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Abstract

In the safety assessment of nuclear waste repositories, sorption of radionuclides on the surfaces of colloids may significantly modify transport behaviour where colloid concentration is sufficiently high. In the case of fractured geological media, colloids may be excluded from matrix pores, in which case radionuclides bound to them are not subject to the retarding effects of matrix diffusion and sorption onto matrix pore surfaces.

A transport model is presented describing colloid facilitated transport through fractured media with non–linear sorption. A simplified model, with linear sorption both on pore surfaces and colloids, is derived from the more general model. Such a model is desirable if it can be demonstrated to be conservative. However, even when the same sorption mechanism is known to operate for pore surfaces and colloids, it is unclear how the same linear model for sorption can be applied conservatively to both, since low sorption onto pore surfaces is conservative, while a high degree of sorption on colloids is also conservative.

The question of whether the use of the simplified model, with a linear sorption co-efficient, calculated for the highest concentration encountered along the flow path, is conservative for colloid facilitated transport is addressed and simple criteria are developed to predict when the presence of colloids will have a significant influence on transport. A series of simulations using the more general model is carried out, illustrating the general behavior to be expected and effects resulting from the non–linearity of sorption are described.

Zusammenfassung

In der Sicherheitsanalyse für Endlager für radioaktive Abfälle kann die Sorption von Radionukliden auf Kolloidoberflächen einen wichtigen Einfluss auf den Nuklidtransport haben, wenn die Kolloidkonzentration genügend hoch ist. In geklüfteten, geologischen Medien können Kolloide in den Matrixporen ausgeschlossen werden; in diesem Fall tragen Matrixdiffusion und -sorption nicht zur Verzögerung der an die Kolloide gebundenen Nuklide bei.

Es wird ein Modell vorgestellt, welches den kolloidgebundenen Nuklidtransport in geklüfteten Medien mit nicht-linearer Sorption beschreibt. Davon wird ein einfacheres Modell mit linearer Sorption auf den Porenoberflächen und Kolloiden abgeleitet. Ein solches Modell ist aber nur dann sinnvoll, wenn gezeigt werden kann, dass es konservativ ist. Wenn der gleiche Sorptionsmechanismus auf den Porenoberflächen und auch auf den Kolloiden wirkt, bleibt unklar, wie das Modell mit linearer Sorption in beiden Fällen konservativ angewendet werden kann, weil auf den Porenoberflächen eine geringe Sorption, auf den Kolloiden eine starke Sorption, konservativ ist.

Es wird auf die Frage eingegangen, ob die Anwendung des vereinfachten Modells, mit einem linearen Sorptionskoeffizienten, der aus der höchsten Konzentration entlang des Fliessweges berechnet wurde, für den durch Kolloide beschleunigten Nuklidtransport als konservativ betrachtet werden kann und es werden einfache Kriterien ausgearbeitet, um Prognosen zu machen, wann Kolloide für den Nuklidtransport einen entscheidenden Einfluss haben werden. Eine Reihe von Simluationen, durchgeführt mit dem allgemeineren Modell, belegen das grundsätzliche Verhalten, das man erwartet, und es werden Effekte diskutiert, die von der Nicht-Linearität der Sorption herrühren.

Résumé

Lors de l'évaluation de la sûreté de dépots finals pour déchets radioactifs, la sorption de radionuclides à la surface des colloïdes peut modifier de façon substancielle le comportement de leur transport lorsque la concentration des colloïdes est suffisament élevée. Dans le cas de milieux géologiques fracturés, on peut négliger la présence des colloïdes dans les pores de la matrice, auquel cas les radionulides qui leur sont attachés ne subissent pas l'effet retardateur de la diffusion matricielle ni celui de leur sorption à la surface des pores de la matrice.

On présente un modèle de transport décrivant une migration à travers un milieu fracturé, facilitée par des colloïdes avec sorption non–linéaire. Un modèle simplifié, avec sorption linéaire sur la surface des pores comme sur les colloïdes, est dérivé du modèle plus général. Un tel modèle est bienvenu si l'on peut démontrer qu'il décrit une situation surestimée. Cependant même si l'on sait que ce mécanisme même de sorption s'applique aux surfaces des pores et aux colloïdes, il n'est pas clair comment ce même modèle linéaire de sorption peut illustrer une scenario pessimiste en considérant une faible sorption sur la surface des pores et qu'un taux élevé de sorption sur les colloïdes.

On s'intéresse à la question de savoir si l'utilisation du modèle simplifié, avec sorption linéaire calculée pour la concentration maximale rencontrée le long de l'écoulement, décrit une situation surestimée lorsque l'on est en présence d'un transport facilité par les colloïdes. Des critères simples sont élaborés pour pronostiquer le moment où la présence de colloïdes aura une influence significative sur le transport. Une série de simulations utilisant le modèle plus général a été realisée, illustrant le comportement général auquel on peut s'attendre et on décrit finalement les effets résultants de la non–linéarité de la sorption.

Principal Notation

a_c ... colloid specific surface $[m^2\,kg^{-1}]$

a_p ... rock matrix specific surface $[m^2\,kg^{-1}]$

b ... fracture half–aperture $[m]$

$f(C)$ ... isotherm for sorption onto the surface of matrix pores $[mol\,kg^{-1}]$

$g(C)$ ... isotherm for sorption onto colloids $[mol\,m^{-3}]$

i ... hydraulic gradient $[m/m]$

k ... hydraulic conductivity $[ms^{-1}]$

v_f ... average water velocity $[m\,s^{-1}]$

v_c ... average colloid velocity $[m\,s^{-1}]$

A ... repository area $[m^2]$

B ... thickness of porous rock matrix $[m]$

C_f ... concentration of the nuclide in true solution within the fracture $[mol\,m^{-3}]$

C_c ... concentration of the nuclide (per unit volume of water) sorbed onto mobile colloids $[mol\,m^{-3}]$

C_p ... concentration of the nuclide in solution within matrix pore water $[mol\,m^{-3}]$

C_0 ... nuclide concentration at which distribution ratios $\Re_c$ and $\Re_p$ have been measured $[mol\,m^{-3}]$

C_1 ... maximum concentration at the point of release to the geosphere $[mol\,m^{-3}]$

D_f ... longitudinal dispersion coefficient for nuclides in solution $[m^2s^{-1}]$

D_c ... longitudinal dispersion coefficient for nuclides sorbed onto colloids $[m^2s^{-1}]$

D_p ... diffusion coefficient for the rock matrix $[m^2s^{-1}]$

G ... total length of fractures intersecting the repository area $[m]$

J ... rate of nuclide release from the repository $[mol\,m^{-2}s^{-1}]$

L ... length of the geosphere flow path $[m]$

K_a ... colloid surface sorption coefficient $[m]$

K_c ... sorption constant for colloids $[m^3kg^{-1}]$

K_d ... sorption constant for the rock matrix $[m^3kg^{-1}]$

K_f ... Freundlich isotherm constant $[mol^{1-N}m^{3N}kg^{-1}]$

K_l ... Langmuir isotherm constant $[m^3kg^{-1}]$

N ... Freundlich isotherm exponent $[-]$

Pe ... Peclet number $[-]$

$R_{eff}(C)$ ... effective retention factor $[-]$

$\Re_c$ ... distribution ratio for colloids $[m^3kg^{-1}]$ at measurement concentration C_0

$\Re_p$ ... distribution ratio for rock matrix $[m^3kg^{-1}]$ at measurement concentration C_0

$\Re_z$ ... derivative of the isotherm for sorption onto matrix pore surfaces $[m^3kg^{-1}]$, evaluated at the nuclide concentration $C = J/v_f$

S_c ... concentration of the nuclide (per unit area of fracture wall) sorbed onto immobile colloids $[mol\,m^{-2}]$

S_p ... concentration of the nuclide (per unit mass of rock matrix) on the matrix pore surfaces $[mol\,kg^{-1}]$

S_{max} ... saturation concentration for the Langmuir isotherm $[mol\,kg^{-1}]$

ϵ_p ... porosity of the rock matrix $[-]$

η ... geosphere barrier efficiency $[-]$

λ ... radioactive decay constant $[s^{-1}]$

$\lambda_{eff}(C)$ ... effective decay factor $[s^{-1}]$

ρ_c ... colloid density $[kg\,m^{-3}]$

ρ_p ... rock density $[kg\,m^{-3}]$

χ ... colloid concentration (volume of colloids per unit volume of water) $[-]$

1 Introduction

The modelling of radionuclide transport through the geosphere is an important component in the safety assessment of nuclear waste repositories in geological formations. In most hard rocks, the dominant transport mechanisms are likely to be advection and dispersion of solutes within groundwater flowing through conducting zones or fractures, with matrix diffusion into the adjacent rock. The retardation provided by matrix diffusion is enhanced if radionuclides sorb on pore surfaces within the matrix. However, where the concentration of colloids in the groundwater is sufficiently high, sorption of radionuclides on their surfaces can also significantly modify transport behaviour. Colloids may be excluded from matrix pores, in which case radionuclides bound to them will be retarded less effectively by matrix diffusion and sorption onto pore surfaces[1]. In Projekt Gewähr 1985, which aimed to demonstrate the feasibility of deep disposal of radioactive waste in Switzerland, the potential rôle of colloids in the transport of radionuclides was not assessed: "the effect of colloids on nuclide transport in the far–field ..... is not modelled ..... as no data are available for calculations"[3]. Since then, effort has been expended in the Swiss programme on the gathering of data on concentrations and physico–chemical properties of colloids in relevant groundwaters and it is intended to employ this data in *Kristallin I*, the current safety assessment for a high–level waste repository in the crystalline basement of northern Switzerland. The purpose of this paper is to present a model describing colloid facilitated transport through fractured media for use in such safety assessments. Current experimental data and the level of understanding of relevant processes are still limited and necessitate a highly simplistic approach. However, with an appropriate choice of conservative parameters, the model can be used to place an upper bound on the consequeces for radionuclides transport of the presence of colloids in fractured systems.

Several models for colloid transport in homogeneous porous media [4], [5], [6] and in fractures [1], [7], [8], [9], [10] have been described previously ([9] and [10] address the problem of so–called 'true' or 'intrinsic' colloids, generated from the radionuclides themselves by hydrolysis and precipitation). For models in which radionuclides sorb onto colloids naturally present in the groundwater, linear sorption of radionuclides is assumed, both on colloids and on pore surfaces. Experiments show, however, that a linear sorption isotherm is the exception rather than the rule and the considerable effects which the non–linearity of sorption can have on the transport of radionuclides in solution has been demonstrated in various modelling exercises [11], [12], [13]. The use of a simple transport model, with linear sorption both on pore surfaces and on colloids, is desirable *if it can be demonstrated to be*

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[1]The mean colloid velocity can also be larger than the mean water velocity, although this is a relatively small effect [1]. The phenomenon is more pronounced for large particles and is employed in hydrodynamic chromatography [2]

conservative, firstly because the lack of comprehensive sorption data prohibits extensive use of more complex isotherms and secondly because the resulting system of linear transport equations is straightforward to solve in comparison with those arising from non–linear sorption. For transport of radionuclides in solution only, in cases where the empirical sorption isotherm is non–linear, *conservative* use of a model based on linear sorption requires a sorption coefficient corresponding to the weakest sorption and therefore the highest concentration encountered along the flow path: generally the concentration at the point of release to the geosphere at the time of highest release flux. For colloid facilitated transport, even if the same sorption mechanism is known to operate on pore surfaces and colloids, it is unclear how the same linear model for sorption can be applied conservatively to both: weak sorption onto pore surfaces, corresponding to high concentrations in solution, is conservative, while strong sorption on colloids, corresponding to low concentrations in solution, is also conservative provided that colloids migrate over long distances. A further aim of the present paper is to clarify this point.

The starting point is to develop a general model for colloid facilitated transport, in which sorption on pore surfaces and on colloids is described in terms of independent non–linear isotherms. A simplified transport model is then described, derived from the more general model, for the special case of linear–sorption. Where sorption is known to be non–linear, sorption coefficients for the simplified model are calculated from the empirical sorption isotherms at the highest concentration encountered along the flow path. The conditions under which the simplified model is likely to give conservative results are then determined. Criteria are developed to predict when the presence of colloids will have a significant influence on transport and the additional influence on non–linear sorption is assessed.

2 Modelling Assumptions

The model presented here generalises the dual–porosity model for solute transport through fractured rock solved by code RANCHMD, which is discussed in detail in [14]. This model was taken as a starting point for reasons of compatibility with previous Swiss safety assessments [3] and because it has been successfully applied to a number of test cases at both laboratory [15], [16], [17] and field scale [18], [19].

As in the model for solute transport, different zones within the rock are distinguished :

- water–conducting zones (fractures) in which transport of radionuclides, both

dissolved and sorbed on colloids, is governed by advection and dispersion. Colloids may become immobilized by attachment to the fracture walls or become mobile again through scouring.

- porous matrix surrounding each fracture. Radionuclides in solution are transported through the pores by diffusion and may sorb onto their surfaces. Colloids are assumed to be excluded from the matrix pores due to their size and, possibly, charge repulsion. Since matrix diffusion is a mechanism for retardation, this is a conservative assumption.

Further assumptions of the model are itemised below :

1. the same Peclet number is applied to nuclides in solution and those sorbed onto mobile colloids. This assumption is justifiable for a model which is applied to fracture networks, where dispersion is dominated by the differing transport times along different paths through the network. Dispersion is then likely to be a function of the geometry of the network, and independent of the smaller–scale mechanisms governing dispersion in individual fractures. A model for the dispersion of colloids within an individual, parallel–walled fracture has given in [1].

2. instantaneous, reversible sorption equilibrium of radionuclides is established. The effect of slow sorption kinetics for colloids was modelled in [8]. However, current experimental data is insufficient to provide the necessary input for such a model.

3. an equilibrium exists between the number of mobile colloids moving with the groundwater and immobile colloids attached to the walls of the fracture, giving a colloid concentration which is constant in space and time (i.e. no net colloid filtration occurs). This assumption is made due to the inadequacy of the DLVO (*Derjaguin, Landau, Verwey, Oberbeek*) theory in describing attachment of colloids [20] and the lack of an accompanying model for colloid generation.

4. nuclides do not distinguish between mobile and immobile colloids in their sorption behaviour (although in reality there may be significant changes in the surface properties of colloids when they become attached to the solid surface of a fracture), so that the sorption behaviour of both may be described by the same isotherm.

5. colloids are neither created nor destroyed in the system and the chemistry of colloids and groundwater is constant along the flow path. A constant colloid surface chemistry is also implicitly assumed in point 3. This requires that

migrating radionuclides are at trace concentrations; in the groundwater of the crystalline basement of northern Switzerland, the concentrations arising from the calculated releases of radionuclides from a repository are much smaller than those of the stable isotopes.

3 General Colloid Transport Model

3.1 Transport Equations

The mathematical description of colloid–facilitated radionuclide transport is based on a mass balance, carried out over a representative elementary volume for a single fracture. A Cartesian coordinate system (x, z) is employed; the z–axis follows the direction of water flow and the x–axis follows the direction of matrix diffusion. $x = 0$ is the line of symmetry along the centre of the fracture, with the origin of the coordinate system at the upstream end. Within the fracture[2],

$$\frac{\partial}{\partial t}\left[(C_f + C_c) + \frac{S_c}{b}\right] = D_f\frac{\partial^2 C_f}{\partial z^2} + D_c\frac{\partial^2 C_c}{\partial z^2} - v_f\frac{\partial C_f}{\partial z} - v_c\frac{\partial C_c}{\partial z} + \frac{1}{b}\epsilon_p D_p\frac{\partial C_p}{\partial x}\bigg|_{x=b} -$$
$$\lambda\left[(C_f + C_c) + \frac{S_c}{b}\right]. \tag{1}$$

Within the porous matrix,

$$\frac{\partial}{\partial t}\left[\epsilon_p C_p + (1 - \epsilon_p)\rho_p S_p)\right] = \epsilon_p D_p\frac{\partial^2 C_p}{\partial x^2} - \lambda\left[\epsilon_p C_p + (1 - \epsilon_p)\rho_p S_p)\right] \; ; \; |x| \geq b \tag{2}$$

The notation, which is based on that in [13], is defined at the start of this document.

Since the Peclet number is the same for nuclides in solution and those sorbed onto colloids,

$$\frac{D_f}{D_c} = \frac{v_f}{v_c} \tag{3}$$

A fixed ratio $K_a\,[m]$ is assumed between the concentration of mobile colloids (those moving with average velocity v_c in the groundwater) and that of immobile colloids (those attached to the walls of the fracture). Since it is further assumed that nuclides do not distinguish between mobile and immobile colloids in their sorption

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[2]Sorption of radionuclides directly on the walls of the fracture is not modelled in this formulation. However, radionuclides sorb on the immobile colloids which coat the fracture walls.

behaviour[3]:

$$S_c = K_a C_c \tag{4}$$

Assuming instantaneous sorption equilibrium, the following isotherms are introduced for nuclide sorption onto colloids and matrix pore surfaces

$$C_c = g(C_f) \tag{5}$$

$$S_p = f(C_p) \tag{6}$$

The functions $g(C)$ and $f(C)$ may be independent if the composition of colloids and rock matrix is different. Furthermore, the specific surfaces of colloids are in general larger than those of the rock matrix (see section 3.3.2).

Substituting eq.3, eq.4 and eq.5 in eq.1 and rearranging,

$$\frac{\partial C_f}{\partial t} = \frac{1}{R_f(C_f)} \left\{ D_f \left[T(C_f) \frac{\partial^2 C_f}{\partial z^2} + U(C_f) \left(\frac{\partial C_f}{\partial z} \right)^2 \right] - v_f T(C_f) \frac{\partial C_f}{\partial z} \right.$$
$$\left. + \frac{\epsilon_p D_p}{b} \left. \frac{\partial C_p}{\partial x} \right|_{x=b} - \lambda C_f \tilde{R}_f(C_f) \right\} \tag{7}$$

Similarly, substituting eq.6 in eq.2 and rearranging,

$$\frac{\partial C_p}{\partial t} = \frac{1}{R_p(C_p)} \left[D_p \frac{\partial^2 C_p}{\partial x^2} - \lambda \tilde{R}_p(C_p) C_p \right] \; ; \; |x| \geq b \tag{8}$$

where the following abbreviations for the six concentration dependent functions $R_f(C_f)$, $\tilde{R}_f(C_f)$, $T(C_f)$, $U(C_f)$, $R_p(C_p)$ and $\tilde{R}_p(C_p)$ have been introduced

$$R_f(C_f) = 1 + \frac{dg(C_f)}{dC_f} \left(1 + \frac{K_a}{b} \right) \tag{9}$$

$$\tilde{R}_f(C_f) = 1 + \frac{g(C_f)}{C_f} \left(1 + \frac{K_a}{b} \right) \tag{10}$$

$$T(C_f) = 1 + \frac{v_c}{v_f} \frac{dg(C_f)}{dC_f} \tag{11}$$

$$U(C_f) = \frac{v_c}{v_f} \frac{d^2 g(C_f)}{dC_f^2} \tag{12}$$

$$R_p(C_p) = 1 + \frac{1 - \epsilon_p}{\epsilon_p} \rho_p \frac{df(C_p)}{dC_p} \tag{13}$$

$$\tilde{R}_p(C_p) = 1 + \frac{1 - \epsilon_p}{\epsilon_p} \rho_p \frac{f(C_p)}{C_p} \tag{14}$$

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[3]If immobile colloids are present as aggregates or multiple layers, then their effective surface area, and hence their ability to sorb nuclides, may be reduced. This possible effect is not modelled. In [10], in which the transport of colloidal Uranium is considered, a Langmuir–like isotherm is proposed for the colloid–wall interaction. Here, a simple, linear relationship quantified by K_a is adopted.

Eq.7 and eq.8 are similar form to the corresponding equations for solute transport in a dual–porosity medium with non–linear sorption (eq.2.7 and eq.2.9 in [13]), with $R_f(C_f)$ and $\tilde{R}_f(C_f)$ redefined, v_f and D multiplied by the function $T(C_f)$ and an additional term $U(C_f)(\partial C_f/\partial z)^2$ introduced.

3.2 Effective Surface Sorption Approximation

When diffusion within a porous matrix of limited thickness B $[m]$ is sufficiently fast [14], the nuclide concentration in the connected pore spaces of the rock matrix can be considered to adjust "instantaneously" to the concentration within the fracture, in which case

$$C = C_p = C_f. \tag{15}$$

The problem then reduces to one dimension in space, with matrix diffusion incorporated as an *effective surface sorption*. Repeating the mass balance for a representative elementary volume, eq.7 and eq.8 are replaced by the single equation

$$\frac{\partial C}{\partial t} = \frac{1}{R_{eff}(C)} \left\{ D_f \left[\frac{\partial^2 C}{\partial z^2} + \frac{U(C)}{T(C)} \left(\frac{\partial C}{\partial z} \right)^2 \right] - v_f \frac{\partial C}{\partial z} \right\} - \lambda_{eff} C \tag{16}$$

In eq.16 the combined effect of matrix diffusion and sorption onto matrix pore surfaces and colloids is described by an *effective retention factor* $R_{eff}(C)$ $[-]$, given by

$$R_{eff}(C) \equiv \frac{R_f(C)}{T(C)} = \frac{1 + \epsilon_p \frac{B}{b} + \frac{dg(C)}{dC} \left(1 + \frac{K_a}{b} \right) + \rho \frac{df(C)}{dC}(1 - \epsilon_p)\frac{B}{b}}{1 + \frac{v_c}{v_f} \frac{dg(C)}{dC}} \tag{17}$$

Radioactive decay is described by an *effective decay factor* $\lambda_{eff}(C)$ $[s^{-1}]$, given by

$$\frac{\lambda_{eff}(C)}{\lambda} \equiv \frac{\tilde{R}_f(C)}{R_f(C)} = \frac{1 + \epsilon_p \frac{B}{b} + \frac{g(C)}{C} \left(1 + \frac{K_a}{b} \right) + \rho \frac{f(C)}{C}(1 - \epsilon_p)\frac{B}{b}}{1 + \epsilon_p \frac{B}{b} + \frac{dg(C)}{dC} \left(1 + \frac{K_a}{b} \right) + \rho \frac{df(C)}{dC}(1 - \epsilon_p)\frac{B}{b}} \tag{18}$$

3.3 Sorption Isotherms

3.3.1 Linear Sorption

If sorption onto colloids and onto the surfaces of matrix pores is described by the linear isotherms:

$$g(C_f) = \rho_c \chi K_c C_f \tag{19}$$

$$f(C_p) = K_d C_p \tag{20}$$

where $K_d\,[m^3kg^{-1}]$ and $K_c\,[m^3kg^{-1}]$ are sorption constants for the matrix and colloids respectively, $\rho_c\,[kg\,m^{-3}]$ is the density of the colloid material and $\chi\,[-]$ is the colloid concentration (volume of colloids per unit volume of water), eq.9 to eq.14 become

$$R_f = \tilde{R}_f = 1 + \rho_c\chi K_c\left(1 + \frac{K_a}{b}\right) \tag{21}$$

$$T = 1 + \frac{v_c}{v_f}\rho_c\chi K_c \tag{22}$$

$$U = 0 \tag{23}$$

$$R_p = \tilde{R}_p = 1 + \frac{1-\epsilon_p}{\epsilon_p}\rho_p K_d \tag{24}$$

The model then reduces to the dual–porosity model for solute transport with linear sorption [14], with modified water velocity, longitudinal dispersion coefficient and retention factor for sorption on fracture surfaces redefined as follows[4]

$$\text{water velocity} \quad : \quad v_f\left(1 + \frac{v_c}{v_f}\rho_c\chi K_c\right) \tag{25}$$

$$\text{dispersion coefficient} \quad : \quad D_f\left(1 + \frac{v_c}{v_f}\rho_c\chi K_c\right) \tag{26}$$

$$\text{retention factor} \quad : \quad 1 + \rho_c\chi K_c\left(1 + \frac{K_a}{b}\right)$$

The retention factor for diffusion in the porous matrix remains unaltered. For linear sorption, the transport equations eq.7 and eq.8 may thus be solved using the solute transport code RANCHMD.

Where the effective surface sorption approximation is valid, eq.17 and eq.18 become

$$R_{eff} = \frac{1 + \epsilon_p\frac{B}{b} + \rho_c\chi K_c\left(1 + \frac{K_a}{b}\right) + \rho_p K_d(1 - \epsilon_p)\frac{B}{b}}{1 + \frac{v_c}{v_f}\rho_c\chi K_c} \tag{27}$$

$$\frac{\lambda_{eff}}{\lambda} = 1 \tag{28}$$

3.3.2 Non–Linear Sorption

It is considered unlikely that sufficient experimental data will be available in the near–future to define independent non–linear isotherms for colloids and matrix.

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[4]Similar expressions appear as eq.31 and eq.32 in [8]. In [8], the sorption constant K_c includes sorption on immobile as well as mobile colloids and is equal to $\rho_c\chi K_c(1 + K_a/b)$ in the present report.

Some sorption isotherms are available for intact rock [21], [22] and some distribution ratios at specific nuclide concentrations are available for colloids [23]. However, for the special case where the composition of both colloids and matrix can be assumed the same[5], then the desities of rock matrix and colloids may be equated

$$\rho_p = \rho_c = \rho \tag{29}$$

as may the quantities sorbed per unit surface area of rock matrix pores and colloids at a concentration C

$$\frac{1}{a_p} f(C) = \frac{1}{a_c} \frac{g(C)}{\rho\chi} \tag{30}$$

where $a_p \ [m^2 \ kg^{-1}]$ and $a_c \ [m^2 \ kg^{-1}]$ are the specific surfaces (area of sorbing surface per unit mass of solid material) of the matrix pores and colloids respectively. In eq.30, the sorption per unit area of matrix pore surfaces and colloid surfaces is equated. The ratio of the specific surfaces of colloids and rock matrix can be determined from sorption data. If $\Re_c \ [m^3 kg^{-1}]$ and $\Re_p \ [m^3 kg^{-1}]$ are the distribution ratio for colloids and matrix for which measurements have been made at a specific concentration C_0, then

$$g(C_0) = \rho\chi\Re_c C_0 \tag{31}$$

$$f(C_0) = \Re_p C_0 \tag{32}$$

From eq.30, eq.31 and eq.32, the ratio of the specific surfaces of colloids and rock matrix is given by

$$\frac{a_c}{a_p} = \frac{\Re_c}{\Re_p} \tag{33}$$

and

$$g(C) = \rho\chi\frac{\Re_c}{\Re_p}f(C) \tag{34}$$

The isotherm $g(C_f)$ describing sorption on colloids may then be eliminated from eq.11 and eq.12 and, where the effective surface sorption approximation is valid, from eq.17 and eq.18:

$$T(C) = 1 + \rho\chi\frac{\Re_c}{\Re_p}\frac{v_c}{v_f}\frac{df(C)}{dC} \tag{35}$$

$$U(C) = \rho\chi\frac{\Re_c}{\Re_p}\frac{v_c}{v_f}\frac{d^2f(C)}{dC^2} \tag{36}$$

$$R_{eff}(C) = \frac{1 + \epsilon_p\frac{B}{b} + \rho\frac{df(C)}{dC}\left[\chi\frac{\Re_c}{\Re_p}\left(1 + \frac{K_a}{b}\right) + (1 - \epsilon_p)\frac{B}{b}\right]}{1 + \rho\chi\frac{\Re_c}{\Re_p}\frac{v_c}{v_f}\frac{df(C)}{dC}} \tag{37}$$

$$\frac{\lambda_{eff}(C)}{\lambda} = \frac{1 + \epsilon_p\frac{B}{b} + \rho\frac{f(C)}{C}\left[\chi\frac{\Re_c}{\Re_p}\left(1 + \frac{K_a}{b}\right) + (1 - \epsilon_p)\frac{B}{b}\right]}{1 + \epsilon_p\frac{B}{b} + \rho\frac{df(C)}{dC}\left[\chi\frac{\Re_c}{\Re_p}\left(1 + \frac{K_a}{b}\right) + (1 - \epsilon_p)\frac{B}{b}\right]} \tag{38}$$

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[5]For the crystalline basement of northern Switzerland, the main components of the colloidal phase are clay (illite) and silica. The rock matrix is more complex, additionally containing a variety of clay minearals, calcite and iron hydroxide[23].

Two specific forms for the isotherm $f(C)$ are :

The Freundlich Isotherm

$$f(C) = K_f C^N \; ; \; N > 0 \tag{39}$$

The Langmuir Isotherm

$$f(C) = \frac{S_{max} C}{S_{max}/K_l + C} \tag{40}$$

$K_f \, [mol^{1-N} m^{3N} kg^{-1}]$ and $N \, [-]$ are empirical constants for the Freundlich isotherm and
$K_l \, [m^3 kg^{-1}]$ and $S_{max} \, [mol \, kg^{-1}]$ are empirical constants for the Langmuir isotherm. The exponent of the Freundlich isotherm $N \leq 1$ for almost all cases of interest and this is assumed in the following analysis. At low concentration $(C \ll S_{max}/K_l)$, the Langmuir isotherm has a linear behaviour and, at high concentration, $f(C)$ becomes constant with a value S_{max}, the saturation concentration.

A code has been written to solve the one–dimensional non–linear transport equation for cases where the effective surface sorption approximation is valid: eq.16 with $T(C)$, $U(C)$, $R_{eff}(C)$ and $\lambda_{eff}(C)$ given by eq.35 to eq.38 and isotherms given by eq.20, eq.39 and eq.40. The code is based around the routine MOLCH in the MATH/LIBRARY of IMSL, Inc. For the case of linear sorption, comparison has been made with results from code RANCHMD: no difference was found between the results from the two codes. Some results from this code are presented in section 6.

4 Simplified Transport Model

The use of a transport model with nuclide sorption approximated by linear isotherms both for pore surfaces and for colloids is generally unavoidable due to the lack of comprehensive sorption data, which prohibits extensive use of more complex isotherms in the transport equations, eq.7 and eq.8. The resulting system of linear transport equations is relatively straightforward to solve; the existing transport code RANCHMD can be used with redefined parameters. However, as sorption of some nuclides is known to be non–linear, the conservatism of such an approach must be demonstrated.

In this section, a simplified transport model is considered in which the composition of matrix and colloids is assumed the same and coefficients of the transport

equations are those for linear sorption, given by eq.21 to eq.24, with

$$K_c \quad = \quad \frac{\Re_c}{\Re_p} \left. \frac{df(C)}{dC} \right|_{C=C_1} \tag{41}$$

$$K_d \quad = \quad \left. \frac{df(C)}{dC} \right|_{C=C_1} \tag{42}$$

$C_1 \; [mol \; m^{-3}]$ is the maximum concentration at the point of release to the geosphere. This choice of sorption constants for the simplified model minimises sorption for both Langmuir and Freundlich isotherms (with $N \le 1$). Where the effective surface sorption approximation applies, R_{eff} and λ_{eff} are given by eq.27 and eq.28.

In the following discussion of the conservatism of the simplified model, it is assumed that the effective surface sorption approximation applies. In this case, the transport equation incorporating non–linear sorption is eq.16, with $R_{eff}(C)$, $\lambda_{eff}(C)$, $T(C)$ and $U(C)$ given by eq.35 to eq.38.

4.1 Effective Retention Factor

R_{eff} in the simplified transport model, given by eq.27, is equal to $R_{eff}(C_1)$, given by eq.37, in the more general model. $R_{eff}(C)$ is differentiated in order to determine the conditions under which a conservative choice of C_1 will be the *highest* value along the flow path : the maximum concentration at the point of release to the geosphere.

$$\frac{dR_{eff}}{dC} = \rho\chi\frac{\Re_c}{\Re_p}\frac{d^2f(C)}{dC^2} \left\{ \frac{1 + \frac{K_a}{b} + (1-\epsilon_p)\frac{B}{b}\frac{1}{\chi}\frac{\Re_p}{\Re_c} - \frac{v_c}{v_f}\left(1 + \epsilon_p\frac{B}{b}\right)}{\left[1 + \rho\chi\frac{\Re_c}{\Re_p}\frac{v_c}{v_f}\frac{df(C)}{dC}\right]^2} \right\} \tag{43}$$

For both Freundlich and Langmuir isotherms (eq.39 and eq.40) $d^2f(C)/dC^2 < 0$. If $dR_{eff}/dC < 0 \; \forall \; C$, then a choice of C_1 as the highest concentration encountered along the flow path will be conservative, giving the lowest effective retention factor.

$$\frac{dR_{eff}}{dC} < 0 \;\; \text{if} \;\; 1 + \frac{K_a}{b} + (1-\epsilon_p)\frac{B}{b}\frac{1}{\chi}\frac{\Re_c}{\Re_p} > \frac{v_c}{v_f}\left(1 + \epsilon_p\frac{B}{b}\right) \tag{44}$$

In general, $v_c \sim v_f$ and $K_a > 0$, in which case

$$\frac{dR_{eff}}{dC} < 0 \;\; \text{if} \;\; \chi < \frac{\Re_p}{\Re_c}\frac{1-\epsilon_p}{\epsilon_p} \tag{45}$$

This criterion applies *irrespective of the form of these sorption isotherms*.

4.2 Effective Decay Factor

The effective decay factor is λ_{eff} (eq.28) in the simplified model and $\lambda_{eff}(C)$ (eq.38) in the more general model. For both the Freundlich isotherm and the Langmuir isotherm,

$$\frac{df(C)}{dC} < \frac{f(C)}{C} \tag{46}$$

and therefore

$$\frac{\lambda_{eff}(C)}{\lambda} > 1. \tag{47}$$

Setting $\lambda_{eff}/\lambda = 1$ in the simplified model is therefore conservative, since it gives a decay factor λ_{eff} which is always less than $\lambda_{eff}(C)$ in the more general model.

4.3 Dispersion

An additional term $D_f U(C)/T(C)(\partial C_f/\partial z)^2$ arises in the more general model due to the combined effects of dispersion and non–linear sorption in eq.16. For both the Freundlich and Langmuir isotherms $df(C)/dC > 0$ and $d^2 f(C)/df(C)^2 < 0$ and therefore, from eq.35 and eq.36, the coefficient of this term, $D_f U(C)/T(C)$, is always negative. The term therefore always reduces radionuclide concentration. In the simplified model, $U = 0$ and so this additional term is absent. Neglecting the term in the simplified transport model is therefore likely to increase conservatism.

5 The Effect of Colloid Concentration

Expressions for the effective retention factor and effective decay factor at high and low colloid concentrations can be obtained from eq.37 and eq.38

$$R_{eff} \sim \frac{v_f}{v_c}\left(1 + \frac{K_a}{b}\right) \text{ if } \rho\chi\frac{\Re_c}{\Re_p}\frac{df(C)}{dC} \gg 1 + \epsilon_p\frac{B}{b} \tag{48}$$

$$R_{eff} \sim 1 + \epsilon_p\frac{B}{b} + \rho\frac{df(C)}{dC}(1 - \epsilon_p)\frac{B}{b} \text{ if } \rho\chi\frac{\Re_c}{\Re_p}\frac{df(C)}{dC} \ll 1 \tag{49}$$

$$\tag{50}$$

$$\frac{\lambda_{eff}}{\lambda} \sim \frac{f(C)/C}{df(C)/f(C)} \text{ if } \rho\chi\frac{\Re_c}{\Re_p}\frac{df(C)}{dC} \gg 1 + \epsilon_p\frac{B}{b} \tag{51}$$

$$\frac{\lambda_{eff}}{\lambda} \sim 1 \text{ if } \rho\chi\frac{\Re_c}{\Re_p}\frac{df(C)}{dC} \ll 1 + \epsilon_p\frac{B}{b} \tag{52}$$

Considering eq.49 and eq.52, the expressions for both effective retention factor and effective decay factor at low colloid concentration are themselves independent of the colloid concentration. Since $\epsilon_p B / b > 0$, low colloid concentration here means $\rho \chi \, \Re_c / \Re_p \, df(C)/dC \ll 1$. _Colloids have no influence on either the effective retention factor or the effective decay factor when $\rho \chi \, \Re_c / \Re_p \, df(C)/dC \ll 1$._ Considering eq.48 and eq.49, where colloids are sufficiently mobile ($K_a < \epsilon_p B(1 + \rho df(C)/dC(1 - \epsilon_p)/\epsilon_p)$) and where $v_f \sim v_c$, the effective retention factor is always lower at high colloid concentration, due to the exclusion of colloids from matrix pores.

The combined effects of the presence of colloids and the non–linearity of the sorption isotherm on $R_{eff}(C_1)$, the effective retention factor used in the simplified transport model, is now examined. It has been established that a conservative retention factor is one based on C_1, the highest concentration encountered along the flow path (generally that at the point of release to the geosphere). If the repository releases radionuclides to the geosphere at a given rate $J \, [mol \, m^{-2} s^{-1}]$, sorption on colloids will decrease C_1, the concentration in solution. Where $dR_{eff}(C)/dC < 0$, non–linearity will tend to increase the effective retention factor.

C_1 is obtained by equating the nuclide flux from the repository to the advective and dispersive fluxes, in solution and on colloids, within the geosphere. For the purposes of illustration, an example without dispersive fluxes is taken :

$$\frac{J}{v_f} = C_1 \left(1 + \frac{g(C_1)}{C_1} \right) = C_1 \left(1 + \rho \chi \frac{\Re_c}{\Re_p} \frac{f(C_1)}{C_1} \right) \tag{53}$$

From eq.53, at zero colloid concentration $C_1 = J/v_f$ and $\Re_z \, [-]$, the derivative of the isotherm with respect to nuclide concentration at zero colloid concentration, is given by

$$\Re_z = \left. \frac{df(C)}{dC} \right|_{C = J/v_f} \tag{54}$$

Sets of Freundlich and Langmuir isotherms are considered which give the same value of $\Re_z$ and thus the same effective retention factor at zero colloid concentration. $R_{eff}(C_1)$ is evaluated from eq.37 with C_1 given by an iterative solution to eq.53.

In the case of the Freundlich isotherm, a set of values for N is chosen and K_f is set to

$$K_f = \frac{1}{N} \Re_z \left(\frac{v_f}{J} \right)^{N-1} \tag{55}$$

As demonstrated above, it is the value of $\rho \chi \Re_c / \Re_p df(C)/dC$, equal to $\rho \chi \Re_z \Re_c / \Re_p$ at the point of release to the geosphere, which determines whether or not the presence of colloids influence radionuclide transport. Figure 1 shows R_{eff} at the point

of release to the geosphere plotted against this quantity for Freundlich isotherms with a range of values of N between 0.4 and 1.0. In the case of the Langmuir isotherm, a set of values for $(S_{max}/K_l)/(J/v_f)$ is chosen and K_l is set to

$$K_l = \Re_z \left(\frac{S_{max}/K_l + J/v_f}{S_{max}/K_l} \right)^2 \qquad (56)$$

Figure 2 shows R_{eff} plotted against $\rho \chi \Re_z \Re_c / \Re_p$ for Langmuir isotherms with a range of values of $(S_{max}/K_l)/(J/v_f)$ between 0.5 and ∞. $(S_{max}/K_l)/(J/v_f) = \infty$ corresponds to a linear sorption isotherm.

In both figures, as anticipated, increasing non–linearity tends to increase R_{eff}, particularly where $\rho \chi \Re_z \Re_c / \Re_p$ lies in the range of approximately 0.1 to 1: sorption on colloids decreases the concentration in solution and the retention factor, which is dominated here by sorption on the matrix pore surfaces, is increased as a result of non–linearity. For the most highly non–linear isotherms, there is even a range of colloid concentrations over which an increase in effective retention factor with colloid concentration occurs.
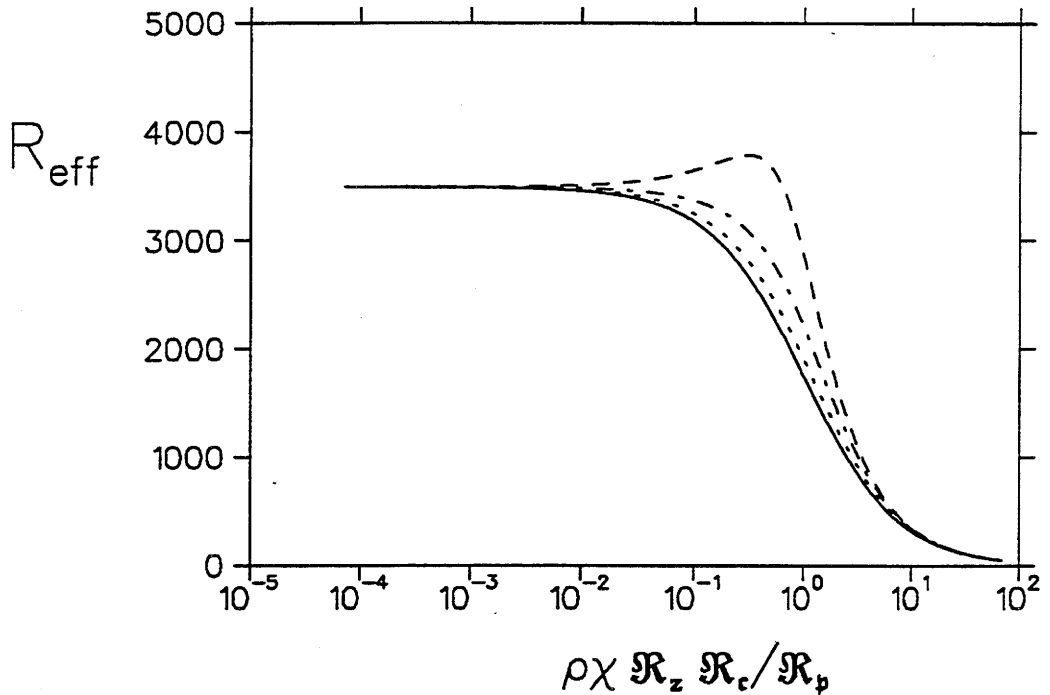
Figure 1: The effective retention factor R_{eff} at the point of release to the geosphere plotted against $\rho\chi\Re_z\Re_c/\Re_p$. A Freundlich sorption isotherm is assumed and results are shown for a range of values of the sorption coefficient N. $\epsilon_p = 0$, $B/b = 20$, $\rho = 2500\,m^3kg^{-1}$ and $\Re_z = 0.07\,m^3kg^{-1}$ (symbols defined in the text). Increasing non–linearity of the isotherm increases R_{eff}, particularly where $0.1 < \rho\chi\Re_z\Re_c/\Re_p < 1$. For the crystallin basement of northern Switzerland, values of $\rho\chi K_c$ ($K_c = \Re_z\Re_c/\Re_p$ for linear sorption) in the order of 0.1 have been measured (see section 7); non–linear sorption was not taken into account in these measurements.

———————	:	$N = 1$
- - - - - - - -	:	$N = 0.8$
— - — - —	:	$N = 0.6$
— — — —	:	$N = 0.4$
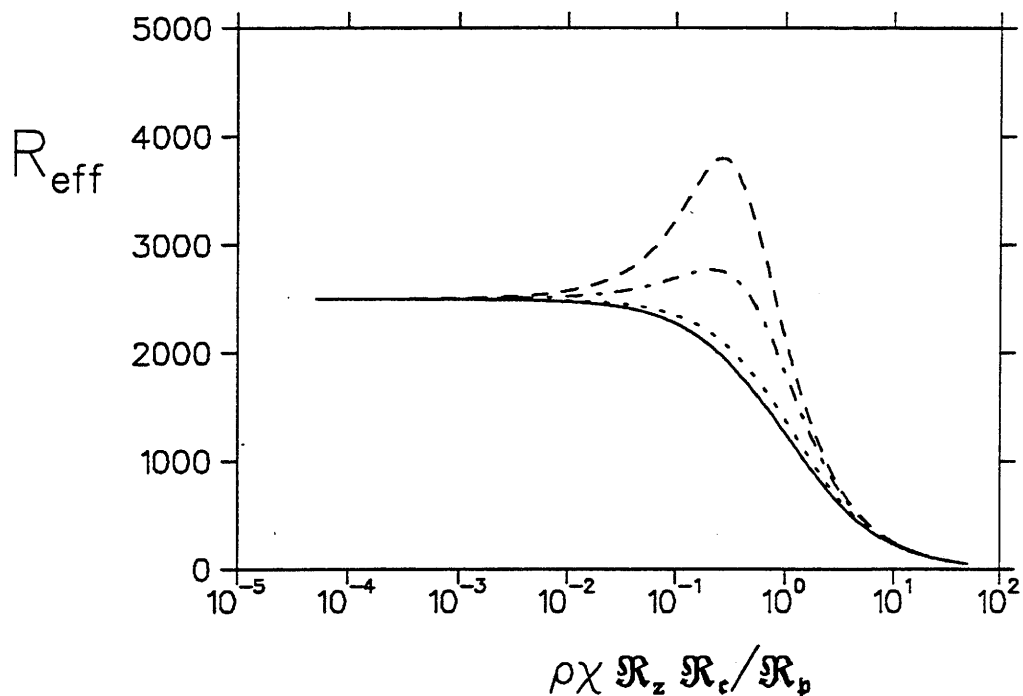
Figure 2: The effective retention factor R_{eff} at the point of release to the geosphere plotted against $\rho\chi\Re_z\Re_c/\Re_p$. A Langmuir sorption isotherm is assumed and results are shown for a range of values of $(S_{max}/K_l)(J/v_f)$. $\epsilon_p = 0$, $B/b = 20$, $\rho = 2500\,m^3kg^{-1}$ and $\Re_z = 0.07\,m^3kg^{-1}$ (symbols defined in the text).

————————	:	$(S_{max}/K_l)(J/v_f) = \infty$
- - - - - - - -	:	$(S_{max}/K_l)(J/v_f) = 5$
— · — · —	:	$(S_{max}/K_l)(J/v_f) = 1$
— — — —	:	$(S_{max}/K_l)(J/v_f) = 0.5$

6 Simulation of Colloid Facilitated Transport

6.1 Model Parameters

Some solutions are now presented to the governing equations for colloid facilitated transport from a repository through a geosphere in which water flows through a network of fractures. Linear and non–linear isotherms are each considered. The set of parameters used in the simulations is given in table 1.

Darcy velocity	$k.i$	1.0×10^{-11}	ms^{-1}
Repository area	A	860×860	m^2
Length of flow path	L	500	m
Total length of fractures	G	1.0×10^5	m
Half–aperture of fractures	b	0.5×10^{-3}	m
Peclet number	Pe	10.0	
Colloid density	ρ_c	2500	kgm^{-3}
Colloid surface–sorption coefficient	K_a	0	m
Matrix thickness	B	0.05	m
Matrix density	ρ_p	2500	kgm^{-3}
Matrix porosity	ϵ_p	0.001	

Table 1: Parameters for Colloid Facilitated Transport Simulations.

The Darcy velocity, the product of the hydraulic conductivity k $[ms^{-1}]$ and hydraulic gradient i $[m/m]$, when multiplied by the repository area A $[m^2]$ gives the rate of flow through the repository. The flow is partitioned between fractures, which have a total length G $[m]$ within the plane of the repository and a combined

cross sectional area of $2bG$. The mean water velocity within the fractures v_f is then given by

$$v_f = \frac{kiA}{2bG} \tag{57}$$

The mean colloid velocity v_c is set to v_f (see footnote 1). For a flow path of length $L\,[m]$, the Peclet number $Pe\,[-]$ is related to the longitudinal dispersion coefficient through the equation

$$D_f = \frac{v_f L}{Pe} \tag{58}$$

$K_a = 0\,m$ implies that all colloids are mobile, which is unrealistic in view of the forces which operate between colloids and fixed surfaces. However, due to the current lack of experimental data, a highly conservative K_a value is used here (see, however, fig.3b for a parameter variation).

6.2 Linear Sorption

It was shown in [24] that, for ^{237}Np, a representative, long–lived sorbing radionuclide, radionuclide transport in solution could generally be approximated by a simple, steady–state, geosphere transport model. In [25], a steady–state solution, in which the degree to which nuclides penetrate the matrix is determined both by decay and by the physical extent of the matrix, was presented. The solution, in which linear sorption is assumed, corresponds to those given by RANCHMD for release to the geosphere of infinite duration may thus be highly conservative for many nuclides. However, the solutions allow the *barrier efficiency of the geosphere* to be predicted readily with parameters varied continuously over the range of interest. The solution applies equally to colloid facilitated transport under the assumption of linear sorption, with modified water velocity, longitudinal dispersion coefficient and retention factor redefined as in section 3.3.1.

The barrier efficiency $\eta\,[-]$ is a measure of how effectively the radionuclide flux is reduced by its passage through the geosphere and is defined as

$$\eta = 1 - \left.\frac{C}{C_1}\right|_{z=L} \tag{59}$$

The nuclide concentration at $z = L$ is calculated from eq.8 in [25]. $\eta = 1$ corresponds to zero radionuclide flux from the geosphere and a high barrier efficiency. $\eta = 0$ corresponds to a flux unaltered by its passage through the geosphere, which therefore provides an ineffective barrier.

In figure 3a, η is plotted as a function of Darcy velocity for a range of values of $\rho_c \chi K_c$. All remaining parameters are set to the values in table 1. In general,

the barrier efficiency of the geosphere behaves as a smoothed step function, with a transition from 1 to 0 where the transit time of the radionuclide through the geosphere exceeds its half–life. As anticipated from the form of the expressions for the redefined model parameters, the presence of colloids has insignificant influence of transport when $\rho_c \chi K_c \ll 1$ (independent of all other model parameters: see also eq.49). However, the flowrate at which the barrier effect of the geosphere breaks down decreases rapidly at higher values of $\rho_c \chi K_c$.

Figure 3b shows the same data plotted in a different way. Here, contours of η, corresponding to 90% and 99% efficiency, are plotted. For a given Darcy velocity, it can therefore be determined from the figure how high a sorption constant or concentration of colloids is required to be in order for the geosphere to break down as an effective barrier to migration. The half–life $\ln 2/\lambda = 2.14 \times 10^6\, yr$ and linear sorption constant for the matrix $K_d = 1.0\, [m^3 kg^{-1}]$ (*realistic* value from Projekt Gewähr 1885 [3]) are specific to the radionuclide ^{237}Np. An effective diffusivity in matrix of $\epsilon_p D_p = 0.7 \times 10^{-12}\, m^2 s^{-1}$ is used.

Results are generally insensitive to the value of K_a if $\rho_c \chi K_c \ll 1$ (in which case the presence of colloids is expected to have no effect on transport). Furthermore, if K_a is less than about one metre, little effect resulting from the interaction of colloids with fracture walls is calculated, whatever the value of $\rho_c \chi K_c$; the case of $K_a = 5\, m$ is also shown in fig.3b. Although there is a lack of experimental data giving K_a values for the colloid–wall interaction, K_a values of the order of a metre are probably higher than would be expected. K_a values for nuclide–wall interaction in crystalline rock have been determined for serveral sorbing nuclides [26]. Even for the relatively strongly sorbing nuclide ^{134}Cs, K_a is of the order of only $10\, cm$.
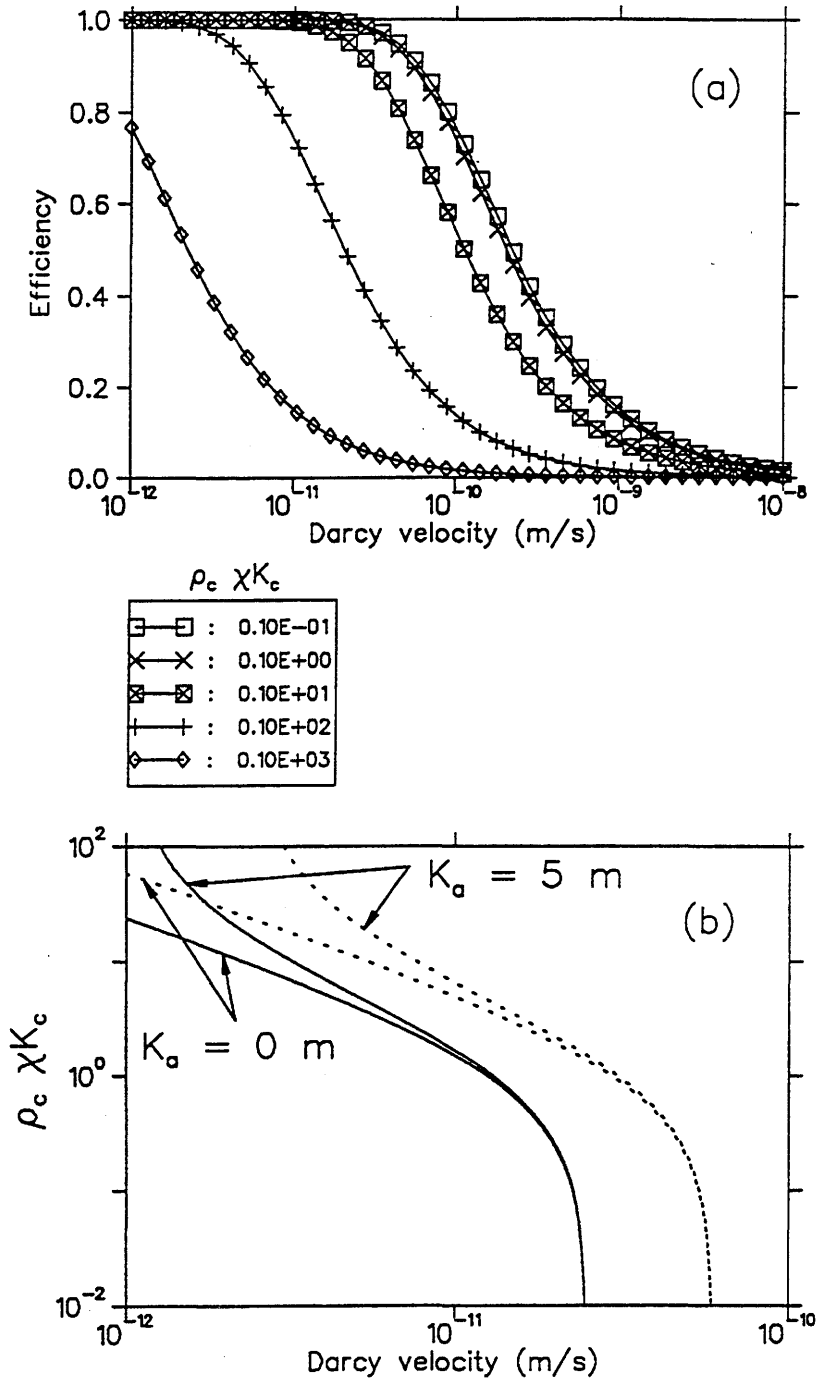
Figure 3: (a) The barrier efficiency of the geosphere η, plotted as a function of Darcy velocity for different values of $\rho_c\chi K_c$. (b) Contours of η, corresponding to 90% (broken line) and 99% (continuous line) barrier efficiency. For the crystallin basement of northern Switzerland, values of $\rho_c\chi K_c$ in the order of 0.1 have been measured (see section 7).

6.3 Non–Linear Sorption

Examples are now given of solutions to the one–dimensional non–linear transport equation for cases where the effective surface sorption approximation is valid: eq.16 with $T(C)$, $U(C)$, $R_{eff}(C)$ and $\lambda_{eff}(C)$ given by eq.35 to eq.38. The example of a non–decaying nuclide, with sorption governed by a Langmuir Isotherm (eq.40) and a constant release to the geosphere over 10^5 $years$, is taken for illustration.

Figures 4 and 5 show the flux of nuclides from the geosphere, both in solution and sorbed on colloids, plotted against time. In all cases $\Re_z$, the distribution ratio at zero colloid concentration defined by eq.54, is kept constant. Figure 4 shows the effect on the fluxes of varying the colloid concentration. As anticipated from the discussion in section 5, colloids have little effect on transport when $\rho\chi\,\Re_c/\Re_p\,\Re_z <$ 1. However, when $\rho\chi\,\Re_c/\Re_p\,\Re_z = 1$, the flux from the geosphere on colloids is larger than that in solution, the total flux increases and the peak flux occurs at an earlier time. When $\rho\chi\,\Re_c/\Re_p\,\Re_z = 10$, the geosphere provides little barrier effect; flux on colloids dominates over that in solution and follows closely the release flux to the geosphere. Figure 5 shows the effect of varying the non–dimensional saturation concentration $(S_{max}/K_l)/(J/v_f)$. As in figure 2, the range of variation is between 0.5 and ∞, with $(S_{max}/K_l)/(J/v_f) = \infty$ corresponding to a linear sorption isotherm. The maximum flux on colloids increases slightly with non–linearity and the tail of the break–through curve is increased in length, while the flux in solution is reduced. As the migrating nuclides spread during their transport through the geosphere, concentration in solution is reduced. Non–linearity of sorption results in more sorption both on colloids and in the matrix. In this example, since $(\Re_c/\Re_p)\chi = 0.03$ and $(1 - \epsilon_p)/\epsilon_p \sim 10^3$, eq.45 indicates that the effective retention factor increases with decreasing concentration in solution. Non–linear sorption therefore results in a higher retention effective factor, a reduced flux from the geosphere and longer tails.
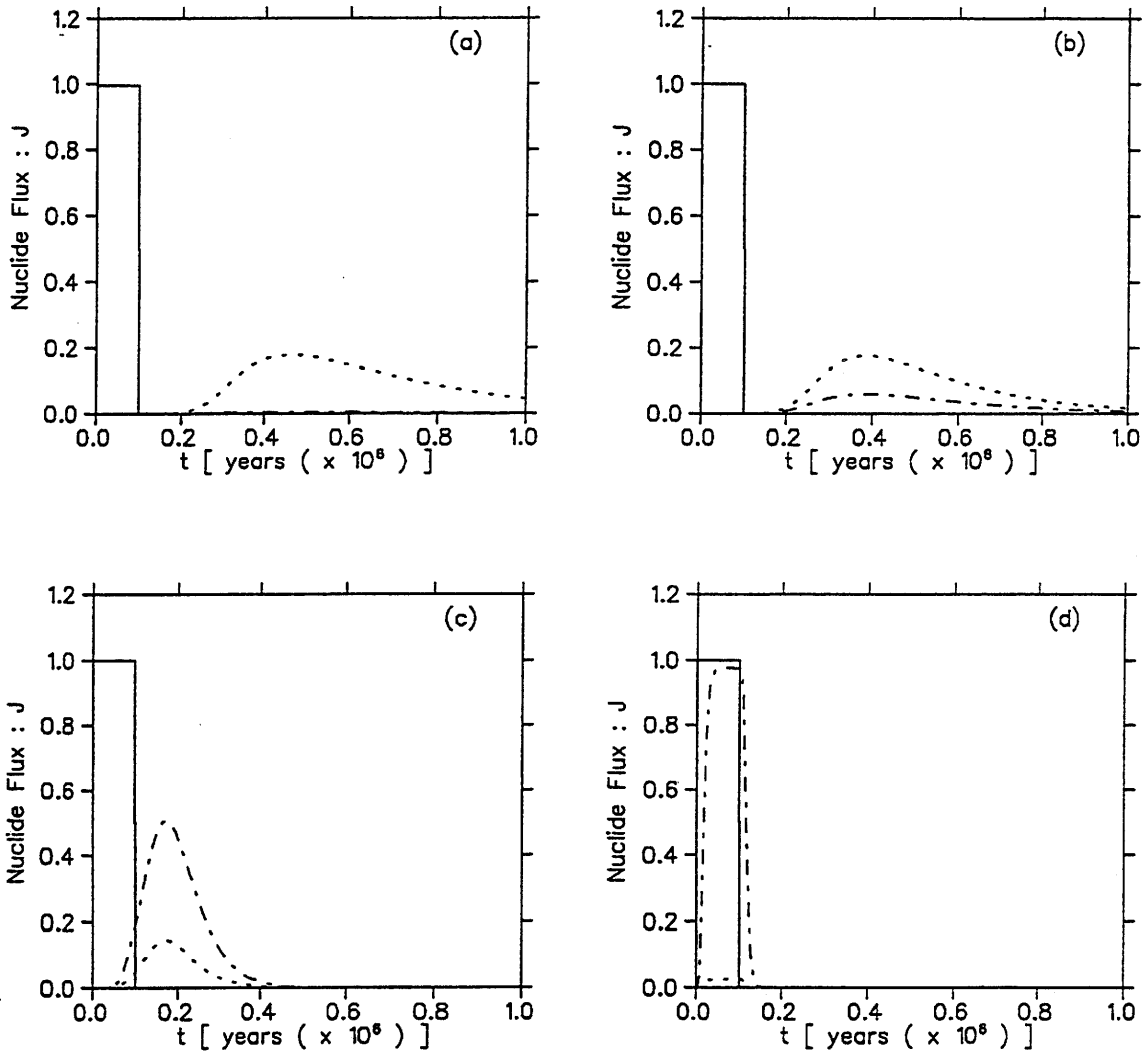
Figure 4: Nuclide flux normalised to J, the maximum release flux to the geosphere, as a function of time. A Langmuir sorption isotherm is assumed and results are shown for a range of values of colloid concentration. $\Re_z = 0.004\,m^3kg^{-1}$, $(S_{max}/K_l)(J/v_f) = 1.0$, (a): $\rho\chi\Re_c\Re_z/\Re_p = 0.01$, (b): $\rho\chi\Re_c\Re_z/\Re_p = 0.1$, (c): $\rho\chi\Re_c\Re_z/\Re_p = 1$, (d): $\rho\chi\Re_c\Re_z/\Re_p = 10$, (symbols defined in the text).

———————	:	release flux to the geosphere
— . — . —	:	flux on colloids from the geosphere
— — — —	:	flux in solution from the geosphere
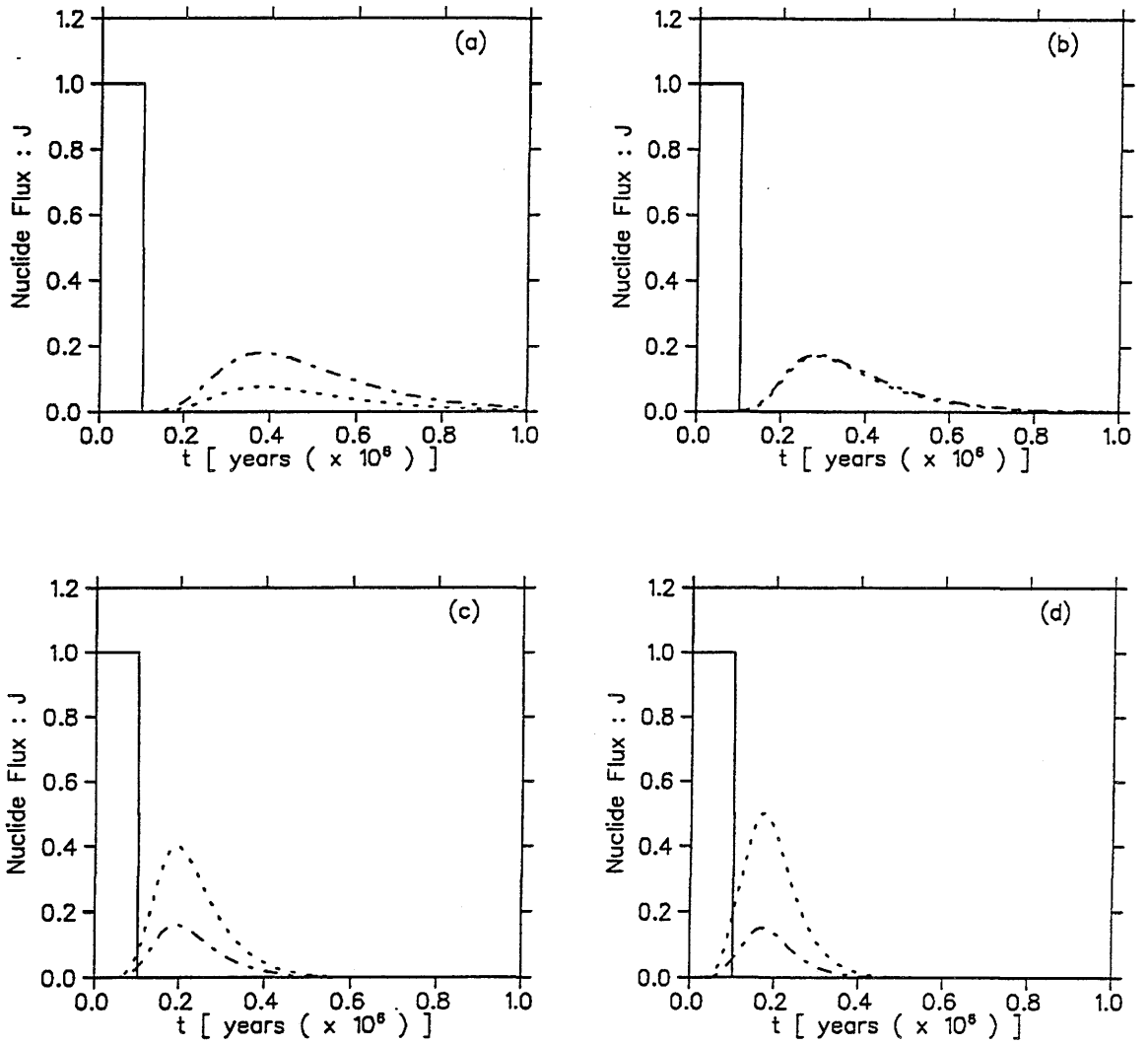
Figure 5: Nuclide flux normalised to J, the maximum release flux to the geosphere, as a function of time. A Langmuir sorption isotherm is assumed and results are shown for a range of values of non–dimensional saturation concentration $(S_{max}/K_l)(J/v_f)$. $\mathfrak{R}_z = 0.004\,m^3kg^{-1}$, $\rho\chi\mathfrak{R}_c\mathfrak{R}_z/\mathfrak{R}_p = 0.3$, (a): $(S_{max}/K_l)(J/v_f) = 0.5$, (b): $(S_{max}/K_l)(J/v_f) = 1$, (c): $(S_{max}/K_l)(J/v_f) = 5$, (d): $(S_{max}/K_l)(J/v_f) = \infty$, (symbols defined in the text).

——————— : release flux to the geosphere
— · — · — : flux on colloids from the geosphere
— — — — : flux in solution from the geosphere

7   Discussion and Conclusions

The conclusions of this work are summarised and discussed below. It should be noted that these conclusions are valid only under the very simplified set of assumptions made in the development of the model.

1. **A model for colloid facilitated transport in fractured geological media has been presented, in which sorption on matrix pore surfaces and on colloids is described in terms of independent non–linear isotherms.**

The model is of similar form to that for solute transport, but with an effective retention factor and an effective decay factor describing the effects of the presence of colloids, matrix diffusion, radioactive decay and non–linear sorption. The governing equations can be reduced to one dimension in space if the porous matrix surrounding the fractures becomes rapidly saturated by migrating radionuclides, in which case the effective surface sorption approximation is valid. For the special case of linear sorption, the governing equations are equivalent to those solved by code RANCHMD, but with redefined parameters. For Freundlich and Langmuir non–linear isotherms, a computer code has been written to solve the governing equations under the effective surface sorption approximation.

2. **A further simplified form of the model, which handles sorption by a linear isotherm, can be used conservatively, even where the empirical sorption isotherm for colloids and matrix is known to be non–linear as long as a simple condition on the colloid concentration is satisfied.**

The simplified modelling approach, for cases where the empirically determined isotherms are known to be non–linear, is one in which sorption coefficients corresponding to the maximum concentration at the point of release to the geosphere are used within the model for linear sorption, with the governing equations solved by the existing code RANCHMD. The conservatism of this approach has been investigated for the special case where sorption on pore surfaces and on colloids can be described by the same isotherm and the effective surface sorption approximation is valid. A comparison was made between the effective retention factor and effective decay factor in the simplified and more general model (the more general model also contains an additional term arising from the combined effects of dispersion and non–linear sorption, which is conservatively omitted in the simplified approach). The effective decay factor in the more general model is always higher

than in the simplified model. At the point of release to the geosphere, the effective retention factor for the more general model and for the simplified model are equal. At other points within the geosphere, where the radionuclide concentration is lower, the effective retention factor for the geosphere in the more general model is higher provided the condition

$$\chi < \frac{\Re_p}{\Re_c} \frac{1 - \epsilon_p}{\epsilon_p}, \tag{60}$$

which is independent of the form of the empirical sorption isotherm, is satisfied. For such cases, the simplified transport model, in which the effective retention factor is fixed, will be conservative.

3. **For colloid concentrations typical of the crystalline basement of northern Switzerland, the condition on the colloid concentration is likely to be satisfied.**

$\Re_p$ and $\Re_c$ are measured distribution ratios for matrix and colloids at a specific nuclide concentration. Their ratio gives a measure of the relative surface areas available for sorption. Data for the clay/silica colloids from the Grimsel Test Site [27] can be used to give an indication of the order of magnitude of this ratio. In [27], $\Re_c$ is $10^3 \, m^3 kg^{-1}$ for $Am(III)$ and $10^2 \, m^3 kg^{-1}$ for $U(VI)$. Equating $\Re_p$ to the *conservative* sorption constants for intact rock from Projekt Gewähr [3] ($0.5 \, m^3 kg^{-1}$ for Am and $0.05 \, m^3 kg^{-1}$ for U) gives $\Re_p/\Re_c \sim 5 \times 10^{-4}$. For a matrix of porosity $\epsilon_p = 0.01$, the simplified colloid transport model is conservative for colloid concentrations $\chi < 5 \times 10^{-2}$. A typical colloid concentration for the groundwater of the crystalline basement of northern Switzerland is $\sim 10^{-7}$ (100 ppb) or less [23].

4. **The simplified transport model indicates that, for colloid concentrations and sorption constants typical for the crystalline basement of northern Switzerland, the presence of colloids may perturb radionuclide transport, though probably not to a large extent.**

In general, both colloid concentration and the degree of sorption determine the radionuclide concentration in solution and hence the conditions under which colloids influence radionuclide transport. In the simplified transport model, colloids have no influence on either the effective retention factor or the effective decay factor when

$$\rho \chi \, K_c \ll 1 \tag{61}$$

Values of K_c and χ have been tabulated in [8] for a range of groundwater colloids, including those from the crystalline basement of northern Switzerland, and for a

number of different sorbing species. In general, $\rho\chi K_c$ is less than unity, but values of the order of 0.1 are common. In such cases, the presence of colloids would be expected to perturb the transport of radionuclides, although it is unlikely to be a dominant effect.

5. **Experimental studies should give priority to determining colloid concentrations and quantifying radionuclide sorption. Provided that sorption is reversible, the investigation of the interaction between colloids on fracture surfaces is of secondary importance, determining the *magnitude* of this effect.**

Colloid concentration and the degree of radionuclide sorption determine whether or not there is an effect on radionuclide transport resulting from the presence of colloids. Only if it is established that such an effect is possible are the parameters which determine its magnitude of interest. The degree of perturbation of radionuclide transport is a function of the colloid surface–sorption coefficient K_a, although, for the test–case presented here, the dependence is weak and an unrealistically high value of K_a is required to produce a significant effect.

6. Provided there is little interaction between colloids and fracture walls, the effect of colloids is generally to enhance transport. Where sorption on matrix pore surfaces and colloids is highly non–linear, however, there are circumstances under which transport may be retarded by increased colloid concentration.

Where it is assumed that all colloids are mobile (attachment to fracture walls is neglected), then the presence of colloids generally reduces the effective retention factor, thus enhancing transport, since colloids are excluded from matrix pores. However, where sorption on matrix pore surfaces and colloids is non–linear, if radionuclides enter at a constant rate into the geosphere, radionuclide concentration in solution falls with increasing colloid concentration and non–linear sorption tends to increase the retention factor. This leads to the surprising result that, for highly non–linear isotherms, an initial *increase* in the retention factor is predicted with increasing colloid concentration before the effect of the colloid exclusion from matrix pores again reduces it.

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