either air or preserved in 96% ethanol). Steel bar reinforced mortar prisms (16x4x4cm), cracked under tension after 28 days curing, were also further incubated in either tapwater or artificial seawater and analysed for surface crack-closure after 0, 28 and 63 days incubation.

3. RESULTS AND DISCUSSION

Mineral formation on surfaces of mortar cubes incubated in respectively fresh and artificial seawater appeared strikingly different both in terms of quantity and type of mineral formed (Figure 1). While moderate amounts of small calcium carbonate based minerals were formed on the surface of tapwater incubated specimens, substantial and dense layers of brucite, dolomite- and calcium carbonate based minerals appeared on surfaces of seawater incubated specimens.

The small calcium carbonate minerals formed on tapwater incubated specimens were likely formed due to carbonation of the cement paste resulting in conversion of Potlandite into calcium carbonate according to: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

EDAX analysis indicated that the substantially thicker layer of minerals formed on the surface of seawater incubated specimens consisted of brucite $(Mg(OH)_2)$ minerals and dolomite $(MgCa(CO_3)_2)$ minerals visible in Fig 1B. Interestingly, a sequence of mineral formation, from brucite to dolomite, with concomitant expansion of reaction products appeared visible. This apparent sequential process can be explained by a reaction of seawater derived magnesium ions reacting with hydroxide ions leaching from the concrete matrix to form brucite: $Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2$, followed by reaction with seawater derived calcium ions and carbon dioxide molecules:

 $2Mg(OH)_2 + Ca^{2+} + 2CO_2 \rightarrow CaMg(CO_3)_2 + Mg^{2+} + 2H_2O$. The expanding mineral reaction results in more efficient crack healing in seawater than in freshwater as was

also visible in crack-healing of mortar prisms incubated in both types of water (Figure 2). During 56 days of curing, seawater incubated specimens showed higher autogenous crack-healing rates than tapwater incubated specimens.



Figure 1: Specimens (10 days cured, 21 days incubated) in tapwater (top image, left: 500x magnification, right:2000x magnification), showing formation of small calcium carbonate minerals, and seawater (bottom image, same magnifications), showing formation of larger brucite minerals (ball-shaped structures) and dolomite minerals (needle shaped structures).

4. CONCLUSIONS

The results of this study indicate that autogenous crack-healing is higher in seawater than in freshwater incubated mortar specimens. The difference can be explained by type of mineral formation, which is predominantly calcium carbonate in freshwater and eventually dolomite in seawater. As the later mineral formation involves more seawater derived molecules (magnesium and carbondioxide) its reaction is more expansive thus resulting in potentially higher autogenous crack-sealing capacity. Our on-going research currently focusses on the role of microbial metabolic CO_2 production as this process could exert a control on brucite to dolomite formation.



Figure 2: Autogenous crack-healing of mortar specimens incubated in fresh water (top image, left picture: crack induced after 28 days curing, crack width at arrow: 292 µm, right picture: imperfect crack closure (arrows) after 63 days incubation) and seawater (bottom image, left picture: crack induced after 28 days curing, crack width at arrow: 400 µm, right picture: crack closure up to 400 µm crack width after 63 days

incubation)

This is important as unrestricted internal dolomite formation in concrete could potentially result in crack formation or crack extension due to the expansive reaction comparable to harmful secondary ettringite formation.

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