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Macroscale investigations on colloid mobility in near-natural systems

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Table of Contents

1	Introduction.....	4
2	WP3: Radionuclide and host rock interactions	4
3	Study of ⁸⁵ Sr transport through crushed granite in the presence of bentonite colloids	5
4	Radionuclide sorption onto bentonite colloids and radionuclide/colloid migration	8

1 Introduction

BELBaR project is based on the desire to improve the long-term safety assessments for repository concepts that combine a clay EBS with a fractured rock. The formation and stability of colloids from the EBS may have a direct impact on assessed risk from the repository in two aspects: Generation of colloids may degrade the engineered barrier; and Colloid transport of radionuclides may reduce the efficiency of the natural barrier. Colloids generated from clay are relevant from the point of view of probability of colloid mediated radionuclide transport and as a consequence of inappropriate degeneration of the engineered barrier system. In the BELBaR description of work it is stated that WP3: Radionuclide and host rock interactions will have the responsibility to ensure that the type and values of the parameters selected for experimental and modelling work should be those that will enable, as far as possible, representation of the range of different situations which can be expected in a repository.

The present deliverable gives a brief overview of the project activities during the period: 01/06/13 – 31/05/14. Macroscale investigations on colloid mobility in near-natural systems performed in NRI-REZ and UH are reported.

2 WP3: Radionuclide and host rock interactions

Clay colloids potentially generated in the radioactive waste repository near-field from the bentonite-buffer/backfill material might be stable under the geochemical conditions of the fractured rock far-field and could be a carrier of radionuclides. Colloid mobility is strongly dependant on fracture geometry (aperture size distribution and fracture surface roughness) as well as chemical heterogeneity induced by the different mineral phases present in the fracture filling material and the chemistry of the matrix pore water. WP3 addresses the following topics:

1. The process understanding of colloid mobility controlling processes and their appropriate description. A bottom-up approach starting from mono-mineralic single crystals over fracture filling mineral assemblages to natural fractures will be used to identify the colloid attachment probability determining processes.
2. The mobility of clay colloids will not necessarily enhance the mobility of strong sorbing radionuclides, if the sorption is reversible. Strong radionuclide clay colloid sorption reversibility kinetics have frequently been observed, but the reasoning for the observed kinetics is still pending and detailed species determination is needed in order to implement these reactions in thermodynamic models.
3. Identifying additional retention processes. Colloid transport and naturally occurring colloid concentrations in fractured rocks are frequently correlated to the water chemistry found in the water conducting features. However, the potential release of divalent cations (Ca^{2+} , Mg^{2+}) via matrix diffusion is expected to increase the colloid attachment probability and reduce the colloid mobility even under glacial melt water/meteoric water conditions and has to be investigated.

3 Study of ^{85}Sr transport through crushed granite in the presence of bentonite colloids

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The migration experiments were continued with ^{85}Sr transport through crushed granite in the presence of bentonite colloids. The main aim of experiments was to prepare stable radiocolloid suspension (^{85}Sr + bentonite colloids) and compare the strontium and radiocolloid suspension behaviour passing through crushed granite and quantification the effect of bentonite colloids presence on strontium migration (mobilization/immobilization). The migration experiments were investigated under dynamic conditions in column set-up which provides an approximation to real conditions, existing in the environment.

Preparing of radiocolloid suspension

Firstly, the stable radiocolloid suspension was prepared from SrCl_2 ($c = 2 \cdot 10^{-6}$ mol/l) solution spiked by ^{85}Sr as a tracer and purified bentonite B75 forming colloid particles as a suspension. The purification was described in previous report (Deliverable D3.2). Radiocolloid suspension was prepared by mixing the specific volume of strontium solution and same volume of bentonite colloids. The final strontium concentration in radiocolloid suspension was 10^{-6} mol/l and bentonite colloids concentration was 100 mg/l. Initially the mean hydrodynamic size of bentonite particles in suspension was about 500 nm (PCCS measurement). The contact time between strontium and the colloid particles before the dynamic experiments was seven days to ensure equilibrium. The sorption of strontium on colloid particles was checked by centrifugation. The radiocolloid suspension of volume 1.5 ml was centrifuged (30 minutes, $30\,000 \times g$) and the activity was measured in upper part (1 ml) and in bottom part, where the colloid particles settled. Over 90% of strontium activity was present in the bottom part, which confirm, that almost all strontium was sorbed (exchanged) on colloid particles.

Transport of strontium and bentonite colloids

The dynamic experiments provide information about important transport parameters (retardation coefficient R , distribution coefficient K_d , Peclet number Pe or hydrodynamic dispersion coefficient D) and respect realistic mass ratio (V/m). Transport of strontium and colloid particles through crystalline rock were studied in column arrangement. Crushed granitic rock from Melechov massif (Czech Republic) was used as solid phase. The grain size of used granitic fraction was 0.125-0.63 mm. Before the start of experiments the granite was washed by deionised water to remove the fine dust particles. All the column experiments were performed in arrangement with continual inlet of tracer. The initial concentration or activity of the tracer in aqueous phase and flow rate of aqueous phase was constant during the column experiment. The concentration or activity of tracer in liquid phase was measured in outlet of column and the breakthrough curve was evaluated from measured data. Before starting the experiments with the tracer the tritium breakthrough curve was obtained to characterize the column parameters.

Firstly, the column experiment only with bentonite colloid suspension was performed. The transport of bentonite colloid particles was fast (24 hours) and comparable with tritium transport, therefore the colloid particles passed through crushed granite without retention. The breakthrough curves of tritium (\blacktriangle) and bentonite colloids (\times) are displayed in Figure 1. The dynamic experiment with radiocolloid suspension was performed after that. The transport of both tracers was completely different. The bentonite colloids in presence of ^{85}Sr passed through crushed granite during first 24 hours and left the strontium in the column (see breakthrough curves of ^{85}Sr (\blacklozenge) and bentonite colloids (\blacksquare) displayed in Figure 1.). The sorption potential of granite material was higher, than the forces of interaction between strontium and bentonite colloids (ion exchange). Also the behaviour of colloids in presence and absence of ^{85}Sr was different. The colloids transport in presence of ^{85}Sr was slightly slower than transport of bentonite colloids without presence of ^{85}Sr (see breakthrough curves of bentonite colloids (\times) and bentonite colloids in presence of ^{85}Sr (\blacksquare) in Figure 1). The strontium transport duration was about 20 days and 400 pore volume of aqueous phase flew through crushed granite. This strontium behaviour differed significantly from the strontium behaviour described in our previous experiments which studied strontium transport in synthetic granitic water without presence of colloid particles. This experiment was completed after 3 days (Palágyi et al., 2013). Completely different strontium behaviour is probably caused by using various aqueous phases. In presented experiments with radiocolloids, the distilled water (flow rate 0.030 ml/min) was used as liquid phase (in order to preserve the stability of colloid particles). Palágyi et al. (2013) used the synthetic granitic water as liquid phase (flow rate 0.050 ml/min) and strontium transport was faster. Other parameters of both column experiments (concentration of strontium, grain size of crushed granite, column dimensions) were similar.

Evaluation of dynamic experiments

The transport of studied tracers through crushed granite is illustrated by breakthrough curve. The number of pore volume n_{PV} is on x-axis, the relative concentration (activity) (c_{rel} , A_{rel}) measured at outlet of column is on y-axis. The obtained breakthrough curve has S-shape with inflection point (see index i). At this point $c_{\text{rel}} = 0.5$ and for experimental values of retardation coefficients it holds that $R = n_{\text{PV},i}$. The retardation coefficient R is equal to number of pore volume provided that $c_{\text{rel}} = 0.5$ (Videnská et al., 2013). The distribution coefficient is calculated by the following equation:

$$K_d = \frac{\theta}{\rho} (R - 1)$$

where K_d is distribution coefficient (ml/g), θ is porosity, ρ is bulk density, R is retardation coefficient. The breakthrough curves were fitted by CXTFIT Code (STANMODE, version 2.08). This computer program allows estimating solute transport parameters from observed experimental concentrations. CXTFIT 2.1 estimates unknown parameters using a nonlinear least-squares optimization approach based on the Levenberg-Marquardt method. The model parameters are determined by minimizing an objective function (the sum of squared residuals, SSQ) (Toride et al., 1995). The one-dimensional transport model was used for the modelling of our experimental data, namely the deterministic equilibrium of the convection-dispersion equation (CDE) model. The input parameters were v , D , R . For initial estimate we used their experimental values and the values of v and D were fitted by CXTFIT Code.

The resulting experimental values (subscript _{exp}) of retardation and distribution coefficients and theoretical values (subscript _{model}) of dispersion coefficients are listed in Table 1.

Table 1. The transport parameters of studied tracers in crushed granite

Tracer	R_{exp}	$K_{d,exp}$ (ml/g)	D_{model} (cm ² /d)	Lower	Upper
				95 % confidence limit	
⁸⁵ Sr - radiocolloid	209.56	56.2	0.0231	0.0204	0.0258
B75 - radiocolloid	1.32	0.1	0.1430	0.0633	0.2228
³ H	1.02	0.0	0.0100	0.0072	0.0128
B75	1.17	0.05	0.0108	0.0000	0.0260

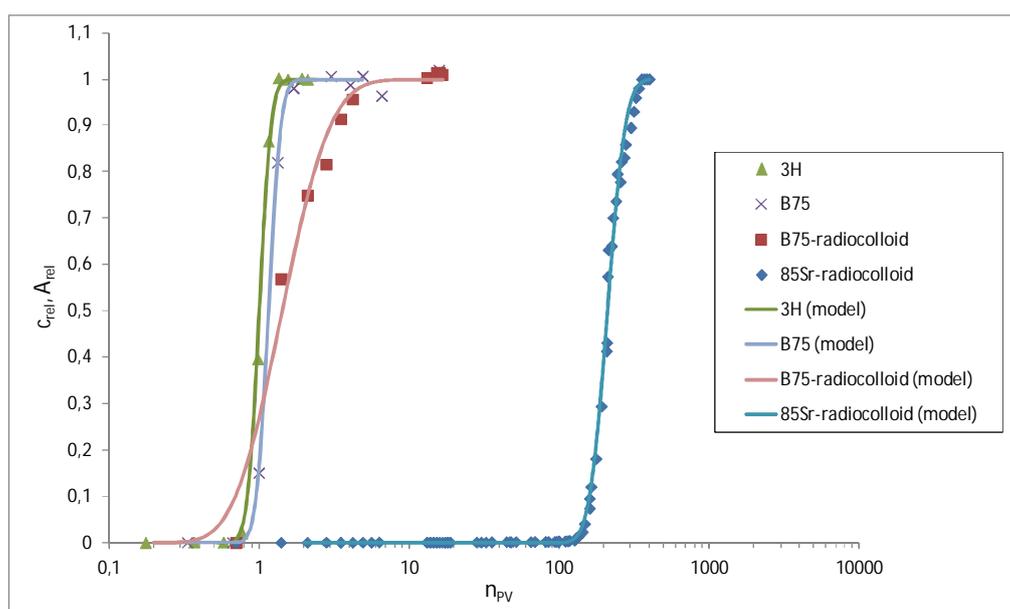


Figure 1. Experimental (points) and model (lines) breakthrough curves of different tracers in crushed granite of 0.125-0.63 mm grain size.

The ongoing research is focused on the modelling of obtained experimental breakthrough curves using the geochemical code PHREEQC and on understanding of colloids behaviour in the system. Further experiments will focus on the dynamic column experiments with other tracers (e. g. cesium and selenium).

References

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- Toride N, Leij FJ, van Genuchten MTh (1995) The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments, version 2.0. Research Report No. 137, U.S. Department of Agriculture, Riverside, California
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4 Radionuclide sorption onto bentonite colloids and radionuclide/colloid migration

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In the BELBaR/WP3, UH focus on macroscale investigations on colloid mobility in near-natural systems. The topics are radionuclide sorption/de-sorption onto colloids and radionuclide/colloid/rock interactions in column experiments. The radionuclide sorption has been studied on bentonite colloids as a function of ionic strength and pH using the batch method. Radionuclide and colloid interaction with a rock has been studied by means of the rock fracture and crushed rock column experiments.

Materials and Methods

The bentonite used is MX-80 Volclay type bentonite powder which consists mainly of montmorillonite. Cation exchange capacity determined using Cu(II)-triethylenetetramine-method is 0.89 eq kg^{-1} . Colloid dispersion solution was made from MX-80 bentonite clay powder which was mixed with Milli-Q water at a solid/solution ratio of 1:20. The suspension was shaken for one week and the colloidal fraction was then separated by centrifugation and the concentration of the bentonite colloids was determined by a gravimetric method after drying the suspension in an oven at $105 \text{ }^\circ\text{C}$ for 3 days. Allard, low salinity granitic ($I = 4.2 \cdot 10^{-3} \text{ M}$) and diluted OLSO ($I = 0.517 \text{ M}$) reference groundwater were used as solutions. OLSO simulates the current saline groundwater in Olkiluoto in oxic conditions. Electrolyte solutions, NaCl ($I = 1 \text{ M} - 1 \cdot 10^{-7} \text{ M}$) and CaCl_2 ($I = 3 \text{ M} - 3 \cdot 10^{-7} \text{ M}$) were used to study the effect of salinity.

The fracture column from Olkiluoto tonalite drill core was artificially fractured along the natural fracture containing an altered zone and filling minerals with where mainly chlorite. The porosity of unaltered tonalite is 0.1 – 0.3 %. The porosities of altered areas were not determined. The fracture width in the column was about 3.5 cm, the column length 6.8 cm and the fracture aperture 100 μm . The crushed rock columns were made of Kuru Grey granite and strongly altered tonalite from the Syryy area in Sievi. The rock matrix of Kuru gray granite is intact, fine-grained, non-foliated and equigranular. The total porosity is 0.2 % and the density is 2660 kg m^{-3} . The rock matrix of Syryy column was strongly and homogeneously altered containing visible mm scale pores. The total porosity is 2 – 8 % and the density is 2400 kg m^{-3} . The crushed rock column diameter was 1.5 cm and length 15 cm or 30 cm. The grain size of crushed rock was 1.95 – 5 mm.

Colloidal particle size distribution was determined applying the dynamic light scattering (DLS) method and zeta potential applying the dynamic electrophoretic mobility (Malvern Zetasizer Nano ZS). Colloid concentration was determined using a standard series made from MX-80 bentonite and a derived count rate obtained DLS measurements. The count rate is roughly proportional to the concentration of particles and can be used to estimate colloid concentrations. The calibration curve was constructed by measuring the known concentrations of particles with the same size and shape as the colloids in the samples. Colloid concentration determination was verified by analyzing the aluminum content of montmorillonite using ICP-MS (Figure 1).

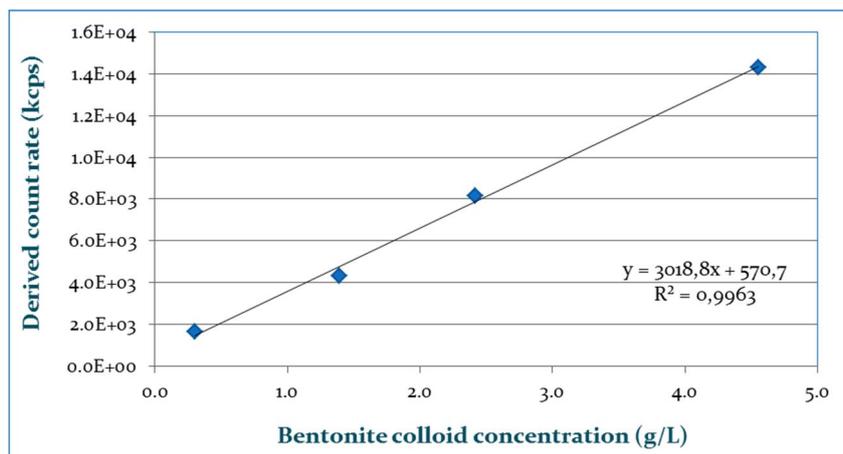


Fig. 1. Correlation of count rate determined by DLS and colloid concentration calculated based on the aluminium content of bentonite colloid suspensions analyzed using ICP-MS.

Experiments

Radionuclide sorption onto bentonite colloids was studied using colloid dispersion solution made from MX-80 bentonite clay powder. Colloid solution was added to the solution spiked with Sr-85 or Eu-152 tracer, 4.7 mL aliquot were taken after 2 h, 1, 2 and 7 days and solid colloid fraction was separated by ultracentrifugation (90000 rpm/60 min). The gamma activity of Sr-85 or Eu-152 was detected from the separated liquid phase using a Wizard gamma counter. Particle size distribution and concentration in the separated liquid phase were determined in order to check the number and size of remaining particles. Sorption was quantified by the determination of the distribution ratio of radionuclide activity between solid and liquid phase. The flow experiments were performed using a set-up shown in Figure 2. Water was pumped through the fracture of crushed rock column at different flow rates of 5–25 $\mu\text{L min}^{-1}$ using a peristaltic pump to control water flow rate. A short tracer pulse (20 μL) was injected into the water flow using an injection loop and the out flowing tracer was collected using a fraction collector.



Fig. 2. The experimental set-up for the fracture and crushed rock column experiments.

The hydraulic properties in the columns were determined using conservative tracer I-125 without colloids. The column experiments were performed in the low salinity Allard reference groundwater, in which the colloids are assumed to be stable and mobile. The transport of Sr-85 or Eu-152 in the columns was studied without and with bentonite colloids. In the experiments, the injected activity was 3 – 6 kBq. When the potential effect of colloids on the migration of Sr-85 or Eu-152 was studied, the tracer pulse was injected in the bentonite colloid suspension flow.

Results

Radionuclide sorption onto bentonite colloids was quantified by batch experiments that give a distribution ratio of radionuclide between solid and a liquid phase. A distribution coefficient, K_d ($\text{m}^3 \text{kg}^{-1}$) was calculated from the equation:

$$\frac{(A_0 - A_L)}{m} \cdot \frac{V}{A_L} \quad (1)$$

where A_0 is tracer activity, A_L is a measured activity in solution after separation, m is a solid phase mass (g) and V is liquid phase volume (mL). The determined distribution coefficient, K_d ($\text{m}^3 \text{kg}^{-1}$) values of Sr-85 for bentonite colloids in OLSO reference groundwater are shown as a function of ionic strength in Figure 3. The corresponding K_d values of Eu-152 are shown in Figure 4. Nearly all of Sr-85 and Eu-152 was rapidly sorbed onto bentonite colloids in 0.001 M solutions. Sorption was nearly 100 % and measured radioactivity in a liquid phase was at the background level resulting in inaccurate K_d determination. The distribution coefficient (K_d) decreased when the ionic strength increased. When the ionic strength was low, there was no difference in sorption between sodium chloride and calcium chloride solutions. The obtained results confirmed the influence of ionic strength and Ca^{2+} concentration on the sorption of Sr-85 and Eu-152 onto bentonite colloids. Radionuclide sorption is dependent also on pH and the concentration of colloids. In the case of small colloid concentrations, obtained K_d -values are not based on the equilibrium and are not accurate.

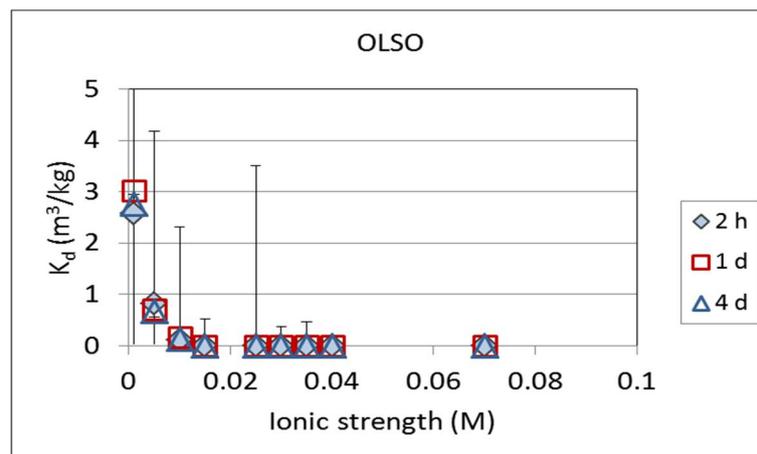


Fig. 3. The distribution coefficient, K_d -values of Sr-85 for bentonite colloids in OLSO reference water.

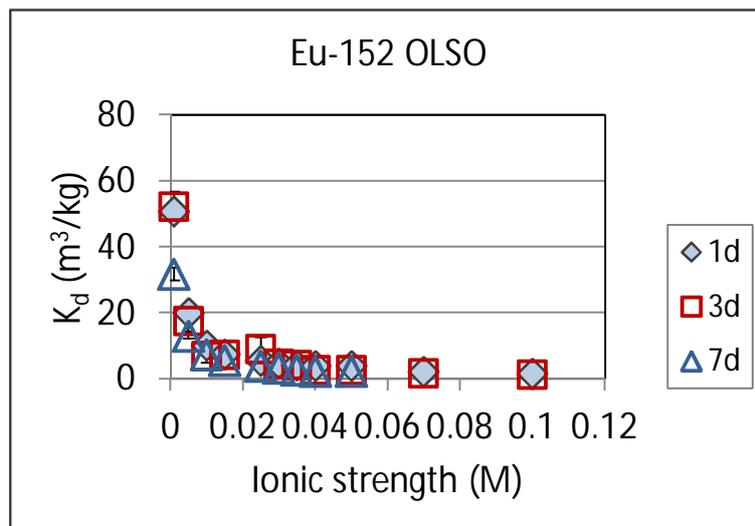


Fig. 4. The distribution coefficient, K_d -values of Eu-152 for bentonite colloids in OLSO reference water.

In the column experiments, different sorption processes taking place on fracture surfaces can be considered the main factor causing radionuclide retardation. The retardation factor can be estimated from the breakthrough curves of the conservative tracer and the radionuclide when the same experimental conditions have been used. The retardation factor is an approximation, because in the course of column experiment equilibrium between sorbed and dissolved species may not have been attained.

In the Olkiluoto fracture column and Syyry altered tonalite crushed rock column, particularly Eu-152 but also Sr-85 was strongly retarded without colloids. In the presence of bentonite colloid suspension, the slow elution of Eu-152 and Sr-85 was obtained. The breakthrough curves of Sr-85 in Olkiluoto tonalite fracture column without and with bentonite colloids are shown in Figure 5. Retardation factor, R_f of 56 was estimated without the presence of colloids at water flow rate of 0.6 mL h^{-1} . In the presence of colloids, R_f of 7.1 was estimated. In the Kuru grey unaltered granite crushed rock column, slight effect of bentonite colloids was found in the breakthrough curves of Sr-85. No breakthrough of Eu-152 activity was detected during two week experiment without the addition of bentonite colloids.

Bentonite colloid filtration in a fracture or crushed rock surfaces was observed and the migration of colloids was affected primarily by colloid size but also by the type of column and/or rock alteration (Table I). The distribution of radionuclides between mobile colloidal and immobile rock phases determines radionuclide mobility. The main uncertainties remain in the quantification of colloids under realistic repository conditions and how mobile colloids are. If colloids are sufficiently stable and thus mobile, irreversible sorption on silica colloids may increase radionuclide transport. The reversibility or irreversibility of radionuclide-colloid association must be further investigated in a simple system and in repository relevant conditions.

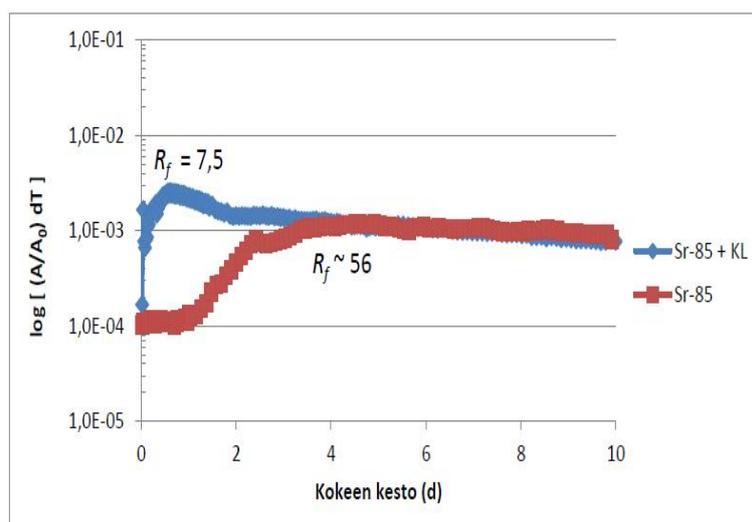


Fig. 5. The breakthrough curves of Sr-85 in Olkiluoto tonalite fracture column without (red) and with (blue) bentonite colloids.

Table I. The recovery of colloids in crushed rock column (KGG c, SY-KR7 c) and fracture column (OT f) experiments.

Column packing material	Flow velocity (mL/h)	Z-Ave. (BC) (nm)	m (BC pumped) (mg)	m (Al) (mg)	m (Al anal.) (mg)	Colloid recovery (%)
KGG c	2,2	274 ± 4	3,133	0,315	0,128	40,5 ± 1,5 (after 22 h) 41,1 ± 2,0 (after 43 h)
	1,2	583 ± 12	3,650	0,367	0,0143	3,9 ± 0,2 (after 28 h)
	2,4	583 ± 12	3,770	0,380	0,0232	6,1 ± 0,2 (after 20 h)
SY-KR7 c	2,2	274 ± 4	3,133	0,315	0,0116	3,7 ± 0,2 (after 22 h) 3,7 ± 0,6 (after 43 h)
	1,2	583 ± 12	4,000	0,402	N/A	N/A
	2,4	583 ± 12	3,790	0,381	0,00572	1,5 ± 0,1 (after 20 h)
OT f	0,6	274 ± 4	0,724	0,073	0,0184	25,3 ± 0,5 (after 43 h)
	1,2	274 ± 4	1,500	0,150	0,0958	62,1 ± 2,0 (after 19 h)

Conclusions

The interaction between radionuclides and bentonite colloids has been studied. The obtained results confirmed the influence of ionic strength and Ca²⁺ concentration on the sorption of Sr-85 and Eu-152 onto bentonite colloids. Bentonite colloids were observed to have a significant influence on the migration of Sr-85 and Eu-152 in the fracture and crushed rock column experiments. Migration of bentonite colloids in columns was affected primarily by colloid size but also by water flow rate and column type.

The main uncertainties remain in the quantification of colloids under realistic repository conditions and how mobile colloids are. If colloids are sufficiently stable and thus mobile, irreversible sorption on colloids may increase radionuclide transport. The reversibility or irreversibility of radionuclide-colloid association must be further investigated in a simple system and in repository relevant conditions. At current conditions in Olkiluoto, the ionic strength of the groundwater is around 0.5 M and the colloids released from the bentonite barrier are aggregated and unstable do not have an influence on the migration of radionuclides. However, this knowledge and understanding about bentonite erosion in colloidal form can be utilized in the estimation performance of the bentonite barrier. The possibility of a future glacial period and subsequent post-glacial phase when the infiltration of fresh, glacial melt water dilutes groundwater, implies that dilute groundwater conditions cannot be excluded and the influence of bentonite and other colloids has to take into consideration.