BELBaR

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Macroscale investigations on colloid mobility in near-natural systems

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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: 01/06/14 – 31/05/15. 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.

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3 Study of ^{137}Cs transport through crushed granite in the presence of bentonite colloids

K. Videnská, R. Červinka, ÚJV Řež, a. s.

The study of ^{137}Cs transport through a column filled with crushed granite in presence of bentonite colloids followed the previous experiments with ^{85}Sr. The main aim of experiments was to quantify the effect of bentonite colloids presence on cesium migration. The cesium migration was investigated under dynamic conditions in column set-up and cesium sorption properties by static batch method. Column experiments stepwise approach included characterization of column by ^{3}H tracer, transport of colloid particles without presence of radioactive tracer, transport of ^{137}Cs without presence of clay colloids and finally transport of radiocolloids. The values of transport parameters (retardation coefficient R, distribution coefficient K_d, dispersion coefficient D) were calculated from experimental breakthrough curves.

With static batch method we study the influence of granite composition on cesium sorption, mainly the contribution of individual minerals (i.e. muscovite). The sorption experiments were performed with granite and muscovite, because mica minerals are considered as dominant cesium sorbent in the literature.

MATERIALS AND METHODS

Preparing of radiocolloid suspension

Radiocolloid suspension was prepared by mixing of specific volume of cesium solution in deionised water and same volume of bentonite colloids. The final cesium concentration in radiocolloid suspension was 10^{-6} mol l^{-1} and bentonite colloids concentration was 100 mg l^{-1}. The colloid suspension was prepared from the purified bentonite "Bentonite 75", denoted as B75 in Na$^+$ form (see purification procedure in Deliverable D3.2). Initially the mean hydrodynamic size of bentonite particles in suspension was 410 nm measured by photon cross-correlation spectroscopy (PCCS). The contact time between cesium 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, RCF 30 000 × g) and the activity was measured in upper part (1 ml) and in bottom part, where the colloid particles settled. Over 80 % of cesium activity was present in the bottom part, which confirmed, that cesium was sorbed (exchanged) on colloid particles. The stability of radiocolloids was controlled by PCCS.
Sorption experiments

Sorption of cesium was studied by static batch method. The crushed granitic rock from Melechov massif (Czech Republic) and separated muscovite were used as solid phases. The grain size of granitic fraction was 0.125-0.63 mm. Solution of 10^{-6} mol/l CsCl spiked by ^{137}Cs in distilled was used as liquid phase. The mixture was shaken for 9 days; solid to liquid ratio was 1:20. The activity of cesium was measured in aqueous phase by gamma spectrometry.

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Column experiments

The crushed granite (Melechov massif, fraction 0.125-0.63 mm) was placed into 5 cm^3 plastic columns. The inlet of liquid phase into column was continuous with constant tracer concentration (colloid concentration, cesium concentration) and flow rate of liquid phase. Defined volumes of liquid phase were taken periodically from the column outlet for the measurement of colloids concentration and cesium activity. The transport results of studied tracers through crushed granite are represented by breakthrough curves, where 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 experimental procedure is described in Palágyi et al. (2013).

RESULTS

Sorption of cesium on granite

The composition of granitic rock is one of the crucial parameters influencing sorption of cesium on granite. The mica minerals are considered as a possible dominant sorbent of cesium in granitic rock. The sorption experiment was focused on the cesium sorption on Czech granite from Melechov massif. The main components of Melechov granite are quartz and feldspars (orthoclase and plagioclase), the minority components are muscovite (mica mineral) and chlorite. The sorption experiment was performed with separated muscovite and bulk crushed granite and resulting K_d were compared. The K_d values are summarised in Table **1**. The assumption of higher cesium sorption on muscovite was not confirmed. The results showed that 13% of cesium was sorbed on muscovite and 87% of cesium was sorbed on other minerals presented in granite. These results are very similar to sorption behaviour of strontium. Also previous experiments have shown that mica minerals are not dominant sorbents for strontium (see Deliverable D3.5).

Table 1. Radionuclides sorption on minerals in granite

Tracer	Sorption on granite (%)	
	Muscovite in granite	Other minerals in granite
Cesium	13	87
Strontium	12	88

Transport of cesium in presence of bentonite colloids

The column experiments were performed in same arrangement as previous ones with strontium and provided information about cesium transport through crushed granite in presence of bentonite colloids. The resulting breakthrough curves are shown in Figure 1.

Before starting the experiments with ^{137}Cs, bentonite colloids and radiocolloid suspension, the tritium breakthrough curve was obtained to characterize the column parameters (▲).

Then the column experiment only with bentonite colloid suspension was performed (✕). The bentonite colloids transport was fast and comparable with tritium transport, therefore the colloid particles passed through crushed granite without retention and behaved as conservative tracer.

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The transport of cesium in deionised water without presence of bentonite colloids was significantly slower, cesium showed strong sorption and passed through column after 350 pore volumes (−). Our previous experiment with cesium was conducted in synthetic granitic water (SGW) (●). This experiment was completed after 9 days and 177 pore volumes of aqueous phase flew through crushed granite (see Deliverable D3.2). The results showed the different sorption behaviour of cesium in deionised water (DW) and SGW, the transport of cesium through granite in DW is significantly slower. Different cesium behaviour is probably caused by different composition of aqueous phases. In case of SGW, the competition of cesium with other ions resulted in lower sorption and thus faster breakthrough. Similar situation was observed in column experiments with strontium (see Deliverable D3.5).
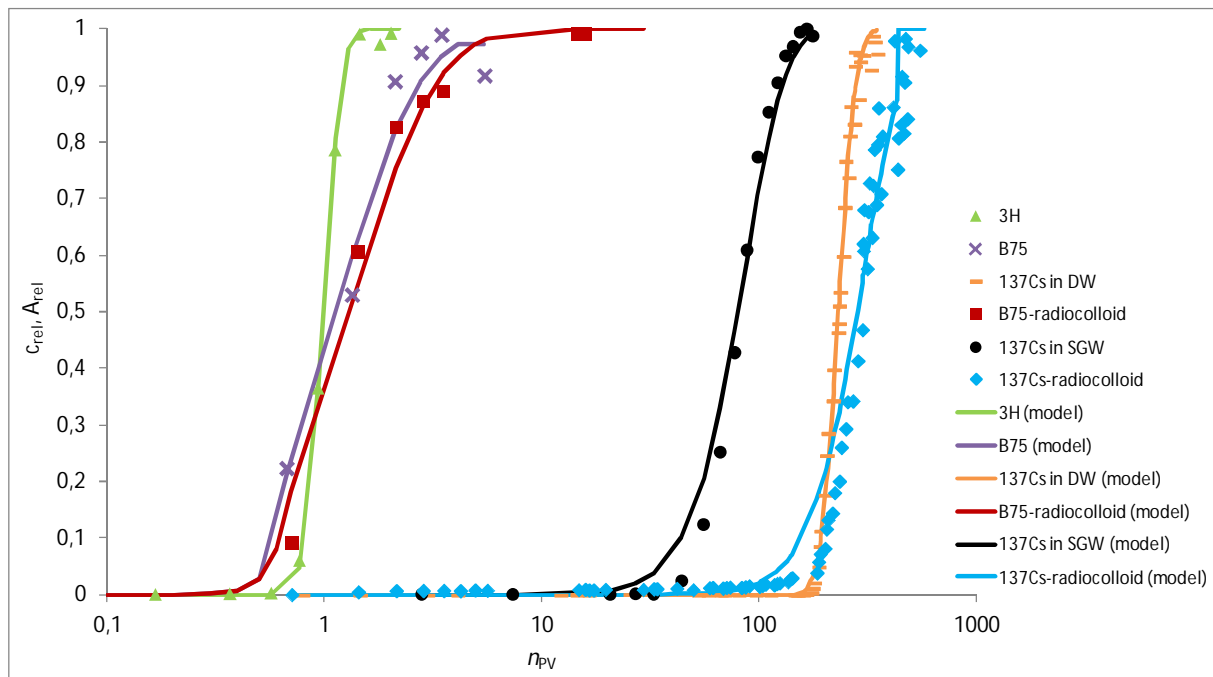

Figure 1. Experimental (points) and model (lines) breakthrough curves of different tracers in crushed granite of 0.125-0.63 mm grain size

The last column experiment was performed with radiocolloid suspension. The concentration of bentonite colloids and activity of cesium were measured at column outlet at the same time and the breakthrough curves were evaluated. The transport of bentonite colloids in presence of cesium (■) was almost similar as transport of bentonite colloids alone (✕). Colloids passed through crushed granite during first several hours, however the transport was slightly slower than transport of bentonite colloids without Cs presence. This result suggested some temporary effect of retardation in the system Cs-colloid-granite.

The transport of cesium in presence of bentonite colloids (◆) differed from transport of cesium alone significantly. The first activity of cesium at column outlet was measured after 68 pore volumes and increased slowly. The rapid increase of cesium activity was observed after 184 pore volume. The results showed that part of cesium (about 1 %) passed through granite with bentonite colloids, the cesium was probably tightly bind at montmorillonite frayed edge sites. Most of cesium was exchanged from montmorillonite layer sites to granite mineral surface. In comparison with cesium transport in presence of colloids, cesium transport without presence of

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bentonite colloids was different, the first activity of cesium was measured after 160 pore volumes and the rapid increase of activity followed immediately (–). Although the resulting breakthrough curves of cesium seem they have similar shapes (see Figure 1), the different cesium behaviour with (♦) and without (–) presence of bentonite colloids is evident from cesium behaviour during passing first 100 pore volumes (see Figure 2). Cesium transport is particularly accelerated by bentonite colloids however the amount of passing cesium with bentonite is limited by number of montmorillonite sorption sites.
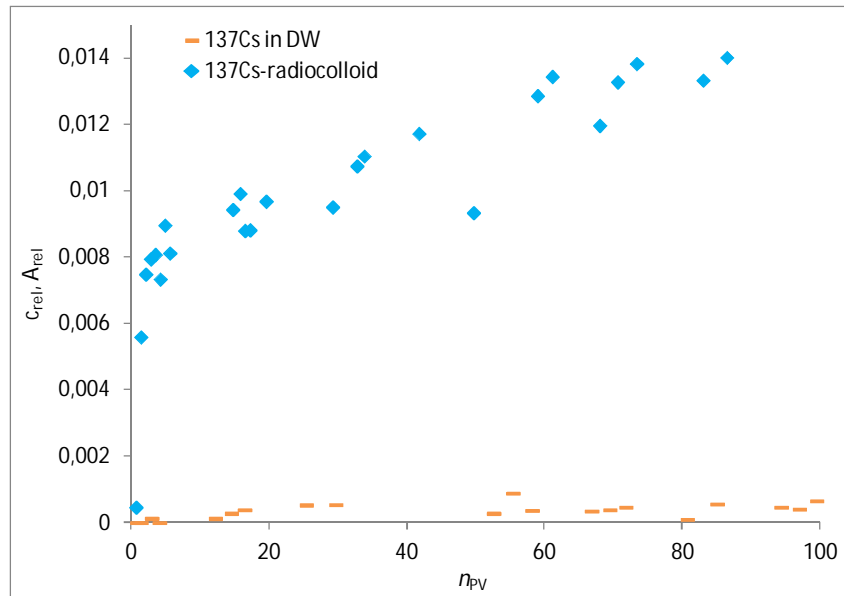

Figure 2. Influence of bentonite colloids on Cs transport

Evaluation of dynamic experiments

The important transport parameters R (retardation coefficient) and K_d (distribution coefficient) are calculated from breakthrough curves. The breakthrough curves were fitted by CXTFIT Code (STANMODE, version 2.08), the evaluation and fitting of breakthrough curves is described in Deliverable D3.5. The values of theoretical dispersion coefficients D_{model} and theoretical retardation coefficient R_{model} were calculated from fitted breakthrough curves. The resulting experimental values (subscript $_{exp}$) and theoretical values (subscript $_{model}$) of transport parameters are listed in Table 2. The values of R and K_d described tracers sorption on granite, the lowest sorption was observed in case of bentonite colloids, they behaved as non-sorbing conservative tracer. The highest values of K_d were observed for cesium in presence of bentonite colloids.

Table 2. The transport parameters of studied tracers in crushed granite

Tracer	R_{exp}	R_{model}	$K_{d,exp}$ (ml/g)	D_{model} (cm^2/d)
^{3}H	1.00	2.50	0.00	0.029
B75	1.27	2.25	0.08	0.412
^{137}Cs in SGW	80.1	44.0	23.8	0.01
^{137}Cs in DW	233.8	276.1	65.9	0.01
^{137}Cs-radiocolloid	298.9	172.7	81.2	0.01
B75-radiocolloid	1.28	4.52	0.08	0.844

Conclusions

The influence of bentonite colloids on cesium transport in crushed granite was studied using column experiments. The results showed that the presence of bentonite colloids affected the cesium transport. The colloid particles partially fulfil the role of radionuclides carrier; part of cesium (about 1 %) passed through crushed granite sorbed on bentonite colloids, however the most of cesium was desorbed from bentonite colloids and retained in granitic rock. Thus, cesium affinity towards granitic rock is higher than affinity towards bentonite colloids and the cesium sorption on bentonite is reversible.

On the other hand, the transport of colloids is also influenced by presence of cesium. The colloid particles passed through granite in presence of cesium slightly slower than without present of cesium, the temporary complex Cs-colloid-granite is probably formed in the column.

References

Palágyi Š, Štamberg K, Havlová V, Vodičková H (2013) J Radioanal Nucl Chem 297:33-39

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 Macroscopic sorption and colloid migration experiments

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In the BELBaR/WP3, UH focus on macroscale investigations on radionuclide sorption and colloid mobility in near-natural systems. The radionuclide sorption has been studied on montmorillonite and 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 crushed rock and drill core column experiments.

Materials and Methods

The bentonite used is MX-80 Volclay type bentonite powder which consists mainly of montmorillonite. It has a mineralogical composition of 76.3 % smectite, 8.3 % muscovite, 4.8 % quartz, 2.3 % plagioclase and illite, tridymite, magnetite, gypsum and pyrite as accessory minerals. Its chemical composition is 64.32 % SiO_2, 19.00 % Al_2O_3, 3.84 % Fe_2O_3, 2.56 % MgO, 2.03 % Na_2O, 1.66 % CaO, 0.73 % SO_3, 0.62 % K_2O, 0.15 % TiO_2 and 0.07 % CO_2. Cation exchange capacity determined using Cu(II)-triethylenetetramine-method was 0.89 eq kg^{-1}. The sodium montmorillonite has been isolated from Wyoming Volclay MX-80 bentonite and purified by B^+Tech Oy, Finland. The specific surface area determined by the N_2-BET method was 49.6 g^2/cm. Corundum (α-Al_2O_3), aluminium oxide, was provided by Taimicron. The specific surface area was 14.5 g^2/cm.

The crushed rock columns were made of Kuru Grey granite and strongly altered tonalite from the Syyry 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 Syyry 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. Drill core columns were constructed from Kuru gray granite cores which were placed inside a tube to form a flow channel (L = 68.5 cm, w = 4.4 cm) representing an artificial fracture formed by the 0.5 mm gap between the core and the tube.

Colloidal particle size distribution was determined applying the photon correlation spectroscopy (PCS) 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 PCS 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 *Agilent 7500ce* ICP-MS (Figure 1).

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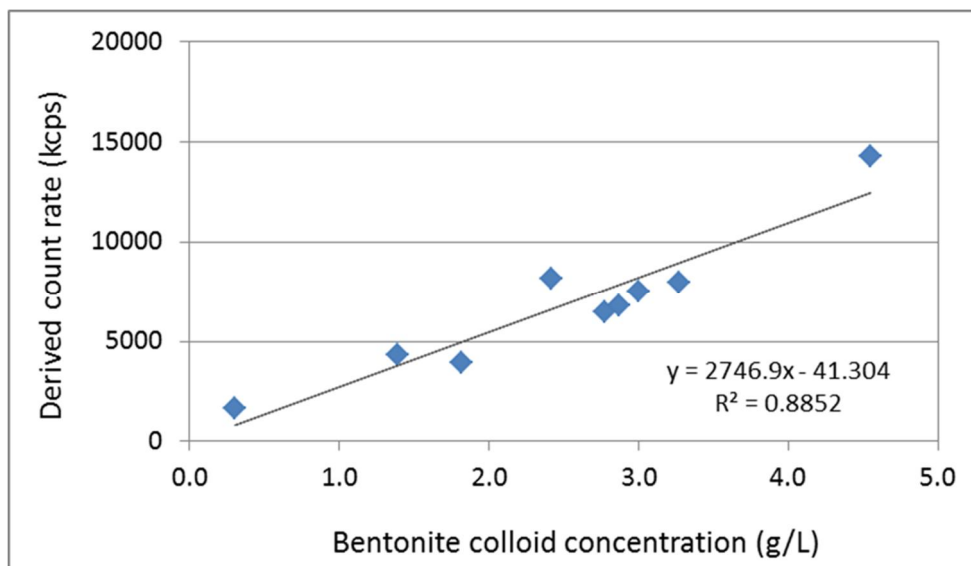Date of issue of this report: **31/05/15**

Figure 1. Correlation of count rate determined by PCS and colloid concentration calculated based on the aluminum content of bentonite colloid suspensions analyzed using ICP-MS.

Experiments

Sr-85 and Eu-152 sorption

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 °C for 3 days. Allard, low salinity granitic ($I = 4.2 \ 10^{-3}$ M) and diluted OLSO ($I = 0.517$ M) reference groundwater were used as solutions. OLSO simulates the current saline groundwater in Olkiluoto in oxic conditions. Electrolyte solutions, NaCl ($I = 1$ M – $1 \ 10^{-7}$ M) and $CaCl_2$ ($I = 3$ M – $3 \ 10^{-7}$ M) were used to study the effect of salinity.

Sr-85 and Eu-152 sorption on bentonite colloids has been investigated as a function of ionic strength and pH (3 to 11). The sorption parameters as a function of pH were determined by conducting batch experiments in a clove box under CO_2 free conditions. The solid liquid–ratio was studied to obtain an optimum mineral concentration needed to conduct batch experiments, in which the amount of mineral or colloid is not the limiting the radionuclide sorption. The kinetic experiments were conducted to optimize the equilibration time for the batch experiments. In the sorption experiments, colloid suspension was added to the solution spiked with a 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). Particle size distribution and concentration in the separated liquid phase are determined in order to check the number and size of remaining particles. The radioactivity of Sr-85 and Eu-152 was detected using an automatic gamma counter (Perkin Elmer, 1480 Wizard 3). Sorption was quantified by the determination of the distribution ratio of radionuclide activity between solid and liquid phase.

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Np-237 sorption

Neptunium(V)-237 sorption on sodium montmorillonite and bentonite colloid dispersion made from MX-80 Volclay bentonite powder has been studied under simplified but environmentally relevant conditions. Aluminium oxide (α-Al_2O_3), corundum was used as a reference mineral in order to study the aluminol surface sites present on clay minerals, which are regarded as the main adsorption sites for radionuclide attachment. Batch sorption experiments were done as a function of pH and neptunium concentration. The experiments as a function of pH (pH-edges) were done using a constant neptunium concentration of 10^{-6} M over the pH range 4 – 11. The sorption isotherm determinations as a function of Np concentration (10^{-9} to 5×10^{-6} M) were done at a constant pH of either 8, 9 or 10. The solid liquid–ratio was studied to obtain an optimum mineral concentration needed to conduct batch experiments, in which the amount of montmorillonite is not the limiting factor for the neptunium sorption. Solid concentrations 0.5 g/L and 5 g/L were used for montmorillonite and 3.3 – 4.0 g/L for bentonite colloids. 10 mM $NaClO_4$ was used as a background electrolyte. The kinetic experiments were conducted to optimize the equilibration time for the batch experiments. All sorption experiments were conducted in a N_2-glove box to exclude the formation of soluble Np-carbonato complexes that influence the uptake and speciation of neptunium on the solid surfaces.

The samples were made by adding a small aliquot of concentrate montmorillonite or colloid stock solution, Np-237 tracer and a background electrolyte to the liquid scintillation bottles. Solution was buffered to the desired pH and after one week or 30 days equilibration time, the solid particles were separated from the liquid by centrifugation (6000 rpm/60 min) and the 1 mL aliquots were taken immediately for liquid scintillation counting (Perkin Elmer Tri-Carb 3100 TR liquid scintillation counter). α/β – discrimination was used to separate out the β disintegrations from the Np daughter nucleus Pa-233.

Two desorption experiments were done to investigate the reversibility of neptunium sorption reaction on montmorillonite. The experimental conditions were: N_2-atmosphere, Na-montmorillonite concentration of 5 g/l, Np(V) concentration of 10^{-6} M and 10 mM $NaClO_4$ background electrolyte. In the first desorption experiment, neptunium was allowed to sorb on the montmorillonite surface at pH 9. After an equilibration time of 7 days, the suspension was acidified to pH 5 and the neptunium desorption was followed as a function of time by taking small aliquots from the suspension until to 15 days. In the second desorption experiment, the background electrolyte (pH 8) of the neptunium spiked montmorillonite suspension was changed every 2 – 3 days or 7 days. A small (1 ml) aliquot for a liquid scintillation counter was taken from the supernatant to measure the desorbed amount of neptunium.

Colloid migration

The colloid migration experiments were performed using a set-up shown in Figure 2. Water was pumped through the crushed rock or drill core column at different flow rates of 5– 30 µL min^{-1} using a peristaltic pump to control water flow rate. Colloid solution was injected into the water flow using an injection loop and the out flowing solution was collected using a fraction collector. The column experiments were performed in the low salinity Allard reference groundwater, in which the colloids are assumed to be stable and mobile. Colloid concentration was determined by analyzing the aluminum content of montmorillonite using ICP-MS.

Figure 2. The experimental set-up for the crushed rock and drill core column experiments.

Results

Sr-85 and Eu-152 sorption

Radionuclide sorption onto bentonite colloids was quantified by batch experiments that give a distribution ratio of radionuclide between solid and a liquid phase. The distribution coefficient, K_d (m^3 kg^{-1}) values of Sr-85 for bentonite colloids as a function of ionic strength in OLSO reference groundwater are shown in Figure 3 and in NaCl and CaCl$_2$ solutions in Figure 4.
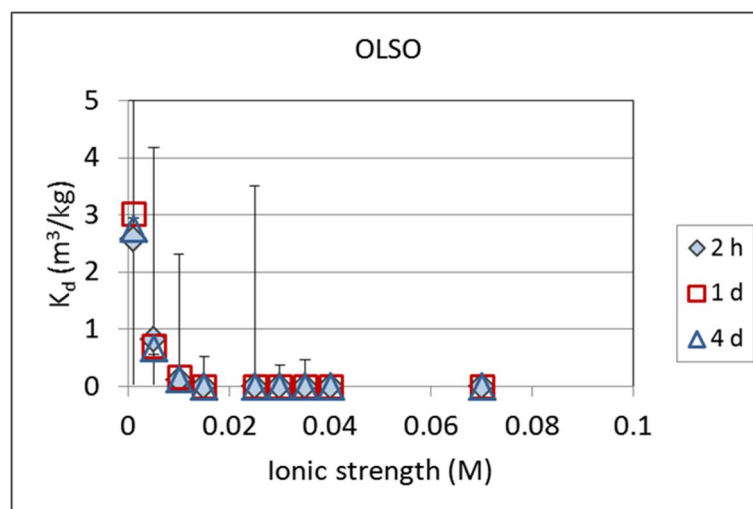
Figure 3. The distribution coefficient, K_d-values of Sr-85 for bentonite colloids as a function of ionic strength in OLSO reference water.
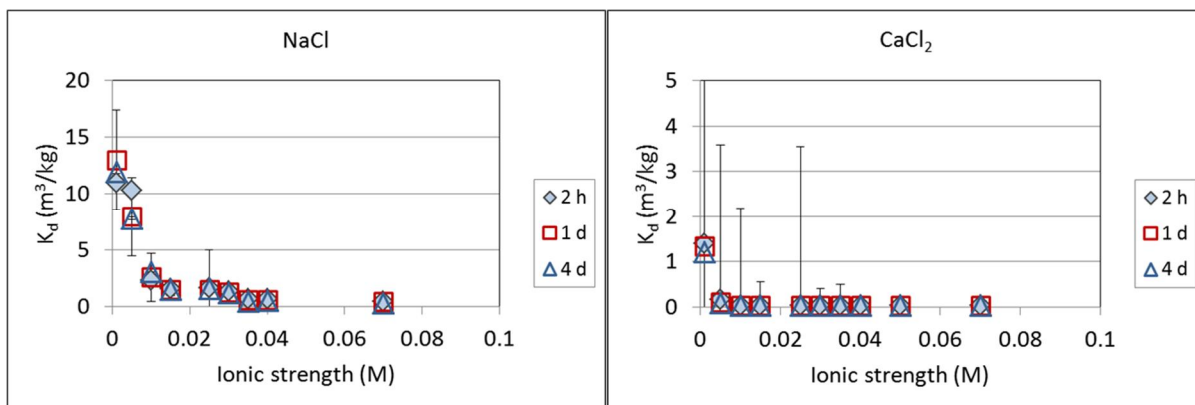
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Figure 4. The distribution coefficient, K_d-values of Sr-85 for bentonite colloids as a function of ionic strength in NaCl (left) and CaCl$_2$ (right) solution.

The distribution coefficient, K_d (m^3 kg^{-1}) values of Eu-152 for bentonite colloids as a function of ionic strength in OLSO reference groundwater and in CaCl$_2$ solutions are shown in Figure 5. 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.
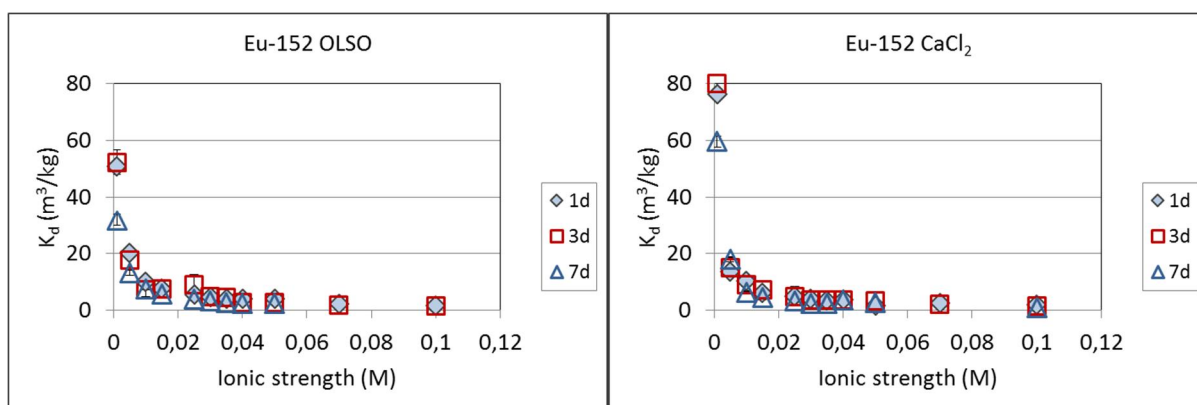

Figure 5. The distribution coefficient, K_d-values of Eu-152 for bentonite colloids as a function of ionic strength in OLSO (left) reference water and CaCl$_2$ (right) solution.

Radionuclide adsorption onto the bentonite colloids and montmorillonite was highly pH dependent, adsorption increasing with increasing pH. Sr-85 sorption onto bentonite colloids in 1 mM and 100 mM OLSO is shown as a function of pH in Figure 6. Eu-152 sorption onto bentonite colloids in 4.2 mM Allard water is shown as a function of pH in Figure 7.
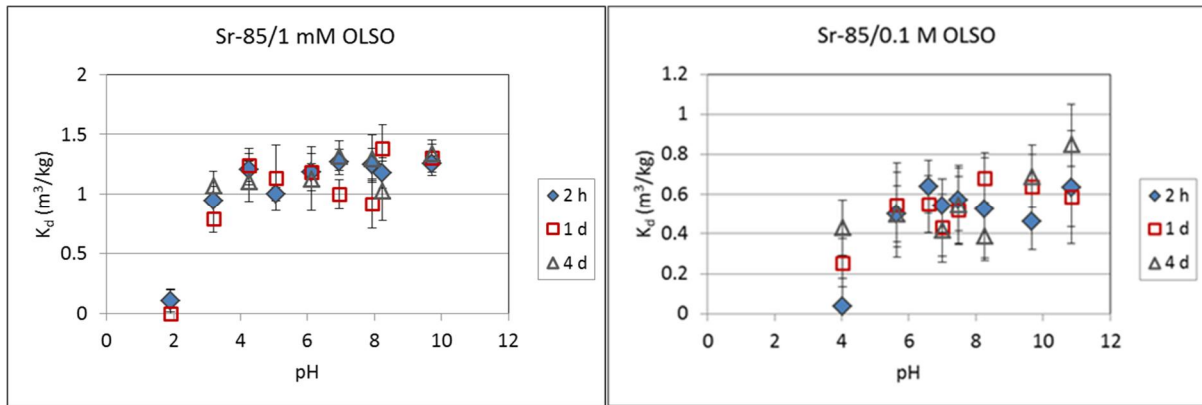
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Figure 6. The distribution coefficient, K_d-values of Sr-85 for bentonite colloids in 1 mM (left) and 0.1 M (right) OLSO reference water as a function of pH.
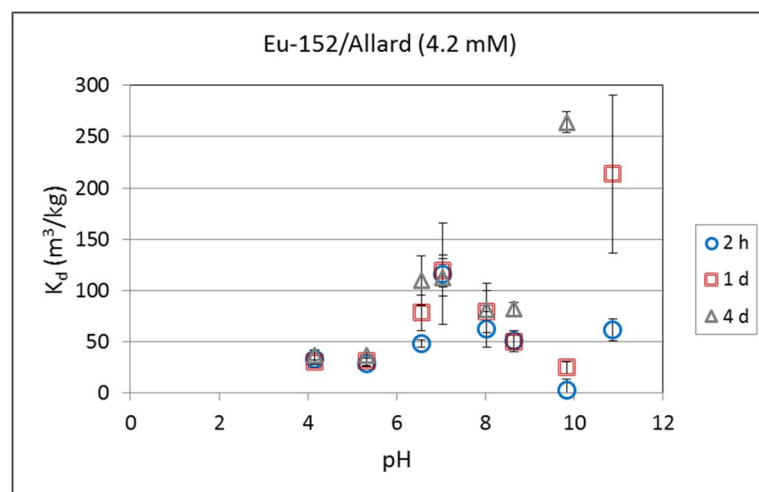

Figure 7. The distribution coefficient, K_d-values of Eu-152 for bentonite colloids in Allard reference water as a function of pH.

Np-237 sorption

Np(V) sorption onto bentonite colloids, Na-montmorillonite (MX-80) and corundum in 10 mM NaClO$_4$ is shown as a function of pH in Figure 8. Sorption onto bentonite colloids was rather weak (20 %) at pH 8 and higher adsorption occurred only above pH 10. Kinetic experiments indicated fast neptunium adsorption onto bentonite colloids. At pH 8, during the first few hours 20 % sorption and 24 hours maximum level of 30 % were reached. The increase in the solid concentration from 0.5 g/l to 5 g/l, neptunium sorption on montmorillonite was increased. Np(V) sorption onto Na-montmorillonite as a function of Np(V) concentration ($1\ 10^{-9} – 5\ 10^{-6}$ M) at pH 8, 9 and 10, in 10 mM NaClO$_4$ at two solid concentrations 0.5 g/l is shown in Figure 9. The difference between solid concentration 5 g/l and 0.5 g/l is unexpected, less Np(V) was adsorbed at the lower solid concentration than at the higher concentration and the effect increased at higher pH 10. This inconsistency might be caused by a carbonate contamination which will be ensured later. Np(V) sorption onto bentonite colloids as a function of Np(V) concentration ($1\ 10^{-9} – 5\ 10^{-6}$ M) at pH 8 and 9, in 10 mM NaClO$_4$ is shown in Figure 10. The

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sorption isotherms for bentonite colloids are as expected, linear and the slopes are close to one another indicating that all added neptunium sorbs on the colloids.
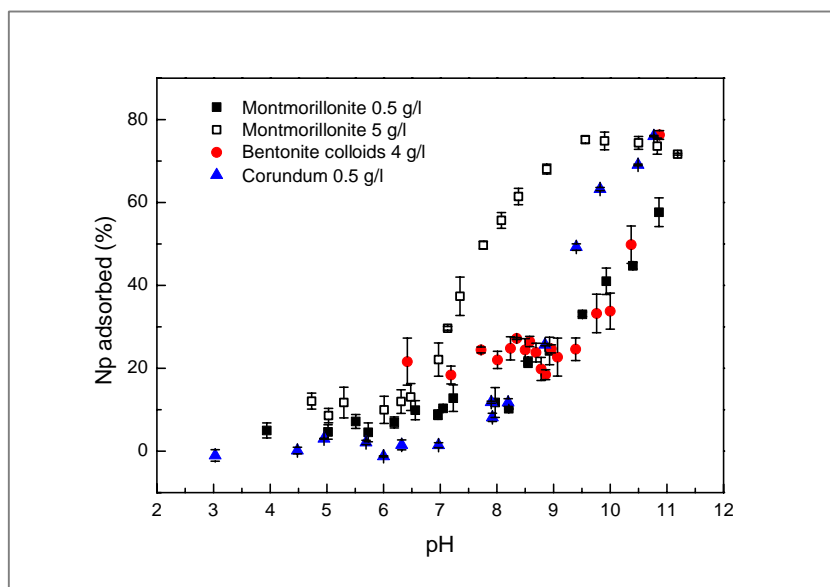

Figure 8. Np(V) adsorption onto bentonite colloids, Na-montmorillonite and corundum as a function of pH in 10 mM NaClO$_4$. Np(V) concentration was 1 10^{-6} M.
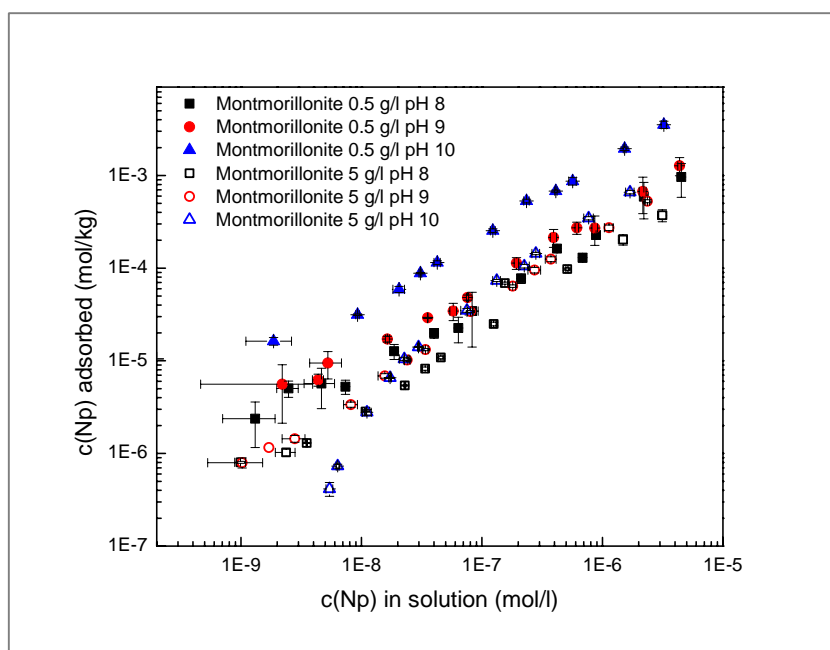

Figure 9. Np(V) sorption onto montmorillonite as a function of Np(V) concentration (1 10^{-9} – 5 10^{-6} M) at pH 8, 9 and 10, in 10 mM NaClO$_4$ at two solid concentrations 0.5 g/l and 5 g/l.

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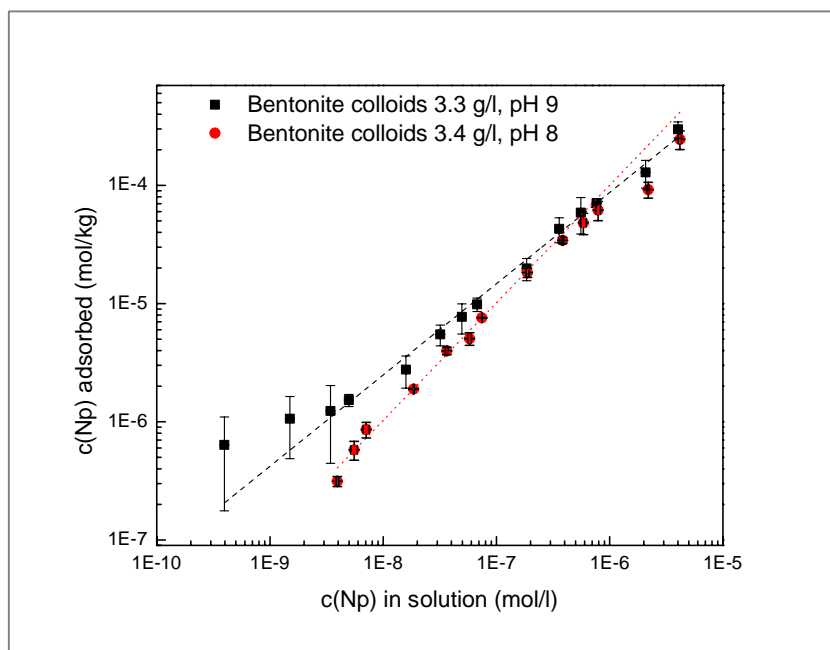Date of issue of this report: **31/05/15**

Figure 10. Np(V) sorption isotherms for bentonite colloids in 10 mM NaClO$_4$ at pH 8 and 9.

Neptunium desorption from Na-montmorillonite surface after electrolyte changes is presented in Figure 11. Neptunium was completely removed from the surface after five electrolyte changes independent of the exchange interval (2 – 3 days or 7 days). Ionic strength or pH were not changed during the course of the desorption experiment indicating that the neptunium detachment from the surface can only be explained by the fast establishment of an equilibrium between adsorbed neptunium and neptunium in the solution. Acidic desorption experiments conducted for montmorillonite (Figure 11, right) show equally fast desorption than the change of electrolyte, almost all Np(V) is desorbed after six hours after the pH was adjusted to acidic. Thus the desorption kinetics occurs to be as fast as the adsorption kinetics. Both desorption studies indicate that Np(V) adsorption onto montmorillonite is highly reversibly.
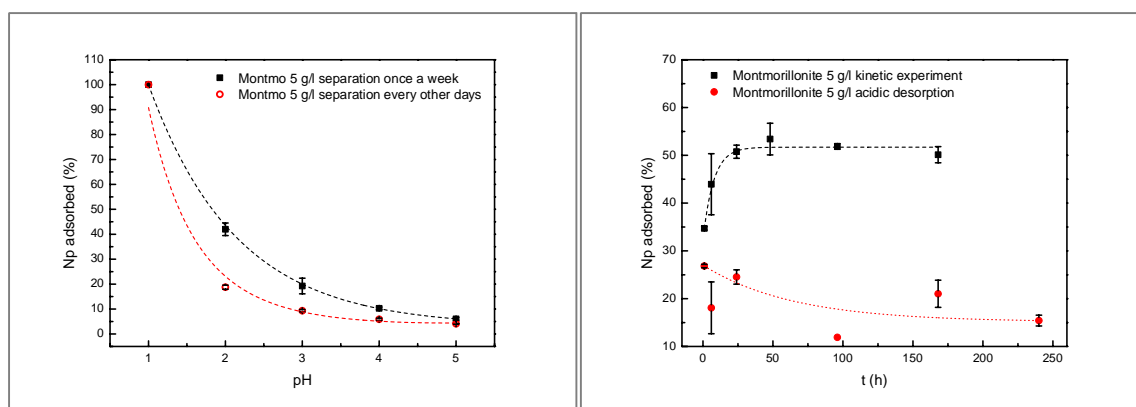

Figure 11. Np(V) desorption of montmorillonite by changing the background electrolyte to a fresh one either every 2 – 3 days or once a week (left). A kinetic experiment of Np(V) sorption onto montmorillonite and desorption from the surface after acidification of the mineral suspension (right).

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Colloid migration

In the column experiments, different filtration processes taking place on fracture surfaces can be considered the main factor causing colloid or radionuclide retardation. In the previous column experiments, 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. In this study, bentonite colloid filtration in crushed rock and drill core surfaces was observed. The low recovery of bentonite colloids in the column experiments is presented in Figure 12. Migration of colloids was affected by the type of column and/or rock alteration, water flow rate and colloid size.
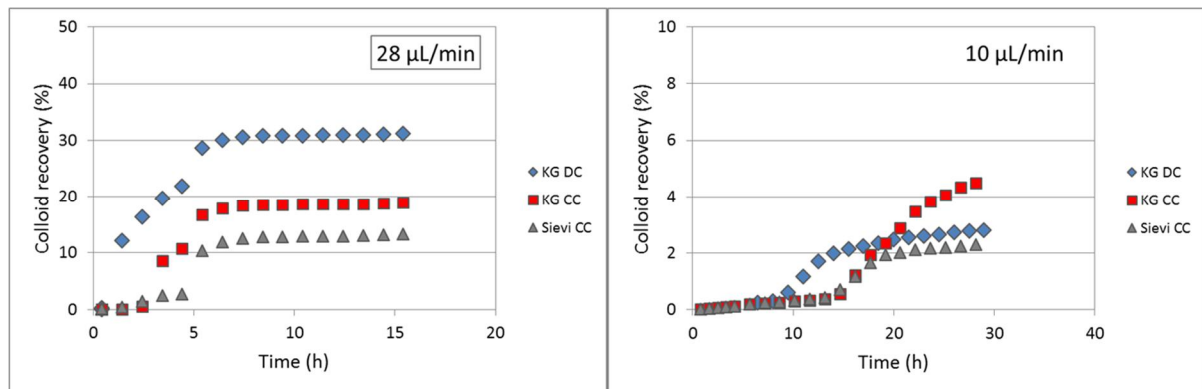

Figure 12. Bentonite colloid recovery in Kuru grey granite drill core column (blue), crushed rock columns (15 cm): Kuru grey (red) and Sievi altered tonalite (grey), flow rate 28 and 10 µl/min, average particle size was 230 nm.

Conclusions

The interaction between radionuclides and Na-montmorillonite or bentonite colloids has been studied. Radionuclide adsorption onto the bentonite colloids and montmorillonite was highly pH dependent, adsorption increasing with increasing pH. The obtained results confirmed the influence of ionic strength and Ca^{2+} concentration also on the sorption. In environmentally relevant oxic conditions for SNF repository, at pH 8, corundum, and montmorillonite had low and almost similar adsorbing capacities for neptunium(V). Colloid recoveries in the column experiments were very low. Migration of bentonite colloids in columns was affected by the water flow rate, column type and colloid size. Batch experiments give valid information of the amount of the sorption though the chemical nature of the sorption cannot be evaluated. The pH and ionic strength have great influence on the chemical form of the actinides, thus the batch results are the important source of data for further studies using specific methods. 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 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.

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