5.3 Colloid impact on radionuclide migration

M. Bouby, K. Dardenne, G. Darbha, N. Finck, F. Geyer, S. Heck, F. Huber, U. Kaplan, C. Marquardt, R. Polly, F. Quinto, Th. Rabung, F. Rinderknecht, Th. Schäfer, D. Schild, M. Stoll, T. Yokosawa

In co-operation with:

S. Brassines[a], M.A. Denecke[b], J. Haigh, E. Prestat[c]

[a]*ONDRAF/NIRAS, Bruxelles, Belgium; [b]Dalton Nuclear Institute, University of Manchester, United Kingdom; [c]School of Materials, University of Manchester, United Kingdom*

Introduction

Aquatic colloids / nanoparticles (NPs), *i.e.* nanoscopic solids of organic or inorganic nature in the size range from ~1 nm up to ~1 µm remaining suspended in water [1], are known to be ubiquitous in natural groundwater (up to 10^6 part./mL in surface fresh waters). They are continuously generated by multiple physico-chemical processes (inter alia erosion, nucleation / precipitation, …) [2]. Naturally occurring nano suspended material (organic detritus, iron and aluminosilicate oxi/hydroxide…), residues and transformation products of alteration and corrosion processes of the multi barrier system (i.e. waste matrix, geotechnical and geological barriers) may potentially contribute to the migration of radionuclides towards the biosphere [3,4].

Long-term safety being a pre-requisite to any deep geological nuclear waste repository (DGR), performance assessment has to consider which parameters to take into account for reliable predictions. To state if the presence of colloids is one of them and to define the boundary conditions for the colloid relevance are our objective.

Our current activities deal with 1) the detection and the identification of the relevant NPs forming or existing in repository specific areas, 2) the control of their stability as a function of geochemical parameters, 3) the thermodynamics and kinetics description of their interaction with radionuclides, 4) the elucidation of their interaction with mineral surfaces and 5) the quantification of the colloid mobility. To do that, from the near-field to the far-field, we are combining laboratory and in-situ migration experiments which need the use and development of highly sensitive and sophisticated analytical techniques. The final goal is to implement our experimental data into reactive transport modelling codes (see following subchapter).

Our work is conducted with the support and in close collaboration with international nuclear waste management agencies (ONDRAF / NIRAS, Belgium; NAGRA, Switzerland), in the framework of several projects like the BMWi project HATT-2 (duration 2012 - 2013), the European FP7 CP-Belbar project and BMWi project KOLLORADO-e (durations 2013-2016) closely related to the international Colloid Formation and Migration (CFM) project performed in the Grimsel Test Site (GTS) in the frame of the investigation Phase VI.

According to the waste matrix (in particular HLW glass), steel container, backfill material (e.g. compacted bentonite) and the host rock selected (i.e. argillaceous, crystalline or saline host rocks) various colloids/nanoparticles might form and play a role which have to be examined individually. This year, in the present report we highlight some specific studies related to that question.

Long-term Lu incorporation into iron (hydr)oxide phases

Iron (hydr)oxides, widespread in nature, can play an important role in the bioavailability and migration of pollutants, such as heavy metal ions or radionuclides. Ferrihydrite and its transformation products (hematite and goethite) are commonly found in nature. In DGR sites, iron (hydr)oxides are also expected to form upon steel canister corrosion and can thus serve as sinks for radionuclides, either by surface adsorption and/or by structural incorporation. In this study, 2-line ferrihydrite was freshly synthesized, Lu(III) used as homologue for trivalent actinides was added to the suspension which was then aged for 12 years under ambient conditions in the dark. Previous characterization started by applying transmission electron microscopy (TEM) with high efficiency energy dispersive X-ray spectroscopy (EDX) and probe-side aberration corrected high-angle annular dark field STEM (HAADF-STEM) on the individual hematite NPs and
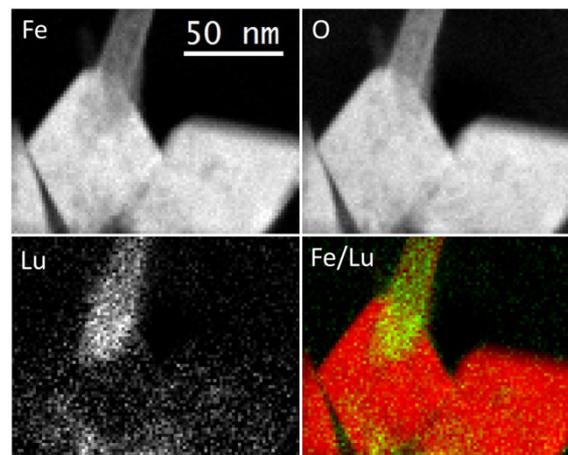

Fig. 1: EDX spectrum images of hematite particles and goethite needle. Fe and Lu distributions in the overlapped image (Fe/Lu) are indicated by red and light green, respectively.
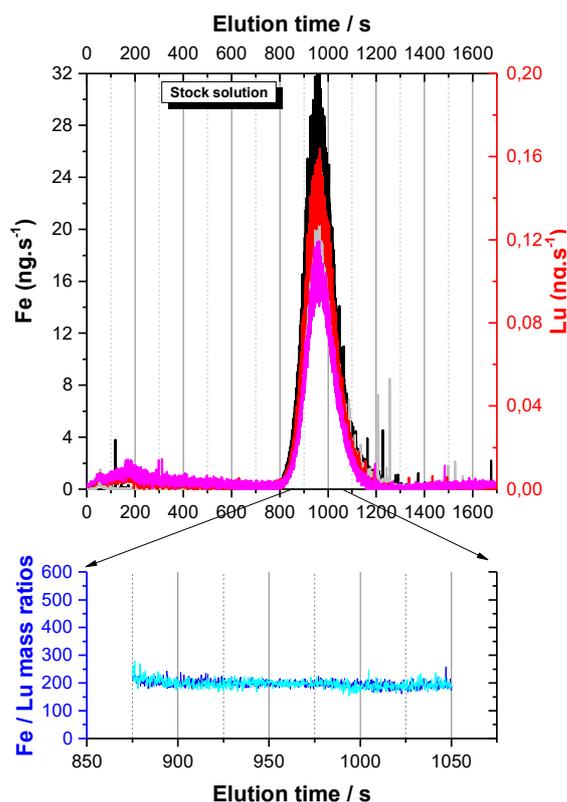
Fig. 2: *AsFlFFF-ICP-MS data, Fe- and Lu-ICP-MS fracto-grams, two successive injections of the stock suspension.*

the goethite needles grown on them (Fig. 1, [5]).

It was completed by using extended X-ray absorption fine structure (EXAFS) spectroscopy and Asymmetric Flow Field-Flow Fractionation (AsFlFFF) coupled to UV-Vis. and ICP-MS techniques [6] while modeling was done by density functional calculations (DFT) [5]. AsFlFFF/UV-vis./ICP-MS results confirm the size obtained previously [5] and indicate a clear correlation between the Fe and Lu signals which strongly hinted to a structural incorporation (Fig. 2).

EXAFS was used to further characterize the binding mode and to identify the host phase. The results do not evidence any surface adsorption or incorporation
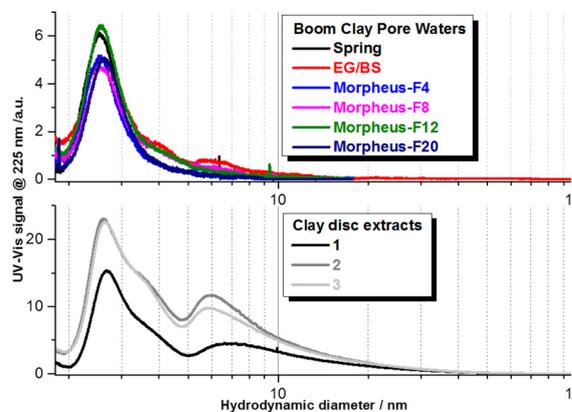

Fig. 3: *UV-fractograms converted in hydrodynamic diameter according to a calibration of the system performed by using PSS standards and carboxylated polystyrene nanoparticles.*

within hematite, but rather that Lu very likely substitutes for Fe within goethite. Consequently, a very consistent picture is obtained by the complementary use of different analytical techniques strongly suggesting that Lu atoms mainly associated with the goethite NPs, where they are occupying (substituting) Fe sites. Results from DFT calculations indicate that Lu incorporation within the goethite or hematite structures are almost equally likely, suggesting that experimental conditions may play an important role.

Accordingly, demonstration has now been done of the possible sequestration over years of trivalent element. In case of effective mobilization, these NPs might transport radionuclides towards the biosphere. Their potential role has thus to be considered.

Characterization of natural organic matter derived from different layers within the Boom Clay formation and their radionuclide interaction

In Belgium, deep geological disposal of nuclear waste is envisaged by ONDRAF/NIRAS in poorly indurated clay formations like the Boom Clay (BC) or Ypresian clays (http://www.ondraf-plandechets.be). These host rocks have favorable intrinsic properties promoting the retention of radionuclides (low hydraulic conductivity, reducing redox capacity, slightly alkaline character, high specific surface area, cationic exchange capacity and plasticity). Organic material (OM) is present in 1 to 5% wt in BC [7]. To complement the Belgian research program conducted so far, our program work focuses on the determination and characterization of the mobile size fraction of dissolved organic matter (DOM) currently present and to be expected within the lifespan of the repository (i.e., taking into account the possible geochemical evolution). Here we report on the size distribution and natural metal association determination of 1) current BC pore water DOM and 2) DOM released from solid clay samples. The pore waters and solid clay samples comes from the HADES underground research laboratory (URL) (Mol, Belgium) and are representative of different horizons of the Boom Clay formation under present-day conditions (i.e., 15 mM NaHCO$_3$), see [8] for details.

Highly sensitive and complementary analytical, imaging and spectroscopic techniques have been used on the original samples or their isolated size fractions, see [8] for details.

The data presented first are those obtained by using the AsFlFFF/UV-Vis./ICP-MS. The present results show a relative OM size homogeneity (Fig. 3): Small size OM fractions (< 10 nm) are found in all natural pore waters and in the leached samples but with various relative quantities.

In the BC pore waters, several elements like Mg, Al, Fe, Mn, Sr, Y and a part of the lanthanides (Lns) and actinides (Ans, e.g. U, Th) are associated with the OM. In the leached extract, the Lns and Ans are mainly detected in bigger sized fractions (4 - 30 nm), the nature of which remains to be identified.
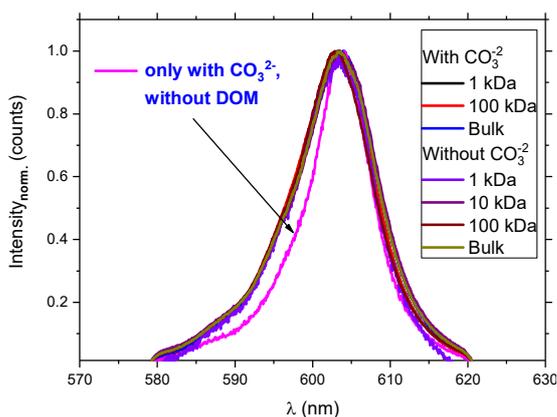
Fig. 4: Compilation of the Cm(III) fluorescence spectra in the EG/BS sample in the presence and absence of carbonate recorded by the "indirect excitation" method. The spectra are scaled to the same peak height. The spectra obtained in the absence of DOM is also added.

Complexation properties have been examined by using the time resolved laser induced fluorescence spectroscopy (TRLFS) applied to Cm(III) ions as representative of trivalent actinides. The two pore waters investigated (Morpheus-F20 and EG/BS) contain two types of strongly complexing ligands: DOM and carbonates. Indirect excitation measurements allow to elucidate the Cm(III) speciation. It is concluded that the Cm(III)-DOM complexes are the dominant species and no ternary complexes (e.g. Cm(III)-carbonato-DOM) are formed. In addition, it can be concluded after examination of specific DOM size fractions isolated by ultrafiltration, that their binding properties are identical or at least very similar, as illustrated exemplary Fig. 4 for one of the BC pore water investigated (EG/BS).

To better characterize and understand the behavior of the BC OM, one has now to concentrate on its origin, on the long-term stability of the leached or fractionated BC OM and on the reversibility of the metal ion complexation process.

Experiments on compacted bentonite erosion and colloid formation at the bentonite pore water interface

In present DGR concepts, low permeability swelling clay material is surrounding the HLW products. Besides acting as a transport vehicle for contaminants, colloid release / bentonite buffer erosion is an issue with respect to the long-term integrity of the geotechnical barrier. Bentonite erosion experiments have been an important component within the Kollorado-e [9] and BelBar projects (http://skb.se/belbar). Erosion processes have been simulated under dynamic but rather stagnant flow conditions simulating repository post-closure conditions. To better understand the FEBEX and MX-80 bentonite erosion behavior, systematic variation of the compaction density, chemistry of the contact water (ionic strength (IS), pH value, cation composition), contact surface and angle, and

type of bentonite (raw material or homo-ionic Na/Ca form) was performed. Results were compared with modeling approaches. Experiments performed in the laboratory with two different setups [10,11] evidence the erosion (clay colloid detachment) whatever the clay composition. For the raw material, three phases can be identified: 1-washing of loosely bound particles, 2-dissolution of accessory minerals and 3-erosion. Remarkably, comparable colloid concentrations (< 2 mg/L) and erosion rates have been reported. The erosion rate for natural FEBEX bentonite in Grimsel ground water is 71.0 ± 20.1 g/m²/y and for natural MX-80 bentonite in a synthetic low glacial melt ground water is 51 ± 7 g/m²/y. More details in [10,11]. In the so-called Long Term In-situ Test (LIT) performed at the GTS, a bentonite source was emplaced in a water conducting feature. After 1 year, colloid concentrations < 1 mg/L have been reported in the effluent samples. These values are consistent with those obtained in the laboratory. Experiments are still on-going.

Colloid stability under specific conditions

Once produced, bentonite clay colloids have to be stable under relevant geochemical conditions to play a role. Numerous experiments have been carried out on that topic over the past years and research programs (CFM&Kollorado, Kollorado-2, Kollorado-e, BelBar). The stability has been proven in NaCl media, up to 0.1 M, whatever the bentonite material considered as clay colloidal source. On the opposite, the presence of divalent cations destabilizes the clay colloids. While numerous studies have been conducted over a rather short time period (fast coagulation) only few are reported over period of more than 1 year [12]. In that case, agglomeration has been reported even under geochemical conditions where colloids are supposed to be highly stabilized. To confirm this observation, a systematic study has been initiated in the frame of the BelBar project. Clay colloid suspensions have been prepared at different concentrations, at two pHs (~6 and 8.4), in various electrolytes at fixed ionic strength (10^{-3} M), in presence or not of organic matter (i.e. fulvic acids (FA)). The few samples tested after 4 years aging confirm previous results with a gradual agglomeration. A complete analysis is planned in 2018.

In the frame of the BMWi HATT-2 project [13], the stability of FA has been tested in very high ionic strength media simulating saline solutions eventually present in rock salts formations. The results demonstrate the high stability of this small sized organic matter up to 5 M IS NaCl and 3 M IS CaCl₂/MgCl₂, i.e. the FAs remain suspended (less than 10% variation of the dissolved organic concentration (DOC) reported). In addition, conformational changes have been evidenced leading to an increase of their size but their mobility might be preserved.

Concerning the BC OM previously characterized (see above), an increase of salinity evidences a dissociation and a coagulation of the different fractions. The largest sizes fractions tend to coagulate under

high IS. On the opposite, the smallest sized fractions dissociate for IS > 0.5 M. As usually observed, divalent cations such as Ca^{2+} have a more pronounced effect than monovalent cation such as Na^+.

Colloids interaction with mineral surface

While adsorption of colloids on rock surfaces has been attributed to electrostatic interactions, contradictory results evidenced colloidal adsorption even under unfavorable (repulsive) conditions. Migration processes have thus to be investigated in more details by looking at the deposition of colloids onto mineral surfaces. In a recent study [14], the impact of gravity, collector surface roughness and fracture orientation on colloid retention kinetics in an artificial fracture has been examined. It appears clearly that the behavior of bigger sized colloids (1000 nm carboxylated polystyrene nanoparticles) is dominated by the gravity and not affected by the mineral surface (granodiorite from Grimsel, Switzerland) roughness. On the opposite, smaller sized nanoparticles (25 nm carboxylated polystyrene nanoparticles) are not subject to sedimentation under the present experimental conditions (pH 5, 1 mM NaCl IS, 7 mL/h laminar flow) but impacted by surface inhomogeneities such as surface roughness.

Bentonite colloids-radionuclides sorption and reversibility

Radionuclides sorption and reversibility studies are on-going, under realistic conditions (pore water and glacial melt water) and long contact time periods (more than 5 years). The aim is to determine radionuclides kinetics rates which are necessary to simulate the field and laboratory experiments when inserted into transport codes. The role played by organic matter or fracture filling material (FFM, consisting mainly of fault gouge) is scrutinized. Batch radionuclides sorption / desorption studies on fault gouge material from Grimsel Test Site have been conducted (PhD work of F. Rinderknecht, 2017). Sorption kinetics rates have been derived by fitting when possible. ^{242}Pu shows the fastest kinetics closely followed by ^{243}Am and ^{233}U, while ^{237}Np present a lower rate of one order of magnitude. No fitting was possible for ^{99}Tc due to its weak interaction with FFM. Kinetics rates for desorption have been fitted using both 1-rate and 2-rate exponential equation approach revealing a simple sorption / desorption process (for ^{242}Pu and ^{243}Am) or a more complex coupled sorption / reduction process (for ^{237}Np).

For in-situ experiment performed at the GTS, the application and further development of Accelerator Mass Spectrometry (AMS) [15] offered new opportunity. AMS does not provide direct information on the association of actinides with colloids and neither on their speciation, however due to its extreme sensitivity, it has enabled to study the long term release and retention of the actinide tracers within the system of groundwater – bentonite colloids – fault gouge minerals at the GTS. Recent investigations consisted in sampling the tailing of the breakthrough
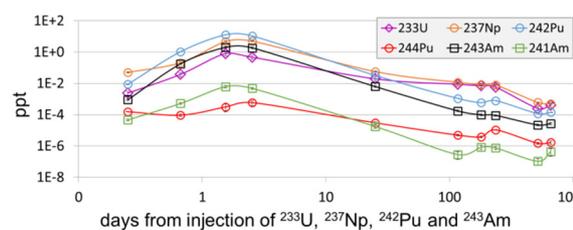

Fig. 5: *Concentrations expressed in ppt of ^{233}U (violet rhombuses), ^{237}Np (orange circles), ^{242}Pu (blue circles), ^{244}Pu (red circles), ^{243}Am (black squares) and ^{241}Am (green squares) determined with AMS in selected samples of CFM run 13-05.*

curve over a period of eight months and more which definitely provided additional details on the sorption / desorption processes / kinetics of the fault gouge. Both in the *in situ* test CFM run 12-02 and CFM run 13-05, AMS has been employed as analytical technique complementary to SF ICP-MS in order to investigate ultra trace levels of actinide nuclides in the Grimsel groundwater samples. In fact, as depicted in Fig. 5, concentrations of ^{233}U, ^{237}Np, ^{242}Pu, ^{244}Pu, ^{243}Am and ^{241}Am have been determined down to values of ca. 1×10^{-7} ppt in samples collected in the tailing of the breakthrough curve of run 13-05. Details on the analytical method as well as the outcome of the study are given in references [15] and [16].

References

[1] Honeyman, B.D., Nature, 397, 23-24, (1999)

[2] Stumm, W. et al., Aquatic Chemistry: chemical equilibria and rates in natural waters, 3rd. Ed., John Wiley & Sons, USA, 1996.

[3] Kim, J.I., Radiochim. Acta, 52/53, 71-81 (1991)

[4] Schäfer, Th. Et al., Appl.Geochem, 27, 390-403, (2012)

[5] Yokosawa, T. et al., Fate of Lu(III) sorbed on 2-line ferrihydrite at pH 5.7 and aged for 12 years at room temperature. II: Insights from STEM-EDXS and DFT calculations (to be submitted to JCIS, 2017).

[6] Finck, N. et al., Fate of Lu(III) sorbed on 2-line ferrihydrite at pH 5.7 and aged for 12 years at room temperature. I: Insights from ICP-OES, XRD, ESEM, AsFlFFF/ICP-MS and EXAFS spectroscopy (to be submitted to JCIS, 2017).

[7] Bruggeman, C. et al., Boom clay natural organic matter. Status report 2011, SCK.CEN-ER206, External report, 2012

[8] Kaplan, U. et al., KIT-internal report 04/2016, 20004085

[9] Huber, F. et al. Project Kollorado-e final report, DOI: 10.5445/IR/1000059756

[10] Rinderknecht, F. et al., Bentonite erosion and colloid mediated transport of radionuclides in advection controlled systems (to be submitted to Applied Clay Science, 2017)

[11] M. Bouby et al., Colloid generation from compacted raw or homo-ionic MX80 bentonite in a low ionic strength carbonated synthetic

(ground)water under quasi stagnant flow conditions: Erosion rates and propagation front determination (to be submitted to Applied Clay Science, 2017)

[12] Bouby, M. et al., Geochim. Cosmochim. Acta, 75, 3866-3880, (2011)

[13] Marquardt, C. et al., HATT-2 final report, in print (2017)

[14] Stoll, M. et al., J. Coll. Int. Sci, 475, 171-183, (2016)

[15] Quinto, F. et al., Anal. Chem, 87, 5766-5773, (2015)

[16] Quinto, F. et al.; (to be submitted to Anal. Chem, 2017).