Integrated Project
Fundamental Processes of Radionuclide Migration
IP FUNMIG
(FP6-516514)

Final Scientific and Technical Report of the Integrated Project "Fundamental Processes of Radionuclide Migration" (6th EC FP IP FUNMIG)

EURATOM

FOREWORD

The EURATOM 6th EC Framework Program Integrated Project FUNMIG (FUNda-men-tal processes of radionuclide MIGration) started 1st January 2005 and lasted for four years. The project was implemented by 51 Contractors from 15 European countries and 29 Associated Groups, including organizations from three non-EU countries (Canada, Korea and Russia). The consortium includes key European Research Institutes, Univer-sities, National Waste Management Agencies and SMEs. The participation and strong financial commitment of Waste Management Agencies have ensured the proper technology transfer and application feedback. The project dealt with the migration of radionuclides in the far-field of nuclear waste repositories in the three different host-rock types presently under investigation in Europe, namely clay, crystalline and salt. The project tackles one of the main challenges for a sustainable European energy mix, scientific and social credibility of geologic HLRW disposal.

The present report gives a comprehensive description of the Scientific and Technical results obtained within the Project. This report is part of the scientific-technical reporting of the FUNMIG project. Other parts are a number of different institutional reports, four annual project workshop proceedings, and a special issue in Applied Geochemistry. The latter is scheduled for publication around end 2010. Bibliographic references to the other documents are given below.

In view of radionuclide migration in the far-field, the overall objectives of the project were to (i) improve the knowledge-base for assessment of the long-term safety of a nuclear waste repository in the three host-rock types presently considered in Europe, (ii) provide tools for application of the knowledge in the repository Safety Case, (iii) involve a broad representation of European countries aiming for a harmonized competence level throughout the EU, and (iv) communicate the outcome of the project to a broader scientific community and other interested groups.

The project was divided into seven components. Six components implement research and technology-related activities (RTDC's) and one component dealt with training, and documentation, management and dissemination of knowledge. The six RTDCs cover basic processes common to all the disposal concepts under consideration in Europe, through to studies of host-rock type specific processes and application of the results to the disposal Safety Case. Two of these RTDC's (RTD components 1 and 2) dealt with well, and with less well established basic processes, respectively. The results of these RTDC's are applicable to the migration of radionuclides under different conditions in all types of host rock under consideration. Three RTDC's dealt with processes that are of specific interest for the three different host-rock types currently under consideration in Europe, namely clay (RTD component 3), crystalline (RTD component 4) and salt (RTD component 5). One RTDC dealt with integration of scientific-technical results for the purpose of generating tools for performance assessment (PA) and application of the RTD results to the Disposal Safety Case (RTD component 6).

Reflecting the structure of the work program, this report is been divided into 5 sections:

- Section 1: RTDC1 and RTDC 2 description focused on the study of a) well defined processes, such as ionic speciation, ionic exchange and surface complexation, organic complexation and solid solution and formation of secondary phases and b) less-well defined processes, such as formation and migration of colloids, redox reactions at surfaces and biogeochemical processes.

- Sections 2, 3 and 4: Description of RTDC's 3, 4 and 5 and the respective host-rock types presently under consideration in Europe, namely clay host-rock (RTDC3), crystalline host-rock (RTDC4) and the overburden of salt formations (RTDC5).

- Section 5: RTDC6 description focused on the integration of scientific results for their application in the disposal Safety Case.

More detailed scientific-technical reporting along with the project can be found in the four annual project workshop proceedings:

- 1st Annual Workshop Proceedings of Integrated Project Fundamental Processes of Radionuclide Migration IP FUNMIG, Eds. P. Reiller, G. Buckau, B. Kienzler, L. Duro, M. Meritxell, Report CEA-R-6122, 2006.

- 2nd Annual Workshop Proceedings of the Integrated Project "Fundamental Processes of Radionuclide Migration" 6th EC FP IP FUNMIG, Eds. G. Buckau, B. Kienzler, L. Duro, V. Montoya, Report SKB-TR-07-05, June 2007

- 3rd Annual Workshop Proceedings 6th EC FP – FUNMIG IP, Eds. G. Buckau, B. Kienzler, L. Duro, V. Montoya, Anne Delos, NDA Report, 2008.

- 4th Annual Workshop Proceedings of the Integrated Project "Fundamental processes of radionuclide migration" (6th EC FP IP FUNMIG). Eds. G. Buckau, L. Duro, B. Kienzler, V Montoya, A Delos, Report FZKA-7461, July 2009.

The source term from the near-field to the subject of the present project, i.e. the far-field, will be published as an ENRESA report 2010.

A more detailed description of the outcome of the project in view of its application to the disposal safety case will be published 2010 as a NAGRA NAB report.

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FUNDAMENTAL RTD COMPONENTS
(RTDC 1 & 2)

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Introduction

Demonstration of safety of an encompassed nuclear waste repository makes use of operational models and descriptions. A solid and sound scientific knowledge of the processes is required in order to ascertain the robustness of these operational models and necessary simplification used. The first two Research and Technical Development Components (RTDCs) of the IP FUNMIG generated fundamental data and information needed therefore.

The main objectives of these components was:

1. To provide fundamental process knowledge and the required data for processes with comparably well established conceptual understanding. The overall impact of natural organic coatings is included. Processes studied are fundamental and applicable to all types of host rocks and the proper parameters are derived for the relevant migration systems. The outcome is the fundamental understanding and quantification of the processes studied. The models are developed at the research model level.

2. To improve the knowledge on radionuclide retention processes which are currently not well understood and which are not fully considered for predictive analysis of the far-field of geological repositories. Far-field radionuclide retention were investigated taking into account inorganic/organic colloid generation, colloid mediated radionuclide transport, redox reactions and biogeochemical processes that potentially control the mobility in the geological barrier. Relevant data and results from previous Community-supported R&D as well as from national and international programs were integrated.

Presentation of the results obtained from these RTDC's is structured around the key scientific questions guiding their activities:

- Are required thermodynamic data available and accurate?

- Can sorption models calculate sorption isotherms measured under chemically realistic conditions?

- What is the influence of radionuclide complexation on sorption and can this influence be quantitatively calculated with the sorption models?

- Is the influence of natural organic matter on sorption described adequately by the available thermodynamics?

- Are the modelling simplification justified regarding analysis and interpretation of spectroscopic investigations used?

- Can we close the gap between sorption and solid solution?

- Which natural redox phases and/or redox processes act as redox buffers in the far-field environment?

- Are redox-sensitive contaminants transformed into equilibrium valence state?

- Which are the main parameters affecting the erosion and generation of bentonite colloids from the compacted bentonite?

- Are we able to reliably predict a "source term" for bentonite colloids?

- Which are the main parameters affecting stability and filtration of colloids in a crystalline rock?

- Which is the mobile fraction of colloids in diffusion controlled systems?

- How well advanced is the mechanistic description of colloid transport? Are there fundamental data are still missing?

- Does the presence of microbial activity/biofilms affect the sorption/mobility of radionuclides in far-field systems?

In RTDC 1 & , there were 25 partners (ARMINES, CEA, CIEMAT, CTH, FZD, FZK-INE, HU, KU, KULEUVEN, KTH, NIREX, NRIRR, NRI-REZ, PSI, SAS-IIC, SCK·CEN, TUM-RCM, UNIMANCH, UNILOUGH, UNICYPRUS, UNIUTRECH, UPC, UPPC, VTT, WU) from 14 countries (BE, CH, CY, CZ, DE, DK, ES, FI, FR, HU, NL, SE, SK, UK) and in addition associated groups, contributing to providing answers to the key questions. In the following comprehensive description of the works done in FUNMIG along these key questions, whenever possible, the citation of the full articles or contributions in the workshop proceedings or already published peer-reviewed articles is given.

Are required thermodynamic data available and accurate?

Some compilations of critically assessed data exist, mainly through the data basis program of the Nuclear Energy Agency (NEA) of the Organisation for Economic Co-operation and Development (Grenthe et al., 1992; Silva et al., 1995; Rard et al., 1999; Lemire et al., 2001; Guillaumont et al., 2003; Gamsjäger et al., 2005; Hummel et al., 2005). Nevertheless, not all

the data needed to perform the speciation calculations were available with the same level of accuracy, or even did not reach the sufficient level of consensus to propose a value for the data, *e.g.*, log $*\beta°_{2,3}$ for $U(OH)_n^{4-n}$, $\Delta_f H°_m$ for $Am(CO_3)_n^{3-n}$. Within WP1.1, contributing to filling the gaps and improving the accuracy of data, investigations were conducted on carbonate, sulphate, phosphate, and the very particular silicate system.

The carbonate system

The carbonate complexation of lanthanides and actinides (III)

$$M^{3+} + pCO_2^{3-} \rightleftarrows M(CO_3)_p^{3-2p} \tag{1}$$

was studied by the **CEA**. The speciation of trace amounts of curium (III) in carbonate solutions at variable temperature was investigated by time-resolved laser-induced fluorescence spectroscopy (TRLFS).

The dissociation reaction

$$Cm(CO_3)_3^{3-} \rightleftarrows Cm(CO_3)_2^- + CO_3^{2-} \tag{2}$$
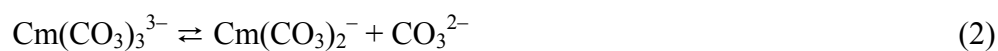
has been examined at high ionic strength as a function of the carbonate concentration between 10 and 70°C. The corresponding equilibrium constant was determined at each temperature. The enthalpy and entropy of the reaction were found to be low, suggesting a very small effect on the aqueous speciation even at 70°C. These data were compared with previous solubility measurements of Am(III) in carbonated solutions at various temperatures, for which the interpretation is not ubiquitous; after the original experimental data had been corrected for a small effect on the speciation calculations, they have been reinterpreted considering the transformation of the solubility-controlling solid, and provided new data in agreement with the TRLFS results on Cm(III). A publication of these works are available (Vercouter et al., 2005c; Vercouter et al., 2005b)

The sulphate system

Sulphur can be present as sulphate at a substantial concentration in the repository far-field. Hence, **CEA** studied the complex formation of Eu and La as analogues of Am/Cm(III) with sulphate at ambient temperature by ESI-MS and TRLFS.

$$M^{z+} + qSO_4^{2-} \rightleftarrows M(SO_4)_q^{z-2q} \tag{3}$$

3

A set of thermodynamic data was obtained by TRLFS for $EuSO_4^+$ and $Eu(SO_4)_2^-$ *vs.* ionic strength. At low ionic strength, the formation of the $LaSO_4^+$ analogous complex could also be quantified by ESI-MS (Vercouter *et al.*, 2005a).

In the case of U(VI), in the framework of an oxidant perturbation, experimental work has been carried out by TRLFS and ESI-MS, to identify the stoichiometries, perform sensitivity analysis of the measurements, and derive thermodynamic data. The interpretation of the fluorescence measurements at 20°C is in good agreement with the formation constants for $UO_2SO_4(aq)$ and $UO_2(SO_4)_2^{2-}$ from the literature. Thermodynamic data were also obtained. The measurements at high sulphate concentrations indicate that $UO_2(SO_4)_3^{4-}$ forms and dominates the speciation. Its formation constant has been determined. Extrapolation to zero ionic strength with the SIT formula provides a value which agrees fairly well with the selection by the NEA based on a single study (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003). The effect of the temperature on complexation was measured and a new set of thermodynamic data is proposed (Vercouter *et al.*, 2008).

The phosphate system

In systems where growing of biofilm can occur, the concentration of phosphate ligands can be important. Hence, the knowledge of the extent of this type of complexes can be critical. The use of thorium as an analogue of other tetravalent actinides is common. There are very few experimental data on these systems but it seems that strong complexes exists for U(IV) (Grenthe *et al.*, 1992); only $PuH_3PO_4^{4+}$ complex was selected in very acidic media for Pu(IV) and no data on Np(IV) are available in Lemire *et al.* (2001). It is thus difficult to predict the phosphate speciation of these metals under these conditions (Ekberg *et al.*, 2008).

CTH determined the constants for the Th(IV)-phosphate system at pH 7, 8 and 8.7. Using the AKUFVE system (Rydberg, 1969), the log β_n value for the reaction

$$Th^{4+} + nHPO_4^{2-} \rightleftarrows Th(HPO_4)_n^{4-2n} \tag{4}$$

with $n = \{1, 2, 3\}$, was determined at 1.0 M (Ekberg *et al.*, 2008). But the constant for $ThHPO_4^{2+}$, log β_1, remains too uncertain to be used with confidence. The reason is that this complex occurs at a too low phosphate concentration, and is extrapolated from log $\beta_{2,3}$. Furthermore, these log β_n are only valid under the experimental conditions used for the investigations ($I = 1$ M, $NaClO_4$).

The silicate system

The complexation of RN by the silicate ions has only been sparingly studied. The formation of the first silicate complex seem to be established for actinide (III) and (VI) (Jensen and Choppin, 1996; Hrnecek and Irlweck, 1999; Wadsak et al., 2000). Contrary to this, the formation of silicate complexes of actinide (IV) is more difficult to assess. Furthermore, formation

of 'high order' complexes or colloids have been proposed (Pazukhin et al., 1990; Lieser and Hill, 1992a, 1992b).

CEA and **CTH** investigated the interactions of Eu(III), Am(III), and Th(IV) with silicate anions by TRLFS, ESI-MS, and liquid-liquid extraction.

$$M^{z+} + OSi(OH)_3^- \rightleftharpoons MHSi(OH)_3^{z-1} \tag{5}$$

For Eu(III), under the experimental conditions (pH < 7 and 0.1 mM < [Si] < 2 mM), Eu(III) is expected either to hydrolyse or to form $EuOSi(OH)_3^{2+}$. At low Si concentrations (0.1-1 mM), the Eu(III) fluorescence changes with time, suggesting slow formation of colloidal particles and molecular complexes. Silicate oligomers were detected in gas-phase by ESI-MS in solutions at pH 4 to 6. This suggests that silica oligomers can easily be formed even under acidic or near-neutral conditions, and thus provide an additional potential inventory of metal ion complexation ligands. An aspect of interaction arises where both the silica and the actinide (IV) are present as colloids.

CEA and **CTH** have conducted a joint study on the speciation of Th(IV) with silicate. A key aspect was the possible formation of colloidal particles. Liquid-liquid extraction experiments were used. For this purpose, the AKUFVE technique was set up in the CEA Saclay center. Th(IV) and silicates in the aqueous phases were analyzed by Photon Correlation Spectroscopy (PCS). Particles were detected in some of the samples with a size distribution between 100 and 250 nm. The chemical nature of these cannot be determined by PCS. They could be Th or Si colloids as well as mixed Th-Si colloids (Lieser and Hill, 1992b).

Can sorption models calculate sorption isotherms measured under chemically realistic conditions?

The sorption of ions on mineral surfaces has been modelled by a large number of mathematical models. Out of them, only the models permitting prediction in a wide 'parametric space' have been envisaged within this project, namely, surface complexation modelling (SCM) and ionic exchange models. These two models rely on the establishment of equilibrium between the solution and the surface, but in quite different way. The SCM defined the equilibrium

$$M^{z+} + nH_2O + m{\equiv}SOH \rightleftharpoons ({\equiv}SO)_mM(OH)_n^{z-m-n} + nH^+ \tag{6}$$

whereas IE requires the net exchange of charges on a site i

$$M^{z+} + nH_2O + z\,\overline{^iNa^+} \rightleftharpoons \overline{^iM(OH)^{z-n}} + z\,Na^+ + nH^+ \tag{7}$$
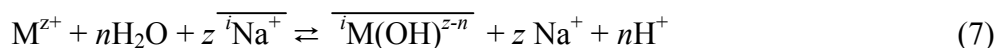
One can see that competition with anions of the solution, which will be developed later on, is taken into account. The SCM can be non electrostatic or the establishment of the charge at the surface can be explicitly accounted for using the Gouy-Chapman theory for instance.

A modelling attempt proposes combination of both approaches to represent both the ionic strength dependencies of the permanent negative charge on clay mineral surfaces, and the pH-dependent component of edge sites of clays (Bradbury and Baeyens, 1997).

Development of models

One of the main problems of thermodynamic sorption model is the lack of theoretical back-ground to account for the ionic strength effect of sorbed species. **CEA**, in the framework of the Ion-Exchangers Thermodynamic theory (IXT2) (Motellier et al., 2003; Beaucaire et al., 2008), verified that the caesium and potassium sorption on illite du Puy followed an ideal thermodynamic behaviour; the sorption at trace caesium concentrations is constant, which means that that the ratios between the activity coefficient of sorbed Cs^+ and sorbed K^+, and between sorbed Cs^+ and sorbed H^+ are also constants. This has been further assessed in potassium salt solution (up to 2 M, variable pH), with illite, under potassic form, and Cs^+, Sr^{2+} or Am(III) at trace level confirm the constancy of corrected selectivity coefficients independently of aqueous phase composition, and the ideal thermodynamic behaviour. Predictions of sodium, potassium, calcium and magnesium sorbed amounts onto illite equilibrated with chloride-rich brines, simulating sea and estuarine waters, have been compared to measurements; an excellent agreement is obtained.

In parallel, the **INE** tested a non-electrostatic SCM model to avoid the ambiguity of the surface potential description, and also to permit the reduction of surface species to account for. The sorption modelling of Se(VI) and Se(IV) on goethite (α-FeOOH) can be considered successful, but the most simplistic model fails to reproduce the results of U(VI)/CO_3^{2-} on quartz (Lützenkirchen and Huber, 2008). **CEA**, also tried to benchmark SCM and IXT2 using aluminium oxide, but problems of polynuclear forms of aluminium (keggin Al_{13}) prevent the study from completion.

Application of already existing models

In this applied part, the major part of the works done was performed on clay systems, either considering it as host rock, fracture infill, or buffer materials. Smectite and illite, were the main substrates, but natural or extracted biotite was also used. The main sorption model used was the 2-site protolysis no electrostatics surface complexation and cation exchange (2SPNE/CE, Bradbury and Baeyens, 1997). The RN considered were Cs(I), Sr(II), Ni(II), Co(II), U(VI), Eu(III), Am(III), Pu(IV), and also Se(VI) and Se(IV).

The data for Sr^{2+} (**CIEMAT**) revealed that the sorption on smectite is an ion exchange process, the sorption is basically independent of pH, however, it is strongly ionic strength dependent. For illite, the dependence on ionic strength is also strong, and in addition there is a slight pH dependency (Missana et al., 2006; Missana et al., 2008). Linear combinations of sorption

properties on illite/smectite mixtures provide a good description of systems that are mixtures of the two clay components.

The use of bottom-up approach for the modelling of the real clays was applied with success both to Opalinus Clay (Mont-Terri, Switzerland) and to Boom clay (Mol, Belgium). The sorption of Ni^{2+} (**PSI**) was insensitive to the concentration of carbonate but was shown to be in competition with Fe^{2+}. In the case of Co^{2+} the blind modelling of the sorption isotherm on Opalinus clay from previous results obtained on Na-illite was successful.

The modelling of the Eu(III) sorption on different batches of illite or montmorillonite was successful, providing consistent sorption data (**CIEMAT**, **PSI**, **SCK-CEN**). For instance the sorption of Eu(III) on illite required the use of $\equiv SOEu(OH)_n^{3-n-1}$ defined in Equation (6) with $n = \{1, 2, 3\}$, and the formation of cation exchange at low pH was verified (**CEA**, **PSI**)

The sorption of Se(IV) on illite (**KULEUVEN**) was modelled in the framework of the 2SPNE SC/CE (log K_{wb} = 8.2 instead of 9.0) to describe the titration behaviour. The selenite pH edges and the sorption isotherm could be adequately described using the sorption of $HSeO_3^-$ and H_2SeO_3 on a combination of four sites: strongly and weakly sorbing sites of the weak basic ($\equiv S_{wb}$) and weak acid ($\equiv S_{wa}$) surface sites.

$$\equiv S_{wb}OH_2^+ + HSeO_3^- \rightleftarrows \equiv S_{wb}OH_2HSeO_3 \tag{8}$$
$$\equiv S_{wb}OH_2^+ + H_2SeO_3 \rightleftarrows \equiv S_{wb}H_2SeO_3^+ + H_2O \tag{9}$$
$$\equiv S_{wa}OH_2^+ + HSeO_3^- \rightleftarrows \equiv S_{wa}OH_2HSeO_3 \tag{10}$$
$$\equiv S_{wa}OH_2^+ + H_2SeO_3 \rightleftarrows \equiv S_{wa}H_2SeO_3^+ + H_2O \tag{11}$$
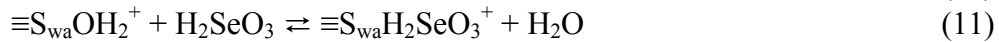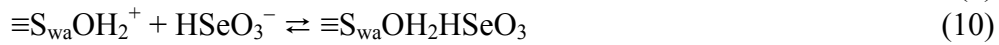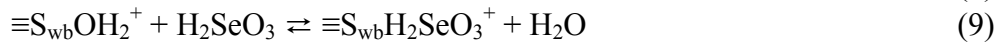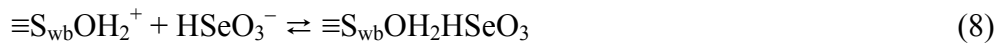
The data on sorption of tetravalent actinides are still scarce, mainly because of the propensity of these ions to form colloids. The formation of these colloids were taken into account to interpret the sorption isotherms of Th(IV) on ferrihydrite, $Fe(OH)_3$(am), and magnetite (Fe_3O_4) by **UPC**. The slope analysis of the pH isotherm suggests the formation of a surface complex with the release of two protons, which can lead to the two hypothesis of the formation of either $\equiv SOThOH^{2+}$ or the bidentate complex $(\equiv SO)_2Th^{2+}$. From complementary spectroscopic study (cf. p. 13) it seems that

$$2\equiv SOH + Th^{4+} \rightleftarrows (\equiv SO)_2Th^{2+} + 2H^+ \tag{12}$$

is forming at the surface.

The application to granitic rocks was done to identify the main minerals responsible for the sorption of RN, namely Cs^+, Ni^{2+}, and Eu^{3+} on graniodiorite and mica-gneiss, *i.e.*, biotite. The minerals were identified by autoradiography (Puukko *et al.*, 2006). Sorption pH isotherms on extracted biotite were obtained and modelled using a 1-pK SCM (Puukko *et al.*, 2008). The outcome was compared to a reference biotite. These results were complemented by molecular modelling of the biotite surface (Puukko et al., 2006; Olin et al., submitted).

A key question is the application of data from crushed rock studied under lab conditions to the real system. More specific, it concerns the surface properties of crushed rocks in comparison to intact clay rock, especially under ambient compaction pressure. **ARMINES** investigated the influence of the compaction on the retention properties of illite for Se(IV) using capillaries for solid-to-liquid ratios of 9000 and 4600 g/L (pH 4 and 8, [Se] = 10^{-6} and 5 10^{-3} mol/L) (Montavon *et al.*, 2009). Almost no influence of 'compaction' was evidenced between these results and a classical batch experiment, *e.g.*, experiments performed by **KULEUVEN**. There is still a need to verify these findings all the way through to formation relevant compaction pressures.

What is the influence of radionuclide complexation on sorption and can this influence be quantitatively calculated with the sorption models?

Inorganic complexant

As the complexation of RN induces a change in the charge of the major species in solution, it is awaited that a change in surface speciation should also be observed. From the competing anions, already discussed above, CO_3^{2-} is the most abundant. The influence of carbonate on Ni^{2+}, UO_2^{2+}, and Eu^{3+} was shown on illite and smectite, in $NaClO_4$ (**CIEMAT**) and in simulated Opalinus Clay groundwaters (**PSI**). If Ni^{2+} sorption is rather insensitive, Eu^{3+} and overall UO_2^{2+} are. In addition with the sorption of hydrolysed species, $\equiv SOEu(OH)_n^{3-n-1}$ defined in Equation (6) with $n = \{0, 1, 2, 3\}$, accounting for the sorption of positive monocarbonato-Eu(III) on smectite and illite (Bradbury and Baeyens, 2006; Missana *et al.*, submitted)

$$Eu^{3+} + CO_3^{2-} + \equiv SOH \rightleftharpoons \equiv SOEuCO_3 + H^+ \qquad (13)$$
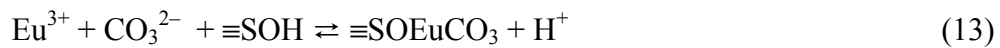
plus a neutral hydroxocarbonato-Eu(III) complexe on illite (Bradbury and Baeyens, 2006)

$$Eu^{3+} + H_2O + CO_3^{2-} + \equiv SOH \rightleftharpoons \equiv SOEuOHCO_3^- + H^+ \qquad (14)$$

was necessary to reflect the synergetic sorption effect for Eu(III).

In the case of U(VI), the formation of neutral non-sorbing ion pair complex

$$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca_2UO_2(CO_3)_3(aq) \qquad (15)$$

was necessary in order to represent the more efficient desorption of U(VI) from illite due to carbonate (Bradbury and Baeyens, 2008).

In addition, a modelling exercise has been performed using the Eu(III)-silicate data from the literature to explain already available data on Eu(III) sorption to montmorillonite. It has been shown that should equation (5) be accounted for Eu(III), given the silicate concentration in

equilibrium with the clay, then sorption of $EuOSi(OH)_3^{2+}$ on surface must be included in the 2SPNE/CE model.

$$\equiv SOH + Eu^{3+} + H_4SiO_4 \rightleftarrows \equiv SOEuSiO(OH)_3^+ + 2H^+ \qquad (16)$$

Simple organic complexant

As for the competition with inorganic ligands, the competition with 'simple' organic complexes can modify the sorption on surface. These organics can either be included within the formation (Glaus et al., 2005; Courdouan et al., 2007a; Courdouan et al., 2007b), or anthropogenic and included in the waste as cellulose degradation products (Glaus et al., 1999; Pavasars et al., 2003; Tits et al., 2005; Glaus and Van Loon, 2008), decontamination agents (Anderegg, 1982; Hummel *et al.*, 2005), cement additives…

The elements were Ni^{2+} and Eu^{3+} – that permit the comparison with the competition of CO_3^{2-} – that will be complexed by ethylenediaminetetracetic acid (EDTA), nitrolotriacetic acid (NTA), picolinic acid, gluconic acid, and iso-saccharinic acid (Figure 1). Here again the main solid samples used were clays, *i.e.*, kaolinite and montmorillonite, but also goethite.

EDTA   NTA   Picolinic acid

ISA   Gluconic acid
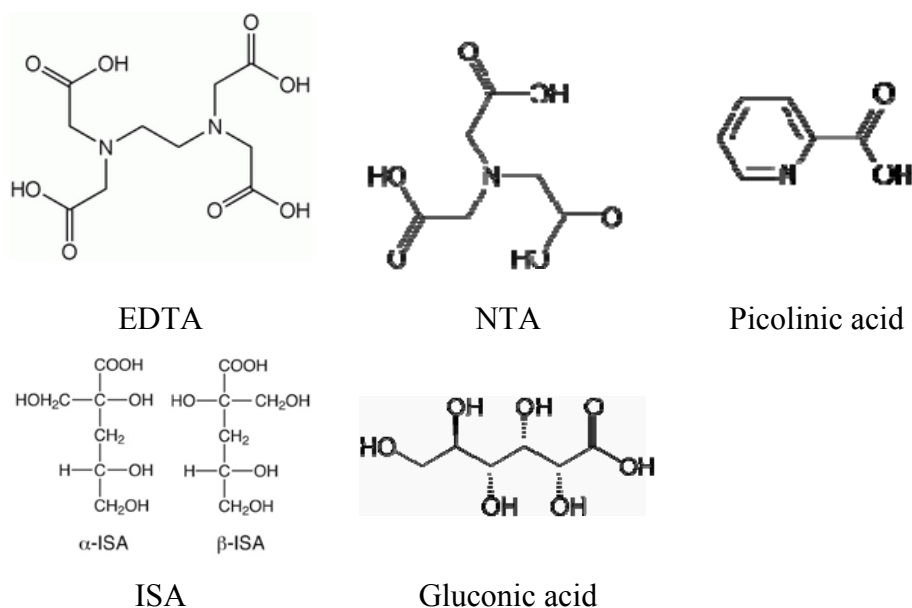
Figure 1: *Structure of the organic ligands used as competitors for sorption of metals on surface in FUNMIG.*

As a general pattern, it can be said that the sorption of the organic ligands to these mineral surfaces is weak, with the exception of picolinic acid (Warwick *et al.*, 2007). The organic ligands reduced the sorption of the metals (Warwick *et al.*, submitted), with the exception of Eu(III)/ISA/goethite system where an enhancement of the sorption is observed. The formation

of weak surface complexes of metals with EDTA can be postulated (Bowers and Huang, 1986).

Is the influence of natural organic matter on sorption described by thermodynamics?

The sorption of natural organic matter (NOM), and its influence on the RN retention, is a subject that has proven difficult to tackle. Given the heterogeneity of NOM, which is composed of a wide variety of molecules from the decomposition of the living, it is not surprising that its comportment is not the simple addition of its component. Actually, modifications of properties, either composition due to fractionation or of conformation induced by the sorption, are proposed to be at the origin of these phenomena. Nevertheless, under some particular conditions, simple addition of the properties, using linear additive models (LAM), may give a reasonable description of the system, as long as the model applied is not outside of its 'parametric space'.

Basic data

The sorption of cationic RN is greatly influenced by the presence of natural organic matter, especially the humic and fulvic acid fractions. This is clearly shown for Am(III) on kaolinite by **FZD**, were an increase is observed before the Am(III)/kaolinite sorption edge –around pH = 6 –, due to the sorption of Am-HA complexes on the clay, and a decrease is induced after the sorption edge, due to the desorption of Am-AH complexes when the surface charge become more and more negative.

Development of models

The complexation and sorption of NOM has been subject to a high number of publications and a large number of models are available. This is especially due to the difficulty to define a thermodynamic standard state for NOM. Within FUNMIG, two complementary definitions were proposed to represent the evolution of the sorption of NOM and its influence on RN retention.

- A purely thermodynamic description, which considers NOM as a distribution of binding sites;
- A kinetic approach, which considers that NOM comprises different compartments with different RN interaction kinetics, including a compartment with a non-exchanging RN inventory.

In complement to the NICA-Donnan model that describes the complexation of metal by NOM (Kinniburgh *et al.*, 1999), **WU** has developed the Ligand and Charge Distribution (LCD) model to account for the modification of the free energy of sorbed NOM (Weng *et al.*, 2007).

The application was tested on the Ca/NOM/goethite and Cu/NOM/goethite systems (Weng *et al.*, 2008). The extent of the modification is much more important for Ca than it is for Cu. Calcium is prone to non-specific binding to NOM in the framework of NICA-Donnan model, whereas Cu is highly specific. Hence, the electrostatic interactions are much in stake in the case of Ca, whereas electrostatic and specific bindings are equally important for Cu. These results points to the importance of the conformation of NOM at mineral surfaces, necessary to regard and leading to the deviation from LAM.

In a dynamic system, these modifications of the NOM were tacked by **UNIMANCH**, using a kinetic model. After an initial RN rapid uptake, a rapidly exchanging fraction is progressively transferred to a slow exchange fraction. This model was first developed on low sorbing sand, and then applied to high sorbing iron oxides: goethite, hematite (α-Fe_2O_3), and magnetite. Two versions were proposed to monitor the heterogeneity of the NOM, *i.e.*, Model 1 assumes that the observed heterogeneity derives from multiple binding sites on the surface of the iron oxide, whilst the second assumes that it is the result of chemical or size heterogeneity of the humic matter itself. The behaviour of the magnetite system is best described by Model 1, but hematite follows Model 2 most closely, whilst goethite shows intermediate behaviour (Farelly *et al.*, 2007).

The different models complement each other. A procedure was proposed to help in the choice of a thermodynamic description or of a kinetic description of the sorption properties. This procedure is based on the application of two dimensionless Damkohler numbers to monitor the ratio of the non-exchangeable first order dissociation rate constant and the residence time in the groundwater column. Sorption of humic/metal complexes at mineral surfaces may reduce mobility. In addition to direct retardation, sorption also increases the residence time of the non-exchangeable fraction, giving more time for dissociation and immobilisation. The magnitude of the effect depends upon the concentrations of the mineral surface humic binding sites and the humic in solution, along with the magnitudes of the equilibrium constant and the forward and backward rate constants. The slow exchanging dissociation reaction and the sorption reaction may be classified in terms of two Damkohler numbers, which can be used to determine the importance of chemical kinetics during transport calculations. These numbers could be used to determine when full chemical kinetic calculations are required for a reliable prediction, and when equilibrium may be assumed, including when the reactions are sufficiently slow that they may be ignored completely (Ivanov *et al.*, 2007).

Application to real system

In the framework of the Boom clay system, a large emphasis is put on the influence of natural organic matter on the migration properties of RN. The sorption of americium (III) and thorium (IV), which are particularly sensitive to this compartment of the rocks, were tested under the conditions of the Boom clay (**SCK-CEN**). The major part of Am and Th were associated with the organic colloidal fraction and not in the kerogen, which do not bear enough functionality (Fourier Transform Infra Red analysis). The sorption isotherms of Am(III) and Th(IV) were obtained with real Boom Clay in equilibrium with real and synthetic Boom clay water.

The metal ions where associated to the NOM. The modelling of the sorption in presence of NOM was difficult with the simple 'additive' model used.

The formation of an organic coating of clay rocks, and its compositions, has been studied at **INE**. The polymerisation of 'simple' organic materials was catalysed by divalent metals and with temperature elevation (25 and 80°C). The formation of aromatic molecules is clearly shown in Scanning Transmission X ray Microscopy (STXM, C1s). The experimental conditions, however, were not sufficient to mimic the natural organo-clay system of host rock formations (Opalinus Clay and Callovo-Oxfordian argillite) (Schäfer *et al.*, 2006). Nevertheless, a series of confined pyrolysis test was conducted on the "*Glucose-Glycine/Calcium/smectite*" polymerized products. The aim was to obtain a kerogen-type material, taking into account the O/C and H/C atomic ratios published for the Toarcian and Callovo-Oxfordian formations of the Paris Basin. Time-temperature parameters of pyrolysis were chosen to be 160°, 180°, 200° and 250°C during 24 hours in agreement with previous works published on Callovo-Oxfordian formation (Elie and Landais, 1997). From kerogen sample from the Callovo-Oxfordian argillite, the C1s spectra and μFT-IR spectra show a high aliphatic and carboxylic content of the organic matter (Schäfer *et al.*, 2009a).

Are the modelling simplification justified regarding spectroscopy?

Species proposed in 'thermodynamic' modelling are *per se* proposition of stoichiometry from fitting or slope analyses. There is a strong desire to verify the actual existence of these species by spectroscopic method, in order to constrain the degrees of freedom of the modelling. Within this project these spectroscopy studies were mainly performed by time-resolved luminescence ("TRLFS"), and X-ray methods (XANES and/or EXAFS).

Luminescence data

In the case of clays, the several different complexes have been proposed for trivalent actinides and lanthanides. The luminescence spectra of Am(III) on kaolinite (**FZD**) is verifying that, between pH 6 and pH 8 different complexes are occurring on the surface. This is in agreement with, *e.g.*, the modelling obtained on Eu(III) on illite (Bradbury and Baeyens, 2006) (cf. p. 8). In the case of montmorillonite and hectorite, the progressive dehydration of Eu(III) with pH was also demonstrated by the increase in the luminescence decay time (**CEA**).

After probing the spectrum of Cm(III) on different crystal planes of sapphire single crystal (Al_2O_3), **INE** performed sorption experiments of Cm(III) on gibbsite. In addition to inner-sphere sorption species, the progressive incorporation of Cm(III) into the structure was shown. This incorporation was confirmed for gibbsite by slightly changing the preparation and storage protocol. In the case of α-Al_2O_3 and bayerite, more than one sorption species is evidenced in TRLFS.

X-Ray

The mechanisms proposed through the sorption modelling have also been verified by polarised EXAFS for the structure of the layered edge of Y, Nd, Lu, and U(VI) surface complexes on hectorite (Schlegel, submitted, 2008). The proposed sorption mechanism (Equation 12) of tetravalent actinides on iron oxides was also examined in XAS (**UPC**). The sorbed species on magnetite are in bidentate-corner arrangement on the both tetraedra and octaedra, and a bidentate-corner sharing surface complex for ferrihydrite. This confirms the postulated release of two protons.

The molecular binding mechanism(s) of selenium surface complexes on illite clay by XANES and EXAFS is studied by **KULEUVEN** (Bruggeman, 2006). Selenite standard solutions and illite sorption sample suspensions are measured in order to elucidate the selenium sorption process. Measurements at three different pH values (3.25, 4.34 and 5.90), all had XANES spectra resembling the spectrum of $HSeO_3^-$. This shows that the two Se species have a similar molecular structure, with two oxygen atoms in the first coordination shell and one atom in the second coordination shell. The same observation is also made with EXAFS, with close resemblance of the sorbed Se species and $HSeO_3^-$. However, in the Fourier-transformed RSFs, new features different from the $HSeO_3^-$ standard were identified. These features point to an inner-sphere sorption complex on the clay platelet edges. An aluminium atom located at 3.05 Å distance of the central Se absorber fits the new peak in the RSFs. Uncertainty concerning the exact molecular structure of the different sorption complexes, and the non-negligible presence of soluble selenite species in the collected spectra however, prevented further interpretation of the spectra in terms of the precise binding mechanism (monodentate, bidentate mononuclear or bidentate binuclear).

Can we mend the bridge between sorption and solid solution?

Reversible sorption is the first step, necessary for incorporation into the structure of minerals and the formation of new solid phases as solid solutions.

Development of models

Vitorge (2008) proposed a common starting point for handling so-called solid solutions, co-precipitation processes or mixtures. The starting point is the thermodynamics of ideal solid solutions non-ideality. Several features of solid solutions were discussed, as typically the chemical meaning of the choice for stoichiometric coefficients, dramatic decrease of aqueous solubility when co-precipitation of elements at trace concentrations, but little influence on aqueous solubilities, when the components of the mixture are at macro concentrations. The stoichiometry of ideal solid mixtures is deduced from the composition of the equilibrated aqueous solution. Stoichiometric coefficients inside the mixture also appeared to be the saturation indexes of the pure components, *i.e.*, end-members. No new thermodynamic parameters are needed: the solubility products of the pure components – or equivalently their Gibb's energy of formation – are sufficient, and make the equations consistent with Standard State. The

dissolution reaction of a three-component mixture was handled as a two advancement variable reaction; one of these reactions is ionic exchange inside the solid solution. For the solid solution $AB_{b(1-x)}C_x$ of the two end members AB and AC, the pseudo solubility product is

$$K_{s,B}^{1-x} \cdot K_{s,C}^{x} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1-x)}\left[C^{z_C}\right]^{cx}}{(1-x)^{b(1-x)} x^{cx}} \tag{17}$$

where $K_{s,B}$ and $K_{s,C}$ are the actual solubility product of AB and AC. The other equation needed is the ratio of the solubility product.

$$\frac{K_{s,C}}{K_{s,B}} = \frac{(1-x)^b \left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b x^c} \tag{18}$$

In that respect, any ionic exchange equilibrium – in solid, surface or liquid phases – can be interpreted as deriving from the dissolution reaction of the ion exchanger matrix; this gives a theoretical link to Standard State for sorption, at least when described as ionic exchange.

Laboratory studies

Solid solution formation, which can be considered as the formation of a new phase, can induce the lowering of solubility compared to the pure 'end-members'. The structural incorporation of actinides in calcite was examined in mixed flow reactors under steady state conditions. Neptunium (V), as neptunyl ion NpO_2^{+}, is actually incorporated in the calcite lattice sites, with higher partition coefficient than UO_2^{2+}. The neptunyl ion is coordinated by 4 carbonate ions (Heberling et al., 2007; Heberling and Bosbach, 2008; Heberling et al., 2008).

Selenium in its –II redox state can be incorporated in the structure of pyrite (FeS_2). To elucidate this mechanism, **ARMINES** performed the sorption incorporation experiment under imposed potential in a specially designed electrochemical cell. The incorporation of Se^{2-} occurs through the oxidation to Se(0), detected by XRD and XPS.

$$HSe^- \rightarrow Se + 2e^- + H^+$$
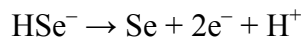
The pyrite reduction is occurring to FeS.

$$FeS_2 + e^- \rightarrow FeS + S^-$$
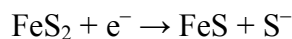
Hence, the incorporation mechanism that can be proposed is the surface reaction

$$\equiv FeS_2 + HSe^- \rightleftarrows \equiv FeS + Se + HS^- \tag{19}$$

This mechanism is also verified in EXAFS by **KULEUVEN** (Breynaert *et al.*, 2008), and the reduction of Se(IV) by pyrite to Se(0) was also demonstrated.

Real systems

For real systems, the estimation of the upper limit of actinide solid solution formation in calcite by analogy to the total concentration of lanthanides was done (**KU**). From sixty carbonate minerals of different origins, the maximum value found is 6.5 mmoles lanthanides per kg calcite. This value is to be compared with the maximum incorporation of Eu(III) in synthetic calcite, namely 6 mmol/kg. It is thus suggested that this value is used as an upper limit for incorporation of trivalent lanthanides and actinides in calcite.

Which natural redox phases and/or redox processes act as redox buffers in the far-field environment?

Direct Eh measurements, or redox buffering capacity of potential host rocks, were not performed within FUNMIG, but the real site analysis within the Swedish site investigation programme was part of RTDC-4. Redox potentials of fractured rock systems were measured during the Redox Zone experiment at Äspö (Sweden). At a depth of 70 m, the redox potentials ranged from -150 to -100 mV. In undisturbed measured native saline water, a value of -145 mV is obtained (Molinero and Samper, 2006). For the Laxemar–Simpevarp sites, the potentiometrically measured Eh ranges from -210 to -380 mV. In general, sulphur redox pairs showed a good agreement with the measured Eh values (Laaksoharju *et al.*, 2008).

Within the FUNMIG project period, some peer-reviewed journal papers appeared with in situ redox conditions in indurated and plastic clays. On-site measurements in the Opalinus Clay at Mont Terri revealed a redox potential of -196 mV at pH 7.6 (Fernández *et al.*, 2007). Eh value in all the waters was calculated with the pyrite/Fe(III), pyrite/goethite and pyrite/siderite redox pairs, obtaining a redox value of -196 mV, -222 mV and -216 mV, respectively. Similar redox values were obtained for the siderite/Fe(OH)$_{3(s)}$ and Fe(II)/Fe(OH)$_{3(s)}$ redox couples, as well as for the siderite/Fe(III) and Fe(II)/Fe(III) values. According to the mineralogy of the Opalinus Clay formation, the Eh is controlled by the sulphate/pyrite or pyrite/Fe(III) couples.

Boom Clay laboratory data and modelling results gave Eh values from -230 mV to -256 mV for a pH between 8.2-8.67. Goethite, siderite and pyrite were selected as the main Fe minerals for the numerical model, in spite of goethite being thermodynamically less favourable than hematite (Zhang *et al.*, 2008).

Are redox-sensitive contaminants transformed into equilibrium valence state?

In general, redox active phases in natural systems can be considered Fe(II) containing minerals as pyrite (FeS_2), troilite (FeS), magnetite (Fe_3O_4) or biotite, Fe(II) adsorbed to clay miner-

als as illite or montmorillonite, natural organic matter (NOM) and microorganisms. Microorganisms can act as direct reductant (terminal electron acceptor) and will be discussed in a separate key question.

The majority of organizations (FZD, KTH, FZK-INE, SCK·CEN) working within FUNMIG to answer the above mentioned key question, focussed on the interaction of U(VI) with Fe(II) containing mineral phases. Uranium(VI) mobility in groundwater is strongly affected by sorption of mobile U(VI) species (e.g. uranyl, UO_2^{2+}) to mineral surfaces, precipitation of U(VI) compounds, such as schoepite $(UO_2)_4O(OH)_6\cdot6H_2O)$, and by reduction to U(IV), forming sparingly soluble phases (uraninite; UO_2). The latter pathway, in particular, could be very efficient for long-term immobilization of U. Redox reactions between U(VI) and Fe(II) depend not only on the availability of Fe(II) in the environment, but also on the chemical conditions in the aqueous solution. Under atmospheric conditions, FZR has shown that U(VI) reduction with Fe(II) containing biotite during uranium adsorption seems to play an insignificant role in the immobilization behaviour. No characteristic U(IV) fluorescence could be detected by TRLFS within the analytical uncertainty. Additional Kryo-TRLFS measurements revealed that the adsorbed ternary uranyl carbonate species plays a role in removing aqueous U(VI) from solution.

KTH together with **FZK-INE** investigated o which extent U(VI) carbonato- complexes can be reduced to UO_2 by Fe(II) structurally bound in a mineral (magnetite, Fe_3O_4) or sorbed to a redox-inert mineral surface (as corundum, Al_2O_3). Batch experiments were conducted under strictly anaerobic conditions, in order to observe U removal from the aqueous phase by the two minerals depending on HCO_3^- addition (1 mM), U concentration (0.01-30 μM) and pH value (6-10). Immediately after the experiments, the mineral surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) to obtain information on the redox state of U bound to the solid surfaces. XPS results gave evidence that U(VI) can be reduced both by magnetite and by corundum amended with Fe(II). In the presence of HCO_3^- the amount of reduced U on the mineral surfaces increased compared to carbonate-free solutions although the total amount of surface sorbed U is lower in the presence of carbonate. This appears to be due to formation of Fe(II) carbonates on the mineral surfaces which represent an easily available Fe(II) pool for the U(VI) reduction. A facilitated U(VI) reduction is also considered possible when U is present as a carbonate complex compared to uranyl (Regenspurg *et al.*, in press).

Real system analyses **were performed in two different rock types, namely** *fractured rocks (Äspö, Sweden) and plastic clays (Boom Clay, Belgium).*

Fracture filling thin sections and post-mortem analysis of migration experiments on overcored natural fractures from the Äspö system (Sweden) was done by **FZK-INE.** It was shown, that under near-natural conditions (recent groundwater conditions) a retention of Np(V), Pu(IV), Tc(VII) and U(VI) is observed. Fe-bearing mineral phases were important in the retention process of all actinides and Tc. It could be evidenced by spectroscopic methods (i.a. XPS) that sorptive reduction (Np(V) => Np(IV) and Tc(VII) => Tc(IV)) on Fe(II) containing mineral phases and a pronounced dependence of the recovery in migration experiments on the fracture residence time (reduction kinetics) is a key parameter for radionuclide

mobility (Kienzler *et al.*, 2009). Therefore, the pH/Eh conditions in laboratory experimental programs as well as field activities (i.e. site investigation programs) are a key parameter and should be routinely measured and cross- checked with the solution speciation found. However, the exact structure/mineralogy of the Fe(II) containing minerals, *i.e.*, magnetite, pyrite, biotite, were not identified in this study.

The partner **KU** focused specifically on the role of green rust (GR; Fe(II),(III)-hydroxide) in fractured rock ground water systems concerning the GR occurrence, structure, composition and reactivity. The composition and structure of green rust (GR) sulphate was determined and proved that it also contains monovalent cations:

$NaFe(II)_6Fe(III)_3(OH)_{18}(SO_4)_2 \cdot 12H_2O$ (Christiansen *et al.*, submitted-a) and the free energy of formation (ΔG_f) has now been established to be -6366 ± 18 kJ/mol. Using an anaerobic sampling technique it was also possible to sample GR in groundwater from the Äspö Hard Rock laboratory at a depth of 500 m (Christiansen *et al.*, submitted-b). The observation has been made that GR forms colloids that aggregate and attach to fracture minerals, but the relative proportion of mobile GR colloids has not been quantified within the project. Furthermore, the reduction and uptake of selenite (SeO_3^{2-}) and neptunyl by GR has been investigated. Selenite ended as metallic Se(0) colloids (Behrends *et al.*, 2006) and Np(V) was reduced to Np(IV) and incorporated into the GR. Simulating complete GR oxidation to goethite (FeOOH), 75% of the Np remained in the Fe(III) phase (Christiansen *et al.*, submitted-c).

SCK·CEN focused on the speciation and solubility of uranium in presence of pyrite (FeS_2) and siderite ($FeCO_3$) under Boom Clay geochemical conditions. In presence and absence of Boom Clay natural organic matter (NOM) the U sorption isotherm follows a Freundlich-type behaviour suggesting an adsorption-like process being responsible for the U solution concentration. In comparison to earlier studies (Delécaut, 2004), the solubility limit of $\sim 2 \cdot 10^{-7}$ M was not observed; instead U concentrations in the supernatant solution ranged from $< 4 \cdot 10^{-10}$ M (detection limit) to $6 \cdot 10^{-6}$ M (after 120 days equilibration).

The presence of NOM in solution decreases the uptake by the FeS_2 surface, possibly by blocking adsorption sites or by altering the surface charge, whereas the overall association of U with NOM is low. XANES and EXAFS measurements showed that U(VI) is partly reduced by FeS_2 via the formation of small UO_2 nanoclusters. In contrast to (Delécaut, 2004), a formation of $UO_{2.33}$ could not be confirmed, but instead, the results from EXAFS indicate a mixture of adsorbed U(VI) species and UO_2 nanoclusters. The amount of U(IV) is higher in absence of NOM, and increases with increasing equilibration time. Similar XANES/EXAFS studies on siderite solid phases suggest also the reduction of U(VI) to UO_2 nanoclusters. The outcome of the study gives further proof that both siderite and pyrite reduce U(VI) to UO_2 and that U(IV) is the stable redox state under Boom Clay conditions (equilibrium redox state). Both siderite and pyrite act as a redox buffer in the Boom Clay far- field environment.

KULEUVEN made a complementary study to elucidate the Se speciation and solubility controlling phases under Boom Clay conditions. Se(IV) sorption experiments were conducted on (a) non-purified pyrite containing Fe(III) amorphous coatings and (b) purified pyrite minerals. Results from the first type of experiments showed a $\sim 90-95\%$ decrease of total Se solution concentration upon contact with FeS_2 after one day equilibration time, then remaining con-

stant over 25 weeks (log K_D = 3.2 ± 0.2). Experiments with purified FeS_2 also showed an initial $^{75}SeO_3^{2-}$ decrease of > 95% in the supernatant total Se concentration after 1 day, but the Se solution concentration slowly decreased afterwards and therefore the distribution coefficients in these systems gradually increased from log $K_D \approx 3.0$ (1 day) to log $K_D \approx 3.7$ (139 days). In both experiments, only inorganic Se(IV) anions as solution species were determined.

The above mentioned experimental results can be explained by a two step process as suggested by (Bruggeman *et al.*, 2005): (1) A rapid adsorption onto illite and/or FeS_2 is followed by (2) a slow reduction onto FeS_2 as thermodynamically expected (pH 8.7-8.9; -80 mV < E_h < -160 mV). However, the observation in the non-purified pyrite system point more to an adsorption mechanism of Se(IV) to Fe(III) phases at the FeS_2 surface.

In mixed illite/pyrite system, Se(IV) is reduced to Se(0) (Breynaert *et al.*, 2008). The kinetics of reduction of Se(IV) by FeS_2 are decreased and metastable plateau concentrations of Se in solution are observed. Solution speciation using SEC, IC, UF (30 kDa) indicated the presence of Se(IV) as major selenium species in solution. FeS in mixtures of illite/FeS proves to be a more efficient reductant than FeS_2. Additional X-ray Absorption Spectroscopy (XANES-EXAFS) studies evidenced the Se(0) formation in presence of FeS_2 and the formation of FeSe in presence of FeS (Breynaert *et al.*, 2008). These results are in accordance with the Se redox speciation expected under the established pH/Eh conditions in equilibrium with FeS_2 or FeS.

Summarizing the results, no selenate (Se(VI)) reduction or uptake by pyrite was observed in the timeframe of the experiments conducted, whereas Se(-II) is oxidised by pyrite to Se(0) and Se(IV) is reduced by pyrite to Se(0) and finally Se(IV) is reduced to S(-II) in the presence of FeS.

The long term Se speciation in Boom Clay is expected to be governed by the presence of reduced Se phases, resulting from interaction with reducing minerals such as, *e.g.*, FeS_2/FeS. The exact nature of the phases formed in real Boom Clay, however, needs to be confirmed experimentally.

Concerning the role of humic substances as a redox partner, **FZK-INE** worked on the plutonium and neptunium redox states in solutions containing humic substances (HS) by both laboratory investigations and equilibrium thermodynamic modelling. The investigations with humic substances focused on fulvic acid (FA), rather than humic acid (HA). To elucidate reaction mechanisms, also simple hydroquinones are used as model compounds (Marquardt and Seibert, 2006). Various types of hydroquinones were used , assuming that these are models for the reducing entities of humic substances. Hydroquinone (HQ) and the 9,10-anthraquinone-2,6-disulfonic acid (AH2DS) with an E^0 of 0.6992 V and 0.228 V, respectively, were chosen to cover a broad range of normal redox potentials (E^0). The normal potential of fulvic acids lies in between both values and is estimated to be about 0.5 V. Specifically it was attempted to answer the question whether or not the behaviour of actinides in humic-rich groundwater can be quantified by the application of thermodynamic equilibrium constants. Pu experiments were started with mostly Pu(VI) and small residues of Pu(V), to ensure colloid free start solution. The final Pu concentrations were typically $1-2\cdot10^{-4}$ M and about < 10^{-8} M, respectively. The neptunium concentrations were typically $2\cdot10^{-5}$ M of Np(V). The FA concentrations were $4 – 200$ mg/L ($2.7\cdot10^{-5} – 1.7\cdot10^{-3}$ eq/L proton exchange capacity).

The hydroquinones were used at various concentrations of $1 \cdot 10^{-4}$ - $3 \cdot 10^{-3}$ eq/L. The pH of solutions varied between pH 1 and 7. All experiments were performed in a glove box under Ar atmosphere (O_2 content < 20 ppm).

The results showed that Pu(V) and (VI) are not stable in the solutions with HQ, AH2DS or FA. Pu in such solutions is quantitatively converted to Pu(IV) within 20 days. The tetravalent Pu oxidation state is the main oxidation state in FA at pH 3 - 7 and in HQ at pH 5 – 7 (relevant for natural aquifers). Reduction of Pu(IV) to Pu(III) was also observed in the same pH range, but only for low Pu concentrations. Np(V) was reduced to Np(IV) in AH2DS, and HS solutions, but not in HQ solution. Eh was monitored in all experiments and those data were compared with calculated pe values. For pe calculations it was assumed that dissolved Pu(III) and Np(V)-species were in equilibrium with colloidal Pu(OH)$_4$, and Np(OH)$_4$, respectively. For Pu the calculation shows that Pu(III) can be stabilized in presence of FA at higher pH values (Marquardt and Seibert, 2007). According to thermodynamic estimations for the Np(V)/Np(IV) redox couple there is a limiting value for the redox potential of -32 ± 41 mV. For all investigated AH2DS systems Eh lies below this value. Therefore, the thermodynamic prediction of Np(V) reduction is in good agreement with experimental data (Shcherbina *et al.*, 2009).

Which are the main parameters affecting the erosion and generation of bentonite colloids from the compacted bentonite?

A number of groups within RTDC-2 and RTDC-4 and outside the FUNMIG consortium have investigated parameters influencing the erosion behaviour of compacted bentonite (Alonso *et al.*, 2008; Seher *et al.*, 2009). These parameters included *inter alia* the dry density of compacted bentonite, the exchangeable cation composition and the contact water solution chemistry (pH, ionic strength, cation composition). The investigations have shown that for an ionic strength below the critical coagulation concentration (CCC) a colloid generation can be confirmed. The strong pH dependency of colloid stability in the sodium system previously investigated in coagulation experiments was confirmed in the colloid generation experiments. A filter pore size dependent colloid generation mechanism could not be observed in the course of the experimental period (two years). In all experiments the colloid concentration with time reaches a plateau value. Higher dry densities of compacted bentonite yielded a higher colloid concentration plateau value. The exchange of the contact water leads to a rapid neo-formation of colloids reaching again a plateau value, sometimes below the first concentration plateau. The reason for these observations as being (a) dynamic generation/ aggregation equilibrium and/or (b) depletion of the colloid source, could not be clarified within the project.

The internal erosion of the sand- bentonite mixtures was not focus of IP FUNMIG and here we refer to published data (Kaoser et al., 2006). Kaoser et al. found that internal erosion is mainly influenced by porosity, which can be reduced by properly selecting the sand particle size distribution and the bentonite percentage. An empirical expression to predict the risk of internal erosion in the sand-bentonite mixtures has been proposed which can be used for designing compacted bentonite.

Other generic studies by **FZK-INE** and **TUM** focused on the formation of montmorillonite precursor phases, namely hydroxyl-aluminosilicates (HAS) and the question whether actinides are prone to co-nucleate with Si and Al under normal conditions of temperature and pressure within a pH range of 4 – 9. Optimum conditions for the formation of HAS pseudocolloids of actinides are derived from a broad parameter screening experiment based on radiometric tracing of the actinides as they are distributed between three phases differentiated by sequential filtrations: solution (< 1.5 nm), colloids (1.5 – 450 nm) and precipitate (> 450 nm). The chemical binding state of the actinides incorporated in the HAS colloids is analyzed by time-resolved laser fluorescence spectroscopy (TRLFS), extended X-ray absorption fine structure spectroscopy (EXAFS) as well as by the ligand displacement method with EDTA. The results prove that increasing pH, increasing actinide concentration and/or co-nucleation elements (Si, Al), long reaction times, etc. also increase the interaction of Cm(III) with HAS colloids (Kim et al., 2005; Panak et al., 2005; Kim et al., 2007). Finally, the interaction of actinides with humate colloids was investigated. Cm(III) and [^{14}C]-labelled humic acid are simultaneously traced during their phase partition, especially at colloid formation. It has been shown that at pH 6, Cm(III) speciation is dominated by humic acid complexation. Additional analysis in systems where competition between two ligands takes place, namely silicic and humic acid, for the complexation of Al and Cm(III) in the neutral pH region (6.6 – 7.8) showed the formation of colloid-borne actinides in a mixed structure of HAS and humic acid aggregates. The investigation shows that aquatic colloids composed of HAS and humic acid combine actinides via different but synergic mechanisms and hence enhance the stability of colloid-borne actinides (Kim *et al.*, 2007). An(III) speciation is dominated under natural conditions by hydroxyl-aluminosilicate (HAS) or polysilicic acid colloids in (Si, Al) containing waters, whereas these colloids are aggregating at ionic strengths > 0.015M in the absence of humic substances.

Are we able to reliably predict a "source term" for bentonite colloids?

The activities within FUNMIG focused on a broad parameter screening of potential parameters controlling the release of bentonite colloids and the erosion of the compacted bentonite buffer (see above). Direct model development or application was not possible within the time-frame of IP FUNMIG. It should, however, be noted that outside the FUNMIG consortium, activities have started on model development starting with a "zero order" conceptual model consisting of the following steps: (a) the clay in the deposition hole will be pushed due to the swelling pressure into the fracture taking up water and equilibrating with the local water composition, (b) if the water composition at the outer edge of the clay change so that it will be lower than the CCC (calcium concentration for simplification determines CCC; 1 mM) clay particles will disperse and be carried away, but (c) calcium from gypsum mineral dissolution inside the bentonite buffer determines porewater Ca concentration (gypsum solubility controlled at 9.8 mM) until all gypsum is dissolved (Liu and Neretnieks, 2006; Neretnieks, 2006). Different bentonite erosion rates were calculated based on the repository evolution (initial stage, intermediate stage with gypsum, intermediate stage without gypsum) (Liu and Neretnieks, 2006). The datasets generated within FUNMIG can be transferred into erosion

rates and an evaluation and comparison with the "zero order" model as well as new approaches published by the same group are the next steps (Liu *et al.*, 2009a; Liu *et al.*, 2009b).

A first evaluation of the data shows that the "zero order" model over-predicts the compacted bentonite buffer erosion for the data obtained within FUNMIG.

Which are the main parameters affecting stability/filtration of colloids in crystalline rock?

Within FUNMIG the studies on colloid stability and especially colloid – fracture surface interaction were subdivided between RTDC-2 and RTDC-4.

The approach used by **FZK-INE** and **TUM** within FUNMIG was twofold, (a) stability analysis were performed on initial stabile colloid suspensions and (b) looking at the potential neo-formation of colloids (i.e. hydroxyl-aluminosilicates, or polysilicilic acid).

Concerning the first topic, the critical coagulation concentration (CCC) of Febex bentonite colloids is determined by colloid coagulation studies under variation of pH, electrolyte concentration and fulvic acid (GoHy-573FA) content. For $CaCl_2$ electrolyte solution, a pH independent Ca-CCC of 1 mmol·L^{-1} was found. In the case of NaCl background electrolyte a pH dependent Na-CCC could be determined with 15 ± 5 mmol·L^{-1} at pH 6, 20 ± 5 mmol·L^{-1} at pH 7, 200 ± 50 mmol·L^{-1} at pH 8, 250 ± 50 mmol·L^{-1} at pH 9 and 350 ± 100 mmol·L^{-1} at pH 10, respectively. The addition of 1 mg·L^{-1} DOC FA increases the Ca/FA-CCC to 2 mmol·L^{-1}. Scanning Transmission X-Ray Microscopy (STXM) showed an FA association with Febex bentonite colloids as surface coating and specific hot spots could be clearly identified. The experimental bentonite stability results were described by means of a DLVO approach summing up hydration forces, short-range Born repulsion, van der Waals attraction and electrical double layer repulsion. The measured zeta (ζ) -potential of the bentonite colloids is used as platelet face charge and the edge charge is estimated by the combination of silica and alumina ζ-potential data in the ratio given by the Febex bentonite structural formula. Adjusting the montmorillonite face charge by a maximum of ± 12 mV was sufficient to successfully reproduce the measured stability ratios. The Na- CCC values, however, could only be reasonably predicted using solely the calculated edge-face interaction energy. The strong deviations of the model predictions and the experimentally determined Na-CCC values found at low electrolyte concentrations, are explained by the spill-over of the platelet face electrical double layer (EDL) shielding the positive platelet edge charge (Seher et al., 2006; Seher et al., 2009, submitted).

The first simplified approach used by **FZK-INE** was to test the colloid formation within the mixing zone of a synthetic Febex bentonite porewater of saturated bentonite with natural groundwater from the Grimsel Test Site (GTS, Switzerland) representing expected glacial melt water composition via batch-type studies. The formation of colloids was investigated by laser-induced breakdown detection (LIBD), SEM-EDX as well as the changes in radionuclide (U, Th, Eu) speciation via ultrafiltration or TRLFS analysis in the case of Cm(III). The colloids generated in the mixing zone aggregate when the synthetic Febex porewater (FPW) content exceeds 10% (I= 0.015M). LIBD analysis after 70 days revealed a low concentration of

stable colloids (~100 ppt, average diameter ~ 30 nm). SEM/EDX mostly identifies Si/Al containing colloidal phases. TRLFS studies show that the Cm speciation is strongly influenced by colloid formation in all solutions. In the FPW/GGW mixing zone with high Grimsel groundwater contents (>80%) colloids are newly formed and Cm is almost quantitatively associated with most likely polysilicilic acid colloids. (Kunze et al., 2008b; Kunze et al., 2008a).

Other work within IP FUNMIG on the generation mechanism of nanoparticular phases, included the generation or formation of U(IV) nanoparticles (Opel *et al.*, 2007).

Concerning the mobility of colloids in crystalline environments, microscopic and macroscopic approaches were used to gain mechanistic understanding, especially on colloid attachment under "unfavourable" conditions (see also RTDC-4). Work both by **CIEMAT** and **FZK-INE** focused on migration studies and observed a mass recovery reduction with increasing residence time indicating a colloid attachment to fracture surfaces (Albarran *et al.*, 2009; Schäfer *et al.*, 2009b). Interestingly, microscopic studies using the so-called colloid probe technique to measure force-distance curves via AFM revealed no snap-in forces for carboxylated microspheres under these hydrogeochemical conditions (Filby et al., 2008; Filby et al., 2009). Consequently, detailed mechanistic understanding on the colloid retention mechanisms in natural fractured systems is lacking also after conclusion of FUNMIG. The microscopic studies, however, indicate that local Ca-concentration variations might be a key to colloid attachment even under "unfavourable" conditions.

Which is the mobile fraction of colloids in diffusion controlled systems?

For far-field environments with diffusion controlled claystone systems, model calculations are made. The basis for the model is a pore size distribution and connectivity argue for nanoparticles << 10nm fitting through pore necks. The model calculations indicate that colloid-related transport is negligible (Nagra, 2002). Several in situ collected water samples from the Opalinus Clay (Mont Terri) were studied with focus on the size range 1-10 nm. A concentration of inorganic colloids around 10-20 ppt was derived and humic colloids below the detection limit (Degueldre *et al.*, 1998). New detailed studies on the organic inventory of the Opalinus and Callovo-Oxfordian porewater performed outside the FUNMIG consortium have shown that a significant fraction of dissolved organic carbon (DOC) belongs to low molecular weight compounds and not colloids with a molecular size < 500Da (Courdouan et al., 2007a, 2007c). For plastic clays (Boom Clay formation) comparison performed by **SCK·CEN** between batch-type studies bringing the whole organic inventory in suspension and the pore water sampled in the HADES underground laboratory gives indications that the pore-size cutoff is ~300 kD. Further support has been obtained within FUNMIG using Asymmetrical Flow-Field Flow Fractionation (AsFFFF)**.**

How far is the possibility of a mechanistic description of colloid transport? Which fundamental data are still missing?

Fundamental data to reliably predict the effect of colloid transport on radionuclide mobility include (a) the presence of colloids, (b) the stability of colloids, (c) the mobility of colloids, (d) the radionuclide interaction with colloids, especially the pozental irreversibility of metal sorption. Some aspects as the stability or mobility of colloids are already discussed in detail.

In RTDC 2, the focus was on the interaction of radionuclides with natural organic matter (NOM), especially humic substances (HS), and on investigations in ternary systems (mineral-humic colloids- metal).

Work by **CEA, NRIRR** and **UNILOUGH** focused on a literature review concerning the coherence of actinide(IV) complexation data by humic substances (HS). Papers where the experimental data are published were recalculated/reinterpreted and compared. In order to have a consistent overall outcome, for example only one hydrolysis constant set taken from U(IV) was used. Hence, the obtained evolution of conditional formation "constant" is much more coherent, differences originating from different basic data-sets and calculation basis are removed, and the remaining uncertainties do not permit to distinguish an An(IV) from one another (Reiller *et al.*, 2007; Reiller *et al.*, 2008). The obtained data are then applied to independent laboratory and in situ experiments in order to delimit the domain of possible applicability. This exercise demonstrates the treatment of data through analogy in the case of An(IV) and would permit to limit and orientate the number of necessary, but difficult, experiment with redox sensitive elements like U, Np, or Pu. If no competition occurs, the humic complexation of tetravalent actinides can be obtained with a rather good approximation from Th(IV) data.

Another activity of **CEA** focused especially on competition effects. Using the NICA-Donnan model, providing a coherent description of the metal-humic substance complexation mechanisms, Co^{2+}/Mg^{2+} competitive experiments were done in Flux Donnan Membrane Technique (FDM). It was shown that Co^{2+} was slightly less sensible to humic complexation than its d-blocks metal 'neighbours' and susceptible to Mg^{2+} competition (Marang *et al.*, 2006).

The same experiments were performed with UO_2^{2+}, evidencing the limitation of FDM due to U(VI) precipitation in the Donnan membrane at pH higher than 4. The use of insolubilized humic acid helped to finish the works and provide evidence of a weak competition with Mg^{2+} (Marang, 2007).

Finally, in collaboration with **UPPC**, the NICA- Donnan parameters for Ca^{2+}, Cu^{2+}, and Eu^{3+} obtained from competitive binding experiments using Ca^{2+} or Cu^{2+} ion selective electrodes were used to model time-resolved laser fluorescence spectroscopy (TRLFS) measurements. Eu^{3+} and Cu^{2+} are in direct competition for the same type of sites, whereas Ca^{2+} has an indirect influence through electrostatic binding (Marang et al., 2008a; Marang et al., 2008b; Marang et al., 2009). It means that alkaline-earth are only merely in competition for strongly sorbing metals like actinides and lanthanides, whereas Fe^{3+} and Al^{3+} and inter-Ln/An competition are awaited to have a stronger competitive effect.

The work of partner **UPPC** focused on advanced TRLFS methods as analytical tools for improved speciation of actinides and secondly on the increase/improvement of fundamental understanding of interaction processes between actinides (lanthanides were used as homologues and luminescence probes) and humic substances (HS). The intrinsic HS fluorescence as well as the sensitized lanthanide (Ln^{3+}) luminescence was used to describe the complex formation. Upon addition of Ln^{3+} to humic acids (HA), a blue shift of the intrinsic HA fluorescence was found in addition to the overall decrease of the intrinsic fluorescence intensity. In contrast, in experiments with fulvic acids (FA) no spectral shift of the intrinsic fluorescence was detectable, but the intrinsic fluorescence intensity also decreases. From the quenching of the HS fluorescence and the sensitized Ln^{3+} luminescence, complex formation constants were derived. In case of FA the value of the complex formation constant determined from the quenching of the intrinsic FA fluorescence was always lower compared to the constant calculated based on the sensitized luminescence intensity of the Ln^{3+} ion. In case of HA, the picture was not that clear, e.g., in some cases no sensitized luminescence signal of the Ln^{3+} could be observed at all. The different behaviour of HA and FA fractions is also confirmed in stopped-flow experiments. For FA a very fast quenching of the intrinsic FA fluorescence (= binding) was found. In measurements with HA, in addition to the fast quenching, a second much slower quenching process was observable. The findings of the steady-state and stopped-flow measurements give raise to the assumption, that FA and HA differ in size and/or association due to metal complexation (Kumke *et al.*, 2006). Time-resolved fluorescence anisotropy measurements additionally support this assumption. Upon increasing of the Ln^{3+} concentration, a decrease of the intrinsic HA fluorescence correlation time was found, which can be directly connected to a decrease of the (rotating) volume of the molecule under investigation. In case of Tb^{3+} HS complexes, the possibility of an energy transfer back from the Tb^{3+} to the HS was implemented in the data evaluation. As a consequence, only one decay time was derived. In addition, parameters reflecting the inhomogeneity of the complexes were calculated from the model applied. In order to get information on the distribution of metal ion bound to HS without a bias due to missing knowledge of HS structure, inter-lanthanoide energy transfer between Eu^{3+} (Tb^{3+}) and Nd^{3+} was investigated and the mean distance between metal ions was calculated. Depending on the origin of HS and on the loading with metal ions distance in the range of ten ionic radii were found (Kumke *et al.*, 2005).

To model the influence of humic substances on the migration of tetravalent actinides (Pu, Np, U) in and around nuclear waste repositories, **NRIRR** has immobilized humic acid on silica gel (Szabó *et al.*, 2007b) or silicon wafer (Szabó *et al.*, 2006b) and investigated its complexation of Th(IV) and Pu(IV). It is anticipated that this material might serve as a geochemical model of the humate-coated minerals that are likely to be present in the vicinity of the repositories. The binding of Th(IV) by the immobilized humic acid was examined at pH 4, 5 and 6 in 0.1 mol L^{-1} $NaClO_4$ by the batch method. Th(IV)-humate conditional interaction constants have been evaluated from data obtained by these experiments using non-linear regression of binding isotherms (Szabo et al., 2006; Szabó et al., 2006a; Szabó et al., 2007a). Examination of Pu(IV) sorption isotherms at different ionic strengths at pH 4 it is apparent that conditional stability constants of Pu(IV)$_{Total}$ (log $^{HA}\beta(Pu_{Total})$) can be computed and by using these values and the side reaction coefficients (α_{Pu}) the conditional stability constants $^{HA}\beta(Pu^{4+})$ can be calculated. Comparing the log $^{HA}\beta(Pu^{4+})$ at different ionic strength with log $^{HA}\beta^0(Pu^{4+})$ indi-

cates that the effect of ionic strength on humate complexation of Pu(IV) is not dramatically pronounced but can be observed. The maximal binding capacity (B_{max}) and loading capacity (LC) decrease gradually with increasing ionic strength. Log $^{HA}\beta(Pu^{4+})$ for zero ionic strength at pH 4 can be calculated using a non linear least square fitting procedure (Szabo *et al.*, 2006), which gives: log $^{HA}\beta^0(Pu^{4+})$ = 16.9 ± 0.5 (Szabó *et al.*, 2008; Szabó *et al.*, 2009).

The complexation of plutonium(III) with humic substances and its reversibility was studied by **FZD**. For the study of the complexation of such redox-sensitive radionuclides, synthetic humic acid model substances with distinct redox properties are used. These humic substances were synthesized by oxidation of diphenolic compounds in the presence of amino acids in alkaline solution. The most promising synthetic humic acid (HA) are the HA type Cat-Gly, which is an oxidation product of catechol synthesized in the presence of glycine, and the HA type Hyd-Glu, which is an oxidation product of hydroquinone synthesized in the presence of glutamic acid. The Fe(III) reducing capacities determined for HA type Cat-Gly and Hyd-Glu range from 10.7-14.5 meq/g HA at pH 3.0 and from 33.6-36.9 meq/g HA at pH 9.2 and are significantly higher than those determined for natural Aldrich HA with 1.2 and 7.2 meq/g HA at pH 3.0 and 9.2, respectively. The formal redox potential of HA type Hyd-Glu is 565 ± 12 mV, decreasing with pH by −64 ± 12 mV/pH. Structural parameters for the near-neighbors surrounding of plutonium(III) in complexes with humic and fulvic acids at pH 1 by means of EXAFS have been quantified (Schmeide *et al.*, 2006). The experiments on Pu(III) complexation by model substances could not be finished in the period of FUNMIG.

Another approach to improve our mechanistic understanding of radionuclide humic substance interaction, focused on the development of new relativistic quantum-chemical methods for interpretation of NMR spectra of lanthanide complexes with humic acids and model ligands. New methods for quantum-chemical calculations of NMR shifts of paramagnetic molecules (based on 1-component approach), as well as calculations of NMR shifts at the four-component Dirac-Kohn-Sham level were developed and implemented in the framework of FUNMIG by partner **SAS-IIC** (Komorovsky *et al.*, 2006; Malkin *et al.*, 2006; Reviakine *et al.*, 2006). The former method was tested for a series of transition metal complexes and calculated PNMR shifts were in good agreement with experimental data. Since the experimental NMR spectroscopic data for lanthanide complexes with humic acids are very scarce and incomplete, SAS-IIC switched their efforts to model complexes. Experimental work was devoted to ^{1}H and ^{13}C paramagnetic NMR chemical shifts (D_2O, 25°C, pH=5.5) in lanthanide $Ln(SSA)_3^{3-}$ complexes (Ln = Dy, Ho, Er, Tm, Yb), where SSA = 5-sulfosalicylic acid (Hrobarik et al., 2007; Hrobárik et al., 2007). The lanthanide induced shifts (LIS), as obtained in PNMR study, were surprisingly small (up to 8 ppm on ^{1}H and 59 ppm on ^{13}C for Dy complexes). That made the major goal of the whole study – to extract the information about the complexation of lanthanides/actinides with humic acids from NMR spectra with the help of quantum-chemical calculations more problematic.

Quantum-chemical DFT calculations performed on model complexes of Gd(III) with salicylic acid and 8 water molecules revealed several geometry minima (among them formation of Gd(III) complex with salicylic acid via carboxyl group with mono-dentate coordination was preferable). Based on those data one can conclude that fast exchange of ligand-coordinated water can also occur (Hrobarik et al., 2007; Hrobárik et al., 2007). In addition, to judge about

the accuracy of new quantum-chemical approaches for calculations of NMR parameters of lanthanide complexes, better suited (more rigid) compounds were required. Thus **SAS-IIC** also studied complexes of 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP) with lanthanides, which form rather rigid structures even in solution and for which the structural information is available. The experimental studies were done in cooperation with **FZK-INE**. The experimental NMR data were in excellent accord with the calculated predictions.

To gain more mechanistic understanding, further experimental studies are required with ^{17}O and ^{13}C enriched nuclei of carboxylate groups of the salicylic and humic acids.

Real system analyses* were performed on two different sites, namely *the rock salt overburden at Ruprechtov (Czech Republic) and plastic clays (Boom Clay, Belgium).

Investigation of **NRI-REZ** aimed on the behaviour and influence of immobile organic matter from real site conditions (Ruprechtov site) on U migration. Sedimentary organic matter (SOM) of the Ruprechtov site seems not to be readily available for the degradation processes as indicated by very low groundwater DOC concentrations and small amount of sediment extractable humic substances. Humic substances (HS), i.e. humic acid (HA) and fulvic acid (FA), were separated and purified from the clay sediment using a modified methyl isobutyl ketone (MIBK) and the alkali method (dissolution and precipitation) with a four times higher HA extraction yield using the alkali method (Cervinka *et al.*, 2008). Purified HA (< 5% ash content) extracted from sample NA12 (4.07 wt.% TOC) yielded 2,38 wt.% of OM as insoluble organic material and 0.22 wt.% as humic substances (0.15 wt.% HA + 0.073 wt.% FA) (Havlová *et al.*, 2009). Sample HA-12/3 revealed total proton exchange capacity (PEC) of 7.14 ± 0.66 mmol/g by back titration of excess $Ba(OH)_2$. Dissociation of acidic functional groups was studied by the continuous potentiometric titration procedure (Cervinka *et al.*, 2008).

U(VI) complexation (1.10^{-4} M) with extracted HA (HA-12/3) was studied as a function of HA concentration (1-40 mg/l) in 0.01M $NaClO_4$ at pH 6. The results were evaluated using the Charge Neutralization Model (CNM). Two slightly different approaches were used to stability constant determination: a) only uranyl ion was considered for complexation, b) two uranium species were considered UO_2^{2+} and $(UO_2)_3(OH)^{5+}$. The average stability constant of U(VI) humate complex was established for case a) log K_{cnm} (log ß) = 4.98 ± 0.619 and for case b) log K_{cnm} (log ß) = 4.58 ± 0.645. Generally, with increasing HA content the complexed U fraction increased and the loading capacity (LC) decreased. Determined stability constants K_{cnm} are lower then the literatures values and probably indicate lower potential of HA to complex U in the system. In conclusion, OM at the Ruprechtov site does not directly influence speciation of uranium as sorbing/complexing agent, but indirectly via maintaining reducing conditions and contributing to U(IV) immobilisation in secondary phases (Noseck *et al.*, 2009).

SCK·CEN investigated in batch-type studies the influence of Boom Clay NOM and Aldrich HA on the solubility of Th(IV) and Eu(III) under Boom Clay conditions and the sorption of Th(IV)/Eu(III) onto Boom Clay isolated kerogen. Analysis was performed both after micro-filtration and 30kD ultra-filtration to distinguish between larger colloids (assumed to be immobile) and small dissolved and presumably mobile species.

Equilibrium was approached from under-saturation starting from synthesized Eu(OH)$_3$(s), which during the experiment transformed into EuOHCO$_3$(s), in agreement with thermodynamic expectations. In the absence of NOM, the Eu solution concentrations after micro-filtration exceeded the thermodynamic solubility of EuOHCO$_3$(s) by several orders of magnitude, indicating the presence of inorganic Eu colloids. In the presence of NOM, the Eu solubility increased with increasing NOM concentration as was expected, both after micro- and ultra-filtration. However, both the total Eu concentration in the filtrate for an identical NOM concentration, and the calculated complexation constant of Eu with NOM, were higher for the micro-filtered solutions. Probably, the aforementioned inorganic Eu colloids are the source of these observations. he data sets were modeled using the Nagra/PSI database for solubility, hydrolysis and inorganic aqueous complexation reactions. The increase of Eu in solution with increasing NOM could be modeled using pure complexation reactions between Eu^{3+} and NOM functional groups. Both, a free ligand approach (with electrostatic correction) and the humic ion-binding model VI (Tipping, 1998), which was for the first time successfully introduced into the PhreeqC geochemical code, were tested and provided equally good fits to the data (Liu *et al.*, 2008). Within the study of the influence of NOM on the Eu-sorption onto BC components, the sorption of Eu onto immobile NOM (BC kerogen) has been determined and was found to be very significant. Additional experiments investigating the interaction of Se(IV) with isolated kerogen were performed by KULeuven.

A similar solubility study was performed for tetravalent Th starting from crystalline ThO$_2$(s). Differently to a previous study conducted by Delécaut (2004), an increase in Th concentration is observed with increasing NOM concentration, but only for NOM concentrations < 60 ppm C (in the previous study, experiments were conducted > 50 ppm C). The data set for Th shows a lot of similarities with the one recorded for Eu.

The results of these experiments further demonstrated the significant influence of NOM on the solution speciation of tri- and tetravalent radionuclides under Boom Clay conditions. A quantitative description of the interaction of Eu and Boom Clay NOM for different size fractions is achieved which will helps in the selection of trustworthy maximum mobile concentrations (PA relevant solubility) for trivalent RN for PA. The dependency of the maximum radionuclide solution concentration on the size of the humic molecules has highlighted the need for further studies on the pore-size cut-off under in situ Boom Clay conditions. Currently the indications are that the pore-size cut-off for Boom Clay is *approx.* 300 kD.

The work performed by **KULeuven** focused on the interaction of Se(IV) and Se(VI) with "mobile" Boom Clay NOM. For Boom Clay, the supernatant of a ~ 0.01 M NaHCO$_3$ Boom Clay extract, centrifuged with a cut-off of 35nm was used as a representative sample for mobile BC NOM. For the Gorleben system, a sample of Gorleben groundwater filtered at 0.4μm was used. The main conclusions of this study were:

- Selenate, Se(VI), remains unaltered in solutions containing Boom Clay HS or Gorleben HS.

- Selenite, Se(IV), decreases dramatically, leaving about 5 % of total Se in solution after 224 days. The solution speciation proved that Se was associated with HS (Bruggeman

et al., 2007). In the case of batch experiments with purified HS extracted from Boom Clay, comparable results were found, but Se disappeared more slowly from solution. XANES-EXAFS data collected at the DUBBLE BM26A beamline (ESRF, Grenoble, France) showed for all samples exclusively selenite species in the supernatant and confirmed that Se(IV) is reduced to Se(0) in presence of Boom Clay HS or Gorleben HS.

Another aspect investigated in the field of natural organic matter (NOM) was the interaction with radionuclides in the presence of mineral phases (ternary systems). Knowledge on the interaction of NOM with mineral surfaces and effect of NOM on the solubility and solid phase stability is of fundamental importance to understand the chemical behaviour and migration of radionuclides in the geosphere.

UNICYPRUS has studied the stability and solubility of $UO_2(OH)_2$ and UO_2CO_3 solids as a function of the humic acid concentration in 0.1 M $NaClO_4$, in the pH range from 4 to 9 under normal atmospheric conditions and 100% CO_2 atmosphere, respectively. Furthermore the solid phases under investigation have been prepared in the presence and absence of humic acid and characterized by TGA, ATR-FTIR, XRD, SEM/TEM and solubility measurements. According to the experimental data $UO_2(OH)_2$ and UO_2CO_3 are stable and remain the solubility limiting solid phases even in the presence of increased humic acid concentration in solution (up to 0.5 g/l). However, the presence of humic acid affects texture, water-holding capacity and particle size of the solid phases. Based on the solubility data, the $logK_{sp}$ of the solubility limiting solid phases in humic acid-free solutions has been determined to amount -22.0 ± 0.3 and -13.2 ± 0.3, for $UO_2(OH)_2$ and UO_2CO_3 solids, respectively (Antoniou *et al.*, 2009). With increasing humic acid concentration and decreasing particle size the solubility of the solid phase increases significantly because of micro-solubility effects e.g. $logK_{sp}(UO_2(OH)_2)=$ -21.7 in 0.3 g/l HA and $logK_{sp}(UO_2(OH)_2) < -21.7$ in 0.5 g L^{-1} HA solutions. The stability constant for the $UO_2OH(HA)$ species has been evaluated to amount log β_{111}=15.3 ± 0.5 at pH 6.5 (Kolokassidou and Pashalidis, 2009).

Another aspect in the ternary system was the role of adsorptive fractionation of natural organic matter on mineral phases and its effect on the interaction with radionuclides. **CEA** evidenced adsorptive fractionation comparing UV-Vis and Total Organic Carbon quantification of humic extracts after sorption on α-Al_2O_3; this phenomenon occurs for the same ratio of humic sites to surface sites for two surface humic extracts via the apparent enrichment of aromatic functionality at the α-Al_2O_3 surface. This was further confirmed in Scanning Transmission X-ray Microscopy studies of **FZK-INE**, where the aromatic and phenolic C1s NEXAFS peaks decreases for site ratios in agreement with UV-Vis/TOC results. Finally the change in chemical environment of Eu(III) in contact with previously sorbed NOM was confirmed in Time Resolved laser induced Luminescence Spectroscopy (Claret *et al.*, 2008).

In the case of NOM from a sedimentary origin, Gorleben, the fractionation was evidenced neither in UV-Vis/TOC nor in STXM. This can be due to the lack of chromism effect in UV-Vis, and to the lesser propensity of Gorleben humic acids to form 'large' aggregates. Nevertheless, as for the surface humic extracts, an actual modification of the Eu(III) chemical environment in TRLS was evidenced. Preliminary results with a brown coal humic acid seem to confirm these hypotheses (Brevet *et al.*, 2009).

A key aspect of colloid facilitated transport is the reversibility of radionuclide sorption. However data on this critical aspect is not found frequently in the literature. For natural organic matter we refer to the topical session of the 3rd Annual meeting of IP FUNMIG on *"Influence of organics on radionuclide migration processes"* (Schäfer and Reiller, 2008) and here especially on the contribution of Nick Bryan on *"Metal ion – humic interactions and the importance of kinetics in radionuclide transport (some results from European Union projects over the last 20 years)"*. Some published data on radionuclide inorganic colloid reversibility can be found in the literature focusing on iron phases (Lu *et al.*, 1998) and silicates (Ulrich and Dedueldre, 1993; Geckeis et al., 2004; Missana et al., 2004; Turner et al., 2006; Nagra, in press).

Batch-type studies on the ternary system Febex bentonite colloids; radionuclides ($3.0·10^{-8}$ mol/L Np(V), $1.5·10^{-9}$ mol/L Am(III) and $7.7·10^{-11}$ mol/L Pu(IV)) and fracture filling material (FFM) from the Grimsel granodiorite were performed within FUNMIG by **FZK-INE**. Analysis of Al (bentonite colloid indicator) in the batch experiments show no significant concentration changes over 14 days suggesting a negligible interaction/sorption of bentonite colloids on the FFM surface. Am and Pu(IV) bentonite sorption reversibility data are in line with (Geckeis *et al.*, 2004) for short contact times (t < 14d). Np data shows increasing retardation values with time and FFM surface area indicating a Np(V) => Np(IV) reduction (redox potential -170mV) and preferential FFM association. Both observations, the constant Al concentration together with the decreasing RN concentration suggests a desorption of initially bentonite colloid associated Pu and Am (Huber and Schäfer, to be submitted). Long-term reversibility kinetic studies by Asymmetrical Flow- Field- Flow- Fractionation (AsFFFF) on Th(IV) bentonite colloid association within FUNMIG have revealed very slow reversibility kinetics (3 years observation period). The reasoning for the "irreversible" sorption is still under investigation (Bouby *et al.*, 2009).

Does the presence of microbial activity/biofilms affect the sorption/mobility of radionuclides in far-field systems?

Three partners worked in the field of microbiology to elucidate the effect of microbial activity on radionuclide sorption/mobility. Whereas **FZD** and **UNIUTRECH** focused on studies using lab grown multispecies biofilms or a bacterium (*Shewanella putrefaciens*), **CTH** directly focused on in- situ grown biofilms (MICROBE site, Äspö HRL) containing acetogens, methanogens and sulfate reducers representing therefore a kind of real system analysis.

FZD studied the influence of exopolymeric substances (EPS), a structural component within biofilms, on the actinide speciation and immobilization of U(VI). The stable multi species biofilms was cultivated under air atmosphere and U(VI) was consciously added (10^{-5} and 10^{-6} M). In order to achieve information about the uranium speciation in these biofilms a combination of laser fluorescence spectroscopy and confocal laser scanning microscopy (CLSM) was used. A fluorescence signal in the wavelength range of 415-475 nm was indicative for metastable uranium(V) and a fluorescence signal in the range of 480-560 nm was identified as uranium(VI), clearly showing that redox processes take place within the bio-films. These findings show the different influence of distinct micro-organisms on the migration of uranium and for the first time in vivo by a combined laser fluorescence spectroscopy and CLSM ap-

proach that within a multispecies biofilm some of the U(VI) was reduced to meta-stable U(V) by a one-electron transfer (Grossmann *et al.*, 2007; Krawczyk-Barsch *et al.*, 2008).

For the determination of the redox processes taking place within the biofilms, numerous concentration profiles of oxygen versus biofilm depths were measured in different multi species biofilms. The measurements were done by electrochemical oxygen microsensors with a tip diameter of 10 μm. For the first time it became obviously that the addition of uranium (VI) in ecologically relevant concentrations (1×10^{-5} M and 1×10^{-6} M) to stable multispecies biofilms has induced a fast decrease of the oxygen concentration with increasing biofilm depth, dependent on the uranium concentration. In addition, oxygen consumption rates were calculated from the steady-state O_2 microprofiles measured in the upper layers (<70 μm) of multispecies biofilms, which were fed with uranium (1×10^{-5} M). The results indicate that the addition of uranium (VI) results in an increase of the microbial metabolic activities in the upper biofilm layers. This response is a prompt reaction of the microbes.

The working hypothesis is put forward that aqueous uranium concentrations may trigger higher O_2 consumption rates, leading to larger reducing zones within the biofilms. Consequently, such zones may be responsible for an increased immobilization of uranium from the surrounding bulk solution (Grossmann *et al.*, 2007; Krawczyk-Barsch *et al.*, 2008).

Based on equilibrium thermodynamics, it is expected that U(VI) is reduced to U(IV) and precipitates as uraninite in environments in which microbial iron reduction and sulfate reduction are the prevailing respiratory pathways. The mechanisms and the U reduction rates under the conditions of such environments, however, are relatively unknown, in particular in relation to the reduction of iron oxides which might also serve as sorbents for U(VI).

UNIUTRECH studied the reduction of U(VI) and its phase distribution in batch experiments (pH 7.5 ± 45mM $[CO_3]_{tot}$) with the metal reducing organism *Shewanella putrefaciens* and nanoparticulate hematite as a substrate for microbial iron reduction and sorbent for U(VI). Sorption of U(VI) increased as a consequence of microbial iron reduction. XANES analyses revealed that only a small part of the decrease of dissolved uranium could be caused by U reduction and precipitation of UO_2. The extent of U reduction in all experiments was less than expected from thermodynamic considerations, irrespective whether siderite or magnetite was the dominant secondary iron mineral formed during the experiment. The only partial reduction of U(VI) can be possibly explained by the kinetic hindrance of forming well crystalline uraninite crystals in these systems. Under these conditions surface catalyzed reduction by Fe(II), which was produced by dissimilatory iron reduction, was the dominant pathway for uranium reduction. Reduction kinetics of U(VI) were identical to those in abiotic controls to which soluble Fe(II) was added. Strong adsorption of U(VI) at the hematite surface apparently favored the abiotic pathway by reducing the availability of U(VI) to the bacteria. The reason for the increased sorption of U(VI) to iron oxides in the presence of Fe(II) is still enigmatic but it can be speculated that adsorbed Fe(II) creates additional adsorption sites for U(VI) (Behrends and Van Cappellen, 2005; Behrends et al., 2006; Behrends and Van Cappellen, 2007; Bots and Behrends, 2008).

A second part of the partner **UNIUTRECH** work program focused on the effect of reductive dissolution of iron oxides by S(-II) on uranium mobility in batch experiments. In the experiments sulfide solution was added to lepidocrocite (FeOOH) containing adsorbed U(VI). U(VI) was strongly adsorbed onto lepidocrocite and equilibrium concentrations in solution were typically less than 2 nM. When sulfide solution was added, concentrations of dissolved uranium increased significantly to about 50-450 nM (up to about 5% of the total concentration of U) depending on the amount of uranium in the system and the added amount of sulfide. When dissolved S(-II) concentrations decreased due to the reaction with lepidocrocite and the concomitant formation of FeS, concentrations of dissolve U decreased as well. XANES analysis indicated that uranium became partially reduced to U(IV), which was most emphasized in experiments with high S(-II) addition and pronounced FeS formation. Hence, FeS seems to be the most efficient reductant for U(VI) in the experiments. From complimentary adsorption studies with silica gel it was concluded that the initial release of U upon S(-II) addition was not caused by the formation of soluble uranium complexes but likely due to the replacement of hydroxide groups at the mineral surface with thiol groups (Alexandratos et al., 2007; Alexandratos et al., 2009).

In addition to be potentially involved in reduction of U(VI), dissolved Fe(II) and S(II) can effect the sorption of U(VI) to mineral surfaces. Reduction of U(VI) can be less than expected at redox equilibrium due to the competition with Fe(III) oxides as an electron acceptor and kinetically hindrance of crystalline uraninite formation.

CTH has investigated the effect of biofilms on the sorption properties of ^{234}Th(IV), ^{241}Am(III), ^{60}Co(II) and ^{134}Cs(I) onto mono-minerally apatite and quartz mineral slides as confirmed by XRD, Scanning electron microscopy (SEM), epifluorescence microscopy and energy dispersive X-Ray spectroscopy (EDS). Biofilms have been grown *in-situ* on these slides placed inside a high-pressure flow-cell at the Microbe site (Hallbeck and Pedersen, 2008) at 450 m in the Äspö Hard Rock Laboratory (30 Bar, 17° C, 30 mL/week, 10 weeks) and compared to slides without biofilm. The attained biofilms on the mineral slides contained about $1 \cdot 10^6$ microbes/cm^2 comparable to earlier work with $2 \cdot 10^6$ microbes/cm^2 (Anderson *et al.*, 2006).

The mineral slides were gently transferred from the flow cell to sterile 50 mL polypropylene tubes inside a glove-box with an N$_2$ / H$_2$ (97 / 3 %) atmosphere and a copper catalyst to reduce oxygen. Sampling and analysis of the activity of the solution has been made over time using a liquid scintillation counter or an HPGe detector. The sorption to the mineral slides is analyzed by autoradiography.

From the time resolved investigations (up to 1400h) it can be seen that the presence of biofilms on the mineral slides have an effect on the sorption of Co and Am, whereas for Cs almost no effect could be observed. For Co the sorption both on quartz and apatite increased in the presence of biofilms, whereas other studies on polished Äspö granite slides (Anderson *et al.*, 2007) have observed a decrease of the rock adsorption capacity. These authors interpreted that the presence of biofilms possibly slows down radionuclide diffusion to the rock. For Am only in the apatite case an increase of 20% sorption could be detected, whereas on quartz in the initial stage of the experiments a higher uptake could be observed that decreases and results in a 20% lower sorption compared to the pure quartz slide after 1400h.

Overall, the results of the microbial work conducted within FUNMIG indicate that an effect on the sorption capacity of biofilms depending on the radionuclide oxidation state can be observed but the clear reasoning and process understanding of sorption suppression or enhancement has not been progressed to an extent that it can be accounted for in performance safety assessment models. Furthermore, tools are available to model the bioavailability of chemical substrates of microbial reactions, and the sequential occurrence of terminal electron accepting pathways. While various model approaches are capable to reproduce field data sets from different environmental settings, they are rarely compared in terms of performance and predictive ability (Thullner *et al.*, 2007). Most approaches incorporate simplifications or empirical rate laws, which limit their range of application. Although in the field of microbial reduction of radionuclides rate laws from laboratory experiments are available, the extrapolation of these rate constants to field conditions are difficult and interferences by other redox couples (inhibitory terms) are not completely clear. Thus, there remains a need for further development of more general, process-based modelling concepts to represent microbial mediated reactive processes after FUNMIG.

Conclusion and prospectives

- *Thermodynamic data*. The works done within the FUNMIG framework has permitted to complement available data. The thermodynamic data for trivalent actinide-carbonate complexes are important as they now permit temperature extrapolation. The sulphate data confirms the value selected (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003), which relied on a limited set of data. Regarding the phosphate system, the existence of complexes with tetravalent actinides is confirmed, but extrapolation to zero ionic strength cannot yet be provided. Also, a stress shall be put on the fact that all the stable stoichiometries should be known in order to propose a thorough speciation calculation; in the future the clarification of the ion-pair complexes implying alkaline-earth should receive interest. Finally, concerning the awkward silicate system, the importance of oligomeric species, probably of colloidal dimension, either for trivalent and tetravalent actinides is confirmed, as is the influence of kinetics for the formation of these colloidal phases. This latter remark permits to make a link with the formation of polysilicilic colloids done concerning the generation and stability of colloids generated in the granite groundwater bentonite porewater mixing zone (KUNZE et al., 2008b).

- *Retention modelling*. In general, the results on radionuclide retention obtained in the framework of FUNMIG gave a consistent picture of the observed systems. On comparable systems, FUNMIG partners were able to model the experimental results with a limited set of mechanistic models and interaction data. The influence of the competition from simple inorganic ligands, *i.e.*, CO_3^{2-}, and $HSiO_3^-$, and between metals, could be accounted for. Most important, the applicability of a bottom-up approach is now validated. Spectroscopic studies have mostly supported the modelling propositions. The influence of simple organics seems to be limited to weak ternary complexes. The influence of natural organic matter is much more complicated, and account for the de-

scription of its heterogeneity is mandatory for accurate modelling, and operational models have been proposed. Nevertheless, there is still a need for the description of conformation/composition evolution of natural organic matter during sorption on surfaces.

- *Solid solution.* The main outcome is that solid solution formation is the final evolution of sorption. A mathematical formalism was proposed, which make a link between sorption and the matrix formation, considering one end member as the solute and the other as the solvent. The formation of solid solution either from co-precipitation ($Np/CaCO_3$) or from evolution of sorption studies ($Cm/CaCO_3$) demonstrated this evolution, as well as the redox processes in the case of Se(IV)/pyrite system.

- *Redox processes.* Concerning redox buffering systems in the Swedish site investigation program, sulphur redox couples and the measured Eh show a good agreement. According to the mineralogy of the Opalinus Clay, its Eh is controlled by the sulphate/pyrite or pyrite/Fe(III) couples. Similar results were found in the Callovo-Oxfordian argillite and in the Boom Clay formation, where siderite and pyrite are considered as redox buffering phases. New data on redox speciation in the Boom Clay have further proofed that U(IV) is the stable redox state and the long-term Se speciation is expected to be governed by reduced Se phases. The exact nature of these Se phases, however, is still matter of ongoing research. The open issues remaining concerning redox processes as i.e. (a) application and modification of existing methods and development of new methods for determination of redox state in relevant systems, (b) quantification and development of process understanding on redox buffer capacity and kinetics of response to redox perturbations, and (c) process understanding of radionuclide redox states (equilibrium/disequilibrium). These topics have already been identified in the last project year of IP FUNMIG and are currently tackled in the EC 7th framework collaborative project CP ReCosy (www.recosy.eu).

- *Colloid stability and bentonite erosion.* Based on the bentonite derived colloid stability investigations and bentonite erosion experiments within FUNMIG, a good knowledge has been gained on the stability controlling geochemical parameters. The determined critical coagulation concentration (CCC) for $CaCl_2$ electrolyte with a solution pH independent Ca-CCC of 1 mmol·L^{-1} gives further confidence in the geosphere safety function indicator criteria $[Me^{2+}] > 1mM$ given in SR-Can (SKB, 2006). The addition of 1 mg·L^{-1} DOC in form of fulvic acids increases the Ca/FA-CCC to 2 mmol·L^{-1}, pointing to a potential influence of organics in crystalline environments. In the case of NaCl background electrolyte a pH dependent Na-CCC could be determined. A huge parameter screening has been performed concerning the erosion of compacted bentonite and a thorough evaluation of the data concerning i.e. erosion rates is now needed. Furthermore, the integration of these results into currently existing models or the improvement of these models based on the new data available should be a focus of future research programs in this field.

- *Colloid mobility and radionuclide association.* The mobility of low molecular weight compounds (< 500Da) and absence of colloidal phases has been shown by porewater analysis in indurated clays (Callovo-Oxfordian argillite and Opalinus Clay). In the

plastic Boom Clay formation a colloid size comparison between suspended material and real Boom Clay porewater has shown a pore-size cut-off ~300kDa. Taking into account the dependency of the maximum radionuclide solution concentration as a function of the humic molecule size clearly highlight the need for further studies linking pore geometry and connectivity to colloid mobility. For crystalline far-field systems the colloid mobility is clearly dependent on the flow path heterogeneity and a residence time dependent colloid recovery has been found even under "unfavourable" colloid attachment conditions. The results obtained within FUNMIG indicate that local calcium concentration variations along the flow path might be a key parameter to create areas of attachment beside a potential filtration due to the flow path geometry. Concerning the interaction of radionuclides with bentonite, data generated within FUNMIG shows reversibility kinetics, strongly dependent on the radionuclide and oxidation state investigated. A mechanistic understanding of the reasons for the observed binding strength differences are still pending and need to be addressed in future research.

- *Influence of microbial activity/biofilms.* The results of the microbial work conducted within FUNMIG indicate that an effect on the RN mineral sorption capacity of biofilms can be observed but the clear process understanding of sorption suppression or enhancement has not been progressed to an extent that it can be accounted for in performance safety assessment models. Although rate laws of microbial reduction of radionuclides from laboratory experiments are available, extrapolation to field conditions is difficult and interferences by other redox couples (inhibitory terms) are not completely clear. There remains a need for further development of more general, process-based modelling concepts to represent microbial mediated reactive processes.

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RADIONUCLIDE MIGRATION IN CLAY-RICH HOST FORMATIONS: PROCESS UNDERSTANDING, INTEGRATION AND UP-SCALING FOR SAFETY CASE USE (RTDC3)

Introduction

Deep underground disposal in low permeability 'clayrock' formations has been put forward by Belgium, Switzerland and France as the most appropriate solution for managing the high and intermediate level, long half life radioactive wastes generated by their respective nuclear energy programs. These concepts rely on various favourable characteristics of the host rock formation to insure that release of radio nuclides (RN) to the biosphere will always remain at levels well below those capable of potentially affecting human health. Stakeholder confidence in these projects is based in large part on the capacity of the corresponding waste management organizations (WMO: i.e. ONDRAF/NIRAS (BE), Nagra (CH), Andra (FR)) to demonstrate that the models used to predict radionuclide migration through the respective clayrock formations (Boom Clay, Opalinus Clay, Callovo-Oxfordian (COx)) are based on a scientifically sound understanding of all contributing phenomena. WMO publish 'Safety Case' (SC) reports (1, 2, 3) describing, among many other aspects, the state of knowledge regarding RN migration phenomena in the geological barrier (GB, i.e. the host rock formation) and the results of Performance Assessment (PA) simulations of RN migration towards the biosphere. While each of these SC has its own specificities, they reveal many common points concerning the state of knowledge, and remaining questions, regarding understanding and modelling RN migration in the respective GB. RTDC3 was conceived based on the state of knowledge in 2004 regarding RN migration in clayrocks and analogous compacted clay mineral materials, the essential aspects of which are presented in the three SC. This state-of-knowledge led to formulation of several 'key questions':

- Do we have a sound theoretical basis for describing RN speciation in the porosity of highly-compacted clay materials and clayrocks, in particular the distribution of total RN mass between dissolved and sorbed species?
- Do we have a coherent conceptual model describing diffusion-driven transport of anionic and cationic RN in clayrocks?
- Do we have credible strategies / methods for carrying out the up-scaling needed to obtain representative parameter values usable for performance assessment simulations of a clayrock geological barrier system, in particular taking into account the effects of spatial heterogeneity of rock physical-chemical properties.

The goal of RTDC3 was to improve our capacity to provide positive answers to these questions for use in upcoming clayrock safety cases.

At the most simplistic level, most of the research carried out in RTDC3 can be structured around conceptual models based on (i) Fick's first and second laws for diffusive driven transport, adapted to take into account the effect of reversible sorption of RN on clayrock surfaces, and (ii) consideration of whether or not the same set of Fick's law parameter values can be used to represent RN migration at all space-time scales considered in clayrock safety cases ($< 10^{-3}$ m to $> 10^2$ m).

- *Fick's first law (for steady state RN flux):* $J = -D_e \frac{dC}{dx}$ with $D_e = D_0 \left(\frac{\delta}{\tau^2}\right) \omega = D_p \omega$ where J: flux (mol·s^{-1}·m^{-2}); D_e, D_0, D_p: 'effective', 'free solution', 'pore' diffusion coefficients (m^2·s^{-1}) respectively; C: concentration (mol·m^{-3}); x: distance (m); δ/τ^2: term representing the effects of pore space geometry on RN diffusion (dimensionless); ω: porosity accessible for RN diffusion (dimensionless).
- *Fick's second law (time dependence of RN mass transfer):* $\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2}$ with $D_a = \frac{D_e}{(\omega + \rho K_d)}$ where D_a: 'apparent' diffusion coefficient (m^2·s^{-1}); ρ: rock density (kg·m^{-3}) and K_d: coefficient representing the partitioning of total RN mass present at position x between mobile dissolved species and immobilized sorbed species (m^3·kg).

Most of the work carried out in RTDC3 was focused on improving conceptual models for diffusion driven transport for two classes of RN of key importance for SC:

- *Non or very weakly sorbing RN*, principally those which are anions (^{36}Cl$^-$, ^{129}I$^-$…). Here the objective was to improve understanding of terms in Fick's 1st law (porosity organization, anion exclusion and mobility in clay domains, effects of mineral composition on porosity…). These aspects are discussed below in sections §2 and §3;
- *Moderately and highly sorbing RN*, principally in cationic form (^{135}Cs$^+$, actinides, analogue elements,…). Here the focus was on the partitioning term in Fick's 2nd law, but interesting information concerning mass transport was also obtained. Sections §2 and §4 describe these aspects.

RTDC3 involved the collaborative and complementary efforts of research teams from 24 different organizations (ANDRA(FR), ARMINES(FR), BRGM(FR), CEA(FR), CIEMAT(ES), ERM(FR), FZK-INE(DE), GRS(DE), II-CRC(HU), NAGRA(CH), ONDRAF/NIRAS(BE), PSI(CH), SCK•CEN(BE), UDC(ES), UNIV-BERNE(CH), UJF(FR), LPEC(FR), LMM(FR), AIED(FR)) including research institutes, laboratories, SME, national radwaste management agencies and four Associated Groups (Hydr'asa(FR), La Trobe University(AUS), CEREGE(FR), UnivAvignon(FR)).

Characterizing and understanding clayrock properties influencing RN migration

Clayrock composition and structure largely govern the migration characteristics for any given RN species. This rather blunt affirmation is in fact the working hypothesis for a significant part of the research carried out in RTDC3, which is why it merits explanation, in particular in relation to the two situations studied in detail in RTDC3: diffusion-driven transport of anionic RN species and retardation-by-sorption of cationic RN species. First, what do we mean by composition and structure? Composition includes both the inorganic (mineralogical) and organic compounds and phases making up the rock solid matrix and, most importantly, the speciation of the pore solution and contacting mineral surfaces. Pore solution and mineral surface speciation will largely determine RN dissolved speciation (e.g. predominance of anionic or cationic forms), solid-solution partitioning of RN mass (K_d) and the intensity of electrostatic field effects on the solution volume accessible to anionic RN. As for structure, it refers to the organization, geometry and dimensions of the connected porosity of a given clayrock, and its relation to contacting minerals. Porosity structure, taken together with the electrostatic field effects on anions mentioned above, will determine the accessible porosity and diffusion path 'tortuosity' for cationic and anionic RN species. In addition, since current knowledge indicates that the permanently negatively charged swelling clay minerals present in clayrocks play a key role in determining RN migration behaviour, the structure and composition of the porosity associated with the clay mineral fraction is expected to be of prime importance. In addition, clayrock formation databases (1, 2, 3) generally show that values measured for a given composition or structure parameter vary for rock samples taken from different positions within the formation, i.e. the formation is not an homogeneous entity as regards parameters which might affect RN migration.

Research carried out in RTDC3 focused on enhancing understanding of clayrock structure and composition at the various scales and spatial resolutions which will be needed for interpreting, integrating and up-scaling the results of studies on RN diffusion and sorption described in subsequent sections, i.e.

- at the formation, i.e. Geological Barrier System (GBS), scale ($\sim 10^2$ m) with a resolution of $\sim 10^{-1}$ m,
- at the 'macroscopic' scale (10^{-1} to 10^{-2} m), typical of that associated with lab and in-situ determinations of RN K_d (or R) and D_e parameters, with resolutions ranging down to $\sim 10^{-5}$ m,
- at the 'mesoscopic' scale ($\sim 10^{-3}$ to 10^{-4} m), characteristic of that of diffusion profiles for high K_d RN (cf. §4.2), with resolutions down to 10^{-6} m.

All scales were studied on the COx formation in order to provide a common 'safety case' context for inter-relating and up-scaling study results. Clayrock samples from all four clayrock formations (Opalinus Clay, Boom Clay, Callovo-Oxfordian, Boda Claystone (HU)) were also characterized in terms of mineralogy, structure, porewater composition and water states at the *macroscopic scale* in order to identify key common characteristics and essential differences likely to impact RN migration (*CIEMAT, ERM*).

Geological formation scale (10^2 – 10^3 m) results

Clayrock safety cases generally present a detailed geological model of the host formation emphasizing its stratigraphic organization and corresponding (vertical) variability in mineralogy. On the other hand, the PA calculations carried out in these same safety cases generally assume that the entire formation has uniform characteristics as regards RN migration, i.e. single values for D_e, K_d, etc. selected based on the results of measurements on many rock samples taken throughout the formation. While this process is robust from a PA standpoint, as demonstrated by an analysis carried out by *SCK•CEN* (cf. §3.4), safety case confidence could be enhanced if a method (tool) existed for evaluating the effect of formation-scale geological variability on the GBS representation in Performance Assessment. The first step in this process was achieved by research carried out by Andra which used signal profiles obtained by high resolution electrical logging of three boreholes traversing the COx to generate profiles of rock carbonate mineral concentrations with sub-cm scale resolution. Geostatistical methods were then used to divide the formation profile into three mineralogical classes based on carbonate content (which is inversely correlated with clay mineral content and porosity). This information was subsequently used to define the meshing of a RN transport model, each class being assigned different values for RN migration parameters (D_e, K_d) based on the results of measurements on representative samples of differing carbonate content (cf. §3.4 and §4.2 for further details). Another RTDC3 action along this same line, i.e. being able to link information concerning the spatial variability of rock characteristics at the formation scale with possible effects on RN migration, was development of a database for the COx formation containing all data regarding parameters likely to influence directly or indirectly RN migration (*BRGM*).

Macroscopic scale (mm-dm) results

The vast majority of the RN migration-related data (rock composition, structure, K_d, D_e, etc.) presented in safety cases are based on measurements made on cm-dm scale rock volumes. There are excellent reasons for this, among which are practical upper limitations on the sample dimensions which can be accommodated in the space-time framework laboratory experiments and lower limits imposed by the need to make measurements on volumes of rock of sufficient size to guarantee that the values measured are sufficiently representative of 'real rock' complexity to be credible for safety case use. Field experiments in underground laboratories complement such measurement. They apply to similar or slightly larger scales and allow a verification of laboratory results under chemically and mechanically more representative in-situ conditions. Several actions in RTDC3 were devoted to enhancing understanding of clayrock composition and structure at this important scale:

- A detailed analysis (*CIEMAT*) of porewater composition and water states in the above mentioned four different clayrocks led to development of a common conceptual model for the distribution and composition of the different types of water (external and internal water) present in highly compacted clayrocks, main inputs needed for constructing models for water-rock interaction, RN speciation and solute transport. The resulting comparative database (PID3.2.1) clearly illustrates the main commonalities and differences of the four rock types (cf. example in Figure 1).

- Investigation of processes controlling the redox state of COx clayrock pore waters (*BRGM, LPEC, La Trobe University*) show that the upper limit of dissolved Fe(II) in pore water must be less than 1/100 of the Ca concentration ($< 10^{-4}$ mol/L). This concentration is certainly linked to the solubility of an identified siderite like mineral (sideroplesite) whose solubility has been estimated. At last clay-associated Fe(II) has been proved to be a highly reactive, redox determining component in the COX, a result in line with the demonstrated reactivity of Fe(II) sorbed onto clay minerals in laboratory systems (see below).

- Macroscopic-scale clayrock volumes can exhibit significant internal variability in terms of structure, mineral composition and porosity, all of which are capable of affecting RN migration. Samples from the four clayrock formations were characterized (*ERM, Hydr'asa, CEA*) using a wide range of methods in order to visualize and map (2D, 3D) the spatial distribution of porosity, mineralogy and structural discontinuities (pyrite inclusions…) with resolutions reaching down to the μm scale. The results of the most complete characterization, that carried out on a single dm-sized COx clayrock sample taken from a diffusion experiment carried out in the Bure URL, were used along with results of studies at the formation scale, mesoscopic and microscopic scales, as the basis for the conceptual model used to integrate and up-scale many of the research results of RTDC3.

- Results from a field experiment in the Mont Terri underground research laboratory were used to validate laboratory results for mobile and sorbing tracers.
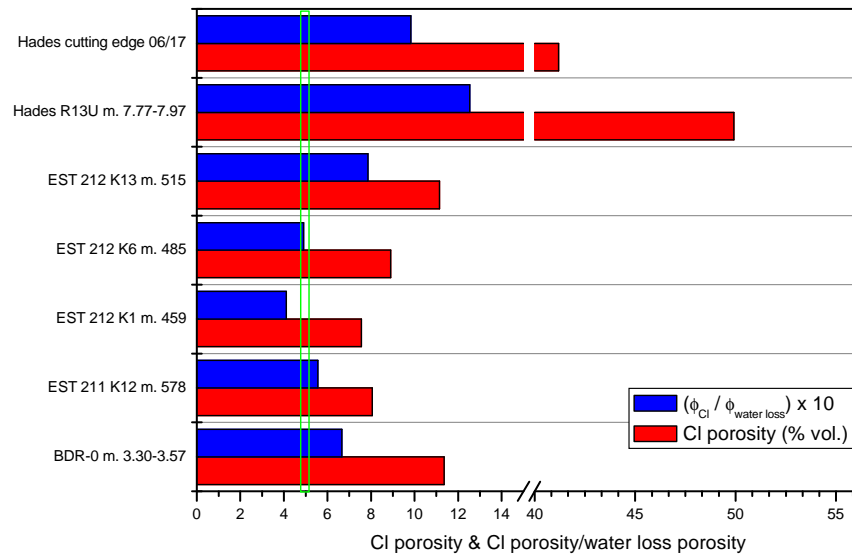
Figure 2: *Chloride porosity and $\phi_{Cl}/\phi_{water\,loss}$ porosity ratio in core samples from the Boom Clay, Callovo-Oxfordian and Opalinus Clay formations*

Mesoscopic scale (< mm) results

An important objective of RTDC3 research was to improve understanding of how clayrock composition and structure influence RN diffusion (mainly for anions) and retention by sorption (mainly for cations). If we set aside the possible effects of discontinuities (pyrite inclusions, fissures…) on RN transport measurements carried out at the macroscopic scale, and if we assume the clay mineral fraction and its associated porosity to be of prime importance, it seems reasonable to expect that a detailed understanding of the latter's organization and connectivity could help in reaching this objective. A major effort was consecrated by *Hydr'asa,*

ERM, Andra and *CEA* on developing and applying methods for quantifying and analyzing the form and organization of clay, quartz, carbonate and other mineral grains in sub-mm volumes of clayrock with sub μm resolution (cf. Figure 2). Two main results were achieved:

- The results of measurements and statistical analysis of the form factors (length to width ratio) and orientations relative to the sedimentation plane of non porous quartz and carbonate mineral grains which show that both grain populations have elongated form factors, are preferentially oriented parallel to the sedimentation plane and that adjacent grains are always separated by the clay matrix. Taken together, these results show that the COx clayrock exhibits two domains of mineral particle organization: 1) the spatial arrangement of clay particles, at the μm scale, inside the clay matrix and 2) the spatial organization of the contiguous clay matrix, at the <mm scale, determined mainly by the organization of the non porous carbonate and quartz grains.
- The building of 3D representations of the pore space and mineral organization in the rock samples used for diffusion and retention experiments. These representations are the basis for defining the meshing, and associated apparent diffusivity values, for the numerical model used to predict and interpret diffusion/retention experimental results (cf. §3.3 and 4.2).
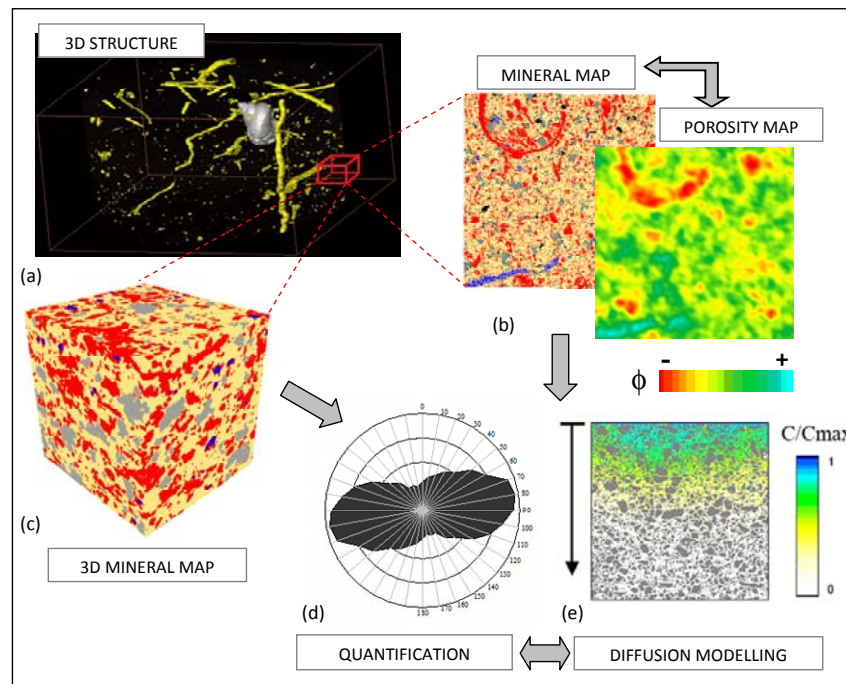
Figure 1: *Methodology used to characterize clayrocks at macroscopic and mesoscopic scales (a) 3D spatial distribution of structure (yellow : pyrite inclusions, white : fossil) acquired for a cm^3 scale sample by X-ray tomography (b) comparison between porosity (^{3}H-MMA method) and mineral (SEM) maps (c) 3D mineral spatial distribution (red: carbonates, grey: quartz, blue: pyrite, yellow: clay matrix) acquired for a sub mm scale sample by synchrotron X-ray tomography (d) statistical analysis of mineral distributions (ex: orientation rose of carbonate grains) (e) diffusion modelling computed from 2D/ 3D mineral and porosity distribution using TDD method.*

Diffusion of 'non-sorbing' RN in clayrocks

The overall objective of RTDC3 research in this domain is to develop a coherent conceptual model for diffusion of non-sorbing tracers (^{36}Cl, ^{129}I, HTO...) in clayrocks at all space-time scales. Very extensive databases have been developed (1, 2, 3) regarding anion and HTO diffusion in intact rock samples at the ~cm scale in order to provide the safety case with a sound basis for evaluating anionic RN diffusion in the GBS. The important role played by this scale in safety cases, and its potential utility in developing links between the geological model of mineralogical variability and diffusion, were the impetus for several studies carried out in RTDC3. The majority of RTC3's efforts were, however, focused on improving understanding of diffusion-governing phenomena operating at under- and over-lying scales.

Diffusion in 'clay mineral domains'

All of the clayrocks studied in Funmig contain significant amounts of permanently negatively charged illitic- and illite/smectite mixed layer type clay minerals. It is known that electrostatic repulsion results in total exclusion of anions from the volume contained within the clay layer stacks, and reduces their concentration in the pore solution near external clay surfaces. As a result, anions can diffuse only in the connected porosity outside the clay interlayer volume, and it is expected that anion repulsion will also affect the amount and 'geometry' of this 'external' porosity accessible for anion diffusion. Cations and neutral species (HTO), on the other hand, are able to access and diffuse in, all of the pore volume. RTDC3 consecrated a significant effort toward increasing understanding and modelling equilibrium mass distribution (accessible porosities) and mobility (diffusion) of anions, HTO (and cations) in *clay mineral domains at the microscopic-scale (~µm)*, and testing the models against experimental data measured on a compacted pure clay mineral (montmorillonite) synthesized and characterized specifically for project needs (*LMPC*).

From a theoretical and modelling perspective, the challenge is to describe and model, in a scientifically rigorous fashion, diffusion of anions, cations and HTO molecules in compacted clay materials as a function of material density (which affects the pore size distribution) and solution composition (cation charge, ionic strength…). The main outcomes and advances in understanding along this line are summarized below:

- Results of molecular dynamics simulations of a montmorillonite in contact with a NaCl solution (*BRGM*, AIED) were used to estimate reasonable bounds for the anion exclusion volume, distance of water structuring and cation partitioning between the diffuse layer and the sorbed plane in the system. Molecular dynamics results on anion exclusion compares well with experimental data obtained on Na-montmorillonite suspensions, enabling to calibrate a macroscopic model for anion exclusion. This model has been extended to compacted systems showing that it is possible to predict anion exclusion volume and anion diffusion coefficients from montmorillonite partial dry density and ionic strength only for experiments carried out in NaCl salts background (Figure 3). Moreover, the H_2O data were consistent with ^{1}H-NMR measurements (*LAIEM*) on the synthetic clay mineral. It is

then possible to build a dual porosity model reproducing transport properties of water and anions. The calculated ion distributions were then used to 'calibrate' the electrical double layer parameters of a surface complexation model contained in a code capable of coupling geochemical speciation and diffusion (PHREEQC2 v2.14). This code was then used to calculate diffusion of HTO, anions and cations through compacted montmorillonite under different conditions (density, solution composition). Comparison of model results with existing data sets show that it is able to simulate the principal observed characteristics. This model must be extended to divalent cation salt backgrounds in order tosimulate the experimental data obtained in Funmig (see below).

- Two new theoretical (and corresponding numerical) models of anion, cation and HTO diffusion in compacted clay domains were developed respectively by *Armines* and *CEA*. The distinctive feature of the *Armine* model is that it proposes that the hydration water associated with cations present in clay interlayers be treated as part of the solid phase, i.e. not as a constitutive part of overall porosity. This paradigm change allows a single value to be used for the porosity accessible for anion, cation and HTO diffusion, with only the latter two molecules being able to exchange mass with the pools of cation and hydration water present in the interlayer (solid). This model, which has many similarities with that developed by *BRGM*, is able to satisfactorily model data sets of anion, cation and HTO diffusion over a wide range of degree of compaction of the clayey material (dry densities).

  The model developed by *CEA* takes a completely different approach, representing the compacted clay in terms of an ordered arrangement of charged, non porous, several nanometre-thick rectangular entities, immersed in a continuous dielectric medium (the pore solution). The rectangles represent the external surfaces (basal and edge) of real clay particles, i.e. the interlayer volume is not considered. Changes in pore size distribution as a function of density is taken into consideration by changing the particle population spacing. It is worth noting that this is the only model approach, at this scale, which yields different values for D_e perpendicular or parallel to particle orientation, i.e. this model allows introduction of diffusion anisotropy in the clay domains. Model simulation results are generally coherent with experimental observations of diffusion in compacted clays; e.g. D_e and accessible porosity values for anions decrease with ionic strength, D_e for the alkaline elements increase from Na to Cs. Effective diffusion coefficients for monovalent and divalent anions measured in illite compacted to different densitiesand for various ionic strengths (from 0.01 to 0.3 M NaCl or $KClO_4$) are in good agreement with those calculated using the model.

- Experimental data sets, for comparison with the blind predictions made using the theoretical models described above, are being generated by carrying out diffusion experiments with an anion (^{36}Cl), HTO and mono and divalent cations (^{22}Na, ^{45}Ca) on compacted synthetic montmorillonite samples, as a function of ionic strength (*CEA*). While these measurements are not completely finished at this time, initial results show for example that, as expected, (i) anion exclusion increases with decreasing ionic strength and there is no impact of ionic strength on HTO diffusion and (ii) ^{45}Ca diffusion is enhanced by and strongly depends on ionic strength (due to reduced Ca^{2+} sorption due to competition of Mg^{2+} for ion exchange sites).
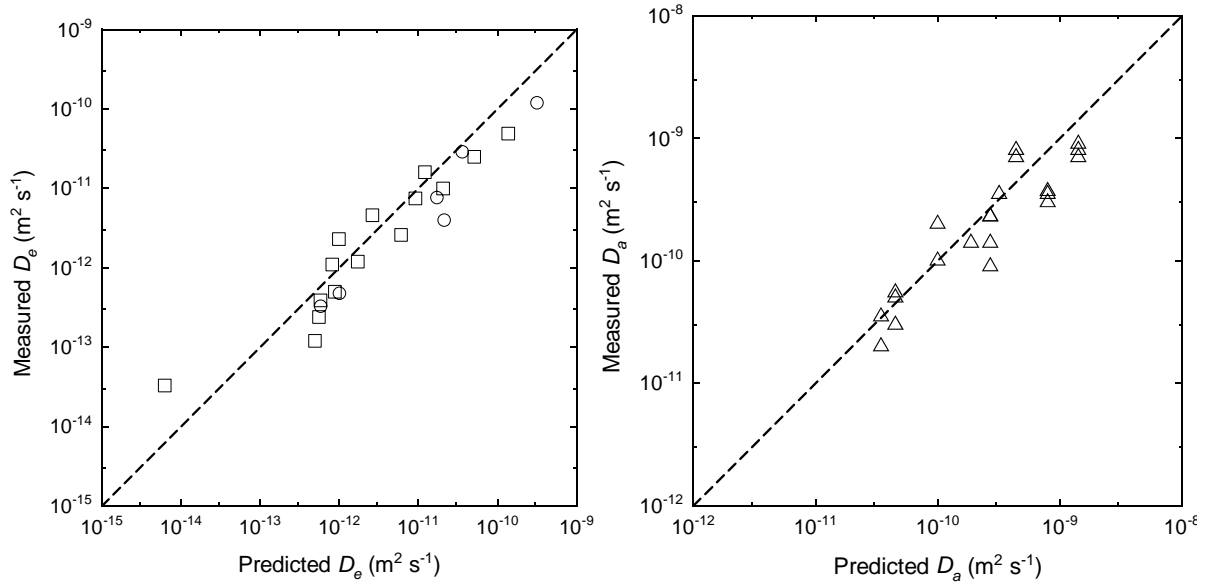
Figure 3. Comparison of the predicted and experimental effective diffusive coefficients (left figure. Circles: data from Van Loon et al., 2007; squares: data from Muurinen et al., 1989) or apparent diffusion coefficient (right figure. Triangles: data from Molera et al., 2003). The dashed line represents the 1:1 relationship.

Diffusion in mesoscopic scale (~mm) clayrock volumes

Considerable effort was invested in improving understanding of how clayrock mineral-porosity organization can affect diffusion of mobile (non sorbing) RN since this seems to be a highly promising approach for establishing links between diffusion properties and observed variations in rock mineralogy. The working hypothesis, based on the observations presented in §2.3 (figure 2), was that the spatial organization of the contiguous clay matrix porosity could affect (i) the value of the apparent diffusion coefficient (D_a) for non sorbing tracers by modifying diffusion path tortuosity and (ii) the anisotropy of D_a values measured in directions perpendicular or parallel to the sedimentation planes. The study, carried out by Hydr'asa/Andra, was based on simulations of anion diffusion in numerical models of the 2D and 3D mineral-porosity distributions quantified in §2.3. These simulations were carried out using the Time Domain Diffusion (TDD) method which simulates diffusion by tracking the 'random walk' of anion particles in the 2D or 3D pixel grids based on the digitized images of mineral grain organization. Each grid pixel is characterized by its porosity (a constant value for all clay pixels, null for all others) and an isotropic D_a value (for the clay pixels). The effects of grain organization were quantified by performing simulations of diffusion, in rock volumes having different compositions, in directions parallel and perpendicular to the sedimentation surface plane. The results show that (i) D_a perpendicular to the sedimentation surface decreases with increasing fraction of non porous minerals and (ii) that the elongated shape of carbonate and quartz grains and their orientation relative to the sedimentation surface introduce geometrical anisotropy in the organization of the connected porosity at the mesoscopic scale, which in turn induces diffusion anisotropy at a larger scale. The anisotropy of diffusion, which is observed experimentally, probably has two components: inside and outside the clay matrix. The global diffusion coefficient is related to the clay matrix diffusion

coefficient by a geometric factor G_m which is specific to the clay matrix geometry. The clay matrix diffusion coefficient is itself related to free diffusion of solute and a geometric factor G_{cp} related to clay particles (as described by the models presented in §3.1).

Diffusion at the macroscopic scale (cm-dm)

Several premises are behind diffusion measurements made at the ~cm scale, among the most important being that (i) they are made on samples representative of the 'average' properties (mineralogical composition, porosity characteristics, etc.) of the rock unit from which they were taken and (ii) the measured parameter values (D_e, D_a(perpendicular to bedding); D_e, D_a(parallel), accessible porosity, mineralogy, etc.) integrate, in a representative fashion, the effects on these parameters of local variations in rock properties at smaller scales. One of the working hypotheses guiding the RTDC3 experimental program at this scale was that the major characteristics of anion diffusion should be coherent with, and explainable by, phenomena which were studied and modelled at the smaller, mesoscopic scale (§3.2), in particular the role of non porous mineral grain organization in determining diffusion anisotropy, i.e. D_a(bedding parallel) > D_a(bedding perpendicular), and the reduction in D_e with increasing proportion of non porous minerals. RTDC3 efforts were therefore focused on (i) improving the capacity to measure, model and quantify the effects of rock heterogeneity and bedding on diffusion at the cm scale and (ii) evaluating the effect of rock mineralogy on diffusion, in part by comparing diffusion in samples from different clayrock formations.

Detailed analyses of HTO diffusion in dm-scale volumes of Opalinus Clay and Callovo-Oxfordian clayrock were carried out by *CIEMAT* using a novel technique consisting of placing a solid source of radioactive anionic and HTO tracers at the centre of a pluri-dm sized clayrock cylinder. 3D tracer distribution maps were obtained at the end of the experiment by coring. Numerical modelling by *UDC* using a code capable of considering bedding plane relative anisotropy was used to (i) carry out sensitivity analyses to identify relevant diffusion and retention parameters and (ii) determine best estimates for parameter values by solving the inverse problem. Results for the Callovo-Oxfordian clayrock give lowest error values of $4 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$ and $2.23 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$ for D_e(bedding parallel) and D_e(bedding perpendicular) respectively, which leads to a diffusion anisotropy ratio of 1.8 (Figure 4). This value is of the same order, but greater than, that calculated by the TDD method (§3.2) which could be due to the fact that the TDD model does not consider possible anisotropy within the clay domains, i.e. at the scale of the models presented in §3.1. Results for HTO diffusion in the Opalinus Clay give higher anisotropy ratios, of the order of 5, which might indicate a higher degree of preferential orientation of clay particles than for the Callovo-Oxfordian formation.
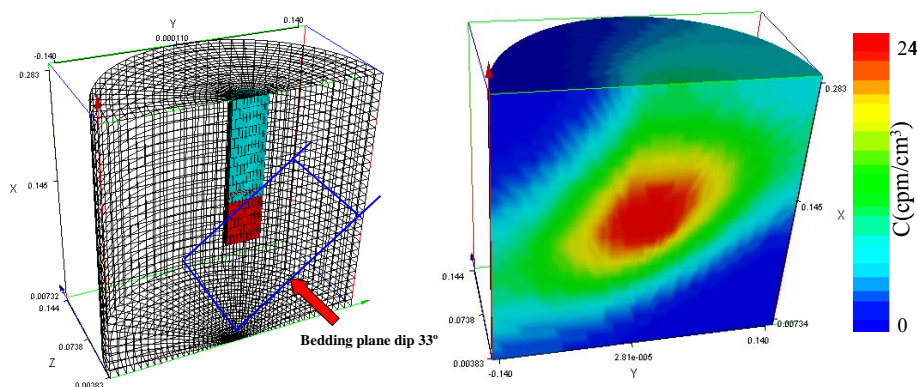
Figure 4: Grid used in PORFLOW calculations (left). HTO results obtained with the best set of diffusion coefficient parallel and perpendicular to the bedding (right).

At Mont Terri rock laboratory a large scale in situ experiment (DR) has been launched to investigate diffusion of non-sorbing to strongly sorbing nuclides. Combined laboratory and large scale in-situ migration studies could show that diffusion is the main transport process for radionuclides in Opalinus Clay [Tevissen et al., 2003]. Retention of radionuclides, on the other hand, has been predominantly investigated by batch sorption measurements. The objectives are threefold: (i) to obtain diffusion and retention data for moderately and strongly sorbing tracers, (ii) to improve diffusion data for rock anisotropy and (iii) to quantify effects of the borehole-disturbed zone for non-reactive tracers. The design has been validated by diffusion tests with non-sorbing and sorbing tracers [Palut et al., 2003; Van Loon et al., 2004; Wersin et al., 2008]. The injected tracers were tritium, I, Br, ^{22}Na, ^{85}Sr, Cs, ^{137}Cs, ^{133}Ba, ^{60}Co, ^{152}Eu, and ^{75}Se (planned). These tracers were added as a pulse to the fluid circulating in a packer system allowing the tracer to diffuse into the clay formation. Funmig allowed an extensive modelling exercise accompanying this experiment in which four distinct reactive transport models from four groups (*PSI, UDC, CSIC, GRS*) are being benchmarked [e.g., Gimmi, 2007; 2008; PID3.3.2].

Effective diffusion coefficients 'bedding perpendicular' were measured (*CEA*) for Cl$^-$ and HTO on a set of Callovo-Oxfordian rock samples having carbonate contents covering the entire observed range in the formation. Rocks having extreme, and relatively rare, high carbonate contents were of particular interest since they will necessarily have very low fractions of the clay minerals governing RN diffusion (and sorption, cf. §4.2). The results for D_e(Cl) show a 'threshold' effect, with D_e(Cl) remaining in the normal range of values for the formation (5.10^{-12} m^2.s^{-1}) for carbonate fractions below ~35 wt%, then falling off progressively to roughly 40% of this value as carbonate increases to 70 wt%. This tendency is similar to that predicted by TDD modelling of the effect of increasing the fraction of non porous grains at the mesoscopic scale (§3.2).

Results of a large-scale, long-term (~10 year) in-situ diffusion test running in the HADES URL (Boom Clay, BE) with ^{14}C-labelled natural organic matter were analyzed, along with

results from small-scale migration tests, in order to evaluate whether the latter could be used to predict the former, i.e. whether small-scale, short-term results for this retarded species could be up-scaled directly. The lab test results were interpreted with the classical diffusion-advection approach, yielding migration parameters which reasonably described the experimental data, without taking colloidal transport into account. The lab-derived parameters were able represent the in-situ experiment, with only a small modification of the diffusion coefficient. Inclusion of a colloid filtration term (attachment and detachment kinetics) in the modelling improved the simulation. A very good match with the experimental data was achieved when considering non-linear sorption (Freundlich isotherm) instead of linear sorption (Kd). It was concluded that more elaborate transport models are indeed able to better describe the migration of the colloidal NOM in the Boom Clay, but it remains a fitting exercise because there are no independent determinations of the attachment/detachment kinetics. Additional studies should allow improved estimation of the sorption term however.

One RTDC3 goal was to develop a comparative database of diffusion properties of different clayrock formations. The characteristics of $^{99}TcO_4^-$, HTO and $H^{14}CO_3^-$ in clayrock samples originating from two depths in the Boda Claystone formation were determined by *II-HAS*. While the two depths show significant differences in mineralogy (e.g. absence or presence of analcime), the D_e values measured for the $^{99}TcO_4^-$ anion and HTO were generally coherent with results on other clayrocks, i.e. $D_e(TcO_4)$: $4.2 \cdot 10^{-12}$ $m^2 \cdot s^{-1}$ < $D_e(HTO)$: $1.4 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$.

Diffusion at geological and Safety Case (SC) time-space scales

Performance assessment calculations in existing SC (cf. 1, 2, 3) show that non sorbing RN diffuse across the entire GBS thickness (roughly 50 meters thick) during typical PA time-frames (10^6 years). In all of these SC, single values for diffusion-determining parameters (D_e, D_a, ω) were used to represent RN diffusion throughout the entire GBS volume. The parameter values chosen for both base case (most probable) and sensitivity (pessimistic) calculations are demonstrably valid and robust, being based on statistical evaluation of measurements made on a representative population of cm-dm scale samples. One of the objectives of RTDC3 was to provide information and methods for supporting homogeneous representations of GBS diffusion properties. Three complementary approaches were taken along this line:

- A theoretical and statistical analysis of the effects of scaling on RN transport (*SCK•CEN*),
- An up-scaling methodology linking (i) diffusion parameter value variation as a function of rock mineralogy measured at the cm scale and (ii) rock mineralogy measured at the GBS scale, followed by comparative diffusion modelling with a homogeneous model (*Andra, CEA*),
- Natural tracer based studies (*UniBerne, GRS*).

A comprehensive evaluation of the potential effects of observed (or induced) spatial variability in the Boom clay formation properties on RN transport was carried out by *SCK•CEN*. The study shows that, from a theoretical standpoint, microscopic flow and transport processes can be up-scaled to the scale of the formation 'layers' so long as parameter values are associated

with rock volumes equal to or exceeding that of a representative volume element (RVE) for the Boom clay (pluri-mm to cm). Consideration of two other types of information, statistical analysis of parameter values measured on cm scale samples from throughout the formation and in situ measurements integrating large rock volumes (hydraulic tests, diffusion experiments), allows a strong case to be made for using parameter values measured on small samples as a basis for determining a representative value and associated uncertainty applicable to the entire geological formation at the repository site.

A similar conclusion was reached regarding anion diffusion through the Callovo-Oxfordian formation using a method developed by *Andra* and *CEA*. The approach is based on a logical extension of the working hypothesis which guided studies at the mesoscopic (§3.2) and macroscopic (§3.3) scales, i.e. that non sorbing tracer diffusion should be determined largely by effects of rock mineral composition on porosity organization. It therefore constitutes the last step in up-scaling process understanding gained at small scales to the parameterization of model for non sorbing RN migration in the GBS for PA purposes. It consists of three main steps:

- Determination of the relationship between diffusion parameter values (D_e, ω) for Cl^- and carbonate mineral content in Callovo-Oxfordian rock samples (cf. §3.3). This relationship was used to define three rock classes having statistically different D_e values.
- Signal treatment and geo-statistical methods were used (i) to obtain vertical profiles of rock carbonate content with cm scale resolution from high resolution borehole log data and (ii) to assign formation intervals (10 cm thick) to one of the three $D_e(Cl)$ rock classes,
- Modelling of diffusion, using the above as a basis for meshing and with an anion source term located in the centre.

The calculated anion flux vs. time curve at the top of the formation was compared to that calculated for the same system but with a single D_e value used for the entire formation, i.e. the configuration used for PA calculations. The difference is insignificant.

In certain geological contexts information obtained by measuring and modelling spatial distributions of conservative (non sorbing) natural tracers can provide a powerful argument for supporting use of Fick's law representations of non sorbing RN transport at the GBS scale, based on parameter values measured at laboratory space-time scales. Such an approach requires measurement of natural tracer concentration profiles within a geological formation (including boundary formations) followed by model interpretation to extract plausible Fick's law parameters[1]. *UniBerne* applied this approach to studying natural tracers (Cl, Br, He and water isotopes) in the Opalinus Clay and adjacent formations in the Mont Russelin anticline (Jura, CH). The Cl^- distribution shows a regular, well-defined profile, with the highest values being found in the centre of the Liassic clayrock anticline, close to the contact with Opalinus Clay. The data were modelled using a 2D geometry and the $D_p(Cl)$ value determined experimentally on Mont Terri samples. The results (Figure 5) show that the observed Cl tracer distributions

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[1] The OECD Nuclear Energy Agency 'CLAYTRAC Project: Natural Tracer Profiles Across Argillaceous Formations' (2008) treats this aspect in detail.

are consistent with diffusion as the dominating transport process, assuming that the ground-water flow system in the overlying Dogger aquifer developed about 4 My ago, which is coherent with independent palaeo-hydrogeological evidence.

GRS modeled tracer profiles measured at the Mont Terri URL with the added objective of testing the benefits and disadvantages of using models of differing complexity to represent RN diffusion driven transport at geological (and GBS) space-time scales. The results show that, while both complex and simple models are able to represent the data satisfactorily, a higher degree in complexity does not improve the agreement between the simulations and the experimental data. The most probable reason for this is considered to be that the complexity of the model is too high and does not correspond with the level of detail and the quality of the input data.
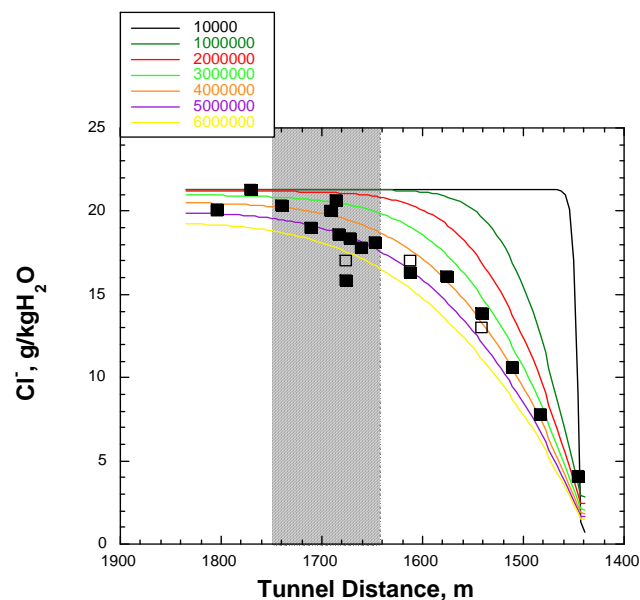
Figure 5: Results of 2D diffusion modelling of chloride tracer concentration profiles using Dp(Cl) value determined on lab-scale sample. The curves indicate the time since imposition of boundary conditions by the overlying aquifer.

Understanding migration of sorbing RN in clayrocks

The principal method used for generating databases of RN sorption behaviour on clayrocks is by 'K$_d$' measurements in batch systems, i.e. using crushed clayrock material. K$_d$ values obtained for many RN (e.g. actinides, ^{135}Cs) are sufficiently high such that, when used in PA modelling, these RN are entirely confined within the GBS over the simulation time frame. Three important questions of interest to future clayrock SC can be raised regarding this approach:

- Can the K_d dataset obtained for a given RN / dispersed clayrock system be interpreted in terms of a chemically plausible thermodynamic model, i.e. mass action laws for adsorbed RN species, surface site types and concentrations, other reactions…?
- Are the migration characteristics observed for a given RN in an intact clayrock coherent with the predicted behaviour based on batch sorption behaviour, i.e. either by direct use of Rd values or using the thermodynamic model?
- If not, can means be provided for selecting a K_d for PA use which compensates for the discrepancy, ideally in terms of justifiable (and robust) adaptations of parameter values in the thermodynamic model (i.e. mass action laws, activity correction model, extensive parameter values)?

Research carried out in Funmig focused mainly on enhancing understanding regarding the first and second questions, mostly for strongly sorbing RN or analogue elements, but also provided some insights into the latter aspect.

Fundamentals of RN sorption reactions on clays and clayrocks

The majority of the work on this subject was carried out within the framework of RTDC1 and the reader is invited to consult the corresponding final report for details. Nevertheless, the highlights of these actions are briefly mentioned hereafter for completeness.

Regarding surface speciation and redox reactions:

- The results of a study (*UJF-LGIT*) of the nature (hydration/hydrolysis state, inner/outer sphere complex) of Sm^{3+} species sorbed on synthetic montmorillonite samples using variety of analytical methods (neutron diffraction (ND), EXAFS, Quasi-elastic Neutron Scattering (QENS)) show somewhat contradictory results. ND measurements indicate that Sm^{3+} is bound to the clay surface and is probably partially hydrolyzed while EXAFS measurements indicate that Sm^{3+} is present as an outer-sphere complex with nine water molecules surrounding the cation. Quasielastic neutron scattering (QENS) experiments were performed with *Na-hectorite*, *Ni-hectorite* and *Sm-hectorite* samples in order to compare the diffusion mobility of water molecules in *Sm-hectorite* with that for other interlayer cations: *strongly hydrated Ni^{2+}* and relatively *weakly hydrated Na^+*. It was found that water mobility in Sm – hectorite sample is very close to the water mobility in the Ni-hectorite. This is only possible if Sm^{3+} ion is fully hydrated. A compromise with the neutron diffraction data can be found, assuming that not all adsorbed Sm interacts with water molecules, probably due to precipitation. It was discovered that water molecules hydrating Ni^{2+} and Sm^{3+} perform diffusion mobility measurable with a backscattering spectrometer. The diffusion coefficients of the exchangeable cations were found using slow exchange approximation to be $D_{Ni} = (0.05 – 0.14) \times 10^{-9}$ m^2/s and $D_{Sm} = (0.04 – 0.18) \times 10^{-9}$ m^2/s.

- The redox reactivity under anoxic conditions of Se(IV) with Fe(II) adsorbed on synthetic, structural Fe-free montmorillonite was studied by *UJF*, in collaboration with *BRGM, LPEC, LMPC/LMM*. The results show slow reduction of Se and formation of a nano-

particulate Se(0) solid phase when selenite is added to a montmorillonite previously equilibrated with Fe^{2+} solution; this was not observed in Fe-free systems. These, and other, results clearly suggest that the Se and Fe redox reactions are not directly coupled, leading to the hypothesis that electrons produced in the absence of Se by oxidation of sorbed Fe(II) are stored, for example by formation of surface H_2 species, and are then available for the later Se(IV) reduction.

Regarding thermodynamic modelling of sorption:

* The results of batch sorption studies (*CIEMAT*) of Sr, Pu, selenite and europium sorption onto Na-smectite, Na-illite and mixed systems showed for selenite that (i) sorption was higher in smectite than in illite and, in both clays, was independent of ionic strength and decreased with pH, (ii) linear sorption isotherms over a broad concentration range ($1 \bullet 10^{-10}$ to $1 \bullet 10^{-4}$ M), and (iii) that data could be satisfactorily modelled (from pH 3 to 8) considering the formation of surface complexes at the edge sites of the clay and using a one site, non electrostatic model. Regarding Eu (III), results show that (i) ionic exchange is important at pH < 4, (ii) surface complexation becomes increasingly important as pH increases to 10, and (iii) that data could be represented satisfactorily using a model incorporating non-electrostatic, two site surface complexation and cation exchange.

* Measurements and modelling of Ni(II), Co(II) and U(VI) sorption on Opalinus Clay, and of Co(II) on illite were carried out by *PSI*, with the results for U(VI) being particularly illustrative. Here, predictive modelling of sorption was carried out using the 2 site protolysis, non electrostatic surface complexation and cation exchange sorption model used in previous studies to represent U(VI) sorption on purified Na-illite assuming that (i) illite is the main sorbing phase in the Opalinus Clay and (ii) only the UO_2^{2+} and the hydrolyzed species sorb. In the case of the clayrock, it was found that the U(VI) sorption isotherm could only be modelled if the neutral $Ca_2UO_2(CO_3)_3(aq)$ complex was included in the calculations and assumed to be non-sorbing.

* Sorption data for Cs, Sr, Am and Th on dispersed Boom Clay were gathered and interpreted (*SCK•CEN*) in terms of surface complexation models, and sorption experiments on compacted samples (clay disks) were performed for Cs and Sr to check the impact of compaction (decreased accessibility to sorption sites) on K_d, with no significant differences being observed. Cs sorption could be modelled using the same 3 site, cation-exchange model used by PSI for modelling sorption on Opalinus Clay using illite as model component. Similarly, Sr sorption could be modelled using a simple cation exchange model for argillaceous rocks based on illite as model clay. SCK•CEN also studied the influence of the natural organic matter (NOM) present in the porewater on sorption of Eu(III) on illite in order to understand the Am(III) sorption onto Boom Clay. Tipping's Humic ion binding model VI was used to account for NOM interactions (succesfully introduced into Phreeqc code). Eu sorption behaviour on illite in presence of NOM could be interpreted with the 2SPNE SC/CE model in combination with the Humic Ion-binding model VI (Tipping). Interpretive modelling of Am and Th sorption onto Boom Clay is done using the Bradbury and Baeyens approach and are based on Am and Th sorption

data on montmorillonite and illite as model components. As a first attempt to capture the interaction with NOM, a 1:1 RN-NOM surface complexation reaction was used. The above simple model currently is not able to describe the sorption isotherms and needs further refinement. In the future the Tipping model will be incorporated.

- *Armines* adapted the retention and porosity model developed for bentonite to COx clayrock by assuming additivity of the various mineralogical contributions, based principally on the content of interstratified illite/smectite (I/S) minerals and the illite to smectite ratio in the I/S minerals. The approach led to a reasonable quantitative representation of the CEC and surface complexation site densities as a function of mineralogical composition. Sorption isotherms calculated for Cs and Ni were in good agreement with measured K_d data.

Migration of (strongly) sorbing RN in intact clayrock

The most convincing (from a safety case stand point) approach for quantifying migration of highly sorbing RN in clayrock is direct measurement of D_a values (cf. Fick's second law, §1) in intact samples under conditions representative of the GBS. While this approach has been used in SC, it is much more frequent to estimate D_a using $D_a = \frac{D_e}{(\omega + \rho K_d)}$ based on (i) assumed D_e values for cationic RN and (ii) K_d datasets measured on crushed rock samples. The reason for this is evident from Fick's second law which tells us that the rate of propagation of a sorbing RN in a clayrock (i.e. the distance travelled by the migration front away from the source in a given period of time) will be inversely proportional to its K_d value. For example, for a RN having a K_d = 10 m3.kg^{-1} (order of magnitude for actinides) and D_e = 10^{-11} m2.s^{-1} (order of magnitude for HTO), RN mass will have penetrated roughly 0.5 or 1.5 mm into a typical clayrock after respectively 1 or 10 years of contact. From a practical standpoint, this means that for a one year experimental time frame, one must be able to quantify RN mass distribution within a <u>sub-mm thickness of rock</u> in order to determine D_a. Despite such a challenge, RTDC3 considered that it was sufficiently important for safety case confidence building to take it on.

The work program was guided by two main objectives: (i) determining if K_d values measured in batch systems under varying conditions could be used to estimate RN sorption behaviour in the intact rock and (ii) determining if D_e values for strongly sorbing RN could be estimated based on values measured for non or weakly sorbing tracers. Studies were carried out on three different clayrocks (Opalinus Clay, Boom Clay, Callovo-Oxfordian clayrock) using elements representing the range of sorption behaviour for cationic RN: strongly-complexing (Am, Eu, Pu, U), moderately-sorbing (Cs Co, Cu), weakly-sorbing (e.g. Sr, Na). The main results concern:
- Development and application of new analytical methods for carrying out in-diffusion experiments and quantifying high K_d tracer migration in intact rock;
- Comparison of sorption equilibrium model parameter values determined in batch and compact rock systems;

- Comparison of D_e + sorption parameter value sets obtained by modelling data from in-diffusion experiments with predictions made using an assumed D_e value and batch sorption parameters.

Analytical method development

It was necessary to develop a variety of innovative analytical methods during Funmig in order to be able to quantify the migration of highly-sorbing tracers in intact clayrock samples. The 'hi-resolution abrasive peeling' method developed by *PSI* consists of diffusing tracer into a flat clayrock surface using a specially developed cell, for a given period of time (e.g. ~170 days for Eu(III)), and then abrasively removing roughly 10 m thick layers of rock for total tracer concentration determination. With this method, tracer concentration profiles extending less than 200 m into the rock could be determined with roughly 10 m resolution. Along this same line, *CIEMAT* demonstrated that nuclear ion beam Rutherford Backscattering Spectroscopy (RBS) could be successfully used to quantify Eu(III) depth profiles extending to ~1.5 m (~50 nm resolution) below a polished clayrock surface, after different in-diffusion times. *FZK-INE* developed a special cell for carrying out actinide in-diffusion experiments on clayrock samples maintained at in-situ confining pressures and an autoradiography technique for quantifying tracer distribution relative to the input surface. A different approach was taken by the *CEA* driven by the need to associate the spatial distribution of tracer mass after an in-diffusion experiment with the corresponding rock mineral-porosity organization for carrying out diffusion modelling by the TDD method (cf. §3.2). The developed method (cf. Figure 6) based on hi-resolution Laser Induced Breakdown Spectroscopy (LIBS), allows the simultaneous determination of tracer and rock mineral element distribution away from the tracer input surface with a ~3 m spatial resolution. *CEA* also developed column-based method for determining D_a parameters for sorbing RN diffusion into and out of ~ 2 mm thick clayrock 'plates', with the number of plates and flow rate being varied depending on RN the sorption and diffusion characteristics.
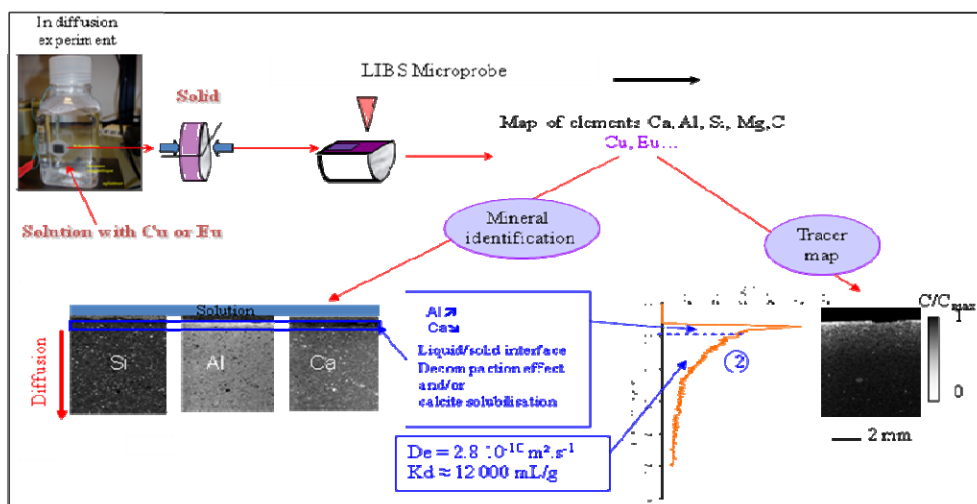

Figure 6: *Methods used for quantifying spatial distributions of both mineral and tracer concentration, here Cu, in intact clayrock samples (CEA).*

Results of comparison of RN sorption equilibrium in batch and intact rock systems

The question addressed here is quite simple – for a given mass of rock equilibrated with a given activity of a sorbing RN under otherwise identical conditions, does one measure the same total sorbed mass of RN if the rock is present as ground particles or as a compact solid? While this question can be answered fairly readily for weakly and moderately sorbing RN as will be shown below, it turns out to be quite difficult in the case of strongly sorbing RN. The key objective here is to reach an equilibrium state in systems containing compact rock samples, i.e. kinetics related to RN mass transport (diffusion) into the sample have reached insignificant levels. When this is the case, results can be interpreted using only a chemical equilibrium model, i.e. without diffusion. The results of measurements carried out by *PSI* (e.g. Figure 7) show that sorption equilibrium reached for Na^+, Sr^{2+} and Cs^+ on compacted Opalinus clayrock are comparable (within a factor of 2) to corresponding states measured on crushed samples (Van Loon et al., 2005; Van Loon et al., 2008).

Similar results were obtained by *SCK-CEN* for Sr and Cs on Boom Clay. The R_d values measured on compacted samples tend to be higher than for crushed rock which might be due to the longer equilibration times used for the compact material studies. Measurements of Co^{2+} sorption, while not completely attaining equilibrium within the nearly 700 day experimental time frame, indicate the same result. Taken together, these results tend to support the following conclusions:
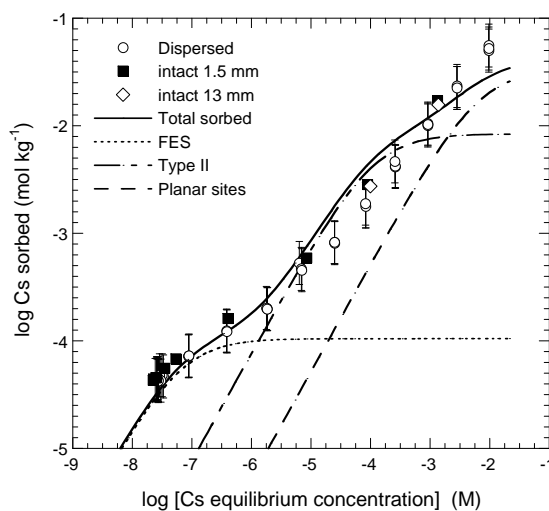
Figure 7: *Cs sorption isotherm on OPA. The solid line is the calculated Cs isotherm using the generalised Cs sorption model and assuming an illite content of 21 wt. %. The contribution of Cs sorbed on the different illite sorption sites are shown by the various curves.*

- Crushed and whole rock samples have similar sorption site populations per unit mass (sorption site types and corresponding total concentrations),
- Similar mass action laws apply for sorption in intact and crushed materials,

- Sorption-induced retardation of RN mass transport (i.e. very low D_a value) results in very long time frames for reaching equilibrium for highly sorbing RN in compact rock systems. This limits the capacity to directly determine sorption equilibrium for actinides in compact rock.

RN migration experiments and model interpretation

A major part of the research carried out in RTDC3 was concentrated on measuring mass transfer of sorbing RN in compact clayrock-containing systems and interpreting the resulting datasets using numerical models coupling the effects of diffusion and sorption equilibrium. A wide variety of experimental techniques were used to study RN migration characteristics in rock volumes ranging from mm (cf. techniques mentioned above) to dm (laboratory and in-situ experiment) scales. Generally speaking, two types of information were sought (i) time-dependent evolution of RN tracer concentration in the source term and, in certain cases, in a 'sink' reservoir, and (ii) tracer mass distribution in the rock volume after a given time(s). Numerical modelling was then used to seek plausible sets of values for diffusion (e.g. D_a, D_e) and sorption (K_d, complexation model) parameters, and in certain cases the degree of spatial variability within the rock, leading to the best possible representation of the experimental dataset. The model results were then compared with those expected based on initial hypotheses concerning RN migration (e.g. K_d(intact rock) = K_d(batch), D_e(cations) = D_e(HTO), homogeneous porous medium), and conclusions drawn regarding the applicability or non applicability of the reference model for representing RN migration. The following sections briefly summarize the principal results of research carried out on three clayrocks: Opalinus Clay, Callovo-Oxfordian and Boom Clay.

Opalinus Clay

Migration in Opalinus clayrock of a wide range of weakly to strongly sorbing cations (Na^+, Sr^{2+}, Co^{2+}, Cs^+, U(VI), Eu(III), Pu(IV)) was studied using a number of differing experimental configurations. The results of Cs^+ in-diffusion and through-diffusion experiments carried out by *PSI* tend to show that RN migration behaviour is generally coherent with the expected sorption model but is significantly affected by relatively complex mass transport processes. One hypothesis is that the porosity is made up of well-connected and 'dead-end' pores, which would necessitate considering at least two D_a terms in the diffusion equation, with that for the 'dead end' pores representing both the kinetics of RN mass transport into this volume and RN retention on the sorption sites in contact with this porosity. In-diffusion studies of Co(II) and Eu(III), with profiles extending to less than 0.2 mm after roughly 200 days for the later (cf. Figure 8, left), also show evidence of mass transport complexity (dual path). The general conclusion is that mass transport of sorbing RN in clayrocks is still not well understood, especially given the difficulties associated with making measurements at such small spatial scales (modifications of surface layer properties….).

CIEMAT carried out in-diffusion studies using four techniques: diffusion from a solid source term in large-scale (dm) clayrock blocks (HTO and Sr), using a 'filter source sandwich' con-

figuration (Sr, Co, Eu, U(VI), Cs) (cf. Figure 8, right), classical in-diffusion experiments (Na, Se, Sr, Cs, Co), and RBS detection (Eu). From the equation used to fit the experimental data of sorbing elements in classical in-diffusion experiments (Put and Henrion, 1992), K_d and D_a are estimated simultaneously. Generally speaking, the obtained K_d values were found to be significantly smaller (10% or smaller for Co and Cs) than those measured in batch experiments. On the other hand, the D_a range obtained for Cs (3 to 12.10^{-14} $m^2.s^{-1}$) is similar to the value obtained by *PSI* ($\sim 6.10^{-14}$ $m^2.s^{-1}$) and D_a values measured for Co and Eu are intermediate between the D_a values for fast and slow diffusion path values fit by *PSI*. This suggests that some of the differences between K_d and observed effects on D_a might be attributable to differences in the modelling approach used for taking sorption into account. For example, had the Kd values been fixed at those measured in batch experiments (cf. results in §4.2.2) and the fit made on the De value, the result would have given cation De values > De(HTO).
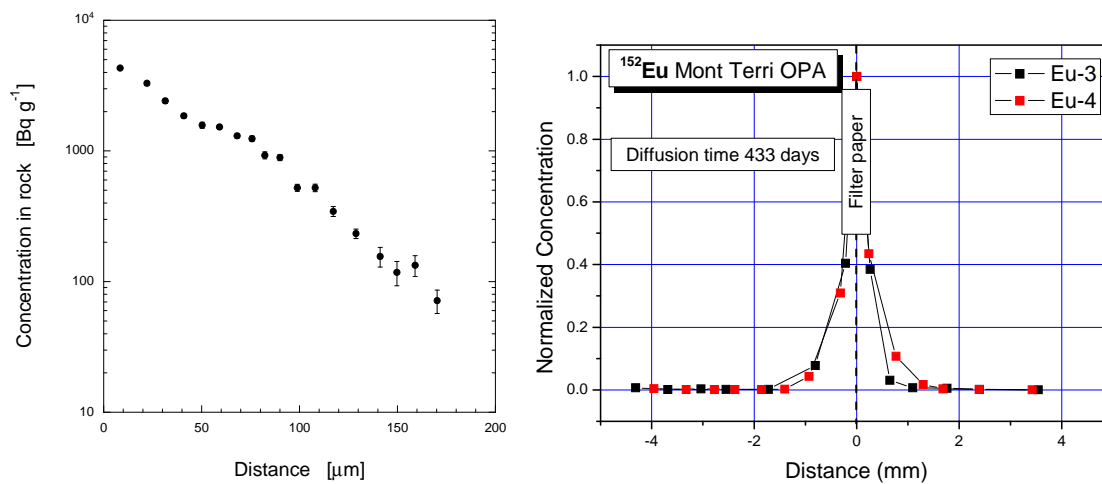

Figure 8: *Activity vs. depth profiles measured after Eu in-diffusion into Opalinus clay samples (left) after 168 days using abrasive peeling method (PSI); (right) filter-sandwich experiment lasting 433 days, followed by slicing (CIEMAT).*

Migration of most of these tracers is also being studied by means of the DR in-situ experiment being carried out by Nagra/*PSI* at the Mont Terri URL, the first step of which was predictive modelling (*PSI, UDC, GRS*) of tracer mass loss from the source solution using a variety of numerical codes. While preliminary data on tracer loss from the injection interval tend to confirm the general behaviour expected based on measurements on rock samples, data modelling also shows that for strongly sorbing tracers, complexities in mass transfer (borehole mixing, diffusion in filters, etc.) strongly influence experimental data, making clear-cut estimations of values for diffusion-retention parameters in the undisturbed clayrock difficult. Some of these ambiguities will certainly be removed, at least for the more mobile tracers, when information on tracer distribution in the surrounding rock becomes available (post-Funmig) for providing further constraints on model interpretations.

Finally, Pu(V) diffusion into Opalinus clayrock samples kept under in-situ confining pressures was measured by *FZK-INE*, with results from both batch and in-diffusion experiments

showing that Pu is reduced to the Pu(IV), probably by Fe(II) contained in rock minerals (probably chlorite), and is retained (sorption or other process?) on preferential sites.

Callovo-Oxfordian

The Callovo-Oxfordian research program is, by design, quite similar to that described for the Opalinus clayrock since one of the objectives of RTDC3 was to generate comparable data sets for different clayrocks in order to identify common characteristics and eventual significant differences in RN migration properties. The principal difference between the two is in the working hypothesis, and consequent experimental approach, taken by a consortium of French partners (*CEA, ERM, Hydr'asa, Andra*) for quantifying and modelling migration of highly-sorbing RN in clayrock. The guiding assumption here was that, given the very small spatial scales covered by RN migration during the time frames of in-diffusion experiments owing to the preponderant effect of sorption, it would be important to be able to quantify how tracer mass present in the diffusion profile was distributed relative to rock mineral constituents and associated porosity. The approach taken (cf. Figures 1 & 7) involved carrying out, on a <u>single, oriented cm-scale volume of clayrock</u>:

- Characterization of the mineral-pore space organization and construction of the corresponding 2-3D numerical models, including analysis of grain organization (cf. §2.2), followed by TDD modelling of diffusion of non sorbing tracers (cf. §3.2);
- In-diffusing a highly-sorbing tracer (Eu, Cu) into the rock (gradient perpendicular to sedimentation plane) for a given period, then sectioning the rock perpendicular to bedding;
- Simultaneous mapping of tracer mass and mineral grain 2D spatial distributions, relative to the in-diffusion surface, using   LIBS and Electron Probe Micro Analyser (calculation of the average diffusion profile), followed by construction of numerical models of the in-diffusion zone;
- Inverse modelling of tracer diffusion (source term, spatial distribution) to determine D_a values for the porous mineral zones (clay matrix + disseminated pyrite), followed by comparison with batch K_d.

The results for Cu(II) (the most complete dataset available) are rich in information concerning both tracer migration phenomena and potential experimental artefacts which can make measurements on such small rock volumes difficult to interpret. Regarding the former, it was found that (i) Cu does not penetrate into, nor sorb significantly onto, the carbonate and quartz grains and associates preferentially with the pyrite minerals dispersed in the clay matrix, (ii) Cu diffusion profiles (clay and pyrite) developed over a distance of roughly 2 mm into the rock and (iii) evaluation of the entire dataset (reservoir + profile) yields values for D_e ($2.5.10^{-10}$ $m^2.s^{-1}$) and Rd (3500 mg/L) which are consistent both with results showing that D_e for cations in the COx are generally significantly higher than the value for HTO ($\sim 2.5.10^{-11}$ m^2s^{-1}) and measurements of $K_d(Cu)$ which give values in the 3000 to 9000 range (note that Rd could be controlled by the redox reactivity of this tracer). On the other hand, detailed analysis also shows that the roughly 50   m layer of rock in contact with the source solution is significantly perturbed, both in terms of its mineral-porosity composition/organization and its Cu(II) retention characteristics - the D_a in this zone is roughly two orders of magnitude less than the rest of the

profile. These observations have, by the way, quite a number of similarities with those for Co(II) in-diffusion in the Opalinus Clay.

CIEMAT carried out a program of 'filter sandwich', in-diffusion, and block-scale diffusion measurements similar to that described for the Opalinus clay rock, and obtained generally similar results, i.e. K_d extracted from fitted D_a values are significantly smaller than those observed in comparable batch (cf. §4.2.4).

Note finally that *FZK/INE* carried out similar measurements of Pu(V) migration in COx samples and obtained similar results as for Opalinus.

K_d values for Cs were determined (*CEA*) on the same set of 'variable carbonate content' COx samples studied in §3.2. As for D_e(Cl), the results exhibit a 'threshold' effect, with Kd remaining in the normal range of values for the formation for carbonate fractions below ~70 wt%, then falling off drastically to roughly 10 wt% of this value. For completeness it can be noted that, when this data is used to parameterize the distribution of Kd(Cs) values at the formation scale (cf. §3.4), the calculated Cs flux vs. time curve at the top of the formation is, as expected, identical to that calculated using a constant K_d for the entire formation.

Boom Clay

For Boom Clay, reliable and reproducible values for the D_a had already been obtained from different types of experiments (column migration type experiments, electromigration experiments), but they did not lead to trustworthy *R* values and thus no good comparison with sorption data was possible. A coupled transport simulation of a Cs diffusion profile implementing the 3 site, cation exchange model for Cs^+ sorption (cf. paragraph 4.1) was used to carry out a sensitivity analysis on the effect of increased pore diffusion coefficients (related to "surface diffusion" effects) and decreasing available sorption sites. Results show that good fits to the migration profile required either that (i) the total sorption site concentration needed to be decreased to a fraction (5%) of that used to model Cs sorption data obtained on dispersed and compact Boom Clay or (ii) the D_p value needed to be raised by an order of magnitude compared to the D_p value of HTO. Sorption experiments with Cs and Sr on compacted clay were performed and showed that compaction did not affect the accessibility of sorption sites seeming to support the second explanation. In-diffusion and through-diffusion were carried out and a good approximation of the R value was obtained by combining the data of the separate fits. Feeding these values for Cs and Sr into the relationship $R=1 + (\rho K_d/\eta)$ resulted in K_d values which matched the values from the sorption experiments. The following parameters for Cs and Sr migration and retention in Boom Clay are obtained: $D_a(Cs)\sim1.4.10^{-13}$ m²/s & $\eta R\sim12700$ (logKd ~3.9), $D_a(Sr) \sim7.8.10^{-13}$ m²/s & $\eta R\sim438$ (log $K_d\sim2.4$). For Cs and Sr migration in Boom Clay, the relationship between *R* and K_d (under the approximation that at low concentrations sorption is a linear reversible process), seems valid. For transport modelling purposes, one can therefore introduce experimental measured sorption values or the mechanistic sorption model to simulate the transport without having to change sorption site densities. The common explanation for D_e values for cations exceeding that for HTO is that a sup-

plementary diffusion 'pathway' is operant for sorbed cations, so-called "surface diffusion", the nature of which is still not understood.

Main messages for Clayrock Safety Cases

The overall results of RTDC3 can be summarized by returning to the three questions posed in the introduction:

- Do we have a sound theoretical basis for describing RN speciation in the porosity of highly-compacted clay materials and clayrocks, in particular the distribution of total RN mass between dissolved and sorbed species?

  A fairly positive response seems justified based on two main results. The first is the observation that similar equilibrium sorption states (K_d) are observed in dispersed and compacted materials for moderately sorbing cations (Sr^{2+}, Cs^+, Co^{2+}) for all clayrocks. This implies that the same sorption site populations are accessible under both conditions and that the corresponding mass action laws are valid. It was not possible to demonstrate this for highly sorbing RN (actinides…) because of the extremely long times needed to reach equilibrium conditions (associated with other problems), but there does not seem to be any clear reason why they should not have a similar behaviour. The work on pure clay systems provides a sound basis for partitioning the mass of both anionic and cationic RN between different porosity volumes (anionic exclusion, interlayer, EDL, bulk).

- Do we have a coherent conceptual model describing diffusion-driven transport of anionic and cationic RN in clayrocks?

  Here the answer is clearly mixed. For anions, yes. The results of the studies carried out at scales ranging from molecular/microscopic, to mesoscopic, to macroscopic, and geological formation scales offer a sound scientific basis for explaining and modelling migration of anionic RN. As for cations, the picture is not so clear, with all of the results tending to show that coupled diffusion-sorption migration is much more complex than expected, leading generally to greater mobility than that predicted by coupling Fick and batch K_d. Several hypotheses have been advanced for this, perhaps the most plausible being that cationic RN diffuse along more than one type of 'pathway' (or porosity) in a clayrock, each having a corresponding D_p value and sorption site population. In this case, mass transport kinetics could limit access to the sites in the lower D_p porosity. It should also not be forgotten that these studies are necessarily carried out on very small rock volumes, with the accompanying possibility that effects of mineral-porosity heterogeneity existing at this scale might also have an influence. It is not impossible that the reduced effect of sorption retardation observed at these mm scales becomes less important when migration over larger space (and time) scales are considered. In any case, more research is indicated in this area.

- Do we have credible strategies / methods for carrying out the up-scaling needed to obtain representative parameter values usable for performance assessment simulations of a clay-

rock geological barrier system, in particular taking into account the effects of spatial heterogeneity of rock physical-chemical properties.

Here the answer is an unqualified yes, backed up by the multiple lines of argument and demonstration provided by the theoretical, experimental, up-scaling and natural tracer studies presented above.

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Publications and Communications

Peer reviewed publications

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RADIONUCLIDE MIGRATION IN CRYSTALLINE HOST ROCKS. (RTDC4)

Abstract

The overall aim of the component 4 of the FUNMIG project (RTDC4) was the investigation, both at laboratory and *in-situ* scale, of specific processes influencing radionuclide migration in crystalline rock formations.

Processes as fluid-flow system, matrix diffusion and sorption, considered fundamental in performance assessment (PA) were studied focusing on those aspects not yet completely understood. Amongst them special attention was paid to understand the role of the heterogeneities on these processes, to the analysis of transport models that adequately describe these heterogeneities and to the development of up-scaling methodologies.

The performed studies comprised basic investigations on the chemistry of the crystalline groundwater, also accounting for the potential consequences caused by the presence of the bentonite barrier, present in most of radioactive repository design, as for instance, the formation of bentonite colloids. A great effort was made in RTDC4, also in collaboration with RTDC2, to elucidate the role of bentonite colloids on radionuclide transport in crystalline rocks, because of their possible high relevance, although *colloids* are not directly included in PA.

Part of these studies benefit from supporting data from real sites (Forsmark and Laxemar) and *in-situ* data from the FEBEX gallery (NAGRA's Grimsel Test Site, GTS, Switzerland). At the GTS, an experiment simulating at real scale a high-level waste repository in granite was installed more than 11 years ago. This was a unique opportunity to study migration processes from the bentonite barrier to granite in a *realistic* environment.

Introduction

Crystalline rocks present suitable properties to host a deep geological repository (DGR) of high level radioactive waste and, for this reason, radionuclide (RN) migration in these systems has been studied for many years in different European countries (Sweden, France, Finland, Switzerland, Spain, UK) as well as in Canada, Japan and USA. Finland approved the disposal for high-level waste in the location of Olkiluoto after the study of different possible sites (Vieno and Nordman, 1999) and Sweden will select in the near future the possible site for the final waste disposal in a granitic location (for example Oskarshamm or Forsmark).

The performance assessment (PA) is an important element to demonstrate the feasibility of geological repositories and their safety at a long-term. A solid *Safety Case* is a prerequisite for obtaining a license for a geological repository: this includes the development of concepts,

methodologies and the testing of application as well as the analysis of possible evolutions of the repository scenario and the analysis of the possible radiological consequences.

In PA of a DGR of radioactive waste in crystalline rocks, the main processes considered fundamental to describe radionuclide migration are: a) <u>distribution of the groundwater flow; b) matrix diffusion and c) sorption.</u> These processes were widely studied in the past and a large knowledge existed before starting FUNMIG.

Nevertheless, the final report of the E.U. RETROCK Project (Retrock 2005), which dealt with the treatment of radionuclide transport in crystalline media within safety assessments, summarised several aspects related to these processes not completely understood (i.e. effects of the heterogeneities, interaction mechanisms, up-scaling...) and additionally pointed out that in certain cases, data obtained under realistic or relevant conditions are scarce or missing, opening new fields of research. PA formulates mathematical models for radionuclide migration in which simplifications are needed. If the level of scientific understanding is not adequate, conservative assumptions are used. Certainly, a better knowledge of the most important processes, providing a better description of the system, decreases the uncertainties and increases confidence in its description. Basically, these were the starting point for the research work to be carried out in FUNMIG.

The following organisations participated to the crystalline rock component, RTDC4: **AITEMIN** Spain; **AMPHOS21**, Spain; **CIEMAT**, Spain; **CSIC**, Spain; **FZK-INE**, Germany; **GEOPOINT**, Sweden; **HUT**, Finland; **IIF**, Germany, **JGUM**, Germany, **KTH**, Sweden; **NILPRP**, Rumania; **NRI-Rez**, Czech Rep; **UDC**, Spain; **UPC**, Spain; **UPV**, Spain; **HU**, Finland; **OVIUNI**, Spain; **VTT**, Finland. Furthermore 5 associated groups collaborated to the work of this component.

RTDC 4 was structured in 6 work packages (WP) corresponding to the main investigations identified as necessary to address within the project: **WP 4.1** "Characterisation of geochemical conditions in crystalline host rocks"; **WP 4.2** "Fluid flow system characterisation"; **WP 4.3** "Generation, quantification, characterisation, stability and mobility of groundwater colloids"; **WP 4.4** "RN transport studies, including the effects of inorganic/organic colloids"; **WP 4.5** "Process identification and verification by real system analysis" and, finally, **WP 4.6** "Up-scaling of processes". Nevertheless, the structure was flexible, there was lot of inter-relation within WPs, as the research work was organised around key-questions.

In particular, to understand the role of the rock heterogeneities on radionuclide migration was an issue from a theoretical and experimental point of view. A large experimental work-plan was settled to gather data under well-defined conditions for assessing the effects of the rock heterogeneities on the fundamental PA processes i.e: distribution of the groundwater flow, matrix diffusion and sorption.

The characterisation of complex water flow-paths in crystalline rocks is essential for the analysis of the main migration and/or retention processes, so that novel and complementary experimental approaches were proposed to analyse the rock matrix and fractures structure at different scales.

The effects of physical and chemical rock heterogeneity on the main parameters needed for PA calculations (i.e. distribution coefficients, diffusion coefficients or porosity) were also analysed within different work packages.

Additional questions were related to the evaluation of models adequacy in describing transport in this complex environment, process understanding and to the development of upscaling method and upscaled effective transport models. The dependence of transport parameters and effective transport dynamic on the scale was analysed. Advantages and limitations of different up-scaling methodologies in the context of underground radioactive repositories were evaluated (**WP 4.6**) (Cassiraga et al., 2005).

Another important point, concerned reactive transport models that, at present, do not take into account the complex dynamics inherent to a heterogeneous reactive transport system. Efforts were made to quantify effective reactions and transport in heterogeneous media for a more realistic large scale modelling and to implement concepts and modelling frameworks in numerical PA tools (**WP 4.6**) (Bea et al. 2008).

On the other hand, as the models developed on the basis of results obtained from laboratory tests might not be directly applied to field conditions, field studies played an important role. Apart from providing site-specific data, they allowed investigating the migration processes at a larger spatial scale and under almost *"real"* conditions.

As an example, in the frame of **WP 4.5**, hydrological and geochemical data from the Swedish Forsmark and Simpevarp sites were analysed as a support of the safety case for nuclear waste disposal in fractured crystalline rock in Sweden. *In-situ* studies were also carried out at the FEBEX site at the Grimsel Test Site (**WP 4.1** and **WP 4.2**). The FEBEX experiment reproduces at a real scale a high-level waste repository in granite. At moment, it represents the only realistic environment where the processes affecting RN migration from the bentonite to granite can be studied.

Different problems may exist even when the processes are well understood, for example in the case of matrix diffusion for which obtaining relevant experimental data, as input for transport models, is not straightforward. The development of new experimental methodologies may overcome the difficulties representing in addition a scientific challenge.

Lastly, it has to be mentioned that some processes are nowadays neglected in PA because they present high degree of uncertainty or because of experimental data obtained in realistic conditions are too scarce. In crystalline rocks, colloids are neglected because of their low concentration in the far-field. However, recent studies showed that bentonite colloids can be generated from the engineered barriers (Missan et al. 2003) and that they could be particularly relevant for the migration of high sorbing elements as tri- or tetravalent actinides (Geckeis et al. 2004), thus in RTDC4 they were thoroughly studied. The complete description of radionuclide transport in the presence of colloids needs to understand colloidal behaviour in crystalline groundwater (generation, stability, colloid-RN interactions and rock-colloid interactions). All these aspects were dealt with in different WPs of RTDC 4 (**WP 4.1**, **WP4.3** and **WP 4.4**).

In summary, the main aim of the work carried out within RTDC4 was to obtain (realistic) data, both from laboratory and *in-situ* for the validation of existing models, and to improve the knowledge on less known processes to facilitate their inclusion in PA models (e.g. colloid behaviour).

In this paper, a short description of the main processes studied in RTDC4, including a summary of the main results obtained is given. Most of the bibliographic references included concerns studies carried out during the project and can provide more detailed information of the research work performed.

Transport in crystalline rocks: PA relevant processes

Groundwater chemistry and real-sites studies

It is important underlying the importance of the groundwater chemistry on RN transport. RNs mainly migrate dissolved in the groundwater: the chemistry of the water (salinity, pH, Eh, complexing agents) is one of the main parameters controlling the aqueous speciation of RNs, their solubility and their retention in the medium. Chemistry influences several other processes, colloid formation and stability, amongst others. When studying a crystalline medium, the first key point is to understand what chemical reactions and sorption processes occur in the host rock and what their effects on RN mobility are. It is also of importance to evaluate possible effects of the presence of the engineered barrier on the chemistry of the system.

The occurrence of chemical reactions and sorption processes occurring in the rocks is mainly site specific and different scenarios and problems (i.e. climate) have to be analysed. One question is whether *in-situ* studies and real system analyses, help to improve the knowledge of RN migration.

Site specific studies, as those carried out in the Swedish sites Forsmark and Laxemar by **GEOPOINT** and several **associated groups**, clearly represent a direct support for PA (Laaksoharju et al. 2007). The evaluation of field geochemical data (Eh, pH, TOC, colloids presence, Mg-Ca, etc…) is needed to verify if they met safety criteria for site selection and to build confidence in the site. On the other hand, these studies are fundamental to understand phenomena that cannot be obtained from laboratory studies. Advanced geochemical modeling applied in these sites helps to generate understanding in terms of concepts, scenarios, spatial and temporal scales and on models validation itself (Laaksoharju et al. 2007). The understanding of the hydro-geochemical conditions of the past and present is the basis to predict future evolutions. Additionally, the complete characterization of a site allows gaining capability and confidence for the extrapolation of data when the information is scarce or not available. A considerable progress on data interpretation and understanding of relevant processes, in particular on groundwater origin and evolution, interactions of surface/deep ground-waters, redox front, microbes, gases and colloids was reached in the last years. Important progresses were also obtained on modelling aspects by the integration of hydrochemistry with mineralogy, microbial data and reaching a closer integration with hydrogeology (Laaksoharju et al., 2008).

Real-site geochemistry studies are important for the site-specific aspects: in certain environments, as the Fennoscandian shield, the climate may also have very important effects on RN migration. For this reason, different methodologies were implemented by **HU** and **HUT** to understand the effects of glacial melt water intrusion (Suksi et al. 2006) and how natural uranium minerals respond to them. **HU** analysed a link between hydro-geochemistry and U isotope fractionation as a possible tool to characterise the groundwater flow system. The $^{234}U/^{238}U$ activity ratio (AR) contains information of the groundwater conditions under which uranium was dissolved. For example high AR (>3) may indicate the existence of short water-rock contact which favours the dissolution of the more mobile ^{234}U isotope. In some cases, analyses suggest the existence of episodes of faster groundwater flow in the past. The analysis of $^{230}Th/^{238}U$ activity ratio in samples from Palmottu made by **HUT** indicated that the precipi-

tation/dissolution of uranium is influenced by glaciations and that the intrusion of oxygenised glacial melt water affects this process (Markovaara-Kovisto and Einsalo, 2008).

CIEMAT, **AITEMIN** and **CSIC** performed different types of investigations in the FEBEX tunnel, at the GTS, trying to focus on mass transfer from the bentonite to granite. In the FE-BEX project (1996-2004) (Huertas, 2000), a real-scale experiment was constructed simulating a high level waste repository in granite. The objective of the project was to demonstrate the feasibility of constructing engineered barrier system and to develop methodologies and models for assessment of the thermo-hydro-mechanical and geochemical behaviour of the bentonite barrier. The heat of the spent fuel was simulated by two heaters within the bentonite (Figure 1) and the hydration was natural, from the formation water. Additionally, different tracers were located into the bentonite blocks and at their surface (Garcia-Gutierrez, 2001).

Figure 1: FEBEX experiment during the installation of the heater. Bentonite blocks are visible in the picture.

The experiment was mounted and switched on in 1996; one of the two heaters and the bentonite around it were dismantled in 2002. The rest of the experiment is still running. This was considered and adequate scenario to obtain data under "repository conditions", taking into account the presence of the bentonite barrier.

In-situ studies carried out at the FEBEX site served to quantify mass transfer processes from the bentonite to granite and to perform in-depth analysis of the effects of the bentonite on the water chemistry, also important for the validation of models. In particular, the migration of natural tracers as Na^+, Ca^{2+} or Cl^-, coming from the bentonite was analysed as well as the migration of tracers as I^- and ReO_2^- placed at the surface of bentonite blocks. Furthermore, they allowed analysing, for the first time, the presence and stability of bentonite colloids in a *realistic* environment.

Attention was focused on hydro-geological structure previously identified by **CSIC** (Perez-Estaún et al., 2007). The surface fracture mapping of the tunnel wall allowed classifying the fracture into different families according to when and how they were developed. The geology of the gallery showed the existence of various sets of fractures with different attributes (geometry, kinematics, fracture infilling, etc.). The first group presented the characteristics of echelon tension fractures, formed in late magmatic stages, according to the paragenesis of the minerals filling the cracks. The second group corresponded to the lamprophyre dikes, of mantellic origin with an orientation oblique to the tunnel and slightly oblique to the first group of fractures. The third group corresponded to very few faults located at the end of the gallery, sub-vertical and normal to the tunnel. Longitudinally to the tunnel, bands with small fractures, at small angles, exist and cataclastic zones that form brittle shear zones (Carbonell et al, submitted).

In FUNMIG, with the objective of studying the mass transfer from the bentonite to granite and analysing the presence of bentonite colloids, at the end of 2005, two investigation boreholes (FU05.001 and FU05.002) were drilled *quasi* parallel to the FEBEX gallery. These most important boreholes were relatively near to the bentonite surface (approximately 20 and 60 cm, respectively) (Gomez et al., 2007), with short packed off section to minimise ion dilution.

To characterize the crystalline rock, three short boreholes were drilled for the geophysical experiments (FU05.003, -4 and -5) (Perez-Estaún et al. 2007). Several other boreholes around the gallery already existed (19 radial boreholes with 41 packed-off sections, and other boreholes as Febex, Bous, etc.) that represented additional source of information both for hydro-geochemistry and hydrogeology. A schematic of the FEBEX tunnel with the location of the new boreholes and main hydro-geological structures is presented in Figure 2. Different types of fractures cut both FU05.001 and FU05.002 boreholes, all showing transmissivity (between $1 \cdot 10^{-11}$ and $1\ 10^{-12}$ m^2/s) with exception of the interval 1 of FU05.001 at the back of the gallery in a fault region (6-8$\cdot 10^{-10}$ m^2/s).

Several water sampling campaigns were carried out by **CIEMAT** for both water chemistry and colloid analyses (**CIEMAT** and **FZK-INE**) in the new and old boreholes. The waters from the new boreholes are HCO$_3$-Ca type waters with neutral or slightly alkaline and with low electrical conductivity.
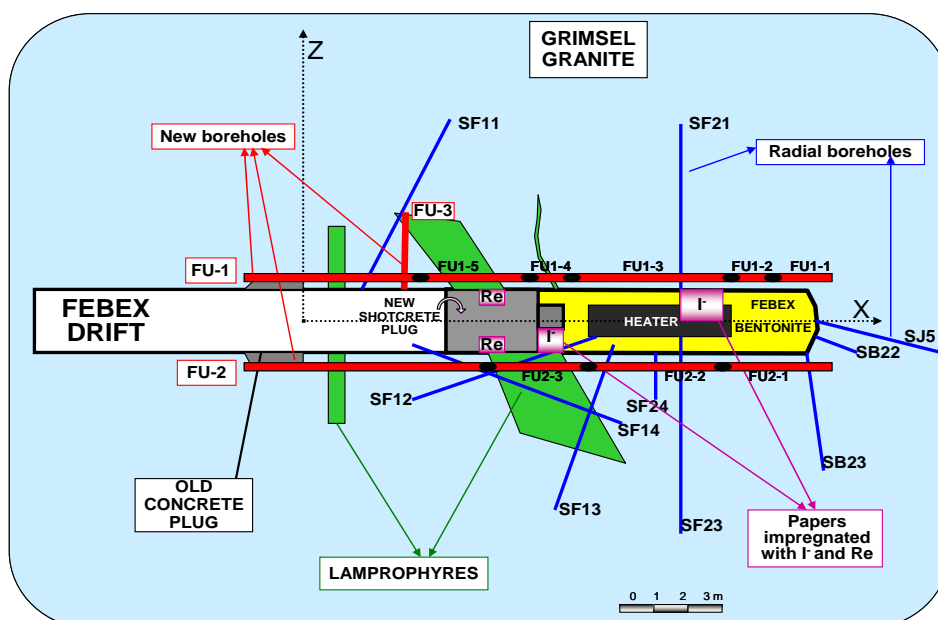

Figure 2: Schematic of the FEBEX drift with the new boreholes, the packed-intervals, the main fractures and the locations of the Re and I tracers in the FEBEX experiment.

The migration through granite of conservative ions like I$^-$ and ReO$_4^-$ (installed in 1996 during the FEBEX experiment, Figure 2) and other "natural" tracers from the bentonite (Cl$^-$, Na$^+$..) was studied. I$^-$ was observed both in FU05.001 (interval 4, 0.46 ppm) and in FU05.002 (interval 3, 0.85 ppm) in correspondence to the initial location of I$^-$ impregnated filter papers (Figure 2). The fact that only iodine and not rhenium was detected must be related to the reducing conditions present in Grimsel waters. The mobility of Re would be greatly affected if reduction to the valence state from (VII) to (IV) occurred.

Mass transfer was observed to be restricted to a few centimeters from the bentonite/granite interface, but the intervals of new boreholes, nearest to the bentonite, showed higher concentration of the main ions than the old radial ones. An increase with time of Na$^+$ and Cl$^-$ was observed in all the intervals of FU05.001, particularly relevant in the packed-off section isolating a small lamprophyre dyke (interval 4, Figure 1). Based on the data obtained in these *in-situ* studies a mass-transfer conceptual model was developed (Gomez et al, 2007, Buil et al., 2008). **CIEMAT** analysed and fit the Cl$^-$ behaviour with a simple 1D diffusive model.

These studies allowed determining in a real scale experiment the mean effective diffusion coefficient for Cl⁻ (D_e = 5.0E-11 m^2/s), as shown in Figure 3. Diffusion results obtained *in-situ* will be compared values obtained coefficients obtained in the large scale migration experiment constructed at **CIEMAT** and modeled by **UDC** that simulates the FEBEX configuration (bentonite+ large block granite) (**WP4.4**) (Samper et al. 2009)
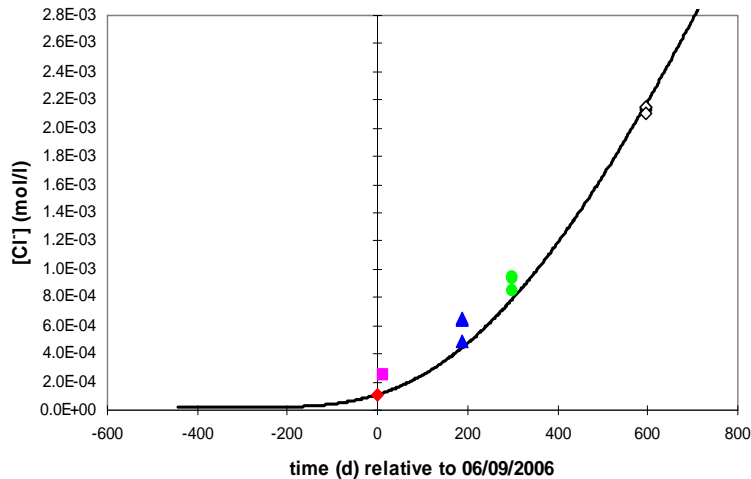

Figure 3: Concentration as a function of time of the natural tracer Cl⁻ in the interval 4 of the FU05.001 borehole (June fracture). Data fit with a simple 1D diffusion model.

De(Cl)= 5.0E-11 m^2/s

The concentration profile of major ions in the new boreholes was also modeled by **AMPHOS21** and **UPC,** their results also suggested that mass transfer from bentonite to granite, in the conditions of the tunnel, is probably governed by diffusion. In any case, they highlighted that results may be sensitive to the groundwater pathway, to the hydration of bentonite, and especially to the existence of fractures.

The packed-off sections of FU05.001 isolated different fractures or fault zones with different characteristics, also in terms of porosity and porosity distribution from the fracture surface to the matrix in depth, which provide quite interesting information. The porous zones are taken into account when evaluating RN migration from the conductive water flow paths into the matrix giving "diffusion depth" values of geosphere model parameters.

Table 1 shows the values of open porosity in the main fractures obtained by **ONIUVI** and **HU** with different techniques (Minicores porometrical analysis; water adsorption; confocal laser scanning microscopy and ¹⁴C-polymethylmethacrylate impregnation technique). Figure 4 shows an example of the porosity distribution in the interval 4 of the FU05.001 borehole (June fracture). This figure gives information on the expected variation of diffusion coefficients within the granite from the surface exposed to the water flow to the matrix.

Table 1: *Open porosity values measured by different techniques.*

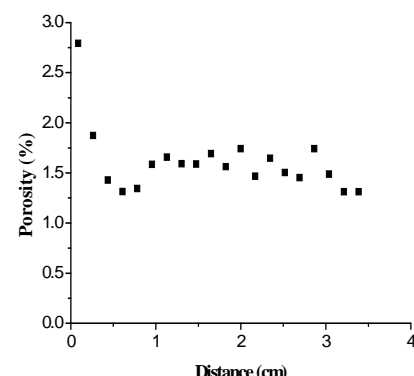| Sample/Depth		MIP (%)	WATER (%)	CLMS (%)	PMMA (%)±10%
FUN05-001; 8,22-8,64 m (June fracture)		1,62	1,81	1,56	1,6
FUN05-001 14,74-15,13 m (August fracture)	Granite	2,01	2,01	2,51	1,3
	Vein	2,96		3,09	0,6

Figure 4: *Porosity distribution from the fracture to the matrix in June fracture.*

Distribution of the groundwater flow: characterisation and modelling

As mentioned before, one of the most important issues for PA is the characterisation of the fluid flow system. In crystalline rocks, water flow takes place in the fractures that are the main conducting paths being advection the dominant transport mechanism. The water flow in the porous rock matrix, with low hydraulic conductivity, is negligible and the main transport mechanism here is diffusion. The predominance of advection over diffusion depends on the characteristics of the fluid flow system.

Therefore, the characterisation of the fluid flow system is a key point for evaluating which paths are actually available for RN transport and retention. Fracture network can be very complex and the pore space can be connected or not. It is recognised that small scale features may have an important influence on the overall transport behaviour, so that a study of the rock pore space from μm to the dm scale was one of the objectives of **WP 4.2**.

At the *in-situ* scale (dm-m) the characterization of the granite in the FEBEX tunnel was carried out by **CSIC** with geophysical experiments. The logging carried out included borehole televiewer, caliper and gamma. These data acquired were used for the identification of the main fracture zones within the old and new drilled boreholes. This provided a calibration for the interpretation of the geophysical images obtained by GPR and Cross-hole ultrasonic monitoring. The main objective of the work was to visualize in a *quasi* 3D-shape the map and geometry of the network of fractures in the rock matrix region between the main boreholes. The most relevant images were those acquired by GPR. GPR is especially sensitive to fluid filled cracks and provided the images of three fracture zones, relatively sub-parallel to the FEBEX gallery, not detected before (in the hydrogeological analysis previously performed in FEBEX) and that could play a role in the solute transport in the region (Carbonell et al. submitted). Obviously, a better system description leads to less uncertainty. This study was also important to validate the use of indirect visualization methods for the determination of fracture network in crystalline rocks.

On the basis of the hydraulic data, **UPC** calibrated the groundwater flow model of the FEBEX tunnel and observed that the pressure expected in the region analysed in FUNMIG was lower

than the expected, especially in those boreholes closer to the gallery. These results indicate the existence of a higher transmissivity zone and are in agreement with **CSIC** findings.

At a laboratory scale (**WP 4.2**) several techniques were used for the characterisation of the pore structure of different granite samples (Grimsel, Äspö, Olkiluoto, selected cores from the FEBEX site) by **HU**, **OVIUNI**, **CIEMAT**, **IIF**, **JGUM** and **NILPRP**. Different rock matrix characterisation methods (PMMA method, X-ray computed tomography (XCT), confocal laser microscopy) were compared to highlight the applicability and limits of each technique (Lahdemaki et al. 2007, Kelokaski et al. 2005). The synergy of the use of different (no destructive) techniques on the same sample was highlighted in several experiments.

The links between pore apertures and mineralogy were studied combining PMMA method and autoradiography with electron microscopy (FESEM/EDAX) by **HU**. Heterogeneity, anisotropy and connective pore-network and heterogeneities were identified as a support of laboratory transport experiments with solutes and/or colloids (**WP 4.3** and **WP 4.4**) by **HU, UNIOVI, IIF** and **JGUM**.

Positron emission tomography (PET) studies were performed by **IIF** to analyse the water flow distribution and colloid transport in a crystalline rock core from Äspö (Grundig et al. 2007, submiteed). Conservative tracers (KF, KI) marked with positron emitting radionuclides (^{18}F, ^{124}I) were used to perform transport experiments in a longitudinal fracture and at different flow rates. This non - destructive technique is applied for the direct 3D visualisation of solute transport using PET tracers. The transport paths through the fracture were observed to be modulated by the flow rate and, at localised sites, matrix diffusion was clearly observed (Kulenkampff et al.).
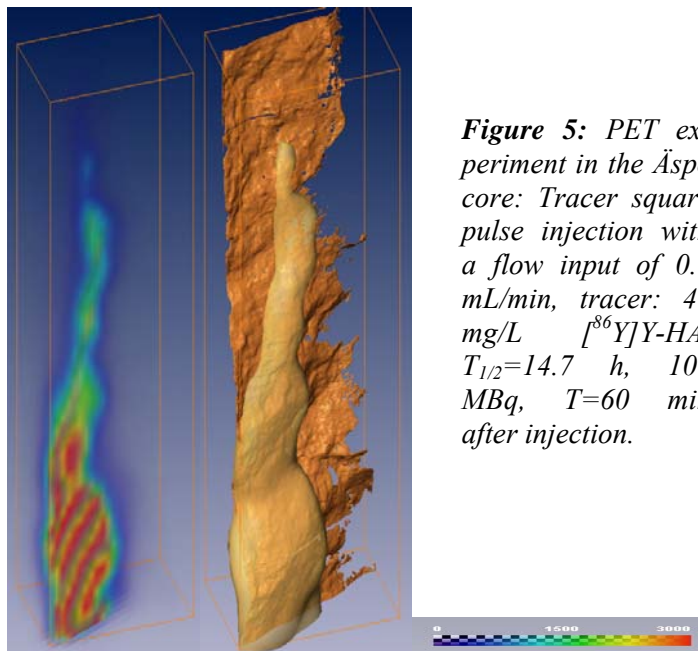

Figure 5: PET experiment in the Äspö core: Tracer square pulse injection with a flow input of 0.1 mL/min, tracer: 40 mg/L [^{86}Y]Y-HA, $T_{1/2}$=14.7 h, 100 MBq, T=60 min after injection.

An example of PET experiment in the Äspö core with the matching of XCT and PET data is shown in Figure 5. On the basis of XCT measurements of the pore structure computer simulations with the lattice Boltzmann methods can be carried out. PET measurements were used for the stepwise refinement and validation of the model. Geometrical description (3D) of the Äspö fractured core was also obtained by X-ray computer micro-tomography (XTC).

Using this information advanced simulation of the fluid flow can be done.

The applicability of PET measurements for investigations of the spatial distribution of transport processes of both dissolved components and colloids in granite was demonstrated. XCT

studies were also performed in the same sample by **JGUM**. The matching of PET and XCT data was carried out by the mathematical concept of geometrical transformation and the correlation between the fracture porosity and the tracer transmissibility was determined

A new experimental approach for non-destructive spatially resolved mapping the mineral composition and the volumetric microstructure of the host rock samples was developed by **NILPRP**, combining 3D dual-energy cone-beam tomography and X-ray fluorescence (Tiseanu et al., 2006) (Figure 6). This approach could be a very useful as a support of transport experiments in **WP 4.4.**
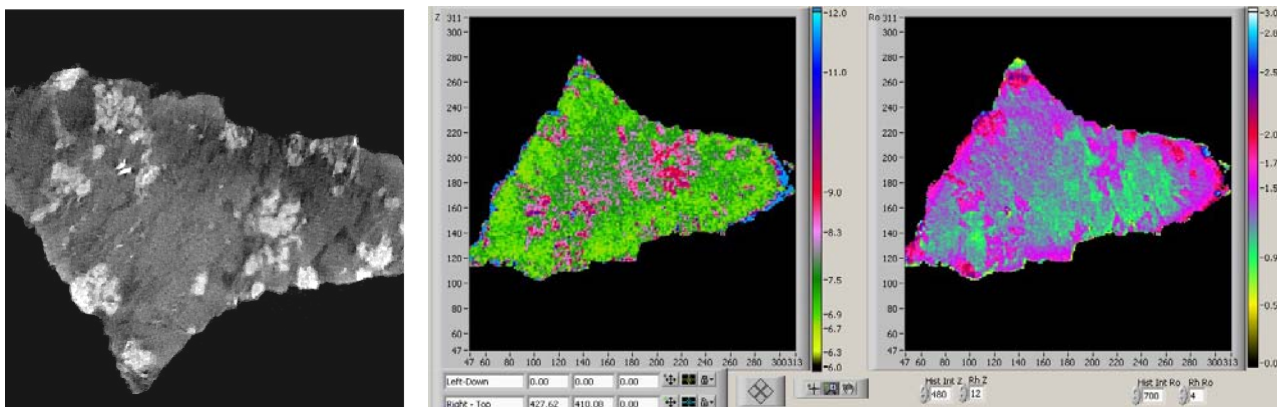

Figure 6: (left) Tomographic image of the X-ray attenuation coefficient. Scanning parameters: X-ray Source: Microfocus (Phoenix); High energy: U= 140 kV, I=0.10 mA; Low energy: U= 70 kV, I=0.15 mA; Detector: Hamamatsu flat panel array 1220x1216 pixels x 0.1 mm pitch;Voxel size: 18x18x18 µm3. (right) Tomographic image of the density and effective atomic number (Z_{eff}).

Matrix diffusion.

Matrix diffusion (MD) is considered a very important retardation process in crystalline rock above all for not sorbing elements. The state of the art of this process was well described in RETROCK and its theoretical bases in Frick et al. 1996. The effectiveness of matrix diffusion as retardation mechanism depends on the penetration depth into the rock from the water conducting zones, and it is very dependent on the porosity of the rock, the flow rate, RN diffusivity as well as on the flow-wetted surface. These studies were carried out in **WP 4.2** and **WP 4.4.**

To assess its relevance as retention mechanism it is necessary to assess the role of diffusion against advection, if the extension of the RN diffusion within the matrix is limited or not and if the pore system is stable over time. Both in *in-situ* and in laboratory tests, matrix diffusion was observed to play an important role. In dynamic experiments in fractures matrix diffusion played a significant role at low water flow rates (Kulenkampff et al.).

Another process of interest is the diffusion of anions, which can be affected by anionic exclusion, because PA calculations showed that doses are mainly controlled by anionic species $^{129}I^-$ and $^{36}Cl^-$.

A large scale laboratory mock-up experiment (MUE) was designed at **CIEMAT** to study tracer diffusion at the bentonite/granite interface. A large granite block (40x40 cm approx.) from GTS was used and characterised previous to the experiment by **OVIUNI.** A small cylindrical block of compacted FEBEX bentonite was placed in the centre of the granite block to mimic the granite/bentonite interface. A series of small boreholes were drilled monitoring tracer migration in the granite. Tracers were injected in a metallic filter placed in the bentonite. Numerical models of the experiment have been developed by **UDC.** Figure 7 shows the schematic of the experiment (upper left), the 2D grid finite element used for modelling the experiment (Samper et al. 2009, Yang and Samper, 2008, Samper and Yang, 2007, Samper and Yang, 2006) (lower left) and the experimental/modelled evolution of tracer concentration (normalised) in the tracer section (right). The diffusive behaviour of elements of different type (conservative as HTO and Cl- and non-conservative as Cs) is being analysed. HTO and Cl concentration remain almost constant during the first 150 days (99 - 98 %), the measured data are satisfactorily fit by the model. The slightly different behaviour of HTO and Cl$^-$ is explained by ionic exclusion. To demonstrate the role of MD on the retention of these non-sorbing radionuclides is a key point. The behaviour of Cs is totally different as it undergoes to sorption in the bentonite. So far, no tracers have reached the sampling points in granite.
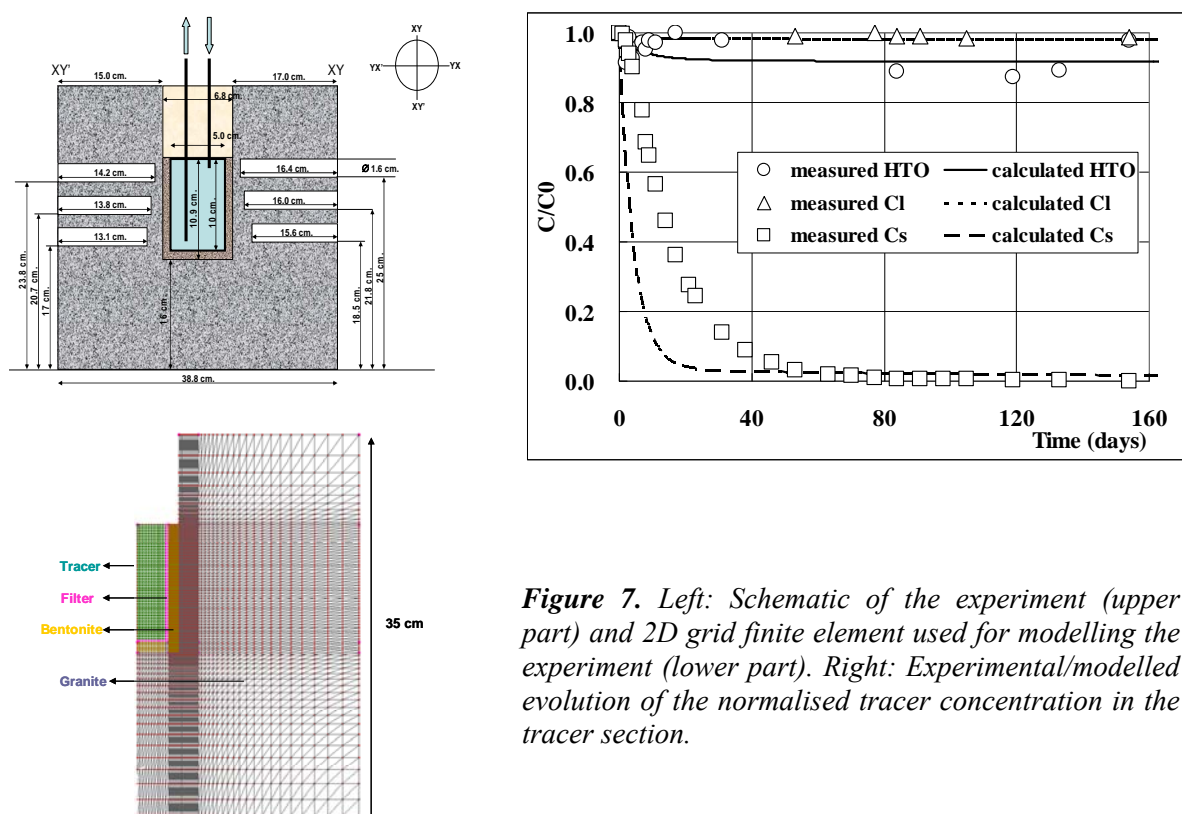
Figure 7. *Left: Schematic of the experiment (upper part) and 2D grid finite element used for modelling the experiment (lower part). Right: Experimental/modelled evolution of the normalised tracer concentration in the tracer section.*

One of the main recognised problems related to diffusion studies is the difficulty of obtaining experimental data; partly because of disturbances and artefacts that may exist in small laboratory samples and partly because, in the matrix, diffusion lengths are extremely short (in experimental time span of months - years), above all for highly sorbing radionuclide. As a con-

sequence, available data on diffusion in granite are scarce. Methodologies that can overcome these problems have been analysed in FUNMIG.

One of the important goals of RTDC4 studies was to analyse the role of heterogeneities for the matrix diffusion process and to develop models that explicitly take into account the heterogeneity of the rock matrix. In most of the models, matrix diffusion is assumed to be Fickian and homogeneous, but some authors suggested that these assumptions may not be valid (Haggerty, 2002, Widestrand et al, 2007, Siitari-Kauppi et al., 1997) the uncertainties in the migration pathways for contaminants may make inappropriate the deterministic treatment of transport and therefore stochastic methods have been also developed. Indeed, simple models do not include the effect of the heterogeneity in rock properties. Apart from the porosity measurements the visualisation of the micro-fracture system (paths, connectivity, depth) was shown to be of great of help in the understanding this mechanism.

First attempts of modelling the diffusion in a rock matrix consisting of heterogeneous porosity patterns exist (Sardini et al, 2003, 2006, 2007, Robinet et al., 2008). In RTDC4, **VTT** analysed spatial up-scaling of the retention by matrix diffusion (Poteri, 2006). However, to validate these models, it is necessary to obtain diffusion coefficients and to correlate diffusion profiles with the physical (and mineralogical) properties of the rock matrix, in the same sample (Leskinen et al. 2007).

CIEMAT proposed a microscale approach to matrix diffusion combining diffusion studies and characterization matrix porosity at a mineral scale (Siitari-Kauppi et al. 2007). The Rutherford backscattering spectrometry (RBS) is a nuclear ion beam technique that allows measuring concentration profiles in a micrometric scale with a resolution that allows measurements within a single mineral. Additionally, as the diffusion profile is measured within micrometers, the diffusion times are reduced to a few days. Apparent diffusion coefficients of uranium could be determined in three different granite types (Grimsel*, El-Berrocal* and *Los Ratones,* both from Spain) in different minerals knowing simultaneously porosity values (Siitari-Kauppi et al. 2007). The measured D_a values for the U diffusion within feldspars in the three granites were comparable but the most interesting difference was found between the various quartz grains. In some granite, where quartz minerals showed no accessible PMMA porosity, uranium access was subject to the existence of micro-cracks or intergranular fissures.

Figure 8 shows the RBS spectra of Grimsel granite obtained on quartz, feldspar and biotite. In Table 2, the values of apparent diffusion coefficients (D_a) obtained for each mineral type and its porosity are shown. Different D_a could be determined in different minerals, showing that diffusion is heterogeneus. These results are important because they provide experimental data to validate the abovementioned models and showed the importance of these studies at a mineral scale.

The RBS technique was also used by **NRI-Rez** to quantify Cs diffusion/sorption on single minerals in Czech granites (Havlova et al. 2007) in combination with auto radiographic techniques.
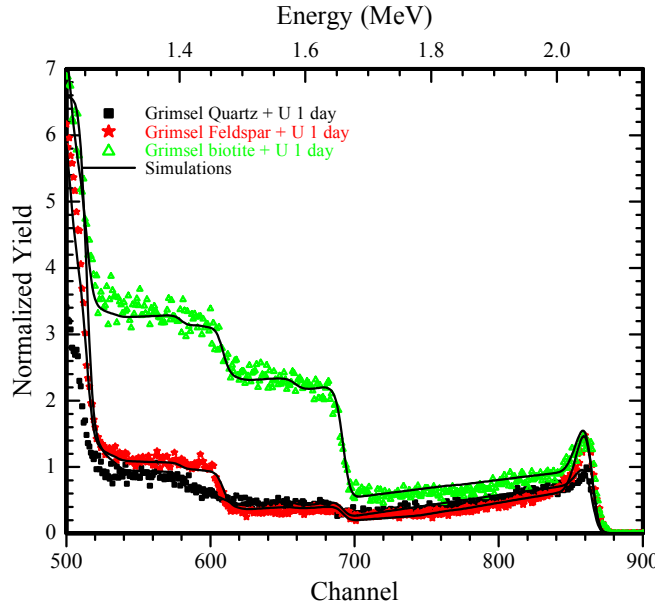
Energy (MeV)

Table 2: *D$_a$ of uranium and porosity in Grimsel granite.*

Mineral	D$_a$ (m2/s)	Porosity
Feldspar	(1.5 ± 0.5) E-13	0.5 %
Quartz	(1.1 ± 0.5) E-13	0.5 %
Dark minerals	(5.2 ± 0.5) E-13	> 1.4 %

Figure 8: *RBS spectra of Grimsel granite main minerals after contact with U solution 1 day: (■) Quartz, (★) Feldspar and (△) Biotite. Simulations are plotted as continuous lines. In the table, the values of apparent diffusion coefficients obtained for each mineral type and its porosity are shown.*

Sorption

"Sorption" is the general term used to define an unknown retention mechanism at a solid surface. RN sorption may take place at the fracture walls, but also on the materials filling the fractures. In PA, sorption is handled as a reversible attachment of dissolved species to surfaces using the "K$_d$ approach". The K$_d$ is experimentally derived, generally from static "batch" experiments under site-specific conditions. Pore surface of the rock matrix is considered to dominate sorption, while the sorption on fracture or infills is minor and neglected in PA. Limitations of the K$_d$ concept are fully recognised: in particular, the K$_d$-approach does not take into account the chemistry of the pore solution and its variability. Besides, other relevant processes as precipitation /co-precipitation and solid solution formation may be hidden in K$_d$ values. Mechanistic approach to sorption and retention processes was widely treated in RTDC 1.

In RTDC 4, two main problems related to K$_d$ values were evaluated. First of all K$_d$ are not obtained directly on intact rocks (RETROCK, 2005): this can be a problem because crushing may dramatically change the properties of granite rock; furthermore, the effect of the heterogeneities on the measurements is totally neglected. These factors lead to a significant variability of experimental sorption data for granite existing in the literature and can introduce uncertainties in the selection of K$_d$ values for PA.

The use of coupons of intact rocks instead of crushed material presents several advantages, as concluded in RTDC 4. In principle, experiments on intact granite provide more realistic values of K$_d$s (sorption generally increases as the grain size of the crushed solid decreases (Havlova et al., 2007a). Different types of analyses with different techniques can be compared. Apart from sorption, other processes can be evaluated in the same sample e.g. porosity distribution and diffusion, so that crossed-information can be obtained. Furthermore, the "scale dependence" can be experimentally evaluated. All these studies may represent an additional experimental support for the creation of transport parameters database.

To perform sorption studies on intact rocks, different "visualisation" techniques are available allowing the observation of the regions in which radionuclides interacts (e.g. modern autoradiography method (Havlova et al, 2007b) used by **NRI-Rez**). Moreover, to account for heterogeneities a micro-scale approach can be also used.

CIEMAT carried out sorption experiments with small rock pieces using the particle induced X-ray emission technique (μPIXE). One of the main challenges of this study was to quantify RN retention at a mineral level and this was done by **CIEMAT** in collaboration with the Instituto Nazionale di Fisica Nucleare (Legnaro, Italy) that developed a methodology for the interpretation of μPIXE spectra. A mapping of the single elements on the solid surface allows identifying both the main minerals present and the reactive areas where the RN is adsorbed. The quantification of RN retention in single minerals can be done only by specific analyses of the individual PIXE spectra in each scanned point within 2x2 mm^2 areas. Figure 9 shows the elemental maps of Si, K Fe and U.

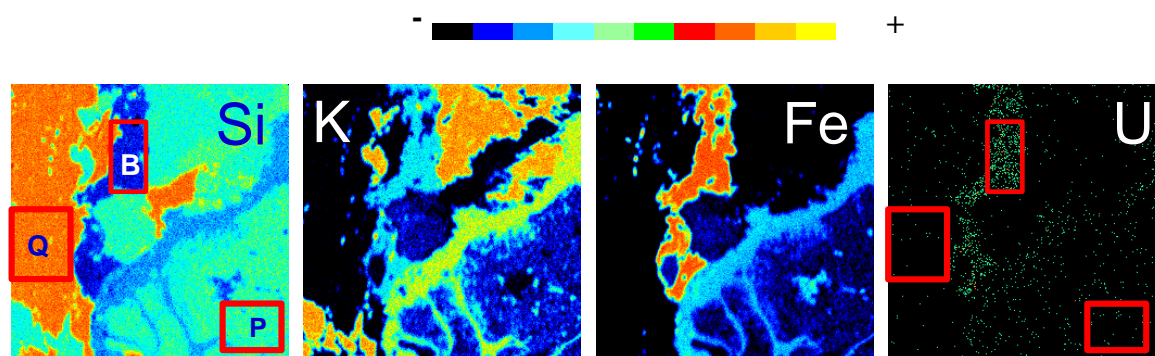***Figure 9:*** *Elemental distribution maps (Si, K, Fe and U) obtained by μPIXE on a 2x2 mm^2 granite area after the contact with uranium (10 days). Red squares refer to the areas selected to obtain the individual PIXE spectra for a quantitative analysis, identified here as (Q) quartz; (B) biotite; (P) plagioclase.*

Small regions within single minerals can be selected and the Ka values in these regions calculated. In Figure 9, it could be seen that uranium is preferentially adsorbed in a biotite. The variability of the surface distribution coefficient (K$_a$) was analysed as the studied areas increased, and this variability is experimentally determined. This investigation tried to understand how the distribution coefficients must be up-scaled for consideration of the mineralogical heterogeneity found in any natural system.

Modelling of fluid and solute transport: up-scaling methodologies.

As the rock characterisation techniques are improved, higher level of detail for the fluid paths description can be obtained. However, in PA the scales of interest are much larger than the variation scale of the fluid path heterogeneity. It is neither practical nor feasible to include the full heterogeneity spectrum in an explicit way into a PA model. Nevertheless, heterogeneity has an important effect on the large scale flow and transport behaviour, which must be taken into account in a realistic large scale flow and transport model Classical transport approaches

are based on advection and dispersion. The latter is quantified by Fick's law. This type of transport model is not suited to described so-called anomalous transport features such as early and late solute arrival times as well as sub- and superdiffusive solute spreading (i.e., the variance of the solute distribution grows super or sublinear). Effective modeling approaches such as continuous time random walks (CTRW) and multirate mass transfer do not have these limitations. The latter models are based on the observation that fast solute transport in high conductivity zones and slow transport in retardation zones can lead to the observed non-Fickian behavior (i.e., anomalous dispersion, breakthrough curve tailing), and take these effects into account explicitly.

A fundamental issue is to validate the application of these models and **UPV** and **UPC** evaluated their advantages/limitations (Salomon et al. 2006, Fernandez-Garcia and Gomez-Hernandez 2007). The state of the art and comparison of different models (macrodispersive, continuous-time random walk (CTRW), multirate mass transfer (MRMT) were analysed for conservative transport. Furthermore, efficient algorithms to model MRMT, which seems to be the most promising to deal with both for conservative and reactive transport, were developed by **UPC** and **CSIC**.

A methodology proposed in RTDC4, to up-scale transport is based upon the MRMT model. A new random walk particle tracking methodology to efficiently simulate MRMT solute transport was developed by **UPV** (Salomon et al. 2006). In contrast with the classical up scaling method, which is based on the standard macrodispersive transport model, the proposed methodology is shown capable to properly reproduce the mean behaviour of the main features associated with observed concentration breakthrough curves.

Performance assessment (PA) of radioactive waste repositories in geological media requires the sound understanding of reaction and transport processes radionuclides (RN) undergo in heterogeneous environments. This understanding is complicated: On one hand, RN undergo a wide range of (bio)geochemical reactions. On the other hand, spatial heterogeneities in the physical and chemical properties of the medium and temporal fluctuations of the state variables lead to non-trivial scale dependences of transport and reaction phenomena (Sanchez-Vila et al., De Simoni et al. 2007, Luo et al. 2008). While this is widely acknowledged, current reactive transport models do not take into account the complicated dynamics inherent to a heterogeneous reactive transport system.

The need to incorporate multi-component reactive transport to PA has also been stressed by the RETROCK project (Retrock 2005). The interplay between transport and chemical reactions is complex but possible and geochemical modeling nowadays can be definitely used as a tool to understand and describe complex systems as mentioned in section 2.1.

Reaction rates can be obtained from mixing ratios and disequilibrium within the medium is often controlled by mixing (Sanchez-Vila et al. 2007, De Simoni et al., 2007, Luo et al. 2008). The MRMT approach was proven to represent well the effective behaviour of conservative elements and seems to be a good methodology to integrate the impact of spatial heterogeneity on effective mass transfer and solute transport (Willmann et al., 2008). A novel effective reactive transport model is being implemented by coupling the MRMT transport equations with multicomponent chemical reactions (Donado et al. 2008).

A methodology for the analytical solution for reaction rates for multi-species equilibrium and non-equilibrium reactive transport in heterogeneous media was developed (Sanchez-Vila et al.

2007, De Simoni et al., 2007, quantifying the impact of heterogeneity on reaction rates (Luo et al., 2008) as well as the effect of heterogeneities on mixing and spreading. The impact of heterogeneity on mixing and spreading in geological media has been quantified and new indicators for mixing have been determined (Dentz and Carrera, 2007, Dent and Tartakovsky, 2008, Gouze et al., 2008, Zavala et al., 2007, 2008).

The stiffness of reactive transport codes is an additional problem for a direct application of these methodologies to PA. Thus, a Fortran 90 tool using object-oriented concepts that simulates complex geochemical processes has been developed (CHEPROO, (Bea et al., 2008). This tool is flexible and extensible and supports all the current demands in reactive transport modeling (e.g. implementation of different numerical approaches, complex geochemical models, spatial heterogeneity). A general structure is implemented with two entities or classes. The first class, called Nodal Chemistry Class accounts for the local composition description and geochemical state variables. The second entity, called Chemical System Class includes all the possible kinetic and thermodynamic models describing the behavior of the phases and reactions within and between them (thermodynamic and kinetic databases, stoichiometry of reactions, standard states and activity models). This tool supports future flexibility, extensibility and modularity, and can be easily linked to complex hydraulic simulation codes, which has been demonstrated in a series of study cases. Due to its flexibility and modular structure, CHEPROO can be readily incorporated into existing PA exercises.

Based on the theoretical and numerical studies on effective reactive transport outlined above, an effective large scale hybrid transport model was implemented. It is an hybrid model in so far, as large scale heterogeneity (obtained by hydraulic test, geo-radar, tracer tests, etc.) is represented explicitly, while the impact of small scale heterogeneity (difficult to determine deterministically) on transport is taken into account implicitly using a MRMT model (Willmann et al., 2008, Silva and Carrera, 2008). The resulting effective conservative transport research code (Silva and Carrera, 2008), coupled with the chemistry module CHEPROO This extended CHEPROO version can be coupled with any conventional flow and transport code and convert the latter into an effective reactive transport simulator.

Transport in crystalline rocks: Effects of colloids.

As mentioned before, a large effort was made in RTDC 4 to analyze the possible role of bentonite colloids on RN transport. To play a role in RN migration, colloids must exist in a non-negligible concentration, be mobile, stable and be able to adsorb radionuclides in an irreversible form (Ryan and Elimelech, 1996). As they are mainly site specific, these conditions must be verified investigating scenarios, geochemistry, hydrogeology, and other physical factors as well as possible artefacts that could bias data interpretation. In poorly mineralized waters, such as those present at the GTS, bentonite colloids may fulfil several of the above-mentioned conditions, so that the determination of the effects on radionuclide migration has to be studied in depth. The hydration and loss of density of the bentonite backfill are necessary conditions for the colloids to be formed at the bentonite/granite interface (Missana et al., 2003, Baik et al., 2007) but the quantification, in realistic conditions, of the colloid source term from the engineered barriers is still an open issue (Retrock 2005, Alonso et al., 2006).

In-situ transport studies at the GTS in the CRR project (Geckeis et al., 2004, Mori et al., 2003) demonstrated that bentonite colloid migration was not retarded with respect to the wa-

ter flow; the colloid recovery depended on not very well identified filtration processes taking place along the flow path as size exclusion, rock/colloid interactions and diffusion in the rock matrix. The recovery of bentonite colloids and highly sorbing tri- and tetravalent elements was very high (Hauser et al., 2002) but water flow conditions were not fully representative of those expected in a geological repository. Thus, it was considered necessary to perform more experimental studies at a laboratory scale, under constrained conditions as similar as possible to the real ones. **CIEMAT** and **FZK-INE** carried out the studies on inorganic colloids. **KTH** studied the kinetics of the complexation/sorption of cations to humic substances.

In particular in RTDC4, different processes related to bentonite colloids were analysed, following the many key-questions related to "the colloid problem": generation (Alonso et al., 2007, Seher et al., 2008), stability and effects on RN speciation (Bouby et al., 2007, Kunze et al., 2008), recovery under different flow rates (Missana et al, 2008), diffusion in the rock matrix (Alonso et al., 2007). Other studies on transport and rock/colloid interactions related with colloid properties (size or surface charge) were carried out also with model colloids (Au, quantum dots composed of CdSe/ZnS).

The generation of bentonite colloids from compacted clay in contact with stagnant (or low flow) water was analysed varying clay density, groundwater chemistry, clay type, surface exposed to hydration, pore size of extrusion layer were analysed. Figure 10 (left) shows an example of colloid generation from compacted bentonite. Colloid concentration initially increases but a steady state is reached in a relatively short time. The higher the clay dry density, the higher the quantity of colloids generated. Water chemistry controls the stability, size and concentration of the generated colloids: the concentration of colloids increase, when the salinity of the water decreases (Figure 9, right) and when pH increases. Ca-homoionised clay did not form colloid in appreciable concentration, but the presence of Na in the exchange complex (20 %) completely changes the generation behaviour (for example, as-received FEBEX bentonite). Finally, the surface exposed to hydration (and the consequent existence extrusion paths) also affects colloid generation. Generated bentonite colloids are stable over month in low mineralised and alkaline pH and their stability may increase in the presence of humic acids.

Liu and Neretnieks, 2006 suggested a 'zero order model' to describe the colloid generation from compacted bentonite for PA purposes. The criterion of colloid release is the critical coagulation concentration corresponding to 1 mmol/L Ca^{2+}. The studies performed within FUNMIG clearly show that taking a certain Ca concentration as a colloid generation criterion might not describe the real behaviour. Calculated colloid release rates according to the 'zero order model' in general are by far higher than measured in experiments. The new experimental data can be used to develop an improved colloid generation model.

The possible formation of bentonite colloids was studied also in-situ at the FEBEX site. Several techniques were used for detection and characterisation of colloids in these waters (PCS, LIBD, SEM, FESEM, EDX). ICP-MS analyses of the water before and after ultra-centrifuging were carried out to know which trace elements are present in colloidal form.

Clay colloids were detected in some intervals of the borehole FU05.001 (20-30 cm far from the bentonite) and compared to those obtained in the laboratory studies of bentonite colloid generation. The similarity in both microstructure and composition was shown.

The precise quantification of bentonite colloids resulted a difficult task but, from the measurements conducted so far and considering the quantity of Al (as indicator of the presence of bentonite), the concentration of colloids at 30 cm far from the bentonite and after 11 year is not higher than 1 ppm.
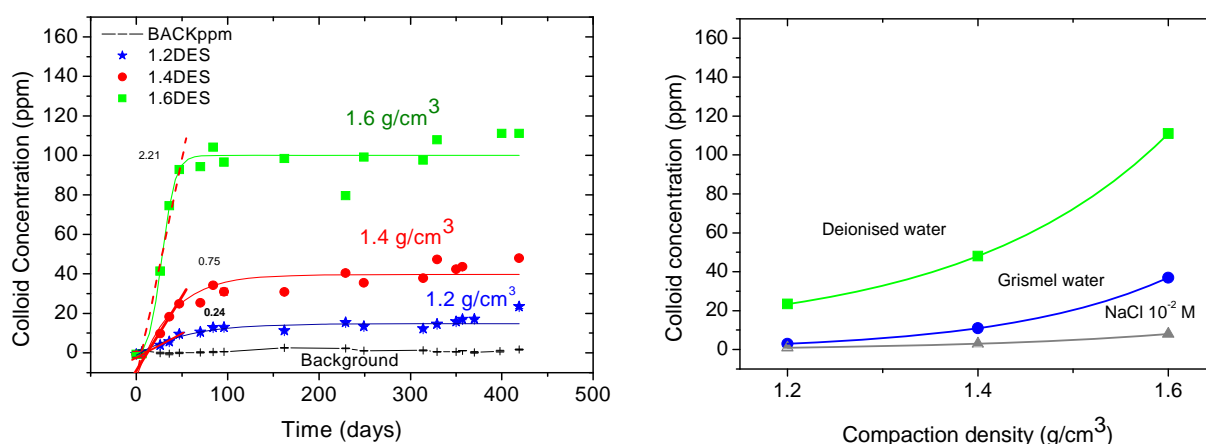

Figure 10. *Left: Generation of bentonite colloids from bentonite plugs at different initial densities in deionised water. Right: Dependence on the colloid concentration with the compaction density in three different waters (deionised, Grimsel groundwater and NaCl 0.01 M. As received FEBEX clay.*

Higher colloid concentration were measured by PCS, showing that artifacts, possibly introduced during the excavation of the new boreholes, exist. The analysis of these artifacts for a better quantification of the "source term" is a very important issue at moment (Missana et al., 2008). Additional studies are still being carried out to analyse the stability of bentonite colloids in the FEBEX tunnel and on the mineralogical characterisation of fracture filling materials that can affect the natural colloid formation and rock-colloids interactions and consequent filtration processes. In particular, the presence of Ca-carbonate in fracture fillings can be relevant in the stability behaviour of bentonite colloids in the FEBEX tunnel.

Filtration of colloids in the rock might be detrimental for radionuclide transport in fractures. In most of the transport studies performed in fractured cores, the breakthrough curves of colloids always presented an elution peak in a position very similar to that of conservative tracers but their recovery critically depended on the colloid concentration and on the water flow rate.

Even in Grimsel water, where the chemical conditions favour high colloidal stability and in spite of the existence of "unfavourable" electrostatic conditions for colloid-rock attachment, filtration of bentonite colloid increased significantly when the hydrodynamic conditions approached the ones expected in a repository (low water flow rates) and when the roughness of the fracture surface increased. Thus, this is an indication that "plugging effects" cannot be ruled out in RN transport under certain conditions (Albarran et al., 2008).

The quantification of colloid retention under conditions unfavourable and favourable to electrostatic attachment was analysed also by μPIXE (Alonso et al., 2008) and fluorescence microscopy (Filby et al., 2008). Under favourable conditions, electrostatic attraction prevailed: strong adsorption of negatively charged colloids was in fact observed at pH values close or below the point of zero charge (pH$_{PCZ}$) of the mineral surface. The adsorption of polyvalent

cations as Eu^{3+} at high concentration increased colloid attachment to minerals (Filby et al., 2008). Under unfavourable conditions colloid attachment was still observed (Filby et al., 2008), for example in minerals like albite or orthoclase, and even in the alkaline regime (Alonso et al, 2008). In this case, colloid retention on granite was found to be strongly dependent on small scale chemical effects, roughness or non-uniform distribution of charge sites.

The effect of matrix diffusion on colloid (2-100 nm) retention was analysed and colloid diffusion coefficients could be experimentally measured for the first time. Apparent diffusion coefficients of colloids in granite (approx. 10^{-18} m^2/s) were at least 3 orders of magnitude smaller than those for radionuclides measured in similar conditions (Alonso et al., 2007). These results revealed the small relevance of this process over others on colloid filtration.

Dynamic experiments in granite column were carried out to study the effect of bentonite colloid (**WP 4.4**), on the transport of Pu(IV), Eu(III), U(VI), Sr(II) and Cs(I) under low flow conditions. In the case of Pu and Eu, only the breakthrough peak corresponding to the colloid-associated transport could be detected. The recovery of Pu adsorbed onto the colloids was approximately the expected considering the previously estimated filtration of bentonite colloid in the medium and its adsorption on colloids, whereas the recovery of Eu was always lower. This probably indicates that, along the flow path, part of Eu desorbed from the colloids and was retained on the fracture walls.

Different desorption behaviour can be supposed for these elements even if they both present high K_d on clay colloids. Studies on the reversibility of bentonite colloid-RN attachment were performed with Eu(III) and Th(IV) (Bouby and Geckeis, 2007). The time-dependent desorption of Eu(III) from colloids studied by addition of humic acid as a competing ligand point to the establishment of equilibrium. A strong kinetic inhibition is however stated for Th(IV) desorption from bentonite colloids, where an equilibrium is not achieved even after several months.

The case of the low sorbing Sr, its transport in the presence of colloids was more complicated: three different Sr elution peaks existed probably related to the following mechanisms: 1) transport of Sr that remain adsorbed on mobile colloids (first peak); 2) transport of Sr retarded by granite and 3) transport of Sr retarded by the colloids retained in the fracture. Transport retarded by the accumulation of colloids was also observed in the case of uranium (Albarran et al., 2008).

The existence of these three different components clearly indicated that sorption onto bentonite colloids is reversible and that sorption/desorption processes occurs during the transport. Thus, the irreversibility of RN-colloid attachment is a point that has to be analysed more in depth and in conditions as similar as possible to the real ones, preferably in dynamic conditions.

A sensitivity study was carried out (Comenanza, 2007) to calculate the effects of the presence of bentonite colloids on radionuclide release from the near-field, based on the near field model for the Spanish repository in granite (Enresa 2000). A colloid concentration of 100 ppm was used in the calculations (the maximum concentration observed in generation experiments) and higher sorption (10 or 100 times, case 1 and 2 respectively) on colloids than in compacted bentonite was assumed. Calculations in these "conservative" conditions allowed calculating an increase factor in the peak rate for several radionuclides in the case 1 and 2

(e.g. ^{135}Cs (1.1, 2); ^{238}U(2, 9.2); ^{239}Pu (10, 93)). Figure 11 shows the effects of colloids on the releases from the near field for ^{238}U, ^{230}Th and ^{242}Pu.
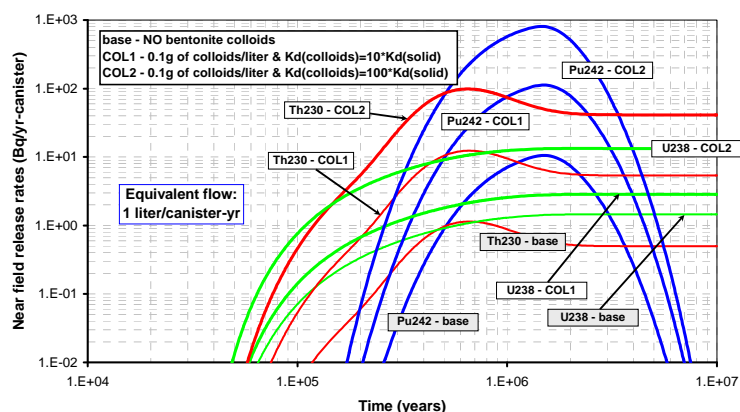

Figure 11. Effect of bentonite colloids on the releases from the near field of ^{238}U, ^{230}Th and ^{242}Pu. (No colloids, Case 1 and Case 2).

Calculations indicated that bentonite colloids have the potential to increase up to factor 100 the near field releases of strongly-sorbing radionuclides, such as curium, plutonium and thorium, compared with the base case. Calculations additionally showed that if radionuclide sorption on bentonite colloids is reversible, the release increase from the near field would lead to a similar increase in the doses that they produce. Doses due to these radionuclides are already very small due to their long travel times through the geosphere and total doses would be little affected. On the contrary, if sorption on bentonite colloids is irreversible and bentonite colloids move un-retarded at groundwater velocity, these radionuclides would move through the geosphere without retardation and the doses can increase significantly. This shows again that the study of the irreversibility of RN-colloid attachment is an issue.

Conclusions

The EC-FUNMIG project gave the opportunity to study more in depth processes affecting radionuclide migration in crystalline media (RTDC 4). Fluid-flow system, matrix diffusion and sorption, were studied focusing on different aspects that are not yet completely understood, in particular on the effects of the physico-chemical heterogeneities affecting the crystalline media.

The following conclusions obtained in the project can be highlighted:

➢ The importance of process identification and verification by real system analysis was shown.

➢ The use of new characterisation techniques of the fluid flow distribution is useful for a better description of the rock and the evaluation of hydraulic parameters, reducing the uncertainty in PA.

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➢ The studies on <u>matrix diffusion</u> were focused on the development of experimental and modelling methodology to account for the physical and mineralogical rock heterogeneity. Results obtained so far are promising to describe this mechanism more adequately. The methodologies have been validated but experimental data in a wider range of conditions are needed.

➢ In a similar way, the quantification of <u>sorption</u> by the determination of K_d and K_a parameters in the intact rock, proposed in RTDC4, provides more realistic data based on more in-depth knowledge of retention processes at the rock surface. The research on this issue should continue on these premises. An important advantage of the proposed methodologies is that retention, diffusion and porosity can be analysed in the same sample, this providing complementary information. The K_d database can be improved and the uncertainties reduced.

➢ Successful studies allowed the development of <u>up-scaling modelling methodologies</u>. The multirate mass transfer (MRMT) approach for effective transport modelling in heterogeneous media has proven to represent well the effective behaviour of conservative elements. Furthermore, MRMT seems to be a good methodology to integrate the impact of spatial heterogeneity on effective mass transfer and solute transport. This is a very interesting field of research to be continued. However, the application of these models to real repository conditions is still missing and this work needs further efforts.

➢ The CHEmical PRocesses Object Oriented code, CHEPROO, was developed as tool for <u>reactive transport</u> in PA A reactive transport model based on MRMT transport mechanisms and coupling with CHEPROO has been developed.

➢ A significant part of the RTDC4 work was devoted to study the <u>relevance of colloids</u> coming from the compacted bentonite barrier on radionuclide migration in crystalline media. The main parameters affecting the generation and stability of colloid were identified; laboratory experiments provided data to update existing models on colloid generation and to quantify the "source term" more precisely.

➢ Both strongly and slight sorbing elements showed, in the presence of colloids, a breakthrough peak related to colloid-driven transport. However, dynamic experiments demonstrated that <u>bentonite colloid recovery decreases significantly as approaching the hydrodynamic conditions expected in a repository</u> (i.e. very low water flow rates) even in conditions unfavourable to colloid attachment to rock surface and that may produce clogging effects. The retention of colloid on the rock surface was analysed and quantification studies were started. To perform experiments in realistic conditions is important to assess the real role of colloids in RN transport.

➢ <u>Apparent diffusion coefficients for colloids</u> (2-100 nm) were experimentally measured in granite for the first time. Colloid diffusion was shown to be a minor "filtration" process.

➢ Results obtained so far, indicated that future experiments should be focused on the study of <u>irreversibility of RN-colloids and rock-colloid interactions</u> in dynamic conditions.

➢ All the studies carried out in real sites always provided valuable inputs. The recently started studies at the FEBEX gallery would improve as far as the effects of disturbance due to new borehole excavation decrease, in particular regarding to the evaluation of

the presence of bentonite colloids. <u>To continue these studies in such a realistic environment is of great interest.</u>

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PROCESSES AND TRANSPORT STUDIES RELEVANT FOR SALT ROCK DISPOSAL CONCEPTS (RTDC5)

Introduction

In component RTDC5 of the integrated EC project FUNMIG the far field of the host rock formation salt is subject of the investigations. In contrast to the two other host-rock specific components RTDC5 is a real system analyses at an analogue site. The study is performed at Ruprechtov site in Czech Republic and represents an analogue for potential migration processes in a similarly structured overburden of a salt dome but also of other geological formations, which are foreseen as potential host rocks for radioactive waste repositories.

Due to the uncertainties in the safety assessment within the very long geological time frame multiple lines of evidence, supporting the modelling results as well as the conclusions to be drawn, will be of increasing importance for a Safety Case. One category of supporting arguments can be derived from natural analogues. The main benefit of natural analogues in a Safety Case is to increase understanding of long-term processes in geological environment and scale. In this context the investigations at Ruprechtov have been performed.

The speciation of uranium is of high relevance for the Safety Case, since uranium is the major constituent of spent nuclear fuel. The migration behaviour of uranium released from a spent fuel repository can be very complex. Retardation and sorption parameters are strongly affected under varying geochemical conditions, i.e. sorption and precipitation processes strongly depend on the groundwater properties such as pH, Eh, pCO_2, complexing agents as carbonates and natural organic matter, which determine the chemical speciation and hence the equilibrium distribution of uranium. Particularly, the redox state of uranium is of high relevance, since U(IV) mineral phases are sparingly soluble in contrast to U(VI) phases. Moreover, U(VI) forms negative species in many geochemical environments compared to the dominating neutral tetravalent $U(OH)_4$ species, resulting in quite different sorption behaviour.

Uranium speciation and interaction with various mineral phases have been analysed in numerous studies. Further, there is knowledge available from several natural analogue studies (e.g. Iwatsuki et al. 2004, Miller et al. 2000 and references therein) or investigations at potential repository sites indicating mobility and/or immobility of uranium. For example radiochemical studies in Boom Clay indicated that in general the Boom Clay is in state of secular equilibrium and no important mobility of uranium has been observed during the last million years (De Craen et al. 2004). Otherwise, at Forsmark site, quite high concentrations of uranium have been found in several groundwater samples in the depth of 200 – 650 m (Laaksoharju et al. 2006). These findings are of interest for the siting and safety assessment programme as they indicate that uranium is mobile in groundwaters at the Forsmark site. Investigations are under way to understand the mobility of uranium and its impact on the site understanding.

The Ruprechtov site was identified as suitable type of study, since the uranium occurrence is shallow close to the surface, and sedimentary layers, typical for the overburden of host rocks, with clay minerals, high organic content and partly sandy water bearing horizons exist here. Beside this a large data set had been already available before the FUNMIG work.

The topics "behaviour of organic matter" and "role of colloids" are investigated in detail in RTDC1 and 2. However, analogue studies can underpin results from lab and field experiments. In the natural environment colloid studies have been addressed in most of the major international analogue studies, for example, Poços de Caldas, Cigar Lake, Oklo and Bangombé, Palmottu and Maqarin where advective flow in fractures is present. In summary, it can be concluded that radionuclides in the groundwater can occur sorbed on colloids and that the possibility that a small fraction will be bound irreversibly to mobile natural colloidal particles cannot be entirely excluded. However, from these analogue results the overall consequence of the naturally occurring colloids for the safety of the repository is regarded as low because of the very small amounts of particles that exist in natural groundwater systems at the depths being considered for disposal (Miller et al. 2000). On the other hand organic colloids have turned out to be rather stable in the sedimentary formation at Gorleben site being present in quite high concentrations, formed by microbial oxidation of lignitic sediments (e.g. Buckau et al. 2000).

Approach and objectives of the work within FUNMIG

The Ruprechtov site, located in the north-western part of the Czech Republic, is geologically situated in a Tertiary basin filled with argillised pyroclastic sediments (Noseck et al. 2004). The study area is characterised by a granitic body, which partly crops out in the west and in the south (see Figure 1) and is widely kaolinised in varying thicknesses (up to several tens of metres) on its top in the central part. The horizon of major interest is the so-called clay/lignite layer, a zone of 1-3 m thickness at the interface of kaolin and overlaying plastic clay sediments in 20 to 50 m depth, with high content of SOC and areas of uranium enrichment. This layer does not represent a continuous aquifer, but rather distinct aquiferous zones. The general groundwater flow direction in the water bearing zones in the Tertiary is from southwest to northeast. The infiltration area is supposed to be in the outcropping granite in the western and south-western part, represented by the boreholes NA10, NA8 and RP1.

Results from site characterisation and a database were already available before this study, e.g. (Noseck et al. 2004). Within the FUNMIG project specific questions have been addressed, to receive an in-depth understanding of the evolution of the natural system and the key processes involved in uranium immobilisation as well as the behaviour of organic matter. Emphasis was put into characterisation of the immobile uranium phases, their long-term stability, uranium speciation and the factors controlling mobility of uranium in the system. The second major issue comprised the behaviour of colloids and organic matter in the system, particularly focused on better understanding the interrelation between sedimentary organic carbon (SOC) and dissolved organic carbon (DOC), its impact on the mobility of uranium and generally the role of microbes involved in these processes. As described above the investigations in RTDC5 are a natural analogue study, where specific questions are addressed, reflected by the following topics. The methodology for each topic is briefly described.
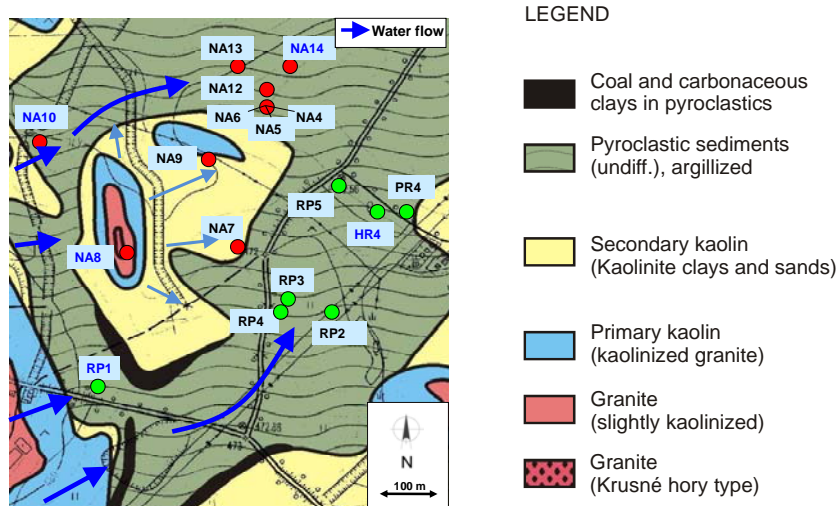
Figure 1. *Geological sketch of Ruprechtov site with location of the boreholes (Noseck et al. 2009a).*

Characterisation of the uranium speciation

Different microscopic and macroscopic methods have been applied to selected samples to characterise the immobile uranium phases. These methods comprise μ-XRF and μ-XAFS spectroscopy, sequential extraction, U(IV)/U(VI) separation with $^{234}U/^{238}U$ ratio determination. Detailed information about the methods can be found in (Noseck et al. 2008). In addition, sorption experiments have been performed and exchangeable uranium determined by isotope exchange with ^{233}U, e.g. (Havlova et al. 2006), (Vopalka et al. 2008). μ-XRD and μ-XAFS were applied the first time to natural samples and the method was further developed within the FUNMIG project. In addition several measurements of U(IV)/U(VI) speciation in the groundwater and accompanying geochemical calculations have been performed.

Characterisation of colloids and organic matter

Colloid characterisation: A borehole groundwater sampling system and a mobile laser-induced breakdown detection equipment (LIBD) for colloid detection, combined with a geo-monitoring unit has been further developed and applied to characterise the natural background colloid concentration in groundwaters of the Ruprechtov natural analogue site. To minimise artefacts during groundwater sampling the contact to atmospheric oxygen has been excluded by use of steel sampling cylinders opening and closing by remote control. The groundwater samples collected in this way are transported to the laboratory where they were eluted from the cylinders under original hydrostatic pressure without contact to oxygen. Behind the LIBD detection cell the system consists of in-series connected detection cells for pH, Eh, electrical conductivity, and oxygen content. More details can be found in (Hauser et al. 2005).

Organic matter behaviour: Additional work was carried out on characterisation of DOC and SOC (see also RTDC2). Generally, humic substances as potential complexing agents that can be released into groundwater due to organic matter degradation were extracted and additionally characterised using elementary analysis, ash and moisture content, UV-Vis spectroscopy,

FTIR spectroscopy, acidobasic titrations and MALDI-TOF. Humic acid complexation reaction with U(VI) as a potential interaction in groundwater was then studied (Cervinka et al., 2008). Moreover, DOC in groundwater was characterised by MALDI-TOF spectroscopy. Details can be found in (Cervinka et al. 2007). This work comprised also analyses of specific environmental isotopes, in particular $\delta^{34}S$ in dissolved sulphates as well as $\delta^{13}C$ and ^{14}C in DIC and DOC. Inverse geochemical modelling using Netpath was performed to understand the changes in the isotope signatures and therewith contribute to the understanding of the carbon chemistry, in particular to identify microbial degradation of organic matter.

Results, achievements for the Safety Case and conclusions

The chemical conditions of the site are characterised by low mineralised waters with ionic strengths in the range from 0.003 mol/l to 0.02 mol/l. The pH-values vary in the range 6.2 to 8 and the Eh-values from 435 mV to -280 mV. More oxidising conditions with lower pH-values are found in the near-surface granite waters of the infiltration area. In the clay/lignite horizon conditions are more reducing with Eh-values as low as -280 mV. The groundwater from nearly all boreholes of the clay/lignite horizon is of Ca-HCO$_3$-type. The waters from the infiltration area in granite (NA8, NA10 and RP1) as well as water from borehole NA12 with significantly lower alkalinity and Ca concentration are defined as Ca-SO$_4$-type water. All DOC values are in a range between 1 mg/l and 5 mg/l. A detailed description of the groundwater chemistry can be found in (Noseck et al. 2009a).

Uranium in the sedimentary system

The application of macroscopic and microscopic methods provided detailed insight into the U enrichment processes at the Ruprechtov site (Noseck et al. 2008). U-series analyses were used to obtain information of U mobility. The activities of ^{238}U, ^{234}U and ^{230}Th were analysed in the bulk samples from several boreholes from the U-enriched clay/lignite horizon. The results were interpreted using a Thiel's plot diagram (Thiel et al. 1983). Nearly all data are plotted in the U-deposition area (see Figure 2) and a high fraction of data points accumulate in segment S1, which is interpreted to represent an open system. Characteristic to S1 is the $^{234}U/^{238}U$ activity ratio below unity, which indicates that ^{234}U has been removed selectively over bulk U.

Selective ^{234}U removal can be considered as evidence for a high chemical long-term stability of the immobile uranium phase (Noseck et al. 2008). Selective removal of ^{234}U over ^{238}U is due to different origin of the isotopes: ^{238}U is primordial and ^{234}U is a decay product whose mobility is further facilitated by α-recoil process contributing to $^{234}U(VI)$ formation in U(IV) phase (see Suksi et al. 2006 and references therein).
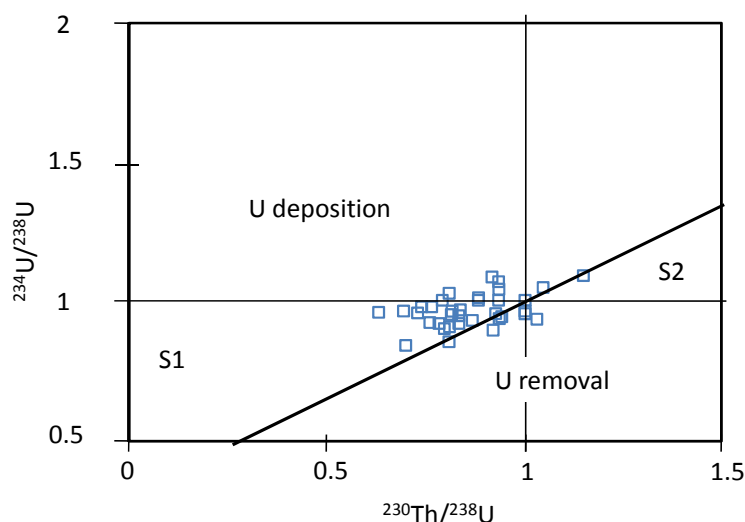
Figure 2. *$^{230}Th/^{238}U$ and $^{234}U/^{238}U$-activity ratios of bulk samples from the clay/lignite horizon plotted in a Thiel's diagram.*

Further insight into the chemical uranium form and stability is achieved by uranium redox state analysis. In order to separate U(IV) and U(VI), a wet chemical method (Ervanne and Suksi 1996) was applied for the first time to Ruprechtov samples. In the method U(IV) and U(VI) are extracted simultaneously from sample material and separated in ion exchange chromatography. A major result is that uranium in all samples consists of both U(IV) and U(VI). Results from all analyses are summarised in Table 1. The extraction did not dissolve all uranium. The content of uranium in this insoluble phase is denoted as U(res). The $^{234}U/^{238}U$ activity ratio denoted as AR was determined in all three phases. The AR differs significantly in the U(IV) and U(VI) phases, with ratios <1 in the U(IV) phase and ratios >1 in the U(VI) phase in nearly all samples. The AR of the U(res) phase is, with exception of NA12, similar to that observed in the U(IV) phase. Different (higher) AR in the NA12 residue may indicate involvement of different U compounds in the sample material, i.e. U(IV) and insoluble U(res) represent different compounds. Taking into account the higher stability of U(IV) phases we assume that insoluble uranium exists as a stable mineral phase in oxidation state IV. Most uranium in all samples is U(IV), with contents between 50 and 90 wt.%.

That U(res) and U(IV) exhibit in nearly all samples an AR below one is a strong indicator for their long-term stability. In order to attain low AR values of approx. 0.2 in the U(IV) phase no significant release of bulk uranium must have occurred during the time period of several half-lives of ^{234}U, i.e. for at least one million years. This is in good agreement with the hypothesis that the major uranium input into the clay/lignite horizon occurred during Tertiary, more than 10 My ago (Noseck and Brasser 2006). The U(VI) fraction or at least part of it has recently formed. The AR in this fraction varies from 1.2 to 3.4 and in general reflects the AR observed in groundwater. However, it is not fully clear, whether all U in this fraction is originally U(VI). There are indications that some oxidation of U(IV) occurs during sample storage (Noseck et al. 2005).

Table 1. *Amount of uranium and $^{234}U/^{238}U$-activity ratios (ARs) in the different phases from uranium separation (Noseck et al. 2008)*

sample	U [ppm]	U(IV)		U(VI)		U(res, IV)		U(IV) total
		[%]	$^{234}U/^{238}U$	[%]	$^{234}U/^{238}U$	[%]	$^{234}U/^{238}U$	[%]
NA6 35a	356±7	28.7	0.54±0.01	41.9	1.42±0.02	29.5	0.65±0.01	58.1
NA6 35b	468±9	45.9	0.56±0.01	33.3	1.69±0.03	20.7	0.64±0.02	66.7
NA6 35c	369±8	23.3	0.47±0.01	47.4	1.16±0.02	29.3	0.67±0.01	52.6
NA6 37a	37.3±2	73.7	0.79±0.03	15.7	2.66±0.07	10.6	0.73±0.01	84.3
NA6 37b	47.5±1,5	66.2	0.52±0.01	9.0	3.37±0.15	24.8	0.86±0.02	91.0
NA6 37c	35.7±2	51.3	0.58±0.01	19.8	2.56±0.08	28.9	0.71±0.04	80.2
NA11 a	52.5±2,2	4.2	0.44±0.02	34.1	0.94±0.01	61.7	0.55±0.02	65.9
NA11 b	53.6±2,5	6.1	0.39±0.02	49.6	0.94±0.02	44.3	0.67±0.02	50.4
NA12 a	27.2±1,4	3.9	0.26±0.02	47.5	1.31±0.04	48.6	1.22±0.03	52.5
NA12 b	31.4±2,1	4.2	0.13±0.02	57.4	1.25±0.04	38.4	1.04±0.03	42.6
NA13 a	216±7	5.4	0.53±0.02	46.8	1.15±0.02	47.8	0.55±0.01	53.2
NA13 b	230±9	1.6	0.58±0.03	46.2	1.15±0.02	52.2	0.53±0.01	53.8
NA14 b	317±10	13.3	0.87±0.02	68.8	1.28±0.02	18.0	0.44±0.01	31.2
NA14 c	354±11	25.4	0.88±0.02	39.6	1.11±0.01	41.5	0.54±0.01	58.5

In order to characterise uranium immobilisation processes notably confocal μ-XRF and μ-XANES were applied. In good agreement with results from chemical separation and other spectroscopic methods like ASEM and electron-microprobe μ-XANES identified U as U(IV) (Denecke et al. 2005). As demonstrated in Figure 3 (left), the shape and intensities show the average valence state of the sampled volume to be U(IV). All three curves do not show the multiple scattering feature 10-15 eV above the white line (WL) characteristic for U(VI) nor do they show a significant decrease in the WL intensity, which would be expected for U(VI) as be seen in the schoepite spectrum.

By μ-XANES and μ-XRF it was also shown that As exists in two oxidation states, As(0) and As(V). The analyses of a number of tomographic cross sections of elemental distributions recorded over different sample areas show a strong positive correlation between U and As(V). By further development of the method, using new planar compound refractive lens (CRL) array at the Fluoro-Topo-Beamline at the synchrotron facility ANKA of the Forschungszentrum Karlsruhe, a higher spatial resolution (focus beam spot size of 2 x 5 μm^2 (V x H)) was achieved. The high resolution made it possible for the first time to discern an As-rich boundary layer surrounding Fe(II)-nodules, see Figure 3, right (Denecke et al. 2007). This suggests that an arsenopyrite mineral coating of framboidal pyrite nodules is present in the sediment. Uranium occurs in direct vicinity of the As-rich layers. In conclusion of these results a driving mechanisms for uranium enrichment as secondary U(IV) minerals in the sediment was suggested. Mobile, groundwater-dissolved U(VI) was reduced on the arsenopyrite layers to less-soluble U(IV), which formed U(IV) mineral phases. As(0) was oxidised to As(V). Uranium, therefore, is associated with As(V).
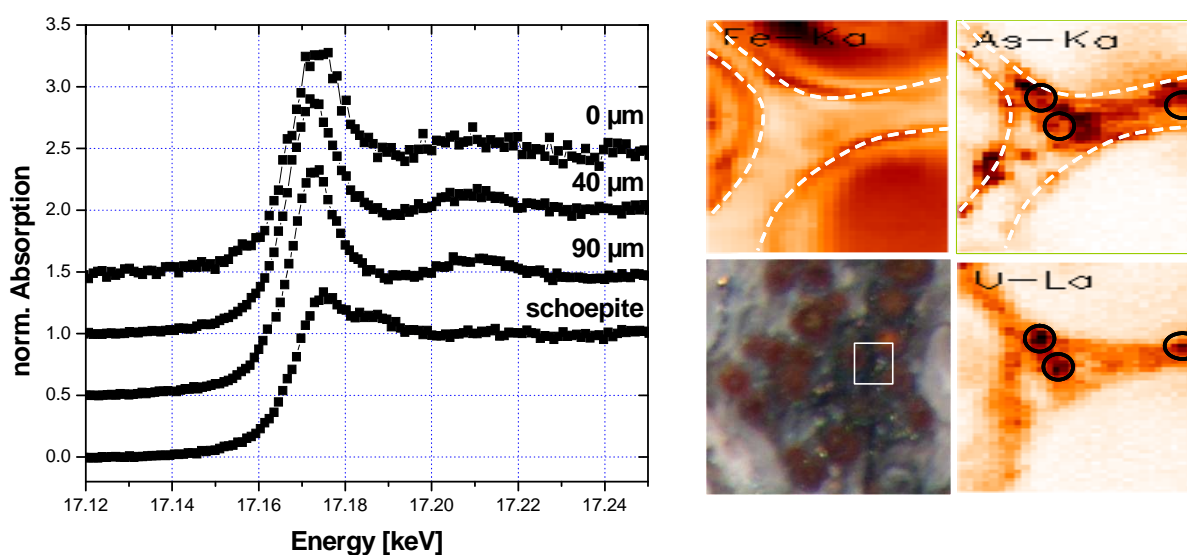
Figure 3. *Results from μ-XANES (left) and μ-XRD (right) of a sample from borehole NA4 (Denecke et al. 2005, Denecke et al. 2007).*

The results from these microscopic methods are supported by cluster analysis of sequential extraction results, which also indicate that U occurs in the tetravalent state, since major part of uranium is extracted in the respective steps for (reduced) U(IV) forms and the residual fraction (Noseck et al. 2008). By cluster analyses, performed to identify possible correlations between elements, a strong correlation of U with As and P was found (see Figure 4), supporting the mechanism postulated above and the existence of uranium phosphate mineral ningyoite identified by SEM-EDX.
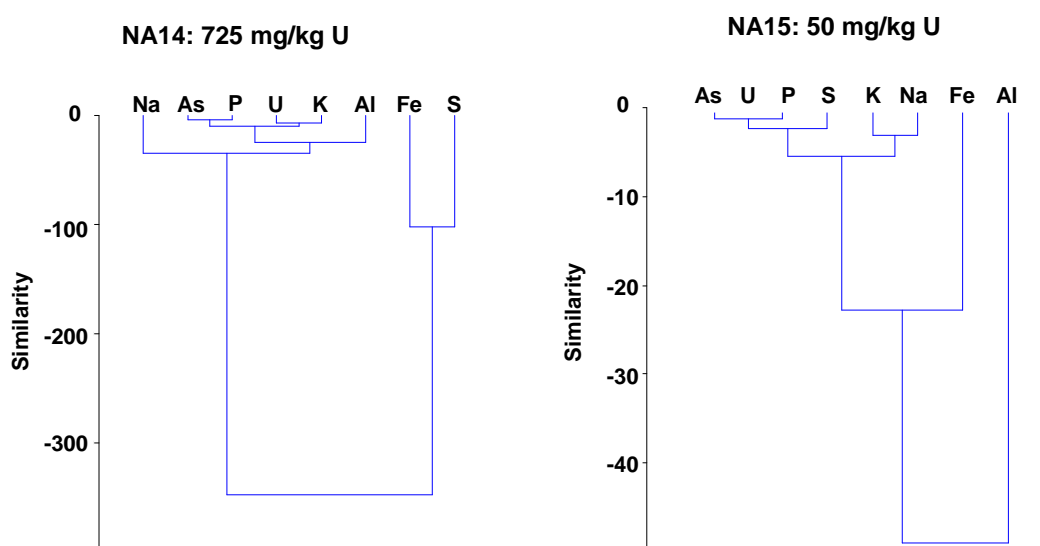

Figure 4. *Cluster analyses for extended SE results of samples from the boreholes NA14 and NA15*

The long-term stability of the immobile uranium phases in the clay/lignite horizon can be understood by a closer look into the current geochemical conditions at the site. Groundwater

analyses show that the uranium concentrations in the clay/lignite horizon are low with values below 1µg/l for nearly all boreholes. In this horizon in-situ Eh-values in the range of -160 to -280 mV seem to be determined by the SO_4^{2-}/HS^- couple (Noseck et al. 2009b).

Uranium speciation calculations have been performed with GWB (Bethke et al. 2006) and the updated NEA TDB database (Guillaumont et al. 2003). The Eh/pH diagram for typical conditions at Ruprechtov site is shown in Figure 5. The data for the more oxidising granite groundwater from the infiltration area are dominated by uranyl-carbonate complexes, whereas the groundwaters from the clay/lignite horizon are at the boundary of the stability fields for the tetravalent aqueous $U(OH)_4$ complex and the hexavalent complexes $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$. First analysis of the U(IV)/U(VI) ratio in groundwater showed the existence of both valence states in solution but only 20% in the U(IV) state (Noseck et al. 2009b). However, the calculations confirmed that due to the high CO_2 partial pressure from microbial SOC degradation and probably CO_2 exhalation (Noseck et al. 2009a) in this system even for the quite reducing conditions a part of the dissolved uranium can be stabilised as U(VI) by carbonate complexes. The calculated fraction of U(IV) in groundwater NA6 at pH 8 assuming equilibrium is shown in Figure 5.

An appropriate method to understand which uranium phases control the uranium solubility in the natural system is the calculation of saturation indices. In many reducing groundwater systems uraninites or pitchblendes with stoichiometry of UO_{2+x} are found to be the phases controlling the dissolved uranium concentration. In the uranium enriched sediments at Ruprechtov site two secondary U(IV) phases have been observed, UO_2 and ningyoite ($CaU(PO_4)_2 \cdot 1$-$2H_2O$). Since no stoichiometric determination of the UO_2 phase was performed, saturation indices of different U(IV) mineral phases are taken into account. Thermodynamic data for ningyoite are not available in the NEA TDB and have been taken from recommendations in (Langmuir 1997).
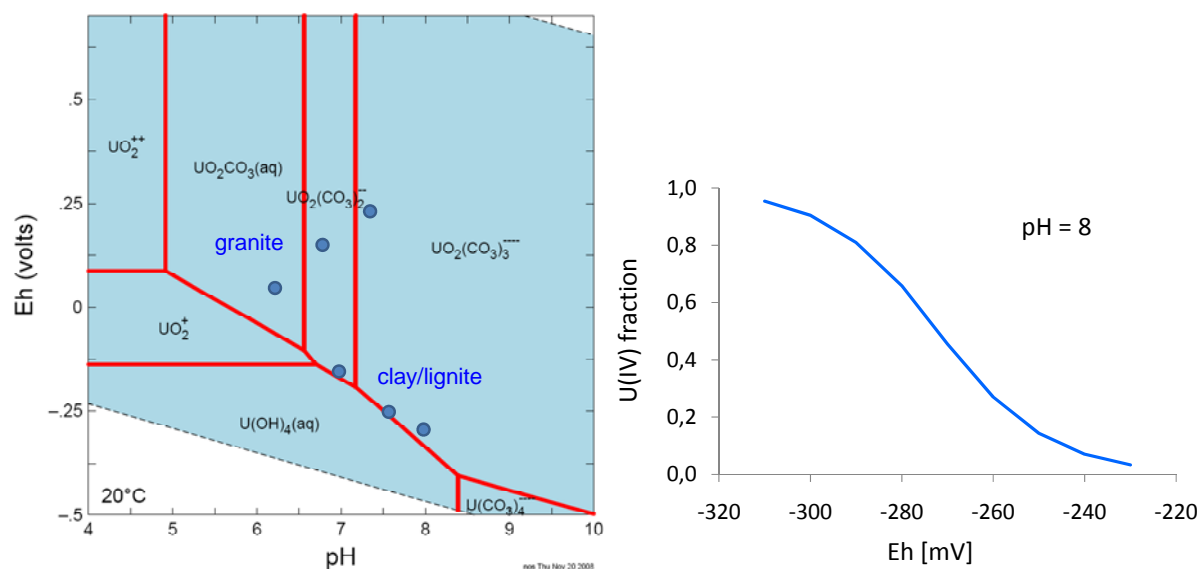

Figure 5. *Left: pH/Eh-diagram for Ruprechtov groundwaters. U concentration 10^{-3} mg/l, CO_2 activity = 10^{-3}. Right: fraction of U(IV) in dependence of Eh-value at pH 8, for conditions of NA6 groundwater.*

The calculation results are shown in Figure 6. The groundwaters from the clay/lignite horizon are strongly oversaturated with respect to the crystalline uraninite and coffinite indicated by saturation indices (SI) in the range between 5 and 7. The mixed valence uranium oxides

$UO_{2.25}$ and $UO_{2.33}$ are also oversaturated (SI between 2.5 and 4). The mixed valence oxide $UO_{2.66}$ is always undersaturated with SI values below -0.8. No saturation of U(VI) minerals was indicated. Assuming an uncertainty range of ±0.6 (shadowed area in Figure 6) for the saturation index, resulting from uncertainties in the thermodynamic data, the results indicate that the uranium concentration in groundwater is controlled by amorphous UO_2. SI values for ningyoite are also close to saturation in groundwater NA6 and NA13, but not for NA12. So, there is generally a good agreement with observed mineralisations in the clay/lignite horizon. Metastable amorphous UO_2 has been shown also in other studies to be likely the uranium controlling mineral phase, e.g. (Iwatsuki et al. 2004). These results also indicate that no significant U-release can be expected under the geochemical conditions in the clay/lignite horizon, in agreement with the very low $^{234}U/^{238}U$ activity ratios observed in the uranium(IV) mineral phases as indicators for their long-term stability.
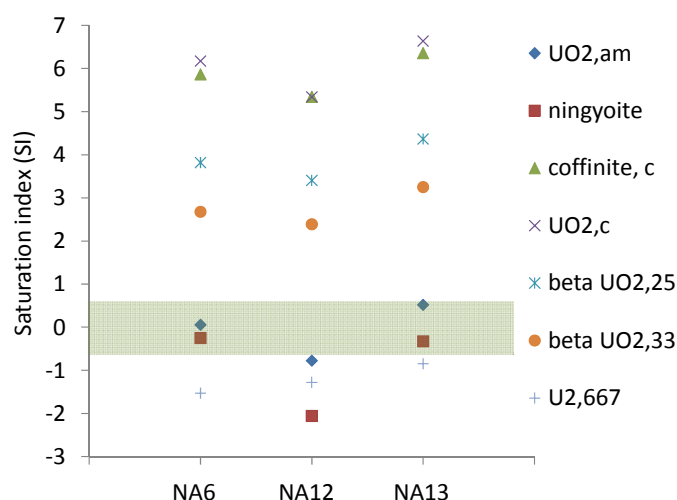

Figure 6. *Saturation indices of various U(IV) minerals calculated for groundwaters NA6, NA12 and NA13.*

Investigation of colloids in natural systems

As discussed above part of the work was dedicated to method-development and qualification. During the project a new mobile geomonitoring system including a system for the laser-induced breakdown detection of colloids (LIBD) was developed (Hauser et al. 2005). It was successfully applied to the detection of colloids in natural groundwater samples from Ruprechtov site and other sites in Sweden.

It could be shown that colloid concentrations down to µg/l can be detected with the special sampling technique. By comparison with in-situ probe measurements in several boreholes it was also demonstrated that reducing conditions with minimal access of atmosphere oxygen are maintained. In-situ experiments in granite demonstrated that colloid generating processes like redox changes (e.g. in the EDZ) and/or mechanical erosion can increase the natural colloid background by up to several orders of magnitude.

The natural background colloid concentrations LIBD determined at Ruprechtov were compared with data of studies performed in Äspö (Sweden) and Grimsel (Switzerland). A comprehensive representation of colloid concentrations in different water samples as determined

by LIBD as a function of the respective ionic strength is given in Figure 7 (Hauser et al. 2005, see also the section about RTDC2). Increasing ionic strength usually forces colloid aggregation which is reflected in lower colloid concentration in the respective groundwater.

In the Ruprechtov groundwater samples the ionic strength varies in the range of $2 \cdot 10^{-3}$ to $1.1 \cdot 10^{-2}$ mol/l without any significant influence on the measured colloid concentration. The broad bandwidth of detected colloid concentrations in groundwater of ionic strength <100 mmol/l (Grimsel, Ruprechtov) suggests that different parameters besides ionic strength as e.g. pH and/or groundwater velocity may control the actual colloid concentrations. However, the studies suggest that an ionic strength of 100 mmol/l represents some kind of upper limit: colloids may persist in groundwater with ionic strengths below this value for considerable time scales and variable colloid concentrations. At ionic strengths above 100 mmol/l natural aquatic colloid stability is effectively decreasing. As a consequence, for groundwater samples from Äspö and simulated NaCl solutions a clear dependency of the maximum colloid concentrations with the salinity of the solution is found.
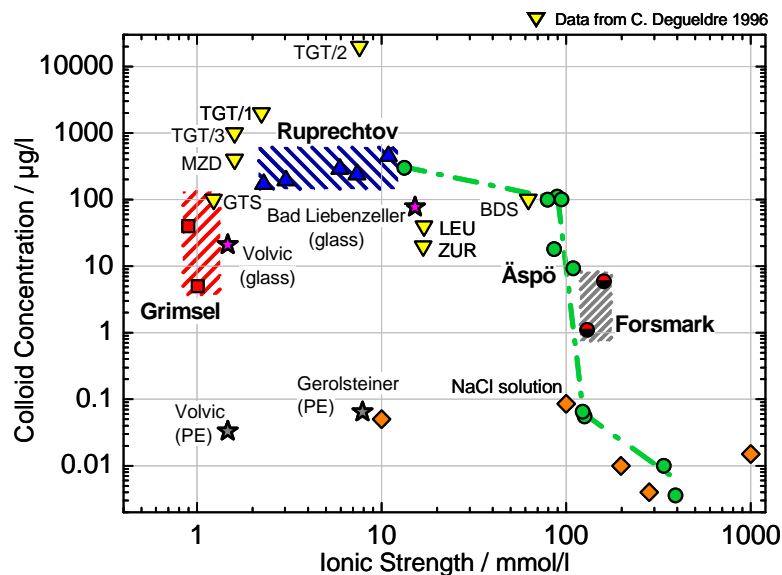

Figure 7. Comparison of colloid concentration in different types of natural groundwater, mineral water and synthetic NaCl-solution versus ionic strength. For details see (Hauser et al. 2005)

Carbon chemistry and role of organic matter in the sedimentary system

One part of the work comprised the re-evaluation of existing, and the evaluation of new hydrological, geochemical and environmental isotope data from groundwater wells at Ruprechtov site to characterise the hydrogeological flow regime and the carbon chemistry in the system. The existing idea about the flow system in the tertiary sediments was confirmed. Additionally, the complexity of the system was demonstrated (see Noseck et al. 2009a). Differences in stable isotope signatures in the northern part of the site indicate very local connections of the flow systems with the flow system in the underlying granite via fault zones.

In order to understand the carbon chemistry and the interrelation between SOC and DOC isotopes of carbon in DIC, DOC and SOC were evaluated. This work is described in detail in

(Noseck et al. 2009a). Here only the major aspects with respect to the formation of DOC in the clay/lignite layer are elaborated. In Figure 8 on the left the correlation between biogenic DIC and DOC is plotted, assuming that the ^{13}C content of the source water is of inorganic origin with -27 ‰ and additional DIC is of organic origin. Besides data for NA8, which well is probably not strongly connected to the clay/lignite water, the other data follow a line, with increase of biogenic DIC from infiltration waters NA10 and RP1 to the waters from the clay/lignite layer. It is an important indication that in this layer DOC is formed by additional release of DIC, as it is observed at other sites, e.g. (Buckau et al. 2000).

Concerning the mechanism of DOC release, important information can be gained from other isotope signatures. Firstly, the evolution of ^{13}C and ^{14}C isotope signatures from the infiltration area to the clay/lignite horizon was investigated by simple open and closed system models and inverse geochemical modelling. The general result is that additional CO_2 input from microbial degradation of SOC into the system is evident and can explain the development of δ^{13}C and ^{14}C isotopes in DIC in the clay/lignite horizon. There is also an evidence that in addition some input of endogenous CO_2 occurs. All data and a detailed explanation can be found in (Noseck et al., 2009). A further strong indicator for microbial degradation of organic matter by sulphate reduction is the δ^{34}S signal in dissolved sulphates. Since sulphate reducing bacteria had been detected at the site, appropriate analyses were performed in groundwater from the infiltration area and from the clay/lignite layers.
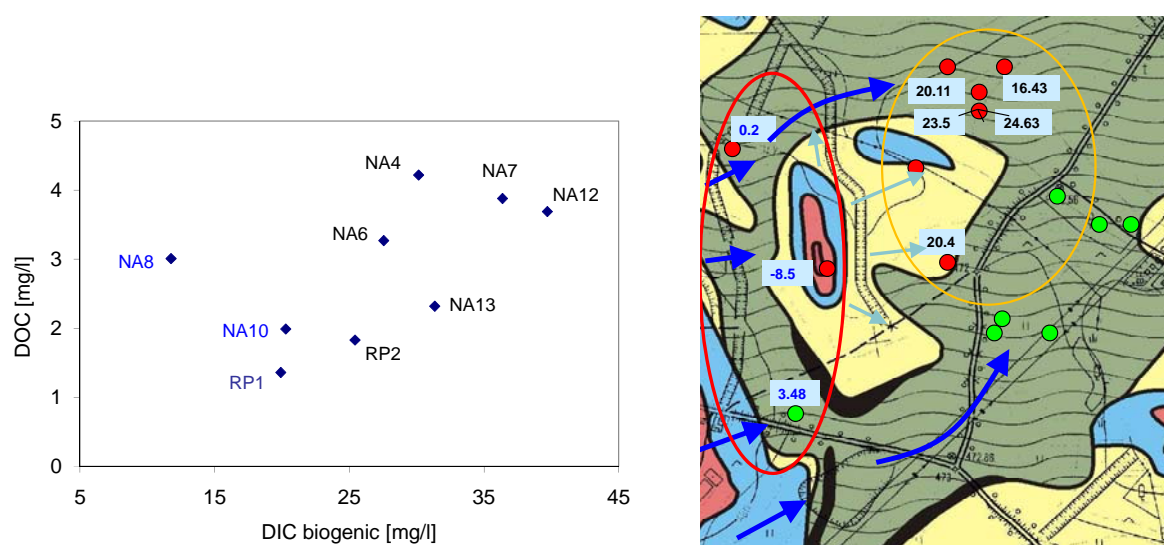

Figure 8. *Correlation of biogenic DIC with DOC (left) and δ^{34}S values in boreholes from the infiltration area (red circle) and clay/lignite layers (yellow circle) (Noseck et al. 2009a).*

The results (see Figure 8, right) show that δ^{34}S-values in waters from the clay-lignite layer (yellow circle) are in a range between 16.4‰ and 24.6 ‰, i.e. strongly increased compared to the values between -8.5 and 3.48 observed in the wells from the infiltration area (red circle). The substantial enrichment of ^{34}S in these boreholes is a clear indication that microbial sulphate reduction occurs in the clay/lignite layers. The microbial sulphate reduction is accompanied by isotope fractionation. The lighter isotope ^{32}S is preferentially metabolised by the microbes leaving residual sulphate enriched in ^{34}S in the solution. With the initial sulphate concentration in the infiltration area and the concentration after sulphate reduction in the clay lignite an enrichment factor ε can be calculated by use of the Rayleigh equation. Based on the data from all wells shown in and the corresponding sulphate concentrations an enrichment

factor of 11‰ was calculated (Noseck et al. 2009a). Compared to other investigations this value is comparably low, but not unusual for bacterial sulphate reduction. Enrichment factors in a similar range of ~10 ‰ have been observed e.g. in (Knöller et al. 2004).

In order to better understand the interrelation between SOC and DOC, in particular to understand the relatively low DOC concentrations below 5 mg C/l in the water from clay/lignite layer compared to other sites with SOC-bearing sediments (Buckau et al. 2000), a more detailed analysis of SOC from selected samples of clay/lignite layers have been performed. SOC was characterised in detail by micropetrographical methods, by the application of different extraction schemes, by degradability experiments, and by interaction experiments of humic acids with natural clay samples.

The micropetrographical study showed that the sedimentary organic matter at Ruprechtov site is generally formed by slightly dispersed matter with low degree of coalification, which only reaches brown coal or lignite degree. However, partly layers of coal clay or even coal seams had formed. The main components of detritic and xylodetritic coal samples and clay-lignite samples are mineral admixtures and huminite of the maceral group (Cervinka et al. 2007).

According to the results from SOC characterisation it seems that the low concentration of dissolved organic matter in the Ruprechtov system is mainly caused by the low degradability of the sedimentary organic matter. Only average of 4 % of SOC can be released into solution and the release rate is increasing with coalification. An additional reason could be the strong sorption properties of the clay that fix humic acids on the sediment matrix. This is indicated in sorption experiments performed by NRI with extracted natural HA-12/3 from Ruprechtov samples on the montmorillonite standard SAz-1 and on low TOC clay samples from borehole NA11 and NA15. The results are shown in Figure 9 and indicate significant sorption of HA on the clay samples with higher sorption values on Ruprechtov samples compared to standard montmorillonite.
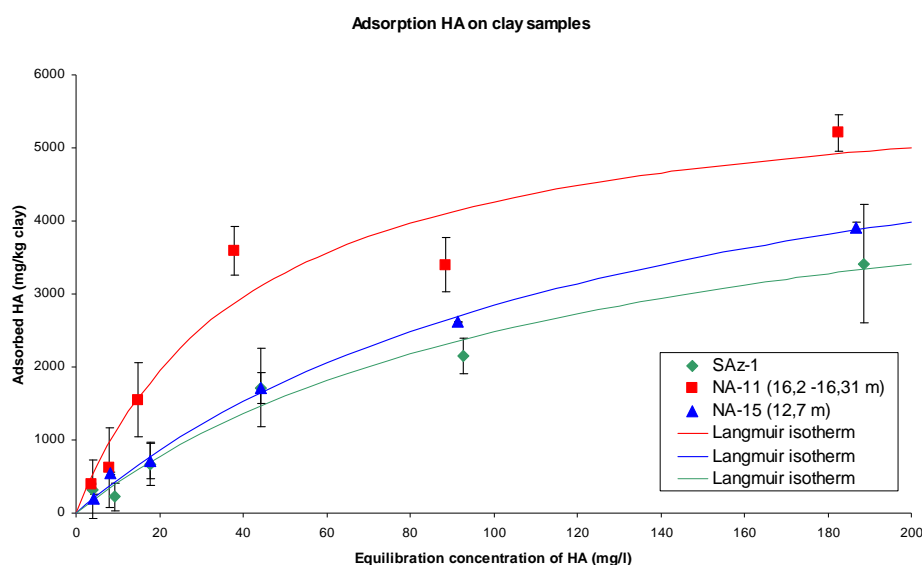

Adsorption HA on clay samples

Figure 9. Sorption isotherm of HA on different clay samples.

The integration of all results showed that organic matter did not play such an important role by direct interaction with uranium, but SOC contributed and still contributes to maintain re-

ducing conditions in the clay/lignite layers. It is supported by the finding that the highest accumulations of uranium were located slightly below the parts, which are highly enriched in organic matter. It can be concluded that SOC within the sedimentary layers was (and to some extent still is) microbially degraded. By this process DOC is released, providing protons to additionally dissolve SIC. Moreover SO_4^{2-} is reduced leading (and has lead in the geological past) to the formation of iron sulphides, especially pyrite. Reducing conditions, being maintained amongst others by sulphate reducing bacteria, caused the reduction of As, which sorbed onto pyrite surfaces, forming thin layers of arsenopyrite. Uranium U(VI), originally being released from the outcropping/underlying granite, was reduced to U(IV) on the arsenopyrite surfaces. UO_2 and uranium phosphates were formed by reaction of U(IV) with phosphates PO_4^{3-}, released by microbial SOC degradation. These U(IV) minerals have been stable and immobile over geological time frames.

Conclusions and outlook

This natural analogue study contributed to the Safety Case regarding the far-field transport of radionuclides in sedimentary layers in different ways. A very important part was the aspect of method development and testing, e.g. colloid sampling under undisturbed conditions with detection limit in the μ-molar range, and further development of μ-XRF and μ-XANES with first application to natural samples as well as application of modern isotope analyses like $\delta^{34}S$ signatures to identify relevant processes in the field. All these methods are important for characterisation of a potential repository site including lab and field experiments.

The key processes occurring at Ruprechtov site have been identified and a consistent picture of the geochemical behaviour of uranium and the role of organic matter and colloids has been reached. Moreover, a strong long-term barrier function of a sedimentary layer and the involved key processes were identified. The sedimentary system at Ruprechtov site provides evidence that uranium is and was effectively immobilised in a sedimentary layer, which was exposed to surface erosion in the geological past. Today the uranium enriched horizons occur in a depth between 20 and 50 metres. All results indicate that uranium was efficiently immobilised in a reducing environment (controlled by the SO_4^{2-}/S^{2-} couple) over millions of years. There is no indication for uranium mobilisation recently and within the geological past. The low uranium concentrations in the groundwater in the range of $1-8\cdot10^{-9}$ mol/l nowadays are determined by amorphous UO_2 and ningyoite, which is underpinned by geochemical modelling and observations of both mineral phases in the clay/lignite horizon.

The role of microbial processes turned out to be very important with respect to the key processes at Ruprechtov site in the geological past and also today. Sulphate reducing bacteria have been identified and typical framboidal shaped pyrites (formed by microbial sulphate reduction) are found in the clay/lignite horizon. In the geological past, arsenopyrite layers have formed on the pyrite surfaces acting as a reductant for U(VI). Today microbes are still active in the clay/lignite horizon proved by a strong increase of the ^{34}S content in dissolved sulphate compared to the infiltration water. By this process DOC and DIC is released leading also to an increase in dissolved phosphate. It is suggested that phosphates released from the organic matter have been the source for the formation of the U(IV) phosphate minerals in the past.

With respect to the behavior of organic matter the situation in Ruprechtov is quite different to that at Gorleben site. The results indicate that DOC does not contribute to mobilisation of U because of the relatively low DOC concentration in the groundwater of the clay/lignite layer.

DOC is formed by microbial degradation of SOC in the clay/lignite layers but only a very small fraction of SOC seems to be accessible. The study also contributed to complement information on stability of colloids in geochemically different natural systems.

The importance of an appropriate handling of the redox-sensitive samples became evident. The samples have to be carefully stored under inert argon atmosphere directly after drilling. However, in some of our samples, an alteration after long storage times, partly even under argon atmosphere, could be observed, which might have affected the U(IV)/U(VI) ratio in the sediment. Another challenge was the determination of the Eh values, under low flow conditions at the site. The planned kaolin mining at Ruprechtov site provides the opportunity to investigate the effect of disturbed geochemical conditions in the clay/lignite horizon and its impact on the uranium behaviour. These issues will be tackled in a specific follow-on investigation.

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IMPLICATIONS FOR THE SAFETY CASE

(RTDC6)

Abstract

The scope of the FUNMIG Integrated Project (IP) was to improve the knowledge base on radionuclide retention processes in the geosphere, relevant for assessment of the safety of radioactive waste repositories. An important part of this project involved the interaction between data producers (research) and data users (European radioactive waste management organisations). The aim thereof was to foster the benefits of the research work for performance assessment (PA), and in a broader sense, for the safety case of radioactive waste repositories. For this purpose, a specifically adapted procedure was elaborated. Thus, relevant features, events and processes (FEPs) for the three host rock types, clay, crystalline and salt, were taken from internationally accepted catalogues and mapped on each of the 108 research tasks by a standardized procedure. The main outcome thereof was a host-rock specific tool (Task Evaluation Table) in which the relevance and benefits of the research results were evaluated both from the PA and research perspective. Virtually all generated data within FUNMIG are related to the safety-relevant FEP-groups "transport mechanisms" and "retardation".

Generally speaking, much of the work within FUNMIG helped to support and to increase confidence in the simplified PA transport and retardation models used for calculating radionuclide (RN) transport through the host rock. Some of the studies on retardation processes (e.g. coupled sorption-redox processes at the mineral-water interface) yielded valuable data for all three rock types dealt with within the IP. However, most of the studies provided improved insight regarding host-rock specific features and processes, the majority of this work being dedicated to clay-rich and crystalline host rocks. For both host rock types, FUNMIG has significantly contributed to improving understanding on a conceptual level, both by providing new experimental data at different spatial scales and by developing new modelling approaches. The disposal concept in salt host rocks differs from those in other host rock types in that the host rock is, at least in part, regarded as near-field from which under normal scenarios no release of radionuclides is possible. Corresponding investigations in FUNMIG concerned therefore not salt host rocks but an example of an overburden.

Selected highlights with regard to FUNMIG's achievements include: For argillaceous host rocks, the systematic effort of investigating and comparing diffusion and sorption processes at different scales in different clay rocks using a variety of methods has substantially increased the knowledge basis for future safety cases. For crystalline host rocks, valuable data on the generation, transport and filtration of clay colloids from the near-field and their impact on RN transport under realistic conditions have been obtained. The results from studies on organic colloids and on biofilms, including their interaction with radionuclides, have been shown to be of interest for future safety cases of salt-host rocks. Among the main research issues from a PA perspective to be addressed in the future, we note the following: (i) the question of irreversibility of RN sorption to colloids in fractures of crystalline rocks, (ii) a comprehensive

model for cation and anion diffusion in clays for different scales and (iii) the applicability of mechanistic retardation models for strongly sorbing radionuclides in intact clay and crystalline host rocks.

An important lesson learnt from the interaction between research and PA is that it would be desirable to conduct an analogous evaluation procedure for the proposed task before the start of the research work. In this regard, the procedures developed within FUNMIG are a useful tool for planning future Integrated Projects.

Introduction

Geological disposal is the favoured final goal for radioactive waste management because it provides long term security and safety in a manner that does not require active monitoring, maintenance and institutional control (NEA, 2004). Geological disposal relies on the multi-barrier concept, including both engineered and natural (geological) barriers. A key function of the geological barrier (the host rock and possibly additional geological units above and/or below the host rock) is to protect the repository and its included engineered barrier systems (EBS) for very long times by ensuring low groundwater fluxes, by providing mechanical stability and by ensuring geochemical conditions that are favourable to the long-term stability of the EBS. Moreover, the host rock should retard radionuclides which eventually might pass through the EBS, leading to attenuation of radionuclide releases to the biosphere due to radioactive decay. Retardation processes that occur during transport are very dependent on geochemical conditions. Thus, it is crucial to understand (1) the geochemical conditions within the host rock formation and (2) the interaction processes between radionuclides and rock constituents (porewater solutes, mineral surfaces, organic matter, biota).

The focus of the FUNMIG (fundamental processes of radionuclide migration) IP was to improve knowledge on biogeochemical processes which affect radioactive species during their transport in the geosphere, sometimes termed the far-field. It complements the sister IP NF-PRO which was focussed on processes relevant to radionuclide transport in the so-called near-field, the engineered barrier system (EC, 2008). A primary objective of FUNMIG was to promote interaction between researchers on one hand and "end users" (i.e. specialists responsible for compiling safety cases for deep geological repositories) on the other hand, as well as to develop tools for application in performance assessment (cf. section 2). This interaction, which in fact was an important part of the IP, was enforced by a specifically adapted organisation and management (cf. section 3).

The general structure of FUNMIG, which included 51 partner organisations, comprised six research and technology development components (RTDCs) and one component on training, knowledge management and dissemination of knowledge transfer (www.funmig.com). RTDC 1 investigated conceptually well-established radionuclide migration processes with the aim of filling in critical data gaps, while RTDC 2 was focussed on improving understanding of conceptually less understood fundamental processes driving radionuclide migration in the geosphere. RTDCs 3 to 5 were focussed on investigations of specific rock types currently under discussion in Europe for hosting HLW repositories (clay-rich sedimentary, crystalline, salt; in the case of salt an example of an overburden was investigated). RTDC 6 provided a forum for documenting the general aspects of performance assessment tool development, bringing the outcome of the other RTDCs under one umbrella. Thus, this last RTDC was largely responsible for promoting, organizing and managing the applied component of the programme - the

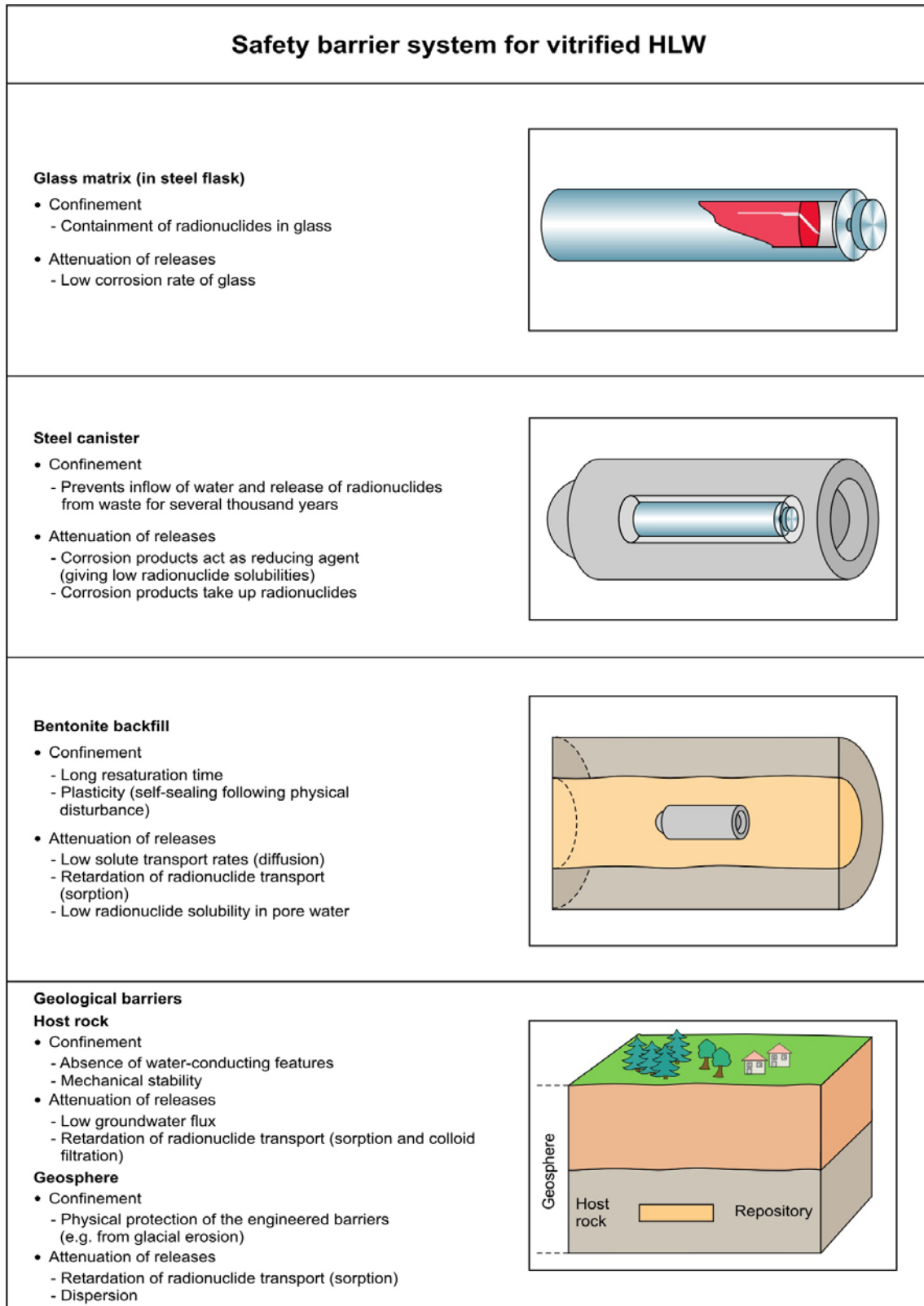use of the generated results for the assessment of the long-term safety of geological HLW disposal.

Figure 1. *The system of safety barriers for vitrified high-level waste (HLW) in the Swiss disposal concept (from Nagra 2002)*

This contribution summarizes the outcome of FUNMIG with regard to the safety case for HLW repositories. In section 2, the main elements necessary for a safety case are presented and the role of the host rock therein is highlighted. The approach adopted in FUNMIG for promoting interaction between research and application for the safety case is described in section 3. The main achievements of FUNMIG for the safety case are outlined in section 4. Finally, the benefits of the programme for the safety case are discussed in section 5.

Safety concepts in geological disposal of high-level nuclear waste

Deep geological disposal relies on efficient isolation of the high-level nuclear waste (HLW) from the human environment for very long time periods (in the order of 10^6 years).

The geological disposal of HLW is based on the multi-barrier safety concept. The disposal system is designed to completely contain the waste for a period of time (steel or copper/steel canister) and, after canister breaching, to retard and attenuate the releases of decaying radionuclides through the backfill material (e.g. bentonite), if present, and the host rock. The safety concept thus provides passive barriers with multiple safety functions, as illustrated in Fig. 1 for the Swiss HLW disposal concept.
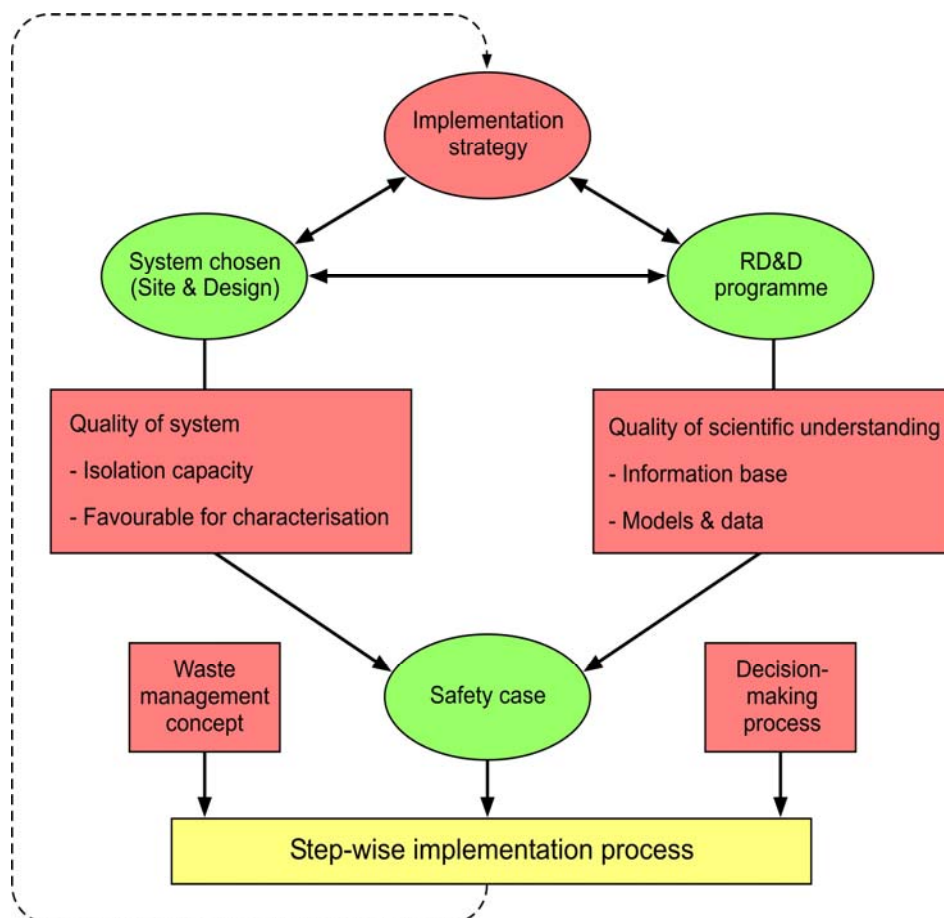

Figure 2. Important elements of decision-making for the step-wise and iterative repository implementation process (from Nagra 2002)

The role of the host rock and the surrounding formations as safety barriers is rock- and concept-specific, but from a general point of view they provide the following safety functions: (1) to isolate the waste from the human environment, (2) to provide long-term confinement of the waste by protecting the engineered barriers due to the mechanical stability and favourable geochemical properties (e.g. redox and pH buffering capacity), and (3) to attenuate releases of radionuclides by retardation and dispersion processes.
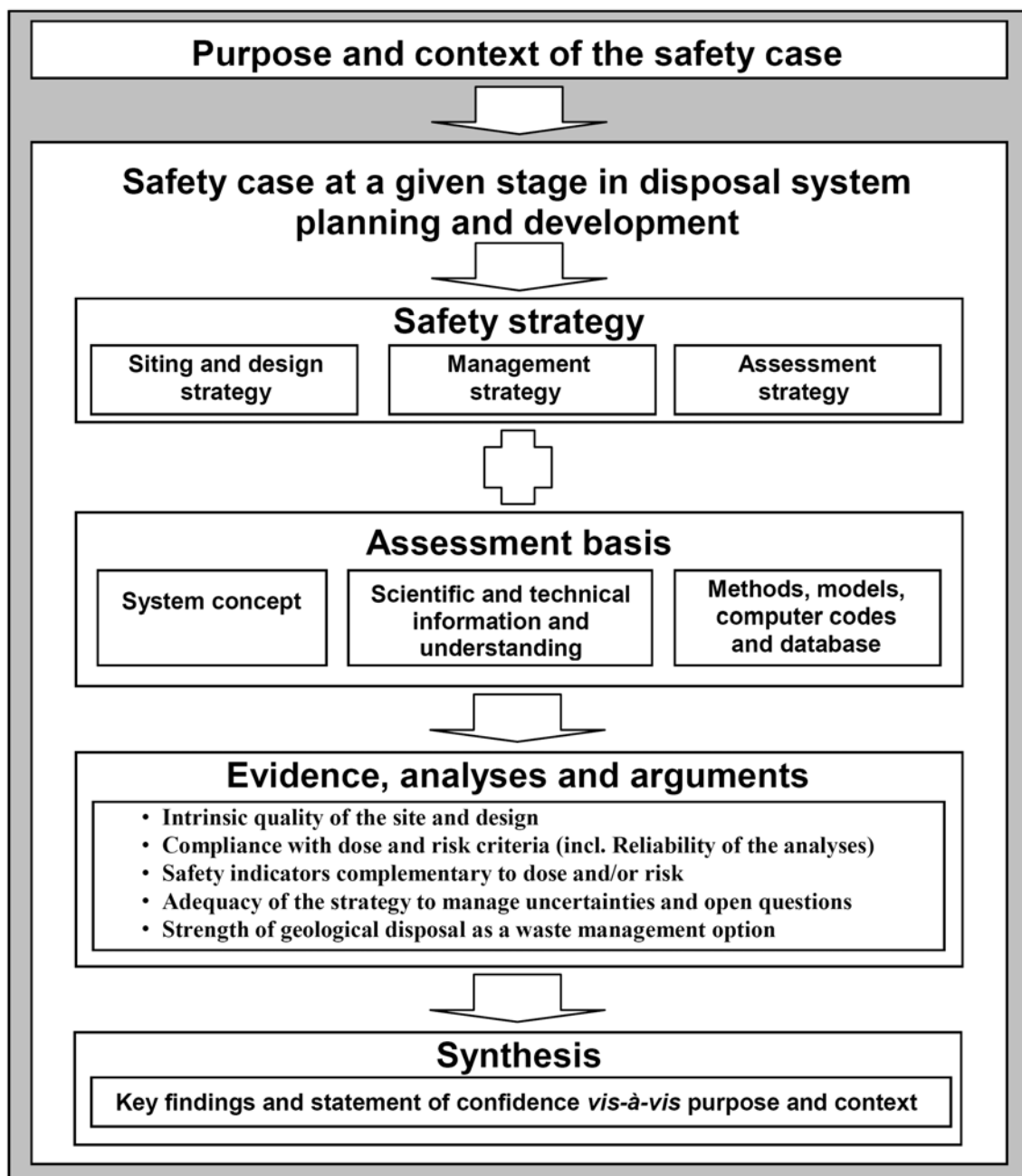

Figure 3. *Methodology for the development of a safety case (from NEA 2004)*

The implementation of a HLW repository is a complex and lengthy process. There is wide international agreement that for this purpose, a staged, iterative approach should be adopted, with the possibility to take into account insights from previous stages (NEA, 2004). The implementation strategy has to ensure that both the design of the system and the associated RD&D programme, which provides system understanding, are adequate for the stage at hand. An example for such an iterative approach is illustrated schematically in Figure. 2.

A key aspect in this implementation process is the assessment of long-term safety, which needs to be addressed in a thorough, transparent and traceable way. In view of the long experience gained with this issue in the different nuclear waste management programmes, established procedures for evaluating long-term safety have been developed (NEA, 2004; IAEA, 2008). Thus, rather than presenting a set of radionuclide transport and resulting dose calculations, as was often the case 20-30 years ago, a comprehensive so-called safety case is presented, which, according to the Nuclear Energy Agency of the OECD (NEA, 2004), can be defined as follows: "A safety case is the synthesis of evidence, analyses and arguments that quantify and substantiate a claim that the repository will be safe after closure and beyond the time when active control of the facility can be relied on." Important elements of the safety case are (Fig. 3): the safety concept (e.g. description of disposal system components and their safety functions), the assessment basis (e.g. methods, models, scientific & technical data for different repository components and geosphere), performance assessment (evidence, analyses and arguments) and a synthesis (overall interpretation of all safety-relevant considerations).

Performance assessment (PA), which is often used synonymously with "safety assessment", can be defined as "… the process of analysing the performance of a repository and showing, with an appropriate degree of confidence, that it will remain safe over a prolonged period, beyond the time when active control of the facility can be guaranteed …" (NEA, 2004).

The interaction between research and PA in FUNMIG

As outlined in the introduction section, an important objective of FUNMIG was to promote and to enforce the interaction between science and PA. Thus, the main task of RTDC 6 was to monitor the scientific outcome of the IP for its use in future safety cases and to provide feedback to the researchers from the PA perspective.

The organisation for the research-PA interaction process in FUNMIG is illustrated in Fig. 4. The Integration Monitoring Group (IMG) was composed of one representative for each of RTDC 1-5. The "PA group" was composed of representatives of European WMOs participating in FUNMIG. The process was coordinated within RTDC 6.
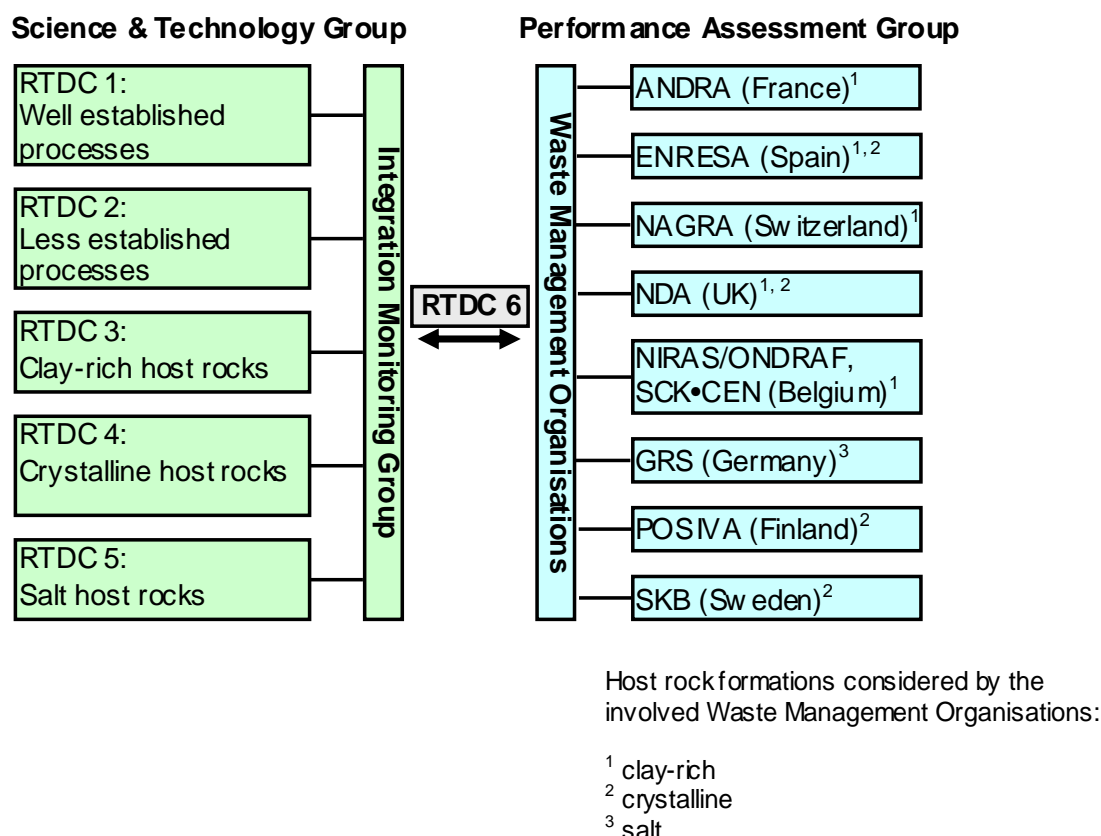
Figure 4. *Organisation in FUNMIG: Interaction between "Science" and Performance Assessment coordinated by RTDC 6*

The interaction process involved four steps (Nagra, 2010):

(1) Definition of boundary conditions: The relevant radionuclides and their respective fluxes passing from the engineered barrier system (near-field) to the geosphere (far-field) were extracted from the documentations of the various European disposal concepts. This compilation confirmed the general assumption that the radionuclides released from the waste enter the far field in trace amounts only. In addition, the results from the sister NF-PRO project regarding the interface between near-field and geosphere were extracted from the final reports of this IP. Thus, not only RN fluxes, but also possible disturbances affecting the far field were discussed in the compilation document. Possible disturbances arising from near-field processes include gas generation by corrosion of steel components, transport of corrosion products and of bentonite colloids, and transport of oxygen, organics and nitrate. With a few exceptions (bentonite colloids, some waste-originated organics) near-field induced disturbances were not subject of the studies carried out in FUNMIG.

(2) Compilation of each research task and mapping to relevant FEPs: A standardized summary - termed Task Abstract Form - was compiled by the researchers for each of the 108 research tasks identified as being carried out within FUNMIG. Based on this information, the tasks were to be interpreted with regard to their relevance for PA by internationally accepted criteria for clay-rich, crystalline and salt host rocks. For argillaceous rocks, FEPCAT (Mazurek et al., 2003), a catalogue of safety-relevant Features, Events and Processes (FEPs) was applied. In the case of crystalline rocks, a catalogue of FEPs based on

RETROCK (EC, 2005), a European project on the treatment of radionuclide migration in crystalline rock with safety assessment was used. For salt host rocks, the FEP list recently developed within the German research project ISIBEL (TEC, 2008) was taken as basis.

(3) Evaluation of research tasks by a standardized procedure: The evaluation of the Task Abstract Forms using the FEP catalogues for the different rock required an adaptation of the project structure (Fig. 5). For this purpose, three Task Evaluation Tables (TETs) for the clay-rich rocks in RTDC 3, crystalline rocks in RTDC 4 and salt rocks in RTDC 5 were prepared. The tasks of the two non-host rock specific components RTDC 1 and RTDC 2 were included in each of the three host-rock specific TETs. The topics (families of tasks) treated in FUNMIG and their relevance for the three host rock types are shown in Table 1. The upper part of Fig. 5 depicts the general structure of the TETs. Based on the information in the Task Abstract Forms, all restructured tasks were evaluated by the PA team of WMO representatives to their relevance and benefit for the different safety cases, on one hand, and with regard to the scientific progress achieved within FUNMIG, on the other. For this purpose, the WMOs used expert judgement based on their experience in previous safety cases and sensitivity analyses carried out therein. As a counterpart in the interaction process, the researchers were asked to give their opinion as to the possible benefits of their work for future safety cases. All this information was included in the host-rock specific TETs. Thus for every task, FEP numbers and affected PA parameters were assigned to and, most importantly, a standardized evaluation consisting of the researcher's view and the WMO's view was included (Nagra, 2010).

(4) Synthesis: After elaboration of the TETs, the achieved results were synthesized by grouping the individual FEPs into "Super-FEPs".
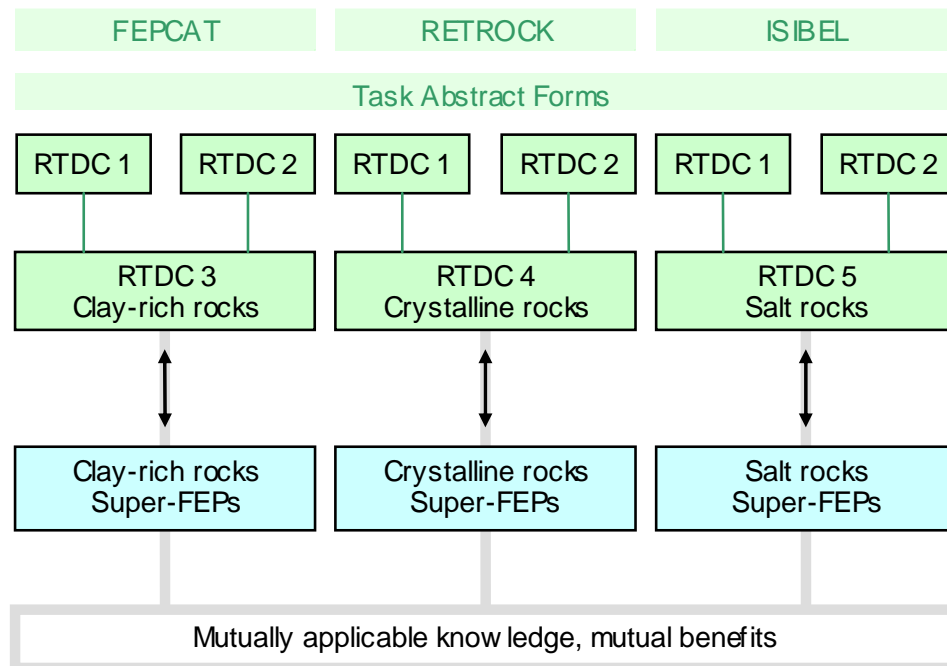

Figure 5. *Structure for task mapping and evaluation in FUNMIG (see text)*

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Table 1: Topics tackled within FUNMIG and their relevance for different host rock types

Process / Topic:	Host rock type		
	Clay-rich host rocks	Crystalline rocks	Overburden of salt host rocks
Key thermodynamic data	×	×	×
Ion exchange and surface complexation	×	×	×
Influence of organics on retention	×	×	×
Retention by the formation of solid solutions, including retardation of anions	×	×	×
Inorganic colloids	(×)	×	×
Organic colloids	(×)	×	×
RN redox transformation on minerals	×	×	×
Biogeochemical processes	(×)	×	×
Thermodynamic equilibria in clay	×		
Diffusion in clay	×		
Up-scaling	×	×	×
Characterization of geochemical conditions		×	
Fluid flow system characterization		×	×
Generation, stability and mobility of colloids		×	×
Process identification and verification by real system analysis	×	×	×

FUNMIG achievements for the safety case

Clay-rich host rocks

The evaluation procedure revealed that virtually all FEPs treated within FUNMIG could be grouped into the two Super-FEPs "Transport mechanisms" (A1) and "Retardation" (A2), as shown in Fig. 6. "Transport mechanisms" includes the FEPs diffusivity, connected matrix porosity, ion exclusion and surface diffusion. For the super-FEP "retardation", the processes tackled within FUNMIG are ion exchange, surface complexation, solid solutions / co-precipitation and dissolution / precipitation of solid phases. The parameters corresponding to the two Super-FEPs and typically used in PA are sorption values (K_d), solubility, effective diffusivity and diffusion-accessible porosity.
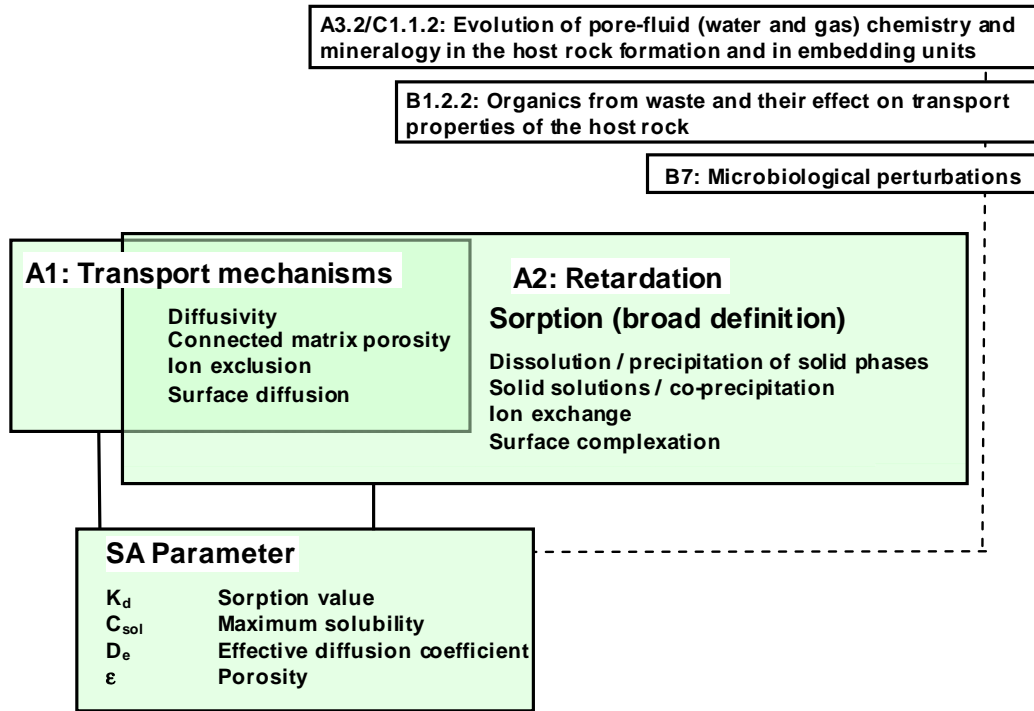
Figure 6. FEP groups and single FEPs (taken from FEPCAT) to which the FUNMIG tasks from RTDC 1, 2 and 3 were mapped, and affected safety assessment parameters for the clay-rich host rock case

In safety cases for argillaceous host rocks, it is often argued that RN transport is adequately described by using simple "averaged" parameters which apply to the entire clay formation. RN migration is hence represented by Fick's two diffusion laws. For a steady-state RN flux:

$$J = D_e \frac{dC}{dx} \text{ with } D_e = D_p \varepsilon = D_0 (\frac{\delta}{\tau^2}) \varepsilon$$

where J: flux (mol·s^{-1}·m^{-2}), D$_e$, D$_p$, D$_0$: 'effective', 'pore', 'free solution' coefficients (m^2·s^{-1}) respectively, C: concentration (mol·m^{-3}), x: diffusion distance (m), δ/τ^2: "tortuosity factor" (ratio between constrictivity and tortuosity), representing effects of pore space geometry on diffusion (dimensionless), ε: diffusion available porosity (dimensionless).

For time-dependent RN mass transfer:

$$\frac{\partial C}{\partial t} = D_a \frac{d^2 C}{dx^2} \text{ with } D_a = \frac{D_e}{\varepsilon + \rho_d K_d}$$

where D_a: 'apparent' diffusion coefficient ($m^2 \cdot s^{-1}$), ρ_d: rock dry density ($kg \cdot m^3$); K_d: distribution coefficient representing partitioning of RN mass between dissolved species and sorbed species at position x (m).

Most clay-based work in FUNMIG was focussed on improving conceptual models and mechanistic understanding for diffusion-driven migration of two classes of radionuclides which are of key importance for the safety case:

- Non or weakly sorbing radionuclides, principally in anionic form (e.g. $^{36}Cl^-$, $^{129}I^-$). Here the main focus was to improve understanding of diffusion-related processes influencing D_e, ε, and δ/τ^2, including ion exclusion, porosity distribution and mineral organisation, and effects of mineral composition.
- Moderately and strongly sorbing radionuclides, principally in cationic form (e.g. $^{135}Cs^+$, actinides, lanthanides). Here the main focus was on retardation processes of diffusing radionuclides, such as cation exchange, surface complexation or co-precipitation of radionuclides which affect the distribution coefficient K_d.

In the following paragraphs, the main achievements with regard to the safety case, grouped into retardation and diffusion-related processes, are summarized.

Retardation:

Significant new results were obtained for a variety of different research areas. The most relevant progress from the safety case view was achieved in the issues listed below.

Sorption models:

A great body of high-quality sorption data for clay minerals and clay rocks is available and system-specific sorption models including cation exchange and surface complexation reactions exist. However, these models are based on intrinsic parameters which have limited general applicability and thus the derivation of K_d parameters for safety assessment is not straightforward. The challenge is to develop equilibrium sorption models offering prediction capability over a wide range of conditions. Within FUNMIG, modelling exercises on the basis of existing sorption data (Lützenkirchen & Huber, 2007; Grambow, et al. 2006) and new interesting concepts on data treatment, based for example on a simple additivity approach, have been performed. The promising results obtained offer a first step to achieve this goal.

Sorption of actinides and other strongly sorbing radionuclides:

In spite of considerable sorption data for divalent, trivalent and tetravalent metals on clay minerals as well as on the clay rock materials, uncertainties with regard to the effective sorption values under repository-relevant conditions remain. One of the reasons for this is related to the methodological difficulties for obtaining reliable data for strongly sorbing tracers in compact systems. Thus, in conventional setups for diffusion tests with strongly sorbing tracers (e.g. Eu), sorption to equipment material occurs, making data interpretation difficult. Moreover, diffusion distances for many relevant nuclides are very short (i.e. generally below 1 cm) within realistic experimental timescales, which poses a challenge for interpreting diffusion

profiles. New designs for diffusion tests have been developed and new high-resolution analytical techniques applied to overcome these technical constraints (Robinet al., 2008a). The results obtained so far indicate that the new technical developments are promising, but considerable methodological work it still necessary for achieving reliable sorption data for strongly sorbing species under compact conditions.

The diffusion data on an array of tracers (HTO, Cl, Br, I, Na, Sr, Cs, Co, Eu) obtained from small-scale and block-scale samples supported in-situ tests performed both in the URLs at Mont Terri (CH) and the Meuse / Haute-Marne site (F) (Alonso et al., 2009a; Cormenzana et al., 2008; García-Gutiérrez et al., 2008; Appelo et al., 2010). A large modelling exercise on a long term in-situ experiment in Opalinus Clay (OPA) enabled improved 2D and 3D description of sorbing tracers within a complex geometry (Gimmi, 2008; Samper & Yang, 2007).

Valuable new sorption data on actinides and chemically related species has been obtained from dilute batch systems on model mineral systems and rock materials, including also the quantification of carbonate complexation on radionuclide sorption (Marques Fernandes et al., 2007). Spectroscopic evidence has been given that lanthanides and actinides form inner sphere complexes at edge sites of the clay surfaces (Schlegel, 2008).

Effect of natural and waste-derived organics:

Natural organic matter (OM) in the clay rock may, depending on its chemical nature and its reactivity, either enhance radionuclide mobility by strong complexation or reduce it by creating additional surface sites or by forming surface complexes rather than dissolved ones. Since the reactivity of the humic-like OM in the plastic Boom Clay (foreseen as host rock in Belgium), on radionuclide complexation is significantly larger than that of the natural OM in the more "mature" clay formations Callovo-Oxfordien (COx, foreseen as host rock in France) and OPA (foreseen as host rock in Switzerland), most work in FUNMIG on this issue is of interest to Boom Clay. Experimental and modelling studies on the interactions of humic acids with actinides and chemical analogues (Eu, Am, Pu) using advanced spectroscopic techniques provided new results on speciation and competition effects, also under conditions relevant for Boom Clay (Liu et al., 2008a; 2008b). Further studies on the interaction of Eu, Am and Th with natural OM provided complementary information on the effect of OM on K_d values (Reiller et al., 2006; 2008).

A comparative experimental study on COx and OPA (Schäfer et al., 2008; 2009) provided new insight into the reactivity of kerogen, its spatial distribution and its complexation properties for radionuclides.

Another combined experimental and modelling study (Evans et al., 2006; 2008) indicated the low influence of simple organic compounds on radionuclide sorption/migration, such as low-molecular weight organic acids, relative to that of humic acids. This finding is particularly relevant for disposal concepts containing a high inventory of organic wastes.

Redox processes affecting selenium and other radioactive elements:

Clayrich host rocks contain reducing minerals (e.g. Fe(II)-bearing minerals, sulphides) and organic matter which endows them with a reducing capacity. Under the expected reducing repository conditions, these compounds may react with redox sensitive radionuclides and thus strongly affect their mobility. So far, little work on this topic has been carried out and uncer-

tainties in the fate of important radioactive elements, such as Se, exist. Several investigations within FUNMIG have provided valuable new data on this issue.

The reducing capacity of Fe(II) minerals and Fe(II) sorbed on the clay in COx together with their reaction kinetics was assessed (Tournassat et al., 2005; Lerouge et al., 2006a; Gehin et al., 2007; Charlet et al., 2007) which helped to clarify their role in immobilizing redox sensitive radionuclides. Several experimental studies have been focussed on the interaction of Se with pyrite, clay minerals and natural OM from Boom clay (Liu et al., 2007; Bruggeman et al., 2007; Breynaert et al., 2008; Montavon et al., 2009a). The results yielded a consistent picture showing that Se(IV) is reduced to insoluble Se(0) in the presence of pyrite and natural OM. Interaction with FeS on the other hand led to the formation of more reduced FeSe compound. The mobile U(VI) species also gets reduced to insoluble tetravalent oxides under Boom Clay-type conditions (Bruggeman & Maes, 2008).

Transfer of sorption values from dilute to compact conditions:

As outlined above, mechanistically derived sorption data is generally obtained from dilute batch-type systems and needs to be extrapolated to appropriate K_d values under compact in-situ conditions. This transfer process is a priori not straightforward since it involves a number of assumptions, both with regard to the solution chemistry and to the electrochemical surface properties of the clay.
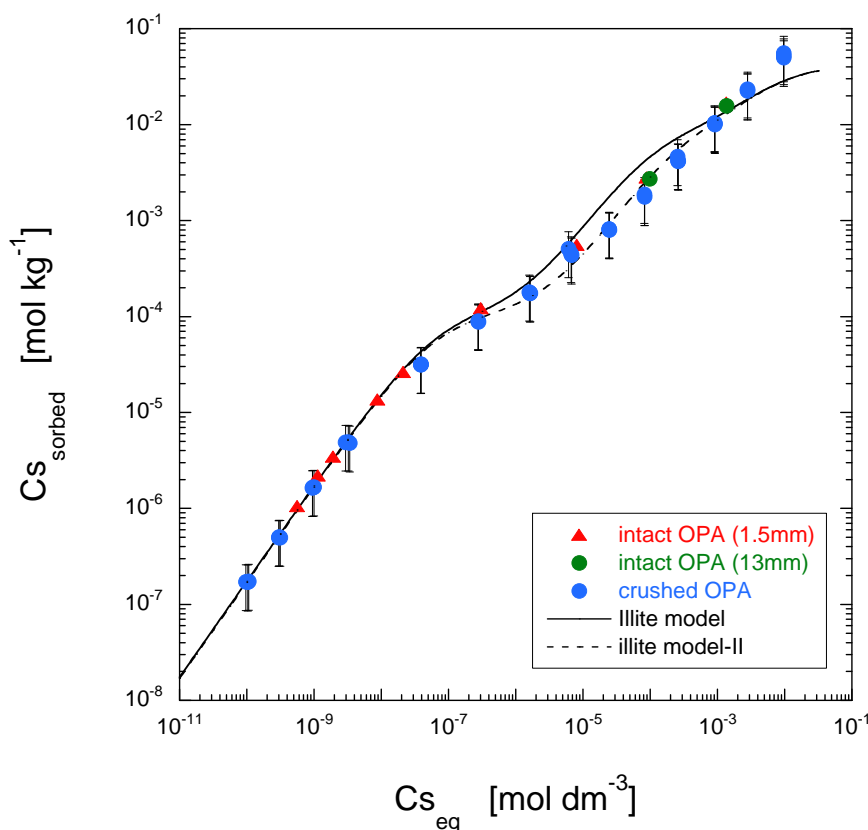

Figure 7. *Experimental study on Cs^+ sorption to crushed and intact Opalinus Clay by Van Loon et al. (2008)*

One key question is whether all surface sites are available for sorption under compact conditions. The validity of this assumption has been tested in different work packages for some specific systems. The data obtained so far suggest that for "simple" cations, such as Sr^{2+} or Cs^+, the assumption of site availability is valid, as indicated by the study of Van Loon et al. (2008), where the sorption behaviour of Cs^+ to OPA under dilute and compacted conditions was shown to be nearly equal (Fig. 7). On the other hand, for the sorption of divalent heavy metals, lanthanides or actinides, further work is necessary to confirm or disconfirm this assumption.

Co-precipitation and solid solution formation:

Co-precipitation or solid solution formation of radionuclides is commonly not considered in PA for the far field, mainly because of incomplete understanding of this process and lack of quantitative data. However, this process can be regarded as reserve-FEP for specific radionuclides, in case this process can be demonstrated to be relevant.

Useful new experimental data on the extent of co-precipitation of actinides with calcite has been obtained (Heberling et al., 2008). A new theoretical study on solid solutions has enabled improvement of the thermodynamic description of solid solutions (Vitorge, 2008).

Diffusion:

As indicated in a number of previous studies and also confirmed by FUNMIG results, the predominant transport mechanism in the studied clay-rich host rocks is diffusion. The diffusion properties in clays have been shown to be strongly affected by the electrochemical properties of the clay surfaces, the structural arrangement of the minerals and the structural heterogeneities (e.g. layering) at different scales.

A remarkable property of clay rocks is the different diffusion behaviour of cations and anions in such materials. From tracer through-diffusion experiments it can be inferred that anions diffuse more slowly than water tracers whereas cations, such as Na^+, Sr^{2+} and Cs^+ show higher effective diffusivities. The lower effective diffusivity and lower diffusion-accessible porosity of anions can be explained by ion exclusion from the negatively charged clay surfaces and interlayers. The reason for the higher diffusivities of cations is less well established. The larger effective diffusivity relative to water has been proposed to be induced by diffusion in the diffuse double layer (often referred to as "surface diffusion") or by diffusion in the interlayers (Appelo & Wersin, 2007; Jougnot et al., 2009; Glaus et al., 2007). In commonly applied diffusion models, the different diffusion properties of anions and cations cannot be accounted for simultaneously, although recent attempts in this regard have been made (e.g. Appelo et al., 2008). One of the difficulties is the lack of data on the micro- and nanostructure of these materials, whose investigation however is technically challenging. One of the main goals within the FUNMIG RTDC 3 was to shed more light on the microstructure of clay materials and to relate it to their diffusion properties. A multi-method approach including both advanced microscopic and spectroscopic techniques and numerical methods was adopted. Moreover, new diffusion data at different spatial scales was collected in order to test potential scale effects on diffusion data and to critically verify and validate existing modelling tools.

Relevant issues related to diffusion, for which remarkable achievements have been obtained, are summarized below.

Conceptual / numerical diffusion models at the nanometre scale:

With aid of a combined innovative numerical and experimental approach the different water and ion states occurring in the vicinity of the clay surface were determined (Tournassat et al., 2008; Montavon et al., 2009b). The results led to a mechanistic description of the water inter-face and ion distributions at the clay-water interface in the compact state. Further work was focussed on the development of a new diffusion model for anions and cations on the basis of both a mono-porosity and a dual porosity concept where so far only preliminary progress could be made.

Diffusion and microstructure at micrometre to centimetre scale:

Most diffusion studies within FUNMIG, which included through- and in-diffusion experi-ments, block scale diffusion and in-situ diffusion, tests were focussed on scales ranging from the micrometre to decimetre (see section above). Various new analytical techniques were applied in order to unravel structural and porosity relationships over this range of scales (Robinet et al., 2007; 2008a). Different imaging techniques were used to obtain the spatial 2D and 3D mineral organisation and porosity distribution in clay rocks as illustrated in Fig. 8. In the case of the COx formation, two domains of mineral organisation could be differentiated: (i) at the μm-scale, the spatial arrangement of clay particles inside the clay matrix; (ii) at the sub mm-scale, the spatial organisation of the clay matrix determined by the arrangement of the (large) non-porous carbonate and quartz minerals. The obtained 3D representations pro-vided the basis for defining model structures for analysing the effects of rock mineral compo-sition on diffusion (Robinet et al., 2008a; Altmann, 2008).

Numerical modelling for non-reactive and reactive diffusive transport on both lab and in-situ data was performed with several different 2D and 3D coupled diffusion-reaction codes (Gimmi, 2008; Samper & Yang, 2007) in order to validate and, if necessary, improve the codes and to quantify the effects of rock anisotropy.
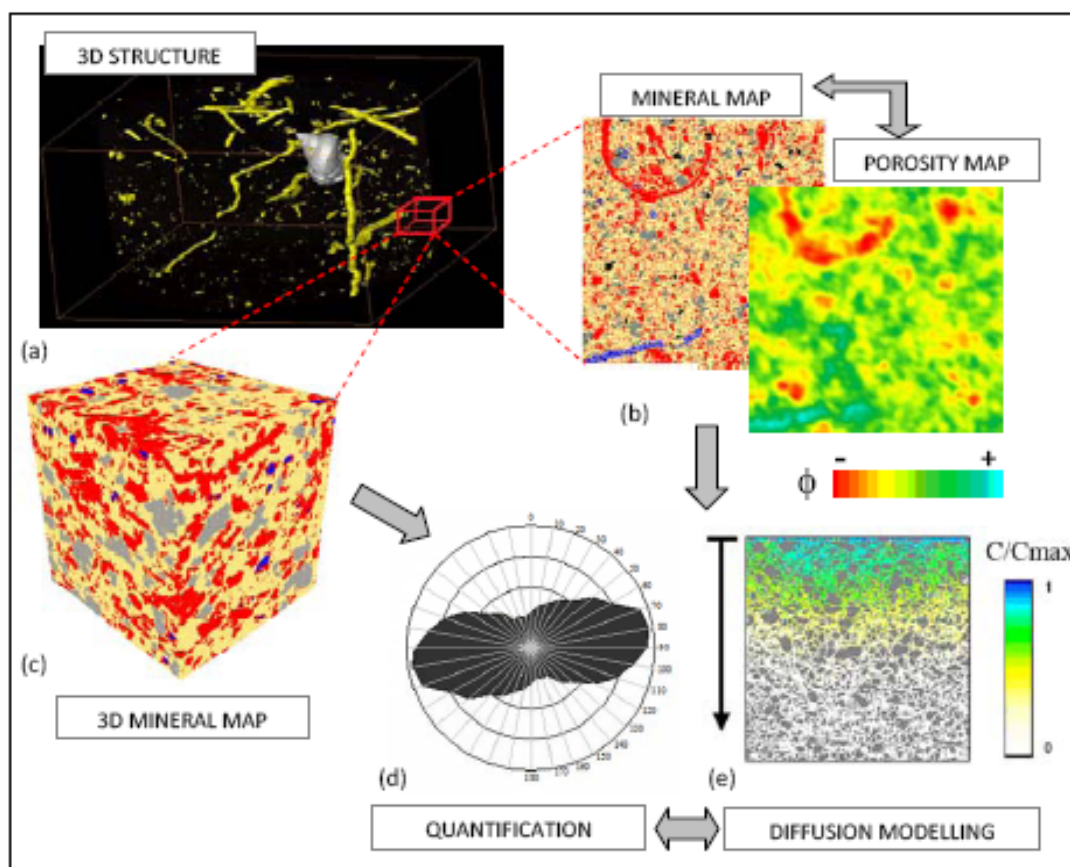
Figure 8. *Methodology used to characterize clay rocks at macroscopic and mesoscopic scales (a) 3D spatial distribution of structure (yellow : pyrite inclusions, white : fossil) acquired for a cm3 scale sample by X-ray tomography (b) comparison between porosity (resin impregnation 3H MMA method) and mineral maps (by SEM) (c) 3D mineral spatial distribution (red: carbonates, grey: quartz, blue: pyrite, yellow: clay matrix) acquired for a sub-mm scale sample by synchrotron X-ray tomography (d) statistical analysis of mineral distributions (ex: orientation rose of carbonate grains) (e) diffusion modelling computed from 2D/3D mineral and porosity distribution using time-domain diffusion (TDD) method (from Altmann 2008)*

Diffusion at large scales:

The study of concentration profiles in the clay formation at the decametre scale provides a good test whether transport concepts derived from smaller scale studies are valid and can be applied for larger spatial distances. Natural tracer profiles were analyzed in separate studies for Boom Clay (CLAYTRAC project; Mazurek et al., 2009) and for OPA (Koroleva et al., 2007). Both studies confirmed that diffusion is the main transport mechanism in these formations and also provided support that diffusion parameters of non-sorbing tracers obtained from smaller-scale studies can be applied over larger spatial and temporal scales for these two formations. A preliminary evaluation of all available experimental diffusion and sorption data for Boom Clay suggests that transport parameters remain valid on decametre scale for this formation, implying that no lab-field scale factor is required in PA. This was supported by a systematic study on many rock samples across the COx formation (Altmann 2008; Lerouge et al., 2006b; Grambow, 2006). By means of geostatistical analysis, three different material

classes with different carbonate content and distinct diffusion properties were obtained, which provided the basis for parametrizing and meshing a diffusion model for the formation. The modelling of anion diffusion from the centre to the boundary revealed that the difference between the "geostatistical" model and a model with a single D_e value for the entire formation is insignificant.

Crystalline host rocks

As for clay-rich rocks, the FEPs for crystalline host rocks can be grouped into the super-FEPs "transport mechanisms" and "sorption". Due to the more complex and spatially variable transport behaviour in crystalline host rocks, this aspect needs to be scrutinized by combined laboratory, field and modelling studies. Various different transport mechanisms for crystalline host rocks are considered in a safety case and, following the recommendation provided by the RETROCK EC project (EC, 2005), transport-and sorption-related FEPs can be grouped into the following more distinct super-FEPs:

- Advection in fractures
- Diffusion in fractures
- Matrix diffusion (diffusive exchange of water and solutes between a fracture and the rock matrix)
- Colloid-related processes
- Sorption processes

All these aspects have been considered and dwelled on with variable detail within FUNMIG, the main achievements of which are summarized below. The work performed could build on substantial knowledge from previous research on RN transport in crystalline rock systems, which to a great extent is summarized in the RETROCK final report (EC, 2005). The work within FUNMIG was focussed on several key issues where significant uncertainties existed. These principally include upscaling effects, model developments for non-reactive and reactive transport to support "simplistic" PA models, matrix diffusion, and colloid-related phenomena.

Understanding in-situ processes which affect RN transport in such heterogeneous fractured media necessitates high quality data at larger scale. A large part of the work performed within RTDC 4 included experimental and modelling studies in the underground research laboratories Grimsel Test Site and Äspö Hard Rock Laboratory and in deep boreholes with realistic repository-type conditions. These studies were complemented with medium-scale mock-up tests in the laboratory. In addition, fundamental laboratory studies from RTDC1 and RTDC2 were considered for specific phenomena, such as radionuclides-clay colloid interactions and radionuclides-organic ligand interactions.

Upscaling phenomena and modelling:

A systematic evaluation of field data from two Swedish sites Forsmark and Laxemar (Laaksoharju et al., 2008) provided a valuable and direct support for the safety case. By putting these data into a comprehensive framework, the hydrogeochemical conditions of the past could be unravelled, which set the basis for predicting future evolutions. Hydrochemical,

mineralogical and microbial data were integrated in a process-based model and thus reaching a closer integration with hydrogeology. An important aspect affecting groundwater hydrology and hydrochemistry in Northern countries are glaciation-induced effects. The impact of glacial meltwater intrusion on uranium migration was investigated at the Palmottu site in Finland (Suksi et al., 2006; Markovaara-Koivisto & Einsalo, 2008)

The determination of actual RN fluxes from the near-field and the understanding of mass transfer processes was the focus of an extensive study (García-Gutiérrez, 2001; Perez-Estaún et al., 2007; Gomez et al., 2007) as follow-up of the FEBEX experiment (Enresa, 2000) at the Grimsel Test Site. Data from hydrogeological, geophysical and geochemical analysis enabled to develop a conceptual model for mass transfer and to derive mean effective diffusion coefficients for a real scale experiment (Buil et al., 2009). The study was complemented with porosity measurements and with 3D imaging analysis (Carbonell et al., 2009) in the different fractures, which led to the identification of sub-parallel fracture zones in the gallery. Such visualization methods were shown to be valuable tools for describing fracture network systems in crystalline rock. The existence of a higher transmissivity zone parallel to the gallery was supported by groundwater flow modelling.

A remaining challenge for PA is the adequate simplification for describing the complex physical heterogeneities in transport models. By application of geostatistical tools, some shortcoming evident with classical models, such as the scale dependence of transport parameters and resulting underestimation of late-time breakthrough behaviour, can be overcome without exact description of the flowpaths. The application of different upscaling methodologies was analyzed and evaluated in the context of their adequacy for PA (Salamon et al., 2006a; Fernández & Gomez-Hernández, 2007). The multi-rate transfer method appears particularly suitable for this purpose and new improvements for this method were developed (Salamon et al., 2006b). They allowed for reproducing main features of breakthrough curves for conservative tracers obtained from in-situ tests.

A further level of modelling complexity is reached when transport in heterogeneous fracture systems is coupled with chemical reactions. An important effort in this area was undertaken by developing a methodology for deriving analytical solutions for transport-controlled reaction rates under chemical equilibrium and non-equilibrium conditions (Sánchez-Vila et al., 2007; De Simoni et al., 2007; Luo et al., 2008; Dentz & Carrera, 2007; Dentz & Tartakovsky, 2008). Thus, the impact of heterogeneity on reaction rates, mixing and spreading could be quantified.

Sorption/diffusion in the rock matrix:

Matrix diffusion is taken into account in PA and contributes significantly in retarding the transport of non-reactive and sorbing radionuclides. The underlying modelling concepts are well established in the safety cases of the different national programmes. However, the averaged parameters used in PA (diffusivities, porosities, sorption values) have so far not been well justified, because of the experimental difficulty to obtain meaningful data.

Within FUNMIG, a large effort has been undertaken to improve the knowledge basis on sorption and diffusion processes in the rock matrix. A multi-method approach involving various visualization techniques was adopted for characterizing the porosity and mineral distribution at μm-cm scales (Tiseanu et al., 2006; Lähdemeki et al., 2007; Kelokaski et al., 2005). The

effects of the deduced physical and chemical heterogeneities were analyzed for their relevance on averaged parameters used for PA.

An important prevailing uncertainty is the RN transfer from the near field to the rock matrix in "tight" sections (i.e. very low flow rates). This was assessed with a large scale laboratory mock up test in which tracer diffusion at the bentonite/granite interface was investigated (Samper et al., 2008) (see Fig. 9). The diffusive behaviour of conservative and reactive tracers was evaluated by a new numerical modelling tool which revealed satisfactory agreement with the observed data using reasonable assumptions for parameter values. Another column-type study demonstrated the increasing importance of matrix diffusion as flow rates are decreased (Kulenkampff et al., 2008).

The effect of scale-dependent heterogeneities was analyzed by Time Domain Diffusion models (Sardini et al., 2003; Sardini et al., 2007; Sardini et al., 2006; Robinet et al., 2008b) in which residence time distributions are related to pore-space geometry and diffusivity. To validate model results, diffusion experiments at the microscale were performed in which diffusion profiles were analyzed with the Rutherford backscattering spectrometry and auto radiographic methods (Siitari-Kauppi et al., 2007).

The quantification of RN sorption behaviour to host rock minerals under realistic conditions remains to be a non-trivial task, in particular for the crystalline matrix. A number of studies involving various new methods were applied within FUNMIG to obtain sorption data for intact rock and compare these with existing batch sorption data on crushed rock material. The general outcome from these studies was that data obtained from intact rock measurements yield more realistic estimates for PA (Missana, 2008) and that, moreover, additional information, such as porosity distribution and diffusion data can be obtained.

Figure 9. Granite block (RB0-1) extracted from the FEBEX gallery at the Grimsel Test Site and used for the mock-up diffusion experiment (from Samper et al. 2008)

Colloidal phenomena:

The release of clay colloids from the bentonite backfill and their advective transport in fractures of crystalline rock is one of most challenging and pertinent issues from both a research and a PA point of view. Under unfavourable chemical conditions (low salinity, high pH), loss of swelling clay material might impair the performance of the bentonite backfill, a process considered to be highly relevant for example in the recent Swedish safety case SR-Can (SKB, 2006). A further safety-relevant process is the migration of radionuclides sorbing strongly to the clay colloids (e.g. actinides) in the geosphere. The scope within FUNMIG was to gain better understanding on bentonite colloid behaviour and radionuclides-colloid migration under realistic conditions.

The geochemical conditions at the Grimsel Test Site (GTS) which display low salt content and relatively high pH offer a favourable framework for conducting colloid-related studies. Moreover, considerable knowledge from previous studies has been made available for this site. The new studies within FUNMIG, which were focussed on colloid generation, transport and filtration under stagnant or low flow rate conditions, included both in-situ work at the GTS and well-constrained systematic laboratory experiments. It was found that bentonite colloid generation strongly depends on salinity, pH, clay density and Calcium concentration (Missana et al., 2008a). Moreover, the stability of such colloids may increase in the presence of humic acids. The data obtained provide a valuable basis for improving models for colloid generation. One interesting result was that microstructure and composition of generated colloids under in-situ and lab conditions are similar, but that the amount of stable in-situ colloids is small in comparison with expected concentrations from lab studies. Further work on this issue is ongoing to understand discrepancies between lab and field measurements. Preliminary data at the GTS site suggest colloid filtration at low flow rates, in spite of unfavourable geochemical conditions (Alonso et al., 2009b). However, filtration efficiency depends on small-scale chemical effects, surface roughness and non-uniform distribution of surface charges in fractures. The effect of matrix diffusion on colloid transport has been experimentally determined for the first time and highlights the strong retardation of colloids, ranging from 2 - 100 nm in size relative to solute tracers (Filby et al., 2008)

The influence of colloid-promoted RN transport was evaluated with a sensitivity analysis with aid of newly derived data from FUNMIG (Cormenzana, 2007). This study reveals the large potential of bentonite colloids to increase near-field releases for actinides, but under the conditions of reversible sorption, the total doses expected in the biosphere are small because of long travel times in the geosphere. In contrast, under the assumption of irreversible sorption, calculated doses increased substantially, since in this case radionuclides attached to colloids were assumed to move un-retarded with water flow. This highlights the need of addressing potential irreversible sorption processes, such as co-precipitation in more detail. Preliminary data with column experiments with RN-doped bentonite colloids indicated lower recovery of Eu(III) relative to Pu(IV), which suggests a lower desorption rate for the latter nuclide (Missana et al., 2008b).

Salt host rocks

The disposal concept in salt host rocks differs from those in other host rock types in that the host rock is, at least in part, regarded as near-field from which under normal scenarios no release of radionuclides is possible. After emplacement of the salt backfill around waste canis-

ters, convergence of the salt rock closes remaining gaps, thus providing an efficient "dry" barrier for very long times. The likelihood of water intrusion, for example by an inadequately sealed shaft, is considered to be low, but treated as special scenario in the safety case. For such a case, the migration of radionuclides in the overburden, consisting of sedimentary rocks is considered. This was also the scope within FUNMIG where various aspects of RN migration processes in the overburden were investigated. As an example for a relevant overburden case, the natural Ruprechtov site in the Czech Republic was studied within RTDC 5, mainly in terms of uranium migration processes. Specific site-independent studies on sorption and colloidal phenomena within RTDC 1 and RTDC 2 were also evaluated for their relevance for salt host rock concepts. In fact, for the Gorleben site in Germany, which is one of the prominent HLW site candidates in a salt formation in Europe, the colloid-induced transport in the overburden has been recognized to be a key issue to consider.

FEPs from the ISIBEL catalogues (TEC, 2008) were mapped with regard to the salt-related work in FUNMIG which resulted in five FEPs, or rather FEP groups. It is important emphasize again that these FEPs are related to the overburden and not to the salt rock itself. They have been selected and evaluated specifically for the German disposal concept and its corresponding safety case. One FEP concerns RN transport processes which depend on the transport characteristics of the overburden of a specific salt host rock. The other four FEPs are:

(1) <u>Sorption / desorption processes:</u> For the German performance assessments carried out so far, reversible and linear sorption in the overburden is assumed and a large sorption database of site-specific K_d-values exists. A number of sorption studies in FUNMIG has helped to support these data and increase confidence in model assumptions. Among these, mechanistic studies on actinide-smectite interactions, demonstrating the occurrence of inner sphere complexes (Schlegel, 2008; Rabung, 2006) and providing improved data for thermodynamic sorption models have been of most value. For certain key elements, such as iodine or selenium, there is still a need for improving the site-specific sorption database. Thus, further work is necessary for improving mechanistic understanding of sorption processes which is prerequisite for assessing the impact of future changes in geochemical conditions by climate change.

(2) <u>Chemical speciation and complexation:</u> The chemical speciation and complexation properties determine the chemical form of a radionuclide and its sorption efficiency in the overburden. For some specific systems useful new thermodynamic data has been produced, such as Th(IV) complexation with silicate and phosphate (Ekberg et al., 2007) or existing data have been improved, e.g. actinide-carbonate complexation (Vercouter et al., 2005). These data will be integrated in the new German thermodynamic database THEREDA (www.thereda.de). Data on the speciation and solubility limitation of U(IV) at the natural analogue Ruprechtov site, including for example the use of new spectroscopic methods (e.g. μ-XRF) for solid phase speciation (Noseck et al., 2008) has increased confidence in existing data.

(3) <u>Colloidal processes</u>: As outlined in the previous section on crystalline host rocks, colloids may have a large impact on RN mobility and, depending on their physico-chemical behaviour, may retard or enhance RN transport. For the Gorleben site, colloids are considered to be potentially relevant for RN transport, because levels of organic colloids in the overburden are high (Buckau et al., 2000). So far, colloid-induced transport of radionuclides has not been considered in PA calculations for sites with salt host rocks in Germany. This as-

pect has been addressed by several experimental studies on interactions between actinides and humic or fulvic substances (Liu et al., 2008a; Křepelová, 2007; Evans et al., 2008; Kim et al., 2007; Cervinka et al., 2007; Marang et al., 2008; Reiller et al., 2008; Pashalidis & Buckau, 2007) and new thermodynamic data on these systems have been obtained. Moreover, field scale studies on the kinetics and reversibility of radionuclides-colloid interactions have increased process understanding for conditions that are relevant for the Gorleben site. All these and further data still need to be evaluated in a comprehensive way to derive the relevance of colloid-facilitated transport in the overburden for the safety case.

(4) <u>Microbial processes:</u> Such processes can affect radionuclides by a number of different ways and much work for various subsystems focussing on biosorption, bioaccumulation and biotransformation already exists. However, this type of information has so far not been scrutinized in a systematic way, and moreover, site-specific data on such processes is limited. Valuable new information with regard to the effect of biofilms on RN sorption and immobilization could be obtained (Grossmann et al., 2008; Krawczyk-Bärsch et al., 2008). Furthermore, the importance of microbial processes on reduction of U(VI) and precipitation of U(IV) at a natural analogue site has been shown (Noseck et al., 2009). However, no direct contribution for the safety case has been provided within FUNMIG. A systematic evaluation of the potential effects of microbial processes on RN transport and retardation for German site from a PA perspective is lacking so far.

Discussion & conclusions

Summary of main achievements and remaining uncertainties for PA

Generally speaking, much of the work within FUNMIG helped to support and to increase confidence in future safety cases and in the simplified PA transport and retardation models used for simulating RN transport through the host rock. Some of the studies on retardation processes (e.g. coupled sorption-redox processes at the mineral-water interface) yielded valuable data for all three rock types dealt with within the IP (cf. lower part of figure 5). However, most of the studies provided improved insight to host-rock specific features and processes. Thus, transport mechanisms in clay host rocks are dominated by diffusion whereas in crystalline host rocks these are more complex, with advection/dispersion in fractures and diffusion in the rock matrix being relevant. For both host rock types, FUNMIG has significantly contributed to improving understanding on a conceptual level, both by providing new experimental data at different spatial scales and by developing new modelling approaches. Innovative spectroscopic and visualization methods applied at the μm-cm scale have led to a refined view on mineral fabric and porosity distribution in these rocks. This is a prerequisite for more realistic modelling of RN transport at a larger scale in so-called process models, which can be used to validate the relatively simple models used in PA, thus increasing confidence in the applicability of the PA models.

The systematic effort of investigating and comparing diffusion and sorption processes at different scales in different clay rocks with a variety of methods has largely increased the knowledge basis for future safety cases. Distinct studies in three different clay rocks using data distributed over a large scale supported the validity of simple PA models with diffusion and sorption parameters averaged for the whole formation. A further highlight was the improved

understanding of sorption and immobilisation of ^{79}Se, a safety-relevant nuclide in most safety cases, in clay media.

For crystalline host rocks, valuable data on the generation, transport and filtration of clay colloids from the near-field and their impact on RN transport under realistic conditions have been obtained. The results from studies on organic colloids and on biofilms including their interaction with radionuclides (RN) have shown to be of interest for future safety cases of salt-host rocks concerning their overburden.

As can be expected from the vast number of studies, a variety of uncertainties for different topics remain. From a PA perspective, we consider the following as particularly relevant:

- The impact of colloids on RN transport through crystalline rock and in particular, the question of sorption irreversibility.
- The conceptual uncertainty regarding the modelling of cation and anion diffusion in clays at different scales.
- The applicability of mechanistic sorption models for strongly sorbing radionuclides in intact rock, both for clay and crystalline host rocks.

General Perspectives

An important part of the FUNMIG IP was the dialogue between the "supplier group", the scientists, and the "customer group" the performance assessors. This interaction between the two groups was inspired by the long-term experience of national waste management organisations in building safety cases for geological disposal concepts. Thus, an adapted organisation was set up in the IP to promote and enforce information exchange and collaboration with both views equally represented. The procedure for evaluating each research task, based on a compilation and re-grouping of FEPs for the three host rock formations was elaborated within a specific RTD component. This resulted in a tool (Task Evaluation Tables), which provided both the researcher's and the PA view on the achievements with regard to future safety cases. This evaluation exercise indicated that the scope of investigated processes in FUNMIG was rather well set and that substantial progress had been made in research areas important for the development of future safety cases.

From the PA point of view, the experience of FUNMIG revealed that it would be desirable to conduct an analogous evaluation procedure for each proposed task before the start of the research work. In this regard, the procedures developed within FUNMIG are a useful tool for planning future Integrated Projects.

The achievements of integrated research projects for safety cases in European waste management programmes are strongly related to the specific disposal concepts and to programme advancement. Nevertheless, some common conclusions can be drawn:

- A scientific programme providing a sound scientific understanding of the disposal system considered is one of the key elements of a safety case. This holds for all stages of the implementation process.
- There is a continuing need for supporting and validating simplified PA models with more elaborate coupled transport and retention models. For improving fundamental understand-

ing of upscaling effects, advanced multi-method tools are required. The main goal for these developments is increased confidence in long-term predictions using simplified PA models.

- The host rock plays an important role as a stable barrier in geological disposal in all concepts. A key issue in this regard is its stable and predictable geochemical environment.

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Acknowledgements

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