SKI Report 02:34

Research

Quantitative Assessment of the Potential Significance of Colloids to the KBS-3 Disposal Concept

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SKI Perspective

Background

The travel times of radionuclides from a spent nuclear fuel repository to the surface environment is mainly determined by the direction and magnitude of groundwater flow as well as chemical reactions of nuclides on solid surfaces. The travel time for a specific nuclide can be regarded as an important characteristic in the overall evaluation of the long-term safety for such repositories. Radionuclides can move with the groundwater either as solutes or colloids (minute particles in the range 1nm to 1 µm), where the latter mechanism generally results in much shorter travel times for radionuclides that interact strongly with solid phases, such as actinides. In performance assessment is it therefore essential to assess the relative importance of these two transport mechanisms for different nuclides. The relative importance of colloids depends on the nature and concentration of colloids in groundwater.

Galson Sciences has previously completed a study for SKI in which international experiences related to the treatment of colloid transport in performance assessment calculations is summarised (SKI Report 00:33). This study complements the previous one by including a quantitative evaluation of the significance of plutonium transport with colloids for conditions representative of deep Swedish groundwaters. Plutonium was chosen as an example of a relevant nuclide because new information was available about its behaviour in groundwater from the Nevada test site.

Relevance for SKI

SKI need to develop, maintain and update independent modelling capability in order to achieve a detailed understanding of different phenomena of relevance for the long-term safety of spent fuel and other nuclear waste and to evaluate key conclusions from previously published safety assessments. This study contributes to the achievement of that goal by testing and implementing the previously developed COLLAGE II code, which considers radionuclide transport as solutes as well as on colloids.

Results

The modelling results show that transport of plutonium by colloids can not be ruled out as a significant transport pathway relative to the solute transport pathway, based on the available information about sorption/desorption kinetics, colloid concentrations, sorption strength, etc. The study also includes a sensitivity analysis that especially contributes to an understanding of the significance of sorption kinetics in the context of colloid transport.

Future work

The present version of the COLLAGE II code can be improved by adding a more detailed model for sorption and desorption reactions and a more realistic representation of the release of nuclides at the inner boundary. It would also be possible to analyse other nuclides apart from plutonium, but additional experimental/field data would then be needed.

Project information

SKI project manager: Bo Strömberg

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Summary

Colloids are minute particles in the size range 1 nm to 1 μm that can remain suspended in water, and may influence radionuclide transport in radioactive waste disposal systems. Galson Sciences Ltd (GSL) has undertaken a quantitative assessment of the impact that colloid-facilitated radionuclide transport may have on the performance of the Swedish KBS-3 concept for disposal of high-level radioactive waste and spent fuel. This assessment has involved the evaluation and application of SKI's colloid transport model, COLLAGE II, modelling of km-scale Pu transport at the Nevada Test Site (NTS), USA, and identification of circumstances under which colloid-facilitated transport could be important for a KBS-3-type environment.

Colloids bearing traces of plutonium from the BENHAM underground nuclear test have been detected in samples obtained from Nevada Test Site (NTS) groundwater wells 1.3 km from the detonation point. Plutonium is generally fairly immobile in groundwater systems, and it has been suggested that colloids may have caused the plutonium from the BENHAM test to be transported 1.3 km in only 30 years. This hypothesis has been tested by modelling plutonium transport in a fracture with similar characteristics to those present in the vicinity of the BENHAM test.

SKI's colloid transport code, COLLAGE II, considers radionuclide transport in a one-dimensional planar fracture and represents radionuclide-colloid sorption and desorption assuming first-order, linear kinetics. Recently published data from both the ongoing NTS site investigation and from the associated Yucca Mountain Project have been used to define a COLLAGE II dataset. The kinetics of radionuclide-colloid sorption and desorption have been found to be crucial in explaining the transport of plutonium associated with colloids, as inferred at the NTS. Specifically, it has been found that for plutonium to have been transported by colloids over the full 1.3 km transport path, it is likely that the plutonium was released in colloidal form and that the rate of plutonium desorption from colloids must have been slow.

For the KBS-3 situation, the *Aberg* fracture from the SR97 performance assessment has been used to provide the basis for a COLLAGE II representation of colloid transport. Colloid concentrations of typical Swedish groundwaters have been used, together with literature information on the strength of radionuclide-colloid sorption.

Modelling results indicate that colloids may play a role in contaminant transport if radionuclides sorb strongly, and irreversibly or nearly irreversibly, to colloids. Furthermore, if the rates of radionuclide sorption and desorption to colloids lie in a certain range, then there exists the possibility that colloid-facilitated transport could lead to relatively rapid (<100 year) transport of radionuclides from the bentonite-host rock interface to the accessible environment. Early release will only occur over a relatively restricted range of low sorption/desorption rates. At these low rates, even if all plutonium is initially released to far-field groundwaters in solution, following diffusion through the bentonite buffer, a small amount is able to associate with groundwater colloids. Because of the slow rate of disassociation, this plutonium is then able to be carried significant distances on colloids before being released to

solution where it is rapidly sorbed onto mineral surfaces. Were the strength of sorption of plutonium to colloids, or the concentration of colloids, to be greater than current best estimates, there could be a relatively greater early release.

Sammanfattning

Kolloider är små partiklar i storleksordningen 1 nm till 1 µm som kan förbli svävande i vatten, och som kan påverka radionuklidtransporten från ett slutförvar med radioaktivt avfall. Galson Sciences Ltd (GLS) har genomfört en kvantitativ studie av vilken betydelse kolloidal radionuklidtransport kan ha för funktionen av ett svenskt KBS-3 förvar med använt kärnbränsle. Denna studie innehåller en utvärdering och tillämpning av SKI:s kolloidtransportmodell (COLLAGE II), modellering av plutonium transport (i km-skala) vid Nevada Test Site i USA, och identifiering av förhållanden under vilka kolloidtransport skulle kunna vara betydelsefull för ett KBS-3 förvar.

Kolloider med spår av plutonium från BENHAM "underground nuclear test" har detekterats i prov tagna från Nevada Test Sites grundvattenbrunnar belägna 1.3 km från detoneringspunkten. Plutonium är vanligtvis relativt immobilt i grundvattensystem, och man tror att kolloider kan vara orsaken till att plutonium från BENHAM testet har transporterats 1.3 km på bara 30 år. Denna hypotes har testats genom modellering av plutoniumtransport i en spricka med liknande egenskaper som de i omgivningen av BENHAM testet.

SKI:s kolloidtransportkod, COLLAGE II, beskriver radionuklidtransport i en endimensionell, plan spricka och representerar radionuklid-kolloid sorption/desorption genom att antaga en första-ordningens linjär kinetik. Nyligen publicerade data, både från de pågående platsundersökningarna vid NTS och från Yucca Mountain projektet, har använts för att definiera ett dataset för COLLAGE II. Radionuklid/kolloid sorptions-desorptionskinetiken har visat sig vara avgörande i förklaringen till transporten av plutonium med kolloider. Mer specifikt har det visat sig att det plutonium som har transporterats av kolloider hela den 1.3 km långa transportvägen troligen släpptes ut i kolloidal form och att hastigheten för plutonium desorptionen i detta fall måste ha varit långsam.

För KBS-3 fallet har data för A-berg (Äspö) från säkerhetsanalysen SR 97 använts som bas för en COLLAGE II representation av kolloidtransport. Kolloidkoncentrationer hos typiska svenska grundvatten har använts tillsammans med litteraturdata om styrkan på radionuklid-kolloid sorption.

Modellresultat visar att kolloider kan ha betydelse för radionuklidtransporten om radionukliderna sorberar starkt och irreversibelt eller nästan irreversibelt till kolloiderna. Om dessutom hastigheten av radionuklidenas sorption/desorption till kolloider ligger inom ett visst intervall så är det möjligt att kolloidtransporten kan leda till en relativt snabb (mindre än 100 år) radionuklidtransport från bentonit-berg-gränsytan till den tillgängliga miljön. Ett tidigt utsläpp sker endast över ett relativt begränsat intervall av låga sorptions/ desorptions-hastigheter. Vid dessa låga hastigheter kan små mängder plutonium bindas till kolloider i grundvattnet, även om allt tillgängligt plutonium initialt släpps ut i grundvatten i närheten av förvaret efter att ha passerat bentonitbufferten via diffusion. På grund av den långsamma dissociationshastigheten så kan detta plutonium bäras långa avstånd på kolloiderna innan de desorberar och släpps ut igen i grundvattnet där de sedan snabbt sorberar på mineralytor. Om sorptionsstyrkan av plutonium till kolloider, eller kolloidkoncentrationen, vore större än de nuvarande bäst uppskattade värdena, skulle ett relativt större utsläpp i ett tidigt skede kunna förekomma.

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1 Introduction

1.1 Background and Objectives

Colloids are minute particles in the size range 1 nm to 1 μm that can remain suspended in water. Groundwaters often contain large populations of natural colloids, and these can interact with pollutants and influence their transport. In radioactive waste disposal systems, natural colloids and waste- and repository-derived colloids may influence radionuclide transport. Since the early 1990s, there has been a growing awareness of the potential importance of colloids, and as greater computing resources and more data have become available, PA models have increasingly included colloids in quantitative analyses of repository safety.

Recent observations made by United States Department of Energy (DOE) researchers at the Nevada Test Site (NTS) have demonstrated migration of Pu 1.3 km from the site of the BENHAM underground nuclear test; the researchers suggest that the migration may have occurred as a result of the attachment of the Pu to colloids (Kersting *et al*., 1999).

The primary objective of this project has been to evaluate the potential for colloids to transport radionuclides in environments relevant to the Swedish disposal concept. In order to assess the role of colloids in the Swedish KBS-3 disposal concept, a review of the mechanisms by which colloids could be introduced into the disposal system environment has been carried out (Wickham *et al*. 2000). This enabled us to form an understanding of which and how many colloids may be present in far-field fractures under normal circumstances.

Modelling of colloid-facilitated transport is a matter of representing the transport of radionuclides in solution and on colloids in a network of fractures in granite. The Swedish Nuclear Power Inspectorate (SKI) has a model designed for the purpose of colloid modelling - COLLAGE II (Grindrod and Cooper, 1993). The observations from the NTS provide an opportunity to test COLLAGE II against independent data, and to assess the level of confidence in the use of COLLAGE II. COLLAGE II may also be used to represent fractures in the KBS-3 concept, and to assess the potential role of colloids in that system.

In the course of the work it has been possible to use the most recent information from the Yucca Mountain Project and the NTS site monitoring programmes from the USA. Colloids are of potential importance in both of these programmes.

1.2 Report Structure

Section 2 of this report provides a brief review of the COLLAGE II model. Details of the mathematical model represented in COLLAGE II and suggestions arising from our experience with the code are summerised in a technical note available from SKI.

The application of COLLAGE II to the NTS system is described in Section 3. This Section includes a review of newly available data from the NTS and Yucca Mountain Project. The ability of COLLAGE II to reproduce the NTS observations is investigated and the consequences for colloid modelling discussed.

Section 4 applies the lessons learned to a model of a representative fracture in the KBS-3 concept. The crucial role of the sorption/desorption rate of radionuclides onto colloidal material is investigated in a deterministic sensitivity study, and a wider probabilistic sensitivity analysis is used to investigate the range of parameters that might give rise to significant colloid-driven effects.

Conclusions from the study are presented in Section 5.

2 Overview of the COLLAGE II Model for Colloid-Facilitated Transport

2.1 Background

COLLAGE II is SKI's colloid-facilitated radionuclide transport code. It is the main tool used by SKI for quantitative assessment of the potential impact of colloids in the KBS-3 disposal concept.

The model and its development are documented in a series of SKI reports (Grindrod, 1989; Grindrod and Worth, 1990; Grindrod, 1991; Grindrod *et al.*, 1992; Grindrod and Cooper, 1993). COLLAGE II calculates the flux of radionuclides released at the end of a saturated planar fracture surrounded by porous media. The flux in solution, the flux attached to mobile colloids, the total flux (solute and colloid), and time-integrated flux are calculated.

Earlier implementations of the code assumed instantaneous irreversible sorption onto colloidal material but included representations of both mobile and immobile colloids. The most recent version of the code includes reversible interactions between radionuclides in solution and on both forms of colloids. These are modelled via first-order kinetics. This project has highlighted the importance of these mechanisms.

Galson Sciences has implemented some modifications to the original COLLAGE II coding. These have had the effect of allowing the user greater flexibility in selecting output times and the code can now be run more easily with groups of input files. A probabilistic version, interfaced to output from the Sandia Latin Hypercube Sampling (LHS) code (Iman and Shortencarrier, 1984), has also been produced for this project.

2.2 Conceptual Model

Figure 2.1 illustrates the features and processes represented in the conceptual model from which the COLLAGE II code is derived. The characteristics of the model are summarised below.

Radionuclides in solution travel with the groundwater flow within the fracture but interact with the rock matrix of the fracture walls. If suspended colloidal material is present in the fracture, radionuclides can sorb onto the colloids and desorb back into solution. Some of the colloids may be captured by the walls of the fracture and some may be released.

The model permits an evaluation of the response of the system, as illustrated in Figure 2.1, to the input of radionuclides at the upstream end of the fracture. The response is given in terms of the radionuclide flux at the downstream end, both in solution and on mobile colloids.

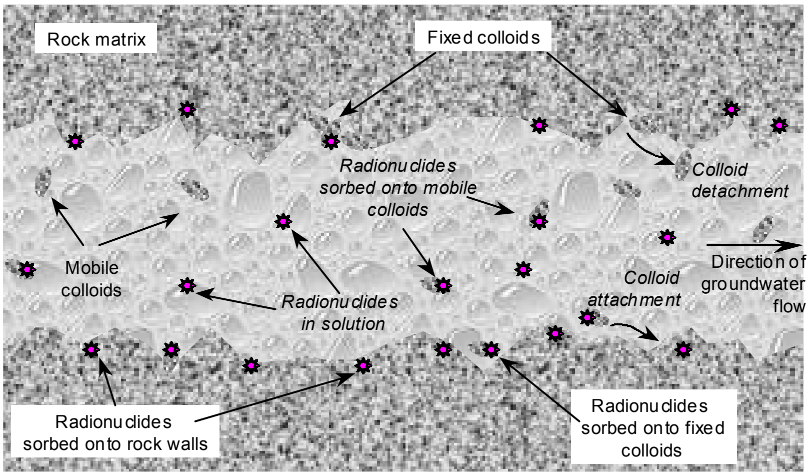

Figure 2.1: Illustration of the COLLAGE II conceptual model for colloid transport in a thin planar fracture.

In common with a number of colloid modelling approaches, COLLAGE II uses a one-dimensional approach to characterise the fracture properties, with matrix sorption into the wall rock perpendicular to the direction of flow. Such descriptions have been used in many cases (e.g., Nagra, 1994; US DOE, 1998; JNC, 2000). A 1-D approach is currently also used in the US YMP programme (Wolfsberg and Reimus, 2000). COLLAGE II differs from contemporary models in its treatment of the kinetics of radionuclide-colloid interactions (see the review by Wickham *et al.*, 2000).

2.3 Mathematical Model

The following provides an overview of the mathematical model represented in COLLAGE II. Details of the model's derivation has been summerised in a technical note available from SKI.

The fracture has length L [m] and the aperture half-width is b [m]. The boundary between the water in the fracture and the wall rock is at $z = 0$ m. Within the fracture ($0 \leq x \leq L$), there are three radionuclide concentrations of interest:

c_s	mol m^{-3}	radionuclide concentration in solution in fracture flow;
c_m	mol m^{-3}	radionuclide concentration sorbed to mobile colloids; and
c_f	mol m^{-3}	radionuclide concentration sorbed to immobile colloids.

Additionally the radionuclide concentration in the rock matrix is used:

c_p	mol m^{-3}	radionuclide concentration sorbed to the rock matrix.

Table 2.1 summarises the other parameters used in the code.

Table 2.1: Parameters in the COLLAGE II code.

parameter	units	Definition
$\tilde{D}$	$m^2\ y^{-1}$	dispersion coefficient of solute
$\tilde{u}$	$m\ y^{-1}$	average groundwater velocity in the fracture
D	$m^2\ y^{-1}$	molecular diffusion coefficient of the solute into the rock matrix
ϕ	-	rock matrix porosity
b	m	half fracture width
D^*	$m^2\ y^{-1}$	dispersion coefficient of mobile colloids
u^*	$m\ y^{-1}$	average mobile colloid flow rate
λ	y^{-1}	decay constant
R	-	rock matrix retardation coefficient - $R = 1 + \frac{1-\phi}{\phi}\rho K_d$ where K_d is the distribution coefficient for radionuclides sorbing onto the rock matrix
κ_1	y^{-1}	rate of sorption/desorption, mobile colloids
κ_2	y^{-1}	rate of sorption/desorption, immobile colloids
β	-	number of mobile colloids/number of immobile colloids
k_1	-	partition coefficient for radionuclides sorbing onto mobile colloids
k_2	-	partition coefficient for radionuclides sorbing onto immobile colloids
η	-	fraction of injected inventory in solute phase
L	m	length of fracture modelled
n	-	scaling factor for zero concentration outer boundary condition at $x = nL$

The advection-dispersion equation representing radionuclide exchange between solution and colloids is:

$$\frac{\partial c_s}{\partial t} = \tilde{D}\frac{\partial^2 c_s}{\partial x^2} - \tilde{u}\frac{\partial c_s}{\partial x} + \frac{\phi D}{b}\left.\frac{\partial c_p}{\partial z}\right|_{z=0} - \lambda c_s + (\kappa_1 + \beta\kappa_2)c_m - (\kappa_1 k_1 + \kappa_2 k_2)c_s \tag{1}$$

for radionuclides in solution, and

$$(1+\beta)\frac{\partial c_m}{\partial t} = D^*\frac{\partial^2 c_m}{\partial x^2} - u^*\frac{\partial c_m}{\partial x} - \lambda(1+\beta)c_m - (\kappa_1 + \beta\kappa_2)c_m + (\kappa_1 k_1 + \kappa_2 k_2)c_s \tag{2}$$

for radionuclides on mobile colloids.

The model implements a zero concentration outer boundary condition in the fracture:

$$c_s(nL,t) = c_m(nL,t) = 0, \qquad t \ge 0 \tag{3}$$

The initial condition at $x = 0$ is a pulse of radionuclides, with zero concentration elsewhere in the fracture.

$$c_s(x,0) = c_m(x,0) = 0, \qquad 0 < x < nL \tag{4}$$

The initial pulse at $x = 0$ is divided into a fraction η in solution and a fraction $(1 - \eta)$ on mobile colloids, so that the evolution can be described as:

$$\left[\tilde{u}c_s - \tilde{D}\frac{\partial c_s}{\partial x}\right]_{x=0} = \eta\frac{1}{2b}\delta(t), \qquad t \ge 0\text{, and} \tag{5}$$

$$\left[u^* c_m - D^*\frac{\partial c_m}{\partial x}\right]_{x=0} = (1-\eta)\frac{1}{2b}\delta(t), \quad t \ge 0\,. \tag{6}$$

In the rock matrix, the boundary and initial conditions are:

$$c_p(x,z,t) \to 0 \qquad \text{as} \qquad z \to \infty\,, \tag{7}$$

$$c_p(x,0,t) = c_s(x,t)\text{, and} \tag{8}$$

$$c_p(x,z,0) = 0\,. \tag{9}$$

The output quantities are the fluxes at $x = L$:

$$f_s(t) = 2b\left[\tilde{u}c_s - \tilde{D}\frac{\partial c_s}{\partial x}\right]_{x=L} \tag{10}$$

$$f_m(t) = 2b\left[u^* c_m - D^* \frac{\partial c_m}{\partial x}\right]_{x=L} . \tag{11}$$

The solution method implemented in COLLAGE II uses a Laplace transform for the equations for solute, mobile and immobile colloids and the rock matrix. This transforms the equations into a more manageable form and requires the implementation of inverse Laplace transform routines to obtain the quantities given in Equations (10) and (11).

The model represented by Equations (1) and (2) is a fairly standard form. However, the kinematic terms which allow for reversible sorption are a notable feature. In the absence of colloids, Equation (1) reduces to a form which is similar to that used in the SKB far-field model FARF31 (Lindgren and Lindström, 1999) for modelling advective/dispersive radionuclide transport in a 1-D fracture in the SR97 PA.

2.4 COLLAGE II Parameterisation

Consistent with the aim of determining the conditions under which colloid-facilitated transport could lead to potentially significant releases of radionuclides on colloids, the calculations carried out with COLLAGE II have not sought to calculate absolute values of radionuclide flux. Rather, the focus has been on the comparison of the release flux on colloids to that in solution (both in time and magnitude). Comparisons have also been made between results from cases with colloid transport, and cases where there are no colloids present in the modelled system.

Bentonite is widely considered to be an excellent filter of colloids. Where it is used as a buffer in waste repository designs, it is considered unlikely that near-field generated colloids would escape into far-field groundwaters (Kurosawa *et al.*, 1997). Radionuclides diffusing through the bentonite are therefore expected to enter the fracture at $x = 0$ in solution only.

In modelling the NTS case, the nature of the source term is essentially unknown. A nuclear explosion may embody some of the features of a δ-function input, at least in comparison with the 30 years elapsed since the detonation. The possibility of prompt injection over the 1.3-km transport distance may be discounted, although such transport over shorter distances may have occurred (Wickham *et al.*, 2000). The colloids found at the NTS comprised a mixture of clays, zeolites, silica and glass (Thompson, 1998). It is possible that colloids were formed as a consequence of the explosion, and that Pu was released into the local groundwater system on colloids. This possibility may be modelled in COLLAGE II through use of the η parameter.

The partition parameters used in COLLAGE II are generally not what is reported in the literature. In practice, the derivation of k_1 and k_2 in the modelling work reported here has assumed that the radionuclide partitioning factor for mobile colloids is

$$k_1 = K_p \alpha_m \text{ [-].} \tag{12}$$

The factor K_p [m^3 kg^{-1}] is the radionuclide-colloid distribution coefficient (analogous to K_d) and α_m [kg m^{-3}] is the suspended load of mobile colloids.

The role of immobile colloids in groundwater systems such as the SR97 fractures is poorly constrained and it is not clear how immobile colloids could be detected in field measurements. There are techniques for determining their potential presence in laboratory rock samples but the implications of the results for colloids in natural systems is not clear. For consistency we have adopted the following form for determining k_2:

$$k_2 = K'_p \alpha_f \text{ [-],} \tag{13}$$

where the population α_f [kg m^{-3}] is now the fixed colloid mass per unit volume of water in the fracture. To allow for the possibility that sorption of solute-phase radionuclides onto immobile colloids might differ from that onto mobile colloids, we assume that the sorption parameter (K'_p [m^3 kg^{-1}]) may have a different value to K_p.

3 Modelling NTS Conditions with COLLAGE II

3.1 Background

At the Nevada Test Site (NTS), colloids bearing plutonium have been found in boreholes. The isotopic composition of the plutonium has been used to identify it as originating from the BENHAM nuclear test, 1.3 km away, which took place in the 1960s (Kersting *et al*., 1999). The implication is that plutonium has migrated in groundwater over a distance of 1.3 km in around 30 years since the test, and that migration could have been facilitated by attachment to colloids. The concentration of colloids in the groundwater samples is low. Nevertheless, the result indicates the potential role of colloids in transporting radionuclides rapidly over fairly large distances. Wickham *et al*. (2000) provide a more thorough review.

The NTS monitoring data do not include concentrations of Pu on colloids as a function of time, nor is the nature of the source term definitively established. However, there are sufficient data to allow COLLAGE II to be used in a semi-quantitative assessment of colloid-facilitated transport at the NTS.

First, it is of interest to see if COLLAGE II can produce results consistent with 1.3 km transport of colloid-associated Pu in 30 years. Second, it is relevant to ask what the implications are for the set of model parameters and features, events and processes (FEPs) that allow COLLAGE II to represent the NTS observations.

3.2 Database

In this subsection, we describe the selection of COLLAGE II parameters used to model NTS colloid transport.

3.2.1 Fracture and Groundwater

New data on groundwater composition are available from the NTS monitoring programme (e.g., Sawyer *et al*., 1999; Brachmann and Kersting, 2000): the data are relevant to the BENHAM test and to other locations within the NTS. Monitoring of groundwater characteristics and radionuclide migration following the CHESHIRE test was more detailed than any other test at the NTS. Many of the data from CHESHIRE are relevant to the BENHAM case since conditions are locally similar. The Yucca Mountain site characterisation programme, geographically adjacent to the NTS, also provides much relevant information (US DOE, 1998).

In using COLLAGE II, the first stage is to assign values to the fracture parameters. In this exercise, the length of the fracture was assumed to be 1.3 km and a suitable range of groundwater velocities was taken as 1 - 80 m y^{-1} (Blankennagel and Weir, 1973). From this we take 40 m y^{-1} as the central value. For dispersion in the groundwater, the value quoted by Grindrod *et al*. (1992) has been used (50 m^2 y^{-1}).

The host rock surrounding the fracture is porous tuff and therefore the base case model simulates diffusion of dissolved Pu tracer into the rock matrix, where it may become sorbed. The porosity of the tuff is relatively low - US DOE (1998) quoted a triangular distribution for this type of material. The central value of porosity, $\phi = 0.02$ [-], is adopted here. For model testing, the rock diffusivity is assumed to be the same as that used in the original COLLAGE II test cases - $D = 7.9\times10^{-4}$ m^2 y^{-1}. A typical fracture half-width for the system is 5×10^{-5} m, which is the central value provided by US DOE (1998).

We assume that the half-life of the plutonium isotopes is long, compared to the 30-year timescale of the observations, and we therefore set the decay constant to zero. Retardation is set to 10^6, consistent with the range of K_d values cited for Pu by USDOE (1998).

The numerical values are summarised in Table 3.1 alongside the data for the colloids.

3.2.2 Colloids

Colloids may move with a velocity that is higher or lower than the mean groundwater velocity. However, as there are little data with which to assign *a priori* colloid velocities, we use the same velocity for colloids as for groundwater (40 m y^{-1}). In recent colloid tracer experiments, Wolfsberg and Reimus (2000) successfully employed unmodified colloid velocity and dispersion parameters derived from non-sorbing solute tracer experiments to their fitting of colloid breakthrough curves. We take as default for the value of colloid dispersion the value quoted by Grindrod *et al.* (1992), which was used in the COLLAGE II test phase. The value is $D^* = 140$ m^2 y^{-1}.

The partition coefficient for mobile colloids in COLLAGE II is defined by the radionuclide-colloid sorption coefficient and the suspended colloid load in groundwater (Equation (12)). The Yucca Mountain TSPA Viability Assessment again provides a good deal of information in this area (US DOE, 1998). There has been much experimental work in relation to colloids. A range of values is cited for the radionuclide-colloid sorption coefficient (K_p). US DOE (1998) considered 1- 1000 m^3 kg^{-1} to be an appropriate range for plutonium. For the default case we take $K_p = 100$ m^3 kg^{-1}, the same as is used in the KBS-3 calculations (Section 4).

Brachmann and Kersting (2000) give details of measurements carried out on groundwaters abstracted from wells in the NTS as part of the CHESHIRE test monitoring programme. The data presented are groundwater concentrations of colloids together with values for particle size. These data can be used to estimate the parameter, α_m [kg m^{-3}], used to derive the partitioning in COLLAGE II.

Table 3.1: Reference dataset for the representation of the BENHAM fracture. These data are used as the basis for the set of investigative COLLAGE II runs in Section 3.3. Shaded entries denote FEPs not modelled in this project.

Parameter	**Value**	**Units**	**Justification**
$\tilde{u}$	40	m y^{-1}	The NTS groundwater flow velocity is between 1 and 80 m a^{-1} (Blankennagel and Weir, 1973) and this represents a central value.
$\tilde{D}$	50	m^2 y^{-1}	Taken from Grindrod *et al*. (1992).
ϕ	0.02	-	Middle value of triangular distributions specified in Table 3-20 of Volume 3 of the TSPA-VA (US DOE, 1998).
λ	0.0	y^{-1}	In the 30-year time period considered, decay of ^{242}Pu is negligible.
R	10^6		Suitable value with ϕ and assuming rock density = 2.65×10^3 kg m^{-3} K_d of plutonium in the 5 - 10 m^3 kg^{-1}. This value is the same as is assumed in the KBS-3 modelling in Section 4.
D	7.875×10^{-4}	m^2 y^{-1}	Value used in calculations presented in Grindrod *et al*. (1992).
L	1300	m	This is consistent with there being no prompt injection and a direct connection between the explosion site and the measurement location, or prompt injection plus tortuosity of the flow path through a connected network of fractures.
b	5×10^{-5}	m	Geometric mean specified in Table 3-18 of Volume 3 of the TSPA-VA (US DOE, 1998).
n	1	-	Downstream boundary at 1,300 m.
u^*	40	m y^{-1}	Colloids may move with a velocity that is higher or lower than the mean groundwater velocity. However, as there are little data with which to assign *a priori* colloid velocities, we use the same velocity for colloids as for groundwater
D^*	140	m^2 y^{-1}	Taken from Grindrod *et al*. (1992).
k_1	5.9	-	Table 3.3.
k_2	0	-	Only mobile colloids considered.
κ_1	3	y^{-1}	See text.
κ_2	0	y^{-1}	Only mobile colloids considered.
β	0	-	Only mobile colloids considered.
η	0	-	All release assumed on colloids

Table 3.2: Colloid load in NTS groundwaters. Colloid density is assumed to be 2650 kg m^{-3}. Data from the CHESHIRE test monitoring programme (Brachmann and Kersting, 2000).

well	**particle size d_m [nm]**	**particle density N_m [particles m^{-3}]**	**colloid load α_m [kg m^{-3}]**
ER-20-5 #1	91	3×10^{16}	3.1×10^{-2}
ER-20-5 #3	81	8×10^{16}	5.9×10^{-2}

Table 3.3: Radionuclide partition coefficient, k_1, used in modelling the NTS case, based on the colloid load given in Table 3.2. The reference value for k_1 in the NTS modelling is 5.9, and is indicated in bold type.

		Colloid sorption coefficient, K_p [m^3 kg^{-1}]			
		1	10	100	1000
colloid load in groundwaters α_m [kg m^{-3}]	3.1×10^{-2}	3.1×10^{-2}	3.1×10^{-1}	3.1	31.0
	5.9×10^{-2}	5.9×10^{-2}	5.9×10^{-1}	**5.9**	59.0

The average colloid size is 91 nm (well reference: ER-20-5 #1) and 81 nm (ER-20-5 #3). In the two wells, ER-20-5 #1 has an average of 3.0×10^{10} particles ml^{-1} (3×10^{16} particles m^{-3}) and ER-20-5 #1 has 8×10^{10} particles ml^{-1} (3×10^{16} particles m^{-3}). These data are summarised in Table 3.2.

The groundwater-colloid load is therefore given by:

$$\alpha_m = N_m \rho_m v_m = \frac{1}{6} N_m \rho_m \pi d_m^3 \tag{14}$$

where the number of mobile colloids is N_m [particles m^{-3}], ρ_m [kg m^{-3}] is the density of the free colloidal material, v_m [m^3] is the volume of each particle, and d_m [m] is the diameter of the particles. With these values, a range of k_1 values for use in COLLAGE II calculations is shown in Table 3.3.

There are many uncertainties in this database. At this stage it was not felt that the role of fixed colloids could be reasonably investigated owing to a lack of data. The presence of mobile colloids may be relatively easily determined in groundwater samples. However, by definition these are mobile rather than immobile colloids, which are bound to the rock and are therefore not extracted. The tendency for colloids to attach to fracture walls can be demonstrated in the laboratory but it is another matter to infer suitable values for deep hydrogeochemical conditions. For these reasons we assume no fixed colloids and set the immobile colloid parameters, k_2 and β, to be equal to zero. Similarly we set the sorption/desorption rate onto immobile colloids (κ_2) to be equal to zero.

The kinematic aspects of COLLAGE II are an important part of the code. Grindrod and Cooper (1993) tested the model with a range of values. Colloid modelling work in relation to radioactive waste performance assessments in the past decade has assumed reversible and irreversible sorption (e.g., Allard *et al*., 1991; Nagra, 1994; JNC, 2000). Recent DOE research has provided information on rate constants for the sorption of actinides on colloids. These data can be used to set COLLAGE II rate parameters.

Lu *et al*. (2000) have recently studied the adsorption of actinides onto colloids. Part of the investigation involved measuring both the rate of adsorption and desorption onto a variety of colloidal materials (hæmatite, montmorillonite and silica) in natural and synthetic groundwaters. The results allow suitable estimates of the COLLAGE II parameter, κ_1 [y^{-1}], to be inferred. Values for the radionuclide-colloid sorption coefficient are also determined. The plot is reproduced in Figure 3.1.

In the experiments of Lu *et al*. (2000), the kinetics of adsorption to colloids are complex and rates of sorption and desorption are not necessarily of the same form as assumed in the COLLAGE II mathematical model. For montmorillonite in natural groundwaters, only around 50% of the Pu (V) had been sorbed after 240 hours and there was an increasing trend which, if extrapolated to 100%, would imply

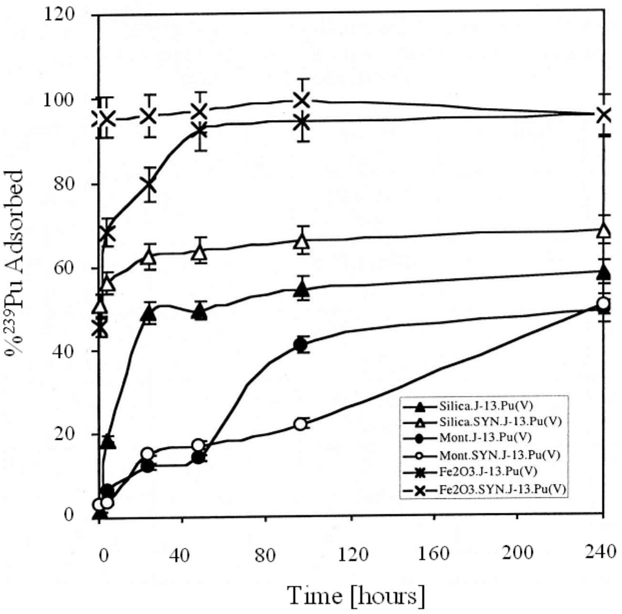

Figure 3.1: Kinetics of plutonium - groundwater interactions (from Lu *et al.*, 2000). The percentage of ^{239}Pu adsorbed onto colloids in a variety of natural and synthetic groundwaters. Montmorillonite in natural groundwater is used as the basis for the selection of a sorption/desorption rate of 3 y^{-1}.

$\kappa_1 = 3\ y^{-1}$. More detailed interaction was observed on timescales of a few tens of hours ($\approx 900\ y^{-1}$). Sorption onto silica was also observed not to have reached equilibrium by the end of the experiments at 240 hours, though results for hæmatite indicated equilibrium at around 100 hours ($\approx 90\ y^{-1}$). Over the timescale of these experiments, the K_p distribution coefficient for Pu was around 100 $m^3\ kg^{-1}$ for hæmatite but only 5.8 $m^3\ kg^{-1}$ for montmorillonite.

Based on the results of Lu *et al.* (2000), a value of $\kappa_1 = 3\ y^{-1}$ is adopted for plutonium. From these results there is no evidence that the rate would be significantly slower, but a faster rate is possible. The US DOE (1998) values for K_p were considered applicable since they are derived from similar rock types under comparable conditions to those at the BENHAM site. For the calculations a value of 100 $m^3\ kg^{-1}$ (as in the KBS-3 modelling) was used.

The experiments were carried out using colloid concentrations of 200 mg $litre^{-1}$ (0.2 $kg\ m^{-3}$). This is higher (by a factor of 3 to 6) than the groundwater colloid concentrations measured by Brachmann and Kersting (2000). It is not clear if this has any influence on the K_p value or the kinetics.

As mentioned above, the exact nature of the source term is not clear. In the reference cases calculated we assume that all radionuclides are input to the fracture already attached to colloids, so that $\eta = 0$, except in case *NTS_ref_NC* where it is assumed that there is no colloidal material present in the fracture and radionuclides are released and transported in solution. Other cases in which radionuclides are released in solution only are listed in Table 3.5 and for these cases, $\eta = 1$. The colloid parameters are summarised together with the fracture values in Table 3.1.

3.3 Results

The reference data in Table 3.1 allows a number of informative cases to be run. Results are summarised in Figure 3.2. These concentrate on the reference dataset (*NTS_ref*), for which both the flux on colloids and in solution are plotted, and two variant cases, summarised in Table 3.4. In the first of these (*NTS_ref_NC*), it is assumed that there is no colloidal material present in the fracture and that radionuclides are released and transported in solution. There is a strong interaction with the fracture walls and retardation is effective to the extent that the breakthrough would peak beyond 10^{10} years and at low levels.

In the second (*NTS_ref_irrev*), all radionuclides are assumed to be released on colloidal material but there is irreversible sorption so that there is no desorption into solution. All radionuclides are transported on colloids, and there are no radionuclides in solution. Breakthrough is comparatively rapid. Unfortunately, in this case, numerical instabilities in the COLLAGE II output are apparent. While it is possible to identify that the colloids contribute to a fairly high flux at times around 30 years, it is not possible to identify clearly the centroid of the initial peak. The tail of the release is similarly noisy[1].

With the large difference in behaviour between the two extremes, it is clear that the role of the sorption/desorption rate (κ_1) is of interest. Another feature of the modelling is that it is assumed that the release is on colloids. There remains the alternative possibility that the Pu has entered the system in solution and has subsequently become attached to colloids.

Two series of additional results have been calculated (summarised in Table 3.5) which explore the role of the rate constant κ_1 and the release form - radionuclides on colloids or in solution. A range of sorption rates has been studied with $10^{-3} \leq \kappa_1 \leq 10^3$ y^{-1}. To contrast with the reference case assumption, the second set of runs assumes that all radionuclides are input in solution, with transfer to colloids by sorption/desorption.

The total flux released is shown in Figure 3.3 (release on colloids) and Figure 3.4 (release in solution).

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[1] The peak can be smoothed but only if the colloid dispersion coefficient $D^* \geq 1000$ m^2 y^{-1}. Using this value of D^* resolves the peak but it has not been included because the value is unrealistically high.

Table 3.4: Variations on the NTS reference case dataset considered in the investigation of the properties of the COLLAGE II representation of the NTS system.

Case	characteristics/comments
NTS_ref	The reference case as defined in Table 3.1.
NTS_ref_NC	Data as in Table 3.1, no colloids ($k_1 = \kappa_1 = 0.0$), Release in solution ($\eta = 1.0$).
NTS_ref_irrev	Reference case data set (Table 3.1) with irreversible sorption ($\kappa_1 = 0.0$), all release on colloids ⇒ no release in solution.

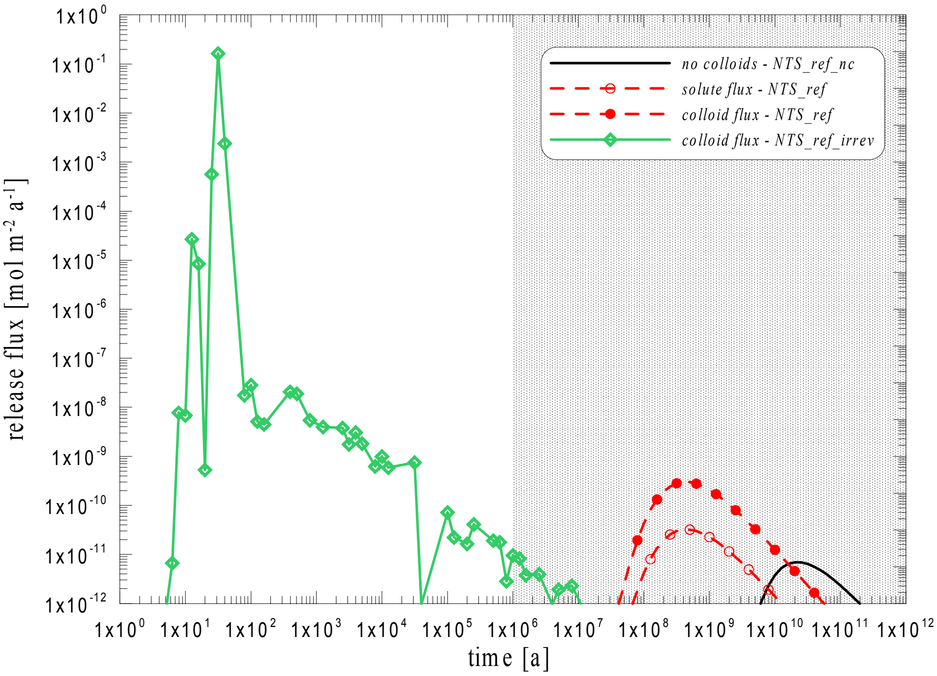


Figure 3.2: Plutonium transport in the NTS reference fracture for a variety of conditions. With no colloids present in the system, releases would occur far into the future as a consequence of the high retardation assumed for Pu in solution on fracture surfaces. The shaded region indicates times greater than one million into the future and demonstrates that releases with no colloids have little significance in terms of performance assessment.

Table 3.5: Summary of NTS simulation test cases investigating the role of sorption/desorption kinetics and the form of the release to the fracture. Modifications with respect to the reference case in Table 3.1 are noted.

	case	**characteristics**
release on colloids	*NTS_k1_1e-3*	$\kappa_1 = 10^{-3}$ y^{-1}, $\eta = 0.0$
	NTS_k1_1e-2	$\kappa_1 = 10^{-2}$ y^{-1}, $\eta = 0.0$
	NTS_k1_1e-1	$\kappa_1 = 10^{-1}$ y^{-1}, $\eta = 0.0$
	NTS_k1_1	$\kappa_1 = 1$ y^{-1}, $\eta = 0.0$
	NTS_k1_10	$\kappa_1 = 10$ y^{-1}, $\eta = 0.0$
	NTS_k1_100	$\kappa_1 = 100$ y^{-1}, $\eta = 0.0$
	NTS_k1_1e2	$\kappa_1 = 10^{3}$ y^{-1}, $\eta = 0.0$
release in solution	*NTS_k1_rs_1e-3*	$\kappa_1 = 10^{-3}$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_1e-2	$\kappa_1 = 10^{-2}$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_1e-1	$\kappa_1 = 10^{-1}$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_1	$\kappa_1 = 1$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_10	$\kappa_1 = 10$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_100	$\kappa_1 = 100$ y^{-1}, $\eta = 1.0$
	NTS_k1_rs_1e2	$\kappa_1 = 10^{3}$ y^{-1}, $\eta = 1.0$

3.4 Discussion

Figure 3.2 shows that the reference case (open circles) cannot reproduce the NTS observations. After 30 years, the colloid concentration is vanishingly small, much lower than the concentrations of Pu on colloids reported by Kersting *et al.* (1999). The reference case data set does indicate that colloid-facilitated transport could have an effect on both the colloid-borne and solute fluxes of Pu at the end of the fracture but only at times very far into the future (> 500 million years). There is a two order of magnitude increase in the peak release compared to the case with no colloids but the result is still at a very low level. Given that plutonium-bearing colloids have apparently travelled 1.3 km in 30 years at the NTS, and are present in detectable quantities, it is clear that the reference dataset does not represent the observations satisfactorily.

The fourth curve in Figure 3.2 (diamonds) illustrates an alternative model calculation in which colloids do transport radionuclides over the 1.3 km distance from the BENHAM test to the sampling point. In this example, radionuclides must enter the fracture *in colloidal form* and the kinetics of desorption must proceed at very low rates compared to those inferred from the work of Lu *et al.* (2000).

In Figure 3.3, a range of curves for various values of κ_1 is shown, with radionuclide release exclusively on colloids. These suggest that for κ_1 in the range 10^{-3} to a few times 10^{-2} y^{-1}, an early peak in the release flux may be anticipated. If κ_1 is 0.1, the initial peak is no longer seen and above around $\kappa_1 = 1.0$ y^{-1} there is no early breakthrough at all.

The results plotted in Figure 3.4 are for the case in which all radionuclides are released in solution. In model runs where the release is in solution, it is generally not possible to obtain an early peak. Nevertheless, some breakthrough of radionuclides at early times is still observed, for κ_1 in the range 10^{-3} to 10^{-1}. It is therefore possible that the NTS inferences of rapid Pu transport could also be associated with release in solution, and sorption/desorption at a rate of around 10^{-2} y^{-1}.

Note that if the release of Pu were in solution and the sorption irreversible ($\kappa_1 = 0.0$), there would then be no release on colloids and no colloid-born plutonium would have been detected. For release in solution, the only results predicting rapid transport of Pu are for the limited range of κ_1 specified above. These results suggest that the BENHAM test probably introduced radionuclides into the fracture that were already associated with colloids.

No breakthrough curve has been measured at the BENHAM observation wells to date but, were it possible to measure it in future, the rate of change of plutonium concentration could be used to better constrain the source term. If the fall-off were rapid, it would correspond to the situation in Figure 3.3 and might add additional support for the suggestion that the release was probably on colloids. If the fall-off was slower, the representation in Figure 3.4 could be more appropriate, and this might add support for the input of plutonium being in solution.

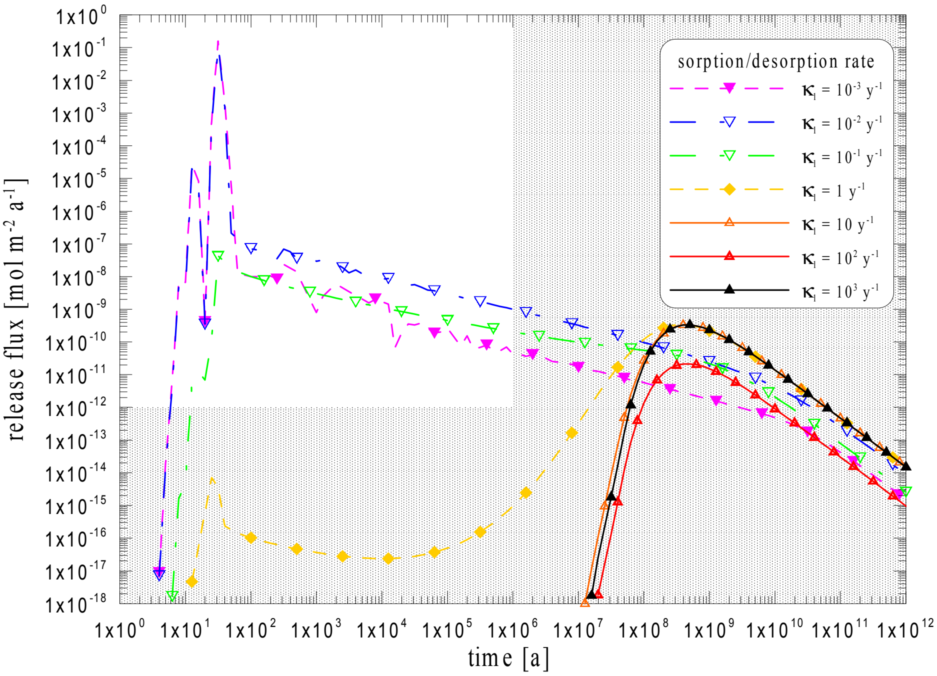


Figure 3.3: Influence of radionuclide-colloid sorption/desorption rate on radionuclide release flux (solute + colloid) at the NTS. Case of all radionuclide release *on colloids*.

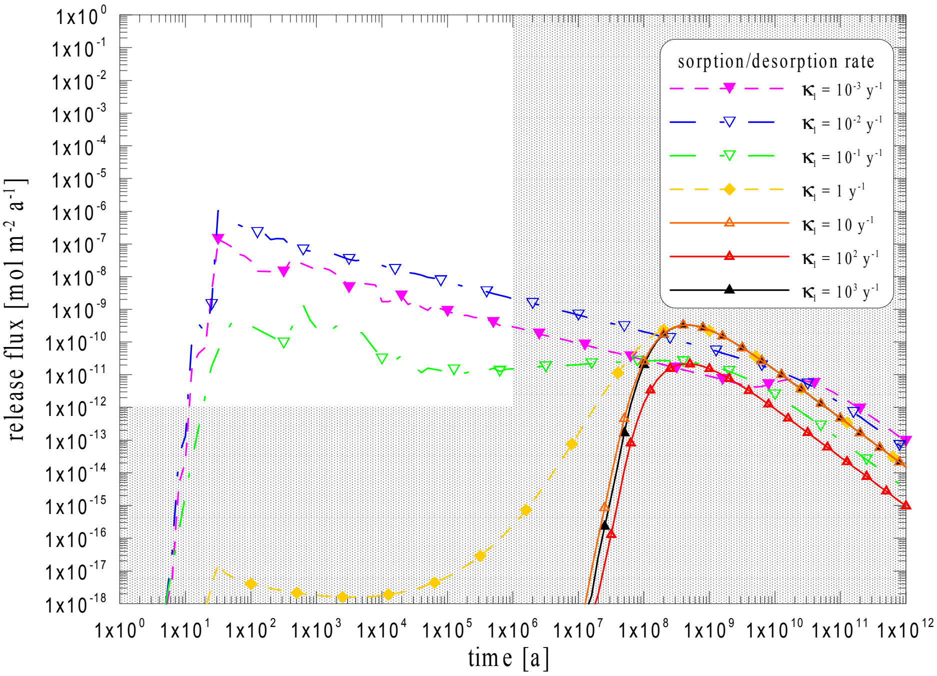


Figure 3.4: Influence of radionuclide-colloid sorption/desorption rate on radionuclide release flux (solute + colloid) at the NTS. Case of all radionuclide release *in solution*.

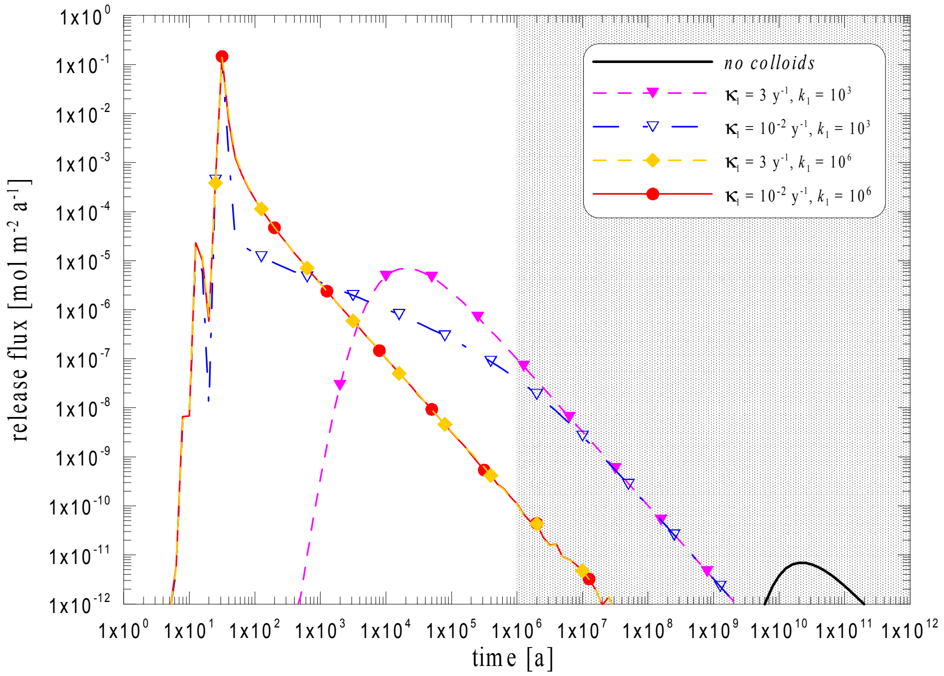


Figure 3.5: COLLAGE II output for artificially increased values of the partitioning coefficient k_1. In these examples the value of k_1 is at a level not supported by observed data for undisturbed geospheres (see text). Release flux shown is solute + colloid.

It is possible that the underground nuclear explosion gave rise to abundant colloid-sized particles, effectively instantaneously. Such a theory is supported by the relatively high colloid concentrations observed at the NTS by Brachmann and Kersting (2000), which are in excess of the theoretical limit of 0.01 kg m^{-3} suggested by Degueldre (1994) on the basis of groundwater hydrogeochemistry. This could be represented in COLLAGE II by increasing the partitioning parameter k_1. The high values at the NTS may represent a groundwater system perturbed from its natural state by the nuclear detonations and it may be the case that the groundwater colloid loads will return to a lower level with time.

Two alternatives are considered in Figure 3.5: $k_1 = 10^3$ and $k_1 = 10^6$. Both cases are plotted for the reference sorption/desorption rate: $\kappa_1 = 3\ y^{-1}$ and for $\kappa_1 = 10^{-2}$. In the case of very high k_1 (10^6), an early pulse occurs with either value of the sorption/desorption parameter. With $k_1 = 1000$, an early peak only occurs with the low value of κ_1.

The likelihood of such high values of the partitioning coefficient is open to question. Degueldre's (1994) work implies $k_1 \approx 1$ is an upper limit. The high values of k_1 in Figure 3.5, although possibly representative of conditions subsequent to an underground nuclear test, cannot meaningfully be applied to conditions in an undisturbed geosphere.

If the BENHAM test generated large amounts of colloids, under such circumstances it might be imagined that colloids would become rapidly attached to the fracture walls and that the colloid load would change with time. However, this process is not currently represented in COLLAGE II and the scenario cannot be explored quantitatively.

A scenario in which radionuclides are introduced into the fracture only on colloids is the favoured modelling option for explaining the NTS interpretation of km-scale Pu-colloid transport in 30 years. This, combined with a low sorption/desorption rate, is the most likely explanation of the BENHAM observations. Without access to a reasonable breakthrough curve for plutonium on colloids in the NTS wells, this is as far as the current analysis can go. The implications of this analysis for Swedish waste disposal assessments are considered in the following section.

4 The Potential Influence of Colloids in Swedish PAs

4.1 Background

Svensk Kärnbränslehantering AB (SKB) has responsibility for disposal of Sweden's radioactive waste. For the disposal of spent nuclear fuel, SKB has developed the KBS-3 concept. In the KBS-3 concept, SKB plans that after 30 to 40 years of interim storage, spent fuel will be placed in copper canisters, surrounded by a bentonite buffer, and disposed at a depth of about 500 m in crystalline bedrock.

The KBS-3 repository for spent nuclear fuel is composed of a system of barriers. The fuel is placed in copper canisters, surrounded by a layer of bentonite clay. The clay provides mechanical protection, and limits access of groundwater and corrosive substances to the canisters. The bentonite also adsorbs radionuclides that may be released from the canisters, and filters colloids that may form within the repository.

Kurosawa *et al*. (1997) indicate that any colloidal material generated in the near-field will be effectively filtered by the bentonite layer. Any radionuclides migrating through the bentonite will therefore probably enter groundwater flow systems in solution rather than already attached to colloids. This provides a contrast with our consideration of the NTS system, in which we suggest that the radionuclides were probably released in colloidal form. COLLAGE II can represent cases in which the radionuclides are initially dissolved, or are initially colloidal, using the parameter η, the fraction of the radionuclide release in solution.

The repository host rock in Sweden is granite whereas at the NTS it is volcanic tuff. Nevertheless, Wickham *et al*. (2000) compared the mineralogy of the two sites and found that they are similar, though texturally contrasting. Radionuclide transport properties may also be similar in the two systems. Retardation will be higher in the KBS-3 granite because the matrix porosity is lower than the NTS tuff (10^{-5} compared with 0.02), although retardation is already high in the NTS dataset.

The aim of the analysis presented in this section is to discover regions of parameter space where colloids might play a role. In order to achieve this objective, both deterministic and probabilistic sensitivity analyses have been carried out. Attention again focuses on plutonium which, as an actinide, is expected to sorb strongly to colloids (Degueldre, 1994). Other actinides tend to have similar properties, and are discussed in Section 4.4.

4.2 Colloid Transport in the KBS-3 Concept

4.2.1 Model Parameterisation

In this section we describe how we have parameterised the COLLAGE II model so that it can be used to represent the transport of plutonium through the fractured geosphere present in the KBS-3 disposal concept. The basis for our parameterisation is derived from the geosphere modelling carried out by Lindgren and Lindström (1999) in the SR97 assessment using the geosphere code FARF31, which considers a one-dimensional representation of a planar fracture.

The SR97 assessment considers three hypothetical sites. The geosphere transport properties of these sites differ principally in terms of the fracture flow path length considered in the assessment. For this analysis we choose the shortest of these - the *Aberg* site - as the basis for the representation of the fracture.

One way in which the FARF31 and COLLAGE II mathematical models differ is in the way in which the total flow in the fracture is represented. In SR97 the *F*-ratio is used, which is the product of the groundwater travel time and the *flow-wetted surface area per unit volume of water*. The *F*-ratio is related to the fracture aperture half-width (b [m]) used by COLLAGE II and may be used to account for transport in multiple fractures. As COLLAGE II considers only a single fracture, we use the data in Table 3-14 of Lindgren and Lindström (1999) in which two fractures are defined, one with width 10^{-4} m, and the other with width 5×10^{-4} m. For COLLAGE II we use $2b = 2\times10^{-4}$ m on this basis.

In the KBS-3 concept, the repository is at a depth of 500 m and the simplest assumption is for a fracture of this length reaching down to the excavation disturbed zone (EDZ) and through which water can flow. There is no discussion of the relevant flow path length in Lindgren and Lindström (1999), and we therefore take a path length $L = 500$ m.

The groundwater travel time corresponds to 500 m in ten years, according to Lindgren and Lindström (1999). However, Appendix 1 of Skagius *et al.* (1999) quotes a porewater velocity of $u_p = 30\ \mathrm{m\ y^{-1}}$ and this has been adopted as the base case value. There is scope for alternative values but the implications for solute transport are not particularly important (see Section 4.3).

Lindgren and Lindström (1999) quoted a Peclet number of 10 and this is similar to assessments elsewhere. Nagra (1994) used this value to define dispersion despite the misgivings about the low value (cf. de Marsily, 1986). The relationship:

$$P_e = \frac{L}{a_L}\ [\text{-}], \qquad (15)$$

is used, where the dispersivity is a_L (longitudinal dispersivity). L is the flow path length, as above. With this relationship, the dispersivity for COLLAGE II is $L/P_e = 500/10 = 50$. Hence, the dispersion coefficient is given by

$$\widetilde{D} = du_D = d\varepsilon_{flow}u_p = \varepsilon_{flow}u_p\frac{L}{P_e} = \frac{1\cdot13\times10^{-3}\times30\times500}{10} = 1.695\ \mathrm{m^2\ y^{-1}}, \qquad (16)$$

where the flow porosity ε_{flow} [-] is 1.13×10^{-3} (Lindgren and Lindström, 1999).

K_d values for plutonium are taken from Lindgren and Lindström (1999). For Pu, the rock diffusivity is quoted as 4×10^{-14} m^2 s^{-1}. The rock K_d of Pu is 5 m^3 kg^{-1}. Together with the rock matrix porosity of 5×10^{-3}, this gives a retardation factor of 2.69×10^6. The rock density quoted is 2.7×10^3 kg m^{-3}.

The parameter values used in the COLLAGE II modelling are summarised in Table 4.1.

It is assumed here that there are no immobile colloids. This simplifies the task of data selection because the colloid component of the model is based on the release form, the velocity and dispersion parameters for the colloidal particles, the partitioning of radionuclides in solution, and the sorption/desorption rate.

Following the analysis given by Grindrod (1989), it is assumed here that colloids move in the centre of the flow channel and so the mean velocity is higher than for the water flow averaged across the aperture. The ratio of colloid velocity to water velocity has been set at 1.3:1. The alternative use of $\tilde{u} = u^*$ was employed in the NTS calculations, corresponding to the assumption of Wolfsberg and Reimus (2000). Here we took the higher value from Grindrod (1989) so as to be able to exercise an additional feature of the conceptual model. However, in the probabilistic sensitivity analysis (Section 4.3) the use of the factor of 1.3 instead of 1.0 is shown to be relatively unimportant.

Values for the dispersion coefficient are taken from Grindrod and Cooper (1993). Values for the kinetics of sorption/desorption are based on the review of Lu *et al.* (1999) as discussed in Section 3.2.2; the rate assumed is $\kappa_1 = 3$ y^{-1}.

Given the nature of the release from the bentonite buffer in the KBS-3 concept, it is assumed that all radionuclides enter the fracture already in solution so that (in contrast to some of the NTS calculation cases) $\eta = 1.0$.

As there are no immobile colloids, all parameters relating to them are set to zero.

Radionuclides are assumed to enter the fracture in solution and it may therefore be assumed that the colloidal content of the fracture groundwater is unperturbed from its natural state. Laaksoharju *et al.* (1995) have noted that the concentrations in typical Swedish groundwaters are very low. Colloid concentration may be estimated based on local hydrogeochemical conditions (Degueldre *et al.*, 2000). Currently the conditions are somewhat saline. The possibility of increased colloid loads may be associated with an influx of non-saline waters under a future glacial melting scenario. However, the impact is not expected to be large.

Table 4.1: Reference dataset for the representation of an *Aberg* fracture in COLLAGE II. Shaded entries denote FEPs not modelled in the project.

Parameter	**Value**	**Units**	**Justification**
$\tilde{u}$	30.0	m y^{-1}	Skagius *et al*. (1999)
$\tilde{D}$	1.695	m^2 y^{-1}	Lindgren and Lindström (1999), based on a Peclet number of 10.
ϕ	5×10^{-5}	-	Lindgren and Lindström (1999).
λ	1.86×10^{-6}	y^{-1}	Value for ^{242}Pu (Lindgren and Lindström, 1999).
R	2.69×10^{6}	-	Derived from other properties. Matrix k_d and rock density from Lindgren and Lindström (1999).
D	1.262×10^{-6}	m^2 y^{-1}	Lindgren and Lindström (1999).
L	500	m	Lindgren and Lindström (1999).
b	10^{-4}	m	Single fracture interpreted from Lindgren and Lindström (1999), Table 3-14.
n	1	-	Downstream boundary at end of fracture, see Section 3.2.1.
u^*	39.6	m y^{-1}	Assumes that colloids move in centre of the aperture
D^*	4.746	m^2 y^{-1}	Using ratio of 140/50 relative to $\tilde{D}$, cf. Grindrod & Cooper, (1993)
k_1	2.0×10^{-3}	-	See text for details.
k_2	0	-	Only mobile colloids considered.
κ_1	3.0	y^{-1}	Default value from the Yucca Mountain analysis (see Section 3.2.2)
κ_2	0	y^{-1}	Only mobile colloids considered.
β	0	-	Only mobile colloids considered.
η	1.0	-	All release assumed in solution - see text.

Table 4.2: Values for colloid load (α_m) in a variety of fractured granites. The reference case is denoted by the bold type.

source	μg ml^{-1}	kg m^{-3}	comments
Assumed for sensitivity analysis	0.002	2.0×10^{-6}	extreme low range - factor of 10 lower than saline case
	0.0045	4.5×10^{-6}	factor of 10 lower than non-saline case
Laaksoharju *et al.* (1995)	**0.02**	$\mathbf{2.0\times10^{-5}}$	50 - 500 nm, saline groundwaters (present day)
	0.045	4.5×10^{-5}	non-saline groundwaters - glacial meltwater dilution
Assumed for sensitivity analysis purposes	0.2	2.0×10^{-4}	high range for Swedish conditions - factor of 10 higher than saline case
	0.45	4.5×10^{-4}	high range for Swedish conditions - factor of 10 higher than non-saline case
Degueldre (1994)	0.1	1.0×10^{-4}	lower detection limits for Swiss granites
	0.4	4.0×10^{-4}	lower detection limits for Swiss granites Canadian, French and Spanish
	10	1.0×10^{-2}	value quoted for special circumstances of very low Na and Ca content in groundwaters

Table 4.3: Values of the radionuclide - colloid partition coefficient (k_1) for a range of radionuclide - colloid sorption coefficients (K_p) and colloid loads (α_m). The reference case value for saline conditions is indicated in bold type.

	α_m [kg m^{-3}]					
K_p [m^3 kg^{-1}]	$\mathbf{2.00\times10^{-6}}$	$\mathbf{4.50\times10^{-6}}$	$\mathbf{2.00\times10^{-5}}$	$\mathbf{4.50\times10^{-5}}$	$\mathbf{2.00\times10^{-4}}$	$\mathbf{4.50\times10^{-4}}$
0.1	2.0×10^{-7}	4.5×10^{-7}	2.0×10^{-6}	4.5×10^{-6}	2.0×10^{-5}	4.5×10^{-5}
1	2.0×10^{-6}	4.5×10^{-6}	2.0×10^{-5}	4.5×10^{-5}	2.0×10^{-4}	4.5×10^{-4}
10	2.0×10^{-5}	4.5×10^{-5}	2.0×10^{-4}	4.5×10^{-4}	2.0×10^{-3}	4.5×10^{-3}
100	2.0×10^{-4}	4.5×10^{-4}	$\mathbf{2.0\times10^{-3}}$	4.5×10^{-3}	2.0×10^{-2}	4.5×10^{-2}
10^3	2.0×10^{-3}	4.5×10^{-3}	2.0×10^{-2}	4.5×10^{-2}	2.0×10^{-1}	4.5×10^{-1}
10^4	2.0×10^{-2}	4.5×10^{-2}	2.0×10^{-1}	4.5×10^{-1}	2.0	4.5
10^5	2.0×10^{-1}	4.5×10^{-1}	2.0×10^{0}	4.5×10^{0}	20.0	45.0

Table 4.2 summarises the information concerning colloid load in fractured granites. Specifically for Swedish fractures, Laaksoharju *et al.* (1995), citing Allard *et al.* (1991), assumed 0.02 μg ml^{-1} for colloidal particles under present-day saline conditions and 0.045 μg ml^{-1} for less saline conditions. The difference in the two colloidal concentrations is small. Table 4.2 also adds some higher and lower values suitable for consideration in sensitivity analyses.

As discussed above, K_p values for plutonium are taken from Lindgren and Lindström (1999), and this together with the colloid concentration, determine the partition coefficient, k_1. Table 4.3 illustrates the choice of a suitable value for k_1. As noted above, the reference case is defined by Table 4.1. Alternative parameter values for additional cases studied are summarised in Table 4.4.

4.2.2 Model Results and Discussion

Figure 4.1 shows breakthrough curves for the no-colloid case and saline and non-saline groundwaters. These results indicate that the no-colloid case has a long delay before radionuclides arrive at the end of the fracture. This is a consequence of high retardation. Based on similar results, Laaksoharju *et al.* (1995) concluded that colloids would be unlikely to play a major role in the transport of radionuclides through fractures. The reference case results for saline groundwaters show that the flux is predominantly in solution with only a small contribution on colloids. Even in the case of non-saline groundwaters, the picture is virtually unchanged, and it is difficult to distinguish the three solute fluxes, which give almost identical results.

However, experience in the modelling of the NTS system implies that kinetic effects might potentially influence the nature of the breakthrough curve. A sequence of cases for different low values of κ_1 were run, as summarised in Table 4.4. All cases were run for the release of radionuclides in solution. The resulting breakthrough curves are shown in Figure 4.2.

With slow kinetics of sorption/desorption, it is possible to obtain peaks at early times that are comparable in magnitude to the peak at later times. This is illustrated in Figure 4.3. Early releases occur over a relatively restricted range of low values of κ_1. At these low rates, even if all plutonium is initially released in solution, a small amount is able to associate with colloids. Because of the slow rate of disassociation, this plutonium is then able to be carried significant distances along the fracture before being released into solution, where it is rapidly sorbed onto mineral surfaces.

If sorption kinetics are consistent with κ_1 being in the range 10^{-3} to 10^{-1} yr^{-1}, then early releases may be seen, although the actual rate values quoted here are specific to the particular length- and time-scales analysed.

Table 4.4: Variations on the KBS-3 reference case. All release in solution. Parameters modified with respect to the reference case (Table 4.1) are indicated.

	case	Characteristics
fast sorption / desorption rate	*KBS3_ref_nc*	$\kappa_1 = 0.0$ y^{-1}, $k_1 = 0.0$, no colloids
	KBS3_ref_s	$\kappa_1 = 3.0$ y^{-1}, $k_1 = 2.0\times10^{-3}$, saline conditions
	KBS3_ref_ns	$\kappa_1 = 3.0$ y^{-1}, $k_1 = 4.5\times10^{-3}$, non-saline conditions
variable sorption / desorption rate*	*kap_a*	$\kappa_1 = 10^{-3}$ y^{-1}, $k_1 = 2.0\times10^{-3}$
	kap_f	$\kappa_1 = 10^{-2}$ y^{-1}, $k_1 = 2.0\times10^{-3}$
	kap_k	$\kappa_1 = 10^{-1}$ y^{-1}, $k_1 = 2.0\times10^{-3}$
	kap_p	$\kappa_1 = 1.0$ y^{-1}, $k_1 = 2.0\times10^{-3}$
	kap_u	$\kappa_1 = 10$ y^{-1}, $k_1 = 2.0\times10^{-3}$

Note:

* Twenty-seven test cases were run *kap_a* - *kap_z* plus *kap_peak*. The dataset was that given in Table 4.1 with κ_1 logarithmically distributed 5 per decade over the range $10^{-3} \leq \kappa_1 \leq 10$ y^{-1}, with *kap_peak* having $\kappa_1 = 8\times10^{-2}$.

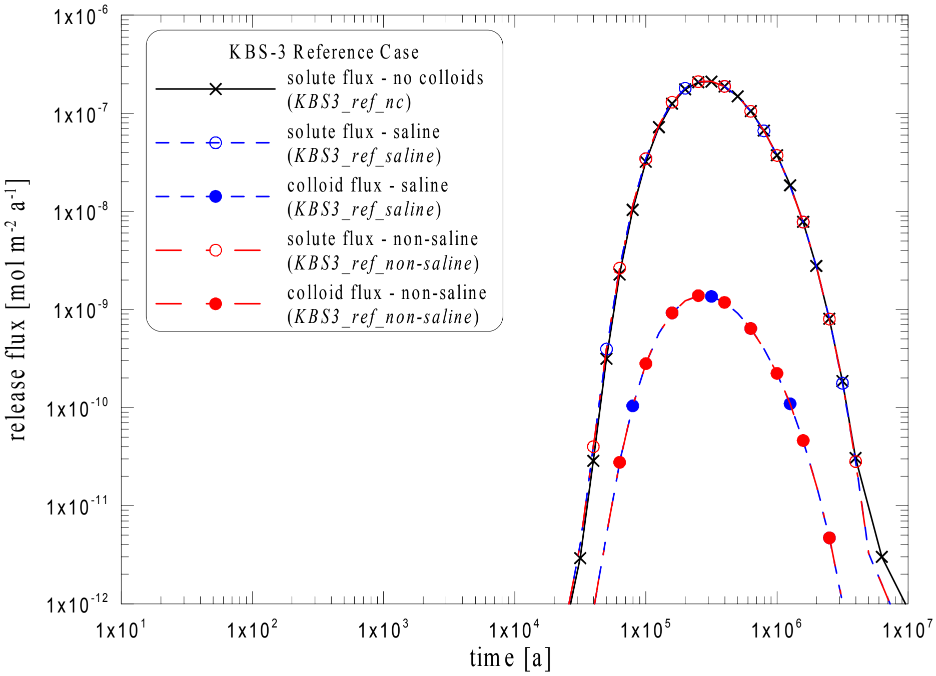


Figure 4.1: Results for the KBS-3 reference case. Fast sorption/desorption kinetics (κ_1 = 3 y^{-1}), radionuclide release in solution.

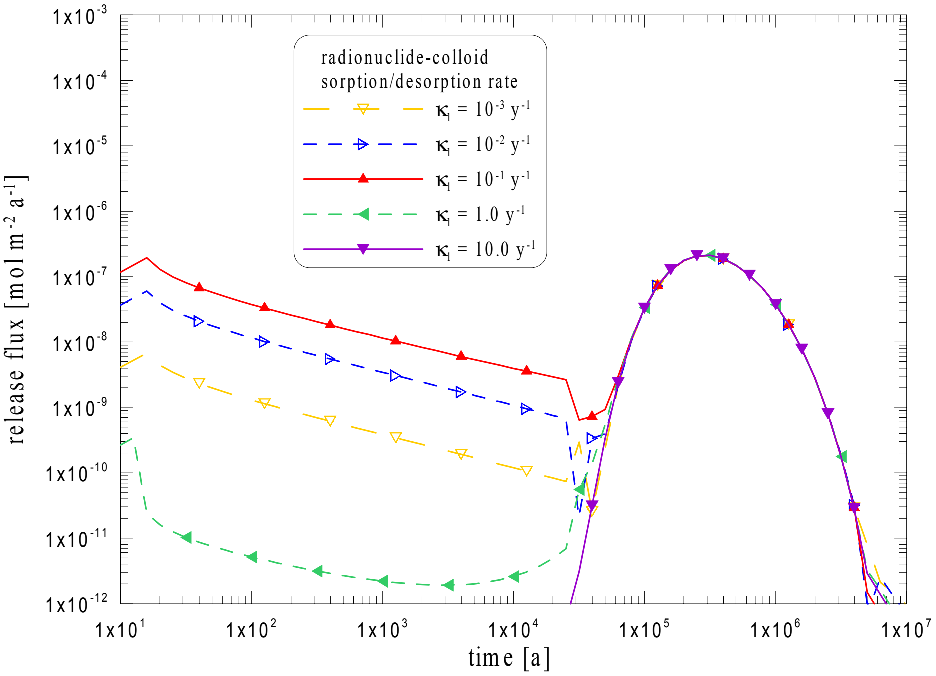


Figure 4.2: Effect of low values of the sorption/desorption rate, κ_1, on plutonium breakthrough curve. Release in solution with all other parameters at reference values (cf. Figure 4.1).

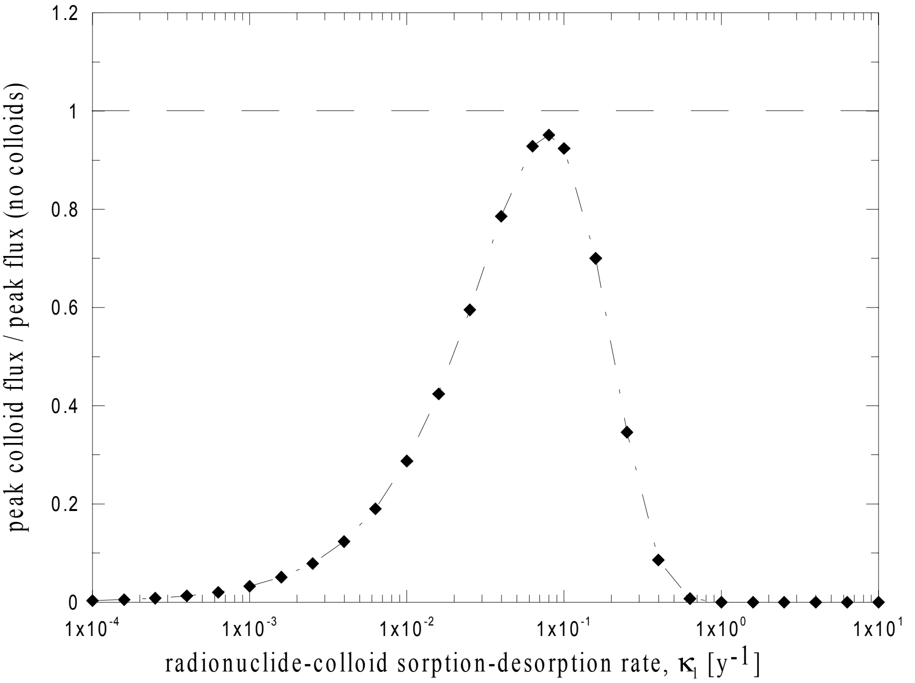


Figure 4.3: Effect of sorption - desorption rate (• $_1$) on the colloid-born release at 12.6 years for the KBS-3 dataset. Flux on colloids at 12.6 years is normalised to the peak solute flux seen in the no-solute case (*KBS3_ref_nc*). The maximum early release peak is for $\kappa_1 = 0.08\ y^{-1}$.

Figure 4.3 illustrates that there are two regions, one each side of the peak, where κ_1 has values implying that there would be no significant radionuclide transport by colloids:

1) If radionuclides are initially in solution and sorption was very slow or irreversible ($\kappa_1 \sim 0.0$), as represented by the extreme left of Figure 4.3, then radionuclides would be virtually unable to sorb to colloids. Colloids would therefore play no role in radionuclide transport.

2) If sorption/desorption was rapid ($\kappa_1 > 1$), as represented by the right of Figure 4.3, colloids would be sorbed and desorbed from colloids rapidly enough for sorption on the fracture walls to effectively retard radionuclide transport.

Between these regions is a critical range of values of κ_1 for which colloids are able to carry plutonium a significant distance along the fracture.

If $\kappa_1^{(sorption)} \neq \kappa_1^{(desorption)}$ more complex effects might be anticipated. However, the mathematical model in COLLAGE II does not allow this to be modelled. Modifications to COLLAGE II would be needed to evaluate the effects of differential sorption rates.

4.3 Probabilistic Sensitivity Analysis

The key parameters in the COLLAGE II model may all exhibit considerable variation. A probabilistic sensitivity analysis has been conducted to identify those combinations that give rise to more significant colloid-facilitated radionuclide transport.

4.3.1 Model Parameterisation

The Sandia Latin-Hypercube Sampling code (LHS) of Iman and Shortencarrier (1984) was used to generate 1000 LHS samples based on variations of the parameters, as discussed below. Simple ranges were used in all cases and loguniform distributions employed.

Seven parameters were varied; the justification of the values selected is given in Table 4.5. Those parameters relating to the fracture itself were not varied. These include the flow velocity and dispersion coefficient of the solute. The fracture half-width was also kept constant as were the rock matrix porosity and path length. Matrix porosity influences the retardation of radionuclides in solution. However, as this is also determined by radionuclide rock K_d, it was the K_d that was varied in order to vary retardation.

4.3.2 Model Results and Discussion

The Kolmogorov-Smirnov test has been used to determine the sensitivity of the model to the values of the parameters considered. In this test, the output distribution is split at the median of the input parameter to be tested, and the cumulative distribution function (cdf) of the two parts of the output are calculated. Two parameters are calculated, the absolute difference of the cdfs for the upper and lower parts of the input distribution, and the probability that the two cdfs are the same.

The results (Table 4.6) show that the key model input determining the impact of the system is the partition parameter k_1. This parameter was not sampled directly, but is itself dependent on two sampled parameters, the radionuclide - colloid sorption coefficient (K_p) and the mobile colloid concentration (α_m) in the water in the fracture. The importance of k_1 comes as no surprise - the more colloids there are and the more strongly radionuclides bind to them, the more the peak total flux increases.

To illustrate the influence of K_p and α_m further, scatter plots of peak total flux in the no-colloid case vs. sorption coefficient and colloid load are shown in Figure 4.4. The time of peak is plotted against K_p in Figure 4.5. Figure 4.6 illustrates the influence of κ_1 on the time of peak flux.

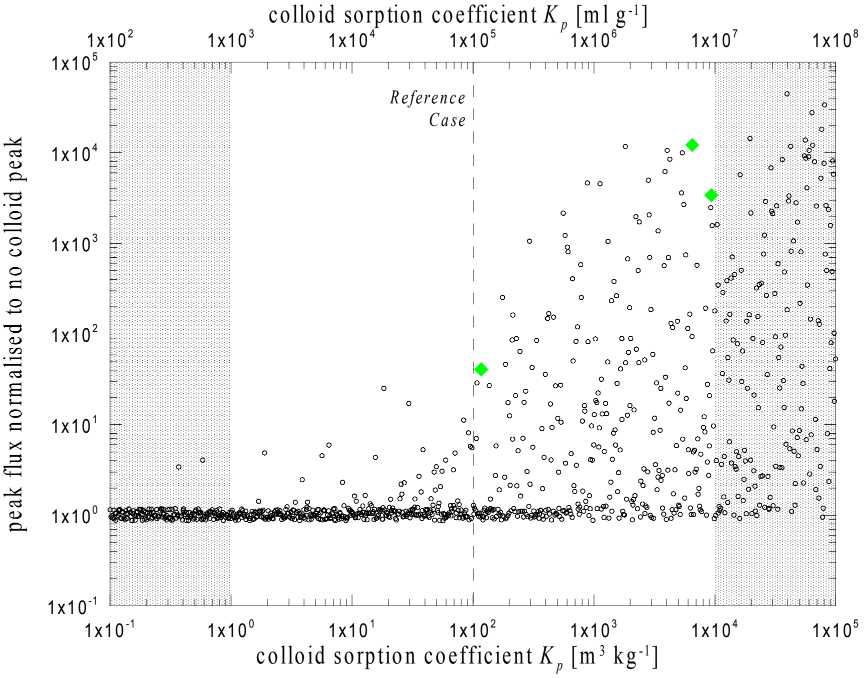
Table 4.5: List and justification of parameters sampled in the probabilistic sensitivity analysis.

Model parameter	**Comments and justification**	**Sampled pdfs and ranges**
u^* [m y^{-1}]	Colloid transport velocity. Grindrod (1989) noted that the ratio of mean colloid to mean water velocities is 1.32. This is used as a central figure and one order of magnitude on either side is allowed for a scaling factor.	scaling factor - loguniform: 0.132 - 13.2
D^* [m^2 y^{-1}]	Mobile colloid dispersion coefficient. Grindrod *et al.* (1993) suggested that the ratio is $\tilde{D}/D^*$ = 140/50. This is used to define D^* in the reference case. In these calculations a scaling factor is used with one order of magnitude on either side of the value of the solute dispersion coefficient.	scaling factor - loguniform: 14/50 - 140/5 m^2 y^{-1}
R [-]	Rock matrix retardation coefficient. Well defined in terms of the rock matrix K_d: $R = 1 + \frac{1-\phi}{\phi}\rho K_d$.	rock K_d - loguniform: 4.5 - 5.5.
k_1, k_2 [-]	Partition parameters. These COLLAGE II parameters are combinations of sorption coefficients and the colloid load in the groundwater (Section 2.4): $k_1 = \alpha_m K_p$ and $k_2 = \alpha_f K'_b$. The range for K_p is consistent with the data observed by Lu *et al.* (2000) and takes into account the data set out by Degueldre (1994), but extends the range by an order of magnitude on either side. The range of groundwater colloid concentrations is determined by the range identified in Table 4.2.	K_p - loguniform: $0.1 \le K_p \le 10^5$ m^3 kg^{-1} α_m - loguniform: $0.002 \le \alpha_m \le 0.45$ kg m^{-3} $K'_b = K_p$ - perfect correlation α_f - defined by parameter β: $\alpha_f = \beta\alpha_m$.
β [-]	Ratio of mobile to immobile colloids. The number of *immobile colloids* is very uncertain. It is not clear how their numbers may be estimated from groundwater analyses carried out by Laaksoharju *et al.* (1995) or Brachmann and Kersting (2000). Degueldre *et al.* (2000) do not address immobile colloids in their review of groundwater and colloids. A broad range is therefore assumed corresponding to situations where there are fewer mobile colloids to situations where there are more immobile than mobile colloids.	loguniform: $10^{-6} \le \beta \le 10^3$
κ_1, κ_2 [y^{-1}]	Sorption/desorption rate coefficients for mobile and immobile colloids. From the deterministic sensitivity analysis carried out above, the sorption/desorption rate for mobile colloids was assigned a range 10^{-3} - 10^3 per year. Given the uncertainties in the treatment of immobile colloids, the same range is set and a perfect correlation is assumed.	κ_1 - loguniform $10^{-3} \le \kappa_1 \le 10^3$ y^{-1}, $\kappa_2 = \kappa_1$.

Table 4.6: Analysis of the probabilistic sensitivity analysis of plutonium transport in a KBS-3 fracture. Kolmogorov-Smirnov test with the input distribution split at the median of the output quantity. Absolute difference in cdf and the probability of the two distributions being the same are shown. Large negative probability of difference (high negative number) and large difference indicate sensitivity. Key values are shown in bold type and are shaded. Results for 1000 LHS samples.

	KS-difference			$\log_{10}$ (KS-probability)		
	Peak total flux	Time of peak total flux	Colloid flux to total flux ratio at time of peak	Peak total flux	Time of peak total flux	Colloid flux to total flux ratio at time of peak
Scaling factor for colloid velocity (u^*)	0.2	0.2	0.2	-7	-7	-5
Scaling factor for colloid dispersion (D^*)	0.0	0.0	0.1	0	0	-1
Radionuclide - colloid sorption K_p (mobile & immobile colloids)	**0.6**	**0.6**	**0.7**	-85	-81	-95
Mobile colloid load in groundwater, α_m	0.3	0.3	0.3	-23	-21	-25
Radionuclide - mobile colloid partitioning factor, k_1	**0.8**	**0.7**	**0.9**	-139	-111	-160
Colloid immobile to mobile population, β	0.0	0.1	0.1	0	-2	-1
Radionuclide - immobile colloid partitioning factor, k_2	0.4	0.3	0.4	-35	-26	-38
Sorption/desorption rate for mobile and immobile colloids, κ_1	0.1	0.3	0.2	-3	-15	-13
Radionuclide - rock matrix sorption coefficient, K_d	**0.5**	0.4	0.1	-62	-44	-1
Rock matrix retardation factor, R	**0.5**	0.4	0.1	-61	-43	-1

(a) radionuclide - colloid sorption coefficient, K_p. Extreme ranges of K_p are indicated by shading.



(b) mobile colloid load in fracture groundwater, α_m.

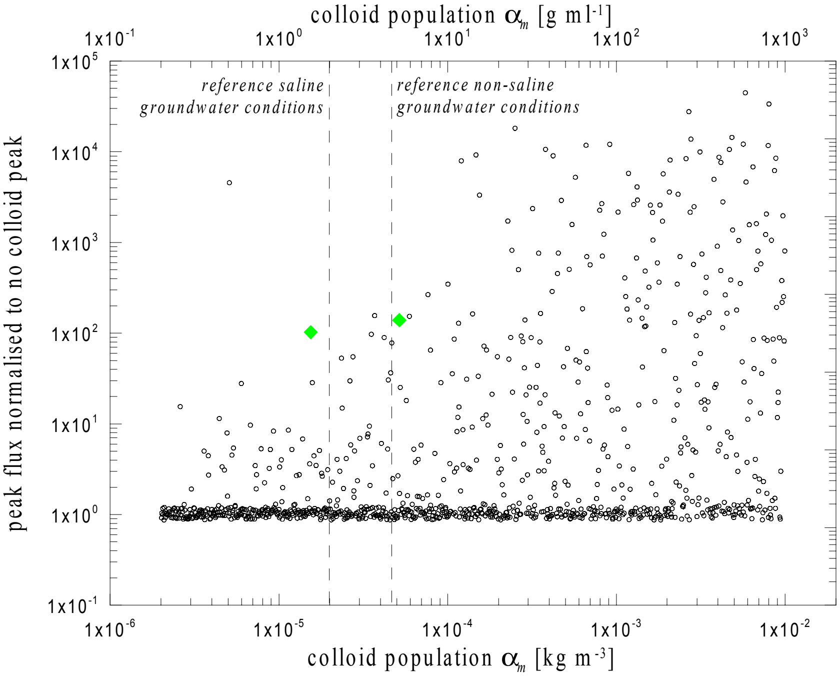


Figure 4.4: Scatter plots of key parameters showing their influence on peak total release flux. Significance of green diamonds is discussed in the text.

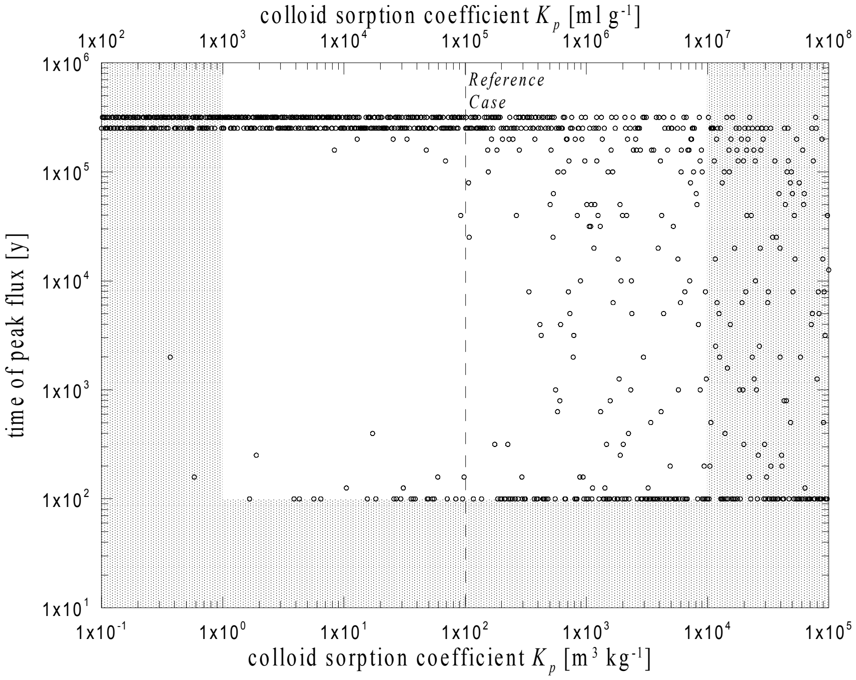


Figure 4.5: Scatter plots of time of peak release vs. radionuclide - colloid sorption coefficient, K_p. Extreme ranges of K_p are indicated by shading as is the region for $t < 100$ years.

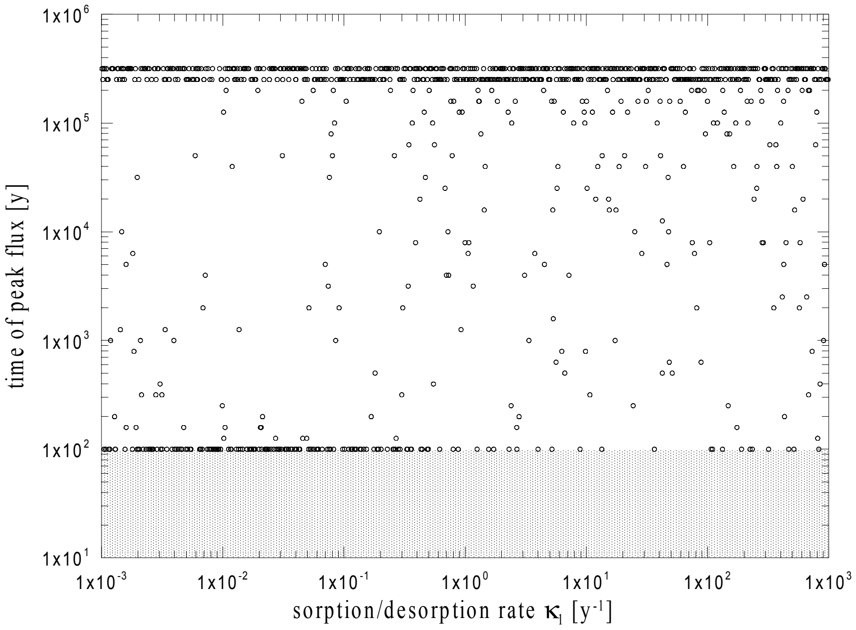


Figure 4.6: Scatter plots of time of peak release vs. sorption/desorption rate, κ_1. The region for time < 100 years is shaded.

Figure 4.4 shows that there is a tendency for colloid transport cases to result in the same peak flux value as in the no-colloid case (normalised flux = 1.0). Only at higher values of K_p than the reference case value do many of the points separate from this level, indicating that the presence of colloids causes higher radionuclide release fluxes (Figure 4.4 (a)). Similar comments apply to Figure 4.4 (b) at α_m values above the reference value for non-saline groundwater, where the separation from the normalised flux = 1.0 starts at low values under the influence of high K_p.

As noted, Table 4.6 indicates that the radionuclide-colloid sorption coefficient, K_p, has the most influence on peak release of all of the individually sampled parameters. In Figure 4.4 (a), at the highest end of the reasonable range, the green diamond at around 10^4 m^3 kg^{-1} gives a flux which is around 5000 times higher than the peak flux in the no-colloid case. Similarly, a slightly smaller K_p value gives a peak release over ten thousand times higher. In addition to high K_p, these two runs also have fairly high values of the colloid load (α_m) - more than a hundred times the non-saline colloid load in the reference case.

Also of interest is the case that has $K_p = 1.17\times10^2$ m^3 kg^{-1} (17% higher than the reference case). For $\alpha_m = 6.54\times10^{-3}$ kg m^{-3} (350 times higher than the saline reference case), the peak release is around fifty times higher than in the no-colloid case. For this run, the colloid sorption/desorption rate is near the critical value determined in Figure 4.3 at 1.9×10^{-2}.

Two points are singled out in Figure 4.4 (b), corresponding to values of colloid load close to the saline and non-saline reference values. They show values of peak release around a factor of 100 higher than the no-colloid case. Each corresponds to a run with very high K_p values - respectively 9.7×10^4 and 1.8×10^4 m^3 kg^{-1} - which are above the reasonable region. One of these runs has κ_1 in the critical region identified in Figure 4.3 ($\kappa_1 = 4\times10^{-2}$ y^{-1}). Thus, the results plotted in Figure 4.4 (b) suggest that for typical Swedish groundwater colloid loads (α_m), the radionuclide - colloid sorption coefficient, K_p, is effectively the only parameter that can significantly affect colloid transport.

The sorption/desorption rate (κ_1) is not indicated in Table 4.6 as being particularly important in its influence on the timing and magnitude of release, despite the fact that the analysis reported in Sections 3.3 and 4.2 might suggest otherwise. This is because it has not been possible to extend the probabilistic analysis to times earlier than 100 years, due to numerical difficulties in COLLAGE II at earlier times. In many model calculations, we have found that the peak release in the colloid case is earlier than in the no-colloids case, and its magnitude is less than or similar to the peak with no colloids. Had it been possible to run the probabilistic case from ten years, it is likely that many of the peaks would have been before 100 years, and the effect of κ_1 may have been more prominent. Individual runs were possible starting before this time and these have been analysed separately below. The 100-year effective working limit is indicated in Figure 4.5 and Figure 4.6 by the shaded region, which denotes $t < 100$ years.

In Figure 4.5 and Figure 4.6, the clustering of points around the same peak-flux value as in the no-colloid case (approximately 3×10^5 years) indicates that the output times requested in the COLLAGE II runs were discretised. The true time of peak flux is probably somewhere between the two bands of points indicated in the plots.

Results for some individual runs in the probabilistic sample set were able to yield results at early times <100 years. For example, one run (#30) had $K_p = 5.4\times10^3$ m^3 kg m^{-1}, $\alpha_m = 3\times10^{-5}$ (mid-way between saline and non-saline cases) and $\kappa_1 = 2.6\times10^{-3}$ y^{-1}. These figures correspond to a reasonable colloid load and sorption/desorption rate in the critical region. The plot of release flux vs. time for this run is shown in Figure 4.7. The run is of interest because it demonstrates an early colloid release flux (green points) that is around two orders of magnitude higher than the solute flux. The value of K_p is 54 times higher than the reference value from Degueldre (1994). While this is quite high, it is not unreasonable.

4.3.3 Key Parameter Sets

Our analyses have identified three key parameters that determine the likely impact of radionuclide transport by colloids:

- Radionuclide-colloid sorption coefficient (K_p).
- Suspended colloid load (α_m).
- Sorption/desorption rate (κ_1).

Consideration of the results described above suggest that it may be useful to define a range of parameter sets relevant to colloid-facilitated transport in Swedish fractures. The sets are determined in terms of the three key parameters and are summarised in Table 4.7. Results illustrating the most pessimistic cases for radionuclide transport by colloids are plotted in Figure 4.8.

The eight parameter sets distinguish themselves by variations in K_p (100 - 5000 m^3 kg^{-1}), in the groundwater colloid load associated with saline and non-saline conditions (respectively 2×10^{-5} and 4.5×10^{-5} kg m^{-3}), and in the rate constant (κ_1). Figure 4.8 shows that for fast sorption/desorption ($\kappa_1 = 3.0$ y^{-1}), the peak flux is barely enhanced by a factor of two, with a slightly earlier peak. If, conversely, the kinetics are slow ($\kappa_1 = 0.08$ y^{-1}), there is the potential for a significantly higher release at times < 1,000 years. The COLLAGE II code is not able to resolve the peak. However, a factor of 50 (saline case) is possible, rising to over 100 in the non-saline case.

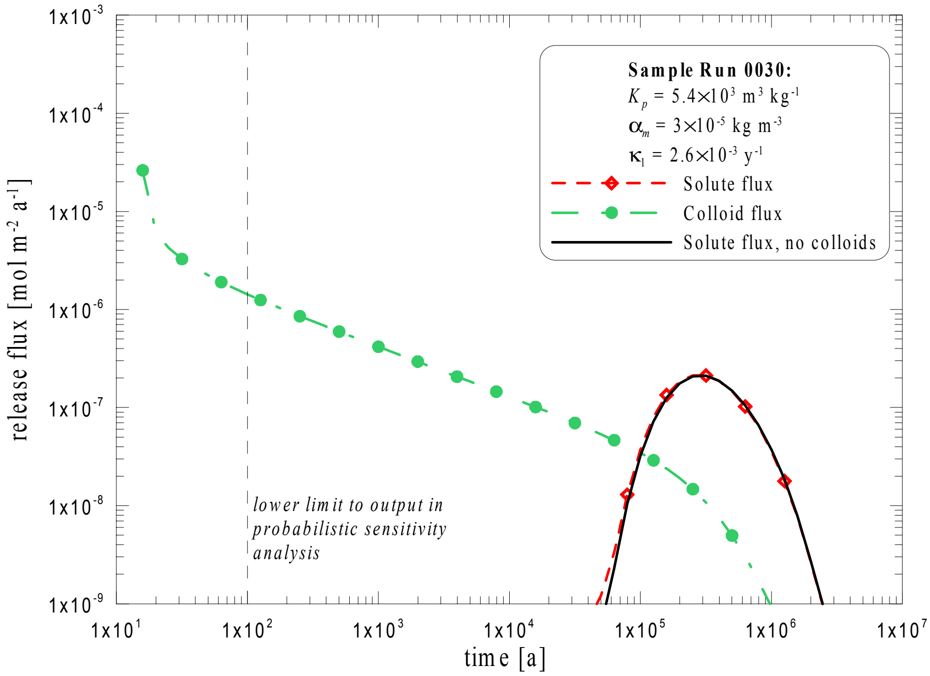


Figure 4.7: Colloid and solute fluxes from sample run 30 compared to the case with no colloids. The combination of parameters represents colloid sorption, colloid load and colloid kinetics within a reasonable range. Enhanced transport on colloids by up to two orders of magnitude is seen.

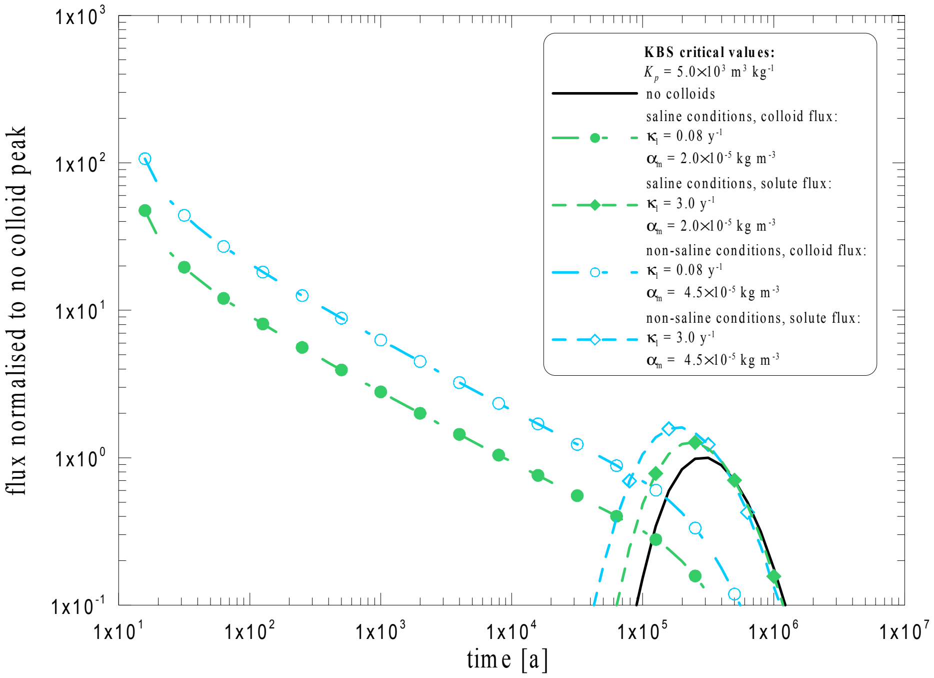


Figure 4.8: Identification of pessimistic case colloid transport parameters for groundwater conditions and colloid populations defined by Swedish saline and non-saline groundwaters.

Table 4.7: Key parameters characterising plutonium transport in Swedish fractures in the KBS-3 concept. Reference and early breakthrough cases.

Parameter			Comments
Best estimate case - present-day groundwater conditions			
K_p - colloid sorption coeff.	100	[m^3 kg^{-1}]	Degueldre (1994)
α_m - mobile colloid load	2×10^{-5}	[kg m^{-3}]	Saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	3	[y^{-1}]	Interpretation of Lu *et al.* (2000)
Best estimate case - future non-saline groundwater conditions			
K_p - colloid sorption coeff.	100	[m^3 kg^{-1}]	Degueldre (1994)
α_m - mobile colloid load	4.5×10^{-5}	[kg m^{-3}]	Non-saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	3	[y^{-1}]	Interpretation of Lu *et al.* (2000)
Saline groundwater conditions - low sorption/desorption rate (BC3)			
K_p - colloid sorption coeff.	100	[m^3 kg^{-1}]	Degueldre (1994)
α_m - mobile colloid load	2×10^{-5}	[kg m^{-3}]	Non-saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	0.08	[y^{-1}]	Peak value, early release (Section 4.2.2)
Best estimate case - future non-saline groundwater conditions			
K_p - colloid sorption coeff.	100	[m^3 kg^{-1}]	Degueldre (1994)
α_m - mobile colloid load	4.5×10^{-5}	[kg m^{-3}]	Non-saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	0.08	[y^{-1}]	Peak value, early release (Section 4.2.2)
High early release case - present-day groundwater conditions			
K_p - colloid sorption coeff.	5000	[m^3 kg^{-1}]	Section 4.3.2
α_m - mobile colloid load	2×10^{-5}	[kg m^{-3}]	Saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	3	[y^{-1}]	Interpretation of Lu *et al.* (2000)
High early release case - future non-saline groundwater conditions			
K_p - colloid sorption coeff.	5000	[m^3 kg^{-1}]	Section 4.3.2
α_m - mobile colloid load	4.5×10^{-5}	[kg m^{-3}]	Non-saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	3	[y^{-1}]	Interpretation of Lu *et al.* (2000)
High early release case - Saline groundwater conditions - low sorption/desorption rate			
K_p - colloid sorption coeff.	5000	[m^3 kg^{-1}]	Section 4.3.2
α_m - mobile colloid load	2×10^{-5}	[kg m^{-3}]	Non-saline conditions (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	0.08	[y^{-1}]	Peak value, early release (Section 4.2.2)
High early release case - Best estimate case - future non-saline groundwater conditions			
K_p - colloid sorption coeff.	5000	[m^3 kg^{-1}]	Section 4.3.2
α_m - mobile colloid load	4.5×10^{-5}	[kg m^{-3}]	Non-saline cond. (Laaksoharju *et al.*, 1995)
κ_1 - sorption/desorp. rate	0.08	[y^{-1}]	Peak value, early release (Section 4.2.2)

4.4 Other Radionuclides

Plutonium has been considered in the numerical assessment carried out here for a number of reasons. First, it is an important component of the KBS-3 spent fuel source term. Second, it is clearly associated with colloids at the NTS. Third, there is a useful body of knowledge relating to plutonium and its interaction with colloids. It is therefore sometimes used as a surrogate for the other actinides in the sense that many of the properties are similar, and our aim is to establish significant areas of parameter space where colloid-mediated effects might be seen.

SR97 (Lindgren and Lindström, 1999) indicates that plutonium and the actinides do not play a significant role in determining dose because they are not released to the biosphere in sufficient quantities. Indeed, Lindgren and Lindström (1999) calculated little release of plutonium from the near-field. The enhanced potential for the release of colloidal plutonium outlined here could certainly lead to higher doses from ^{242}Pu but, to assess this properly, the release from the near-field in Figure 4.1 of Lindgren and Lindström (1999) would need to be used as an input to the COLLAGE II code.

Other radionuclides are released from the near-field, including ^{226}Ra, ^{237}Np and ^{229}Th. These nuclides have similar behaviour to plutonium. They all appear in the release at late times but retardation in the far-field means that they do not play a significant role in the determination of dose. The analysis performed in this study suggests that higher radionuclide-colloid sorption coefficients might lead to increased dose. The data given by Degueldre (1994) suggest that the actinides all have similar but uncertain K_p values.

For groundwater colloid concentrations relevant to Swedish fractures, the K_p values suggested by Degueldre might lead to an early peak in the release flux when combined with slow sorption/desorption rates. Lu *et al.* (2000) have considered the kinetics of a number of actinides in addition to Pu (Am, Np, and U) but the experiments were all conducted over a timescale for which the critical range of κ_1 is probably not detectable. Enhanced transport of these radionuclides leading to release from KBS-3 fractures at times comparable to the groundwater travel time cannot be ruled out. The potential impact in PAs cannot be fully assessed without enhancements to existing capabilities for representing colloids in PA.

The other radionuclides indicated as relevant in SR97 (Lindgren and Lindström, 1999) are either anions (^{129}I, ^{36}Cl) or are otherwise not strongly sorbed to colloids (^{135}Cs, ^{59}Ni, ^{79}Se - see Degueldre, 1994).

5 Conclusions

The main objective of this project was to investigate the potential role of colloids in the KBS-3 concept, taking account of recent developments in the study of radionuclide transport by colloids.

The understanding of colloid transport and dynamics arising from a review of current colloid research activities in the US, combined with the analysis of the BENHAM observations from the NTS, implies that **colloids could play a more important role than previously recognised in the KBS-3 concept** if similar processes operated. This is in contrast to earlier PA modelling in the context of radioactive waste management (e.g., Nagra, 1994; Laaksoharju *et al*., 1995). The conditions under which significant transport might arise have been identified and the range of parameters determined.

5.1 Modelling Plutonium Transport at the Nevada Test Site

Study of groundwater in the vicinity of the BENHAM test at the NTS has detected Pu at a point 1.3 km downstream from the source. The Pu is currently associated with colloids. Isotopic measurements have established that the Pu definitely came from the BENHAM test, which was conducted over 30 years ago. Plutonium is generally fairly immobile in groundwater systems, and it has been suggested that colloids may have caused the plutonium to be transported 1.3 km in only 30 years. This hypothesis has been tested by modelling plutonium transport in a fracture with similar characteristics to those present in the vicinity of the BENHAM test.

Recently published data from both the ongoing NTS site investigation and from the Yucca Mountain Project have been used to define a COLLAGE II dataset. The kinetics of radionuclide-colloid sorption and desorption have been found to be crucial in explaining the transport of plutonium associated with colloids, as inferred at the NTS. Specifically, it has been found that for plutonium to have been transported by colloids over the full 1.3-km transport path, it is likely that the plutonium was released in colloidal form and that the rate of plutonium desorption from colloids must have been slow.

The results obtained suggest that a programme of future monitoring observations would be necessary in order to properly understand colloid transport associated with the BENHAM test. If future observations at the NTS indicate a relatively short-lived pulse of Pu-bearing colloids, then it is likely that the Pu-bearing colloids were generated at the time of the nuclear explosion and that they have migrated through fractures in the intervening years. If the fall-off in colloid concentration at the observation wells is slow, and no peak is clearly resolved, our results imply that the plutonium on the colloids became attached during transport from the detonation point.

On the balance of the available evidence, we consider that the most appropriate interpretation of the BENHAM observations is that:

- Most of the plutonium inventory was released into the fracture on colloids.
- Plutonium - colloid interaction kinetics at the NTS proceeded at a rate less than 0.1 y^{-1}.

5.2 Colloids in Swedish PA

COLLAGE II has been used to evaluate the possible role of radionuclide transport by colloids in the Swedish KBS-3 disposal concept. Sensitivity analyses using parameter values relevant to Swedish fractures and groundwater hydrogeochemistry, combined with lessons from modelling the NTS observations, imply that colloid-facilitated transport of plutonium could be significant for the KBS-3 concept if:

1) Groundwater colloid concentrations are at or above observed levels.

2) Plutonium sorption to colloids is as strong as is currently estimated,

3) Pu - colloid sorption/desorption rates (κ_1) are in a critical range from 0.02 to 0.2 per year.

A combination of these factors could lead to releases of colloidal radionuclides at similar levels to releases estimated in previous PA studies, but at a much earlier time.

Early releases will only occur over a relatively restricted range of low Pu - colloid sorption/desorption rates. At these low rates, even if all plutonium is initially released in solution following diffusion through the bentonite buffer, a small amount is able to associate with groundwater colloids. Because of the slow rate of disassociation, this plutonium is then able to be carried significant distances on colloids before being released to solution, where it is rapidly sorbed onto mineral surfaces.

The key to our results is the dynamic representation of radionuclide - colloid interactions in COLLAGE II. Earlier performance assessments have not modelled these interactions dynamically and so have not accounted explicitly for the kinetics of radionuclide-colloid sorption.

We recommend, therefore, that a full PA-type calculation is made involving the $4N + i$ decay chains and including the near-field source term as input. This would help to assess the potential for colloid-facilitated transport to affect PA results.

On the basis of the COLLAGE II modelling carried out in this project, the relevant ranges of key parameters likely to give rise to early releases of radionuclides bound to colloids are:

- Radionuclide - colloid sorption - K_p: $100 \leq K_p \leq 5000$ m^3 kg^{-1}. $K_p = 5000$ m^3 kg^{-1} is suitable for scoping calculations and is consistent with the values cited by Degueldre (1994).
- Colloid load in groundwater - α_m: $2\times10^{-5} \leq \alpha_m \leq 0.01$ kg m^{-3}.
- Radionuclide - colloid sorption/desorption rate - κ_1: $0.02 \leq \kappa_1 \leq 0.2$ y^{-1}.

A set of eight reference parameter sets have been suggested for future use in the assessment of the impact of colloid-facilitated transport in Swedish fractures.

Published data on present-day Swedish groundwater hydrogeochemistry, and colloid sorption kinetic data, suggest the following values: radionuclide - colloid sorption coefficient, $K_p = 100$ m^3 kg^{-1}, groundwater colloid load (saline conditions) $\alpha_m = 2\times10^{-5}$ kg m^{-3}, and plutonium - colloid sorption/desorption rate κ_1 of the order 1 to 10 y^{-1}.

Modified colloid loads arising from an inflow of non-saline glacial meltwater might result in $\alpha_m = 4.5\times10^{-5}$ kg m^{-3}, and our analysis indicates that at this value of α_m, if the sorption/desorption rate is 0.08 y^{-1}, then there is the potential for colloid-born release at early times.

Disposal concepts that do not employ bentonite may also give rise to significantly higher groundwater concentrations of colloids, because there is no bentonite to filter waste- and repository-derived colloids. Moreover, in cementitious repositories, colloids may be generated as a result of the interaction of the near-field with the far-field. Higher concentrations of colloids may also occur for specific scenarios, such as earthquake or human intrusion scenarios involving breaching or degradation of the bentonite buffer. These are in most cases likely to be transient effects that will require further investigation before their potential PA impact can be assessed.

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