

INVERSE ANALYSIS IN MASS DIFFUSION WITH ELECTRICAL CONDUCTIVITY MEASUREMENTS

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Abstract. The proposed work is aimed at the analysis of the molecular diffusion of contaminants through porous materials, such as soils and engineering barriers, for utilization in surface repositories of toxic waste. We first describe the experimental apparatus and the different 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 diffusion coefficient of Potassium Bromide in sandy soils are illustrated.

Keywords. Mass transfer, diffusion coefficient, inverse problem, experimental analysis

1. Introduction

The numerical simulation of the dispersion of radioactive materials in soils and in engineering barriers plays an important role in the safety analysis of nuclear waste repositories. Accurate numerical simulations of such phenomenon require the knowledge of reliable values for the physical properties appearing in the formulation, including, among others, the apparent diffusion coefficient. Such coefficient is defined as the ratio between the effective diffusion coefficient (which includes the effects of tortuosity on the molecular diffusion) and the retardation factor (Shackelford and Daniel, 1991.a).

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).

The *two-cell technique* consists in saturating two equal cells with different solutions and assembling them together to allow diffusion to occur. After a sufficiently long period, when significant changes from the initial concentration can be observed in both cells, the apparatus is disassembled. The soil in each cell is then sectioned to determine the resulting concentration profile and the experimental results are curve-fit with an analytical solution to determine the diffusion coefficient. Besides the clear disadvantage of being a destructive technique, the two-cell technique may also be inappropriate for compacted clay soils, because it is difficult to obtain good contact between the half-cells.

In the *reservoir technique*, compacted and saturated soil in a mold is put into contact with a leachate in a reservoir. A concentration gradient is then established between the reservoir and the compacted soil and the concentration of solutes in the reservoir decreases with time. As for the two-cell technique, after a sufficiently long period, the soil is extruded and sectioned, in order to determine the concentration profile. The diffusion coefficient can be obtained from the time variation of the concentration in the reservoir, as well as from the concentration profile in the soil at the end of the test. However, some inconsistencies have been observed with the results obtained with these two approaches in the reservoir technique (Shackelford and Daniel, 1991.b).

Electrical conductivity cells placed inside the soil (Shackelford and Redmond, 1995) have also been used to measure the solute concentration profile in order to estimate the diffusion coefficient. Although it permits the use of transient measurements for the estimation procedure, resulting in faster experiments, and being a non-destructive technique, it clearly involves a perturbation of the medium under study because intrusive measurements are used in the analysis (Shackelford and Redmond, 1995).

The use of non-intrusive *radiation measurement techniques* has also been considered for the estimation of the apparent diffusion coefficient (Pereira et al. 1999). The experimental setup consisted of a cylindrical column filled with compacted soil saturated with water. A radioactive salt solution was injected in the bottom of the column and, due to the

concentration gradient, the salt diffused through the column. A radiation detector was used to measure the number of counts, which was associated to the salt concentration at several positions along the column during the experiment. Such measurements were then used to estimate the apparent diffusion coefficient of the salt in the column by inverse analysis. This measurement technique is especially suitable for diffusion experiments involving radioactive materials found in nature; but it can also be used for the study of diffusion of several non-radioactive materials, which can be irradiated before the experiments. Also it has the advantages of being non-intrusive and non-destructive, as an opposition to other techniques referred to above. It is based on transient measurements, which may result in faster experiments in many cases. On the other hand, it involves the manipulation of radioactive materials, thus requiring strict safety procedures.

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 by using electrical conductivity cells to measure concentration. Such a fact was confirmed with the use of simulated experimental data containing random errors.

In this work we examine the use of actual measured concentration data obtained from electrical conductivity cells for the estimation of the apparent diffusion coefficient of Potassium Bromide (KBr) in a column filled with sandy soil saturated with distilled water. 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 apparent mass diffusion coefficient are described below.

2. Experimental Apparatus and Experimental Procedure

The experimental apparatus consisted of a cylindrical Plexiglas column, with inner and outer diameter of 50 mm and 60 mm, respectively and height of 180 mm, as depicted in figure 1. The base of the column was closed with a Plexiglas plate. The top of the column was left open to allow the filling and compaction of the tested soil.

The soil used in the present study was sand. The sand was sieved and grains larger than 48 tyler and less than 20 tyler were retained and thoroughly washed with distilled water. The sand was gently poured into the column with distilled water in order to obtain a homogeneously packed porous medium with an estimated porosity level of 0.36. The sand was completely saturated with distilled water prior to the experiments.

In previous experiments using radiation detection techniques (Pereira et al, 1999) the salt solution was injected through a capillary tube at the bottom of the column. For these cases, we noticed inconsistencies among the obtained results because of uncertainties in the volume of the salt solution really injected into the column. Such a fact required that the injected volume of the salt solution be also estimated *via* the inverse analysis parameter estimation approach, together with the apparent mass diffusion coefficient, which was actually the parameter of interest. In fact, during the present study, dye injected into the column revealed that the above procedure resulted in a non-uniform distribution of the salt solution into the column. Therefore, for the present study the contamination of the bottom of the column with the salt solution for the diffusion experiment was performed in an alternative manner; before filling the column with saturated sand, the column was filled with contaminated sand to a height of 18 mm. This sand was saturated with inactive Potassium Bromide (KBr) dissolved in distilled water in an appropriate concentration.

To measure the concentrations of the inactive salt along the column, a total of 8 pairs of electric conductivity cells were used. Each cell is rectangular, 10 mm wide and 5 mm high. The salt concentration was indirectly determined by measuring the electrical conductivity in $\mu\text{Si}/\text{cm}$ of the fluid in the porous medium. The spacings between the cells were 10 mm. From the base of the column to the first cell, the spacing was 2.5 mm. These cells were fixed on the inner column wall. The information collected by the cells was passed to an electrical conductivity measurement system, DM30, manufactured by DIGIMED. In order to collect the measurements, an automatic data acquisition system was used. With the help of a four-channel electronic switch, it was possible to obtain sequential measurements of the conductivity for 4 different cells. To transform these values of electrical conductivities into concentrations, calibration curves were used. The calibration was performed in the column filled with sand saturated with inactive salt solution of (KBr), in concentrations varying from 0 to 2%.

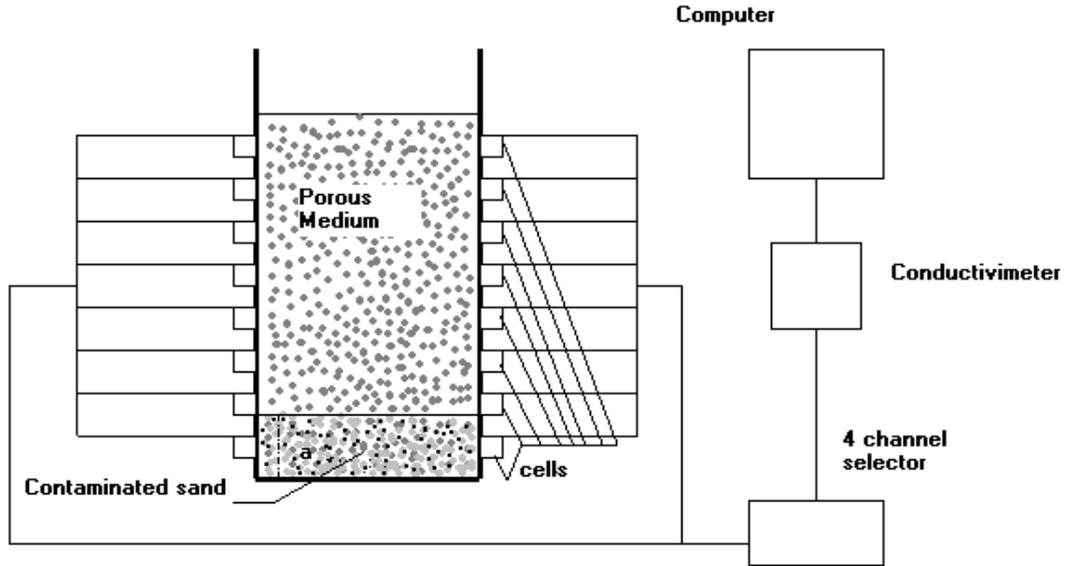


Figure 1: Experimental Apparatus for Apparent Diffusion Coefficient Estimation

3. Mathematical Formulation

The physical problem associated with the experiment described above can be mathematically formulated by considering the column as a semi-infinite medium, since the diffusion process is so slow that the boundary condition at the open end of the column does not influence the solution during the time range of interest. Due to the symmetry of the column and due to the no-flux boundary conditions on its surfaces, the diffusion process can be formulated in terms of a one-dimensional problem given by:

$$\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial z^2} \quad \text{for } t > 0 \text{ and } z > 0 \quad (1.a)$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = 0, \text{ for } t > 0 \quad (1.b)$$

$$C = f(z) = \begin{cases} C_0 & \text{for } t = 0 \text{ and } 0 < z < a \\ 0 & \text{for } t = 0 \text{ and } z > a \end{cases} \quad (1.c)$$

where D^* is the apparent mass diffusion coefficient, C_0 is the initial concentration of the salt into the column and a is the initial height of the column filled with the salt solution.

The apparent mass diffusion coefficient (Shackelford and Daniel, 1991.a) is defined as

$$D^* = \frac{D}{K} \quad (2)$$

where D is the effective diffusion coefficient, which takes into account the tortuosity of the porous media, and K is the retardation factor.

The above problem (1) is denoted as a *direct problem* when D^* , C_0 and a are known. The objective of the direct problem is then to determine the transient concentration field $C(z,t)$ in the column.

The analytical solution for the direct problem, obtained by Fourier transform (Ozisik, 1993), is given by:

$$C^*(z,t) = \frac{C(z,t)}{C_0} = \frac{1}{2} \left[\operatorname{erf} \left(\frac{a+z}{2\sqrt{D^*t}} \right) + \operatorname{erf} \left(\frac{a-z}{2\sqrt{D^*t}} \right) \right] \quad (3)$$

where $C^*(z,t)$ is the normalized concentration and $\operatorname{erf}(\cdot)$ is the error function (Ozisik, 1993).

4. Inverse Analysis

The objective of the present study is to estimate the apparent mass diffusion coefficient D^* appearing in problem (1), by using transient concentration measurements taken along the column. Such kind of problem is denoted as an *inverse problem of parameter estimation* (Beck and Arnold, 1977, Alifanov, 1994, Ozisik and Orlande, 2000). As in our previous work involving the use of radiation detection techniques (Pereira et al, 1999), the initial height occupied by the salt solution, a , was also considered as an unknown parameter.

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

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

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

$$[\mathbf{Y} - \mathbf{C}(\mathbf{P})]^T = [(\bar{Y}_1 - \bar{C}_1), (\bar{Y}_2 - \bar{C}_2), \dots, (\bar{Y}_I - \bar{C}_I)] \quad (5.a)$$

where $(\bar{Y}_i - \bar{C}_i)$, $i=1, \dots, I$ is a row vector containing the differences between the measured and estimated concentrations at the measurement positions z_m , $m=1, \dots, M$ at time t_i , that is,

$$(\bar{Y}_i - \bar{C}_i) = [Y_{i1} - C_{i1}, Y_{i2} - C_{i2}, \dots, Y_{iM} - C_{iM}] \quad (5.b)$$

The estimated concentrations C_{im} are obtained from the solution of the direct problem, Eq. (3), at the measurement location z_m 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:

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

where the superscript k denotes the number of iterations, μ^k is the so called damping parameter and $\mathbf{\Omega}^k$ 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

$$\mathbf{J}(\mathbf{P}) = \left[\frac{\partial \mathbf{C}^T(\mathbf{P})}{\partial \mathbf{P}} \right]^T = \begin{bmatrix} \frac{\partial \bar{C}_1^T}{\partial P_1} & \frac{\partial \bar{C}_1^T}{\partial P_2} & \frac{\partial \bar{C}_1^T}{\partial P_3} & \dots & \frac{\partial \bar{C}_1^T}{\partial P_N} \\ \frac{\partial \bar{C}_2^T}{\partial P_1} & \frac{\partial \bar{C}_2^T}{\partial P_2} & \frac{\partial \bar{C}_2^T}{\partial P_3} & \dots & \frac{\partial \bar{C}_2^T}{\partial P_N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial \bar{C}_I^T}{\partial P_1} & \frac{\partial \bar{C}_I^T}{\partial P_2} & \frac{\partial \bar{C}_I^T}{\partial P_3} & \dots & \frac{\partial \bar{C}_I^T}{\partial P_N} \end{bmatrix} \quad (7.a)$$

$$\text{where: } \bar{C}_i = [C_{i1}, C_{i2}, \dots, C_{iM}] \quad \text{for } i=1, \dots, I \quad (7.b)$$

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):

$$\text{cov}(\mathbf{P}) = (\mathbf{J}^T \mathbf{J})^{-1} \quad (8)$$

We note that different experimental variables, such as the number of measurement locations, frequency of measurements and the duration of the experiment, can be determined from the analysis of the sensitivity coefficients, i.e., the elements of the sensitivity matrix, and of the determinant of the matrix $\mathbf{J}^T \mathbf{J}$. The maximization of the

determinant of such matrix is generally aimed in order to obtain estimates with minimum confidence regions (Beck and Arnold, 1977).

5. Results

The analyses of the sensitivity coefficients and of the determinant of the information matrix were performed by Pereira et al (2001), for experimental conditions similar to those of the present work, involving electrical conductivity measurements. Such analyses revealed that accurate estimations for the apparent mass diffusion coefficient of KBr could be obtained with the measurements of 4 conductivity cells located along the sand column, during the time interval $0 < t < 80$ h. Thus, for the experimental results presented below, the measurements of cells 1 through 4, located at $z = 2.5, 32.5, 42.5$ and 52.5 mm, respectively, were used for the inverse analysis. Measurements were taken until 80 hours after the beginning of the experiment, with a frequency of 1 measurement per cell every 20 minutes. The standard-deviation of the normalized concentration measurements was 0.03. The initial guesses for the iterative procedure of the Levenberg-Marquardt method were taken as $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ and 2.00 cm, for D^* and a , respectively. However, the results presented below were not sensitive to the initial guesses used for such iterative procedure.

Under such experimental conditions, the apparent mass diffusion coefficient of KBr, estimated with the Levenberg-Marquardt method described above, was $1.43 \times 10^{-5} \text{ cm}^2/\text{s}$. The 99% confidence level for the estimated parameter was $1.40 \times 10^{-5} \text{ cm}^2/\text{s} < D^* < 1.46 \times 10^{-5} \text{ cm}^2/\text{s}$. The initial height of the column filled with the salt solution was estimated as 2.18 cm, with the 99% confidence interval given by $2.17 \text{ cm} < a < 2.20 \text{ cm}$.

Figure 2 shows a comparison between estimated normalized concentrations (obtained from the solution of the direct problem with the values of the parameters estimated above) with the measured normalized concentrations, for the different electrical conductivity cells. Generally, the agreement between measured and estimated normalized concentrations is very good.

Figure 3 illustrates the residuals, defined as the difference between measured and estimated concentrations, for the 4 cells used in the inverse analysis. The residuals are quiet small at the different measurement positions, but, on the other hand, they exhibit some degree of correlation. Therefore, the mathematical model utilized is not completely consistent with the physical problem under picture. Among possible inconsistencies we can find wall effects and non-linearities, such as the dependence of the diffusion coefficient with concentration. These effects are currently under investigation.

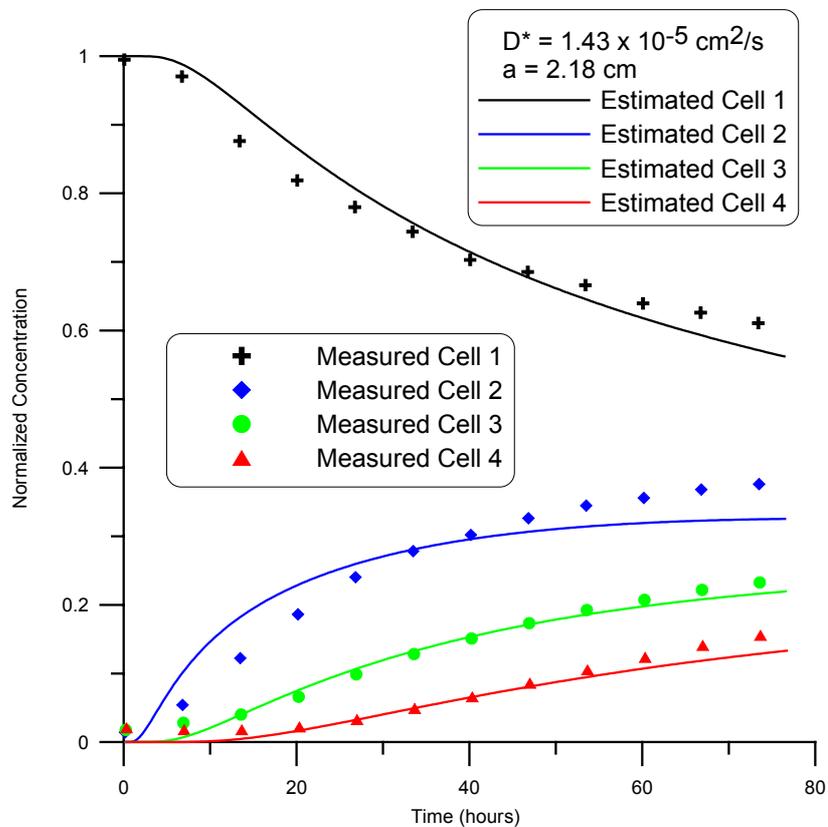


Figure 2: Measured and estimated normalized concentration values

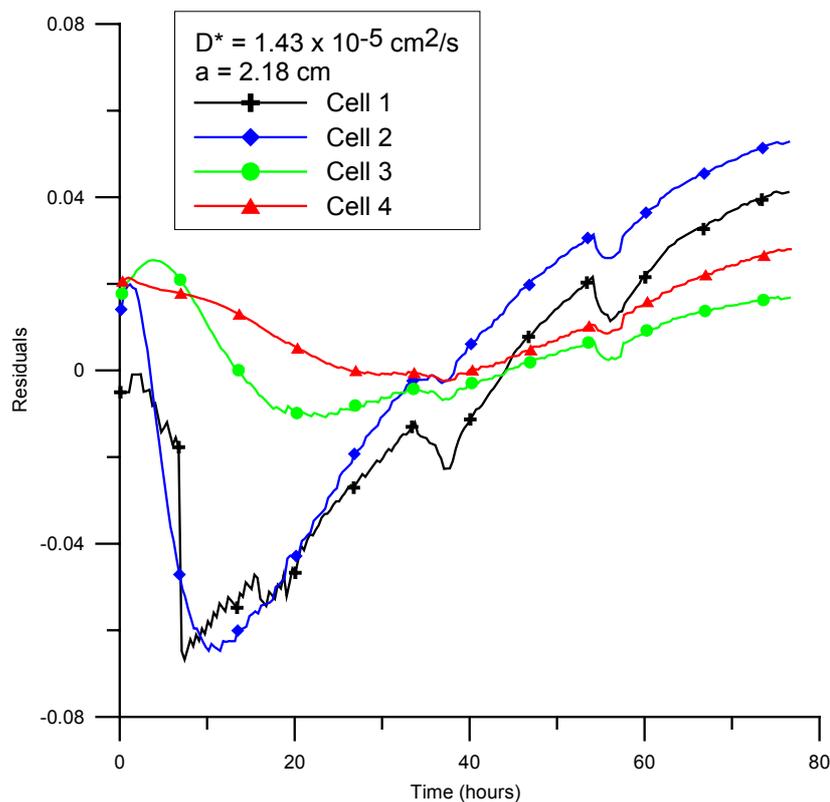


Figure 3: Residuals between measured and estimated concentrations

6. Conclusions

This paper dealt with the use of electrical conductivity measurements for the estimation of the apparent diffusion coefficient of salts in sandy soils. 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 diffusion of Potassium Bromide (KBr) in sand saturated with distilled water, as well as for the initial height of the column filled with the salt solution. The concentration residuals obtained are small but correlated, indicating that the mathematical model is not completely consistent with the physical problem. Possible causes for such inconsistencies are currently under investigation.

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