Computational Modeling of Sand Cementation by Bio-mineral $CaCO_3$

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Abstract. An innovative sand cementation method of bio-mineral carbonate formation in sand spacing through urea hydrolysis inspired by microbial urease was introduced in the present investigation. A sand column prepared for experimental data and a set of engineering equations for 1-D numerical modeling data of the sand cementation process were adopted. Important characteristic of CaCO3 weight vertically along the sand column and the urea concentration variation under the effect of microbial urease was investigated based on the experiment and the modeling. Future study was suggested to focus on the model's parameters modification in order to construct an applicable model for industrial up-scaling application in sand or soil strengthening.

Introduction

Bio-mineralization is discovered and applied in geological material consolidation [1-2]. It is adopted in sand bio-cementation as the in-situ micro-inspired calcite precipitation technique (MCP technique for abbreviation) in the specific way that at first mixed solution of urease-producing bacteria, urea and calcium chloride is injected in sand, then the bacteria-producing urease dehydrates urea, shown in Eq. (1), and consequently calcium carbonate precipitates and fills in the spacing of sand, shown in Eq. (2) [3].

$$CO(NH_2)_2 + 2H_2O \rightarrow CO_3^{2-} + 2NH_4^+ \qquad (1)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow \qquad (2)$$

MCP technique is introduced to cement the incompact particles which leads to a reduction in permeability and an increase in strength. The mechanism of MCP is easily understood and was successfully applied in lab-scale experiment [4]. However, since the final objective is an industry-scale application for geological material consolidation and strengthening, an engineering model is required to predict the desired variables and even properties to meet the criteria set ahead. The modeling concerns hydrological aspect, geochemical aspect and microbiological aspect. Therefore, different modeling softwares (Matlab, Microsoft Excel and Geochemist's Workbench) were combined to discuss the complex physico-chemical phenomena in MCP [5]. This paper focused on the predicted urea hydrolysis and CaCO3 formation in comparison with experimental data in order to discuss more possibilities about a potential environmental friendly application in sand and soil treatment.

Principles

All the parameters are defined here [6]. r: urea hydrolysis rate, mM/min; A: area of cross-section of column, cm2; L: length of reactive part of column, cm; η: initial porosity; q: reaction fluid flow rate, ml/s; C_i: input urea concentration, mol/L; l_{box}: unit length, cm; ρ: density of CaCO3, g/cm3; t_{bac}:

linear reduction time of urease activity ($v_{\max\to0}$), hr; n : number of unites; k_v : urease activity decreasing ratio, mmol/(L h2); t : any moment in reaction, h.

For unit 1 (Fig. 1), the following statements are defined for the first trial. Eq. (3) - Eq. (16) are listed below.

Initial pore volume, cm3:
$$V_{pore,initial} = \eta V_{unit} \tag{3}$$

Initial sand volume, cm3:
$$V_{\min eral,initial} = V_{unit} - V_{pore,initial} \tag{4}$$

Time of fluid flow through an unit, s:
$$t_{unit} = V_{pore,initial} / q \tag{5}$$

Time since start, h:
$$t_{total} = t_{unit} / 3600 \tag{6}$$

Urea degraded per litre, mol:
$$U_L = t_{unit}(r - t_{total} r / t_{bac}) / 60000 \tag{7}$$

Urea degraded per unit, mol:
$$U_{unit} = U_L V_{pore,initial} / 1000 \tag{8}$$

Amount of urea left in solution, mol:
$$N_{urea} = V_{pore} C_i / 1000 - U_{unit} \tag{9}$$

New concentration of urea, mol/L:
$$C_{new} = 1000 N_{urea} / V_{pore} \tag{10}$$

Amount of CaCO3 formed, mol:
$$N_{calcite} = U_{unit} \tag{11}$$

Mass of CaCO3 formed, g:
$$M_{calcite} = 100.1 N_{calcite} \tag{12}$$

Volume of CaCO3 formed, cm3:
$$V_{calcite} = M_{calcite} / \rho_{calcite} \tag{13}$$

New pore volume after one cycle
of reaction in 3 units, cm3:
$$V_{pore,new} = V_{pore,initial} - V_{calcite} \tag{14}$$

Unit length, cm:
$$L_{unit} = L / n \tag{15}$$

Unit volume, cm3:
$$V_{unit} = A L_{unit} \tag{16}$$

In order to prevent all the above data from becoming negative, IF-statements are used [7-9].

Amount of urea left in the unit should not be negative;

New concentration of urea should not be negative;

Amount of CaCO3 formed should not be negative.

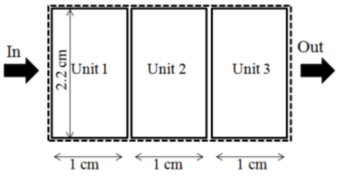

Fig. 1. 1-D modeling frame of a sand column

For unit 2 (Fig. 1), the same statements as unit 1 are applied, but there are also a few differences. Eq. (17) and (18) are listed below.

Time since start，h：
$$t_{total} = (t_{0\to unit1} + t_{unit2}) / 3600 \tag{17}$$

Amount of urea left in solution，mol：
$$N_{urea} = \left(V_{pore} / 1000 \times C_{new}\right) - U_{unit} \tag{18}$$

For unit 2, IF-statements are also applied. Some statements in the second time step depend on results of the first time step, shown in Eq. (22) - Eq. (23). Eq. (19) - Eq. (23) are listed below.

Pore volume relationship：
$$V_{pore,initial,timestep2} = V_{pore,new,timestep1} \tag{19}$$

Sand volume relationship：

$$V_{\min eral,initial,timestep2} = V_{\min eral,initial,timestep1} + V_{calcite,timestep1} \quad (20)$$

Total time since start，h：

$$t_{total} = t_{0 \to timestep1} + t_{unit} / 3600 \quad (21)$$

Urea concentration at any moment calculated in linear equation，mol/L：

$$C_{urea} = C_i - 60rt / 1000 \quad (22)$$

Urea concentration at any moment calculated in non-linear equation，mol/L：

$$C_{urea} = C_i - 60t(r - k_v t) / 1000 \quad (23)$$

Discussions

Eq. (3) - Eq. (23) were used to present three important physico-chemical relationships, urea concentration variation with a function of time, CaCO3 volume fraction variation with a function of time and CaCO3 weight variation with a function of time, in Fig. 2.

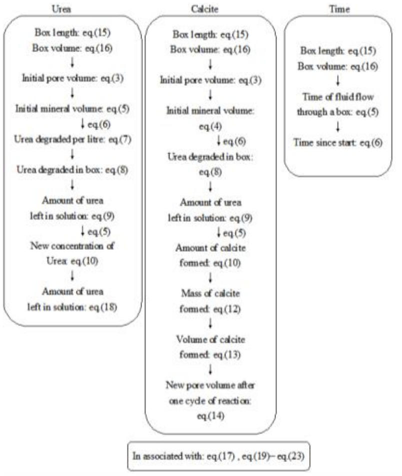

Fig. 2. Computational procedure of equations of 1-D modeling

In order to evaluate the reliability and the accuracy of 1-D numerical modeling results, experimental data were used to compare with the modeling data. Experimental conditions were listed in Tab. 1 and modeling parameters were assigned in Tab. 2.

Table 1. Experimental conditions

Experimental parameters	Value / unit
Temperature	(20±2)/ ℃
Particle diameter	< 200 / μm
Accumulated density	1.74 / (g/cm3)
Initial inflow velocity	0.01 / (mL/s)

The first trial based on Eq. (3) - Eq. (10) and Eq. (15) - Eq. (23) of the 1-D numerical modeling was run on with a constant of urea hydrolysis rate. The result of this trial was plotted in dots with the experimental data shown in a dash line in Fig. 3a. Clearly, the feature of the modeling data was in resemblance with the one of the experimental data. It was also obvious that the urea concentration decreased as a function of time at the presence of urease-producing bacteria in each unit. However, the computational data were much lower than the experimental ones of unit 2 and 3, indicating that the actual hydrolysis rate was lower than the assumed constant adopted in the modeling.

Table 2 1-D modeling parameter’s values

Simulating parameters	Value / unit
Urea hydrolyzing velocity， r	0.5 / (mM/min)
Cross section of sand column， A	3.80 / (cm2)
Total length of sand column， L	3.0 / cm
Initial porosity volume ratio， η	0.03 / (cm3/cm3)
Initial flow velocity， q	0.011 / (ml/s) or 40 / (ml/h)
Initial urea concentration， C_i	2.0 / (mol/L)
Length per unit of sand column， l_{box}	1 / cm
CaCO3 density， ρ	2.71 / (g/ cm3)
Time of urease activity from initial to 0， t_{bac}	> 240 / h

A remarkable improvement was obtained in agreement between the computational data and the experiment data in considering of a constant of linear reduction of urea hydrolysis rate at the second trial, in Fig. 3b. The constant of linear reduction of urea hydrolysis rate varied from 0.0009 mM/h2，0.0015 mM/h2 to 0.002 mM/h2, which represented an inspiring approach to modify the numerical data.

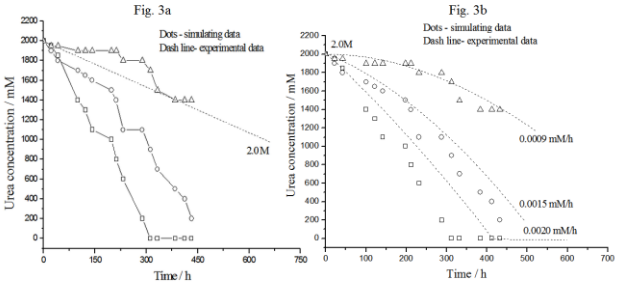

Fig. 3 Urea concentration
(a) no counting urease catalytic activity,
(b) counting urease catalytic activity

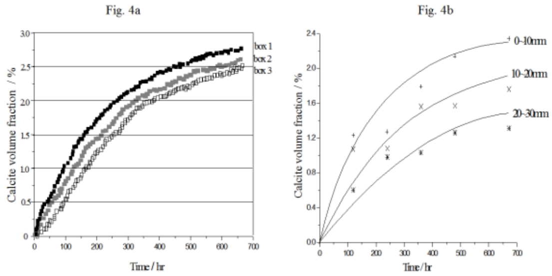

Fig. 4. CaCO3 volume fractions
(a) 1-D simulating data;
(b) Experimental data

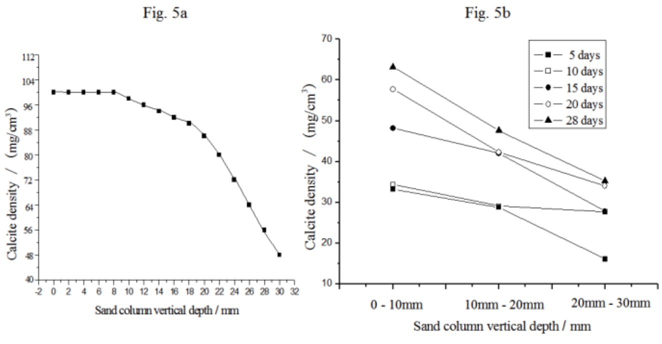

Fig. 5. calcite density of various cementing ages along depth
(a) 1-D simulating data; (b) Experimental data

The urea hydrolysis immediately inspired the precipitation of CaCO3 only if there were calcium ions at presence according to Eq. (1) and (2). The amount of dehydrated urea equaled to the amount of CaCO3 on a 1:1 basis (assuming that all carbonate formed through urease-catalyzed urea hydrolysis instantaneously converted to CaCO3). The CaCO3 formed in each unit could be computed out as a function of time. The volume fraction variations of CaCO3 of unit 1, 2 and 3 were plotted in Fig. 4a. Obviously, the feature of the modeling data (Fig. 5a) was in resemblance with the one of the experimental data (Fig. 4b).

The “endpoints” of the curves in Fig. 4a were plotted in Fig. 5a with the necessary mathematical derivation. The experimental data of the CaCO3 weight were driven out from the thermo-gravimeter, which was the amount of CaCO3 per unit volume of solid only. In fact, the numerical data were defined as the amount of CaCO3 per unit volume of solid and pores. The original numerical data coming from the thermo-gravimeter test were multiplied with a correction factor, which was a reciprocal of solid volume fraction. The result in Fig. 5a was the CaCO3 weight after the pretreatment. The experimental data were presented in Fig. 5b. A decrease of the amount of CaCO3 per unit volume of solid from the inlet to the outlet of each unit in modeling agreed with the experimental result, especially for the fact that the cementation in sand column was far more sufficient in the head than the tail of the column.

Conclusions

The precipitation of CaCO3 initially starting in the first part of the column is resulting in a variation of porosity along the column during the cementation process. Future study should be focused on the refinement of the model in order to construct an environmental application model for sand or soil consolidation that can be used to input more flexible variables and work out more reliable results.

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