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Technical Note

Optimum conditions for microbial carbonate precipitation

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ABSTRACT

The type of bacteria, bacterial cell concentration, initial urea concentration, reaction temperature, the initial Ca^{2+} concentration, ionic strength, and the pH of the media are some factors that control the activity of the urease enzyme, and may have a significant impact on microbial carbonate precipitation (MCP). Factorial experiments were designed based on these factors to determine the optimum conditions that take into consideration economic advantage while at the same time giving quality results. *Sporosarcina pasteurii* strain ATCC 11859 was used at constant temperature (25 °C) and ionic strength with varying amounts of urea, Ca^{2+}, and bacterial cell concentration. The results indicate that the rate of ureolysis (k_{urea}) increases with bacterial cell concentration, and the bacterial cell concentration had a greater influence on k_{urea} than initial urea concentration. At 25 mM Ca^{2+} concentration, increasing bacterial cell concentration from 10^6 to 10^8 cells mL^{-1} increased the $CaCO_3$ precipitated and CO_2 sequestrated by over 30%. However, when the Ca^{2+} concentration was increased 10-fold to 250 mM Ca^{2+}, the amount of $CaCO_3$ precipitated and CO_2 sequestrated increased by over 100% irrespective of initial urea concentration. Consequently, the optimum conditions for MCP under our experimental conditions were 666 mM urea and 250 mM Ca^{2+} at 2.3×10^8 cells mL^{-1} bacterial cell concentration. However, a greater $CaCO_3$ deposition is achievable with higher concentrations of urea, Ca^{2+}, and bacterial cells so long as the respective quantities are within their economic advantage. X-ray Diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray analyzes confirmed that the precipitate formed was $CaCO_3$ and composed of predominantly calcite crystals with little vaterite crystals.

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1. Introduction

Microbial carbonate precipitation (MCP) occurs as a byproduct of common microbial metabolic processes, such as photosynthesis (McConnaughey and Whelan, 1997), urea hydrolysis (Fujita et al., 2000; Hammes et al., 2003; Dick et al., 2006; De Muynck et al., 2007a,b; Ercole et al., 2007) and sulfate reduction (Castanier et al., 1999; Knorre and Krumbein, 2000; Hammes et al., 2003). Microorganisms whose net cell surface charge is negative have also been reported to act as scavengers for divalent cations including Ca^{2+} and Mg^{2+} in aquatic environment by binding them onto their cell surfaces, thereby making microorganisms ideal crystal nucleation sites (Ferris et al., 1986, 1987; Schultze-Lam et al., 1996; Stocks-Fischer et al., 1999; Ramachandran et al., 2001) and another source of MCP. Another basic advantage of MCP is its ability to sequestrate atmospheric CO_2 through calcium carbonate formation (Ferris et al., 1994; Rodriguez-Navarro et al., 2003; Manning, 2008). The uptake of CO_2 from the atmosphere by surface waters form carbonic acid which reacts with soluble products of weathered silicate minerals in the aquatic environment, and consequently raises the pH which creates a suitable condition for $CaCO_3$ precipitation.

MCP has been used for crack repair in concrete (Bang et al., 2001; Ramachandran et al., 2001; Bachmeier et al., 2002; DeJong et al., 2006), sand consolidation (Ferris and Stehmeier, 1992; Gollapudi et al., 1995; Stocks-Fischer et al., 1999; Nemati and Voordouw, 2003), repair of calcareous monuments (Le Metayer-Levrel et al., 1999; Tiano et al., 1999, 2006; Rodriguez-Navarro et al., 2003; De Belie et al., 2006; Dick et al., 2006; Jimenez-Lopez et al., 2008), concrete compressive strength improvement (Bang et al., 2001; Ramachandran et al., 2001; Ghosh et al., 2005; Jonkers et al., 2010), concrete durability improvement (De Muynck et al., 2007a,b), selective plugging for enhanced oil recovery (Gollapudi et al., 1995), wastewater treatment (Hammes et al., 2003), and soil improvement (Whiffin et al., 2007; Ivanov and Chu, 2008; DeJong et al., 2010).

MCP by urea hydrolysis has been used by many researchers especially its application in bioremediation because ureolytic bacteria are widespread in the environment (Fujita et al., 2000), and an in situ remediation scheme based on urea hydrolysis is not likely to require the introduction of foreign microorganisms. In addition, using ureolytic bacteria to increase pH is preferable to direct addition of a basic solution because the gradual hydrolysis of urea is

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likely to promote a wider spatial distribution of calcite precipitation in the subsurface than the direct addition of base (Ferris et al., 2003), and the rate and quantity of the carbonate precipitated can also be easily controlled (De Muynck et al., 2010).

Ureolytic bacteria especially *Sporosarcina pasteurii* (formerly *Bacillus pasteurii*) and *Bacillus sphaericus* have generated a lot of interest in this area, and have been studied extensively (Fujita et al., 2000; Hammes et al., 2003; Dick et al., 2006; De Muynck et al., 2007a,b; Ercole et al., 2007). These facultative bacteria are able to precipitate calcite through the enzymatic hydrolysis of urea. The microbial urease enzyme hydrolyzes urea to produce dissolved ammonium, dissolved inorganic carbon and CO_2, and the ammonia released in the surroundings subsequently increases pH, leading to accumulation of insoluble $CaCO_3$ in a calcium rich environment. Quantitatively, 1 mol of urea is hydrolyzed intracellularly to 2 mol of ammonium (Eqs. (1) and (2)).

$$CO(NH_2)_2 + 2H_2O \xrightarrow{Urease} 2NH_4^+ + CO_3^{2-} \quad (1)$$

$$CO(NH_2)_2 + 2H_2O + Ca^{2+} \xrightarrow{Urease} 2NH_4^+ + CaCO_3 \downarrow \quad (2)$$

These reactions occur under the influence of natural environmental factors that control the activity of the urease enzyme. Factors such as the type of bacteria, bacteria cell concentration, temperature, urea concentration, calcium concentration, ionic strength, and the pH of the media may have a significant impact on MCP. The bacteria should possess high ureolytic efficiency, alkalophilic (optimum growth rate occurs at pH around 9, and no growth at all around pH 6.5), non-pathogenic, and posses the ability to deposit calcite homogeneously on the substratum. The bacteria should also have a high negative zeta-potential (Dick et al., 2006; De Muynck et al., 2007a,b) to promote adhesion and surface colonization, and produce enormous amounts of urease enzyme in the presence of high concentrations of ammonium (Kaltwasser et al., 1972; Friedrich and Magasanik, 1977) to enhance both the rate of ureolysis and MCP (Nemati and Voordouw, 2003).

Urease-catalyzed ureolysis like any other enzymatic reaction is temperature dependent. However, the optimum temperature ranges from 20 to 37 °C depending on environmental conditions and concentrations of other reactants in the system. Ferris et al. (2003), Nemati and Voordouw (2003), and Mitchell and Ferris (2005) reported that increasing the temperature from 15 to 20 °C increased rate of ureolysis, k_{urea} 5 times (from 0.18 to 0.91 d^{-1}) and 10 times greater than k_{urea} at 10 °C (0.09 d^{-1}). It can therefore be emphasized that increasing temperature within the optimum range enhances rate of ureolysis.

Nemati and Voordouw (2003) established that increasing urea and Ca^{2+} concentration beyond 36 and 90 g L^{-1} respectively do not increase the amount of $CaCO_3$ obtained by MCP. In addition, since Ca^{2+} is not likely utilized by microbial metabolic processes, it would accumulate outside the cell where it would be readily available for MCP (Silver et al., 1975).

Ionic charge influences enzymatic reactions like temperature and concentration. In bacteria transport in porous media, the total interaction energy needed by microbial particles to adhere and attach themselves to solid surfaces as explained by the classical Derjaguin–Landau–Verwey–Overbeek theory, is composed of the repulsive electrostatic forces and the attractive Van Der Waals forces. High ionic strength increases electrical double layer (EDL) compression by decreasing EDL repulsive forces leaving attractive Van Der Waals forces to dominate, and in the process promotes bacterial adhesion and attachment to the substratum (Faibish et al., 1998; Foppen and Schijven, 2006). Increase in ionic strength from 0.1 to 1.0 may increase the equilibrium constant for ammonia speciation from 9.3 to 9.4 (Martell and Smith, 1974).

A pH increase is an indication of urea hydrolysis, and is an important property of alkalophiles (optimum growth at pH 9 and no growth below pH 6.5). At any media pH, NH_3 gas and dissolved NH_4^+ exist at different concentrations. Higher concentrations of NH_3 provide favorable conditions for MCP.

The main objective of this research is to determine the optimum conditions for urease catalyzed MCP. The urease enzyme will be supplied by the soil bacteria *S. pasteurii* strain American Type Culture Collection (ATCC) 11859, and the optimum conditions will be determined by the factorial experiments. The factorial experiments will be designed based on the important factors that affect MCP as previously been outlined.

2. Materials and methods

2.1. Stock culture

S. pasteurii strain ATCC 11859, (Manassas, VA) was grown at 30 °C for 72 h with agitation in brain heart infusion (BHI) broth. After growth, cells were platted in an agar plate to confirm their viability and storage.

2.2. Culture medium

The culture medium consisted of 3 g of BHI broth, 10 g of ammonium chloride, and 2.1 g of sodium bicarbonate (Fisher Scientific, Pittsburgh, PA) per liter of distilled water. A varied amount of urea was added to the mixture and the pH was adjusted to 6.5 using 1 N HCl (Fisher Scientific, Pittsburgh, PA) before addition of a varied amount of $CaCl_2$ (Fisher Scientific, Pittsburgh, PA) to avoid premature $CaCO_3$ precipitation. The mixture was then autoclaved at 121 °C for 20 min.

2.3. Factorial experimental design

Factorial experiments were designed based on the important factors that affect MCP (Table 1). Bacterial cell concentration was varied from 10^6 to 10^8 cells mL^{-1} by dilution using ultrapure water (Milli-Q Gradient, Molsheim, France) and quantified by measuring the absorbance (optical density) of the suspension using Spectronic Genesys five Spectrophotometer (Thermo Electron Corporation, Madison, WI) at 600 nm wavelength (OD_{600}). The concentration of cells suspended in the stock culture was estimated by the expression.

$$8.59 \times 10^7 \cdot Z^{1.3627} \quad (3)$$

(Ramachandran et al., 2001), where Z is reading at OD_{600}, and Y is the concentration of cells mL^{-1}.

For each test, 20 mL of the culture medium was mixed with 10 mL of the stock culture in a beaker, and the mixture was stirred slowly using a magnetic stirrer. A pH meter (accumet AB 15, Fisher Scientific, Pittsburgh, PA) and ammonia gas electrode (Cole Parmer, Vernon Hills, IL) were then dipped into the solution in succession to measure pH and ammonia concentration (in millivolts) of the mixture. Measurements were done after 15 min, 30 min, 1 h, 3 h, 6 h, 12 h, 24 h, and every 24 h for 7 d. The ammonia gas concentration was converted to molarity using the ammonia electrode calibration curve provided by the manufacturer. Finally, NH_3 gas concentration was converted to [NH_4^+] by the equations derived from the chemistry of buffer solutions involving ammonium ion (pKa = 9.25). All experiments were done in triplicate.

Table 1
Mean k_{urea}, mean mass of $CaCO_3$ precipitated, and mean mass of CO_2 sequestrated during the factorial experiments using *S. pasteurii* strain ATCC 11859 to determine the optimum conditions for MCP. C1: 2.5 mM Ca^{2+}, C2: 25 mM Ca^{2+}, C3: 250 mM Ca^{2+}, U1: 333 mM urea, and U2: 666 mM urea. Mean mass of $CaCO_3$ is ± standard deviation. The means and standard deviations were calculated from triplicates (n = 3).

Combination	Bacteria cell concentration (cells mL^{-1})		Mean k_{urea} (d^{-1})	Mean mass of $CaCO_3$ precipitated (mg d^{-1})	Mean mass of CO_2 consumed (mg d^{-1})
C1U1	B1	8.4×10^6	0.77	–	–
	B2	7.1×10^7	0.84	–	–
	B3	2.7×10^8	0.93	–	–
C2U1	B1	5.5×10^6	0.77	5.3 ± 0.02	2.3
	B2	7.4×10^7	0.84	5.6 ± 3.17	2.5
	B3	3.1×10^8	0.91	7.1 ± 1.06	3.1
C3U1	B1	8.9×10^6	0.78	4.3 ± 0.02	1.9
	B2	7.2×10^7	0.85	7.6 ± 2.40	3.3
	B3	2.9×10^8	0.92	9.5 ± 0.89	4.2
C1U2	B1	8.7×10^6	0.78	–	–
	B2	8.2×10^7	0.84	–	–
	B3	2.7×10^8	0.90	–	–
C2U2	B1	8.2×10^6	0.77	6.2 ± 1.34	2.7
	B2	8.1×10^7	0.80	7.6 ± 2.34	3.3
	B3	3.1×10^8	0.92	8.1 ± 4.13	3.6
C3U2	B1	8.5×10^6	0.78	6.4 ± 0.28	2.8
	B2	7.5×10^7	0.84	9.5 ± 2.74	4.2
	B3	2.3×10^8	0.92	13.0 ± 1.30	5.7

2.4. Estimation of urea replenishment time

In order to determine urea replenishment time, the rate of urea hydrolysis must first be determined. The determination of k_{urea} is based on the assumption that ureolytic reactions follow a first order differential equation. By integrating this equation, and combining it with urea hydrolysis reaction stoichiometry, the rate of ureolysis, k_{urea} and the concentration of urea remaining at time t, $[urea]_t$ may be computed for each experimental combination from Eqs. (4) and (5) respectively since $[NH_4^+]_t$ and the initial urea concentration $[urea]_0$ are known.

$$[NH_4^+]_t = 2[urea]_0(1 - \exp(-k_{urea}t)) \quad (4)$$

$$[urea]_t = [urea]_0 \exp(-k_{urea}t) \quad (5)$$

3. Results and discussion

3.1. pH changes and NH_4^+ generated

The pH changes and ammonium generated during urea hydrolysis are presented in Fig. 1. The time taken for the experiments to reach equilibrium pH decreased with increase in bacterial cell concentration (Fig. 1a, c and e). There is a significant difference between the control and the inoculated experiment (Fig. 1a and b), indicating the greater influence urease enzyme has on urea hydrolysis. Ammonium production was generally constant at about 0.09 M (Fig. 1b, d and f).

3.2. Rate of urea hydrolysis, k_{urea}

Table 1 shows results from the experiments. Bacterial cell concentration and Ca^{2+} concentration were varied by an order of magnitude from 2.5 to 250 mM and 10^6 to 10^8 cells mL^{-1} for Ca^{2+} and bacteria respectively. However, urea concentration was varied by a factor of 2, from 333 to 666 mM. The k_{urea} values increased consistently with increase in bacterial cell concentration irrespective of initial urea concentration. These results show that k_{urea} is controlled much by the bacterial cell concentration.

The mean k_{urea} values obtained by bacterial cell concentrations 10^6 (B1), 10^7 (B2) and 10^8 (B3) cells mL^{-1} were statistically compared at 95% confidence limit. The results indicate that k_{urea} values obtained by B1 and B2 were not statistically different (p-value = 0.153). However, both B1 and B2 k_{urea} values were statistically different from those obtained by B3 (p-value = 0.001 and 0.017 respectively). Although individual k_{urea} values obtained by B3 were not statistically different (stdev = 0.07) as compared with B1 (stdev = 0.11) and B2 (stdev = 0.10) for all the factorial experiments, the amount of the carbonate precipitated and the speed at which the precipitation took place were significantly different, and subsequently formed the basis for acceptance or rejection of a combination. After carefully analyzing k_{urea} values and the amount of $CaCO_3$ precipitated from Table 1, combination C3U2 with the highest bacterial cell concentration (B3 = 2.3×10^8 cells mL^{-1}) was chosen as the optimum condition for MCP in this experiment. Generally, so long as all other factors are constant, higher urea, Ca^{2+} and bacterial cell concentration would enhance the amount of $CaCO_3$ precipitated and the rate of urea hydrolysis.

3.3. Estimation of urea replenishment time

The amount of urea remaining at any given time estimated by Eq. (5) is presented in Fig. 2. From this graph, it would be economical to replenish both the bacterial cell concentration and the amount of urea after approximately 80 h. In addition, our data shows the existence of a linear relationship (R^2 = 0.9048) between the bacterial cell concentration and rate of urea hydrolysis (Fig. 3). Using this relationship, the rate of urea hydrolysis could be estimated when bacterial cell concentration is known and under the same conditions. It is also worth noting that the mean k_{urea} values obtained by 333 and 666 mM urea are in approximately 1:1 ratio (Fig. 4). Subsequently, a lower amount of urea not exceeding 36 g L^{-1} would be needed to enhance the rate of urea hydrolysis and the amount of $CaCO_3$ precipitated.

3.4. Estimation of the amount of $CaCO_3$ precipitated and CO_2 sequestrated

At the end of the experiments (7 d), the carbonate precipitate was vacuum-filtered through a 0.20 μm filter paper of known mass, and then allowed to dry in air inside a Petri dish at room temperature for 4 d before being weighed. The mass of $CaCO_3$ deposited was then determined by subtracting the mass of the filter paper from the mass of filter paper with $CaCO_3$. From ureolysis and $CaCO_3$ formation stoichiometry, hydrolyzing 1 mol of urea sequestrates 1 mol of CO_2. Consequently, the amount of CO_2 sequestrated is directly proportional to the amount of $CaCO_3$ precipitated by MCP. The concentration of CO_2 was therefore calculated using a simple ratio 44/100 = X/Y which yields to $X = (44.Y)/100$ where X is the amount of CO_2 sequestrated and Y the amount of $CaCO_3$ precipitated. The results presented in Table 1 indicate that the amount of $CaCO_3$ precipitated and CO_2 sequestrated increase monotonically with bacterial cell concentration. In addition, at the same bacterial cell concentration, increasing urea and Ca^{2+} concentrations increases the amount of carbonate precipitated. At 25 mM Ca^{2+} concentration, increasing bacterial cell concentration from 10^6 to 10^8 cells mL^{-1} increases the $CaCO_3$ precipitated and CO_2 sequestrated by more than 30%. However, when Ca^{2+} concentration is increased 10-fold to 250 mM Ca^{2+}, the $CaCO_3$ precipitated and CO_2 sequestrated increased by over 100% irrespective of urea concentration. This result indicates that the amount of $CaCO_3$

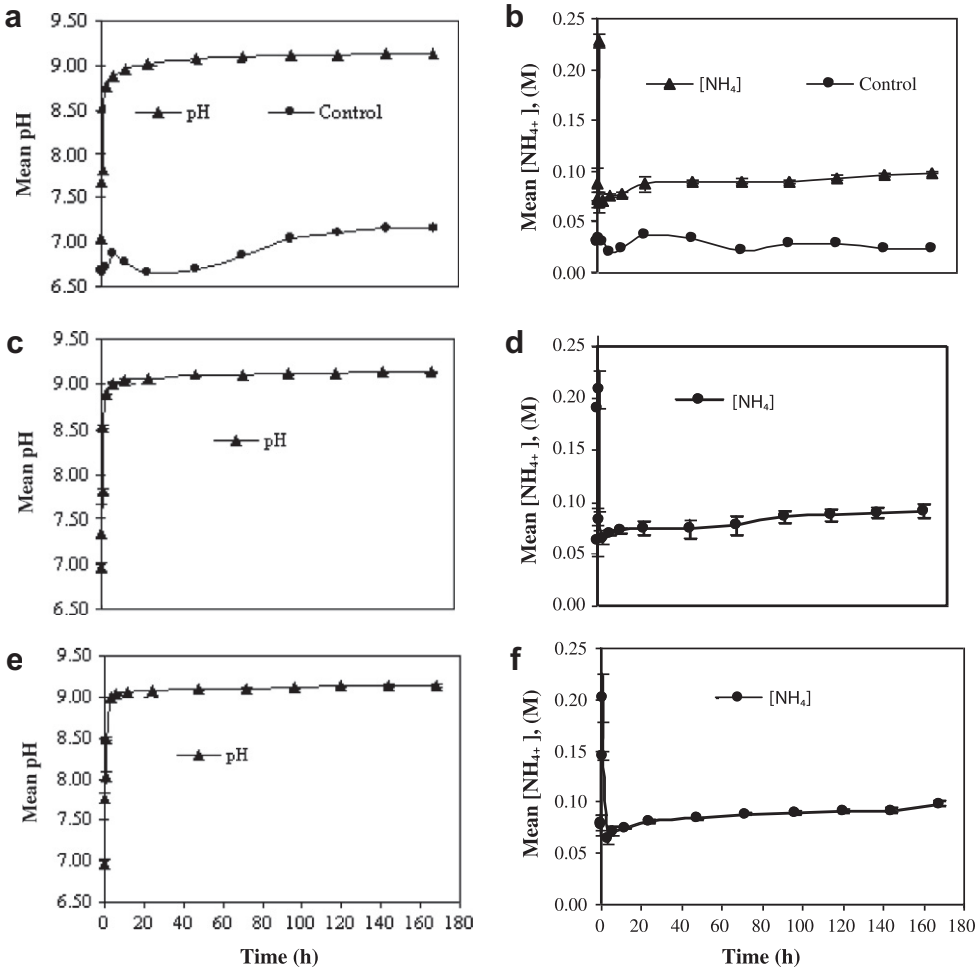

Fig. 1. Graphical representation of changes in mean pH and $[NH_4^+]$ generated during urea hydrolysis: (a) and (b) at 8.5×10^6 cells mL^{-1}, (c) and (d): at 7.5×10^7 cells mL^{-1}, (e) and (f): at 2.3×10^8 cells mL^{-1}. (a) Takes longer time to reach pH 9 than (c) and (e).

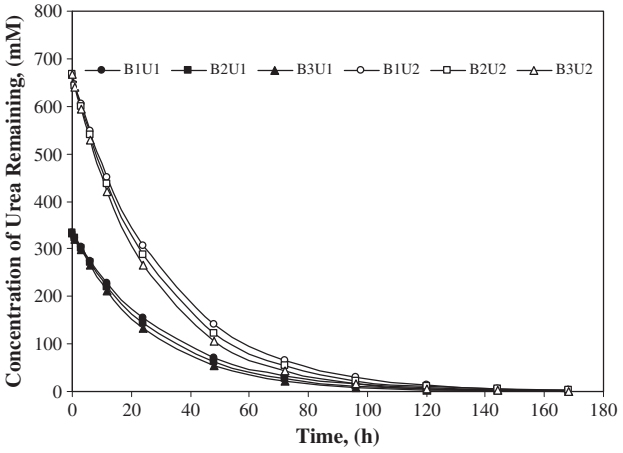

Fig. 2. Estimation of the concentration of urea remaining at any given time using *S. pasteurii* strain ATCC 11859. B1, B2 and B3 are bacterial cell concentrations at 8.9×10^6, 7.2×10^7 and 2.9×10^8 cells mL^{-1} respectively for combination C3U1, and 8.5×10^6, 7.5×10^7, and 2.3×10^8 cells mL^{-1} respectively for combination C3U2. U1 and U2 are initial urea concentrations at 333 mM and 666 mM respectively.

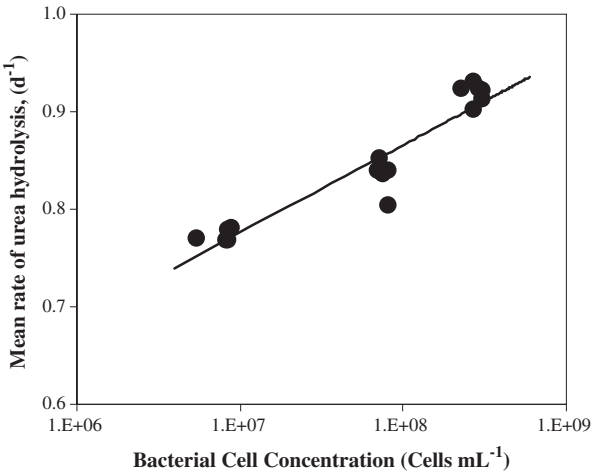

Fig. 3. Variation of bacterial cell concentration (cells mL^{-1}) with mean rate of urea hydrolysis (k_{urea}).

precipitated and CO_2 sequestrated depend more on the Ca^{2+} concentration than the amount of urea.

3.5. X-ray Diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray analysis

X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX) analysis of the precipitated

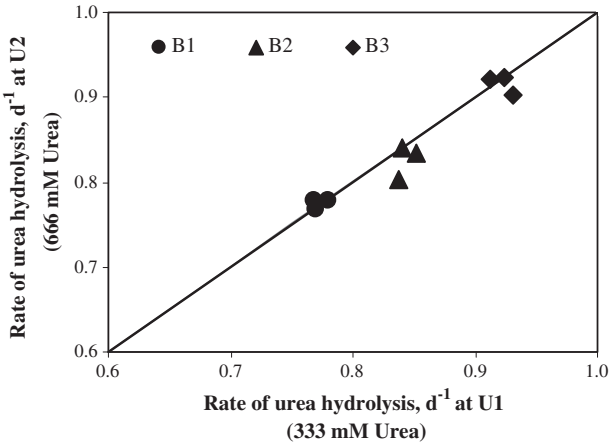

Fig. 4. A comparison between mean rate of urea hydrolysis (k_{urea}) obtained by U1 (333 mM urea) and U2 (666 mM urea) at bacterial cell concentrations B1 (10^6 cells mL^{-1}), B2 (10^7 cells mL^{-1}) and B3 (10^8 cells mL^{-1}).

calcium carbonate powder are given in Fig. 5. The $CaCO_3$ precipitate is composed of calcite and vaterite crystals (Fig. 5a) but predominantly calcite with a rhombohedra crystalline structure (Fig. 5b). The EDX (Fig. 5c) peaks show that the elemental composition of the precipitate is mostly calcium, carbon and oxygen. This is further evidence that the precipitate formed is calcium carbonate.

4. Conclusions

The rate of urea hydrolysis, k_{urea} and the amount of $CaCO_3$ precipitated formed the basis of selecting the optimum conditions for MCP. Our results indicate that k_{urea} is dependant more on the bacterial cell concentration than initial urea concentration so long as there is enough urea to sustain the bacteria. The bacterial cell concentration, initial urea concentration and Ca^{2+} concentration all influence the amount of $CaCO_3$ precipitated and CO_2 sequestrated. At 25 mM Ca^{2+} concentration, increasing bacterial cell concentration from 10^6 to 10^8 cells mL^{-1} increased the $CaCO_3$ precipitated and CO_2 sequestrated by over 30%. However, when Ca^{2+} concentration was increased 10-fold to 250 mM Ca^{2+}, the $CaCO_3$ precipitated and CO_2 sequestrated increased by over 100% irrespective of initial urea concentration. Consequently, the optimum condition for MCP for this work are 250 mM Ca^{2+}, 666 mM urea (combination C3U2), and the highest bacterial cell concentration (B3 = 2.3×10^8 cells mL^{-1}). These results also indicate that a greater amount of $CaCO_3$ would be precipitated with greater concentrations of urea, Ca^{2+}, and bacterial cells so long as these quantities are within their economic advantage. XRD, SEM and EDX analysis confirmed that the precipitate formed was $CaCO_3$, and composed of predominantly calcite crystals with little vaterite crystals.

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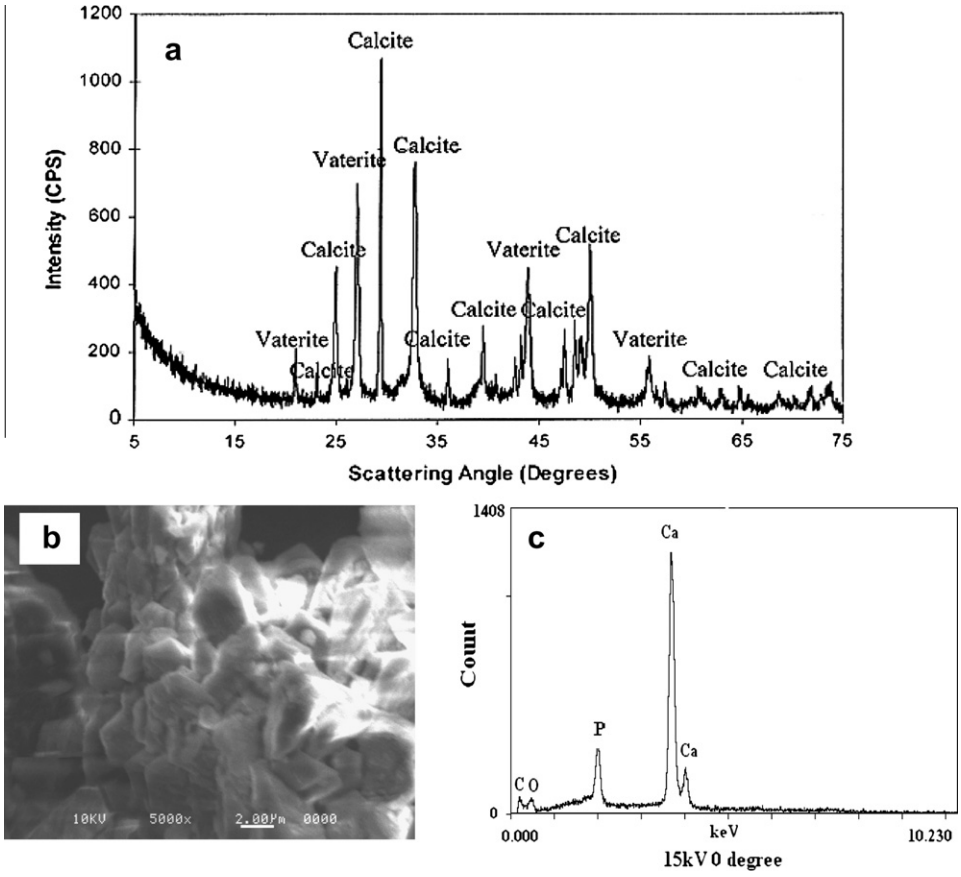

Fig. 5. The X-ray Diffraction at a continuous scanning rate of 2° min^{-1}: (a) Scanning Electron Microscopy (b) at 5000× magnification, and Energy Dispersive X-ray and (c) analysis of the precipitated calcium carbonate powder.

References

Bachmeier, K.L., Williams, A.E., Warmington, J.R., Bang, S.S., 2002. Urease activity in microbiologically-induced calcite precipitation. J. Biotechnol. 93, 171–181.

Bang, S.S., Galinat, J.K., Ramakrishnan, V., 2001. Calcite precipitation induced by polyurethane-immobilized *Bacillus pasteurii*. Enzyme Microb. Technol. 28, 404–409.

Castanier, S., Le Metayer-Levrel, G., Perthuisot, J.-P., 1999. Ca-carbonates precipitation and limestone genesis – the microbiogeologist point of view. Sediment. Geol. 126, 9–23.

De Belie, N., De Muynck, W., Verstraete, W., 2006. A synergistic approach to microbial presence on concrete: cleaning and consolidating effects. Struct. Concr. 7, 105–109.

De Muynck, W., Cox, K., De Belie, N., 2007a. Bacterial carbonate precipitation reduces the permeability of cementitious materials. In: Chun, Y.-M., Claisse, P., Naik, T.R. (Eds.), Sustainable Construction Materials and Technologies. Taylor & Francis Group, London, pp. 411–416.

De Muynck, W., De Belie, N., Verstraete, W., 2007b. Improvement of concrete durability with the aid of bacteria. In: Proceedings of the 1st International Conference on Self Healing Materials, Noordwijk aan Zee, The Netherlands, April 18–20, 2007.

De Muynck, W., De Belie, N., Verstraete, W., 2010. Microbial carbonate precipitation in construction materials: a review. Ecol. Eng. 36, 118–136.

DeJong, J.T., Fritzges, M.B., Nusslein, K., 2006. Microbially induced cementation to control sand response to undrained shear. J. Geotech. Geoenviron. Eng. 132, 1381–1392.

DeJong, J.T., Mortensen, B.M., Martinez, B.C., Nelson, D.C., 2010. Bio-mediated soil improvement. Ecol. Eng. 36, 197–210.

Dick, J., De Windt, W., De Graef, B., Saveyn, H., Van der Meeren, P., De Belie, N., Verstraete, W., 2006. Bio-deposition of a calcium carbonate layer on degraded limestone by *Bacillus* species. Biodegradation 17, 357–367.

Ercole, C., Cacchio, P., Botta, A.L., Centi, V., Lepidi, A., 2007. Bacterially induced mineralization of calcium carbonate: the role of exopolysaccharides and capsular polysaccharides. Microsc. Microanal. 13, 42–50.

Faibish, R.S., Elimelech, M., Cohen, Y., 1998. Effect of interparticle electrostatic double layer interactions on permeable flux decline in crossflow membrane filtration of colloidal suspensions: an experimental investigation. J. Colloid Interf. Sci. 204, 77–86.

Ferris, F.G., Stehmeier, L.G., 1992. Bacteriogenic Mineral Plugging. USA Patent 5, 143, 155. US Patent Office, Washington, DC.

Ferris, F.G., Beveridge, T.J., Fyfe, W.S., 1986. Iron–silica crystallite nucleation by bacteria in a geothermal sediment. Nature 320, 609–611.

Ferris, F.G., Fyfe, W.S., Beveridge, T.J., 1987. Bacteria as nucleation sites for authigenic minerals in metal-contaminated lake sediment. Chem. Geol. 63, 225–232.

Ferris, F.G., Wiese, R.G., Fyfe, W.S., 1994. Precipitation of carbonate minerals by microorganisms: implications of silicate weathering and the global carbon dioxide budget. Geomicrobiol. J. 12, 1–13.

Ferris, F.G., Phoenix, V., Fujita, Y., Smith, R.W., 2003. Kinetics of calcite precipitation induced by ureolytic bacteria at 10–20 °C in artificial groundwater. Geochim. Cosmochim. Acta 67, 1701–1722.

Foppen, J.W.A., Schijven, J.F., 2006. Evaluation of data from the literature on the transport and survival of *Escherichia coli* and thermotolerant coliforms in aquifers under saturated conditions. Water Res. 40, 401–426.

Friedrich, B., Magasanik, B., 1977. Urease of *Klebsiella aerogenesis*: control of its synthesis by glutamine synthetase. J. Bacteriol. 8, 313–322.

Fujita, Y., Ferris, F.G., Lawson, R.D., Colwell, F.S., Smith, R.W., 2000. Calcium carbonate precipitation by ureolytic subsurface bacteria. Geomicrobiol. J. 17, 305–318.

Ghosh, P., Mandal, S., Chattopadhyay, B.D., Pal, S., 2005. Use of microorganism to improve the strength of cement mortar. Cem. Concr. Res. 35, 1980–1983.

Gollapudi, U.K., Knutson, C.L., Bang, S.S., Islam, M.R., 1995. A new method for controlling leaching through permeable channels. Chemosphere 30, 695–705.

Hammes, F., Boon, N., De Villiers, J., Verstraete, W., Siciliano, S.D., 2003. Strain-specific ureolytic microbial calcium carbonate precipitation. Appl. Environ. Microbiol. 69, 4901–4909.

Ivanov, V., Chu, J., 2008. Applications of microorganisms to geotechnical engineering for bioclogging and biocementation of soil in situ. Rev. Environ. Sci. Biotechnol. 7, 139–153.

Jimenez-Lopez, C., Jroundi, F., Pascolini, C., Rodriguez-Navarro, C., Pinar-Larrubia, G., Rodriguez-Gallego, M., Gonzalez-Munoz, M.T., 2008. Consolidation of quarry calcarenite by calcium carbonate precipitation induced by bacteria activated among the microbiota inhabiting the stone. Int. Biodeterior. Biodegrad. 62, 352–363.

Jonkers, H.M., Thijssen, A., Muyzer, G., Copuroglu, O., Schlangen, E., 2010. Application of bacteria as self-healing agent for the development of sustainable concrete. Ecol. Eng. 36, 230–235.

Kaltwasser, H., Kramer, J., Conger, W.R., 1972. Control of urease formation in certain aerobic bacteria. Arch. Microbiol. 81, 178–196.

Knorre, H., Krumbein, K.E., 2000. Bacterial calcification. In: Riding, R.E., Awramik, S.M. (Eds.), Microbial Sediments. Springer-Verlag, Berlin, Germany, pp. 25–31.

Le Metayer-Levrel, G., Castanier, S., Orial, G., Loubiere, J.-F., Perthuisot, J.-P., 1999. Applications of bacterial carbonatogenesis to the protection and regeneration of limestones in buildings and historic patrimony. Sediment. Geol. 126, 25–34.

Manning, D.A.C., 2008. Biological enhancement of soil carbonate precipitation: passive removal of atmospheric CO_2. Mineral. Mag. 72, 639–649.

Martell, A., Smith, R., 1974. Critical Stability Constants. Plenum Press, New York.

McConnaughey, T.A., Whelan, J.F., 1997. Calcification generates protons for nutrient and bicarbonate uptake. Earth Sci. Rev. 42, 95–117.

Mitchell, A.C., Ferris, F.G., 2005. The coprecipitation of Sr into calcite precipitates induced by bacterial ureolysis in artificial groundwater: temperature and kinetics dependence. Geochim. Cosmochim. Acta 69, 4199–4210.

Nemati, M., Voordouw, G., 2003. Modification of porous media permeability using calcium carbonate produced enzymatically in situ. Enzyme Microb. Technol. 33, 635–642.

Ramachandran, S.K., Ramakrishnan, V., Bang, S.S., 2001. Remediation of concrete using microorganisms. ACI Mater. J. 98, 3–9.

Rodriguez-Navarro, C., Rodriguez-Gallego, M., Chekroun, K.B., Gonzalez-Munoz, M.T., 2003. Conservation of ornamental stone by *Myxococcus xanthus*-induced carbonate biomineralization. Appl. Environ. Microbiol. 69, 2182–2193.

Schultze-Lam, S., Fortin, D., Beveridge, T.J., 1996. Mineralization of bacterial surfaces. Chem. Geol. 132, 171–181.

Silver, S., Toth, K., Scribner, H., 1975. Facilitated transport of calcium by cells and subcellular membranes of *Bacillus subtilis* and *Escherichia coli*. J. Bacteriol. 122, 880–885.

Stocks-Fischer, S., Galinat, J.K., Bang, S.S., 1999. Microbiological precipitation of $CaCO_3$. Soil Biol. Biochem. 31, 1563–1571.

Tiano, P., Biagiotti, L., Mastromei, G., 1999. Bacterially bio-mediated calcite precipitation for monumental stones conservation: methods of evaluation. J. Microbiol. Methods 36, 139–145.

Tiano, P., Cantisani, E., Sutherland, I., Paget, J.M., 2006. Biomediated reinforcement of weathered calcareous stones. J. Cult. Herit. 7, 49–55.

Whiffin, V.S., Van Paassen, L.A., Harkes, M.P., 2007. Microbial carbonate precipitation as a soil improvement technique. Geomicrobiol. J. 24, 417–423.