BELBaR
(Contract Number: FP7 *295487*)

Macroscale investigations on colloid mobility in near-natural systems
DELIVERABLE D3.2

Author(s):
P. Hölttä, University of Helsinki
T. Schäfer, KIT-INE
K. Videnská, R. **Č**ervinka, ÚJV **Ř**ež, a. s.
T. Missana, Ciemat

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities (2007-2011)		
Dissemination Level		
PU	Public	PU
RE	Restricted to a group specified by the partners of the BELBaR project	
CO	Confidential, only for partners of the BELBaR project	

DISTRIBUTION LIST

Name	Number of copies	Comments
Christophe Davies (EC) BELBaR participants		

Table of Contents

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 first 15project months. Macroscale investigations on colloid mobility in near-natural systems performed in CIEMAT, KIT-INE, 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 Macroscale investigations on colloid mobility in near-natural systems: CIEMAT's contribution

The focus of CIEMAT is on bentonite colloids interaction processes with the rock surface (filtration), which can significantly affect colloid mobility and how they can affect radionuclide transport in granite fractures. Of special interest, is to understand which can be the mechanisms related to colloid filtration under "unfavorable conditions" to colloid attachment, that is when colloid and the rock surface are both negatively charged.

Previous studies [1] recently showed the large importance of the residence time on colloid filtration in a fracture (Figure 1), this means that, under natural low flow rates, colloid attachment to the rock surfaces will occur, even under unfavorable conditions.
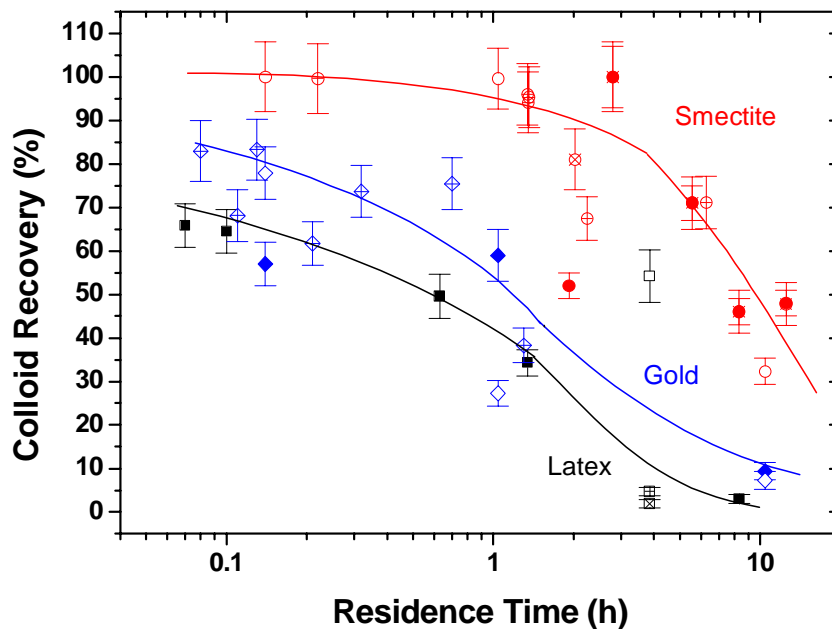

Figure 1: Colloid recovery in artificial fractures (Grimsel Granite) as a function of the residence time.

Under similar water flow rates and using chemically similar waters (in which colloids were stable), the retention of the colloids in the fractures increased with the macroscopic roughness. In natural fractures, the observed colloid recovery was less than in artificial smooth fractures.

The comparison of the recovery as a function of the residence time (Figure 1) showed that natural smectite colloids show, in general, higher recovery than gold or latex artificial colloids with similar surface charge. This is an interesting point, because indicates that artificial colloids might not be totally representative of the clay colloids behavior.

These colloid transport tests were all done under chemical conditions favorable to colloid stability using $5 \cdot 10^{-4}$ M NaClO$_4$ as electrolyte.
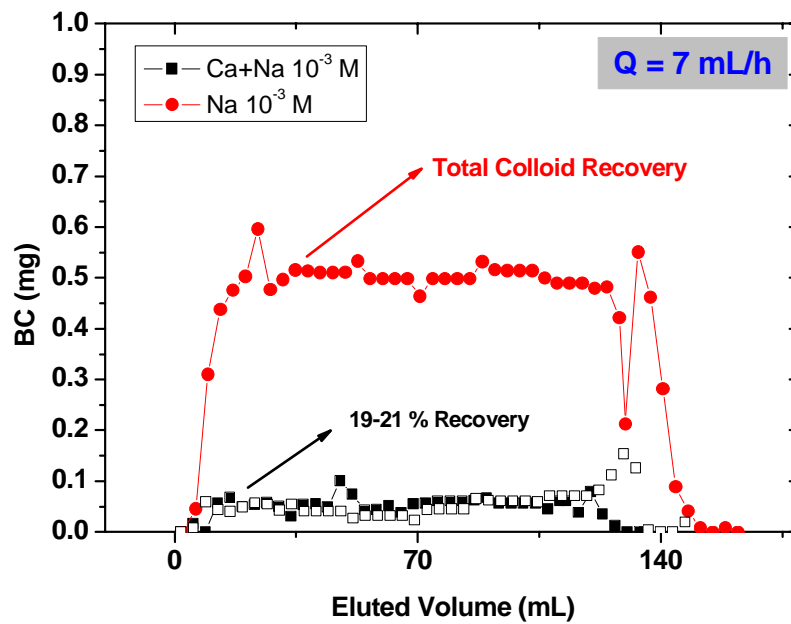
Figure 2: Colloid recovery in an artificial fracture (Grimsel Granite). Red points correspond to the Na- system and black points correspond to the (Na, Ca)-system. Water flow rate in the fracture was 7 mL/h.

An important point, however, is to analyze how the chemistry of the water can affect the mobility of bentonite colloids. Using "high" water flow rates (7 mL/h), the transport of bentonite colloid in fracture with two different aqueous solution of low ionic strength ($I \approx 1 \cdot 10^{-3}$ M), the first one mono-cationic (Na) and the second bi-cationic (Na and Ca), was analyzed (Figure 2).

Results showed that a small quantity of calcium significantly affected the recovery behavior. Whereas in the case of Na mono-cationic aqueous solution colloids were completely recovered, a large quantity of bentonite colloids was retained in the fracture when the bi-cationic (Na, Ca) solution was used. Furthermore, in the sodium solution, the size of the colloid eluted was very similar to the initial one, but in presence of calcium, colloids eluted presented a significantly larger size than the initial. Thus, even small quantities of calcium in the systems promoted aggregation and filtration under dynamic conditions. This effect was more evident, when the injected colloids where not in equilibrium with the groundwater.

Flow velocity and water chemistry are both substantially affecting the mobility of smectite colloids in the fracture, and they must be considered together. Figure 3 shows the summary of different tests performed in the same fracture with smectite colloid dispersed in a $NaClO_4$ solution at different flows. In a low saline ($5 \cdot 10^{-4}$ M), Na-electrolyte, water flow rates as high as $5 \cdot 10^{-4}$ m/s lead to a complete recovery of bentonite colloids; however increasing the calcium content in the water or its ionic strength (Na+Ca, $1 \cdot 10^{-3}$ M electrolyte solution or Äspö water) under the same flow conditions, the colloid recovery might be significantly lower and even null.
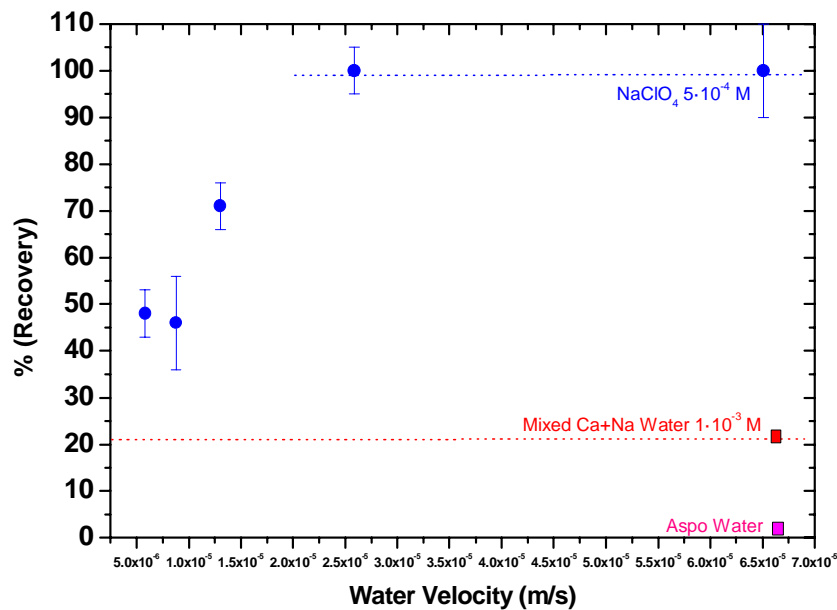
Figure 3: Comparison of the recovery of bentonite colloids under the same water flow velocity and different water chemistry.

However, colloid attachment was not completely irreversible, as colloid can be removed from the surface increasing the water flow rate.

The different mobility behavior, under different chemical conditions, also greatly affects radionuclide transport. Cesium migration (with and without bentonite colloids) in geometrically similar artificial granite fractures, under the Grimsel and Äspö conditions, was compared.

These two specific cases are of interest because: a) Grimsel (Switzerland) and Äspö (Sweden) are underground laboratories, where investigations on radionuclide migration in crystalline rocks have been performed for years; b) the chemistry of the groundwater of these two sites is very different, providing a very different environment for colloids stability and mobility.

In the Grimsel case, cesium transport was significantly different in the presence or absence of colloids, whereas the cesium breakthrough curves were very similar in the Äspö case.

Transport experiments were carried out using water flow velocity from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ m/s in two artificial fractures (of Grimsel and Äspö granite, respectively), injecting 100 ppm of bentonite colloids in which cesium ([Cs]=$1 \cdot 10^{-7}$ M) was previously adsorbed (80 % in the Grimsel case and 20 % in the Äspö case) and suspended in synthetic waters representative of the two different cases.

The eluted water was analysed to measure cesium activity and the presence of bentonite colloids by photon correlation spectrometry (PCS) in the same samples and to obtain simultaneously colloid and cesium breakthrough curves. The breakthrough curve of cesium, without colloids, presented a single peak with a retardation factor (R_f) of ~200 in the Grimsel case and of ~170 in the Äspö case.

In the presence of bentonite colloids, in the Grimsel case, the breakthrough curve clearly showed a small cesium peak in a position very similar to that of the conservative tracer (HTO), with an R_f of 0.8,

coincident with the colloid breakthrough peak measured by PCS. However, the quantity of cesium recovered after this peak was only the 0.15 % of the injected.

Since the colloid recovery was quite high (80%), this clearly demonstrated that cesium desorbed from the colloid during the transport in the column. Other two peaks were observed in the breakthrough curve with R_f of 200 and 370 approximately. In the Äspö case, no elution of colloids was seen at all, which was no surprising considering that they aggregate fast under the Äspö water conditions, and are completely retained in the fracture. The "split" of the main cesium peak in two peaks with Rf of approximately 170 and 270 was also clearly observed. The appearance of new peaks with retardation factors higher than those showed in the same system without colloids, is most probably due to the modification of the sorption properties of the fracture surface caused by bentonite colloid deposition [2].

It is important to remark that in similar experiments made at CIEMAT with other radionuclides (Sr [2], Eu [3] and U[4]) and bentonite colloids, desorption was also clearly observed. Desorption from the colloids is a very important factor limiting the role of colloids in radionuclide transport.

As a main conclusion, in both the Grimsel and Äspö cases, the presence of bentonite colloids did not facilitate cesium transport in the medium, rather produced a slight increase in the overall cesium retardation in the fracture.

References

[1] Albarran N., Missana T., Alonso U., García-Gutiérrez M., Mingarro M., Analysis of latex, gold and smectite colloid transport and retention in fractured crystalline rocks. Colloids and Surfaces A (2013, in press): doi:10.1016/j.colsurfa.2013.02.002

[2] Albarran N., Missana T., Garcia-Gutierrez M., Alonso U., Mingarro M, Journal of Contaminant Hydrology 122 (2011) 76-85.

[3] Missana T., Alonso U., Garcia-Gutierrez M., Mingarro M, Applied Geochemistry 23 (2008) 1484-1497.

[4] Albarran N., Ph.D Thesis, Procesos de migración de contaminantes asociados a coloides en un almacenamiento geológico de residuos radiactivos. (2010) Universidad Autónoma de Madrid (In Spanish).

4 Column migration experiments with crushed granitic material: radionuclides and colloids system behavior

The main aim of these experiments is to estimate the influence of bentonite colloids on radionuclide retention through rock columns under defined conditions. Column experiments allow determination of transport parameters such as the retardation and distribution coefficients (R and K_d), Peclet number and hydrodynamic dispersion coefficient under dynamic conditions. Those are determined by fitting the experimental breakthrough curves using regression procedures based on the erfc-function, assuming a non-linear reversible equilibrium sorption/desorption isotherm.

At first the sorption and desorption of radionuclides were studied in columns of crushed granite and fracture infill of various grain size. These experiments represent an introduction providing information about the transport of radionuclides through crushed granite material of different composition in order to determine the start-up behaviour of the system without colloid presence. The radioactive (^{3}H, ^{36}Cl$^-$, ^{85}Sr^{2+}, ^{137}Cs$^+$) and stable (SeO$_3^{2-}$, SeO$_4^{2-}$) tracers and two type of crystalline rock materials were investigated (pure granite, coded as PDM1-1 and fracture filling materials, coded as PDM1-2). Synthetic granitic water (SGW) was used.

The breakthrough curves showed that behaviour of ^{3}H and ^{36}Cl is different in comparison with other tracers, both displaying behaviour of conservative tracers without any sorption. The anionic exclusion was observed in case of ^{36}Cl in granite PDM 1-1. The selenate (Se(VI)) showed similar behaviour as ^{36}Cl and ^{3}H. The sorption of ^{85}Sr is significant in comparison with breakthrough curves of ^{3}H or ^{36}Cl. The values of K_d and R showed differences on different granite material for ^{85}Sr; the presence of fracture infill minerals (chlorite) significantly increased sorption of ^{85}Sr in comparison with pure granite. On the other hand selenite (Se(IV)) showed completely different sorption behaviour. The sorption of selenite was observed on the both type of granitic rock. The values of R and K_d showed influence of granitic size and granite composition on selenite sorption. The experimental and theoretical breakthrough curves are displayed in Fig. 1. For more details see publication Videnská et al., 2013.
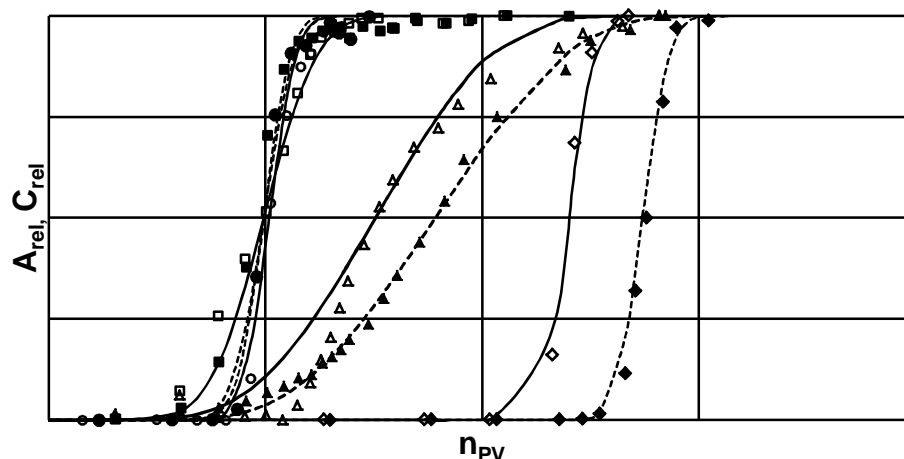

Fig. 1.: Theoretical breakthrough curves (solid line, resp. dashed line) and experimental breakthrough curves of transport: ^{3}H$^+$ (○, ●), Se^{IV}(Δ, ▲), Se^{VI} (□, ■) and ^{85}Sr^{2+} (◊, ♦) in crushed granite (blank symbols) and in fracture infill materials (dark symbols) with grain size 0.125 – 0.63 mm in synthetic granitic water. A$_{rel}$, C$_{rel}$ – relative activities and concentrations, n$_{pv}$ – number of column pore volumes.

Second step was to study the migration behaviour of bentonite colloids using the same columns with crushed granite. For this purpose the purified bentonite B75 in Na^+ form was used. The purification procedure contained several steps:

- the carbonates were removed by sodium acetate-acetic acid buffer

- iron was removed using sodium dithionite in acetic acid buffer and washed by NaCl

- clay fraction < 2 μm were obtained by sedimentation in enough amount of distilled water

- transfer to homoionic Na^+ form by treatment with NaCl and washing with distilled water

- dialysis as a last step was performed until the conductivity of solution was > 10 μS/cm

- the final product was air dried or lyofilised (freeze drying)

From this powder the suspension of purified bentonite B75 and distilled water was prepared for experiments with concentration 100 mg/L. Initially the mean hydrodynamic diameter of bentonite particles in suspension was about 500 nm (photon cross correlation spectroscopy (PCCS) measurement).

Also the reference material cerium(IV) oxide nanopowder (CeO_2) from Sigma-Aldrich was used. The suspension of CeO_2 and distilled water with same concentration 100 mg/L was prepared. The size distribution of particles in suspension was bimodal with two main peaks around 140 nm and 740 nm (PCCS measurement).

The concentrations of colloids in effluents from column experiments were measured again with PCCS. Calibration curves were obtained plotting the response of the photomultiplier (kcps) vs. the known concentration of bentonite colloids (linear calibration curve). The detection limit for bentonite colloid with PCCS is around 1mg/L.

Results from the migration of colloids in columns with crushed granite (the experimental breakthrough curves) are showed in Fig. 2. The breakthrough curves for ^{3}H and bentonite colloids are almost similar. Bentonite colloids did not interact with crushed granite and relatively small particles had low dispersion in column flow. Conversely, larger particles of CeO_2 demonstrated greater dispersion as it shows breakthrough curve. For comparison the breakthrough curve for sorbing radionuclide [85]Sr is situated to the graph from previous experiments.
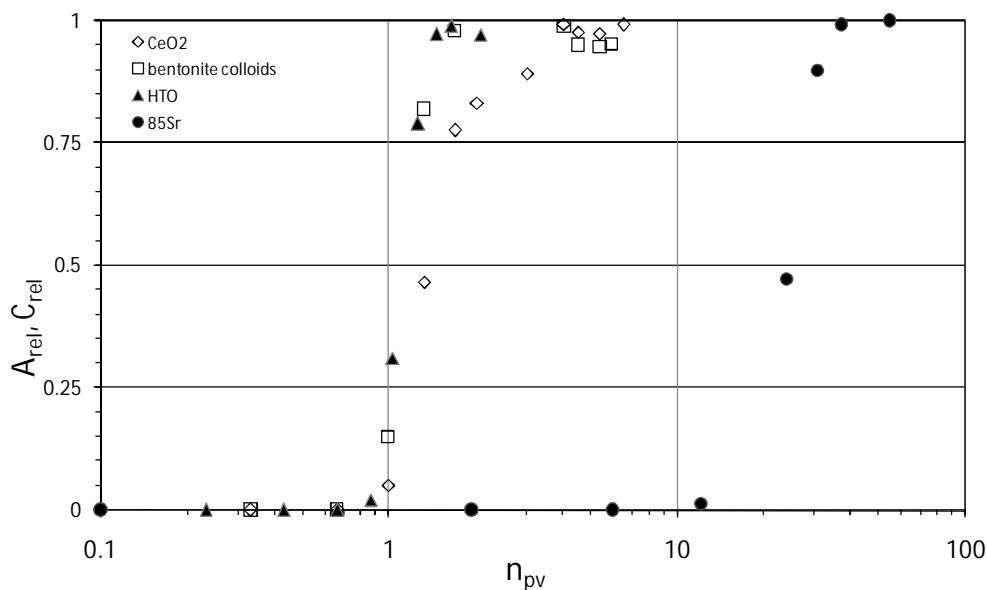
Fig. 2.: Experimental breakthrough curves of transport: ^{3}H (▲), ^{85}Sr^{2+} (●), CeO$_2$(◊) and bentonite colloids (□) in crushed granite with grain size 0.125 – 0.63 mm in synthetic granitic water (radionuclides) and distilled water (colloids). A$_{rel}$, C$_{rel}$ – relative activities and concentrations, n$_{pv}$ – number of column pore volumes.

The next step, further following, is migration of bentonite radiocolloids again in the columns with crushed granite. This step also includes the preparation of stable radiocolloid suspension (^{85}Sr + bentonite colloids/CeO$_2$). At the end the comparison of breakthrough curves of given radionuclide, bentonite colloid and radiocolloid will distinguish the contribution of colloid for radionuclide transport.

Reference

Videnská, K., Palágyi, Š., Štamberg, K., Vodičková, H., Havlová, V. (2013) EFFECT OF GRAIN SIZE ON THE SORPTION AND DESORPTION OF SEO42- AND SEO32- IN COLUMNS OF CRUSHED GRANITE AND FRACTURE INFILL FROM GRANITIC WATER UNDER DYNAMIC CONDITIONS. Journal of Radioanalytical and Nuclear Chemistry, DOI : 10.1007/s10967-013-2429-7.

5 The latest results on colloid associated radionuclide mobility from the CFM project, Grimsel (Switzerland)

T. Schäfer[1*], I. Blechschmidt[2], M. Bouby[1], S. Büchner[1], J. Brendlé[3], G. Darbha[1], H. Geckeis[1], T. Kupcik[1], R. Götz[1], W. Hauser[1], S. Heck[1], F. Huber[1], M. Lagos[1], A. Martin[2]

[1] *Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Karlsruhe, Germany;* [2]*NAGRA Natl. Cooperat. Disposal Radioact. Waste, Wettingen, Switzerland;* [3]*Lab. Mat. Mineraux, UMR CNRS, Univ. Haute Alsace, Mulhouse, France *thorsten.schaefer@kit.edu*

The influence of colloidal/nano-scale phases on the radionuclide (RNs) solubility and migration behavior is still one of the uncertainties in repository safety assessment [1]. In our work, we aim 1) to identify the presence and the formation of relevant colloids in repository specific areas, 2) to determine their stability as a function of geochemical parameters, 3) to elucidate the thermo-dynamics and kinetics of the colloid interaction with radionuclides, 4) to perform laboratory and field experiments to quantify the colloid mobility and their interaction with surfaces. The final goal is to state on the relevance of the nanoparticles (NPs)/colloids for the radionuclide migration under natural geochemical conditions. In this contribution we report on the progress concerning the colloid migration under near natural hydraulic conditions at the Grimsel Test Site.

Within the Colloid Formation and Migration (CFM) project at the Grimsel Test Site (GTS Switzerland) [2] a huge geo-technical effort was taken to isolate hydraulically a shear-zone from the artificially introduced hydraulic gradient due to the tunnel construction. The construction is a combination of polymer resin impregnation of the tunnel surface and a steel torus to seal the tunnel surface. The steel tube with reinforcement rings is sealed at both ends with rubber based hydraulic "donut" packers and the annulus between resin and steel ring is filled and pressurized with water to counteract the hydrostatic pressure of the water conducting feature giving mechanical support to the resin. Natural outflow points of the MI shear zone were localized prior to the construction and sealed by surface packers. This design gives the opportunity to regulate outflow and thereby adjust the flow velocity in the fracture.

After optimization of the experimental setup and injection procedure through a number of conservative tracer tests using fluorescence dyes so-called "homologue" tracer tests were performed by injecting a suspension of Febex bentonite colloids containing adsorbed Eu, Tb, Hf in addition to the conservative tracer. A license was granted in January 2012 by the Swiss regulator (BAG) to perform the first radionuclide tracer test under these low-flow conditions. The injection cocktail of 2.25L volume was prepared at INE and transferred to the GTS. A total colloid concentration of 101.4 ± 2.5 mg/L montmorillonite clay colloids were used, whereas 8.9 ± 0.4mg/L were present as synthetic montmorillonite with structural incorporated Ni. For details on the structural characterization of the Ni-montmorillonite phyllosilicate, see [3]. Beside the colloids and the conservative tracer Amino-G (1646 ± 8ppb) the radioisotopes ^{22}Na, ^{133}Ba, ^{137}Cs, ^{232}Th, ^{237}Np, ^{242}Pu and ^{243}Am were injected. The trivalent and tetravalent actinides were quantitatively associated with the colloids present as well as a part of the Cs, whereas Np(V) and Na are not bentonite colloid bond.

The injection of the radionuclide bentonite colloid cocktail was performed through borehole CFM 06.002-i2 into the MI shear zone and the water extracted under a constant flow rate of approx.

25mL/min from the "Pinkel" surface packer (dipole distance 6.08m). The tracer cocktail was recirculated in the injection loop to monitor the fluorescence decrease of the conservative tracer (Amino-G) and therefore providing an injection function for consequent transport modeling. For on-site colloid analysis a mobile Laser- Induced Breakdown Detection (LIBD) system similar to the one used in the CRR experiments [4] was transferred to Grimsel and installed in-line at the "Pinkel" outlet to directly monitor the mobile colloid fraction throughout the experiment.

The conservative tracer Amino-G was recovered quantitatively both by on site inline and off-site fluorescence detection. Analysis of the weakly sorbing tracers by ☐-spectrometry performed by PSI-LES and INE showed very good conformity and revealed recoveries for ^{22}Na, ^{137}Cs and ^{133}Ba of 64%, 10% and 1%, respectively. The clay colloid recovery (integration until 11.4 days) determined by LIBD was quantified to be ~66%, whereas HR-ICP-MS provided 33-38% by analyzing Al and Ni as structural components of the clay particles. . The Al/Ni ratio taken as an indicator for the injected clay colloids did not vary during the experiment (injection cocktail: Al/Ni ratio = 21.6 ± 0.5; effluent samples: Al/Ni ratio = 20.4 ± 0.5) and thus a mobilization of Al containing colloid phases from additional sources in the fracture can be excluded. Reasons for the divergent colloid recovery data are currently investigated.

Based on a number of colloid migration experiments performed in the MI shear zone a colloid attachment/filtration rate can be estimated, which is lower than the value of $2 \cdot 10^{-2}$ estimated by filtration theory in [5]. All injected radionuclides including the strongly sorbing tri- and tetravalent actinides could be detected in the effluent. For the initial quantitatively colloid associated actinides Am(III) and Pu(IV) a recovery of at least 16% and 28-32%, respectively, could be determined. Np recovery is significantly reduced to ~4 % in comparison to the CRR experiment of 82 ± 4 % [4], which hints to a kinetic controlled Np(V) reduction observed through the increased residence time in Run 12-02 in line with the measured pH/Eh conditions. The data of Run 12-02 obtained so far clearly show the mobility of bentonite derived montmorillonite colloids under near-natural flow conditions in the MI shear zone of the Grimsel Test Site [6]. The experimental data will be discussed in detail in the presentation.

Acknowledgement

References

[1] T. Schäfer, et al. Appl. Geochem., 27 (2012) 390-403.

[2] H. Geckeis, et al., Actinide - Nanoparticle interaction: generation, stability and mobility, in: S.N. Kalmykov, M.A. Denecke (Eds.) Actinide Nanoparticle Research, Springer- Verlag, Berlin, Heidelberg, 2011, pp. 1-33.

[3] Reinholdt, et al., Nanomaterials, 3 (2013) 48-69.

[4] H. Geckeis, et al., Radiochim. Acta, 92 (2004) 765-774.

[5] T. Schäfer & U. Noseck, Colloid/ Nanoparticle formation and mobility in the context of deep geological nuclear waste disposal (Project KOLLORADO; Final report), FZKA report 7515, 2010.

[6] www.grimsel.com

6 Radionuclide/colloid migration experiments

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 powdered bentonite and bentonite colloids as a function of ionic strength 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.

The bentonite used was MX-80 type bentonite powder which consists mainly of montmorillonite. Sr-85 and Eu-152 sorption was determined in NaCl and $CaCl_2$ solutions as well as in diluted OLSO reference groundwater which simulates the current saline groundwater in Olkiluoto in oxic conditions. The ionic strengths of the solutions were adjusted between 0.001 and 0.1 M. All of these experiments were made in ambient conditions. Sorption was quantified by the determination of the distribution ratio of radionuclide activity between solid and liquid phase.

MX-80 bentonite powder was added to the solution spiked with the tracer. Aliquots were taken after 2 hours, 2 and 7 days. The solid phase was separated from the colloids containing liquid phase by centrifuging. The activity of the liquid was measured and the size and zeta potential of particles in the solution was analyzed. The liquid was then returned to the sample vial and the sample was shaken until the centrifugation and activity, particle size and zeta potential measurements were repeated after three and after seven days. Finally, after the last centrifugation, the remaining particles in the liquid were separated by filtering the sample with polycarbonate filters (pore size 1.2 and 0.05 µm) and the colloids contribution to the sorption was determined.

Radionuclide sorption onto bentonite colloids was studied using colloid dispersion solution made from MX-80 bentonite clay powder which was mixed with Milli-Q water at a solid to 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. In the case of sorption on separated colloids, 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 using a Wizard gamma counter. From the separated liquid phase, colloidal particle size distribution was determined applying the photon correlation spectroscopy 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 as well as using the Al content of montmorillonite analyzed using ICP-MS.

When the ionic strength was low, there was no difference in sorption between sodium chloride and calcium chloride solutions or Sr-85 and Eu-152. At First, the tracers were mostly adsorbed on solid bentonite but during one week, the activity was increasing in the liquid phase as the colloid concentration was also increasing. The mean particle size was increasing slightly during one week but a great majority of particles were in the size range of colloids' definition, i.e. 1–1000 nm. Practically all of the activity in the electrolyte solution disappeared in the filtration, which indicates that the tracers were adsorbed on the colloids in the solution. When the ionic strength of the electrolyte solutions got higher, there were differences between the different tracers and the electrolyte

solutions. Using europium, practically all of the activity was in the solid phase from the beginning to the end of the experiment regardless of the electrolyte solution. The particle size was large (1400–5000 nm) and the particle concentration low, no colloids were present. Using strontium and sodium chloride solution, about 70 % the activity adsorbed immediately on the solid phase. The mean particle size was again large and no activity disappeared from the liquid phase during filtration. In calcium chloride solution, the activity of Sr-85 was much lower in the solid phase.

The fracture column from Olkiluoto tonalite drill core was artificially fractured along the natural fracture containing an altered zone and filling minerals. The fracture width 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 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. In the flow experiments water was pumped into the columns at different flow rates of 5–25 µl 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.

At the beginning, the hydraulic properties in the columns were determined using non-sorbing tracers, Cl-36 and I-125 without colloids. In the low salinity Allard reference ground water, the colloids are assumed to be stable and mobile. The transport of Sr-85 and Eu-152 in the columns was studied without and with bentonite colloids. Colloid dispersion solution was made from MX-80 bentonite clay powder which was mixed with Milli-Q water. The beta activity of Cl-36 was detected using liquid scintillation counting (Perkin Elmer Tri-Carb) and the gamma activity of I-125, Sr-85 and Eu–152 was detected using a Wizard gamma counter. The colloidal particle size distribution was determined applying the photon correlation spectroscopy 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 as well as using the Al content of montmorillonite analysed using ICP-MS.

The transport of tracers through the columns will be interpreted using a numerical compartment model modified to calculate the advection and hydrodynamic dispersion in the columns. Based on the retention time distribution without matrix diffusion in the column, the effect of matrix diffusion is calculated for each short time interval by means of analytic expression of the matrix diffusion. The effects of matrix diffusion were observed in the elution curves of I-125 in the Olkiluoto fracture column and altered Syyry tonalite column. Particularly Eu-152 but Sr-85 were strongly retarded in the Olkiluoto fracture column and altered Syyry tonalite column without colloids. In the presence of bentonite colloid suspension, the slow elution of Eu-152 and Sr-85 was obtained. The results showed the effect of the water flow rate and thus the residence time on the colloid recovery indicating colloid filtration in a fracture or crushed rock surfaces.