THE POTENTIAL OF BIO-BASED REPAIR SYSTEM TO INCREASE THE DURABILITY OF REPAIRED CONCRETE STRUCTURES

Virginie Wiktor and Henk M. Jonkers

Section of Material and Environment, Faculty of Civil Engineering and Geosciences, Delft, the Netherlands

Abstract

Periodic maintenance operations for concrete structures are generally focused on repairing concrete damages while not considering the relevant durability issues of the repair system itself. The main goal is to develop a bio-based repair system which features improved durability and sustainability characteristics compared to currently commercially available systems. The authors investigated (i) the effect of the pH of two transportation solutions on the bacterial activity, the biological part of the repair system, and (ii) the influence of the nutrient source, i.e. the mineral precursor compound of the repair system, on the cement paste microstructure, with or without bacterial activity. Two distinct surface layers have been observed depending of the treatment performed. The first type is a thick Ca-based layer formed with the treatment with glucose with or without bacteria. The second type has been observed for the treatment with glucose+NaS (sodium silicate) with or without bacteria. In the latter case a silica-based layer was noticed at 7 days and at 28 days some few locations only exhibit a glucose/NaS surface layer. The results have shown that treatment of mortar specimen with glucose repair solution with or without bacteria promoted vaterite formation instead of calcite. This was probably due to the neutral pH of the solution and the possible adsorption of glucose on $CaCO_3$ nuclei.

1. INTRODUCTION

Concrete is one of the most used construction material worldwide as it is strong, and relatively cheap. However, concrete is subjected to a number of degradation processes which hamper the structure to reach its required service life [1]. Currently available concrete curing and repair systems aiming to decrease porosity and repair of cracks in aged structures are largely based on environmental unfriendly materials systems. Moreover, periodic maintenance operations for concrete structures are generally focused on repairing concrete damages while not considering the relevant durability issues of the repair system itself [2, 3]. Premature failure of repairs and lack of certainty in the durability and performance of some

repaired concrete structures affects Europe and many parts of the world. Accordingly, there is a need to achieve more durable repaired concrete structures [1].
With respect to these considerations, the present study focuses on the development on a bio-based repair system. The basic idea is considered a spin-off of the recently developed bio-based self-healing concrete where cracks are filled with calcite produced by incorporated bacteria [4, 5]. The main goal is to develop a bio-based repair system which features improved durability and sustainability characteristics compared to currently commercially available systems [6].
The bio-based repair system as presented in this paper is a liquid-based system which transports a bio-based agent into concrete. The bio-based repair agent consists of concrete compatible bacteria and feed which produce calcite-based minerals decreasing concrete matrix porosity. The first step in the development of this bio-based repair system is to determine the best combination between the nutrient source for bacteria and the transportation solution in order to have an optimum bacterial activity but also to insure a good compatibility with the concrete matrix.
In this paper, the authors investigated (i) the effect of the pH of two transportation solutions on the bacterial activity and (ii) the influence of the nutrient source on the cement paste microstructure, with or without bacterial activity.

MATERIAL AND METHODS

Bacteria

Based on the promising results from previous work on bacteria-based self-healing concrete [4, 5], the same alkali-resistant spore-forming bacteria are being used for the development of the current bio-based repair system. These bacteria are alkaliphilic species from the genus *Bacillus* which can metabolically convert dissolved precursor compounds (food) into calcite-based minerals in alkaline environment.

Transportation solution

A silicate-based solution has been selected as transportation solution to ensure alkaline pH within the liquid bio-based repair system. Moreover, alkali silicate solutions are known to react with calcium hydroxide in the hydrated cement paste to form insoluble calcium silicate gels [7, 8], which results in the decrease of the matrix porosity.
In this study, sodium silicate (water glass) solution at 34.9% is used. It is diluted 50% in demineralized water to decrease the viscosity and have a better penetration in the matrix.

Nutrient source

To produce calcite-based minerals bacteria need organic carbon and a calcium source. As previously mentioned, silicate-based solutions are also highly reactive with calcium ions, therefore to avoid immediate precipitation of calcium within the transportation solution, the nutrient source should not contain calcium. In the present study, the calcium source comes from the cement paste only.

Glucose (D(+)Glucose mono hydrate, Boom, The Netherlands) is selected as the carbon source. To investigate the effect of the pH of the solution on the bacterial activity, glucose solutions were prepared either in demineralized water (neutral pH) or in water-glass (alkaline pH) at a concentration of 148 g/L.

Experimental procedure and treatments

Preparation of mortar test specimens

Three prismatic mortar test specimens (4x4x16 cm) were casted with ready mix mortar (Weber.tec SBN 175) and kept 28 days at room temperature, under plastic foil to avoid evaporation of water. They were then sawed in small cubes of $1cm^3$. Only cubes which were cut on all sides were used for experiments.

Relating to the treatment procedure, small cubes of $1cm^3$ 28 days old mortar were immersed for 1 hour in a repair solution. The composition of each solution is given is Table 1. The cubes were then kept in water saturated atmosphere until further testing.

Testing

After 7 and 28 days in water saturated atmosphere, for each treatment, one cube was broken in two pieces.

(i) one part was immediately frozen in liquid N_2, and kept in freeze-drying device until polished section preparation. The polished sections are analyzed with Environmental Scanning Electron Microscope (ESEM, Philips XL30 series) equipped with an Energy Dispersive X-ray (EDAX) element analyzing system for element mapping.

(ii) The second part of the cube was directly monitored with ESEM/EDAX to study the influence of the treatment on the sample surface and to observe the morphology of the newly formed minerals.

Two other cubes were tested for compressive strength with an Instron 8872 machine equipped with a device to test $1cm^3$ cubes in compression.

Table 1: Summary of the different treatments performed with the composition of the solutions

	Repair system solution composition				
Treatment	Bacteria	C - source	Solution	pH	Studied effect
Control	∅	∅	∅	∅	Carbonation of the cement paste
H_2O	∅	∅	* demi H_2O	~ 6	Leaching of Ca^{2+} from the cement paste
H_2O + bacteria	10^6 spores/mL	∅	demi H_2O	~ 6	Effect of non-active bacteria
Glucose	∅	Glucose (148 g/L)	demi H_2O	~ 7	Influence of the C-source on the cement paste microstructure
Glucose + bacteria	10^6 spores/mL	Glucose	demi H_2O	~ 7	Influence of the pH on the bacterial activity
Glucose + NaS	∅	Glucose	water glass	~ 11	Influence of the pH on the C-source behavior
Glucose + NaS + bacteria	10^6 spores/mL	Glucose	water glass	~ 11	Influence of the pH on the bacterial activity

* demi H_2O = demineralized water

RESULTS AND DISCUSSION

Control

ESEM observations from the polished sections show that, 7 days after the treatment, the surface area (~15µm thick) is more porous than the bulk area, and is lined by a very thin Ca-based layer. At 28 days, Ca-based mineral formation within the porosity of the porous area is noticed, resulting in a densification of the microstructure (Figure 1).

Relating to compressive strength results, it should be emphasis that the treatment affects essentially the specimen surface. Therefore, changes in the cement paste microstructure, if

any, should not highly influence the compressive strength values. However, these values may reflect a trend.

For the control specimen, the compressive strength tends to slightly increase between 7 and 28 days, which may be explained by a denser microstructure of the surface area (Table 2).The control specimen has not been in contact with a repair solution, but changes in the cement paste microstructures are observed. However, it has been kept in water saturated atmosphere for 7 and 28 days. This allows the matrix to be partially saturated with water and penetration of gaseous carbon dioxide within the cement paste initiates the carbonation process and the formation of a thin calcite layer on the surface at 7 days. At 28 days the formation of calcite in replacement of portlandite reduces the porosity of the matrix [9].

Table 2: Compressive strength at 7 and 28 days

#	Treatment	Compressive strength	
		7 days (Mpa)	28 days (Mpa)
1	Control	24.8 ± 3.8	27.3 ± 0.5
2	H_2O	23.1 ± 3.2	28.7 ± 0.2
3	H_2O + bacteria	19.7 ± 3.7	28.6 ± 1.6
4	Glucose	21.1 ± 3.7	23.3 ± 0.2
5	Glucose + bacteria	33.0 ± 0.8	26.4 ± 0.2
6	Glucose + NaS	27.0 ± 0.4	28.4 ± 0.8
7	Glucose + NaS + bacteria	32.9 ± 1.2	30.40 ± 3.7

Reference treatment: H_2O, H_2O+bacteria

The cubes immersed in H_2O with or without bacteria exhibit the same behavior, but different from the control.

At 7 days, as for the control specimen, a porous surface area of about 15-20μm thick is observed. However, the surface layer is thicker and composed of large crystals. EDAX analyses reveal that this layer is also Ca-based. At 28 days, the surface layer is denser but not thicker, and Ca-based mineral partly fills the porous area (Figure 1).

In the present case, the immersion of the samples in demineralized water leads to the leaching of ions (mainly calcium and hydroxide) from the pore solution to the external environment (repair solution). This is due to the pH difference and results in the dissolution portlandite and C-S-H [9]. Then, during the conservation of the specimens in water saturated atmosphere a thin film of H_2O remains on the surface and permits the precipitation of calcium carbonate. The thickness of this layer does not increase between 7 and 28 days as no more leaching is occurring. However, high humidity and presence of carbon dioxide favors more calcium carbonate precipitation especially within the porosity of the surface area. That also supports the tendency of increased compressive strength values at 28 days (Table 2).

The treatment with H_2O with or without bacteria can be used as reference in this study to investigate the effect of neutral pH solution on the cement paste.

Glucose

At 7 days a Ca-based layer is observed and the surface area seems less porous than the control and the treatment with H_2O. At 28 days this surface layer is denser and slightly thicker (Figure 2a).

The cement matrix reacts differently depending of the type of the C-source. It has been reported that treatment with Na-gluconate (148 g/L) leads to the leaching of calcium and hydroxide ions. This was due to the low pH of the Na-gluconate solution compared to that of the pore solution. Furthermore, as Ca-gluconate is less soluble than Na-gluconate, its immediate precipitation in the repair solution acted as a pump of calcium promoting portlandite and C-S-H dissolution [10].

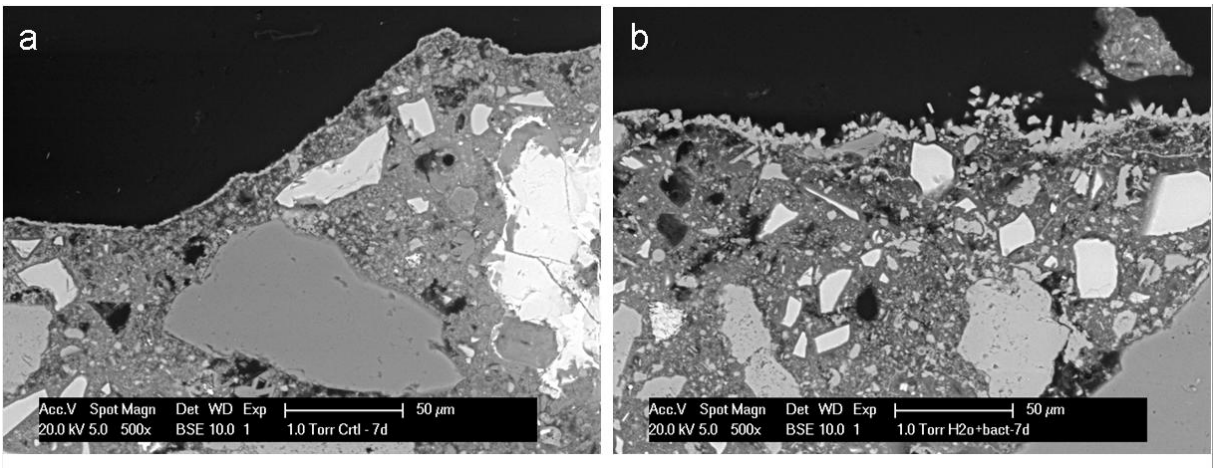


Figure 1: ESEM observations of polished sections 7 days after treatment – (a) Control, (b) H_2O+bacteria

In the present case, although the pH of the glucose solution is the same as the Na-gluconate one, no extensive leaching of calcium ions is noticed. This may be due to the absence of counter ion in the case of glucose and as a result there is no competition between the precipitation of the Ca- or Na- form of the salt.

Glucose+bacteria

The observations for this treatment are nearly the same to the previous treatment with glucose only that is the formation of a surface Ca-based layer at 7 days which becomes thicker at 28 days, and absence of porous surface area. The only difference is that in the present treatment, the surface layer is thicker than the one observed with the glucose treatment (Figure 2a,b). Moreover, observation of the surface of the specimen at 28 days reveals that the Ca-based layer is indeed composed of spherules. Lower values for the compressive strength at 28 days (Table 2) compared to control and reference treatment with H_2O are noticed.

Glucose+NaS

A thin silica-based surface layer is observed at 7 days, and the surface appears denser than in the previous treatments. At 28 days, the surface layer almost disappeared and the surface area is bright and dense (Figure 3a). This may be explained by the reaction of the Na-silicates solution with calcium hydroxide in the hydrated cement paste to form insoluble calcium

silicate gels [7, 8]. However, the treatment does not result in a significant increase of the compressive strength (Table 2).

Glucose+NaS+bacteria

At 7 days, similarly to the treatment with glucose+NaS, a silica-based surface layer is observed. However, at 28 days, the observations differ, and Ca-based mineral is formed at the surface of glucose/NaS layer and its interface with the cement matrix (Figure 3b). The alkaline pH of this repair solution favour bacterial activity which promotes $CaCO_3$ formation due to metabolic conversion of glucose. However, additional measurements have to be carried out to conclude on the activity of bacteria in the present case.

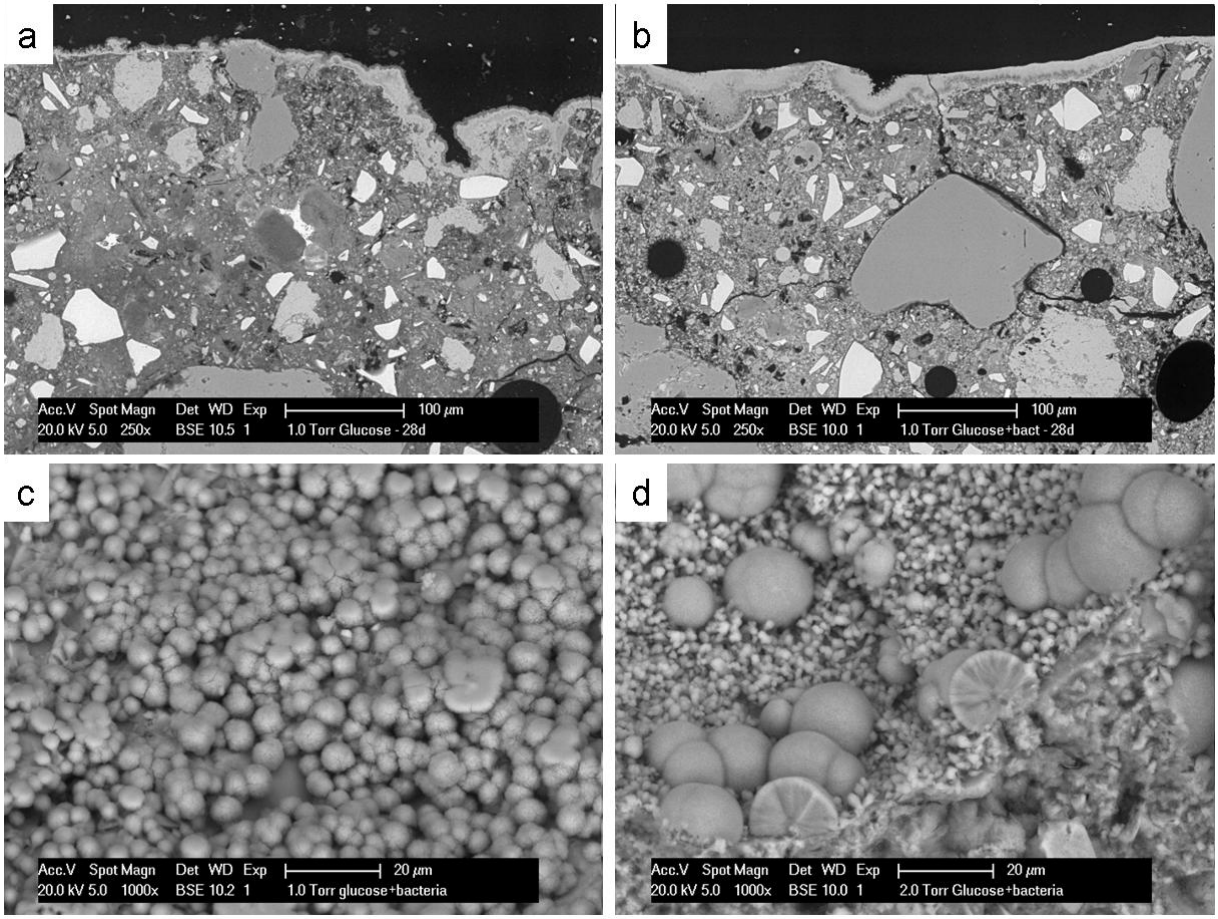


Figure 2: ESEM observations of polished section at 28 days of specimen treated with (a) glucose and (b) glucose+bacteria. (c,d) Surface observations with ESEM of fresh fractured specimens 28 days after treatment with glucose+bacteria

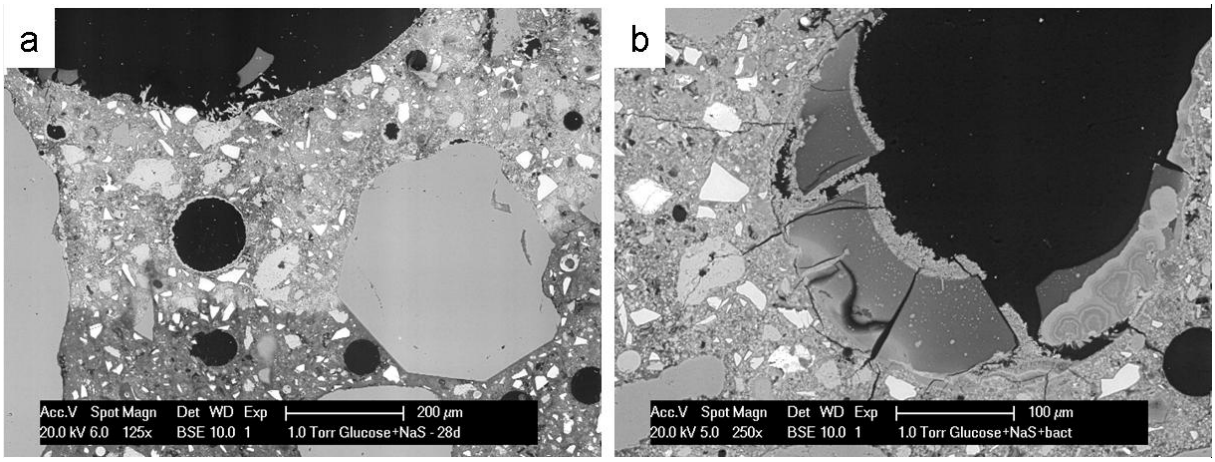


Figure 3: ESEM observation of polished section 28 days after treatment with (a) glucose+NaS, (b) glucose+NaS+bacteria

Discussion

Two distinct surface layers have been observed depending of the treatment performed. The first type is a thick Ca-based layer formed with the treatment with glucose with or without bacteria. The second type has been observed for the treatment with glucose+NaS with or without bacteria. In the latter case few locations only exhibit a glucose/NaS surface layer.

These two categories of treatment differ mainly by the pH of the repair solution. Hence, as mentioned in table 1, a glucose solution with or without bacteria has a pH around 7 while a solution with water glass has an alkaline pH.

In the present study, the Ca-based mineral is expected to be formed as the result of the reaction between Ca^{2+} from the cement matrix and the CO_2 from atmosphere or produced by bacteria. It has been reported that pH influence the formation of $CaCO_3$ polymorphs [11, 12] and organic additive are known to affect the crystal morphology [13-15].

In the case of $CaCO_3$ crystallization, it has been proposed that the system initially forms prenucleation nanoparticles of amorphous material that turns into vaterite and then calcite with aging [14, 15]. Han *et al* [12] reported that at low pH (less than 9) spherical particles with different sizes are formed and that the sample was mainly composed of vaterite.

Furthermore, sugars are known in concrete field to have retarder effect on the hydration of cement. They may form a complex with calcium and can adsorb onto calcium hydroxide and C-S-H thereby inhibiting their growth during hydration process [16].

In the present study, it can be assumed then that some dissolution of portlandite occurs due the pH difference between the repair and the pore solutions, but that the calcium ions are trapped within the glucose layer at the surface of the specimen. The calcium ions can therefore react with carbon dioxide to form calcium carbonate. Glucose may attach or adsorb to the $CaCO_3$ crystal surface subsequently affecting the crystal growth. Moreover, due the low pH of the glucose repair solution vaterite is favoured to the formation of the more stable polymorph calcite.

In the presence of water glass, vaterite formation is no longer favoured, and although bacterial activity is promoted due to alkaline conditions portlandite is also less prone to dissolution. Moreover, from the results it is not clear whether bacteria were really active or not. Additional measurements have to be undertaken to clarify this case.

CONCLUSION

The results have shown that treatment of mortar specimen with glucose repair solution with or without bacteria promoted vaterite formation instead of calcite. This was probably due to the neutral pH of the solution and the possible adsorption of glucose on $CaCO_3$ nuclei.

Glucose as C-source for bacteria reacts in different way than Na-gluconate, and the treatment with glucose+NaS+bacteria seems to promote only limited bacteria activity. Therefore, glucose as C-source does not appear as a promising approach for the development of the bio-based repair system.

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