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ESTIMATION OF THE APPARENT MASS DIFFUSION COEFFICIENT BY USING INVERSE ANALYSIS AND RADIATION MEASUREMENT TECHNIQUES

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ABSTRACT

This paper deals with the use of radiation measurement techniques for the estimation of the apparent diffusion coefficient of salts. The Levenberg-Marquardt method is applied for the solution of the present parameter estimation problem. The experimental apparatus and experimental procedure are described and results are presented for the diffusion of Potassium Bromide (KBr) in sand saturated with distilled water. The experiment was designed with respect to the number of measurement locations, frequency of measurements and duration of the experiment through the analysis of the sensitivity coefficients and by using a D-optimum approach.

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) 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.

In this paper we describe a technique for the estimation of the apparent diffusion coefficient based on non-intrusive radiation measurements. The experimental setup consists of a cylindrical column filled with compacted soil saturated with water. A radioactive salt solution is injected in the bottom of the column and, due to the concentration gradient, the salt will diffuse through the column. A radiation detector is used to measure the number of counts, which is associated to the salt concentration, at several positions along the column during the experiment. Such measurements are then used to estimate the apparent diffusion coefficient of the salt in the column by inverse analysis. 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, 1999). The present 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 experimental apparatus, as well as the results obtained for the apparent mass diffusion coefficient of Potassium Bromide (KBr) in a column filled with sand saturated with distilled water, are described below.

EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental apparatus consisted of a cylindrical Plexiglas column, with inner and outer diameters of 0.075 m and 0.081 m, respectively, and 0.30 m of height. The base of the column was closed with a Plexiglas plate, while its top end was left open to permit the filling and compaction of the soil tested. Another column with same outer and inner diameters and 0.15 m of height supported this test column, as illustrated in Fig. 1. For the tests, both columns were filled with soil under the same compaction, in order to allow for the continuity of the medium at their interface. The radioactive salt was injected into the column through a capillary Teflon tube with length of 0.80 m. Such a tube penetrates into the test column through its lateral surface. The outlet of the injection tube was located at the center of the column at 0.001 m from its base. The inlet was connected to a 15 ml syringe through a Teflon tube.

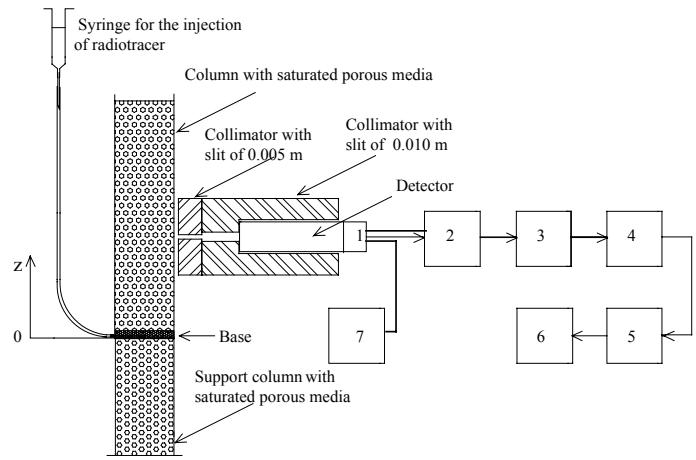

Figure 1 – Experimental apparatus

The system was adjusted to detect only the most abundant energies emitted by the Br 82, which was the radioactive ion obtained from the irradiation of Potassium Bromide (KBr) used in our experiments. Table 1 shows the energies emitted by Br82 and their respective abundancies, where those discriminated for the measurements are marked in bold characters. Therefore, the system was set to detect only the energies above 500KeV and below 850KeV.

Table 1- Energies emitted by the Br82 with respective abundancies

Energy E(γ), MeV	Abundance (%)
0.09	0.40
0.221	2.30
0.273	1.20
0.554	**73.00**
0.619	**43.00**
0.698	**27.00**
0.776	**83.00**
0.828	**24.00**
1.044	29.00
1.084	0.40
1.318	28.00
1.475	17.00
1.651	0.80
1.778	0.12
1.874	0.05
1.959	0.05
2.056	0.02
	329.34

The radiation detection system consisted of (see Fig. 1): (1) Sodium Iodide Tallium activated NaI(Tl) scintillation detector; (2) Pre-amplifier; (3) Amplifier; (4) Analyzer of pulse height

and discriminator; (5) Pulse counter (scaler); (6) Multi-channel analyzer and (7) High-voltage source. The resolving time of the detection system was determined as 1.62×10^{-6} s. The detector was manufactured by EG&G ORTEC.

The collimating system was constituted of two plumb blocks. One of them surrounded the detector. Its frontal part, ahead of the detector, was 0.05 m deep, 0.10 m wide and 0.10 m high, containing a slit with width of 0.05 m and height of 0.01 m. The second plumb block was placed in front of the first one. It was 0.05 m deep, 0.10 m wide and 0.10 m high, as the frontal part of the first block. However, its slit was smaller (0.05 m wide and 0.005 m high) than that of the other block, in order to reduce the collimating volume of the column viewed by the detector.

The soil used in the present study consisted of sand. The sand was sieved and grains larger than 180 tyler and less than 20 tyler were retained and thoroughly washed with distilled water. The sand was gently poured into the columns, together with distilled water, and compacted to a porosity level of 0.35. The sand was completely saturated with water prior to the experiments. After filling the columns with sand and properly adjusting the detection system, the radioactive salt was carefully injected into the test column by gravity. The injected salt initially filled the bottom of the column and diffusion occurred due to the concentration gradient. The salt concentration along the column was measured through the number of counts in 20 seconds, obtained with the radiation detector. Such a detector was manually moved along the column, with the front face of the second collimating block (as referred to above) almost touching its outer surface. Each measurement reading was replicated and the average value was used for the analysis, after deducting the measured background radiation. The frequency of measurements, number of measurement positions along the column and duration of the experiment are addressed later in the paper, in the discussion of the results.

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

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

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

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

where D^* is the apparent mass diffusion coefficient, λ is the radioactive decay coefficient, C_0 is the initial concentration of the salt injected into the column and a is the initial height of the column filled with the salt solution injected, under the hypothesis that such injected solution perfectly displaces the water in the pores.

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

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

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, λ 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 of the direct problem can be obtained by Fourier transform (Ozisik, 1993) as

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

where *erf*(.) is the error function (Ozisik, 1993).

The normalized concentration $C^*(z,t)$ can be related to the number of counts in 20 seconds measured with the radiation detector by

$$C^*(z,t) = \frac{C(z,t)}{C_0} = \frac{M(z,t)}{M_0} \qquad (4)$$

where M_0 is the measured number of counts corresponding to the salt concentration C_0 and $M(z,t)$ is the number of counts measured at position z at time t.

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, 1999). The other quantities appearing in the formulation of the direct problem are considered exactly known for the analysis, with the exception of the initial height occupied by the solution. Such quantity was also regarded as unknown and left to be estimated as part of the solution procedure, because we detected some inconsistencies

between different experiments, when using actual experimental data for the estimation of the apparent diffusion coefficient.

Inverse problems are generally *ill-posed* (Hadamard, 1923, Beck and Arnold, 1977, Alifanov, 1994, Ozisik and Orlande, 1999). The accurate solutions of inverse problems generally involve their reformulation in terms of well-posed problems. By assuming the measurement errors to be additive, uncorrelated and normally distributed, with zero mean and known standard deviations, the apparent mass diffusion coefficient was estimated here through the minimization of the *weighted 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

$$S(\mathbf{P})=[\mathbf{Y}-\mathbf{C}(\mathbf{P})]^T\,\mathbf{W}[\mathbf{Y}-\mathbf{C}(\mathbf{P})] \tag{5}$$

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

$$[\mathbf{Y}-\mathbf{C}(\mathbf{P})]^T \equiv \left[(Y_1-C_1),(Y_2-C_2),\ldots,(Y_I-C_I)\right] \tag{6.a}$$

where $\left(Y_i - C_i\right)$, i=1,...,I is a row vector containing the differences between the measured and estimated concentrations at the measurement positions z_m, m=1,...,M at time t_i, that is,

$$\left(Y_i - C_i\right) = \left[Y_{i1}-C_{i1}, Y_{i2}-C_{i2},\ldots,Y_{iM}-C_{iM}\right] \tag{6.b}$$

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.

The weighting matrix **W** contains the inverse of the variances of the measured concentrations on its diagonal. It is given by

$$\mathbf{W} = \begin{bmatrix} 1/\sigma_{11}^2 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & \ddots & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1/\sigma_{1M}^2 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \ddots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1/\sigma_{I1}^2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & & \ddots & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & 0 & 1/\sigma_{IM}^2 \end{bmatrix} \tag{6.c}$$

We note that the ordinary least squares norm, where the weighting matrix is given by the identity matrix, was not used in the present work because the standard-deviations of the measurements are not constant (Tsoulfanidis, 1983). The use of the weighted least squares norm (5) is recommended in such cases, in order to obtain minimum variance estimates (Beck and Arnold, 1977, Ozisik and Orlande, 1999).

For the minimization of the weighted least squares norm (5), we considered here the Levenberg-Marquardt method (Levenberg, 1944, Marquardt, 1963, Beck and Arnold, 1977, Ozisik and Orlande, 1999). The iterative procedure of such method is given by

$$\mathbf{P}^{k+1}=\mathbf{P}^k+(\mathbf{J}^T\mathbf{W}\mathbf{J}+\mu^k\,\Omega^k)^{-1}\mathbf{J}^T\mathbf{W}[\mathbf{Y}-\mathbf{C}(\mathbf{P}^k)] \tag{7}$$

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 $\mathbf{J}^T\mathbf{W}\mathbf{J}$. The sensitivity matrix **J** is given by

$$\mathbf{J}(\mathbf{P})=\left[\frac{\partial \mathbf{C}^T(\mathbf{P})}{\partial \mathbf{P}}\right]^T=\begin{bmatrix} \frac{\partial C_1^T}{\partial P_1} & \frac{\partial C_1^T}{\partial P_2} & \frac{\partial C_1^T}{\partial P_3} & \cdots & \frac{\partial C_1^T}{\partial P_N} \\ \frac{\partial C_2^T}{\partial P_1} & \frac{\partial C_2^T}{\partial P_2} & \frac{\partial C_2^T}{\partial P_3} & \cdots & \frac{\partial C_2^T}{\partial P_N} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{\partial C_I^T}{\partial P_1} & \frac{\partial C_I^T}{\partial P_2} & \frac{\partial C_I^T}{\partial P_3} & \cdots & \frac{\partial C_I^T}{\partial P_N} \end{bmatrix} \tag{8.a}$$

where: $C_i = \left[C_{i1}, C_{i2},\ldots,C_{iM}\right]$ for i=1,...,I (8.b)

After estimating the unknown parameters by using the iterative procedure of the Levenberg-Marquardt method, Eq. (7), subjected to appropriate stopping criteria (Ozisik and Orlande, 1999), we can estimate the standard-deviations for the parameters with the covariance matrix given by (Beck and Arnold, 1977):

$$\mathbf{cov}(\mathbf{P}) = \left(\mathbf{J}^T\mathbf{W}\mathbf{J}\right)^{-1} \tag{9}$$

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 $\mathbf{J}^T\mathbf{W}\mathbf{J}$, as described next. The maximization of the determinant of such matrix is generally aimed in order to obtain estimates with minimum confidence regions (Beck and Arnold, 1977).

RESULTS AND DISCUSSIONS

Before proceeding to the estimation of the apparent diffusion coefficient, by using actual experimental data obtained in the apparatus described above, let us examine first the variation of the sensitivity coefficients and of the determinant of the matrix $\mathbf{J}^T\mathbf{W}\mathbf{J}$.

The analytical expressions for the sensitivity coefficients with respect to the initial height occupied by the salt in the column, a, and with respect to the apparent mass diffusion coefficient, D^*, can be obtained from the solution of the direct problem, Eq. (3), respectively as

$$\frac{\partial C^*}{\partial a} = \frac{1}{2} e^{-\lambda t} \left[\frac{e^{\frac{-(a-z)^2}{4D^* t}} + e^{\frac{-(a+z)^2}{4D^* t}}}{\sqrt{\pi D^* t}} \right] \tag{10.a}$$

$$\frac{\partial C^*}{\partial D^*} = -\frac{1}{2} e^{-\lambda t} \frac{\left\{ t(a^2 - z^2) \left[\frac{e^{\frac{-(a-z)^2}{4D^* t}}}{(a+z)} + \frac{e^{\frac{-(a+z)^2}{4D^* t}}}{(a-z)} \right] \right\}}{2\sqrt{\pi D^{*3}}} \tag{10.b}$$

We note that the present estimation problem is non-linear, since the sensitivity coefficients depend on the unknown parameters D^* and a. As a result, the following analysis of the sensitivity coefficients and of the determinant of $\mathbf{J}^T\mathbf{WJ}$ is local and dependent on the values of D^* and a assumed for the simulation.

Figure 2 presents the normalized concentration, while Figs. 3.a and 3.b present the sensitivity coefficients obtained with Eqs. (10.a and 10.b), respectively, for different positions along the column and for a test-case involving the diffusion of KBr. For such a test-case, we used the values $a=2$ *cm* and $D^* = 10^{-5}$ cm^2/s.

Figure 2 shows a reduction of the maximum value of concentration as the measurement location distances from the boundary $z=0$ *cm*. Such behavior can also be noticed in Fig. 3.a for the sensitivity coefficients with respect to a.

An analysis of Fig. 3.b reveals that the sensitivity coefficients with respect do D^* for the positions $z=1$ *cm* and $z=2$ *cm* are negative, while the sensitivity coefficients for the remaining positions are positive. This is in accordance with the physics of the problem, since the first two positions are located inside the region initially occupied by the salt (recall that $a=2$ *cm* for the test-case). Therefore, an increase in the diffusion coefficient tends to decrease the concentration in such positions. On the other hand, the concentrations on the other positions, not located inside the region initially occupied by the salt, tend to increase when the diffusion coefficient is increased. Figure 3.b shows that the magnitude of the negative sensitivity coefficients with respect to D^* is larger for the location $z=1$ *cm*, which is fully inside the region initially occupied by the salt. The magnitude of the positive sensitivity coefficients decreases as the measurement location distances from the region initially occupied by the salt. However, it is interesting to note that measurements taken at the locations $z=1$ *cm* and $z=3$ *cm* have basically the same sensitivity to variations in the diffusion coefficient D^*. This is also the case for measurements taken at $z=2$ *cm* and $z= 6$ *cm*.

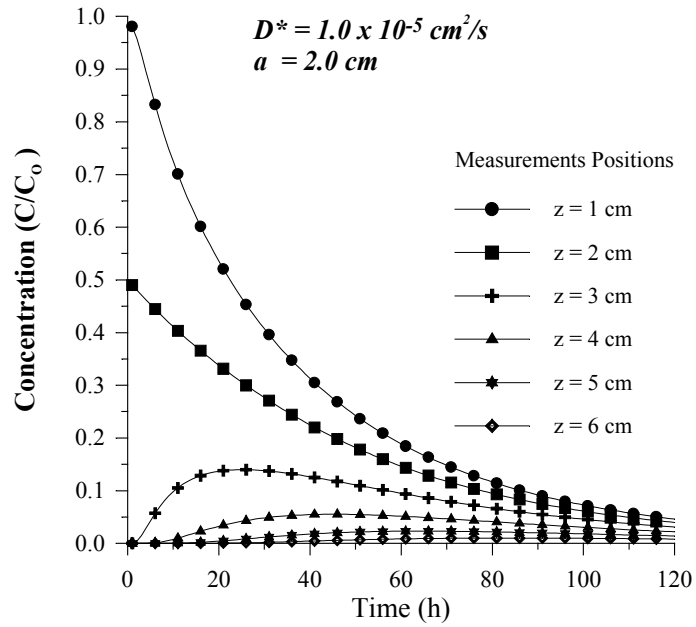

Figure 2. Normalized concentration for $a=2$ *cm* and $D^* = 10^{-5}$ cm^2/s.

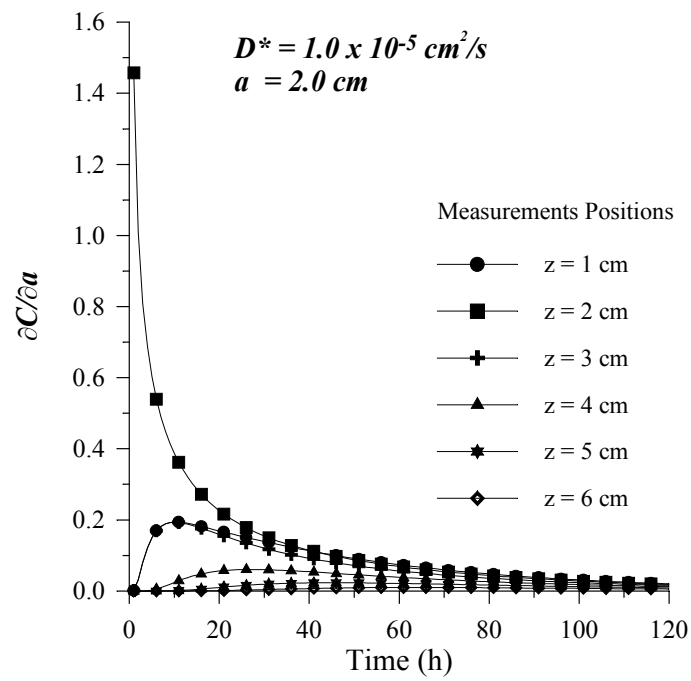

Figure 3.a. Sensitivity coefficients with respect to a for $a=2$ *cm* and $D^* = 10^{-5}$ cm^2/s.

A comparison of Figs. 3.a and 3.b shows that the sensitivity coefficients with respect to a and with respect to D^* are not linearly-dependent. The analysis of the *relative sensitivity coefficients* (Ozisik and Orlande, 1999), obtained by multiplying the sensitivity coefficients of Fig. 3.a by the value of the parameter a and of Fig. 3.b by the value of the parameter D^*, that is, 2 *cm* and 10^{-5} cm^2/s, respectively, reveals that they may attain the same order of magnitude of the concentration.

Therefore, the conditions for the estimation of both parameters appear to be favorable.

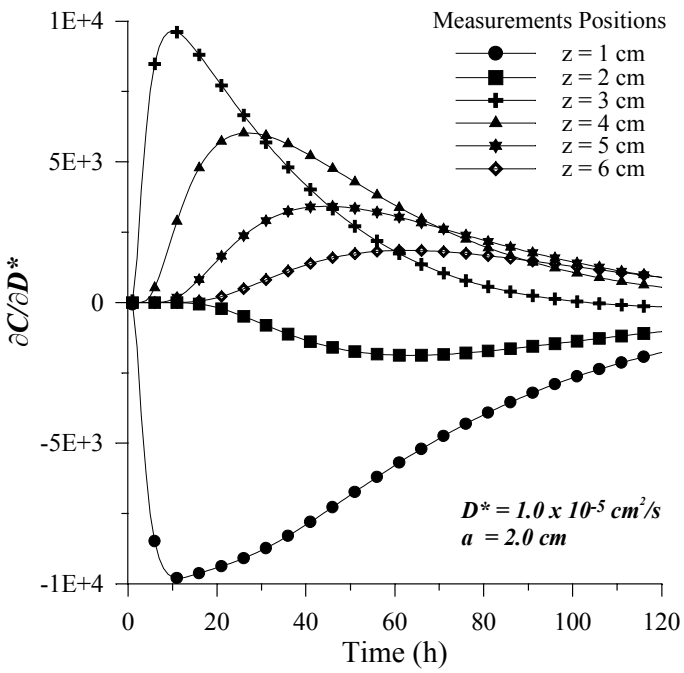

Figure 3.b. Sensitivity coefficients with respect to D^* for $a=2\ cm$ and $D^* = 10^{-5}\ cm^2/s$.

Figures 4.a and 4.b present the variation of the determinant of the matrix $\mathbf{J}^T\mathbf{WJ}$, for frequencies of 1 measurement every 8 hours and 1 measurement every 4 hours, respectively, and by considering different number of sensors. For the case involving one single sensor, the measurement position was considered to be z=1 cm; for two sensors, the measurement positions were considered to be z=1 cm and z=2 cm, and so on. Figures 4.a and 4.b reveal an increase in the determinant when the number of measurement locations is increased, since more information is available for the estimation of the unknown parameters. However, the values of the determinant basically do not increase when the number of measurement locations is larger than 6. Such is the case because the magnitudes of the sensitivity coefficients are strongly reduced for measurements taken far from the boundary z=0 cm, as can be seen from the analysis of Figs. 3.a and 3.b. Also, Figs. 4.a and 4.b show that the determinant is practically constant for times greater than 90 hours, for any number of measurement locations used in the analysis. This is due to the reduction of the magnitude of the sensitivity coefficients for large times. As expected, a comparison of Figs. 4.a and 4.b reveals an increase in the value of the determinant when the frequency of measurements is increased.

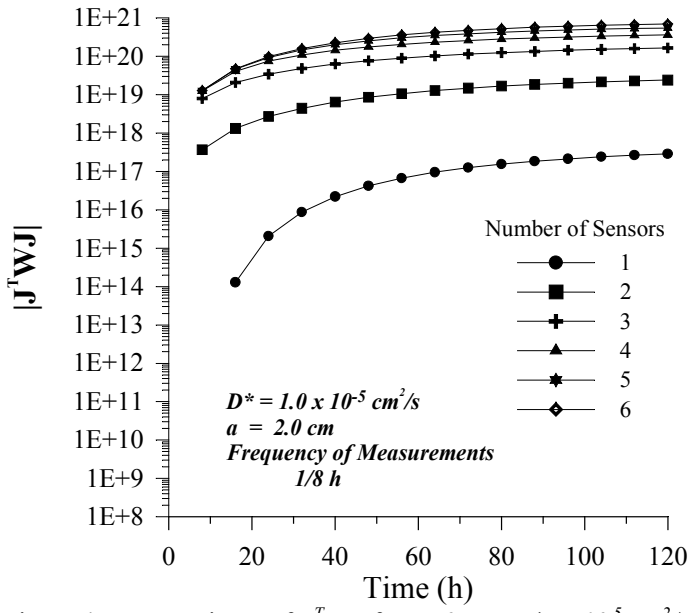

Figure 4.a. Determinant of $\mathbf{J}^T\mathbf{WJ}$ for $a=2\ cm$, $D^* = 10^{-5}\ cm^2/s$ and a frequency of 1 measurement every 8 hours.

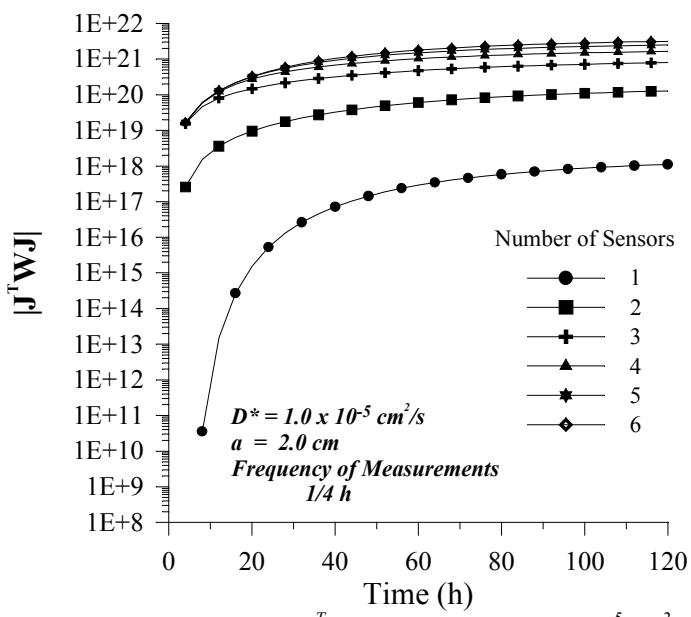

Figure 4.b. Determinant of $\mathbf{J}^T\mathbf{WJ}$ for $a=2\ cm$, $D^* = 10^{-5}\ cm^2/s$ and a frequency of 1 measurement every 4 hours.

The foregoing analysis points in the direction that the use of six measurement locations and an experimental duration around 100 hours appears to be sufficient to obtain accurate estimates for the unknown parameters. In fact, results obtained with simulated measurements, by using 1 measurement per sensor every 4 hours or every 8 hours, with and without random errors, revealed that such is actually the case. For those cases involving simulated errorless measurements the parameters were exactly recovered and reasonably accurate estimates were obtained with measurements containing simulated errors.

After choosing the number of measurement locations, duration of the experiment and frequency of measurements through the analysis of the sensitivity coefficients and of the determinant of $\mathbf{J}^T\mathbf{WJ}$, and assessing the accuracy of the estimates through the use of simulated measurements, we utilized actual experimental data for estimating the apparent mass diffusion coefficient of KBr in sand saturated with distilled water. Two experiments were run by using basically the same conditions for the porosity and concentration of the salt injected. They were 0.35 and 1.40 g/cm^3, respectively. The activities of the solutions injected were 14.18 μCi for the first and second experiments. Measurements were taken every 4 hours during the day and generally an 8 hours interval was considered for measurements taken during the night. The duration of the first experiment was taken as 120 hours and of the second experiment as 92 hours, resulting in 20 and 17 measurements available per measurement location, respectively. The readings taken at the locations z = 1, 2, 3, 4, 5 and 6 cm were used in the analysis.

Figures 5.a and 5.b present the measured and estimated normalized concentrations at the different measurement locations, for the first and second experiments, respectively. In both experiments, the values estimated for the apparent diffusion coefficient were identical. At the 99% confidence level, we obtained $D^*=(1.25\pm 0.01)\text{x}10^{-5}\ cm^2/s$. On the other hand, the values estimated for the height of the column initially occupied by solution injected were not identical for the two experiments, despite the fact that care was taken to inject the same solution volume. At the 99% confidence level, for the first experiment the initial height estimated was $a=(1.566\pm 0.004)$ *cm*, while for the second experiment we estimated $a=(2.021\pm 0.005)$ *cm*. The different values for the initial heights of the two experiments can be due to variations of the local porosity in the base of the column or due to some part of the solution that was inevitably left in the capillary tube used for the injection. The immediate dilution of the solution injected can also be the cause for such different values for the initial height, since in our model we assumed the injected solution to perfectly displace the water in the pores. We note that the above values estimated for a and D^* were independent of the initial guess used for the iterative procedure of the Levenberg-Marquardt method.

Figures 5.a and 5.b show an excellent agreement between measured and estimated concentrations. The relative residuals $(C_{im} - Y_{im})/Y_{m,max}$, where $Y_{m,max}$ is the maximum normalized concentration measured at the location m (m=1,…,6), are shown in Fig. 6a and 6.b, for the first and second experiments, respectively. Figure 6.a shows residuals with very small bias, specially for the measurement positions of z=5 *cm* and z=6 cm. The largest residuals occur for the measurement positions z=1 *cm* and z=2 *cm* at small times. The residuals are slightly correlated indicating some inconsistency between the model and the experiment. Correlated residuals can also be observed in the second experiment, as shown in figure 6.b. However, differently from the first experiment, the residuals for the second experiment attained relatively large values for all measurement positions. The probable cause for such behavior of the residuals is the initial conditions (1.c) used for the model, resulting in different estimated values for the initial height occupied by the salt, as discussed above.

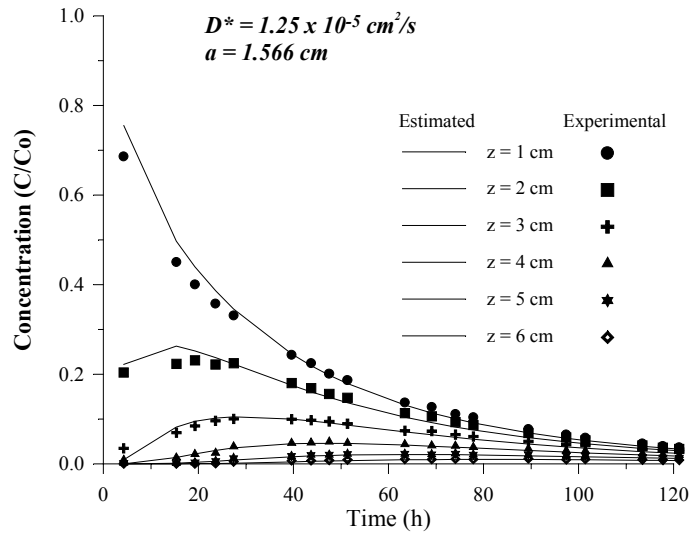

Figure 5.a. Measured and estimated concentrations for the first experiment

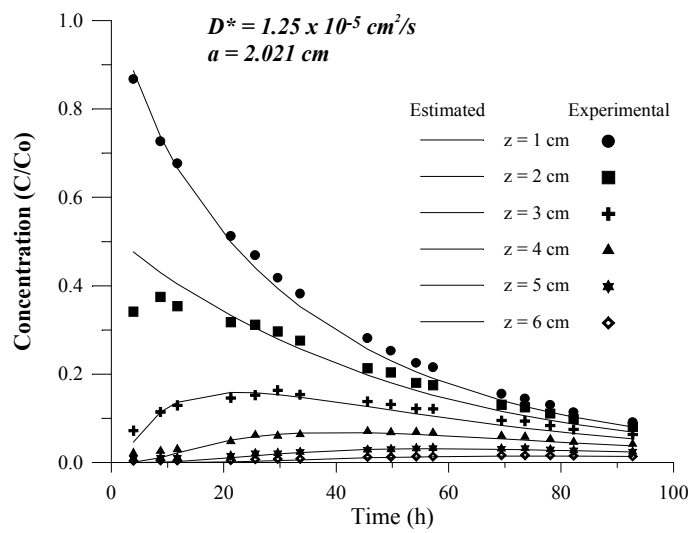

Figure 5.b. Measured and estimated concentrations for the second experiment

In accordance with Shackelford and Daniel (1991.a), the free-diffusion coefficient of KBr in water is $D^*=2.02\text{x}10^{-5}cm^2/s$. Therefore, the reduction on the diffusion coefficient, as a result of the tortuous path in the porous media and of any retardation effects, is of the order of 38%, for the sand soil studied in our experiments.

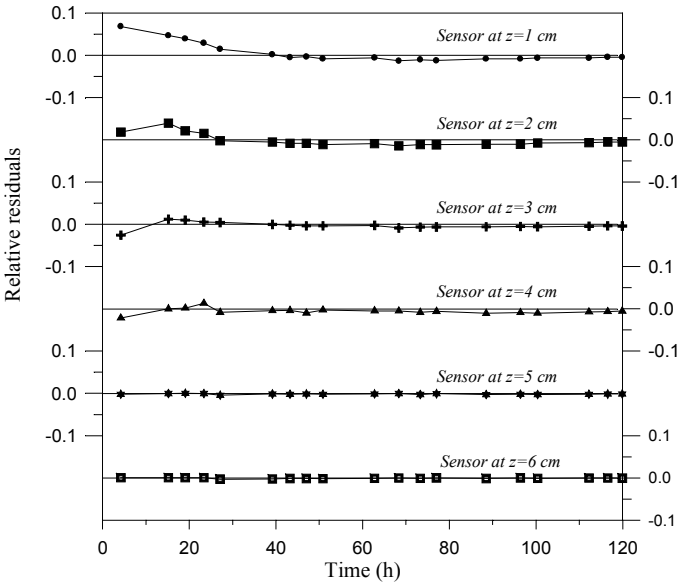

Figure 6.a. Relative residuals $(C_{im} - Y_{im})/Y_{m,max}$ for the first experiment

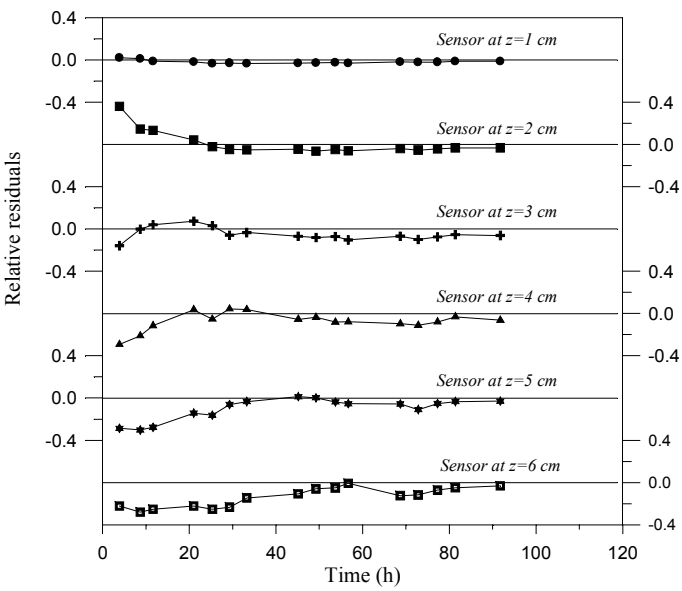

Figure 6.b. Relative residuals $(C_{im} - Y_{im})/Y_{m,max}$ for the second experiment

CONCLUSIONS

The experimental apparatus developed in the present work, based on radioactive measurement techniques, together with the Levenberg-Marquardt method of inverse analysis, was capable of providing accurate and reproducible estimates for the apparent diffusion coefficient of KBr in sand saturated with distilled water. For the present diffusion problem, the analysis of the sensitivity coefficients and of the determinant of the matrix $\mathbf{J}^T\mathbf{W}\mathbf{J}$, where $\mathbf{J}$ is the sensitivity matrix and $\mathbf{W}$ is the weighting matrix (inverse of the covariance matrix of the measurements), revealed that the use of six measurement locations, with a frequency of 1 measurement per position every 8 hours, and an experimental duration of approximately 100 hours, was sufficient to provide accurate estimates for the apparent diffusion coefficient.

The inverse analysis involving actual measured data revealed uncertainties in the height of the column initially occupied by the injected solution. Hence, we decided to estimate such height together with the apparent diffusion coefficient. The optimization of the experiment with respect to the initial height of the solution and different approaches to accurately control such variable are currently under investigation.

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