

Rock-matrix diffusion and its implications for radionuclide migration

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ABSTRACT. Diffusion into the rock matrix is potentially an important retardation mechanism for nuclides leached from an underground radioactive waste repository in a fractured hard rock. A technique for measuring the intrinsic diffusion coefficient and rock capacity factor is briefly described. Simple solutions to migration model equations are used, together with diffusion results and typical hydrogeological parameters, to estimate the impact of matrix diffusion on radionuclide migration. It is shown that retardation factors in excess of 100 and reductions in the peak concentration by 3-4 orders of magnitude are possible for non-sorbed ions, which would otherwise be carried by the flow and not retarded at all.

KEYWORDS: radionuclides, radioactive waste, diffusion.

ONE of the options being considered for the safe long-term disposal of radioactive waste from the nuclear power industry is deep burial in stable fractured rock formations. The most probable way in which radionuclides from the waste could reach the biosphere is by groundwater transport. The man-made barriers surrounding the waste, the waste form and its packaging will all serve to delay, possibly for thousands of years, contact between the waste and the circulating groundwater. Eventually, however, the barriers will be breached and the process of leaching and dissolution will begin, releasing radionuclides into the flowing water. In fractured rock bodies such as granite, migration will take place predominantly along existing open fracture networks, since these generally offer the path of least hydraulic resistance. Fortunately, nuclides will not usually advect with the ground water, but will rather be retarded by two primary mechanisms: sorption and diffusion into the rock matrix.

The main subject of this paper is the latter process—namely diffusion of radionuclides from water flowing in the fractures to stagnant water in the rock matrix. Recently, models incorporating diffusion into the rock matrix have been increasingly studied (Neretnieks, 1980; Rasmuson and Neretnieks, 1980, 1981; Grisak and Pickens, 1980;

Curtis, 1980; Glueckauf, 1980, 1981; Rae and Lever, 1980; Kipp, 1982; Barker, 1982; Bibby, 1981; Tang *et al.*, 1981; Kanki *et al.*, 1981), and experimental programmes have started to measure the important parameters (Bradbury *et al.*, 1982; Skagius and Neretnieks, 1982; Wadden and Katsube, 1982). In addition, a model incorporating rock-matrix diffusion has been used to interpret a field experiment (Hodgkinson and Lever, 1983). In the next section we briefly describe laboratory experiments to measure the parameters characterizing the diffusion process—the intrinsic diffusion coefficient and the rock capacity factor. These data, together with a typical range of realistic hydrogeological parameters pertaining to granite formations, are used in solutions of migration equations. Estimates are given for the retardation factor and the variation of the maximum concentration as a function of distance from the source. The case chosen is that for a non-sorbing species, for example the iodide ion, since such species would be expected to migrate the most rapidly. Therefore, for the situation considered, the calculations represent an upper bound on the migration rate. It should be emphasized that all species will be retarded and dispersed by diffusion phenomena to a similar extent. For sorbing species, diffusion-related retardation and dispersion will be in addition to delays originating from sorption processes, whether taking place in the bulk rock, on fracture surfaces, or on fracture infill material.

1. Experimental procedure and results. Diffusion has been measured through cylindrical samples of granite approximately 75 mm in diameter and up to 50 mm thick. Briefly, the method consists of sealing a previously saturated sample in a perspex cell. One face of the sample is maintained at a constant concentration by contact with a large volume of a KI solution. Diffusion across the sample is monitored continuously by measuring the iodide ion concentration using calibrated ion specific electrodes in a stirred solution contacting the opposite face of the sample (Bradbury *et al.*, 1982). It was

found that small variations in temperature had no discernible effects.

The diffusion through the slab is modelled by the diffusion equation

$$\alpha' \frac{\partial c'}{\partial t} = D_i \frac{\partial^2 c'}{\partial x^2}, \quad (1.1)$$

where D_i is the intrinsic diffusion coefficient (the flux per unit area of rock is $-D_i \partial c' / \partial x$) and α' is the rock capacity factor. This has two contributions,

$$\alpha' = \varphi' + \rho' K'_m, \quad (1.2)$$

where φ' is the porosity, ρ' the rock density and K'_m the partition coefficient assuming a linear equilibrium isotherm. In (1.1), c' is the concentration per unit volume of pore water, and so $\alpha' c'$ is the concentration per unit volume of rock in the pore-water and sorbed to the rock.

For the present case of a porous slab initially at zero concentration, with constant inlet concentration C_1 at $x = 0$ and outlet concentration $C_2(t)$ ($C_2(t) \ll C_1$) at $x = l$, the total quantity, $Q(t)$, diffused through the slab in time t is found by solving (1.1) to be:

$$\frac{Q(t)}{AlC_1} = \frac{D_i t}{l^2} \frac{\alpha'}{6} - \frac{2\alpha'}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left\{-\frac{D_i n^2 \pi^2 t}{l^2 \alpha'}\right\}, \quad (1.3)$$

where $Q(t) = C_2(t)V$, (1.4)

V is the solution volume in the measurement cell, l is the sample thickness, and A the area of the sample.

As t increases, the exponential term in (1.3) rapidly decreases leaving the asymptotic solution

$$C_2(t) = \frac{D_i A C_1}{V l} t - \frac{C_1 A l \alpha'}{6 V}. \quad (1.5)$$

In this asymptotic limit, plots of $C_2(t)$ against t become straight lines from which D_i and α' can be calculated from the slope and extrapolated intercept on the time axis respectively (fig. 1).

It is important to realize that the intrinsic diffusion coefficient is an inherent property of the three component system: porous solid, diffusing

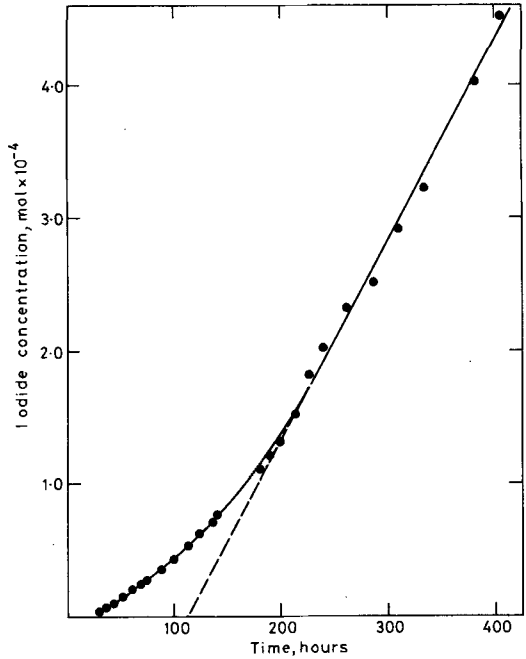


FIG. 1. The concentration in the measurement cell as a function of time for iodide ion diffusion through a disc of Ossian granite.

species, and solvent. Since it is measured when the system has attained a steady state its value is independent of the sorption characteristics of the diffusing nuclide.

Diffusion measurements using iodide ions as tracer have been carried out on over twenty granite samples obtained from four different regions of the United Kingdom (these were available commercially and have no direct significance for waste disposal). The main thrust of this paper centres on the impact of matrix diffusion on the radionuclide migration from a repository. In this context it is important to know the anticipated range of values for D_i and α' . These results are given in Table I. It is also interesting to note that similar measurements

TABLE I. Diffusion parameters for granites obtained from laboratory diffusion experiments

Granite	D_i ($\text{m}^2 \text{ s}^{-1}$)	α'
Ossian	6.4×10^{-13} – 1.6×10^{-12}	3.1×10^{-3} – 2.2×10^{-2}
Scottish Lowland	2.7×10^{-13} – 4.0×10^{-13}	2.2×10^{-3} – 2.7×10^{-3}
Skene Complex	2.8×10^{-13} – 7.4×10^{-13}	1.2×10^{-3} – 4.6×10^{-3}
Cornish Carnmenellis	2.3×10^{-14} – 3.2×10^{-14}	6.0×10^{-4} – 8.8×10^{-4}

carried out on granites from Sweden (Skagius and Neretnieks, 1982) and Canada (Bradbury, 1983, unpublished results) yield very similar diffusion parameters to those given here.

2. *Migration model.* In this section we describe the one-dimensional migration model used in subsequent sections. We start by giving the conservation equations for the radionuclide concentration. These equations are considered in more detail by Lever *et al.* (1983).

In the absence of radioactive decay, the concentration per unit volume of water in the fracture, $c(x,t)$, and the concentration in the rock, $c'(x,w,t)$, satisfy

$$\underbrace{K \frac{\partial c}{\partial t}}_{\text{Retardation}} + \underbrace{u \frac{\partial c}{\partial x}}_{\text{Advection}} = \underbrace{D_{B\parallel} \frac{\partial^2 c}{\partial x^2}}_{\text{Dispersion}} + \underbrace{\frac{D_i}{h} \frac{\partial c'}{\partial w}}_{\text{Flux to rock matrix}} \Bigg|_{w=0}, \quad (2.1)$$

$$\alpha' \frac{\partial c'}{\partial t} = D_i \frac{\partial^2 c'}{\partial w^2}. \quad (2.2)$$

Diffusion in the rock

In these equations u is the mean flow velocity, $D_{B\parallel}$ is the longitudinal bulk dispersion coefficient, D_i is the intrinsic diffusion coefficient for diffusion into the rock, h is the mean fracture half-width, x and w are the coordinates along and perpendicular to the fracture respectively, α' is the rock capacity factor (1.2), and K is the fracture retardation factor, given by

$$K = 1 + K_f/h, \quad (2.3)$$

where K_f is the distribution coefficient per unit area of fracture wall. If dispersion and diffusion were absent the nuclide would move at velocity u/K .

Sorption has been modelled by a linear equilibrium isotherm, and this has given the simple factors K and α' . Kinetic and non-linear effects have both been neglected. The impact of sorption will be very different (usually reduced) if either the kinetics are slow compared with other time-scales or if the concentrations are sufficiently large for the quantity sorbed not to be proportional to the concentration in the water. However, rock-matrix diffusion will be most important for non- or weakly sorbed ions, and the example taken at the end of this paper is of a non-sorbed nuclide. So equilibrium sorption is included in the analysis to give an idea of how the results are affected.

Hydrodynamic dispersion arises from the different transit times for various paths through the fracture network. In this analysis dispersion in the direction of the flow is modelled by a diffusion-like term, with a 'geometric' dispersivity (Bear, 1972)

$$D_{B\parallel} = D_o + a_{\parallel} \gamma u, \quad (2.4)$$

where a_{\parallel} is an empirical constant and γ is a length scale between fracture intersections. This is assumed

to be similar to the diffusion length or mean half fracture separation l . Hydrodynamic dispersion is only represented by a diffusion-like term after a moderate number of fracture intersections, which can in practice be quite a large distance from the source. Nevertheless, it will be used to give an estimate of the spreading even before it is a truly valid concept.

Transverse dispersion, spreading orthogonal to the flow direction, has not been included in the model considered here. Generally it leads to a further significant dilution of the concentration at all times, although at early times the decrease will depend on the spatial distribution of the source. Therefore, the maximum concentrations calculated here are on the pessimistic side. An alternative interpretation of the solution considered here is that it is the total quantity integrated over a plane perpendicular to the flow direction. When this integration is carried out the transverse dispersion term, here neglected, disappears. This quantity is relevant when looking at the total flux returning to the biosphere.

Finally, initial and boundary conditions are required to complete the equations. Initially the concentrations in the rock and fracture are assumed to be zero. At the fracture surface the concentration is continuous,

$$c(x,t) = c'(x, w = 0, t). \quad (2.5)$$

There will be no flux of nuclide mid-way between the fractures, thus

$$\frac{\partial c'}{\partial w} \Bigg|_{w=l} = 0, \quad (2.6)$$

where $2l$ is the mean fracture spacing. For a fracture network it is an oversimplification to take a single value of l ; however, it is sufficient to give a guide to the importance of the effect. At the inlet, the concentration $c(0,t)$ is assumed to be specified as a function of time. There are a number of possible downstream boundary conditions. They can be applied either at the point where the quantity of nuclide is being monitored or at a point far from both the source and the monitoring point. The latter course leads to simpler solutions, and so is adopted here.

3. *Analytic solutions of the migration equations.* The equations described in the previous section do not have simple analytic solutions for general parameter values. However, there are some simple solutions for certain values of the parameters (l, u, D_L, \dots) and for certain boundary conditions. From these an understanding of diffusion into the rock matrix can be gained, and so two are examined here.

We consider two inlet boundary conditions. The

first is a step function with zero concentration for $t < 0$ and constant thereafter,

$$c(0,t) = \begin{cases} 0 & t < 0, \\ c_0 & t > 0. \end{cases} \quad (3.1)$$

The other condition is a 'top-hat' condition with zero concentration until $t = 0$ and after $t = T$, and a constant concentration between,

$$c(0,t) = \begin{cases} 0 & t < 0, t > T, \\ c_0 & 0 < t < T. \end{cases} \quad (3.2)$$

As the equations in section 2 are linear, the solution for (3.2) can be obtained as the sum of two step-function solutions. We will be particularly interested in the case of a short pulse input, when T is short compared with other time scales.

The first analytic solution considered is the case of non-zero hydrodynamic dispersion in the fracture and no diffusion into the rock ($D_i = 0$). Then the solution for the step function boundary condition (3.1) is (Harada *et al.*, 1980; Hodgkinson *et al.*, 1984):

$$c(x,t) = \frac{c_0}{2} \left\{ \operatorname{erfc} \left[\left(\frac{x^2 K}{4D_{B||} t} \right)^{\frac{1}{2}} - \left(\frac{u^2 t}{4D_{B||} K} \right)^{\frac{1}{2}} \right] + \exp \left(\frac{xu}{D_{B||}} \right) \operatorname{erfc} \left[\left(\frac{x^2 K}{4D_{B||} t} \right)^{\frac{1}{2}} + \left(\frac{u^2 t}{4D_{B||} K} \right)^{\frac{1}{2}} \right] \right\}. \quad (3.3)$$

The first term is the solution for an infinite medium with the initial concentration at $t = 0$ that $c = 0$ for $x > 0$ and $c = c_0$ for $x < 0$. This distribution is then convected with velocity u/K and spread over a distance of order $(D_{B||} t/K)^{\frac{1}{2}}$. Thus, after the front has travelled a distance x from the source, the time-scale it has been spread over is of order

$$\sigma = \left(\frac{D_{B||} x K^2}{u^3} \right)^{\frac{1}{2}}. \quad (3.4)$$

The second term in (3.3) is the correction term required to satisfy the boundary condition at $x = 0$. Once the step-function has been convected away from the source, as the distance over which it has dispersed is much smaller than the convection distance, it can be neglected.

The solution for a 'top-hat' inlet profile is found by taking the difference of two solutions of the form (3.3). The approximate solution for a pulse is found to be

$$c(x,t) = \frac{c_0 T x}{2(\pi D_{B||} t^3/K)^{\frac{1}{2}}} \exp \left(-\frac{(x-ut/K)^2}{4D_{B||} t/K} \right). \quad (3.5)$$

This clearly shows an exponential fall-off at large t after the pulse has passed. Once the pulse has been convected away from the source, the maximum arrives at $t = Kx/u$ and the time-scale over which the arrival is spread is again given by σ (3.4).

Secondly, we consider the solution for the case $D_{B||} = 0$ and $l = \infty$, i.e. negligible hydrodynamic dispersion in the fractures and effectively infinite rock perpendicular to the fracture. The solution for the step function input (3.1) is for no nuclide to arrive before $t = Kx/u$, while after this the concentration is given by

$$c(x,t) = c_0 \operatorname{erfc} \left[\left(\frac{\tau}{t - Kx/u} \right)^{\frac{1}{2}} \right], \quad (3.6)$$

$$\text{where} \quad \tau = \frac{D_i \alpha' x^2}{4u^2 h^2}, \quad (3.7)$$

(Neretnieks, 1980; Lever *et al.*, 1983). τ is the characteristic time-scale of diffusion into the rock matrix. If $t - Kx/u \ll \tau$, the argument of the complementary error function is very large and so the concentration is negligible. For $t - Kx/u \approx 0(\tau)$ the argument of the complementary error function is order 1, and so significant quantities of the nuclide are arriving. For $t - Kx/u \gg \tau$, the concentration is effectively c_0 .

The solution for the 'top-hat' condition (3.2) is obtained by taking the difference of two solutions of the form (3.6) and this can be simplified when the release time is short compared to the transit time to give the approximate solution

$$c(x,t) = \frac{c_0 T \tau^{\frac{1}{2}}}{\pi^{\frac{1}{2}} (t - Kx/u)^{3/2}} \exp \left\{ -\frac{\tau}{t - Kx/u} \right\}. \quad (3.8)$$

An extremely important feature of the solution is now clear. For large times, as long as the thick-rock ($l = \infty$) solution is valid, c falls off algebraically as $t^{-3/2}$ (Gleuckauf, 1981), rather than exponentially, as is the previous case with no diffusion into the rock but with dispersion in the fracture (3.5).

We have seen in this section that there are two important time-scales. When there is hydrodynamic dispersion and no rock-matrix diffusion, there is no additional delay and the time-scale over which the concentration changes is given by σ (3.4). When there is diffusion into the rock and no hydrodynamic dispersion τ (3.7) gives both the time-scale of the delay of nuclide and also the time-scale for either the pulse to pass or for the step function to attain its constant value.

4. General form of the solution. In the last section two ideal solutions to the equations for special values of the parameters were discussed for two boundary conditions, (3.1) and (3.2). In this section the simple solutions already described are used to examine more general forms of the solution for values of the parameters when no simple analytic solution is available.

As the nuclides migrate from the repository, different physical processes will determine how the concentration changes in different regions along

the migration path. At very short times the effects of diffusion and dispersion are not important. The principal effect, if it takes place, is retardation by sorption on the fracture walls, otherwise the nuclide is advected at the flow velocity.

The next process to become important is hydrodynamic dispersion. This can be seen by comparing the time-scales on which diffusion spreads the front or pulse, τ (3.7), and the time-scale for dispersion, σ (3.4).

$$\frac{\tau}{\sigma} = \frac{D_i \alpha' x^{3/2}}{4D_{B\parallel}^{\frac{1}{2}} u^{\frac{3}{2}} h^2 K}. \quad (4.1)$$

For small enough x , this is less than 1, suggesting that spreading by hydrodynamic dispersion dominates that by diffusion. An estimate of the distance, $x = L_{dt}$, at which the transition takes place, can be obtained by setting the ratio τ/σ (4.1) to unity. This gives the transition distance as:

$$L_{dt} \approx 3 \left(\frac{D_{B\parallel} u h^4 K^2}{D_i^2 \alpha'^2} \right)^{1/3}. \quad (4.2)$$

In deriving the time-scale for spreading by dispersion, we neglected retardation by diffusion. However, even though dispersion is spreading the front more than diffusion, diffusion into the rock could still be retarding the nuclide, and so rather than include in (4.2) the retardation factor in the absence of diffusion, K , it is better to include the value appropriate to that value of L_{dt} . This retardation factor, $\kappa(L_{dt})$, will be discussed shortly. Thus, instead of being given by (4.2), L_{dt} is the solution of

$$L_{dt} = 3 \left(\frac{D_{B\parallel} u h^4 [\kappa(L_{dt})]^2}{D_i^2 \alpha'^2} \right)^{1/3}. \quad (4.3)$$

Initially, nuclides diffuse into the rock as though it were infinite, and the thick-rock solutions discussed in the previous section are valid. However, the influence of neighbouring fractures is eventually felt. If at some point along the fracture, the nuclide has been diffusing into the rock for a time t_d , there will be appreciable concentrations at a distance $2(D_i t_d / \alpha')^{\frac{1}{2}}$ from the fracture. Once this becomes comparable with half the fracture separation l , the thick-rock solution breaks down. The position, $x = L_{dq}$, at which this occurs if the maximum is being monitored, can be found by substituting $t_d = \tau(x)$, given by (3.7), and this gives:

$$L_{dq} \approx \frac{luh}{D_i}. \quad (4.4)$$

Much further from the repository a region of quasi-equilibrium is reached when the nuclide concentration in the rock and fractures are approximately in equilibrium. In this region the migration can be modelled by an equivalent porous

medium and the concentration again approximately satisfies the convection-diffusion equation (Glueckauf, 1980; Lever *et al.*, 1983):

$$K' \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D_e \frac{\partial^2 c}{\partial x^2}, \quad (4.5)$$

with enhanced values of the retardation factor and dispersion coefficient given by

$$K' = K + \frac{\alpha' l}{h} \\ D_e = D_{B\parallel} + \frac{\alpha'^2 l^3 u^2}{3h D_i K'^2}. \quad (4.6)$$

In this region the solutions (3.3) and (3.5), obtained for pure hydrodynamic dispersion, are again appropriate, and the slow fall-off in concentration at large times for the thick-rock solutions, (3.6) and (3.8), is no longer found. Curtis (1980) found that at large distances, the time of arrival of the maximum was shifted by a constant, corresponding to the time taken to diffuse across the rock between the fractures. Clearly, as the distances get larger, this constant becomes less significant. He also found that the transition from the thick-rock solutions was fairly slow.

The distances (4.3) and (4.4) have been expressed in terms of the flow velocity in the fracture u . It is helpful to relate this to the hydraulic gradient driving the flow, Δ

$$u = \frac{g \Delta h^2}{3\nu}, \quad (4.7)$$

where ν is the kinematic viscosity and g the acceleration due to gravity. When this is substituted it is seen that the distances L_{dt} and L_{dq} are very sensitive to the values of the fracture aperture $2h$.

5. *The retardation factor.* One of the main effects of diffusion into the rock matrix is increased nuclide retardation. There are a number of ways of defining the retardation factor, depending on the form of input. For a pulse it is convenient to define the retardation of the maximum concentration, whilst for a step-function it is more sensible to define it by the breakthrough of a fraction of the constant limiting value. However, we saw in section 3 that when the nuclide is diffusing into thick-rock both of these are determined by τ , and so different definitions will only differ by a constant factor. Later, in the quasi-equilibrium region, the retardation factor tends to a constant, given by (4.6), and all definitions are equivalent. So in this section we will concentrate on the retardation of the maximum concentration in a pulse, bearing in mind that it is typical of more general definitions.

The retardation of the maximum is not affected by hydrodynamic dispersion, which simply spreads

the pulse. So at very short times, when diffusion effects are negligible, the retardation is determined by sorption on the fissure walls, given by (2.3). As diffusion into the rock matrix becomes more important the retardation of the maximum increases. Initially the nuclide diffuses into the rock as though it were infinite in extent; the influence of neighbouring fractures is not felt. The concentration is given approximately by (3.8) and the maximum arrives at time

$$t_{\max} = \frac{KL}{u} + \frac{2}{3}\tau = \frac{KL}{u} + \frac{D_1\alpha'L^2}{6u^2h^2}. \quad (5.1)$$

Thus, the retardation factor, κ , of the maximum is

$$\kappa(L) = \frac{ut_{\max}}{L} = K + \frac{D_1\alpha'L}{6uh^2}, \quad (5.2)$$

κ increases linearly with distance from the repository in the region where the thick-rock solution is valid.

However, this solution starts to break down when the influence of diffusion from neighbouring fractures becomes important. This occurs at a distance L_{iq} from the repository, given by (4.4). After this the retardation stops increasing linearly with distance and tends to the constant retardation factor characteristic of the quasi-equilibrium region, where the concentration in the rock is approximately the same as in the fracture. The limiting value of the retardation factor is given by (4.6)

$$\kappa = K' = K + \frac{\alpha'l}{h}. \quad (5.3)$$

It is worth noting that the term $\alpha'l/h$, by which rock-matrix diffusion enhances the retardation factor K , is simply the ratio of the amount of nuclide held immobile in the rock matrix (sorbed and in solution in the pore-water) to the amount flowing in the fissure.

The transition from the thick-rock solution to the quasi-equilibrium solution takes place over a large distance. This can be seen by equating (5.2) and (5.3) to find the distance from the repository where the two asymptotes meet, this is at

$$L = \frac{6uhl}{D_1} = 6L_{\text{iq}}. \quad (5.4)$$

6. *The maximum concentration.* Having studied the retardation factor we now consider the variation along the migration path of the maximum concentration, first for a pulse input, and then for a decaying step function.

The behaviour of the maximum concentration of the pulse is different in the various regions described in section 4. Initially the characteristics of the input pulse are retained. The first significant effect arises

from longitudinal dispersion for distances less than L_{dt} , given by (4.3). The concentration is given by (3.5) and the maximum is

$$c_{\max} = \frac{c_0 T}{2} \left(\frac{u^3}{\pi D_{\text{B||}} K^2 L} \right)^{\frac{1}{2}}. \quad (6.1)$$

An important point to note is that c_{\max} falls off as $L^{-\frac{1}{2}}$. For distances greater than L_{dt} , diffusion into the rock becomes the dominant process, and for $L_{\text{dt}} < L < L_{\text{iq}}$ the nuclide diffuses into the rock as if it were infinite in extent. The maximum concentration arrives at the time given by (5.1) and is

$$c_{\max} = 0.93 \frac{c_0 T u^2 h^2}{D_1 \alpha' L^2}. \quad (6.2)$$

Consequently as long as the thick-rock approximation is valid, the maximum concentration will decrease as L^{-2} , i.e. more rapidly than (6.1).

Eventually the thick-rock solution breaks down and the system tends slowly to a quasi-equilibrium characterized by an enhanced retardation and an enhanced dispersion, given by (4.6). The migration equation is again approximately a convection-diffusion equation and so the maximum concentration is similar to (6.1), with $D_{\text{B||}}$ replaced by D_e and K by K' , and is

$$c_{\max} = \frac{c_0 T}{2} \left(\frac{u^3}{\pi D_e K'^2 L} \right)^{\frac{1}{2}}. \quad (6.3)$$

Now, as in the region dominated by longitudinal dispersion, the maximum decreases as $L^{-\frac{1}{2}}$. One simple way to characterize the effect of rock-matrix diffusion is to compare the asymptote (6.3) with the asymptote when there is no matrix diffusion but only dispersion (6.1). This ratio is determined by the hydrogeologic and diffusion parameters, and does not depend on L or q . It is given by

$$E = \frac{c_{\max}(D_e)}{c_{\max}(D_{\text{B||}})} = \left(\frac{D_{\text{B||}} K^2}{D_e K'^2} \right)^{\frac{1}{2}}. \quad (6.4)$$

Thus the maximum will be significantly reduced if K' is greater than K (i.e. there is a substantial increase in retardation), or if D_e is much greater than $D_{\text{B||}}$. E gives the fractional reduction in the quasi-equilibrium region. The fractional reduction, ε , along the migration path is a function of the migration distance, and is found from (6.1) to (6.3) to be approximately

$$\varepsilon(L) = \begin{cases} 1 & L < L_{\text{dt}}, \\ 3.3 \left(\frac{u^3 h^2 D_{\text{B||}}^{\frac{1}{2}} K}{D_1 \alpha' L^{3/2}} \right) & L_{\text{dt}} < L < L_{\text{iq}}, \\ E & L_{\text{iq}} < L. \end{cases} \quad (6.5)$$

Finally, we examine a step-function boundary condition. There is only a reduction in maximum concentration if the nuclide is decaying, including

that in the source. Then if it is retarded sufficiently for the transit time to become comparable to, or greater than, the half-life, there is a significant reduction. Of course, the nuclide probably decays into another radionuclide. However, as most nuclides are significantly sorbed, this may be much less mobile.

The maximum concentration in the absence of retardation by diffusion is approximately

$$c_{\max} = c_0 \exp(-\lambda KL/u), \quad (6.6)$$

where λ is the decay constant. With diffusion it is approximately

$$c_{\max} = c_0 \exp(-\lambda \kappa(L) L/u), \quad (6.7)$$

where the retardation factor is given by (5.2) and (5.3), depending on whether L is less than or greater than $6L_{\text{tq}}$. So the approximate fractional reduction, ε , is given by

$$\varepsilon(L) \simeq \begin{cases} \exp(-D_i \alpha' l^2 \lambda / 6u^2 h^2) & L < 6L_{\text{tq}}, \\ \exp(-\alpha' l L \lambda / uh) & L > 6L_{\text{tq}}. \end{cases} \quad (6.8)$$

7. *Estimates of the enhanced retardation and reduction in maximum concentration.* As an example of the sort of delays that may be expected from diffusion into the rock we consider the migration of a non-sorbed ($K = 1$), non-decaying pulse of nuclide. This is a good example because non-sorbed nuclides are probably not retarded by other physical processes, only dispersed, so they are the ones most likely to return rapidly to the biosphere.

The following values for physical constants and hydrogeological parameters are used:

$$\begin{aligned} g &= 10 \text{ ms}^{-2} \\ v &= 10^{-6} \text{ m}^2 \text{ s}^{-1} \\ \Delta &= 10^{-3}. \end{aligned}$$

We take two sets of diffusion parameters, based on the range given in Table I for granites:

$$\begin{aligned} D_i &= 10^{-12} \text{ m}^2 \text{ s}^{-1}, & \alpha' &= 10^{-2}, \\ D_i &= 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}, & \alpha' &= 5 \times 10^{-4}, \end{aligned}$$

and two values of the dispersion length constant:

$$a_{\parallel} = 1 \quad \text{and} \quad a_{\perp} = 10,$$

to reflect the way the quantities we calculate depend on D_i , α' , and a_{\parallel} . Bourke *et al.* (1982) recently reported fracture separations ($2l$) of 10 m and fracture apertures ($2h$) of 5×10^{-5} m. So we consider two values of l , 2 m, and 5 m, and two values of h , 2.5×10^{-5} m and 10^{-4} m, to see the dependence of the quantities of interest on the fracture parameters. These quantities are: (i) the distance from the repository at which diffusion into the rock starts to dominate hydrodynamic dispersion, L_{dt} (4.3);

(ii) the distance at which the thick-rock solutions break down and the quasi-equilibrium solutions start to be appropriate, L_{tq} (4.4); (iii) the maximum retardation factor K' (5.3), attained in the quasi-equilibrium region; (iv) the maximum fractional reduction, E (6.4), in the maximum concentration compared to its value without diffusion into the rock, again attained in the quasi-equilibrium region. The results are shown in Table II.

The limiting values of the retardation shown vary from 10 (for the case of low rock capacity, small fracture separation and wide fracture aperture) to 2000 (for high capacity, wide separation and small aperture), and the fractional reduction in maximum concentration are in the range 10^{-4} to 10^{-3} . The distances at which the transitions take place vary considerably: L_{dt} from 3 m to 6.5×10^3 m (6.5 km) and L_{tq} from 100 m to 3.3×10^5 m (330 km). Clearly the highest values are much larger than any migration distances that would be encountered in practice, indicating that the maximum retardation and reduction could not be attained. The wide range shows how important it is to have accurate field data for the separation and aperture of the major water-bearing fractures.

We further illustrate the retarding effects by calculating the travel times for water and a non-sorbed nuclide along a path of given length for a given set of rock parameters. These values, referred to as the central case, are migration distance $L = 2000$ m, diffusion parameters $D_i = 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $\alpha' = 0.01$, fracture parameters $l = 5$ m and $h = 2.5 \times 10^{-5}$ m, dispersivity $a_{\parallel} = 1$ and hydraulic gradient $\Delta = 10^{-3}$. The effect on the travel times of varying each in turn is examined, and the results given in Table III. The nuclide travel time is calculated from the retardation factor, based on the arrival time of the maximum of a pulse. Clearly the breakthrough or initial arrival time is somewhat earlier, but the above value provides a suitable estimate for the purpose here.

For the central case, the water travel time is 30 years, and the time for the non-sorbed nuclide about 2000 times longer, i.e. 60 000 years, as the migration path is sufficiently long for the quasi-equilibrium region to be attained ($L > 6L_{\text{tq}}$). Changing the dispersivity a_{\parallel} does not alter these results (although it would alter the initial breakthrough time). Decreasing l to 2 m decreases the limiting retardation factor to 800, the quasi-equilibrium solution is still relevant, and so the nuclide travel time is decreased to 24 000 years. The other four variations all result in the migration distance being smaller than $6L_{\text{tq}}$, so the quasi-equilibrium region is not attained, and the thick-rock solution (5.1) has to be used instead as an estimate. The effects of reducing the migration

TABLE II. *The effect of rock-matrix diffusion on nuclide migration*

h (m)	l (m)	u (ms^{-1})	L_{dt} (m)	L_{dq} (m)	K'	E
(i) $D_i = 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $\alpha' = 10^{-2}$, $a_{ } = 1$						
2.5×10^{-5}	2	2.1×10^{-6}	2.6	100	800	2.9×10^{-4}
2.5×10^{-5}	5	2.1×10^{-6}	5.0	260	2000	1.2×10^{-4}
10^{-4}	2	3.3×10^{-5}	45	6700	200	1.5×10^{-4}
10^{-4}	5	3.3×10^{-5}	64	17000	500	6.0×10^{-5}
(ii) $D_i = 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, $\alpha' = 5 \times 10^{-4}$, $a_{ } = 1$						
2.5×10^{-5}	2	2.1×10^{-6}	59	2.1×10^3	41	1.3×10^{-3}
2.5×10^{-5}	5	2.1×10^{-6}	84	5.2×10^3	100	5.4×10^{-4}
10^{-4}	2	3.3×10^{-5}	2200	1.3×10^5	11	6.7×10^{-4}
10^{-4}	5	3.3×10^{-5}	3000	3.3×10^5	26	2.7×10^{-4}
(iii) $D_i = 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $\alpha' = 10^{-2}$, $a_{ } = 10$						
2.5×10^{-5}	2	2.1×10^{-6}	16	100	800	7.6×10^{-4}
2.5×10^{-5}	5	2.1×10^{-6}	39	260	2000	3.0×10^{-4}
10^{-4}	2	3.3×10^{-5}	110	6700	200	4.7×10^{-4}
10^{-4}	5	3.3×10^{-5}	170	17000	500	1.9×10^{-4}
(iv) $D_i = 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, $\alpha' = 5 \times 10^{-4}$, $a_{ } = 10$						
2.5×10^{-5}	2	2.1×10^{-6}	1.5×10^2	2.1×10^3	41	4.2×10^{-3}
2.5×10^{-5}	5	2.1×10^{-6}	2.2×10^2	5.2×10^3	100	1.7×10^{-3}
10^{-4}	2	3.3×10^{-5}	4.8×10^3	1.3×10^5	11	2.1×10^{-3}
10^{-4}	5	3.3×10^{-5}	6.5×10^3	3.3×10^5	26	8.5×10^{-4}

L_{dt} is the distance where thick-rock diffusion dominates hydrodynamic dispersion, L_{dq} where the thick-rock solutions break down, K' and E the limiting retardation factor and fractional reduction in maximum concentration in the quasi-equilibrium region.

distance to 500 m or increasing the hydraulic gradient to 4×10^{-3} are identical; the water and nuclide travel times are reduced respectively to 7.6 and 4900 years, giving a retardation factor of 640. If the rock porosity is lower and the intrinsic diffusivity is correspondingly lower ($\alpha' = 5 \times 10^{-4}$,

TABLE III. *The effects on the travel times for water and a non-sorbed nuclide of a variation of the parameters*

Variation	Water travel time (yrs.)	Non-sorbed nuclide travel time (yrs.)
Central case	30	60000
$L = 500 \text{ m}$	7.6	4900
$D_i = 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$	30	230
$\alpha' = 5 \times 10^{-4}$		
$l = 2 \text{ m}$	30	24000
$h = 10^{-4} \text{ m}$	1.9	21
$a_{ } = 10$	30	60000
$\Delta = 4 \times 10^{-3}$	7.6	4900

The central case has a migration length $L = 2000 \text{ m}$, $D_i = 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $\alpha' = 0.01$, $l = 5 \text{ m}$, $h = 2.5 \times 10^{-5} \text{ m}$, $a_{||} = 1$, and $\Delta = 10^{-3}$.

$D_i = 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$), then the retardation is only 7.4, compared with a maximum value of 100 in the quasi-equilibrium region, and the nuclide travel time is 230 years. If the half fracture aperture h is increased by a factor of 4, to 10^{-4} m , the retardation factor is only 11. The water travel time is reduced to 1.9 years (as the hydraulic gradient is kept constant) and the nuclide travel time is a mere 21 years. Thus, a comparatively small change in h leads to a dramatic change in the retardation, because in the thick-rock diffusion region the increase in the travel time (5.1) is proportional to h^{-6} (as u is proportional to h^2). This again emphasizes the need for a good characterization of the major water-bearing fractures.

Finally, we give two illustrative curves to show how the formulae developed in sections 4 to 6 can be used to construct approximate curves showing the development of the solution. We again take as the specific example the values: $h = 2.5 \times 10^{-5} \text{ m}$, $l = 5 \text{ m}$, $D_i = 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $\alpha = 0.01$, $a_{||} = 1$, $\Delta = 10^{-3}$. First, the retardation factor is shown in fig. 2. This increases from 1 at $L = 0$ to the constant value of 2000 in the quasi-equilibrium region. The two asymptotic regions are shown: the solution

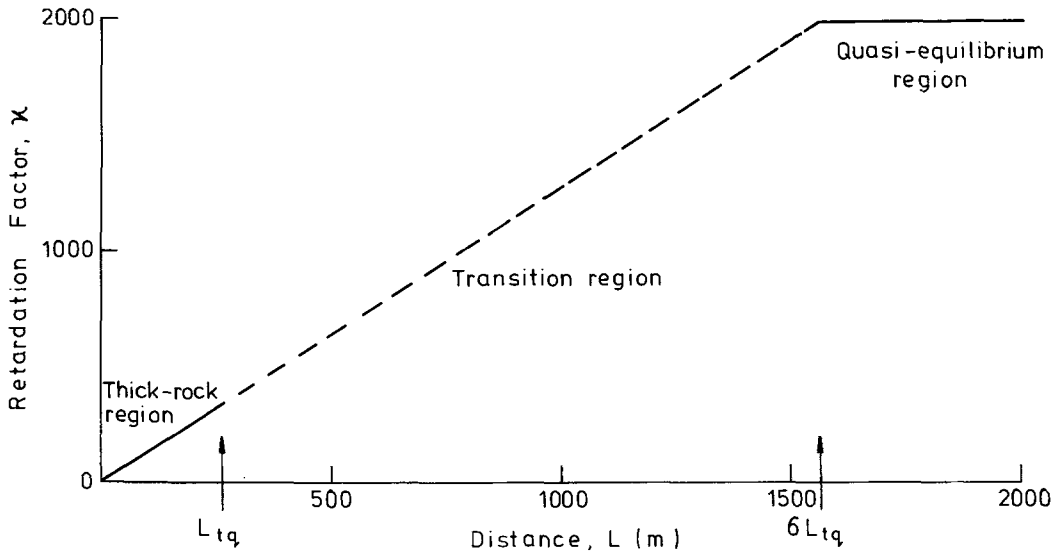


Fig. 2. The retardation factor κ as a function of distance from the repository showing the asymptotic behaviour in the thick-rock and quasi-equilibrium regions, for $h = 2.5 \times 10^{-5}$ m, $l = 5$ m, $D_i = 10^{-12}$ m² s⁻¹, $\alpha' = 0.01$, $a_{||} = 1$, $\Delta = 10^{-3}$.

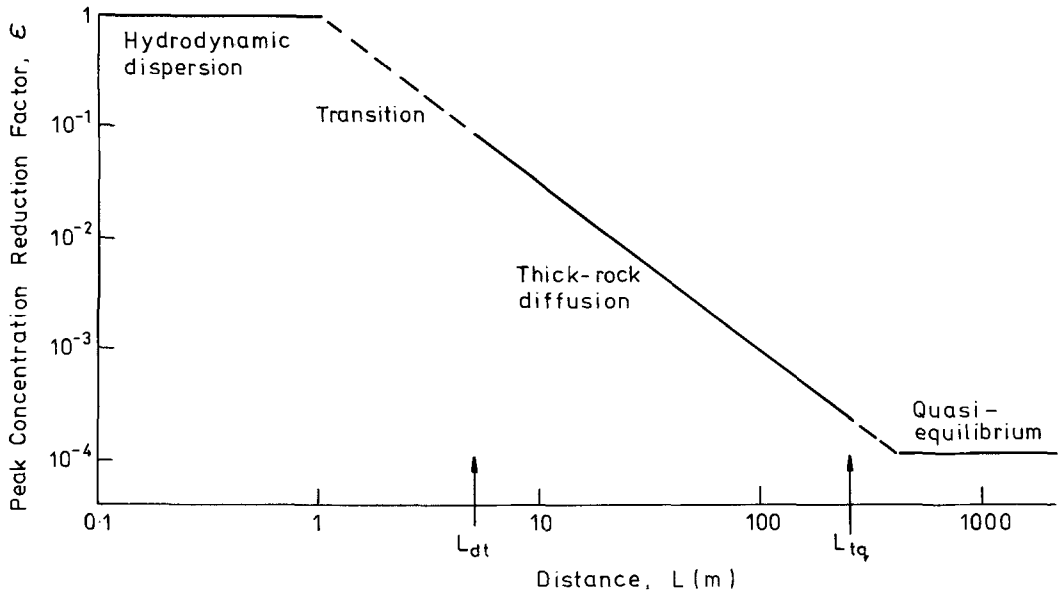


Fig. 3. Logarithmic plot of the reduction in the maximum concentration, ϵ , against distance from the repository, showing the asymptotic behaviour for $h = 2.5 \times 10^{-5}$ m, $l = 5$ m, $D_i = 10^{-12}$ m² s⁻¹, $\alpha' = 0.01$, $a_{||} = 1$, $\Delta = 10^{-3}$.

when it is diffusing into effectively infinite rock (5.2) and the quasi-equilibrium constant (5.3). The position of the breakdown of the former, L_{tq} , is marked, and the long transition to the equilibrium seen. Then in fig. 3 the fractional reduction, ε , in the maximum concentration arising from diffusion into the rock matrix is plotted as a function of distance from the source. The three asymptotes are given by (6.5). Initially diffusion has no effect, hydrodynamic dispersion dominates and $\varepsilon = 1$. Then there is a transition region before the thick-rock solutions dominate after L_{dt} . This long transition arises because diffusion retards the pulse, and so increases spreading by dispersion, before it dominates in the spreading of the pulse. After this the thick-rock region is seen, which in turn gives way to the quasi-equilibrium solution at L_{tq} . Here the fractional reduction is again a constant (1.2×10^{-4}), determined by the enhanced dispersivity and retardation.

8. *Conclusions.* We have described the results of laboratory experiments measuring the intrinsic diffusivity and rock capacity factors for weakly sorbed ions in granitic rocks. These values have been used when the effects of diffusion from water flowing in fractures into immobile water in the rock pores is important for radionuclide migration. Simple solutions have been presented, which enable the positions of the transitions between regions where different phenomena dominate to be calculated. The retardation factor and reduction in maximum concentration have been calculated in the different regions and their asymptotic behaviour plotted. We have seen that for non-sorbed ions, which would not otherwise be retarded, retardation factors in excess of 100 and reductions in the maximum concentration of 3 or 4 orders of magnitude are possible.

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