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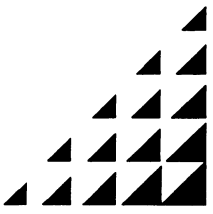

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1 Introduction

In any consideration of the transport and dispersal of radionuclides through saturated fractured and porous rock it is important to assess the possible effect of colloids. To date, this is poorly understood (although both laboratory and field data regarding colloid and groundwater chemistry is available), and there have been few attempts to incorporate such information into a dynamic colloid migration model able to quantify the impact of colloids upon radionuclide breakthrough.

The central objective of this report is to develop and use such a model in order to scope the effects of colloids upon radionuclide migration through the geosphere.

Radionuclides present in groundwater sorb strongly on to rock surfaces. Not all such surfaces are immobile though, and it is well known that radionuclides may become sorbed to colloidal particles present within the groundwater. Despite their small size, the colloids present a large surface area to the radionuclides, and volume for volume, may adsorb the solute species more efficiently than the surfaces of the surrounding rock mass. Once sorbed to colloids, the transportation characteristics of the radionuclides becomes altered radically to those of the colloids.

Within fractures, mobile colloids tend to stay centre stream where the flow rate is highest (as in hydrodynamic chromatography experiments), and are also subject to surface forces causing their motion relative to the fracture surfaces. For instance, colloids may have an opposite net charge to the radionuclide species sorbed to them, such as when a cationic metal becomes sorbed to an organic particle yet the net charge remains anionic. Hence the net retardation of the colloid-bound species is dependent upon the host colloid population, and is distinct from that of the solute species.

In Phase I of the SKI radionuclide-colloid modelling project a number of conceptual factors were identified, reviewed and formulated as a mathematical radionuclide-colloid transport model [1]. In Phase II this work was utilised as the basis for both modelling and calculations of colloid migration and the subsequent effect upon the transport and dispersal of radionuclides in fractured rock [2].

In this report we extend such calculations in order to test the sensitivity of some of the geosphere base-case calculations carried out for Project 90 [4] to the presence of mobile and immobile colloid material within the fracture space.

Prior to the model calculations it was necessary to develop a mathematical

technique capable of reducing the microscopic mathematical models of the processes affecting colloids in water-filled fractures, to the macroscopic parameters defining colloid dynamics over much larger scales. This work provided a firm theoretical basis for the subsequent model calculations, and allowed the derivation of dynamic parameters that were otherwise unavailable.

There is a large literature concerning the chemistry of colloids and complexes. This documents the analysis of naturally occurring colloids, groundwater chemistry, and batch experiments on radionuclide-colloid sorption [6] [7]. Use of such data in migration modelling, relating the parameters controlling colloid dispersal (within both fractured rock and porous media) to the underlying colloid science, appears long overdue.

2 The colloid transport model

The underlying model scenario considered previously in [2] is that of colloid dispersal within an idealised fracture. As discussed in [1], this must present the colloids with their best opportunity to migrate over *long* distances, at average flow rates 20-30% in excess of that of any solutes present. Since the real flow paths are irregular and tortuous, this would both perturb the assumed flow rate, and increase the rock surface area available for colloid adsorption.

The idealized fracture is also suggestive of dynamic colloid migration experiments that could be carried out utilizing capillary tubes, of suitable material in order to measure colloid dispersal and validate the modelling approach.

Rather than analyse fully three dimensional fractures, it is more relevant, and more tractable, to consider the dispersal of colloids in a single direction - the direction of the groundwater flow: particularly when calculations commensurate with geosphere reference cases are to be made, where such a simplification is standard.

Thus the model starts out by specifying those processes effective over small scales, affecting the motion of colloids within a three dimensional fracture (subject to diffusion, fluid advection, surface forces, and capture at the rock surfaces). This model is next averaged across the fracture, in order to derive and compute parameters effective at the macroscopic scales associated with the geosphere calculations. This process is a generalization of the argument used to derive Taylor dispersion coefficients for solutes [3]. It results in the calculation of an axial dispersal coefficient, an average flow rate, and an average capture rate for colloids moving along the aver-

aged, one dimensional , fracture. These parameters can subsequently be incorporated in colloid radionuclide geosphere models generalizing those employed in the solute geosphere calculations, such as CRYSTAL [4].

In the initial, three-dimensional model, the diffusivity, D, of a population of colloids is given as a function of their radius, a, by the Stokes-Einstein relation. The groundwater flow is assumed to be so slow that the Poiseuille approximation (slow flow) is valid. Colloids are subject to surface forces acting across fractures. Free colloids are also subject to drag forces opposing their motion relative to the groundwater.

The surface force term is the sum of various separate terms: the force due to electric double layers, and the van der Waals force (due to the interaction of molecules on the colloid and rock surfaces), for example. Other long or short range forces may be considered within the model approach. Indeed in view of the ongoing debate concerning surface forces, it seems wise to allow for alternative theories to be included. For example DLVO theory, based upon surface charges and molecular interactions, has been recently questioned [2].

Once colloids come into contact with the fracture surfaces, they are assumed to become captured there, and immobilized. In fact, the surface forces are localized near the fracture surfaces, whereas diffusion will dominate the cross-fracture dispersal at more centre stream positions. Since the rate of fluid flow is zero at the fracture surface, any colloid close to the rock, but not yet captured, migrates at a flow rate much less than those midstream, making the assumption of immediate immobility acceptable.

In [1] and [2] the fractured rock colloid migration model was analyzed, assuming that the groundwater was flowing through a representative planar fracture, of half aperture L, with average flow rate $\overline{u}$.

As the size of the colloids was varied, calculations were made for the effective colloid dispersivity, D^*, the average colloid flow rate, u^*, the colloid capture rate, s^*, as well as the mean distance travelled by each colloid [2].

If necessary, a distribution of colloids transported according to such parameters can be tracked [2]: the conclusion being that such individual colloids are highly unlikely ever to travel over distances greater than one metre, before becoming captured,

Natural colloids may migrate, become captured on rock faces, be released via hydrodynamic scouring, say, migrate further, and so on. The effect would be a constant supply of free colloids along the fracture, each migrating according to the processes described above.

Thus in considering the impact of colloids upon radionuclides, we shall assume that there is an ambient background population of such colloid material, constantly being released and captured along the fracture, providing an alternative means of radionuclide transport.

3 Colloid sizes

Measurements of colloid populations within natural groundwater are well documented within the literature, see [1] and the references therein. Of particular interest is the work at Grimsel [7], where the distribution of colloids in the groundwater is dominated by those with radii in the 15-50 nm range. There the host rock is granodiorite, whilst the colloids were composed of illite, biotite, muscovite, quartz, ca-silicate, iron hydroxide, organic material and bacteria. The inorganic colloids were assumed to result from the scouring of fracture infill material.

Colloids having hydrodynamic radii, a, in the range 10-1000 nm are considered for the purpose of the calculations in [2] and below. Moreover, the models are linear with respect to the colloid density functions, so the distributions of colloids of different sizes may be superimposed. Hence there is no loss of generality in assuming a population of colloids having uniform radius a, and allowing this to vary.

4 Radionuclide transport in the presence of colloids

Once the transport characteristics of the colloids have been established they can be utilised within the colloid-radionuclide migration model.

In the calculations which follow, we shall employ the conceptual and mathematical models developed in [1] and [2], and integrate this approach within the geosphere modelling carried out for Project 90 [4].

Firstly we describe the conceptual model for radionuclide transport: the full equations, and their development are given in [2].

In figure 1 we show the fractured rock scenario, into which the radionuclides will be released. Colloid material exists within the fracture space in both mobile and immobile forms, in a state of dynamic equilibrium.

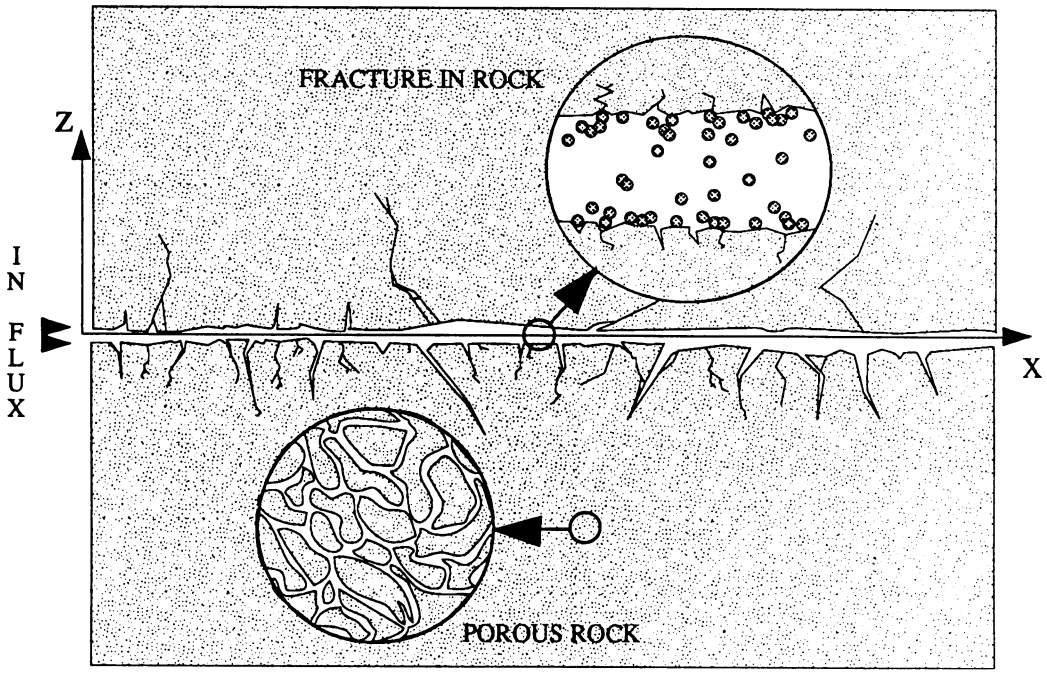


Figure 1: Colloids present within a single fracture, surrounded by porous saturated rock.

Radionuclides are present in one of the following ways:

- free, in solute form within the fracture;
- sorbed to free colloids;
- sorbed to stationary colloids;
- in solute within the water-filled pore space;
- sorbed to the rock mass, in equilibrium with the concentration within the pore space.

This is summarised schematically in figure 2.

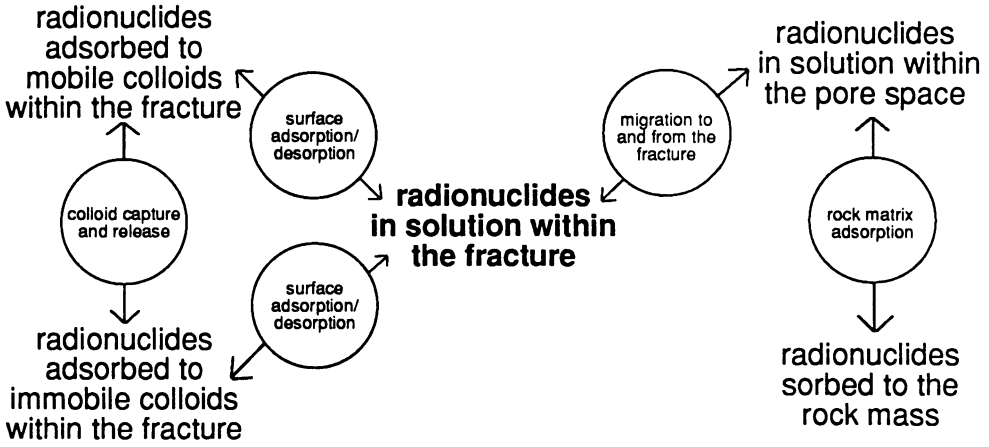


Figure 2: The partition of the radionuclide population, and exchange between the classes.

There are three major effects of radionuclide colloid interaction upon the transport and breakthrough of radionuclides.

Firstly, colloid bound radionuclides proceed at a faster flow rate (on average) than the solute species. In [2] and [3], this is shown to be around a 30% increase, for a variety of situations. Indeed, this is also seen in evolution rates of colloids through both packed columns and capillaries [1].

Secondly, the colloids may become immobile, thus also entrapping currently adsorbed radionuclides. The retardation of radionuclides due to colloid-rock sorption is dependent upon both the colloid radionuclide sorption behaviour as well as the colloid-rock/desorption rates. However, it is clear that the more colloidal material that becomes immobile, the stronger will be the effective retardation. For this reason natural colloids would be advantageous within porous media since they present a large surface area for adsorption of radionuclides, and yet are filtered out efficiently in such circumstances (as described by standard theory of filtration, see [1] for a further discussion).

In the radionuclide-colloid migration model of [2], this adsorption behaviour is represented by two partition coefficients k_1 and k_2. k_1 represents the ratio of the density of radionuclides sorbed to free colloidal material, to the density of the dissolved species. Similarly, k_2 represents the ratio of the density radionuclides sorbed to immobile colloid material, to the

density of the dissolved species.

In [2], formal expressions are derived for k_1 and k_2, assuming colloid numbers are small. There is considerable uncertainty regarding their likely values. Accordingly, in the calculations given below, they will each be varied over five orders of magnitude. The extreme cases covered are where less than 1% of radionuclides present within the fracture are bound to either free or immobile colloid material, and where over 98% of radionuclides are bound to either free or immobile colloid material.

At Grimsel [7], uranium analysis of samples showed that between 7.5 ± 2 and 25 ± 4 % of the total uranium recovered was found to be colloid-bound. This corresponds to the sum $k_1 + k_2$ taking values between 0.05 and 0.5. At the lower end of this scale we shall see that there is little change in breakthrough behaviour from the *no colloid* ($k_1 = k_2 = 0$) case; whereas for larger values of k_1 and k_2 ,breakthrough is enhanced or retarded.

Thirdly, the dispersion behaviour of colloids is distinct from that of solutes. Accordingly, the dispersion of free colloid-bound radionuclides must be then taken into account. On a small scale, the dispersion of colloids within a single fracture is analyzed via a generalization of Taylor dispersion theory [3]. Such dispersion is a result of the colloids diffusing or being advected (due to surface forces) across the flow profile of the groundwater. In [2], a number of calculations are made, whilst the effect of surface forces is varied. It is demonstrated that for colloids having radii less than around 5×10^{-4}mm (500nm), the effect of surface forces is highly localized at the rock face. As a consequence, the generalized Taylor dispersivity of such colloids is given by the approximation

$$\frac{L^2\overline{u}^2}{D}[2.665 \times 10^{-3}],$$

which was derived in [2] (and should be added on to the particle diffusivity term in order to represent the net dispersal along the length of the fracture). Here L and $\overline{u}$ are as before, while D is the colloid diffusivity. Substituting for D from the Stokes-Einstein relation, the dispersivity of the colloid population is

$$\text{colloid dispersivity} = aL^2\overline{u}^2[0.49] \qquad \text{mm}^2/\text{yr}$$

where a, L and $\overline{u}$ are measured in mm's and yr's.

By comparison, the Taylor dispersivity of a solute within an identical fracture is

$$\text{solute dispersivity} = L^2\overline{u}^2[2.42 \times 10^{-4}] \qquad \text{mm}^2/\text{yr}.$$

Here it is assumed that the solute diffusivity is 78.75 mm^2/yr so as make our calculations consistent with the geosphere reference cases, VG0, see [5], which we shall generalize below.

Notice that the ratio of these dispersivities is independent of the flux or fracture size:

$$\frac{\text{colloid fracture dispersivity}}{\text{solute fracture dispersivity}} \simeq a.2 \times 10^3$$

which is valid for $0 \ll a < 5 \times 10^{-4}$mm.

Thus the generalized Taylor dispersivity of colloids is always less than that of a solute within the same fracture. For a representative colloid of hydrodynamic radius 10^{-4}mm (100nm), it is 1/5 of the corresponding solute dispersivity.

In the geosphere reference case model calculations [4], described below, the single fracture incorporated is, in effect, a representation of a system of many such fractures and indeed a consequent network effect. Accordingly, solute dispersion is represented via a dispersion length of 50m over the length scale of 200m, rather than a single fracture dispersivity.

In order to generalize this model, so as to include the effect of colloids, a corresponding dispersion length must be estimated for the free colloid-bound radionuclides. This estimate is made as follows.

The assumption of the dispersion length for the solute relies on complete mixing at all fracture intersections, whereas, in fact, this takes place via diffusive mixing along the length of each fracture. That is, via the same process that yields the Taylor dispersion described above. As we have noted, such mixing occurs less for colloids than for solutes, and consequently the total dispersive effect of the fracture network is lessened for colloids. In the extreme case of no cross-fracture mixing, all mobile colloids leaving from a single point would travel along the same stream line, and exit the flow path no more dispersed than at the start. On the other hand, if colloids were dispersed within each fracture in an identical manner to solutes then the network dispersion lengths would be identical. Consequently, it is assumed that

$$\begin{bmatrix} \text{colloid} \\ \text{dispersion} \\ \text{length} \end{bmatrix} = \begin{bmatrix} \text{solute} \\ \text{dispersion} \\ \text{length} \end{bmatrix} \times \left[\frac{\text{colloid fracture dispersivity}}{\text{solute fracture dispersivity}} \right]$$

Accordingly, for colloids of radius $a = 10^{-4}$mm, and a solute dispersion length of 50m, an estimate of 10m is obtained for the free colloid dispersion

length to be employed within the 200m reference case calculations such as the example given below.

For the single fracture colloid migration calculations in [2], the total axial colloid dispersion rate is the sum of the particle diffusivity, proportional to a^{-1}, and the generalized Taylor dispersivity, proportional to a. In the geosphere calculations given in the next section the particle diffusivity is negligible when compared to the effective network dispersion constant (defined via the colloid dispersion length, above), and is consequently omitted.

5 Geosphere calculations

By employing the parameters derived controlling the migration and sorption of colloids, we shall make calculations for radionuclide transport assuming a background population of colloids and colloidal material within the fracture space.

In the absence of colloidal matter (or alternatively any radionuclide-colloid sorption), such calculations reduce to reference cases considered in the Project 90 base case calculations [4] [5]. Consequently, the addition of various populations of mobile and immobile colloids, with various radionuclide adsorption properties, is best regarded as a perturbation of a central case, such as those already covered in the geosphere models.

Consider the geosphere reference cases VG0, $K_d = 0.05,\ 0.1$, and $5.0\text{m}^3/\text{kg}$ given in [5], where a molar concentration of a non-decaying radionuclide is released into a representative fracture, of width 0.1mm and length 200m, surrounded by porous rock. The outflux is calculated at 200m resulting in a typical breakthrough curve. The parameters employed are discussed in [4] and listed belowin Table 1.

The generalization of these cases to include the effect of colloids may be made, once values have been set for the colloid dispersivities, flow rates and the partition coefficients k_1 and k_2, see Table 1.

Average groundwater fracture flow rate	$\bar{u}$	1.0 m/yr
Average free colloid flow rate	u^*	1.3 m/yr
Dispersion length for solute	d_{sol}	50 m
Dispersion length for free colloids	d^*	10 m
Dispersivity of solute	$D_{\text{sol}} = d_{\text{sol}}\bar{u}$	50 m^2/yr
Dispersivity of free colloids	$D^* = d^*u^*$	13 m^2/yr
Diffusivity of solute within the rock matrix	D^m	7.875E-4 m^2/yr
Retardation of solute within the rock matrix	R^m	set from K_d value
Fracture/rock matrix solute exchange coefficient	$\frac{(\text{area})\theta_m D^m}{\theta}$ see [4]	15.75E-5 m/yr
Partition constant for free colloid-bound radionuclides	k_1	.005-50
Partition constant for immobile colloid-bound radionuclides	k_2	.005-50
Decay rate	λ	0.0

Table 1: Colloid-radionuclide transport parameters employed in the extension of reference cases VG0.

Let c denote the dissolved concentration of radionuclides within the fracture, and let c^m denote the dissolved concentration of radionuclides within the surrounding porous rock matrix. Employing the notation used in the set of Project 90 reference case calculations [4], the model becomes:

$$(1+k_1+k_2)\frac{\partial c}{\partial t} = (D_{\text{sol}}+k_1D^*)\frac{\partial^2 c}{\partial x^2} - (\bar{u}+k_1u^*)\frac{\partial c}{\partial x} - (1+k_1+k_2)\lambda c + \frac{(\text{area})\theta_m D^m}{\theta}\frac{\partial c^m}{\partial z}|_{z=0},$$

$$0 < x < 200, \quad t > 0,$$

$$R^m\frac{\partial c^m}{\partial t} = D^m\frac{\partial^2 c^m}{\partial z^2} - R^m\lambda c^m,$$

$$0 < x < 200, \quad 0 < z < p, \quad t > 0;$$

together with the initial and boundary value conditions

$$c(x,0) = c^m(x,z,0) = 0,$$

$$\left[(\bar{u}+k_1u^*)c - (D_{\text{sol}}+k_1D^*)\frac{\partial c}{\partial x}\right]_{x=0} = \delta(t), \quad c(200,t) = 0.$$

As in the VG0 reference case calculations, we shall calculate the outflux at $x = 200$ via a technique base on the numerical inversion of the Laplace transform.

The breakthrough curves for the VG0 family of test cases (K_d= 0.005, 0.1, 5.0 m^3/kg, respectively) are depicted in Figures 3, 5 and 7. For each fixed value of k_2, breakthrough curves are plotted for k_1= 0.05, 0.5, 5.0, and 50.0: the higher values resulting in the sharper peaks. In each graph the dashed curve depicts the appropriate VG0 central reference cases. In figures 4, 6 and 8 the peak flux values and the peak flux times are mapped as functions of k_1 and k_2 (again for K_d= 0.005, 0.1, 5.0 m^3/kg, respectively). Notice that as k_2 increases the breakthrough curves become retarded (a fraction $k_2/(1 + k_1 + k_2)$ of all radionuclides within the fracture being sorbed to immobile colloid material); while as k_1 increases the breakthrough curves become advance and less disperse (a fraction $k_1/(1 + k_1 + k_2)$ of all radionuclides within the fracture being sorbed to mobile colloids).

Recall that the estimates obtained from the uranium analysis at Grimsel [7] suggest that the values for k_1 and k_2 lie between 0.05 and 0.5.

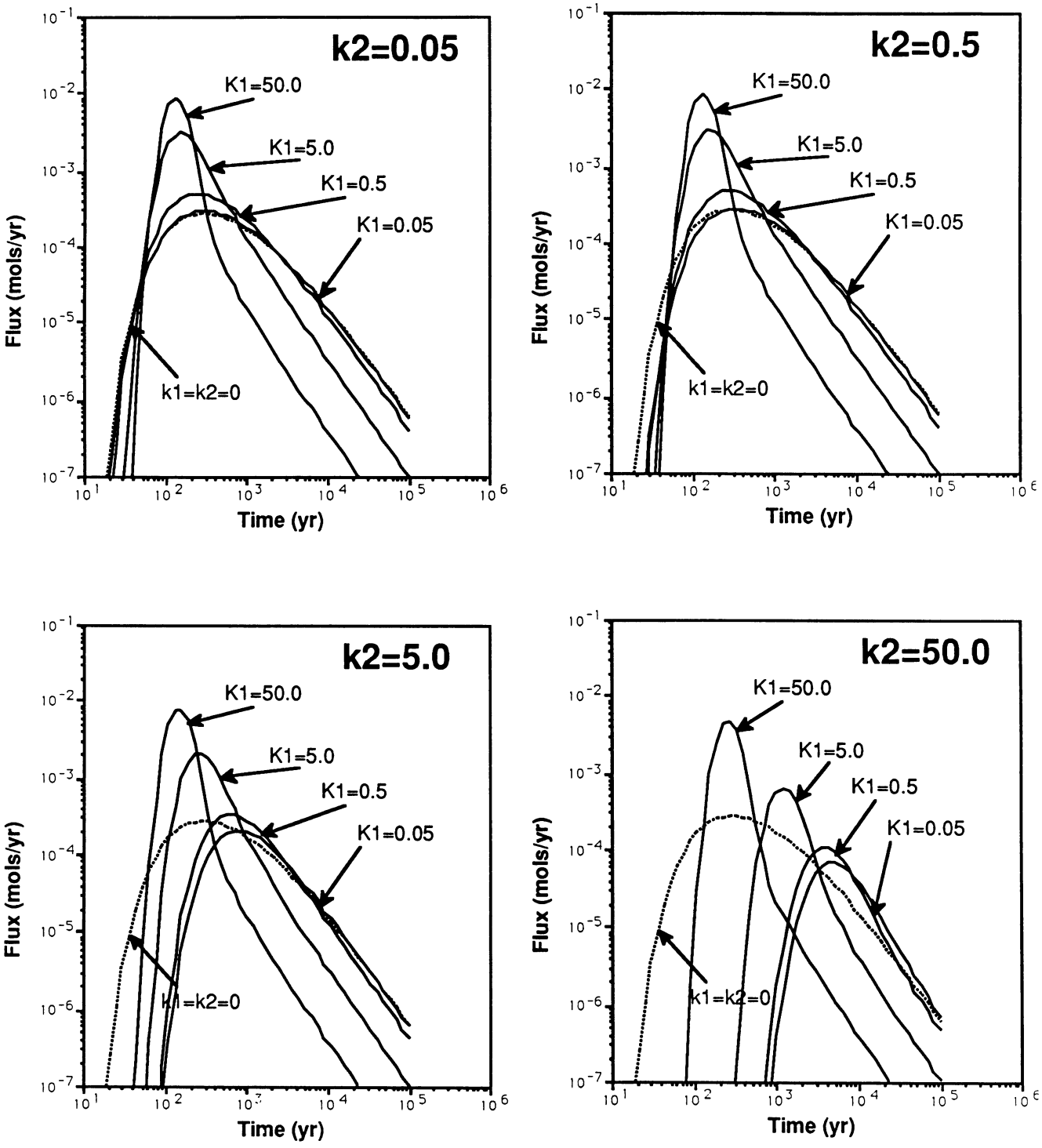
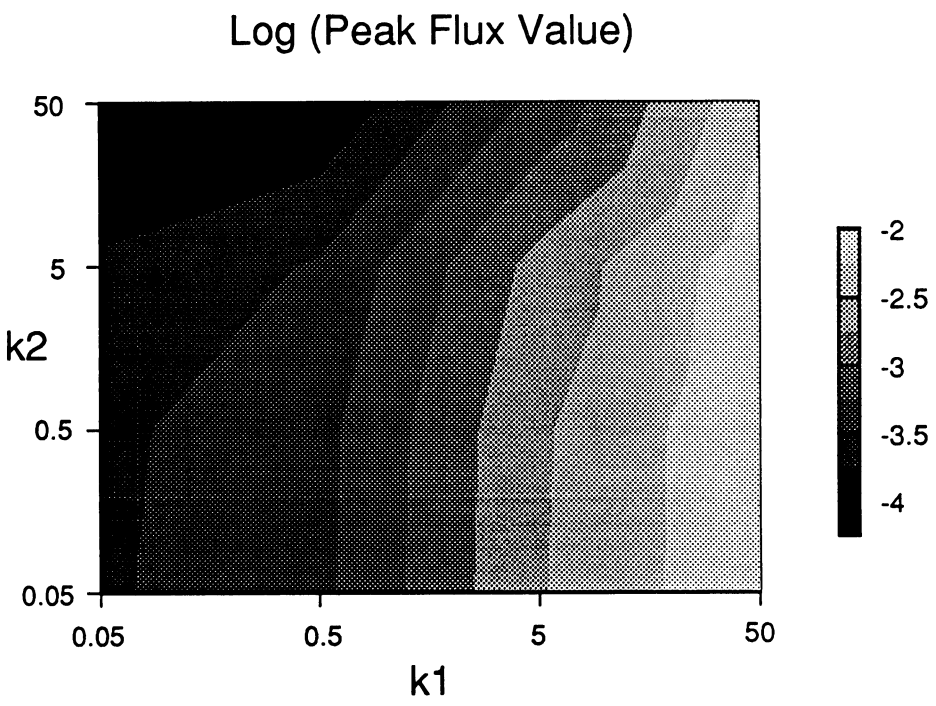


Figure 3: Breakthrough curves as k_1 and k_2 vary for base case calculation VG0, K_d=0.005 m^3/kg



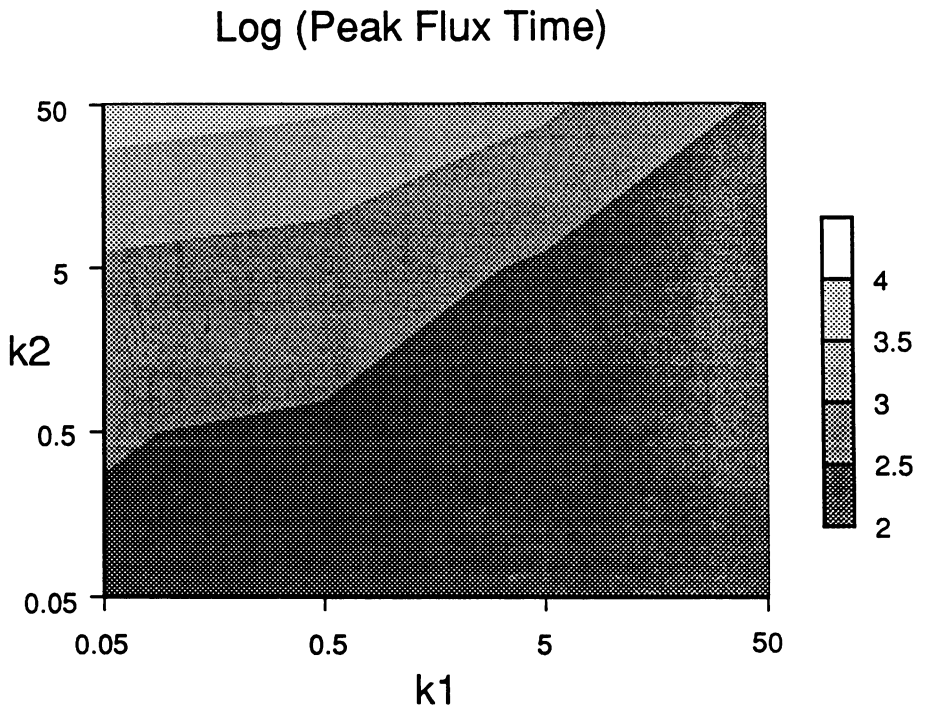


Figure 4: Log values of peak flux, and peak flux breakthrough time for the curves depicted in figure 1: base case VG0, K_d=0.005 m^3/kg

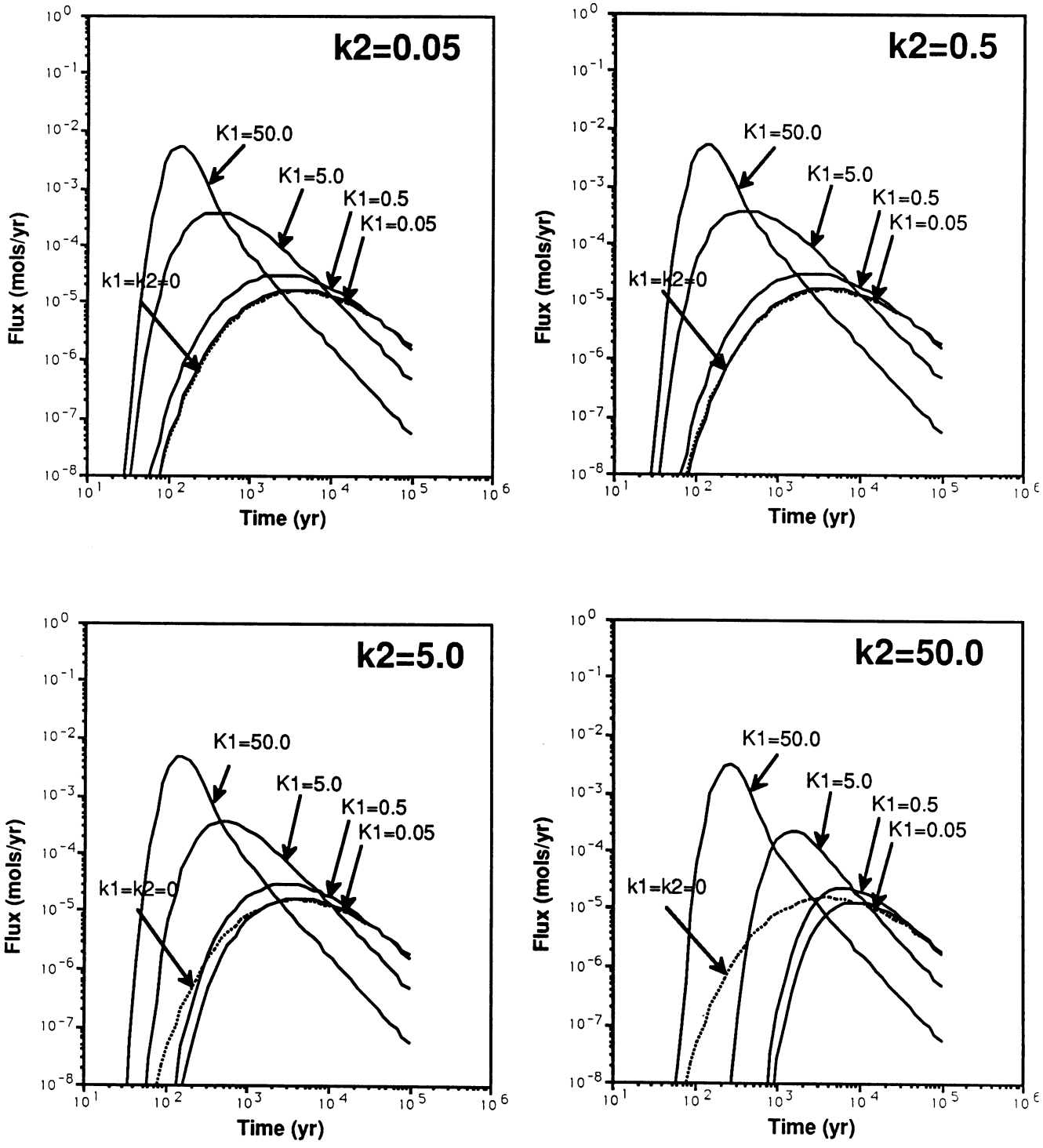


Figure 5: Breakthrough curves as k_1 and k_2 vary for base case calculation VG0, K_d=0.1 m^3/kg

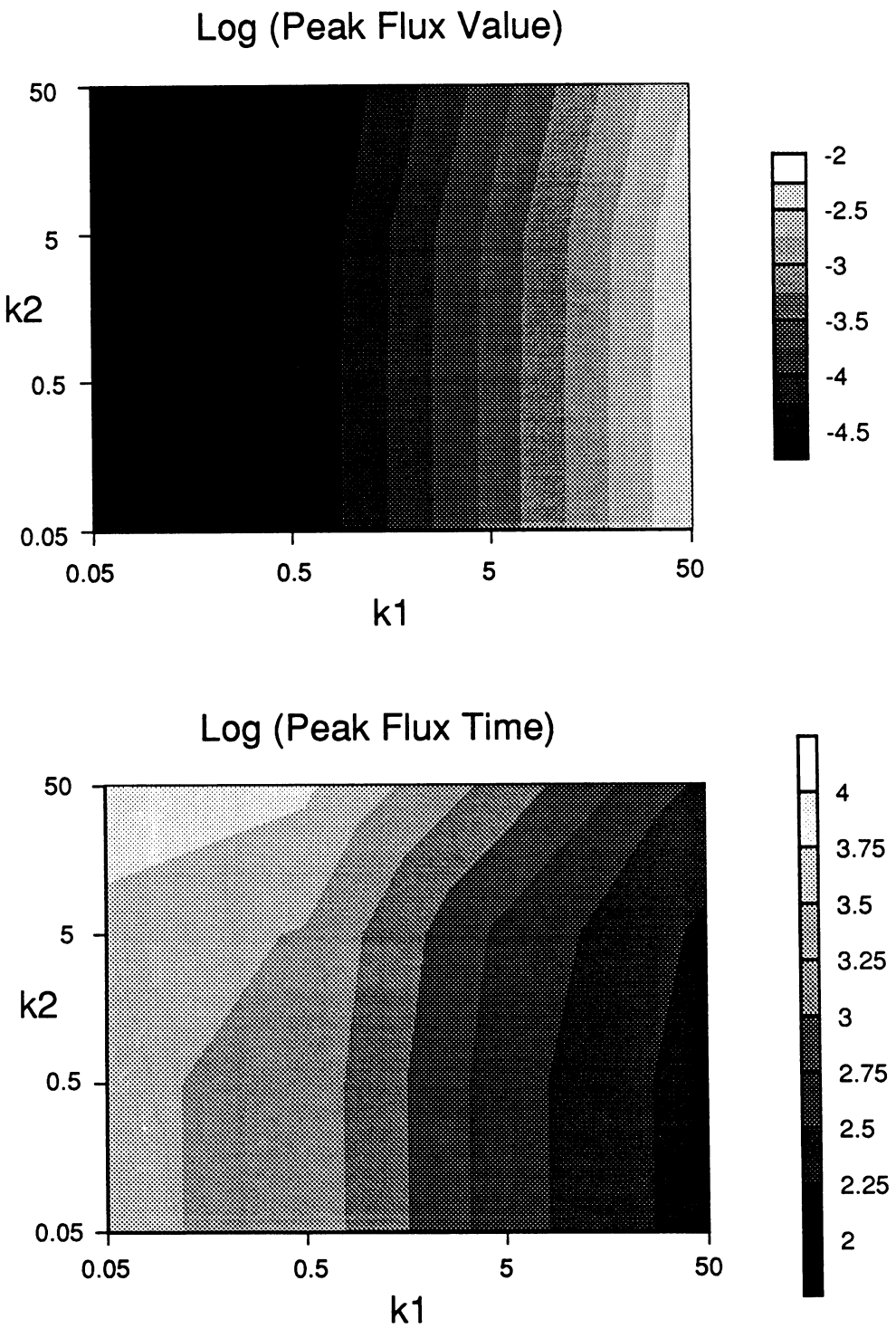


Figure 6: Log values of peak flux, and peak flux breakthrough time for the curves depicted in figure 3: base case VG0, K_d=0.1 m^3/kg

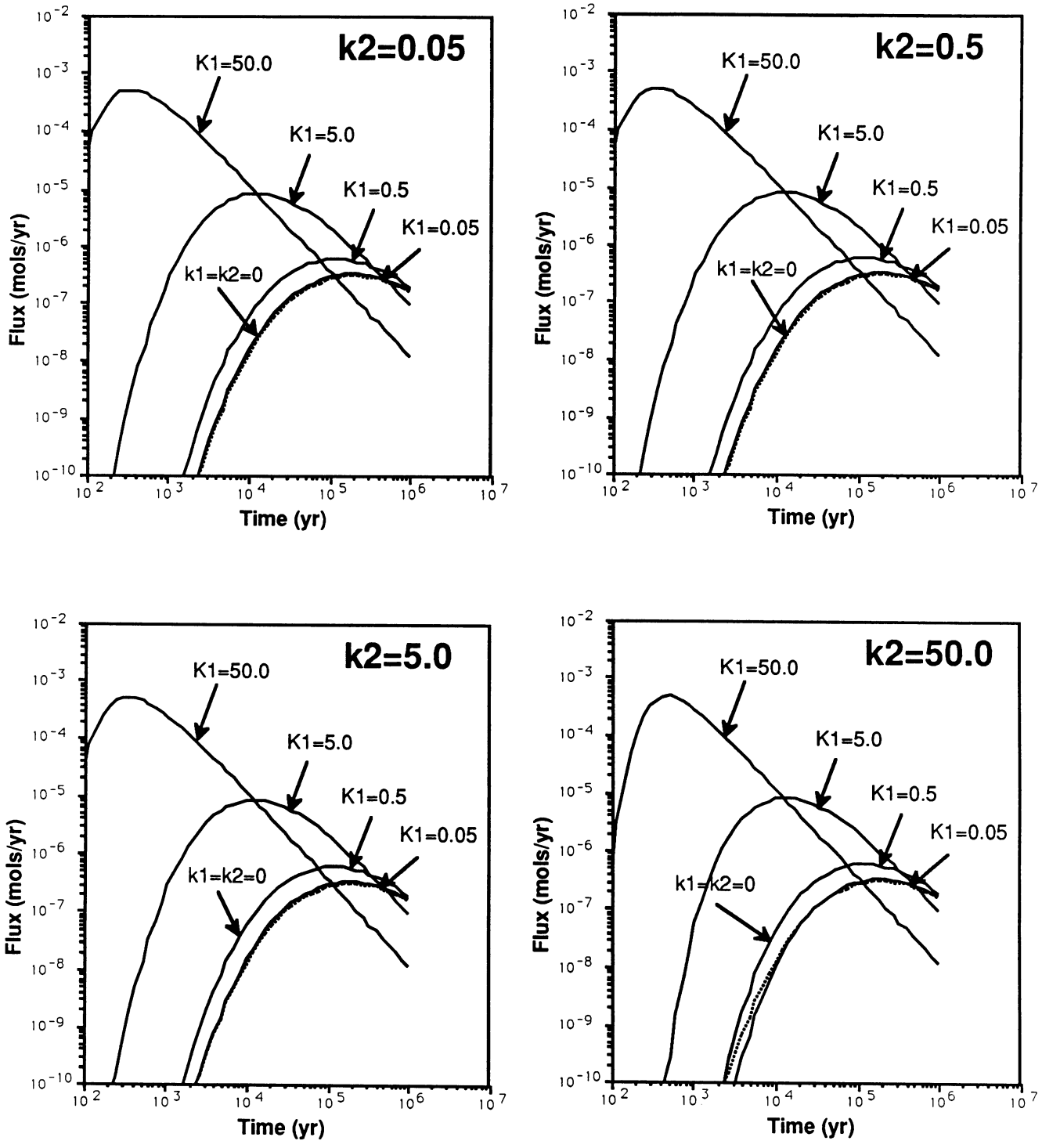


Figure 7: Breakthrough curves as k_1 and k_2 vary for base case calculation VG0, K_d=5 m^3/kg

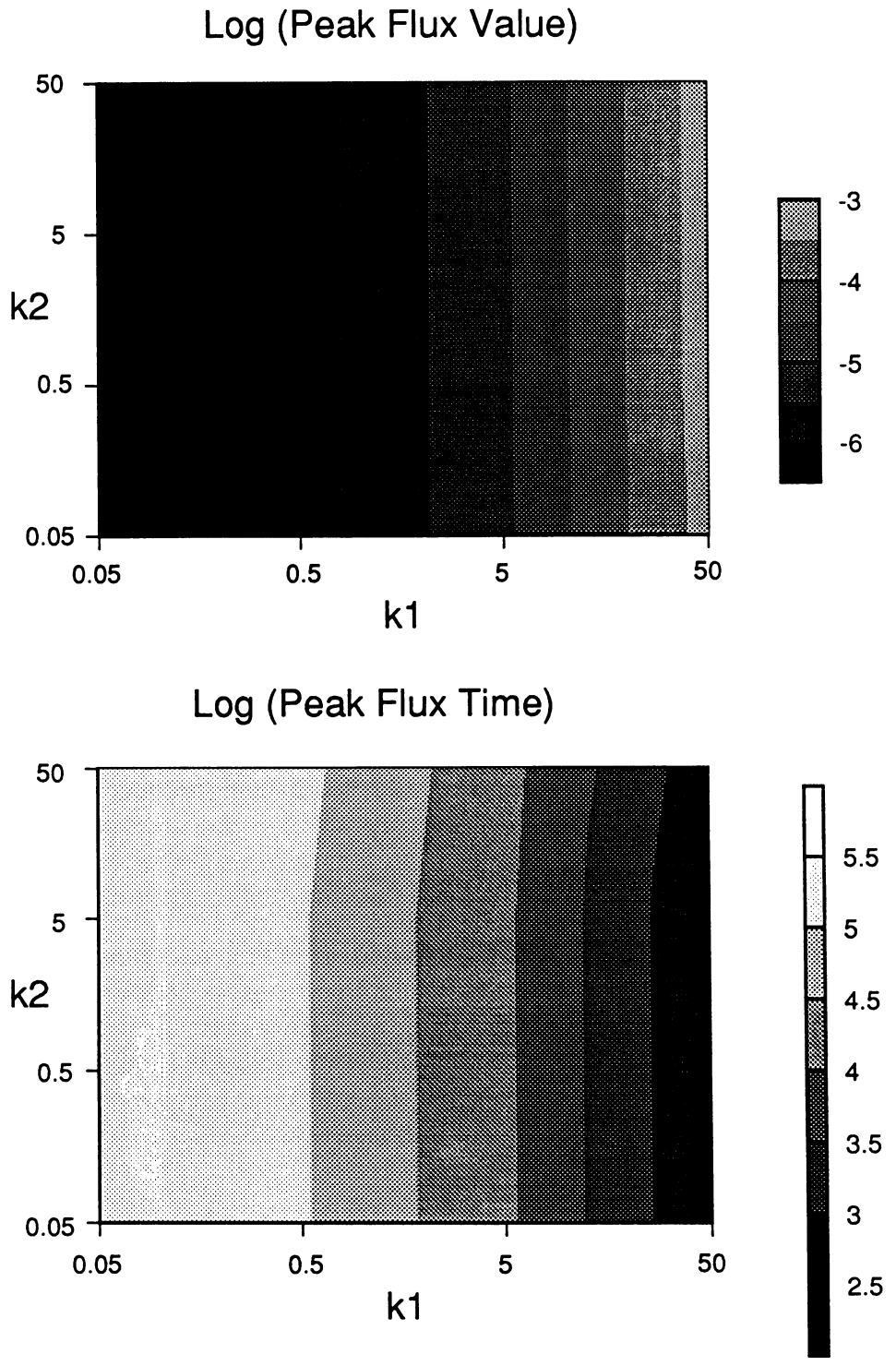


Figure 8: Log values of peak flux, and peak flux breakthrough time forthe curves depicted in figure 5: base case VG0, K_d=5 m^3/kg

6 In Conclusion

A central objective of this colloid-radionuclide modelling programme was to make calculations such as those made above for radionuclide dispersal in the presence of colloids, extending the cases calculated for the geosphere. Geosphere model data requirements included colloid dispersion rates, capture rates, and flow rates. Accordingly such data has been derived and its dependence upon colloid size, composition, fracture dimensions, and microscopic surface forces were analyzed [2]. The calculations made required a generalization of standard dispersion theory [3] so as to incorporate the effects of advection relative to the fluid flow and rock surface capture of colloids.

All analysis was based on theoretical considerations, presenting a unified approach to dispersal from the scale of individual colloids up to that of geosphere breakthrough problems. A major achievement was to bridge the gap between the standard continuum models of macroscopic transport and the considerations of colloid science, where colloids and complexes are subject to microscopic experimental analysis.

Predictions have also been made for the migration of individual colloids, relevant to the dispersal of *true* colloids [2].

In the radionuclide-colloid analysis it was shown that breakthrough curves could be both enhanced and retarded by the presence of colloids, according to the levels assumed for sorption to free and immobile colloid material. However, any enhancement is limited above by a 30% faster average breakthrough.

This modelling programme was focused first and foremost upon the dynamic behaviour of colloids and their impact on radionuclide dispersal, rather the chemistry of colloids and complexes. A number of predictions regarding colloid and radionuclide migration within fractured rock have been made which will become the subject of further experiment and analysis in future international radioactive waste programmes.

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