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INTRODUCTION

To improve the performance assessment of geologic disposals of high-level radioactive waste in crystalline rocks, it is necessary to decrease the uncertainties related to radionuclide retention in such heterogeneous systems. 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 well-understood processes, as the kinetic of retention processes or the parameters dependence on the hydrodynamic conditions of the system or on the heterogeneity of the medium, as well as on up-scaling factors. This leads to biased data interpretation and poor modeling.

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: 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 lower 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 for determining 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 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 participate to WP 2: **KIT-INE** and **HZDR** (Germany); **CIEMAT** (Spain); **CTH** (Sweden); **NRI-Rez** (Czech Republic); **MSU** (Russia).

SUMMARY OF THE WORK PERFORMED WITHIN WP 2 DURING THE 1st REPORTING PERIOD.

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) and ^{233}U(VI) onto the 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). Additionally, they studied the sorption behavior of Tc (VII) and the results are summarized in an S+T contribution (Totsikiy et al., 2012).

One of the objectives of their work was to compare sorption data, for the radionuclides of interest, 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 they used for sorption experiments was synthetic Äspö groundwater, which composition was provided by Heck and Schäfer (2012) at the beginning of the project, whereas 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).

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.

Desorption experiments did not show evidences for irreversible sorption; less of 10 % of tracer was desorbed for Cs and Eu, this value being independent on time, whereas desorption of U was increasing with time. Desorption depended on the chemistry of the fresh water (Äspö or Grimsel) and its redox potential, but it did not seem to depend on the solid used (oxidized or not-oxidized).

HZDR objective is to perform batch sorption experiments to determine the sorption capacity of granite and fracture infill materials, respect to neptunium, uranium and selenium. The results obtained for the sorption of U(VI) and Np(V) onto Äspo diorite are summarized in the S+T contribution at the first CROCK workshop (Schmeide et al., 2012). Additional results are presented in Gürtler (2012).

HZDR analyzed the influence of several parameters (solid to liquid ratio, grain size, temperature) on actinides sorption. These investigations are complemented by fluorescence spectroscopy and vibrational spectroscopy.

The speciation of U(VI) and Np(V) in the synthetic Äspö groundwater (Heck and Schäfer, 2012) was dominated by $Ca_2UO_2(CO_3)_3(aq)$ or NpO_2^+, respectively. For U, the speciation is very sensitive to the groundwater composition, thus possible ions leached out from the solid, particularly calcium and carbonate, may significantly affect speciation and consequently its sorption behavior. On the other hand, the speciation of Np(V) is less sensitive to the water composition. This was seen performing studies at different solid to liquid ratios and with different aqueous phases.

Adsorption of both actinides in Äspö diorite was comparable and decreased with the temperature. U adsorption decreased with decreasing surface area, whereas for Np the correlation with the surface area was not clear.

In situ time-resolved attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy was applied to analyze the surface species formed upon sorption experiments onto Äspö diorite and compared with those previously observed in SiO_2 or illite. For U the identified surface specie was $UO_2(CO_3)_3^{4-}$ whereas for Np the surface specie was NpO_2^+, possible formation of Np(IV) surface specie.

CIEMAT aim is to determine diffusion and sorption parameters on granite a different scales by means of the combination of different techniques (radio-analytical, μPIXE, RBS autoradiography, SEM-EDAX), with the objective of identifying the main source of uncertainties; matrix diffusion processes are being studied in a large block scale (30 x 30 cm). The block scale diffusion experiment, started at CIEMAT in 2007 and simulates a high level radioactive waste repository in granite: it includes a central compacted bentonite in which the radionuclide (Cs, Cl and HTO) reservoir is placed. The evolution of the activity of Cs, Cl and HTO in the tracer reservoir has been analyzed and modeled; the evolution of the activity of the conservative Cl and HTO has been periodically measured in 11 different boreholes placed in granite at different distances from the source during approximately 5 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)

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 is analyzing in detail ^{137}Cs sorption in different minerals (biotite, muscovite, K-feldspar, quartz) in parallel to sorption onto granite. 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 to an international conference (Missana et al., 2012).

Cs adsorption in the different materials was studied under as similar as possible experimental conditions to reduce the experimental uncertainties and data were analyzed as a whole with the aim of evidencing the possible differences in the sorption behavior amongst the different rocks (mineral content, BET area, chemistry of the water, competitive ions in solution, radionuclide concentration, etc.,). In all the solids, Cs sorption showed a similar behavior which could be satisfactorily modeled according to a three-site ionic exchange simplified model.

Additionally, CIEMAT performed first micro-scale analyses on uranium retention on Äspö diorite samples under anoxic conditions were and the results were published in a S+T contribution (Alonso et al., 2012a) and two international congresses (Alonso et al, 2012 b,c). Experiments were carried out maintaining anoxic conditions from the rock core extraction to the micro-scale analyses. Uranium distribution and sample elemental concentration was analyzed by the ion beam technique μPIXE. Results showed that U retention on Äspö diorite surface was heterogeneous. Quantitative distribution coefficients (K_a) on selected minerals were obtained by PIXE spectra analyses. Higher sorption values were generally observed on Fe-bearing minerals.

These experiments were compared to those previously obtained with granite from the Grimsel Test Site (Switzerland) and El Berrocal (Spain).

CTH will study radionuclide diffusion and sorption by cell experiments. The drill cores will be transferred into an inert atmosphere glove-box and sawn into sections of about 2-5 cm. Some sections will be used for in-diffusion studies of radiotracer cocktails and other sections will be crushed and sieved for batch sorption experiments. Complementary analyses of the in-diffusion process are also foreseen, where the sections are gradually grinded down, or sawed, from the low-activity side to reveal sorption profiles and autoradiogram patterns. Batch sorption experiments will be made both from the fracture surface and the undisturbed zone. Surface area normalized sorption coefficients (Ra) will be determined. All diffusion and batch sorption experiments will be made in inert atmosphere and at a precisely regulated low temperature, simulating the sampling site conditions.

At present, CTH carried out the preparation of drill core sections for diffusion experiments and started HTO diffusion experiments.

NRI will study sorption and diffusion processes in different rock materials (crushed or in disks) under both anoxic and oxic conditions to emphasize the potential O_2 effect on the determination of retention/transport parameters. Most of NRI's activities is focused on sorption experiments with redox sensitive tracer (Se) and on electromigration measurements for diffusion parameter determination. The main results obtained by NRI are reported in Vecernik et al (2012) and in Videnska et al (2011 and 2012).

Firstly, the O_2 protected Äspö rock samples from KIT INE were safely removed to the anaerobic box where some of them were prepared for further analyses (grinding, cutting). Synthetic groundwater was prepared on the basis of KIT-INE information about Aspo groundwater composition (Heck and Schäfer, 2012).

Selenium speciation calculations were performed using Geochemist´s Workbench prior the experiments in order to assume which phases might be present in the Äspo system.

Afterwards, the very first round of oxic sorption experiments with Se(IV) and Se(VI) in the concentration level of 10^{-5} M were performed. It was found that the sorption of Se(VI) was almost negligible. Sorption of Se(IV) was detectable, however still very low (below 10 ml/g). The anaerobic sorption experiments with Aspo granodiorite material were started also in the glove box, gaining the very first results by the end of reported period.

Moreover, sorption experiments with Se(IV) and Se(VI) and Äspö granite disks were performed in order to determine Se distribution and oxidation state in the rock surface. ICP-LA and ESCA respectively will be used for those analyses.

The other part of activities was focused on electromigration method and its use for Aspo rock samples. The apparatus was successfully tested for samples 10 mm thick and also also for samples of 30 mm thickness.

The formation factor (F_f) and the effective diffusion coefficient (D_e) were measured in 3 samples, for iodine. The aim of the work is to use electromigration cell for longer samples (up to 100 mm) to look on migration parameters dependency on the sample length. The cell for longer samples is under constructing and verification.

MSU will study sorption onto actual fracture samples collected from different nuclear waste disposal sites in Russia accompanied by various spectroscopic investigations with micro- to nano-resolution and bulk scale. Sorption onto different mineral grains within the fracture samples will be studied by radiographic techniques accompanied by various microscopic and mass-spectrometric measurements. Core materials from two areas (area Kamenny, drilling depth down to 700 m, and area Itatsky, drilling depth down to 500 m) have been studied in terms of petrographic and mineralogical characterization.

Sorption experiments were carried out under atmospheric conditions in synthetic groundwater with ^{137}Cs and ^{233}U 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 concentration of U. This work has been reported in a S+T contribution to the first workshop (Petrov et al., 2012).

The details of the work carried out so far by the different organization can be found in the following references:

Alonso U., Missana T., Garcia-Gutierrez M., Patelli A., Rigato V., Ceccato D (2012a) "Ion beam analyses of radionuclide migration in heterogeneous rocks." Ion Beams'12: Multidisciplinary Applications of Nuclear Physics with Ion Beams. Legnaro, Italia, 6-8 June 2012 ORAL

Alonso U., Missana T., Patelli A., Rigato V., Ceccato D. (2012b), "Uranium retention under anoxic conditions on Äspö diorite: first micro-scale analyses"- 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER & POSTER;

Alonso U., Missana, A. Patelli, D. Ceccato, M. García-Gutiérrez, V. Rigato (2012c) "Micro-scale study of uranium retention on granite" – Interface Against Pollution (IAP 2012) Conference, Nancy France 11 -14 June 2012.POSTER

García-Gutiérrez M., Mingarro M., Missana T. "Block scale experiment at CIEMAT" – 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) ORAL;

Gürtler, S.: Sorption von U(VI) und Np(V) an Äspö-Granit unter anaeroben und aeroben Bedingungen (Sorption of U(VI) and Np(V) onto Äspö granite under anaerobic and aerobic conditions). Hochschule Fresenius, University of Applied Sciences, Zwickau, 2012 (Diploma Thesis).

Heck, S. and Schäfer T. (2012) "Short Note: CP Crock groundwater sample characterization.

Missana T. and García-Gutiérrez M. (2012a) "Analysis of the caesium sorption behaviour on biotites of different origin"- 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER & POSTER;

Missana T. and García-Gutiérrez M. (2012b) "Comparison of the caesium adsorption on different crystalline rocks" – 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER & ORAL;

Missana T., Garcia Gutierrez M., Alonso U. (2012) ""Adsorption processes in heterogeneous rock: top-down vs bottom-up modelling approach in modelling experimental data"- Interface Against Pollution (IAP 2012) Conference, Nancy France 11 -14 June 2012. POSTER

Petrov V.G., Vlasova I.E., Kuzmenkova N.V., Petrov V.A., Poluektov V.V., Grivot A., Kalmykov S.N. (2012) "Characterisation of rock samples from areas of the proposed Russian HLW and SNF repositories (Nizhnekansky massive) and first sorption studies - 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER;

Schmeide, K., Gürtler, S., Müller, K., Steudtner, R., Joseph, C., Bok, F., Brendler, V. (2012): Sorption of U(VI) and Np(V) onto diorite from Äspö HRL" – 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden)PAPER & ORAL

Stage E., Huber F., Heck, S., Schäfer T. (2012) "Sorption desorption of 127Cs(I), ^{152}Eu(III) and ^{233}U(VI) onto new crock derived Äspö diorite - A batch type study" – 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER & ORAL

Totsikiy Y., Geckeis H., Schäfer T." Sorption of Tc(VII) on Äspö diorite" (2012) -1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER

Vecernik P., Havlova V., Lögfren M (2012) "Determination of rock migration parameters (Ff, De): application of electromigration method on samples of different length"- 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER;

Videnska K. (2011): Study of Se(IV) and Se(VI) sorption processes in granitic environment. Seminar of the project Research on barriers of deep geological repository (CZ, 1H-PK/25), December 9, 2011, Rez.

Videnska K., Havlova V., Vecernic P., Vejsadu J., Sajdi P. (2012) "Speciation of selenium sorbed species on Äspo granodiorite surface"- 1st CROCK Workshop (May 22-24, 2012, Stockholm, Sweden) PAPER ;