Radionuclide/colloid interaction and transport – Summary of laboratory experiments

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Outline

Objectives

Materials and methods

Sorption experiments (Sr-85, Eu-152)

Np-237 sorption on montmorillonite and bentonite colloids

Colloid/radionuclide transport experiments

Conclusions

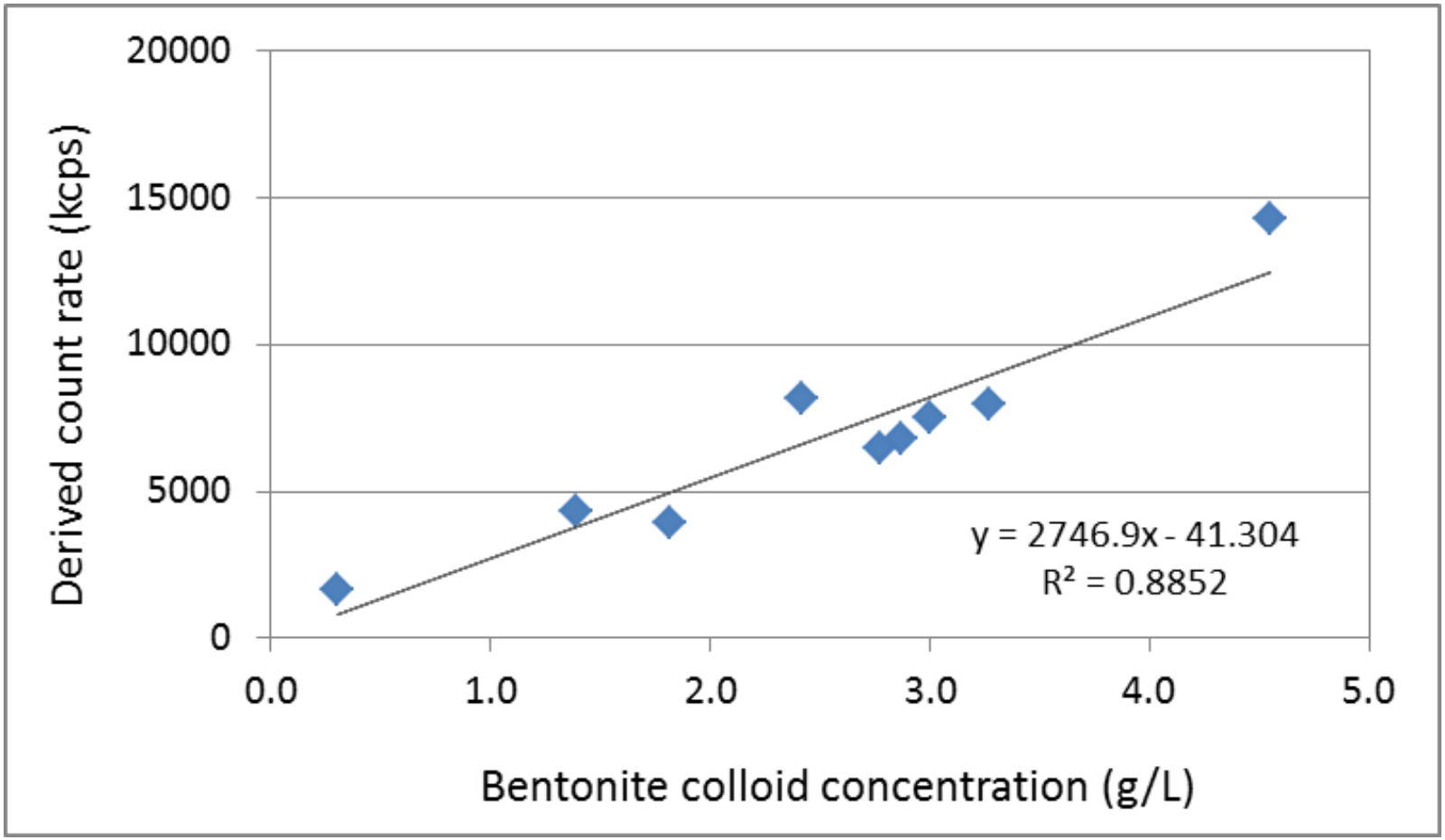
On-going work

Objectives

- To determine radionuclide sorption on MX-80 bentonite suspension, colloids and montmorillonite
- To study colloid/radionuclide and host rock interaction in dynamic conditions
- To apply new methods to study radionuclide sorption

Materials and methods

- MX-80 Volclay bentonite (76 %), purified Na-Montmorillonite and Nanocor PGN Montmorillonite (98 %) provided by B+Tech
- Reference groundwater: OLSO (I = 0.517 M) and Allard (I = 4.2 mM)
- NaCl and $CaCl_2$ solutions (I = 1 mM - 0.1 M)
- Photon correlation spectroscopy (PCS): particle size, concentration and zeta potential
- ICP-MS: Colloid concentration: Al determination
- In-situ ATR FT-IR, EXAFS



Correlation of count rate determined by PCS and colloid concentration calculated based on the aluminium content of bentonite colloid suspensions analysed using ICP-MS

Radionuclide sorption

Sorption onto powdered bentonite:

1 g bentonite powder + 20 mL solution + ^{85}Sr or ^{152}Eu → Sentrifugation (7500 rpm/30 min) → Filtration 1.2 µm and 0.05 µm → Radioactivity, particle size and zeta potential measurements

In low salinity solutions, about 10 % of the tracer was adsorbed on the colloidal fraction

Sorption including colloidal fraction $K_d \sim 3$ m^3/kg.

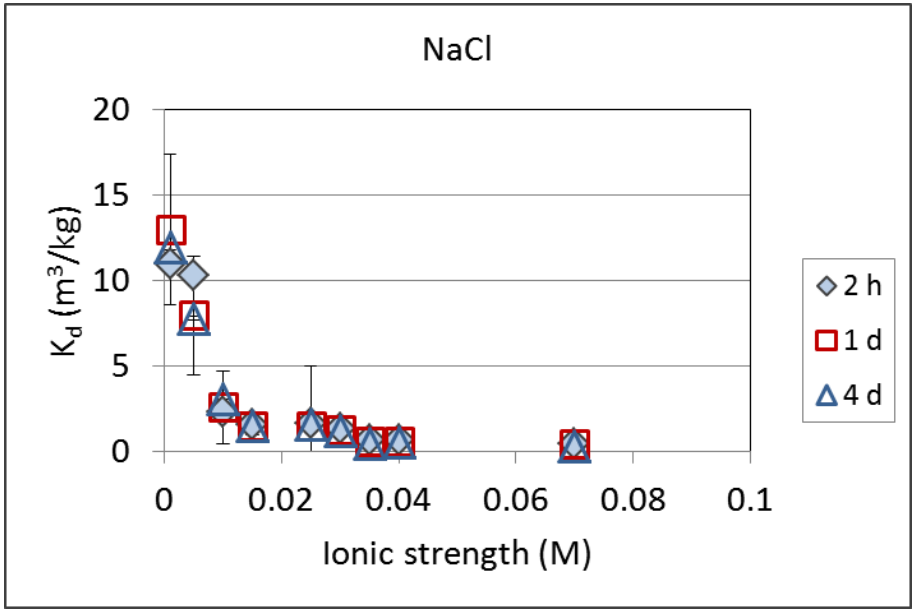
Sr-85 and Eu-152 sorption onto colloids

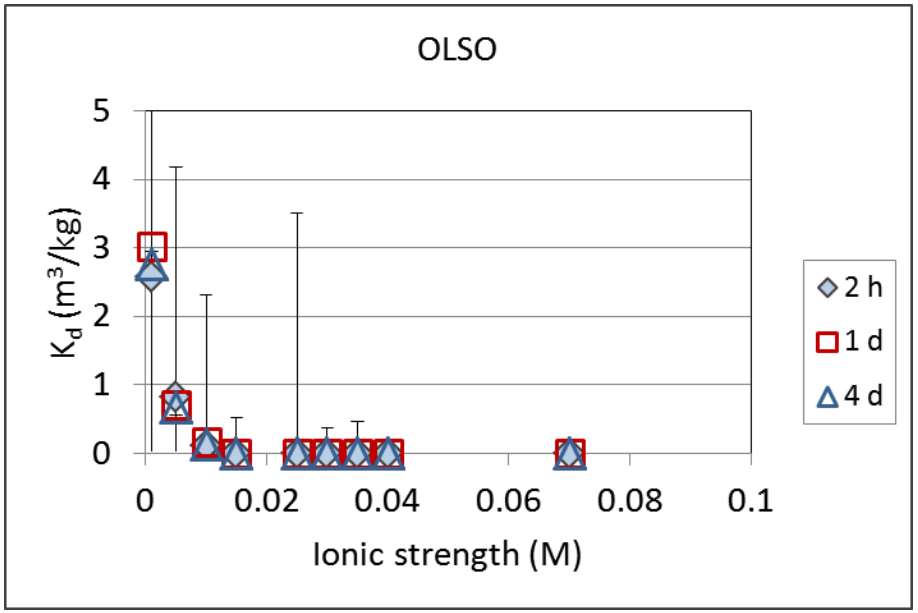
- MX-80 and Nanocor colloid solution separated ultrasonically (2 h), centrifugation (12000 rpm/20 min)
- 270 – 530 nm, 2.4 - 5.9 g/L
- Batch experiments in a clove box under CO_2 free conditions (pH)
- Colloid dispersion + 90 mL solution + tracer → 4.7 mL aliquot after 2 h, 1, 2 and 7 days → Ultracentrifugation (90000 rpm/60 min) → Radioactivity measurement
- The solid liquid–ratio and kinetic experiments
- Zeta potential of the system as a function of pH at the presence and absence of Sr-85 or Eu-152 → information about the sorption mechanisms.

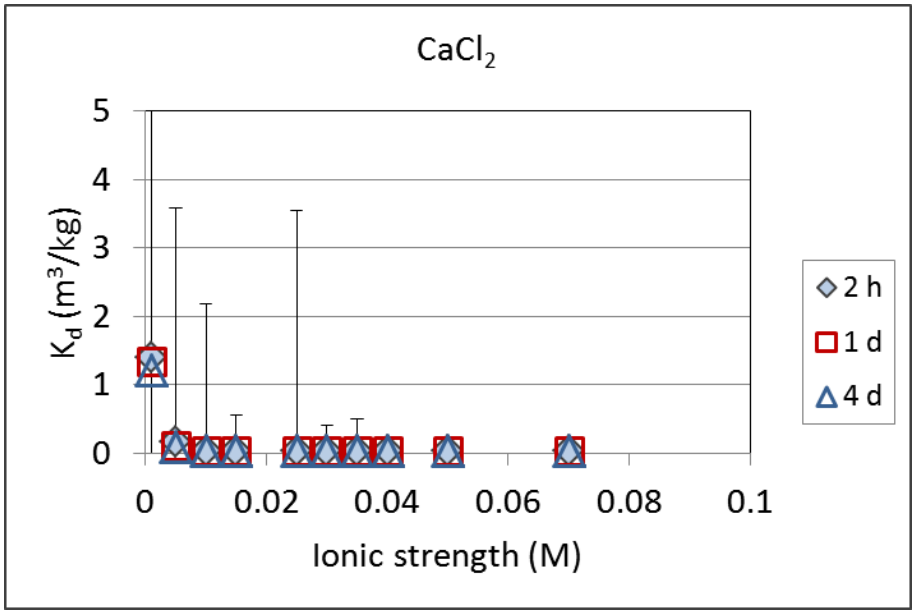
Sr-85 sorption on bentonite colloids

Nearly all of ^{85}Sr was sorbed onto bentonite colloids in 0.001 M solutions.

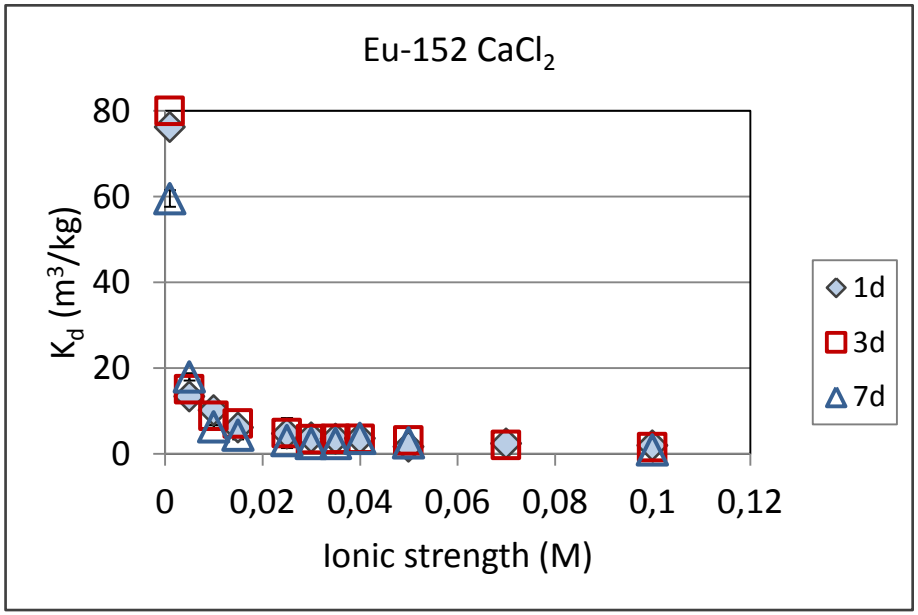
The distribution coefficient (K_d) decreased when the ionic strength increased.

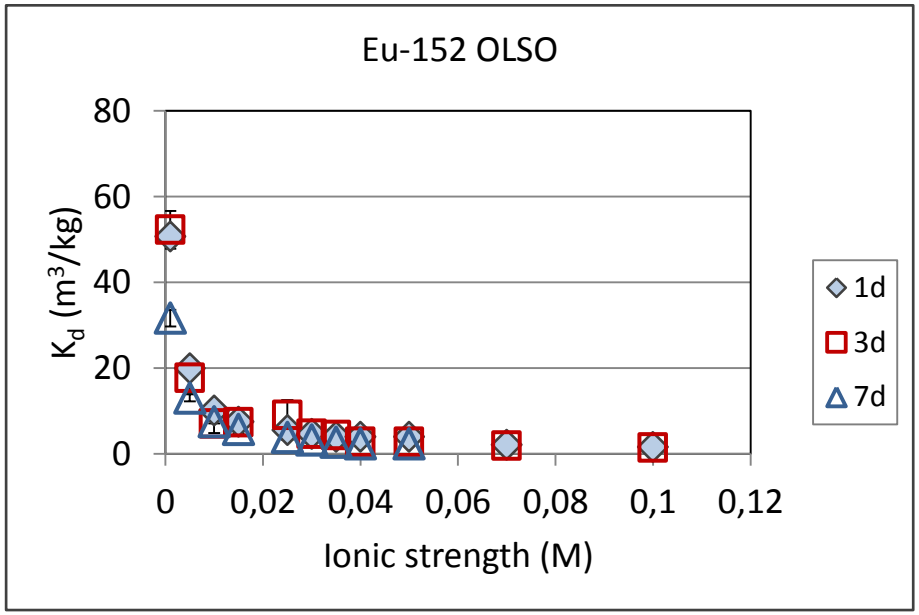




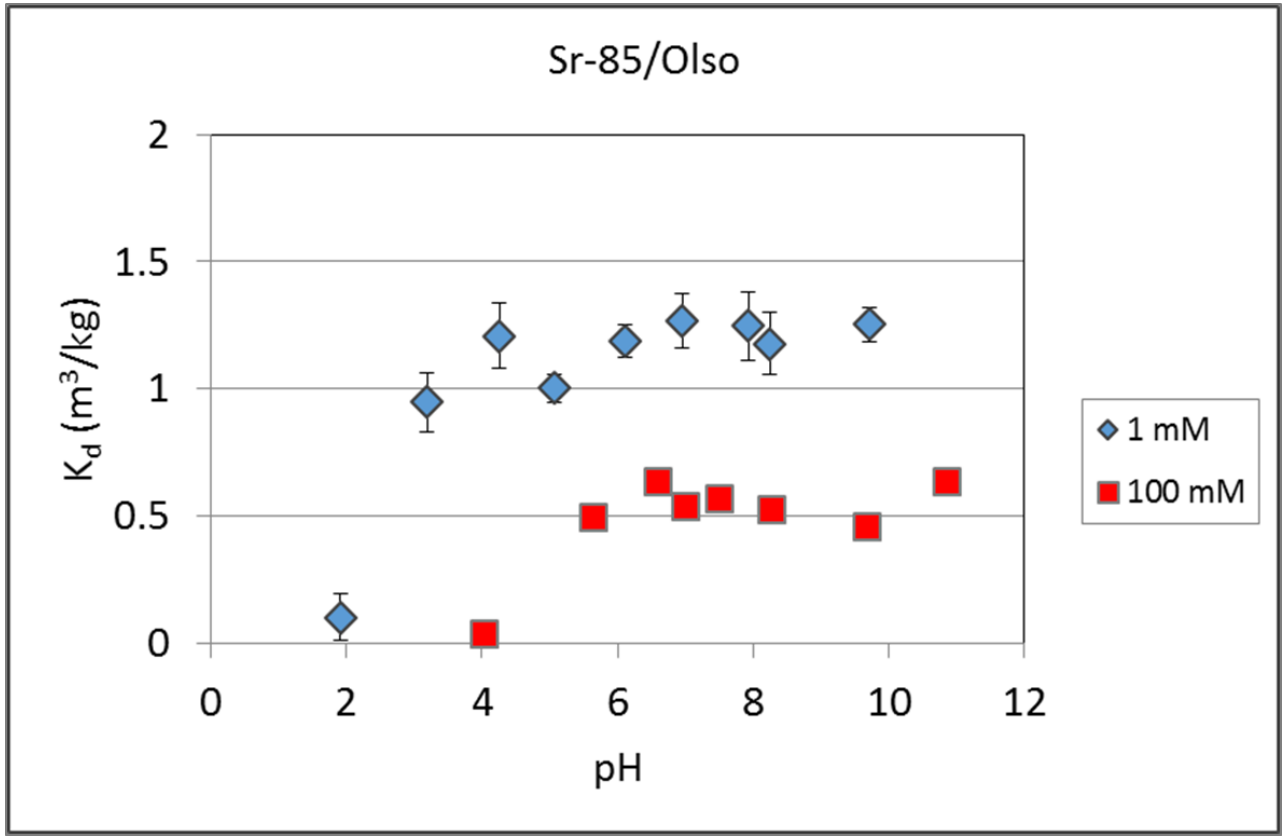


Eu-152 sorption on bentonite colloids

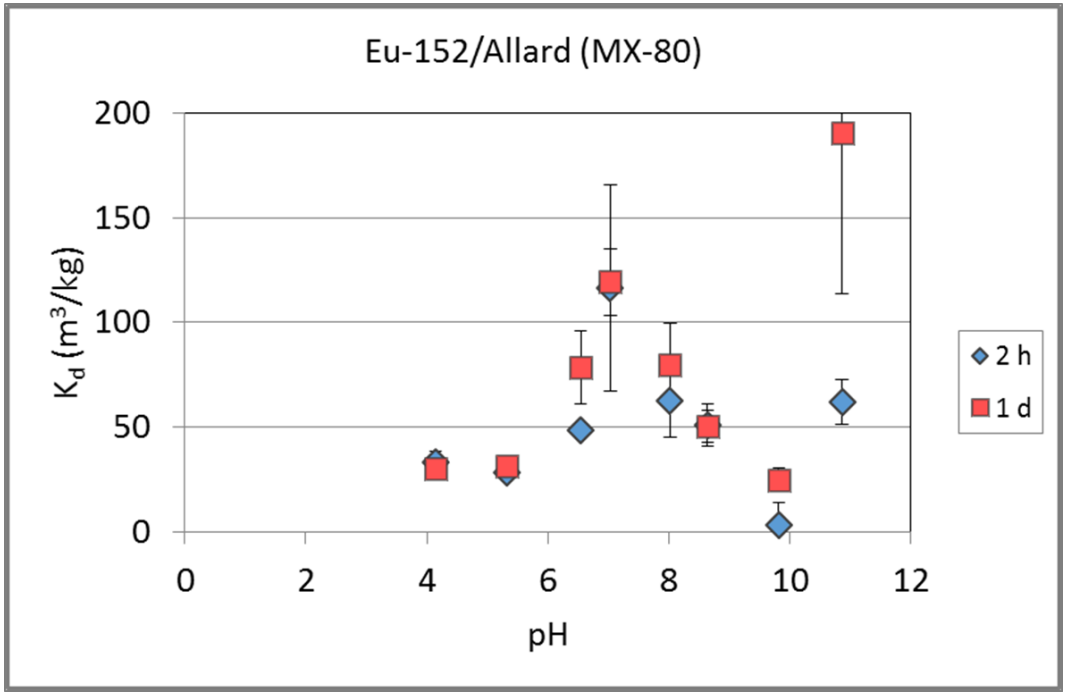




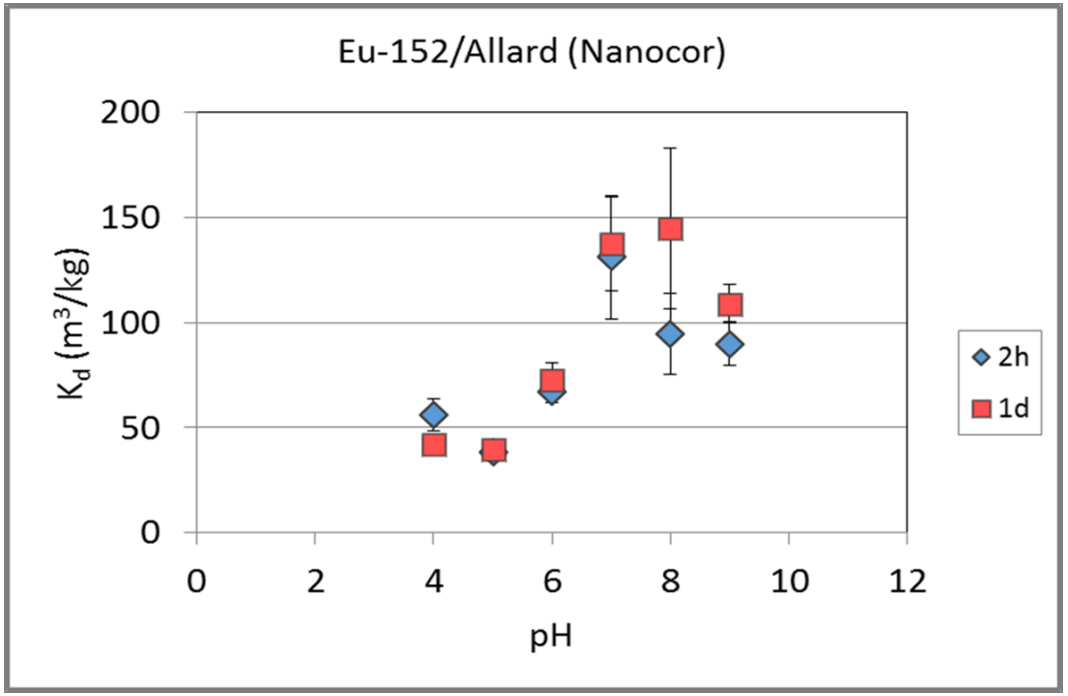
Sr-85 sorption on MX-80 bentonite colloids

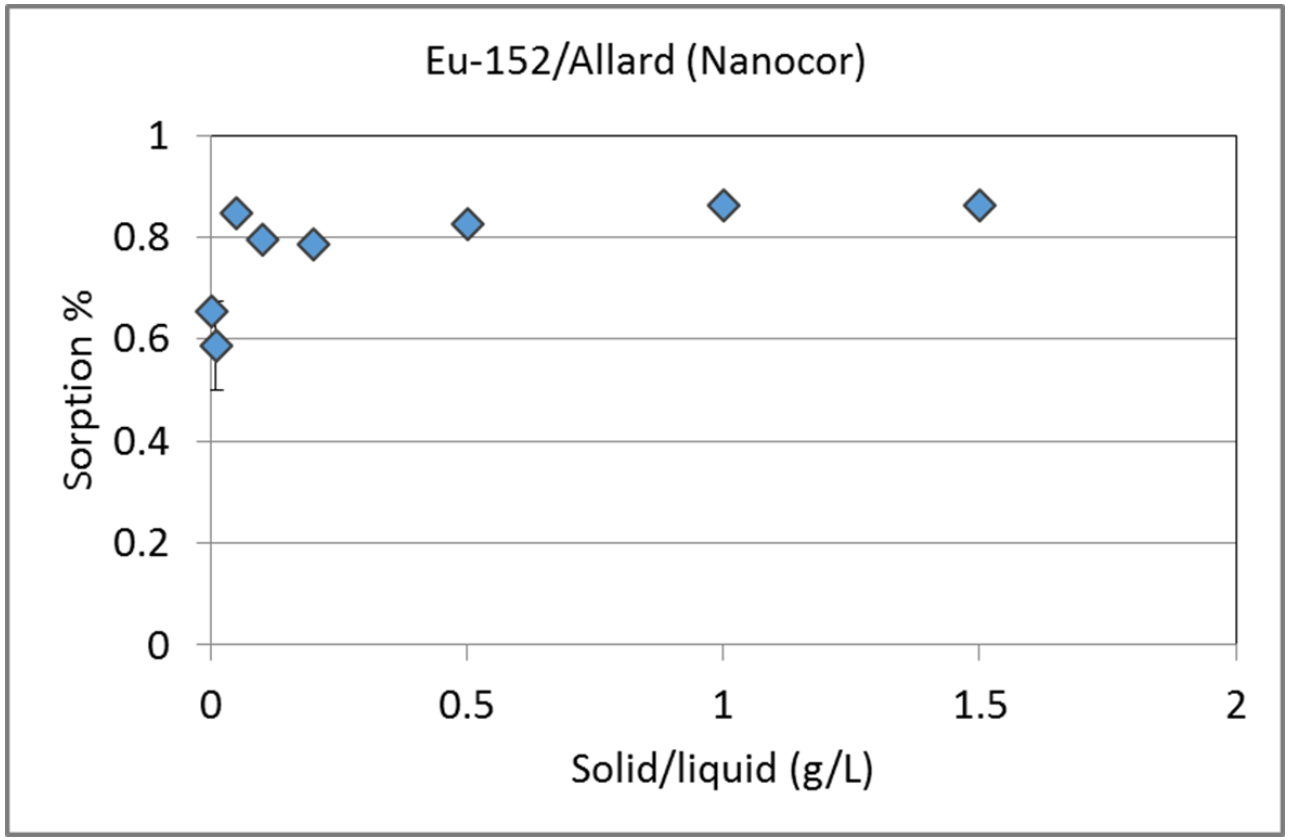


K_d-values of Eu-152 for MX-80 bentonite colloids in Allard reference water.



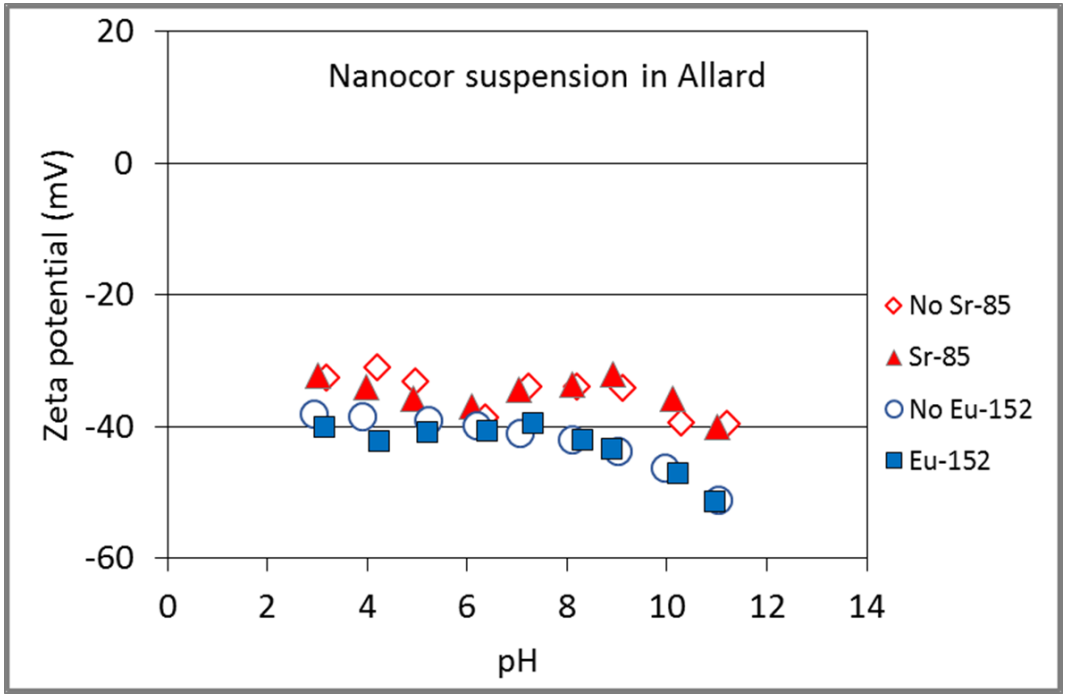
K_d-values of Eu-152 for Nanocor PGN Montmorillonite colloids in Allard reference water.



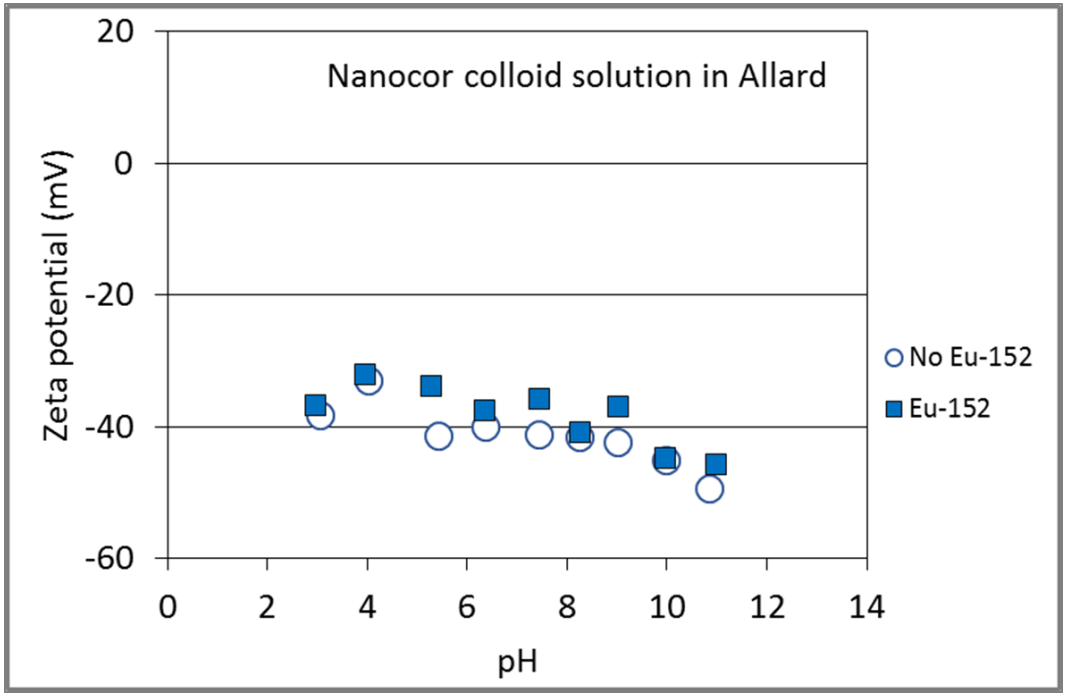


Eu-152 sorption on Nanocor colloids in Allard reference groundwater as a function of solid/liquid ratio.

Zeta potential of Nanocor suspension in Allard water as a function of pH at the presence and absence of Sr-85 or Eu-152.



Zeta potential of Nanocor colloid solution in Allard water as a function of pH at the presence and absence of Eu-152.



Np-237 sorption on corundum, montmorillonite and colloids

Batch experiments

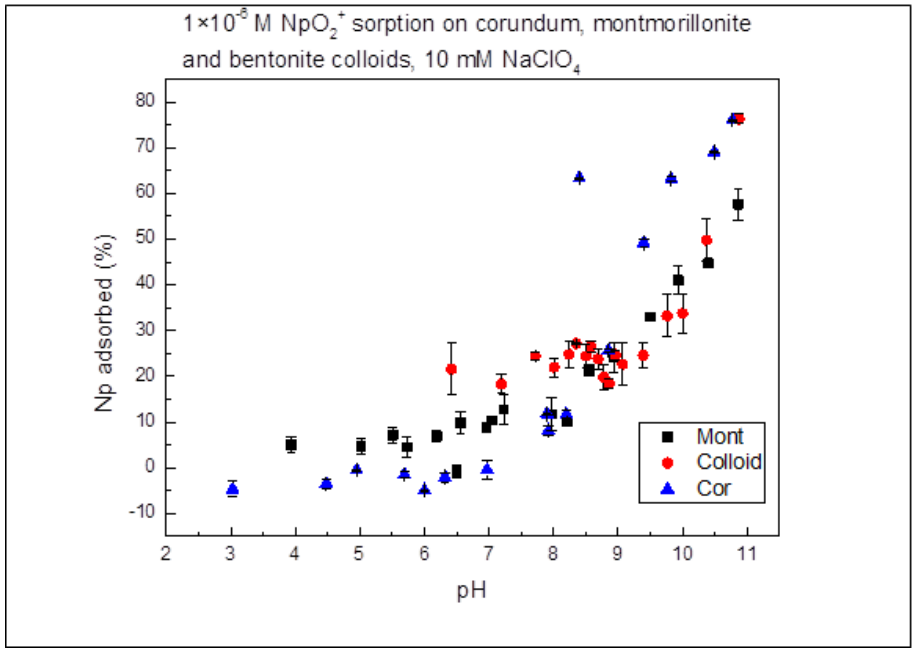
- Under anoxic conditions
- 10 mM $NaClO_4$ (batch)
- 10 mM NaCl (IR, ζ-potential)
- pH edges
- Np-237(V) sorption isotherms
- effect of time and the amount of mineral concentration

In-situ ATR FT-IR measurements in HZDR

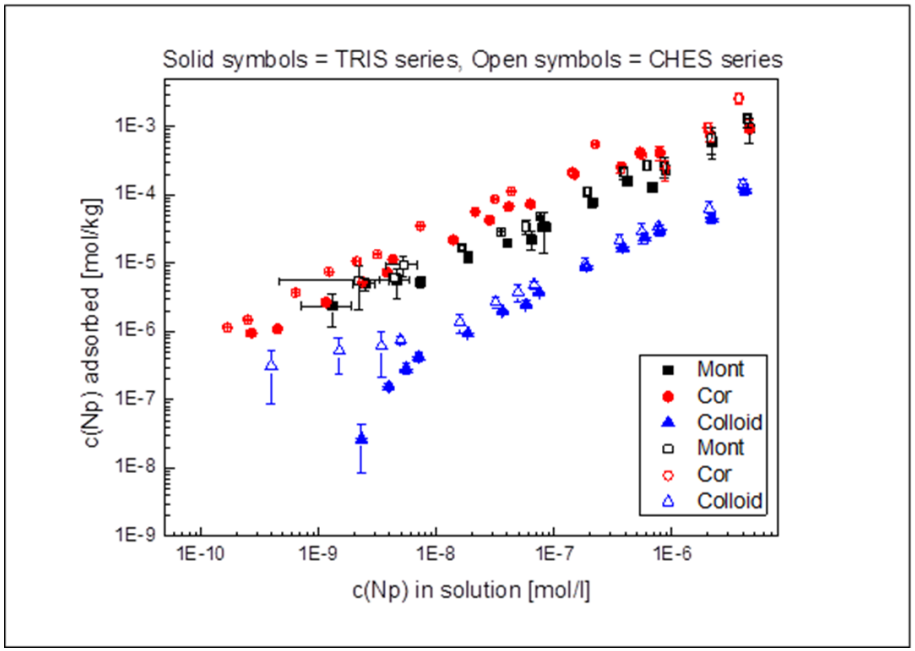
(attenuated total reflection Fourier transform infrared spectroscopy)

EXAFS

The neptunium(V) adsorption onto corundum, montmorillonite and MX-80 bentonite colloids

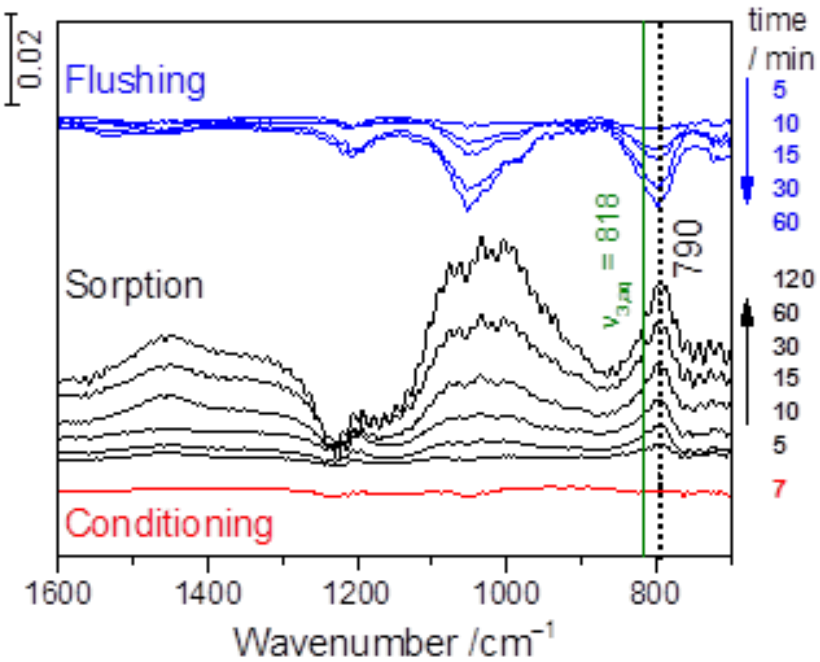


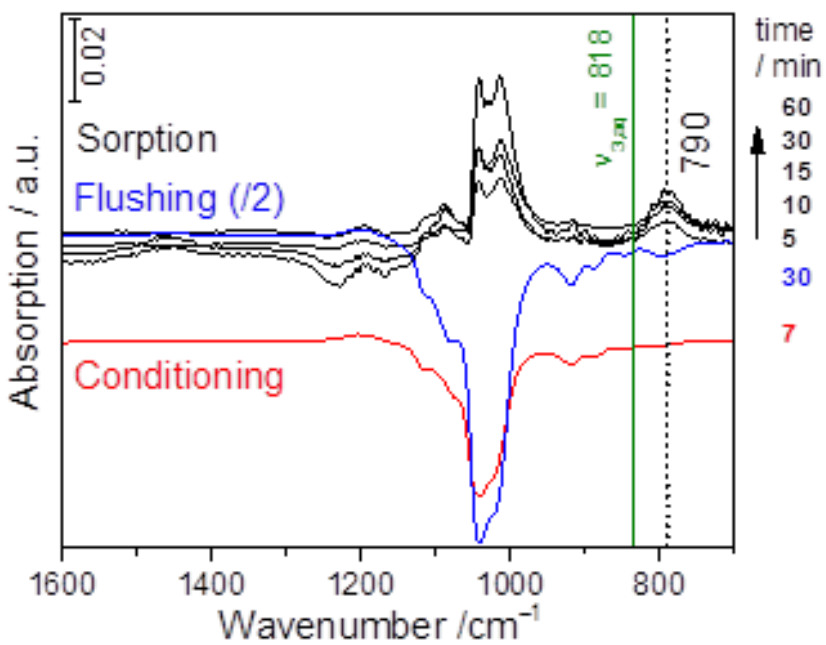
pH - edge



The sorption isotherms in TRIS and CHES buffer solution

ATR FT-IR measurements of Np(V) sorption





Sorption of 50 µM Np(V) in 0,01 M NaCl in D_2O on corundum at pD 9,6, flow rate 0,1 mL/min.

Sorption of 50 µM Np(V) in 0,01 M NaCl in D_2O on montmorillonite at pD 9,6, flow rate 0,1 mL/min.

Column experiments

Crushed rock columns:

Kuru grey granite and Sievi strongly altered tonalite

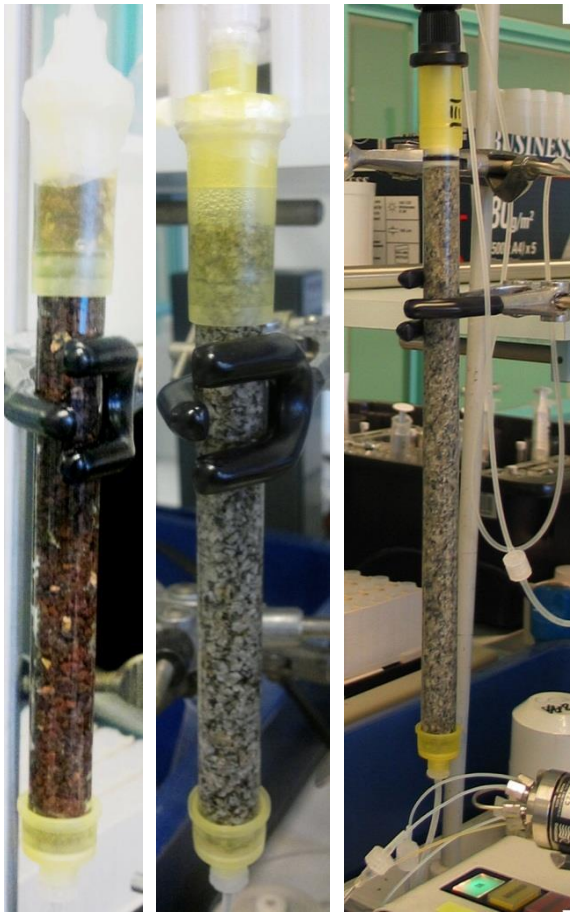
L = 15 cm, i.d. = 1.5 cm

Drill core column:

Kuru grey granite, core placed inside a tube

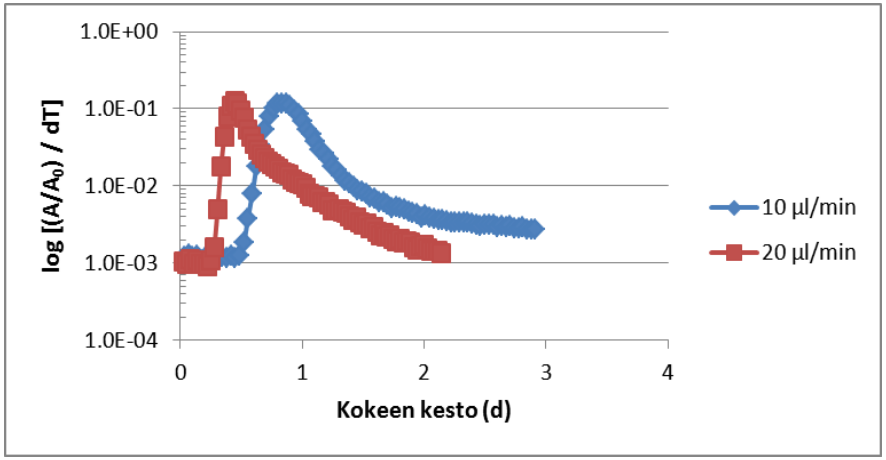
Flow channel in a 0.5 mm gap between the core and the tube

L = 28 cm, w = 4.4 cm

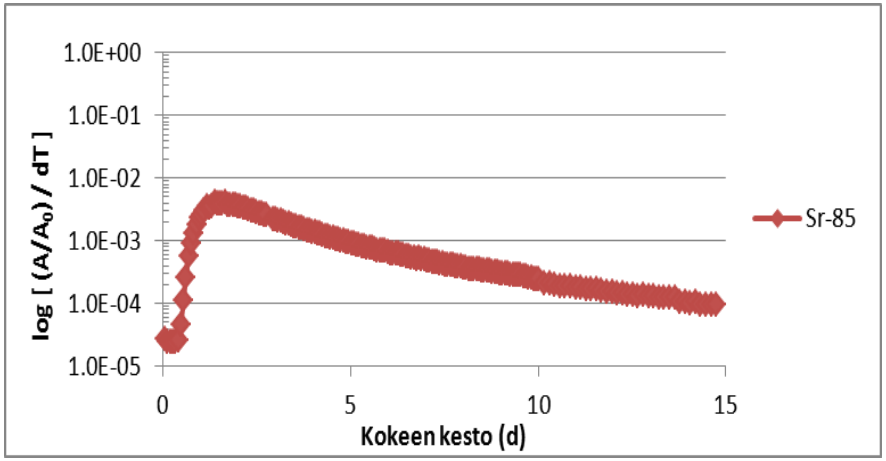


Kuru grey granite crushed rock column (30 cm)

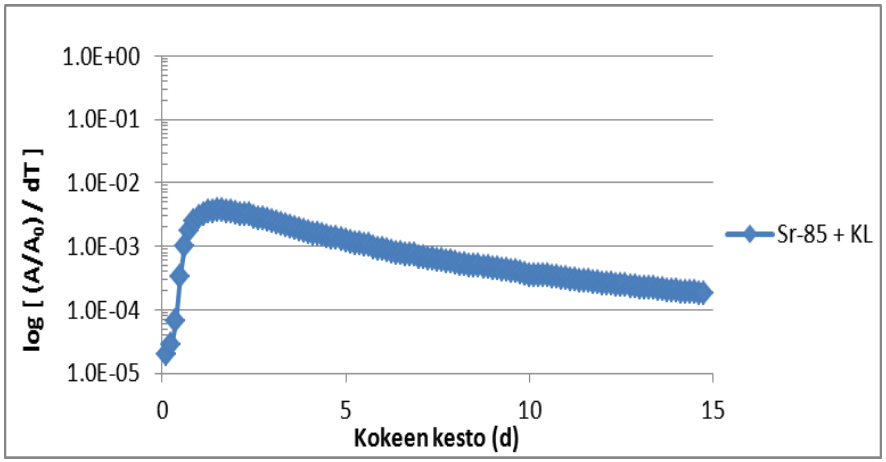
Breakthrough curves of ^{125}I



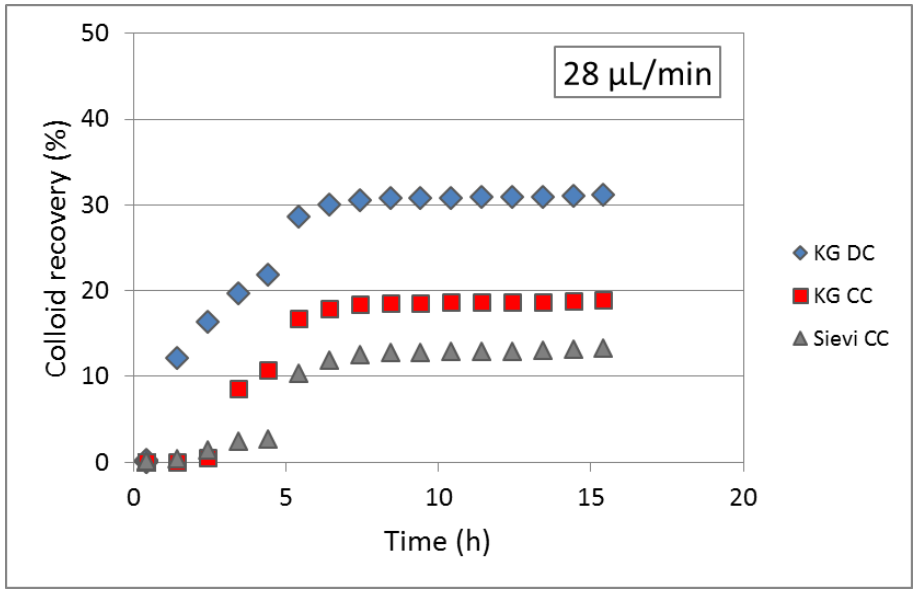
Breakthrough curve of ^{85}Sr without bentonite colloids

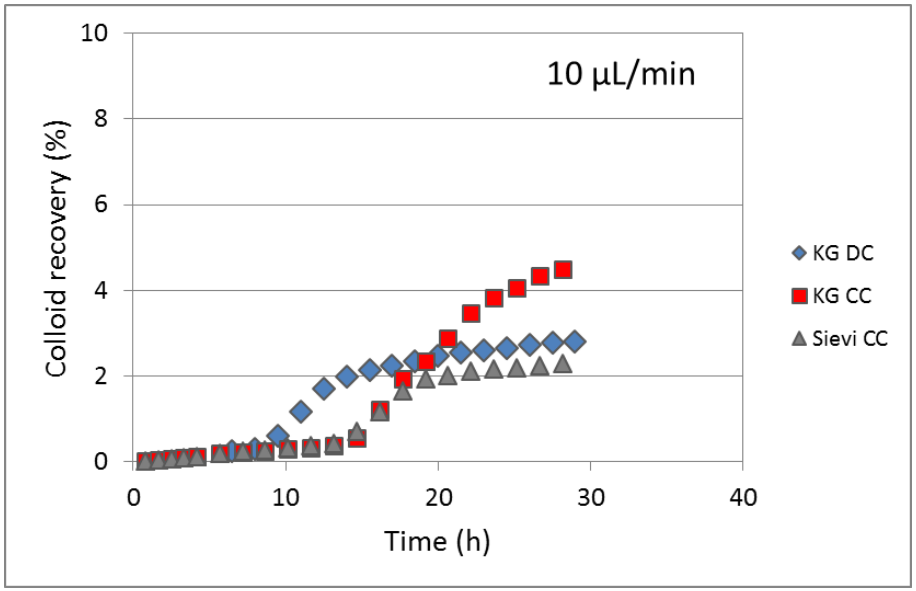


Breakthrough curve of ^{85}Sr with bentonite colloids



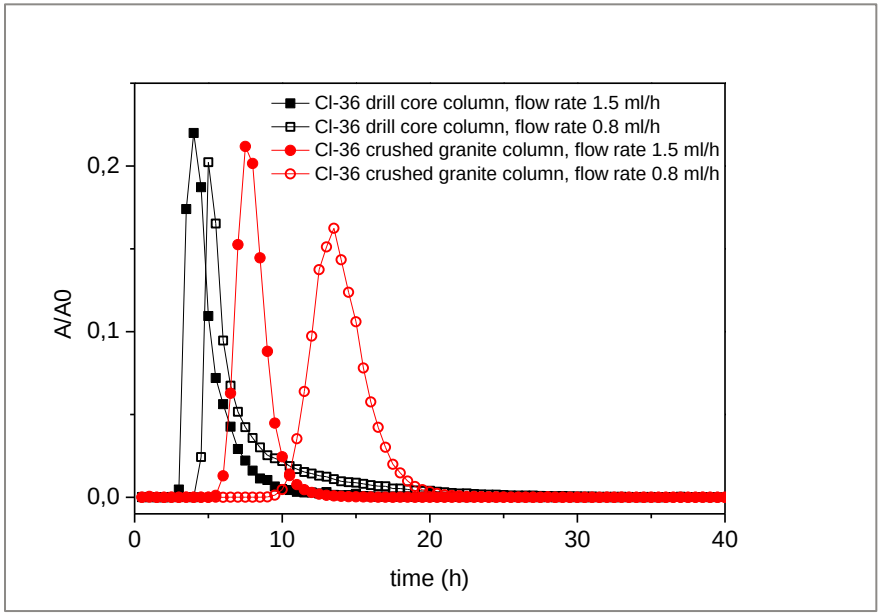
Colloid recovery

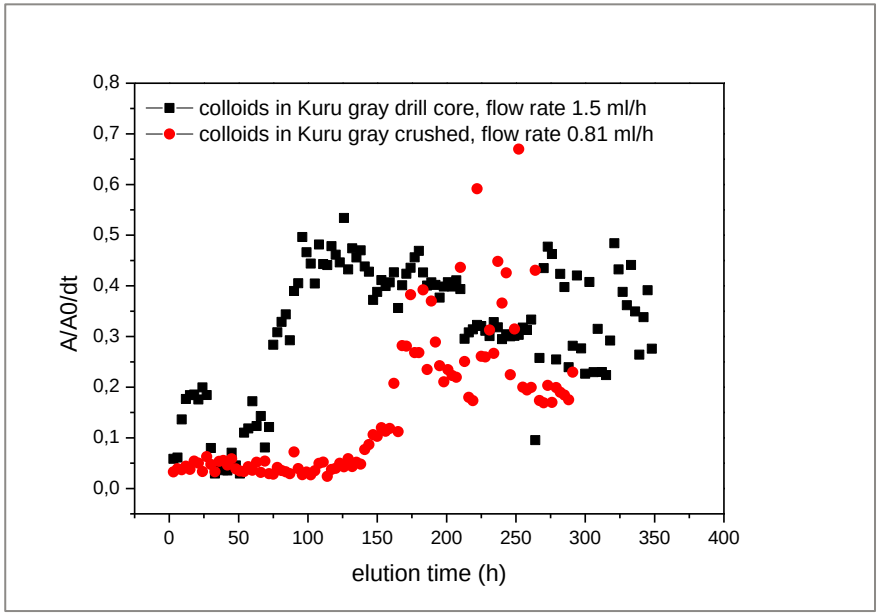




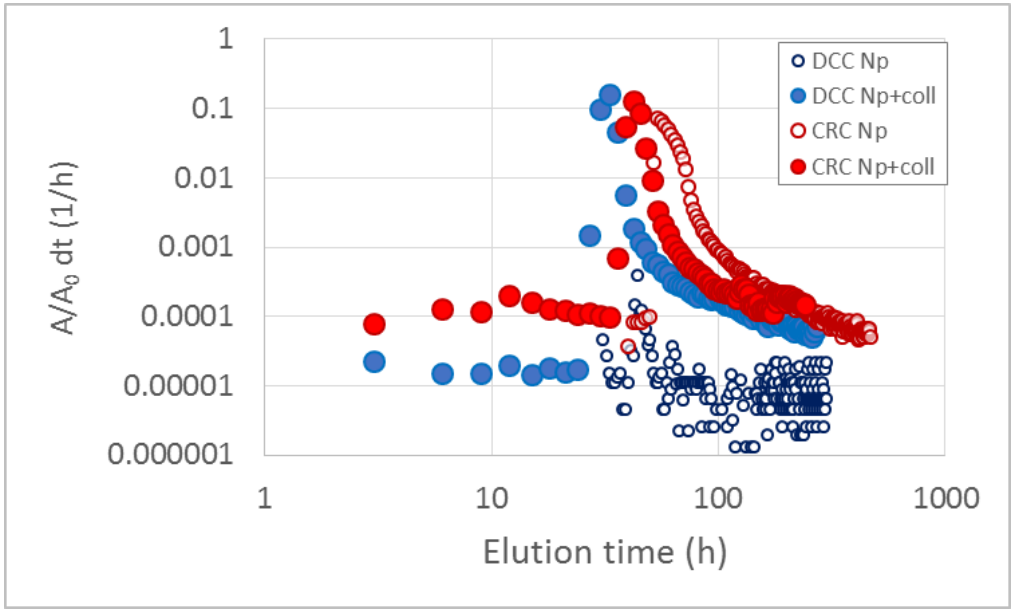
Kuru grey granite drill core column (28 cm) (blue), crushed rock columns (15 cm): Kuru grey (red) and Sievi altered tonalite (grey), flow rate 28 and 10 ul/min, particle size 230 nm

Np-237 Column experiments

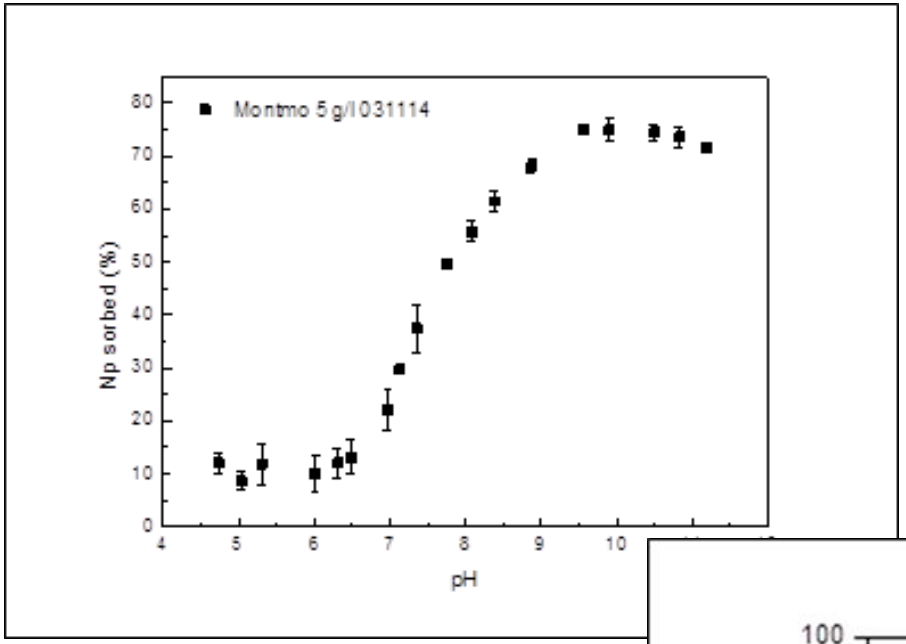


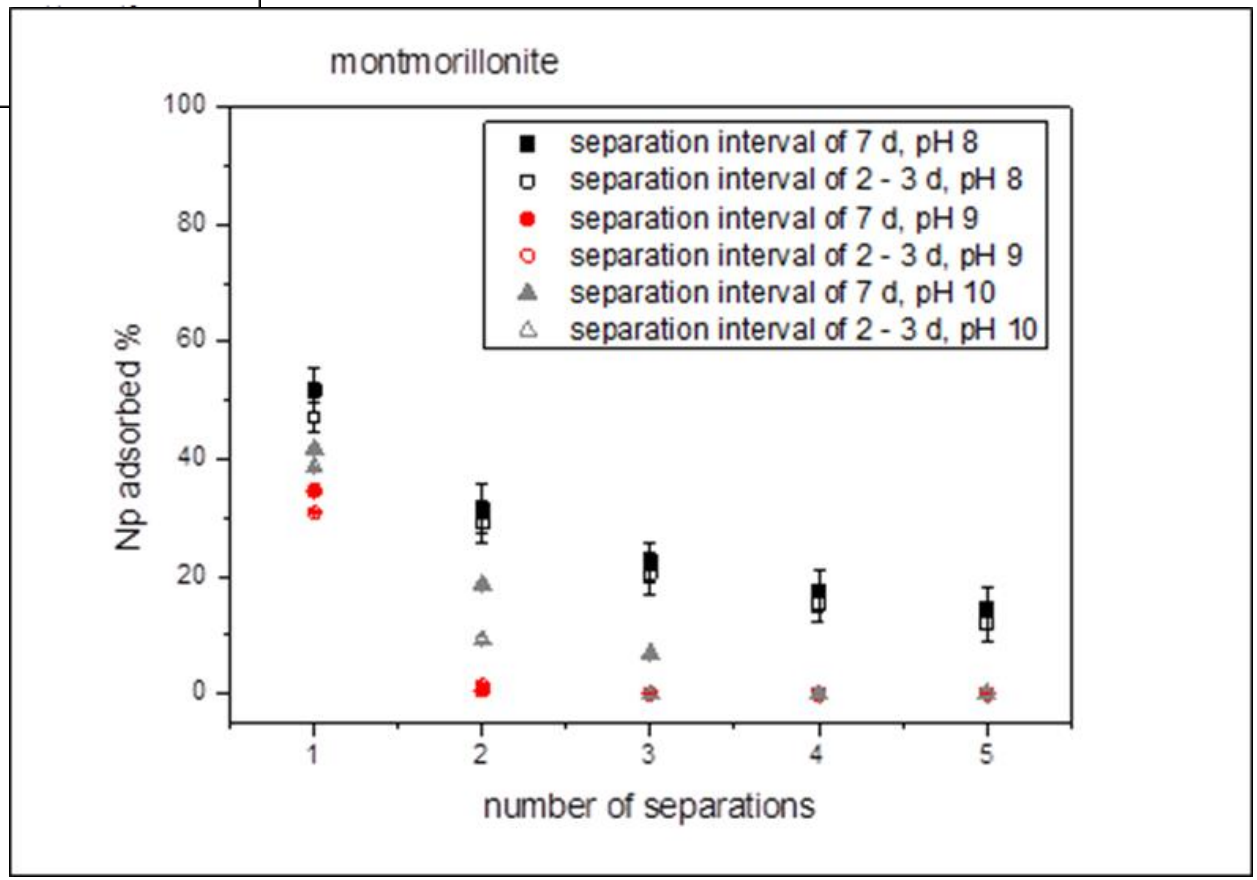


Breakthrough curves of Np-237 through drill core column (blue dots) and crushed rock column (red dots) with flow rates of 1.5 ml/h and 0.8 ml/h, respectively, in 10 mM $NaClO_4$. Open symbols in the absence of colloids and solid symbols in the presence of colloids.



Neptunium(V) adsorption and desorption on Na-montmorillonite





Conclusions

pH had a great influence on the chemical form of the radionuclides (Eu-152) and thus on their sorption onto colloids.

Eu speciation calculations are needed to explain its sorption behavior.

Zeta potential was less negative with europium only in colloid solutions suggesting also outer-sphere or inner-sphere complex due to the aluminol sites present on clay minerals.

No change in the Zeta potential curve with strontium suggest electrostatic ion-ion interactions.

Mobility of colloids was affected by water flow rate, colloid size, column material and type.

Key questions

What are the colloid mobility controlling processes and can we describe them appropriate?

- Water flow rate, colloid size, column material and type
- Groundwater salinity

Is the sorption of strongly sorbing radionuclides fully reversible, why do we observe kinetics?

- Np(V) sorption was reversible, Np(IV) ??
- Eu(III) ??

Have we indications for additional retention processes occurring?

- No matrix diffusion was seen in the breakthrough curves owing to the high flow rates.

On-going and future work

- Zeta potential determinations of the system as a function of pH with and without a radionuclide to provide information about the adsorption mechanisms (outer-sphere or inner-sphere complexation)
- Desorption experiments
- The sorption of neptunium(V) on montmorillonite (Nanocor) and bentonite colloids
- The effect of bentonite colloids on neptunium(V) transport in the column experiments
- Colloid mobility in the block scale natural fracture

Acknowledgements

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