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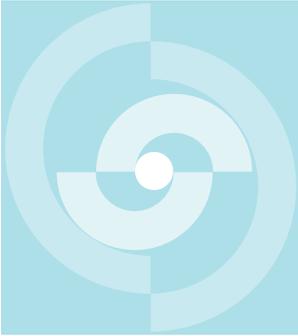
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TECHNICAL REPORT 90-11

MODELLING OF A DIFFUSION- SORPTION EXPERIMENT ON SANDSTONE

P.A. SMITH

FEBRUARY 1990

Paul Scherrer Institute, Villigen, Switzerland

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Vorwort

Im Rahmen des Programmes Entsorgung werden im PSI Arbeiten zur Analyse der Ausbreitung radioaktiver Elemente in geologischen Medien durchgeführt. Diese Untersuchungen werden in Zusammenarbeit und mit teilweiser finanzieller Unterstützung der Nationalen Genossenschaft für die Endlagerung radioaktiver Abfälle (NAGRA) vorgenommen. Die vorliegende Arbeit erscheint gleichzeitig als PSI-Bericht und NAGRA Technischer Bericht.

Abstract

The results of a diffusion-sorption experiment on a sample of Darley Dale sandstone, using simulated groundwater spiked with a mixture of ^{125}I , ^{85}Sr and ^{137}Cs , are modelled by a one-dimensional porous medium approach in which sorption is described by Freundlich isotherms. The governing equations are solved analytically for the special case of a linear isotherm, and numerically using the computer code RANCDIFF for non-linear isotherms. A set of time-dependent, ordinary differential equations is obtained using the Lagrange interpolation technique and integrated by Gear's variable order predictor-corrector method.

It is shown that the sorption behaviour of ^{85}Sr can be modelled successfully by a linear isotherm, using a sorption parameter consistent with batch-sorption tests. The behaviour of ^{137}Cs may be modelled by a non-linear isotherm, but the amount of ^{137}Cs sorbed is less than that anticipated from batch-sorption tests. ^{125}I is assumed to be non-sorbing and is used to determine the porosity of the sandstone.

Zusammenfassung

Die Resultate von Diffusions-Sorptions-Experimenten mit ^{125}I , ^{85}Sr und ^{137}Cs an einer Darley Dale Sandsteinprobe werden mit Hilfe eines Modelles für eindimensionale poröse Medien und einer Freundlich Isotherme interpretiert. Für den Spezialfall einer linearen Isotherme werden die Transportgleichungen analytisch und für die nicht-lineare Isotherme mit dem Computercode RANCDIFF gelöst. Durch Lagrange Interpolation erhält man ein System von zeitabhängigen gewöhnlichen Differentialgleichungen, welche mit Hilfe von Gears Prediktor-Korrektor-Methode variabler Ordnung integriert werden.

Es wird gezeigt, dass das Sorptionsverhalten von ^{85}Sr durch eine lineare Isotherme erklärt werden kann, wobei die Parameter mit Werten aus statischen Batch-Experimenten übereinstimmen. Das Verhalten von ^{137}Cs kann mit einer nicht-linearen Isotherme interpretiert werden. Die Menge sorbierten Caesiums ist jedoch geringer als in den Batch-Experimenten. ^{125}I wird als nichtsorbiierend angenommen und die Resultate der Experimente zur Bestimmung der Porosität des Sandsteines benützt.

1 Introduction

Batch-sorption experiments, which measure the sorption of radionuclides on geological materials, are often performed on crushed material or on small coupons in order to obtain experimental results on a reasonable time scale ($\sim 10^3$ hours). The preparation of such samples, however, may disrupt the internal pore structure of a rock and creates fresh fracture surfaces, which may seriously modify sorption behaviour. Results are found to depend on both the water volume / rock mass ratio (W/R) and the particle size range (PSR). Furthermore, prediction of the migration of radionuclides through intact rock in the field requires separate experiments to determine transport properties, such as the diffusion coefficient [Bradbury *et al.* (1982)].

In order to overcome these difficulties, Bradbury *et al.* (1986) designed experiments in which sorption and diffusion parameters could be extracted from the same set of measurements. The experiments were carried out on intact rock samples, so that the internal pore structure was unchanged and the need to choose values for W/R and PSR was avoided.

The radionuclides used were ^{125}I , ^{85}Sr and ^{137}Cs . Diffusion coefficients were obtained for all three radionuclides for samples of sandstone, anhydrite and upper magnesian limestone. ^{125}I was assumed to be non-sorbing, and the results were used to extract the porosity of the samples. Distribution ratios (R_D) were then obtained for ^{85}Sr and ^{137}Cs by a simplistic modelling approach.

Batch-sorption tests were also carried out over a wide concentration range for each of the radionuclides, using three different $PSRs$ and two different W/Rs . The sorption data were compared with those extracted from the diffusion-sorption experiment. Although batch-sorption tests give a range of values, due to the dependence of R_D on W/R and PSR , values from the diffusion-sorption experiment were generally significantly below this range, with ^{137}Cs exhibiting the greatest discrepancies. A further observation was that the diffusion coefficient for ^{85}Sr was higher by a factor of 4 or 5 compared with ^{125}I and ^{137}Cs .

The analysis of Bradbury *et al.* (1986) assumed firstly that, at the end of the experiment, the system had reached a steady state and secondly that sorption is linear (i.e. that R_D is independent of concentration). For ^{85}Sr , batch-sorption tests indicated that the latter seemed to be a valid assumption. For ^{137}Cs , however, batch-sorption tests indicated non-linear behaviour; the value of R_D extracted from the diffusion-sorption experiment was interpreted as a mean value for the concentration range in the experiment. In the present work, these data are re-examined. A more detailed analysis of the results of the diffusion-sorption experiment is presented, in which the assumptions of steady state and linear sorption are not made. Governing equations are given for the experimental system and an analytical solution is given for the special case of linear sorption. For non-linear sorption, the equations are integrated numerically. Both types of solution are taken as regression models and fitted to the experimental data by the method of least squares. This allows us to determine whether it is necessary to invoke non-linear sorption to model the behaviour of the different nuclides and enables us to extract the sorption and diffusion parameters.

2 Experimental Procedure

The apparatus for the diffusion-sorption experiment is shown schematically in figure 1. The experimental fluid was a simulated groundwater spiked with a mixture of ^{125}I , ^{85}Sr and ^{137}Cs . In order to simulate groundwater, distilled water had been "equilibrated" with crushed rock over a 5 month period and filtered prior to use. The particular rock sample used to produce the data modelled here was a disc of Darley Dale sandstone with a diameter of 25mm and a thickness of 5mm. The composition of the simulated groundwater and the mineralogy of the rock are given in Bradbury *et al.* (1986). However, the concentration of stable cesium is omitted. Near-constant concentrations of the radionuclides were maintained on both sides of the sample. The fluid volume in the cells on either side of the sample was approximately 25ml. In order to minimise concentration change on the high-concentration side, fluid was circulated continuously between the cell and a reservoir of volume 400ml. The reservoir concentrations (C_0) of the radionuclides were $1.3 \times 10^{-7} mol.m^{-3}$ for ^{125}I , $1.4 \times 10^{-3} mol.m^{-3}$ for ^{85}Sr and $1.9 \times 10^{-2} mol.m^{-3}$ for ^{137}Cs . On the low-concentration side (the measurement cell), samples were taken at frequent intervals and the activity counted. The samples were replaced by equal volumes of simulated groundwater, maintaining a near-zero concentration in the cell. Results for each nuclide are given in the form of a time-history of a quantity C_t , with units of concentration. C_t , obtained by a summation of the counted activities, is defined as

$$C_t = \frac{A}{V} \int_0^t T(t') dt' \quad (1)$$

where A is the cross-sectional area of the sample, V is the volume of the measurement cell and T is the nuclide flux into the measurement cell.

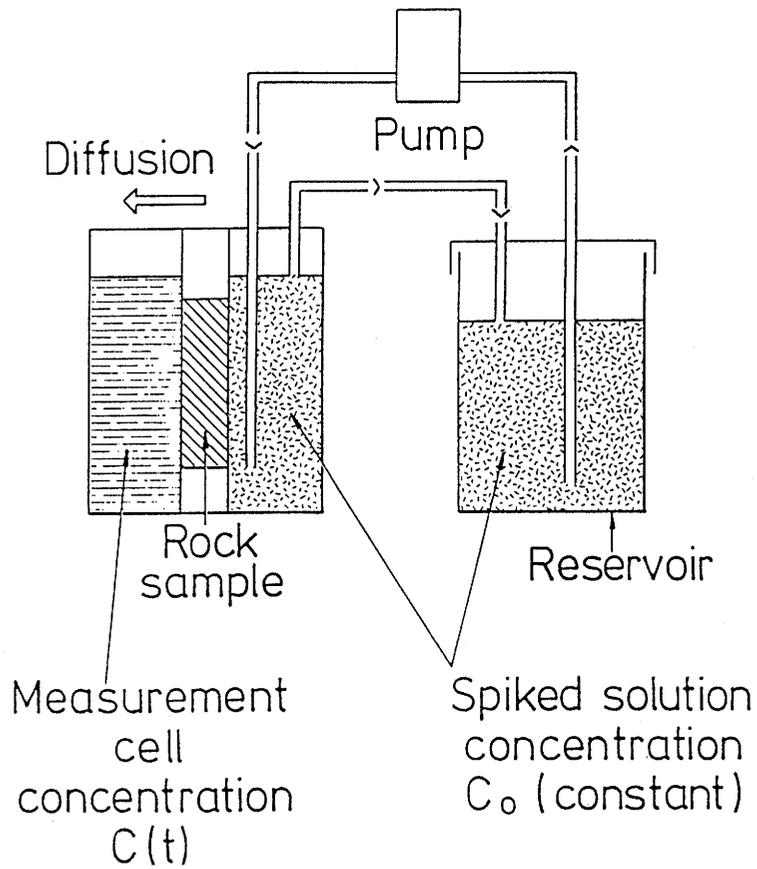


Figure 1: Experimental apparatus for the diffusion-sorption experiment. From Bradbury *et al.* (1986).

3 Governing Equations

We assume that the diffusion-sorption experiment may be described in terms of a one-dimensional, single-porosity medium, in which the pore water diffusion coefficient D is constant in time and space. Consideration of mass-balance yields the following diffusion equation [Bear (1979)]

$$\frac{\partial}{\partial t}(C + \rho S/\epsilon) = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

where ρ is the bulk density, ϵ is the porosity, C is the concentration of solute in the liquid phase and S is the mass of solute in the solid phase per unit mass of porous medium.

We further assume instantaneous sorption, which is described by a Freundlich isotherm

$$S = KC^N \quad (3)$$

where K and N are constants. The distribution ratio R_D is defined as the ratio of S to C and is therefore given by

$$R_D = KC^{N-1} \quad (4)$$

Combining equations (2), (3) and (4) gives the governing equation for the experiment

$$\frac{\partial C}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where $D_e = \epsilon D$ is the effective diffusion coefficient and

$$\alpha = \epsilon + \rho N R_D \quad (6)$$

Equation (5) must be solved for each nuclide with boundary conditions

$$C = C_0 \text{ at } x = 0 \text{ and } C = 0 \text{ at } x = L$$

No analytical solution is known to this general problem; solutions are obtained by integrating equation (5) numerically. However, if a nuclide sorbs linearly, so that $N = 1$, $R_D (= K)$ is not a function of concentration and an analytical solution for equation (5) may be derived. Methods for obtaining such solutions have been widely published [e.g. Carslaw and Jaeger (1959)].

$$\frac{C}{C_0} = 1 - \frac{x}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{D_e n^2 \pi^2 t}{\alpha L^2}\right) \quad (7)$$

The flux T across $x = L$ is given by

$$T = -D_e \frac{\partial C}{\partial x} \Big|_{x=L} \quad (8)$$

Substituting equations (7) and (8) into (1) and integrating

$$\frac{C_t V L}{A C_0} = D_e t \left[1 - \frac{\alpha L^2}{6 D_e t} - \frac{2 \alpha L^2}{D_e \pi^2 t} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_e n^2 \pi^2 t}{\alpha L^2}\right) \right] \quad (9)$$

4 Regression Models

The experimental time-histories of C_t for ^{85}Sr and ^{137}Cs are modelled both with and without the assumption of linear sorption. ^{125}I is assumed to be non-sorbing; it is simply used to extract a value for the porosity by the graphical analysis described below.

4.1 Linear Sorption

If the nuclides are assumed to be either non-sorbing or to sorb linearly, equation (9) can be taken as a regression model, with D_e and K as regression parameters, and the Levenberg-Marquardt method used to fit the model to the experimental data by the minimisation of the χ^2 merit function, as described in the appendix. This approach yields the regression parameters themselves, together with standard errors and a correlation coefficient.

Bradbury *et al.* (1986) used a more simple, graphical analysis, which is possible if the experimental results are known to extend to times for which the asymptotic linear solution

$$\frac{C_t V L}{A C_0} = D_e t - \frac{\alpha L^2}{6} \quad (10)$$

is valid. Equation (10) is obtained from equation (9) by letting $t \rightarrow \infty$. If C_t is plotted against t and the linear part of the curve (large times) extrapolated to the time axis, the value of D_e may be obtained from the gradient and α from the intercept. $\alpha = \epsilon$ for non-sorbing nuclides and $\alpha = \epsilon + \rho K$ for linearly sorbing nuclides, where $N = 1$ and $R_D = K$.

4.2 Non-Linear Sorption

Equation (5) has been solved using both the computer codes RANCDIFF and MOLCH. RANCDIFF is based on the more general code RANCDMDNL [Jakob *et al.* (1989)], which solves the advection-dispersion and diffusion transport equations for a dual porosity medium. A set of time dependent, ordinary differential equations is obtained using the Lagrange interpolation technique and integrated by Gear's variable order predictor-corrector method. The parts of this code dealing with matrix diffusion and advection have been removed in RANCDIFF. MOLCH is a subprogram in the MATH/LIBRARY of IMSL, Inc., which solves second order partial differential equations of a more general form. In MOLCH, cubic Hermite polynomials are used for the spatial approximation and Gear's method is again used for the time integration. No difference has been found between the results from the two codes; RANCDIFF was used in most of the work presented here. The output of RANCDIFF gives a time-history of the flux T across $x = L$. This is substituted into equation (1) and integrated using Simpson's rule to yield C_t . The solution thus obtained can be taken as a regression model of the experimental data, with D_e , K and N as regression parameters.

5 Results

5.1 ^{85}Sr

Table 1 shows the fitted parameters obtained from the time-development of ^{85}Sr concentration, together with the minimum value of the χ^2 merit function for the fitted model and the standard deviation in the experimental errors σ , on the assumption that the model used represents a good fit and that the experimental errors are normally distributed. Values of $\rho = 2500 \text{ m}^3\text{kg}^{-1}$ and $\epsilon = 0.1$ were taken from Bradbury *et al.* (1986). The uncertainties in the fitted parameters in table 1 are the standard errors, derived from the diagonal elements of the covariance model (see appendix).

| <i>sorption model</i> | D_e ($\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) | K ($\text{mol}^{1-N} \text{ m}^{3N} \text{ kg}^{-1}$) | N (-) | χ_{min}^2 ($\times 10^{-9} \text{ m}^4$) | σ ($\times 10^{-6} \text{ m}^2$) |
|-----------------------|---|--|-----------------|--|--|
| linear | 14.8 ± 0.6 | 0.060 ± 0.004 | | 2.99 | 7.97 |
| non-linear | 15 ± 1 | 0.07 ± 0.02 | 1.04 ± 0.02 | 2.93 | 7.90 |
| non-linear † | 22 ± 3 | 0.07 ± 0.03 | 0.95 ± 0.02 | 9.83 | 14.5 |

Table 1: Fitted parameters for diffusion of ^{85}Sr .

† experimental results shifted to compensate for experimental error (see text).

The two regression models, incorporating linear and non-linear sorption, were used. To investigate the possibility of several χ^2 minima, various initial guesses were used for the regression parameters in the Levenberg-Marquardt iteration, but the same minimum was obtained in each case. It can be seen from table 1 that allowing for non-linear sorption gives only a small ($\sim 2\%$) reduction in χ_{min}^2 and small changes in the regression parameters. Allowing the parameter N to vary, however, results in an increase in the standard errors in the other parameters.

Table 2 shows the results of the batch-sorption tests on coupons of intact rock and on crushed rock, using different W/R s and PSR s, reported in Bradbury *et al.* (1986). For coupons and for crushed rock with a PSR of $1 - 2\text{mm}$, the tests gave ranges of $0.48 - 0.104 \text{ mol}^{1-N} \text{ m}^{3N} \text{ kg}^{-1}$ and $0.95 - 1.00$ for K and N respectively, consistent with the fitted parameters in table 1. Larger values of K , however, were obtained in the batch-sorption tests for PSR s of less than 0.1mm .

| PSR (mm) | W/R | | | |
|-------------|--|------------|--|------------|
| | 20 : 1 | | 3 : 1 | |
| | K ($\text{mol}^{1-N}\text{m}^{3N}\text{kg}^{-1}$) | N (-) | K ($\text{mol}^{1-N}\text{m}^{3N}\text{kg}^{-1}$) | N (-) |
| < 0.1 | 0.200 | 0.97 | 0.301 | 1.07 |
| 1 - 2 | 0.090 | 0.95 | 0.061 | 0.99 |
| coupons | 0.104 | 0.99 | 0.048 | 1.00 |

Table 2: The results of batch-sorption tests for ^{85}Sr on sandstone, using different water volume / rock mass ratios (W/R) and particle size ranges (PSR).

The effective diffusion coefficient of ^{125}I in Bradbury *et al.* (1986) is $2.4 \times 10^{-11}\text{m}^2\text{s}^{-1}$, which is smaller than that of ^{85}Sr by a factor of more than 6.

The experimental data and the two regression models are plotted in figure 2. It can be seen that the models overlie each other almost exactly. Also plotted is the asymptotic solution (equation (10)), obtained from the regression parameters of the linear-sorption model, showing that the simple, graphical analysis of the results would have been inaccurate, since the experiment had not proceeded for a sufficient time. This is not apparent from an inspection of the experimental data alone. The graphical analysis carried out in Bradbury *et al.* (1986), underestimated both D_e ($12 \times 10^{-11}\text{m}^2\text{s}^{-1}$) and K ($0.025\text{m}^3\text{kg}^{-1}$).

In the definition of the correlation coefficient, we use the indices 1, 2 and 3 denote D_e , K and N respectively. In the case of linear sorption, the correlation coefficient R_{12} between the uncertainty in the fitted parameters D_e and K is equal to 0.9970. The meaning of this large, positive correlation is illustrated in figure 3, in which contours of χ^2 have been plotted in the (K, D_e) -plane. χ_{min}^2 lies in a trough, the axis of which has a positive gradient in the (K, D_e) -plane, so that a positive error in the D_e -coordinate of χ_{min}^2 is likely to result in a positive error in its K -coordinate. In the case of non-linear sorption, the correlation coefficients are $R_{12} = 0.9778$, $R_{23} = 0.9882$, $R_{31} = 0.9214$.

Examining figure 2, the experimental errors seem not, in fact, to be randomly distributed about the best-fit lines. Rather, there is a tendency for the experimental value of C_t to increase more rapidly with time for several successive points, before undergoing a small negative shift. This process occurs repeatedly, with the negative shifts following the 9th, 13th, 18th, 23rd, 32nd, 37th and 43rd points. This indicates a possible systematic experimental error. In figure 4, the experimental points have been displaced to compensate for the shifts, and the displaced points fitted using the non-linear sorption model. The distances by which the points were displaced were judged roughly by eye. The purpose of this crude procedure was to investigate qualitatively whether this apparent systematic error has a significant influence on diffusion and sorption parameters. The fitted parameters are given in table 1. The values of K and N are almost unchanged, but D_e is increased; a systematic experimental error does not account for the large effective diffusion coefficient of ^{85}Sr . Furthermore, the increase in χ_{min}^2 indicates that the adjusted points are fitted less well by the model than are the original points.

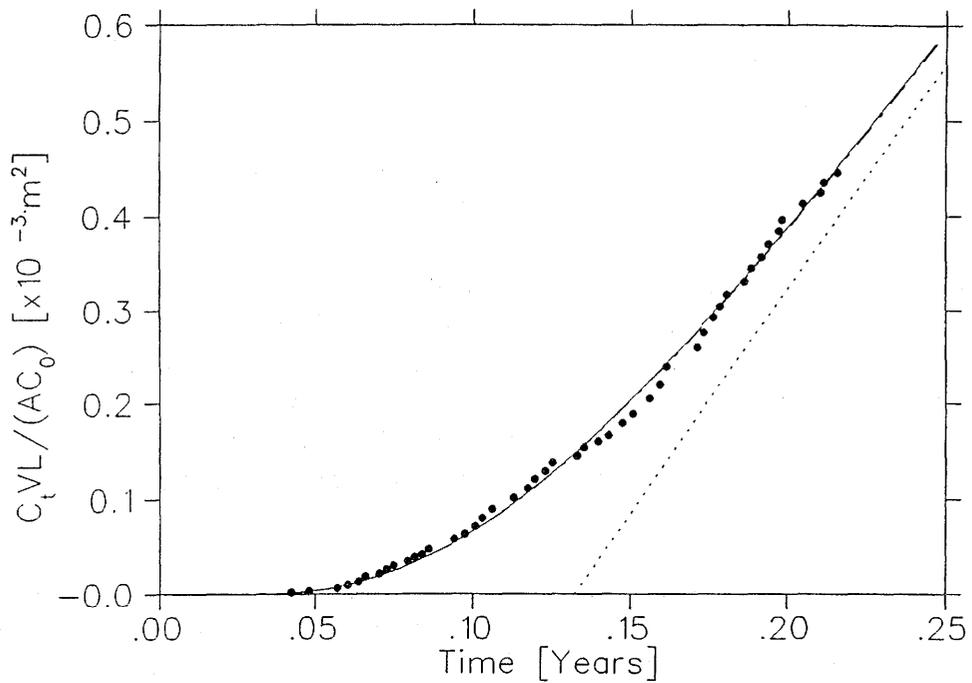


Figure 2: Diffusion-sorption curve for ^{85}Sr .

●●●● experimental data

----- regression model with linear sorption
 ($D_e = 1.48 \times 10^{-10} \text{m}^2 \text{s}^{-1}$, $K = 0.060 \text{m}^3 \text{kg}^{-1}$)

----- asymptote (linear-sorption model)

———— regression model with non-linear sorption
 ($D_e = 1.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$, $K = 0.07 \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 1.04$)

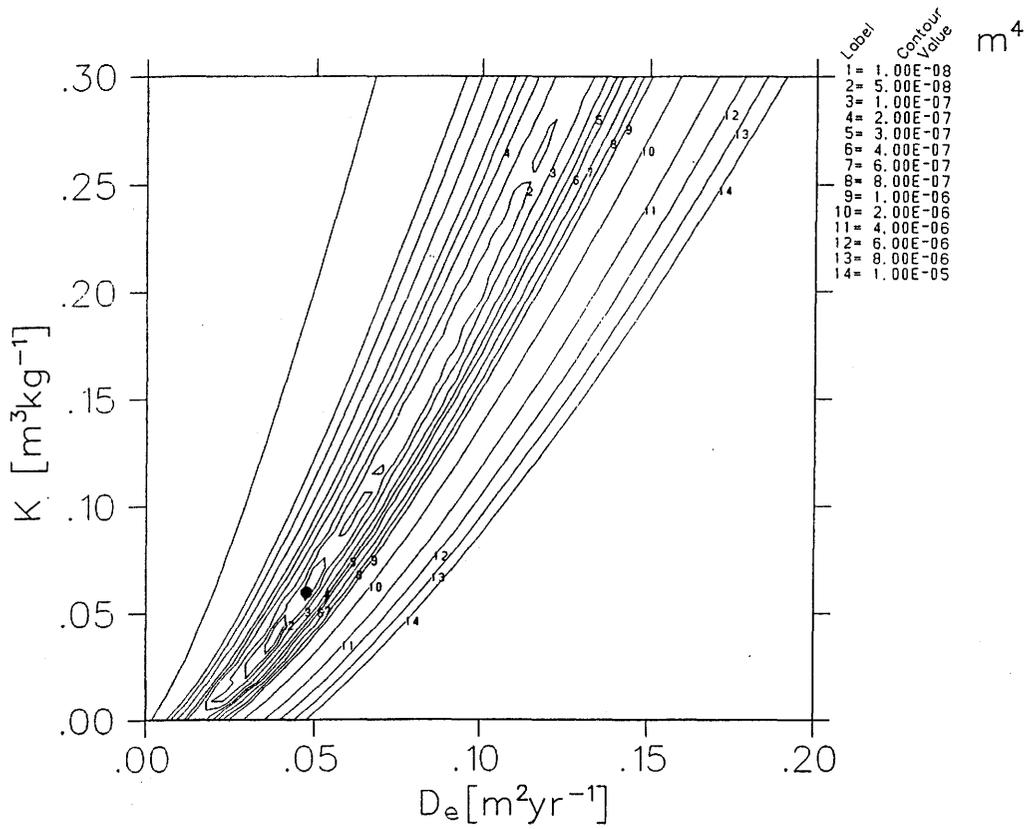


Figure 3: Contours of the χ^2 merit function for ^{85}Sr in the (K, D_e) -plane, corresponding to the fitted diffusion-sorption curve (with linear sorption) in figure 2.

- minimum value of χ^2

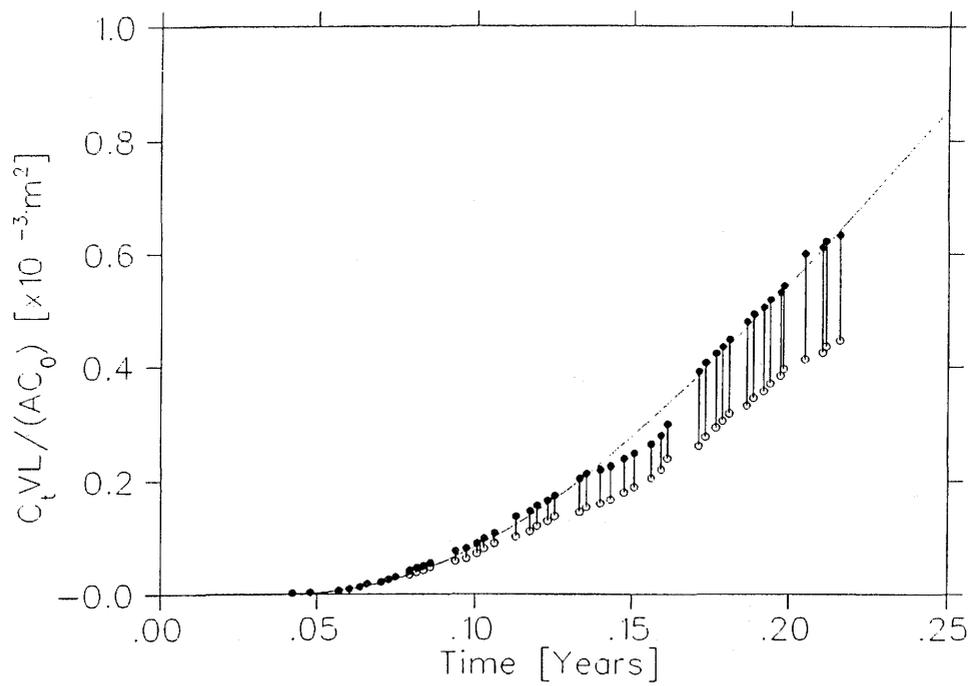


Figure 4: Diffusion-sorption curve for ^{85}Sr , with the experimental data shifted to compensate for the apparent systematic error.

○ ○ ○ ○ original experimental data

● ● ● ● manually shifted experimental data points under the assumption of a systematic error (see text)

— regression model with non-linear sorption

$(D_e = 2.2 \times 10^{-10} \text{m}^2 \text{s}^{-1}, K = 0.07 \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}, N = 0.95)$

5.2 ^{137}Cs

Table 3 shows the fitted parameters, obtained from the time-development of ^{137}Cs concentration, together with χ^2 and σ . As before, the two regression models were used and the possibility of several χ^2 minima was investigated by beginning the Levenberg-Marquardt iteration with various initial guesses for the regression parameters. In the case of linear sorption, a single χ^2 minimum was located, but several minima were located with non-linear sorption indicating that, in order to obtain a unique set of regression parameters, more experimental data (or data of greater precision) would be required. Three of the minima are given in table 3 (the sets of regression parameters corresponding to these minima will be referred to as 1, 2 and 3).

| sorption model | $D_e (\times 10^{-11} \text{ m}^2 \text{ s}^{-1})$ | $K (\times 10^{-3} \text{ mol}^{1-N} \text{ m}^{3N} \text{ kg}^{-1})$ | N (-) | χ_{min}^2 ($\times 10^{-11} \text{ m}^4$) | σ ($\times 10^{-7} \text{ m}^2$) |
|-------------------------|--|---|-------------------|---|--|
| linear | 4.5 ± 0.2 | 44 ± 3 | | 14.22 | 16.7 |
| non-linear ¹ | 2.31 ± 0.03 | 1.29 ± 0.06 | 0.550 ± 0.006 | 3.922 | 8.77 |
| non-linear ² | 2.57 ± 0.05 | 3.4 ± 0.2 | 0.705 ± 0.005 | 3.870 | 8.71 |
| non-linear ³ | 4.6 ± 0.6 | 40 ± 10 | 1.00 ± 0.02 | 14.23 | 16.7 |

Table 3 : Fitted parameters for diffusion of ^{137}Cs . The parameters of the non-linear model have been derived from three different initial guesses.

There is little difference in χ_{min}^2 obtained with parameter sets 1 and 2. Parameter set 3 is essentially the same as that obtained with linear sorption, with a larger value of χ_{min}^2 than those of sets 1 or 2, although allowing N to vary again results in an increase in the standard errors in the other parameters. Therefore, in contrast to the results for ^{85}Sr , a reduction in χ_{min}^2 can be obtained by allowing for non-linear sorption.

The experimental data and the non-linear sorption model with the three sets of regression parameters of table 2 are plotted in figure 5 and figure 6, with different time scales. In figure 5, the asymptotic solution (equation(10)), obtained from regression parameters of the linear-sorption model, is also plotted. Figure 5 shows that the experimental data and the fitted curves match closely over the time interval covered by the experiment, diverging at later times. A unique χ^2 minimum could probably have been located if the experiment had proceeded to longer times (0.6 years, say). The figure also indicates that a steady state (C_t increasing with time at an approximately constant rate) is reached more rapidly for parameter sets having greater non-linearity (with smaller values of N).

A graphical analysis was carried out in Bradbury *et al.* (1986), assuming linear sorption. This gave a values of $2.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $9 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ for D_e and K respectively. These are again smaller than values for the linear-sorption model in table 3, since the experiment had not proceeded to a sufficient time for the linear-sorption model to reach steady state and again this is not apparent from an inspection of the experimental data alone. There is, however,

fair agreement between the value of D_e in Bradbury *et al.* (1986) and those of parameter sets 1 and 2 for the non-linear sorption model, indicating that these models have reached a steady state. This value also matches that of ^{125}I .

Figure 6 shows that, for the time interval over which experimental data is available, the greatest difference between the curves generated from the different parameters sets occurs between about 0.1 and 0.2 years, where C_t begins to increase with time and $^{137}C_s$ breaks through into the measurement cell. This change in gradient takes place over a shorter time for parameter sets with smaller values of N , providing a better fit to the experimental data.

In figure 7, the liquid-phase concentration profiles of $^{137}C_s$ corresponding to linear sorption and non-linear sorption (parameter set 1) are plotted for different times. In general, values of N less than unity give concentration profiles with smaller curvatures. This is consistent with the observations (above) that initial breakthrough of $^{137}C_s$ becomes more sudden and a steady state is reached more rapidly: with smaller values of N , when breakthrough first occurs, the concentration is already close to a linear profile.

The results of batch-sorption tests reported in Bradbury *et al.* (1986) are reproduced in table 4. For coupons and for crushed rock with a PSR of $1 - 2mm$, the tests gave ranges of $(62 - 141) \times 10^{-3} mol^{1-N} m^{3N} kg^{-1}$ and $0.71 - 0.76$ for K and N respectively. Again, larger values of K were measured for crushed rock with $PSRs$ of less than $0.1mm$. While these ranges are consistent with the value of N in parameter set 2, K is an order of magnitude larger. Graphs of R_D vs. concentration (Freundlich isotherms) for the linear and non-linear regression models of the diffusion-sorption experiment data and for the batch-sorption tests on coupons and crushed rock with a PSR of $1 - 2mm$ are plotted in figure 8 using logarithmic scales. At the end of the diffusion-sorption experiment, Bradbury *et al.* (1986) found an appreciable reduction in the reservoir concentration C_0 (see discussion). They were therefore able to estimate the amount of $^{137}C_s$ sorbed during the experiment, giving average value of R_D for the range of concentration across the sample. This value is also shown in figure 8.

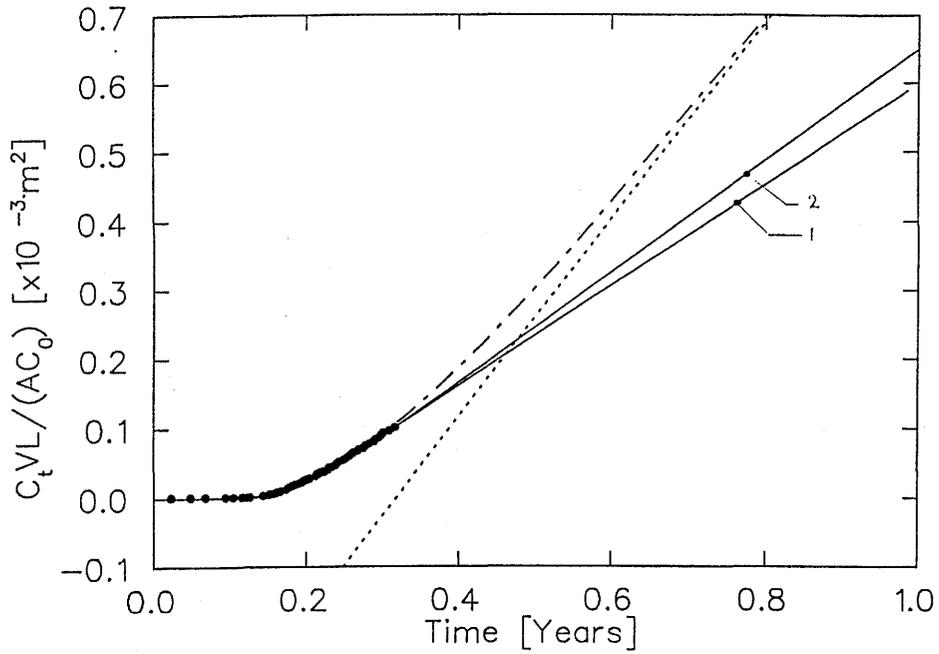


Figure 5: Diffusion-sorption curve for ^{137}Cs .

••••• experimental data

----- regression model with linear sorption
 ($D_e = 4.5 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 0.044 \text{m}^3 \text{kg}^{-1}$)

- - - - asymptote

—— regression model with non-linear sorption

1: $D_e = 2.31 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 1.29 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.550$

2: $D_e = 2.57 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 3.4 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.705$

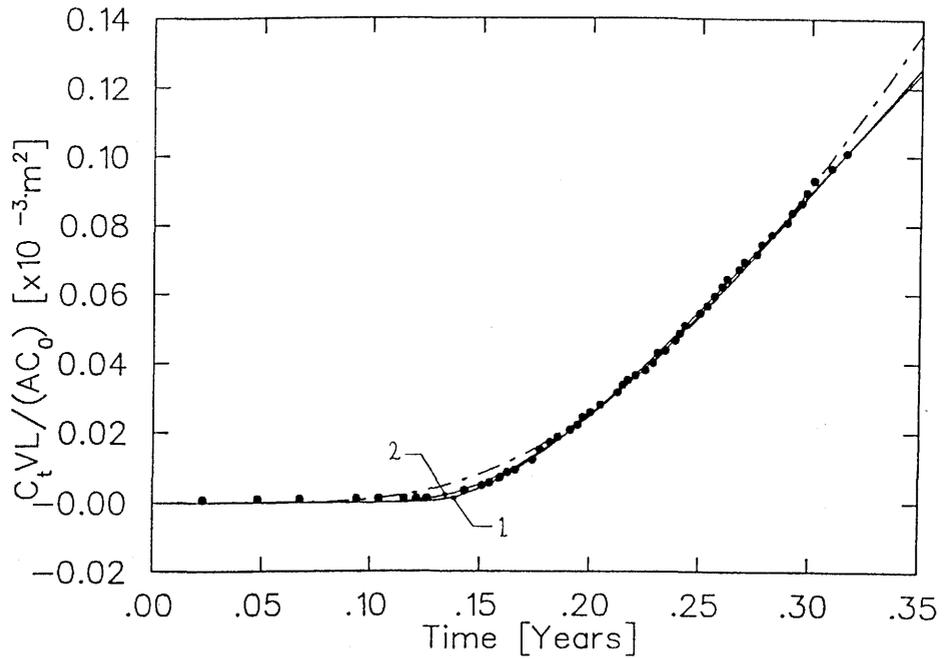


Figure 6 Diffusion-sorption curve for ^{137}Cs .

●●●● experimental data

----- regression model with linear sorption

($D_e = 4.5 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 0.044 \text{m}^3 \text{kg}^{-1}$)

———— regression model with non-linear sorption

1: $D_e = 2.31 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 1.29 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.550$

2: $D_e = 2.57 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 3.4 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.705$

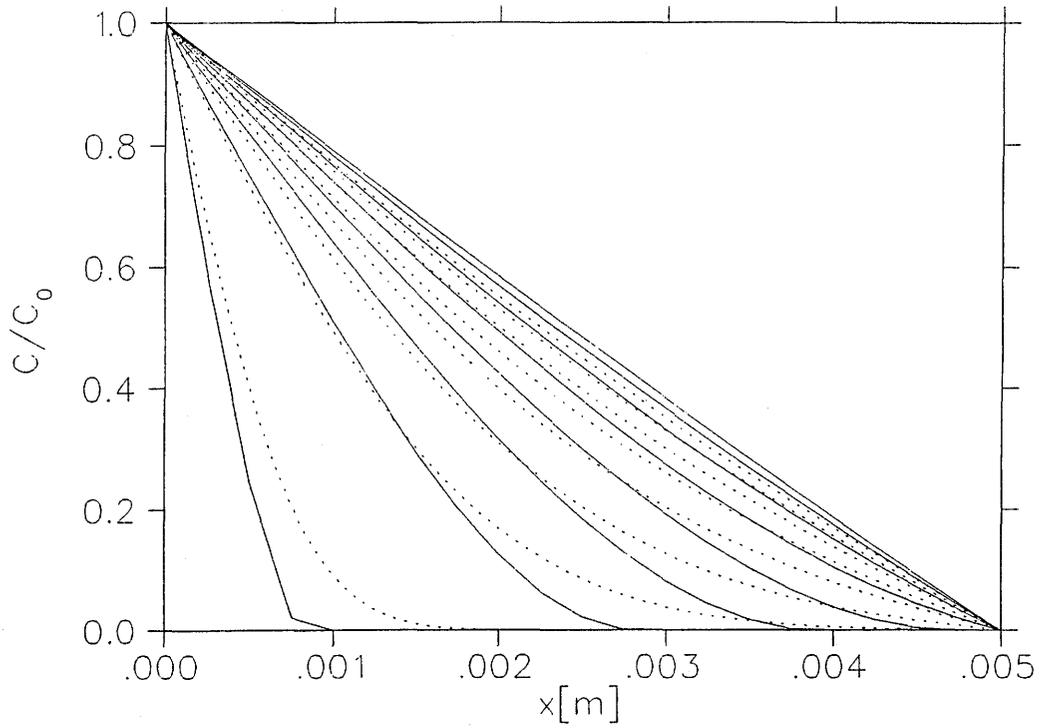


Figure 7: Profiles of the liquid-phase concentration of ^{137}Cs across the sample, generated using the linear and non-linear sorption models. Time increment between profiles is 0.04 yrs.

----- linear sorption ($D_e = 4.5 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 0.044 \text{m}^3 \text{kg}^{-1}$)

———— non-linear sorption

($D_e = 2.31 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, $K = 1.29 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.550$)

| PSR (mm) | W/R | | | |
|-------------|---|------------|---|------------|
| | 20 : 1 | | 3 : 1 | |
| | K ($\times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$) | N (-) | K ($\times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$) | N (-) |
| < 0.1 | 164 | 0.75 | 356 | 0.94 |
| 1 - 2 | 141 | 0.71 | 79 | 0.77 |
| coupons | 85 | 0.76 | 62 | 0.75 |

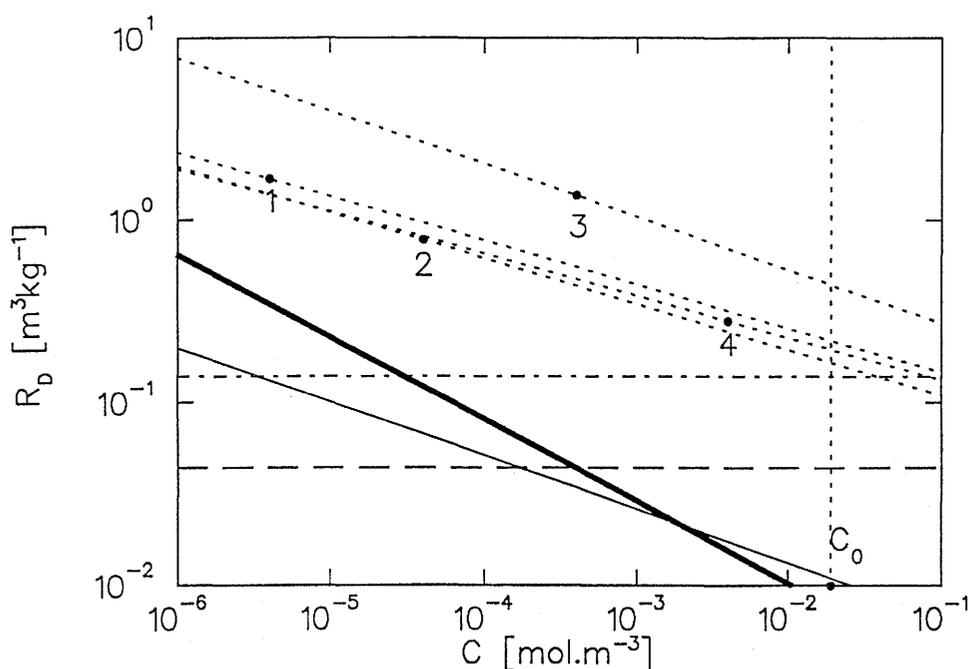
Table 4: The results of batch-sorption tests for ^{137}Cs on sandstone.

Figure 8: Freundlich Isotherms for ^{137}Cs from batch sorption experiments and from the linear and non-linear sorption model of the diffusion-sorption experiments.

..... batch sorption experiments

1 : $W/R = 20 : 1$, coupons 2 : $W/R = 3 : 1$, coupons

3 : $W/R = 20 : 1$, $PSR = 1 - 2\text{mm}$ 4 : $W/R = 3 : 1$, $PSR = 1 - 2\text{mm}$

----- mass balance calculation, from Bradbury *et.al.* (1986).

----- linear sorption; $K = 0.044 \text{m}^3 \text{kg}^{-1}$

———— non-linear sorption; $K = 1.29 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.550$

———— non-linear sorption; $K = 3.4 \times 10^{-3} \text{mol}^{1-N} \text{m}^{3N} \text{kg}^{-1}$, $N = 0.705$

6 Discussion

In this work, the results of the diffusion-sorption experiment have been re-examined by fitting time-dependent solutions of the governing equations, incorporating linear and non-linear sorption. We have thus extracted diffusion coefficients and a Freundlich isotherms for each radionuclide from a single experiment on an intact rock sample.

It has been shown that the original graphical analysis of the results was inappropriate. This is because the experiment had not attained the asymptotic steady state and also, in the case of ^{137}Cs , because sorption is non-linear. For linear sorption, the analysis used here allows the parameters of the models to be determined from a relatively short-term experiment. Provided the data is of sufficient accuracy, the experiment can be terminated while the system is still in a transient state; it is no longer necessary for the steady state to be attained. This was demonstrated for ^{85}Sr . For ^{137}Cs , however, we were unable to obtain a unique fit using the non-linear sorption model; the data would need to be extended to longer times ($\sim 0.6\text{years}$) in order to choose between the curves from parameter sets 1 and 2 in figure 5. Alternatively, greater accuracy in the data would be required for an experiment of the present duration. A criticism of the data used here is that an estimate of experimental errors was not given. It was therefore not possible to assess the "goodness of fit" of the models. However, from table 3, assuming that either of the curves from parameter sets 1 and 2 represents a good fit and that the experimental errors are normally distributed, the standard deviation in the experiment errors (σ) is $\sim 10^{-6}m^2$. Comparing the curves at $\sim 0.15\text{years}$ in figure 6, the maximum difference between the curves from parameter sets 1 and 2 is also $\sim 10^{-6}m^2$; the experimental errors would have to be reduced below this value (by an order of magnitude, say) in order to choose between the two parameter sets.

The best fit to the experimental data for ^{85}Sr was obtained using a linear isotherm (or non-linear isotherm with $N = 1.04 \pm 0.02$). D_e of ^{85}Sr was found to be higher than that of ^{125}I or ^{137}Cs by a factor of more than 6. Important mechanisms influencing diffusion through pores include the effect of charge (anion exclusion) and ion diameter. However, an interpretation at the calculated diffusion coefficients in terms of these mechanisms is beyond the scope of the present work. K , however, is inside the range of results from batch-sorption tests on coupons and on crushed samples with a PSR of $1 - 2mm$. For $PSRs$ of $< 0.1mm$, the batch-sorption tests give larger values of K . For ^{137}Cs , the best fit to the experimental data was obtained using a non-linear isotherm, with a value of N less than unity (consistent with the batch-sorption experiments). This gives a smaller least-squares merit function than the linear-sorption model. However, according to these analyses of the results from the sorption-diffusion experiment, batch-sorption measurements tend to overestimate sorption by at least an order of magnitude.

If the concentration of a radioactive tracer is lower than that of the stable element, then sorption is determined by isotopic exchange and the distribution is ratio becomes independent of concentration, i.e. the isotherm becomes linear. In the diffusion sorption experiment, if a radioactive tracer and a stable element have a similar concentration, then this inflection in the isotherm should be taken into account. Although an analysis was made of the simulated

groundwater used in the experiment, the concentration of stable cesium was omitted and an isotherm without inflection was assumed. The same assumption was made for strontium, but, since the best fit isotherm for strontium was in any case linear, this approach was justified. The reason why ^{137}Cs is sorbed less than would be anticipated from batch-sorption tests (and why in the batch-sorption tests the largest values of K for both ^{85}Sr and ^{137}Cs are found at the smallest PSR) may lie in the preparation of the samples for such tests, during which fresh fracture surfaces are created, so increasing the surface area available for sorption. Furthermore, the one-dimensional description of the porous medium is certainly an oversimplification. In the diffusion-sorption experiment, although diffusion takes place through all interconnected pores, those pores which run parallel to the direction of the concentration gradient make a greater contribution to the flux through the sample than those which run perpendicular to it. The two types of pores therefore make different contributions to the calculated sorption. In batch-sorption tests, there is no such distinction between types of interconnected pores; all interconnected surfaces contribute to the measured sorption. Hemmingway *et al.* (1983) devised a dual-porosity model, in which interconnected pores were divided into "through-transport" pores and "dead-end" pores. An attempt was made to fit the dual-porosity model to the present diffusion-sorption data. However, the model introduces two new adjustable parameters and a unique fit to the data could not be obtained.

The problem experienced in obtaining a unique parameter set from a diffusion-sorption experiment with a nuclide which sorbs non-linearly might be overcome by sectioning the rock sample following the experiment (without redistributing the radionuclides) and measuring the radionuclide concentrations. This would also provide a check on the consistency of the model. For a sorbing species, the concentrations in the sections are dominated by the solid-phase concentration S ($\rho S \gg C$). If the diffusion experiment is continued until the flux through the sample reaches a steady state, then the gradient of the liquid-phase concentration is uniform and, from equation (3), the profile of S is given by

$$S = KC_0^N(1 - x/L)^N \quad (11)$$

a plot $\log S$ against $\log x$ will therefore be linear, and will yield N from its gradient and K from its intercept with the $\log x$ axis. Figure 9 gives profiles of the solid-phase concentration of ^{137}Cs for parameter sets 1 and 3 at different times, corresponding to the liquid-phase concentration profiles of figure 7. Practically, the maximum number of sections which could be cut from the sample used in the diffusion-sorption experiment would be small, with errors in the measured concentration of around 10%. These results may, however, still be informative since a clear change in the shape of the profiles can be seen for the two values of N : $N = 0.550$ gives a negative curvature and $N = 1.00$ a positive curvature.

Bradbury *et al.* (1986) analysed the results for ^{137}Cs assuming linear sorption and therefore a constant R_D (the graphical analysis). However, since ^{137}Cs exhibits non-linear sorption behaviour, R_D would be expected to vary across the width of the sample as the nuclide concentration varies. They interpreted the calculated distribution ratio (R'_D) as a mean value for the concentration range across the sample. It is of interest to establish how R'_D is related to R_D at these concentrations. Figure 10 shows five numerical solutions of equations (5), each with $C_0 = 1.9 \times 10^{-2} \text{ mol.m}^{-3}$ and each having the same asymptote as $t \rightarrow \infty$, but with different values of N (the figure demonstrates that the transition from $C_t \approx 0$ to the

asymptotic solution at large times takes place over a shorter time as N is reduced i.e. as sorption becomes more non-linear). In the case of $N = 1$, the asymptotic solution is given by equation (10). Since they have the same asymptote, if we apply the graphical analysis, they will all give the same R'_D . R'_D is defined by:

$$R'_D = \frac{6D_e t_{int}/L^2 - \epsilon}{\rho} \quad (12)$$

where t_{int} is the intercept of the asymptote with the time axis. From equation (10), if $N = 1$ then $R'_D = R_D$. If we define the quantity F such that, in general, $R'_D = R_D$ when $C = FC_0$, and evaluate F for each value of N in figure 10 using the hypothetical relationship

$$R'_D = K(FC_0)^{N-1} \quad (13)$$

we find that it takes a value of about 0.4, independently of N . In other words, R'_D is equal to R_D , evaluated at 40% of the reservoir concentration. Although F cannot be expected to be independent of the reservoir concentration, this result indicates that, for a diffusion experiment using a species which sorb non-linearly, a simple, graphical analysis of the results will give a guide to the average distribution ratio within the sample.

From the modelling point of view, the duration of the diffusion-sorption experiment is of great importance. A unique set of diffusion and sorption parameters for each nuclide could have been extracted if the experiment has proceeded to longer times. It is not, however, simple to judge beforehand what the duration of the experiment should be. In any future experiment of this type, it is therefore recommended that the analysis of the data be carried out while the experiment is proceeding. The decision to stop the experiment could then be made once it is possible to obtain a unique set of parameters for the chosen model.

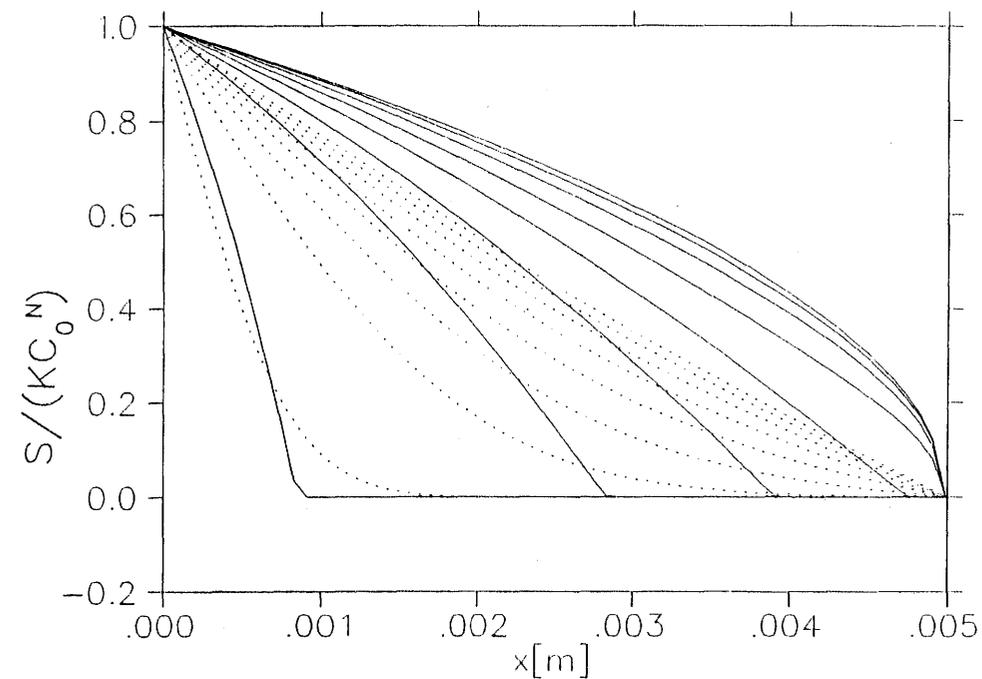


Figure 9: Profiles of the solid-phase concentration of ^{137}Cs across the sample, generated using the linear and non-linear sorption models. Time increment between profiles is 0.04yrs .
 - - - - linear sorption ($D_e = 4.5 \times 10^{-11}\text{m}^2\text{s}^{-1}$, $K = 0.044\text{m}^3\text{kg}^{-1}$)
 ——— non-linear sorption
 ($D_e = 2.31 \times 10^{-11}\text{m}^2\text{s}^{-1}$, $K = 1.29 \times 10^{-3}\text{mol}^{1-N}\text{m}^{3N}\text{kg}^{-1}$, $N = 0.550$)

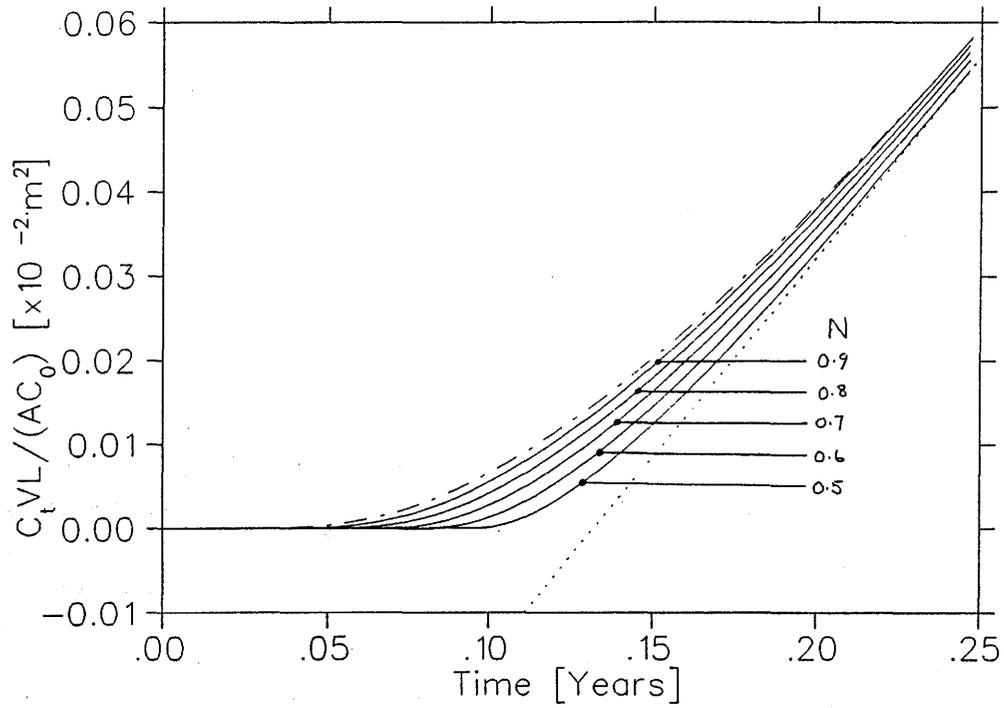


Figure 10: Diffusion-sorption curves, each having the same asymptote for $t \rightarrow \infty$, but with a range of values of N .

- linear sorption
- non-linear sorption
- asymptote

7 Conclusions

- The analysis presented here allows diffusion coefficients and Freundlich isotherms for different radionuclides to be extracted from one experiment on an intact rock sample, thus avoiding the need for separate experiments to measure diffusion and sorption parameters and the problems associated with sample preparation in batch-sorption tests. From an experimental point of view, this means that long term diffusion-sorption experiments are more attractive.
- The analysis uses time-dependent solutions of the governing equations, allowing diffusion and sorption parameters to be extracted from an experiment which has not reached steady state. Experiments of relatively short duration can be used, provided data is of sufficient accuracy.
- The sorption of ^{85}Sr is modelled by a linear isotherm, consistent with batch-sorption results on coupons and on crushed samples with large $PSRs$.
- The sorption of ^{137}Cs is modelled by a non-linear isotherm, but is sorbed less than anticipated from batch-sorption tests. Batch-sorption data on coupons and crushed samples with a range of $PSRs$ and W/Rs between 3:1 and 20:1 seem to overestimate sorption in the concentration range considered by at least an order of magnitude.
- The diffusion coefficients calculated for ^{137}Cs from the diffusion-sorption experiment is similar to that of ^{125}I , but that of ^{85}Sr is larger by a factor of more than 6. Although this observation is currently unexplained, the effects of anion exclusion and ion diameter may be important.
- The simple graphical analysis enables diffusion coefficients and distribution ratios to be extracted for nuclides which exhibit linear sorption. For nuclides which exhibit non-linear sorption, the analysis gives a measure of the mean distribution ratio within the sample. However, it is not necessarily clear, from an inspection of the experimental data, at what point the system has reached steady state.
- Further experiments, in which the sample is sectioned to give profiles of the solid-phase concentration, would assist in determining the sorption parameters of non-linear sorbing species and would provide a check on the consistency of the models.
- In future experiments, analysis of the data should be carried out while the experiment is proceeding. The experiment could then be continued until the data gives a unique set of parameters for the chosen model.
- In future experiments, the analysis of simulated groundwater should include the concentrations of the stable isotopes of all the tracer elements.

8 Appendix

FITTING A REGRESSION MODEL TO EXPERIMENTAL DATA

Consider a set of n experimental data points (x_i, y_i) . A general, non-linear regression model $f(x; \theta)$ which fits this set of points may be written

$$y_i = f(x_i; \theta) + e_i(\theta), i = 1, 2, \dots, n \quad (14)$$

where θ is a vector containing the p regression parameters of the model and $e_i(\theta)$ are the residuals of the model. Each experimental data point has a measurement error σ_i . A merit function χ^2 for this fit is then defined by

$$\chi^2 = \sum_{i=1}^n [e_i(\theta)/\sigma_i]^2 \quad (15)$$

The value of θ which minimises the merit function is taken to give the best-fit regression model. If the measurement errors are normally distributed, with standard deviations σ_i , then a minimisation of χ^2 is also a "maximum likelihood estimator". If the experimental errors are unknown, then an assessment of the "goodness of fit" of the model is not possible. However, if it is assumed that all the measurement errors are normally distributed with the same standard deviation σ and that the model represents a good fit, then we can assign an arbitrary constant $\sigma_i = 1$ to all the points, obtain regression parameters for the model by minimising χ^2 and recompute the standard deviation from

$$\sigma^2 = \chi^2/n \quad (16)$$

We use an IMSL statistical library routine to minimise χ^2 by the iterative Levenberg-Marquardt method. \mathbf{A} , the Hessian matrix, defined by

$$A_{ij} = \frac{\partial^2 \chi^2}{\partial \theta_i \partial \theta_j}, i = 1, 2, \dots, p \quad j = 1, 2, \dots, p \quad (17)$$

is then calculated. The inverse of the Hessian matrix is proportional to \mathbf{C} , the covariance matrix of the standard errors in the fitted parameters of the model

$$\mathbf{C} = 2\mathbf{A}^{-1} \quad (18)$$

The standard errors in the regression parameters $\sigma(\theta_i)$ are related to the diagonal elements of \mathbf{C} by

$$\sigma(\theta_i) = [C_{ii}\chi^2/(n-p)]^{1/2}, i = 1, 2, \dots, p \quad (19)$$

The correlation matrix \mathbf{R} is given by

$$R_{ij} = \frac{C_{ij}}{(C_{ii}C_{jj})^{1/2}}, j = 1, 2, \dots, p \quad (20)$$

R_{ij} is the coefficient of correlation between the uncertainty in θ_i and the uncertainty in θ_j , with a positive value indicating that errors in θ_i and θ_j are likely to be of the same sign and a negative value indicating that they are likely to be of opposite sign.

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