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Modeling of Microbial Induced Carbonate Precipitation in Porous Media

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The latest researches show that certain types of microorganism can obviously accelerate the precipitation of calcium carbonate (MICP) in porous media, and therefore effectively improve the strength of material. In this new technology, bacterium solution and nutrient salt solution are in-situ transported to the pores of porous media to induce the process of MICP, and it will have important application prospects in restoration of ancient masonry heritages and in foundation improvement. In this paper, a detailed mathematical model for the MICP process in porous media, considering both the bio-chemical reaction and solute transport, is described based on convection-diffusion-reaction equation and crystallization theory. Three different types of microbial induced calcium carbonate crystal are distinguished in the model. 1D finite element simulations based on this model are carried out for the MICP process in sand columns. . Comparisons of model results to experimental results are made for the validation of the model.

Key words: Microbial induced carbonate precipitation, Bio-chemical reaction, Solute transport, finite element model; porous media.

Recent research has found that certain types of microorganism can obviously accelerate the natural process of diagenesis. For instance, Sporosarcinapasteurii, which produces urease, is able to induce carbonate precipitation in a short amount of time through a series of microbial-chemical reactions, given that urea and calcium is provided. This discovery introduces new concepts of foundation reinforcement in construction field. If certain types of bacterial and nutrition solution are grouted into the pores of foundation soil, the formation of calcium carbonate precipitation will effectively fill the pores and bond soil particles together, therefore improves the strength of soil. The construction process can be called as bio-grout method. With the concept, Whiffinformed sand columns in the laboratory which had a height of 20cm and uniaxial compression strengths range from 0.2MPa to 20MPa[1](Whiffin *et al*., 2007). Leon applied the method of biogrout to sand column with height of 5 m, and sand foundations with volume of 1 m^3 and 100 m^3, respectively (Leon *et al*., 2008). The results of which verified the feasibility of applying biogrout to foundation reinforcement.

Compared with traditional chemical grouting materials, biogrout materials possess the advantage of low viscosity and high fluidity, which is able to enhance the effective distance of a single grouting point, therefore reducing economic costs.

Meanwhile, microorganism has low energy consumption, low emission and no negative effect on human body. The harmful ions

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formed in the reinforcement process, such as Ammonium ion, are able to be eliminated with special methods. Therefore, biogrout is hopefully an environment-friendly ground reinforcement method.

The method is especially useful for the reinforcement of liquefiable foundation, for this purpose the improved liquefiable foundation usually needs a uniaxial compression strength of 100-200kPa, which is relatively low compared with other ground improvement works. Besides, other than calcium carbonate formed among particles, those formed in pore solution away from particles also contributes to strength enhancement for liquefied foundation. This is because calcium carbonate in the solution is able to reduce porosity and therefore increase the liquefaction-resistance ability. The ability is also enhanced by the air formed while grouting, for it can reduce the saturation of the sand soil. All these reasons show that biogrout can be very powerful in dealing with reinforcement of liquefied foundation.

The research group from Department of Civil Engineering, Tsinghua University, has done a series of works focusing on the improvement of property of soil materials using microorganism. The control of calcium carbonate formation in sand column has been accomplished, and some in-situ test has been done. Based on these work, a further research about the key technology in reinforcement of liquefiable foundation using biogrout is carried out. An essential part of the research is to deal with the nonuniformity of calcium carbonate distribution. Leonfound an obvious nonuniformity of calcium carbonate distribution in their large scale experiments (Leon *et al.*, 2008). The reasons include the inhomogeneity of nutrient transport, the distribution of microorganism, the nonuniformity of transport path, etc. For high precision constructions such as foundations of high-speed railway, the large nonuniformity of strength is forbidden. The inhomogeneity of reinforcement also makes the quality and cost control a much more difficult job. Therefore, the paper introduces a detail mathematical model of the process of MICP, based on convection-diffusion-reaction equation and crystallization theory. A 1D finite element simulation of biogrout in sand column is made, and the verification of the method is made with existing experiment data. Based on the model, the paper presents a preliminary study of the main factors affecting the nonuniformity and the way of improvement. The paper has important significance for the application of biogrout on liquefiable foundation improvement.

The biochemical processes of micp within porous medium (leon *et al.*, 2009; jason *et al.*, 2010)

The organism used in our experiments is called Sporosarcinapasteuriiÿwhich is a alkaliphiles, it can produce urease to catalyze the hydrolysis of urea, producing ammonium (NH_4^+) and carbonate ions(CO_3^{2-})according to Eq. (1).The products further react into a wide range of dissolved species according to Eq. (2), Eq. (3) and Eq. (4).

$$NH_2-CO-NH_2+3H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad ...(1)$$

$$H^+ + CO_3^{2-} \rightleftarrows HCO_3^- \quad ...(2)$$

$$NH_4^+ \rightleftarrows NH_3 + H^+ \quad ...(3)$$

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^- \quad ...(4)$$

Meanwhile,decomposition of water in the porous medium can react according to Eq. (5),

$$H_2O \rightleftarrows H^+ + OH^- \quad ...(5)$$

Usually, in water with a PH value of around 7, Bicarbonate ions (HCO_3^-) surpasses Carbonate ions (CO_3^{2-}) in the ability of existence. Hence, Eq. (2) tends to the right direction. The reduction of H^+ allows Eq. (3), Eq. (4), Eq. (5) heading towards the direction of Producing more H^+, until the Eq.s above reach the equilibrium. In general, the hydrolysis of urea will consume the H^+ in the environment, resulting a higher concentration of Hydroxide ion (OH^-) and hence a higher PH value. With the calcium ion (Ca^{2+}) from porous medium, further reactions can happen according to Eq. (6), Eq. (7) and Eq. (8),

$$Ca^{2+} + HCO_3^- \rightleftarrows CaHCO_3^+ \quad ...(6)$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(aq) \quad ...(7)$$

$$Ca^{2+} + OH^- \rightleftarrows CaOH^+ \quad ...(8)$$

After the concentration of $CaCO_3$ (aq) surpassing its solubility, the calcium carbonate can be precipitated according to Eq. (9),

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(\downarrow) \quad ...(9)$$

Unlike the transport-reaction process of biogrout which is counted in the magnitude of hours, the reaction of Eq. (2) to Eq. (8) finishes instantaneous. Therefore, it is reasonable to assume that the reactions above are in the condition of dynamic equilibrium at any time. The transient equilibrium value is decided by the hydrolysis rate of urea, the precipitation rate of calcium carbonate and the equilibrium constants of each reaction. For reactions of the typical form: A+B’!C+D, the reaction rate can be written as C_AC_B-C_CC_D·10^{pK}=0, where k is a reaction constant, C is the concentration of reactants or resultants, pK is the equilibrium constant of the reaction. When the reaction reaches an equilibrium (r=0),C_AC_B-C_CC_D·10^{pK}=0. Table 1 shows the equilibrium constants, reaction constants and reaction rates in Eq. (2) to Eq. (8). Where a_i represents the product of activity coefficient and concentration of ion i, the hydrolysis rate of urea and the precipitation rate of calcium carbonate will be discussed in Section 2 of the paper.

Table 1. Constants and reaction rates for the equilibriums included in this model (Parkhurst, 1995)

Eq.	Reaction rate
(2)	$r_2 = 10^{12} \times (a_{CO_3^{2-}} a_{H^+} - a_{HCO_3^-} 10^{-10.329})$
(3)	$r_3 = 3 \times 10^5 \times (a_{H^+} a_{HCO_3^-} - a_{CO_2} 10^{9.25})$
(4)	$r_4 = 3 \times 10^5 \times (a_{CO_2} a_{OH^-} - a_{HCO_3^-} 10^{6.681})$
(5)	$r_5 = 10^{12} \times (a_{NH_3} a_{H^+} - a_{NH_4^+} 10^{14})$
(6)	$r_6 = 10^{12} \times (a_{CaOH^+} a_{H^+} - a_{Ca^{2+}} 10^{0.42})$
(7)	$r_7 = 10^{12} \times (a_{CaHCO_3^+} a_{Ca^{2+}} a_{CO_3^{2-}} - a_{H^+} 10^{-3.22})$
(8)	$r_8 = 10^{12} \times (a_{CaCO_3} - a_{Ca^{2+}} a_{CO_3^{2-}} 10^{-1.22})$

Eq. (1) to Eq. (9) altogether set up the biochemical reaction system of MICP. Meanwhile, in reality, diffusion, convection and adsorption of ions, as well as the complex internal structure of porous media will make the system quite complicated. Thus, in order to get a deeper understanding of the variance and distribution of calcium carbonate, it is necessary to simulate the process in more details.

Modeling of MICP

Hydrolysis Rate of Urea

Factors that affects the hydrolysis rate of urea in porous media includes concentration of urea and calcium ion, PH value, temperature, aging of microorganism, insulation of nutrients by calcium carbonate crystals . Leonstudied the impact of these factors on the hydrolysis rate of urea (Leon, 2009). Table 2 shows the details, where r represents the real hydrolysis rate of urea, r_0 is the optimal hydrolysis rate considering this factor. It can be shown that the hydrolysis rate of urea increases with the rise of temperature and concentration of urea. Meanwhile, calcium ion inhibits the hydrolysis rate of urea, with an optimal value of 43% when the concentration of calcium ion reaches 500mMÿ$K_{37\%,Ca2+}$ is 0.6M ÿ0Later in this paper it is suggested that the inhibition of calcium ion towards hydrolysis rate of urea is an important factor that affects the distribution and variance of calcium carbonate on the grouting path. If the PH value drops out of [pH_{LL}, pH_{UL}] interval, the hydrolysis rate of urea would reduce significantly. The results of Leon (Leon, 2009) will be used in this paper to calculate the variation of the hydrolysis rate of urea. Since data of the precipitation quantity of calcium carbonate is not mentioned, it is assumed that the term exp[-t/t_d] has already included the influence. Assume that the factors in Table 2 are independent and r_0 is the initial hydrolysis rate, then the hydrolysis rate of urea can be presented as,

$$\frac{r}{r_0} = \frac{C_{urea}}{K_{m,urea} + C_{urea}} \cdot \frac{1 + 2 \cdot 10^{0.5(pH_{LL} - pH_{UL})}}{1 + 10^{(pH - pH_{UL})} + 10^{(pH_{LL} - pH)}} \cdot \exp(-C_{Ca^{2+}} / K_{37\%,Ca^{2+}}) \cdot \exp[(T - T_0)\frac{\ln Q_{10}}{10}] \cdot \exp[-\frac{t}{t_d}] \qquad \text{...(10)}$$

In this paper, the results of Leon (Leon, 2009) will be used to prove the rationality of modeling. However, it is necessary to point out that the strains and culture conditions used by Whiffin and Leon van Paassen may not be exactly the same. This should be taken into account when analyzing the results of numerical simulation.

Crystal Type and Precipitation Rate of Calcium Carbonate

The precipitation and crystallization of calcium carbonate is not decided only by the equilibrium constant from Eq. (9), because the amount of different allotropes of calcium carbonate may affect the whole process. Usually, the crystal type of calcium carbonate includes Calcite, Vaterite, Aragonite, Amorphous calcium carbonate (ACC), MCC and HCC, etc. Meanwhile, according to

Table 2. Environmental Impact on hydrolysis rate of urea

Environment factors	Rates of the impact	Remark
Concentration of urea	$\frac{r}{r_0}=\frac{C_{urea}}{K_{m,urea}+C_{urea}}$	C_{urea}: urea concentration $K_{m,urea}$: urea concentration when the hydrolysis rate become 50%.
pH value	$\frac{r}{r_0}=\frac{1+2\cdot 10^{0.5(pH_{LL}-pH_{UL})}}{1+10^{(pH-pH_{UL})}+10^{(pH-pH_{LL})}}$	pH: pH value of the solutionpH_{LL}, pH_{UL}: The lower limit and upper limit of PH values when the hydrolysis rate is reduced by 50%.
Concentration of Ca^{2+}	$\frac{r}{r_0}=\exp(-C_{Ca^{2+}}/K_{37\%,Ca^{2+}})$	C_{Ca2+}: Concentration of calcium ion$K_{37\%,Ca2+}$: Hydrolysis rate of urea when hydrolysis rate of urea become 37%.
Temperature	$\frac{r}{r_0}=\exp[(T-T_0)\frac{\ln Q_{10}}{10}]$	Q_{10}=3.4, when T_0=25°C.
Microbial decay/ decomposition	$\frac{r}{r_0}=\exp[-\frac{t}{t_d}]$	t:Time usedt_d: Time used when hydrolysis rate of urea become 37%.
Nucleation of MICP	$\frac{r}{r_0}=\exp[-\frac{S_{CaCO_3}}{S_d}]$	S_{CaCO3}: Total MICP S_d: the amount of MICP when hydrolysis rate of urea become 37%.

Whiffin (Whiffin, 2004), Leon (Leon, 2009) and Jiyun (Jiyun *et al.*, 2008), scanning electron microscope (SEM) of the MICP samples only showed the existence of Calcite, Vaterite and ACC. Thus, the paper assumes that only these three types of calcium carbonate are formed in the biogrout process. Among the three, Calcite possesses the best stability and density, while ACC has the worst. It is widely believed that the precipitation morphology of calcium carbonate greatly influences the strength of MICP improved material. So in this paper, the precipitation rate and quantity of three types of calcium carbonate is going to be calculated separately.

The precipitation rate of calcium carbonate can be presented as (Nancollas *et al.*, 1971),

$$r_p = k_p(S-1)^2 \qquad ...(11)$$

Table 3. Parameters used for the hydrolysis rate of urea in this model

$K_{m,urea}$	pH_{LL}	pH_{UL}	$K_{37\%,Ca^{2+}}$	T_0	Q_{10}	t_d
55mM	5	9.5	0.6M	25°C	3.4	14 day

Where k_p is the precipitation rate constant (mol/L·h), S is the supersaturation degree of calcium carbonate in the solution. k_p is decided by the type, nucleus quantity and growth speed of the crystal. Previous research has shown that microorganism actually acts as the nucleus in the crystallization of calcium carbonate. For siliceous sand, it is assumed that the quantity of crystal nucleus N remains constant, which is equal to the number of bacteria. At the same time, it is assumed that the crystalline grows in a spherical form, with a radius of R. The growth speed of crystalline can be presented as (Sohnel *et al.*, 1982),

$$r_g = \frac{dR}{dt} = k_g(S-1)^2 \quad ...(12)$$

Where k_g is the growth constant (m/s), S is the supersaturation degree of calcium carbonate in the solution, which can be calculated by the following equations:

$$S = \sqrt{\frac{IAP}{K_{sp}}} \quad ...(13)$$

$$IAP = \gamma_{Ca^{2+}} C_{Ca^{2+}} \gamma_{CO_3^{2-}} C_{CO_3^{2-}} \quad ...(14)$$

$$\log \gamma_{Ca^{2+}} = \log \gamma_{CO_3^{2-}} = -2 \cdot \left(\frac{\sqrt{IS}}{1+\sqrt{IS}} - 0.3IS\right);\ IS = 0.5 \sum_i C_i z_i \quad ...(15)$$

Where LAP is the ion activity products of Ca^{2+} and CO_3^{2-} (mol^2/L^2) , γ_i is the activity coefficient of iron *i*, C_i is the concentration of ion *i* (mol/L), z_i is the valence of ion i,K_{sp} is the solubility of the specific type of calcium carbonateÿ IS is depend on the concentration of all the ion in the solution. The solubility product depend on the type of calcium carbonate, for Calcite, Vaterite and ACC, the solubility product K_{sp} is decided according to Eq. (16) Eq. (17) and Eq. (18) (Plummer *et al.*, 1982; Breèeviæ *et al.*,1989).

$$\log K_{sp} = -171.9065 - 0.077993T + 2839.319/T + 71.595 \log T \quad ...(16)$$

$$\log K_{sp} = -172.1295 - 0.077993T + 3074.688/T + 71.595 \log T \quad ...(17)$$

$$\log K_{sp} = -6.1987 + 0.00053369t + 0.0001096t^2 \quad ...(18)$$

Where t is in Fahrenheit and T is in Kelvin. Under the same condition, the precipitation rate of Calcite, Vaterite and ACC may not be the same because of the difference in solubility and therefore supersaturation. The difference can be presented by k_g mathematically. The relationship between temperature and the growth constant of Calcite and Vaterite is shown in Figure 1. For 25 °C, the growth constant of Calcite is 1.2×10^{-11} m/s, while that of Vaterite is 5×10^{-9} m/s. The growth constant of ACC is usually larger than the former two(Leon, 2009).

Figure 1 indicates that the precipitation rate of Vaterite will be much larger than that of Calcite in the same solution (i.e. the same the solubility product), if the supersaturation degree of Calcite surpasses 2.5. However, if the solubility product is relatively low (also results in a low supersaturation degree), the precipitated calcium carbonate will be mainly Calcite. This is one of the main reasons that cause the variance of crystal morphology of calcium carbonate on the biogrout path mentioned in (Ferris*et al.*, 1992; Leon, 2009). The paper assumes that there always exits the three types of crystal morphology in porous media (as long as the relating supersaturation degree is larger than 1), and distinguishes the three types on both quantity and distribution.

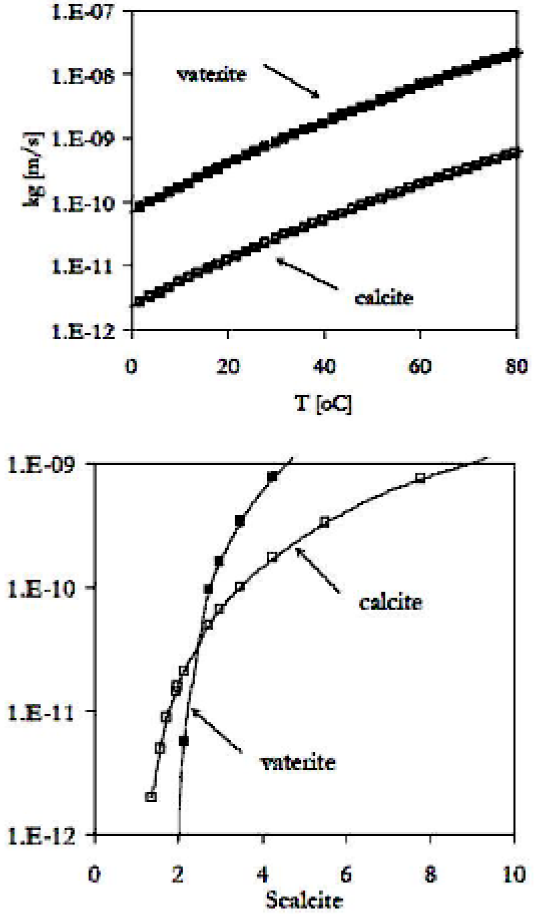

Fig. 1. Solubility product as a function of temperature and solubility of calcite

The precipitation rate of a certain type of calcium carbonate can be calculated if the growth speed of a single crystal is known. The radius R of a single crystal is calculated by Eq. (12). Thus, the surface area of a single crystal is $A_c=4\rightarrow R^2$, and the precipitation rate of the integrity is shown as,

$$r_p=\frac{dS_{CaCO_3}}{dt}=\frac{\rho_c}{M_c}A_c\frac{dR}{dt}N=4\pi R^2k_g\frac{\rho_c}{M_c}N(S-1)^2 \quad ...(19)$$

The precipitation rate constant in Eq. (11) can be presented by,

$$k_p=4\pi R^2k_g\frac{\rho_c}{M_c}N \quad ...(20)$$

Where ρ_c is the density of calcium carbonate minerals, which is 2.71 t/m^3, 2.54 t/m^3 and 2.23 t/m^3 for Calcite, Vaterite and ACC, respectively. M_c is the molar mass of calcium carbonate, which is 100.09 g/mol. According to Eq. (11) to Eq. (20), we can calculate the precipitation rate of each three types of calcium carbonate and its final precipitation ratio.

Differential Equation of Porosity

With the increasing precipitation of calcium carbonate, the porosity of porous media will become smaller, which can be described by the following differential equation,

$$\frac{\partial n}{\partial t}=-\frac{m_{CaCO_3}}{\rho_{CaCO_3}}\frac{\partial C_{CaCO_3}}{\partial t}=-\sum_{i=1,2,3}\left(\frac{m_{CaCO_3}}{\rho_{CaCO_3}}nr_p\right)_i \quad ...(21)$$

Where m_{CaCO3} is the molar mass of calcium carbonate, ρ_{CaCO3} is the density calcium carbonate, subscript i indicates the crystal type of calcium carbonate.

Percolation Differential Equation

Suppose that the soil and solution are incompressible. Then, in a certain amount of time, the volume of outflow equals to the reduction of pore volume. The percolation differential equation can be written as,

$$\nabla q=-\frac{\partial n}{\partial t} \quad ...(22)$$

$$q=-\frac{k}{\mu}\nabla(p+\rho_f gz) \quad ...(23)$$

Where k is the permeability of porous media, μ is the dynamic viscosity of fluid. The density of fluid within the pores changes with biochemical reactions, which causes density flow. This means that we need to take the whole process of biochemical reactions and the couple between reactions and convection into consideration. At the temperature of 20 °C, assume that the density of the solution only depend on the concentration of urea, calcium and ammonium ion (Bear, 1972).

$$\rho_f=1000+15.4996C_{urea}+86.7338C_{Ca^{2+}}+15.899C_{NH_4^+} \quad ...(24)$$

The permeability k is affected by porosity n, as is shown by the Kozeny-Carman Relationship (Bear, 1972),

$$k=\frac{d_{50\%}^2}{180}\frac{n^3}{(1-n)^2} \quad ...(25)$$

Where $d_{50\%}$ is the average diameter of the particles.

Finite element modeling og biogrout in porous media

The process of biogrout in porous media is actually a solution-transport-reaction-precipitation problem of multi-component (gas, solid, liquid) biochemical reaction system. It is a very complicated system, including the absorption/desorption of different ions. Based on the transport theory of solutes in porous media, a 1D numerical model is set up using Eq. (1) to Eq. (9). The basic formula is the convection-diffusion-reaction equation,

$$\frac{\partial nC_i}{\partial t}=\frac{\partial}{\partial x}\left(nD\frac{\partial C_i}{\partial x}\right)-\frac{\partial}{\partial x}(nuC_i)+n\sum_{k=1}^{N}r_k \quad ...(26)$$

Where n is the porosity; D is the diffusion coefficient; C is the concentration of component i in the solution; u is the actual flow rate of fluid inside the pores; r_k represents the concentration change of reagent i caused by reagent k (bio/chemical) within a unit time. The first item on the right of the equation represents diffusion, while the second item refers to convection and the third microbial-chemical reactions. For 1D problems, the diffusion coefficient D can be represented by the product of longitudinal diffusion coefficient $á_L$ (m) and flow rate u, i.e. $D=á_L u$. For reaction terms, the major concern should be focus on the reactions in Eq. (1) to Eq. (9) and the surface absorption of porous media. The main ions simulated in the paper includes H^+, CO_3^{2-}, HCO_3^-, OH^-, NH_4^+, NH_3, CO_2, Ca^{2+}, $CaHCO_3^+$, Urea and Cl^-. Since the amount of liquid calcium carbonate in the solution is very small compared with that of solid one, it is assumed that there exists only solid calcium carbonate in the solution. Thus, we use Eq. (9) for modeling, whereas Eq. (7) is neglected. For the reagent i, the mass absorbed by unit mass of porous medium is $\bar{C}_{si}$, and the concentration change caused by biochemical reaction is R_i, the Eq. (26) can change to the following form.

$$\frac{\partial nC_i}{\partial t}=\frac{\partial}{\partial x}(nD\frac{\partial C_i}{\partial x})-\frac{\partial}{\partial x}(nuC_i)-\rho_b\frac{\partial \bar{C}_s}{\partial t}+nR_i \quad ...(27)$$

The absorption and retention of ion i to the porous media can be defined by the following retardation factor:

$$R_d=1+\frac{\rho_b}{n}\frac{\partial \bar{C}_s}{\partial C_i} \quad ...(28)$$

The change value of concentration R_i, which is caused by microbial-chemical reactions, can be decided by the reaction rate of Eq. (1) to Eq. (8), as is shown in Eq. (29).

$$R_i=\sum_{k=2}^{7}m_k r_k+m_p r_p+m_u r_u \quad ....(29)$$

Where m_k is the contribution coefficient of k to ion i (the value includes 1, -1 and 0); m_p and m_u represents the contribution to ion i by calcium carbonate sedimentation and hydrolysis reaction of urea, respectively, and r_k is the reaction rate. Therefore, Eq. (27) can be rewritten as:

$$R_d n\frac{\partial C_i}{\partial t}=\frac{\partial}{\partial x}(nD\frac{\partial C_i}{\partial x})-\frac{\partial}{\partial x}(nuC_i)-C_i\frac{\partial n}{\partial t}+nR_i \quad ...(30)$$

Now we consider a 1D problem with length L. Assume that the initial condition is given by Eq. (31), and the boundary condition is given by Eq. (32) and Eq. (33). Where Eq. (31) represents the concentration of the outflow equals to zero.

$$\{C\}_{t=0}=0,\ 0<x\le L \quad ...(31)$$

$$\{C\}_{x=0}=\{C\}_{input},\ t\ge 0 \quad ...(32)$$

$$nD\frac{\partial\{C\}}{\partial x}\bigg|_{x=L}=0,\ t\ge 0 \quad ...(33)$$

Discrete the length L into N equal-length units, and use variational principle for the finite element analyses of Eq. (30). Define $\{C\}=\sum_{j=1}^{N+1}\{C(t)\}_j\phi_j(x)$, where $\phi_j(x)$ is the basis function (j represents the nodes). Then we can get the following equation.

$$\int_0^L[\frac{\partial}{\partial x}(nD\frac{\partial\{C\}}{\partial x})-\frac{\partial}{\partial x}(nu\{C\})-\{C\}\frac{\partial n}{\partial t}+n\{R\}-[R_d]n\frac{\partial\{C\}}{\partial t}]\phi_i dx=0 \quad ...(34)$$

The second derivative for the first part of the integrand above can be transformed to a first derivative using partial integration, and substitute $\{C\}=\sum_{j=1}^{N+1}\{C(t)\}_j\phi_j(x)$ into the equations above, then we can get the following equations.

$$\begin{gathered}E_{ij}^I C_j^I+U_{ij}^I\frac{\partial C_j^I}{\partial t}=F_i\\ E_{ij}^I=\sum_e\int_e[nD\frac{\partial\phi_j}{\partial x}\frac{\partial\phi_i}{\partial x}+q\frac{\partial\phi_j}{\partial x}\phi_i]dx\\ U_{ij}^I=\sum_e\int_e[R_d]^I n\phi_i\phi_j dx,\ F_i^I=-\sum_e\int_e R^I n\phi_i dx\end{gathered} \quad ...(35)$$

Where subscript i and j represents the nodes; superscript I shows the number of ions or chemical components. We can also change Eq. (22) and Eq. (23) into finite element scheme.

$$\begin{gathered}K_{ij}H_j=-S_i\\ K_{ij}=\sum_e\int_e\frac{k}{\mu}\frac{\partial\phi_j}{\partial x}\frac{\partial\phi_i}{\partial x}dx-\frac{k}{\mu}\{\frac{\partial\phi_j}{\partial x}\phi_i\}\bigg|_{x=L}\\ S_i=\sum_e\int_e\{\sum_{k=1,2,3}(\frac{m_{CaCO_3}}{\rho_{CaCO_3}}nr_p)_k\}\phi_i dx\end{gathered} \quad ...(36)$$

With the help of Eq. (35) and Eq. (36), initial condition (Eq. (31)) and boundary condition (Eq. (32) and Eq. (33)), it is able to analyze the concentration and mass of ions and chemical components anytime anyplace within the process. The precipitation of calcium carbonate, distribution of different types of crystal, porosity and change of permeability coefficient can also be calculated. The paper applies backward Euler method and Newton-Raphson iterative method to solve the finite element equations mentioned above. A preliminary analysis will be given. The basis function Φ is given by Eq. (37).

$$\phi_i(x)=\begin{cases}\dfrac{x-x_{i-1}}{\Delta x} & x_{i-1}<x\le x_i\\ \dfrac{x_{i+1}-x}{\Delta x} & x_i<x\le x_{i+1}\\ 0 & \text{others}\end{cases} \quad ...\ (37)$$

Analyses of calculation results

In this paper, the model mentioned above is used for the 1D finite element simulation of biogrout in sand column. It is assumed that bacteria solution distributes homogeneously in the pores of the sand columns. The initial hydrolysis rate of urea is 0.152mol-urea/(L·h). The concentration of urea and calcium chloride in nutrient solution at the entrance of biogrout is 1.1mol/L, and the filling rate remains constant (2.84×10^{-5} m/s and 2.84×10^{-6} m/s is used, respectively). The length of sand columns is 5 m, and the average particle diameter is 0.164 mm. The longitudinal diffusion coefficient α_L is supposed to be 0.01m, while the rest of the parameters is summarized in Table 1,2,3.

Figure 2 shows the difference of precipitation quantity of the three types of calcium carbonate along the length of sand column, provided that the filling rate is 2.84×10^{-5} m/s and the duration is 5.9h. We may come to the conclusion that the major crystal type in this case is Vaterite and ACC with approximately the same amount. Meanwhile, the precipitation quantity of calcite is much smaller. This is in consistence with the results of experimental studies under similar conditions

Figure 3 to 6 shows the precipitation quantity of calcium carbonate, concentration of urea, porosity and hydrolysis rate of urea along the length of sand column at certain time under two different filling rates.

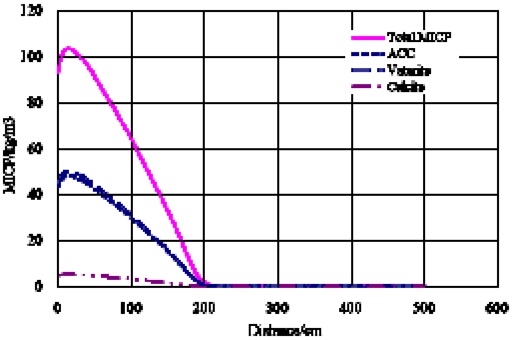

Fig. 2. Different types of calcium carbonate precipitation distribution along the column

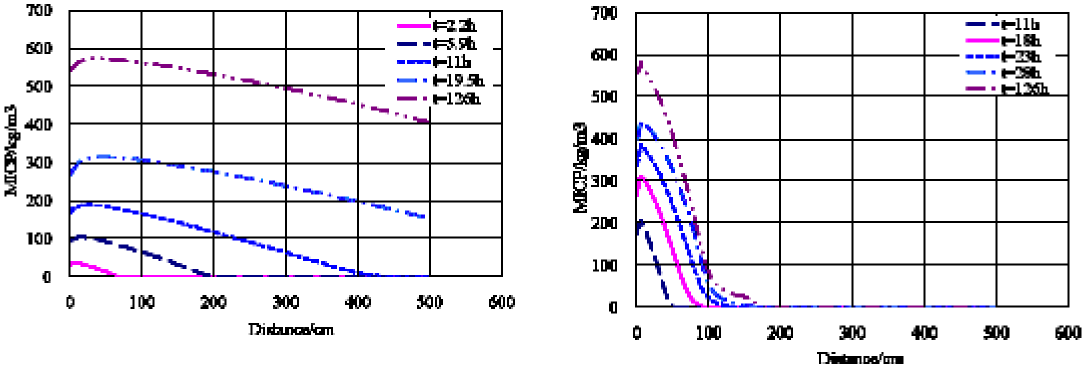

Fig. 3. MICP distribution along the column (left qin=2.84×10-5 m/s, right qin=2.84×10-5 m/s)

In the figures, the peak of calcium carbonate precipitation is 580 kg/m^3, which occurs at a certain distance away from the inflow (at the distance of 18cm to 40 cm). After the peak, the precipitation quantity reduces to zero almost linearly, this agrees with the data from experiments (Leon, 2009). Accordingly, the porosity of sand column got a reduction, and the final porosity at the peak position can reduce to one third of the initial.

The concentration of urea changes with time, and finally becomes a uniform distribution along the length of sand column. The hydrolysis rate of urea has a major peak, which appears when the concentration of urea is reducing rapidly. The peak point moves from the inflow towards the far end and gets lower with time. The hydrolysis rate of urea is nearly zero all along the length after the duration of 126 hours, mainly because the metabolism of microorganism gets much slower due to the insulation of nutrients by the precipitated calcium carbonate. (The higher t_d in Table 2 is, the longer the hydrolysis rate of urea remains nonzero). There is significant difference of distribution and moving speed of precipitation quantity along the length for the two filling rates. For $q_{in}=2.84\times10^{-5}$ m/s, the distribution of precipitation quantity along the length is already nearly homogenous before the hydrolysis of urea ends. Meanwhile, for $q_{in}=2.84\times10^{-6}$ m/s, only a length of 200 cm exists

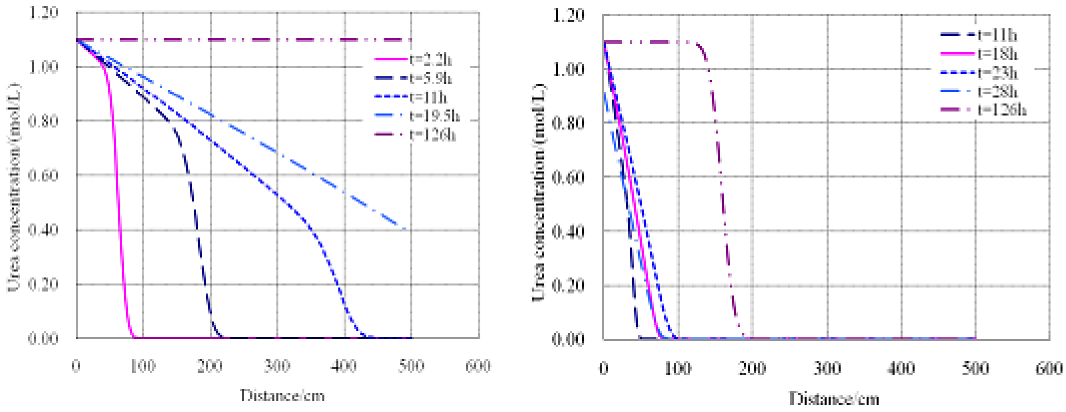

Fig. 4. Distribution of urea concentration along the column (left qin=2.84×10-5 m/s, right qin=2.84×10-5 m/s)

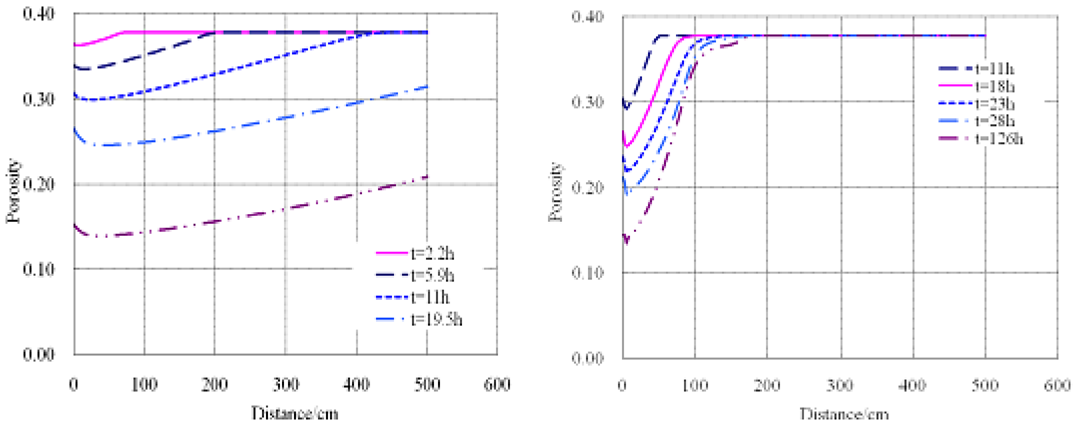

Fig. 5. Distribution of porosity along the column (left qin=2.84×10-5 m/s, right qin=2.84×10-5 m/s)

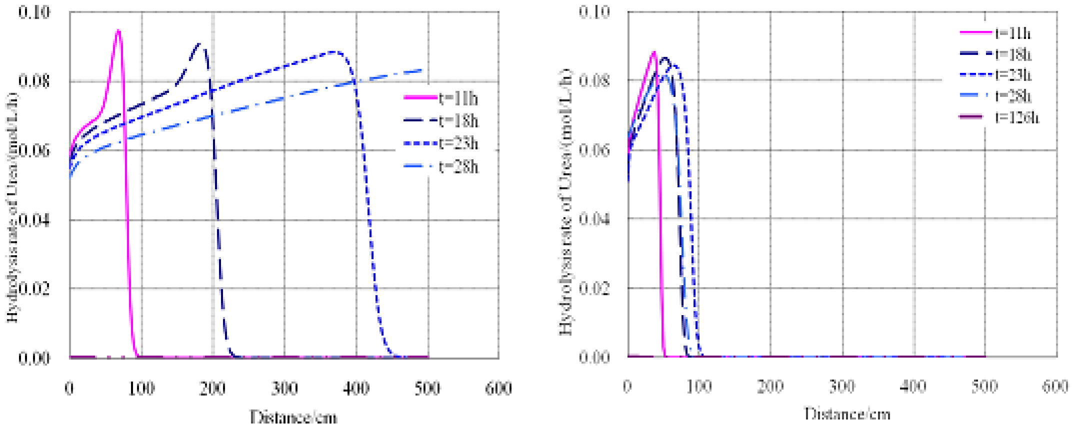

Fig. 6. Distribution of urea hydrolysis rate along the column (left qin=2.84×10-5 m/s, right qin=2.84×10-5 m/s)

precipitation of calcium carbonate at the time when hydrolysis of urea ends. Unless new bacteria solution is injected into the sand column, there will be no more precipitation of calcium carbonate. The difference is also caused by aging and death of microorganism. Therefore, as long as there is no huge disturbance to the main structure of porous media, the filling rate should be as high as possible in order to enhance the rate and homogeneity of precipitation.

CONCLUSIONS

Based on convection-diffusion-reaction equation and crystallization theory, the paper presents a detailed mathematical model of the process of MICP, which is able to make 1D finite element simulation for biogrout problems of sand column. A preliminary analysis is made about the precipitation quantity of calcium carbonate, the distribution of different crystal type along the length of sand column and its change with time. The model as presented in this paper is verified by the experimental data reported in the literature. The paper has a scientific relevance for the application and optimization of MICP technology.

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REFERENCES

1. Bear, J.: Dynamics of Fluids in Porous Media, Dover Publications, New York, 1972.
2. Breèeviæ, L. and Nielsen, A. E., Solubility of amorphous calcium carbonate. *J. Cryst. Growth*. 1989; **98**: 504 - 510.
3. Ferris FG, Setehmeir LG., Bacteriogenic mineral plugging. United States Patent 1992; 664769.
4. Jason T. DeJonga, Brina M. Mortensen. Bio-mediated soil improvement. *Ecological Engineering,* 2010; **36**: 197~210
5. Kralj D, Brecevic L, Kontrec J., Vaterite growth and dissolution in aqueous solution III. Kinetics of transformation. *Journal of Crystal Growth* 1997; **177**: 248-257.
6. L.A. Van passen, *et al.* In Situ Soil Reinforcement by Microbial Denitrification. 1st international conference BGCE 2008.
7. Leon van Paassen. Biogrout, Ground Improvement by Microbially Induced Carbonate Precipitation. Delft University of Technology, Ph.D thesis, 2009.
8. Microbial Carbonate Precipitation. 1st international conference BGCE 2008.
9. Nancollas, G.H. & Reddy, M.M. 1971. “The crystallization of calcium carbonate. II. Calcite growth mechanism.” Journal of Colloid and Interface Science 37(4): 824.
10. Parkhurst, D.L., “User’s guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations.” Report 1995; 95-4227: 143 p.
11. Plummer, L. N. and Busenberg, E., 1982. The solubilities of calcite, aragonite and vaterite in Co2-H2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO3-CO2-H2O. *Geochim. Cosmochim. Acta* **46**: 1011-1040.
12. Sohnel, O. & Mullin, J.W. Precipitation of calcium carbonate. *Journal of Crystal Growth* 1982; **60**(2): 239.
13. Whiffin, V.S., Microbial CaCO3 Precipitation for the production of Biocement. Science and Engineering, School of Biological Sciences & Biotechnology Perth, Western Australia, Murdoch University. Ph.D thesis 2004; 154.
14. Whiffin, V.S., van Paassen, L.A. & Harkes, M.P., “Microbial Carbonate Precipitation as a Soil Improvement Technique.” *Geomicrobiology Journal* 2007; **24**(5): 417-423.