Strål
säkerhets
myndigheten
Swedish Radiation Safety Authority

Authors: Richard Kłos
Adrian Bath

Research

2010:08

Development of COLLAGE 3

Report number: 2010:08 ISSN: 2000-0456
Available at www.stralsakerhetsmyndigheten.se

Title: Development of COLLAGE 3
Report number: 2010:08
Author: Richard Kłos and Adrian Bath; Aleksandria Sciences, UK; Intellisci Ltd., UK
Date: December 2009

SSM Perspective

Background

The issue of colloid-facilitated radionuclide transport (CFRT) was last addressed by the Swedish nuclear regulators (SKI at that time, now integrated into SSM) in 2001 – 2002. SKI had commissioned the Collage code with subsequent development as Collage 2. This code was employed to investigate the potential role for colloids to have been involved in the transport of radionuclides at the Nevada Test Site and to examine the implications for CFRT in the Swedish disposal programme. It was concluded that colloids could not be ruled out as a mechanism for rapid transport and early release from the geosphere.

Recently the “bentonite erosion scenario” has become of concern. In it the generation of large quantities of bentonite colloids in fractures as a result of fresh water ingress at repository depth is possible. Potentially, these could carry radiologically significant quantities of radionuclides to an early release to the surface system.

Objectives of the project

The objectives of this work are to update the knowledge of colloid-facilitated radionuclide transport through a fractured geosphere and to provide review capability within the SSM.

Results

Recent developments in CFRT (reviewed here) indicate that additional parameters needed to be added to the existing Collage 2 plus code in order to adequately represent colloid transport in Swedish fractures.

This report looks at modifications to the model and discusses the implications of the implementation of the new processes. Authors conclude that the process of colloid filtration is an important mitigating mechanism. A new code – Collage 3 – is demonstrated and suggestions for further work are given.

Project information

Project manager: Shulan Xu
Project reference: SSM 2009/2590 and 2009/2591
Project number: 1693 and 1794

Content

1. Introduction

The issue of colloid-facilitated radionuclide transport (CFRT) was last addressed by the Swedish nuclear regulators (SKI at that time, now integrated into SSM) in 2001 – 2002. SKI had commissioned the COLLAGE code (Grindrod *et al*., 1992) with subsequent development as COLLAGE 2 (Grindrod & Cooper, 1993). This code was employed by Kłos *et al*. (2002) to investigate the potential role for colloids to have been involved in the transport of radionuclides at the Nevada Test Site and to examine the implications for CFRT in the Swedish disposal programme. It was concluded that colloids could not be ruled out as a mechanism for rapid transport and early release from the geosphere. A subsequent revision to the numerical solution method employed in COLLAGE 2 gave rise to the COLLAGE 2 plus code (Kłos, 2003) which exhibited more stable results, particularly at early times. Recently there has been interest in the "bentonite erosion scenario", where ingress of fresh water at repository depth during deglaciation could lead to the erosion of bentonite with the subsequent generation of large numbers of colloids. Coupled to a release of radionuclides from a damaged canister, there is scope for CFRT with potentially greater radiological consequences than in scenarios identified previously.

Since the early parts of the decade there has been ongoing work on the characterisation and quantification of CFRT, primarily in the context of the yucca Mountain project. The process of filtration/straining of colloid particles due to the geometry of the fracture through which water flows has emerged as an important factor. Other processes not directly implemented in COLLAGE 2 plus are also known to be important.

This report has been produced with the aims of

i. assessing how the COLLAGE 2 conceptual model could incorporate the newly identified FEPs,
ii. providing a preliminary assessment of the potential importance of the bentonite erosion scenario, and
iii. identifying the options and requirements for developing the COLLAGE 2 plus to take into account the new information.

In the event, the COLLAGE 2 framework has been successfully modified to deal with the process of filtration/straining) and, at the same time differential rates of sorption / desorption have been include. The current model is COLLAGE 3, though the current version of the code should be thought of as a fully functioning prototype.

Section 2 of this report details recent developments in CFRT which led to the requirement to revise the dynamics modelled in COLLAGE 2 plus. Section 3 describes the revised interpretation of the COLLAGE 2 equations and their modification to address some of the issues identified in Section 2, leading to a new implementation of CFRT in the COLLAGE framework. Section 4 illustrates the results from COLLAGE 3 dealing with the representation of a typical Swedish fracture into which a pulse of radionuclide bearing colloids has been injected. The results, with parametric sensitivity analyses, indicate the importance of the rate parameter commonly used in CFRT to describe the process of filtering of colloidal particles during transport through the fracture. Section 6 concludes the report with a summary of results and provides some recommendations.

2. Recent developments in CFRT modelling

2.1 Background of SSM's development of COLLAGE

SSM has carried out research and development to inform itself about and provide modelling capability on CFRT over many years. This work has been documented in the SKI report series (Grindrod & Worth, 1990; Grindrod, 1991; Grindrod & Cooper, 1993; Wickham *et al.*, 2000; Kłos *et al.*, 2002; Kłos, 2003). The 1991 'Grindrod' reports developed a model based on theoretical considerations of irreversible sorption of radionuclides to both mobile and immobile colloids; subsequently that was changed so that sorption was reversible for both mobile and immobile colloids. Sorption of colloids to surfaces was assumed to be at equilibrium, i.e. no net gain or loss, so that the ratio of sorbed to non-sorbed colloids remains constant. This was the basis of the original COLLAGE 2 model for simulating dispersion and migration of radionuclides associated with colloids. Dispersion was modelled by COLLAGE 2 due to the faster advective velocity of colloids relative to true solutes due to preferential movement of colloids in the centre of the advective streamlines in fractures.

Kłos et al. (2002) used the COLLAGE 2 code to assess potential impacts of CFRT on a KBS-3 repository, conditioning the model by simulation of the observed migration of colloid-associated Pu at the Nevada Test Site. It was concluded that the key variables are the kinetics of sorption and desorption of radionuclides onto mobile and immobile colloids, i.e. that CFRT could lead to migration over significant distances with respect to migration through the geosphere only in the case of a fairly narrow range of low sorption/desorption rates. At that time, COLLAGE 2 was the only such model that incorporated sorption kinetics and thus would replicate that behaviour. The numerical method was upgraded by Kłos (2003) to produce the more stable and efficient COLLAGE 2-PLUS code, but the basic conceptual model remained the same, i.e. kinetic sorption of radionuclides onto both mobile and immobile colloids and a constant ratio of mobile to immobile colloids. The model for colloid filtration, i.e. for the attachment/detachment or sorption/desorption of colloids onto fracture surfaces, is inflexible in that it is assumed to be at equilibrium with a constant ratio of sorbed to non-sorbed colloids throughout the modelled system. Furthermore, the underlying conceptual model does not include colloid 'straining', i.e. the trapping of colloids due to physical size within fracture apertures.

2.2 CFRT modelling by SKB

CFRT effects superimposed onto the TRUE tracer experiments carried out at the Äspö HRL were considered for SKB in a modelling report by Cvetkovic

(2004). A sensitivity analysis was carried out with respect to sorption rate of tracers onto colloids and to rate or efficacy of colloid filtration, i.e. irreversible colloid removal by sorption to fracture surface. It was concluded that, under experimental constraints of restricted distance and time scales that were typical of the TRUE tests, a controlling factor would be kinetics of sorption of tracers onto colloids. Reversibility of sorption onto colloids was less important because of the short timescale.

SKB also carried out in situ experiments on latex colloid stability and mobility in the Äspö HRL. These were supported by laboratory investigations of migration of bentonite and latex colloids through a fracture in an ex situ granite block (Laaksoharju & Wold, 2005; Vilks et al., 2008). These showed that bentonite colloids, predominantly in the upper part of the particle size range, were retained in the experimental fracture as the flow velocity of low ionic strength elution water was reduced towards natural flow conditions. When the ionic strength of the elution water was increased to values typical of Äspö groundwater, bentonite colloids were fully immobilised. Moreover, under the experimental conditions, immobilised colloids were not remobilised by a subsequent low ionic strength flush.

The conceptual model of CFRT in COLLAGE 2 was incorporated into a probabilistic program using the finite volume method with numerical solvers for SKB by Vahlund & Hermansson (2006), for use in sensitivity analysis alongside FARF31, which does not include CFRT. The enhanced program is called FARF33 (or sometimes FVFARF). For simulations of CFRT in a KBS-3 repository, FARF33 assumed that all colloids are fully mobile, i.e. no filtering occurs.

In the SR-Can safety evaluation (SKB, 2006), SKB concluded that CFRT would not have to be included in consequence calculations except, possibly, for the glacial stage of the reference evolution. To bound the possible impact of CFRT under glacial conditions, geosphere retention was neglected in a scoping calculation. SKB reached its conclusion in SR-Can concerning CFRT on the basis of confidence that divalent cation concentrations in pore water would be sufficient to resist colloidal erosion and dispersion of buffer, with the caveat that there are still significant uncertainties about the hydraulics and chemical evolution of dilute melt water infiltration under an ice sheet.

SKB’s SDM-Site report for Forsmark (SKB, 2008) considers CFRT in Section 10.6 (‘Transport of radionuclides’). It states that, for the case of the strongly-sorbing trivalent actinides and lanthanides in constant groundwater compositions, ‘colloid …… transport mechanisms may dominate the release to the biosphere, particularly ….. if sorption is deemed to be irreversible’. SKB states that ‘the status of sorption reversibility for key radionuclides on colloids is not conclusively established at present, although recent studies …… suggest that sorption of Ac(III)-Ln solutes is most likely to be reversible under normal groundwater conditions’.

Scoping calculations for SKB in Crawford (2008) imply that there will be a negligible effect of CFRT due to natural colloids if sorption is reversible. The calculations assume a constant concentration of colloids along a transport path and no attachment or detachment of colloids, i.e. no filtration or straining.

A conceptual model for the formation of bentonite colloids due to hydrodynamic erosion of material that has expanded into adjacent fractures from its original compacted state in deposition holes is described in Pusch (1999). Dispersion and stabilisation under such conditions would presumably be enhanced by a very dilute groundwater composition. Colloid transport and CFRT in this case is deduced to be significant in terms of overall transport through the geosphere only if filtration, i.e. sorption and other mechanisms of attachment of colloids to fracture surfaces, and straining, i.e. trapping by fracture-filling minerals, are insignificant.

2.3 CFRT in the RETROCK and FUNMIG projects

Both SKI and SKB were partners in the EU's RETROCK project (EC, 2005), part of which was a task on geosphere retention phenomena in safety assessments (WP2; reported in SKB, 2004a). CFRT is dealt with in Sections 3.1 and 4.5 of the RETROCK report. It is stated that 'a conservative approach is to assume that radionuclides are irreversibly bound to colloids'. The two models for CFRT mentioned in RETROCK are COLLAGE 2 and a similar model that was at that time being developed for the USDOE project at Yucca Mountain (Wolfsberg & Reimus, 2000). It also states that 'the modelling of filtration in fractured rock systems (as opposed to idealised filters) presents particular difficulties', although it is not clear whether this refers to filtration in the sense used here or to straining which is the physical process of colloid trapping rather than the sorption at surfaces. In summarising the status of inclusion of CFRT in performance assessment modelling, it states that mechanistic models used in PAs by Nagra (Kristallin-1), Nirex (Nirex 97), JAEA (H-12) and USDOE (TSPA-VA/LA) have been fairly similar in simulating reversible sorption to mobile and immobile colloids. The USDOE model is the only one to include irreversible sorption in addition to reversible sorption (see below).

The Nirex 97 assessment of the Sellafield site in the UK was supported by transport calculations with various scoping calculations for the near field that assumed constant waste-derived colloid concentrations and distributions, reversible sorption of radionuclides to colloids, no sorption of colloids onto cementitious backfill, and the likelihood that colloids would be physically excluded from backfill pores (Swanton et al., 2000). The far field model considered sorption of colloids to rock, reversible or irreversible sorption of radionuclides to colloids, and also the exclusion of colloids from some pores in the fractured rock matrix. However physical retention, i.e. straining, of colloids during migration through fractures was not considered.

The latest EU project to represent the 'state of science' on CFRT has been FUNMIG, in which Task 4 investigated processes influencing radionuclide migration in crystalline rock formations. An overview of Task 4 (Missana et al., 2008) refers to the CRR and CFM experiments in the Grimsel laboratory which found that bentonite colloid migration was not retarded with respect to water flow and that recovery of the colloidal bentonite with sorbed solutes was high. But the Grimsel results also indicate that some poorly identified filtration was evidently occurring, although the dilute hydrochemical conditions there would support colloid stability – correlation between 'filtration' and fracture surface roughness suggests that straining (or 'plugging effects') may affect the bentonite colloids. However the hydraulic conditions of this experiment are considered to be of questionable comparability to natural geosphere conditions. Nevertheless, it was possible to measure apparent diffusion coefficients for colloids in the granite matrix which were at least 3 orders of magnitude lower than for true solute radionuclides, confirming that diffusion of colloids into matrix is negligible for transport modelling.

Experiments for the FEBEX programme, reported in FUNMIG, have shown that the concentrations of bentonite colloids passed into water adjacent to compacted Na-bentonite increase as salinity decreases and pH increases, as expected from basic colloid stability considerations. FUNMIG experiments also seem to indicate that the hydrochemical ‘suitability requirement’ of 1 mmol/L Ca2+ is not an adequate criterion to constrain likely colloid release.

2.4 CFRT modelling in USDOE’s Yucca Mountain project

A scientific basis for colloid mobility in groundwaters which is referred to in USDOE’s model of CFRT is summarised in Ryan & Elimelech (1996). The DLVO theory for attractive and repulsive forces between colloidal particles and mineral surfaces describes mobilization and retention of colloids: the basis of this is that sorbed colloids are likely to be retained on surfaces unless a change of solution chemistry (i.e. ionic strength and/or pH) makes the repulsive forces between colloids and the charged double layer on mineral grains greater than the van der Waals attractive forces. There are two theoretical approaches for modelling the kinetics of colloid attachment and filtration: a Lagrangian stochastic representation of Brownian motion, or Eulerian geometrical/deterministic representation of convection-diffusion. Using an Eulerian approach, a detailed analytical representation of colloid attachment from water flowing in a fracture with uniform aperture was produced by James & Chrysikopoulos (1999).

The model for CFRT that was used in the Safety Analysis Report for the proposed Yucca Mountain repository in the USA assumed a conceptual model with reversible sorption onto colloids (smectite or iron oxide products from wasteform degradation) for most radionuclides plus irreversible sorption for Pu and Am only (USDOE, 2008; Moridis et al., 2003). For those colloids with irreversibly sorbed Pu or Am, it was assumed that the dominant fraction would be reversibly or irreversibly filtered by kinetic attachment/detachment whilst a very small fraction (<0.01) would migrate through the unsaturated and saturated zones with no effective retardation because of the very slow kinetics of attachment. It seems that the filtration term was assumed to include physicochemical attachment and also ‘mechanical clogging’ (Moridis et al., 2003). Diffusion of colloids into pores of the rock matrix was assumed to be limited by ‘straining filtration’ to the smaller colloids only.

Important aspects of the CFRT model for Yucca Mountain are that it simulates dynamic generation of different types of colloids with variable size distributions and concentrations and stabilities that depend on water composition, i.e. ionic strength. CFRT is implemented in the TOUGH2-3D flow-transport code using a forward filtration kinetic coefficient $\kappa+$:

$$\kappa^{+} = \varepsilon f u G \tag{2.1}$$

where

ε is a colloid size-dependent 'filter coefficient', $\varepsilon = 1.5 \frac{1\text{-}\phi}{d_m} \alpha_c \, \eta_c$

f is a velocity modification factor that accounts for the higher relative 'centre-stream' advective velocity of colloids,

u is the Darcy velocity,

G is a dynamic blocking function accounting for variations of porosity and specific surface in relation to filtered colloids concentration,

d_m is the grain size of porous medium or size of fracture aperture,

ϕ is porosity,

α_c is the 'sticking efficiency' for colloids (0.001 to 1),

η_c is the 'collector efficiency' for attachment of colloids:

$$\eta_c = 0.9\left(\frac{k_b T}{\mu_w d_c d_m u}\right)^{2/3} + 1.5\left(\frac{d_c}{d_m}\right)^{2} + (\rho_c - \rho)\frac{g\, d_c^{\,2}}{18\mu\, u}$$

k_b is Boltzmann's constant,

d_c is colloid diameter,

μ_w is dynamic viscosity of water,

ρ_c is density of colloids,

ρ is density of water.

The change of filtered concentration, σ (volume of colloids per volume of water), of colloid at any point in the system is modelled as:

$$\frac{\partial \sigma}{\partial t} = \kappa^{+}\, \mathrm{X} - \kappa^{-}\, \sigma \tag{2.2}$$

where X is the mass fraction of colloid in water and κ^{-} is the reverse filtration ('declogging') coefficient. κ^{-} is commonly assumed to be zero, i.e. filtration is assumed to be irreversible, but 'there is insufficient evidence to support this' (Moridis *et al.*, 2003). Straining is not explicit in these expressions, but is implicit in the conceptual model for CFRT.

The conceptual model that lies behind the application of these equations in the transport model for the Yucca Mountain SAR is indicated in a report by Moridis & Bodvarsson (2001). Straining is inferred to take place mainly in the layered fracture system where the misalignment of fractures means that preferential flow and transport pathways must pass through the rock matrix between adjacent fractures. Straining is also envisaged to take place within fractures where the aperture becomes constricted, but this is regarded as a less effective straining mechanism. Straining is allowed for by a simple adjustment factor, χ^{f} (value between 0 and 1), which operates on the Laplace transform solution for radionuclide flux (eqn. 75 in Moridis & Bodvarsson, 2001). In illustrative calculations, χ^{f} is given arbitrary values of 0.95 for 5 nm diameter colloids and 0.35 for 500 nm colloids (Table 12 in Moridis & Bodvarsson, 2001).

Other models for CFRT in the Yucca Mountain system have focused on the details of the mechanism, kinetics and reversibility of sorption onto colloids for specific radionuclides (Contardi et al., 2001; Cvetkovic et al., 2004). The Cvetkovic et al. paper highlighted the sensitivity of the model to parameterisation of desorption rates and of filtration processes. For a fixed rate of colloid filtration, the attenuation of radionuclide breakthrough was found to be sensitive to the rate of desorption of radionuclide from colloids. Cvetkovic et al. concluded that experimental calibration of radionuclide desorption rates and in situ studies of colloid filtration are needed. They adopted the experimental rate of sorption of Pu onto montmorillonite obtained by Lu et al. (1998, 2000) and converted it to a site-specific sorption rate for relatively high colloid concentrations in the alluvial aquifer downgradient from Yucca Mountain, deriving a rate of 0.1 a-1. Converting the same experimental data to the low natural colloid concentrations and low porosity in repository host rock at Forsmark would give a sorption rate of about 10-5 a-1. They also estimated the rate of irreversible filtration of colloids using a formula based on filtration theory which is the same one that Moridis et al. (2003) used for the ‘filtration coefficient’:

$$\varepsilon = 1.5U\frac{1-n}{d}\eta\alpha \qquad (2.3)$$

where

U is flow velocity

n is porosity

d is a characteristic grain diameter (assuming porous medium)

η is a ‘single collector efficiency term’

α is a ‘collision efficiency factor’.

For example, Cvetkovic *et al.* estimate that ε would be about 53 a^{-1} for a 0.45 µm diameter colloid in a porous medium with grain size 0.2 mm and about 230 a^{-1} for a 0.05 µm colloid in the same medium.

2.5 Models of colloid straining

A model for colloid straining in porous media has been developed and empirically calibrated by Xu *et al.* (2006), using column experiments with latex microspheres and quartz sand cleaned to remove coatings likely to cause physicochemical attachment. The experimental measurements showed an exponential decrease of straining as immobilised colloids increased, suggesting a conceptual model whereby colloids will follow non-straining flowpaths once those with constrictions and dead-ends have been occupied. The transport equation used was:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\phi}\frac{\partial S}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} \qquad (2.4)$$

where
C is concentration of colloids in water
ρ_b is bulk density
ϕ is porosity
S is concentration of strained colloids
v is linear velocity of water
D is hydrodynamic dispersion coefficient.

The variation of strained colloids, S, is represented by a simple kinetics expression with exponential relationship:

$$\frac{\rho_b}{\phi}\frac{\partial S}{\partial t} = k_o C \exp\left(-\frac{S}{\lambda}\right) \tag{2.5}$$

where
k_o is a rate coefficient for colloid straining in the particular conditions
λ is a coefficient defining the exponential decline of straining rate as S increases.

Xu *et al.* found that k_o was generally zero, i.e. no significant straining, if the ratio of colloid diameter to sand grain diameter, d_c/d_m, was < 0.008, or typically for colloid sizes ≤ 0.5 µm. k_o increased to about 35 hr^{-1}, approximately linearly with d_c/d_m above 0.008, for grain sizes up to 0.78 mm and colloid sizes up to 5.1 µm. They found that λ increased with increasing colloid size and decreasing grain size, $\lambda = 1.44\ d_c/d_m - 0.004$ ($\lambda \sim 0.008$ to 0.07). In a similar studies, Bradford *et al.* (2003) measured a k_o-value of 67 hr^{-1} for a maximum d_c/d_m ratio of 0.021, whilst Bradford *et al.* (2004) found that straining became important relative to attachment when $d_c/d_m > 0.005$, i.e. reasonably consistent with the finding of Xu *et al.* (2006).

Xu & Saiers (2009) carried out further experiments to test the effect of non-uniformity of colloid size on the validity of the above rate expression for straining in porous media, especially with respect to the importance of dc/dm. It was found that straining of larger colloids enhances the straining of smaller colloids, so the rate expression was modified to account for this additional size-dependent effect.

Bradford et al. (2004) and Bradford & Bettahar (2006) found that experimental results could be fitted to a slightly simpler kinetic expression:

$$\frac{\partial(\rho_b S)}{\partial t} = \phi k_0 \psi_{str} C \tag{2.6}$$

where
ψ_{str} is a ‘straining function’ which is a function of distance from the flow inlet or a textural interface where straining tends to occur:

$$\psi_{str} = \left(1 - \frac{S}{S^{max}}\right)\left(\frac{d_m + z}{d_m}\right)^{-\beta}$$

where

S^{max} is the maximum concentration of strained colloids,

z is distance from flow inlet,

β is a parameter for the shape of the power law spatial function (for which Bradford *et al.*, 2003, reported a value of 0.432).

2.6 Potential development of COLLAGE

COLLAGE 2 represents CFRT by the solution of two transport equations: one for radionuclides in solution, i.e. as true solutes, and one for radionuclides sorbed onto mobile colloids. Radionuclides are distributed by sorption onto mobile and immobile colloids. The ratio of mobile to immobile colloids is specified, the rates of sorption and desorption of radionuclides to mobile colloids are considered equal, and similarly for immobile colloids. Therefore the CFRT process is quite prescribed and constrained in the COLLAGE 2 model. Straining is not explicitly considered.

Of the formulations for colloidal sorption, filtration and straining, only that used for the Yucca Mountain safety analysis is specifically aimed at CFRT in fractured rock (though it is primarily developed for unsaturated fractured rock and therefore not directly transferable to the hydrogeological conditions in Swedish rock). The other formulations are for general colloidal migration in porous media, e.g. clean sands or sandstones, and have been developed with the focus on contaminant transport in shallow aquifers.

Three potential developments are suggested for implementation in COLLAGE-3:

1. Decoupling the rates of sorption and desorption for radionuclides on to mobile and immobile colloids (noting that it is commonly assumed that sorption is instantaneous and only desorption is kinetically-controlled);
2. Introducing a term for sorption-desorption of colloids onto surfaces, i.e. the attachment-detachment or ‘filtration’ term, so that the ratio of mobile/immobile colloids is variable;
3. Introducing a term for straining of colloids due to trapping in fractures, e.g. due to varying apertures, and migration into dead-end fractures.

Decoupling of sorption and desorption rates for radionuclides would require that the rate coefficients κ_1 and κ_2 in COLLAGE-II are divided into distinct rate coefficients for sorption, κ_1^{sorb} and κ_2^{sorb}, and desorption, κ_1^{desorb} and κ_2^{desorb}.

A filtration term would take the form, as shown above for the Yucca Mountain transport model:

$$\frac{\partial \sigma}{\partial t} = \kappa^{+} X - \kappa^{-} \sigma \qquad (2.7)$$

in which $\kappa^{+} = \varepsilon f u G$ and $\kappa^{-} = 0$ (or a specific expression for detachment rate if non-zero and colloid attachment is modelled as reversible).
The straining term is the most problematic to implement in a model for colloids moving in a fractured rock. Either an arbitrary straining factor, χ^{f} (see above) could be applied to the colloid or radionuclide transport solution to attenuate the colloid concentration at any point, or the conceptual model for exponentially reducing straining rate in relation to concentration of strained colloids could be adopted. In the latter case, it could be assumed, as an initial approximation, that the relationship of aperture in the case of fractured rock is equivalent to that of grain size in the case of the porous medium.

The two alternative expressions for straining rate in a porous medium are: (i) from Xu et al. (2006):

$$\frac{\rho_b}{\phi}\frac{\partial S}{\partial t} = k_o C \exp\left(-\frac{S}{\lambda}\right) \tag{2.8}$$

in which k_{o} and λ are related to colloid size versus grain size (or fracture aperture) and to concentration of strained colloids as explained above;
or (ii) from Bradford *et al.* (2004):

$$\frac{\rho_b}{\phi}\frac{\partial S}{\partial t} = k_o \psi_{str} C \tag{2.9}$$

in which k_{o} and ψ_{str} are related to grain size (or fracture aperture), concentration of strained colloids, and to distance along flow path, as explained above.

A pragmatic alternative approach would be to assume that immobilisation of colloids by straining is implicitly included in the filtration term for sorption of colloids to the fracture surface. This would involve two assumptions: (a) that straining is reversible with the same kinetics as apply to desorption, and (b) that straining is a spatially homogeneous process and that there is no interest in simulating the likely prevalence of straining at the start of a flowpath, e.g. in fractures close to deposition holes that are the source of dispersed bentonite.

3. Review of CFRT modelling in COLLAGE 3

3.1 Conceptual and mathematical background

COLLAGE 2 is a one-dimensional representation of radionuclides transport in a fracture. As well as advection and dispersion of radionuclides in solution and on mobile colloids. The conceptual model is illustrated in Figure 2. Water flows in the fracture with an non-uniform profile. Colloids move with the water flow, but with potentially higher velocity since they tend to flow in the centre of the fracture being electrostatically repelled from the fracture walls. Solute and colloids therefore have different velocities and dispersivities. Radionuclides in solution can diffuse into the rock matrix of the fracture walls.

Within the fracture any colloids present can sorb and desorb radionuclides from solution. Conceptually there are two populations of colloids – mobile and fixed. Colloids can be generated and may be input to inlet of the fracture some of these may attach to the walls of the fracture or otherwise be lost from the mobile population. Remobilisation may also occur.

Radionuclides entering the fracture in solution and/or sorbed onto mobile colloids can migrate between the three populations: solution, mobile and fixed. Radioactive decay also reduces the amount of radionuclides in the system.

Radionuclide concentration in solution (cs) can be represented by the advection-dispersion transport equation, allowing for matrix diffusion. The concentration on mobile colloids (cm) similarly obeys an advection-dispersion relation. The exchange of radionuclides between solute and mobile and fixed colloids can be represented by linear first order dynamics. The system is illustrated in Figure 2 (a).

Four equations therefore define radionuclide transport in the fracture (the parameters are summarised in Table 1):
The radionuclide concentration in the fracture solution (cs) is given by,

$$\begin{aligned}\frac{\partial c_s}{\partial t} &= D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} + \frac{\phi D_r}{b} \left.\frac{\partial c_p}{\partial z}\right|_{z=0} \\ &\quad - \left(\lambda + \kappa_{sm} p_m + \kappa_{sf} p_f\right) c_s + \kappa_{ms} c_m + \kappa_{fs} c_f\end{aligned} \qquad (3.1)$$

and the concentration on *mobile* colloids (c_m) is

$$\begin{aligned}\frac{\partial c_m}{\partial t} &= D_m \frac{\partial^2 c_m}{\partial x^2} - u_m \frac{\partial c_m}{\partial x} \\ &\quad - \left(\lambda + \kappa_{ms} + \kappa_{mf}\right) c_m + \kappa_{fm} c_f + \kappa_{sm} p_m c_s\end{aligned} . \qquad (3.2)$$

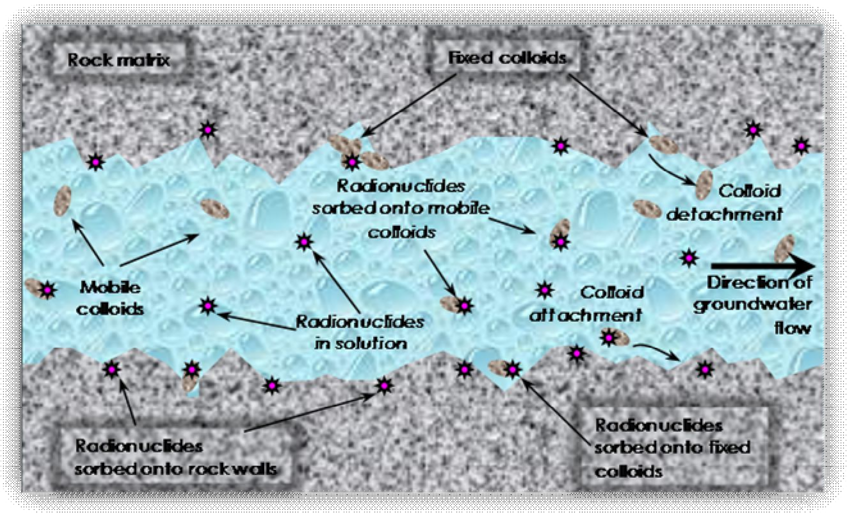
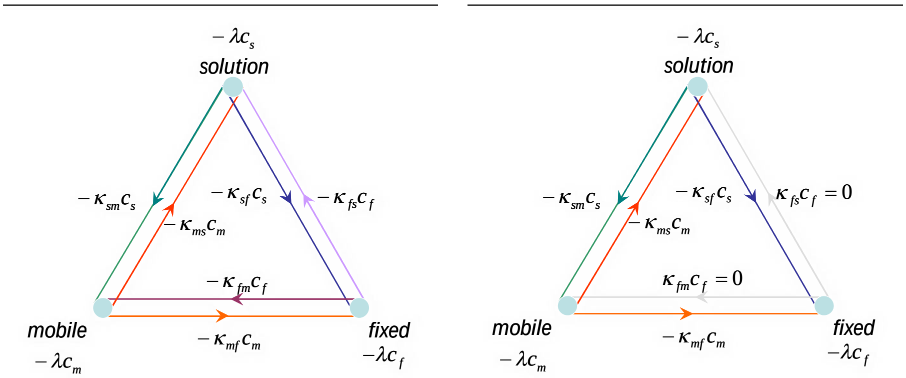


Figure 2: COLLAGE 3 conceptual model for radionuclide transport in a one-dimensional planar fracture.



(a) Generalised system interactions between all three components

(b) Restricted system in COLLAGE 3 – irreversible interactions with fixed colloids

Figure 2: Radionuclide-colloid dynamic processes in the fracture. Restrictions imposed by the COLLAGE 2 mathematical model restrict interactions in COLLAGE 3 to those indicated in (b). This is further discussed in Section 3.2.

Table 1: Summary of parameters used in the mathematical model of CFRT on which the COLLAGE 3 code is based.

name	units	definition
D_s	$m^2\ y^{-1}$	dispersion coefficient of solute
u_s	$m\ y^{-1}$	average groundwater velocity in the fracture
D_r	$m^2\ y^{-1}$	molecular diffusion coefficient of the solute into the rock matrix
ϕ	-	rock matrix porosity
b	m	fracture half width
D_m	$m^2\ y^{-1}$	dispersion coefficient of mobile colloids
u_m	$m\ y^{-1}$	average mobile colloid flow rate
λ	y^{-1}	radionuclides decay constant
R	-	rock matrix retardation coefficient - $R = \phi + \rho K_D$ where K_D is the distribution coefficient for radionuclides sorbing onto the rock matrix
p_m	-	partition coefficient for radionuclides sorbing onto mobile colloids: $p_m = k_c \alpha_m$
p_f	-	partition coefficient for radionuclides sorbing onto immobile colloids: $p_f = k_c \alpha_f$
f_s	-	fraction of injected inventory in solute phase, $f_m = 1 - f_s$
L	m	length of fracture modelled
n	-	scaling factor for zero concentration outer boundary condition at $x = nL$
κ_{ij}	y^{-1}	Transfer rates between the dynamic components of the system: i, j = s, m, f, solute, mobile colloids and fixed colloids, respectively

The accumulation of radionuclides on *fixed* colloids (c_f) is given by

$$\frac{\partial c_f}{\partial t} = -\left(\lambda + \kappa_{fm} + \kappa_{fs}\right)c_f + \kappa_{mf} c_m + \kappa_{sf}\, p_f c_s \tag{3.3}$$

The radionuclide concentration in the rock matrix (c_p) is given by:

$$R\frac{\partial c_p}{\partial t} = D_r \frac{\partial^2 c_p}{\partial z^2} - R\lambda c_p \tag{3.4}$$

Of these, Equations (3.1) and (3.2) are the main interest since their solution gives the flux of *radionuclides* at the outlet of the fracture. NB, these are the governing equations for a *single* radionuclide. Chains are not yet modelled in COLLAGE.

In the absence of colloids, the equations reduce to a standard one-dimensional advection-dispersion model. It is in the dynamics of radionuclides interactions between solution, mobile and fixed colloids that the code comes into its own. According to the conceptual model in Figure 2, there are six dynamic interactions between radionuclides in the different components of the system. Figure 2 illustrates the dynamic relationships between solute, mobile and fixed colloids in the fracture. However, given the structure of the pre-existing COLLAGE 2 mathematical model it is only possible to include four of these in the current structure. The reason for this and the interpretation of the transport equations in COLLAGE 3 are discussed in the following section.

3.2 The COLLAGE 2 mathematical framework

The COLLAGE mathematical framework has been developed through two phases. The most recent is COLLAGE 2 (Grindrod and Cooper, 1993). The basic equations for radionuclide transport are those given in Equations (3.1) to (3.4) but with modification and simplifications to facilitate the solution for the radionuclide flux at the fracture outlet where a zero concentration boundary condition is imposed.

Of concern therefore is the radionuclides flux from the fracture. The colloid distribution is not at issue. COLLAGE 2 employs the following assumptions:

1) Equal sorption/desorption rates from solute to mobile colloids: $\kappa_{sm} = \kappa_{ms}$
2) Equal sorption/desorption rates from solute to fixed colloids: $\kappa_{sf} = \kappa_{fs}$
3) Non-dynamic populations of fixed and mobile colloids, radionuclide dynamics between the two populations are modelled only in terms of

sorption/desorption. There is a constant ratio between mobile and fixed colloid populations – parameter, f_{fm}. This allows the nuclide concentration on the two populations to be written as $c_f = f_{fm} c_m$

4) No dynamic relationship directly between mobile and fixed colloids: $\kappa_{mf} = \kappa_{fm} = 0$

From assumptions 3 and 4 the colloid concentrations can be written as a linear combination so that Equations (3.2) and (3.3) become

$$\begin{aligned}(1+f_{fm})\frac{\partial c_m}{\partial t} &= D_m \frac{\partial^2 c_m}{\partial x^2} - u_m \frac{\partial c_m}{\partial x} \\ &\quad - \left[(1+f_{fm})\lambda + \kappa_{ms} + f_{fm}\kappa_{fs}\right]c_m + \left(\kappa_{sm} p_m + \kappa_{sf} p_f\right)c_s\end{aligned} \qquad (3.5)$$

for the concentration on colloids, and

$$\begin{aligned}\frac{\partial c_s}{\partial t} &= D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} + \frac{\phi D_r}{b} \left.\frac{\partial c_p}{\partial z}\right|_{z=0} \\ &\quad - \left(\lambda + \kappa_{sm} p_m + \kappa_{sf} p_f\right)c_s + \left(\kappa_{ms} + f_{fm}\kappa_{fs}\right)c_m\end{aligned} \qquad (3.6)$$

for the solute transport equation.

These equations are implemented in the original COLLAGE 2 code. NB, the sorption / desorption rate parameters are written in the non-symmetric form for future reference.

To solve for the flux at the outlet of the fracture the boundary and initial conditions are required:

$$c_s(x,0) = c_m(x,0) = 0, \qquad 0 < x < nL, \qquad (3.7)$$

$$c_s(nL,t) = c_m(nL,t) = 0, \qquad t \ge 0. \qquad (3.8)$$

Initially there is no radionuclide in the system and there is a zero downstream concentration at *n* times the length *L* of the fracture.

COLLAGE assumes a delta-function input at the inlet with the release of the radionuclide partitioned between solution and mobile colloids, according to parameter f_s:

$$\left[u_s c_s - D_s \frac{\partial c_s}{\partial x}\right]_{x=0} = f_s \frac{1}{2b}\delta(t), \qquad t \ge 0, \qquad (3.9)$$

$$\left[u_m c_m - D_m \frac{\partial c_m}{\partial x}\right]_{x=0} = (1-f_s)\frac{1}{2b}\delta(t), \ t \ge 0. \qquad (3.10)$$

COLLAGE uses a Laplace transform method to solve for the radionuclide flux across the fracture outlet. In the Laplace domain, (3.7) and (3.8) can be reduced to a single 4th-order ordinary differential equation in $\hat{c}_s$, the Laplace transform of the radionuclide concentration in solution. In turn this can be used to solve for $\hat{c}_m$, the Laplace domain transform of the mobile colloid concentration.

Assuming that the solution for the transform of the outlet concentration is a linear superposition of states:

$$\hat{c}_s = \sum_{i=1,4} A_i e^{r_i(x-nL)} . \tag{3.11}$$

where $r_i = p_i + iq_i$, the ode becomes a 4th order polynomial. COLLAGE 2 plus (Kłos, 2003) used an analytic solution (in place of the original matrix inversion approach of Grindrod & Cooper, 1993) to provide a solution for $\hat{c}_s$ and $\hat{c}_m$ at the outlet.

A numerical Laplace inversion is used to obtain the radionuclide fluxes in solution and on mobile colloids (the Talbot algorithm is used as documented by Grindrod & Cooper). In practice the algebraic solution to the ode has been found to be particularly robust at the early times of interest in the rapid transport of pulses of colloids along the fracture in the bulk solute flow.

3.3 The COLLAGE 3 model

The assumptions listed on page 15, on which COLLAGE 2 is based, limit what it is possible to do in terms of expanding the capabilities of the code in line with the description of recent developments in CFRT set out in Section 2. In particular the restriction imposed by the third assumption means that it is not possible to model the populations of fixed and mobile colloids independently.

However, using the form of the linear dynamics illustrated in Figure 2 (b), a set of equation can be formulated which allow unequal sorption / desorption rates to be implemented, so that, generally, $\kappa_{ij} \neq \kappa_{ji}$. Furthermore by setting the parameter describing the population ration of fixed to mobile colloids to zero in the COLLAGE expressions (f_{fm} = 0) the model then takes into account solute and mobile colloids only. Filtering of mobile colloids then leads to a loss term from the transport equation for mobile colloids, ie, filtering is represented by the rate κ_{mf}. However, because the fixed colloids are not modelled explicitly the return process cannot be modelled so the processes must be regarded as irreversible. Similarly desorption from fixed colloids cannot be modelled.

The transport equations in COLLAGE 3 are therefore:

$$\begin{aligned}\frac{\partial c_s}{\partial t} &= D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} + \frac{\phi D_r}{b} \left.\frac{\partial c_p}{\partial z}\right|_{z=0}, \\ &- \left(\lambda + \kappa_{sm} p_m + \kappa_{sf} p_f\right) c_s + \kappa_{ms} c_m\end{aligned} \tag{3.12}$$

For radionuclides in solution, and

$$\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x^2} - u_m \frac{\partial c_m}{\partial x} - \left(\lambda + \kappa_{ms} + \kappa_{mf}\right) c_m + \kappa_{sm} p_m c_s \,. \tag{3.13}$$

For radionuclides on mobile colloids.

There are two partition parameters used in these equations: p_m, for radionuclides on mobile colloids and p_f for fixed colloids. In each case these are derived from the populations of mobile and fixed colloids per unit volume of fracture water, according to

$$p_i = \alpha_i K_i, \qquad \text{with } i = f, m \tag{3.14}$$

The effective k_d for colloids on the two populations is K_i and the mass of each per unit volume of the fracture is α_i.

Some recoding is also required, not only to account for this additional parameters but also to modify the internal coefficients of the 4th order polynomial that has to be solved. For the record, the modified versions are as described below (refer to the code for further information and to Grindrod & Cooper, 1993, for deeper description).

Internally to the COLLAGE 3 code the two 4th order polynomials (for each of the solute and colloid concentrations) have the form

$$y = a_i x^4 + b_i x^3 + c_i x + d_i \,. \tag{3.15}$$

For the solute:

$$\begin{aligned} a_1 &= D_s \\ b_1 &= -u_s \\ c_1 &= -\left[\lambda + s + \frac{\phi D_r}{b}\sqrt{\frac{(s+\lambda)R}{D_r}} + \kappa_{sm} p_m + \kappa_{sf} p_f\right] \\ d_1 &= -\kappa_{ms} \end{aligned} \tag{3.16}$$

For the colloids the coefficients are:

$$\begin{aligned} a_2 &= D_m \\ b_2 &= -u_m \\ c_2 &= -\left[\lambda + s + \kappa_{ms} + \kappa_{mf}\right]. \\ d_2 &= -\left(\kappa_{sm} p_m + \kappa_{sf} p_f\right) \end{aligned} \tag{3.17}$$

4. Application of COLLAGE 3

4.1 Best estimate dataset for the bentonite erosion scenario

This project has the aim of implementing the conceptual changes discussed in Section 2 in the COLLAGE 3 framework. This section sets out a suitable test case dataset for the revised model in which a best estimate representation of the SR-Can fracture with impulse release of ^{242}Pu on colloids is implemented, illustrating the bentonite erosion scenario. This model demonstrates the revised code and provides an indication of the potential significance of colloid filtration.

The revision of mathematical model described above means that the data requirements for COLLAGE 3 differ from the earlier versions and, unlike the modification to COLLAGE 2 plus, which allowed the original datafile format to be used. The enhanced capabilities of COLLAGE 3 require a modified format in that there are additional parameters input, namely the kinematic transfers from mobile colloids to solution and to fixed colloids. Additionally the effective kd for sorption onto colloidal particles is input directly as are the mass loadings of suspended and fixed colloids per unit volume of the fracture.

Numerical values for the best estimate case follow in the order they appear in the input files (including redundant parameters). Those items in the data file which are not directly related to the mathematical model of CFRT are greyed-out in the text. Data for the fracture transport are taken from the interpretation of the SR-Can fracture discussed in Broed & Xu (2008). Data for the kinematics of radionuclide colloid – solute interactions are described below.

Fracture characterisation:

- **Mean solute velocity**, u_s is taken from Broed & Xu, based on a fracture length of 500 m and a groundwater travel time of 40 a. The mean colloid velocity is taken to be 1.32 greater as discussed by Grindrod & Cooper (1993):

  $u_s = 12.5$ m a^{-1} $\qquad$ $u_m = 16.5$ m a^{-1}
- **Dispersion coefficients for solute and colloids**. Broed & Xu quote the value for D_s (with an implicit Peclet number of 10). Grindrod and Cooper note that the dispersion coefficients for colloids should be higher and cite 140 m^2 s^{-1} for colloids compared to 50 m^2 s^{-1}. Lacking more detailed information we adopt this ratio here:

  $D_s = 625$ m^2 a^{-1} $\qquad$ $D_m = 1750$ m^2 a^{-1}
- **Matrix porosity** (Broed & Xu):

$\phi = 1\times10^{-3}$

- **Radionuclide decay constant** – data for ^{242}Pu (halflife = 3.7×10^5 years):

  $\lambda = 1.86\times10^{-6}$ a^{-1}
- **Rock matrix retardation factor** $R = \phi + \rho K_D$. Lindgren & Lindström (1999) quote a realistic value for the rock K_D of Pu as 5 and a pessimistic value of 1 m^3 kg^{-1}. These were the values used in SR97 and Sr-Can, and derive from the review of rock K_Ds carried out by Carbol & Engkvist (1999). The rock density is assumed to be 2700 kg m^{-3}. The realistic value gives a retardation factor:

  $R = 1.30\times10^4$
  The pessimistic value gives $R = 2.6\times10^3$.
- **Molecular diffusion coefficient** of the solute into the rock matrix. The realistic value from SKB (2004b), the interim data report for SR-Can is used :

  $D_r = 1.26\times10^{-6}$ m^2 a^{-1}
  A pessimistic alternative, $D_r = 1.26\times10^{-7}$ m^2 a^{-1} is also considered in conjunction with the pessimistic retardation factor.
- **Fracture length, fracture width** (aperture) - Broed & Xu - and scaling factor for the zero concentration boundary condition (taken to be $x = nL$):

  $L = 500$ m $\quad b = 10^{-4}$ m $\quad n = 2$

Inverse Laplace transform parameters (Grindrod & Cooper, 1993):

- Talbot algorithm parameters

  $N = 64 \quad Q = 16 \quad \Lambda = 6$

Redundant parameters in COLLAGE 2 files for backwards compatibility:

- Superseded parameter

  1 (not used in COLLAGE 3, used to maintain compatibility with COLLAGE 2)
- Superseded parameter

  1 (not used in COLLAGE 2 plus, used to maintain compatibility with COLLAGE 2 datafiles)
- Partition coefficients for mobile colloids (now evaluated using additional parameters in the COLLAGE 3 datafile)

  $p_m = 5\times10^{-4}$
- Partition coefficients for fixed colloids (now evaluated using additional parameters in the COLLAGE 3 datafile)

  $p_f = 9.5\times10^{-3}$

Dynamics involving transfers from solute :

- **Sorption rate of solute to mobile colloids**, solute to fixed colloids, based on interpretation of Cvetkovic *et al.* (2004):

  $\kappa_{sm} = 0.1$ a^{-1} $\quad \kappa_{sf} = 1.9$ a^{-1}

basing κ_{sf} on the relation $\kappa_{sf} = \kappa_{sm}\,\kappa_{mr}$, in which κ_{mr} is the distribution coefficient for colloids being filtered on to rock matrix, $\kappa_{mr} = 19$.

Scenario defining conditions:

- **Ratio of fixed to mobile colloids**: this parameter can be set to zero (see Section 0)

  $f_{fm} = 0.0$
- **Fraction of radionuclides injected in solution** (remainder are injected on colloids):

  $f_s = 0.0$
  Injection on colloids is the assumption for the bentonite erosion scenario.

Time stepping options for the solution:

- Parameter defining time at which output starts (0 $\Rightarrow$ at initial time step, > 0 $\Rightarrow$ at time of first breakthrough):

  $DELT = 0$
- Exponent of first time and number of time points per decade in the output - $t = 10^{p+\frac{k}{t_i}}$:

  $p = 0$ $t_i = 50$
- Final output time:

  $t_{fin} = 2\times10^{7}$ a
- Parameter used after COLLAGE 2 plus to turn diagnostic output on or off:

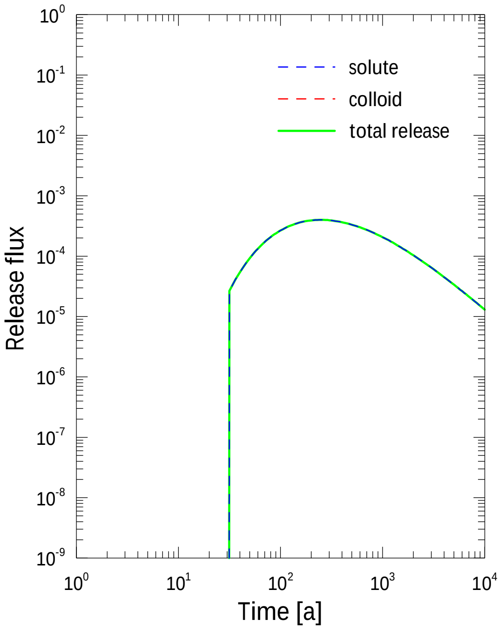
  $OVERFLOW = 0$
  No diagnostic information generated in the results files. Overflow < 0 full diagnostics, > 0 limited diagnostics. Beware Overflow < 0.

Additional parameters used in COLLAGE 3

- **Desorption rate for radionuclide from mobile colloids, filtration loss from mobile colloids** (based on interpretation of Cvetkovic *et al*. (2004):

  $\kappa_{ms} = 10^{-3}$ a^{-1} $\kappa_{mf} = 1.15$ a^{-1}
  $\kappa_{ms} = \kappa_{sm} / a$, where $a \sim 100$ is a reversibility ratio, and κ_{mf} is based on Appendix F in Cvetkovic *et al*. for colloid size 0.45 µm, water flow velocity 10 m a^{-1}, collision efficiency factor 0.005 and aperture 2×10^{-3} m [assuming that aperture width is equivalent to grain size in the diffusion-only formulation for single-collector efficiency of a porous medium in eqn. 6 of Yao *et al*. (1971) as used in Appendix F of Cvetkovic *et al*. (2004)]. For aperture 2 x 10^{-4} m, $\kappa_{mf} = 53.5$ a^{-1}
- **Effective solid – liquid distribution coefficients for colloidal particles**:

  $K_c = 5.0$ m^3 kg^{-1}
  Assumed equal to sorption on fracture walls. The pessimistic case uses $K_c = 1.0$.



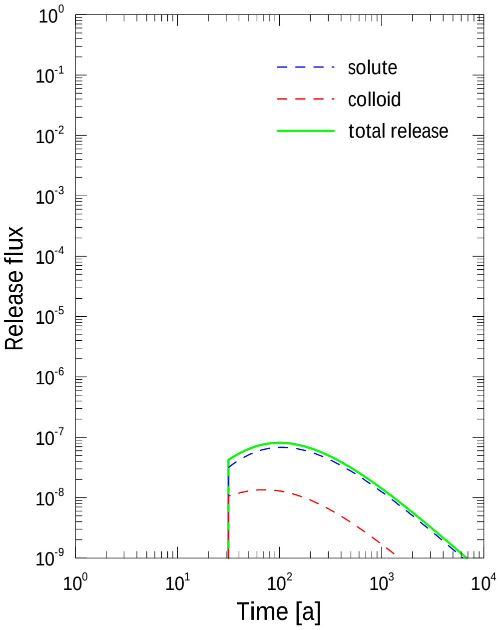
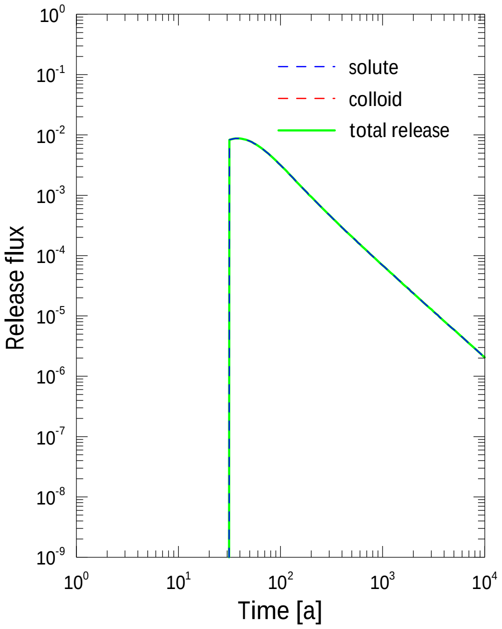


Figure 3: Breakthrough curve calculated using COLLAGE 3 for the case of a fracture transporting radionuclides in solution only. Injection in solution, no colloids present. Best estimate dataset.

Figure 4: Best estimate breakthrough curve calculated using COLLAGE 3 Mobile colloids filtered during transport. Injection on colloids cf. bentonite erosion scenario.



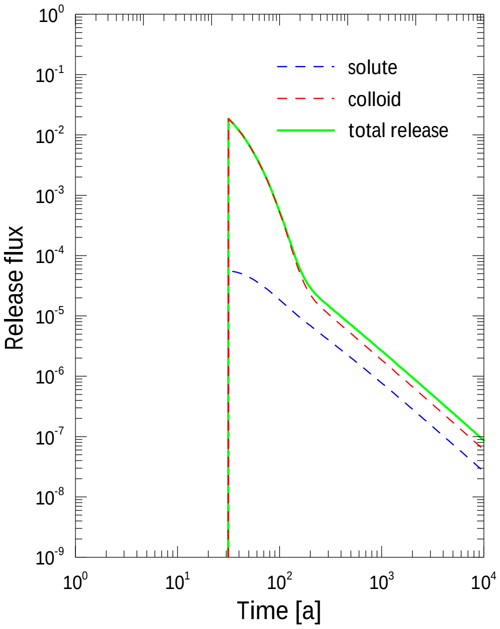


Figure 5: Breakthrough curve calculated with COLLAGE 3 with pessimistic values for sorption in the rock matrix in the absence of colloids. Injection in solution.

Figure 6: Breakthrough curve calculated using COLLAGE 3. Best estimate dataset but no filtration ($\kappa_{mf} = 0.$) Injection on colloids.

- **Density of mobile colloids per unit volume of fracture water**:

  $\alpha_m = 5\times10^{-4}$ kg m^{-3}
  based on assumed concentration of 0.5 mg litre^{-1}.
- **Density of fixed colloids per unit volume of fracture water**:

  $\alpha_f = 9.5\times10^{-3}$ kg m^{-3}
  based on assumed concentration of 9.5 mg litre^{-1}.

The parameters describing colloid interactions mainly attempts to give 'typical' values, though their variability in real systems may range over many orders of magnitude. For preliminary sensitivity tests of the model, it was decided that only two terms in the above list should be varied:

- Desorption rate for radionuclide from mobile colloids: $10^{-5} \leq \kappa_{ms} \leq 10^{-3}$ a^{-1}
- Filtration loss of mobile colloids becoming irreversibly immobilised: $10^{-2} \leq \kappa_{mf} \leq 10$ a^{-1}.

Results for the best estimate case, a pessimistic sorption case and an investigation of the sensitivity to colloid dynamics are presented in the following section.

4.2 Results and discussion

The primary motivation in the application of COLLAGE has always been to illustrate the potential effects of CFRT in fractures. Figure 3 illustrates the case for a pulse of radionuclides entering the fracture *in solution* at $t = 0$. In this case there are no colloids in the system. Matrix diffusion provides the retardation mechanism and the peak release occurs around 250 years after the release but with a peak flux at around 4×10^{-4} compared with the input unit pulse.

The best estimate of CFRT is shown in Figure 4. In comparison with the no colloid case the overall release is much lower at ~ 8×10-8. The presence of the colloids in the fracture brings the peak release forward to 100 years. However, the filtration of the colloids, leading to a loss of radionuclide from the fracture's flow system leads to a marked reduction in the overall release.

With the pessimistic values for matrix sorption (rock kd reduced from 5 m3 kg-1 to 1 m3 kg-1 and matrix diffusivity reduced by an order of magnitude to 1.26×10-7 m2 a-1), Figure 5 shows that a peak release of around 10-2 is possible close to the groundwater travel time (the peak is actually at 38 years. Compared to Figure 3, this illustrates the importance of matrix diffusion as a mechanism for retardation. This can be considered a pessimistic result for the fracture.

With the best estimate filtration rate there is around a four order of magnitude reduction in the peak release of radionuclides from the fracture compared to the no colloid case. However, if there is no filtration (Figure 6) there is an initial peak of 1.85×10-2 which arrives with a travel time of around 30 years. In this case release of radionuclides on the colloids transported along the fracture remains greater that solute-born release beyond 10 ka from the injection of the radionuclide pulse. There is appreciable spreading of the pulse along the flowpath. In the best estimate case radionuclides in solution dominate the release. Clearly, between the no-filtration and best estimate filtration cases there is a transition from early colloid dominated releases to a slower solute driven release.

Comparing Figure 6 and Figure 5 the release from the colloid-mediated no-filtration case gives a higher release than the pessimistic case for matrix sorption. This illustrates the potential significance of colloidal filtration. The parametric sensitivity analysis further illustrated the influence of the filtration and desorption terms, κmf and κms. The results investigated are the initial flux at first breakthrough and the peak flux over all time.

The mobile colloid to solute desorption rate shows a linear influence on the peak and initial fluxes. For all values of κms in the range considered the initial release is less than the later solute driven peak. Other than increasing the release with decreasing transfer rate from mobile colloids to solution, there is no other influence. For the values of the dispersion parameters used here this parameter does not lead to a higher initial flux.

In contrast there is a much greater sensitivity to the filtration parameter, κmf (Figure 8). This might be expected since the filtration effectively removes radionuclides from the system. The best estimate value is close to the point where the colloid-mediated early peak dominates. If the filtration parameter were to be lower by a factor of 10, the early peak would have a magnitude of around 5×10-3 relative to the initial pulse and would then be comparable to the pessimistic matrix sorption case. For values of κmf up around 0.8 a-1 the early peak dominates. Thereafter the later peak is higher. At this value the peak release is already five orders of magnitude lower than the no-filtration case.

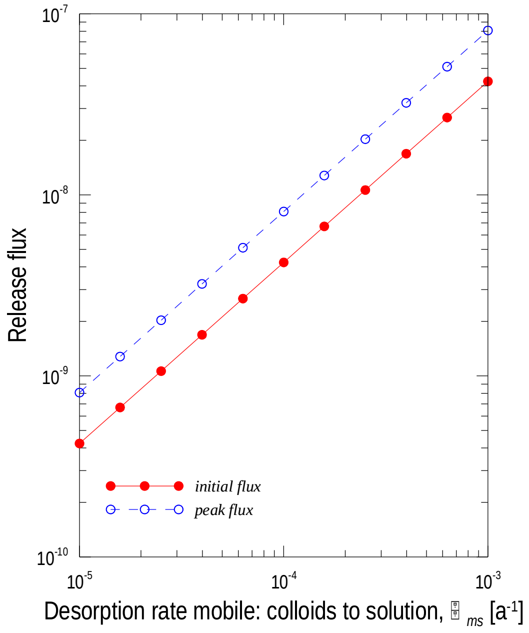


Figure 7: Effect of κ_{ms} on the initial peak and the peak at over all time, keeping all other parameters at their best estimate values. Best estimate value is $\kappa_{ms} = 10^{-3}$ a^{-1}.

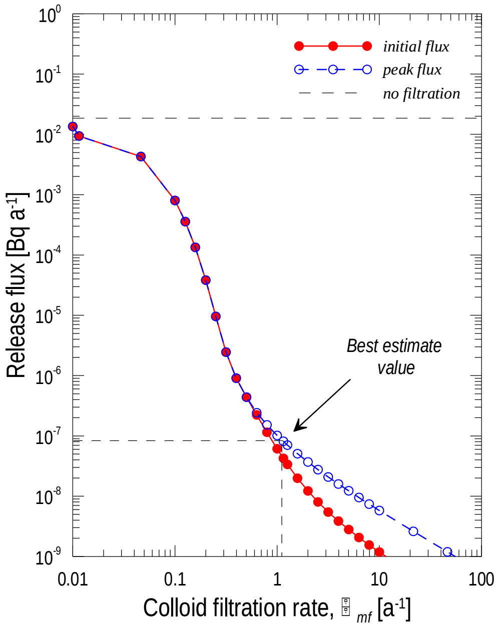


Figure 8. Effect of varying the filtration parameter, κ_{mf}, on the initial peak and the peak at over all time, keeping all other parameters at their best estimate values.

It is likely that filtration would be beneficial in reducing any colloid-mediated releases from the fracture. However, the results are sensitive to the value of the filtration rate and a one order of magnitude reduction compared to the best estimate value could lead to a higher release than the no-colloids case. This may be significant and it should be noted that because there is no remobilisation of filtered colloids and no desorption from fixed colloids to solution, the use of this high filtration value may be non-conservative. To investigate this influence it might be considered reasonable to use a reduced value for the filtration rate. It should also be noted that, as intuitively expected, the filtration rate increases as the fracture aperture width decreases, i.e. by a factor of ~50 for an order of magnitude decrease in aperture. This suggests that there is a better need to understand the mechanics of colloid filtration and , potentially, to include the fixed colloid population so as to be able to explicitly model the remobilisation of fixed colloids.

These preliminary results show that the key processes outlined in Section 2 of this report can be represented using modifications to the original COLLAGE code. The resulting model – COLLAGE 3 – shows the importance of colloid filtration as a mechanism for reducing potential early releases of radionuclides on colloids in the bentonite erosion scenario.

The structure of the COLLAGE mathematical model imposes restriction on the dynamical system that can be represented. In particular the issue of desorption of radionuclides from mobile colloids to solution is represented but, in the presence of a fixed (ie, filtered) colloid population the same process can not currently be modelled. Nevertheless, the potential importance of filtration as a limiting mechanism of CFRT mediated early release is clearly indicated. The reverse process is also not modelled in the current code (remobilisation of filtered colloids).

In the bentonite erosion scenario it is assumed that an episodic intrusion of dilute water to repository depth and in contact with bentonite buffer at the deposition hole-rock interface could cause the smectite gel to expand and thus be eroded and dispersed into fractures as a colloidal suspension. Loss of buffer performance might increase the risk of corrosion of canisters, for mechanical or hydrochemical reasons. If leakage from corroded canisters were to coincide with mobilisation of dispersed bentonite, then the consequences of colloid-facilitated radionuclide transport should be taken into account in the safety analysis. There are many uncertainties in how this mass of eroded and dispersed material might interact with the fracture and whether all of the injected colloids would be strained (i.e. physically trapped) close to deposition holes and/or filtered irreversibly (i.e. immobilised by sorptive attachment to fracture surfaces). SKB have research and modelling of these processes ongoing, the results of which are not yet published. Currently the only way to model this conservatively is to scale-down the filtration parameter κmf, so as to represent the possibility of a reversible filtration process plus the possibility that straining might be incomplete due to the large initial concentration of bentonite colloids. As the results show, the best estimate value of this parameter is close to the tipping point between CFRT early release dominated radionuclide fluxes and solute dominated later releases. Potentially of greater significance is the observation that a one order of magnitude reduction in the filtration rate would lead to an release of radionuclides of comparable magnitude to the pessimistic matrix diffusion case.

A further limitation of the current code concerns the fixed populations of colloids in the fracture. In reality these might vary in time as mobile colloids are filtered. The use of constant average values for the colloidal densities in the fracture water, αm and αf are therefore weakness of the current approach. A clearer picture would emerge from a revision of COLLAGE’s mathematical structure explicitly to include the concentration of radionuclides on fixed colloids as well as on mobile colloids and in solution.

5. Conclusions and recommendations

5.1 COLLAGE 3

Taking account of the recent developments in colloid facilitated radionuclide transport discussed in Section 2, the COLLAGE 2 plus code has been modified and reinterpreted to take into account additional processes – particularly colloid filtration. The new code – COLLAGE 3 – has been demonstrated (in prototype form) and the results indicate the potential importance of colloid filtration as one of the processes in colloid-facilitated radionuclide transport and retention in fractured rock that typifies the selected geological repository location at Forsmark. The best-estimate dataset has a filtration term which is close to the point where early release could become important. The modifications to the code introduced in COLLAGE 2 plus mean that the results at early times are reliably expressed.

Given the structure of the code, two processes are neglected here:

- the desorption of radionuclides on fixed colloids back to solution
- the remobilisation of fixed colloids, 'detachment'

These are non-conservative assumptions which act to limit the number of colloids reaching the outlet. However, irreversible trapping of colloids by filtration and straining is probably realistic.

A more complete description would account for the populations of fixed and mobile colloids but this would require a significant reworking of the code.

5.2 Implications for CFRT in SKB's PA modelling

In the bentonite erosion scenario it is supposed that large quantities of potentially radionuclide-bearing colloids are injected into a fracture. Depending on the mechanisms for filtration there can be a potentially significant early release of radionuclides. Filtration is a key issue.

Additional understanding is required to better characterise the mechanisms for colloid generation in such circumstances and to understand the scope for the filtration of colloids along the length of the fracture. Such investigations are beyond the scope of COLLAGE but the results should help to characterise parameters and FEPs to be include in PA codes for CFRT in SR-Site.

5.3 Suggestions for future work

Options for future work include

1. This work aimed to investigate if the COLLAGE 2 plus model could be developed to represent additional FEPs. This has been successfully carried out but the current code should be considered as a prototype for COLLAGE 3. Although fully functioning, it could be tidied up and made more user friendly. The code is written in Fortran 95. This is primarily because of the use of high-precision complex arithmetic in the Laplace Transform inversion. Nevertheless there are ways in which the user interface could be improved.

2. As the issue of CFRT has re-emerged recently a verification of the results from COLLAGE 3 against other CFRT codes would be useful. This could include a revised interpretation of a typical Forsmark fracture.

3. A more detailed review of classical filtration theory (Cvetkovic, 2004, citing Yao *et al*., 1971) could provide a better framework for filtration in a fracture characterised by aperture size.

4. As noted there are some mechanisms that the current form of the model cannot represent. Consideration should be given as to whether it is necessary to revise the mathematical model to include explicit representation of the three radionuclide concentrations: in solution, on mobile colloids and on fixed colloids.

5. Ultimately the significance of the bentonite erosion scenario lies in the radiological impact. For this the dose conversion factors are required for the nuclides implicated (^{242}Pu, americium, uranium, and neptunium). Similarly the potential source term needs to be approximated. Currently the model uses a delta-function release. The amount of colloidal material releases and the quantity of radionuclide are therefore also required. Alternatively, DCFs generated using GEMA3D, say, could be used to determine the radiologically acceptable limits on the release.

6. The code does not currently handle decay chains these could be added to the mathematical framework. However, the main importance of CFRT lies in the potential early release it may not be necessary to build decay chains into the code since it is the early release of the parents that are at variance with the non-CFRT case.

References

Bradford, S.A. and Bettahar, M. (2006). Concentration dependent transport of colloids in saturated porous media. Journal of Contaminant Hydrology, 82, 99-117.

Bradford, S.A., Bettahar, M., Šimunek, J. and van Genuchten, M.T. (2004) Straining and attachment of colloids in physically heterogeneous porous media. Vadose Zone Journal, 3, 384-394.

Bradford, S.A., Šimunek, J., Bettahar, M., van Genuchten, M.Th. and Yates, S.R. (2003) Modeling colloid attachment, straining, and exclusion in saturated porous media. Environmental Science and Technology, 37, 2242-2250.

Broed R. & Xu, S., (2008). User’s manual for Ecolego Toolbox and the Discretization Block, SSI Report, SSI 2008:10, Swedish Radiation Protection Institute (Now SSM, Swedish Radiation Protection Authority), Stockholm, Sweden

Carbol P, & Engkvist I, (1997). of radionuclide sorption coefficients for safety assessment. SKB R-97-13, SKB, Stockholm , cited by Lindgren & Lindström (1999)

Contardi, J.S., Turner, D.R. and Ahn, T.M. (2001). Modeling colloid transport for performance assessment. Journal of Contaminant Hydrology 47, 2-4, pp 323-333

Crawford, J. (2008). Bedrock transport properties Forsmark, Site descriptive modelling: SDM-Site Forsmark, Report R-08-48, SKB, Stockholm.

Cvetkovic, V. (2004). Colloid-facilitated radionuclide transport in single fractures: Sensitivities and scoping calculations for tracer tests at Äspö. Report R-04-49, SKB, Stockholm.

Cvetkovic, V., Painter, S., Turner, D., Pickett, D and Bertetti, P. (2004) Parameter and model sensitivities for colloid-facilitated radionuclide transport on the field scale. Water Resources Research, 40, W06504, doi:10.1029/2004WR003048.

EC (2005). Treatment of radionuclide transport in geosphere within safety assessments (RETROCK). Final report. EUR 21230. EC Directorate-General for Research, European Commission.

Grindrod, P. (1991) Radionuclide migration within fractured rocks: the impact of colloids upon geosphere calculations. Report 91:12, SKI, Stockholm.

Grindrod, P. and Worth, D.J. (1991) Radionuclide and colloid migration in fractured rock: model calculations. Report 91:11, SKI, Stockholm.

Grindrod, P. Brown, R. C. and Gealy, N.D. (1992). COLLAGE: A numerical code for radionuclide migration through a fractured geosphere in aqueous and colloidal phases. SKI Technical Report 92:19, Stockholm.

Grindrod, P. and Cooper, N. (1993). COLLAGE 2: A Numerical Code for Radionuclide Migration through a Fractured Geosphere in Aqueous and Colloidal Phases. SKI Technical Report 93:45, Stockholm.

James, S.C. and Chrysikopoulos C.V. (1999). Transport of polydisperse colloid suspensions in a single fracture Water Resources Research, Vol 35, No. 3 pp707-718

Kłos, R.A., (2003). COLLAGE 2 plus ~ User Guide, Aleksandria Sciences Note, ASN-03-01, Aleksandria Sciences, Sheffield, United Kingdom

Kłos, R.A., White, M.J., Wickham, S.M., Bennett, D.G. and Hicks, T.W. (2002). Quantitative assessment of the potential significance of colloids to the KBS-3 disposal concept. Report SKI 02:34, Swedish Nuclear Safety Inspectorate, Stockholm.

Laaksoharju, M. and Wold, S. (2005). The colloid investigations conducted at the Äspö Hard Rock Laboratory during 2000-2004. Report TR-05-20, SKB, Stockholm.

Lindgren, L. & Lindström, F., (1999). SR 97 Radionuclide transport calculations, SKB Report TR-99-23, SKB, Stockholm

Lu, N., Triay, I., Cotter, C., Kitten, H.D. and Bentley, J. (1998). Reversibility of sorption of Pu-239 onto colloids of hematite, goethite, smectite and silica: A milestone final report of YMP. Tech. Rep. LA-UR-98-3057, Los Alamos Natl Lab, Los Alamos, USA.

Lu, N., Conca, J., Parker, G., Leonard, P., Moore, B., Strietelmeier, B. and Triay, I. (2000) Adsorption of actinides onto colloids as a function of time, temperature, ionic strength and colloid concentration. Tech. Rep. LA-UR-00-5121, Los Alamos Natl Lab, Los Alamos, USA.

Missana, T., Alonso, U., García-Gutiérrez, M. and Mingarro, M. (2008). Role of bentonite colloids on europium and plutonium migration in a granite fracture. Applied Geochemistry, 23, 1484-1497.

Moridis, G.J, and Bodvarsson, G.S. (2001). Semi-analytical solutions of radioactive or reactive tracer transport in layered fractured media. Work supported by Office of Civilian Radioactive Waste Management US Department of Energy.

Moridis, G.J., Hu, Q., Wu, Y-S. and Bodvarsson, G.S. (2003). Preliminary 3-D site-scale studies of radioactive colloid transport in the unsaturated zone at Yucca Mountain, Nevada. Journal of Contaminant Hydrology, 60, 251-286.

Moridis, G.J., Yongkoo, S. and Wu, Y.-S (2003). Modelling studies of mountain-scale radionuclide transport in the unsaturated zone at Yucca Mountain, Nevada. Proceedings TOUGH Symposium Lawrence Berkeley National Laboratory, California May 12-14 pp1-9

Pusch, R. (1999). Clay colloid formation and release from MX-80 buffer. Report TR-99-31, SKB, Stockholm.

Ryan, J.N. and Elimelech, M. (1996). Colloid mobilization and transport in groundwater. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 107, 1-56.

SKB (2004a). RETROCK Project. Treatment of geosphere retention phenomena in safety assessments. Scientific basis of retention processes and their implementation in safety assessment models (WP2). Report R-04-48, SKB, Stockholm.

SKB (2004b). Interim data report for the safety assessment SR-Can, Report R-04-34, SKB, Stockholm.

SKB (2006). Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. Report TR-06-09. SKB, Stockholm.

SKB (2008) Site description of Forsmark at completion of the site investigation phase: SDM-Site Forsmark. Report TR-08-05, SKB, Stockholm.

Swanton, S.W., Atkinson, R., Sinclair, J.E. and Poole, M.J. (2000) Calculations of the potential impact of colloid transport on repository performance. Report AEAT/R/ENV/0222. AEA Technology, for UK Nirex, Harwell.

USDOE (2008) Yucca Mountain Repository Safety Analysis Report (SAR). Section 2.3.9.3.2.3 Colloid-facilitated Transport. US Department of Energy Report DOE/RW-0573, Rev 0.

Vahlund, F. and Hermansson, H. (2006) A direct numerical approach to solving the transport equations for radionuclide transport in fractured rock. Report R-04-50, SKB, Stockholm.

Vilks, P., Miller, N.H. and Vorauer, A. (2008) Laboratory bentonite colloid migration experiments to support the Äspö Colloid Project. Physics and Chemistry of the Earth, Parts A/B/C, 33, 14-16, 1035-1041.

Wickham, S.M., Bennett, D.G. and Higgo, J.J.W. (2000). Evaluation of colloid transport issues and recommendations for SKI performance assessments. Report SKI 00:33, SKI, Stockholm.

Wolfsberg, A. and Reimus, P. (2000) Saturated Zone Colloid-facilitated Transport. Report ANL-NBS-HS-000031, Rev 00. Los Alamos National Laboratory, for Office for Civilian Radioactive Waste Management, US Department of Energy.

Xu, S. and Saiers, J. (2009) Colloid straining within water-saturated porous media: Effects of colloid size nonuniformity. Water Resources Research, 45, W05501, doi: 10.1029/2008WR007258.

Xu, S., Gao, B. and Saiers, J. (2006) Straining of colloidal particles in saturated porous media. Water Resources Research, 42, W12S16, doi: 10:1029/2006WR004948.

Yao, K-M., Habibian, M. and O’Melia, C. (1971) Water and waste filtration: Concepts and applications. Environmental Science and Technology, 5, 1105-1112.

Additional bibliography on colloids and CFRT

Abdel-Salam, A. and Chrysikopoulos, C.V. (1995). Modeling of colloid and colloid-facilitated contaminant transport in a two-dimensional fracture with spatially variable aperture. Transport in Porous Media, 20, 3, 197-221

Albarran, N., Alonso, U., Missana, T., García-Gutiérrez, M. and Mingarro, M. (2008). Evaluation of geochemical conditions favourable for the colloid-mediated uranium migration in a granite fracture. e-Terra, 5, 2. http://e-terra.geopor.pt

Alonso, U., Missana, T., Geckeis, H., García-Gutiérrez, M., Turrero, M.J., Möri, R., Schäfer, Th., Patelli, A. and Rigato, V. (2006). Role of inorganic colloids generated in a high-level deep geological repository in the migration of radionuclides: Open questions. Journal of Iberian Geology, 32, 1, 79-94.

Bradford, S.A., Kim, H.N., Haznedaroglu, B.Z., Torkzaban, S. and Walker, S.L. (2009). Coupled factors influencing concentration-dependent colloid transport and retention in saturated porous media. Environmental Science and Technology, 43, 6996-7002.

Bradford, S.A., Šimunek, J., Bettahar, M., van Genuchten, M.T. and Yates, S.R. (2006). Significance of straining in colloid deposition: evidence and implications. Water Resources Research, 42, W12S15, doi: 10.1029/2005WR004791.

Bradford, S.A., Torkzaban, S. and Walker, S.L. (2007). Coupling of physical and chemical mechanisms of colloid straining in saturated porous media. Water Research, 41, 3012-3024.

Bradford, S.A., Torkzaban, S., Leij, F., Šimunek, J. and van Genuchten, M.T. (2009). Modeling the coupled effects of pore space geometry and velocity on colloid transport and retention. Water Resources Research, 45, W02414, doi: 10.1029/2008WR007096.

Bradford, S.A., Yates, S.R., Bettahar, M. and Simunek, J. (2002). Physical factors affecting the transport and fate of colloids in saturated porous media. Water Resources Research, 38, 1327, doi: 10.1029/2002WR001340.

Chrysikopoulos, C.V. (1998). Transport of colloids in saturated fractures. In: Advances in Fracture Mechanics: Fracture of Rock (E.B. Ahiabadi, ed.).

Chapter 10, pp 297-330. Computational Mechanics Publications, WIT Press, Southampton, U.K.

Filby, A., Plaschke, M., Geckeis, H. and Fanghänel, Th. (2008). Interaction of latex colloids with mineral surfaces and Grimsel granodiorite. Journal of Contaminant Hydrology, 103, 3-4, 273-284

Gardiner, M.P., Grindrod, P. and Moulin, V. (2001). The role of colloids in the transport of radionuclides from a radioactive waste repository: implication on safety assessment. Report EUR 19781, Directorate-General for Research, European Commission, Brussels.

Geckeis, H. (2004). Colloid influence on the radionuclide migration from a nuclear waste repository. In: Energy, Waste and the Environment: a Geochemical Perspective. Special Publications vol. 236, 529-543, Geological Society London.

Geckeis, H., Schäfer, T., Hauser, W., Rabung, T., Missana, T., Degueldre, C. Möri, A., Eikenberg, J., Fierz, Th. and Alexander, W.R. (2004). Results of the Grimsel Test Site (GTS), Switzerland – Impact of reaction kinetics and speciation on radionuclide migration. Radiochimica Acta, 92, 765-774.

Grindrod, P., Peletier, M and Takase, H. (1999). Mechanical interaction between swelling compacted clay and fractured rock, and the leaching of clay colloids. Engineering Geology 54 159-165

Honeyman, B.D. (2002). The role of colloids in radionuclide retention by and transport through geological media. In: Radionuclide Retention in Geological Media, GEOTRAP Workshop Proceedings, Oskarshamn, Sweden, 7-9 May 2001, pp 91-99. Nuclear Energy Agency of OECD, Paris.

James, S.C., Bilezikjian, T.K. and Chrysikopoulos, C.V. (2005). Contaminant transport in a fracture with spatially variable aperture in the presence of monodisperse and polydisperse colloids. Stochastic Environmental Research and Risk Assessment Volume 19, Number 4 pp266-279

Kersting, A.B., Efurd, D.W., Finnegan, D.L., Rokop, D.J., Smith, D.K. and Thompson, J.L. (1999). Migration of plutonium in ground water at the Nevada Test Site. Nature, 397, 56-59.

McKay, L.D., Sandford, W.E. and Strong, J.M. (2005). Field-scale migration of colloidal tracers in a fractured shale saprolite Ground Water, 38, 1, 139-147.

Möri, A., Alexander, W.R., Geckeis, H., Hauser, W., Schäfer, T., Eikenberg, J., Fierz, Th., Degueldre, C. and Missana, T. (2003). The colloid and radionuclide retardation experiment at the Grimsel Test Site: influence of bentonite colloids on radionuclide migration in a fractured rock. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 217, 33-47.

Novikov, A.P., Kaimykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V. and Myasoedov, B.F. (2006). Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia. Science, 314, 5799, 638-641.

OCRWM (2000). Colloid-associated radionuclide concentration limits. ANL-EBS-MD-D000020 Rev 00 ICN 01, Los Alamos Natl Lab, USA

OCRWM (2004). Radionuclide transport models under ambient conditions. MDL-NBS-HS-000008 Rev 2, Los Alamos Natl Lab, USA

OCRWM (2004). Unsaturated zone colloid transport model. ANL-NBS-HS-000028, Rev 00, Los Alamos Natl Lab, USA

Plaschke, M., Schäfer, T., Bundschuh, T., Ngo Manh, T., Knopp, R., Geckeis, H. and Kim, J.I. (2001) Size characterisation of benotnite colloids by differnet methods. Analytical Chemistry, 73, 4338-4347.

Schäfer, Th., Geckeis, H., Bouby, M. and Fanghänel, T. (2004). U, Th, Eu and colloid mobility in a granite fracture under near-natural flow conditions. Radiochimica Acta, 92, 731-737.

Shangping, X., Bin, G and Saiers, J.E. (2006). Straining of colloidal particles in saturated porous media. Water Resources Research, 42 W12S16

Swanton, S.W., Alexander, W.R., Berry, J.A. and Kelly, M.J. (2009) Review of colloids in the geosphere and their treatment in performance assessment. NDA Technical Report 2009-XY, NDA-RWMD, Harwell (not yet published).

Utsunomiya, S., Kersting, A.B. and Ewing, R.E. (2009). Groundwater Nanoparticles in the Far-Field at the Nevada Test Site: Mechanism for Radionuclide Transport. Environmental Science and Technology, 43 (5) pp1293-1298

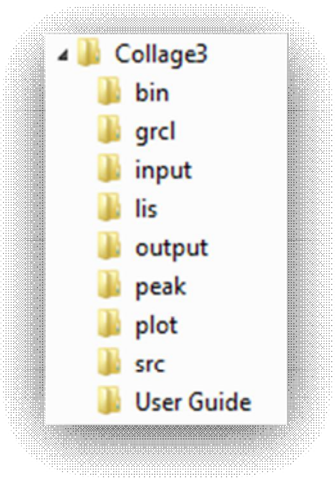
Zheng, Q., Dickson, S and Guo Y. (2007). Effect of aperture field variability, flow rate, and ionic strength on colloid transport in single fractures: laboratory-scale experiments and numerical simulation. American Geophysical Union, Fall meeting 2007, abstract #H23G-1733.

Appendix A – Implementation of COLLAGE 3

A.1 Datafiles, command line and results

The COLLAGE codes are written in Fortran and extensive use is made of complex arithmetic in the Laplace domain. The codes are rather old though there have been some enhancements to make use of the Fortran 95 standard, particularly use of increased precision models for all key variables enhancing the performance at earlier times. As a fortran application the code is command-line based and ruins in a Windows command window. Development took place in Linux and was also compiled for use in Cygwin. The MinGW compiler has also been used to produce native Windows executables. Compiler issues are discussed further in the following section.

As a text-based application basic i/o is accomplished using text files. The best estimate datafile described in Section 0 is illustrated in Table A-1. The numerical values are read in as free format numbers. The most secure way of generating the files is to employ a template in Excel and to copy the contents of the file to a text file for use with the code. In this way the parameters can be stored as tab-separated numbers. This is format is illustrated in Figure A-1. One option might be to integrate the execution of the code into an Excel spreadsheet as a macro.



Running the code requires the use of batch files (in the main directory) with a fixed subdirectory structure: the executables are stored in the `bin` path. Input files are in the `input` path. The command to run the code is (DOS window, Cygwin or Linux):

```
> c3_x c3_BE
```

This reads the `c3_BE.in` file from `input`. A listing of the run is directed to `lis` and the output from the code is stored in `output`. The command `c3_x` also runs a code from the `grcl` code which extracts details from the output files as columns of fluxes vs time. These are then stored in the `plot` path for use with plotting utilities. Additionally the peak folder contains details of the time of initial flux , the initial flux, the time of peak flux and the peak flux. All data files use the same name with the file extension used to denote the type of file:

`.in`	input files	`.out`	results files
`.lis`	listing files	`.dat`	tab delimited plot files
`.tab`	tab delimited peak flux files		

Source codes are in the `src` path.

A.2 Compilers

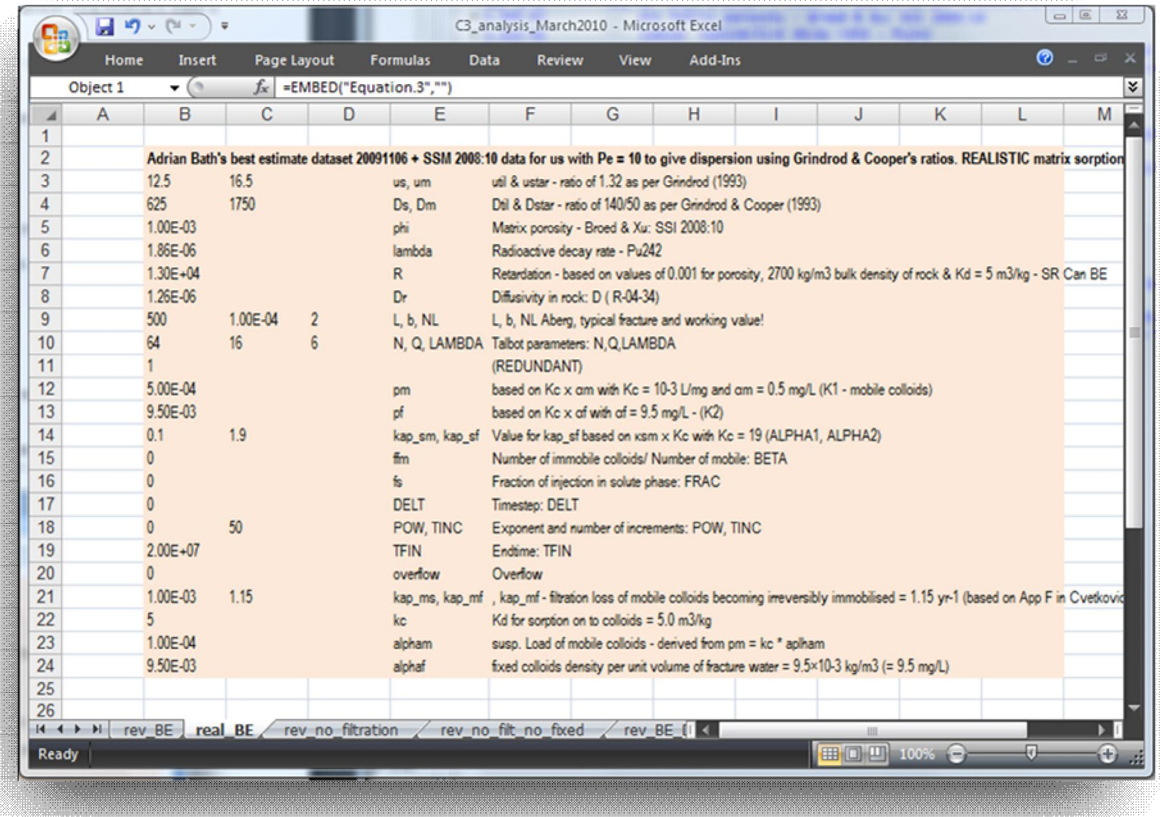
COLLAGE uses Fortran because of the need to perform complex arithmetic. The current version of the code includes several Fortran 95 features, such as the `real(10)` or `cmplx(10)` options which increase numerical precision beyond the normal double precision (`real(8)`) numbers. This additional precision helps provide numerical stability at early times in the solution.

Table A-1: The Best estimate data file for the COLLAGE 3 calculations.

```
Adrian Bath's best estimate dataset 20091106 + SSM 2008:10 data for us with Pe = 10 to give dispersion using
Grindrod & Cooper's ratios. REALISTIC matrix sorption

12.5       16.5                              us, um           util & ustar - ratio of 1.32 as per Grindrod
(1993)
625        1750                              Ds, Dm           Dtil & Dstar - ratio of 140/50 as per Grindrod &
Cooper (1993)
1.00E-03                                     phi              Matrix porosity - Broed & Xu: SSI 2008:10
1.86E-06                                     lambda           Radioactive decay rate - Pu242
1.30E+04                                     R                Retardation - based on values of 0.001 for
porosity, 2700 kg/m3 bulk density of rock & Kd = 5 m3/kg - SR Can BE
1.26E-06                                     Dr               Diffusivity in rock: D ( R-04-34)
500        1.00E-04         2                L, b, NL         L, b, NL Aberg, typical fracture and working
value!
64         16               6                N, Q, LAMBDA     Talbot parameters: N,Q,LAMBDA
1                                                             (REDUNDANT)
5.00E-04                                     pm               based on Kc x αm with Kc = 10-3 L/mg and αm =
0.5 mg/L (K1 - mobile colloids)
9.50E-03                                     pf               based on Kc x αf with αf = 9.5 mg/L - (K2)
0.1        1.9                               kap_sm, kap_sf   Value for kap_sf based on κsm x Kc with Kc = 19
(ALPHA1, ALPHA2)
0                                            ffm              Number of immobile colloids/ Number of mobile:
BETA
0                                            fs               Fraction of injection in solute phase: FRAC
0                                            DELT             Timestep: DELT
0          50                                POW, TINC        Exponent and number of increments: POW, TINC
2.00E+07                                     TFIN             Endtime: TFIN
0                                            overflow         Overflow
1.00E-03   1.15                              kap_ms, kap_mf   , kap_mf - filtration loss of mobile colloids
becoming irreversibly immobilised = 1.15 yr-1 (based on App F in Cvetkovic et al for colloid size 0.45 µm and
aperture 2 mm)
5                                            kc               Kd for sorption on to colloids = 5.0 m3/kg
1.00E-04                                     alpham           susp. Load of mobile colloids - derived from pm
= kc * aplham
9.50E-03                                     alphaf           fixed colloids density per unit volume of
fracture water = 9.5×10-3 kg/m3 (= 9.5 mg/L)
```

Figure A-1: Data file stored as an Excel spreadsheet.



=EMBED("Equation.3","")

	A	B	C	D	E	F
1						
2		**Adrian Bath's best estimate dataset 20091106 + SSM 2008:10 data for us with Pe = 10 to give dispersion using Grindrod & Cooper's ratios. REALISTIC matrix sorption**				
3		12.5	16.5		us, um	util & ustar - ratio of 1.32 as per Grindrod (1993)
4		625	1750		Ds, Dm	Dtil & Dstar - ratio of 140/50 as per Grindrod & Cooper (1993)
5		1.00E-03			phi	Matrix porosity - Broed & Xu: SSI 2008:10
6		1.86E-06			lambda	Radioactive decay rate - Pu242
7		1.30E+04			R	Retardation - based on values of 0.001 for porosity, 2700 kg/m3 bulk density of rock & Kd = 5 m3/kg - SR Can BE
8		1.26E-06			Dr	Diffusivity in rock: D (R-04-34)
9		500	1.00E-04	2	L, b, NL	L, b, NL Aberg, typical fracture and working value!
10		64	16	6	N, Q, LAMBDA	Talbot parameters: N,Q,LAMBDA
11		1				(REDUNDANT)
12		5.00E-04			pm	based on Kc x αm with Kc = 10-3 L/mg and αm = 0.5 mg/L (K1 - mobile colloids)
13		9.50E-03			pf	based on Kc x αf with αf = 9.5 mg/L - (K2)
14		0.1	1.9		kap_sm, kap_sf	Value for kap_sf based on κsm x Kc with Kc = 19 (ALPHA1, ALPHA2)
15		0			ffm	Number of immobile colloids/ Number of mobile: BETA
16		0			fs	Fraction of injection in solute phase: FRAC
17		0			DELT	Timestep: DELT
18		0	50		POW, TINC	Exponent and number of increments: POW, TINC
19		2.00E+07			TFIN	Endtime: TFIN
20		0			overflow	Overflow
21		1.00E-03	1.15		kap_ms, kap_mf	, kap_mf - filtration loss of mobile colloids becoming irreversibly immobilised = 1.15 yr-1 (based on App F in Cvetkovic
22		5			kc	Kd for sorption on to colloids = 5.0 m3/kg
23		1.00E-04			alpham	susp. Load of mobile colloids - derived from pm = kc * aplham
24		9.50E-03			alphaf	fixed colloids density per unit volume of fracture water = 9.5×10-3 kg/m3 (= 9.5 mg/L)
25						
26						

Development of the code has been carried out using the Linux environment with the gfortran compiler and the Photran integrated development environment for fortran. The developed code has been implemented in Windows XP and Vista using the Cygwin Linux-like enhancements for the DOS command window and using the G95 fortran compiler. This requires Cygwin to be installed on the host system, so the MinGW implementation of G95 which produces native Windows executables has also been implemented on XP and Vista. The results shown here were obtained in Vista using the MinGW G95 compiler (http://www.g95.org).

All codes produce the same results. As a verification, the results from COLLAGE 2 plus and COLLAGE 3 have been compared for equivalent datasets and the results are identical.

Strålsäkerhetsmyndigheten
Swedish Radiation Safety Authority

SE-171 16 Stockholm
Solna strandväg 96

Tel: +46 8 799 40 00
Fax: +46 8 799 40 10

E-mail: registrator@ssm.se
Web: stralsakerhetsmyndigheten.se