23rd Australasian Conference on the Mechanics of Structures and Materials

2014

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Publication details

Mukherjee, A, Achal, V 2014, 'A biological route for producing low energy binders', in ST Smith (ed.), *23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23)*, vol. II, Byron Bay, NSW, 9-12 December, Southern Cross University, Lismore, NSW, pp. 893-898. ISBN: 9780994152008.

23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23)
Byron Bay, Australia, 9-12 December 2014, S.T. Smith (Ed.)

A BIOLOGICAL ROUTE FOR PRODUCING LOW ENERGY BINDERS

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ABSTRACT

Building materials almost certainly consist of some form of binders. Presently used binders, such as cement, consume a high amount of energy consumption in its manufacturing and transportation. This paper reports a biomimetic strategy for production of binders at ambient conditions based on microbially induced calcium carbonate precipitation (MICP). Microorganisms such as *Sporosarcina pasteurii* and *Bacillus megaterium* are used for precipitation of calcium carbonate on substrates such as concrete and brick. The deposition reduces permeability and corrosion in the substrate. The paper demonstrates the methods of increasing efficiency and cost reduction of the process. Effect of microbial action on strength, permeability of concrete, particularly near its surface, and ingress of moisture and chloride are discussed. Result of calcite deposition on reinforced concrete in terms of current passed when exposed to harsh corrosive conditions and *Icorr* is presented. Further, the role of MICP has been presented to develop highly efficient and durable soil-cement brick that requires very low embodied energy for production and also emit least CO_2.The current work demonstrates that production of biocalcification by urease producing bacteria can at least partially replace the industrial binders and provide a more sustainable alternative.

KEYWORDS

Biomineralisation, microbial concrete, strength, permeability, corrosion.

INTRODUCTION

Being one of the largest consumers of energy and raw materials, construction industry emits a high quantity of greenhouse gases (GHG). In order to become more sustainable, it needs to limit its environmental impact and in particular it has to reduce the use of both raw materials and energy. At the same time, construction industry needs to be cost efficient and minimizing the embodied energy of their products, such as cement, steel and bricks, can result in considerable energy savings as well as reduction of CO_2 emission (Mukherjee et al. 2013). Many building materials use huge quantities of energy and produce high volumes of CO_2 (Table 1). Developing a novel technology that does not hinder the progress of infrastructure and at the same time does not cross the boundaries of sustainability would be a great step forward. Nature has been building its habitats for millions of years in a sustainable way utilising biological processes. It is worthwhile to examine the natural-biological routes of building habitats and to what extent they can be emulated in engineering construction. Early evidences suggest that bacteria can have a role in producing cement like binders with dramatically lower energy consumption and CO_2 emission. The binder can alter the pore structure of concrete and brick and drastically reduce their water and chloride ion permeability (Achal et al. 2009a, 2010). Moreover, bacteria can seal the cracks developed in building materials through MICP. Thus, it is feasible to have self healing structures. The present paper provides a brief account on the biological route for producing low energy binders through biomineralisation.

In addition to dramatically lower embodied energy and green house gas emission biomineralisation is promising in developing recycled and recyclable, reversible, functionally graded and self-healing building materials. Moreover, it process is capable of sequestering atmospheric CO_2.

Table 1. Embodied energy and emission of building materials

Material	Energy (MJ/kg)	Carbon (kg CO_2/kg)	Density (kg /m^3)
Aggregate	0.083	0.0048	2240
Concrete (1:1.5:3 eg in-situ floor slabs, structure)	1.11	0.159	2400
Concrete (eg in-situ floor slabs) with 25% PFA RC40	0.97	0.132	-
Concrete (eg in-situ floor slabs) with 50% GGBS RC40	0.88	0.101	-
Bricks (common)	3.0	0.24	1700
Concrete block (Medium density 10 N/mm^2)	0.67	0.073	1450
Aerated block	3.50	0.30	750
Limestone block	0.85	-	2180
Cement mortar (1:3)	1.33	0.208	-
Steel (general - average recycled content)	20.10	1.37	7800
Steel (section - average recycled content)	21.50	1.42	7800

(Source: http://www.greenspec.co.uk/embodied-energy.php)

BIOMINERALISATION

Biomineralisation is a process by which living organisms produce minerals, more specifically an inorganic mineral phase with a biopolymer (Chen et al. 2012). Microbially Induced Calcium-carbonate Precipitation (MICP) is the most common process of biomineralisation (Achal et al. 2013). MICP is a result of complex biochemical reactions often governed by an enzyme urease (urea amidohydrolase; EC 3.5.1.5) produced by microbes. This reaction or precipitation requires urea as a substrate while a calcium source as the chief agent for calcite production. During microbial urease activity, 1 mole of urea is hydrolysed intracellularly to 1 mole of ammonia and 1 mole of carbamate (Eq. 1), which spontaneously hydrolyses to form an additional 1 mole of ammonia and carbonic acid (Eq. 2). These products subsequently equilibrate in water to form bicarbonate and 2 moles of ammonium and hydroxide ions (Eqs. 3 and 4). It causes an increase in pH and ultimately shifts the bicarbonate equilibrium, resulting in the formation of carbonate ions (Eq. 5). The high pH condition favours the formation of CO_3^{2-} from HCO_3^- (Knoll 2003). Finally, the carbonate concentration increases inducing an increase in super-saturation level leading to $CaCO_3$ precipitation around the cell in the presence of soluble calcium ions (Eqs. 6 and 7).

$$CO(NH_2)_2 + H_2O \rightarrow NH_2COOH + NH_3 \tag{1}$$

$$NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3 \tag{2}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{3}$$

$$2NH_3 + H_2O \leftrightarrow 2NH_4^+ + 2OH^- \tag{4}$$

$$HCO_3^- + H^+ + 2NH_4^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2NH_4^+ + 2H_2O \tag{5}$$

$$Ca^{2+} + Cell \rightarrow Cell - Ca^{2+} \tag{6}$$

$$Cell - Ca^{2+} + CO_3^{2-} \rightarrow Cell - CaCO_3^- \tag{7}$$

Biomineralisation can be applied to civil and construction engineering processes through two primary strategies, bio-augmentation and bio-stimulation. In bio-augmentation the required microbes are introduced into the structure, while in bio-stimulation the naturally residing microbes are stimulated by making the environment favourable for their growth. Bio-stimulation is preferred because it uses only the native microbes that are adapted to the environment and avoids introduction of exogenous organisms. However, the main challenges in bio-stimulation are the necessity of longer time for stimulation and growth and variable deposition over a large length scale. A bacteria augmentation at a low dosage has been attempted to leverage the advantages of the two approaches (Martinez 2012).

MICROBIAL BINDERS

Biomineralisation process has been successfully implemented in binding together the aggregates of construction materials such as soil, sand and stone. Soil at earth’s surface contains around 10^{14} bacterial cells per kilogram regardless of saturation, pH, mineralogy and other environmental factors. They have been engineering soil for nearly 3 billion years. This factor is being increasingly included in geotechnical engineering (DeJong et al., 2006). Application of MICP has been demonstrated in the remediation of heavy metals (Achal et al. 2012a), restoration of stone monuments (Tiano et al. 1999; Rodriguez-Navarro et al. 2003), sand consolidation (Achal et al. 2009a), strengthening of concrete (Ramchandran et al. 2001), and durability of building materials (De Muynck et al. 2008; Achal et al. 2010a, 2011a, 2011b).

MICP can be utilised in a variety building materials either at the time of construction or later as a means of protection. Biomineralisation can alter the mechanical properties by two means- reduction of pore spaces and cementation between grains. The effect is reduced hydraulic conductivity (especially at the surfaces), and to a smaller extent gain in stiffness and strength. Moreover, one can exercise topological preferences by selectively altering the properties at pre-determined areas. For example, the surface of the building materials can be treated with MICP to seal the mouths of the pores to dramatically reduce the hydraulic permeability of those materials. It is observed that the reduction in permeability impedes environmental degradation and improves durability. The cumulative implication of MICP can be potential to substantially reduce the embodied energy of the building materials (Rong and Qian 2012). In this discussion applications on cement concrete and brick are illustrated.

Microbial Concrete

Microbial concrete has aggregates as in the conventional concrete. The binder, however, can be a bacterial mixture or a combination of other cementitious materials and the bacterial mixture. The bacterial mixture consists of four materials, namely, alkalophilic bacteria, nutrient solution, urea as substrate solution and calcium ion solution. When introduced in the concrete mix, bacteria use the nutrient to grow and multiply its cells, urea as a substrate to hydrolyse, and calcium as the energy source to form the bio-mineral. The bacterial mixture can be available in various forms such as powder and liquid. The material may be mixed directly with other constituents of concrete or it could be mixed with the water that is used for mixing concrete. The bacterial mixture can also be used in curing water. Sometimes it is sprayed on the surface of concrete. When it is used for autogenous healing it is introduced in concrete in capsules.

When the ca-carbonate producing bacterial solution is first introduced into the sand particles, numerous bacteria bind on the surface of sand particles after the solution is fully exudative (Rong and Qian 2012). MICP was proposed as a novel method for cementing loose sands to produce structural materials, termed as bio-sandstone. A typical setup for the sand consolidation experiment to develop bio-sandstone was simplified in Reddy et al (2012). A plastic column was filled with loose sand for bacterial action. The bacterial culture was either pre-mixed with sand or injected into the sand column along with the cementation fluid consisting of nutrient media with urea and a calcium source. The bacterial sand consolidation resulted into porosity reduction from sand, as reported by Kantzas et al. (1992) when they found up to 50% and 90% reduction in porosity and permeability, respectively in sand consolidated by *Bacillus pasteurii*. Such reduction is due to deposition of calcite in column, as Achal et al. (2009a) found 40% calcite deposition in the sand column consolidated by a mutant of *Sporosarcina pasteurii*. The sand column 32.10mm high and 18.40mm in diameter had a compressive strength up to 2 MPa (Qian et al. 2010b). Further the MICP in sand plugs resulted in high amount of calcite precipitates with 28% and 24% reductions in water absorption and porosity, respectively, compared to the control specimens (Dhami et al. 2013a).

Ramachandran et al. (2001) investigated MICP technology by casting mortar cubes of dimension 50.8mm with urease producing *Bacillus pasteurii* and reported a significant improvement in the compressive strength of cement mortars at 28 days. Our previous studies showed 17% higher compressive strength of mortars (dimension 70.6 mm^3) at 28 days with a bacterium, *Sporosarcina pasteurii* (Achal et al. 2009b), which was later enhanced by 35% after optimizing with best of nutrient sources to grow bacterial cells (Achal et al. 2010). The overall trend of an increase in compressive strength might be attributed to the behaviour of microbial cells within the cement matrix. Upon cell growth, calcium carbonate would precipitate on the cell surface as well as within the cement mortar matrix. Once many of the pores in the matrix are plugged, the flow of the nutrients and oxygen to the bacterial cells is impeded. Eventually, the cells that either died or turned into endospores acted as organic fibres. This phenomenon may be associated with the increase of compressive strength of the mortar cubes (Ramachandran et al. 2001; Achal et al. 2011a).

The MICP has been proved to reduce the water permeability at a very significant rate since initiation of such experiments on limestone by Tiano et al (1999), resulted in 60% reduction in the porosity of limestone. *Bacillus sphaericus* was found to decrease water uptake of mortars by 45%, 43% and 24% with increasing water-cement ratios (De Muynck et al. 2008). The chloride migration coefficient also reduced by 19%. It was concluded that the carbonate precipitation was mainly a surface phenomenon due to the limited penetration of the bacteria into the porous matrix but it resulted in considerable decrease of water absorption and gas permeability. In a study with concrete cubes it was observed that over a period of 168 hours the specimens with bacterial cells absorbed nearly six times less water than the control cubes (Achal et al. 2011a). The chloride ion permeability tests carried out according to ASTM C1202-05 indicated that the permeability class lowered from ‘‘moderate’’ for control concrete specimens to ‘‘low’’ with bacterial cells. For control samples, the average charge passed was 3177 C, whereas for samples prepared with bacterial cells it was 1019 C (Achal et al. 2011b).

Corrosion of steel and reinforcing bar is a predominant factor causing widespread premature deterioration of concrete constructions worldwide (Raupach and Schiebl 2001). As MICP promises to alleviate permeability and transport of pollutants inside concrete, it can be effective in reducing corrosion in reinforced concrete by making a protective layer of calcite precipitates. To determine the effect of MICP, Achal et al (2012b) prepared the RC specimens with bacterial cells (*Bacillus* sp. CT-5) and induced corrosion by applying a constant anodic potential of 40 V for 7 days. The control specimens had significantly higher *Icorr* (60.83 mA/m^2 [39.25 $mA/in.^2$]) compared to MICP samples (14.78 mA/m^2 [9.53 $mA/in.^2$]) in nutrient and 20.03 mA/m^2 (12.92 $mA/in.^2$) in CSL media. An approximate four-fold reduction in *Icorr* by *Bacillus* sp. CT-5 suggests that the calcite precipitation has the effect of greatly reducing corrosion. Achal et al (2012b) concluded that the formation of calcite might facilitate the protective passive film around the steel and act as a corrosion inhibitor by interrupting the transport process in such samples.

Microbial Bricks

One of the most high embodied energy materials used by the construction industry is brick that utilizes agricultural soil as its raw material and bakes at a high temperature with energy consumption around 3 MJ/Kg. It is imperative to look for alternative materials, methods and techniques for brick making for cutting down emission and embodied energy. Reddy and Jagdish (2003) reported a combined soil-cement brick that consumes only one-fourth of the energy of burnt clay bricks. These bricks are produced by combining sand with locally available soil that is stabilised with a small quantity of cement. These bricks are dried in the sun and not baked. Thus, they have very low embodied energy. Though these bricks have adequate strength and durability, during humid conditions, ingress of moisture leads to non-homogeneous expansions that ultimately lead to cracking. A barrier layer on the surface of these bricks that impedes moisture ingress can significantly improve their usefulness. MICP precipitates calcium carbonate crystals in the pores of soil-cement bricks and resists the ingress of moisture by reducing their porosity (Dhami et al. 2013b). Mercury intrusion porosimetry test of such bacterial and control brick specimens reflected that total porosity of control specimens was 25.3% while upon MICP resulted in 31% reduction with porosity only 17.4%. Further, the bricks treated with bacterial cells improved compressive strength by 22% compared to control bricks (Dhami et al. 2013b).

MICP RESEARCH IN AUSTRALIA

MICP research in Australia has mainly been in the domain of sand plugging and soil stabilisation (Cheng et al. 2013). A bacterial strain for MICP has been isolated and it is argued that bio-stimulation is a more cost effective source for production of urease (Al-Tawadi, 2008). Surface percolation I 1m deep sand bed has been attempted (Cheng and Cord-Ruwisch, 2012). A non-sterile process using activated sludge has been explored (Cheng and Cord-Ruwisch, 2013). Scaling the technology up with 2m sand columns reported clogging at the injection points and strategies to alleviate the problem (Cheng and Cord-Ruwisch, 2014). Compressive strength of 2.5MPa was achieved in this process.

CONCLUDING REMARKS

This paper has presents a brief review on biological route for producing low energy binders based on microbial calcium carbonate precipitation. The early indications promise development of a low embodied energy binder through MICP that can improve the existing materials of construction. The main improvement is promised by intervening the pore structure of the substrate and thereby impeding moisture ingress. However, formidable challenges exist in scaling the technology up from the lab to the field. MICP research in Australia has mainly explored soil stabilisation. Researchers of materials, construction and biotechnology need to work together for further development of this transformative technology.

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