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TRANSPORT OF CONTAMINANTS IN POROUS MEDIA COLUMNS: DIRECT AND INVERSE ANALYSIS

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Abstract. The proposed work is aimed at the analysis of the dispersion of contaminants through porous materials, such as soils and engineered barriers. We first describe the experimental apparatus and the porous media employed, besides the corresponding experimental procedure. Then, the computational strategies for the properties identification analysis are presented in detail. Typical results for the dispersion coefficient and retardation factor of Potassium Bromide in sandy soils are illustrated.

Keywords. Mass transfer, *dispersion coefficient, inverse problem, experimental analysis*

1. Introduction

The numerical simulation of the dispersion of pollutants, such as fertilizers, pesticides, heavy metals and radioactive waste, in soils and in engineering barriers, plays an important role in safety analysis procedures. Accurate numerical simulations of such phenomenon require the knowledge of reliable values for the physical properties appearing in the formulation, including, among others, the dispersion coefficient.

Different experimental techniques have been used in the past for the identification of the diffusion coefficient. They include, the two-cell technique (Gillham *et al*., 1984; Shackelford and Daniel, 1991.a), the reservoir technique (Barone *et al*., 1989; Shackelford and Daniel, 1991.a,b), radioactive techniques (Pereira *et al*. 1999; Pereira *et al*. 2001) and the use of electrical conductivity cells (Shackelford and Redmond, 1995; Moreira *et al*, 2003). The use of electrical conductivity measurements and of radiation measurement technique were compared by Pereira *et al*. (2001) in terms of the accuracy of the estimated parameter via inverse analysis techniques. Analyses of the sensitivity coefficients and of the determinant of the information matrix revealed that more accurate estimates could be obtained for the diffusion coefficient by using electrical conductivity cells to measure concentration. Such a fact was confirmed with the use of simulated experimental data containing random errors as well as with the use of actual measurements (Moreira *et al*., 2003).

In this work we examine the use of actual measured concentration data, obtained from electrical conductivity cells, for the estimation of the dispersion coefficient and the retardation factor of Potassium Bromide (KBr) in sandy soil. The experiments were run on a saturated breakthrough column (Van Genuchten, 1981). Two experimental techniques are used to measure the salt concentration of the outflow solution. The inverse problem of parameter estimation is solved with the Levenberg-Marquardt Method of minimization of the least-squares norm (Levenberg, 1944; Marquardt, 1963; Beck and Arnold, 1977; Ozisik and Orlande, 2000). The experimental apparatus, as well as the results obtained for the unknown parameters are described below.

2. Experimental Apparatus and Experimental Procedure

The experimental apparatus consists of a plexiglas column with 0.095 mm of internal diameter and 380 mm of length. The column base is closed with a plexiglas plate. A flexible nylon tube at the column outlet permits the measurement of the solution concentration by using two different measurement techniques. In this tube, a valve is used to control the flow through the column. A constant-level distilled water reservoir on the column top maintains a

constant flow through the column. The salt solution is injected into the column through a cell containing contaminated sand, as illustrated in figures 1 and 2.

The salt concentration is measured with two different techniques at the column outlet. These techniques are:

- Technique I – The outflow solution is stored periodically in a glass reservoir for 3 minutes. The solution concentration is then measured with a commercial electrical conductivity cell DIGIMED DMC-010.
- Technique II – The outflow solution concentration is measured in line with the nylon tube at the column outlet, by using an electrical conductivity cell manufactured in the Laboratory of Heat Transmission and Technology of COPPE.
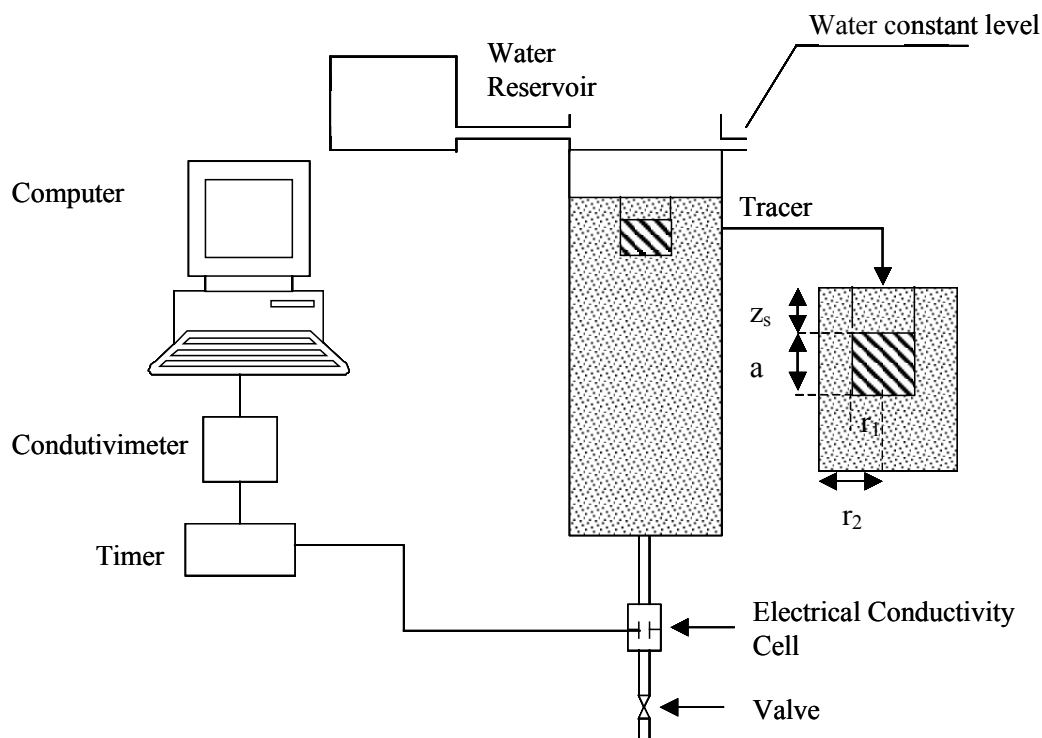

Figure 1. Experimental apparatus components


Figure 2. Experimental apparatus

The sand soil was sieved and grains larger than 48 Tyler and smaller than 16 Tyler were used in the experiments. The results of the sieving process are shown in Tab. (1). After sieving, the sand was thoroughly cleaned with distilled water before being carefully poured into the column. Distilled water was then added to the column in order to obtain a homogeneous saturated porous medium. The experimentally obtained porosity of the column is 0.35.

Table 1- Sieving results for the sand used in the experiments

Diameter (mm)	Diameter (Tyler)	Mass (kg)	% Retained	Total (%)
> 1.1	—	—	—	—
0.84 – 1.00	20 – 16	0.012	5.22	5.22
0.59 – 0.84	28 – 20	0.076	33.04	38.26
0.50 – 0.59	32 – 28	0.062	26.96	65.22
0.297 – 0.50	48 – 32	0.070	30.43	95.65
—	—	0.010	4.35	100.00

A cylindrical plexiglass cell with 58 mm of height and 51.6 mm of internal diameter was used to inject the saline tracer into the column. The cell bottom was closed with and impermeable membrane. Before letting the water to flow through the column, the cell was placed on the top of the column. The cell contained 30 ml of a 0.05 % solution of KBr (Potassium Bromide). Dry and clean sand was then poured into the cell. Wet sand was poured in the column beside and above the cell, in order to make the porous medium as continuous as possible. The saline solution, mixed with the sand, occupied a length of 40 mm inside the cell. At the initial time for the experiment, the cell membrane was ruptured, permitting the saline solution dispersion through the column.

The salt concentration of the column outflow solution was measured with two different techniques, as described above. Calibrations of the two different electrical conductivity cells used in this work were performed before the experiments, so that the concentration could be obtained from the electrical conductivity measurements. Standard KBr solutions were used for the calibration. The calibration curves are presented in Figs. (3.a,b), for the cells used in techniques I and II, respectively.

(a)   (b)
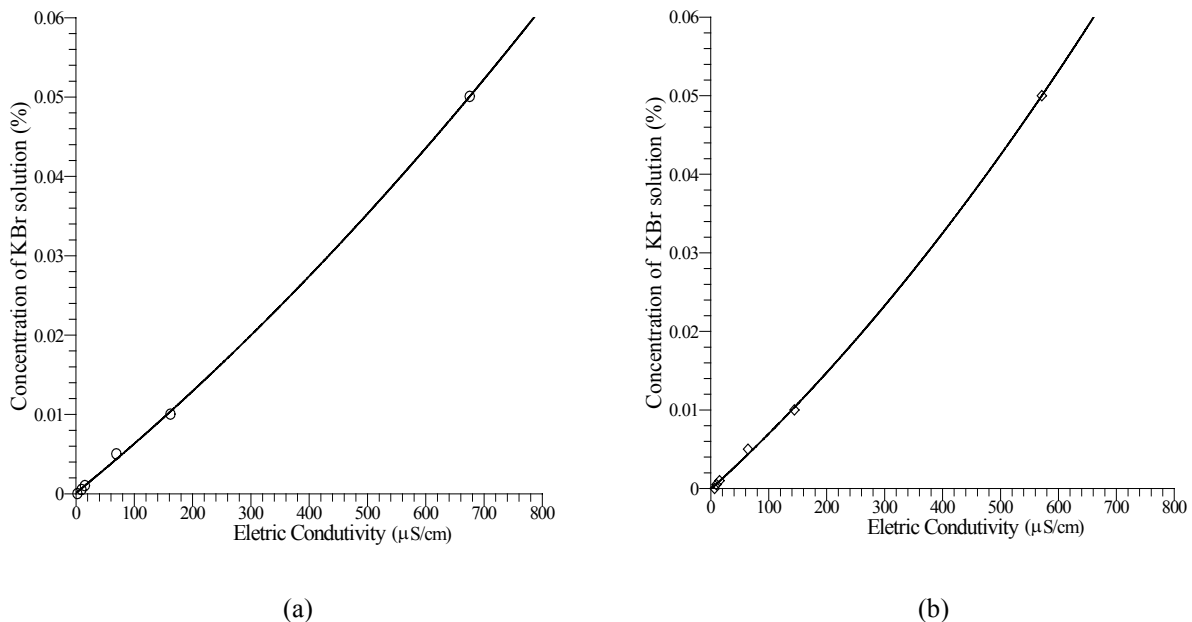
Figures 3. Calibration curves for the cells used in (a) Technique I and (b) Technique II

3. Mathematical Formulation

For the physical problem described above, we assume that, initially, the KBr solution with concentration C_0 inside the cell occupies the region $z_s < z < z_s + a$, while the salt concentration in other regions of the column is taken as a

background value C_b. The water flowing into the column is also supposed to contain a salt concentration C_b. Dispersion is assumed to be one-dimensional along the longitudinal direction through the column. Also, we assume that the relation between adsorbed and solution concentrations is described by a linear isotherm (Van Genuchten, 1981), that the diffusion-advection equation describing the salt dispersion through the column is given by:

$$R\frac{\partial c(z,t)}{\partial t} = D\frac{\partial^2 c(z,t)}{\partial z^2} - V\frac{\partial c(z,t)}{\partial z}; \quad \text{for} \quad 0 < z < L \ \text{e} \ t > 0 \tag{1.a}$$

The initial condition is given by:

$$c(z,0) = \begin{cases} C_b, & em \quad 0 < z < z_s \\ C_0, & em \quad z_s < z < a + z_s \\ C_b, & em \quad z_s + a < z < L \end{cases} \quad \text{for} \quad t = 0 \tag{1.b}$$

and the boundary conditions as:

$$c(0,t) = C_b \qquad \text{in} \quad z = 0 \quad e \quad t > 0 \tag{1.c}$$

$$D\frac{\partial c(L,t)}{\partial z} + h_m\, c(L,t) = h_m C_b \qquad \text{in} \quad z = L \ \text{e} \ t > 0 \tag{1.d}$$

where D is the dispersion coefficient, R is the retardation factor, V is the porous velocity and L is the column length.

Note in Eq. (1.c) that the boundary condition at z =0 is taken as of the first kind, by assuming that the advective effects are locally dominant. Also, note in Eq. (1.d) that the boundary condition at z =L was taken as of the third-kind, where h_m is the mass transfer coefficient between the column and the outflow plenum. Such was the case because a paper filter as used to hold the porous medium inside the column. Any salt retention on this filter is mathematically taken care of by the mass transfer coefficient h_m.

For the solution of the problem given by Eqs. (1) we use finite-differences with the McCormack predictor-corrector scheme (Anderson, 1984).

The dispersion coefficient can be written as:

$$D = \alpha V^n + \tau D_{dm} \tag{2}$$

where α is the dispersivity, τ is the tortuosity, D_{dm} is the molecular diffusion coefficient and n is an empirical constant usually taken between 1 and 2.

4. Inverse Analysis

The objective of the present study is to estimate the apparent the following vector of unknown parameters:

$$\mathbf{P} = [\, D\,,\, R\,,\, h_m\,] \tag{3}$$

appearing in problem (1), by using transient concentration measurements of the column outflow solution. Such kind of problem is denoted as an *inverse problem of parameter estimation* (Beck and Arnold, 1977; Alifanov, 1994; Ozisik and Orlande, 2000). The other quantities appearing in the formulation of the direct problem are considered exactly known for the analysis.

Estimating the dispersion coefficient without making any specific assumption regarding its inner structure, such as in Eq. (2), is interesting because there is evidence that dispersion be non-Fickian in nature, especially in the presence of preferential flow paths (Knowles and Yan, 2004).

By assuming the measurement errors to be additive, uncorrelated and normally distributed, with zero mean and known standard deviation, the unknown parameters were estimated here through the minimization of the *ordinary least squares norm*. For a general case involving N unknown parameters $P_1, P_2, \ldots, P_N$, such a norm can be written as

$$S(\mathbf{P}) = [\mathbf{Y} - \mathbf{C}(\mathbf{P})]^T [\mathbf{Y} - \mathbf{C}(\mathbf{P})] \tag{4}$$

The superscript T above denotes transpose and $[\mathbf{Y}\text{-}\mathbf{C}(\mathbf{P})]^T$ is given by

$$[\mathbf{Y} - \mathbf{C}(\mathbf{P})]^T \equiv \left[(Y_1 - C_1), (Y_2 - C_2), ..., (Y_I - C_I) \right] \tag{5}$$

where, $i=1,...,I$

The estimated concentrations C_i are obtained from the solution of the direct problem at the measurement location and at time t_i, by using estimated values for the unknown parameters.

For the minimization of the ordinary least squares norm (4), we considered the Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1963; Beck and Arnold, 1977; Ozisik and Orlande, 2000). The iterative procedure of such method is given by:

$$\mathbf{P}^{k+1} = \mathbf{P}^k + (\mathbf{J}^T \mathbf{W} \mathbf{J} + \mu^k \, \Omega^k)^{-1} \, \mathbf{J}^T [\mathbf{Y} - \mathbf{C}(\mathbf{P}^k)] \tag{6}$$

where the superscript k denotes the number of iterations, μ^k is the so called damping parameter and Ω^k is a diagonal matrix, which can be taken as the identity matrix or as the diagonal of $\mathbf{J}^T\mathbf{J}$. The sensitivity matrix $\mathbf{J}$ is given by

$$\mathbf{J}(\mathbf{P}) = \left[\frac{\partial \mathbf{C}^T(\mathbf{P})}{\partial \mathbf{P}} \right]^T = \begin{bmatrix} \dfrac{\partial C_1}{\partial P_1} & \dfrac{\partial C_1}{\partial P_2} & \dfrac{\partial C_1}{\partial P_3} & \cdots & \dfrac{\partial C_1}{\partial P_N} \\[2mm] \dfrac{\partial C_2}{\partial P_1} & \dfrac{\partial C_2}{\partial P_2} & \dfrac{\partial C_2}{\partial P_3} & \cdots & \dfrac{\partial C_2}{\partial P_N} \\[2mm] \vdots & \vdots & \vdots & & \vdots \\[2mm] \dfrac{\partial C_I}{\partial P_1} & \dfrac{\partial C_I}{\partial P_2} & \dfrac{\partial C_I}{\partial P_3} & \cdots & \dfrac{\partial C_I}{\partial P_N} \end{bmatrix} \tag{7}$$

After estimating the unknown parameters by using the iterative procedure of the Levenberg-Marquardt method, Eq. (6), subjected to appropriate stopping criteria (Ozisik and Orlande, 2000), we can estimate the standard-deviations for the parameters with the covariance matrix given by (Beck and Arnold, 1977):

$$\mathbf{cov}(\mathbf{P}) = \left(\mathbf{J}^T \mathbf{J} \right)^{-1} \sigma^2 \tag{8}$$

5. Results

Figure 4 presents a comparison of the two techniques used in this work to measure the outflow solution concentration, for a velocity of 5.19×10^{-3} cm/s. We note that the agreement between the two techniques is very good. For the results presented below we have used Measurement Technique II, since the electrical conductivity is automatically measured with the data acquisition system, without sources of errors, such as in the manual procedure of Technique I.
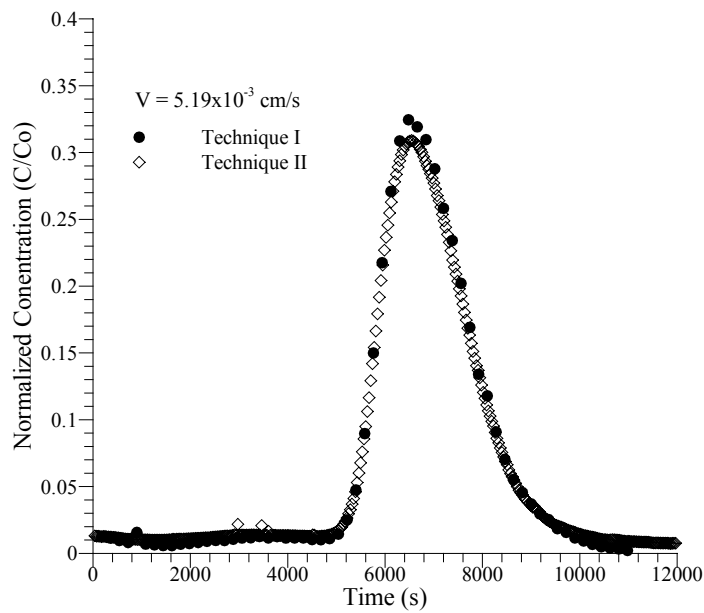
Figure 4. Comparison between techniques I and II of measurement

Figure 5 presents the normalized sensitivity coefficients with respect to the different unknown parameters. We note that, for nonlinear estimation problems such as the one under picture in this work, these analysis of the sensitivity coefficients is not global, because they are functions of the unknown parameters. Therefore, *a priori* estimated values for the parameters are required for such analysis. In this work, we have used $D = 1.33 \times 10^{-4}$ cm^2/s, $R = 1$. $h_m = 5.19 \times 10^{-3}$ cm/s. The analysis of the sensitivity coefficients was performed for $V = 5.19 \times 10^{-3}$ cm/s, which was the porous velocity during the experiments (see Fig. 4). Figure 5 shows that the sensitivity coefficients with respect to D and h_m are very small, as compared to the sensitivity coefficient with respect to R. Therefore, the estimation of these two parameters is quite difficult, requiring initial guesses for the Levenberg-Marquardt method quite close to the exact values. On the other hand, the sensitivity coefficients are not linearly-dependent, as shown by Fig. 6, which presents an amplification of the region of small sensitivity coefficients. Figure 5 also shows that the sensitivity coefficients are null before and after the solution plume passes through the measurement location. Therefore, only the measurements taken during the period that the plume passes through the sensor are useful for the inverse analysis.
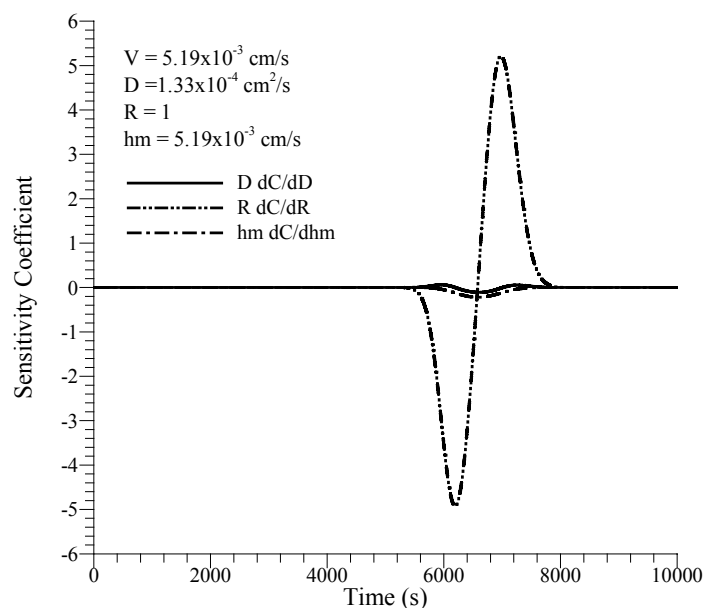

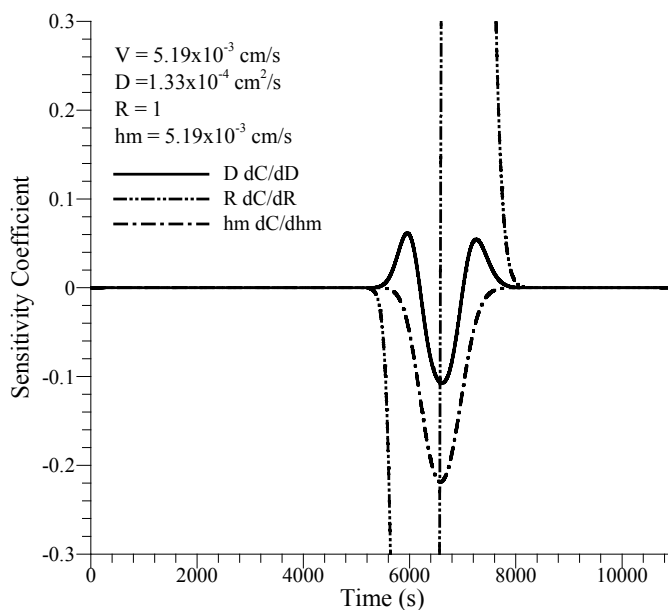Figure 5. Sensitivity coefficients

Figure 6. Amplification of the region of small sensitivity coefficients

We now use the experimental data shown in Fig. 4, obtained with Technique II, for the simultaneous estimation of $\mathbf{P} = [\, D\,,\, R\,,\, h_m\,]$. The estimated parameters, with their respective 99% confidence intervals, were:

$$D = (1.21 \pm 0.01)\ \text{x}10^{-3}\ \text{cm}^2/\text{s}$$
$$R = (1{,}0321 \pm 0.0004)$$
$$h_m = (1.49 \pm 0.02)\ \text{x}10^{-3}\ \text{cm/s}$$

Figure 7 presents a comparison of experimental and estimated concentrations obtained with the above estimated parameters. The agreement between measured and estimated concentrations is excellent. Despite this fact, we note in Fig. 8 that the residuals are correlated. Hence, the mathematical model used in this work needs improvement in order to accurately represent the physical problem.
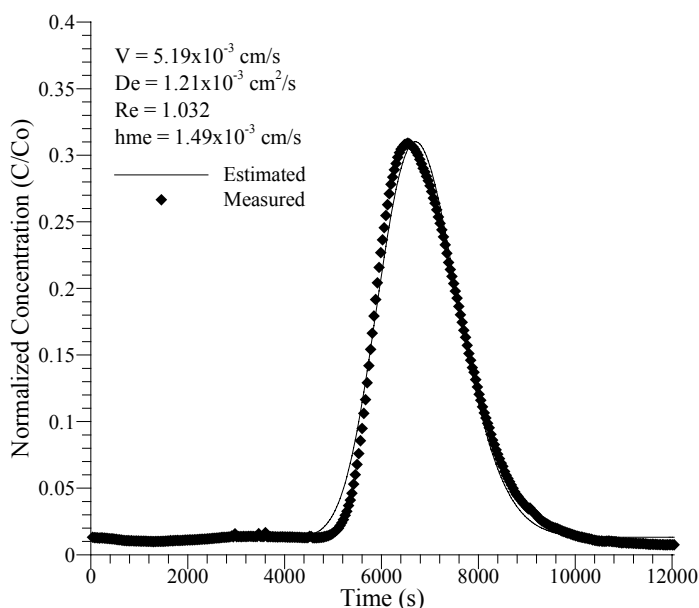

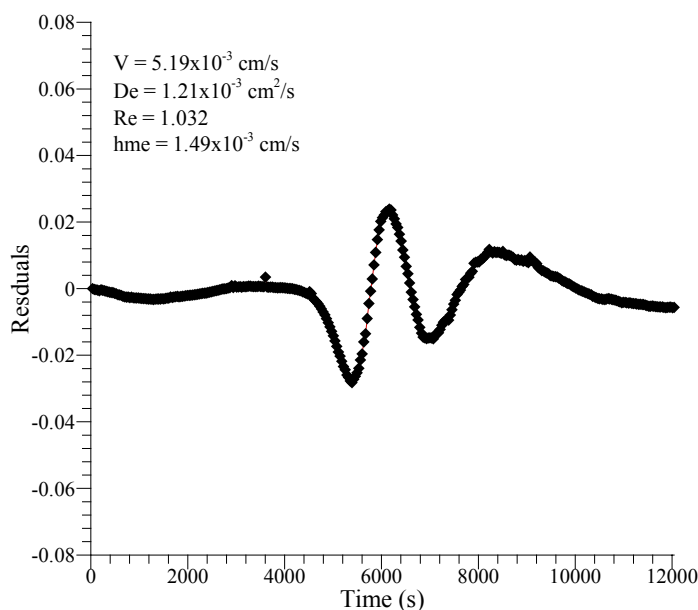Figure 7. Comparison of experimental and estimated concentrations

Figure 8. Concentration residuals

6. Conclusions

This paper dealt with the use of electrical conductivity measurements for the simultaneous estimation of the dispersion coefficient, retardation factor and mass transfer coefficient of salts in sandy soils, by using a breakthrough column. The Levenberg-Marquardt method was applied for the solution of the present parameter estimation problem. The experimental apparatus and experimental procedure were described and results were presented for the dispersion of Potassium Bromide (KBr) in sand saturated with distilled water.

The results obtained so far indicate that both measurement techniques under study provide accurate results for the outflow salt concentration. Although quite small, the concentration residuals are correlated indicating that there are inconsistencies between the mathematical and the physical models. Possible sources for such inconsistencies can be multi-dimensional effects, non-linear behavior, uncertainties in parameters judged as exactly known for the inverse analysis and inappropriate boundary conditions. In fact, since the sensitivity coefficient for the mass transfer coefficient at the outflow boundary is very small, it appears that a second-kind boundary condition can be used. The choice for this boundary condition would result in a reduction of one unknown parameter, and would improve the accuracy of the other estimated parameters. The investigation of non-linear effects is now being undertaken. The effects of uncertainties on parameters assumed as exactly know for the inverse analysis, such as the pore velocity, are also now under investigation, by using Bayesian statistics.

7. Acknowledgements

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