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 $(D-N^{\circ}:2.1)$ – Status of radionuclides sorption and transport studies Dissemination level: PU Date of issue of this report : 3^{rd} April 2013

AIM OF THE WORK

To decrease the uncertainties related to radionuclide retention in the performance assessment of geologic disposals of high-level radioactive waste in crystalline rocks is still a necessary task. The large discrepancies, obtained in retention data from different sources, or the lack of reproducibility in the determination of transport parameters in crystalline rocks are often not easily explicable.

Existent uncertainties might be related to conceptual aspects, including not wellunderstood processes, as the kinetic of retention processes or to the dependence of retention parameters on the hydrodynamic conditions of the system. Other important factors are the heterogeneity of the medium and up-scaling factors. These uncertainties may lead to a biased data interpretation and therefore a poor modeling, which would preclude good predictions of radionuclide migration.

Additionally, problems related to experimental determinations still exist. Experimental data are sometimes gathered under conditions not fully representative of the scenario of interest or using samples not correctly characterized or handled.

Some main factors, which can represent source of uncertainty and have to be taken into account and evaluated are, for example: the origin of samples, their mineralogical composition or their accessible surface area. The characteristic of the groundwater and rock/water interactions are also of importance. Additionally, factors as sampling, crushing or cutting and storing of the solid samples together to the conservation of the natural groundwater might be very important in the outcome of the experiments. In particular, the oxidation of the solid or aqueous phase may strongly affect the results for redox sensitive elements.

The main objective of the work performed in Work Package 2 (WP2, Radionuclide Transport and Sorption Studies) is to provide methodologies to decrease the degree of uncertainty on the determination of retention parameters in crystalline rocks and consequently on the prediction of radionuclide migration in the host rock at a long-term.

In WP2, radionuclide transport and sorption studies have been planned to determine radionuclide transport properties in crystalline rock systems over different spatial



scales, thus experiments are conducted with small to large block-scale samples, using different complementary techniques.

Granite from different sites will be used and the results obtained, with the same material (Äspö diorite) in different laboratories, will be compared trying to identify the main source of uncertainties.

In parallel, an improvement of the knowledge on retention mechanisms is foreseen. Their kinetic and irreversibility as well as their relation to different relevant minerals and mineral components will be analyzed. This will allow developing sorption models for a more reliable description of retention in heterogeneous rocks.

Data generated within WP2 will feed models developed in WP4 (Conceptualization and Modeling) and WP5 (Application to the Safety Case).

The following organizations are participating to WP 2: **KIT-INE** and **HZDR** (Germany); **CIEMAT** (Spain); **CTH** (Sweden); **UJV Rez, a.s.** (formerly NRI-Rez) (Czech Republic); **MSU** (Russia).

SUMMARY OF THE WORK PERFORMED WITHIN WP 2 from the staring of the project up to 31 March 2013.

KIT-INE focused on the study of sorption and desorption of radionuclides. In particular, they studied the sorption/desorption of $^{137}Cs(I)$, $^{152}Eu(III)$, $^{233}U(VI)$ and Tc(VII) onto the Äspö diorite obtained from the new samplings performed, within the frame of the CROCK Project, at the Äspö Hard Rock Laboratory (Sweden).

One of the objectives of KIT-INE work was to compare sorption data obtained with well-preserved rock samples with those obtained with oxidized samples. Previous to sorption experiments, the solid phases were characterized by different techniques. The aqueous phase used for sorption experiments was a synthetic Äspö groundwater, which composition was provided by Heck and Schäfer (2012) at the beginning of the project. Desorption studies (with Cs, Eu and U) were carried out with both the synthetic Äspö water and with natural groundwater coming from the Grimsel Test Site (GTS, Switzerland).



Adsorption of Cs and Eu onto the Äspö diorite was rapid and almost quantitative; the adsorption of U was lower but presented a slower kinetic. The distribution coefficients of Cs, Eu and U and their time-evolution were not significantly different when obtained on the well-preserved or oxidized samples. This was expected in the case of Cs and Eu because they are non-redox sensitive elements. In the case of U, the Eh measurements in the aqueous solution indicated that U should not have been reduced in the solution. However, XPS results indicated that the U adsorbed on the well-preserved sample could have been reduced to U(IV).

Additional work focused on the study of sorption and desorption of radionuclides onto granitic material. In particular, KIT-INE studied the sorption/desorption of ¹³⁷Cs(I),¹⁵²Eu(III) and ²³³U(VI) onto crushed material of Äspö diorite obtained from the new samplings performed within the frame of the CROCK Project. A summary of these results was presented at the first CROCK Workshop as an oral contribution (Stage et al., 2012)

Instead, in the case of Tc, large differences on distribution coefficients obtained with oxidized and non-oxidized samples were observed, indicating the importance of working with well-preserved samples and the results are summarized in an S+T contribution (Totskiy et al., 2012).

Precisely, in the second part of the project, the work focused on the interaction of Tc(VII) with new crystalline rock core material drilled under anoxic conditions. Batchtype sorption studies on Äspö diorite (ÄD) in contact with Äspö groundwater show that low Tc concentrations (< 10^{-8} M) are almost fully retained by un-oxidized granite after 1-2 months contact time, whereas considerably less retention was found in the case of elevated concentration (10^{-5} M). Immobilization of Tc(VII) strongly depends on sample preservation conditions. Tc sorption onto oxidized material shows approximately 2.4 times less adsorption compared to samples drilled, transported and stored under anoxic conditions. This results can be explained by Tc(VII) reduction to poorly soluble and strongly sorbing Tc(IV) by the ion–exchangeable ferrous iron pool available in the ÄD.



The measured Eh(SHE) values of -80 to -150mV after one month equilibration time of the anoxic samples corroborate the proposed Tc oxidation state and predict the stability of $TcO_2 \cdot 1.6H_2O(s)$ for the 10^{-5} M and 10^{-8} M samples and $TcO(OH)_2$ for the 10^{-9} M samples. Based on this thermodynamic calculations a Tc(IV) species sorption in the low concentration samples and a reduction to poorly soluble $TcO_2 \cdot 1.6H_2O(s)$ solid phase in the higher concentrated samples can be expected.

Tc(VII) reduction was proven by XPS analysis of granite surfaces after sorption. Exclusively Tc(IV) was found. Surface ion-exchangeable Fe(II) was quantified as approx. 1-3 μ g/g for oxidized material, whereas for the un-oxidized samples higher values of around 4-6 μ g/g were obtained. Experimentally determined solid/liquid distribution ratios for experiments with the lowest Tc concentration are at ~10³ mL/g under reducing conditions and at ~3 mL/g for partially oxidized material.

These values are in good agreement with previous work on comparable materials of 10^3 mL/g for reducing and 0 mL/g for oxidizing conditions. Only small Tc desorption from ÄD was found under reducing conditions (< 6%) and was independent of contact time (from 1 day to 1 month) and groundwater composition (natural Äspö: pH=7.8, I =0.18 M and Grimsel: pH=9.6; I=1.3·10⁻³ M ground water were used). Colloidal phase formation was not detected during both sorption and desorption studies via ultracentrifugation experiments (90,000 rpm for 60 min).

These data were compared to sorption characteristics of oxidized crystalline material obtained from the Nizhnekansk massif (Russia) foreseen as the deep geological repository site.

Furthermore, migration studies with Äspö core material containing a natural fracture, which has been preserved under anoxic conditions, were performed. The core was sealed into a Plexiglas container and characterized by micro-computer tomography (µCT) for 3D reconstruction of the fracture geometry (voxel size 15µm) and simulation of fluid dynamics. After hydraulic characterization using the conservative tracer tritium (HTO) and ³⁶Cl⁻ to evaluate matrix diffusion (anion exclusion) under different fluid velocities, the technetium migration is studied using ⁹⁹Tc(VII) with ^{95m}Tc(VII) isotope admixture for detection of low concentrations. The results of the Tc migration experiments at variable flow rates will be discussed in the light of sorption



kinetic studies in batch experiments in detail in a S&T contribution (Totskiy et al, 2013).

In addition to the radionuclide batch sorption experiments with crushed Äspö diorite material, a new experimental program is conducted, at the moment, using non-oxidized "Ävrö diorite" and "fine grained granite" crushed material, respectively. Both types of rock are also derived from the drill core sampling campaign within the CROCK project. Although the geological frequency of both rock types are minor compared to the Äspö diorite kinetic batch sorption experiments were conducted to study their sorption behavior in addition to the Äspö diorite sorption data obtained so far within CROCK, as radionuclides ¹³⁷Cs(I), ⁴⁵Ca(II), ²⁴¹Am(III), ²³³U(VI) and ⁹⁹Tc(VII) are used to span a range of different chemical elemental properties ranging from e.g. ion exchange, surface complexation and redox sensitivity.

HZDR objective is to analyze the retention behavior of the crystalline rock diorite from the Äspö Hard Rock Laboratory (HRL, Sweden) toward the redox-sensitive actinides U and Np by means of batch sorption experiments.

Preliminary results, obtained during the first period of the project for the sorption of U(VI) and Np(V) onto Äspo diorite, were summarized in the S+T contribution at the first CROCK workshop (Schmeide et al., 2012). Additional results were presented in Gürtler (2012).

The influence of various parameters, such as grain size (0.063 - 0.2 mm, 0.5 - 1 mm, 1 - 2 mm), temperature (25 and 10°C) and atmosphere was studied using a synthetic Äspö groundwater (pH 7.8, I = 0.178 M) as background electrolyte.

Distribution coefficients, Kd values, were determined. The Kd values decrease with increasing grain size of the diorite and with decreasing temperature. The Kd values determined under aerobic conditions are lower than those determined under anaerobic conditions.

Furthermore, the interaction of U(VI) and Np(V) with diorite (1 - 2 mm fraction) in synthetic Äspö groundwater under anoxic conditions (N₂) was also studied as a function of contact time (5 to 108 days).



These investigations were complemented by fluorescence spectroscopy and vibrational spectroscopy.

In the U sorption system, the speciation of U(VI) in solution and thus, its sorption onto diorite is strongly influenced by the groundwater composition. From the ions leached out of diorite, calcium and carbonate ions have the strongest influence. $Ca_2UO_2(CO_3)_3(aq)$, which sorption onto diorite is relatively weak, was detected as dominating U(VI) species in solution by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Kinetic experiments showed that sorption equilibrium ($K_d = 1.44 \pm 0.30$, 1 - 2 mm fraction) is reached relatively fast (after 10 to 20 days). As surface species on diorite, $UO_2(CO_3)_3^{4-}$ was identified by in situ time-resolved attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy.

In the Np sorption system, the effect of the groundwater composition on speciation and sorption behaviour is much weaker. By in situ time-resolved ATR FT-IR spectroscopy, NpO₂⁺ was detected in solution as well as surface species on diorite. However, this surface species is only valid for short sorption times as applied for ATR FT-IR spectroscopy (90 min). During longer sorption experiments (up to 108 days) Np(V) is reduced to Np(IV) by the Fe(II) of the diorite which leads to a very strong Np sorption (>95% sorption for [Np]₀ = 1×10⁻⁶ M, S/L = 200 g/L).

Currently, the U(VI) sorption onto diorite is studied as a function of total actinide concentration (5×10^{-9} M to 7×10^{-5} M). The experiments are not finalized so far.

CIEMAT aim is to determine diffusion and sorption parameters on granite a different scales by means of the combination of different techniques (radio-analytical, μ PIXE, RBS autoradiography, SEM-EDAX), with the objective of identifying the main source of uncertainties; matrix diffusion processes are being also studied in a large block scale (30 x 30 cm). The block scale diffusion experiment, started at CIEMAT in 2007, simulates a high level radioactive waste repository in granite: it includes a central compacted bentonite in which the radionuclide (Cs, CI and HTO) reservoir is placed. The evolution of the activity of Cs, CI and HTO in the tracer reservoir was analyzed and modeled; the evolution of the activity of the conservative CI and HTO has been



periodically measured in 11 different boreholes placed in granite at different distances from the source during approximately 6 years now. The work performed during the 1st reporting period has been presented as an Oral Presentation at the 1st Workshop of the CROCK Project (García-Gutiérrez, et al 2012) and the update of the main results will be presented in a S+T contribution at the CROCK final meeting (García-Gutiérrez, et al 2013).

An additional objective of the work carried out by CIEMAT is to analyze sorption onto granite and granite minerals of different origin (Spain, Switzerland, Sweden) to develop sorption models to allow a more reliable description of retention in heterogeneous rocks. The understanding of the sorption behavior of radionuclides in the main minerals composing the rock can be very useful for the mechanistic understanding of retention processes in such a heterogeneous system. Therefore, within the frame of the CROCK project, CIEMAT analysed in detail ¹³⁷Cs sorption in different minerals (biotite, muscovite, K-feldspar, quartz) in parallel to sorption onto granite. Experiments with these materials exchanged with Na, Ca and K, were also done in order to determine selectivity coefficients to carry out detailed sorption modeling. The effects of pH, ionic strength and radionuclide concentration were analyzed.

Sorption onto the different materials was studied under experimental conditions as similar as possible to reduce the experimental uncertainties. Sorption data were analyzed to evidence all the possible differences (mineral content, BET area, chemistry of the water, competitive ions in solution, radionuclide concentration, etc.,).

The results of these studies carried out so far with Cs have been published in S+T contributions to the 1st Workshop (Missana and García-Gutiérrez, 2012a, b) and in an international conference (Missana et al., 2012). A paper to be published in the open literature is being prepared (Missana and García-Gutiérrez, 2013).

In the second part of the Project, similar tests were also carried out onto granites of different origin, biotite and muscovite with U(VI), Tc(VII) and Eu(III). The modeling of



uranium sorption data has been initiated. A summary of sorption data will be published in the Final Workshop Proceedings (Missana et al, 2013).

The micro-scale sorption studies onto non crushed rocks carried out by CIEMAT aims to provide sound sorption parameters, through the determination of radionuclide surface distribution coefficients (K_a) directly measured on intact rocks and single minerals by micro-Particle induced X-ray Emission (μ PIXE) analyses. The first results on uranium retention on Äspö diorite samples under anoxic conditions were published in a S+T contribution (Alonso et al., 2012a) and two international congresses (Alonso et al., 2012 b,c).

Previous experiments were carried out on granite samples from Grimsel (Switzerland) and El Berrocal (Spain). However, Äspo samples were extracted, handled, transported and stored under anoxic conditions: the maintenance of redox conditions, from extraction to final sorption measurements, represents an additional challenge, not previously considered but, deemed essential to reduce uncertainties associated to sorption data obtained for redox sensitive radionuclides. Another relevant redox sensitive radionuclide considered for these analyses was selenium.

 μ PIXE technique allows mapping of a studied area on diorite samples, allowing material characterisation. Main minerals and tracers distribution could be visualised. Typical areas analysed showed major presence of plagioclase, biotite, titanite and quartz. Minerals identified as hornblende, apatite or zircon were detected as well. The natural presence of U or Se in the studied samples was undetectable under experimental conditions.

Results showed that both uranium and selenium distribution on Äspö diorite surface was heterogeneous, and the most retentive minerals were identified. By the analyses of the individual PIXE spectra obtained on selected regions, surface distribution coefficients (Ka) were obtained. The Ka values measured on specific minerals on the rock surface were used to obtain average surface distribution coefficients accounting for the mineral occurrence (%) of diorite samples. The main retentive minerals were identified, and this contributes to evaluate the heterogeneity on Kd selection.

These values are compared to the bulk distribution coefficients (Kd) determined on same samples by batch experiments, considering the surface area. Results obtained



under anoxic conditions are compared to previous studies carried out under oxic conditions.

CTH is studying radionuclide diffusion and sorption. One drill core sample (label: "1.30a"), taken at depth 12.11-12.39 m from the tunnel wall in borehole KA2368A-01 of drilling campaign at Äspö was selected for providing material for batch sorption and diffusion experiments with radionuclides. The sample was chosen because it was taken perpendicular to two (possibly sealed and re-opened) fractures, which are present at both ends of this particular sample. The drill core sample was first cut into 9 sub-samples of about 3 cm length. These were then further divided into two samples each of about 1.5 cm length. For each of eight sections, one half was crushed for providing material for batch sorption experiments, the other half was used for diffusion experiments.

At moment, only results for batch sorption of Cs, Ra and U have been evaluated for some sections in the middle of the drill core sample. The size fractions used were 0.063-0.125, 0.125-0.250, 0.250-0.5 and 0.5-1.0mm. Results for Cs gave: $R_d = 0.43\pm0.10, 0.24\pm0.05, 0.11\pm0.03$ and $0.046\pm0.005m^3/kg$, respectively.

Results for Ra gave: $R_d = 0.015 \pm 0.011$, 0.010 ± 0.003 , 0.0079 ± 0.0027 and $0.0048 \pm 0.0004 \text{m}^3/\text{kg}$, respectively. Results for U gave: $R_d = 0.0051 \pm 0.0010$, 0.0030 ± 0.0015 , 0.0017 ± 0.0008 and $0.00099 \pm 0.00052 \text{m}^3/\text{kg}$, respectively.

If corrected for the measured specific surface area of the fractions: 0.379, 0.240, 0.153 and 0.0987 m²/g, respectively, this gives Cs R_a of 1.13, 0.99, 0.71 and 0.47 \cdot 10⁻³m, respectively. Corresponding R_a values for Ra are 3.98, 4.21, 5.17 and 4.85 \cdot 10⁻⁵m, respectively. Corresponding R_a values for U are 1.33, 1.26, 1.12 and 1.00 \cdot 10⁻⁵m, respectively. The conclusion is that, while U and Ra sorption seem to be dependent on specific surface area, Cs sorption seems also to depend on some other factor, presumably the cation-exchange capacity of the mineral fractions, which may then increase with the smaller fractions.

The activities of **UJV Rez, a.s.** (formerly *NRI*) were focused on studies of sorption and diffusion of radionuclides under aerobic and anaerobic conditions.



Batch sorption experiments were conducted on granitic cubes and crushed granite under aerobic and anaerobic conditions. Two fractions of crushed granite were used for experiments (fraction AD-A: grain size 0,5 - 1 mm, fraction AD-B: grain size 1 -1,2 mm). Äspö synthetic granitic water (SGW) was used as liquid phase. Se(IV) and Se(VI) were used as tracers. After 100 days selenium concentration in liquid phase was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and values of K_d were calculated. Eh and pH were also measured in liquid phase. Resulting K_d for Se(IV) under aerobic conditions reached 1,3 mL/g in case of fraction AD-A and 1,6 mL/g in case of fraction AD-B. The sorption of selenite was thus very low. This fact is probably caused by composition of used Aspö synthetic granitic water, specifically by high concentrations of anions (SO₄²⁻, Cl⁻). Speciations of Se in Äspö synthetic water was presented as S+T on CROCK 1st Annual meeting (Videnska et al., 2012). K_d for Se(VI) approached 0. The results confirmed assumption that selenate is a non sorbing, mobile specie. Sorption experiments conducted under anaerobic conditions showed similar results as the experiments under aerobic conditions. K_d of selenite were in case of fraction AD-A only slightly higher than in case of aerobic experiment, generally sorption of selenite was also very low. Sorption experiment with sodium selenite and granitic fraction AD-B is under way. No sorption of selenate was observed on both granitic fractions.

Surface analyses of Se forms on the granite surface were performed on Äspö diorite cubes. The concentration of Na₂SeO₃ or Na₂SeO₄ in SGW was 2.10⁻³ mol/L. After one week the surface of granitic cubes was analysed by Electron Spectroscopy for Chemical Analysis (ESCA) and by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Results of ESCA and LA-ICP-MS methods were interpreted as surface maps which illustrated distribution of elements (Se, Fe, Na, Al, etc.) on granite. The results of surface analysis are not complete; evaluation of LA-ICP-MS measurements and other ESCA measurements is under way.

Electromigration method was also applied on the samples of Äspö diorite. The method enable speeding up the laboratory diffusion experiments to gain rock migration parameters (formation factor F_f and effective diffusion coefficient D_e) in relatively short times (hours) in comparison with through diffusion experiments (months or even years). The method and the first results were presented in S+T



presentation on the 1st annual meeting (Vecernik et al., 2012). The second generation of electromigration cell was then designed in order to be able to use samples of different diameters and lengths. Nowadays rock samples of 4 - 5 cm in diameter and 1 - 10 cm long of drilled core can be placed into the experimental cell. The apparatus and method was successfully applied on rock samples of different lengths from Czech Republic (Melechov granite) and Sweden (Äspö diorite). The results are under evaluation.

Finally, diffusion properties of Äspö diorite under aerobic conditions were determined, using ³H as a conservative non-sorbing tracer and ³⁶Cl as anionic species. The migration of the anion through the AD samples might be influenced by anionic exclusion, causing their delay in comparison with conservative tracer. Firstly, the porosity of the samples AD1 and AD3 (borehole KA2368A-01, depth 1,29 m) were measured, using water-saturation method by Melnyk and Skeet (1986). The porosity determined was 0,22% and 0,21% respectively.

The conventional through-diffusion methodology was used for diffusive breakthrough curve determination. The multitracer solution of ³H (1350 Bq/ml) and ³⁶Cl (216 Bq/ml) in synthetic Äspö groundwater was used. Activity of both radionuclides was measured using liquid scintilation spectroscopy (HIDEX 300 SL). The experiment is still on-going (140 days). The experimental breakthrough curve will be compared with modelled one, being calculated using compartmental diffusion module, based on the environment of GoldSim transport code with the use of the Contaminant Transport Module (Vopálka et al., 2006; Havlová and Vopálka, 2010). Finally, effective diffusion coefficients D_e and F_F values will be calculated.

MSU is studying sorption onto actual fracture samples collected from different proposed Spent Nuclear Fuel and High-Level Radioactive Waste repository in Russia. Sorption studies are accompanied by various spectroscopic investigations with micro- to nano-resolution and bulk scale.

These rock samples were previously characterized in terms of petrographic and mineralogical characterization; defining their filtration, elastic, petro-physical and



strength properties and estimating their hydrothermal-metasomatic transformation. Then they were used in uranium sorption studies.

Four undisturbed slices from perspective areas "Kamenny" and "Itatsky" (Nizhnekansky Granite Massive) were collected to perform sorption experiments to reveal mineral phases responsible for the U(VI) retention. The following rock samples from different depths were chosen: granodiorite biotite (K-106.8) and granodiorite-tonalite biotite (K-524.3) from "Kamenny" area; hornblende diorite from "Itatsky" area (I-408.2). Rock samples were crushed and sieved with size from 1 to 2 mm.

Sorption experiments were performed in glove box with inert atmosphere (N₂) to exclude possible influence of carbonates. Sodium perchlorate was used as a background electrolyte (0.01 M). Initial concentration of uranium was $1 \cdot 10^{-7}$ mol/L and isotope ²³³U (T_{1/2} = $1.59 \cdot 10^5$ years) was used for liquid-scintillation counting. The solid to liquid ratio was 1:4.

Preliminary results show significant differences between used rock samples in sorption rate and pH-dependence. Equilibration time is five days and two weeks in the case of samples K-524.3 and both K-106.8, I-408.2, respectively. The pH-dependence of sorbed uranium fraction has typical hump-shape for samples K-524.3 and I-408.2: increase of sorption percentage with increasing pH values to 6, plateau (90-98 % of uranium sorbed), decrease of sorption percentage with increasing pH values to 6, plateau values from 8 due to U(VI) hydrolysis. In contrast, the fraction of sorbed uranium (VI) was around 95-98 % in the pH range from 4 to 10 in the case of sample K-106.8.

Local distribution and preferential sorption of uranium (VI) onto different minerals within the sample was studied by radiography, SEM-EDX, SIMS, etc. These data accompanying with rock sample composition allow the development of quantitative model for U(VI) sorption onto investigated rocks.

Previous sorption experiments were carried out under atmospheric conditions in synthetic groundwater with ¹³⁷Cs and ²³³U onto granite disks. One side of the disk was polished and reverse side was left rough to determine the roughness effect on sorption of radionuclides. First results show that sorption kinetic for Cs is quite slow and probably depends on diffusion and equilibrium were reached after 100 hours of experiments. U showed lower sorption that can be explained by relatively high



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concentration of U. This work was reported in a S+T contribution to the first workshop (Petrov et al., 2012).



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