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Numerical Inversion of Multi-Parameters in Multi-Components Reactive Solutes Transportation in an Undisturbed Soil-Column Experiment

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Abstract: In this paper, an undisturbed soil-column infiltrating experiment is investigated, and a mathematical model describing multi-components solutes transport behaviors in the column is put forward by combing hydro-chemical analysis with advection dispersion mechanisms, which is a group of advection-dispersion-reaction partial differential equations. Since the model involving six reaction coefficients which can not be obtained directly, an optimal perturbation regularization algorithm of determining these parameters is performed, and numerical simulations under different conditions are carried out. Furthermore, the inversion algorithm is applied to solve the real inverse problem by utilizing the measured breakthrough data. The reconstruction data basically coincide with the measured data showing that the inversion algorithm is efficient to the inverse problem of determining multi-parameters in a group of advection-dispersion equations arising in solutes transportation. The model and the inversion coefficients can be utilized to describe the experimental process and the experimental result.

Keywords: Multi-components solutes transport; soil-column experiment; breakthrough data; inverse problem of multi-parameters identification; optimal perturbation regularization algorithm; simulation; numerical inversion.

1 Introduction

Soil and groundwater pollution has become a serious threat to sustainable development throughout the world. It is important for pollution controlling and remedying to characterize contaminants transport behaviors quantitatively in the soil and groundwater. From the 1980s, there has been much researches on solutes transport models and inverse problems [Yeh (1986); Nielsen, Van Genuchten, and Biggar

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(1986); Van Genuchten and Wagenet (1989); Sun (1994, 1996); Atmadja and Bagtzoglou (2001); Mahar and Datta (2001); Zhang and Bennett (2002)]. In mathematics, convection-dispersion equation(s), stochastic model, and hydro-geochemical model have widely applications on the researches of solute transport behaviors, especially for single solute transport, or non-reactive solutes transport in porous medium. However, there seem to have few effective methods in a view of applying mathematics for multi-components reactive solutes transportation. Although there are some researches by combing convection dispersion mechanism with geochemical analysis, the researching methods mainly focus on numerical simulations and parameter discussions depending upon extra experiments and experimental data analysis [Miller and Benson (1983); Cederberg and Street (1985); Rafael and Antonis (1997); Kenneth (1998); Delolme, Hebrard, Spadini, and Gaudet (2004)].

Actually, since some model parameters can not be measured directly in many cases, we are always encountering with inverse problems of identifying and determining the parameters when coping with problems of soil and groundwater. It is noticeable that with development of computational techniques, inverse problem methods and inversion algorithms have been developed and utilized in a wide variety of applications in science and engineering [Toride, Leij, and Van Genuchten (1995); Engl, Hanke, and Neubauer (1996); Keung and Zou (1998); Guo and Zou (2001); Ling and Atluri (2006); Liu (2006); Li, Tan, Yao, Wang, and Liu (2008)]. Most of the numerical methods are based on regularization strategies so as to overcome ill-posedness and data noises, and one should choose suitable regularization algorithms for different kinds of inverse problems. For example, method of fundamental solutions [Ling and Takeuchi (2008); Marin (2009)], one-step group preserving scheme and lie-group estimation method [Liu, Liu, and Hong (2007); Liu, Chang, and Chang (2008)], level set method [Shim, Ho, Wang, and Tortorelli (2008); Lin, Chen, Cheng, and Wang (2009)], and optimal perturbation algorithms [Su (1995); Li, Cheng, Yao, Liu and Liu (2007)] have been testified to be effective methods in dealing with corresponding inverse problems. As for the inverse problem of multi-parameters identification of multi-components reactive solutes transport with limited experimental data, the situation becomes very complicated. One difficulty is how to give quantitative analysis on physical/chemical reactions occurring in the solutes transportation, the other is how to uniquely determine multi-parameters with higher precision as can as possible.

This paper will deal with a multi-parameters inversion problem arising from an undisturbed soil-column infiltrating experiment. As we know, there are disturbed and undisturbed soil-column experiments. For an undisturbed soil-column experiment, the soil may preserve its original structure and ingredient which can result in complicated physical/chemical reactions in the solutes transportation in the liquid

and solid phases when solute ions are being penetrated through the column with the inflow. On the other hand, there are quite a few investigations on disturbed soil-column experiments, but few for undisturbed experiments in the literatures we have [Pang and Close (1999); Inoue, Simunek, Shiozawa, and Hopmans (2000); Kamra, Lennartz, Van Genuchten, and Widmoser (2001); Cui, Li, Li, and Yang (2004)]. The reason may be that for an undisturbed soil-column experiment involving in multi-components reactive solutes transportation, it is not easy to describe complicated physical/chemical reactions possibly occurring in the column in mathematics [Zhang and Su (2004); Zhang, Xu, and Zhang (2006)].

As stated above, an effective way of researching multi-components reactive solutes transport is to combine hydro-chemical analysis with advection dispersion mechanisms to get a coupled model. Actually, for a real solutes transport problem, when geochemical analysis and preliminary principles known, the problem left is to identify and determine the model parameters in mathematics as can as possible. In this paper, we will employ a modified optimal perturbation regularization algorithm to determine reaction coefficients so as to explore transport behaviors of multi-components reactive solutes, and give a good-fit reconstruction to the measured breakthrough data for an undisturbed soil-column infiltrating experiment.

The paper is arranged as follows.

In section 2, a real soil-column infiltrating experiment carried out in Zibo, Shandong Province, China is introduced. In section 3, by combing hydro-chemical analysis with advection dispersal principles, a mathematical model describing multi-component solutes transport behaviors in the column is put forward, which is a group of advection-dispersion-reaction equations, and an inverse problem of determining multi-parameters in the model ensues based on the additional breakthrough data. Section 4 gives a modified optimal perturbation regularization algorithm with which numerical simulations are carried out under different conditions. In section 5, the optimal perturbation algorithm is applied to solve the real inversion problem, and the reaction coefficients are worked out by which the measured breakthrough data are reconstructed successfully. Finally, several conclusions and discussions are given in section 6.

2 The soil-column experiment

In order to describe and reveal transport behaviors and characteristics of the solutes ions when they penetrating through the soils, soil-column infiltrating experiments are often carried out in Lab or in field. This paper will deal with an undisturbed

soil-column experiment[1]. The experiment was carried out in a laboratory in Zibo, Shandong Province, China, by taking an original soil-column nearby a coal mine region, and infiltrating with the coal mine water. The soil belongs to sub-sandy clay whose main components are calcium sulphate, limestone, and magnesium sulfate, etc. On the other hand, SO_4^{2-}, and Ca^{2+} and Mg^{2+} are rich in coal-mine water. So, an undisturbed soil-column infiltrating experiment was done so as to investigate transport behaviors of acid mine pollutants when across through the sulphates soils.

The experimental device is installed by three parts: infiltrating system, soil-column system and sample collector system. The diameter of the lucite tube loading the soil-column is 20cm, the height of the column is 45cm, the total infiltrating time with the coal mine water is 119 hour, and the total infiltrating quantity is about 70 liter.

Throughout the experiment, the fluid that reaches the bottom of the column was collected as samples by time and analyzed immediately, and then the solutes concentrations at the bottom of the column were obtained which are called breakthrough data. Although quite a few solutes ions were taken into considerations in hydrochemical testing and analysis, we will pay attention to three kinds of solutes ions which are SO_4^{2-}, Ca^{2+} and Mg^{2+}. As for other solutes ions, we will take Cl^- as example to do hydro-dynamical dispersal analysis due to its conservative property. In the follows, some basic parameters for the experiment which can be estimated directly are listed in Tab.1, and the measured breakthrough data of the four solutes ions are plotted in Fig.1, respectively.

Table 1: Basic parameters in the soil-column experiment

l[cm]	a_L[cm]	v[cm/s]	D[cm^2/s]	T_1[h]
45	1	3.76e-3	3.76e-3	119

Where l is the length of the column, a_L is the dispersitivity which is determined based on known experimental results [Sun, 1996], v is the average pore water velocity which is estimated by the experiment, and then the dispersion coefficient is obtained by $D = a_L v$; T_1 denotes the total infiltration time with the coal mine water.

By Fig.1, and noting that initial concentrations in the inflow of the four kinds of ions are known as $[Ca^{2+}]_0$=338.28 mg/L, $[SO_4^{2-}]_0$=1062.9 mg/L, $[Mg^{2+}]_0$=104.42 mg/L and $[Cl^-]_0$=219.1 mg/L, respectively, we can find that the first outflow concentrations of Ca^{2+}, SO_4^{2-} and Mg^{2+} at $t = 0.5$ h are almost double more than

[1] The experiment was supplied by The Inspecting Station of Geology and Environment in Zibo, Shandong.

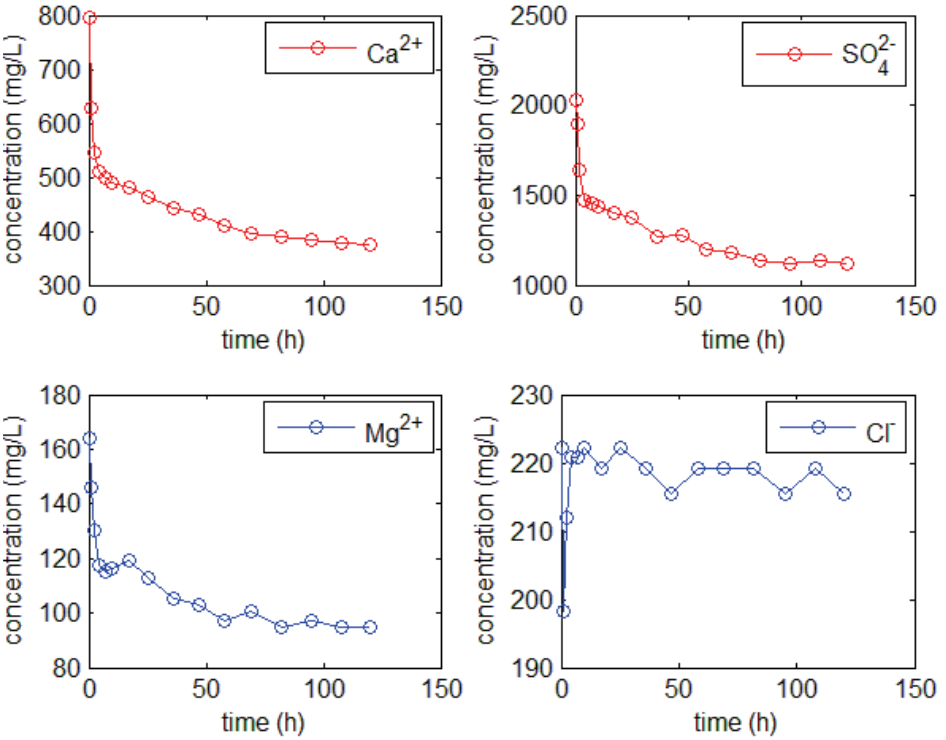

Figure 1: Breakthrough data of the four solutes ions.

those in the inflow, and their breakthrough data go down rapidly at the initial stage, and then decrease with time going on. Maybe rapid dissolutions of ion species happened in the solid phase into the liquid phase for the three solutes ions, and after the short dissolution stage, some chemical decay reactions may play an important role for their transporting behaviors through the column, and the solutes concentrations in the outflow have decreasing trends. As for Cl^-, its concentration only has small changes so that we think there are no more physical/chemical reactions occurring to it.

Let us investigate main physical/chemical reactions between solid and liquid phases in the column for the three solutes ions of Ca^{2+}, SO_4^{2-} and Mg^{2+}. Noting that there exist quite a few calcium sulphate ($CaSO_4$), crystallized gypsum ($CaSO_4 \cdot 2H_2O$) and magnesium sulfate ($MgSO_4 \cdot 7H_2O$) in the experimental soil, which could have some reactions of dissolution and precipitate with the inflow infiltrating into the column. We will consider the following reactions:

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \tag{1}$$

$$MgSO_4 \cdot 7H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 7H_2O \tag{2}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O_{\downarrow} \tag{3}$$

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2 \downarrow \tag{4}$$

where (1) and (2) represent dissolution reactions, and (3) and (4) represent precipitation reactions. In the next section, we will construct a mathematical model of partial differential equations based on the above chemical reactions and hydrodynamic dispersion mechanism.

3 Mathematical model and the inverse problem of determining multi-parameters

Denote c_1, c_2, c_3 and c_4 as the concentrations of Ca^{2+}, SO_4^{2-}, Mg^{2+}, and Cl^{-} at time t and space point x in the liquid phase respectively, and s_1,s_2 represent the intrinsic concentrations of calcium sulphate and crystallized magnesium sulfate in the soils respectively, and k_a, k_s denote dissolved coefficients of the calcium and the crystallographic magnesium sulfate, and k_g, k_m denote precipitation coefficients of the gypsum and magnesium hydrate respectively.

By general advection-dispersion mechanism combing with the analysis of chemical reactions as indicated in (1), (2), (3) and (4), a transport model for the four kinds of solutes ions penetrating through the column can be described as follows for $0 < x < l$, and $0 < t < T_1$:

$$\begin{cases} \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} + k_a s_1 - k_g c_1 c_2, \\ \frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} + k_a s_1 - k_g c_1 c_2 + k_s s_2, \\ \frac{\partial c_3}{\partial t} = D\frac{\partial^2 c_3}{\partial x^2} - v\frac{\partial c_3}{\partial x} + k_s s_2 - k_m c_3, \\ \frac{\partial c_4}{\partial t} = D\frac{\partial^2 c_4}{\partial x^2} - v\frac{\partial c_4}{\partial x}. \end{cases} \tag{5}$$

Furthermore, suppose that $s_1(t) = s_{10}\exp(-k_a t)$, and $s_2(t) = s_{20}\exp(-k_s t)$, here $s_{10} = s_1(0)$, $s_{20} = s_2(0)$, and setting $r_1 = k_a$, $r_2 = k_a s_{10}$, $r_3 = k_g$, $r_4 = k_s$, $r_5 = k_s s_{20}$, and $r_6 = k_m$, we can get the following equations:

$$\begin{cases} \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} + r_2 e^{-r_1 t} - r_3 c_1 c_2, \\ \frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} + r_2 e^{-r_1 t} - r_3 c_2 c_1 + r_5 e^{-r_4 t}, \\ \frac{\partial c_3}{\partial t} = D\frac{\partial^2 c_3}{\partial x^2} - v\frac{\partial c_3}{\partial x} + r_5 e^{-r_4 t} - r_6 c_3, \\ \frac{\partial c_4}{\partial t} = D\frac{\partial^2 c_4}{\partial x^2} - v\frac{\partial c_4}{\partial x}. \end{cases} \tag{6}$$

It is noticeable that the six parameters $r_j (j = 1, 2, \cdots, 6)$ are unknown which represent the chemical reactions occurring in the soil-column. Denote $C_i = c_i / c_{i0} (i =$

$1,2,3,4$), here $c_{i0}(i=1,2,3,4)$ are the initial concentrations of the four ion species in the inflow. Let $Z=x/l$, $T=vt/l$, $P=vl/D$, and $a_j=r_jl/v(j=1,2,\cdots,6)$, we have the following dimensionless model:

$$\begin{cases} \frac{\partial C_1}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2}-\frac{\partial C_1}{\partial Z}+\frac{1}{c_{10}}a_2e^{-a_1T}-c_{20}a_3C_1C_2, \\ \frac{\partial C_2}{\partial T}=\frac{1}{P}\frac{\partial^2 C_2}{\partial Z^2}-\frac{\partial C_2}{\partial Z}+\frac{1}{c_{20}}a_2e^{-a_1T}-c_{10}a_3C_1C_2+\frac{1}{c_{20}}a_5e^{-a_4T}, \\ \frac{\partial C_3}{\partial T}=\frac{1}{P}\frac{\partial^2 C_3}{\partial Z^2}-\frac{\partial C_3}{\partial Z}+\frac{1}{c_{30}}a_5e^{-a_4T}-a_6C_3, \\ \frac{\partial C_4}{\partial T}=\frac{1}{P}\frac{\partial^2 C_4}{\partial Z^2}-\frac{\partial C_4}{\partial Z}. \end{cases} \tag{7}$$

For the above advection-dispersion-reaction equations, the initial conditions are given as

$$C_i(Z,0)=0, \quad i=1,2,3,4, \tag{8}$$

and the boundary conditions are set to be

$$C_i(0,T)=1, \ \frac{\partial C_i}{\partial Z}(1,T)=0, \quad i=1,2,3,4. \tag{9}$$

Then a forward problem is formulated by the dimensionless model (7) together with the initial boundary value conditions (8) and (9). Just as stated in the above, by the soil-column experiment, the so-called breakthrough data are obtained which given in Fig.1. In other words, we have the following measured breakthrough data:

$$C_i(1,T_k)=\hat{C}_{ik}, i=1,2,3,4, \quad k=1,2,\cdots K, \tag{10}$$

where K represents the number of measured breakthrough data. As a result, an inverse problem of identifying the unknown parameters $a_j(j=1,2,\cdots,6)$ in the model (7) is encountered which is the forward problem (7)-(9) with the additional condition (10).

In the follows, an optimal perturbation regularization algorithm will be introduced, and the unknown reactive coefficients can be determined with which the measured breakthrough data will be reconstructed.

4 Optimal perturbation algorithm and numerical simulations

4.1 The inversion algorithm

Denote $\mathbf{a}=(a_1,a_2,\cdots,a_6)^T$, then it is transformed to the following minimization problem to solve the above inverse problem (7)-(10) numerically:

$$\min_{S_a}\{\max_{i=1,2,3,4}\sum_{k=1}^{K}[C_i(1,T_k;\mathbf{a})-\hat{C}_{ik}]^2+\alpha||\mathbf{a}||_2^2\}, \tag{11}$$

where S_a denotes an admissible set of the unknown parameters vector, for example for positive constant E, $S_a = \{\mathbf{a} : \ ||\mathbf{a}||_2 \leq E, a_j > 0, j = 1,2,\cdots,6\}$ is suitable, and $\alpha > 0$ is regularization parameter, K is the number of the samples given in (10). In the concrete computations, the above minimization problem (11) can be solved by obtaining $\mathbf{a}^{n+1}$ for given $\mathbf{a}^n$ by the following iteration procedure:

$$\mathbf{a}^{n+1} = \mathbf{a}^n + \boldsymbol{\sigma}\mathbf{a}^n, \ n = 0,1,\cdots, \tag{12}$$

here $\boldsymbol{\sigma}\mathbf{a}^n = (\delta a_1^n, \delta a_2^n, \cdots, \delta a_6^n)^T$ is called perturbation vector for each n, which is worked out by minimizing the following functional for given $\mathbf{a}^n$:

$$F(\boldsymbol{\sigma}\mathbf{a}^n) = \max_{i=1,2,3,4} \sum_{k=1}^{K} [C_i(1,T_k;\mathbf{a}^n + \boldsymbol{\sigma}\mathbf{a}^n) - \hat{C}_{ik}]^2 + \alpha ||\boldsymbol{\sigma}\mathbf{a}^n||_2^2, \tag{13}$$

If the best perturbation $\boldsymbol{\sigma}\mathbf{a}^n$ is obtained by minimizing (13), then the optimal parameter can be approximated by iterations (12) as long as the perturbation satisfying a given precision. The iterative procedures are listed below:

Step 1. Given initial iteration vector $\mathbf{a}^n$ $(n = 0,1,\cdots)$, compute the output errors

$$E_i = \sum_{k=1}^{K} [C_i(1,T_k;\mathbf{a}^n) - \hat{C}_{ik}]^2, \quad i = 1,2,3,4$$

for the four ions respectively, and suppose the largest error is E_m, where m is one number from 1 to 4, then define the error functional as follows:

$$F(\boldsymbol{\sigma}\mathbf{a}^n) = E_m + \alpha ||\boldsymbol{\sigma}\mathbf{a}^n||_2^2. \tag{14}$$

Step 2. By the above expression (14), and utilizing ordinary optimal perturbation algorithm [Li, Cheng, Yao, Liu and Liu (2007); Li, Tan, Yao, Wang, and Liu (2008)], the perturbation vector can be worked out via

$$\boldsymbol{\sigma}\mathbf{a}^n = (\alpha \mathbf{I} + \mathbf{G}^T\mathbf{G})^{-1}\mathbf{G}^T(\boldsymbol{\eta}_m - \boldsymbol{\xi}_m), \tag{15}$$

where $\mathbf{G} = (g_{kj})_{K\times 6}, g_{kj} = [C_m(1,T_k;\mathbf{a}^n + \tau\mathbf{e}_j) - C_m(1,T_k;\mathbf{a}^n)]/\tau$, $k = 1,\cdots,K$, $j = 1,\cdots,6$, here $\mathbf{e}_j = (0,\cdots,1,\cdots,0)^T (j = 1,\cdots,6)$ is basis functions of $\mathbf{R}^6$; and

$$\boldsymbol{\xi}_m = (C_m(1,T_1;\mathbf{a}^n), C_m(1,T_2;\mathbf{a}^n)\cdots, C_m(1,T_K;\mathbf{a}^n))^T, \quad \boldsymbol{\eta}_m = (\hat{C}_{m1}, \hat{C}_{m2}\cdots, \hat{C}_{mK})^T, \tag{16}$$

and τ is numerical differential step.

Step 3. If the perturbation satisfies a given precision eps by $||\boldsymbol{\sigma}\mathbf{a}^n||_2 \leq eps$, then the algorithm is terminated, and $\mathbf{a}^{n+1} = \mathbf{a}^n + \boldsymbol{\sigma}\mathbf{a}^n$ is taken as the parameter solution what we just want to determine; otherwise, go to **Step 1** by replacing $\mathbf{a}^n$ with $\mathbf{a}^{n+1}$.

In the follows, numerical simulations for determining the reaction coefficients will be carried out based on the inverse problem (7)-(10) by applying the above optimal perturbation regularization algorithm. All computations are performed in a PC of Dell Dimension 9200.

4.2 Impacts of regularization parameters with numerical differential steps

Set the true coefficient vector as $\mathbf{a}^{true} = (1, 0.5, 0.01, 1, 0.8, 1.5)$, and the additional data are generated by substituting the true coefficient into the forward problem (7)-(10) to work out. In this subsection, we will perform the algorithm by fixing initial iteration $\mathbf{a}^0 = \mathbf{0}$ so as to investigate impacts of regularization parameters with numerical differential steps on the inversion algorithm.

1) $\tau = 0.1$

By applying the above inversion algorithm with convergent precision as $eps = 2e-4$, the reaction coefficient can be reconstructed and the inversion results to different regularization parameters are listed in Tab.2, where αrepresents regularization parameter, n denotes number of iterations, $\mathbf{a}^{inv}$ represents reconstruction coefficients vector, and $Err = ||\mathbf{a}^{true} - \mathbf{a}^{inv}||_2/||\mathbf{a}^{true}||_2$ denotes relative inversion error.

Table 2: Impacts of regularization parameters with $\tau = 0.1$

α	n	$\mathbf{a}^{inv}$	Err
$\leq$ 4.5e-4		divergent or failure	
4.6e-4	270	(0.9680, 0.4566, 0.0100, 0.9877, 0.7700, 1.5000)	2.77e-2
4.7e-4	373	(1.0010, 0.5025, 0.0100, 0.9800, 0.7543, 1.5001)	2.24e-2
4.8e-4	383	(1.0071, 0.5114, 0.0100, 0.9761, 0.7448, 1.5000)	2.72e-2
4.9e-4	382	(1.0055, 0.5098, 0.0100, 0.9762, 0.7443, 1.5001)	2.72e-2
5.0e-4	386	(1.0040, 0.5069, 0.0100, 0.9774, 0.7475, 1.5000)	2.54e-2
5.1e-4	730	(1.0388, 0.5604, 0.0100, 0.9674, 0.7258, 1.5001)	4.77e-2
5.2e-4	749	(1.0218, 0.5331, 0.0100, 0.9792, 0.7522, 1.5001)	2.89e-2
5.3e-4	821	(1.0259, 0.5396, 0.0100, 0.9769, 0.7472, 1.5000)	3.29e-2
5.4e-4	589	(1.0719, 0.6174, 0.0100, 0.9456, 0.6804, 1.5001)	8.39e-2
$\geq$ 5.5e-4		divergent	

By Tab.2, we find that regularization parameters should be chosen in a suitable range for a given differential step. In this example, optimal regularization param-

eters should belong to a trustworthy domain of [4.6e-4, 5.4e-4] in which the algorithm is convergent, and the inversion errors belong to [0.0224, 0.0839]. Fig.2 plots inversion errors varying with regularization parameters in such case for $\alpha \in$[4.5e-4, 5.42e-4].

2) $\tau = 0.01$

In this case, the convergent precision is taken as $eps = 1e-4$, the inversion results are listed in Tab.3, where α also represents regularization parameter, and n, $\mathbf{a}^{inv}$, and Err have the same meanings as used in Tab.2.

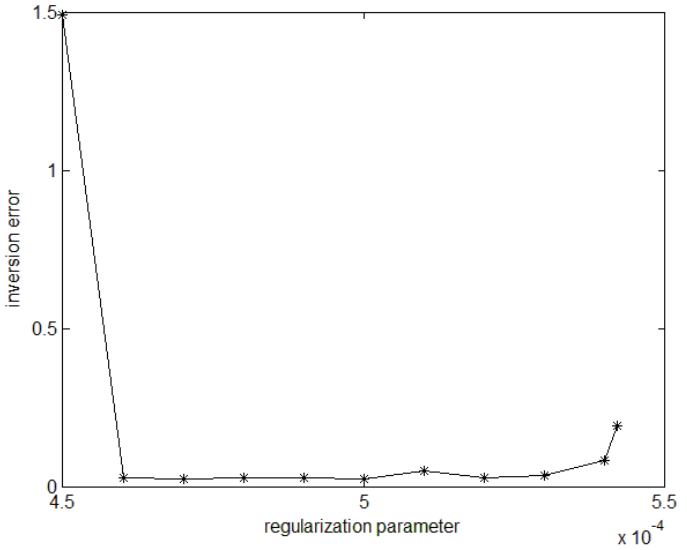

Figure 2: Inversion errors with regularization parameters for $\tau = 0.1$.

By Tab.3, we find that regularization parameter should be chosen a little larger in the case of $\tau = 0.01$ than that of $\tau = 0.1$, and optimal regularization parameters should belong to a trustworthy domain of [0.00390, 0.00394] in which the inversion errors are smaller than 0.0754. In addition, we also find that convergent precision plays a special role in the realization of the inversion algorithm. Fig.3 plots the inversion errors vary with the convergent precisions for α =0.0039.

3) $\tau = 0.001$

In this case, the convergent precision is taken as $eps = 2e-5$, and the inversion results are listed in Tab.4, where α, n, $\mathbf{a}^{inv}$, and Err also have the same meanings as in Tab.2.

Table 3: Impacts of regularization parameters with $\tau = 0.01$

α	n	$\mathbf{a}^{inv}$	Err
$\leq$ 3.88e-3		divergent	
3.89e-3	1282	(1.1570, 0.7920, 0.0100, 0.8988, 0.5913, 1.5002)	1.79e-1
3.90e-3	842	(1.0099, 0.5201, 0.0100, 0.9296, 0.6458, 1.5000)	7.54e-2
3.91e-3	1034	(1.0186, 0.5322, 0.0100, 0.9387, 0.6645, 1.5001)	6.76e-2
3.92e-3	1072	(1.0301, 0.5502, 0.0100, 0.9366, 0.6608, 1.5000)	7.22e-2
3.93e-3	1230	(1.2696, 1.1004, 0.0100, 0.8612, 0.5291, 1.5003)	3.20e-1
3.94e-3	1065	(1.0300, 0.5497, 0.0100, 0.9358, 0.6594, 1.5000)	7.28e-2
3.95e-3		divergent	
3.96e-3	1285	(1.1528, 0.7825, 0.0100, 0.9002, 0.5943, 1.5002)	1.74e-1
$\geq$ 3.97e-3		divergent	

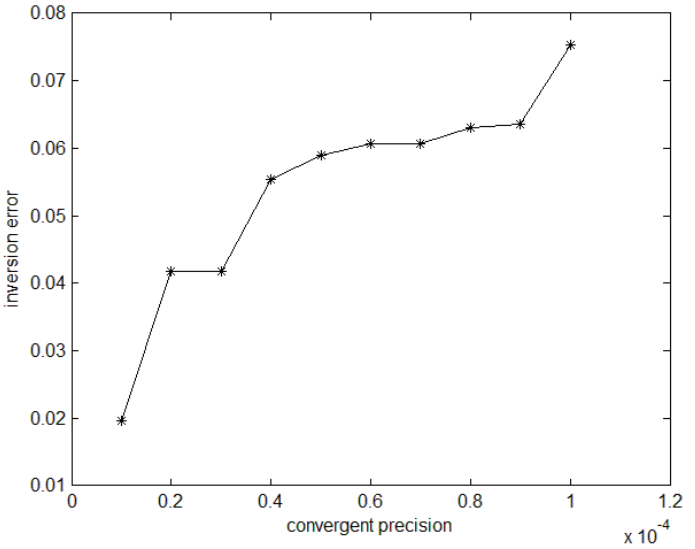

Figure 3: Inversion errors with convergent precisions for α =0.0039 and τ =0.01.

By Tab.4, we can find that regularization parameter should be chosen much more larger in the case of $\tau = 0.001$ than those of $\tau = 0.1$ and $\tau = 0.01$, and optimal regularization parameters should belong to a trustworthy domain of [0.010, 0.014] in which the inversion errors belong to [5.80e-2, 2.10e-1]. In addition, by the above computations, we can also see that the smaller of numerical differential steps, the greater of number of iterations, and the larger of the inversion errors. For the inverse

Table 4: Impacts of regularization parameters with $\tau = 0.001$

α	n	$\mathbf{a}^{inv}$	Err
$\leq$ 9e-3		divergent or failure	
1.00e-2	2836	(1.1848, 0.8592, 0.0100, 0.8890, 0.5749, 1.5002)	2.10e-1
1.10e-2	4140	(1.0146, 0.5254, 0.0100, 0.9348, 0.6830, 1.5000)	5.80e-2
1.20e-2	2365	(1.0034, 0.5093, 0.0100, 0.9358, 0.6585, 1.5001)	6.87e-2
1.25e-2	4317	(1.0065, 0.5145, 0.0100, 0.9347, 0.6561, 1.4999)	7.00e-2
1.30e-2	3764	(1.0972, 0.6650, 0.0100, 0.9334, 0.6552, 1.5001)	1.10e-1
1.40e-2	4829	(1.0264, 0.5435, 0.0100, 0.9391, 0.6661, 1.5001)	6.87e-2
$\geq$ 1.50e-2		divergent	

problem investigated here, it seems to be better to perform the inversion algorithm with relatively large numerical differential steps. In the follows, the inversion algorithm will be applied to solve the inverse problem (7)-(10) of determining the unknown parameters by real measured breakthrough data.

4.3 Numerical convergence of the inversion algorithm

In this subsection, we will investigate convergence of the above inversion algorithm by numerical testification. According to the above computations, also set the true parameter as $\mathbf{a}^{true} = (1, 0.5, 0.01, 1, 0.8, 1.5)$ as that in the last subsection, and choose numerical differential step as $\tau = 0.1$, regularization parameter as α=5e-4, and initial iteration as zero. The inversions errors vary with number of iterations are plotted in Fig.4.

By the computations and Fig.4, we can see that the more of iterations, the smaller of the inversion errors showing that the inversion algorithm is at least of numerical convergence.

5 Determination of model parameters and reconstruction of the breakthrough data

It is much more complicated to solve a real problem with real data than to do numerical simulations. As for a regularization algorithm, it always needs larger regularization parameters for real problems than for artificial simulations. In the concrete computations for the inverse problem of (7)-(10) with the real breakthrough data, we will choose large regularization parameters and numerical differential steps based on the numerical simulations carried out in the last section.

By setting initial iteration as $\mathbf{a}^0 = \mathbf{0}$, convergent precision as $eps = 1e-5$, and

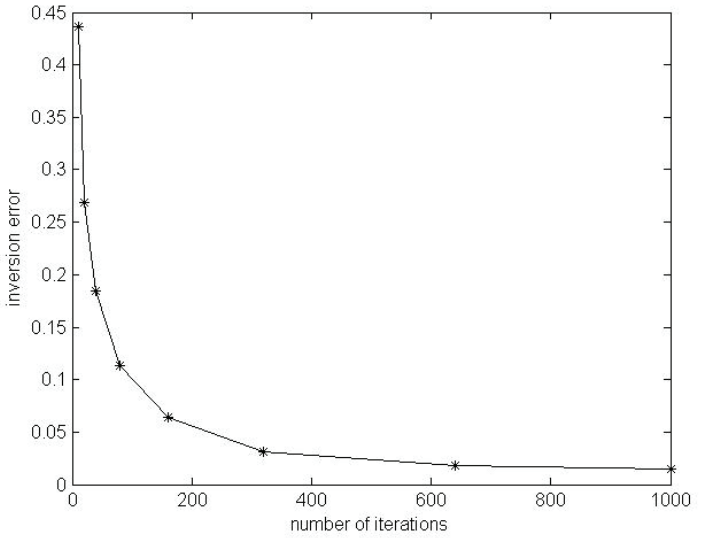

Figure 4: Inversion errors with number of iterations.

choosing regularization parameter as α=0.0392, and numerical differential steps vector as $\tau = 0.1$, the six parameters in the model (7) can be worked out, which is

$$\mathbf{a}^{inv} = (0.0226, 7.9755, 11.2678, 10.8256, 1.8089, 0.0379), \tag{17}$$

Furthermore, by substituting the above inversion coefficients into the model (7), the breakthrough data can be reconstructed which are plotted in Fig.5 as compared with the real measured data.

On the other hand, define average absolute and relative computational errors for the four solutes ions by

$$Err^i_{abs} = ||\boldsymbol{\eta}_i - C_i(1,T;\mathbf{a}^{inv})||_2,\ i = 1,2,3,4, \tag{18}$$

and

$$Err^i_{rel} = Err^i_{abs}/||\boldsymbol{\eta}_i||_2,\ i = 1,2,3,4, \tag{19}$$

respectively, where $\boldsymbol{\eta}_i$ is the measured breakthrough data vector given in (16) ($i = 1,2,3,4$), $\mathbf{a}^{inv}$ is the inversion coefficients vector given by (17), and $C_i(1,T;\mathbf{a}^{inv})$ is the reconstruction breakthrough data for $i = 1,2,3,4$, respectively. The computational errors are listed in Tab.5.

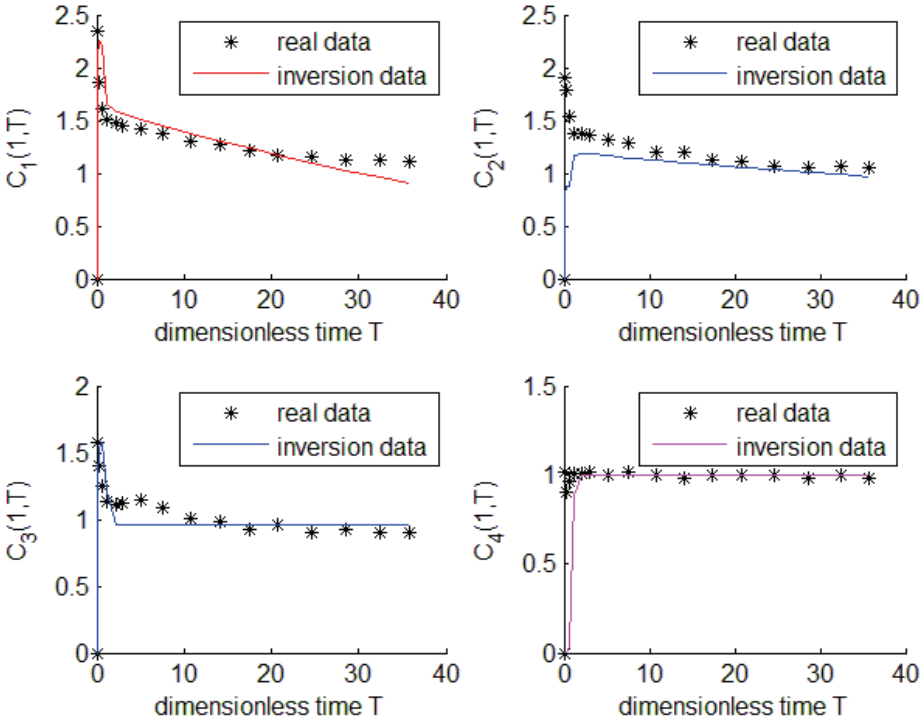

Figure 5: Reconstruction data and real breakthrough data.

Table 5: Computational errors for the four kinds of solutes ions

	Ca^{2+}	SO_4^{2-}	Mg^{2+}	Cl^-
Err_{abs}	0.2068	0.4010	0.1372	0.4011
Err_{rel}	0.0358	0.0756	0.0312	0.1010

By Fig.5 and Tab.5, we can see that the reconstruction breakthrough data are basically agree with the real data, and the relative inversion errors are not too large showing that the inversion for the reaction coefficients in model (7) are satisfactory.

6 Discussions and conclusions

6.1 On the reaction coefficients

Let us come back to original dimensions for the six reaction coefficients given by (17). Noting $a_j = r_j l/v$ for $j = 1,2,\cdots,6$, and with *hour* as time dimension we

have

$$\mathbf{r}^{inv} = (0.0068, 2.3990, 3.3894, 3.2563, 0.5441, 0.0114), \tag{20}$$

by which we get
$k_a = 0.0068$[/h], $k_s = 3.2563$[/h], $k_g = 3.3894$[L/g/h], $k_m = 0.0114$[/h];
and
$s_{10} = 352.9$[g/L], $s_{20} = 0.1671$[g/L].

By the above parameters, we can see that the dissolution speed of calcium sulphate is much smaller than that of crystallized magnesium sulfate in the column, and the precipitation speed of gypsum is much greater than that of magnesium hydrate in the column. Moreover, there are plenty of calcium sulphates in the original soils as compared with the crystallized magnesium sulfate, and calcium sulphate plays an essential role throughout the solutes transport process.

6.2 On space distributions with time

By substituting the inversion coefficients into the forward problem, we can get time-space concentration distributions of the four ions. Fig.6, Fig.7, Fig.8, and Fig.9 plot space distributions of the four solutes ions at different time, respectively.

By the above figures, we find that there really occurred dissolution processes for the solutes of Ca^{2+}, SO_4^{2-} and Mg^{2+} as soon as the experiment began, which resulted in increasing trends of the space distributions at the initial stage; and with time going on, precipitation actions or some decay actions played dominating roles so that the space distributions were in decreasing situations until they arrived at asymptotic equilibriums. However, as for Cl^-, all of its space distributions were in a falling mode at the interval of $t \in (0, 4h)$, which maybe resulted from convection actions, and after $t > 5h$, it reached its equilibrium rapidly.

On the other hand, we can see that Mg^{2+} participated chemical reactions with Ca^{2+} and SO_4^{2-}, but it displayed different behaviors, and got its equilibrium at about $t = 6h$ which is greatly ahead of Ca^{2+} and SO_4^{2-}. It is fortunate that the above statements are basically in keeping with those inferences given in section 2.

6.3 On the model and the inversion algorithm

By the numerical simulations and data reconstruction results, we can see that based on inversion method, it is feasible to combine hydro-chemical analysis with advection-dispersion principles on the researches of multi-components reactive solutes transport behaviors. The reconstruction breakthrough data basically coincide with the measured data, and the model with the reaction coefficients can be utilized to describe the solutes transport behaviors in the experiment and explain the experimental results to some extent.

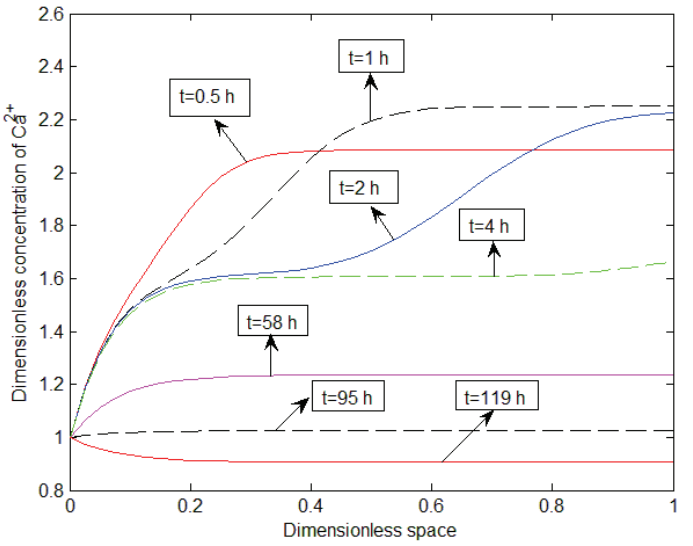

Figure 6: Space distributions of Ca^{2+}.

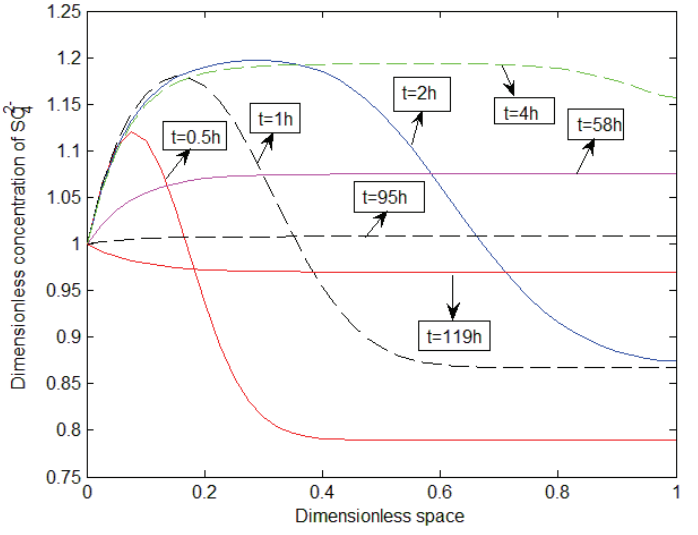

Figure 7: Space distributions of SO_4^{2-}.

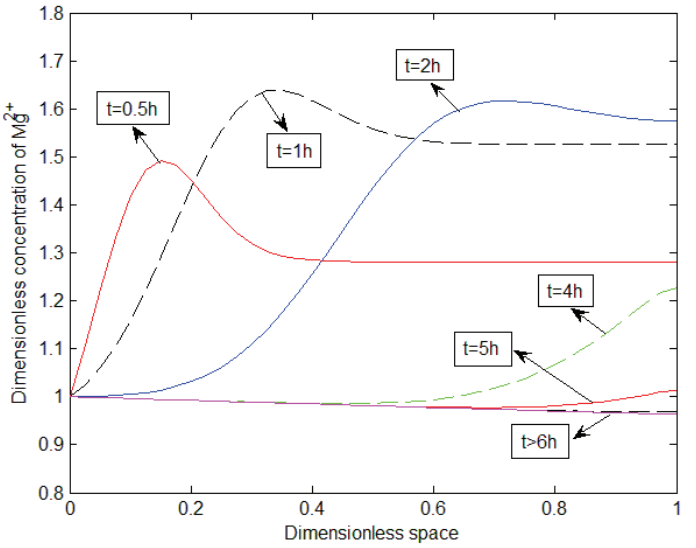

Figure 8: Space distributions of Mg^{2+}.

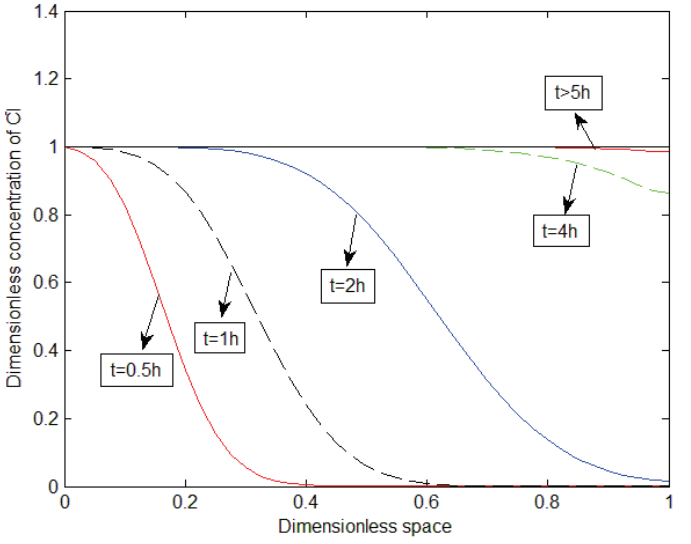

Figure 9: Space distributions of Cl^{-}.

However, at the initial stage of $t \in (0, 0.5h)$ for the experiment, it is still a trouble to describe the solutes transport behaviors with much more accuracy due to lack of measured data. Maybe better experimental devices, and other mathematical tools are needed.

As for the inversion algorithm utilized in this paper, it is an improvement to the ordinary optimal perturbation algorithm which can be applied to solve parameters identification problem numerically arising from a group of equations. Just as stated in subsections 4.2 and 4.3, it needs suitable conditions in realization of the inversion algorithm. For example, regularization parameters should be in a trust range so that an optimal solution can be obtained for given numerical differential step, and differential steps should not be too small. We will make more investigations on the optimal inversion algorithm in our sequent works.

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