

Technical Report 09-01

6th EC FP IP FUNMIG

**Topics and processes dealt with in
the IP FUNMIG and their treatment
in the Safety Case of geologic
repositories for radioactive waste**

August 2017

P. Wersin (ed.)

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**National Cooperative
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Abstract

The scope of the FUNMIG Integrated Project (IP) was to improve the knowledge base on biogeochemical processes in the geosphere which are relevant for 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, an 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 standardised 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".

In a general sense, 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 within the IP. However, most of the studies provided improved insight to host-rock specific features and processes, whereby the majority of this work was 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.

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 with 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 radionuclide 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 radionuclide sorption to colloids in crystalline fractures, (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 analogue 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.

Zusammenfassung

Das FUNMIG Integrated Project (IP) hatte zum Ziel, den Kenntnisstand über biogeochemische Prozesse in der Geosphäre zu verbessern, die für die Sicherheit von geologischen Tiefenlagern für radioaktive Abfälle relevant sind. Ein wichtiger Teil dieses Projekts beinhaltete dabei die Wechselwirkung zwischen Datenproduzenten (Forschung) und Datennutzern (europäische Entsorgungsorganisationen radioaktiver Abfälle). Dabei sollte der Nutzen der Forschungsarbeiten für die Sicherheitsanalyse und im weiteren Sinne für den Sicherheitsnachweis der Tiefenlager für radioaktive Abfälle gefördert werden. Zu diesem Zweck wurde ein angepasstes Verfahren erarbeitet. Demzufolge wurden relevante Vorgänge und Ereignisse (abgekürzt mit der englischen Bezeichnung FEPs für "features, event and processes") für die drei Wirtgesteinstypen Ton-, Kristallin- und Salzgesteine international anerkannter FEP-Kataloge entnommen und jede der 108 Forschungsaufgaben durch ein standardisiertes Verfahren erfasst. Das wichtigste Ergebnis war dabei die Schaffung eines wirtgesteinspezifischen Tools ("Task Evaluation Table"), bei dem die Bedeutung und der Nutzen der Forschungsergebnisse evaluiert wurden, beides aus Sicht der Sicherheitsanalyse und der Forschung. Praktisch alle innerhalb des Projekts FUNMIG gewonnenen Daten beziehen sich auf die sicherheitsrelevanten FEP-Gruppen "Transportmechanismen" und "Retardation".

Generell unterstützte und verbesserte ein Grossteil der Arbeiten innerhalb von FUNMIG das Vertrauen in die vereinfachten Transport- und Retardationsmodelle der Sicherheitsanalyse, die für die Berechnung des Radionuklidtransports durch das Wirtgestein verwendet werden. Einige der Studien über Verzögerungsprozesse (z.B. gekoppelte Sorptions-/Redoxprozesse an der Mineral/Wasser-Grenzschicht) ergaben wertvolle Daten für alle drei Gesteinstypen innerhalb des IP. Jedoch lieferten die meisten Studien verbesserte Erkenntnisse über die wirtgesteinspezifischen Vorgänge und Ereignisse, wobei diese Forschungsarbeiten hauptsächlich an tonreichen und kristallinen Wirtgesteinen durchgeführt wurden. Für beide Wirtgesteinstypen hat FUNMIG wesentlich zur Verbesserung des Verständnisses auf konzeptioneller Ebene beigetragen, indem jeweils neue experimentelle Daten auf unterschiedlichen räumlichen Massstäben bereitgestellt und neue Modellierungsansätze entwickelt wurden.

FUNMIG erbrachte u.a. folgende wichtige Ergebnisse: Für tonige Wirtgesteine haben systematische Untersuchungen und der Vergleich der Diffusions- und Sorptionsprozesse in verschiedenen Tongesteinen auf unterschiedlichen räumlichen Skalen mit einer Reihe von Methoden den Kenntnisstand für künftige Sicherheitsnachweise wesentlich erhöht. Für kristalline Wirtgesteine wurden wertvolle Daten zu Bildung, Transport und Filtration von Tonkolloiden aus dem Nahfeld und deren Auswirkung auf den Radionuklidtransport unter realistischen Bedingungen gewonnen. Es zeigte sich, dass Ergebnisse von Studien über organische Kolloide und Biofilme und ihrer Wechselwirkung mit Radionukliden für künftige Sicherheitsnachweise von salzreichen Wirtgesteinen von Belang sind. Die wichtigsten künftigen Forschungsaufgaben hinsichtlich der Sicherheitsanalyse sind die folgenden: (i) die Frage der Irreversibilität der Radionuklidisorption an Kolloiden in Kluftzonen im Kristallin, (ii) ein umfassendes Modell für die Diffusion von Kationen und Anionen in Tonstein auf unterschiedlichen Skalen und (iii) die Anwendbarkeit von mechanistischen Retardationsmodellen für stark sorbierende Radionuklide in intakten tonigen und kristallinen Wirtgesteinen.

Eine wichtige Erkenntnis aus der Wechselwirkung zwischen Forschung und Sicherheitsanalyse ist der Wunsch nach der Durchführung eines analogen Bewertungsverfahrens für die jeweils vorgeschlagenen Forschungsarbeiten vor deren Beginn. In diesem Zusammenhang stellen die innerhalb des Projekts FUNMIG entwickelten Verfahren ein nützliches Werkzeug für die Planung zukünftiger IPs dar.

Résumé

Le projet intégré FUNMIG avait pour objectif l'amélioration de la base de connaissances existante concernant les processus biogéochimiques de la géosphère qui sont susceptibles d'avoir un impact significatif sur la sûreté des dépôts de déchets radioactifs. Le projet impliquait pour une grande part des interactions entre les équipes chargées de l'acquisition des données (recherche) et celles chargées de leur utilisation (organisations européennes de gestion des déchets radioactifs). Il s'agissait d'encourager l'utilisation des résultats des travaux de recherche dans l'évaluation des performances et, plus généralement, dans la démonstration de la sûreté des dépôts de déchets radioactifs. À cette fin, une procédure adaptée a été définie. Les caractéristiques, événements et processus (FEP) pertinents pour les trois types de roche d'accueil (argileuse, cristalline, saline) envisagés ont ainsi été collectés parmi les catalogues reconnus à l'échelle internationale, puis affectés aux 108 tâches de recherche au moyen d'une procédure normalisée. Le résultat principal de ce travail a été la constitution d'un outil spécifique à chaque roche d'accueil (tableau d'évaluation des tâches), dans lequel une évaluation de la pertinence et des bénéfices des résultats était proposée, tant du point de vue de l'évaluation des performances que de la recherche. La quasi-totalité des données générées par le projet FUNMIG est associée aux groupes de FEP « mécanismes de transport » et « retard » relatifs à la sûreté du dépôt.

Sur un plan plus général, une grande partie du travail au sein du projet FUNMIG a permis d'apporter crédit et confiance aux modèles simplifiés d'évaluation des performances en matière de transport et de retard, utilisés pour les calculs de transport de radionucléides (RN) à travers la roche d'accueil. Certaines des études portant sur les processus de retard (processus couplés sorption-rédox au niveau de l'interface eau-minéral) ont fourni de précieuses données valables pour les trois types de roches étudiées dans le cadre du projet intégré. Cependant, la plupart des études ont permis d'améliorer la connaissance des caractéristiques et des processus spécifiques à l'une ou l'autre roche d'accueil, en précisant que ce travail concernait surtout les roches cristallines et argileuses. Pour ces deux types de roche d'accueil, le projet FUNMIG a largement contribué à une meilleure compréhension sur le plan conceptuel, à la fois par l'apport de nouvelles données expérimentales à différentes échelles physiques et par le développement de nouvelles approches de modélisation.

Parmi les accomplissements importants du projet FUNMIG figurent, entre autres : pour les roches d'accueil argileuses, l'effort systématique d'étude et de comparaison des processus de diffusion et de sorption à différentes échelles et pour différents types d'argiles, à l'aide de diverses méthodes, a permis d'accroître considérablement la base de connaissance à disposition pour les démonstrations de sûreté futures. Pour les roches cristallines, des données précieuses ont pu être collectées sur la génération, le transport et la filtration de l'argile colloïdale depuis le champ proche, ainsi que sur son impact sur le transport de radionucléides en conditions réalistes. Les résultats des études sur les colloïdes organiques et biofilms, notamment sur leur interaction avec les radionucléides, se sont avérés intéressants pour les démonstrations de sûreté qui seront menées dans l'avenir sur les roches d'accueil salines. Sur le plan de l'évaluation des performances, les recherches futures devront s'attacher à résoudre les problèmes suivants: (i) la question de l'irréversibilité de la sorption des radionucléides sur les colloïdes des zones cristallines fracturées, (ii) un modèle global rendant compte de la diffusion des cations et anions dans les argiles à différentes échelles et (iii) l'application des modèles mécanistiques de retard pour les radionucléides à forte capacité de sorption dans les roches argileuses et cristallines intactes.

Une importante leçon tirée de l'interaction entre les équipes de recherche et d'évaluation des performances a été la nécessité de conduire une procédure d'évaluation similaire pour la tâche proposée avant le démarrage du travail de recherche. À cet égard, les procédures développées au cours du projet FUNMIG s'avéreront utiles pour la planification de projets intégrés futurs.

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1 Introduction

1.1 Objectives and scope

IP FUNMIG (Integrated Project on Fundamental Processes of Radionuclide Migration) was a project conducted within the 6th Framework Programme of the European Commission in the period between January 2005 and December 2008. 51 partners from 7 national waste management organisations, 17 research organisations of different sizes and types, 24 universities and 3 small and medium sized enterprises were involved in the project. The names of all the partners are listed in Appendix A. In addition to the partners, other institutions, not financed by the project, including research organisations and national regulatory bodies participated in FUNMIG (also listed in Appendix A).

The project dealt with radionuclide migration in the far-field, i.e. hydrological and geochemical processes taking place in the generally undisturbed host-rock zone between the near-field and the biosphere. FUNMIG complemented the sister IP NF-PRO which was focussed on processes relevant to radionuclide transport in the near-field and engineered barrier system (EC 2008).

A primary objective of FUNMIG was to promote interaction between researchers and "end users" (i.e. specialists responsible for compiling safety cases for deep geological repositories), as well as to develop tools for application in performance assessment (*cf.* Chapter 3). This interaction, which was in fact an important part of the IP, was enforced by a specifically adapted organisation and management (*cf.* Fig. 2-1).

The objectives of the present report are to document the scientific basis developed within FUNMIG and to evaluate the consequences for Performance Assessment (PA) and the Safety Case (SC), in particular the potential to reduce uncertainties in PA/SC.

The topics, processes and methodological developments treated in the IP FUNMIG are listed as Task Abstract Forms (TAFs) in Appendix B of the present report. The evaluation of the FUNMIG results with regard to the Safety Case is documented in three host rock specific Task Evaluation Tables (TETs) in Appendix C.

The Project organised Annual Workshops with topical sessions. These topical sessions were selected so as to provide in-depth treatment of selected topics the outcome of which is documented in the Annual Workshop Proceedings (Reiller et al. 2006, Buckau et al. 2007, 2008 and 2009).

As mentioned above, near-field processes including the excavation disturbed zone (EDZ) were treated within the complementary IP NF-PRO (Integrated Project on Near-Field Processes) (EC 2008). Within the work package WP 6.1, outcomes relevant for FUNMIG were documented in a report dealing with the boundary condition between near-field and host rock (Cuñado et al. 2009).

PA specific issues were treated within PAMINA (Performance Assessment Methodologies in Application to Guide the Development of the Safety Case). Both, NF-PRO and PAMINA were conducted within the Commissions EURATOM 6th Framework Programme.

The present report documents the output of FUNMIG WP 6.2 (Tab. 2-1) and is a key outcome of the project. It provides an overview of the scientific results of the IP FUNMIG evaluated with respect to their use in Performance Assessment and in making the Safety Case. It permits performance assessors to quickly access the knowledge acquired within FUNMIG.

The development of the method to evaluate the scientific results achieved within FUNMIG is documented in two interim reports (Nagra 2006 and 2007).

1.2 The "art" of combining the researcher's and implementer's views

The initiation of FUNMIG was not straightforward. In fact, it started with discussions and debates between the partners. These primarily originated from the different viewpoints between some research organisations and the involved waste management organisations (WMOs). In fact, such conflicts were not new in the nuclear waste community in which there had always been some tension between the "researcher" and the "implementer", or in more specific terms, between those who do research on processes relevant for safety of disposal schemes and those responsible for safety assessment and making a safety case for these schemes. This tension has proved to be creative in that the involvement of the "external" scientists assures that process-understanding is improved and also "new" potentially-relevant processes are considered while the conductance of the safety assessment itself evaluates the importance of the various processes considered.

In the case of the FUNMIG project, some of the research organisations, and in particular the Forschungszentrum Karlsruhe who had launched the project, advocated the need for fundamental research on processes occurring in the geosphere. On the other hand, WMOs were in favour of focussing on specific research issues relevant to repository safety in specific host rock environments (clay, crystalline rock). After several discussion sessions, a compromise was reached, which led to a structuring of the proposed research work into "fundamental processes" and "host rock-specific processes". In addition, and this turned out to be one of the main achievements of FUNMIG, a novel organisational instrument was created, namely a platform that created the link between the scientific work carried out in FUNMIG and its application for the safety case. This instrument was assigned to a separate component in the project – RTDC 6 (see next chapter). The procedures that were established to link to research and safety issues to evaluate the different activities in terms of their safety relevance are described in Chapter 3.

2 Project structure

As stated in the previous section, the project structure was preceded by controversial discussions between the partners which finally led to an agreement to structure the research activities into fundamentally-oriented processes and host-rock specific processes. Contrary to the situation nowadays, no Technological Platform existed during the project initiation process which would have screened and selected the proposed research activities. In the case of FUNMIG, these activities were strongly driven by the needs of the (fundamental) scientists, but, did indeed contain an applied component relevant for repository safety, as was later confirmed during the project.

The Project was divided into seven Components. Six of them were Research and Technological Development Components (RTDCs) and the seventh one dealt with training, knowledge management and dissemination of knowledge (Component 7).

RTDCs 1 and 2 activities were focused on conceptually well defined (RTDC 1) and conceptually less established processes (RTDC 2), not oriented towards a specific host-rock type or disposal concept. RTDCs 3, 4 and 5 were focused on specific processes of relevance in clay-rich, crystalline and salt host-rock types, respectively. In salt, this refers to the overburden far-field beyond the salt rock formation.

Each RTDC was divided into several work-packages, as detailed in Tab. 2-1.

RTDC 6 was focussed on the application of the scientific knowledge generated by the RTDCs 1 – 5 for Performance Assessment and the Safety Case.

Thus, RTDC 6 (WP 6.2) had a key function for establishing the present document. To link the scientific programme carried out within FUNMIG with performance assessment an information exchange forum was established. As depicted in Fig. 2-1, this forum included on one hand the Waste Management Organisations (WMOs) involved in FUNMIG and on the other the Integration Monitoring Group (IMG), representing the organisations carrying out RTDCs 1 – 5.

Tab. 2-1: Structure of research oriented RTDCs with work-packages.

RTDC 1: Well established processes (well defined)	
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data
WP 1.2	Ion exchange and surface complexation
WP 1.3	Influence of organics on the retention of radionuclides by minerals
WP 1.4	Formation of solid solutions and secondary phases, including retardation of anions
RTDC 2: Less established processes (ill defined)	
WP 2.1	Formation, migration and transport processes of inorganic colloids
WP 2.2	Formation, migration and transport processes of organic/humic colloids
WP 2.3	Radionuclide redox transformation on minerals
WP 2.4	Impact of biogeochemical processes
RTDC 3: Radionuclide migration in clay-rich host formations: Process understanding, integration and up-scaling for safety case use	
WP 3.1	Understanding key, basic processes affecting radionuclide transport in clay-rich porous media (small-scale, simplified model laboratory systems)
WP 3.2	Radionuclide chemistry and transport in natural clay-rich host rocks at small scales
WP 3.3	URL experiments for characterising radionuclide chemistry and migration in clay-rich host rock formations at intermediate time and space scales
WP 3.4	Up-scaling to formation scale, furnishing of tools useful for safety case studies
RTDC 4: Processes and transport studies relevant for crystalline rock disposal concepts	
WP 4.1	Characterisation of geochemical conditions in crystalline host rock
WP 4.2	Fluid flow system characterisation
WP 4.3	Generation, quantification, characterisation, stability and mobility of groundwater colloids
WP 4.4	Radionuclide transport studies, including the effects of inorganic/organic colloids.
WP 4.5	Processes identification and verification by real system analysis
WP 4.6	Up-scaling of processes and generation of tools for PA
RTDC 5: Processes and transport studies relevant for salt rock disposal concepts	
WP 5.1	Determination and characterisation of colloids under variation of geochemical conditions
WP 5.2	Geochemical behavior of radionuclides in the natural host rock
WP 5.3	Real system analysis
RTDC 6: Integration of processes and their abstraction to PA	
WP 6.1:	Boundary conditions
WP 6.2:	Treatment of processes in the Safety Case
WP 6.3:	Available sorption data-bases

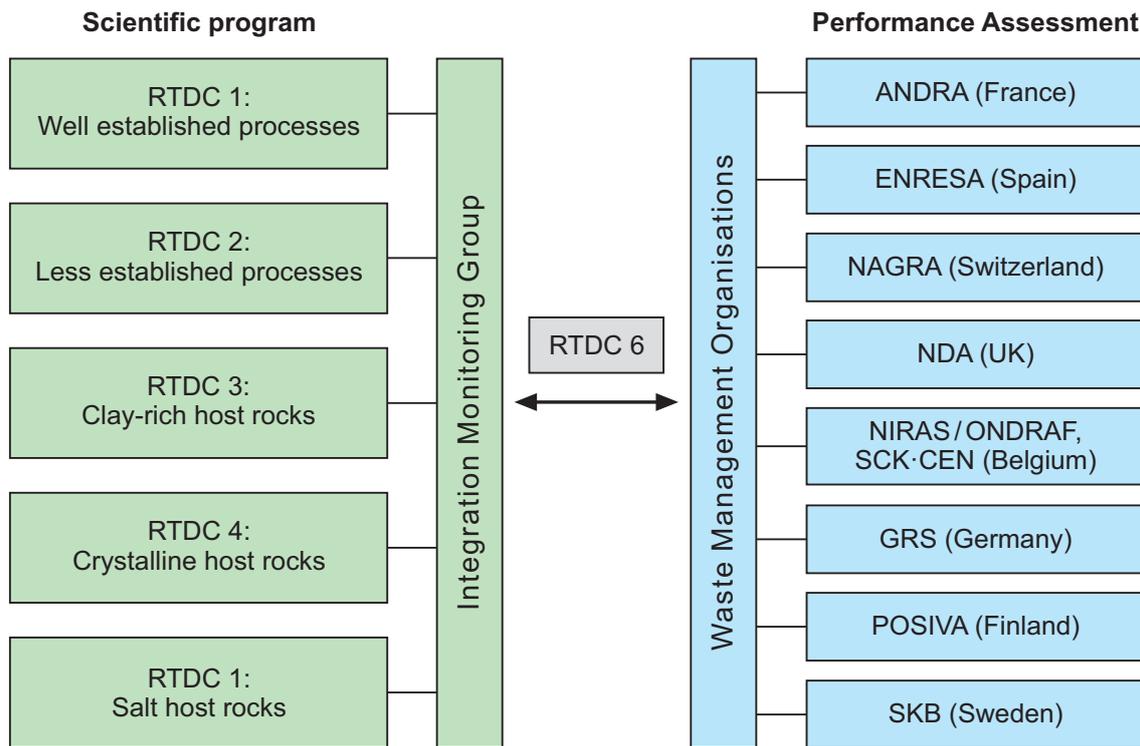


Fig. 2-1: Organisation of information exchange between science (RTDCs 1 – 5) and Performance assessors.

The Integration Monitoring Group consisted of one delegate for each RTDC, each Waste Management Organisation participating in FUNMIG was represented by at least one person. RTDC 6 was the platform for the information exchange leading to the present report.

3 Processes and key topics treated in IP FUNMIG and their mapping on FEPs

3.1 Introduction, FUNMIG and the safety case

The Safety Case may be defined as (IAEA 2006):

The **Safety Case** is an integration of arguments and evidence that describe, quantify and substantiate the safety, and the level of confidence in the safety, of the geological disposal facility.

Safety Assessment and Performance Assessment are parts of the Safety Case, and are described as:

Safety Assessment is the process of systematically analysing the hazards associated with the facility and the ability of the site and designs to provide the safety functions and meet technical requirements.

and, accordingly,

Performance Assessment is the process of systematically analysing the performance of the facility and the ability of the site and designs to provide the required performance and meet the technical requirements.

The contribution of the FUNMIG Project to demonstration of repository safety is aptly described in a letter to the US-DOE, Office of Civilian Radioactive Waste Management (US-DOE 2000), concerning scientific studies (although that was not the original purpose of the letter):

"Another way to address uncertainties is to attempt to reduce them through additional scientific and engineering studies. Presentations on scientific studies at the January Board meeting indicated that significant new information continues to be generated and plans for important future work are being developed. Expert judgment and careful interpretation of data will be needed to accurately characterise and quantify the uncertainties associated with data and their use in predicting repository performance."

The FUNMIG IP aimed at providing useful insights on radionuclide migration processes associated with a deep geologic repository for nuclear waste. The project structure and resource allocation are defined such as to move forward in the required continuous development in process understanding and implementation of the findings in the Safety Case.

Enough fundamental research has been undertaken to show that geological disposal is a viable concept. The structure of the FUNMIG work programme reflected this knowledge by emphasising studies which assess the suitability of specific geological environments.

However, lessons from past experience (e.g. in the UK) showed that key stakeholders, including the regulators, require that the underlying fundamental science and technology is state-of-the-art, relevant and robust. It is for this reason that fundamental research will continue to be needed even during the operational phase of a repository. This will support the decision on the appropriate closure time of the facility. The use of steel and cement in construction provides a useful analogy for this process. These materials are in daily use but fundamental research is still continuing into their properties. Thus, the continued need for fundamental research should not be seen as a weakness in the case for repository development, but as support for decision-making. Likewise, repository development should not be seen as precluding fundamental research.

3.2 Definition of boundary conditions

This pre-step was carried out within the WP 6.1 early in the project (Cuñado et al. 2009). The goal was to obtain reliable data on the relevant radionuclides and their respective fluxes passing from the engineered barrier system (near-field) to the geosphere. It involved a compilation extracted from the documentations of the various European disposal concepts. The extracted data confirmed the general assumption that the radionuclides released from the waste enter the geosphere in trace amounts only. In addition the results from the sister NF-PRO project regarding the interface between the near-field and the geosphere were extracted from the final reports of this IP. Thus, not only radionuclide fluxes, but also 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.

3.3 List of topics and relevance for different host-rock types

Topics (families of tasks) addressed within IP FUNMIG are listed in Tab. 3-1. As some of the processes are relevant for different host-rock types, whereas others are generic. The topics "Diffusion in Clay" (Buckau et al. 2007) and "Ion exchange and surface complexation" (State-of-the-art as reflected in the NEA Sorption Project: Davis et al. 2005) were discussed in the Topical Session of the 1st Annual Project Workshop (Saclay, November 2005). The Topical Session of the 2nd Annual Project Workshop (Stockholm, November 2006) dealt with issues concerning crystalline rocks, including the influence of biogeochemical processes on radionuclide migration, the characterisation of geochemical conditions and fluid flow system characterisation (Buckau et al. 2007). The influence of organics on radionuclide migration processes was the main focus at the Topical Session of the 3rd Annual Project Workshop (Edinburgh, November 2007, Buckau et al. 2008). In the Topical Session of the 4th Annual Project Workshop (Karlsruhe, November 2008, Buckau et al. 2009) a number of interesting outcomes from the FUNMIG research work were presented including mechanistic transport models in clay and crystalline rock, colloidal processes and radionuclide sorption to different mineral and rock surfaces.

Tab. 3-1: Topics tackled within FUNMIG and their relevance for different host rock types.

Process/topic:	Host rock type		
	Clay-rich host rock	Crystalline rock	Far-field of salt host rock
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	(×)	×	×
Radionuclide redox transformation on minerals	×	×	×
Biogeochemical processes	(×)	×	×
Thermodynamic equilibria in clay	×		
Diffusion in clay	×		
Up-scaling	×	×	×
Characterisation of geochemical conditions		×	
Fluid flow system characterisation		×	×
Generation, stability and mobility of colloids		×	×
Process identification and verification by real system analysis	×	×	×

3.4 Task Evaluation Tables and rules for entries

The main task of FUNMIG RTDC 6 was the development and application of a methodology to facilitate the close interaction between the research organisations and the waste management organisations (WMOs). In the section below, the applied steps are listed and explained in detail.

3.4.1 Step 1: Mapping of FUNMIG tasks

The individual topics, processes and method developments within IP FUNMIG were listed and mapped to internationally accepted views for clay-rich and crystalline host rocks. FEPCAT (Mazurek et al. 2003) is a catalogue of Features, Events and Processes (FEPs) for argillaceous rocks. RETROCK (EC 2005) was a European project on the treatment of radionuclide migration in fractured rocks within safety assessment. A list of processes identified by the participants as safety relevant was used as a quasi FEP catalogue. A salt specific FEP list was developed in the German national research project ISIBEL (Buhmann et al. 2008). For the FEP mapping, a project structure was adopted as depicted in Fig. 3-1.

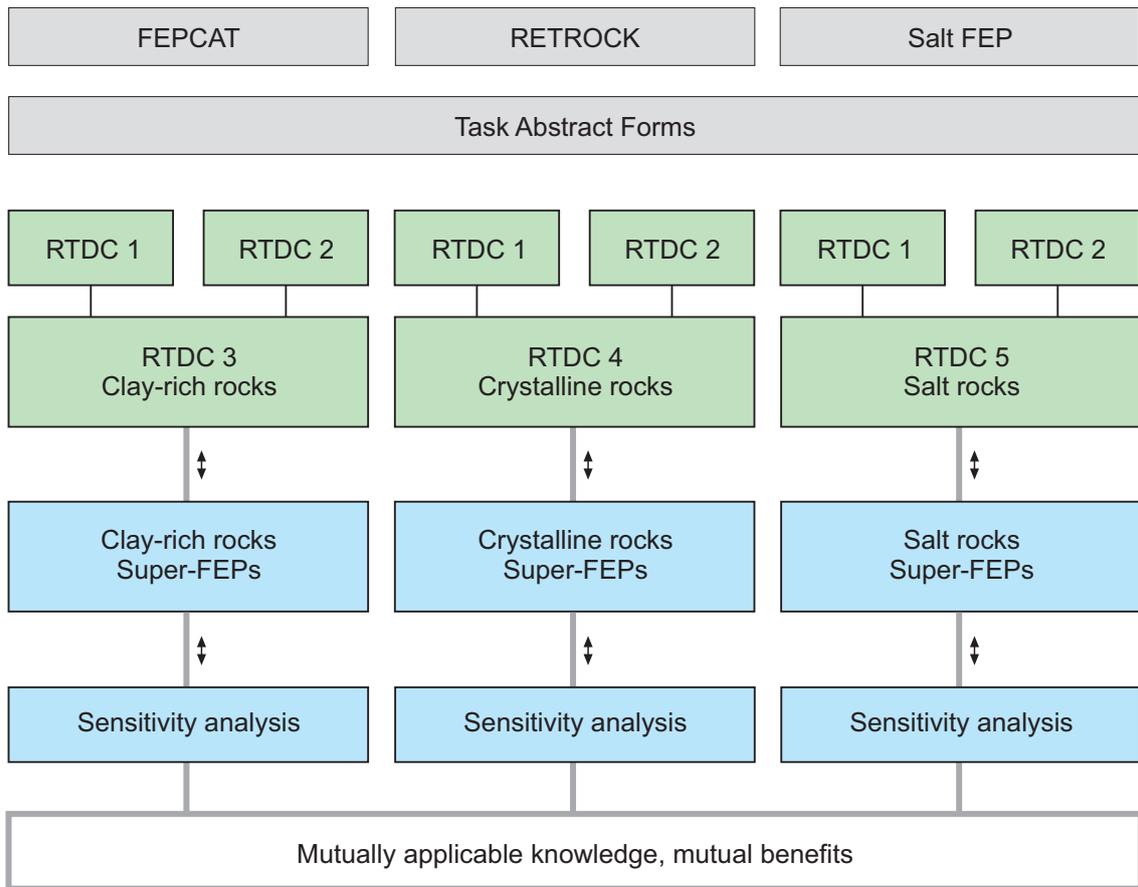


Fig. 3-1: Structure of task mapping and evaluation.

3.4.2 Step 2: Evaluation of FUNMIG tasks by WMOs

In an early stage of the project, the WMOs evaluated all research activities based on the task proposals provided by the individual research groups (Nagra 2007). The evaluation was split into several topics, where each topic was qualified following a pre-defined set of qualifiers (Tab. 3-2). To organise the answers provided by the WMOs, a table was set up for each host rock (clay, crystalline and salt). These tables, the so-called Task Evaluation Tables (TETs), were summarised and presented to the researchers.

Note that the WMOs' evaluation was mainly based on their country-specific safety assessment. Some of these safety cases were performed for specific sites, others are more generic, thus still including some degree of freedom regarding the design of the repository or the specific host rock properties.

Tab. 3-2: Instruction to task evaluation table as distributed among the WMOs.

TET column	Description	Qualifier
FUNMIG tasks	description (from RTDCs 1-5)	
Investigated processes	"translation" into terminology used by FEPCAT/RETROCK/Salt FEP	
SA parameter	if appropriate, you may indicate whether applicable to Reference Case or Alternative Cases, but exclude "what if?" cases	<p>Examples of SA parameters include:</p> <ul style="list-style-type: none"> • K_d [m³/kg]: sorption coefficient • C_{sol} [mol/m³]: max. solubility • D_e [m²/s]: effective diffusion coefficient • ε [-]: matrix porosity • R [-] retention factor • K [m/s]: hydraulic conductivity • T [m²/s]: fracture transmissivity • i [-]: hydraulic head
Relevance for SA	Qualify the overall relevance of the task (parameter and/or process) for the SA	<p>Select one of the following 4 qualifiers:</p> <ul style="list-style-type: none"> • "must have" • "should have" • "nice to have" • irrelevant
	Specify in which sense the task is relevant for SA	<p>Select any combination from the following 7 qualifiers (as appropriate):</p> <ul style="list-style-type: none"> • host-rock specific • site-specific • inventory-specific • design-specific • demonstrating process understanding • enhancing process understanding • basis for deriving SA parameter values
Influence of investigated process on SA parameter uncertainty	How strongly does the proposed improvement of a parameter/process improve the SA parameter uncertainty?	<p>Select one of the following 5 qualifiers:</p> <ul style="list-style-type: none"> • strong • medium • low • non-existent • not applicable

Tab. 3-2: (continued)

TET column	Description	Qualifier
Relevance of SA parameter uncertainty	How important/sensitive is the parameter for the overall SA	Select one of the following 5 qualifiers: <ul style="list-style-type: none"> • high • medium • low • irrelevant • not applicable
Benefits of improvements ("added value" of investigation of process in FUNMIG)	Entries in this column are based on an evaluation of the information given in columns "Relevance for SA", "Influence of investigated process on SA parameter uncertainty" and "Relevance of SA parameter uncertainty"	Select one of the following 3 qualifiers: <ul style="list-style-type: none"> • strong • medium • low

3.4.3 Step 3: Summary of researcher's results through Task Abstract Forms (TAFs)

Each research group and each task provided a one-page summary of the main outcomes. The structure of the TAFs included a self-evaluation of the researchers (Tab. 3-3) which was then transferred into the TETs because it was seen as important that the final TETs would provide a complete picture (i.e. WMOs and researchers) of the task evaluation. This way the reader will be able to compare the views of researchers and WMOs.

The final TAFs are shown in Appendix B.

Tab. 3-3: Task abstract form as distributed among the researchers.

x.x.x Task Title (Times New Roman, 11pt, bold)	
Motivation and aim: Why did you choose the particular materials and approach? What did you want to achieve?	
Type of work:	
Participants:	
State of the art before FUNMIG:	
Main results (abstract): Font (for the whole form): Times New Roman, 11pt, single space (Please do not use more than 1 page for this form including Task Title and references)	
Guidance: This abstract will be used by the Waste Management Organisations as the basis for filling in the last column of the Task Evaluation Tables “Achieved improvements within FUNMIG, PA view (Safety Case)”. Please consider the following aspects (if applicable) in your concise description of work: <ul style="list-style-type: none"> – Improvement of knowledge: How does this work contribute to scientific understanding of the investigated processes? – Methodology: Did you improve methods or develop new ones within your work? – Improvement of data: Do the results reduce data uncertainty? To what extent? Compare outcome with planning and note discrepancies (above expectation or aim not fully reached or even failure)	
Achievements for the safety case	One sentence only! → intended to be transferred to Task Evaluation Tables, last column “Achieved improvements within FUNMIG, researcher’s view”
References: Author(s) (year) title, journal, nr, pages (Please cite only references relevant for tracing back your work!)	

3.4.4 Step 4: Evaluation of achieved improvements within FUNMIG

In order to make the final TETs more comprehensible, the task evaluation criteria as shown in Tab. 3-2 had to be reduced considerably. The last four columns were therefore summarised into a single column named "Importance of improvements for SA parameter uncertainty reduction" (Tab. 3-4).

At the end of the project, each task was evaluated by the group of WMO representatives following the template in Tab. 3-4. Note that consideration of the scientific quality of the work beyond its relevance to performance assessment was outside the scope of this evaluation procedure.

Entries in this last column were filled in based on an evaluation of the TAFs, using the Waste Management Organisations (WMOs) experience with their safety cases and taking into account the entries in the previous columns. The criteria applied in filling in this column were related to the benefits for the WMOs future safety cases for the specific host rocks they consider (clay-rich, e.g. Boom Clay, Callovo Oxfordian, Opalinus Clay, crystalline rock and salt), i.e. improvements of the state of knowledge during FUNMIG and host rock specific conditions were considered and commented.

The tasks were evaluated considering the

- improvement of knowledge with regard to the safety case and
- improvement of data influencing PA

with respect to the WMOs safety cases using the following qualifiers:

- Important
- Supporting
- Not applicable

The results of a task were considered to "improve the knowledge" when they can be used to support a safety case in terms of system understanding. This may include new insights into specific processes or new methodologies that may lead to a deeper scientific understanding.

The results of a task are considered to "improve the data" when they can be used to quantify data used in PA and/or to reduce uncertainties of such data.

A specific improvement of knowledge or data is labelled "important" when it is essential for a future safety case and the corresponding WMO has therefore put a high priority on such an improvement within its RD&D plan ("must have").

It is labelled "supporting" when it contributes to a safety case but has a lower priority within the WMOs RD&D plan ("nice to have").

A specific improvement of knowledge or data is labelled "not applicable" when it is judged not to contribute to a future safety case of a WMO (e.g. irrelevant topic or no improvement).

The evaluation generally considered the current state-of-the-art procedures; however one has to be aware that the procedure for making a safety case may be further developed in the future.

Tab. 3-4: Template for final TETs.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Explanations	Description (from RTDCs 1 – 5)	"Translation" into terminology used by salt-specific FEP DB	If appropriate, you may indicate whether applicable to Reference Case or Alternative Cases, but exclude "what if?" cases		Entries in this column are filled in according to the researchers view given in the task abstract forms (TAFs)	Entries in this column are filled in based on an evaluation of the task abstract forms, using the WMO's experience with their safety cases and taking into account the entries in the previous columns
			Examples of SA parameters include: <ul style="list-style-type: none"> • K_d [m^3/kg]: sorption coefficient • C_{sol} [mol/m^3]: max. solubility • D_e [m^2/s]: effective diffusion coefficient • ϵ [-]: matrix porosity • R [-]: retention factor • K [m/s]: hydraulic conductivity • T [m^2/s]: fracture transmissivity • i [-]: hydraulic head 	Select one of the following 4 qualifiers: <ul style="list-style-type: none"> • high • medium • low • not applicable (n/a) Select any combination from the following 7 qualifiers (as appropriate): <ul style="list-style-type: none"> • host-rock specific • site-specific • inventory-specific • design-specific • demonstrating process understanding • enhancing process understanding • basis for deriving SA parameter values 	For each of the following: <ul style="list-style-type: none"> • improvement of knowledge • improvement of data influencing PA Insert one of the following 3 qualifiers: <ul style="list-style-type: none"> • important • supporting • not applicable (n/a) Rules: <ul style="list-style-type: none"> • thermodynamic databases – support knowledge and data for all countries • new/improved analytical method or technique – supports knowledge but n/a for data • literature search – Does not generate data, so data n/a • individual clay minerals (not host rock) – supporting for both knowledge and data site specific natural systems – supporting for data • modelling studies – supports knowledge but n/a for data 	

Tab. 3-4: (continued)

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Explanations (continued)	Description (from RTDCs 1 – 5) (continued)		Please include a short description of the conceptual model used to derive SA parameter (use references as appropriate)		Please also include a short description of the achieved improvements within FUNMIG for the safety case	
Responsibilities		"Translation" by RTDC6	Compilation by RTDC6 with input from WMOs (based on their general experience in SA)	Compilation by RTDC6 with input from WMOs (based on experience/ sensitivity analyses for specific cases)	Compilation by IMG with input from RTDCs 1 – 5	Compilation by RTDC6 with input from WMOs (An: Andra, En: Enresa, Na: Nagra, NDA, ON: Ondraf/Niras, Po: Posiva, SKB)

The final TETs for each host rock are shown in Appendix C.

4 Clay-rich host rocks

4.1 Clay specific FEPs and their links to FUNMIG work packages

In disposal concepts which include an argillaceous host rock, the properties of the clay formation play a central role in safety considerations. Because of their very low permeability and their high sorption capacity, together with their substantial thickness, these clay rocks provide an effective barrier for radionuclides that may have escaped the engineered barrier system. For the clay formations under consideration for host rocks, such as the Boom clay, Callovo-Oxfordian formation (COx) and the Opalinus Clay (OPA), it has been shown in previous investigations that the main transport process is diffusion.

Research on clays that serve as potential host rocks is relatively recent compared to that on crystalline or salt host rocks. Nevertheless, considerable progress in the last years has been made on the physico-chemical properties of clay rocks in the context of their role as geological barrier. Thus, rock-specific and URL-based studies on the plastic Boom clay and on the two stiff clay rocks, COx and OPA, led to the development of a sound methodology for rock characterisation and to high-quality data on transport properties. The knowledge obtained thereof has been an important foundation for the FUNMIG project and enabled to focus on key issues as outlined below. One of the main benefits of FUNMIG relative to previous projects is the parallel investigation of the three clay rocks where both host rock specific processes and phenomena relevant for all three host rocks have been studied. For example, the fundamental processes of sorption and diffusion are similar in all three rock materials because of their similar mineralogical assemblage. However, the impact of organic matter on radionuclide mobility in the Boom Clay is clearly more pronounced than in the other two formations because of the higher content and reactivity of organics in the Boom Clay.

The safety-relevant features, events and processes (FEPs) for clay host rocks have been presented in the FEPCAT list elaborated by the Clay Club of the NEA in 2003 (Mazurek et al. 2003). In this catalogue FEPs are grouped into three types:

- A. Undisturbed system properties ("far field")
- B. Repository-induced perturbations (EDZ, "affected field")
- C. External perturbations (geologic, climatic, human)

In alignment with the FUNMIG research topics Tab. 4-1 mainly lists FEPs related to undisturbed system properties (type A) but includes two B-type FEPs, "Effects of organics originating from the waste" and "Microbiological perturbations". C-type FEPs were only marginally touched in FUNMIG.

The evaluations were made based on the results obtained in RTDCs 1, 2 and 3. The host rock independent RTDCs 1 and 2 studied well established processes (e.g. speciation, ion exchange or solid solutions) and less established processes (e.g. migration of colloids or humic substances). The Task Evaluation Table for clay-rich host rocks (Tab. C-1) is found in Appendix C.

Tab. 4-1: Classification of FEPs according to state of knowledge and PA relevance (taken from Mazurek et al. 2003) and links to FUNMIG work packages.

FEP No.	FEP name	Availability of PA relevant knowledge on FEP	Relevance of FEP for PA (or, more generally, a safety case)	WP in FUNMIG
A1.1	Advection/dispersion	Good for matrix flow, more limited for fracture flow	Important transport process with limited consequences in diffusion-dominated systems (applies to most sites investigated), highly relevant in advection dominated systems with fracture flow	
A1.1.1	Size and geometry of the host rock and of surrounding units, migration path length	Good	High	
A1.1.2	Migration pathways, including heterogeneity and anatomy	Sedimentary structures well known, database for tectonic structures and their hydraulic significance is limited, and up-scaling in space and time may be problematic mainly in highly indurated formations where fracture flow could be important. However, they can often be avoided by design.	High	
A1.1.3	Undetected geological features	Currently variable, but can be much improved by applying available techniques (e.g. 3D seismics).	Limited in diffusion dominated systems (due to the expected hydraulic irrelevance of undetected features), more relevant in highly indurated, advection-dominated systems with fracture flow (higher degree of heterogeneity).	
A1.1.4	Hydraulic potentials and gradients in the host rock, including boundary conditions	Generally good (except for the understanding of abnormal pressures)	Necessary input for quantifying advection, which is an important transport process. Its consequences are limited in diffusion-dominated systems (applies to most sites investigated), but it is relevant in advection dominated systems with fracture flow.	
A1.1.5	Hydraulic properties of the host rock	Good, except for spatial up-scaling (namely in systems where fracture flow dominates)	High	
A1.1.6	Units over- and underlying the host formation: local and regional hydrogeologic framework	Good	High	
A1.2.1 A2.1.1	Diffusivity	In general good, more limited for retarded species	High	3.1, 3.2, 3.3

Tab. 4-1: (continued)

FEP No.	FEP name	Availability of PA relevant knowledge on FEP	Relevance of FEP for PA (or, more generally, a safety case)	WP in FUNMIG
A1.2.2 A2.1.2	Connected matrix porosity	Good	High	3.1, 3.2, 3.3
A1.2.3 A2.1.4	Ion exclusion	Good	High	3.1
A1.2.4 A2.1.5	Surface diffusion	Limited	Limited, if any at all	3.1
A1.3	Colloid formation, transport and filtration	Limited, but the functionality of the matrix of argillaceous rocks as a colloid filter is established.	Limited in diffusion dominated systems, relevant in advection dominated systems with fracture flow	2.1, 3.2,
A2.1.3	Flow-wetted surface and accessibility of matrix	Fair	Irrelevant in diffusion dominated systems, more relevant in advection dominated systems with fracture flow	
A2.2.1	Lithology, mineralogy of rocks and fracture in-fills	Good	High	3.2
A2.2.2	Natural organics, complexation	Fair	Variable (depending on the nature of the organic matter involved and the nuclide inventory), complexation: high	1.3, 2.2, 3.2
A2.2.3	Mineral-surface area	Good	High	
A2.2.4	Pore- and fracture water composition	Good except for 1) modelling uncertainty and 2) distinction between fracture and matrix water.	High	2.3, 3.1
A2.2.5	Dissolution/precipitation of solid phases	Major phases: good, phases limiting solubilities of radionuclides: limited.	High (solubility limits of radionuclides)	
A2.2.6	Solid solutions/coprecipitation	Moderate, can be modelled in principle.	Potentially high, often (conservatively) neglected	1.4
A2.2.7	Ion exchange	Good, can be modelled in principle but data are limited.	High	1.1, 1.2, 1.3, 2.3, 3.2
A2.2.8	Surface complexation	Fair (empiric data sufficient, mechanistic understanding limited)	High	1.1, 1.2, 1.3, 2.3, 3.2
A2.2.9	Thermodynamic and kinetic modelling data	Variable (depending on element)	High	1.1, 1.2, 1.3
A3.1 C1.1.1	Palaeo-hydrogeology of the host formation and of embedding units	Good in principle even though not available in full at all sites	High	

Tab. 4-1: (continued)

FEP No.	FEP name	Availability of PA relevant knowledge on FEP	Relevance of FEP for PA (or, more generally, a safety case)	WP in FUNMIG
A3.2 C1.1.2	Evolution of pore-fluid (water and gas) chemistry and mineralogy in the host formation and in embedding units	Good in principle even though not available in full at all sites	High	3.2
A3.3	Water residence times in the host formation	Good in principle even though not available in full at all sites	High	
B1.2.2	Organics from the waste and their effects on transport properties of the host rock	Limited	Effects are spatially limited at least in diffusion-dominated systems, otherwise not well known due to the scarcity of information	1.3
B7	Microbiological perturbations	Limited	Unclear, limited in the unfractured matrix due to space constraints	2.4

4.2 Discussion on a Super FEP level and key questions

In Fig. 4-1 the information compiled in Tab. 4-1 is summarised graphically. It shows that virtually all FUNMIG activities are related to the Super-FEPs "Transport mechanisms" (A1) and "Retardation mechanisms" (A2). The affected parameters used in safety assessment calculations are also shown.

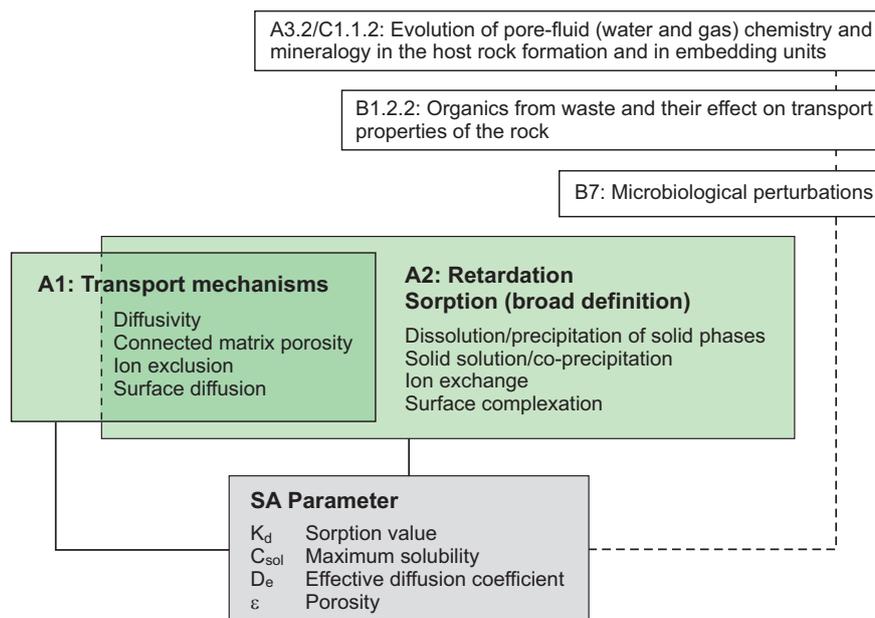


Fig. 4-1: FEPs (taken from FEPCAT) to which the tasks were mapped, and relevant safety assessment parameters for clay-rich host rocks.

The parameters corresponding to the two Super-FEPs and typically used in PA are sorption values (K_d), solubility (C_{sol}), effective diffusivity (D_e) and diffusion-accessible porosity (ε).

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

$$J = D_e \nabla C \quad (1)$$

$$\text{with } D_e = D_p \varepsilon = D_0 \left(\frac{\delta}{\tau^2}\right) \varepsilon \quad (2)$$

where J: flux ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$), D_e , D_p , D_0 : 'effective', 'pore', 'free solution' coefficients ($\text{m}^2\cdot\text{s}^{-1}$) respectively, C: concentration ($\text{mol}\cdot\text{m}^{-3}$), 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 radionuclide mass transfer:

$$\frac{\partial C}{\partial t} = D_a \nabla^2 C \quad (3)$$

$$\text{with } D_a = \frac{D_e}{\varepsilon + \rho_d K_d} \quad (4)$$

where D_a : 'apparent' diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$), ρ_d : rock dry density ($\text{kg}\cdot\text{m}^{-3}$), K_d : distribution coefficient ($\text{m}^3\cdot\text{kg}^{-1}$) representing partitioning of RNs between dissolved species and sorbed species at position x,y,z. The term "sorbed species" does not imply any mechanistic process behind.

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. $^{36}\text{Cl}^-$, $^{129}\text{I}^-$). 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 rock fabric, and effects of mineral composition.
- Moderately and strongly sorbing radionuclides, principally in cationic form (e.g. $^{135}\text{Cs}^+$, 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 summarised.

In Tab. 4-2, the FEPs listed in Tab. 4-1 are grouped into the Super-FEPs, mentioned above, and the latter are linked to the key issues studied within FUNMIG. The corresponding FUNMIG Tasks (see Appendix B) are also given.

Tab. 4-2: FUNMIG key issues investigated for clay host rocks and corresponding FUNMIG Tasks.

FEP	FUNMIG Key issues	FUNMIG Tasks
<i>Retardation</i>		
Sorption processes	Conceptual/numerical sorption model (dilute system)	1.2.4a, 1.2.4b 1.2.5, 1.2.8, 3.1.4b
	Sorption of actinides and other strongly sorbing species (dilute & compact conditions)	1.2.2, 1.2.3, 1.2.9, 1.3.1, 1.3.5, 3.2.4, 3.2.6, 3.3.1, 3.3.2
	Effect of natural and waste-derived organics on sorption	1.3.1, 1.3.2, 2.2.1a, 2.2.1b, 2.2.1c, 2.2.2a, 2.2.2b, 2.2.2c, 2.2.2d, 2.2.2e, 2.2.2f, 2.2.2g
	Redox processes (e.g. Se, role of reducing minerals)	1.2.3, 1.4.2a, 1.4.2b, 2.2.1b, 2.3.1a, 2.3.1b, 2.3.1c, 2.3.2a, 2.3.2b, 2.3.3, 3.1.1
	Transfer of sorption values from dilute to compact conditions	1.4.2a, 3.1.4b, 3.2.4, 3.2.5
Co-precipitation and solid solution formation	Conceptual/numerical solid solution models	1.4.5
	Co-precipitation with model compounds	1.4.3, 2.1.1
<i>Transport mechanisms</i>		
Diffusion processes	Conceptual/numerical diffusion models at nanometer scale	3.1.2, 3.1.4a
	Diffusion and microstructure at micrometre to centimetre scale	3.1.3, 3.2.1, 3.2.2, 3.2.6, 3.3.1, 3.3.2;
	Diffusion at large scales	3.4.1, 3.4.3, 3.4.4a

In the following paragraphs, the main achievements with regard to the safety case, grouped into retardation and diffusion-related processes, are summarised. It should be noted that retardation and diffusion are inter-related processes in clays, as particularly evident for diffusing cations. Most data on retardation and more specifically on sorption mechanisms however is obtained from static batch systems.

4.2.1 Retardation

Retardation processes of radionuclides in clays can be divided into sorption and (co-) precipitation processes. Sorption processes includes cation exchange in the interlayer of the clays and surface sorption or adsorption to external surfaces of the clay minerals, accessory minerals or organic matter (e.g. kerogen). Precipitation processes treated within FUNMIG are limited to co-precipitation and solid solution formation.

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.

Conceptual/numerical sorption models (dilute system)

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 dependent on geochemical conditions which have limited general applicability (Davis et al. 2005) 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. This topic was treated in tasks: 1.2.4a+b, 1.2.5, 1.3.2, 3.1.4b.

Sorption of strongly sorbing actinide and other species

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 et al. 2008a). The results obtained so far indicate that the new technical developments are promising, but considerable methodological work is still necessary for achieving reliable sorption data for strongly sorbing species under compact conditions. This topic has been addressed in tasks: 3.2.4, 3.2.5, 3.3.1.

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 (tasks: 3.2.6, 3.3.1) 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) (task: 3.3.2) enabled improved 2D and 3D description of sorbing tracers within a complex geometry (Gimmi 2008, Samper & Yang 2008).

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. 2008). Spectroscopic evidence has been given that lanthanides and actinides form inner sphere complexes at edge sites of the clay surfaces (Schlegel 2008). This topic has been presented in tasks: 1.2.2, 1.2.4b, 1.2.4c, 1.2.9, 1.3.1.

Effect of natural and waste-derived organics

Natural organic matter (NOM) 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 NOM in the plastic Boom Clay (foreseen as host rock in Belgium), on radionuclide complexation is significantly larger than that of the NOM 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 and 2009). Further studies on the interaction of Eu, Am and Th with NOM provided complementary information on the effect of NOM on K_d values (Reiller et al. 2007 and 2008). This topic has been presented in tasks: 1.3.1, 1.3.2, 2.2.1a – b, 2.2.2a – g.

A comparative experimental study on COx and OPA (Schäfer et al. 2009a und b) provided new insight into the reactivity of kerogen, its spatial distribution and its complexation properties for radionuclides (see Task 1.3.5).

Another combined experimental and modelling study (Evans et al. 2007 and 2011) 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 (see Task 1.3.3).

Redox processes affecting selenium and other radioactive elements

Clay-rich 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 uncertainties 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. 2006, Gehin et al. 2007, Charlet et al. 2007) which helped to clarify their role in immobilising redox sensitive radionuclides. Several experimental studies have been focussed on the interaction of Se with pyrite, clay minerals and NOM 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 NOM. 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 2009). This topic was addressed in tasks: 1.2.3, 1.4.2b, 2.2.1b, 2.3.1a+b+c, 2.3.2a+b, 3.1.1.

Transfer of sorption values from dispersed to compact conditions

As outlined above, mechanistically derived sorption data is generally obtained from dispersed 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.

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. (2009), where the sorption behaviour of Cs^+ to OPA under dilute and compacted conditions was shown to be nearly equal (Fig. 4-2). On the other hand, for the sorption of divalent heavy metals,

lanthanides or actinides, further work is necessary to confirm or disconfirm this assumption (see task: 1.4.2a, 3.1.4b, 3.2.4, 3.2.5).

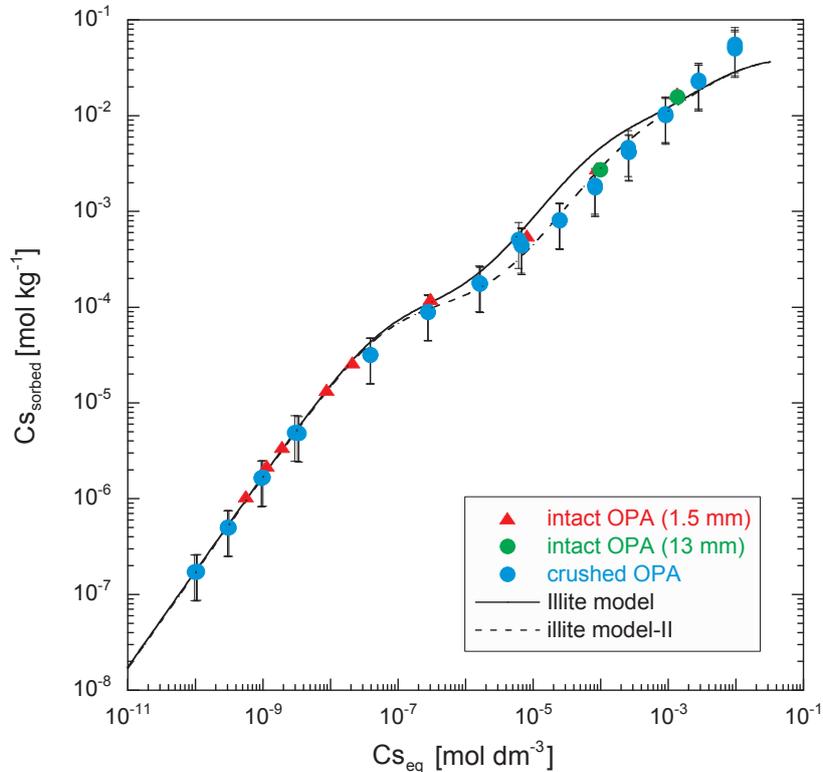


Fig. 4-2: Experimental study on Cs^+ sorption to crushed and intact Opalinus Clay by Van Loon et al. (2009).

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. 2008a). A new theoretical study on solid solutions has enabled improvement of the thermodynamic description of solid solutions (Vitorge 2008). This topic was addressed in tasks: 1.4.3, 1.4.5.

4.2.2 Transport (diffusion) mechanisms

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 were 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 summarised 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. 2009, Montavon et al. 2009b). The results led to a mechanistic description of the water interface 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 monoporosity and a dual porosity concept where so far only preliminary progress could be made (see Tasks 3.1.2, 3.1.4a).

Diffusion and microstructure at micrometre to centimetre scale

Most diffusion studies within FUNMIG, which included through- and in-diffusion experiments, 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 (see Tasks 3.1.3, 3.2.1, 3.2.2, 3.2.6, 3.3.1, 3.3.2) to obtain the spatial 2D and 3D mineral organisation and porosity distribution in clay rocks, as illustrated in Fig. 4-3. In the case of the CO_x 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 provided the basis for defining model structures for analysing the effects of rock mineral composition on diffusion (Robinet et al. 2008a, Altmann 2009).

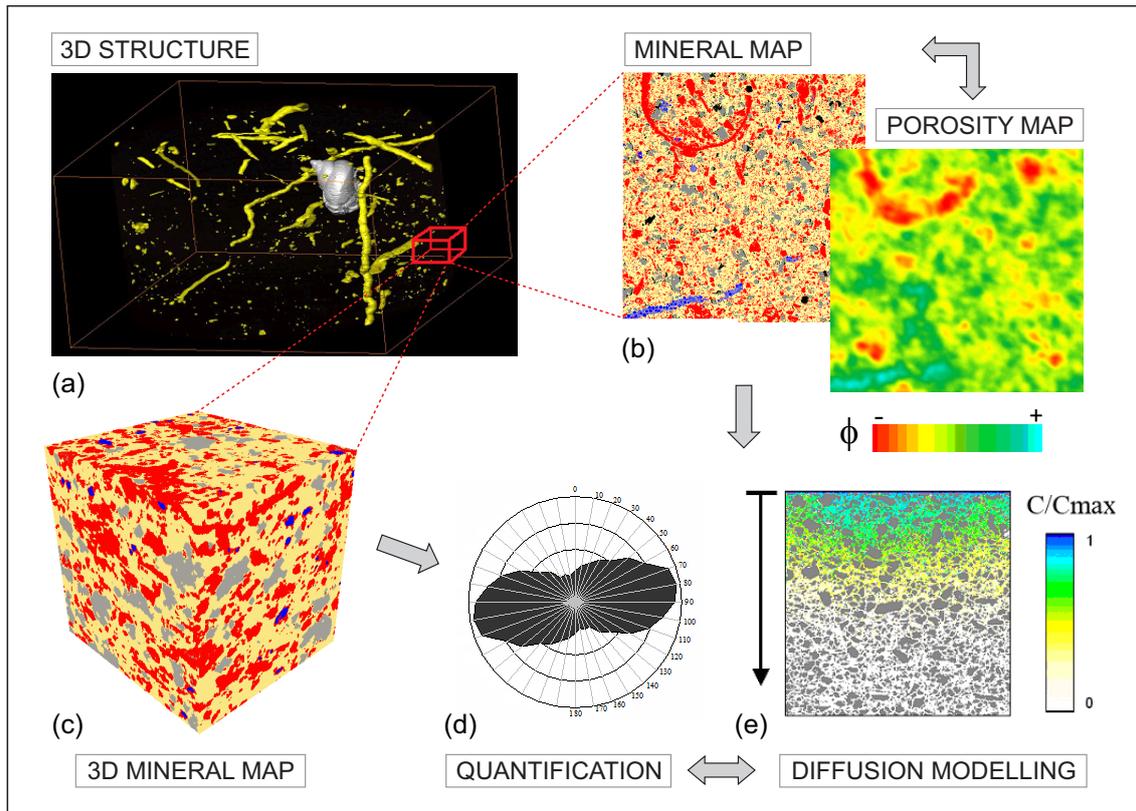


Fig. 4-3: Methodology used to characterise clay rocks at macroscopic and mesoscopic scales.

- (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)

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 2008) in order to validate and, if necessary, improve the codes and to quantify the effects of rock anisotropy (see Tasks 3.3.1, 3.3.2).

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 analysed 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 2009). By means of geostatistical analysis, three different material classes with different carbonate content and distinct diffusion properties were obtained, which provided the basis for parametrising 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.

5 Crystalline host rocks

5.1 Safety-relevant processes identified in the RETROCK Project and their link to FUNMIG work packages

To evaluate tasks of RTDC 1, 2 and 4, the findings of the EC project RETROCK were used, in particular, a list of processes which is based on responses of participating organisations to a questionnaire. In Tab. 5-1 work packages dealing with corresponding topics are assigned to processes of the RETROCK list.

The Component RTDC 4: "Processes and transport studies relevant for crystalline rock disposal concepts" of the IP FUNMIG was devoted to flow and transport studies being characteristic in sparsely fractured rock. The engineered barrier system is essential in such a locally conductive medium to isolate the waste packages from the high flow rate flow paths. However, low transmissive fractures may eventually intersect with waste package positions forming the interface between the EBS near-field and the far-field bedrock. This interface is the source term for the far-field migration.

The overall objectives of this RTD component dealing with crystalline host rocks were to:

- Characterise the prevailing geochemical conditions
- Characterise the fluid flow system with respect of dual porosity, fractures, crystalline matrix and its heterogeneity and complexity
- Analysed the effects of the presence of different colloid types and their potential influence on the radionuclide transport
- Investigate the generation, meta-stability and mobility of colloids through crystalline media
- Investigate radionuclide transport mechanisms (advection, diffusion)
- Identify and verify processes by analysis of real systems, and
- Provide up-scaling of the processes

To structure the studies aiming to reach the objectives the RTDC was divided into the following work-packages:

WP 4.1: Characterisation of geochemical conditions in crystalline host rock

WP 4.2: Fluid flow system characterisation

WP 4.3: Generation, quantification, characterisation, stability and mobility of groundwater colloids

WP 4.4: Radionuclide transport studies, including the effects of inorganic/organic colloids.

WP 4.5: Processes identification and verification by real system analysis

WP 4.6: Up-scaling of processes

In addition to RTDC 4 tasks relevant tasks performed within RTDC 1 and 2 were included in the evaluation.

In the course of the RETROCK project preceding the IP FUNMIG many waste management organisations and stakeholders were asked to summarise their experiences regarding the role of radionuclide transport in geosphere. The transport and retention processes identified as relevant to safety by the different organisations that responded to the RETROCK questionnaire were grouped to a set of most important processes which are listed in Tab. 5-1. Work packages dealing with corresponding processes are also given in Tab. 5-1.

Tab. 5-1: The transport and retention processes identified as relevant to safety by the different organisations that responded to the RETROCK questionnaire.

Major ("lumped") processes mentioned by all respondents	Detailed or related processes mentioned by one or more respondents	WP in FUNMIG
R1: Advection within fractures	a) Longitudinal and transverse dispersion b) Channeling	4.2 --
R2: Diffusion within fractures	a) Diffusion parallel to the direction of advective transport b) Diffusion into stagnant water caused by constrictions in fracture openings	4.2, 4.4 --
R3: Matrix diffusion	a) Anion exclusion b) Surface diffusion c) Plugging of matrix pores by precipitates	-- -- --
R4: Sorption on matrix pore surfaces and on fracture walls and infill	a) Speciation, including formation of complexes b) Adsorption c) Ion exchange d) Surface complexation	1.1, 1.3, 2.2, 2.4, 4.1 2.1, 1.3 1.2 1.2, 1.3
R5: Immobilisation	a) Precipitation/coprecipitation (solid solution formation) b) Very slow desorption	1.4 --
R6: Colloid-related processes	a) Advection/dispersion b) Sorption of radionuclides on colloids c) Generation and filtration in rock mass d) Sorption/desorption of colloids e) Colloid/bubble attachment	4.4 2.1, 2.2, 4.4 2.1, 4.3, 5.1 4.3, 2.1, 2.2 <i>Not far-field relevant</i>
Other processes mentioned by one or more respondents		
R7: Microbiological processes		2.4
R8: Gas-mediated transport		Not far-field relevant
R9: Off-diagonal Onsager processes		RTDC 3
R10: Radionuclide accumulation due to non-stationary flow conditions		--

The evaluations were made based on the results obtained in RTDCs 1, 2 and 4. The host rock independent RTDCs 1 and 2 studied well established processes (e.g. speciation, ion exchange or solid solutions) and less established processes (e.g. migration of colloids or humic substances). The Task Evaluation Table for crystalline host rocks (Tab. C-2) is found in Appendix C.

5.2 Discussion on a Super-FEP level and key questions

The contributions of the performed tasks within the IP FUNMIG to safety case are assessed here in terms of five "Super-FEPs" based on the RETROCK grouping:

- Advection within fractures (R1)
- Diffusion within fractures (R2)
- Matrix diffusion (matrix porosity) (R3)
- Sorption on matrix pore surfaces and fracture walls and infill (R4)
- Colloid-related processes (R6)

These are discussed in the following sub-sections. In addition, the main achievements within FUNMIG related to these Super-FEPs are summarised therein.

The Super-FEP "Immobilisation" (R5) which includes precipitation and co-precipitation phenomena was treated only marginally within FUNMIG and is therefore not considered here further.

5.2.1 Transport within fractures

Advection with fractures (R1)

The RETROCK project, being an important starting point for the IP FUNMIG, discussed the influence of flow on transport and retention processes and described the flow paths in the following way (EC 2005):

"The dominating transport mechanism for solutes in fractured rock is transport with the flowing water. Since water flow is restricted to the fractures, the dimensions, shape, orientation and connectivity of the fractures determine the properties of the flow paths in the rock. Very small scale features of the fractures such as aperture variations may have an important influence on the flow paths. Preferential flow paths or channels may develop through parts of the fractures with larger aperture. Of special interest are fast flow channels with very small interaction area with the rock. Such channels may exist on a local scale, but it is unlikely that they prevail over such long distances that they constitute important transport pathways on the scale of interest for a performance assessment. One hypothesis for the occurrence of fast channels is along fracture intersections where they may act as essentially one-dimensional connectors.

The flow paths are often conceptualised as meandering "streams" following the fractures through the rock, although in reality it is a complex flow field within the fractures. The flow paths should not be considered as fixed but variable depending on the direction of the gradient. In a stationary flow field only limited mixing due to molecular diffusion occurs within the flow paths. At fracture intersections flow paths can combine and separate after mixing of the water. The extent of mixing in fracture intersections is largely unknown.

Since it is not possible to investigate or model the flow field or even the physical fractures within the large rock volumes of interest for PA, simplifications and assumptions have to be made in the modelling. These simplifications have generally been based on available model concepts and their restrictions. However, recently more and more efforts have been put into evaluating which properties are of vital importance for the radionuclide transport and what level of simplification can be made while still obtaining results that are suitable for the purpose of performance assessment. The simplifications made in the modelling are also closely linked to the type of data that is possible to obtain in site investigations. Simplifications can be made in many ways and from different starting points. Thus, a multitude of different model concepts have evolved that differ in many aspects, but also have many similarities."

The flow in fractures has an important role, in addition to the transport function described above, as the interface of radionuclide releases from the near field to the far field. This role as the interface has been studied both under real site conditions at the FEBEX site and in the large scale mock-up test in the laboratory (Tasks 4.4.1a and b). These results provide information and support for future safety cases in general taking into account that site conditions at different sites have to be accounted for separately. Characterisation of the advective field at any disposal site and in principle at every disposal position and along the flow path downstream is a prerequisite for transport analyses. In practice the characterisation of every position and along every path line may be possible only in the statistical sense. Processes that take place in a very detailed scale can be studied in laboratory in generic way. This has been done also in the IP FUNMIG.

Diffusion within fractures (R2)

Depending on the flow velocities in fractures molecular diffusion within fractures may play a dominant role. There are two main aspects of diffusion in an advective field. Longitudinal diffusion, especially over shorter distances up to several metres, may govern or significantly enhance transport in slowest flow fields. On the other hand, the coupling of transverse diffusion and a heterogeneous advective field affects strongly the dispersive characteristics of the mass fluxes. In very heterogeneous advective fields the dispersion (due to different velocities) would be very high and the flow could be described in terms of strong channelling, thus weakening the retention processes whereas in cases with high transverse diffusion over relevant distances in the advective field the dispersion diminishes and the mean velocities and flow rates are more important.

Models for reactive transport in heterogeneous media and flow conditions are useful tools to support a safety case because they provide the possibility to simulate realistic scenarios even without detailed site specific data. It is usually a big challenge or even be impossible to acquire sufficient site specific data in such a detail to describe the flow field accurately enough. In addition, boundary conditions change over time. In any case, modelling tools are needed to study the remaining uncertainties with different conceptual assumptions and sensitivity analyses. Typical examples of complex flow situations should be studied and compared with more simple safety analysis modelling to enhance further confidence in the transport analyses.

Main FUNMIG achievements on transport modelling and upscaling

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 melt-water intrusion on uranium migration was investigated at the Palmottu site in Finland (Suksi et al. 2006, Markovaara-Koivisto & Einsalo 2009).

The determination of actual radionuclide fluxes from the near-field and the understanding of mass transfer processes was the focus of an extensive study (Pérez-Estaún et al. 2006, Gómez 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. 2010) in the different fractures, which led to the identification of sub-parallel fracture zones in the gallery. Such visualisation 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 analysed and evaluated in the context of their adequacy for PA (Salamon et al. 2006a, Fernández-García & Gómez-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.

5.2.2 Matrix diffusion and sorption phenomena

Matrix diffusion (matrix porosity) (R3)

The quantification of groundwater flow and solute transport in crystalline rock is especially interesting for regions with only few fractures where repositories will preferably be located. Solutes are retarded when they interact with material around the flowing water such as fracture walls, material in the fracture, and, most importantly, the rock matrix around the fracture itself. A short description of the situation was given in the RETROCK final report (EC 2005) in the following way:

"On a microscopic scale rock has an intricate network of micro fractures and interconnected pores. The void space arises from processes such as crystallisation sequence, brittle or ductile deformation, dissolution and alteration of minerals. The void space is affected by geochemical processes and pores may be opened, closed or isolated. The dimensions of the voids are also dependent on the lithostatic pressure.

The pores in the rock matrix are so small that there is no or very little water flow in them. However, solutes (e.g. dissolved radionuclides) may enter these pores through molecular diffusion. This process is called matrix diffusion. Through matrix diffusion radionuclides have access to the stagnant water inside the rock matrix and can thus be removed from the water flowing in the rock fractures. Matrix diffusion is a very important process for retention of radionuclide transport in the geosphere, especially for sorbing radionuclides that through matrix diffusion have access to the very large inner surfaces of the rock matrix. These surfaces can typically be 3 to 6 orders of magnitude larger in area than the surfaces of the fractures where the water flows. An extensive overview of matrix diffusion can be found in the Work Package 2 report (RETROCK 2004) and also published in Jakob (2004)."

Both theoretical and experimental studies conducted within the IP FUNMIG have further addressed important aspects of matrix diffusion and have given more insight into the microscopical structure and solute behaviour in the matrix. Main points that are needed for assessing the retardation in safety case include the geometrical structure of the pore space, mineralogical and pore water chemical conditions, and solute speciation and interactions with the pore walls. FUNMIG has produced new information on all these areas.

Many of these properties and conditions are site specific and should be determined in each case separately but the FUNMIG results, which include improvement of overall understanding and development of methods, provide support for site specific studies. Results of theoretical studies and developed up-scaling methods are helpful in safety analysis calculations.

Sorption on matrix pore surfaces and fracture walls and infill (R4)

Radionuclide speciation and adsorption on granite are the main factors affecting retardation during advective transport. The advective transport times themselves are usually too short to cause decisive decay of important radioactive nuclides. Other processes contribute significantly to the retardation. An especially important one is the already discussed matrix diffusion combined with sorption on pore surfaces. In the Final Report of the RETROCK project sorption was described in the following way:

"Sorption is a general term describing a number of different processes that attach dissolved species to mineral surfaces. Examples of processes are ion-exchange, physical adsorption and surface complexation. Sorption is generally considered as a reversible process, but may also be partly irreversible, especially in the case of surface complexation. Sorption can also act as the first step to form a solid solution leading to precipitation (see Section 4.3.3 in RETROCK 2005).

Sorption of aqueous species on solids has been described according to different models. The first group of models are empirical, where the partitioning of solute in solution and adsorbed solute is described by coefficients derived from experiments. Another group of models aims at representing the mechanism of sorption reactions with a thermodynamic formulation (Thermodynamic Sorption Models, TSM), e.g. surface complexation models and ion-exchange models.

In most performance assessment models radionuclide sorption is described as linear equilibrium sorption (the K_d model). The constant K_d model is based on considerable simplifications of the sorption processes. For example, it is assumed that the number of sorption sites is very large with no competition between species for a particular site, both solutes in solution and sorbed species behave ideally and there is only one species of a given solute in solution.

The sorption coefficients or K_d values are empirically derived for conditions as similar as possible to the conditions prevailing at the site. However, using a lumped parameter such as a K_d value means that variations in water chemistry cannot be directly taken into account.

Alternative empirical models are the Freundlich and the Langmuir isotherms. The Freundlich isotherm allows for non-linear sorption while the Langmuir isotherm also allows for a limited amount of sorption sites. However, these empirical models do not take into account competition effects with other solutes and are thus only valid for specific water chemistry."

The multitude of chemically different radionuclides and prevailing chemical conditions in bedrock calls for a quite extensive set of studies. In the IP FUNMIG a large variety of studies on sorption has been accomplished. The outcome supports well the safety cases both in generic and also in specific way. Even if sorption is very important as such, the exact values of parameters are not very critical for safety considerations. The reason is that in most cases the sorption is strong enough and safety can be shown to be achieved with much lower K_d values than normally measured in experiments. This means that generic information and understanding on sorption processes and confidence that sorption exists can be very useful for safety cases. The IP FUNMIG has produced a substantial amount of information on sorption to both clay and bedrock minerals for many nuclides and thus strongly supports the handling of retardation in crystalline rock. It is important to note that clay minerals occur frequently in rock fractures. As a special task a sorption data base has been produced within WP 6.3.

The quantification of radionuclide 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 2009) and that, moreover, additional information, such as porosity distribution and diffusion data can be obtained.

Main FUNMIG achievements from matrix diffusion and sorption studies

A significant contribution within FUNMIG was to improve the knowledge basis on sorption and diffusion processes in the rock matrix. A multi-method approach involving various visualisation techniques was adopted for characterising the porosity and mineral distribution at μm -cm scales (Lähdemeki et al. 2007, Kelokaski et al. 2005). The effects of the deduced physical and chemical heterogeneities were analysed for their relevance on averaged parameters used for PA.

An important prevailing uncertainty is the radionuclides 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. 2009) (see Fig. 5-1). 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 analysed 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 analysed with the Rutherford backscattering spectrometry and auto radiographic methods (Siitari-Kauppi et al. 2007).



Fig. 5-1: 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. 2009).

5.2.5 Colloid-related processes (R6)

Research on colloid related subjects is going on in several research institutes and universities producing more information on colloids in general. From the point of view of safety case the IP FUNMIG started from what was concluded in the RETROCK project referred to, below:

"Colloids could be important for geosphere transport, but there is only limited and controversial evidence that long-distance colloid transport occurs. This comes from grossly disturbed systems such as nuclear weapons test sites and liquid waste injection sites. Although there is a reasonable understanding of how colloids form, there is only limited conceptual understanding of their stability and transport mechanisms. Due to the paucity of basic information, development of mechanistic models is difficult.

PA uses data on colloid populations in undisturbed groundwater systems within sensitivity analyses to draw inferences on their transport relevance. Clearly, there is a continuing requirement for better field data on colloid populations in relevant systems and for evidence of their mobility or immobility (e.g. from experimental studies in underground research facilities and natural analogues). In addition, more research would be useful to understand the interaction between radionuclides and different types of colloids, as well as the nature, characteristics and transport properties of colloids in different environments. In future PAs, further development of the modelling framework for quantification and sensitivity analysis of colloid transport will be beneficial. One issue that should be explored is the potential impact of future changes in groundwater chemistry favouring colloid formation or stability."

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 2006a). 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.

Transport of radionuclides attached to colloids or large organic molecules, thus decreasing retardation, has been the subject in many tasks of the IP FUNMIG. The interactions of radionuclides with colloids and colloid formation and their stability have been studied. Radionuclide interactions with minerals occurring in fractures or in rock matrix have been studied in the presence of different organic compounds. The consequences of these various processes have been also analysed by model calculations. The outcome from the whole set of tasks grouped into this Super-FEP support safety cases by helping to scope and limit the effects of possible processes that may enhance radionuclide transport.

Main FUNMIG achievements from colloid studies

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). Furthermore, 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 radionuclide transport was evaluated with a sensitivity analysis with aid of newly derived data from FUNMIG. 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).

6 Salt host rocks

6.1 Salt specific FEPs and their link to FUNMIG work packages

The safety concept for a repository in a rock salt formation differs from those for clay-rich and crystalline host rocks. For a repository in a rock salt formation the near field includes the engineered barrier system and at least parts of the host rock. The overburden above a salt dome is referred to as the far field which is considered as additional barrier. The work within FUNMIG is focussed on the far field only where various aspects of radionuclide migration processes were assessed. The properties of the far field of a waste repository in rock salt formations are in most cases site-specific depending on the type of rocks in the overburden of the salt dome. The overburden of the Gorleben salt dome e.g. consists of quaternary and tertiary sandy and argillaceous sediments.

Specific processes of interest are investigated in RTDC 5 of FUNMIG at the natural analogue site Ruprechtov in the Czech Republic. This site which has been fairly well geologically characterised displays properties similar to the overburden of the Gorleben salt dome. However, the same types of sediments are also found in the covering rocks of repositories in clay or granite formations. Most of the work conducted in RTDC 5 refers to the overburden and not the salt host rock and therefore it is also of interest for the other host rocks studied within FUNMIG.

A salt specific FEP list was developed in a German national research project (Buhmann et al. 2008). The FEP list includes about 170 FEPs of which most are related to the repository system and the host rock. Only 21 of the FEPs are related to the far field. This subset of FEPs is shown in Tab. 6-1. Since the salt specific FEP list was developed in the German language, the original German titles are given for better identification along with an English translation. The work performed in FUNMIG is mapped against this FEP list and the FUNMIG work packages which are related to a specific FEP are shown in the last column of Tab. 6-1. It can be seen that the work in FUNMIG is related to not more than six FEPs. A rating of the availability of the current PA relevant knowledge for all far field related FEPs is given in the third column of the table.

The evaluations were made based on the results obtained in RTDCs 1, 2 and 5. The host rock independent RTDCs 1 and 2 studied well established processes (e.g. speciation, ion exchange or solid solutions) and less established processes (e.g. migration of colloids or humic substances). The Task Evaluation Table for salt host rocks (Tab. C-3) is found in Appendix C.

Tab. 6-1: Salt specific FEP list for the far field (Buhmann et al. 2008).

FEP No.	FEP Title Original German FEP title (<i>English translation</i>)	Availability of PA relevant knowledge	FUNMIG WP No.
1.2.10.1	Einfluss geologischer Veränderungen auf die Hydrogeologie (<i>Impact of geological changes on hydrogeology</i>)	Limited Detailed impact uncertain Site specific	
1.3.7.1	Hydrogeologische Veränderungen aufgrund Klimawandels (<i>Hydrogeological changes due to climatic change</i>)	Limited Detailed impact uncertain Site specific	
2.2.3.1	Deck- und Nebengebirge (<i>Overburden</i>)	Good Site specific	
2.2.5.1	Geosphäre: Eigenschaften der Transportpfade (<i>Geosphere: Characteristics of the transport pathways</i>)	Good for current situation Limited for future situation Site specific	
2.2.7.3	Geosphäre: Grundwasserströmung (<i>Geosphere: groundwater flow</i>)	Good for current situation Limited for future situation Site specific	
2.2.8.1	Hydrochemische Verhältnisse im Deck- und Nebengebirge (<i>Hydrochemical conditions in the overburden</i>)	Good for current situation Limited for future situation Site specific	
2.2.9.1	Mikrobielle Prozesse in der Geosphäre (<i>Microbial processes in the geosphere</i>)	Limited Site specific	2.4, 5.3
2.2.10.4	Temperaturänderung am Salzspiegel (<i>Temperature changes at the top of salt dome</i>)	Good	
2.3.3.1	Aquifere (<i>Aquifers</i>)	Good for current situation Limited for future situation Site specific	
3.2.2.1	Chemische Speziation (<i>Chemical speciation</i>)	Fair to good, depending on the element	1.1, 1.2, 1.3, 5.2, 5.3
3.2.3.1	Sorption, Desorption (<i>Sorption, desorption</i>)	Fair Empiric data good Mechanistic understanding limited Empiric data is site specific	1.1, 1.2, 1.3, 2.3, 5.2, 5.3
3.2.4.1	Kolloide (<i>Colloids</i>)	Fair Site specific	1.3, 2.1, 2.2, 5.1, 5.3
3.2.5.1	Komplexbildung (<i>Complexation</i>)	In general good, but variable depending on element and ligand	1.1, 1.3, 5.3

Tab. 6-1: (continued)

FEP No.	FEP Title Original German FEP title (<i>English translation</i>)	Availability of PA relevant knowledge	FUNMIG WP No.
3.2.7.2	Advektion (<i>Advection</i>)	Good	
3.2.7.3	Konvektion (<i>Convection</i>)	Good	
3.2.7.4	Diffusion (<i>Diffusion</i>)	Good	
3.2.7.5	Matrixdiffusion (<i>Matrix diffusion</i>)	Good	
3.2.7.6	Mechanische Dispersion (<i>Mechanical dispersion</i>)	Good	
3.2.7.7	Sonstige Transportprozesse in der flüssigen Phase (<i>Other transport processes in the liquid phase</i>)	Limited	2.4
3.2.9.1	Radionuklidtransport in der Gasphase (<i>Radionuclide transport in the gas phase</i>)	Fair	

6.2 Discussion on a Super-FEP level and key questions

The normal evolution scenario of a repository in a rock salt formation is characterised by the closing of all voids and a high compaction of the crushed salt backfill in the waste repository due to the convergence of the salt formation. These two processes result in a complete sealing of the wastes in the salt. In contrast to the clay-rich and crystalline host rocks, a release of radionuclides to the far field is not expected for the normal evolution of a repository in rock salt formations. Therefore, the far-field processes listed in Tab. 6-1 are of no relevance for the normal evolution scenario. The far field is only regarded for those altered evolution scenarios of the waste repository which lead to a release of radionuclides to the far field. Potential altered evolution scenarios are e.g. the early intrusion of brines through a failed shaft seal.

Since the probability of occurrence of an altered evolution scenario itself is already low, the relevance of all FEPs listed in Tab. 6-1 could also be referred to as being low in respect of the whole safety assessment of a repository in rock salt formations. Therefore the definition of so called Super-FEPs as it has been used for the clay and crystalline host rocks might be misleading with regard to their overall importance for the repository system. There are five FEPs for which major research efforts have been performed within FUNMIG. One FEP is related to transport processes, while the other four are related to other processes. The two processes speciation and complexation are closely related and may be grouped together, leaving the following four topics as subject of research in FUNMIG:

1. Sorption, desorption
2. Chemical speciation and complexation
3. Colloids
4. Microbial processes in the geosphere

These four FEPs are discussed in the following with regard to their relevance for PA, the additional knowledge achieved within FUNMIG and the remaining open issues.

6.2.1 Sorption, desorption

Sorption of radionuclides leads to a retardation of the transport and due to radioactive decay during the time of retardation also to a decrease in the radionuclide fluxes. Sorption and desorption are considered as important for the radionuclide transport in the overburden of a repository in salt and both have been accounted for in the integrated performance assessment calculations for repositories in salt in Germany so far in terms of linear sorption according to the K_d model and a large database of site-specific K_d values exists.

FUNMIG contributed to an increase of knowledge in sorption mechanisms of some PA relevant systems like for actinides on smectite, showing the occurrence of inner sphere complexes (e.g. Schlegel 2008, Rabung et al. 2006). The derivation of additional data for thermodynamic sorption models and the application/evaluation of the use of electrostatic/non-electrostatic models on several systems increased the confidence in the use of the models. Therewith they contribute to the confirmation/support of K_d values used in the performance assessment.

For some specific elements like selenium and iodine the site specific data base has to be improved. In general, the process level models like surface complexation models have to be further developed both to reproduce the K_d values measured in laboratory experiments and to estimate the uncertainty ranges of the K_d values. Furthermore these models are intended be used in transport programmes to investigate the impact of temporal and spatial changes in geochemical conditions caused by climate changes on the sorption properties of selected radionuclides.

6.2.2 Chemical speciation and complexation

Chemical speciation and complexation both determine the chemical form in which radionuclides occur in the overburden. They affect the interactions of radionuclides with other substances and consequently also transport and retardation processes. Speciation and complexation are considered important considerations for radionuclide transport in the overburden of a repository in salt and have been accounted for in the integrated performance assessment calculations for repositories in salt in Germany. So far this has been done by selecting model parameters for modelling the transport processes that are appropriate for the expected speciation state of a radionuclide.

For some specific systems useful new thermodynamic data has been produced, such as Th(IV) complexation with silicate and phosphate (Ekberg et al. 2008) or existing data have been improved, e.g. actinide-carbonate complexation (Vercouter et al. 2005a). This information will be integrated in the development of the new German thermodynamic database THEREDA. Results from the NA study at Ruprechtov on the speciation of U(IV) and solubility controlling uranium (IV) mineral phases, increases confidence in existing data for uranium. Here, the use of new methods like μ -XRF (Noseck et al. 2008a) strongly improved the understanding of speciation in the solid phase of the natural system.

A new consistent German thermodynamic database for use in the near and far field is currently under development. Furthermore the speciation of dose relevant elements will be re-evaluated, e.g. the redox state of selenium under PA relevant conditions, will be matter of a future investigation.

6.2.3 Colloids

Colloids found in the groundwaters in the overburden can adsorb radionuclides and therefore affect their transport behaviour. Depending on the transport behaviour of the colloids this influence can result in an acceleration or retardation of the radionuclides. The importance of colloids is depending on their presence and mobility at the considered site. For the Gorleben site in Germany colloids are considered as potentially important for the radionuclide transport since high organic colloid concentrations of up to $200 \text{ mg C}\cdot\text{L}^{-1}$ have been found in groundwater in the overburden of the Gorleben site (Buckau et al. 2000). Colloids have not been accounted for so far in the integrated performance assessment calculations for repositories in salt in Germany.

FUNMIG contributed in different ways to this topic. To some extent the database was improved, e.g. for Pu(III) and Np new thermodynamic data for interactions with humic substances have been derived and for tetravalent actinides similar complexation behaviour with fulvic acids was shown (Liu et al. 2008a, Křepelová 2007, Evans et al. 2011, Kim et al. 2007, Cervinka et al. 2007, Marang et al. 2008, Reiller et al. 2008, Pashalidis & Buckau 2007). Results from field scale transport studies on the kinetics/irreversibility of radionuclide-colloid interactions in ternary systems increased understanding and modelling, which are of relevance for the conditions at Gorleben site. One additional contribution from FUNMIG, which is not directly applicable in the safety case, is the improvement and successful testing of methods for in situ colloid detection.

A comprehensive evaluation of all available data and information relevant for the colloid-facilitated transport in the overburden and its application to performance assessment is still outstanding.

6.2.4 Microbial processes in the geosphere

Dependent on the groundwater conditions different microorganisms are found in the groundwaters in the overburden. The microorganisms can interact in different ways with radionuclides and sediments and therefore alter radionuclide transport. A number of investigations on the processes biosorption, bioaccumulation and biotransformation have been performed in the past. However, the availability of knowledge on the influence of microorganisms on radionuclide transport is still quite limited and the relevance of these processes for performance assessment currently cannot satisfyingly be estimated.

The work in FUNMIG contributed to some better understanding of microbial processes in biofilms and on the reduction of uranium. The importance of microbial processes in the reduction and immobilisation of uranium could also be shown in a natural system. However, there is no direct contribution of microbial investigations in FUNMIG for performance assessment.

The potential impact of microbial processes on transport and retention of radionuclides in the overburden from the viewpoint of performance assessment was not systematically evaluated in Germany so far. This will be the subject of future investigations.

6.3 Conclusions

All FEPs examined in FUNMIG are considered as important for the radionuclide transport in the overburden of a repository in salt. Sorption and desorption as well as chemical speciation and complexation have been accounted for in the integrated performance assessment calculations for repositories in salt in Germany so far and a large database of site-specific data exists. Colloids are of importance for the Gorleben site because of high colloid concentrations in the local ground water and the issue will most probably be regarded in a future Safety Case. Microbial processes have not been accounted for in any of the past safety cases for repositories in salt in Germany. Due to lack of knowledge it is also not expected that these processes will be accounted for in the near future.

7 Summary and conclusions

7.1 Summary of main achievements and remaining uncertainties for PA

The FUNMIG IP produced new knowledge, data and methods which are of relevance for the safety case. Thus, 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 radionuclide 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 Fig. 3-1). 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 transport is 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 visualisation methods applied at the μm -cm scale have led to improved understanding of mineral fabric and porosity distribution in these rocks. This is a prerequisite for more realistic modelling of radionuclide 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 radionuclide 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 radionuclide 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.

7.2 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 in spite of the fact that no initial screening procedure of the proposed research activities had been carried out. The WMO's rated the majority of the research tasks as "supporting" the safety case by improved knowledge or by improved data for PA. A fairly few number of tasks was rated as not relevant for the safety case (~ 10 %). In the case of tasks potentially relevant for clay host rocks, about 40% were judged to be "important" for the safety case. For crystalline host rocks this percentage was clearly lower (~ 10 %). This may – at least partly- be explained by (i) the more "mature" R&D programmes for crystalline rocks and (ii) the less significant role of crystalline rock as barrier compared to clay in the safety case. With regard to salt, none of the tasks was rated as important. This is because salt is considered to completely seal the waste in a normal evolution of a repository. FUNMIG only investigated processes in the far field which for the salt case is considered only as an additional barrier for altered evolution scenarios.

Further it could be shown that substantial progress was 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, such as the catalogue of FUNMIG tasks (Appendix B), 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 being 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 understanding 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.

The Integrated Project FUNMIG has made a significant contribution with regard to the first two points and corroborated the third point.

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Appendix A

List of organisations in FUNMIG

Tab. A-1: List of partners.

Waste management organisations marked in grey.

No.	Partner	Name	Country
1	FZK-INE www.fzk.de/	Forschungszentrum Karlsruhe G.m.b.H.	DE
2	AITEMIN www.aitemin.es	Asociación para el Desarrollo Industrial de los Recursos Naturales	ES
3	ANDRA www.andra.fr	Agence Nationale pour la Gestion des Déchets Radioactifs	FR
4	ARMINES www.armines.fr	Association pour la Recherche et le Développement des Méthodes et Processus Industriels	FR
5	BRGM www.brgm.fr	Bureau de Recherches Géologiques et Minières	FR
6	CEA www.cea.fr	Commissariat à l'Énergie Atomique	FR
7	CIEMAT www.ciemat.es	Centro de Investigaciones Energéticas Medioambientales y Tecnológicas	ES
8	CSIC www.csic.es	Consejo Superior de Investigaciones Científicas	ES
9	CTH www.chalmers.se	Chalmers University of Technology	SE
10	ENRESA www.enresa.es	Empresa Nacional de Residuos Radioactivos S.A.	ES
11	AMPHOS XXI www.amphos21.com	Amphos XXI Consulting S.L.	ES
12	ERM www.erm-poitiers.fr	Études-Recherches-Matériaux	FR
13	FZR www.fz-rossendorf.de	Forschungszentrum Rossendorf e.V.	DE
14	GEOPOINT	Geopoint AB	SE
15	GRS www.grs.de	Gesellschaft für Anlagen- und Reaktorsicherheit mbH	DE
16	HU www.helsinki.fi/university	University of Helsinki	FI
17	HUT www.hut.fi	Helsinki University of Technology	FI
18	IIF www.iif-leipzig.de	Institut für Interdisziplinäre Isotopenforschung	DE
19	II-CRC-HAS www.mta.hu	Hungarian Academy of Sciences	HU
20	JGUM www.uni-mainz.de/	Johannes Gutenberg Universität Mainz	DE

Tab. A-1: (continued)

No.	Partner	Name	Country
21	KTH www.kth.se	Royal Institute of Technology	SE
22	KU www.ku.dk	Københavns Universitet	DK
23	KULEUVEN www.kuleuven.ac.be	Katholieke Universiteit Leuven	BE
24	NAGRA www.nagra.ch	Nationale Genossenschaft für die Lagerung radioaktiver Abfälle	CH
25	NILPRP http://alpha2.infim.ro	National Institute for Laser, Plasma and Radiation Physics	RO
26	NIRAS www.nirond.be	Nationale Instelling voor Radioactief afval en verrijkte splijtstoffen	BE
27	NIREX www.nirex.co.uk	United Kingdom Nirex Limited	UK
28	NRI-REZ www.nri.cz	Nuclear Research Institute Rez plc	CZ
29	NRIRR www.osski.hu	National Center of Public Health, National Research Institute for Radiobiology and Radiohygiene	HU
30	OVIUNI www.uniovi.es/	Universidad de Oviedo	ES
31	POSIVA www.posiva.fi	Posiva Oy	FI
32	PSI www.psi.ch	Paul Scherrer Institut	CH
33	SAS-IIC www.sav.sk	Slovak Academy of Sciences	SK
34	SCK·CEN www.sckcen.be	Studiencentrum voor Kernenergie·Centre d'Étude Nucléaire	BE
35	SKB www.skb.se	Svensk Kärnbränslehantering AB	SE
36	TUM-RCM www.tum.de	Technische Universität München	DE
37	UDC www.udc.es	Universidad de La Coruña	ES
38	UNIBERN www.unibe.ch/	Universität Bern	CH
39	UNICYPRUS www.ucy.ac.cy	University of Cyprus	CY
40	UNILOUGH lboro.ac.uk	Loughborough University	UK

Tab. A-1: (continued)

No.	Partner	Name	Country
41	UNIMANCH www.manchester.ac.uk	The Victoria University of Manchester	UK
42	UNIUTRECH www.uu.nl	Universiteit Utrecht	NL
43	UPC www.upc.edu	Universitat Politècnica de Catalunya	ES
44	UPPC www.uni-potsdam.de/	University of Potsdam	DE
45	UPV www.upv.es	Universidad Politécnica de Valencia	ES
46	VTT www.vtt.fi	Technical Research Centre of Finland	FI
47	WU visit	Wageningen University	NL
48	UJF www.floralis.fr	UJF-Filiale	FR
49	LPEC www.univ-lemans.fr	Laboratoire de Physique de l'Etat Condensé de l'Université du Maine	FR
50	LMM	Laboratoire de Matériaux Minéraux	FR
51	AIED	Alpine Institute of Environmental Dynamics	FR

Tab. A-2: List of associated groups.

Associated groups were organisations participating in FUNMIG at their own cost.

No.	Partner	Name	Country
1	STUK www.stuk.fi	Radiation and Nuclear Safety Authority	FI
2	IRSN www.irsn.fr	Institut de Radioprotection et de Sûreté Nucléaire	FR
3	GRS www.grs.de	Gesellschaft für Anlagen- und Reaktorsicherheit	DE
4	SNSA www.sigov.si	Slovenian Nuclear Safety Administration	SI
5	HSK www.hsk.psi.ch	Swiss Federal Nuclear Safety Inspectorate	CH
6	RPII www.rpii.ie	Radiological Protection Institute of Ireland	IE
7	SKI www.ski.se	Swedish Nuclear Power Inspectorate	SE
8	CONTERRA AB	Conterra AB	SE
9	UNIZAR www.unizar.es	Universidad de Zaragoza	ES
10	GSI www.gsi.ie	Geological Survey of Ireland	IE
11	USC www.usc.es	Universidade de Santiago de Compostela	ES
12	KHNP www.khnp.co.kr	Korea Hydro & Nuclear Power Co. Ltd	KR
13	TERRALOGICA AB	Terralogica AB	SE
14	CTU www.cvut.cz	Czech Technical University	CZ
15	CNCAN www.cncan.ro	National Commission of Nuclear Activities Control	RO
16	OEKO www.oeko.de	Öko-Institut eV – Institut für angewandte Ökologie	DE
17	LAIEM www.sciences.univ-nantes.fr	Laboratoire d'Analyse Isotopique et Electrochimique de Métabolismes	FR
18	3D TERRA		CA
19	UMR-CNRS http://ic2mp.labo.univ-poitiers.fr/index.php/equipes/	Laboratoire Synthèse et réactivité des substances naturelles, Poitiers University	FR
20	LEI www.lei.lt	Lithuanian Energy Institute	LT

Tab. A-2: (continued)

No.	Partner	Name	Country
21	MSU www.msu.ru	Moscow State University	RU
22	ARAO www.arao.si	Agency for Radioactive Waste Management	SI
23	PURAM www.rhk.hu	Public Agency for Radioactive Waste Management	HU
24	CEREGE www.cerege.fr	Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement	FR
25	GI-BAS w.w.w.geology.bas.bg	Geological Institute of Bulgarian Academy of Sciences	BG
26	HYDRASA http://ic2mp.labo.univ-poitiers.fr/index.php/equipes/	HydrASA, Laboratoire d'Hydrogéologie, Argiles, Sols, Altérations, Poitiers University	FR
27	RAWRA www.rawra.cz	Radioactive Waste Repository Authority	CZ
28	BGR www.bgr.de	Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)	DE
29	KAERI www.kaeri.re.kr	Korea Advanced Institute of Science and Technology	KR

Appendix B

Task abstract forms

Task abstract forms

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1.1.1a Ionic species/speciation

<p>Aim: The objective was to determine the thermodynamic parameters related to the formation of the sulphate complexes $\text{UO}_2(\text{SO}_4)_i^{2-2i}$ ($i = 1 - 3$), and confirm the stability of the third complex $\text{UO}_2(\text{SO}_4)_3^{4-}$.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CEA (N°6).</p>
<p>State of the art before FUNMIG: Many data on the speciation of U(VI) in sulphate solutions are available at 20 – 25° C, and were already reviewed in the NEA/OECD database (Guillaumont et al. 2003). However, the influence of the temperature on complexation was only investigated in a few calorimetric studies in which possible bias in the interpretations of the raw data have been pointed out in the present investigation (Vercouter et al. 2008).</p>
<p>Main results (abstract): The speciation of U(VI) was studied in acidic sulphate solutions in the temperature range 10 – 80° C by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The interpretation of the fluorescence measurements at 20° C is in good agreement with the formation constants ($\log_{10} K^\circ$) for $\text{UO}_2\text{SO}_4(\text{aq})$ and $\text{UO}_2(\text{SO}_4)_2^{2-}$ from the literature, and particularly with the values selected by the NEA (Guillaumont et al. 2003). The thermodynamic parameters, $\Delta_r G$, $\Delta_r H$, and $\Delta_r S$, were determined from the Van't Hoff equation. The value of $\Delta_r H$ for the formation of $\text{UO}_2\text{SO}_4(\text{aq})$ is significantly higher than that recommended by the NEA, while the other values either confirm or complete the database.</p> <p>The measurements at high sulphate concentrations indicate that the complex $\text{UO}_2(\text{SO}_4)_3^{4-}$ forms, and indeed dominates the speciation. Its formation constant has been determined at 3 M ionic strength. Extrapolation to zero ionic strength with the SIT formula (based on estimated parameters) provides a value which agrees fairly well with the selection by the NEA based on a single study.</p> <p>The thermodynamic data and the spectroscopic observations were discussed regarding the coordination of the sulphate ligands in the U(VI) complexes.</p> <p>This work is fully described in a publication (Vercouter et al. 2008).</p>
<p>Achievements for the safety case: In oxidative conditions, the influence of sulphate might be taken into account for their complexing properties toward U(VI) (and other radionuclides). The complex formation is even strengthened by increase of temperature.</p>
<p>References: Guillaumont et al. (2003), Vercouter et al. (2008).</p>

1.1.1b Comparison between TRLFS and ESI-MS results in the case of the Eu(III)/U(VI)-SO₄ systems

<p>Aim: Determination of thermodynamic data by TRLFS for the Eu(III)/U(VI)-SO₄ systems, and validation of the use of ESI-MS for quantitative analysis of species concentrations and for mixed complexes detection.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CEA (N°6).</p>
<p>State of the art before FUNMIG: The formation of sulphate complexes of Eu(III) and U(VI) have already been investigated by different techniques, and provided thermodynamic data. Under particular conditions, especially near neutral pH, other complexes with sulphate can be expected to form. Then, a technique such as ESI-MS may be useful for the determination of stoichiometries.</p>
<p>Main results (abstract): This work has been focused on a representative trivalent ion, Eu³⁺, and on UO₂²⁺ in aqueous solutions. The stoichiometries and formation constants of sulphate complexes were determined by both time-resolved laser-induced fluorescence spectroscopy (TRLFS) and electrospray ionisation mass spectrometry (ESI-MS). Thermodynamic data for sulphate complexes of Eu(III) and U(VI) have been successfully measured by TRLFS. ESI-MS has been used for both systems in order to check the reliability of a quantitative analysis of the MS spectrograms, and its potential use for the detection of mixed complexes of U(VI) that can have a significant importance in environmental conditions. Whereas the quantitative treatment gave results in consistency with the speciation expected from the TRLFS results, the detection of mixed complexes of U(VI) by ESI-MS failed, but the strategy for such measurements can be improved.</p> <p>The results of these investigations are presented and discussed in the associated report, available at the Intranet under RTDC1, WP 1.1.</p>
<p>Achievements for the safety case: Evaluation of analytical methods for speciation analysis of radionuclides in environmental conditions.</p>

1.1.2a Ionic species/speciation

Aim: State of the art on the formation of silicate complexes of trivalent f-element cations and identify the needs of experimental work that could be done in a collaborative work between CEA and CTH. The few available studies have been reviewed for a better understanding in a thermodynamic point of view.

Type of work: Bibliographic.

Participants: CEA (N°6).

State of the art before FUNMIG: The silicate ions and derivatives such as oligomers or colloids are expected to affect the speciation of radionuclides in natural waters, and their complexing properties should therefore be well known for speciation calculations.

Main results (abstract): A survey of the data for the interactions between silicate species and Eu(III), Am(III) and Cm(III) is presented in the PID 1.1.2 report. It is concluded that the formation of monosilicic complexes of these trivalent metal ions is well known, and that the values of the corresponding equilibrium constants support a good analogy between these three elements. Colloidal particles or oligomeric species containing silicate have been observed to play an important role in the speciation of these elements, even at low Si concentrations. As a consequence, the formation of disilicic complexes of M(III) is doubtful and should be confirmed. The present task has helped to define a programme of experimental work, which is presented in another report (see PID 1.1.5), for the investigation of interactions between silicate oligomeric species and radionuclides in aqueous solutions.

Achievements for the safety case: Possible role of oligomeric and/or colloidal silicate species in the speciation (and migration) of trivalent radionuclides in groundwaters.

1.1.2b Determination of stability constants

Motivation and aim: Determination of missing key thermodynamic constants and their uncertainties for phosphate and silicate complexation in aqueous solutions with selected metals by solvent extraction.

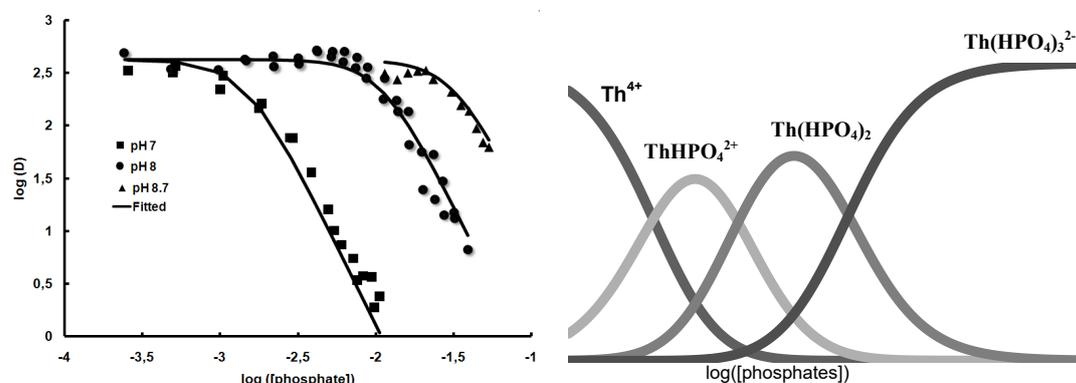
Type of work: Experimental.

Participants: CTH (#9).

State of the art before FUNMIG: Few or no previous investigations on this subject in literature with inconclusive results.

Main results (abstract): Studies of the complexation and determination of stability constants for thorium and americium with silicic acid and phosphates have been performed by liquid-liquid extraction with the AKUFVE-technique. Acetylacetone (HAa) (2,4-pentanedione) was chosen as competitive extractant for the thorium experiments and TBP (Tri-n-butyl phosphate) was used for the americium experiments. Preliminary results gives the value for the first stability constant ($\log \beta_1$) of 4.7 ± 0.1 for americium at pH 6.5 ($AmOSi(OH)_3^{2+}$) and 5.2 ± 1 for thorium ($ThOSi(OH)_3^{3+}$) at pH 7.5 and at 25 °C and $I = 1.0$. The occurring formation of polymeric species at low silicate concentration is seen to possibly influence the complexation. The thorium-silicate system have been investigated with Photon Correlation Spectroscopy in order to determine the effect these formed complexes have on the speciation under natural conditions.

For the complexation formation between Th(IV) and phosphate we have concluded that the phosphate species participating is HPO_4^{2-} . The stability constants of the 1:1, 1:2 and 1:3 complexes formed were evaluated in 1 M (Na,H)ClO₄ at 15, 25 and 35 °C and at pH 7, 8 and 8.7 with enthalpy and entropy determined with the obtained stability constants for the 1:2 and 1:3 complexes. The stability constants of the 1:1, complexes are seen as good approximations since it is difficult to determine with this method due to the problem in reaching low enough acetylacetone concentrations in the water phase so that the phosphate complexation can compete.



Left: Extraction curves for thorium phosphates (Log D vs. log [HPO₄²⁻]) at: ■ pH 7, ● pH 8, ▲ pH 8.7. *Right:* Speciation of the thorium-phosphate system at pH 8 and at 25° C with $\log \beta_{1002} = 17.0$ and $\log \beta_{1003} = 23.7$.

The outcome of this study was as expected.

Achievements for the safety case: This work contributes to providing missing key thermodynamical data for phosphate and silicate complexation that can be implemented in modeling of the migration of Th(IV) and Am(III) in groundwaters.

References: Ekberg et al. (2008).

1.1.2c Complexation constants update

<p>Aim: Determinations of thermodynamic data for relevant chemical species of Am(III), Cm(III), Eu(III) and U(VI) in the presence of carbonate and sulphate.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CEA (N°6).</p>
<p>State of the art before FUNMIG: The radionuclides (or analogue) and the ligands have been chosen according to the issues addressed by the safety assessment of geological disposals of high-level radioactive waste, and because of discrepancies between thermodynamic data as emphasised in the NEA/OECD database (Guillamont et al. 2003). Moreover, very little information was available concerning the temperature effect on the stability of the carbonate complexes.</p>
<p>Main results (abstract): From new interpretations of raw solubility data for Am(III) up to 80°C, a set of thermodynamic parameters have been determined for both complexation and dissolution reactions. The AmCO_3^+, $\text{Am}(\text{CO}_3)_2^-$, and $\text{Am}(\text{CO}_3)_3^{3-}$ stoichiometries have been confirmed, while the complexation constants and the relative stabilities of the solid compounds $\text{Am}_2(\text{CO}_3)_3(\text{s})$, $\text{AmOHCO}_3(\text{s})$ et $\text{NaAm}(\text{CO}_3)_2(\text{s})$ were significantly different from the original interpretations. The stabilities of EuCO_3^+, $\text{Eu}(\text{CO}_3)_2^-$, and $\text{Eu}(\text{CO}_3)_3^{3-}$ have been determined at 25° C by TRLFS. The limiting carbonate complex of Eu(III) was confirmed by solubility curves of $\text{NaEu}(\text{CO}_3)_2(\text{s})$ in carbonate solutions (Vercouter et al. 2005a). The temperature influence on the formation constant K_3 for $\text{Cm}(\text{CO}_3)_3^{3-}$ was also determined by TRLFS. The temperature-dependence of $\lg K_3$ compared very well with that for Am(III). The reaction enthalpy and entropy have been derived from Van't Hoff plots (Vercouter et al. 2005b).</p> <p>The EuSO_4^+ and $\text{Eu}(\text{SO}_4)_2^-$ complexes were also identified at 25° C by TRLFS (Vercouter et al. 2005c). Some preliminary results on the UO_2^{2+} complexes with sulphate at 25° C have also been obtained by TRLFS (see PID 1.1.3 for the complete study). All the results (equilibrium constants, reaction enthalpy and entropy) are summarised in the PID 1.1.1 report.</p>
<p>Achievements for the safety case: Carbonate and sulphate complexes can be major actinide species in groundwaters. Their stabilities can be assessed by using thermochemical data such as those determined in this work, particularly for temperatures higher than 25° C.</p>
<p>References: Guillamont et al. (2003), Vercouter et al. (2005a, b and c).</p>

1.2.1 Batch sorption studies on apatite and quartz

<p>Motivation and aim: Investigation of sorption behaviour of different radionuclides on natural apatite and quartz minerals under near natural conditions.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CTH (#9).</p>
<p>State of the art before FUNMIG: Sorption behaviour on quartz and some apatite minerals have been investigated previously and can be found in literature.</p>
<p>Main results (abstract): The sorption behaviour of the silicate mineral quartz and the phosphate mineral apatite is investigated via batch sorption experiments and titrations in order to provide needed information for investigations within task 2.4.1 were the effect of in situ grown biofilm on these surfaces is investigated.</p> <p>The chemical conditions for the investigation is designed to assess as far as possible the conditions present at the MICROBE site in the Äspö Hard Rock Laboratory at which biofilms where grown on mineral surfaces at in situ pressure and temperature with natural groundwater flowing over the surfaces. In this study we used a synthetic groundwater based on the actual groundwater present and all the experiments are performed in glove-box at near reducing conditions with measurements of the inside atmosphere by Gas-MS. The temperatures in the experiments are 25 °C and the pressure is atmospheric.</p> <p>The mineral material used are both the same type of real mineral slides used for the biofilm experiments in task 2.4.1 and also crushed and sieved material of those slides as well as reference apatite and quartz used in titrations. The materials have been analysed and characterised with XRD, SEM and EDX, BET and image analysis.</p> <p>The reason for using crushed mineral and reference apatite and quartz material is to better correlate the obtained results with what has previously been published in literature since sorption data for natural mineral slide type surfaces investigated at near natural repository conditions are rather poor. The comparable surface areas available for the mineral slides are rather small and the sorption behavior assessment is hard to asses by only looking at these types of surfaces for near natural systems. The results from the first experiment on the sorption on the mineral surfaces for Th(IV), Am(III) Co(II) and Cs(I) are being correlated to the ongoing studies with titrations on the crushed and reference materials.</p> <p>The experiment with Th(IV) have shown difficulties in the performed batch sorption experiments due to loss of activity in the samples because of the short half-life 24.1 d of Th-234 used in the study in combination with hydrolysis.</p>
<p>Achievements for the safety case: The investigation helps in providing needed reference data for modelling the retention capacity of silicate and phosphate minerals under near real repository conditions and the assessment of the effect of biofilm on these minerals.</p>

1.2.2 Influence of inorganic carbonate on the sorption of Ni(II), Eu(III) and U(VI) on illite and Opalinus Clay: experimental and modelling studies

Aim: The main objective of the work is to investigate, quantify and model the influence of inorganic carbonate complexation on the uptake characteristics of nickel, europium and uranyl on Na-illite and Opalinus Clay. Illite is a dominant clay mineral component of Opalinus Clay considered as a potential host rock for a high-level waste repository (Nagra 2002). Carbonate is, together with hydroxide, one of the most important inorganic ligands for radionuclide complexation in natural groundwaters.

Type of work: Sorption: Experimental and modelling.

Participants: PSI.

State of the art before FUNMIG: The influence of inorganic carbon on the sorption behaviour of fission and actinides on illite and Opalinus Clay was not modelled.

Main results (abstract): Experimental sorption edge and isotherm data for Ni(II), U(VI) and Eu(III) on Na-illite have been modelled using the two site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) model. A first estimate of the potential influence of carbonate was obtained by performing scoping calculations for the sorption of the three radionuclides on illite in simulated Opalinus Clay groundwaters compositions in the pH range 6.3 to 7.8. Sorption was calculated assuming that only metal cations and positively charged and neutral hydroxy complexes sorb. Little influence was calculated in Ni(II) systems but the effects for Eu(III) and especially U(VI) were significant.

The experimental sorption results on illite (du Puy) indicated that Ni(II) sorption is rather insensitive to the presence of inorganic carbon at levels up to 20 mM and pH values below 9. Only at very high inorganic carbon concentrations (0.1 M) was a more pronounced effect on sorption observable. On the other hand, a clear effect of the presence of inorganic carbon on Eu(III) and an even more pronounced effect on U(VI) sorption on illite was obtained in the pH range 7 to 9.

Experimental sorption isotherm data for Ni(II), Co(II), U(VI) and Eu(III) on Opalinus Clay under relevant chemical conditions have been measured and modelled using the 2SPNE SC/CE sorption model. Sorption was calculated assuming that only metal cations and positively charged and neutral hydroxy complexes sorb. A further key assumption in the model was that the sorption is only taking place on the illite fraction of the Opalinus Clay. This procedure is based on the so-called "bottom-up" approach.

The results for Ni(II) at trace concentrations indicated that the presence of Fe(II) could play a role in sorption. Inclusion of Fe(II) competition improved the predicted sorption isotherm. In the case of Co(II) the blind prediction was generally good except at the highest Co equilibrium concentrations where the model slightly underpredicted the sorption. From the modelling evidence presented for U(VI) it appeared plausible that a neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complex exists in solution which is non-sorbing. With the inclusion of this complex the U(VI) sorption on the Opalinus Clay could be modelled. The modelling of Eu(III) sorption results is planned in 4th project year. The final aim of this work is to generate a thermodynamic sorption data base to be used in performance assessment.

Achievements for the safety case: Extend the currently available thermodynamic sorption models for Ni(II), Eu(III) and U(VI) onto illite and Opalinus Clay for performance assessment purposes by including the influence of carbonate complexation on radionuclide sorption.

References: Nagra (2002).

1.2.3 Interaction of Se(VI) and Se(IV) with Na-Illite du Puy

<p>Motivation and aim: Investigate and quantitatively describe the mechanism of interaction of Se(VI) and Se(IV) with Na-Illite du Puy based on batch experiments.</p>
<p>Type of work: Experimental.</p>
<p>Participants: KULeuven.</p>
<p>State of the art before FUNMIG: The speciation and quantitative description of Se sorption in illite is unknown.</p>
<p>Main results (abstract):</p> <p>Se(VI) sorption: Sorption of selenate (1.6×10^{-6} M SeO_4^{2-}, 10 g/L Na-Illite in 0.01; 0.05; 0.1 M NaCl) was measured in the pH range 3.0 – 10.0 and was found to be negligible beyond pH 4 and low ($K_d \sim 0.50$ L/Kg) below pH 4. No modeling was undertaken.</p> <p>Se(IV) sorption: The sorption kinetics were studied for selenite (2.0×10^{-5} and 4.0×10^{-8} mol/L SeO_3^{2-}; 3 g/L Na-Illite in 0.01 mol/L NaCl buffered at pH 7) over a period of 100 days. After an initial fast (< 30 minutes) adsorption step, a constant $\text{Log } K_d \sim 1.2$ was observed up to about 7 days. Hereafter a slow linear increase in $\text{Log } K_d$ (up to $\text{Log } K_d \sim 2.5$) versus log time was observed. The nature of this long-term interaction process is still unknown.</p> <ul style="list-style-type: none"> - The sorption mechanism at short (< 7 days) equilibration times: <p>First, adsorption edges (pH range 3 to 10) were studied for 3 constant doses of Se(IV) (5.3×10^{-6}; 5.3×10^{-7}; 5.3×10^{-8} mol/L SeO_3^{2-}; 5 g/L Na-Illite in 0.01 mol/L NaCl). Sorption edges typical for anion sorption on oxides and corresponding to a ligand exchange mechanism were found.</p> <p>Second, sorption isotherms were recorded at pH 4.0 for a range of Se(IV) concentrations and ionic strengths (1.0×10^{-8} to 5.0×10^{-4} mol/L SeO_3^{2-}; 5 g/L Na-Illite in 0.01, 0.05, 0.1 mol/L NaCl). The sorption isotherms were fairly linear and independent of the electrolyte concentration, a feature which is typically observed for an innersphere sorption mechanism.</p> - The surface complexation modeling used the SPNE model of Bradbury & Baeyens (1997) to model the titration behaviour. The selenite adsorption was adequately described by the sorption of HSeO_3^- and H_2SeO_3 on two positively charged weak basic (-SwbOH_2^+) and two positively charged weak acid (-SwaOH_2^+) surface sites. - The XANES/EXAFS spectroscopy of Se(IV) on Na illite surface was studied at three pH values (3.25, 4.34 and 5.90) and proved that Se(IV) species are adsorbed. Data quality did not allow identifying the precise surface complex structure. Therefore, the proposed binding mechanism remains uncertain. - The sorption on mixtures of Illite/FeS_2 and Illite/FeS were investigated as a possible route (bottom up approach) to understand the complex host rock (Boom Clay). The presence of illite decreases the reduction kinetics of Se(IV) by FeS_2 or FeS and metastable plateau concentrations of Se in solution, corresponding to respectively the Se(0) and FeSe solubility are observed. These observations are in agreement with an independent XAS study (RTDC 2) identifying the formation of Se(0) and FeSe in presence of respectively pyrite and troilite.
<p>Achievements for the safety case: Experimental results indicate that the long term Se speciation in Boom Clay will be governed by the presence of reduced Se phases, due to interaction with reducing minerals such as e.g. pyrite.</p>
<p>References: Bruggeman (2006), Breynaert et al. (2008), Bradbury & Baeyens (1997).</p>

1.2.4a Test of a NEM with non-integer proton stoichiometry

<p>Motivation and aim: Evaluation of the capabilities of a simple non-electrostatic model allowing for non-integer proton stoichiometry in describing adsorption data. The Motivation was to further simplify existing non-electrostatic models. Simple robust models should be used in performance assessment. Current non-electrostatic models can be further simplified without loss of robustness. The aim was to test a highly simplified model, compare it with a benchmark electrostatic model and to develop general modelling tools for comprehensive data sets.</p>
<p>Type of work: Modelling of available adsorption data, when required supplement the data with new experimental data.</p>
<p>Participants: FZK-INE (J. Lützenkirchen).</p>
<p>State of the art before FUNMIG: Non-electrostatic models were used with integer proton stoichiometry. Measured proton stoichiometries are often non-integer. This typically requires use of various surface complexes to model the data with the conventional non-electrostatic models. Since the simplicity is the reason for using non-electrostatic models, it was intended here to further simplify. A comprehensive tool treating multiple data sets was not available.</p>
<p>Main results (abstract): Improvement of knowledge: The highly simplified model performs well on a restricted set of data, comparable to those data sets typically used in parameterising non-electrostatic models. For such data sets surface spectroscopic information could be included into the model (i.e. using the determined binding mechanism). The new approach was as successful as the benchmark electrostatic model in this respect for a restricted set of data for Se adsorption to goethite. If the data set was more elaborate (i.e. with more variation in solution composition and pollutant to surface ratios) the new approach did not describe the experimental data with the desired accuracy and sometimes trends could not be described.</p> <p>Methodology: The available data were analysed by a general optimisation shell coupled to a speciation code. The combination allows simultaneous inverse modelling of all available macroscopic data. Spectroscopic (mechanistic) information defines the appropriate surface complexes and remaining parameters are H⁺-stoichiometry and respective stability constants.</p> <p>The modelling tools were found to be extremely efficient in simultaneously treating an arbitrary amount of experimental data for different conditions and sources (with respect to the physicochemical conditions, but also coming from different investigators and potentially different kinds of data [this was not tested here, but should be no problem to implement]).</p> <p>Improvement of data: For the uranyl-quartz system new experimental data were obtained (1,2) in absence of CO₂. From previous studies only data in presence of CO₂ were available.</p> <p>Model calculations were carried out as planned. The combination of the two codes was found to be successful and is deemed to be an extremely useful tool for modelling extensive adsorption data sets. The outcome of the modelling exercises was as expected in that the limited data sets could be well described. For the more extensive data sets it could have been expected that the model is too simple given that the electrostatic benchmark model includes a higher number of adjustable parameters.</p>
<p>Achievements for the safety case: A parameter estimation tool for treating multiple data sets was developed and its application with a non-electrostatic model was tested, where the non-electrostatic approach was found to be inferior compared to the respective benchmark electrostatic model.</p>
<p>References: Lützenkirchen & Huber (2007).</p>

1.2.4b Batch sorption studies of Cm, Eu and Gd on various substrates

<p>Motivation and aim: Trivalent actinide and lanthanide sorption onto different aluminium oxides/hydroxides to get information on sorption mechanism and metal ion surface speciation. The selected solids are model minerals for iron oxides/hydroxides (cannot be investigated using laser fluorescence spectroscopy, TRLFS) and for clay minerals containing also aluminol surface sites.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZK-INE.</p>
<p>State of the art before FUNMIG: Some TRLFS data available for gamma alumina and sapphire single crystals, but not for gibbsite.</p>
<p>Main results (abstract): The Cm sorption study onto sapphire single crystals of different crystallographic orientations clearly show some differences in the surface speciation what can be deduced from the fluorescence peak positions and fluorescence lifetime. The (001) surface seems to be quite similar to that of gamma alumina, whereas the (110), (012), (104) and (018) show significant larger peak shifts and higher fluorescent lifetimes. The results could also be confirmed by XPS measurements. In addition also the amount of sorbed curium differs by more than one order of magnitude for the different faces.</p> <p>It also comes out from this study that the surfaces of the different aluminium oxides are not stable in contact with water and transform to the thermodynamic more stable pure aluminium hydroxides gibbsite and bayerite.</p> <p>Therefore gibbsite was synthesised and intensively characterised. The sorption study was performed with Gd to quantify the pH dependent sorption and with Cm to get information on the sorption mechanisms.</p> <p>From the TRLFS results a very similar surface speciation can be concluded compared to the sapphire single crystals without the (001) surface. Two different surface bound inner-sphere complexes can be identified together with a third species which is a coprecipitated or incorporated curium species. The formation of these species is a result of adjusting the pH from a higher mineral solubility region to a lower one. At the solubility minimum aluminum hydroxide is precipitated and either covers already adsorbed curium or forms a coprecipitate with curium still be in solution.</p> <p>When starting experiments from solubility limit and only increase or decrease pH this species will not be observed.</p> <p>In general, solubility, precipitation, phase transformation and/or surface relaxation of $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$ affect the surface properties of the minerals and therefore also the speciation of sorbed metal ions.</p>
<p>Achievements for the safety case: The bulk composition of a mineral phase does not necessarily reflect the properties of its surface when contacted with water and therefore the nature and the amount of the sorbed metal ion complex can be strongly affected.</p>
<p>References: Huittinen (2013), Huittinen et al. (2009), Rabung et al. (2006).</p>

1.2.4c Spectroscopic study of lanthanide and actinide by clay minerals

<p>Motivation and aim: This research work is motivated by the importance of actinides and their chemical surrogates, lanthanides, in the nuclear waste. These radionuclides may migrate out of the waste matrix into the bentonite barriers or clay host rocks. The research work then aims at providing a molecular basis for the sorption mechanisms of actinides and lanthanides on clay minerals such as hectorite and montmorillonite.</p>
<p>Type of work: Experimental, solution chemistry, TRLIF and polarised EXAFS spectroscopy.</p>
<p>Participants: CEA.</p>
<p>State of the art before FUNMIG: There were several studies on the retention of actinides by montmorillonite, but not using polarised EXAFS spectroscopy. The sorption mechanism of lanthanides and actinides on hectorite had not been probed. Finally, the possible oxydo-reduction of actinides and lanthanides at the surface of clay minerals was largely ignored.</p>
<p>Main results (abstract): The Eu-hectorite and Eu-montmorillonite systems were probed by TRLIF spectroscopy. For Eu-hectorite, the $^5D_0 \rightarrow ^7F_1$ transition manifests itself at interaction $pH \geq 4$, revealing an anisotropic environment for sorbed Eu. Furthermore, an observed increase in the amplitude of the $^5D_0 \rightarrow ^7F_2$ relatively to the $^5D_0 \rightarrow ^7F_1$ confirmed that Eu was binding ligands with increasing strength. The fluorescence lifetime also increased with sorption pH, suggesting substitution of hydroxyls or water ligands from the Eu coordination sphere by anhydrous oxygens. These results confirmed the formation of inner-sphere complexes for Eu sorbed on hectorite. Similarities in sorption mechanisms on montmorillonite and hectorite were established from the comparable TRLIF features observed for these two sorbent phases.</p> <p>The Y-hectorite system was probed by P-EXAFS spectroscopy to ascertain the presence of angular effects for P-EXAFS spectra of trivalent large cations retained by clay minerals. The spectral analysis confirmed that Y sorbed at $pH 6.5 - 7$ was located at the layer edges of hectorite, and surrounded by two Mg/Si shells at ~ 3.16 and ~ 3.50 Å. These data were interpreted by Y polyhedra sharing edges, and possibly corners, with Mg octahedra and Si tetrahedra. A similar study on Lu- and Nd-sorbed hectorite and montmorillonite failed to display significant angular dependence of P-EXAFS spectra.</p> <p>P-EXAFS spectra were recorded for U(VI) sorbed on hectorite and montmorillonite at near-neutral pH. No angular dependence of P-EXAFS data was observed for the montmorillonite substrate. In contrast, a clear angular dependence was observed for hectorite-sorbed U. Angular analysis confirmed that the uranyl moiety was located at the hectorite edges.</p> <p>The Ce(III)- and Ce(IV)-montmorillonite were probed to evaluate the impact of the lanthanide oxidation state on the sorption magnitude. The macroscopic data revealed a clear discrepancy, as Ce(III) was significantly adsorbed on montmorillonite (> 5 % of totCe) at $pH \geq 6$, whereas Ce(IV) was already noticeably adsorbed (30 % of totCe) at pH 4, with sorption magnitude increasing with pH. Interestingly, P-EXAFS spectroscopy revealed differences in environments of sorbed Ce(III) and Ce(IV) in line with these macroscopic observations.</p> <p>In conclusion, all of our studies on lanthanides were performed as scheduled. Rather weak angular dependence was observed for Ln-sorbed clay minerals, raising doubt as to the interest of performing similar experiments on actinides. As a test case, no angular dependence was observed for U(VI) sorbed montmorillonite. In contrast, the angular dependence observed for U(VI)-sorbed hectorite, providing a motivation to perform the last part of the study, i.e., P-EXAFS characterisation of trivalent actinide on clay minerals.</p>
<p>Achievements for the safety case: In near-neutral pH conditions, lanthanide (and, by analogy, actinide) retention on clay mineral occurs essentially by specific sorption at the layer edge, an additional mechanism of radionuclide retention.</p>
<p>References: Schlegel (2008).</p>

1.2.5 Activity coefficients of sorbed species – Benchmarking SCM and IXT2

<p>Motivation and aim: Very commonly found in clayey rocks, illite was chosen as material support for assessing eventual non-ideal behaviour of sorbed species in the framework of IXT2 – Another aim was cross-evaluation of SCM and IXT2 in the modelling of sorption properties of the same and often studied mineral, gibbsite.</p>
<p>Type of work: Batch and isotherm measurements – Titrations – Modelling.</p>
<p>Participants: CEA.</p>
<p>State of the art before FUNMIG: Recently few published theoretical proposals about sorbed species activity coefficients (SCM modelling) on mineral oxides may be found, but not yet in the modelling according to the Ion-Exchangers Thermodynamic Theory (IXT2). Besides, these two modelling options were not yet compared on the ground of their respective performance and limitation.</p>
<p>Main results (abstract):</p> <p><i>First aim:</i> Activity coefficients of sorbed species</p> <p>Potassium conditioned illite (Puy-en-Velay, France) was involved in many batch experiments measuring the distribution coefficient of monovalent (cesium), divalent (strontium) and trivalent (americium) elements in ultra-trace amount (radiotracers), varying the pH and concentration of potassium in the aqueous phase (up to 2 M in the case of Cs). The choice of potassic clay form was dictated by the need to ensure that potassium and protons are the sole ionic competitors, especially in the case of sorption onto minor surface sites presenting very high affinity for elements at trace level. This enabled to non-ambiguously analyse experimental measurements. The main conclusion is that, at least for the investigated mineral, insofar multivalent aqueous speciation and illite's sorption sites multiplicity are taken into account, the sorbed species (as defined in the framework of IXT2) behave ideally from thermodynamic point of view. This was further confirmed by measured Cs isotherms, which besides afforded clear evidence of a new kind of minor surface sites.</p> <p>In order to verify whether the conclusion may or not be extended to the case of high-concentration elements, such as alkalis and alkaline-earths i.e. major elements in natural waters, their sorption have been measured in equilibrated illite with synthetic salt brines mimicking sea and estuarine waters. Results match fairly well with predictions made by using the appropriate sorption equilibrium constants (in fact corrected selectivity coefficients) assuming that sorbed species activity coefficients ratio is constant, independently of aqueous phase ionic strength and composition. We may thus finally conclude to general ideal behaviour of sorbed species, at least on clay mineral such as illite.</p> <p><i>Second aim:</i> Benchmarking SCM and IXT2</p> <p>This aim is presently not reached. Batch sorption measurements of chloride and sodium ions on gibbsite (synthesised according to the classical protocol of Gastuche and Herbillon) in variable pH sodium chloride solutions gave very erratic results and even "negative" for many of them. Our analysis led us to put forward the hypothesis of the presence of high quantity of kinetically stable aluminium polyoxocations (keggin Al_{13}) in our material. Results obtained with another synthesised lot (obtained with another protocol) did not improve the situation.</p>
<p>Achievements for the safety case: Illite thermodynamic sorption data (IXT2 version) outcoming from this research are potentially useful for PA.</p>

1.2.6 Final report on experiments and modelling of Ni and Eu adsorption for minerals and rocks

<p>Aim: To interpret from experimental data and molecular modelling of mineral surfaces the chemical reactions governing the sorption of Ni(II) and Eu(III) on biotite and the crystalline metamorphic gneisses.</p>
<p>Type of work: Experimental and modelling</p>
<p>Participants: HU, VTT</p>
<p>State of the art before FUNMIG: Molecular modelling is a new method to be coupled with sorption modelling.</p>
<p>Main results (abstract): Studies are performed aiming at thermodynamic sorption model for nickel and europium on biotite and crystalline metamorphic rocks. As a reference material a sorption on a pegmatitic biotite was studied.</p> <p>The characterisation of biotite samples showed that the metamorphic biotites included also other exchangeable cations than potassium. Titration results for the pegmatitic biotite were possible to fit into a 1-pK surface complexation model.</p> <p>The sorption pH edges of nickel (II) and europium (III) on biotites and crushed rocks were determined in 0.05 M and 0.5 M NaClO₄ solutions under inert atmosphere.</p> <p>The sorption of nickel and europium on the two biotite types were modelled. The models that were optimised for the two ionic strengths, 0.05 M and 0.5 M, consisted of different values for the cation-exchange selectivity constants.</p> <p>The sorption modelling was supported by molecular-level calculations to obtain better optimised models and model parameters. Sorption modelling on annite and phloegopite gave insight to differences between potassium and nickel on the mineral surfaces. A spatially larger model should be used for calculations of the substitution of europium on three potassium sites.</p>
<p>Achievements for the safety case: Knowledge of sorption at molecular level and sorption models backup sorption data for safety case calculations.</p>
<p>References: Olin et al. (2009).</p>

1.2.7 Report on sorption and modeling of Th(IV) onto magnetite and ferrihydrite

Aim: Investigation of the Th(IV) sorption onto magnetite and 2-line ferrihydrite at acidic pH and modeling of the experimental data.															
Type of work: Experimental.															
Participants: UPC.															
State of the art before FUNMIG: there are no previous investigations on this subject published.															
<p>Main results (abstract): Sorption of Th(IV) onto commercial magnetite and synthetic two-line ferrihydrite has been investigated in batch experiments at 25° C in air atmosphere including the effects of pH (pH 1.5 to 3.6), ionic strength (0.1 or 0.01 M NaClO₄) and thorium concentration. The pH-dependent sorption data are sharp sigmoid profiles with pH₅₀ ~ 2.2 and ~ 2.9, for magnetite and ferrihydrite respectively. Thorium sorption was negatively affected by increasing ionic strength which suggests the formation of inner-sphere complex in both iron oxides. In addition, an evaluation of the pH-edge data (through a "log-log" plot) reveals the presence of only one Th surface sorbed species with the release of a total of two protons ions exchanged in the sorption process.</p> <p>This evidence has been corroborated by EXAFS investigations collected in Th sorption samples. The spectroscopic data analysis indicated that a corner-sharing bidentate-mononuclear inner-sphere surface complex of Th(IV) ion onto the ferrihydrite surface was formed, where the Th atom shares one O atom with each of two coordinated octahedra. A similar interpretation was achieved with the Th(IV) sorbed onto magnetite samples: Th(IV) ion most probably sorbs onto magnetite surface as bidentate-corner arrangements both onto the [FeO₆] octahedra and onto the [FeO₄] tetrahedra.</p> <p>Based on a bidentate surface complexation reaction, three different models have been tested to model the sorption edges of magnetite and ferrihydrite using the FITEQL 4.0 code. Averaged surface complexation constants obtained are:</p> <table border="1"> <thead> <tr> <th>Solid phase</th> <th>logK_{avg}^{int} (NEM)</th> <th>logK_{avg}^{int} (CCM)</th> <th>logK_{avg}^{int} (DLM)</th> </tr> </thead> <tbody> <tr> <td>magnetite</td> <td>12</td> <td>12</td> <td>12</td> </tr> <tr> <td>ferrihydrite</td> <td>8</td> <td>8</td> <td>8</td> </tr> </tbody> </table> <p>These equilibrium constants were also then tested against the equilibrium isotherm data at several starting solid-liquid ratio. Reasonable good fits indicates a self-consistent model.</p> <p>This work contributes to better understanding of Th sorbed process onto magnetite and ferrihydrite.</p>				Solid phase	logK _{avg} ^{int} (NEM)	logK _{avg} ^{int} (CCM)	logK _{avg} ^{int} (DLM)	magnetite	12	12	12	ferrihydrite	8	8	8
Solid phase	logK _{avg} ^{int} (NEM)	logK _{avg} ^{int} (CCM)	logK _{avg} ^{int} (DLM)												
magnetite	12	12	12												
ferrihydrite	8	8	8												
Outcome: As expected.															
Achievements for the safety case: The retention of thorium onto iron oxides, such as magnetite and ferrihydrite, could be taken into account in PA calculations.															
References: Seco et al. (2009), Rojo et al. (2009).															

1.2.8 Batch sorption experiments on clay minerals

Aim: Development of Sorption models for mixed clays.
Type of work: Batch Sorption experiments and geochemical modelling.
Participants: CIEMAT.
State of the art before FUNMIG: Sorption data existed for many radionuclides on separated purified clay systems. Much less data existed on mixed-clay systems.
<p>Main results (abstract): Exhaustive batch sorption experiments were performed to analyse the sorption behavior of different radionuclides (^{85}Sr, ^{239}Pu, ^{75}Se and ^{152}Eu) separately on homionised Na-smectite and Na-illite. Selectivity coefficients and complexation constants were derived on these individual systems by modelling the experimental data.</p> <p>The parameters obtained from the individual clays were successfully used to describe the sorption behaviour of Sr and Se onto mixed illite - smectite clay systems. The Pu and Eu experiments onto mixed systems are still ongoing.</p> <p>Experiments were performed in a wide range of conditions: ionic strength (from 10^{-3} to 0.2 M), pH (from 3 to 11) and radionuclide concentration (from 10^{-10} M to 10^{-3} M) to reduce the uncertainties on the obtained parameters.</p> <p>It has been demonstrated (for the Sr, Se, and Eu cases) that the knowledge of parameters obtained from the individual cases can be used to describe more complex systems.</p> <p>Moreover, in the case of Se, where surface complexation dominates over ionic exchange, it has been shown that the complexation constants are similar for both clays, and that differences in sorption can be just explained accounting for the proper sorption site density.</p> <p>The work carried out so far indicated that the proposed methodology is adequate to face the understanding of sorption in mixed clay systems.</p>
Achievements for the safety case: The thorough analyses of sorption data, based on a quasi-mechanistic description of simplified systems is the basis for the understanding of mixed clay systems.
References: Missana & García-Gutiérrez (2007), Missana et al. (2008c), Missana et al. (2008d), Missana et al. (2009).

1.2.9 Batch sorption studies of trivalent & tetravalent actinides in Boom Clay

<p>Aim: Acquire sorption datasets of tri- and tetravalent radionuclides onto Boom Clay host rock in order to set up a Thermodynamic Sorption Model (TSM) that provides confidence for the selection of radionuclide retention parameters for PA.</p>
<p>Type of work: 1. Batch sorption studies of Am(III)/Eu(III) and Th(IV), as analogues for tri- and tetravalent RN, on Boom Clay host rock and purified phases (i.e. illite, montmorillonite, kerogen) in binary (no NOM) and ternary (including NOM) systems. 2. TSM development.</p>
<p>Participants: SCK·CEN.</p>
<p>State of the art before FUNMIG: Good sorption data for tri- and tetravalent radionuclides onto Boom Clay are lacking, sorption modelling not well developed.</p>
<p>Main results (abstract): Sorption isotherms for both Am and Th onto Boom Clay (at pH ~ 8.3, anaerobic & 0.4 % CO₂) were measured in Boom Clay water to assess the influence of the dissolved organic matter present in the Boom Clay water (~ 100 ppm C). The determined LogK_d values for Am and Th are similar. The presence of dissolved OM clearly decreases the K_d values by one order of magnitude. First modelling attempts are based on montmorillonite (MoMo) and illite as model component for Boom Clay and a 3 NOM functional group model to describe the RN-NOM interaction (RN-NOM conditional interaction constants are fitted). These modellings are premature and did not provide a good description of the experimental data. A more detailed study on the influence of mobile NOM onto sorption was performed using Eu as model component for trivalent radionuclides and illite as model clay component. Sorption was investigated for different binary systems (NOM/illite, Eu/illite) and for ternary systems (Eu/NOM/illite). In absence of NOM, the measured K_d values could be explained using the 2 SPNE SC/CE surface complexation model and complexation constants reported earlier for Eu/illite interaction (Bradbury et al. 2005). In ternary systems, the Eu-NOM interactions decreased the Eu distribution coefficients by an order of magnitude. Due to the high affinity of trivalent radionuclides for natural OM, their sorption to mineral assemblages will be decreased under BC geochemical conditions. However, the overall retention may be increased because of the immobility of high molecular-weight NOM molecules under <i>in situ</i> conditions, as was verified from the distribution coefficients measured after ultrafiltration. The sorption isotherms in the ternary systems are currently being described by applying a simple additivity rule and allowing for reasonable modifications of model parameters derived from respectively the 2 SPNE SC/CE model (Eu/illite interaction) and the Tipping VI model (Eu/NOM interaction; Tipping 1998) which was successfully incorporated in the PHREEQC geochemical code. The results refined the working hypotheses concerning the retardation of tri- and tetravalent radionuclides under Boom Clay conditions. Retention is dominated by the OM pools present in the solid phase and in solution. A TSM for such mixed systems is under development, but preliminary results are already quite satisfactory. The outcome is as expected.</p>
<p>Achievements for the safety case: Site specific sorption data for Am and Th are obtained which can be used for selection of retention data for PA.</p> <p>Increased process understanding in the interaction of trivalent radionuclides with clays in presence of NOM.</p>
<p>References: Liu et al. (2008a), Liu et al. (2009), Bradbury et al. (2005), Tipping (1998).</p>

1.3.1 Batch sorption studies of Am on clay minerals in the presence of humic acids

<p>Motivation and aim: Study of the influence of humic acid on the Am(III) sorption onto kaolinite as model mineral</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZD.</p>
<p>State of the art before FUNMIG: There were no comprehensive quantitative and qualitative sorption data on the Am(III) sorption onto kaolinite in absence and presence of humic acid.</p>
<p>Main results (abstract): The influence of humic acid (HA) on the sorption of Am(III) onto kaolinite KGa-1b (Clay Minerals Society Source Clay Repository) was studied in batch experiments ($[Am(III)]_0 = 1 \times 10^{-6}$ M, $[HA]_0 = 0$ or 10 mg/L, $I = 0.01$ M NaClO₄, pH = 3 – 10, solid/solution ratio (S/L) = 1 or 4 g/L, $pCO_2 = 10^{-3.5}$ atm). Kinetic experiments were performed to evaluate the time to reach the sorption equilibrium ($[Am(III)]_0 = 1 \times 10^{-6}$ M, $I = 0.01$ M NaClO₄, pH = 5, S/L = 4 g/L, $pCO_2 = 10^{-3.5}$ atm).</p> <p>The sorption equilibrium was achieved very fast. 98 % of Am(III) is adsorbed already after half an hour and the amount of adsorbed Am(III) did not change significantly within the time.</p> <p><i>S/L = 4 g/L:</i> In absence of HA, Am(III) exhibits a very strong sorption onto kaolinite. It is almost independent of the pH value. The percentage of sorbed Am(III) amounts to 98 % at pH 3 and to almost 100 % at higher pH values. There are small changes in the Am(III) sorption in presence of HA. At pH < 5, HA enhances very slightly the sorption of Am(III). Conversely, at pH ≥ 5.5, HA slightly decreases the Am(III) sorption due to the formation of dissolved Am(III) humate complexes. Generally, the trend in the sorption behavior of Am(III) in presence of HA is consistent with the results reported in the literature for trivalent actinides. At low pH values the sorption is enhanced by the presence of HA, while at high pH values HA lowers the sorption. At pH >8.5, HA has no influence on the Am(III) sorption onto kaolinite, which reaches almost 100 % as in the binary system without HA.</p> <p><i>S/L = 1 g/L:</i> The decrease of S/L from 4 g/L to 1 g/L shows a significant impact on the Am(III) sorption onto kaolinite in the binary and ternary system. In absence of HA a sorption edge occurs at pH 6 and the influence of carbonate at higher pH values becomes evident. Furthermore, the impact of HA on the Am(III) sorption is more pronounced. Between pH 3 and 4, HA slightly enhances the Am(III) sorption onto kaolinite. Due to the formation of soluble Am(III) humate complexes, HA decreases the Am(III) sorption in the environmentally relevant pH range between pH 5 and 8. It can be concluded that HA can increase the mobility of Am(III) in the environment.</p> <p>In addition to the batch experiments, laser-induced fluorescence spectroscopy was applied to study Am(III) kaolinite surface complexes in absence and presence of HA. The fluorescence spectra of Am(III) adsorbed onto kaolinite differ from the fluorescence spectrum of Am(III) in solution. The presence of HA decreases the fluorescence intensities of Am(III) adsorbed onto kaolinite indicating varieties in the surface speciation in the studied systems.</p>
<p>Achievements for the safety case: New sorption data were obtained which indicate that humic acid may affect the Am(III) migration under environmentally relevant conditions by enhancing or lowering the Am(III) sorption in the acidic and in the environmentally relevant pH range (pH 5 – 8), respectively.</p>
<p>References: Křepelová (2007).</p>

1.3.2 Task title influence of organics on the retention of radionuclides by minerals

Motivation and aim: The objective of our study is to develop a procedure to determine the effective surface area of minerals and an advanced modelling method for ion adsorption to the mixtures of natural organic matter (NOM) and minerals. The effective surface area of minerals in the natural samples is a crucial parameter that is required in modelling ion adsorption. The presence of NOM influences ion adsorption to mineral surface. The knowledge gained from this study will give insight in the effects of NOM on ion adsorption. The outcome can be applied to improve the methodology used for the performance assessment.

Type of work: Lab and field data collection, modelling, methodology development.

Participants: WU.

State of the art before FUNMIG: The lack of a model framework that can deal with the adsorption of both inorganic ions and organic particles in a consistent manner is at present one of the major obstacles that hinder the application of advanced surface complexation models for ion adsorption to field systems. The determination of the amount of Fe-oxides in natural samples is commonly based on chemical extractions. This approach involves large uncertainties because the chemical extractions are based on indirect identification of mineral phases.

Main results (abstract):

Improvement of knowledge:

Adsorption behaviour of fulvic acids and humic acids fractions of NOM and their effects on ion adsorption.

Methodology:

New modelling methodology has been developed to describe ion adsorption to Fe-oxides in the presence of adsorbed NOM. Methodology is under development to estimate the reactive surface area of Fe-oxides in natural samples.

Compare outcome with planning and note discrepancies (above expectation or aim not fully reached or even failure): The project is not yet finished and we expect to reach the planned goals.

Achievements for the safety case: Improve prediction of ion adsorption to natural samples.

References: Weng et al. (2006a), Weng et al. (2006b), Weng et al. (2007), Hiemstra & Van Riemsdijk (2006), Rahnemaie et al. (2007a), Rahnemaie et al. (2007b), Van Riemsdijk et al. (2006).

1.3.3 Batch sorption studies of Ni, Eu, Cs, U(IV), Cd, Fe on montmorillonite, kaolinite, goethite in the presence of various organics

Aim: Quantify the influence of organics on sorption of radionuclides.
Type of work: Batch sorption studies.
Participants: Loughborough University UNILOUGH.
State of the art before FUNMIG: A few studies published on humic acid, but none on the other organics, EDTA, ISA, ACDP, Gluconate, NTA, TPPB.
<p>Main results (abstract):</p> <ul style="list-style-type: none"> • Batch sorption experiments have been completed on binary systems using all five radionuclides with all three solids (metal – surface interactions). The data have been incorporated in the FUNMIG sorption database. • Batch sorption experiments have been completed on binary systems using all organic ligands with all three solids (organic – surface interactions). Sorption was detected in measurable quantities for humic acid, ISA and picolinic acid. • Ternary system experiments have been completed on the systems involving ISA, picolinic acid and humic acid on all three minerals, i.e. where the organic showed sorption to the surfaces. The data have been incorporated in the FUNMIG sorption database. • The linear additive model (LAM) has proved an appropriate technique for modelling the behaviour of the humic acid systems with Ni and Eu. Cd, U(IV) and Fe have also been modelled this way, but the fit between prediction and data is not as good. It has not been possible to model the systems involving Cs and humic acid with the LAM. This is thought to be due to the relatively low binding strength of the Cs-HA interaction. • The ternary systems involving ISA and picolinic acid have not yet proved susceptible to modelling using the LAM.
Achievements for the safety case: Whilst the simple organics do show interactions with mineral surfaces and radionuclides, their effect on PA is likely to be considerably less than the ubiquitous humic acids in the geosphere.
References: Evans et al. (2007), Evans et al. (2011).

1.3.4 Batch sorption studies in the presence of humics

Aim: To produce a physico-chemical model of humic-radionuclide-surface ternary systems.
Type of work: Batch experiments and modelling.
Participants: Universities of Manchester and Loughborough.
State of the art before FUNMIG: Prior to FUNMIG, the binary interactions of humic acids (HA) and radionuclides (RN) had been studied and kinetic and equilibrium batch data had been determined. However, the rate constants that were applicable in RPA calculations were uncertain, and ternary system behaviour was poorly understood.
<p>Main results (abstract): In all HA/RN/mineral ternary systems studied, ternary complexes have been significant. That is, radionuclide speciation and partition between solid and solution phases can only be predicted if the formation of surface ternary complexes between the RN, HA and mineral phase are included in the calculation. Fortunately, for all systems at trace RN conc. ($< 1 \times 10^{-9}$ M), the stability/rate constants that describe the sorption of the HA itself CAN be used to predict the formation of the ternary complexes. Further, only surface complexes of the type Surf-HA-RN are significant; the other class of complex, Surf-RN-HA are not. The work has shown that equilibrium cannot be assumed, and kinetics may be important (depending upon flow rate calculation time and distance of calculation). Analysis of the results from this work has shown that the critical parameters for RN migration calculations will be:</p> <ul style="list-style-type: none"> • Dissociation rate constant of the humic/RN non-exchangeable fraction, and that for all RN studied, the most appropriate value is 10^{-7} s^{-1} (for a conservative prediction). • Rate constants for formation (k_f) and dissociation (k_d) of surface ternary complexes. For both parameters there is a continuum of values that will depend upon the HA sample and the mineral (not RN though at trace concs). k_f will depend on the surface area of the mineral ($\sigma \text{ m}^2\text{g}^{-1}$) and the fractional coverage of the mineral surface humic binding sites with sorbed humic (θ) and is expected to vary between $k_f = (1-\theta).\sigma.3 \times 10^{-7}$ and $(1-\theta).\sigma.1 \times 10^{-5} \text{ s}^{-1}$, whilst k_d (independent of σ and θ) varies between 3×10^{-7} and $1 \times 10^{-5} \text{ s}^{-1}$. The effective R_d will be given by, $R_d = k_f / k_d$ (see below). • Ambient HA concentration at site ([HA]): not because of the effect on the binary humic-RN interaction, but because θ increases with increasing [HA], and this affects k_f. Note, the effect may be predicted using the values of k_f and k_d given above. <p>We have developed a set of rules and a flow sheet that predicts for given values of [HA], flow rate and calculation time and distance whether chemical kinetics will be important and so the calculation must be made using rate equations and constants, or using the effective R_d method. We have also provided the kinetic (and hence R_d) parameters that are needed to make the calculations.</p>
Achievements for the safety case: A methodology has been developed that predicts the impact of humic colloid kinetics in field scale transport calculations, and parameters have been provided to allow the calculation of RN transport through ternary systems via either equilibrium and/or kinetic speciation.
References: Bryan et al. (2007), Farrelly et al. (2007), Abrahamsen et al. (2007).

1.3.5 Batch sorption studies of Eu, Cm on smectite in presence of organics

<p>Motivation and aim: The scientific work focused on the following four topics:</p> <ol style="list-style-type: none"> 1. Extraction of organic matter from natural argillaceous clay-rich formations (OPA), 2. Clay induced polymerisation of natural organic matter building blocks, 3. μFTIR and STXM (Scanning Transmission X-Ray Microscopy) analysis of the sedimentary organic matter (SOC) on whole rock microtomes (OPA and COx) and measurements on the reactivity of kerogen-type material under thermal stress in presence of clay. and 4. Radionuclide complexation of mobile organics, clay/organic associates and kerogen.
<p>Type of work: Experimental.</p>
<p>Participants: FZK-INE.</p>
<p>State of the art before FUNMIG: Characterisation of SOC in undisturbed whole rock samples (COx, Opa) under nanoscopic resolution has not been published. Following the maturation of organic matter building blocks polymerisation/ pyrolysis in presence of clay minerals in order to mimic a second sediment burial is a new approach.</p>
<p>Main results (abstract): Kerogen extraction from the Opalinus Clay whole rock (Mont Terri) has been conducted based on an optimised extraction protocol of Vandenbrouke and Largeau (2007). Inorganic phases are still present and sum up to 18.3 wt.% (Al, Si, Fe, S), which is clearly an improvement compared to e.g. Deniau et al. (2008) (34 – 68 wt.% S, Fe) for different kerogens. Isolated kerogen is characterised. Polymerisation of low molecular weight compounds (synthesis of kerogen containing solely the elements C, O, H and N) as natural organic matter building block under well-defined conditions and presence of swelling clay has been conducted. Pyrolysis-gas chromatography-mass spectrometric (py-GC/MS) and C1s-STXM measurements have been realised. Taking the C1s STXM measurements of the pyrolysed products the polymerised organic material found shows quite comparable organic functionality to the smectite associated organics found in the Callovo-Oxfordian formation. Clay-organic matter interactions were conducted using isolated kerogen (Toarcian) and Volclay bentonite applying confined pyrolysis which has shown its ability to reproduce thermal maturation of organic matter. Run products were characterised by XRD, TEM-EELS and STXM. Direct comparison of TEM-EELS and carbon-edge STXM data is showing an increase of oxygenated functional groups in kerogen associated with clay particles, which was proposed in models (Seewald, 2001), but is proven spectroscopically in this study. To 4) In a subset of samples on clay induced polymerisation Eu (3.2×10^{-6} mol/L, pH 6) was added before polymerisation. The ultracentrifugation results show that a minor fraction of organics is associated with the clays in the glucose/glycine (GG) system. In the GoHy573FA system a dependency with the clay exchangeable cation is observed with the highest mineral surface association in the Fe case. Ultrafiltration experiments reveal that only a minor fraction of Eu is associated with the organics (dominantly to molecules < 1 – 10 kDa range) present in the supernatant of the Ca and Fe system (0.4 – 5.1 % of Eu_{tot}), whereas in the Na system 21.9 – 33.7 % of Eu_{tot} is found in solution. In the FA-bentonite system a smectite exchangeable cation dependent size fractionation of the FA seems to occur.</p>
<p>Achievements for the safety case: New data on sedimentary organic matter (OPA, COx) spatial distribution, functionality, reactivity and radionuclide complexation is provided.</p>
<p>References: Schäfer et al. (2006a), Schäfer et al. (2009a), Schäfer et al. (2009b).</p>

1.4.1 Generation and characterisation of uranium reference minerals

<p>Motivation and aim: The identification of even minor amounts of secondary uranium phases is a necessity to develop a better understanding of the uranium chemistry and consequently its migration behavior around contaminated sites. Many of these secondary uranium phases occur as a coating on rock surfaces or in coexistence with other minerals, so that their isolation from the surrounding matrix is very difficult to achieve or even impossible. For qualitative and quantitative analysis, the non-destructive time-resolved laser-induced fluorescence spectroscopy (TRLFS) is very sensitive to uranium(VI). The fluorescence spectrum of known reference minerals can then be used as a fingerprint to determine the mineralogy of coatings of unknown uraniumiferous samples.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZD (old: FZR).</p>
<p>State of the art before FUNMIG: Spectroscopic fingerprints by TRLFS of many secondary uranium phases were missing before the start of FUNMIG. Within this working package such spectroscopic fingerprints were obtained by TRLFS for boltwoodite and compregnacite.</p>
<p>Main results (abstract): Synthetically prepared boltwoodite and compregnacite were characterised with time-resolved laser-induced fluorescence spectroscopy (TRLFS). The obtained TRLFS emission spectra of both synthesised uranium minerals differ from each other in their positions of the vibronic peak maxima and in their fluorescence lifetimes. Also, the shapes of the spectra and their respective intensities are different. The TRLFS-spectrum of boltwoodite showed well-resolved sharp vibronic peaks at 485.1, 501.5, 521.2, 543.0, 567.4, and 591.4 nm with deep notches between them and compregnacite is characterised by two broad peaks with various shoulders. Here five emission bands were identified at 500.7, 516.1, 532.4, 554.3, and 579.6 nm. The shape of the TRLFS spectra of compregnacite is typical for uranium in a hydroxide coordination environment. For both minerals two fluorescence lifetimes were extracted, each indicative for a unique coordination environment. The two species of boltwoodite and compregnacite, respectively, showed the same positions of the peak maxima showing that the coordination environments are similar, but differ in the chemistry and number of possible quenchers, e.g. water molecules and hydroxide groups. For boltwoodite fluorescence lifetimes of 382 and 2130 ns, and for compregnacite shorter ones of 202 and 914 ns, respectively, were determined.</p> <p>The presented TRLFS method is a suitable technique for identifying spectroscopically in a fingerprinting procedure unknown U(VI) phases in mixtures with other phases, in small amounts, or as thin coatings on mineral and rock surfaces. The spectroscopic signatures of the two uranyl minerals could be useful for identifying uranyl(VI) mineral species as colloids, as thin coatings on minerals or as alteration products of nuclear waste. The TRLFS data may also provide a link between the fluorescence properties of fluorescent minerals and possible unidentified adsorbed uranium(VI) mineral complexes in natural ecosystems. A comparison of the spectroscopic information, obtained for well characterised uranium minerals with unknown uranium samples can be used to obtain information on the coordination environment and structure of unknown adsorbed uranium(VI) surface species on minerals.</p>
<p>Achievements for the safety case: Very small amounts of boltwoodite and compregnacite are identifiable by TRLFS in complex geological samples. The identification of such uranium minerals contributes to a better understanding of the uranium chemistry and its migration behavior around contaminated sites.</p>
<p>References: Arnold & Baumann (2009).</p>

1.4.2a Sorption of Se(IV) on compacted clay materials

<p>Motivation and aim: The goal of the work is to provide sorption data for high solid-to-liquid ratios to assess the effect of compaction on the sorption properties of clay minerals.</p>
<p>Type of work: Improvement of knowledge.</p>
<p>Participants: Armines, Leuven University.</p>
<p>State of the art before FUNMIG: The effect of material consolidation on sorption data is unclear. It has, in some cases, no effect. In other cases, it has a positive (increase of the retention) or negative (decrease of the retention) effect.</p>
<p>Main results (abstract): Two model clay minerals have been studied: illite du puy and a synthetic Na-montmorillonite. Sorption data in the dispersed state with illite were measured by Leuven University.</p> <p>The knowledge of the porosities is a prerequisite for the determination of the sorption data, i.e. they allow the determination of the solid-to-liquid ratio to be used for the determination of the K_d values. The liquid phase, or the pore water refers to the free water, i.e. the water not bound to the material. This pore water volume (θ_p) was experimentally determined using I(-I). The pore volume, composed of the bound+free water, was determined using HTO tracer (θ_{HTO}). The porosity was defined in this work by the volume of pore water (in 10^{-3} m^3) per kilogram of dry material. $\theta_{HTO} = 0.61 \pm 0.11$ and 0.22 ± 0.04 for synthetic montmorillonite and illite, respectively. The free pore water volume θ_p was found to be equal to 0.22 (S/L = 4600 g/L) and 0.11 (S/L = 9000 g/L) for synthetic montmorillonite and illite, respectively.</p> <p>Sorption data were measured as a function of pH and Se concentration. The results obtained show that the compaction do not alter the sorption properties of clay materials for Se(IV).</p>
<p>Achievements for the safety case: Sorption data between Se(IV) and clay materials are not affected by compaction ($600 - 1300 \text{ kg/m}^3$). The results must be checked for highly compacted states.</p>
<p>References: Montavon et al. (2009a).</p>

1.4.2b Incorporation of Selenium into pyrite

<p>Motivation and aim: Selenium is a potentially dose contributing radionuclide from deep geological disposal. In reducing geochemical environments of European repositories, pyrite is omnipresent. The interaction of pyrite with selenium may consider an important retention mechanism.</p>
<p>Type of work: Model development.</p>
<p>Participants: SUBATECH.</p>
<p>State of the art before FUNMIG: While some data exists for Se(IV) interaction with pyrite no such data exist for Se(-II) This is why the work was concentrated on Se(-II).</p>
<p>Main results (abstract): Pyrite (FeS_2) is a mineral phase often present as inclusions in temperate soils. Moreover, it turns out to be a sorption sink for certain radionuclides in deep geological disposals. The present study was thus initiated to determine the capacity of pyrite to immobilise selenide ($\text{Se}(-\text{II})$). Due to the fact that pyrite surface oxidises readily, potentials were applied in order to minimise its surface evolution, and ensure the reducing conditions necessary for stabilising $\text{Se}(-\text{II})$. The sorption experiments were carried out in NaCl electrolyte and were amperometrically controlled. After only several minutes of reaction, at least 97 % of $\text{Se}(-\text{II})$ initially present in solution was disappeared. The K_d values vary from 7 – 65 L/g and the isotherm curve shows site saturation at higher initial selenide concentrations and no pH-dependence. By means of several spectroscopic techniques, the reaction mechanism was investigated. The XRD and in situ XANES results indicate the presence of $\text{Se}(0)$ on pyrite surface, which explain the rapid disappearance of Se observed in the sorption experiments. Moreover, XPS results obtained from Se-reacted pyrite particles reveal cleavage of S-S bonding which resulted in formation of S^{2-} on pyrite surface. Thus, we conclude that $\text{Se}(-\text{II})$ can be immobilised by pyrite via surface redox reaction: $\equiv \text{FeS}_2 + \text{HSe}^- \equiv \text{FeS} + \text{Se}(0) + \text{HS}^-$</p>
<p>Achievements for the safety case: A full Se retention model for reducing repository near- and far field environments does not yet exist, but the clarification of the interaction of $\text{Se}(-\text{II})$ with pyrite is an important cornerstone for the creation of such a model. It is particularly important that both the interaction of $\text{Se}(-\text{II})$ and of $\text{Se}(\text{IV})$ (literature data) lead to the formation of $\text{Se}(0)$.</p>
<p>References: Liu (2007), Liu et al. (2008b).</p>

1.4.3 Uptake of Np(V) and U(VI) by calcite

<p>Aim: Obtain a molecular level process understanding of sorption including structural incorporation and adsorption. Demonstrate whether NpO_2^+ becomes structurally incorporated into the calcite structure upon coprecipitation, quantify partition coefficients, and derive a thermodynamic description of solid solution formation.</p>
<p>Type of work: Experimental.</p>
<p>Participants: INE-FZK.</p>
<p>State of the art before FUNMIG: There were no published results on that subject before FUNMIG.</p>
<p>Main results (abstract): NpO_2^+ and UO_2^{2+} doped calcite has been synthesised in a mixed flow reactor. NpO_2^+ samples were analysed by EXAFS spectroscopy, XRD, Raman spectroscopy, NIR spectroscopy, and polarisation dependent EXAFS spectroscopy. UO_2^{2+} doped calcite was analysed by EXAFS spectroscopy.</p> <p>The linear NpO_2^+ ion becomes structurally incorporated into calcite upon coprecipitation. In the calcite structure it seems to substitute one calcium and two carbonate ions. In the equatorial plane it is hence coordinated by four monodentate bound carbonate groups. It keeps its axial oxygen atoms. It has a much higher affinity for calcite than UO_2^{2+}, which is upon coprecipitation, incorporated onto a strongly distorted site which is not compatible to the calcite structure. The higher affinity of NpO_2^+ for calcite is also displayed in an about two orders of magnitude higher partition coefficient compared to UO_2^{2+}.</p> <p>It is possible to formally describe the experimental results on the uptake of NpO_2^+ by calcite as a simple regular solid solution between calcite and a hypothetical $\text{Ca}_{0.5}\text{NpO}_2(\text{CO}_3)$ endmember ($\log_{10} K_{\text{SP}} \approx -13$) with one Guggenheim parameter, $a_0 \approx 2$, but available structural information indicates that the substitution scheme is more complex than a regular or subregular solid solution. Further process understanding is needed to test the model assumptions.</p> <p>NpO_2^+ adsorption to calcite has been studied. The reaction products were characterised by EXAFS spectroscopy. NpO_2^+ is likely to adsorb to the calcite surface as an inner-sphere complex. Adsorption isotherms show a "Freundlich" like behaviour. Adsorption is pH dependent with maximal adsorption at pH 8.3.</p>
<p>Achievements for the safety case: Formation of a solid solution with calcite can lead to effective entrapment of NpO_2^+ in calcite particles.</p>
<p>References: Heberling et al. (2008a), Heberling et al. (2008b).</p>

1.4.5 Theoretical expression of thermodynamics of solid solutions (co-precipitation)

Motivation and aim: Co-precipitation is an important natural retardation phenomenon for the migration of radio-nuclides and other toxics. Well established and accepted scientific descriptions are needed to take advantage of such a retardation phenomenon for typically performance assessment. While Thermodynamics of such equilibria is well known, various modelling approaches are used: it needs clarification. The aim is to recall scientific bases to facilitate comparisons of the various interpretations used to account for co-precipitation.

Type of work: Recalling Thermodynamics of Mixtures, which provides scientific bases for modelling and interpreting ideal Solid Solutions and associated co-precipitation and ion exchange equilibria.

Participants: CEA.

State of the art before FUNMIG: Co-precipitation has typically been used to identify radioactive isotopes. Co-precipitation can also lower solubility. For this reason it is also important for geochemistry, waste management and (de)pollution studies. Two terms – Solid Solution or Mixture – reflect two different thermodynamic approaches. Thermodynamic equations are widely used for calculating aqueous speciation, including the aqueous solubilities controlled by pure compounds, while it is often a bit confusing for aqueous solubilities controlled by solid solutions, despite the basic Thermodynamics equations for Solid Mixtures and Solutions are well known and implemented in computer codes. As an example of the complexity for modelling co-precipitation, one can cite a recent compilation published by AEN-TDB.

Main results (abstract): We essentially provided a mathematical demonstration of equations based only on Thermodynamics for describing Solid Solution in Appendix of the final report (Vitorge 2008), and gave the resulting working equations in the course of the FUNMIG Project (Vitorge 2008). We also indicated some consequences of the equations to finally point out their qualitative chemical meanings that confirm similar discussion by typically Lipmann or Michard. Several features are pointed out:

- (i) no new equation neither thermodynamics parameter is needed for such modelling,
- (ii) however, the single solubility product of a pure compound is replaced by a set of equations, one corresponds to formation/dissolution of the matrix, the other one(s) account for ionic exchange(s) on the matrix,
- (iii) the set of equations can be rearranged into well known classical formula,
- (iv) Mole Fractions are not intensive variables, hence not concentration units,
- (v) vacancies need to be taken into account,
- (vi) any ionic exchange equilibrium can be considered as deriving from a solid solution,
- (vii) where –conversely the precipitation/dissolution equilibrium of the matrix is obtained by mathematical integration.

Achievements for the safety case: Modelling solubilities provides Thermodynamics bases for validating predictions of the retention of radionuclides here by not-pure solids.

References: Vitorge (2008).

2.1.1 Inorganic colloid formation and radionuclide interaction

<p>Aim: Radionuclide hydroxy-aluminosilicates (HAS) interaction: sorption, co-precipitation and/or incorporation.</p>
<p>Type of work: Batch type laboratory experiments.</p>
<p>Participants: TUM-RCM, FZK-INE.</p>
<p>State of the art before FUNMIG: Speciation of radionuclide colloidal actinide migration is a well known but until today not predictable fact, due to poor knowledge of the underlying mechanisms on a molecular scale.</p>
<p>Main results (abstract): The study comprises four parts: Optimum conditions for the formation of HAS pseudocolloids of actinides are derived from a broad parameter screening experiments (pH 4 – 9; [Si], [Al], [radionuclide]) based on radiometric tracing of the actinides between three phases differentiated by sequential filtrations: solution (< 1.5 nm), colloids (1.5 – 450 nm) and precipitate (> 450 nm). The radionuclide chemical binding state associated to HAS colloids is analysed by time-resolved laser fluorescence spectroscopy (TRLFS), extended X-ray absorption fine structure spectroscopy (EXAFS) and ligand displacement method (EDTA). Increasing pH, increasing actinide concentration and/or co-nucleation elements (Si, Al) and long reaction times increase the interaction of radionuclides with HAS colloids. The second part concerns the actinide humate colloids interaction. Actinides and [¹⁴C]-labelled humic acid are simultaneously traced and it could be shown that at pH 6 radionuclide speciation is dominated by humic acid complexation. The third part of the study analyses the behavior of actinides in systems where competition between two ligands takes place, namely silicic and humic acid, for the complexation of Al and actinides in the neutral pH region (6.6 – 7.8). 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. In the fourth part the contact between the engineered barrier (Febex bentonite) and granite host rock (Grimsel) was simulated in a batch-type study and the formation of colloids investigate by laser-induced breakdown detection (LIBD), 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 = 0.015 M). LIBD analysis revealed a low concentration of colloids to be stable (~ 100 ppt, diameter ~ 30 nm) after 70 days at FPW admixture > 10 %. 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 polysilicic acid colloids.</p>
<p>Achievements for the safety case: Am(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 > 0.015 M in the absence of humic substances.</p>
<p>References: Kim et al. (2005), Kim et al. (2007), Panak et al. (2005), Kunze et al. (2008).</p>

2.1.2 Backfill-derived clay colloid stability in far-field groundwaters of crystalline host rocks

Aim: Investigations on conceptual understanding of colloid stability and transport mechanisms
Type of work: Batch type laboratory experiments
Participants: FZK-INE
State of the art before FUNMIG: Clay colloid stability data has been published in the literature, but data on smectite and intercomparison between different smectite types and influence of low DOC (1 – 10 mg/L) is not published. The bentonite buffer erosion can be predicted based on the conceptual model (see Liu & Neretnieks 2006), experimental proof of proposed erosion rates has not been done. Only a few publications (e.g. Geckeis et al. 2004) on radionuclide sorption reversibility on smectite colloids can be found.
Main results (abstract): Colloid stability measurements are conducted for Febex bentonite and the SWy-2 bentonite by varying ionic strength, pH and electrolyte (Na, Ca, Mg). The Febex bentonite colloid stability increases with increasing pH and edge-face interactions delimit the colloid stability at low pH. Measureable colloid stability can be observed for NaCl at ionic strengths $< 0.5 \text{ mol}\cdot\text{L}^{-1}$ at $\text{pH} > 6$ and for CaCl_2 as well as MgCl_2 for ionic strength $< 0.003 \text{ mol}\cdot\text{L}^{-1}$ at $\text{pH} > 6$ in accordance with the Schulz-Hardy-Rule. The Febex bentonite being of hydrothermal origin having impurities of amorphous silica shows a considerable higher stability in the pH range 7 – 9 compared to SWy-2 smectite. Addition of amorphous SiO_2 to SWy-2 bentonite shows the same colloid stability increase possibly explaining the observed discrepancies. Low dissolved organic carbon concentrations (DOC, here fulvic acid GoHy-573) significantly increase the colloid stability especially in the pH range < 7 . Bentonite erosion experiments ($2.0 \text{ g}/\text{cm}^3$ dry density) show production of colloids in contact with different waters (Na-, Ca-solutions and Grimsel groundwater). Maximum initial erosion rates ($t = 120$ days) were determined for Grimsel groundwater and 10mM NaHCO_3 solution to be $5.5 - 8.2 \times 10^{-7} \text{ mg}/\text{cm}^2/\text{sec}$ which leads to a maximum initial bentonite buffer mass loss of $\sim 50 \text{ mg}/\text{year}$. Batch-type studies on the ternary system Febex bentonite colloids; radionuclides and fracture filling material (FFM) from the Grimsel granodiorite were performed. The added radionuclide concentrations were $3.0 \times 10^{-8} \text{ mol}/\text{L}$ Np(V), $1.5 \times 10^{-9} \text{ mol}/\text{L}$ Am(III) and $7.7 \times 10^{-11} \text{ mol}/\text{L}$ Pu(III). Analysis of Al 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 in line with Geckeis et al. (2004) for short contact times ($t < 14 \text{ d}$). Np data shows increasing retardation values with time and FFM surface area indicating a $\text{Np(V)} \Rightarrow \text{Np(IV)}$ reduction and preferential FFM association. Both observations made above suggests a desorption of initially bentonite colloid associated Pu and Am.
Achievements for the safety case: Smectite colloid stability as a function of pH, ionic strength and cation composition; bentonite buffer erosion rates and radionuclide smectite reversibility kinetics were determined.
References: Liu & Neretnieks (2006), Geckeis et al. (2004), Seher et al. (2007), Schäfer et al. (2006b).

2.1.3 Colloid stability in far-field groundwaters of crystalline host rocks

<p>Motivation and aim: Studies on the formation, behaviour and stability of real colloids and pseudocolloids of actinides under reduced groundwater conditions. The work was focused on uranium(IV). The objective was to provide new information on U(IV) mobility.</p>
<p>Type of work: Experimental</p>
<p>Participants: FZD</p>
<p>State of the art before FUNMIG: The solubility of U(IV) had been studied fairly extensively in the past. However, there was still wide scatter in the data available. Very little was known about the formation of uranium colloids (real colloids and pseudocolloids) in strongly reducing waters. Such colloids might significantly influence the mobility of uranium in reduced waters.</p>
<p>Main results (abstract): Investigations into the formation of real colloids and pseudocolloids of uranium(IV) were performed. Coulometric titrations of strongly acidic U(IV) solutions in $\text{HClO}_4/\text{NaClO}_4$ medium were carried out in order to find the pH of first colloid formation. Laser-induced breakdown detection (LIBD) was applied for the detection of traces of uranium colloids as the pH was increased. The pH values at the onset of colloid formation were used for thermodynamic calculations aimed at determining the solubility products of crystalline and amorphous uranium dioxide. Solubility products of $\log K_{\text{sp}}^0 = -59.6 \pm 1.0$ for the crystalline uranium dioxide, $\text{UO}_2(\text{cr})$, and $\log K_{\text{sp}}^0 = -54.2 \pm 1.0$ for the amorphous hydrous uranium oxide, $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$, were found. Thus, new and more reliable solubility data for U(IV) were obtained which had been measured with a technique quite different from the techniques of the earlier measurements. Furthermore, the $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ colloids were investigated for their colloidal stability. Zeta potentials of ≥ 30 mV were found for pH values of less than 4. The isoelectric point was at $\text{pH} \sim 6.9$. Colloidal suspensions of 1 mMol/L $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ at a pH value of 2.5 proved to be stable over > 1.5 years. The interaction of the forming $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ colloids with other colloid-forming species was tested. Therefore, coulometric titrations of U(IV) solutions in the presence of (a) dissolved Al(III) and (b) dissolved silicate were carried out. The presence of Al(III) does not significantly influence the formation of the $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ colloids, and the presence of U(IV) does not significantly influence the behaviour of Al(III). The presence of silicate does not significantly influence the onset pH of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ colloid formation (i.e. the U(IV) solubility). However, the presence of U(IV) significantly influences the behaviour of the silicate (formation of pseudocolloids due to co-precipitation). The nature of the interaction between the silicate and the U(IV) is not yet known. It may be either adsorption or the formation of a coffinite precursor. EXAFS experiments to elucidate the local structure around the U(IV) atoms in the pseudocolloids are underway.</p>
<p>Achievements for the safety case: Improved knowledge on uranium mobility in strongly reducing environments was obtained; it refers to both the thermodynamic solubility of U(IV) and the formation of U(IV) colloids.</p>
<p>References: Opel et al. (2007).</p>

2.2.1a Radionuclide interaction with clay formation derived natural organic matter (NOM)

<p>Motivation and aim: Investigation of immobile organic matter from real site conditions (Ru-prechtov site), its behaviour and influence on U migration. Selection of appropriate extraction technique. Characterisation and U(VI) complexation of extracted humic substances.</p>			
<p>Type of work: Experimental, modelling.</p>			
<p>Participants: NRI-REZ (No. 28).</p>			
<p>State of the art before FUNMIG: only general knowledge about solid organic matter (SOM) and humic substances (HS) content in natural sediment, no verified methodology for HS extraction, only general knowledge about behaviour of U(VI) with HS.</p>			
<p>Main results (abstract): SOM on Ruprechtov site seems not to be readily available for the degradation processes. That could be confirmed by very low contents of DOC in groundwater and small amount of humic substances extracted from the sediment. Humic substances (HS), i.e. humic acid (HA) and fulvic acid (FA), were separated and purified from the clay sediment. Two different schemes were used and adjusted: MIBK method and Alkali method (dissolution and precipitation). Comparing both extraction methods with regard to HA extraction, the Alkali method showed to be 4 times more efficient than the MIBK method. In both cases, but mainly for the MIBK method, the separation and purification processes were less efficient with increasing sample weight. HA were purified till less than 5 % of ash was determined. 64 % of OM was extracted from sample NA12 (4.07 wt.% TOC), 2.38 wt.% of this OM part was formed by insoluble organic material and 0.22 wt.% was formed by humic substances (HA+FA). Humic substance fraction can be divided in to humic acid 0.15 wt.% and fulvic acid 0.073 wt.%. About 1.467 wt.% of non extracted OM was left. Effectiveness of HA separation ranges from 10 % to 20 %. Separated HA-12/3 was characterised using elementary analysis, ash content, UV-Vis spectra, FTIR spectra and acidobasic titrations. The total proton exchange capacity (PEC) was determined by back titration of excess Ba(OH)₂ to be 7.14 ± 0.66 mmol/g. Dissociation of acidic functional groups was studied by the continuous potentiometric titration procedure. Two types of carboxyl groups (K_{LS}, K_{LW}) and one type of phenolic groups (K_{LP}) were selected for determination.</p> <table border="0" style="width: 100%;"> <tr> <td style="vertical-align: top;"> <p>Protonation constants:</p> <p>$K_{LS} = 1.34 \times 10^4 \pm 4.06 \times 10^2$</p> <p>$K_{LW} = 1.36 \times 10^6 \pm 4.46 \times 10^5$</p> <p>$K_{LP} = 1.92 \times 10^9 \pm 5.18 \times 10^8$</p> </td> <td style="vertical-align: top;"> <p>Concentration of functional groups:</p> <p>carboxyl groups S = $3.61 \pm 8.41 \times 10^{-2}$ mmol/g</p> <p>carboxyl groups W = $1.60 \pm 1.387 \times 10^{-1}$ mmol/g</p> <p>phenol groups = 1.93 mmol/g</p> </td> </tr> </table> <p>U(VI) complexation (1.10^{-4} M) with HA (HA-12/3) was studied as a function of HA concentration (1 – 40 mg/l) in 0.01 M NaClO₄ at pH 6. The results were evaluated using the Charge Neutralisation 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 UO₂²⁺ and (UO₂)₃(OH)⁵⁺. The average stability constant of U(VI) humate complex was established for case A) log K_{cnm} (log β) = 4.98 ± 0.619 and for case B) log K_{cnm} (log β) = 4.58 ± 0.645. Generally, with increasing content of HA increases the complexed fraction of U and decreases LC. Determined stability constants K_{cnm} are lower than the literature values and probably indicate lower potential of HA to complex U in the system.</p>		<p>Protonation constants:</p> <p>$K_{LS} = 1.34 \times 10^4 \pm 4.06 \times 10^2$</p> <p>$K_{LW} = 1.36 \times 10^6 \pm 4.46 \times 10^5$</p> <p>$K_{LP} = 1.92 \times 10^9 \pm 5.18 \times 10^8$</p>	<p>Concentration of functional groups:</p> <p>carboxyl groups S = $3.61 \pm 8.41 \times 10^{-2}$ mmol/g</p> <p>carboxyl groups W = $1.60 \pm 1.387 \times 10^{-1}$ mmol/g</p> <p>phenol groups = 1.93 mmol/g</p>
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<p>Achievements for the safety case: OM on the Ruprechtov site does not influence speciation of uranium directly as sorbing/complexing agent, but indirectly via maintaining reducing conditions and contributing to U(IV) immobilisation in secondary phases.</p>			
<p>References: Cervinka et al. (2007).</p>			

2.2.1b Radionuclide interaction with clay formation derived natural organic matter (NOM)

<p>Motivation and aim: Investigate the interaction of Se with mobile and immobile NOM from Boom Clay, using batch experiments and spectroscopy to elucidate the interaction mechanism and reaction products.</p>
<p>Type of work: Batch type lab experiment – XANES/EXAFS speciation.</p>
<p>Participants: 23, KULeuven.</p>
<p>State of the art before FUNMIG: In batch systems containing dissolved NOM and a reducing solid (FeS₂ or Boom Clay) Se is observed to be partly associated with dissolved NOM. The reaction of Se with dissolved NOM alone is unknown, as well as the identity of the reaction products.</p>
<p>Main results (abstract): The work performed by KULeuven was focused on the interaction of Se(IV) and Se(VI) with "mobile" natural organic matter (NOM). For Boom Clay, the supernatant of a ~0.01 M NaHCO₃ BC extract, centrifuged with a cutoff of 35 nm was used as a representative sample for mobile BC NOM. For the Gorleben system, a sample of Gorleben groundwater filtered at 0.4 µm was used.</p> <p>The main conclusions from batch experiments were:</p> <ul style="list-style-type: none"> • Added Selenate, Se(VI), remains unaltered in solutions containing Boom Clay HS and Gorleben HS. • Added Selenite, Se(IV), decreases dramatically, leaving about 5 % of total Se in solution upon centrifugation after 224 days. The solution speciation proved that Se was associated with HS. However, the chemical nature (speciation) of the Se species formed could not be determined. Either metallic selenium (Se(0)) formed colloid-colloid associations with HS or Se(IV) complexed with HS or minor components (e.g. clay minerals, oxides) present in HS. The Se speciation in the pellet was unknown. • An additional study was performed in which the interaction of Se(IV) was studied in presence of purified HS extracted from Boom Clay. Compared to the previous published experiments, Selenium disappeared from solution more slowly. • Spectroscopy experiments: The working hypothesis for all previous batch experiments was that Se(IV) is reduced to Se⁰ in presence of HS and is centrifuged off in the pellet. To test this hypothesis, two types of samples containing selenium and purified Boom Clay HS (BKHS) were prepared: SeO₃²⁻ + Boom ClayHS and SeO₃²⁻ + Boom ClayHS + hydrazine. <p>XANES-EXAFS data were collected at the DUBBLE BM26A beamline at the ESRF (Grenoble, France). Reference spectra were collected for Se(IV) solution species and reduced Se solid phases such as amorphous and crystalline elemental Selenium and FeSe. The XANES spectra for all samples showed that in the supernatant exclusively selenite species were present, and confirmed that Se(0) was formed and precipitated in the pellet.</p> <ul style="list-style-type: none"> • Experiments investigating the interaction of Se(IV) with immobile NOM were performed using a similar setup as used at SCK·CEN. The Se concentration associated with each BC solid phase fraction was obtained. However the Se/C ratio could not be determined due to problems with the organic carbon measurement.
<p>Achievements for the safety case: Se(VI) is unaffected by NOM, while Se(IV) interacts with Boom Clay NOM.</p>
<p>References: Bruggeman et al. (2007).</p>

2.2.1c Radionuclide interaction with clay formation derived organic matter (NOM)

<p>Aim: Investigation of radionuclide interaction with both mobile and immobile NOM (Boom Clay NOM), aiming at a quantitative description.</p>
<p>Type of work: Batch experiments investigating the influence of OM on the solubility of Th(IV) and Eu(III) under Boom Clay conditions. Batch sorption experiments of Th(IV) and Eu(III) onto Boom Clay immobile NOM (isolated kerogen).</p>
<p>Participants: SCK·CEN.</p>
<p>State of the art before FUNMIG: Previous studies on the influence of NOM on the solubility of U(IV)/Th(IV) and Am(III) under Boom Clay conditions were not satisfactory, as no quantitative description could be given. Radionuclide interaction with kerogen was not studied yet.</p>
<p>Main results (abstract): The influence of natural organic matter (NOM) on the speciation and solubility of europium (Eu) was studied under geochemical conditions representative for the Boom Clay. Different organic matter types were used, and analysis was performed both after microfiltration and 30 kD ultrafiltration to distinguish between larger colloids (assumed to be immobile) and small dissolved species. In the absence of NOM, the Eu solution concentrations after microfiltration exceeded the thermodynamic solubility of $\text{EuOHCO}_3(\text{s})$ 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. The data sets were modeled using the Nagra/PSI database (Hummel et al. 2002) for solubility, hydrolysis and inorganic aqueous complexation reactions. The Eu-NOM interaction is 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.</p> <p>A similar solubility study was performed for Th(IV) starting from crystalline $\text{ThO}_2(\text{s})$. 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 (different from previous study, in which NOM > 50 ppm C in all experimental systems). The data set for Th shows a lot of similarities with the one recorded for Eu. Humic-ion binding model VI could reproduce the results but the problem lays in the correct choice of the Th aqueous species. 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 we have indications that the pore-size cut-off for Boom Clay is ~ 300 kD.</p> <p>The sorption of Eu onto immobile NOM (BC kerogen) has been determined and was found to be very significant but modeling is not yet possible. The outcome is as expected.</p>
<p>Achievements for the safety case: The successful implementation of a thermodynamically consistent metal-humic complexation model into Phreeqc provides a tool to quantitatively describe the interaction of tri and tetravalent radionuclides with NOM. This will help in the selection of trustworthy maximum mobile concentrations relevant for PA.</p>
<p>References: Hummel et al. (2002), Tipping (1998), Liu et al. (2008a).</p>

2.2.2a Radionuclide interaction with natural organic matter (NOM)

<p>Aim: Within this task the redox behaviour of plutonium and neptunium in solutions containing humic substances (HS) is investigated and modelled by equilibrium thermodynamic. To elucidate reaction mechanism simple hydroquinones as model compounds are used beside the HS.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZK-INE.</p>
<p>State of the art before FUNMIG: It was only known that HS reveal reducing properties and can reduce plutonium to Pu(IV) and maybe to Pu(III), and Np(V) to Np(IV). The thermodynamic modelling of the redox reaction of HS has not been done so far, because of lack of reliable data like redox potential of HS. Also the role of colloids on the redox process was unknown.</p>
<p>Main results (abstract): The investigations have been focused on fulvic acid (FA). In addition various types of hydroquinones have been used as model for the reducing entities of humic substances. Here, the 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. We specifically attempt 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 for the purpose of safety analysis of nuclear waste disposal. Our Pu experiments were started with mostly Pu(VI) and small residues of pentavalent Pu (Pu(V)), to ensure colloid free start solution. The final Pu concentrations were typically $1 - 2 \times 10^{-4}$ M and about $< 10^{-8}$ M, respectively. The neptunium concentrations were typically 2×10^{-5} M of Np(V). The FA concentrations were 4 – 200 mg/L ($2.7 \times 10^{-5} - 1.7 \times 10^{-3}$ eq/L proton exchange capacity). The hydroquinone were used at various concentrations of $1 \times 10^{-4} - 3 \times 10^{-3}$ 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 all aqueous solutions containing HQ, AH2DS or FA. Pu in such solutions is converted totally to Pu(IV) within 20 days. The tetravalent 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 stabilised in presence of FA at higher pH values. 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, prediction of Np(V) reduction is in good agreement with experimental data.</p>
<p>Achievements for the safety case: Plutonium can exist in trivalent oxidation state at low concentration of $< 10^{-8}$ M. At higher plutonium concentrations colloid formation dominates and only Pu(IV) is present at pH > 3. At the end of the project thermodynamic constants are given that will update modelling of plutonium and neptunium.</p>
<p>References: Marquardt & Seibert (2006), Marquardt & Seibert (2007).</p>

2.2.2b Radionuclide interaction with natural organic matter (NOM)

<p>Motivation and aim: i) advance TRLFS methods as analytical tools for improved speciation of actinides and ii) increase/improve fundamental understanding of interaction processes between actinides (lanthanides were used as surrogates and luminescences probes!) and humic substances (HS).</p>
<p>Type of work: Experimental.</p>
<p>Participants: UPPC.</p>
<p>State of the art before FUNMIG: no previous investigations on interlanthanide energy transfer in HS.</p>
<p>Main results (abstract): The intrinsic HS fluorescence as well as the sensitised Ln³⁺ luminescence were used to describe the complex formation. Upon addition of Ln³⁺ 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 sensitised Ln³⁺ 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 sensitised luminescence intensity of the Ln³⁺ ion. In case of HA, the picture was not that clear, e.g., in some cases no sensitised luminescence signal of the Ln³⁺ could be observed at all. The different behavior 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. Time-resolved fluorescence anisotropy measurements additionally support this assumption. Upon increasing of the Ln³⁺ 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.</p> <p>In case of Tb³⁺ HS complexes the possibility of an energy transfer back from the Tb³⁺ 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.</p> <p>In order to get information on the distribution of metal ion bound to HS without a bias due to missing knowledge of HS structure, interlanthanide energy transfer between Eu³⁺ (Tb³⁺) and Nd³⁺ 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.</p>
<p>Achievements for the safety case: Improvement of spectroscopic-based speciation analysis and stressing importance of differentiation between FA and HA fractions for modelling approaches.</p>
<p>References: Kumke & Eidner (2005).</p>

2.2.2c Radionuclide interaction with natural organic matter (NOM)

<p>Aim: Study of the competition between radionuclides – Co^{2+}, UO_2^{2+}, and Eu^{3+} – and major cations – Ca^{2+} and Mg^{2+} – for humic substances complexation.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CEA, UPPC.</p>
<p>State of the art before FUNMIG: No direct evidences.</p>
<p>Main results (abstract): Using the NICA-Donnan model, providing a coherent description of the metal-humic substance complexation mechanisms, $\text{Co}^{2+}/\text{Mg}^{2+}$ 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.</p> <p>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 immobilised humic acid helped to finish the works and provide evidence of a weak competition with Mg^{2+}.</p> <p>Finally, combined potentiometric and spectroscopic experiments between Eu^{3+}, Cu^{2+}, and Ca^{2+} showed that only the metals that can compete for Eu^{3+} specific binding are the one that are not in non-specific binding, <i>i.e.</i> mainly in electrostatic binding as Ca^{2+} and Mg^{2+} in a lesser extent. It means that alkaline-earth are only merely in competition for strongly sorbing metals like actinides and lanthanides, whereas Fe^{3+} and Al^{3+} are awaited to have a stronger competitive effect.</p>
<p>Achievements for the safety case: The alkaline earth metals, Ca^{2+} and Mg^{2+}, are merely in competition with actinides and lanthanides for natural organic matter complexation: Fe^{3+}, Al^{3+}, and inter-Ln/An competition should be accounted.</p>
<p>References: Marang et al. (2006), Marang et al. (2008).</p>

2.2.2d Radionuclide interaction with natural organic matter (NOM)

<p>Motivation and aim: Determination of stability constants for the complexation of plutonium(III) with humic substances.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZD.</p>
<p>State of the art before FUNMIG: There was no comprehensive description of the plutonium(III) complexation by humic substances.</p>
<p>Main results (abstract): We are studying the complexation of plutonium(III) with humic substances and its reversibility. This is in continuation of our former study where we determined structural parameters for the near-neighbor surrounding of plutonium(III) in complexes with humic and fulvic acids at pH 1 by means of EXAFS (Schmeide et al. 2006).</p> <p>For the study of the complexation of such redox-sensitive radionuclides, synthetic humic acid model substances with distinct redox properties are applied, that were developed by Sachs et al. (2004a). These humic acid model substances were synthesised by oxidation of diphenolic compounds in the presence of amino acids in alkaline solution. The most promising synthetic humic acid (HA) with distinct redox functionality are the HA type Cat-Gly, which is an oxidation product of catechol synthesised in the presence of glycine, and the HA type Hyd-Glu, which is an oxidation product of hydroquinone synthesised in the presence of glutamic acid. The Fe(III) reducing capacities determined for HA type Cat-Gly and Hyd-Glu amount to 10.7 ± 0.2 and 14.5 ± 1.6 meq/g HA at pH 3.0 and to 33.6 ± 4.0 and 36.9 ± 0.2 meq/g HA at pH 9.2, respectively. These are significantly higher than those determined for natural Aldrich HA with 1.2 ± 0.1 and 7.2 ± 1.9 meq/g HA at pH 3.0 and 9.2, respectively. The formal redox potentials of HA type Cat-Gly and Hyd-Glu are 517 ± 12 and 565 ± 12 mV, decreasing with pH by -57 ± 12 and -64 ± 12 mV/pH, respectively (Sachs et al. 2005).</p> <p>The reduction capability of these humic acid model substances with distinct redox properties towards neptunium(V) and uranium(VI) was already studied under anaerobic conditions and compared to that of natural humic substances (Sachs et al. 2005).</p> <p>The plutonium(III) complexation study is performed in a glove box under N₂ atmosphere. Applying the specific humic acid model substances, the low oxidation state of plutonium can be stabilised. The plutonium species are monitored by UV-Vis spectroscopy and liquid-liquid extraction. However, due to experimental problems with the dissolution of a hardly soluble plutonium oxide for preparing the plutonium stock solution, the experiments have been delayed and are not finished up to know. We will finalise our experiments in the next months. After that, we will revise our report and final results will be presented.</p>
<p>Achievements for the safety case: The stability constants for the complexation of plutonium(III) with humic substances obtained within this study will improve the basic process understanding and contribute to the enhancement of the existing thermodynamic data base.</p>
<p>References: Schmeide et al. (2006), Sachs et al. (2004a), Sachs et al. (2005).</p>

2.2.2e Radionuclide interaction with natural organic matter (NOM)

<p>Aim: Development of new relativistic quantum-chemical methods for interpretation of NMR spectra of lanthanide complexes with humic acids and model ligands.</p>
<p>Type of work: combined, theoretical & experimental.</p>
<p>Participants: SAS-IIC.</p>
<p>State of the art before FUNMIG: There were no relativistic quantum-chemical calculations of NMR spectra of these compounds published.</p>
<p>Main results (abstract): 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. 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, we switched our efforts to model complexes. The study of model compounds let us to get a better insight into the accuracy of theoretical methods for lanthanide complexes. Experimental work was devoted to ^1H and ^{13}C paramagnetic NMR chemical shifts (D_2O, 25°C, $\text{pH} = 5.5$) in lanthanide $\text{Ln}(\text{SSA})_3^{3-}$ complexes ($\text{Ln} = \text{Dy, Ho, Er, Tm, Yb}$), where SSA = 5-sulfosalicylic acid.</p> <p>The lanthanide induced shifts (LIS), as obtained in PNMR study, were surprisingly small (up to 8 ppm on ^1H and 59 ppm on ^{13}C for Dy complexes). That made the major goal of the whole study – to extract the information about complexation of lanthanides/actinides with humic acids from NMR spectra with the help of quantum-chemical calculations more problematic.</p> <p>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 uni-dentate coordination was preferable). Based on those data one can conclude that fast exchange of ligand-coordinated water can also occur. Further experimental studies with the enriched ^{17}O and ^{13}C nuclei of carboxylate groups of the salicylic and humic acids are desirable but lie outside of our capacity. 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 we 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 INE-FZK. The obtained by our group experimental NMR data were in excellent accord with our calculated predictions.</p>
<p>Achievements for the safety case: Quantum-chemical predictions of paramagnetic NMR spectra of Gd with a model ligand (salicylic acid) in water solution were performed. The results of these calculations demonstrate that complexes formed via carboxyl group with mono-dentate coordination are preferable but fast exchange of ligand-coordinated water is expected.</p>
<p>References: Hrobárik et al. (2007), Komorovsky et al. (2008).</p>

2.2.2f Radionuclide interaction with natural organic matter (NOM)

Aim: Consistency of tetravalent actinide humic acid complexation.
Type of work: Review.
Participants: CEA, NRIRR, UNILOUGH.
State of the art before FUNMIG: –
Main results (abstract): The coherence of actinide(IV) complexation by humic substances (HS) is reviewed and new data are proposed. In a first attempt, the values of independent data from literature on Th(IV), U(IV), and Pu(IV) are collected, selected, and compiled. The data obtained follow the "classical" trend of increasing conditional formation "constant" with pH, led both by the increasing ionisation of HS and by the extensive hydrolysis of the tetravalent actinides. Even though a fair agreement is evident, the experimental uncertainties do not permit a full analogy between the actinides(IV) to be ascertained. In a second attempt, the experiments from which the original data are available were reinterpreted using only one hydrolysis constant set for U(IV) as an example, considering that all actinides(IV) have analogous humic complexation behaviour. Hence, the obtained evolution of conditional formation "constant" is much more coherent and the uncertainties do not permit to distinguish an actinide(IV) from one another. 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 actinides(IV) and would permit to limit and orientate the number of necessary, but difficult, experiment with redox sensitive elements like U, Np, or Pu. It also demonstrates that complexation-only mechanisms may not be sufficient to understand field observations.
Achievements for the safety case: If no competition occurs, the humic complexation of tetravalent actinides can be obtained with a rather good approximation from Th(IV).
References: Reiller et al. (2007), Reiller et al. (2008).

2.2.2g Radionuclide interaction with natural organic matter (NOM)

Motivation and aim: It is well-known that the ionic strength and pH the two main factors that effect the complexation of metals with humic substances, so we intended to determinate the effect of ionic strength on complexation of Pu(IV) with humic acid.

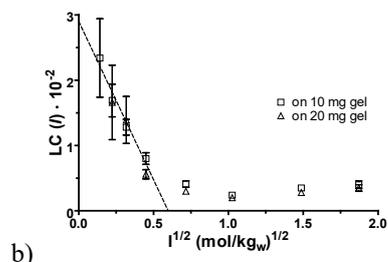
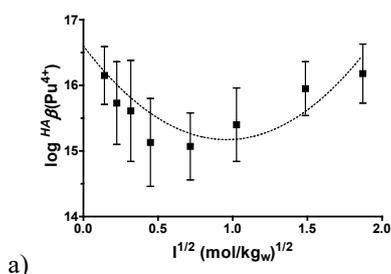
Type of work: Experimental.

Participants: NRIRR.

State of the art before FUNMIG: There is no data on this subject in literature.

Main results (abstract): The potential of SiO₂-HA as a model substrate for predicting the complexation of species such as Pu⁴⁺ by humate-coated minerals has been demonstrated. Examination of the Pu(IV) sorption isotherms at different ionic strengths (pH 4) it is apparent that conditional stability constants of Pu(IV)_{Total} ($\log^{HA}\beta(\text{Pu}_{\text{Total}})$) can be calculated. Using these values and the side reaction coefficients (α_{Pu}) the conditional stability constants $\log^{HA}\beta(\text{Pu}^{4+})$ can be calculated. Comparing the $\log^{HA}\beta(\text{Pu}^{4+})$ at different ionic strength with $\log^{HA}\beta^0(\text{Pu}^{4+})$ indicates that the effect of ionic strength on humate complexation of Pu(IV) is not dramatically pronounced but can be observed. The effect of ionic strength on maximal binding capacity (B_{max}) and loading capacity (LC) appear to be significant. The B_{max} and LC decrease gradually with increasing ionic strength. $\log^{HA}\beta(\text{Pu}^{4+})$ for zero ionic strength at pH 4 can be calculated using a non linear least square fitting procedure, which gives: $\log^{HA}\beta^0(\text{Pu}^{4+}) = 16.6 \pm 0.3$.

I	B_{max}	LC 10^{-2}	$\log^{HA}\beta(\text{Pu})_{\text{total}}$	$\log \alpha_{\text{Pu}}$	$\log^{HA}\beta(\text{Pu}^{4+})$
0.020	157.2	2.33	7.25±0.13	8.87	16.12±0.13
0.050	113.8	1.69	7.16±0.17	8.51	15.73±0.17
0.101	86.2	1.28	7.40±0.14	8.18	15.58±0.14
0.202	53.8	0.79	7.35±0.14	7.85	15.14±0.14
0.513	27.6	0.41	7.60±0.17	7.46	15.07±0.17
1.051	16.2	0.24	8.01±0.27	7.35	15.40±0.27
2.212	24.1	0.35	8.32±0.41	7.63	15.95±0.41
3.502	27.2	0.40	7.99±0.45	8.19	16.18±0.45



Hypothetical variation vs. \sqrt{I} for SiO₂-HA of: a) $\log^{HA}\beta(\text{Pu}^{4+})$, B) Loading capacity of the SiO₂-HA: □ on 10 mg gel, Δ on 20 mg gel.

Achievements for the safety case: The present work provides interaction parameter of Pu(IV) humate that varies with ionic strength. This parameter can be applied in the geochemical modeling of the migration of Pu(IV) under the influence of humic substances.

References: Szabó et al. (2008), Szabó et al. (2010), Reiller et al. (2008).

2.2.3a Radionuclide interaction with natural organic matter (NOM) in the presence of mineral phases (ternary systems)

<p>Aim: Role of the adsorptive fractionation of natural organic matter on alumina, on the interaction with radionuclides.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CEA, INE.</p>
<p>State of the art before FUNMIG: Adsorptive fractionation was evidence with different techniques, but there was no direct indication of a different chemical environment for radionuclides.</p>
<p>Main results (abstract): Adsorptive fractionation was evidenced comparing UV-Vis and Total Organic Carbon quantification of humic extracts after sorption on α-Al₂O₃; 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-Al₂O₃ surface. This was further confirmed in Scanning Transmission X-ray Microscopy 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 europium(III) in contact with previously sorbed NOM was confirmed in Time Resolved laser induced Luminescence Spectroscopy.</p> <p>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.</p>
<p>Achievements for the safety case: The humic acid like structures obtained after micro-organism mediated oxidation in sedimentary formation are not comparable to surface extracts, but the complexation properties are similar.</p>
<p>References: Claret et al. (2007), Claret et al. (2008).</p>

2.2.3b Radionuclide interaction with natural organic matter (NOM) in the presence of mineral phases (ternary systems)

<p>Motivation and aim: The role of natural organic matter (e.g. HA) is an important parameter in metal/radionuclide ion chemistry as HA is ubiquitous in natural aquatic systems and therefore knowledge of the impact of NOM on the solubility and solid phase stability of solid phases is of fundamental importance to understand the chemical behaviour and migration of metal ions in the geosphere.</p>																						
<p>Type of work: Experimental.</p>																						
<p>Participants: UNICYPRUS.</p>																						
<p>State of the art before FUNMIG: there are no previous investigations on this subject published.</p>																						
<p>Main results (abstract): The stability and solubility of $\text{UO}_2(\text{OH})_2$ and UO_2CO_3 solids has been studied as a function of the humic acid concentration in 0.1 M NaClO_4, in the pH range from 4 to 9, and 4 and 6, 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 characterised by TGA, ATR-FTIR, XRD, SEM/TEM and solubility measurements. According to the experimental data $\text{UO}_2(\text{OH})_2$ 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.</p> <table border="1" data-bbox="225 918 766 1176"> <thead> <tr> <th rowspan="2">[HA] [in mg/l]</th> <th colspan="2">Particle size [nm]</th> </tr> <tr> <th>$\text{UO}_2(\text{OH})_2$</th> <th>UO_2CO_3</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>22</td> <td>40</td> </tr> <tr> <td>0.1</td> <td>18</td> <td>10</td> </tr> <tr> <td>0.3</td> <td>12</td> <td>10</td> </tr> <tr> <td>0.5</td> <td>11</td> <td>11</td> </tr> <tr> <td>0.1 (coprecipitated)</td> <td>11</td> <td>10</td> </tr> </tbody> </table> <p>Based on the solubility data, the $\log K_{\text{sp}}$ of the solubility limiting solid phases in humic acid-free solutions has been determined to amount -22.0 ± 0.3 and -13.4 ± 0.5, for $\text{UO}_2(\text{OH})_2$ and UO_2CO_3 solids, respectively. With increasing humic acid concentration and decreasing particle size the solubility of the solid phase increases significantly because of microsolubility effects e.g. $\log K_{\text{sp}}(\text{UO}_2(\text{OH})_2) = -21.7$ in 0.3 g/l HA and $\log K_{\text{sp}}(\text{UO}_2(\text{OH})_2) < -21.7$ in 0.5 g/l HA solutions. The stability constant for the $\text{UO}_2\text{OH}(\text{HA})$ species has been evaluated to amount $\log \beta_{1101} = 15.3 \pm 0.5$ at pH 6.5.</p>			[HA] [in mg/l]	Particle size [nm]		$\text{UO}_2(\text{OH})_2$	UO_2CO_3	0	22	40	0.1	18	10	0.3	12	10	0.5	11	11	0.1 (coprecipitated)	11	10
[HA] [in mg/l]	Particle size [nm]																					
	$\text{UO}_2(\text{OH})_2$	UO_2CO_3																				
0	22	40																				
0.1	18	10																				
0.3	12	10																				
0.5	11	11																				
0.1 (coprecipitated)	11	10																				
<p>Achievements for the safety case: The presence of humic acids may affect both solid phase stability and the solution chemistry and this has to be included in PA calculations.</p>																						
<p>References: Pashalidis & Buckau (2007).</p>																						

2.3.1a Radionuclide redox transformation on minerals

<p>Motivation and aim: The aim was to find out if redox reactions on the biotite surface influence the U immobilisation by reducing adsorbed U(VI) species to U(IV) species. The studies were initiated by two XPS studies by Ilton et al. (2004). In these studies U(IV) and U(V) species were observed on the surface of the Fe²⁺ containing silicate indicating that redox processes occurred and may influence the adsorption behavior of aqueous U(VI) by reducing adsorbed U(VI) species to adsorbed U(IV) species.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZD (old: FZR).</p>
<p>State of the art before FUNMIG: It was not clear if sorptive reduction of actinides (U) on ferrous iron containing sheet silicates occur and if yes to what extent.</p>
<p>Main results (abstract): FZD studied the adsorption of uranium(VI) on the ferrous iron containing sheet silicate biotite by batch sorption experiments and time resolved laser fluorescence spectroscopy (TRLFS). All samples were in equilibrium with atmospheric CO₂. Due to quenching effects of Fe present in the biotite lattice no utilisable TRLFS spectra could be obtained at room temperature. Only in some instances a weak signal for uranium(VI) was found with fluorescence emissions bands for the four strongest lines at 498, 513, 528 and 545. To overcome these quenching effects and to improve the fluorescence intensity Kryo-TRLFS measurements with similar samples were carried out at -120° C. These Kryo-TRLFS investigations clearly showed that significant amounts of uranium(VI) species on the biotite surface had formed. The respective U(VI) fluorescence emission bands were shifted by approximately 10 to 15 nm for the first two peaks to lower wavelengths, compared to U(VI) surface species commonly found on silicate minerals. This shift may indicate the presence of ternary uranium carbonate species, since the positions of the respective fluorescence emission bands at 478.9, 498.5, 519.7, and 541.6 is comparable to the aqueous uranium carbonate species (UO₂)₂(OH)₃CO₃⁻ and UO₂(CO₃)₃⁴⁻ published by Wang et al. (2004) with emissions bands at 479.9, 499.1, 519.8, and 541.4 for the first aqueous carbonate species and 481.6, 501.3, 522.0, and 544.5 for the second aqueous uranium(VI) carbonate species. The fluorescence of such ternary uranium(VI) carbonate surface species is quenched at room temperature, however not at -120° C. To find out if redox reaction influences the adsorption behavior of uranium(VI) respective samples were excited with an excitation wavelength of 245 nm. This wavelength specifically excites U(IV) and triggers a characteristic U(IV) fluorescence spectrum. To trace U(IV) on the biotite surface TRLFS at room temperature was applied using an excitation wavelength of 245 nm. However, with this analytical system it was not possible to detect any characteristic U(IV) fluorescence on the biotite surfaces, indicating that such redox reactions, i.e. U(VI) is reduced to U(IV) and simultaneously Fe(III) is oxidised to Fe(II), does not occur or take place to an insignificant extent. However, currently we can not rule out the possibility of minor amounts of U(IV) forming on the biotite surface, since the sensitivity of our U(IV) TRLFS measuring device is not fully established and, in particular, the question concerning the possible quenching effects caused by the presence of iron is not answered yet. Such quenching effects might suppress any emitted U(IV) fluorescence. In conclusion it can be stated that the uranium reduction during the uranium adsorption seems to play an insignificant role in the immobilisation behaviour of aqueous U(VI). However, the sensitivity of the method and in addition possible quenching effects caused by the presence of Fe impede a final statement to this topic. Kryo-TRLFS measurements revealed that adsorbed ternary uranyl carbonate species play a role in removing aqueous U(VI) from solution.</p>
<p>Achievements for the safety case: It can be stated that U reduction during the U adsorption process on the Fe²⁺ containing silicate minerals, biotite (typical for granitic host rocks) seems to play an insignificant role in the immobilisation behaviour of aqueous U(VI).</p>
<p>References: Ilton et al. (2004), Wang et al. (2014).</p>

2.3.1b Radionuclide redox transformation on minerals

<p>Motivation and aim: This study aimed at investigating the uptake of U(VI) on Fe(II) minerals in granite in presence of carbonate at near-neutral pH conditions. Pairs of structurally related minerals, containing and free-of structural Fe(II) were used to test the importance of reduction.</p>
<p>Type of work: Experiments using batch and flow through reactors, and spectroscopic investigations.</p>
<p>Participants: KTH and FZK-INE.</p>
<p>State of the art before FUNMIG: The reduction of U on Fe(II) minerals had been proposed and observed in the scientific literature. However, little was known about the extent at near-neutral pH conditions, particularly in presence of carbonate in the aqueous solution.</p>
<p>Main results (abstract): Results of batch experiments using biotite/phlogopite, magnetite/ hematite and pyrite/galena showed that reduction of U(VI) at surface of Fe(II)containing minerals (silicates, oxides and sulphides) at near-neutral pH conditions can not be excluded, but that reoxidation may occur and lead to release of the uranium again. After such treatment, EXAFS results indicated U(VI)-carbonato complexes to dominate the surface accumulation of uranium. The experiments furthermore showed all six minerals to considerably remove U(VI) from solution, thereby potentially immobilising uranium in granitic environments. The removal of U(VI) from the aqueous solution was confirmed to be strongly pH and concentration dependent.</p> <p>Ferrous iron sorbed to corundum as well as structural Fe(II) in magnetite was shown to be able to reduce U(VI). If reoxidation was prevented, XPS showed presence of both U(VI) and U(IV) at the corundum and magnetite surfaces. The presence of carbonate in the aqueous solution had complex effects on the uranium being removed from the aqueous solution; on the one hand, for the surface accumulated uranium, oxidation state +IV seemed to be favoured. On the other hand, uranium to a greater extent remained in the aqueous solution.</p> <p>Flow-through experiments using magnetite and hematite showed sorption to take place over time scales of more than weeks. They also showed that uranium accumulation in the solid phase was dominantly reversible, with change in carbonate or pH conditions leading to release of uranium into the aqueous phase. These experiments showed the potential of studying radionuclide-mineral surface interactions using flow-through reactors, in terms of assessing reaction kinetics and reversibility. However, they also highlighted difficulties in keeping experimental conditions constant and connected interpretative challenges.</p>
<p>Achievements for the safety case: Experimental results have shown reduction of U(VI) on Fe(II) minerals to potentially be important for the immobilisation of uranium in granitic environments at near-neutral pH and in presence of carbonate.</p>
<p>References: Regenspurg et al. (2006), Regenspurg et al. (2007a), Regenspurg et al. 2007b).</p>

2.3.1c Radionuclide redox transformation on minerals

Motivation and aim: Investigation and quantification nonlinear sorption processes: Retention of redox sensitive actinides onto pristine and altered granite.

Type of work: Experimental.

Participants: FZK-INE.

State of the art before FUNMIG: In PA, sorption of radionuclides was treated by means of sorption isotherms which means that by flushing of a sufficient amount of groundwater, the whole amount of radionuclides is mobile.

Main results (abstract): Sorption experiments with redox sensitive actinide elements such as Pu, Np and U as well as the fission product Tc are performed onto fracture filling material, which are obtained from Äspö Hard Rock Laboratory. Migration experiments using these elements showed a complex retention pattern along the flow path. For this reason a new SEM/EDX analysis technique was applied for identification retaining mineral phases. From previous investigations, it is known that Np(V) is retained by reduction to Np(IV) in the presence of Fe(II) minerals. Sorption of U is also strongly correlated with the occurrence of Fe oxide phases. The retention mechanism onto Fe(II) phases is evaluated for Np but is not yet confirmed for U and Tc. These tracer concentrations were too low along the flow path. Additionally, the internal surface areas of the fracture play a dominating role for retaining the redox sensitive radionuclides.

Even if the K_d approach will be used in PA, this work reduces uncertainty by showing the retention mechanism for Np and Tc.

The study was successful.

Achievements for the safety case: The retention of Np(V) occurs by redox transformation to Np(IV) forming a low soluble solid at iron phases in the granite.

References: Kienzler et al. (2004), Kienzler et al. (2009).

2.3.2a Radionuclide redox transformation on minerals

<p>Motivation and aim: Investigate the role of Fe(II) bearing minerals on the retention of Se in reducing conditions (reaction mechanism- formed Se species).</p>
<p>Type of work: Batch type lab experiment – XANES/EXAFS speciation.</p>
<p>Participants: KULeuven.</p>
<p>State of the art before FUNMIG: Selenate, Se (VI), is not reduced in presence of FeS₂. Selenite, Se(IV), is assumed to be controlled by a sorption-reduction process onto FeS₂. The identity of the reaction products is unknown.</p>
<p>Main results (abstract):</p> <p>The interaction of Se(IV) with FeS₂ was studied versus time in two types of batch experiments.</p> <p>In the first type, the FeS₂ was used with no further purification. SEM analysis showed that these FeS₂ crystals were covered with an amorphous crust. In a second type, FeS₂ was purified before use to eliminate the presence of Fe(III) phases at the FeS₂ surface which could have a profound impact on Se(IV) sorption.</p> <p>Results from the first type of experiments showed that upon contacting several concentrations (ranging from 10⁻⁸ – 10⁻⁵ M) of ⁷⁵SeO₃²⁻ with FeS₂, a decrease of ~ 90 – 95 % in total Se solution concentration after centrifugation was noted after 1 day of equilibration. Hereafter, and up to 25 weeks of equilibration, Se solution concentrations remained constant. Solution speciation studies showed only inorganic Se(IV) anions. The distribution coefficient in these systems remained constant from 1 day to 25 weeks equilibration time (log K_D = 3.2 ± 0.2).</p> <p>Results from experiments with purified FeS₂ also showed a decrease of > 95% in the supernatant total Se concentration after 1 day of equilibration upon contacting with several concentrations (ranging from 2 × 10⁻⁷ – 2 × 10⁻⁵ M) of ⁷⁵SeO₃²⁻. Hereafter, and up to 20 weeks of equilibration, Se solution concentrations slightly varied (log K_D = 3.5 ± 0.2). Solution speciation studies also showed only inorganic Se(IV) anions. It was concluded that no significant difference between type 1 and 2 systems could be observed.</p> <p>Thermodynamically a reduction of Se(IV) is expected in both Type 1 and Type 2 systems (pH 8.7 – 8.9; -80 mV < E_h < -160 mV). The experimental observations confirm this expectation and point to an adsorption/reduction mechanism in both system types.</p> <p>X-ray Absorption Spectroscopy (XANES-EXAFS) was used to investigate the solid phase Se speciation after short term (3 weeks) contact of selenite [Se(IV)] oxyanions with FeS₂ and FeS.</p> <p>It was found that (for both purified and non purified samples) the nature of the sulfide mineral (FeS₂ and FeS) dictates the final speciation since respectively Se(0) and FeSe were formed, meaning that the reaction mechanism is different and that these phases cannot be regarded as geochemically similar.</p>
<p>Achievements for the safety case: Proof was provided that Se⁰ and FeSe_x will be the solubility limiting phases in Boom Clay conditions.</p>
<p>References: Breynaert et al. (2008).</p>

2.3.2b Radionuclide redox transformation on minerals

<p>Aim: Investigation of radionuclide -U(VI)- sorption/sorptive reduction on pyrite/siderite in presence/absence of Boom Clay NOM.</p>
<p>Type of work: Batch type lab experiment – XANES/EXAFS speciation analysis.</p>
<p>Participants: SCK·CEN.</p>
<p>State of the art before FUNMIG: Redox transformations of U(VI) on Fe-containing minerals have been described in literature, but are highly specific to the geochemical conditions. In Tracom-II (Maes et al. 2004) and in the PhD thesis of Delécaut (2004), a preliminary study was made on the U(VI) interaction with pyrite for Boom Clay geochemical conditions, but doubts remained concerning the final, stable oxidation state of U under such conditions.</p>
<p>Main results (abstract): An experimental programme was set up to assess the speciation and solubility of U in presence of pyrite (FeS₂) and siderite (FeCO₃) under Boom Clay (BC) geochemical conditions (pH 8.3 (± 0.1); 99.6 % N₂/0.4 % CO₂ atmosphere; background electrolytes: Synthetic BC Water (SBCW, ~ 0.014 mol·l⁻¹ NaHCO₃) and Real BC Water (RBCW, containing ~ 100 ppm NOM)).</p> <p>To study U(VI) reduction on FeS₂ in absence and presence of Boom Clay NOM, samples were prepared by adding increasing concentrations of U(VI) (10⁻⁸ M – 10⁻⁴ M) to centrifuge tubes containing crushed and purified FeS₂ (~ 5.0 g/L). These samples were equilibrated with either SBCW or RBCW. Both in SBCW and RBCW electrolyte, the final U solution concentration (120 days equilibration time) follows a Freundlich-type behavior. This suggests that an adsorption-like process is responsible for the U solution concentration. The presence of NOM in solution decreases the uptake by the FeS₂ surface, possibly by blocking adsorption sites or by altering the surface charge. In solution, the association of U with NOM is low. The valence of U in solution is likely to be U(VI), although in the samples with the lowest final U concentration it might also be composed of U(IV). XANES and EXAFS measurements were performed to elucidate the U solid phase speciation in presence of FeS₂, following the experimental set-up which was presented above.</p> <p>On the solid phase, mixtures of uranium(IV) (uraninite-like structures and possibly UO₂ nanocolloids) and uranium(VI) (probably adsorbed onto Fe(III) oxide sites) were observed.</p> <p>The amount of U(IV) was the highest in systems without NOM and increased with increasing equilibration time. This points to a kinetically-driven reduction process, which seems somewhat inhibited by the presence of NOM.</p> <p>We can state that the uranium solid-liquid distribution on pyrite is governed by both reduction and sorption processes.</p> <p>XANES-EXAFS measurements on U(VI)-FeCO₃ systems showed no reduction of U(VI).</p> <p>The outcome of the experiments is as expected.</p>
<p>Achievements for the safety case: Confidence building with respect to the U speciation in the Boom Clay far field: dominant U speciation for Boom Clay conditions is the tetravalent state.</p>
<p>References: Bruggeman & Maes (2009), Maes et al. (2004), Delécaut (2004).</p>

2.3.3 Radionuclide redox transformation on minerals

Aim: Investigations of radionuclide sorption/sorptive reduction on green rust (GR).
Type of work: Batch-type lab experiments and ultra-high resolution microscopy and spectroscopy.
Participants: KU.
State of the art before FUNMIG: The role of green rust (GR) in ground water systems under possible repository conditions was poorly understood. There were many holes in understanding of GR structure, composition and reactivity. Its occurrence had not yet been documented in ground water.
Main results (abstract): The composition and structure of green rust (GR) sulphate are now known. One investigation proved it also contains monovalent cations: $\text{NaFe(II)}_6\text{Fe(III)}_3(\text{OH})_{18}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ (Christiansen et al. 2009 a). The free energy of formation (ΔG_f) has now been established as $-6366 \text{ kJ/mol} \pm 18 \text{ kJ/mol}$ (using USGS database, 1995). We developed a sampling technique that could prevent oxidation of GR and succeeded in proving its present in the fracture water from the Äspö Hard Rock lab at a depth of 500 m (Christiansen et al. 2009b) as well as from an artesian well from sedimentary rocks on Bornholm, south of Äspö. GR forms colloids that aggregate and attach to fracture minerals, suggesting that some are not readily transportable, but the relative proportion has not yet been quantified. The small particles can act as a transport vector for groundwater contaminants. The reduction and uptake of selenite and neptunyl by green rust was investigated. In both cases they were reduced. Selenite ended as metallic selenium colloids (Behrends et al. 2006) and neptunium was reduced to Np(IV) and incorporated into the GR. When the green rust was oxidised completely to goethite (FeOOH), 75 % of the Np remained in the Fe(III) phase. Studies of naturally formed Fe oxides in Äspö boreholes demonstrated that oxygen can penetrate at least 120 m below ground surface in the granitic fractures.
Achievements for the safety case: Green rust (Fe(II),(III)-hydroxide) has been documented in groundwaters when little or no oxygen is present. Composition and structure for the sulphate, sodium phase are now known and thermodynamic constants are available. This is important for PA because GR has not been included in safety assessment modelling but it is highly reactive, especially in the presence of redox active species. Green rust forms colloidal particles that could be mobile in the near or far field, thus acting as vectors for contaminant transport. More work needs to be done to establish the relative proportion of GR colloids that stick to fracture walls and that move in the groundwater. Natural concentrations are too low for conventional particle methods, but nano-scale techniques are very effective.
References: Christiansen et al. (2009a), Christiansen et al. (2009b), Behrends et al. (2006).

2.4.1a Radionuclide mobility influenced by biofilms

<p>Motivation and aim: Investigate the time dependent sorption and desorption of select radionuclides onto in situ grown biofilms and assess the effect of microbiologically generated ligands on sorption.</p>
<p>Type of work: Experimental.</p>
<p>Participants: CTH.</p>
<p>State of the art before FUNMIG: No previous investigations on this subject in literature.</p>
<p>Main results (abstract):</p> <p>Investigations of microbiologically mediated retention capacity in the geosphere by sorption studies of $^{234}\text{Th(IV)}$, $^{241}\text{Am(III)}$, $^{60}\text{Co(II)}$ and $^{134}\text{Cs(I)}$ onto mineral slides of apatite and quartz have been performed.</p> <p>The mineral slides have been characterised using XRD and ESEM/EDX and the mineral compositions showed to be quite homogenous.</p> <p>The experiments are divided into two sets of mineral slides; one with biofilm in situ grown on the slides placed inside a high-pressure flow-cell at the Microbe site at 450 m in the Äspö Hard Rock Laboratory (30 bar, 17 °C, 30 mL/week, 10 weeks); one without biofilm. The attained biofilms on the mineral slides contain about 1×10^6 microbes/cm².</p> <p>The sorption experiments are performed in sterile 50 mL polypropylene tubes. The mineral slides were gently transferred from the flow cell to the tubes inside a glove-box with an N₂/H₂ (97/3 %) atmosphere and a copper catalyst to reduce oxygen. The radionuclides used are $^{234}\text{Th(IV)}$, $^{241}\text{Am(III)}$, $^{60}\text{Co(II)}$ and $^{134}\text{Cs(I)}$. Afterwards 50 mL of synthetic groundwater and stock solutions were added to each tube and the pH was adjusted to approximately 7 in all samples. 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 analysed by autoradiography. The microbes in the synthetic groundwater in the batch sorption experiments have been looked at by fluorescence microscopy. Isotherm titrations of ground and sieved mineral slides have been performed. Changes in the synthetic groundwater and possible dissolution of minerals during the batch sorption experiments as well as titration experiments have been investigated by ICP/OES.</p> <p>From our investigation we can see that the presence of biofilm on the mineral slides have an effect on the sorption. The magnitude of the effect is also dependent on the radionuclide investigated. Additional sorption experiments on mineral slides, crushed and sieved minerals have been performed and are under evaluation.</p> <p>The thorium containing series is difficult to assess, as the half-life is 24 d and in addition, activity is lost due to hydroxide formation. Results however, suggest negligible or un-detectable desorption.</p>
<p>Achievements for the safety case: The results indicate that the effect of biofilms in most cases is not vividly distinct but can be observed but the effect of different oxidation states and radionuclides on the sorption capacity appears to be significant and should be considered.</p>

2.4.1b Radionuclide mobility influenced by biofilms

<p>Motivation and aim: For the determination of the structural components, e.g. exopolymeric substances (EPS) within biofilms and their influence on the actinide speciation and immobilisation of actinides (U) we used stable multi species biofilms which were cultivated under air atmosphere to achieve nearly ecological biofilms and ecologically relevant U concentrations (1×10^{-5} M and 1×10^{-6} M). In order to achieve information about the U speciation in these biofilms we used a combined laser fluorescence spectroscopy (LFS) and confocal laser scanning microscopy approach (CLSM). Redox processes within biofilms were determined by microprofiles of electrochemical oxygen microsensors with tip diameters of 10 μm.</p>
<p>Type of work: Experimental.</p>
<p>Participants: FZD (old: FZR).</p>
<p>State of the art before FUNMIG: Before starting FUNMIG, no investigations were known concerning the determination of pH, Eh, and dissolved oxygen in multi species biofilms which were contaminated by actinides (uranium).</p>
<p>Main results (abstract): The influence of microbes on the mobility and immobilisation of radionuclides in surface and subsurface environments lacked a profound understanding. In our studies we were able to get information about the effect of microbes on the immobilisation of actinides (U) within biofilms by using a combination of different methods. First, laser fluorescence spectroscopy was used to identify in situ and in a non-invasive fashion the U speciation within the biofilms. A fluorescence signal in the wavelength range of 415 – 475 nm was indicative for metastable U(V) and a fluorescence signal in the range of 480 – 560 nm was identified as U(VI), clearly showing that redox processes take place within the biofilms. These findings show the different influence of distinct microorganisms on the U migration and for the first time in vivo by a combined LFS and CLSM approach that within a multispecies biofilm some of the U(VI) was reduced to metastable U(V) by an one-electron transfer. For the determination of the redox processes taking place within the biofilms numerous oxygen concentration profiles versus biofilm depths were measured in different multi species biofilms by electrochemical oxygen microsensors. For the first time it became obviously that the addition of uranium (VI) in ecologically relevant concentrations (10^{-5} M and 10^{-6} M) to stable multispecies biofilms has induced a fast decrease of the oxygen concentration with increasing biofilm depth, which is dependent on the uranium concentration. The results indicate that the addition of U(VI) results in an increase of the microbial metabolic activities in the upper biofilm layers. We consider that aqueous U in environmentally relevant concentrations may trigger higher O₂ consumption rates which lead to larger reducing zones within the biofilms. Consequently, such zones may be responsible for an increased U immobilisation from the bulk solution.</p>
<p>Achievements for the safety case: The results reveal that the addition of uranium in ecologically relevant concentrations to stable multispecies biofilms has a strong effect on the O₂ concentration and consumption rates in biofilms. This increased respiratory activity results in O₂ depleted zones closer to the biofilm air interface which may trigger uranium redox processes, which may lead to precipitation of uranium(IV) solids and consequently to a removal of uranium from the aqueous phase.</p>
<p>References: Grossmann et al. (2007), Krawczyk-Bärsch et al. (2008).</p>

2.4.2 Radionuclide mobility influenced by microbes

<p>Aim: Evaluate the consequences of microbially driven redox transformations of iron oxides on the phase distribution, speciation, and oxidation state of uranium.</p>
<p>Type of work: Experimental.</p>
<p>Participants: UNIUTRECHT.</p>
<p>State of the art before FUNMIG: 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. However, little was known about the mechanism and the rates of U reduction under the conditions of such environments, in particular in relation to the reduction of iron oxides which might also serve as sorbents for U(VI).</p>
<p>Main results (abstract):</p> <p><i>Microbial iron reduction accompanied by biogenic magnetite formation</i></p> <p>Reduction of U(VI) and its phase distribution was studied in batch experiments with the metal reducing organism <i>Shewanella putrefaciens</i> 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 UO₂. 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. 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).</p> <p><i>Reductive dissolution of iron oxides by S(-II)</i></p> <p>Microbial sulfate reduction leads to the formation of sulfide, which, in turn, can react with iron oxides by forming FeS. The effect of reductive dissolution of iron oxides by S(-II) on uranium mobility was investigated 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 dissolved U decreased as well. XANES analysis indicated that uranium became partially reduced to U(IV), which was most emphasised 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.</p>
<p>Achievements for the safety case: 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 if the formation of crystalline uraninite is kinetically hindered.</p>

3.1.1 Analysis and modelling of redox potential and reaction kinetics of synthetic and natural Fe bearing minerals

<p>Motivation and aim: Redox potential in clayey host rocks is a parameter of importance for calculating the speciation and hence the mobility of radionuclides like Se. The determination of the exact nature of the most redox reactive phases in the clayey formation and their reducing capacity was then explored.</p>
<p>Type of work: Wet chemistry, spectrometry (Mössbauer, EXAFS), electrochemistry, clay synthesis.</p>
<p>Participants: LMM, UJF, BRGM, LPEC, La Trobe.</p>
<p>State of the art before FUNMIG: Redox potentials have been estimated based on thermodynamic calculations including equilibrium with siderite and pyrite. The result can be compared to redox potentials that have been measured in URL experiments. However, uncertainties linked to the measurement are high principally due to bacterial disturbance and contact with atmosphere during drilling.</p>
<p>Main results (abstract): Methodology consisted of: (i) synthesis of model Fe free and Fe doped smectites. This material enables to perform experiment with clays without having interfering impurities; (ii) evidence of redox reactivity of Fe(II) associated to clay minerals in the COx: we have associated this finding with a warning about the sample preservation and preparation procedure to interpret batch experiments with redox sensitive elements; (iii) Ferrocene redox sensor development: this new sensor that has been tested on solute Fe(II)/Fe(III) oxides system will enable to measure the redox reactivity (potential, kinetics and capacity) of model minerals representative of the COx.</p> <p>Improvement of data involved determination of the Fe mineral distribution and the amount of Fe(II) in cation exchange position in the COx (Tournassat et al. 2008). This enables reducing the uncertainties on the porewater equilibrium model and then on the redox speciation in COx porewater. Improvement of knowledge: evidence of redox reactivity of sorbed Fe(II) on model clay minerals (Charlet et al. 2007, Gehin et al. 2007) and other minerals present in the COx towards selenium (Scheinost & Charlet 2008). These findings linked to on-going results on the COx reactivity should enable to build a comprehensive model of the redox reactivity towards Se.</p>
<p>Achievements for the safety case: Refinement of the COx redox reactivity (kinetics, potential and capacity ("stock")).</p>
<p>References: Charlet et al. (2007), Gehin et al. (2007), Scheinost & Charlet (2008), Tournassat et al. (2008).</p>

3.1.2 Modeling and measurement of H₂O and ion states in clay-solution interface zone

<p>Motivation and aim: The determination of the water and ion states in clay-solution interface zone is important for the understanding of transport parameters (mainly accessible porosity), for mass balance calculation for porewater composition modelling and speciation calculation for interlayer species.</p>
<p>Type of work: molecular dynamics, NMR spectrometry, neutron diffraction.</p>
<p>Participants: AIED, BRGM, LMM, UJF, LGIT, SUBATECH, LAIEM, CEREGE.</p>
<p>State of the art before FUNMIG: Estimation of the anionic exclusion volume was mostly empirical (e.g. 50 % assumption by Pearson et al. 2003) without quantitative and mechanistic description of the phenomenon.</p>
<p>Main results (abstract): Improvement of knowledge and data: results from various techniques from nanometric to macroscopic scale have been (or are currently) compared with each other in order to assess water and ions distribution and activities in the vicinity of clay surfaces:</p> <ul style="list-style-type: none"> • Molecular dynamics of basal surface/porewater interactions (e.g. Tournassat et al. 2007a) • H-NMR studies of water associated to illite and smectite surfaces (Montavon et al. 2009b) • Triple layer models based on zeta potential measurements (Leroy et al. 2007) • Neutron diffraction study of the hydrolysis of trivalent Sm in the interlayer space of smectite. <p>The results of the first three techniques have been compared in Tournassat et al. (2007b) and Montavon et al. (2009b) and give a coherent picture of water and ion distributions that can be now compared to results from Task 3.1.3 and from the literature (e.g. Appelo et al. 2008). The description of the data down to nanometric scale has enabled to refine macroscopic parameters values (e.g. capacitance values, surface compensated charge fraction values, surface diffusion coefficients) comparable to empirical derived values from transport models. The next step will be the understanding of surface effect on the solute speciation of elements like Sm.</p>
<p>Achievements for the safety case: Mechanistic description and parameterisation of clay surface effect on cations, anions and water distribution.</p>
<p>References: Appelo et al. (2008), Leroy et al. (2007), Montavon et al. (2009b), Tournassat et al. (2007a), Tournassat et al. (2007b), Pearson et al. (2003).</p>

3.1.3 Determination of diffusion parameters (D_e , e) for compacted model clay materials

<p>Motivation and aim: The motivation is to obtain a set of experimental data on a synthetic clay (as pure as possible) for all the species (anion, neutral, cation) at the centimetric scale in order to validate the model developed in 3.1.2.</p>
<p>Type of work: model clay, effective diffusion coefficient, permeation, through-diffusion.</p>
<p>Participants: CEA, LMM, BRGM, ERM.</p>
<p>State of the art before FUNMIG: Data are available on montmorillonite for different solutions and various compaction rates, but there is no coherent set of effective diffusion coefficient and K_d value for the different species for a unique pure clay.</p>
<p>Main results (abstract):</p> <p><i>Methodology:</i></p> <ul style="list-style-type: none"> • Retention isotherm (K_d value) for Ca and Na in 0.1 or 1M $MgCl_2$ electrolyte • Through-diffusion experiment on compacted clay in 0.1 or 1M $MgCl_2$ electrolyte. • Out-diffusion for cations • Advection experiments on the compacted clay in 0.1M $MgCl_2$ electrolyte. • Hg porosity measurement and porosity map by MMA impregnation <p><i>Improvement of data:</i></p> <ul style="list-style-type: none"> • A full set of data is available. Effective diffusion coefficient has been measured for Cl, HTO, Na and Ca in the two solutions. Dispersive coefficient for Cl, HTO has been obtained. • Porosity map of the compacted clay <p><i>Improvement of knowledge:</i></p> <ul style="list-style-type: none"> • Comparison between batch sorption and through-diffusion interpretation. • Improvement in modelling the diffusion process from the nanometric scale to the centimetric scale.
<p>Achievements for the safety case: Comparison between description of diffusion from nanometric to centimetric scale.</p>

3.1.4a Mono- and double-porosity model for simulating radionuclide transfer in compact clay materials

<p>Motivation and aim: Provide a consistent treatment for simultaneous diffusion of anions, cations and neutral species in clay rock.</p>
<p>Type of work: Model development.</p>
<p>Participants: SUBATECH.</p>
<p>State of the art before FUNMIG: The diffusion of anions, cations and neutral species is typically described by separate datasets allowing to model the transport of only one species at the time since both diffusion coefficients and porosity are different. This is a drawback for coupled modelling. In particular, there do not exist geochemical codes which would provide both individual diffusion coefficients and porosity values for each migrating species. Hence, a model which would avoid choices of individual diffusion coefficient and porosity values is urgently needed.</p>
<p>Main results (abstract): Both, a mono and a dual porosity model have been developed, which give similar results for the diffusion coefficients. A significant change in paradigm has been proposed to describe diffusion accessible porosity in compacted bentonite: Only a single micro-porosity value is considered for anions, cations and neutral species. Hydration water in the interlayers is considered as part of the solid phase and is not considered as a constitutive part of overall porosity. Since hydration water takes part of the solid phase, it is now possible to explicitly account for retention of HTO by formulating exchange between HTO and water in the interlayers.</p> <p>In the adaptation of the model to experimental data, a single fit constant, the geometric factor $G = 7$ was used, common to all ions and neutral species and for densities between 0.2 and 1.8 kg dm⁻³. The only input parameters to describe the effect of dry density on diffusion coefficients are the micro porosity (total porosity minus interlayer porosity) and the hydration numbers of exchanging cations in the interlayers, both of which can be measured by independent means (DRX, water sorption isotherms).</p> <p>The modelling of simultaneous mass transfer of HTO, Cs, Br and Ni has been undertaken. From the results apparent diffusion coefficients were obtained. Effective diffusion coefficients can of course only be compared to literature data if the the same porosity hypothesis is used for $D_a - D_e$ conversion as used in literature (total porosity for anions and HTO, micro-porosity for anions. Then, the calculated apparent diffusion coefficients for HTO match closely the measured values in the mentioned density range. Considering large experimental data uncertainty.</p> <p>The agreement between anion diffusion data and calculations is acceptable, while a slight underestimation for Cs is observed at low bentonite densities.</p> <p>There are little advantages for the dual porosity model compared to the mono-porosity model. Even though the dual porosity model opens the door to describe transport processes in the interlayer explicitly, it seems that transport in interlayers is fast compared to transport in the micro pores, hence, local equilibria between both pore spaces are expected to be established rapidly. Hence, the mono porosity model is considered for further developments. The developments consider the effect of ionic strength, of accessory minerals present in the pore space.</p>
<p>Achievements for the safety case: The model development is a potential key cornerstone when heading towards overall systems geochemical interaction modelling coupling speciation, diffusion and reaction simultaneously for anions, cations and neutral species.</p>

3.1.4b Mechanistic model and associated database for one radioelement for Callovo-Oxfordian clay rock conditions

<p>Motivation and aim: Translation to clay rock of the retention model developed for bentonite.</p>
<p>Type of work: Model development.</p>
<p>Participants: SUBATECH.</p>
<p>State of the art before FUNMIG: A radionuclide retention model for bentonite has been developed (Grambow et al. 2006) for mono to tetravalent cations and for some anions but this model was not applicable to clay rock due to the multiminerall phase assemblage and to the complicated porosity relationships in clay rock.</p>
<p>Main results (abstract): The approach taken was to refrain from any fitting of data but to adapt the model by a simple additivity approach, concerning the variation in mineralogy such as smectite and illite contents. An exception from this approach has been done for Cs in which case frayed edge sites on illite (not present in bentonite) were particularly accounted for. Surface complexation/ion-exchange of the PHREEQC based model of Grambow et al. (2006) is closely similar to the model proposed by Bradbury & Baeyens (1997) without electrostatic contributions ("non-EDL"), considering one strong and two weak surface sites, refitted with respect to sorption constants, in order to describe Na-, Ca- and Cs-montmorillonite and bentonite MX-80 with a single set of surface complexation constants and to account as well for carbonate and sulphate concentrations in groundwater. Ion exchange reactions of major elements and associated exchange constants were taken as well from Grambow et al. (2006). Site occupancies were obtained for each argillite sample from the observed values obtained from ANDRAs characterisation programme. Site densities for surface complexation and ion exchange are derived by 2 steps:</p> <ol style="list-style-type: none"> (1) the determination of illite and smectite mass fraction in each sample considering the interstratified illite/smectite (I/S) as a mechanical mixture of illite and smectite, and (2) the comparison with literature data for pure illite and smectite. <p>The mass fractions of illite and of smectite in illite/smectite were derived from an overall fit of measured CEC data from all samples of the drill core EST205 considering the measured mass fraction of illite, I/S, and kaolinite. The working hypothesis was made that the mass fractions of illite and smectite in I/S are constant in either horizon R0 and R1 and that the site densities of illite and if the illite fraction in I/S were similar. Five values were fitted simultaneously in the overall fit: the CECs of the kaolinite, the smectite and illite components as well as illite fraction in the I/S of both R0 and R1 allowing the accurate prediction of whole rock CEC values in the drill core, considering only the measured mineralogical composition (mass fractions of illite, I/S, kaolinite).</p> <p>Considering this general agreement of measured CEC and calculated values based on mineral fractions the same approach has been used for surface complexation (here without the possibility to test the model to measured data) Ratios of micropores to interlayer pore space were obtained as well. Close relation of calculated and measured retention data for Cs and for Ni gave reasonable justification to apply the model for the prediction of K_d variations of Cs all along a drill core. Predicted values vary by about a factor of 10.</p>
<p>Achievements for the safety case: It is very important that a simple additive model can be used to predict retention properties of clay rock based on measured mineral fractions, provided the multiple geochemical interactions are taken into account.</p>
<p>References: Grambow et al. (2006), Bradbury & Baeyens (1997).</p>

3.2.1 Determination of clayrock physical characteristics, mineral and pore water composition & conceptual model of water and porosity distribution in clayrocks

Motivation and aim: Depending of their structure and degree of compaction, clays can be hydrated by a variable amount of water molecules in the interlamellar space and on external surfaces. Because of the structure and nature of water molecules is influenced by the clay surfaces; different types of waters are involved in clayey systems (internal/external water, adsorbed/free water) giving a double porosity structure. The water volume accessible to ions is a key parameter in order to determine the pore water chemistry affecting the radionuclide transport in clayrocks. The material from different clay formations (Boom Clay, Opalinus Clay and Callovo-Oxfordien) offers the opportunity of understanding the nature of water in clayey systems because of their variations in parameters affecting to the amount of adsorbed and capillary water such as: degree of compaction, water content, clay content, type of clays, salinity, nature of exchangeable cations etc.

Type of work: Wet chemistry, DRX, water and gas sorption isotherms, FTIR, TG/DSC, squeezing, data analysis, data comparison.

Participants: CIEMAT.

State of the art before FUNMIG: Natural consolidation induces significant physical and structural changes to clays as a function of time, leading to a progressive compaction and agglomeration of particles, reduction of crystallinity and an increase of microstrain, which affects both the tetrahedral and octahedral layers. At high degrees of compaction, the diffusive transport of the solvated ions and the solvent molecules in clays are substantially retarded compared to the free electrolyte solution because of the surface complexation of ions and the strong ordering of solvent molecules at the solid-liquid interphase. Structural and dynamic properties of water confined between basal planes of clays have been extensively studied by means of water adsorption isotherms, neutron scattering, molecular dynamics (MD) and Monte-Carlo simulations. However, most of the works are related to purified clays and dispersed systems. In real clayey formations, the amount of accessory minerals, type of clays and water contents affect the amount and distribution of the external and internal water; and the combination of such properties is not well understood.

Main results (abstract): The study of water states, types of water (adsorbed, free water); and the water volume accessible to ions is obtained in different materials in order to determine the pore water chemistry. The results are compared with those obtained in experimental lab and in situ studies. The research is accomplished by a careful and detailed characterisation of the clay samples using various methodologies to better interpret the results. Parameters such as particle size, layer spacing, chemical composition, mineralogy, external and total surfaces, porosity and pore water chemistry were determined. The methodology used is innovative in the sense that combines different types of methodologies to obtain a representative description of double porosity systems and the amount of free, adsorbed and confined water involved in real-type porous media: diffuse reflectance FTIR, water adsorption isotherms, XRD, TG and calorimetric measurements. Besides, a comparison between different types of clayey formation is given, in which there are variations in types of clays, water contents, dry densities, pore water chemistry and type of exchangeable cations. No similar data were obtained in previous works. Therefore, the results reduce the lack of data in this sense; and the uncertainty involved in the use of total porosity or effective porosity in the modelling of pore water chemistry which influence the migration of radionuclides.

Achievements for the safety case: Ion exclusion and evolution of pore water chemistry and mineralogy in different host rocks, connected matrix porosity, surface diffusion, double porosity models.

3.2.2 Development & application of appropriate characterisation, quantification methods for quantifying the spatial distribution of porosity and minerals in rock samples

<p>Motivation and aim: Data appropriate for constraining numerical model(s) of mineral & porosity characteristics and spatial distribution in clayrocks at μm – cm scale (in support of transport model and up-scaling).</p>
<p>Type of work: Analytical method development; application to rock samples.</p>
<p>Participants: ERM, ARMINES, HYDRASA.</p>
<p>State of the art before FUNMIG: Partial development of methods for quantification of spatial distribution of minerals and porosity in clay-rich compacted materials from micrometer to centimeter scale.</p>
<p>Main results (abstract):</p> <p><i>Improvement of knowledge:</i> Improvement of the porosity/mineralogy spatial distribution and their relationships.</p> <p><i>Methodology:</i> <p>X-ray tomography laboratory: integration of this technique in the analytical chain and systematic use for the control of samples used in diffusion experiments (detection of structural heterogeneities at a centimetric scale.</p> <p>X-ray synchrotron tomography: Development of a method for the interpretation of high resolution microtomographic data (micrometric scale): 3D spatial distribution of main minerals like carbonates, quartz and clay matrix.</p> <p>Autoradiography: application to various clay rock samples (Boda, Boom Clay, OPA and CO_x); superimposition of EDS-SEM mineral maps with porosity maps; improvement of spatial resolution by using ³H-labelled MMA and detection with new higher resolution films; it improves the knowledge on the relationship of minerals with porosity.</p> <p>Beta imager: constructed a new geometry in 2007 in order to be able to image a mineral sample. The new system was tested on a piece of CO_x labelled with ¹⁴C and the results, while not quantitative, demonstrate the ability of such a new geometry. Many optimisation tests of the geometry and other parameters must still be performed since the spatial resolution is only 100 μm. This resolution could be largely improved compared to the spatial resolution obtained with biological sample labelled with ¹⁴C (resolution close to 40 μm). Nevertheless the quantification process in terms of concentration of radioactivity, spatial resolution is already achieved.</p> <p><i>Improvement of data:</i> The set of applied techniques has provided a best location of heterogeneities in clay rich rocks for micrometer to centimeter scale. It has revealed the specificities of each investigated clay rock.</p> </p>
<p>Achievements for the safety case: Provide a model for structural organisation (including comparison between different clays) for input in transport models.</p>
<p>References: Mazurier et al. (2008), Robinet et al. (2008c).</p>

3.2.3 Development of numerical model(s) of clayrock porosity for transport modelling

<p>Motivation and aim: Numerical model(s) of mineral & porosity spatial distribution at μm – cm scale as support for diffusive transport simulations.</p>
<p>Type of work: Conceptual and numerical model development.</p>
<p>Participants: ERM, HYDRASA, CEA.</p>
<p>State of the art before FUNMIG: Existing solute-diffusion models do not take into account mineral and porosity spatial distribution at μm – cm scale.</p>
<p>Main results (abstract): The TDD (<i>Time Domain Diffusion</i>) method was improved to simulate the results of solute in-diffusion experiments based on the actual microstructure of the rock sample. The input data are coming from Task 3.2.2.</p> <p>Using 3D spatial distribution of minerals obtained by high resolution tomography in COx and 2D spatial distribution of minerals obtained by electronic microprobe (EPMA), simulations of solute diffusion show that nonporous grain (quartz and carbonates) orientation at a μm scale provokes a diffusion anisotropy at a larger scale (mm to cm).</p> <p>The inversion procedure combined with TDD was also improved in order to obtain local diffusion coefficients and porosity (μm scale) from in-diffusion experiments.</p> <p>The microprobe LIBS is used to analyse diffusion profiles combined with mineral maps. Developments were made to improve the reliability of profile with mineral map.</p> <p>This approach allows obtaining a specific diffusion coefficient of the clay matrix. This was made for Eu and Cu tracers on COx.</p> <p>The whole obtained data improve the understanding of the diffusion process at small scale regarding porosity and mineral spatial distribution. Real diffusion coefficient in clay matrix can be measured.</p>
<p>Achievements for the safety case: Obtaining of small scale diffusion coefficient.</p>
<p>References: Robinet et al. (2008c).</p>

3.2.4 Development and application of new methods for quantifying transport parameters of moderate and high K_d species

<p>Motivation and aim: Diffusion and sorption of $^{134}\text{Cs}^+$, $^{60}\text{Co}^{2+}$ and $^{152}\text{Eu}^{3+}$ in Opalinus Clay and Callovo-Oxfordien argillites. Determination of effective diffusion coefficients and in situ R_d values.</p>
<p>Type of work: Experimental work/modelling.</p>
<p>Participants: PSI, CEA.</p>
<p>State of the art before FUNMIG: No diffusion and in situ sorption data were available for $^{134}\text{Cs}^+$, $^{60}\text{Co}^{2+}$ and $^{152}\text{Eu}^{3+}$.</p>
<p>Main results: Sorption of Cs^+ on intact Opalinus Clay (OPA) was found to be similar as or even higher than on crushed material as measured in batch sorption experiments. It was also observed that in long-term experiments, the K_d values are higher than in short-term experiments. Recent modelling of through-diffusion experiments of Cs^+ in OPA showed evidence for dead-end pores what could explain this discrepancy: continuous pores guide Cs^+ relatively quickly towards the zero-concentration end, while part of the mass is taken up by the dead-end pores. The latter process is a slow process. The effective diffusion coefficient of Cs^+ in OPA was shown to be a factor of 8 larger than that of HTO. Although a better understanding of the diffusion and sorption of Cs^+ in OPA has been reached, a complete picture is still missing.</p> <p>Sorption experiments with $^{60}\text{Co}^{2+}$ showed that the sorption on intact OPA is larger than on crushed OPA. The diffusion of $^{60}\text{Co}^{2+}$ and $^{152}\text{Eu}^{3+}$ in OPA turned out to be difficult from a technical point of view because of the more or less strong interaction of the tracers with the equipment. In the case of $^{60}\text{Co}^{2+}$ the interaction with the equipment was moderate and could be taken into account in the modelling. The decrease of the concentration in the source reservoir could be modelled successfully. However, the diffusion profile of $^{60}\text{Co}^{2+}$ in OPA showed a dual porosity behaviour and could not be modelled with a single porosity model using the parameters derived from the reservoir. The reasons for this behaviour are still unclear and further investigations are necessary.</p> <p>In the case of $^{152}\text{Eu}^{3+}$ the interaction with the equipment was so strong that only a very small amount of the tracer was transported into the clay. A proper modelling neither of the decrease of the tracer in the reservoir, nor of the diffusion profile was possible.</p> <p>The CEA developed a μLIBS-based method for measuring both in-diffusion profiles and mineral phase distribution in clayrock. Profiles were determined for Eu and Cu, and the latter interpreted in terms of D_a values. CEA also developed and tested a column-based method for determining D_a values for sorbing tracers.</p>
<p>Achievements for the safety case: Transferability of K_{dS} from batch sorption data towards PA seems to be justified because the sorption on intact material is similar, and in some cases higher.</p>
<p>References: Van Loon & Müller (2010), Yaroshuk & Van Loon (2008).</p>

3.2.5 Comparative measures of K_d and migration of radionuclide representative species in different clay rocks

<p>Aim: Determination, demonstration of the correlation of batch sorption data and retardation factors determined from transport measurements on compacted samples coming from a variety of formations.</p>
<p>Type of work: Data comparison, specific measurement programmes, data analysis.</p>
<p>Participants: SCK·CEN.</p>
<p>State of the art before FUNMIG: Transfer of batch sorption data for dispersed state to compacted state has been shown plausible for some radionuclides (Na^+, Sr^{2+}) on bentonites, some natural clay host rock (OPA), but for Boom Clay this transfer is disputed based on the comparison of migration data with a limited set of sorption data. A systematic study is needed.</p>
<p>Main results (abstract): For Cs and Sr, sorption on dispersed or intact Boom Clay are not significantly different, hence compaction does not seem to influence the accessibility of sorption sites. The sorption of Cs and Sr can also be described in a mechanistic way using a simple cation exchange model based on illite as model component for Boom Clay.</p> <p>Migration experiments with Cs and Sr of different types (In- and Through diffusion, column migration, electromigration) resulted in reproducible D_a values and a trustworthy value can be obtained. However, retrieving trustworthy retention parameters was more difficult. Despite these difficulties, the obtained retention values for Cs and Sr from migration experiments were comparable to the data from batch sorption experiments. As such, the relationship between R and K_d (under the approximation that at low concentrations sorption is a linear and reversible process) seems valid. These observations are in line with observations made on other clay host rocks and therefore, we might state that this can be generalised for simple cationic species. For transport modeling 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. However, combining the $D_e/D_p(\text{HTO})$ and sorption data will not result in correct D_a values for ion-exchangeable radionuclides. As observed on the different clay host rocks, D_e/D_p values are always higher than $D_e/D_p(\text{HTO})$ which is attributed to a "surface diffusion" kind of mechanism. It is therefore not recommended to derive D_a values for cations using a general D_e/D_p value for HTO in combination with batch sorption data.</p> <p>Am retention in Boom Clay is influenced by the presence of NOM and the migration of Am in Boom Clay is further governed by colloid filtration aspects. First steps in describing the sorption processes of Am onto clay systems in presence of NOM were done but still need further efforts. Nothing can yet be concluded from these experiments with respect to transferability of batch sorption K_d to migration retardation. The outcome of the experiments is as expected.</p>
<p>Achievements for the safety case: For species that sorb via pure cation exchange, the relationship $R - K_d$ seems valid. However, combining the $D_e/D_p(\text{HTO})$ and sorption data will not result in correct D_a values for ion-exchangeable radionuclides.</p>
<p>References: Maes et al. (2008).</p>

3.2.6 In-diffusion experiments of doped solutions into polished sections of Callovo-Oxfordian clay rock

<p>Motivation and aim: Analyse spatial distribution (if possible 3D) of mobile radionuclides after diffusion in clay.</p>
<p>Type of work: Autoradiographie using beta imagers.</p>
<p>Participants: SUBATECH, ERM.</p>
<p>State of the art before FUNMIG: Spatial analyse was done using autoradiographie with the help of photographic films.</p>
<p>Main results (abstract): The high spatial resolution β-imager developed in Subatech has suggested to test this technique to follow diffusion of mobile radionuclides in slices of clay rock obtained from a diffusion profile. The method was tested both on tritium doped and ^{14}C doped samples. For the latter case a sample slice doped with $^{14}\text{C}/\text{PMMA}$ was obtained from J.C. Parneix, ERM, Poitiers. However, the spatial resolution was not sufficient to obtain any meaningful results.</p> <p>Even though improvements of the proposed technique can be envisioned, the quality of the images obtained is clearly insufficient to characterise the clay samples. The technique can not compete with typical auto radiographic analyses using photographic paper. It is therefore decided not to continue to develop this technique.</p>
<p>Achievements for the safety case: No achievements.</p>

3.3.1 Diffusion (and sorption) measurements for developing data sets in support of in situ experiments (DR at Mont Terri, DIR at Bure)

<p>Aim: Generation of databases for use in interpreting in situ DR experiment, validation and inter-comparison of large-scale sample datasets, identification of effects of anisotropy. 3D description of diffusion paths.</p>
<p>Type of work: Diffusion + sorption measurements on OPA and COx clays, diffusion from solid source in large scale clay rock blocks, measurements, interpretative modelling.</p>
<p>Participants: CIEMAT, UDC.</p>
<p>State of the art before FUNMIG: Only "classical" diffusion experiments were carried out to determine diffusion parameters. In situ diffusion experiments were carried out with standard methodologies not totally representative of real conditions (e.g. large quantity of water in which tracer is dissolved).</p>
<p>Main results (abstract): A new methodology that allows carrying out diffusion experiments, in laboratory, at a large-scale has been developed and improved. This methodology is proposed as a possible alternative to conventional in situ diffusion test. Compared to conventional in situ tests, this set-up is more realistic since the contact between tracer and clay is improved. A 3D analysis of diffusion pathways can be carried out after a thorough sampling of the solid block at the end of the experiment. Graphical representations of experimental results along vertical and horizontal planes obtained according the samples situation demonstrated the 3D capacity of this methodology and his capability to evaluate anisotropy and heterogeneities. With this technique the diffusion coefficients of HTO, Sr⁺, Cl⁻ was successfully determined in the OPA and COx clay formations. The same technique was used for studying high sorbing tracers (Cs, Co and Eu) diffusion but no satisfactory results were obtained because a bad contact between tracers plugs and clay blocks existed in the last experiments. A large amount of additional diffusion data on both clays have been obtained with conventional through-diffusion and in-diffusion techniques, improving the original database for many radionuclides and reducing data uncertainty. Instantaneous planar source method was successfully used to obtain Da for Eu. Diffusion in clays was also investigated by RBS (Rutherford Backscattering Spectrometry). The technique is particularly useful for high sorbing tracers since it permits measuring concentration profiles at a micrometric scale, reducing the experimental time.</p>
<p>Achievements for the safety case: Improvement of diffusion database and reduction of the uncertainty on diffusion parameters. The 3D description and modelling of large-scale experiments it is adequate for evaluation rock anisotropy.</p>
<p>References: Cormenzana et al. (2008), García-Gutiérrez et al. (2008), Samper et al. (2008b), García-Gutiérrez et al. (2009), Alonso et al. (2009a).</p>

3.3.2 Evaluation of a diffusion and retention experiment at the Mont Terri URL

<p>Motivation and aim: Diffusion experiments at the field scale in an URL offer the possibility to verify laboratory diffusion and retention data under more relevant in situ conditions. We intended to develop and compare various conceptual and numerical models as well as to simulate the data of the field experiment.</p>
<p>Type of work: Development of conceptual and numerical models; code comparisons; modelling of experimental data.</p>
<p>Participants: PSI, UDC, GRS, Nagra, Andra.</p>
<p>State of the art before FUNMIG: Various codes were available that can be used to model the diffusion experiment in the URL, but no or only limited code comparisons for diffusion of mobile and strongly sorbing tracers in an anisotropic rock in two or three dimensions existed. For some of the used tracers, no or only few diffusion and retention data were available.</p>
<p>Main results (abstract): Numerical models for the DR experiment with a 2D radial or an explicit 3D geometry were set up by several research groups using various codes (Th. Gimmi, PSI: Flotran; J. Samper et al., UDC: Core2D; A. Rübél, GRS: r3t; J.M. Soler, CSIC [not a direct participant of FUNMIG]: Crunch). Some of the codes had to be modified to be able to handle anisotropic, heterogeneous solute diffusion, which is important for clay rocks. Additionally, semi-analytical solutions (PSI) were used to check and verify the results.</p> <p>Scoping calculations based on a preliminary set of input data for HDO, Γ, Na^+, Sr^{2+}, and Cs^+ for the DR experiment, performed by the different groups, allowed to eliminate a bug in one of the codes. They also revealed that for strongly sorbing tracers, the numerical representation of the borehole zone and the adjacent rock can considerably affect the simulation results. The robustness of the simulation results has thus to be checked carefully by varying the numerical representation of this zone. Moreover, for strongly sorbing tracers the details of the geometry of the injection area (filter, fluid gaps) affect the decrease of the borehole concentrations with time. The simulations clearly identify possible sources of uncertainty for diffusion and retention data obtained from such field tests. In this sense, our work does not necessarily reduce the uncertainty of the data, but it allows a better quantification of this uncertainty.</p> <p>The available borehole data (HDO, HTO, Γ, Br^-, $^{22}\text{Na}^+$, $^{133}\text{Ba}^{2+}$, $^{85}\text{Sr}^{2+}$, $^{60}\text{Co}^{2+}$, $^{137}\text{Cs}^+$, and Eu^{3+}) of the still ongoing DR experiment were compiled and distributed to the different modelling groups. Based on these data, a very preliminary estimation of diffusion and retention parameters was possible. Final parameter estimates will be available at a later stage only, as planned, after the overcoring of the rock and the determination of the tracer profiles in the rock around the borehole. The data obtained so far allow to check various results from laboratory studies.</p>
<p>Achievements for the safety case: More robust 2D and 3D modelling of diffusion experiments in anisotropic rock, better quantification of uncertainties.</p>
<p>References: Gimmi (2008), Samper & Yang (2008).</p>

3.4.1 Studying of 'natural proofs' of retention/diffusion mechanisms

Aim: Studying of 'natural proofs' of retention/diffusion mechanisms.
Type of work: Data gathering on in situ speciation data, spatial distribution of natural tracers.
Participants: SCK·CEN.
State of the art before FUNMIG: From granulometric, mineralogic, geochemical and radiochemical studies performed on Boom Clay samples from various drillings, proof of radionuclide retention processes were found (changes in natural Cs, Sr, U, Th,...contents; De Craen et al. 2006).
<p>Main results (abstract): From a new drilling at Essen (NIRAS-ONDRAF contract), clay cores were taken from the entire thickness of the Boom Clay and upper/lower aquifers for chemical analysis and for migration experiments.</p> <p>It provided the opportunity to assess the transferability aspects of migration properties of the Boom clay, which were up to now essentially studied at the Mol site. The pore water chemistry of the Boom clay could be thoroughly examined in order to compare it with other locations in the Campine area, as the Mol site, Zoersel and Doel and to provide natural tracer profiles that were used in the CLAYTRAC project (Mazurek et al. 2008).</p> <p>Profiles of major anions and cations as well as stable isotopes data are currently available and interpretation is currently on-going within the CLAYTRAC project.</p>
Achievements for the safety case: Major transport process in Boom Clay is diffusion. Sufficient natural proof for retention is available.
References: De Craen et al. (2006), Mazurek et al. (2009).

3.4.2 Development of a GIS (geographical information system) for parameters and properties of CO_x potentially important for radionuclide transfer

<p>Motivation and aim: This task consists in the development of a database including as much referenced and localised data as possible for the CO_x formation: from mineralogy and chemistry to physical properties. Statistical analysis would then be more easily performed.</p>
<p>Type of work: Data collection, AccessTM database creation and coupling with visualisation tools.</p>
<p>Participants: BRGM.</p>
<p>State of the art before FUNMIG: no "public" database was available for the CO_x. One published paper (Gaucher et al. 2004) made the synthesis of the data from EST205 borehole. Other data (even from BRGM only) were dispersed.</p>
<p>Main results (abstract): A database has been created and released on the FUNMIG project website, including collected data on chemistry, mineralogy, physical parameters (porosity, specific surface area...), isotopy and localisation. The database has been coupled to the GDM software for visualisation in 3D.</p> <p>The database should be completed with incoming information from the other partners.</p> <p>The database has been used to calibrate mineralogical/sorption models.</p>
<p>Achievements for the safety case: Development of a GIS (geographical information system) for parameters and properties of CO_x potentially important for radionuclide transfer.</p>
<p>References: Gaucher et al. (2004).</p>

3.4.3 Overview of upscaling strategies for transport parameters in clay rock

<p>Aim: Provide advice on how to pursue upscaling for transport parameters for safety case studies.</p>
<p>Type of work: Advice, documenting.</p>
<p>Participants: SCK·CEN.</p>
<p>State of the art before FUNMIG: There were already strong indications that upscaling of transport parameters is not a problematic issue in the case of disposal in a clay rock.</p>
<p>Main results (abstract): Typical grain size of Boom Clay particles is 30 μm. The dimension of a representative elementary volume is around 3 mm. Consequently, as far as the Boom Clay can be considered as homogeneous, most experimental and modeling scales are much larger than the dimension of a representative elementary volume.</p> <p>In formations where heterogeneities offer possibilities for accelerated water flow or transport, those heterogeneities can be important elements for the upscaling of the hydraulic and transport parameters. Faults and fractures occur at different scales in the Boom Clay. Various laboratory and in situ tests illustrate that the Boom Clay has a strong sealing potential, what leads to a fast return to values of the hydraulic conductivity close to its original value in zones disturbed by excavation.</p> <p>In situ measurements of the hydraulic conductivity of the Boom Clay made from a tunnel with a length of a few meters or on decimeter long filters placed in the host formation yield values that are very similar to values measured in the laboratory on samples with a thickness of a few centimeters. Long-term, large scale (m-scale) migration tests with HTO, I and HCO_3^- were blind predicted using lab determined migration data. Consequently, parameter values measured on a centimeter scale can also be applied when the scale is upscaled to meters, for so far as the clay volume can be considered as homogeneous for that parameter.</p> <p>The Boom Clay is characterised by a banded structure consisting of an alternation of more silty and more clayey beds of several decimeters thickness. Equivalent values of the hydraulic conductivity can be derived from profiles measured over the whole thickness of the clay layer. Transport parameters of non retarded elements have also been measured over the whole thickness of the clay layer. The variability of the measured diffusion parameters is limited.</p> <p>A more considerable variability of the values of transport parameters can be expected for retarded elements. It is therefore advisable to perform experiments with sorbing tracers on samples of known variation to scope the effect. Large scale migration experiments with retarded tracers are not considered to be a realistic option, because of the time scales (several tens or hundreds of years) needed for the observations. However, the necessity to make detailed investigations of this variability is questionable, because the safety evaluations show that even by applying very conservative transport parameters most of the retarded elements do not migrate out of the host clay formation at significant amounts.</p>
<p>Achievements for the safety case: The conclusions confirm that transport parameters determined at a centimetre-scale remain valid on the decametre-scale that has to be considered in the safety assessments, for so far as the characteristics of the host clay formation are sufficiently homogeneous.</p>

3.4.4a Natural tracer profile characterisation and modelling of tracer transport in compact clay rocks

Motivation and aim: Tracer profiles in argillaceous rock formations can be considered as large-scale and long-term natural experiments by which the transport properties can be constrained. They provide complementary information to that obtained from experiments in laboratories or underground facilities. Natural tracer profiles provide an independent line of evidence for system understanding as well as for safety considerations in qualitative and quantitative terms, relating to time scales required for performance assessment. The interpretation of tracer profiles is useful for the upscaling of laboratory experiments.

Type of work: Field sampling, lab experiments and analyses, num. modelling in 1D and 2D.

Participants: Uni Bern, Nagra.

State of the art before FUNMIG: A number of natural tracer profiles have already been available before FUNMIG. What was missing was an integrated approach that considers several conservative tracers for a given site, together with a well elaborated palaeo-hydrogeological scenario. Also, all previous modelling efforts were 1D, whereas 1D and 2D models were developed at Mont Russelin (i.e. the site studied within FUNMIG).

Main results (abstract): Natural tracers (anions, water isotopes, He) in pore water of Opalinus Clay were studied in cores drilled from the Mont Russelin tunnel near St. Ursanne, Switzerland. The tunnel penetrates an anticline of the thin-skinned belt of the Jura Mountains. Opalinus Clay is overlain by Dogger limestones that constitute an active aquifer. However, there is no active aquifer below Opalinus Clay. Therefore, anion and He concentrations as well as the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of pore water increase steadily with depth. The observed tracer profiles also differ from those obtained at Mont Terri, but the difference can be well explained by the much weaker erosion at Mont Russelin.

Model calculations indicate that the observed tracer distributions can be explained by a simple scenario considering out-diffusion to the overlying aquifer over a time scale of a few Ma, which is consistent with independent palaeo-hydrogeological evidence (folding of the mountain chain, erosion). 1D and 2D models yield similar results, indicating that, in the specific situation of Mont Russelin, the simplification of the complex geometry to a 1D problem does not result in a major error. The consistency of modelled evolution times with independent information suggests that laboratory-derived diffusion coefficients are applicable on the formation scale, i.e. can be upscaled without major corrections. Model calculations were also made considering advective in addition to diffusive transport. The fit of these models to the data is generally worse than when considering diffusion alone, suggesting that the tracer distributions essentially reflect diffusion profiles.

A major fault zone cross cuts the tunnel and correlates with anomalies of He contents and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of pore water. In contrast, Cl- shows no disturbance. The interpretation of these anomalies is uncertain, as obvious mechanisms (natural or man-made) are not at hand. All samples were obtained from 4 m deep boreholes. At Mont Terri, it has been shown that this depth is sufficient to obtain samples undisturbed by the presence of the tunnel. However, it is possible that the effects of the tunnel reach deeper into the formation in faulted areas.

Achievements for the safety case: Confirmation of diffusion as the dominating transport mechanism on the formation scale, together with the demonstrated applicability of laboratory derived diffusion coefficients of that scale.

References: Koroleva et al. (2006), Koroleva et al. (2007).

3.4.4b Natural tracer profile characterisation and evaluation of relative merits of two models of differing complexity to represent tracer transport in compact clayrocks

<p>Motivation and aim: The work in this task consisted of modelling of Mont Terri profiles: The aim was to analyse modelling results in respect of the influence of modelling complexity, e.g. influence of anisotropy.</p>
<p>Type of work: Numerical modelling.</p>
<p>Participants: GRS.</p>
<p>State of the art before FUNMIG: Simulations with a highly simplified, one dimensional model did exist and were used as reference.</p>
<p>Main results (abstract): Existing data of natural tracer profiles from Mont Terri was modelled multiple times with an increasing resolution or complexity of the geometry or transport data set. The modelling has shown that a higher degree in complexity did not improve the agreement between the simulations and the experimental data. This may be either because the model on which the simulations are based on is still not complex enough and that the most relevant influences on the profile are still not included in the model or that the complexity of the model is already too high and does not correspond with the level of detail and the quality of the input data. We currently trend to a combination of both explanations. On the one hand, a consideration of higher resolute transport parameters did not improve the model. The high heterogeneity of the transport properties on a small scale and the high anisotropy tends to flatten out the variability on a larger scale. On the other hand, a better understanding of the paleohydrological history (improvement of the boundary conditions), which was not regarded in this work, might improve the model.</p>
<p>Achievements for the safety case: A better insight about the uncertainty in modelling natural tracer profiles was achieved.</p>
<p>References: Rübel (2008), Rübel et al. (2007).</p>

4.1.1 Study of the response of the bedrock to past redox perturbations

Motivation and aim: Development of Fe/Mn based methodology to study past redox conditions in crystalline bedrock.

Type of work: Experimental and literature.

Participants: HU.

State of the art before FUNMIG: Few studies can be found in literature.

Main results (abstract): Summary of literature survey concerning chemical separation methods of oxidised Fe and Mn in rocks (PID 4.1.1: Separation of oxidised Fe and Mn from rocks – A literature survey).

Experimental work was stopped. The resources were moved to Task 4.5.1.

Achievements for the safety case: No achievements.

**4.1.2a Design of the experimental set-up for chemistry and colloid analyses:
boreholes drilling and water sampling**

Motivation and aim: To provide technical support and investigation tools in order to improve the research methods for understanding the geochemical conditions in crystalline rock.
Type of work: Development of borehole instrumentation for in situ geochemical investigations.
Participants: AITEMIN, CIEMAT and UPC.
State of the art before FUNMIG: -
Main results (abstract): Two hydrochemical investigation boreholes have been instrumented with multi-packer systems. Two outlets for water recirculation and sampling were installed in every interval. Packers and water intervals pressure are monitoring with pressure transducers and their signals are logged by an automatic datalogger. The data transfer is done via modem. New design of the instrumentation has been used, allowing the smaller intervals isolation. It has supposed a notable improve in the precision and quality of the taken water samples
Achievements for the safety case: Improvement of geochemical sampling quality. Experimental data obtained in a environment simulating a deep geological repository in granite and in "realistic" conditions.

4.1.2b Presence of geochemical gradients in the crystalline rocks

<p>Motivation and aim: To work in an underground laboratory as the Grimsel Test Site, implies to obtain data similar to those expected in a repository for high level radioactive waste. The main aim of this work is to highlight the solute migration mechanisms in crystalline host rock, influenced by the presence of the bentonite buffer and by the geochemical gradients generated at the bentonite/granite interface.</p>
<p>Type of work: Experimental work, in situ conditions, geochemical modelling.</p>
<p>Participants: CIEMAT.</p>
<p>State of the art before FUNMIG: Before FEBEX experiment it was difficult to evaluate in realistic conditions the effect of the bentonite barrier into the granite. Now, the FEBEX experiment is the unique opportunity to tackle the problem realistically.</p>
<p>Main results (abstract): There is a mass transfer processes from the bentonite to the granite based on:</p> <ul style="list-style-type: none"> • There is an appreciable increase of Na and Cl concentration in time in the waters sampled from the borehole FU-1 located at 20cm from the bentonite surface, especially in the interval FU1-4. On the other hand, the Na/Cl ratio in waters from the interval FU1-4 is similar to the Na/Cl ratio in the bentonite porewater. For this reason Cl and Na are considered as the main natural tracers indicating the mass transfer process between the bentonite porewater and the granite. Reactive transport modelling was used to describe the mass transfer process. The results show that the Cl and Na concentration in the interval FU1-4 is the result of a diffusive transport from the bentonite to the granite, with a $De \approx 5.0 \times 10^{-11}$. • There is small concentration of iodine and rhenium (tracers installed at the external surface of some bentonite blocks during their installation in 1996) in the waters from the boreholes nearest to the bentonite surface (FU2-3 and FU1-4). <p>These results could have some implications for the performance assessment due to the analogy between ^{36}Cl (one of the dominant radionuclides in the average annual doses in the reference scenario) and the Cl ion. Safety case should take into account the transport of conservative solutes from the bentonite into the granite.</p>
<p>Achievements for the safety case: Slight solute mass transfer from the near-field to the far field should be considered.</p>
<p>References: Gómez et al. (2007), Buil et al. (2008), Peña et al. (2008), Buil et al. (2009).</p>

4.1.2c Modelling of mass transfer at the bentonite/granite interface: The FUNMIG experiment at the Grimsel Test Site

<p>Motivation and Aim: The aim of this task is to develop a predictive model of the mass transfer at the near-field/far field interface, which will be calibrated and validated by new data gathered from the FEBEX gallery, where new boreholes will be drilled and installed in situ sensors for the main geochemical parameters.</p>
<p>Type of work: Modelling.</p>
<p>Participants: AMPHOS21, CSIC and UPC.</p>
<p>State of the art before FUNMIG: The assessment of the mass transfer from near to far field has been always based on models. In a few cases, the modelling results were validated through some laboratory experiments, which usually deviate significantly from the repository conditions (especially when referring to the bentonite dry density) or complete set of chemical data were not measured.</p>
<p>Main results (abstract): The results up to date indicate that the mass transfer is restricted to a few centimetres from the bentonite-granite interface (for the 9 years period simulated in the calculations).</p>
<p>Figure 1. Evolution of chloride concentration (mol/kg water) profiles. Time in years.</p> <p>The results are very sensitive to the groundwater pathways (i.e. fractures intersected by the bentonite) and the hydraulic properties of the system (i.e. hydraulic conductivity, diffusion coefficients, matrix diffusion, etc.). Moreover, the effect of the water saturation of the bentonite, could affect substantially this mass transfer. The results obtained from the NF-PRO integrated project (to be finished by the end of this year) can contribute in a significant way to the understanding of the effect of bentonite saturation to the mass transfer from near to far field.</p>
<p>Achievements for the safety case: The mass transfer from near to far field is very dependent on the bentonite saturation and therefore, minor mass transfer is expected until full saturation of bentonite.</p>

4.1.2d Analysis of bentonite colloids generation at the FEBEX site

Motivation and aim: The role of bentonite colloids on radionuclide transport in a crystalline medium still present large uncertainties. First in situ studies on bentonite colloid generation were carried out at the Grimsel Test Site (Switzerland), where the FEBEX experiment, reproducing at a real scale a high-level waste repository in granite, was installed 10 years ago.

Type of work: Experimental work, in situ conditions.

Participants: CIEMAT, FZK_INE.

State of the art before FUNMIG: Only a scarce quantity of laboratory data on bentonite colloid generation and stability existed.

Main results (abstract): To analyse the possible formation of bentonite colloids, in realistic conditions, two hydro-geochemical investigation boreholes (FUN1 and FUN2) were drilled quasi-parallel to the tunnel and at a distance of approximately 30 and 60 cm from the bentonite surface. Other 19 boreholes in radial position in respect to the tunnel already existed. Water sampling was performed both in the new and old boreholes. The water in the FEBEX tunnel is slightly alkaline (pH 7 – 8) and with low (~ 100 – 200 $\mu\text{S}/\text{cm}$) electrical conductivity. In these conditions, bentonite colloids are expected to be stable.

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 interval of the FUN 1 borehole and compared to those obtained in the laboratory studies of bentonite colloid generation. The similarity in both microstructure and composition was shown.

The quantification of bentonite colloids is still a difficult issue even it is clear that, at approximately 30 cm from the bentonite, the quantity of bentonite colloids cannot be higher than 1 ppm. Higher colloid concentration was 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" it's a very important issue at moment.

Achievements for the safety case: After 10 years from the bentonite emplacement, and in a very favourable environment for the stability of bentonite as it is Grimsel water, the quantity of bentonite colloids in the groundwater at 30 cm far from the bentonite-granite interface is not higher than 1 ppm.

References: Missana et al. (2008a).

4.2.1a Transport by matrix diffusion: experimental work

Aim: Development and validation of a novel experimental methodology to measure radionuclide diffusion coefficients in granite at a mineral scale.

Type of work: Experimental. Application of Rutherford Backscattering Spectrometry (RBS) combined to porosity measurements at the mineral scale.

Participants: CIEMAT, HU.

State of the art before FUNMIG: Scarce data of diffusion coefficients for sorbing radionuclides in granite. Absence of diffusion data obtained at a mineral scale.

Main results (abstract): The Rutherford backscattering spectrometry (RBS) is a nuclear ion beam technique that allows measuring concentration profiles in a micrometric scale. Measurements can be done within a single mineral. Apparent diffusion coefficients of uranium could be determined in three different granites types and different minerals. This represents the development of a new methodology for determining diffusion coefficients in the crystalline rock accounting for its heterogeneity.

For what concerns the improvement of knowledge it is interesting remarking that the differences observed in the measured diffusion coefficients can be related with the nature of the mineral grains. The combination of these studies with the PMMA studies of the porosity at the mineral scales (HU) suggested that the main parameter affecting diffusion is the grain porosity. The main difference observed in uranium diffusion in different granites was, in fact, mainly related to the porosity of quartzes. In Spanish granites quartz was not porous to PMMA and lower diffusion coefficients were measured whereas in Grimsel granite were quartz showed higher porosity, the diffusion coefficients were higher.

Achievements for the safety case: The methodology allowed measuring apparent diffusion coefficients of radionuclides at a mineral scale accounting for heterogeneity of the material.

References: Alonso et al. (2008), Siitari-Kauppi et al. (2007), Leskinen et al. (2007).

4.2.1b **Transport by matrix diffusion: experimental work (quantification of spatial porosity distribution in crystalline rock)**

<p>Motivation and aim: An important component of safety for the disposal of high-level nuclear waste in a crystalline geologic formation is the retention of radionuclides in the bedrock. Several chemical and physical processes affect the migration of solutes driven mainly by groundwater flow in rock fractures. Therefore, it is essential to know the structures of these systems in different scales i.e. from m. to nm scales. In this study the structure characterisation was performed from nm to cm scales. The Grimsel granodiorite was chosen in the first place to link the structure data for already profoundly studied site. The final goal is to study a few examples from the Olkiluoto site too. The key issue to be dealt with is the heterogeneities in the flow and the non-flow environments. The work will focus on the porosity and pore geometry of the non flow environment giving the initial data for evaluating the retention capacity of rock by matrix diffusion and sorption from flow. The main goal is to understand the meaning of heterogeneities for the matrix diffusion process.</p>
<p>Type of work: Laboratory work for matrix structure characterisation using ^{14}C-(PMMA method) and autoradiography and electron microscopy to study the pore apertures and links to mineralogy in detail. Quantitative petrography is performed for mineral specific porosity determinations. Image analyses methods are used for visualising the heterogeneous structures of porosity and mineralogy at all studied scales. The pore apertures and fissure geometry are studied in detail by electron microscopy (FESEM/EDAX).</p>
<p>Participants: HU, HYDRASA, CIEMAT, OVIUNI, VTT.</p>
<p>State of the art before FUNMIG: Granitic rock samples had been studied by the PMMA method. However a wide intercomparison with other structure characterisation methods was not performed, either the structure heterogeneities were not used in the diffusion models.</p>
<p>Main results (abstract): The different rock matrix characterisation methods (PMMA method, X-ray tomography and Confocal laser microscopy) were compared and limits of these methods were found during Funmig project. Microstructure was compared to diffusion data and process understanding concerning the rock matrix heterogeneities in diffusion processes was increased. The porosity and pore geometry was achieved in micrometric to centimetric scales. The overall picture of 3D structure of granitic rock matrix came closer. The work was focused on the porosity of the non flow environment giving the initial data for evaluating the retention capacity of rock by matrix diffusion and sorption from flow. Mineral specific porosities, the minerals elemental composition and the centimetric scale 3D structure of granitic rock adjacent to water flowing fractures gives the data needed for evaluation of radionuclide retention capacity of rocks.</p>
<p>Achievements for the safety case: Improvement of process understanding concerning matrix diffusion from water flowing fractures.</p>
<p>References: Hellmuth et al. (2007), Sardini et al. (2007), Leskinen et al. (2007).</p>

4.2.1c **Transport by matrix diffusion: quantification of spatial porosity distribution in crystalline rock**

Motivation and aim: The aim of this task is the characterisation of water pathways, at the rock matrix scale or intact rock (μm - mm), in granitic rock samples taken from de FEBEX gallery (Boreholes: FUN-01, FUN-02 and FUN-03).

Type of work: Observation and quantification of the granite microfractographic network (rock water pathways), under a combination of different techniques (POL, FM, CLSM, SEM and MIP). In this sense, water circulation is restricted to fissured paths of intergranular, transgranular or intragranular character. This textural and mineralogical location of the water pathways had been evaluated in terms of their specific surface in relation to the main rock-forming minerals.

Participants: UNIOVI and HU.

State of the art before FUNMIG: Since From the 90's, plenty of granitic rock samples had been studied by Confocal Laser Scanning Microscopy (CLSM). Will be very interesting the integration of data from different techniques (CLSM, PMMA method, X-ray CT, etc.).

Main results (abstract): All rock cores from FUN-01, FUN-02 and FUN-03, used in task 4.2.1, had been reported and distributed into the participants. Previously, the heterogeneity and anisotropy of these rock cores had been studied by mean of p-waves velocity. The ultrasonic profiles showed the presence of different anisotropies planes, in relation to rock discontinuities (fissures, foliation, veins, etc). The efforts in the microfractographic characterisation (under a combination of different techniques: POL, FM, CLSM, SEM and MIP) are concentrate in the rock cores nearly to the most hydraulically actives fractures (June, September and December fractures).

Achievements for the safety case: Compared and optimised the microfractographic network characterisation techniques.

References: Lähdemäki et al. (2007), Kelokasi et al. (2005), Montoto & Mateos (2006).

4.2.2a Transport by Matrix Diffusion: experimental work

Motivation and aim: Colloidal mobility is treated in transport models mostly according to the empirical approach of filter theory. The documented filter factors in the literature are strongly site dependent. A detailed understanding of processes driving reversible/irreversible colloid attachment and detachment from fracture surfaces is still lacking.

Type of work: The experimental and modelling work combines information based on laboratory migration experiment on fractured rock core samples from the Äspö granodiorite with detailed information on fracture geometry, aperture and surface roughness obtained by X-Ray Computer Tomography (XCT) implemented in transport codes.

Participants: FZK-INE, JGUM.

State of the art before FUNMIG: Migration studies in low-ionic strength, high pH groundwater systems showed surprisingly a fracture residence time dependent mobility of bentonite colloids. These results cannot be interpreted on the basis of simply electrostatic approaches predicting negligible colloid attachment probability. The calculations are based on simplified geometrical assumptions and implementing information on real fracture geometry/surface roughness might explain the observed deviations reducing the uncertainty concerning colloid mobility.

Main results (abstract): Migration studies with conservative tracers (HTO) and new synthetic colloids (carboxylated Quantum dots; QD) under variation of groundwater flow velocity have been performed. QD represent according to their hydrodynamic diameter of ~10nm as determined by ultrafiltration and AsFIFF combined with ICP-MS a good homologue for the smallest colloid fraction found in fractured rock environments and also a good homologue for the largest size fraction of natural organic matter (namely humic acids) found in groundwater systems.

Migration experiments using QDs show considerable steeper tailing compared to the conservative tracer HTO and surprisingly a flow rate dependent recovery under the Grimsel ground water conditions. Matrix diffusion cannot be observed for QD under the experimental conditions which is in line with the significant lower diffusion coefficient (bentonite colloids $\sim 10^{-17} \text{ m}^2/\text{sec}$, see Alonso et al. 2007a). Final experiments under near natural flow velocities ($\sim 10 \text{ m/a}$) will be finalised within the last project year.

The XCT information showing a broad aperture distribution with a maximum around $500 \mu\text{m}$ has and will be implemented in the last project year in a stepwise approach (Semi 2D to real 3D) in the finite element transport code ADINA-F. The calculated flow velocity fields and breakthrough curves calculated are compared to results of the Lattice-Boltzmann model of JGUM.

Achievements for the safety case: Improvement of process understanding on colloid retention mechanisms in real fractured rock systems.

References: Alonso et al. (2007a).

4.2.2b Transport by matrix diffusion: experimental work

<p>Motivation and aim: Further development and application of the new experimental method Positron Emission Tomography (PET) for spatially and temporally resolved studies of advective flow and matrix diffusion of dissolved components and colloids in granite fractures.</p>
<p>Type of work: Experimental work.</p>
<p>Participants: Institut für Interdisziplinäre Isotopenforschung (IIF) Leipzig.</p>
<p>State of the art before FUNMIG: Non-destructive 3D spatially resolved studies of fluid flow and colloid transport in fractures of crystalline rock cores of potential host rock formations for spent nuclear fuel were not executed.</p>
<p>Main results (abstract): First time the applicability of PET measurements for non-destructive investigations of the spatial distribution of transport processes of dissolved components and colloids in granitic cores (Åspö, Grimsel) is demonstrated. The transport of colloids plays an important role for the radionuclide migration in the potential host rock formations and the long time safety analysis.</p> <p>PET investigations can be used for the validation of the transport model conceptions. PET data are also the basis for the direct development, validation, and parameter estimation of mesoscale transport models which consider the influence of the real pore and fracture structures. Conservative tracers (KF, KI) marked with the positron emitting radionuclides ^{18}F ($T_{1/2} = 110$ min), ^{124}I ($T_{1/2}=4.15$ d) and humic acid colloids marked with ^{86}Y ($T_{1/2}=14.74$ h) were used as radiotracers to describe transport processes of dissolved components and colloids in the crystalline matrix along a longitudinal fracture at flow rates ranging from 0.1 to 0.001 mL/min. The spatial PET tracer concentration distributions were measured in the granitic fracture using the PET technique.</p> <p>On the basis of temporally resolved tracer experiments the data of the spatial distribution of the flow velocity and of the local dispersion parameters were calculated, which show large variations in different regions of the fracture cross sections. At low flow rates an influence of matrix diffusion processes was detected. Theoretical studies have shown the great influence of the heterogeneous transport distribution in the single fracture on the transport properties of the fracture network.</p>
<p>Achievements for the safety case: A new experimental approach for non-destructive spatially resolved studies of fluid flow and colloid transport in fractured drilled rock cores with PET was developed, and new data sets for transport modelling of heterogeneous transport processes in crystalline host rock were evaluated.</p>
<p>References: Richter et al. (2007), Gründig et al. (2007), Kulenkampff et al. (2008).</p>

4.2.2c **Transport by matrix diffusion: experimental work (combined X-ray microtomography and microfluorescence description)**

<p>Motivation and aim: Further development and application of the new experimental method of combined X-ray microtomography and microfluorescence for spatial resolved analysis of crystalline host rock microstructure and composition.</p>
<p>Type of work: RTD.</p>
<p>Participants: National Institute for Lasers, Plasma and Radiation Physics, Bucharest.</p>
<p>State of the art before FUNMIG: There are no studies reported in the open literature so far for the non-destructive space resolved microstructure and micro-composition of crystalline host rock.</p>
<p>Main results (abstract): For the Grimsel sample 05.001 we carried out three types of non-destructive analyses: 3D microCT for small fragments with space resolution of cca. 50 microns, 3D macroCT for full sample (large Field of View - FOV) with space resolution of cca. 150 microns and composition mapping by X-Ray fluorescence with energy resolution of cca. 150 eV. The elemental analysis was complemented with density and effective atomic number information obtained by dual energy tomography. Dual-energy cone-beam tomography is a powerful technique for direct characterisation/visualisation of mineral composition and of heterogeneities of fluid transport in core samples.</p> <p>The reconstructed data was used for extraction of cavities boundary by image post-processing of the 3D reconstructed volumes.</p> <p>Currently we are working at the fabrication of a microbeam fluorescence facility for surface composition mapping (20 μ resolution) and the implementation of innovative combined transmission-fluorescence tomography method.</p>
<p>Achievements for the safety case: A new experimental approach for non-destructive spatially resolved studies of mapping the mineral composition and the volumetric microstructure of the host rock samples.</p>
<p>References: Tiseanu & Craciunescu (2006), Craciunescu et al. (2006).</p>

4.2.3a Transport by advection: in situ work

Motivation and aim: To improve the knowledge of the granite hydrogeological properties influence in the groundwater flow and in the radionuclide transport.

Type of work: Hydrogeological studies and in situ hydraulic tests

Participants: AITEMIN, CIEMAT, CSIC and UPC.

State of the art before FUNMIG: -

Main results (abstract): Hydraulic testing campaign has been carried out. Single hydraulic tests were performed in the new boreholes intervals.

The tests results have contributed to improve the knowledge of the near field fluid flow in granite rocks in order to understand the advective transport contribution to the radionuclides migration.

Achievements for the safety case: Improvement the knowledge of the near field fluid flow in granite rocks.

4.2.3b Transport by advection: in situ work

Aim: The aim of this task is to characterise the hydrogeological behaviour at the scale of the granite-bentonite contact within the FEBEX experiment. We have made a change from the FEBEX experiment scale (metric) to the centimetric scale. This change can be made using the results obtained from the geophysical, hydraulic and chemical experiments at the new boreholes.

Type of work: Experimental tasks and modelling.

Participants: AITEMIN, CIEMAT, CSIC, UPC, UNIOVI.

State of the art before FUNMIG: Characterising the medium hydrogeology was limited to the metric scale. It is important to have an accurate hydrogeological knowledge of the field near the granite-bentonite contact to understand the transport processes, if they exist, from the bentonite to the granite.

Main results (abstract): Groundwater heads measured at the FUNMIG-scale boreholes' intervals (FU1, FU2 and Fbx2) have recovered their natural trend. However, FU1-2, FU1-3 and FU1-4 intervals have been showing quite low pressure values. This fact can be explained if the intervals are connected to low pressure zones, but we have not identified these connections yet.

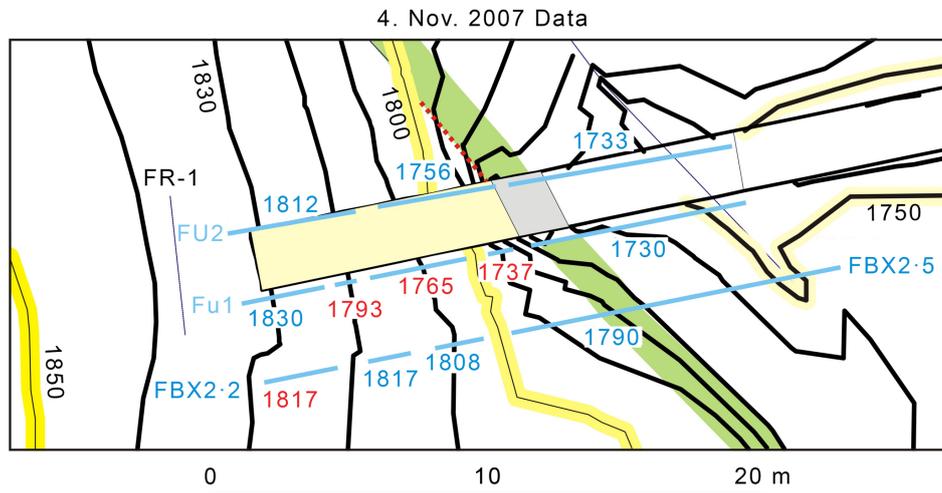


Figure 1: Piezometric heads at the FUNMIG-scale.

Achievements for the safety case: Identifying the main structures and their connectivity is essential to identify potential paths suitable for the migration of contaminants.

4.2.3c **Transport by advection: in situ work (System characterisation: determination of the detailed internal structure of a granitic rock body)**

<p>Motivation and aim: To characterise the internal structure of the Granitic rock around the FEBEX Gallery by means of Geophysical methodologies, providing an indirect way to determine the distribution, geometry of the fracture system.</p>
<p>Type of work: Experimental field data acquisition. Data from geophysical logging, in particular borehole televiewer, ground penetrating radar, and crosshole ultrasonic monitoring. Data processing and interpretation.</p>
<p>Participants: CSIC.</p>
<p>State of the art before FUNMIG: The structure of the granitic massif had been constrained by geological studies and some large scale geophysical experiments. The surface distribution of the fractures on the walls of the FEBEX gallery was known. However the timing, evolution of the fracturing and the distribution and the fracture geometry in the rock was unknown.</p>
<p>Main results (abstract): The FEBEX gallery was excavated in the heterogeneous Aar Granite, containing from very leucocratic facies to granodiorites. The geology of the gallery shows the existence of various sets of fractures with different attributes: geometry, kinematics, fracture infilling, etc. The study of the structural data, new observations on the FEBEX gallery and borehole televiewer data acquired in the new boreholes, allowed identifying four sets of fractures. The first group has a typical distribution and characteristics of an echelon tension fractures and was formed in late magmatic stages, according with the paragenesis of the minerals that filled the cracks. The main strike is around 300 (280 – 300). These fractures are deformed and displaced by the other group of faults. The second group corresponds to the lamprophyre dikes, of mantelic origin, with an orientation oblique to the tunnel, and slightly oblique to the first group of fractures (strike, 310 – 330). They were formed during an extension event well evidenced by their irregular margins and flame structures into the granite. The margins of these dikes show several reactivations as strike slip faults. Geophysical data was acquired to characterise the fracture network of the surrounding volume within the FEBEX gallery. The geophysical data include new borehole logging such as Natural Gamma and Borehole GPR. The processing and integration of these different data sets indicates that the GPR record can provide images of a third set of fractures, which are probably fluid filled. This set of fractures is subparallel to the tunnel axis and appears to intersect older boreholes which are nearly perpendicular to the axis of the FEBEX gallery. No evidences for these fractures existed before the acquisition of the geophysical datasets. These identified new structures needed to be integrated within the fluid flow studies.</p>
<p>Achievements for the safety case: Detailed high resolution geophysical characterisation is mandatory in order to design realistic fluid flow models. The structural constraints provided by the geophysical imaging techniques are an asset for successful 3D model building.</p>
<p>References: Pérez-Estaún et al. (2006), Carbonell et al. (2007), Pérez-Estaún & Carbonell (2007).</p>

4.3.1a Study the nature of natural colloids generated from the fracture infill minerals in samples from the Grimsel test site: laboratory tests on colloid release rates from compacted bentonite.

Aim: Inorganic colloids can contribute to enhancement of radionuclide migration. Possible sources for inorganic colloids in groundwater in a granitic host rock are secondary alteration aluminosilicate minerals and notably clay colloids eroded from the bentonite barrier. Aim of the study is to identify possible colloidal mineral phases, which can be used to model colloid-mediated radionuclide migration and to quantify clay colloid release from compacted bentonite.

Type of work: Focus of INE activities in this WP was to study the nature of natural colloids generated from the fracture infill minerals in samples from the Grimsel test site (GTS). Characterisation of the < 2 µm fraction of crushed material was done by XRD. Studies on colloid generation from compacted bentonite were performed under stagnant or close to stagnant conditions at variable pH and ionic strength. Various experimental techniques and arrangements have been developed for those studies.

Participants: FZK-INE, CIEMAT.

State of the art before FUNMIG: Characterisation of colloids in granitic groundwater has been studied by Degueldre et al. (1996). They found mainly phyllosilicate and silica colloids.

Liu & Neretnieks (2006) suggested a 'zero order model' to describe the colloid generation from compacted bentonite for P.A. purposes. The criterion of colloid release is the critical coagulation concentration corresponding to 1 mmol/L Ca²⁺.

Main results (abstract): The analysis revealed the occurrence of non-expandable illite or mica (biotite) clay minerals. Unexpectedly, also smectite type expandable phases have been identified by XRD, showing that inorganic colloids found in earlier studies basically are derived from erosion of fracture filling minerals. In bore core experiments obtained from GTS a continuous release of such colloidal material is observed also at low groundwater velocities.

Colloid release rates from compacted bentonite under near stagnant conditions are determined by the compaction degree, pH and ionic strength of the groundwater. High compaction, high pH and low ionic strength increase the swelling pressure and thus the colloid release rates. As one should expect, the release rate dependence on geochemistry reflect colloid stability behaviour. The studies performed within FUNMIG clearly show that taking a certain Ca concentration as a colloid generation criterion does 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.

Achievements for the safety case: Improvement of knowledge on colloid generation from fracture filling material and compacted bentonite.

References: Degueldre et al. (1996), Liu & Neretnieks (2006).

4.3.1b Study of the bentonite colloid generation source term in realistic conditions

Aim: Study of the bentonite colloid generation source term in realistic conditions.
Type of work: Laboratory tests and in situ work.
Participants: CIEMAT, FZK-INE.
State of the art before FUNMIG: No data available on bentonite colloids under realistic conditions.
<p>Main results (abstract): Special cells for studying the generation of bentonite colloids from compacted bentonite in stagnant flow conditions were designed.</p> <p>The generation of bentonite colloids from compacted clay plugs, in contact with stagnant water was analysed as a function of (a) the density of the clay and (b) the groundwater chemistry. Results showed that the higher the clay dry density, the higher the quantity of colloids initially generated from the plugs. Colloid concentration increase rapidly when the clay is hydrated but a steady state is reached after approximately 2 months. Additionally, it has been observed that the water chemistry controls the stability, size and concentration of the generated colloids. Additional studies are needed to understand the effects of the type of the clay (main exchange ion) on the clay colloids generation, also by means of geochemical modelling. In principle Ca-homoionised clay did not form colloid in concentration much higher than the detection limit during the first 80 days of experiment. The presence of some Na in the exchange complex (20 %) completely changes the behaviour. ("As-received" FEBEX bentonite, for example, forms colloids in no negligible quantity). The analysis and modelling of these tests has been started. The importance of accounting for water/clay interactions has been evidenced.</p>
<p>Achievements for the safety case: Many parameters have been identified as relevant for colloid generation related to the clay nature and the chemistry of the groundwater. Another interesting parameters affecting colloid generation are the clay compaction density and the surface exposed to hydration (and consequent extrusion paths). Nevertheless to analyse the impact of colloid generation is necessary to account for mobility studies (see 4.3.2).</p>
References: Alonso et al. (2007b), Alonso et al. (2007c).

4.3.2a Mobility and stability of natural and bentonite colloids

Aim: Dynamic colloid transport study to evaluate their mobility in a granite fracture.
Type of work: Laboratory tests.
Participants: CIEMAT.
State of the art before FUNMIG: Lack of understanding on colloid filtration processes in fractures.
<p>Main results (abstract): Migration experiments in a granite fractured column, using low water flow rates trying to approach realistic natural conditions, were carried out with bentonite colloids. The objective was to quantify the filtration of colloids in the medium and to evidence the main factors affecting the retention, as well as possible experimental uncertainties, as a previous step to the analysis of radionuclide migration in presence of colloids. Results showed the breakthrough curves of bentonite colloids always presented an elution peak in a position very similar to that of conservative tracers but that their recovery critically depended on the colloid concentration and on the water flow rate. Additional experiments were carried out with synthetic colloids for studying the effects of colloid size.</p> <p>Even in conditions very favourable for colloids stability and mobility (e.g. Grimsel groundwater) retention of colloid in the rock has observed to be high in certain hydrodynamic conditions. Roughness effects are important for colloid retention. The quantification of colloid retention under conditions unfavourable to electrostatic attachment were analysed also by μPIXE.</p>
Achievements for the safety case: Even in conditions favourable for colloid stability and mobility (e.g. Grimsel water) bentonite colloids are extensively filtered in the fractures when the water flow is low (mL/h).
References: Missana et al. (2008b), Albarran et al. (2009), Alonso et al. (2006).

4.3.2b Development of a methodology to experimentally measure colloid diffusion coefficients in crystalline rocks

<p>Aim: To develop a methodology to experimentally measure apparent diffusion coefficients for colloids in crystalline rocks.</p>
<p>Type of work: Laboratory tests.</p>
<p>Participants: CIEMAT.</p>
<p>State of the art before FUNMIG: No experimental data available colloid diffusion. Lack of understanding on colloid filtration processes in fractures.</p>
<p>Main results (abstract): Diffusion coefficients of colloids in granite have been experimentally measured for the first time. Apparent diffusion coefficients for colloids were at least 3 order of magnitude smaller than those for radionuclides measured in similar conditions.</p> <p>Diffusion coefficients were measured for gold colloids of different size and for bentonite colloids. Small size dependence was observed for gold colloid diffusion.</p> <p>Results demonstrated that diffusion cannot be considered the main filtration mechanisms for colloids in a fracture.</p>
<p>Achievements for the safety case: Apparent diffusion coefficients for colloids experimentally measured are in the range of 10^{-17} m²/s.</p>
<p>References: Alonso et al. (2007a), Alonso et al. (2007d), Patelli et al. (2006).</p>

4.4.1a **Mock-up experiment, transport of HTO, Cl and Cs from the bentonite to granite: experiment design and first experimental results**

Aim: Mock-up experiment simulating the FEBEX configuration (granite+bentonite).
Type of work: Laboratory and mock-up tests.
Participants: CIEMAT, UDC.
State of the art before FUNMIG: Small quantity of radionuclide transport data in the presence of bentonite.
Main results (abstract): A large scale-migration experiment in granite in the presence of bentonite was designed and constructed. This experiment simulates the in situ FEBEX configuration, with a compacted bentonite plug in the centre, where the radionuclides are injected. The large Grimsel granite block was saturated with low mineralised water and, after its saturation, HTO, Cl and Cs were injected. Tracers' evolution in the reservoir is monitored. A previous modeling was carried to predict the radionuclide migration in the system and to plan the sampling at different distances from the bentonite. Dilution data are already available for Cs.
Achievements for the safety case: Determination of radionuclide diffusion coefficients under realistic conditions.
References: Samper et al. (2008a).

4.4.1b Transport of radionuclides (Pu, Eu, Sr and U) in granite fractures in the presence of bentonite colloids

Aim: Study of radionuclide migration in the presence of bentonite colloids. Mock-up experiments.
Type of work: Laboratory and mock-up tests.
Participants: CIEMAT.
State of the art before FUNMIG: Small quantity of radionuclide transport data in the presence of bentonite colloids.
<p>Main results (abstract): Column experiments with europium and plutonium in the presence of bentonite colloids were carried out at different flow rates and their recovery was analysed. Both elements presented high adsorption onto the colloids (> 80 %) thus the migration of colloids should affect their migration. A peak of Eu or Pu in the same position than the conservative tracers was observed, clearly indicating that migration of these radionuclides is mostly colloid-driven. The recovery of Pu adsorbed onto the colloids was approximately the expected considering the filtration of bentonite colloid in the medium, whereas the recovery of Eu was always lower. This probably indicates that, along the flow path, part of Eu desorbs from the colloids and is retained on the fracture walls. The transport of elements that present lower sorption onto the clay like strontium or uranium is being investigated. The transport behaviour of the less sorbing elements is also affected by the presence of colloids retained in the fracture.</p> <p>Sensitivity analysis to quantify the consequences of bentonite colloids generation on radionuclide releases from the near field were carried out by Cormenzana (ENRESA).</p>
<p>Achievements for the safety case: Model calculation showed that the presence of colloids could increase significantly (a factor 100) the release rates from the near field for strongly sorbing RNs (Th, Pu). Calculation was made considering high concentration in water of bentonite colloids (0.1 g/litre) and much higher sorption on colloids than in compacted bentonite (100 times). The effect of bentonite colloids on less sorbing elements (Cs) is much smaller (just a factor 2 of increase), and negligible for weakly sorbing or conservative RN. The irreversibility of sorption from colloids would increase the effects.</p>
References: Missana et al. (2006a), Missana et al. (2008b).

4.4.1c Scoping calculations of mock-up experiment and modelling of the first results

Aim: Develop improved numerical models of radionuclide transport and of the mass transfer from NF to FF under controlled conditions.

Type of work: Modelling laboratory and in situ experiments in granite blocks (mock up) (advection, diffusion, ionic exclusion will be considered), using very low flow rates.

Participants: CIEMAT, UDC.

State of the art before FUNMIG: Only "classical" diffusion models were used to determine diffusion parameters. In situ diffusion experiments were carried out with standard methodologies not totally representative of real conditions (e.g. large quantity of water in which tracer is dissolved).

Main results (abstract): Numerical modeling of radionuclide diffusion in clays and granite has been carried out. Numerical models have been performed for clay and granite. Numerical models have been developed which have been used to design and interpret a large-scale laboratory mock-up experiment in granite in collaboration with CIEMAT to study tracer migration at the bentonite/ granite interface and provide support for field investigations of FEBEX in situ test. Identifiability of effective diffusion and K_d for sorbing tracers has been evaluated.

Achievements for the safety case: 3D models of large-scale experiments provide reliable estimates of rock diffusion anisotropy. Numerical models overcome the limitations of analytical methods which cannot account for non-ideal effects such as sinter filters, gaps, and damaged zones. Interpretation of lab and in situ experiments and estimation with numerical models provides unbiased estimates of diffusion and retention parameters.

References: García-Gutiérrez et al. (2008), Samper et al. (2008b).

4.4.1d Experimental programme to understand colloids – radionuclide interactions and the effects of colloids on radionuclide migration

Motivation and aim: The inorganic colloid-mediated radionuclide transport still belongs to the uncertainties in the long-term safety of various repository concepts. Recent findings on colloid and radionuclide migration in laboratory and field experiments, however, reveal colloid and radionuclide retention even under colloid stabilising groundwater conditions (Geckeis et al. 2004, Missana et al. 2003). The 'reversibility' of the radionuclide-colloid binding is one of the critical parameters for the assessment of colloid relevance to radionuclide migration. Colloid attachment to mineral surfaces under various geochemical conditions another one. The underlying mechanisms are still not clear.

Type of work: The experimental programme combines (1) colloid migration studies in granite bore-cores (from the Grimsel test site) under low groundwater flow rates (2) reversibility studies on trivalent and tetravalent lanthanide/actinide clay colloid interaction and (3) microscopic studies on the colloid interaction with mineral surfaces (all those studies are ongoing and not completed).

Batch sorption studies in the conditions of transport experiments to evaluate the degree of retention of radionuclides onto colloids.

Participants: FZK-INE, CIEMAT.

State of the art before FUNMIG: In general it is found that colloid-bound actinides are mobile under low ionic strength, high pH conditions. Colloid migration has been found under those conditions, however, potential retention mechanisms have not been investigated systematically. Many studies have outlined the necessity to gain information on metal ion – colloid interaction.

Main results (abstract): Due to leakage problems, the bore core experiments are presently running. Results for colloid migration and recovery as a function of groundwater flow rate are expected until the end of the project.

Reversibility studies were performed for Eu(III) and Th(IV) interaction with clay colloids in Grimsel groundwater. The time-dependent desorption of Eu(III) from colloids studied by addition of humic acid as a competing ligand point to the establishment of equilibria. 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 reason for the strong kinetics in Th(IV) binding to clay colloid surfaces is not clear and presently under investigation. The question to be answered is whether new solid Th(IV) phases have formed at the colloid surface or whether the surface complexation equilibria for tetravalent actinide ions are extremely slow. Interaction of carboxylated fluorescent latex colloids with natural Grimsel granodiorite and some of its component minerals is studied by fluorescence microscopy. Experiments show sorption only at pH values up to the point of zero charge of the minerals. Presence of polyvalent cations increases colloid attachment to minerals. Colloid sorption takes place predominantly at mineral edges.

Achievements for the safety case: Improvement of knowledge on reversibility of actinide – colloid interaction and colloid-rock interaction.

References: Geckeis et al. (2004), Missana et al. (2003).

4.4.2a Kinetics of complexation/sorption of humic substances to cations

Motivation and aim: Humic substances are rather complex. They may coil and shield their active groups at high ionic strengths while at lower ionic strengths they open up and show their active groups. We therefore tried to keep the ionic strength as low as possible, allowing all active groups to possibly contribute to the complexation to cations.

Type of work: Laboratory.

Participants: Pooja Yadav, Thomas Müller, Mats Jansson, all Royal Inst. of Technology, KTH.

State of the art before FUNMIG: Very little on the rate constants for sorbing/complexing humic substances to cations has been found in the literature.

Main results (abstract): Batch sorption experiments have been performed to study the kinetics of the complexation/sorption of cations to humic substances. With the methods used it was not possible to get sufficient time resolution to see any transient part of the complexation/sorption, indicating that the complexation is very fast, close to diffusion controlled.

Achievements for the safety case: Sorption/complexation of humic substances to cations is very fast. The rates are or are near to being diffusion controlled.

4.4.2b Study of the retention properties of the Czech granitic reference samples

Motivation and aim: Quantification of retention and migration processes of PA relevant radionuclides in Czech granitic rock samples using different approaches (batch, column and diffusion experiments, RBS, autoradiography).						
Type of work: Experimental, modelling.						
Participants: NRI-REZ.						
State of the art before FUNMIG: Only few basic data on sorption; RBS was not used before for sorption/diffusion experiments on geologic samples, modelling of diffusion was not used.						
Main results (abstract): Batch sorption experiments were performed using ^{125}I , ^{137}Cs , ^{85}Sr and $^{152,154}\text{Eu}$ to derive R_d and/or K_d on either crushed samples or rock coupons (Havlova et al. 2007b and c). Sorption of Cs and Sr depended on grain size: coarser fraction and coupons exhibit lower sorption whereas sorption of Eu was independent on grain size. Cs sorption (diffusion) into rock coupons continued even in long-period time scale, most probable due to binding of radionuclide to inner sorption sites in sheet silicate microstructure and to migration into mineral grain microcracks, as it was proved in RBS study. Diffusion experiments with ^3H , ^{125}I , ^{134}Cs , ^{85}Sr and $^{152,154}\text{Eu}$ continued using reference samples. Experimental diffusion coefficients D_a were determined for non-sorbing radionuclides and modelled for Cs (GOLDSIM diffusion module, invented in NRI/CTU).						
Radionuclide	Rock type	α	D_a [$\text{m}^2\text{-s}^{-1}$]	D_e [$\text{m}^2\text{-s}^{-1}$]	F_r	G
^3H	Tonalite	8×10^{-4}	6.7×10^{-11}	5.36×10^{-14}	2.23×10^{-5}	0.01
	Gabro	1.8×10^{-3}	8.3×10^{-11}	1.49×10^{-13}	6.23×10^{-5}	0.035
^{125}I	Granite	8×10^{-4}	9.0×10^{-11}	7.2×10^{-14}	3×10^{-5}	0.0375
	Diorite	2×10^{-3}	3×10^{-12}	3×10^{-14}	2.5×10^{-6}	0.00125
^{125}Cs	Granite	83				
	Modelled	160	5.3×10^{-14}	8.49×10^{-12}	4.5×10^{-3}	2.34
$^{152,154}\text{Eu}$	Tonalite		No breakthrough			
^{85}Sr	Tonalite	0.27	No breakthrough			
New microscale methodologies invented: RBS study with non-active Cs diffusion was performed to quantify D_a and distribution in the rock samples. Cs sorption/migration on the granitic rock surface follows different pattern according to mineral grain distribution. Cs was sorbed on the surface of mica and then decreased rapidly and diffusing into feldspar mineral grains: Cs concentration decreased in gradual diffusion profile. Sorbed Cs distribution on mineral grains was studied using modern autoradiography method (Image plating). Outcome of the project: above expectation (mainly due to methodology input).						
Achievements for the safety case: Advanced methodology to study micro and medium scale radionuclide distribution, was invented for Czech rock samples and groundwater.						
References: Havlová et al. (2007).						

4.5.1a Process understanding under present hydrological and hydrogeochemical conditions

<p>Motivation and aim: Large data set collected and analysed in association with the Swedish site investigation. Better understanding of natural processes of interest for SA.</p>
<p>Type of work: Real site data analysis to support SA.</p>
<p>Participants: GEOPOINT, FZK-INE; Associated Groups.</p>
<p>State of the art before FUNMIG: -</p>
<p>Main results (abstract): Processes determining the groundwater system in crystalline rock are described, based on site investigations within the Swedish programme for constructing and operating a HLWR in such a rock formation. Two sites are investigated: Forsmak and Laxemar. The present analysis builds on Laaksoharju et al. (2007a), reflecting some increase in the data base and considerable progress in interpretation of data and understanding of the relevant processes. There is an improved description and understanding of issues related to groundwater origin and evolution, interactions of surface/deep groundwater systems, redox fronts and U and Mn values, as well as microbes, gases and colloids. Mathematical modelling improved with respect to a) redox conditions, b) uncertainty analyses of mixing proportions and mass balance deviations, c) integration of hydrochemical data with mineralogical and microbial data, and d) to the role of monosulphides. In addition, M3 issues as proper selection of end-members and variables in the modelling were addressed, and also issues related to the drilling impact study (DIS) and the use of electrical conductivity to address the spatial variability issue. There is also (i) an improvement in the conceptual modelling, including 2D and 3D large- and small-scale conceptualisation approaches, (ii) a closer and better integration with hydrogeology and (iii) increasing understanding concerning the application and impact for PA.</p>
<p>Achievements for the safety case: The collected values and the process understanding can be used for: 1) input parameter values in calculating long-term repository safety, and 2) to understand the present undisturbed hydrogeochemical conditions and how these conditions will change in the future.</p>
<p>References: Laaksoharju et al. (2008), Laaksoharju et al. (2007a), Laaksoharju et al. (2007b), SKB (2005a), SKB (2005b), SKB (2006b), SKB (2006c).</p>

4.5.1b **To study freezing processes in crystalline bedrock: effect of recent glacial events on the naturally occurring uranium**

Motivation and aim: Information was gathered from many scientific journals world wide, and a report about their relevant content was gathered into a form of a report. A general understanding of the freezing processes was achieved. Effect of recent glacial events on the naturally occurring uranium were studied with leaching experiments on uranium rich rock samples from Palmottu natural analogue site in south-west Finland.

Type of work: Writing a report about freezing processes in crystalline rock during permafrost.

Participants: HUT, Mira Markovaara-Koivisto, Klaus Einsalo.

State of the art before FUNMIG: Freezing processes have been studied in many countries world wide, data is scattered.

Main results (abstract): Knowledge of freezing processes in crystalline rock have existed, but it has been scattered. This report gathered the relevant information considering especially crystalline bedrock, deep depths and salty environments.

Effects of recent glacial events on the naturally occurring uranium in bedrock was studied with sequential leaching experiments, and by studying the uranium and thorium isotopes in the separated fractions.

The plan was to study freezing processes in crystalline bedrock by a vast literature survey. Literature was abundant and relevant data for nuclear waste disposal conditions was found. Results of the sequential leaching experiments of naturally uranium rich rock samples were interpreted but the existing uranium phases (primary and secondary) and thorium phases degrade the reliability of the interpretations.

Achievements for the safety case: Better understanding of the freezing processes of crystalline bedrock deep in the repository level.

4.5.1c Development of integration of isotope methodology into groundwater flow modelling – utilisation of U isotopes

<p>Motivation and aim: Development of integration of isotope methodology into groundwater flow modelling – utilisation of U isotopes.</p>
<p>Type of work: Data analysis and literature study.</p>
<p>Participants: HU, FZK-INE, GEOPOINT.</p>
<p>State of the art before FUNMIG: Systematic study on U isotope system in glaciated terrain is missing.</p>
<p>Main results (abstract): Use of U isotope system as an indicator for hydrodynamic and hydrogeochemical processes in glaciated terrain is discussed. U isotope data from site investigations in Finland and Sweden and data from <i>in situ</i> migration experiments in Äspö HRL were utilised. The role of α-recoil in the formation of the $^{234}\text{U}/^{238}\text{U}$ activity ratio in groundwater was clarified. Following conclusions were drawn from the work: i) groundwater conditions affect the $^{234}\text{U}/^{238}\text{U}$ activity ratio, ii) groundwater flow rate (water-rock contact time) plays a role and iii) U isotope system has not been utilised to its full power.</p> <p>The task was not in the original plan. Resources allocated to Task 4.1.1 were moved to this task to carry out the work.</p>
<p>Achievements for the safety case: Increased understanding of the behavior of U isotopes helps to develop models for simulating future groundwater system.</p>
<p>References: Suksi et al. (2006).</p>

4.6.1 Retention caused by the matrix diffusion

Motivation and aim: Task aims to understanding of the retention caused by matrix diffusion in heterogeneous fractured rock under varying flow conditions and migration distances. Matrix diffusion is studied by modelling because this task should also serve needs of the PA.

Type of work: RTD/Innovation activities.

Participants: VTT.

State of the art before FUNMIG: Heterogeneous properties along the flow paths have been studied theoretically and applied in the modelling of the tracer tests. However, heterogeneity is not taken into account in the PA modelling.

Main results (abstract): Modelling of the retention properties in fractured rock over different scales requires that characteristic behaviour of the processes is well understood. Retention by matrix diffusion is very sensitive to flow distribution. Therefore, it seems that it is favourable to take into account the multi-scale structure of the fractured rock directly in the modelling approach, for example, like fracture network modelling does.

Present work has been able to provides tools for conceptualisation and modelling of the heterogeneity that can be applied in the PA geosphere retention modelling for fractured rock.

Achievements for the safety case: Supports more realistic modelling of the geosphere retention in PA.

References: Poteri (2006), Poteri (2008).

4.6.2 Sorption upscaling

<p>Aim: Development of methodologies to account for the heterogeneity in radionuclide sorption onto granite.</p>
<p>Type of work: Experimental. Application of μ Particle induced X-ray emission (μPIXE).</p>
<p>Participants: CIEMAT.</p>
<p>State of the art before FUNMIG: Most of K_d values are determined with batch experiments in crushed solids.</p>
<p>Main results (abstract): The objective of the work proposed is to analyse experimentally the effects of the crystalline rock heterogeneities on the sorption of several radionuclides. In this study, sorption experiments are performed onto small pieces of granite, previously characterised, to obtain surface normalised distribution coefficients (K_a) determined on every single mineral and the bulk distribution coefficient K_d. The most reactive area and the quantification of sorption in these areas are evaluated by the nuclear ion beam technique micro-Particle Induced X-Ray Emission (μPIXE). The methodology has been applied to study the retention behavior of Cs(I), U(VI), Eu(III) and Se(IV) on different granites. The physical characteristics, pore structure and porosity, of the samples were also taken into account.</p> <p>A method to improve the quantitative evaluation of the elements retention and K_d determination within different mineral areas has been developed. It included the improvement of both the data acquisition and analysis. To complete the quantification and the verification of the methodology, sorption tests in a wider range of conditions are needed.</p>
<p>Achievements for the safety case: K_d values determined in the material not previously crushed are more realistic. The effects of heterogeneity in K_d values can be accounted for.</p>
<p>References: Missana et al. (2006a), Missana et al. (2006b).</p>

4.6.3a Development of a model for implementation of multicomponent reactive transport in PA (upscaling and effective modelling of reactive transport in heterogeneous media)

Aim: The main objective of the UPC-CSIC contribution to WP4.6 is to develop a methodology that explains and correctly models the transport of solutes that react amongst themselves and with the solid matrix in heterogeneous media with temporally fluctuating boundary conditions.

Type of work: Modelling.

Participants: UPC and CSIC.

State of the art before FUNMIG: Performance assessment (PA) of radioactive waste repositories in geological media requires the sound understanding of reaction and transport processes radionuclides undergo in heterogeneous environments. This understanding is complicated: On one hand, radionuclides 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 dependence of transport and reaction phenomena. While this is widely acknowledged, current reactive transport models do not take into account the complicated dynamics inherent to a heterogeneous reactive transport system.

Main results (abstract):

Reaction, Transport and Heterogeneity: A methodology for the analytical solution for reaction rates for multispecies equilibrium and non-equilibrium reactive transport in heterogeneous media has been developed. The impact of heterogeneity on reaction rates has been quantified. Mixing and spreading in geological media has been quantified. Effective reaction and transport.

Numerical reactive transport code: A Fortran 90 tool using object-oriented concepts that simulates complex geochemical processes has been developed (CHEPROO). 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 has been implemented implemented and coupled with CHEPROO.

Achievements for the safety case: The quantification of effective reaction and transport in heterogeneous media is a pre-requisite for the realistic large scale modelling and thus prediction of the fate of radionuclides in geological media. The developed concepts and modelling frameworks are implemented in numerical PA tools.

References (out of about 30 journal publications): Bea et al. (2006), Dentz & Carrera (2007), Dentz & Tartakovsky (2008), Dentz & Castro (2009), De Simoni et al. (2007), Donado et al. (2009).

4.6.3b Analysis of modelling methodologies for upscaling transport parameters in porous fracture system (abstraction of transport processes to performance assessment analysis)

<p>Motivation and aim: Performance assessment analysis requires easy-to-use transport models of radionuclide migration. Upscaling encompasses the methods that transfer small-scale information to the scale used by a simplified transport model. The work conducted by the UPV is devoted to develop and evaluate upscaling methodologies for radionuclide transport.</p>
<p>Type of work: We evaluate the advantages/limitations of upscaling through performance assessment exercises developed in the context of underground radioactive repositories.</p>
<p>Participants: UPV: D. Fernández-García, G. Llerar-Meza, J. Gómez-Hernández.</p>
<p>State of the art before FUNMIG: Although upscaling of hydraulic conductivity in groundwater problems has been extensively addressed in the literature and reviewed in several papers and books, the impact of upscaling on the evolution of a solute plume is still largely unknown. The problem of upscaling solute transport stems from the fact that the classical advection-dispersion equation is not always the best choice to characterise solute transport behavior at large scales. Several models have been proposed in the literature to overcome this problem. Yet, the application of these models to real problems has not been adequately addressed and their advantages/limitations never evaluated.</p>
<p>Main results (abstract): We have evaluated the use of dual-domain models for upscaling:</p> <ol style="list-style-type: none"> 1) We have developed a methodology to upscale (homogenise) solute transport. The system is conceptualised as being formed by two distinct domains. A highly conductive region in which transport is mostly advective-dispersive, and a less conductive region in which mass particles can get trapped and eventually released. The latter mechanism is crucial to characterise the movement of slow mass particles. 2) We have developed a new Random Walk Particle Tracking Methodology to efficiently simulate transport defined over a large support scale. The large scale model represents the simplified transport model obtained by upscaling. 3) We have evaluated the advantages/limitations of two upscaled transport models through performance assessment exercises: (i) The standard macrodispersive transport model, and (ii) the dual-domain transport model. Results demonstrate that the dual-domain transport model can capture slow mass particles more adequately. In comparison with the original planning, the work conducted should be considered as "above expectation". The original planning only considers task (4).
<p>Achievements for the safety case: The upscaling methodology we have developed provides an efficient tool to simplify the transport problem involved in the safety case.</p>
<p>References: Salamon et al. (2006a), Fernández-García et al. (2007), Salamon et al. (2006b), Fernández-García et al. (2008), Cassiraga et al. (2005), Sánchez-Vila et al. (2009).</p>

5.1.1 Geo-monitoring of groundwater under undisturbed conditions

Motivation and aim: Development of a geo-monitoring unit to collect undisturbed water samples and analysis of colloid concentration and groundwater data in existing boreholes.

Type of work: Device development, groundwater sampling, water analysis in the lab, in situ water probing and qualification of the method by comparison with in situ data.

Participants: FZK-INE, GRS, NRI-REZ.

State of the art before FUNMIG: There are no previous investigations on this subject published.

Main results (abstract): A borehole ground water sampling system and a mobile laser-induced breakdown detection (LIBD) equipment for colloid detection combined with a geo-monitoring unit have been applied to characterise the natural background colloid concentration in ground waters of the Ruprechtov natural analogue site (Czech Republic). Ground water has been sampled using steel cylinders. To minimise artifacts during ground water sampling the contact to atmospheric oxygen has been excluded. The ground water samples collected in this way are transported to the laboratory where they have been connected to a series of flow-through detection cells. Argon gas is used to press the ground water through these detection cells for colloid analysis (LIBD), pH, Eh, electrical conductivity and oxygen content. After the above mentioned analysis additional samples are taken for chemical analysis by ICP-AES, ICP-MS, IC- and DOC-detection.

The investigations demonstrate that the mobile LIBD with a geo-monitoring unit and a borehole sampling system allows the characterisation of natural ground water and colloids under in situ conditions. In cases where on-site analysis is not possible, a remote borehole sampling technique with steel cylinders and the subsequent sample characterisation with in-line LIBD detection of colloids and measurement of electrical conductivity, pH, Eh is found to provide reasonable data. For this strategy it is shown that the genuine redox conditions of samples can be maintained in most cases with minimal access of atmosphere oxygen.

Achievements for the safety case: This new method improves quality of and therefore confidence in in situ colloid analyses to be used for site characterisation and field experiments in a safety case.

References: Hauser et al. (2007).

5.1.2 Interpretation of results with regard to colloid stability in natural systems

<p>Motivation and aim: Increase knowledge under which conditions colloids can exist in natural systems.</p>
<p>Type of work: Compilation of colloid concentrations and size distributions at different sites and information from laboratory experiments/Evaluation and interpretation of data.</p>
<p>Participants: FZK-INE, NRI-REZ, GRS.</p>
<p>State of the art before FUNMIG: Analyses of colloids by conventional sampling at Ruprechtov site showed formation of iron oxide colloids because of contamination with atmospheric oxygen. First test of the apparatus was performed.</p>
<p>Main results (abstract): Colloid analysis has been performed in groundwater samples collected at a site near Ruprechtov, Czech Republic. The investigations demonstrate that the mobile LIBD with a geo-monitoring unit and a borehole sampling system allows the sensitive characterisation of natural ground water and colloids under in situ conditions. In cases where on-site analysis is not possible, a remote borehole sampling technique with steel cylinders and the subsequent sample characterisation with inline LIBD detection of colloids and measurement of electrical conductivity, pH, Eh is found to provide reasonable data. For this strategy it is shown that the genuine redox conditions of samples can be maintained in most cases with minimal access of atmosphere oxygen.</p> <p>The data are compared with data from in situ measurements in various groundwaters in the underground laboratories Äspö, Sweden, Grimsel, Switzerland and groundwater from the site investigation programme at Forsmark and Laxemar, Sweden. Our data obtained in in situ- and laboratory- measurements point out that the relevant natural colloid concentration can be strongly limited by the ionic strength of the natural ground water. A critical value of 100 mmol/l for the ionic strength is suggested. Above this limit natural groundwater colloids appear to be rather unstable. The quantitative role of dissolved natural organic matter as a colloid stabilising component is still unclear and requires further studies in this context. The ionic strength of the Ruprechtov ground water samples is still fairly below this limit ($I < 100$ mmol/l) so that the relatively high colloid concentrations are comprehensible.</p>
<p>Achievements for the safety case: These analyses complements information from various laboratory- and field- investigations on formation and stability of colloids in geochemically different natural systems.</p>
<p>References: Hauser et al. (2007).</p>

5.2.1 Natural sample characterisation by μ -spectroscopical multi method strategy

<p>Motivation and aim: Characterisation of immobile uranium phases and identification of immobilisation processes</p>
<p>Type of work: Experimental. Development and application of a X-ray techniques with high lateral resolution for U speciation in natural analogue samples.</p>
<p>Participants: FZK-INE (M.A. Denecke)</p>
<p>State of the art before FUNMIG: Results entail the first published 3D μ-XRF and μ-XANES/μ-EXAFS investigation and one of the first scanning, combined μ-XRF/μ-XRD studies published.</p>
<p>Main results (abstract): We investigated uranium-rich tertiary sediment originating from an aquiferous clay/lignite horizon with an anomalously high uranium concentration found in a nuclear waste disposal natural analog site located in the north-west of the Czech Republic using micro-focused X-ray techniques. The overall aim was to assess immobilisation mechanisms leading to actinide enrichment.</p> <p>Results from spatially resolved μ-XRF, μ-XAFS studies provided information allowing us to formulate a hypothesis for one mechanism of U immobilisation during diagenesis of the sediment involving arsenopyrite, AsFeS, as reducing agent. In this mechanism U dissolved from nearby and underlying weathered granite is groundwater-mobile as a U(VI) species. The U(VI) migrates to the anoxic clay/lignite horizon and is reduced on arsenopyrite in the sediment, leading to precipitation of less-soluble U(IV). The arsenopyrite has been identified from its As K-edge X-ray absorption near edge structure (XANES) signature and the observed linear dependence between Fe and As(0) distributions obtained from μ-XRF measurements on As-rich coatings on the surface of sediment framboidal Fe nodules. Combined μ-XRF and μ-XRD investigations of the same uranium-rich tertiary sediment did not secure evidence of arsenopyrite in the sediment from its diffraction pattern. However, these did show pyrite and siderite to be found in the same sample, indicating that the pH of the sediment environment during diagenesis must have been neutral. This allowed us to refine our hypothesis for the mechanism of uranium immobilisation.</p>
<p>Achievements for the safety case: One of the processes leading to U immobilisation in the natural system on a long term scale was successfully identified.</p>
<p>References: Noseck et al. (2008a), Denecke et al. (2005), Denecke et al. (2007a), Denecke et al. (2007b), Denecke et al. (2008).</p>

5.2.2 U(IV)/U(VI) separation

<p>Motivation and aim: The redox state of uranium in sediments from Ruprechtov site is a crucial parameter to fully understand the behaviour of uranium in this natural system. The aim is to quantify the amount of uranium in different oxidation states and to get information about the time frame of formation and long-term stability of the respective phases.</p>
<p>Type of work: Adaption of the U(IV)/U(VI) separation method to samples from Ruprechtov site, determination of the uranium amount and $^{234}\text{U}/^{238}\text{U}$ activity ratio in the different oxidation states and comparison with results from other methods.</p>
<p>Participants: UH, GRS.</p>
<p>State of the art before FUNMIG: By SEM EDX and microprobe a number of U(IV) minerals and no U(VI)-bearing phases had been observed in U-enriched sediments from Ruprechtov site.</p>
<p>Main results (abstract): A method for separation of uranium (IV) and uranium (VI) has been further developed and applied to sediment samples from the uranium-enriched tertiary clay horizon at Ruprechtov site. The method is based on dissolution of U(IV) and U(VI) phases simultaneously by extracting the sample material in anoxic conditions with a mixture of 4 M HCl and 0.03 M HF under Ar atmosphere. Separation between U(IV) and U(VI) is achieved by anion exchange columns.</p> <p>The results show, that both forms U(IV) and U(VI) exist in the tertiary clay horizon. The $^{234}\text{U}/^{238}\text{U}$ activity ratio significantly differs between the forms with values below unity between 0.45 and 0.91 in the U(IV) phase and values above unity between 1.26 and 3.37 in the U(VI) phase. It was shown that the major part of U occurs in the tetravalent state, in agreement with results from spectroscopic methods. It was established that the U(IV) phase remained stable over geological times under the reducing conditions in the clay/lignite horizon. Additionally, an easier accessible fraction of U(VI) was identified in the clay/lignite horizon, which was formed more recently.</p> <p>The comparative analyses of $^{234}\text{U}/^{238}\text{U}$ activity ratios in extracts from a sequential extraction applied to neighboured samples verified the method by confirming the results, i.e. that the major uranium fraction is found in steps 4 and 5 expected to represent U(IV) redox state with similar ratios clearly below 1 and easily accessible (hexavalent) uranium in steps 1 and 2 with values significantly above 1.</p> <p>These results also agree well with those from SEM-EDX and μ-XANES and μ-EXAFS, which identified uraninite and U(IV)-bearing phosphate (or sulphate) minerals like ningyoite in hot spots found in the same horizon. The results strongly support the assumptions for the main uranium enrichment scenario at this natural site.</p>
<p>Achievements for the safety case: The results contribute to the understanding of the behaviour of uranium in a complex natural system over very long time scales.</p>
<p>References: Noseck et al. (2008a), Noseck et al. (2009b).</p>

5.2.3 Extraction experiments

<p>Motivation and aim: Identification and quantification of uranium in different immobile phases in sediments from Ruprechtov site.</p>
<p>Type of work: Development of suitable (sequential) extraction procedures, application to different sediment samples and comparison with other information (especially from geochemical and mineralogical analyses).</p>
<p>Participants: NRI-Rez.</p>
<p>State of the art before FUNMIG: Only previously published extraction procedures were used for studying U forms. No comparison with other methods (e.g. μ-XAFS, U(IV)/U(VI) separation) was done.</p>
<p>Main results (abstract): The adjusted sequential extraction (SE) scheme was applied to Ruprechtov samples of different origin (6 boreholes, different depths, different rock types – kaolinised granite/ Tertiary argillised clay). The SE scheme consists of the following steps:</p> <ol style="list-style-type: none"> 1. U bound on exchangeable sites (leaching with $MgCl_2$) 2. U bound on carbonates (leaching with ammonium acetate with acetic acid) 3. U bound to Fe/Mn oxides (leaching with hydroxylaminehydrochloride in acetic acid) 4. U bound onto organic matter/in reduced form (using H_2O_2 and HNO_3) 5. U in residuum (using boiling with HNO_3) <p>In Tertiary clay samples U was found to be mainly present in reduced form. This form fraction also arises with increasing content of TOC within the sediment however the direct dependence of U on organic matter content could not be shown. In granitic samples carbonates and/or aluminosilicates played a more important role in the U distribution.</p> <p>Extended element analyses (Na, K, S, Fe, As, P) of SE leachates were accomplished. Cluster analyses of these results was used for identifying possible correlations between elements and for comparing those with previous correlations derived from μ-XRF and μ-XAFS investigations. According to the SE cluster analysis P, As and U can be assigned into one group. Fe and S were separated from U, i.e. there was no direct dependence of U on Fe and S identified. K and Na were mainly associated with residual minerals.</p> <p>These analyses underpin the results obtained from microscopic methods, that U immobilisation is caused by As(0), i.e. on arsenopyrite layers where U(VI) from groundwater was reduced to U(IV) being bound into newly formed phosphate minerals (ningyoite). Phosphate is released by microbial degradation of organic matter on the site.</p>
<p>Achievements for the safety case: The quantification and characterisation of uranium in different chemical forms in the sediment, contributes to the understanding of the main immobilisation processes of U in the complex natural system.</p>
<p>References: Denecke & Havlová (2007), Havlová et al. (2007b), Havlová et al. (2006).</p>

5.2.4 Uranium desorption experiments

Motivation and aim: Quantification of easily accessible uranium in sediments from Ruprechtov site.						
Type of work: Determination of exchangeable uranium by isotope exchange with ^{233}U /interpretation of results obtained by different methods.						
Participants: NRI-REZ, CTU (AG).						
State of the art before FUNMIG: Only week studies were performed and limited information about interaction of U(VI) with natural clay samples containing uranium existed.						
Main results (abstract): The isotopic exchange tests with ^{233}U were used to compare the determined amount of exchangeable uranium (U_{ex}) with the amount obtained in the first two steps of sequential leaching (SE) tests. The distribution of ^{233}U was determined using liquid scintillation counting, evaluation of concentration changes of natural uranium during the experiments was based on determination by means of ICP-MS. Evaluation of equilibrium batch experiments (4 weeks contact with modelled seepage water) was performed using a previously presented method. The phase ratio V/m did not significantly affect the U_{ex} values. The results of U_{ex} determination was for most samples in a good comparison with results of the first two steps of sequential leaching: (i) 1M MgCl_2 , 1 hour, pH 7; 1M $\text{NaCH}_2\text{COOH} + \text{CH}_3\text{COOH}$, 5 hours, pH 4.8). The influence of mineralogical composition of rock material on both total uranium content (U-total) and its exchangeable portion is significant.						
Borehole	Real depth [m]	U_{ex} [mg/kg]	SE(1+2) [mg/kgw]	equil. pH	U-tot [mg/kg]	
NA10	15.40	18 ± 3.8	17.5	7.9	23	Gr
NA11	16.28	29 ± 2.5	39	8.5	94	Cl.
NA11	38.08	10 ± 2	7.15	8.2	39	Cl.
NA13	46.37	134 ± 12	74	2.6	212	Cl.
NA14	51,72	325 ± 48	70.5	2.6	724	Cl.
NA15	12,68	3.3 ± 4	22.4	8.5	55	Cl.
NA15	30.97	7.4 ± 4	33.6	8.2	62	Gr
<i>Gr</i> = granitic samples (quartz, biotite, feldspar), <i>Cl.</i> = clay samples (quartz, illite, clay minerals, feldspar).						
In experiments with the two samples NA13 and NA14 pH dropped rapidly due to the significant content of sulphates, the subsequent self-leaching caused in this cases high values of U_{ex} , which can not be compared to SE results.						
Achievements for the safety case: An independent method for determination of accessible uranium by ^{233}U was successfully verified by comparison with sequential extraction tests and showed that the amount of exchangeable U minerals in sedimentary samples increases with increasing content of clay minerals.						
References: Sachs et al. (2004b), Havlová et al. (2006).						

5.2.5 Uranium adsorption experiments

Motivation and aim: Characterisation of the sorption behaviour of uranium on tertiary sediments from Ruprechtov site.																													
Type of work: Batch adsorption experiments with uranium in groundwater/sediment systems from Ruprechtov site.																													
Participants: CTU (AG), NRI-Rez.																													
State of the art before FUNMIG: Only few studies were performed before with limited information about U sorption on natural clay samples from Ruprechtov site.																													
<p>Main results (abstract): The isotopic exchange tests with ^{233}U were used to compare results of exchangeable uranium (U_{ex}) determination with the results of the first steps of standardised sequential leaching tests. U_{ex} amount, found with ^{233}U experiment, reached almost the same values as the sum of the first two steps (U bound on exchangeable sites and on carbonates).</p> <p>The variability of rock material (granite/clay samples) from the site caused variability in uranium release/uptake behaviour in batch tests (artificial groundwater used). The decrease of K_d values, determined with the use of ^{233}U as a spike, with increasing values of initial concentration of uranium (C_{init}) in the liquid phase reflects the non-linear shape of the equilibrium isotherm.</p> <p>The table shows examples of such dependences (K_ds in l/kg):</p> <p>Sample: Borehole NA11; depth 16.63 m; U_{ex}: 29 ± 2.5 mg/kg ; U-total: 94 mg/kg; contact time: 4 weeks</p> <table border="1"> <thead> <tr> <th>C_{init} [mol/L]</th> <th>V/m [l/kg]</th> <th>400</th> <th>100</th> <th>20</th> </tr> </thead> <tbody> <tr> <td>1×10^{-7}</td> <td>K_d:</td> <td>30000</td> <td>22000</td> <td>1900</td> </tr> <tr> <td>1×10^{-6}</td> <td></td> <td>24000</td> <td>6060</td> <td>3470</td> </tr> <tr> <td>6×10^{-6}</td> <td></td> <td>7400</td> <td>4630</td> <td>1150</td> </tr> <tr> <td>2×10^{-5}</td> <td></td> <td>2940</td> <td>1010</td> <td>638</td> </tr> </tbody> </table> <p>In systems, in which the solid phase contains known amount of the exchangeable species (here U_{ex}), it is possible to convert a set of measured K_d data into the functional dependence of the solid phase concentration q on the liquid phase concentration C by means of simple balance relations. In the equilibrium state the dependence represents the equilibrium (sorption) isotherm. In our study this transformation was performed for four different samples.</p> <p>The transformed isotherms showed a significant dependence on the phase ratio (V/m) values. This fact was explained by changes in liquid phase composition caused by dissolution of mineral phases. The modelling of changes in solution of liquid phase during batch experiments performed using PHREEQC supported this conclusion.</p>					C_{init} [mol/L]	V/m [l/kg]	400	100	20	1×10^{-7}	K_d :	30000	22000	1900	1×10^{-6}		24000	6060	3470	6×10^{-6}		7400	4630	1150	2×10^{-5}		2940	1010	638
C_{init} [mol/L]	V/m [l/kg]	400	100	20																									
1×10^{-7}	K_d :	30000	22000	1900																									
1×10^{-6}		24000	6060	3470																									
6×10^{-6}		7400	4630	1150																									
2×10^{-5}		2940	1010	638																									
Achievements for the safety case: K_d values for U sorption on clay sediments was found to be directly dependent on V/m value and indirectly on U concentration in solution; the mineralogical composition of samples (granite, clay) also play a role in U uptake.																													
References: Havlová et al. (2006).																													

5.3.1 Isotope geochemical characterisation of Ruprechtov site

<p>Motivation and aim: The aim is to characterise hydrogeological flow pattern and hydrochemical conditions, in particular carbon chemistry to better understand the behavior of organic matter in a sedimentary system with high DOC content.</p>
<p>Type of work: Compilation of geochemical and isotope data, update of the hydrogeological flow regime at the site and interpretation of all isotope data with emphasis on carbon chemistry including microbial degradation of SOC.</p>
<p>Participants: GRS, NRI-REZ, FZK-INE.</p>
<p>State of the art before FUNMIG: Analyses of ^2H and ^{18}O in a number of boreholes and derived from that a first description of the hydrogeological flow pattern. As well as some analyses of ^{13}C and ^{14}C isotopes were available.</p>
<p>Main results (abstract): All measured stable isotope data from groundwater wells at Ruprechtov natural analogue site are evaluated with respect to the hydrogeological flow regime in the Tertiary sediments close to the clay/lignite layers and especially to the behaviour of carbon in the system. Differences in stable isotope data indicate two different infiltration areas in the outcropping granites in the western part as a source for water in clay/lignite layers in the middle and north and another in the southern part as source for the clay lignite layers in the eastern part of the investigation area. Differences in signatures in the northern part indicate very local connections probably via fault zones of the water system in the underlying granite and the tertiary sediments.</p> <p>Analyses of Carbon isotopes in DOC and DIC in additional wells and ^{34}S isotope analyses in selected wells have been performed. Based on the conceptual model of the hydrogeological flow regime, the data for $\delta^{13}\text{C}$ and ^{14}C in DIC and DOC as well as $\delta^{34}\text{S}$ in dissolved sulphate were evaluated. The groundwater ages calculated from carbon isotope data are unexpectedly high which is caused by reactions of carbon compounds. A lot of results show that DOC and DIC formation by microbial degradation of sedimentary organic matter in the so-called clay/lignite horizon are one important reaction. It is underpinned by the increase of biogenic DIC and phosphate with increasing DOC concentration and the increase of $\delta^{34}\text{S}$ in water from the clay/lignite layers compared to water from granite in the infiltration areas. Enrichment factor is about 13 ‰, which is low but similar values are observed at other sites. ^{14}C values in DOC are difficult to interpret due to contamination of DOC in two water wells.</p> <p>The very low DOC concentrations of app. 5 mg C/l in the clay/lignite horizon with an organic matter content up to 50 % C is a strong difference compared to the situation at Gorleben site, where microbial degradation of lignite material also acts as a source for DOC with resulting concentrations up to 200 mg C/l. This is attributed to a different composition of the sedimentary organic matter. Characterisation of the material from Ruprechtov site showed a very low availability of organic matter for the processes of DOC degradation and release.</p>
<p>Achievements for the safety case: This work shows the potential of isotope analyses for characterisation of a site to be used in a safety case building the basis for understanding of chemical reactions in particular the role of organic matter in a natural system.</p>
<p>References: Noseck et al. (2008b), Noseck et al. (2007).</p>

5.3.2 Inverse modelling and PCA

<p>Motivation and aim: The aim is to identify and quantify processes with impact of carbon chemistry occurring on the pathway from the infiltration area to the tertiary sediments.</p>
<p>Type of work: Principal component and hierarchical cluster analysis with actual groundwater data set. Selection of suitable up-gradient (granite) and down-gradient (tertiary) boreholes and inverse geochemical modelling with emphasis on isotopic signature/concentration of C compounds.</p>
<p>Participants: GRS, NRI-REZ.</p>
<p>State of the art before FUNMIG: No results from these methods were available.</p>
<p>Main results (abstract): The results of the principal component analyses show that the major information is covered by two components: Principal component 1 accounts for 80.6 % variability and is representative for geochemically evolved reducing groundwater with increased concentrations of cations and with high concentration of HCO_3^- as observed in clay/lignite horizons. Principal component 2 accounts for 15.3 % of variability in the data set and represents more immature ground water probably dominated by dissolution of silicates close to recharge areas in the granitic formation. By the hierarchical cluster analysis the similarity between different wells is illustrated, and clearly the clay/lignite wells on the one hand and the wells with granite water and those where contamination from infiltration water on the other hand are clearly grouped together.</p> <p>Inverse geochemical modelling is applied to identify the impact of the different sources for DIC, especially to understand the decrease in $\delta^{13}\text{C}$ values and the low ^{14}C values observed in the clay/lignite horizon. Two pairs of wells with water from infiltration and clay/lignite horizon are selected. As infiltration wells with typical granite water NA10 in the western and RP1 in the south-western area were chosen. Transport from NA10 to clay/lignite well NA12 in the north, and from RP1 to clay/lignite well RP2 in the east is considered, respectively. The results from these calculations show, that concentrations and isotope ratios can not be reached by carbon input from one source only, in particular input by microbial degradation of organic carbon is necessary to describe the data. These results support those from reaction path modelling and evaluation of all other geochemical and isotope data, especially $\delta^{34}\text{S}$ values.</p>
<p>Achievements for the safety case: The modelling exercises illustrate the evolution of the geochemical conditions and contributes to the understanding of carbon chemistry and therewith the behaviour of organic matter in the natural system.</p>
<p>References: Noseck et al. (2009a).</p>

5.3.3 Description of behaviour of organic matter at Ruprechtov site

<p>Motivation and aim: Characterisation of the interrelation between SOC and DOC as a basis to understand the impact of DOC on uranium mobility in the complex natural system at Ruprechtov site.</p>
<p>Type of work: Characterisation of SOM by micropetrographical methods, organic matter extraction using different schemes and characterisation, degradability experiments and interaction of extracted HA with natural clay samples.</p>
<p>Participants: NRI-REZ.</p>
<p>State of the art before FUNMIG: Only week studies were performed. No SOM characterisation technique was introduced before.</p>
<p>Main results (abstract): Sedimentary organic matter (SOM) was characterised in detail and probably originated from the peat bogs with clastic sedimentation under changing redox conditions. Total organic carbon (TOC) content varies between 0.1 to app. 40 wt.%. $\delta^{13}\text{C}$ values of about -27‰.</p> <p>Natural humic acid content in OM is very low 0.22 %, kerogen (residuum) 2.38 %. The humic acid characterisation confirmed, that these natural extracted humic substances, originating from low grade coal contain higher amount of sulphur, which is an indication of sulphate reducing (anoxic) conditions. Mass spectra (MALDI-TOF MS) proved presence of rather low molecular weight substances, which were predominated by substances with the molecular weight up to 1000 Da.</p> <p>DOC analyses at Ruprechtov site showed very low DOC concentration only few mg C/l. Colloid $< 0.450\ \mu\text{m}$ content was identified to be 0.107 mg/l maximally. MALDI-TOF measurement revealed a fingerprint for mobile organic matter (MOM) on the site. MOM fraction can be represented by extracted humic acid HA12/3 (low molecular weight substance). Degradation (leaching) experiments of organic-rich sediments showed that only small amount of leachable organic carbon was released into the solution (2.8 %).</p> <p>Microbial induced SOM degradation was identified within clay horizon. Degradation of the SOM influenced U(VI) migration, reduction of U(VI) to U(IV) and its retention due to both maintaining reducing conditions within the layers and production of PO_4^{3-}, forming U(IV) phosphate minerals.</p> <p>Sorption experiments with natural extracted humic acids and rock samples from Ruprechtov site demonstrated higher sorption on Ruprechtov clays then on montmorillonite standard SAz-1. This finding confirms the initial presumption that the organic matter can be strongly bound on inorganic constituents of sediment (e.g. clay minerals), which resulted both in low DOC concentrations in groundwater and in low yields HS using different extraction techniques.</p>
<p>Achievements for the safety case: Concerning U mobility degradation of natural organic matter at Ruprechtov site is/was important for establishing reducing conditions and phosphate release but do not cause high amounts of dissolved organic substances due to its low availability and sorption on clays.</p>
<p>References: Cervinka et al. (2007), Havlová et al. (2008a).</p>

5.3.4 Application of geochemical models to the natural system at Ruprechtov site

<p>Motivation and aim: The aim is to understand the geochemical development of the site, occurring processes and to test existing thermodynamic models and data.</p>
<p>Type of work: Application of thermodynamic models to describe the evolution of the geochemical conditions and speciation of uranium as well as application of surface complexation models to describe uranium sorption in the natural sediment system.</p>
<p>Participants: GRS, NRI-REZ</p>
<p>State of the art before FUNMIG: Scoping calculations to describe uranium concentrations in the different groundwater types were performed.</p>
<p>Main results (abstract): Reaction path modelling with GWB was performed to understand the development of the geochemical conditions at the site. The reaction of infiltration water from granite wells with the main minerals in the clay/lignite horizon kaolinite, montmorillonite, pyrite and siderite quite well explain the observed conditions and show that Eh and pH are determined by pyrite and montmorillonite. The calculations also show that the high bicarbonate concentrations can not be reached without additional CO₂ input.</p> <p>Uranium speciation in the infiltration area (granite waters) is controlled by the carbonate complexes UO₂(CO₃)_{aq}, UO₂(CO₃)₂²⁻ and to some extent by UO₂(CO₃)₃⁴⁻. In the clay/lignite horizon in situ Eh-values in the range of -160 to -280 mV seem to be determined by the SO₄²⁻/HS⁻ couple. Under these conditions U(IV) is expected to be the preferential redox state in solution. However, measurements in borehole NA6 showed only an U(IV) fraction of about 20%. Thermodynamic calculations revealed that the high CO₂ partial pressure in the clay/lignite horizon can stabilise hexavalent uranium, which can explain the occurrence of U(VI). The calculations indicated that the low uranium concentrations in the range between 0.2 and 2.1 µg/l are controlled by amorphous UO₂ and/or ningyoite. Both mineral phases have been observed by SEM-EDx and µ-XAFS. This also confirms the findings from previous work that the U(IV) phases are long-term stable under the reducing conditions in the clay/lignite horizon.</p> <p>Since U(IV) and U(VI) are observed in groundwater adsorption experiments with uranium in both redox states have been performed. Modelling of U(VI) sorption and desorption experiments was performed with Phreeqc. The results show that the pH dependence, in particular for the desorption data, can be well described by assuming only the fraction of montmorillonite in the natural sediment as sorbent using the model from Bradbury and Bayens for U on Na-montmorillonite. Relatively low sorption data from adsorption experiments could be explained by low sorption kinetics.</p>
<p>Achievements for the safety case: This work contributes to the understanding of the geochemical evolution of the site and shows that uranium concentration, speciation and sorption can be described with existing thermodynamic models and data which increases confidence in both.</p>
<p>References: Noseck et al. (2009b), Noseck et al. (2009c).</p>

5.3.5 Description of behaviour of uranium in the natural system at Ruprechtov site

<p>Motivation and aim: Identify and characterise immobilisation processes in particular for uranium in a natural system similar to the overburden of salt formations.</p>
<p>Type of work: Evaluation of all existing information, development of an updated model for uranium enrichment at Ruprechtov site and comparison of boundary conditions at Ruprechtov site with conditions in sedimentary cap rocks of radioactive waste repository host rocks.</p>
<p>Participants: GRS, NRI-REZ, FZK-INE, UH.</p>
<p>State of the art before FUNMIG: Knowledge about uranium (IV) minerals and uranium distribution in clay/lignite layers at Ruprechtov site.</p>
<p>Main results (abstract): This work shows the great potential of combining macroscopic and microscopic methods to provide insight into U enrichment processes at the Ruprechtov site, and at similar sites elsewhere. Microscopic methods aided in identifying important mineral phases and their origin, i.e. primary minerals of detrital origin or secondary minerals. Detailed X-ray spectroscopic investigations with a micro-focussed beam identified U as a tetravalent phosphate or sulphate mineral phase, in good agreement with ASEM and electron-microprobe results. Furthermore, the spatial distribution of elements and element correlations, i.e. Fe with As(0) and U with As(V), have revealed important information about the immobilisation mechanism of U(VI). The results from microscopic methods are supported by cluster analysis of sequential extraction results, demonstrating the correlation of U with As and P. Furthermore, U(IV)/U(VI)-separation and SE, coupled with analysis of AR in each phase, identified that the major part of U occurs in the tetravalent state, in agreement with results from spectroscopic methods.</p> <p>On the basis of all these results a conceptual model of Uranium immobilisation was developed. Sedimentary organic matter did not play a so important role as a direct sorbent but as a mediator for reducing conditions and the source of substance necessary for uranium mineral formation. It can be concluded that SOC within the sedimentary layers was (and to some extent still is) microbially oxidised. DOC was released by this process, providing protons to dissolve SIC. Oxidising agents, in particular SO_4^{2-} were reduced leading to the formation of iron sulphides like pyrite (FeS_2). Reducing conditions, being maintained amongst others by sulphate reducing bacterias, caused reduction of As. Arsenic sorbed onto FeS_2 surfaces, formed thin layers of arsenopyrite (FeAsS) precipitate. Uranium U(VI), originally being released from the underlying granite, was reduced to U(IV) on the arsenopyrite layers and reacted with phosphates, produced by microbial SOC oxidation. Uranium(IV) phosphates (ningyoite) were thus formed and have been stable and immobile over geological time frames.</p> <p>Today U(IV) and U(VI) are observed in the system in agreement with geochemical calculation for the current conditions in the uranium enriched clay/lignite horizons. U(VI) in the reducing groundwater is stabilised by the high bicarbonate concentrations.</p>
<p>Achievements for the safety case: This work shows the strengths of the combination of microscopic and macroscopic methods to understand radionuclide behaviour in a complex natural system and illustrates the potential barrier effect of a sedimentary layer for uranium migration under specific boundary conditions.</p>
<p>References: Noseck et al. (2008a), Havlová et al. (2008b).</p>

Appendix C

Task evaluation tables (TETs) for clays, crystalline rocks, salt

Tab. C-1: Task evaluation table for clays

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data						
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data					
1.1.1a	Determine the thermodynamic parameters related to the formation of the sulphate complexes $UO_2(SO_4)_i^{2-2i}$ ($i = 1-3$), and confirm the stability of the third complex $UO_2(SO_4)_3^{4-}$.	A2.2.9: Speciation	Base for K_d & C_{sol}	High: An, Na, ON Medium: NDA, En Enhancing process understanding: NDA Basis for deriving SA parameter values: An, En, Na, ON Complements an already extensive database	CEA: In oxidative conditions, the influence of sulphate might be taken into account for their complexing properties toward U(VI) (and other radionuclides). The complex formation is even strengthened by increase of temperature.	Improvement of knowledge: Supporting: An, NDA, ON, Na, En Improvement of data influencing PA: Supporting: Na, An, NDA, ON, En Reliable thermodynamic data are essential to support a safety case. Sulphate complexation data are more relevant in waters with high sulphate concentration, such as in OPA. It is noted that sulphur may be expected to be present as sulphide (rather than sulphate) under strongly reducing conditions.
1.1.1b	Determination of thermodynamic data by TRLFS for the $Eu(III)/U(VI)-SO_4$ systems, and validation of the use of ESI-MS for quantitative analysis of species concentrations and for mixed complexes detection.				CEA: Evaluation of analytical methods for speciation analysis of radionuclides in environmental conditions.	Improvement of knowledge: Supporting: An, ON, En, NDA n/a: Na Improvement of data influencing PA: n/a: An, ON, Na, En, NDA Improvements in analytical methods are always useful, but not of direct application to PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)						
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)					
1.1.2a	<p>State of the art on the formation of silicate complexes of trivalent f-element cations and identify the needs of experimental work that could be done in a collaborative work between CEA and CTH</p> <p>The few available studies have been reviewed for a better understanding in a thermodynamic point of view</p>	A2.2.9: Speciation			<p>CEA: Possible role of oligomeric and/or colloidal silicate species in the speciation (and migration) of trivalent radionuclides in groundwaters.</p> <p>Improvement of knowledge: Supporting: Na, An, ON, NDA, En</p> <p>Improvement of data influencing PA: n/a: Na, En, NDA, An, ON</p> <p>This bibliographic work is useful in bringing existing data together.</p>	<p>Improvement of knowledge: Supporting: ON, Na, En, NDA, An</p> <p>Improvement of data influencing PA: Supporting: Na, En, NDA, An, ON</p> <p>Although good thermodynamic data on Th from NEA exist, this work provides useful complementary data. Silicate complexation has wider applicability than phosphate.</p>
1.1.2b	<p>Determination of stability constants</p> <p>Determination of missing key thermodynamic constants and their uncertainties for phosphate and silicate complexation in aqueous solutions with selected metals by solvent extraction</p>	A2.2.9: Speciation	Base for K_d & C_{sol}	<p>Medium: ON, En</p> <p>Low: NDA</p> <p>n/a: An, Na</p> <p>Enhancing process understanding: An, Na, NDA</p> <p>Basis for deriving SA parameter values: En, ON</p>	<p>CTH: This work contributes to providing missing key thermodynamic data for phosphate and silicate complexation that can be implemented in modelling of the migration of Th(IV) and Am(III) in groundwaters.</p> <p>Improvement of knowledge: Supporting: ON, Na, En, NDA, An</p> <p>Improvement of data influencing PA: Supporting: Na, En, NDA, An, ON</p> <p>Although good thermodynamic data on Th from NEA exist, this work provides useful complementary data. Silicate complexation has wider applicability than phosphate.</p>	<p>Improvement of knowledge: Supporting: ON, Na, En, NDA, An</p> <p>Improvement of data influencing PA: Supporting: Na, En, NDA, An, ON</p> <p>Although good thermodynamic data on Th from NEA exist, this work provides useful complementary data. Silicate complexation has wider applicability than phosphate.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)					
1.1.2c	Determinations of thermodynamic data for relevant chemical species of Am(III), Cm(III), Eu(III) and U(VI) in the presence of carbonate and sulphate				CEA: Carbonate and sulphate complexes can be major actinide species in groundwaters. Their stabilities can be assessed by using thermochemical data such as those determined in this work, particularly for temperatures higher than 25° C.	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA</p> <p>Improvement of data influencing PA: Supporting: An, ON, Na, En, NDA</p> <p>Useful exercise of re-evaluating thermodynamic data of Am, Cm, Eu and U(VI) in presence of carbonate and sulphate.</p>
WP 1.2	Ion exchange and surface complexation					
1.2.1	<i>cf.</i> crystalline					
1.2.2	Batch sorption studies of Ni, Eu, U(VI) on illite, OPA in the presence of carbonate	A2.2.7, A2.2.8, A2.2.9: CO ₃ complex	K _d	High: An, Na, Medium: NDA, En Low: ON Enhancing process understanding: An, En, ON, NDA Host-rock specific: En, Na, ON Influence of carbonate on K _d	PSI: Extend the currently available thermodynamic sorption models for Ni(II), Eu(III) and U(VI) onto illite and Opalinus Clay for performance assessment purposes by including the influence of carbonate complexation on radionuclide sorption.	<p>Improvement of knowledge: Important: An, Na Supporting: NDA, ON, En</p> <p>Improvement of data influencing PA: Important: An, Na Supporting: NDA, ON, En</p> <p>This work is most important to Nagra and Andra, as materials most closely represent their host rock. General relevance to other systems as carbonate can be present in clays. However range of RN not relevant to all countries.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ion exchange and surface complexation (continued)						
WP 1.2	Ion exchange and surface complexation (continued)					
1.2.3	Batch sorption studies of Tc, Se on Pyrite, illite, Boom Clay	A2.2.7, A2.2.8, A2.2.9: CO ₃ complex	K _d	High: An Medium: ON, En, Na Low: NDA Enhancing process understanding: An, En, ON, NDA Host-rock specific: En, Na, ON Boom Clay useful as analogue for OPA, COx etc.	KULeu: Experimental results indicate that the long term Se speciation in Boom Clay will be governed by the presence of reduced Se phases, due to interaction with reducing minerals such as e.g. pyrite.	Improvement of knowledge: Important: An, ON Supporting: Na, En, NDA Improvement of data influencing PA: Important: An, ON Supporting: Na, En, NDA The Se study was considered important for PA. Although the work was carried out on Boom Clay, the results were useful for other clay rocks that contain reducing minerals, such as pyrite.
1.2.4a	Batch sorption studies of Cm, Eu, U(VI) on various substrates Test of a NEM with non-integer proton stoichiometry	A2.2.7, A2.2.8, A2.2.9: CO ₃ complex	K _d	High: Na Medium: En, An Low: ON, NDA Enhancing process understanding: An, En, ON, NDA Basis for deriving SA parameter values: En, Na Knowledge level already high	FZK-INE: A parameter estimation tool for treating multiple data sets was developed and its application within a non-electrostatic model framework was tested, where the non-electrostatic approach was found to be inferior compared to the respective benchmark electrostatic model.	Improvement of knowledge: Supporting: Na, An, ON, En, NDA Improvement of data influencing PA: N/a: Na, An, ON, En, NDA Useful information on sorption on different materials has been generated. The conclusion on the convenience of using electrostatic models is relevant for the development of TSM, that are used to support K _d values for PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.4b	Batch sorption studies of Cm, Eu, U(VI) on various substrates				<p>FZK-INE: The bulk composition of a mineral phase does not necessarily reflect the properties of its surface when contacted with water and therefore the nature and the amount of the sorbed metal ion complex can be strongly affected.</p> <p>Improvement of knowledge: Supporting: An, ON, En, Na, NDA</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, En, NDA This basic study has limited benefit to PA. The processes examined have little direct application to PA.</p>	
1.2.4c	Molecular scale mechanisms	A2.2.7, A2.2.8	Base for K_{ds} D_e	<p>Medium: ON, NDA, Na, An, En Enhancing process understanding: An, Na, NDA, ON</p>	<p>CEA: Sorbent clay minerals are representative of the clay phases in bentonite as argillaceous host rocks. These studies clarify the molecular-scale mechanism of lanthanide (and, by analogy, actinide) retention on clay mineral. They confirm that in near-neutral pH conditions, retention occurs essentially by specific sorption at the layer edge, providing an additional mechanism of radionuclide retention. These results validate modelling of An and Ln retention by clays as a combination of cation exchange and surface complexation.</p> <p>Improvement of knowledge: Supporting: An, Na, ON, NDA, En</p> <p>Improvement of data influencing PA: Supporting: An, Na, En, NDA, ON Spectroscopic study confirms that lanthanides and actinides sorb specifically (inner sphere) to smectite surfaces and as such can be used to support sorption values used for PA.</p>	

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.5	Activity coefficients of sorbed species – Benchmarking SCM and IXT2	A2.2.7, A2.2.8, A2.2.9	K _d	High: An, Na, En Medium: ON, En Low: NDA Enhancing process understanding: An, En, ON, NDA Basis for deriving SA parameter values: En, Na Knowledge level already high	CEA: Illite thermodynamic sorption data (IXT2 version) outcoming from this research are potentially useful for PA.	Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: n/a: An, En, ON, Na, NDA This modelling study can be regarded as preliminary and may have some potential for the future in terms of generalising sorption of RN in clays.
1.2.6	<i>cf.</i> crystalline					
1.2.7	Sorption studies of Th on magnetite and ferrihydrite	A2.2.7, A2.2.8		High: An Low: NDA, ON n/a: En, Na	UPC: In order to be included or considered the sorption process of thorium onto magnetite and ferrihydrite in PA, K _d values and surface complexation constants have been obtained from batch experiments and surface complexation modelling.	Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: n/a: ON, Na, En, NDA, An The topic is of general relevance and provides useful sorption data for the safety case. However, the pH range of the study is much lower than the expected neutral conditions in the host formation.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ion exchange and surface complexation (continued)						
WP 1.2						
1.2.8	Batch sorption experiment on clay minerals	A2.2.7, A2.2.8, A2.2.9	K _d	High: En, Na, Medium: ON, An Low: NDA Enhancing process understanding: An, En, ON, NDA Basis for deriving SA parameter values: En, ON Knowledge level already high.	CIEMAT: The thorough analyses of sorption data, based on a quasi-mechanistic description of simplified systems is the basis for the understanding of mixed clay systems.	Improvement of knowledge: Important: Na, En Supporting: ON, NDA, An Improvement of data influencing PA: Important: Na, En Supporting: ON, NDA, An This study provides relevant new sorption data and puts these data into a generalised semi-mechanistic framework so that for some radionuclides, sorption on complex materials can be predicted on the base of sorption parameters in simple minerals.
1.2.9	Batch sorption studies of tetravalent & trivalent actinides on Boom Clay	A2.2.7, A2.2.8, A2.2.9: CO ₃ complex	K _d	High: An, En, Na, Medium: ON Low: NDA Enhancing process understanding: An, NDA Host-rock specific: En, Na Basis for deriving SA parameter values: En, Na, ON Boom Clay useful as analogue for OPA, Cox etc.	SCK-CEN: Site-specific sorption data for tri- and tetravalent RN are obtained which can be used for selection of retention data for PA. Increased process understanding (sorption, complexation, colloid mobility) in the interaction of trivalent RN with clays in presence of NOM.	Improvement of knowledge: Important: ON Supporting: An, Na, En, NDA Improvement of data influencing PA: Important: ON Supporting: An, Na, En, NDA Site-specific data are generated. NOM content and relevance will be different for other formations but similar methodologies can be used.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.3 Influence of organics on the retention of radionuclides by minerals						
1.3.1	Batch sorption studies of Am on clay minerals in the presence of humic acids	A2.2.7, A2.2.8, A2.2.2: humic complex	K_d	High: An, Na, Medium: ON, NDA, En Enhancing process understanding: An, En, Na, NDA, ON Low humic concentration in OPA	FZD: New sorption data were obtained which indicate that humic acid may affect the Am(III) migration under environmentally relevant conditions by enhancing or lowering the Am(III) sorption in the acidic and in the environmentally relevant pH range (pH 5 – 8), respectively.	Improvement of knowledge: Supporting: ON, Na, An, NDA, En Improvement of data influencing PA: Supporting An, Na, NDA, ON, En This is a very basic study on a model system. It is most relevant for those systems with water extractable humics.
1.3.2	<i>cf.</i> crystalline					
1.3.3	Batch sorption studies of Ni, Eu, Cs, Cd, Fe on montmorillonite, kaolinite, goethite in the presence of various organics	A2.2.7, A2.2.8, A2.2.2: humic complexes, B1.2.2: various org. complexes	K_d	Medium: An, En, NDA Low: ON, Na, Enhancing process understanding: En, ON, NDA Basis for deriving SA parameter values : An, Na Low concentration of complexing organic compounds in OPA and COx NDA: important process but not priority radionuclides	Uni Lough: Whilst the simple organics do show interactions with mineral surfaces and radionuclides, their effect on PA is likely to be considerably less than the ubiquitous humic acids in the geosphere.	Improvement of knowledge: Important: An, NDA Supporting: Na, ON, En Improvement of data influencing PA: Important: An, NDA Supporting: En, ON, Na The complexing behaviour of waste-derived organics is not significant when compared with the expected complexing behaviour of humics. Study is particularly useful for An and NDA as their wastes have a higher organic inventory.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.3	Influence of organics on the retention of radionuclides by minerals (continued)					
1.3.4	Batch sorption studies of Np, U, Eu, Cu, Ag, Cd, Am on silica, magnetite, calcite, goethite in the presence of humics	A2.2.7, A2.2.8, A2.2.2: humic complex	K _d	High: An Low: ON, NDA n/a: En, Na	Uni Man & Lough: Basically, kinetics lead to slower reversibility. A methodology has been developed that predicts the impact of humic colloid kinetics in field scale transport calculations, and parameters have been provided to allow the calculation of RN transport through ternary systems via either equilibrium and/or kinetic speciation. Damkohler numbers are used to decide when full kinetics should be included for an accurate transport prediction and when approximations may be used instead. All of the parameters have been provided to allow predictions to be made either by the exact (kinetic) method or via the approximations (including an equilibrium approach).	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA</p> <p>Improvement of data influencing PA: Supporting: An, Na, NDA, ON, En</p> <p>This study considers the irreversibility of RN binding in the presence of organics and is useful to support PA.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Influence of organics on the retention of radionuclides by minerals (continued)						
WP 1.3 1.3.5	Batch sorption studies of Eu, Cm on smectite in the presence of organics	A2.2.7, A2.2.8, A2.2.2: humic complexes, B1.2.2: various org- complexes	K_d	High: An, Na Medium: En Low: ON, NDA Enhancing process understanding: En, ON, NDA Basis for deriving SA parameter values : An, Na Low concentration of complexing organic compounds in OPA	FZK-INE: New data on clay host rock (OPA, COx) sedimentary organic matter spatial distribution, functionality, kerogen reactivity and RN complexation is provided.	Improvement of knowledge: Important: An, Na, ON Supporting: En, NDA Improvement of data influencing PA: Supporting: An, Na, En, ON, NDA The study represents an important step improving knowledge on characteristics of OM in OPA and its role as RN sorbent. The results are site-specific but the methodology can be applicable to other formations.
Formation of solid solutions and secondary phases, including retardation of anions						
WP1.4 1.4.1	Generation and characterisation of uranium reference minerals	A2.2.6	C_{sol}	Medium: ON Low: An, Na, En, NDA Enhancing process understanding: An, Na, ON, En Not relevant for geochemical conditions in Boom Clay, COx, OPA etc.	FZD: Very small amounts of boltwoodite and co-preignacite are identifiable by TRLFS in complex geological samples. The identification of such uranium minerals contributes to a better understanding of the uranium chemistry and its migration behaviour around contaminated sites.	Improvement of knowledge: Supporting: NDA, An, Na, En, ON Improvement of data influencing PA: n/a: NDA, An, Na, ON, En Work on oxidised states of actinides are supporting process understanding but this information may not be relevant for reducing conditions expected in clay host formations.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP1.4 Formation of solid solutions and secondary phases, including retardation of anions (continued)						
1.4.2a	<p>Coprecipitation and sorption studies of Se on clay minerals</p> <p>Sorption of Se(IV) on compacted clay materials</p>	A2.2.6	C_{sol}	<p>High: An, Na, ON</p> <p>Medium: En, NDA</p> <p>Enhancing process understanding: An, En, Na, ON, NDA</p>	<p>Armines, Leuven University: Sorption data between Se(IV) and clay materials are not affected by compaction (600 to 1300 kg/m³). High compactions are not possible with this methodology.</p>	<p>Improvement of knowledge: Important: An, Na, ON, En, NDA</p> <p>Improvement of data influencing PA: Important: An, Na, ON, En, NDA</p> <p>This work provides valuable insight into sorption of Se(IV) on compacted clay minerals, however, the range of compaction is quite narrow (600 to 1300 kg/m³).</p>
1.4.2b	<p>Incorporation of Selenium into pyrite</p>				<p>SUBATECH: A full Se retention model for reducing repository near- and far field environments does not yet exist, but the clarification of the interaction of Se(-II) with pyrite is an important cornerstone for the creation of such a model. It is particularly important that both the interaction of Se(-II) and of Se(IV) (literature data) lead to the formation of Se(0).</p>	<p>Improvement of knowledge: Important: An, ON, Na, En, NDA</p> <p>Improvement of data influencing PA: Important: An, Na, ON</p> <p>Supporting: En, NDA</p> <p>This study is an important step to understand the immobilisation of reduced Se in argillaceous rocks and suggests the important role of pyrite in this process. A potential mechanism for Se immobilisation has been identified: formation of Se(0) in the pyrite surface.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Formation of solid solutions and secondary phases, including retardation of anions (continued)						
WP1.4 1.4.3	Coprecipitation experiment of U, Np, Pu with calcite	A2.2.6	C_{sol}	Medium: ON Low: An, En, Na, NDA Enhancing process understanding: An, En, Na, ON, NDA	FZK-INE: Formation of a solid solution with calcite can lead to effective entrapment of NpO_2^{2+} in calcite particles.	Improvement of knowledge: Supporting: An, Na, En, ON, NDA Improvement of data influencing PA: Supporting: An, Na, En, ON, NDA <i>Cf.</i> see comment in 1.4.1 This experimental study on Np calcite system adds to understanding of solid solutions. Where clay formations contain calcite, formation of solid solutions with calcite can be an additional barrier mechanism for some radionuclides.
1.4.4	Determine radionuclide sorption/incorporation by calcite				KU: New data for PA modelling: Lanthanide analogues allowed estimation of actinide uptake in calcite to be significant and low concentrations of nickel were observed to adsorb onto calcite and substitute as solid solution with a distribution coefficient near 1. The source of the calcite in a PA framework is the secondary calcite that forms down gradient from concrete, or weathering of rock containing Ca.	Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: Supporting: An, Na, En, NDA, ON This experimental study on Np calcite system adds to understanding of solid solutions. Where clay formations contain calcite, formation of solid solutions with calcite can be an additional barrier mechanism for some radionuclides.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP1.4	Formation of solid solutions and secondary phases, including retardation of anions (continued)					
1.4.5	Theoretical expression of thermodynamics of solid solutions (co-precipitation)				CEA: Modelling solubilities provides Thermodynamics bases for validating predictions of the retention of radionuclides here by non-pure solids.	<p>Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA</p> <p>Improvement of data influencing PA: n/a: ON, Na, En, NDA, An</p> <p>This theoretical study is considered as significant improvement of thermodynamic description of solid solutions. Although solid solutions are not usually considered in PA calculations, they can be used as an additional argument in the safety case.</p>
WP 2.1	Formation, migration and transport processes of inorganic colloids					
2.1.1	Inorganic colloid formation and RN interaction	A1.3	R	Medium: ON n/a: An, En, Na, NDA Enhancing process understanding: NDA No colloids considered in clay formations	TUM-RCM & FZK-INE: 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.	<p>Improvement of knowledge: Supporting: ON, An, Na, NDA, En</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, En, NDA</p> <p>Supporting information because it helps to understand colloid formation processes, but colloids are expected to be filtered by the clay formation.</p>
2.1.2	<i>cf.</i> crystalline					
2.1.3	<i>cf.</i> crystalline					

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction						
WP 2.2						
2.2.1a	<p>Radiocolloid interaction with clay formation derived natural organic matter</p> <p>Investigation of immobile organic matter from real site conditions (Ruprechtov site), its behaviour and influence on U migration. Selection of appropriate extraction technique. Characterisation and complexation of extracted humic substances with U(VI).</p> <p>Refers to overburden</p>	A2.2.2 (NOM)	R	<p>High: An, Na</p> <p>Medium: ON, En</p> <p>Low: NDA</p> <p>Enhancing process understanding: An, En, Na, ON, NDA</p> <p>Host-rock specific: An, En, Na, ON</p> <p>Low concentration of complexing organic compounds in OPA</p>	<p>NRI-RES: OM on the Ruprechtov site does not influence speciation of uranium directly as sorbing/complexing agent, but indirectly via maintaining reducing conditions and contributing to U(IV) immobilisation in secondary phases.</p>	<p>Improvement of knowledge: n/a: An, Na, ON, En, NDA</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, NDA, En</p> <p>This study has been focussed on the Ruprechtov site and its outcome has little relevance for the safety case. Future studies may wish to address the application of mechanisms observed in other formations.</p>
2.2.1b	<p>Investigate the interaction of Se with mobile and immobile NOM derived from the Boom Clay (BC) formation, using batch experiments and spectroscopy to elucidate the interaction mechanism and reaction products</p>				<p>KULeuven: Se(VI) is unaffected by NOM. Se(IV) is reduced by BC NOM, resulting in Se⁰ precipitation. Final Se solution concentrations of 4.4×10^{-8} M (BC HS) and 1.3×10^{-7} M (Gorleben HS) were measured after six months observation.</p>	<p>Improvement of knowledge: Important: ON</p> <p>Supporting: An, Na, NDA, En</p> <p>Improvement of data influencing PA: Important: ON</p> <p>Supporting: An, Na, En, NDA</p> <p>The identified uptake processes of Se are mainly of interest for Boom clay, but applied methodology can also be useful for other clay formations.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2 Inorganic colloid formation and RN interaction (continued)						
2.2.1c	Investigation of RN interaction with both mobile and immobile NOM (Boom Clay NOM), aiming at a quantitative description				<p>SCK-CEN: The successful implementation of a thermodynamically consistent metal-humic complexation model into Phreeqc provides a tool to quantitatively describe the interaction of tri and tetravalent RN with NOM. This will help in the selection of trustworthy maximum mobile concentrations relevant for PA.</p> <p>Improvement of knowledge: Important: ON Supporting: Na, En, An, NDA</p> <p>Improvement of data influencing PA: Important: ON Supporting: Na, En, An, NDA</p> <p>This study leads to improved understanding of the influence of Boom Clay OM on Eu, and is useful for comparison with OPA and COx.</p>	
2.2.2a	<p>Radionuclide interaction with natural organic matter (NOM)</p> <p>Within this task the redox behaviour of plutonium and neptunium in solutions containing humic substances (HS) is investigated and modelled by equilibrium thermodynamic. To elucidate reaction mechanism simple hydroquinones as model compounds are used beside the HS</p>	A2.2.2 (NOM)	R	<p>High: An, Na Medium: ON, En Low: NDA</p> <p>Enhancing process understanding: An, En, Na, ON, NDA</p> <p>Host-rock specific: En, ON</p> <p>Low concentration of complexing organic compounds in OPA</p>	<p>FZK-INE: Plutonium can exist in trivalent oxidation state at low concentration of $< 10^{-8}$ M. At higher plutonium concentrations colloid formation dominates and only Pu(IV) is present at pH > 3. At the end of the project thermodynamic constants are given that will update modelling of plutonium and neptunium.</p> <p>Improvement of knowledge: Supporting: ON, En, NDA, An, Na</p> <p>Improvement of data influencing PA: Supporting: ON, An, Na, En, NDA</p> <p>This preliminary study on the interaction of hydroquinones (as proxy for HS) with Pu and Np, generates thermodynamic data for Np and Pu in the presence of HS.</p>	

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2						
2.2.2b	<p>Twofold: i) advance TRLFS methods as analytical tools for improved speciation of actinides and ii) increase/improve fundamental understanding of interaction processes between actinides (lanthanides were used as surrogates and luminescences probes!) and humic substances (HS)</p>				<p>UPPC: Improvement of spectroscopic-based speciation analysis and stressing importance of differentiation between FA and HA fractions for modelling approaches.</p>	<p>Improvement of knowledge: Supporting: ON, En, NDA, An, Na Improvement of data influencing PA: n/a: An, ON, Na, En, NDA Improvements in analytical techniques are always useful to increase the knowledge but are not of direct application to PA.</p>
2.2.2c	<p>Study of the competition between radionuclides – Co^{2+}, UO_2^{2+}, and Eu^{3+} – and major cations – Ca^{2+} and Mg^{2+} – for humic substances complexation</p>				<p>CEA & UPPC: Functionalised NOM can be generated by an alkaline fluid in clay media. The alkaline earth metals, Ca^{2+} and Mg^{2+}, are merely in competition with actinides and lanthanides for natural organic matter complexation: Fe^{3+}, Al^{3+}, and inter-Ln/An competition should be accounted.</p>	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: Supporting: An, En, ON, Na, NDA Although studied system is not representative for all repositories, the obtained data on competitive effects is of general value.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2						
2.2.2d	Determination of stability constants for the complexation of plutonium(III) with humic substances				FZD: The stability constants for the complexation of plutonium(III) with humic substances obtained within this study will improve the basic process understanding and contribute to the enhancement of the existing thermodynamic data base.	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA</p> <p>Improvement of data influencing PA: Supporting: ON, Na, An, En, NDA</p> <p>This study on Pu(III)-humic substances complexation is useful for improvement of the thermodynamic database, but it is not of direct application to PA.</p>
2.2.2e	Development of new relativistic quantum-chemical methods for interpretation of NMR spectra of lanthanide complexes with humic acids and model ligands				SAS-IIC: Quantum-chemical predictions of paramagnetic NMR spectra of Gd with a model ligand (Salicylic acid) in water solution were performed. The results of these calculations demonstrate that complexes formed via carboxyl group with mono-dentate coordination are preferable but fast exchange of ligand-coordinated water is expected.	<p>Improvement of knowledge: n/a: An, Na ON, En, NDA</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, En, NDA</p> <p>This is a very fundamental study with no direct application to the safety case.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2						
2.2.2f	Consistency of tetravalent actinide humic acid complexation				CEA & NRIRR & Uni Lough: If no competition occurs, the humic complexation of tetravalent actinides can be obtained with a rather good approximation from Th(IV).	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA</p> <p>Improvement of data influencing PA: Supporting: En, An, ON, Na, NDA</p> <p>This prediction exercise on An-humics complexation on the basis of Th(IV) is useful. Since all tetravalent actinides have similar complexation behaviour with fulvic acid, the need of generating radionuclide-specific data is reduced.</p>
2.2.2g	Determination of the effect of ionic strength on complexation of Pu(IV) with humic acid				NRIRR: The present work contributes to providing interaction parameter of Pu(IV) humate that varies with ionic strength. This parameter can be applied in the geochemical modelling of the migration of Pu(IV) under the influence of humic substances.	<p>Improvement of knowledge: Supporting: ON, En, NDA, An, Na</p> <p>Improvement of data influencing PA: n/a: An, Na, En, NDA, ON</p> <p>This study on Pu(IV) – humate complexation is preliminary.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2 Inorganic colloid formation and RN interaction (continued)						
2.2.3a	<p>Radionuclide interaction with natural organic matter (NOM) in the presence of mineral phases (ternary systems)</p> <p>Role of the adsorptive fractionation of natural organic matter on alumina, on the interaction with radionuclides</p>	A2.2.2 (NOM)	R	<p>High: An, Na Medium: ON, En Low: NDA</p> <p>Enhancing process understanding: An, En, Na, ON, NDA</p> <p>Low concentration of complexing organic compounds in OPA</p>	<p>CEA & INE: The humic acid like structures obtained after micro-organism mediated oxidation in sedimentary formation are not comparable to surface extracts, but the complexation properties are similar. These extracts can only be obtained out of a normal evolution scenario.</p>	<p>Improvement of knowledge: n/a: An, NDA, ON, Na, En</p> <p>Improvement of data influencing PA: n/a: An, NDA, ON, Na, En</p> <p>This theoretical study on adsorptive fractionation for model compounds provides limited benefit for the safety case.</p>
2.2.3b	<p>Study of solubility of $UO_2(OH)_2$ and UO_2CO_3 as a function of the humic acid concentration</p>				<p>Uni Cyprus: The presence of humic acids may affect both solid phase stability and the solution chemistry.</p>	<p>Improvement of knowledge: n/a: An, Na, NDA, ON, En</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, En, NDA</p> <p>This rather preliminary study on humic acid interaction with model U(VI) compounds is of very limited benefit for the safety case.</p>
WP 2.3 Radionuclide redox transformation on minerals						
2.3.1a	<i>cf.</i> crystalline					
2.3.1b	<i>cf.</i> crystalline					
2.3.1c	<i>cf.</i> crystalline					<p>FZK-INE: The retention of Np(V) occurs by redox transformation to Np(IV) forming a low soluble solid at iron phases in the granite.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide redox transformation on minerals (continued)						
WP 2.3	Radionuclide redox transformation on minerals, pyrite, siderite Investigate the role of Fe(II) bearing minerals on the retention of Se in reducing conditions (reaction mechanism-formed Se species)	A2.2.4: redox, A2.2.7, A2.2.8	K_d	High: An, Na Medium: ON, En Low: NDA Enhancing process understanding: An, En, Na, ON, NDA Boom Clay redox regime useful as analogue for other clay host rocks	KULeuven: Proof was provided that Se^0 and $FeSe_x$ will be the solubility limiting phases in Boom Clay conditions.	Improvement of knowledge: Important: An, ON, Na Supporting: En, NDA Improvement of data influencing PA: Important: An, Na, ON Supporting: En, NDA The outcome of the study is an important step to understand the role of Fe sulphides in immobilising Se (<i>cf.</i> also I.4.2b). Useful data on Se and U speciation in Boom Clay has been generated. This can be used as analogue for other clay formations.
2.3.2a						
2.3.2b	Investigation of radionuclide – U(VI) – sorption/sorptive reduction on pyrite/siderite in presence/ absence of Boom Clay NOM				SKC-CEN: Confidence building with respect to the U speciation in the Boom Clay far field: dominant U speciation for Boom Clay conditions is the tetravalent state.	Improvement of knowledge: Important: ON Supporting: Na, En, An, NDA Improvement of data influencing PA: Supporting: ON n/a: An, Na, NDA, En From a methodological view point the study bears some potential.
2.3.3	<i>cf.</i> crystalline	A2.2.4: redox, A2.2.7, A2.2.8				

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.4 Impact of biogeochemical processes						
2.4.1a	<i>cf.</i> crystalline	B7				
2.4.1b	<i>cf.</i> crystalline					
2.4.2	<i>cf.</i> crystalline	B7				
WP 3.1 Understanding key, basic processes affecting RN transport in clay-rich porous media (small-scale, simplified model laboratory systems)						
3.1.1	Analysis and modelling of redox potential and reaction kinetics of synthetic and natural Fe bearing minerals	A2.2.4: redox	Base for K_d & C_{sol}	High: An, Na Medium: ON, NDA, En Enhancing process understanding: An, En, Na, ON, NDA Basis for deriving SA parameter values: An, En, Na	LMM, UJF, BRGM, LPEC, La Trobe: refinement of the COx redox reactivity (kinetics, potential and capacity ("stock")).	Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: Important: An, Na Supporting: En, ON, NDA This is a highly relevant and challenging study that has led to improved understanding of the role of Fe in clay formations for immobilising redox sensitive RN.
3.1.2	Modelling and measurement of H ₂ O & ion states in clay-solution interface zone	A1.2.1 & A2.1.1, A1.2.2 & A2.1.2, A1.2.3 & A2.1.4, A1.2.4 & A2.1.5,	D_{cs} , ϵ	High: An, Na Medium: NDA, En, ON Enhancing process understanding: An, En, Na, ON, NDA Basis for deriving SA parameter values: An, Na	AIED, BRGM, LMM, UJF, LGIT, SUBATECH, LAIEM, CEREGE: Mechanistic description and parameterisation of clay surface effect on cations, anions and water distribution.	Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: Important: An, Na Supporting: ON, En, NDA This study represents an important step to improve the theoretical basis to the description of clay surfaces in the compacted state.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 3.1	Understanding key, basic processes affecting RN transport in clay-rich porous media (small-scale, simplified model laboratory systems) (continued)					
3.1.3	Determination of diffusion parameters (D_e , ϵ) for compacted model clay materials	A1.2.1 & A2.1.1, A1.2.2 & A2.1.2, A1.2.3 & A2.1.4, A1.2.4 & A2.1.5,	D_e , ϵ	High: An, En, Na, ON Medium: NDA Enhancing process understanding: An, En, Na, NDA Basis for deriving SA parameter values: En, ON	CEA, LMM, BRGM, ERM : Comparison between description of diffusion from nanometric to centimetric scale.	Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: n/a: Na, NDA An, ON, En This study which should provide the experimental background for task 3.1.2 is apparently still at a preliminary stage and results are not yet available.
3.1.4a	Development of conceptual/numerical model(s) of ion diffusion in compacted clay materials Mono- and double-porosity model for simulating radionuclide transfer in compact clay materials	A1.2.1 & A2.1.1, A1.2.2 & A2.1.2, A1.2.3 & A2.1.4, A1.2.4 & A2.1.5,	D_e , ϵ	High: An, Na, ON Medium: NDA, En Enhancing process understanding: An, En, Na, ON, NDA Basis for deriving SA parameter values: An, En, Na	SUBATECH: The model development is a potential key cornerstone when heading towards overall systems geochemical interaction modelling coupling speciation, diffusion and reaction simultaneously for anions, cations and neutral species.	Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: n/a: ON, Na, NDA, An, En This modelling study is an important discussion basis for a coherent description of anion and cation diffusion in compacted clays.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
<p>WP 3.1 3.1.4b</p>	<p>Mechanistic model and associated database for one radioelement for Cellovo-Oxfordian clay rock conditions</p>				<p>Understanding key, basic processes affecting RN transport in clay-rich porous media (small-scale, simplified model laboratory systems) (continued)</p> <p>Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: n/a: ON, Na, An, En, NDA This modelling exercise, although still preliminary, is useful for providing the theoretical background of sorption values used in PA.</p>	
<p>WP 3.2 3.2.1</p>	<p>Determination of clay rock physical characteristics, mineral and pore water composition & conceptual model of water and porosity distribution in clay rocks</p>	A2.2.4	Base for K_d & C_{soil}	<p>High: An, En, Na, ON, NDA Enhancing process understanding: En, NDA Basis for deriving SA parameter values: An, En, Na, ON Comparison between different clays</p>	<p>Ion exclusion and evolution of pore water chemistry and mineralogy in different host rocks, connected matrix porosity, surface diffusion, double porosity models.</p>	<p>Improvement of knowledge: Supporting: An, ON, Na, En, NDA Improvement of data influencing PA: Supporting: An, Na, NDA, ON, En This task is expected to provide a useful comparative database for three clay rock formations. This comparison between different clays will allow identifying common features of different argillaceous formations. This information will allow to justify the transfer of data between clay formations on the base of their similarities (e.g. if "generic" clay is considered in the actual safety case).</p>
<p>Radionuclide chemistry and transport in natural clay-rich host rocks at small scales</p>						

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide chemistry and transport in natural clay-rich host rocks at small scales (continued)						
WP 3.2	Development & application of appropriate characterisation, quantification methods for quantifying the spatial distribution of porosity and minerals in rock samples	A2.2.1, A1.2.2 & A2.1.2	Base for K_d , ϵ , D_e	High: An, En, Na, NDA Medium: ON Comparison between different clays	ERM, ARMINES, HYDRASA: Provide a model for structural organisation (including comparison between different clays) for input in transport models.	<p>Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA</p> <p>Improvement of data influencing PA: Supporting: An, Na, En, ON, NDA</p> <p>The study provides improved insight into structural organisation of compacted clays at the $\mu\text{m-cm}$ scale. Comparison of the mineral and porosity distribution in different clays provide useful information that can be applied to other clay systems.</p>
3.2.3	Development of numerical model(s) of clayrock porosity for transport modelling	A2.2.1, A1.2.2 & A2.1.2	Base for K_d , ϵ , D_e	High: An, Na, NDA Medium: ON, En Enhancing process understanding: An, En, Na, ON, NDA Basis for deriving SA parameter values: An, En, Na, ON Comparison between different clays	ERM, HYDRASA, CEA: Obtaining of small scale diffusion coefficient. Simulation of a map at a millimetric scale using diffusion coefficients obtained at a micrometric scale then comparison with diffusion profiles and maps obtained with μLIFS ; this work is on the way and were discussed during RTDC3 meeting in Paris.	<p>Improvement of knowledge: Supporting: ON, Na, En, NDA, An</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, En, NDA</p> <p>This new numerical method for analysing micro-structural and micro-spectroscopic data bears potential for the future.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide chemistry and transport in natural clay-rich host rocks at small scales (continued)						
WP 3.2	Radionuclide chemistry and transport in natural clay-rich host rocks at small scales (continued)					
3.2.4	Development & application of new methods for quantifying transport parameters (sorption+ diffusion) of moderate and high K_d species	A1.2.1 & A2.1.1	K_d, ϵ, D_e	High: An, En, Na, NDA Medium: ON Enhancing process understanding: En, ON, NDA Basis for deriving SA parameter values: En, ON	PSI & CEA: Transferability of K_{ds} from batch sorption data towards PA seems to be justified because the sorption on intact material is similar, and in some cases higher.	Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: Important: An, Na Supporting: ON, En, NDA This challenging lab diffusion study is highly relevant for understanding diffusion behaviour of strongly sorbing tracers in OPA and COx.
3.2.5	Comparative measures of K_d and migration for RN representative species in different clayrocks	A2.2.7, A2.2.8	K_d, ϵ, D_e	High: An, En, Na Medium: ON, NDA Enhancing process understanding: ON, NDA Basis for deriving SA parameter values: En, ON	SCK-CEN: For species that sorb via pure cation exchange, the relationship $R-K_d$ seems valid. However, combining the D_e/D_p (HTO) and sorption data will not result in correct D_a values for ion-exchangeable RN.	Improvement of knowledge: Important: ON Supporting: An, Na, En, NDA Improvement of data influencing PA: Important: ON Supporting: An, Na, En, NDA This interesting study intends to make the link between batch sorption and diffusion data in Boom clay. Results are probably of lower value for other clay formations.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 3.2						
Radionuclide chemistry and transport in natural clay-rich host rocks at small scales (continued)						
3.2.6	In-diffusion experiments of doped solutions into polished sections of COx	A2.2.7, A2.2.8 A1.3, A2.2.2	K_d , ϵ , D_e	Medium: NDA, Na, An, ON, En Enhancing process understanding: An, En, Na, ON Basis for deriving SA parameter values: An, En, Na, ON	SUBATECH, ERM: none.	Improvement of knowledge: n/a: An, Na, En, NDA, ON Improvement of data influencing PA: n/a: An, ON, Na, En, NDA This attempt to develop a new methodology did not in the end yield sufficient resolution to compete with existing methods.
WP 3.3						
URL experiments for characterising radionuclide chemistry and migration in clay rich host rock formations at intermediate time and space scales						
3.3.1	Diffusion (and sorption) measurements for developing data sets in support of in-situ experiments (DR at Mont Terri, DIR at Bure)	A1.2.1 & A2.1.1 A2.2.7, A2.2.8	K_d , ϵ , D_e	High: An, Na Medium: ON, NDA, En Enhancing process understanding: En, ON, NDA Basis for deriving SA parameter values: En, ON Host-rock specific: An, Na, ON	CIEMAT & UDC: Improvement of diffusion database and reduction of the uncertainty on diffusion parameters. The 3D description and modelling of large-scale experiments it is adequate for evaluation rock anisotropy.	Improvement of knowledge: Important: Na, An Supporting: En, NDA, ON Improvement of data influencing PA: Supporting: Na, An, NDA, ON, En Useful lab study of diffusion in OPA and COx using innovative approach at block-scale.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 3.3	URL experiments for characterising radionuclide chemistry and migration in clay rich host rock formations at intermediate time and space scales (continued)					
3.3.2	Evaluation of a diffusion and retention experiment at the Mont Terri URL	A1.2.1 & A2.1.1 A2.2.7, A2.2.8	K_d , ϵ , D_e	High: An, En, Na, NDA Medium: ON Enhancing process understanding: En, ON, NDA Basis for deriving SA parameter values: En, ON Host-rock specific: An, En, Na, ON	PSI, UDC, GRS, Nagra, Andra: More robust 2D and 3D modelling of diffusion experiments in anisotropic rock, better quantification of uncertainties.	Improvement of knowledge: Important: An, Na Supporting: ON, En, NDA Improvement of data influencing PA: Important: An, Na Supporting: ON, En, NDA This modelling exercise enabled improved 2D and 3D description of diffusion of sorbing tracers in in-situ experiments and better insight into modelling uncertainties.
WP 3.4	Up-scaling to formation scale, furnishing of tools useful for safety case studies					
3.4.1	Studying of 'natural proofs' of retention/diffusion mechanisms (Boom)	A3.2 & C1.1.2	ϵ , D_e	Medium: ON, En Low: NDA n/a: An, Na Enhancing process understanding: An, En, Na, ON, NDA Basis for deriving SA parameter values: En Host-rock specific: An, En, Na, ON	SCK-CEN: Major transport process in Boom Clay is diffusion. Sufficient natural proof for retention is available.	Improvement of knowledge: Important: ON Supporting: An, Na, En, NDA Improvement of data influencing PA: Important: ON Supporting: An, NDA, Na, En Interpretation of natural tracer profiles are strong arguments in support of the safety case. Although results are site-specific, they confirm the diffusion/retention mechanisms in clay.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 3.4	Up-scaling to formation scale, furnishing of tools useful for safety case studies (continued)					
3.4.2	Development of a GIS (geographical information system) for parameters and properties of COx potentially important for RN transfer	- (synthesis)	All relevant SA parameters	Medium: En Low: NDA, ON n/a: An, Na Enhancing process understanding: En, NDA Basis for deriving SA parameter values: En Host-rock specific: An, Na	BRGM: Development of a GIS (geographical information system) for parameters and properties of COx potentially important for RN transfer.	<p>Improvement of knowledge: Supporting: Na, NDA, An, ON, En</p> <p>Improvement of data influencing PA: Supporting: An, ON, Na, En, NDA</p> <p>This is a site-specific task dealing with the management of the huge amount of information that will be generated during site characterisation. It can serve as a useful model for other clay formations.</p>
3.4.3	Overview of upscaling strategies for transport parameters in clayrock	- (synthesis)	All relevant SA parameters	High: An, En, Na Medium: ON, NDA Enhancing process understanding: An, En, Na, NDA Basis for deriving SA parameter values: En Host-rock specific: An, Na Comparison between different clays	SCK-CEN: The conclusions confirm that transport parameters determined at a centimetre-scale remain valid on the decametre-scale that has to be considered in the safety assessments, for so far as the characteristics of the host clay formation are sufficiently homogeneous.	<p>Improvement of knowledge: Important: ON Supporting: An, Na, En, NDA</p> <p>Improvement of data influencing PA: Important: ON n/a: An, Na, NDA, En</p> <p>This study on upscaling strategies for transport parameters provides rather preliminary results at this point, but may yield useful conclusions in the future.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 3.4 Up-scaling to formation scale, furnishing of tools useful for safety case studies (continued)						
3.4.4a	Natural tracer profile characterisation and modelling of tracer transport in compact clay rocks				<p>UniBern & Nagra: The confirmation of diffusion as the dominating transport mechanism on the formation scale, together with the demonstrated applicability of laboratory derived diffusion coefficients of that scale, are the main achievements.</p> <p>Improvement of knowledge: Important: Na Supporting: ON, En, NDA, An</p> <p>Improvement of data influencing PA: Supporting: Na, En, ON, NDA, An</p> <p>This study represents an important milestone for understanding diffusion in OPA at large spatial and temporal scales. However, it is site-specific and therefore less relevant to other countries.</p>	<p>Improvement of knowledge: n/a: An, NDA ON, Na, En</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, NDA, En</p> <p>This modelling study did not yield much additional information on tracer profiles at Mont Terri, but provided useful insight with regard to model and data sensitivity analysis.</p>
3.4.4b	Natural tracer profile characterisation and evaluation of relative merits of two models of differing complexity to represent tracer transport in compact clay-rocks				<p>GRS: A better insight about the uncertainty in modelling natural tracer profiles was achieved.</p>	<p>Improvement of knowledge: n/a: An, NDA ON, Na, En</p> <p>Improvement of data influencing PA: n/a: An, ON, Na, NDA, En</p> <p>This modelling study did not yield much additional information on tracer profiles at Mont Terri, but provided useful insight with regard to model and data sensitivity analysis.</p>

Tab. C-2: Task evaluation table for crystalline rocks

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data						
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data					
1.1.1.a	Determine the thermodynamic parameters related to the formation of the sulphate complexes $UO_2(SO_4)_i^{2-2i}$ ($i = 1-3$), and confirm the stability of the third complex $UO_2(SO_4)_3^{4-}$	R4a: Speciation	Base for K_d & C_{sol}	Medium: Po, NDA, En Low: SKB Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, Po, En Complements an already extensive database	CEA: In oxidative conditions, the influence of sulphate might be taken into account for their complexing properties toward U(VI) (and other radionuclides). The complex formation is even strengthened by increase of temperature.	Improvement of knowledge: Supporting: NDA, En, Po, SKB Improvement of data influencing PA: Supporting: NDA, En, Po, SKB Reliable thermodynamic data are essential to support a safety case. Sulphate complexation data are more relevant in waters with high sulphate concentration, such as in OPA. It is noted that sulphur may be expected to be present as sulphide rather than sulphate under strongly reducing conditions.
1.1.1.b	Determination of thermodynamic data by TRLFS for the $Eu(III)/U(VI)-SO_4$ systems, and validation of the use of ESI-MS for quantitative analysis of species concentrations and for mixed complexes detection				CEA: Evaluation of analytical methods for speciation analysis of radionuclides in environmental conditions.	Improvement of knowledge: Supporting: NDA, En, Po, SKB Improvement of data influencing PA: n/a: NDA, En, Po, SKB Improvements in analytical methods are always useful, but not of direct application to PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)						
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)					
1.1.2a	<p>State of the art on the formation of silicate complexes of trivalent f-element cations and identify the needs of experimental work that could be done in a collaborative work between CEA and CTH</p> <p>The few available studies have been reviewed for a better understanding in a thermodynamic point of view</p>	R4a: Speciation	Base for K_d & C_{sol}		<p>CEA, CTH: Possible role of oligomeric and/or colloidal silicate species in the speciation (and migration) of trivalent radionuclides in groundwaters.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: En, NDA, Po, SKB</p> <p>This bibliographic work is useful in bringing existing data together.</p>
1.1.2b	<p>Determination of missing key thermodynamic constants and their uncertainties for phosphate and silicate complexation in aqueous solutions with selected metals by solvent extraction</p>			<p>Low: SKB, Po, NDA, En</p> <p>Enhancing process understanding: NDA</p> <p>Basis for deriving SA parameter values: SKB, Po, En</p>	<p>CTH: This work contributes to providing missing key thermodynamic data for phosphate and silicate complexation that can be implemented in modelling of the migration of Th(IV) and Am(III) in groundwaters.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, SKB, NDA</p> <p>Although good thermodynamic data on Th from NEA exist, this work provides useful complementary data. Silicate complexation has wider applicability than phosphate.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)						
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)					
1.1.2c	Determinations of thermodynamic data for relevant chemical species of Am(III), Cm(III), Eu(III) and U(VI) in the presence of carbonate and sulphate				CEA: Carbonate and sulphate complexes can be major actinide species in groundwaters. Their stabilities can be assessed by using thermochemical data such as those determined in this work, particularly for temperatures higher than 25° C.	<p>Improvement of knowledge: Supporting: NDA, En, Po, SKB</p> <p>Improvement of data influencing PA: Supporting: NDA, En, Po, SKB</p> <p>Useful exercise of re-evaluating thermodynamic data of Am, Cm, Eu and U(VI) in presence of carbonate and sulphate.</p>
WP 1.2						
Ion exchange and surface complexation						
1.2.1	Batch sorption studies of Am, Cm, Th on apatite, quartz	R4b-d	K _d	Medium:SKB, En Low: Po, NDA Enhancing process understanding: NDA, En Basis for deriving SA parameter values: SKB, Po, En	CTH: The investigation helps in providing needed reference data for modelling the retention capacity of silicate and phosphate minerals under near real repository conditions and the assessment of the effect of biofilm on these minerals.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA, SKB</p> <p>Additional data for sorption onto relevant materials.</p>
1.2.2	<i>cf.</i> clay (general comment on potential use for fault gauge)					
1.2.3	<i>cf.</i> clay (general comment on potential use for fault gauge)					

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Ion exchange and surface complexation (continued)						
WP 1.2						
1.2.4a	Batch sorption studies of Cm, Eu, U(VI) on various substrates Test of a NEM with non-integer proton stoichiometry	R4a-d (a: CO ₃ complex)	K _d	Medium: En Low: SKB, Po, NDA Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, En Knowledge level already high	FZK-INE: A parameter estimation tool for treating multiple data sets was developed and its application within a non-electrostatic model framework was tested, where the non-electrostatic approach was found to be inferior compared to the respective benchmark electrostatic model.	Improvement of knowledge: Supporting: En, NDA, Po, SKB Improvement of data influencing PA: Supporting: NDA, Po, En, SKB Useful information on sorption on different materials has been generated. The conclusion on the convenience of using electrostatic models is relevant for the development of TSM, that are used to support K _d values for PA.
1.2.4b	Batch sorption studies of Cm, Eu, U(VI) on various substrates	R4a-d	K _d		FZK-INE: The bulk composition of a mineral phase does not necessarily reflect the properties of its surface when contacted with water and therefore the nature and the amount of the sorbed metal ion complex can be strongly affected.	Improvement of knowledge: Supporting: En n/a: Po, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB This basic study has limited benefit to PA. The processes examined have little direct application to PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.4c	Molecular scale mechanisms	R4a-d	K_d	Low: Po, NDA, En n/a: SKB Enhancing process understanding: Po, NDA	CEA: These studies confirm that in near-neutral pH conditions, lanthanide (and, by analogy, actinide) retention on clay mineral occurs essentially by specific sorption at the layer edge, providing an additional mechanism of radionuclide retention.	Improvement of knowledge: n/a: Po, NDA, En, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB This study is focussed on sorption on clays and can be relevant only for fracture infills.
1.2.5	<i>cf.</i> clay					
1.2.6	Sorption studies of Ni, Eu on biotite and gneissic rocks TSM of Ni and Eu on gneissic rocks Back-up of TSM sorption reactions by molecular level modelling	R4a-d	K_d	Medium: Po, En, SKB Low: NDA Host-rock specific: SKB Site-specific: SKB Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, En	HU & VTT: Knowledge of sorption at molecular level and sorption models, backup sorption data for safety case calculations.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Experimental data and models for Eu and Ni sorption on granite have been obtained. Both are useful to generate and justify sorption data for PA.
1.2.7	Sorption studies of Th on magnetite and ferrihydrite	R4a-d	K_d	Medium: Po, NDA Low: SKB, En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po, NDA	UPC: In order to be included or considered the sorption process of thorium onto magnetite and ferrihydrite in PA, K_d values and surface complexation constants have been obtained from batch experiments and surface complexation modelling.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: En, Po, NDA, SKB The range of pH in the study (1.8 – 4.8) is very different from the neutral conditions expected in the host rock.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2						
Ion exchange and surface complexation (continued)						
1.2.8	<i>cf.</i> clay					
1.2.9	<i>cf.</i> clay (general comment on potential use for fault gauge)	R4a-c (a: CO ₃ complex)				
WP 1.3						
Influence of organics on the retention of radionuclides by minerals						
1.3.1	<i>cf.</i> clay	R4a-c (a: humic complex)				
1.3.2	Characterisation of goethite and soil surfaces, sorption of humics	R4a (humic sorption)	Base for K _d & C _{soil}	Low: SKB, Po, NDA, En enhancing process understanding: Po, NDA	WU: Improve prediction of ion adsorption to natural samples	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: NDA, Po, En, SKB Sorption in ternary systems RN-HS-Fe oxides is studied. This is useful for fracture materials.
1.3.3	Batch sorption studies of Ni, Eu, Cs, Cd, Fe on montmorillonite, kaolinite, goethite in the presence of various organics	R4a-d (a: various organic complexes)	K _d	Medium: En Low: SKB, Po, NDA Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB	Uni Lough: Whilst the simple organics do show interactions with mineral surfaces and radionuclides, their effect on PA is likely to be considerably less than the ubiquitous humic acids in the geosphere.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: NDA n/a: Po, En, SKB This study is of little relevance to PA for countries which do not have a high organic waste content in their inventory.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.3 Influence of organics on the retention of radionuclides by minerals (continued)						
1.3.4	Batch sorption studies of Np, U, Eu, Cu, Ag, Cd, Am on silica, magnetite, calcite, goethite in the presence of humics	R4a-d (a: humic complex)	K _d	Medium: NDA, En Low: SKB, Po Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB	Uni Man & Lough: A methodology has been developed that predicts the impact of humic colloid kinetics in field scale transport calculations, and parameters have been provided to allow the calculation of RN transport through ternary systems via either equilibrium and/or kinetic speciation. Damkohler numbers are used to decide when full kinetics should be included for an accurate transport prediction and when approximations may be used instead. All of the parameters have been provided to allow predictions to be made either by the exact (kinetic) method or via the approximations (including an equilibrium approach).	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: En, NDA, Po, SKB Useful data on sorption kinetics in ternary systems RN-HS-solids have been generated. This study considers the irreversibility of RN binding in the presence of organics and is useful to support PA.
1.3.5	<i>cf.</i> clay	R4a-d (a: various organic complexes)	K _d			

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.4	Formation of solid solutions and secondary phases, including retardation of anions					
1.4.1	Generation and characterisation of uranium reference minerals	R5a	C_{so1}	Low: SKB, Po, NDA, En Host-rock specific: NDA Enhancing process understanding: Po	FZD: Very small amounts of boltwoodite and compregnacite are identifiable by TRLFS in complex geological samples. The identification of such uranium minerals contributes to a better understanding of the uranium chemistry and its migration behaviour around contaminated sites.	Improvement of knowledge: Supporting: En, NDA, Po, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB Work on oxidised states of actinides are supporting process understanding but this information may not be relevant for reducing conditions expected in clay host formation.
1.4.2a	<i>cf.</i> clay	R5a				
1.4.2b	Incorporation of selenium into pyrite	R5a	C_{so1}	Low: SKB, Po, NDA, En Enhancing process understanding: Po, NDA	SUBATECH: A full Se retention model for reducing repository near- and far field environments does not yet exist, but the clarification of the interaction of Se(-II) with pyrite is an important cornerstone for the creation of such a model. It is particularly important that both the interaction of Se(-II) and of Se(IV) (literature data) lead to the formation of Se(0).	Improvement of knowledge: Supporting: Po, En, NDA Improvement of data influencing PA: Supporting: Po, En, NDA, SKB This mechanism of Se immobilisation could be present in granite formations with Fe bearing minerals.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.4 Formation of solid solutions and secondary phases, including retardation of anions (continued)						
1.4.3	Coprecipitation experiment of U, Np, Pu with calcite	R5a	C_{sol}	Medium: Po, NDA Low: SKB, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB	FZK-INE: Formation of a solid solution with calcite can lead to effective entrapment of NpO_2^{2+} in calcite particles.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA, SKB</p> <p>Calcite can be present in fracture infills. Coprecipitation with calcite can be a useful additional barrier mechanism for the safety case.</p>
1.4.4	Determine radionuclide sorption/incorporation by calcite	R5a	C_{sol}		KU: Lanthanide analogues allowed estimation of actinide uptake in calcite to be significant and low concentrations of nickel were observed to adsorb onto calcite and substitute as solid solution with a distribution coefficient near 1. The source of the calcite in a PA framework is the secondary calcite that forms down gradient from concrete, or weathering of rock containing Ca.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA, SKB</p> <p>Calcite can be present in fracture infills. Sorption/incorporation by calcite can be a useful additional barrier mechanism for the safety case.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.4	Formation of solid solutions and secondary phases, including retardation of anions (continued)					
1.4.5	Theoretical expression of thermodynamics of solid solutions (co-precipitation)	R5a	C_{sol}		CEA: Modelling solubilities provides Thermodynamics bases for validating predictions of the retention of radionuclides here by non-pure solids. Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB This is a theoretical study that improves the description of solid solutions. Although solid solutions are not usually considered in PA calculations, they can be used as an additional argument in the safety case.	
WP 2.1	Formation, migration and transport processes of inorganic colloids					
2.1.1	Inorganic colloid formation and RN interaction	R6b	R	Medium: En Low: SKB, Po, NDA Demonstrating process understanding: En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, En	TUM-RCM & FZK-INE: 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 > 0.015 M in the absence of humic substances.	Improvement of knowledge: Important: Po, SKB Supporting: En, NDA Improvement of data influencing PA: Supporting: Po, En, NDA, SKB The study found that actinides are incorporated into bentonite colloids and this effect is increased by humic acids. Humic acids increase the stability of these colloids too. This is an important topic for PA because colloidal transport can reduce significantly the barrier function of the granite formation.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Formation, migration and transport processes of inorganic colloids (continued)						
WP 2.1	Formation, migration and transport processes of inorganic colloids (continued)					
2.1.2	Backfill-derived clay colloid stability in far-field groundwater of crystalline host rocks	R6a,c	R	High: En Medium: Po, SKB, NDA Design-specific: SKB Demonstrating process understanding: En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po, En	FZK-INE: Smectite colloid stability as a function of pH, ionic strength and cation composition; bentonite buffer erosion rates and RN smectite reversibility kinetics were determined.	Improvement of knowledge: Important: En, Po, SKB Supporting: NDA Improvement of data influencing PA: Important: En, Po, SKB Supporting: NDA Very useful data have been generated to understand and quantify the generation of bentonite colloids at the bentonite-granite interface. However, the work is less important for the UK safety case where the HLW/SF concept has not been finalised.
2.1.3	Colloid stability in far-field groundwater of crystalline host rocks	R6ac	R	Medium: Po, NDA, En Low: SKB Demonstrating process understanding: En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po	FZD: Improved knowledge on uranium mobility in strongly reducing environments was obtained; it refers to both the thermodynamic solubility of U(IV) and the formation of U(IV) colloids.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB This study is n/a to improvement of data, as the conditions under which this work was carried out are not repository relevant.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction						
WP 2.2						
2.2.1a	<p>Radiocolloid interaction with clay formation derived natural organic matter</p> <p>Investigation of immobile organic matter from real site conditions (Ruprechtov site), its behaviour and influence on U migration. Selection of appropriate extraction technique</p> <p>Characterisation and complexation of extracted humic substances with U(VI)</p>	R4a, R6b	R	<p>Low: SKB, Po, En</p> <p>n/a: NDA</p> <p>Enhancing process understanding: Po, NDA</p>	<p>NRI-RES: OM on the Ruprechtov site does not influence speciation of uranium directly as sorbing/complexing agent, but indirectly via maintaining reducing conditions and contributing to U(IV) immobilisation in secondary phases.</p>	<p>Improvement of knowledge: n/a: NDA, Po, En, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB</p> <p>Data obtained with NOM from a sedimentary formation. Some generic knowledge can be obtained but without applicability to the safety case.</p>
2.2.1b	<p>Investigate the interaction of Se with mobile and immobile NOM derived from the Boom Clay (BC) formation, using batch experiments and spectroscopy to elucidate the interaction mechanism and reaction products</p>				<p>KULeuven: Se(VI) is unaffected by NOM. Se(IV) is reduced by BC NOM, resulting in Se⁰ precipitation. Final Se solution concentrations of 4.4×10^{-8} M (BC HS) and 1.3×10^{-7} M (Gorleben HS) were measured after six months observation.</p>	<p>Improvement of knowledge: Supporting: Po, En, SKB, NDA</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB</p> <p>Data obtained with NOM from a clay formation. Some generic knowledge can be obtained but without applicability to the safety case.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2	Investigation of RN interaction with both mobile and immobile NOM (Boom Clay NOM), aiming at a quantitative description				<p>SCK-CEN: The successful implementation of a thermodynamically consistent metal-humic complexation model into Phreeqc provides a tool to quantitatively describe the interaction of tri and tetravalent RN with NOM. This will help in the selection of trustworthy maximum mobile concentrations relevant for PA.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB</p> <p>Data obtained with NOM from a clay formation. Some generic knowledge can be obtained but without applicability to the PA.</p>
2.2.2a	<p>Radionuclide interaction with natural organic matter (NOM)</p> <p>Within this task the redox behaviour of plutonium and neptunium in solutions containing humic substances (HS) is investigated and modelled by equilibrium thermodynamic. To elucidate reaction mechanism simple hydroquinones as model compounds are used beside the HS</p>	R4a, R6b	R	<p>Medium: Po</p> <p>Low: SKB, NDA, En</p> <p>Enhancing process understanding: Po, NDA</p> <p>Basis for deriving SA parameter values: SKB</p>	<p>FZK-INE: Plutonium can exist in trivalent oxidation state at low concentration of $< 10^{-8}$ M. At higher plutonium concentrations colloid formation dominates and only Pu(IV) is present at pH > 3. At the end of the project thermodynamic constants are given that will update modelling of plutonium and neptunium.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB</p> <p>Thermodynamic data for Np and Pu in presence of HS are generated, expanding the knowledge base. Not of direct application to PA</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2						
2.2.2b	Two-fold: i) advance TRLFS methods as analytical tools for improved speciation of actinides and ii) increase/improve fundamental understanding of interaction processes between actinides (lanthanides were used as surrogates and luminescence probes!) and humic substances (HS)				UPPC: Improvement of spectroscopic-based speciation analysis and stressing importance of differentiation between FA and HA fractions for modelling approaches.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB Improvements in analytical techniques are always useful to increase the knowledge but are not of direct application to PA.
2.2.2c	Study of the competition between radionuclides – Co^{2+} , UO_2^{2+} , and Eu^{3+} – and major cations – Ca^{2+} and Mg^{2+} – for humic substances complexation				CEA & UPPC: Functionalised NOM can be generated by an alkaline fluid in clay media. The alkaline earth metals, Ca^{2+} and Mg^{2+} , are merely in competition with actinides and lanthanides for natural organic matter complexation: Fe^{3+} , Al^{3+} , and inter-Ln/An competition should be accounted.	Improvement of knowledge: Supporting: Po, En, NDA Improvement of data influencing PA: Supporting: En n/a: Po, NDA The data are most relevant for high humic content systems.
2.2.2d	Determination of stability constants for the complexation of plutonium(III) with humic substances.				FZD: The stability constants for the complexation of plutonium(III) with humic substances obtained within this study will improve the basic process understanding and contribute to the enhancement of the existing thermodynamic data base.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Improvement in thermodynamic data of Pu in presence of HS increases the knowledge, but is not of direct application to PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction (continued)						
WP 2.2						
2.2.2e	Development of new relativistic quantum-chemical methods for interpretation of NMR spectra of lanthanide complexes with humic acids and model ligands				<p>SAS-IIC: Quantum-chemical prediction of paramagnetic NMR spectra of Gd with a model ligand (salicylic acid) in water solution were performed. The results of these calculations demonstrate that complexes formed via carboxyl group with mono-dentate coordination are preferable but fast exchange of ligand-coordinated water is expected.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB</p> <p>Very fundamental study without direct application to PA.</p>
2.2.2f	Consistency of tetravalent actinide humic acid complexation				<p>CEA & NRIRR & Uni Lough: If no competition occurs, the humic complexation of tetravalent actinides can be obtained with a rather good approximation from Th(IV).</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA, SKB</p> <p>The study found that all tetravalent actinides have similar complexation behaviour with humic acids. This result reduces the need of producing radioisotope specific data on complexation with HS for actinides.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2 Inorganic colloid formation and RN interaction (continued)						
2.2.2g	Determination of the effect of ionic strength on complexation of Pu(IV) with humic acid				NRIR: The present work contributes to providing interaction parameter of Pu(IV) humate that varies with ionic strength. This parameter can be applied in the geochemical modelling of the migration of Pu(IV) under the influence of humic substances.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Very specific topic useful to increase knowledge but without direct application to PA.
2.2.3a	Radionuclide interaction with natural organic matter (NOM) in the presence of mineral phases (ternary systems) Role of the adsorptive fractionation of natural organic matter on alumina, on the interaction with radionuclides	R4a, R6bd	K _d	Low: SKB, Po, NDA, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB	CEA & INE: The humic acid like structures obtained after micro-organism mediated oxidation in sedimentary formation are not comparable to surface extracts, but the complexation properties are similar. These extracts can only be obtained out of a normal evolution scenario.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB Humic acids of different origins present similar complexation properties. This is a useful result although not directly applicable to PA.
2.2.3b	Study of solubility of UO ₂ (OH) ₂ and UO ₂ CO ₃ as a function of the humic acid concentration				Uni Cyprus: The presence of humic acids may affect both solid phase stability and the solution chemistry and this has to be included in PA calculations.	Improvement of knowledge: n/a: Po, En, NDA, SKB Improvement of data influencing PA: n/a: NDA, Po, En, SKB This rather preliminary study on humic acid interaction with model U(VI) compounds is of very limited benefit for the safety case.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide redox transformation on minerals						
WP 2.3	Radionuclide redox transformation on minerals, fracture infills. Áspö, Grimsel Find out if redox reactions on the biotite surface influence the U immobilisation by reducing adsorbed U(VI) species to U(IV) species	R4ab (a: redox)	K _d	High: En, NDA Medium: SKB, Po Demonstrating process understanding: En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po, En	FZD: It can be stated that U reduction during the U adsorption process on the Fe ³⁺ containing silicate minerals, biotite (typical for granitic host rocks) seems to play an important role in the immobilisation behaviour of aqueous U(VI) under oxidising conditions. Note that the investigations performed in collaboration with FZK & KTH (task 2.3.1b) were conducted under inert gas (Argon glove box) conditions and the samples were directly transferred to XPS for redox state analysis in an environmental chamber preserving oxygen free atmosphere (see PID 2.3.7). FZD work was conducted under atmospheric conditions (see PID 2.3.2).	Improvement of knowledge: Supporting: En, NDA, Po, SKB Improvement of data influencing PA: Supporting: NDA, En, Po, SKB Fe bearing minerals in granite can uptake Uranium or other redox sensitive radionuclides, providing an additional immobilisation mechanism.
2.3.1b	Investigating the uptake of U(VI) on Fe(II) minerals in granite in presence of carbonate at near-neutral pH conditions				KTH & FZK-INE: Experimental results have shown reduction of U(VI) on Fe(II) minerals to potentially be important for the immobilisation of uranium in oxygen free granitic environments at near-neutral pH and in presence of carbonate.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Fe bearing minerals in granite can uptake Uranium or other redox sensitive radionuclides, providing an additional immobilisation mechanism.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.3	Radionuclide redox transformation on minerals (continued)					
2.3.1c	Investigation and quantification nonlinear sorption processes: Retention of redox sensitive actinides onto pristine and altered granite				FZK-INE: The retention of Np(V) occurs by redox transformation to Np(IV) forming a low soluble solid at iron phases in the granite.	<p>Improvement of knowledge: Supporting: NDA, Po, En, SKB</p> <p>Improvement of data influencing PA: Supporting: NDA, Po, En, SKB</p> <p>This study presents evidence of the immobilisation of Np(V) by reduction to Np(IV) by iron phases in granite, reducing Np concentration in dissolution. This is an additional immobilisation mechanism that can be included in the safety case.</p>
2.3.2a	Radionuclide redox transformation on minerals, pyrite, siderite Investigate the role of Fe(II) bearing minerals on the retention of Se in reducing conditions (reaction mechanism- formed Se species)	R4ab (a: redox)	K_d	Medium: Po Low: SKB, En, NDA Demonstrating process understanding: En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po	KULeuven: Proof was provided that Se^0 and $FeSe_x$ will be the solubility limiting phases in Boom Clay conditions.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: NDA, Po, En, SKB</p> <p>Additional evidence of the reduction of redox sensitive radionuclides by pyrite and other Fe bearing minerals.</p>
2.3.2b	<i>cf. clay</i>					

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.3	Radionuclide redox transformation on minerals (continued)					
2.3.3	Radionuclide redox transformation on minerals, green rust, fracture infill Aspö	R4ab (a: redox)	K _d	Medium: Po, En Low: SKB, NDA Demonstrating process understanding: En Enhancing process understanding: NDA Basis for deriving SA parameter values: SKB, Po, En	<p>KU: Green rust (Fe(II),(III)-hydroxide) has been documented in groundwaters when little or no oxygen is present. Composition and structure for the sulphate, sodium phase are now known and thermodynamic constants are available. This is important for PA because GR has not been included in safety assessment modelling but it is highly reactive, especially in the presence of redox active species. Green rust forms colloidal particles that could be mobile in the near or far field, thus acting as vectors for contaminant transport. More work needs to be done to establish the relative proportion of GR colloids that stick to fracture walls and that move in the groundwater. Natural concentrations are too low for conventional particle methods, but nano-scale techniques are very effective.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA, SKB</p> <p>Green rust has proved capable of reducing and uptaking redox sensitive radionuclides. This can provide an additional immobilisation mechanism for radionuclides in the host formation.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Impact of biogeochemical processes						
WP 2.4						
2.4.1a	Radionuclide mobility influenced by biofilms Time-dependent sorption and desorption of selected radionuclides onto in situ grown biofilms and assess the effect of microbologically generated ligands on sorption	R4ab, R7	K _d	Medium: En Low: SKB, Po, NDA Demonstrating process understanding: En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, En	CTH: The results indicate that the effect of biofilms in most cases is not vividly distinct but can be observed but the effect of different oxidation states and radionuclides on the sorption capacity appears to be significant and should be considered.	Improvement of knowledge: Supporting: Po, En, NDA Improvement of data influencing PA: n/a: Po, NDA, En, SKB Biofilms do no affect significantly the sorption of radionuclides on granite. Although data is limited it has been found that the potential effect of biofilms of PA is small.
2.4.1b	Determination of the structural components, e.g. exopolymeric substances (EPS) within biofilms and their influence on the actinide speciation and immobilisation of actinides (U) we used stable multi species biofilms				FZD: The addition of uranium in ecologically relevant concentrations has a strong effect on the O ₂ concentration and consumption rates in biofilms due to a stimulation of the metabolism of the microbes and on their respiratory activity and oxygen consumption. This increased respiratory activity results in O ₂ depleted zones closer to the biofilm air interface which may trigger uranium redox processes, which may lead to precipitation of uranium(IV) solids and consequently to a removal of uranium from the aqueous phase.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB This study has improved the understanding of redox processes in biofilms at a fundamental level, but is not of direct application to PA.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Impact of biogeochemical processes (continued)						
WP 2.4						
2.4.2	Radionuclide mobility influenced by microbes	R4ab (a: redox), R7	K_d	Low: SKB, Po, NDA, En Demonstrating process understanding: SKB, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB	Uni Urecht: 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 if the formation of crystalline uraninite is kinetically hindered.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB This study found that microbes can cause the reduction of U(VI) to U(IV). A potentially useful result, but at an early stage.
Characterisation of geochemical conditions in crystalline host rock						
WP 4.1						
4.1.1	Analysis of Fe and Mn oxides as indicators of past oxygen intrusions in the rock	R4a (redox conditions)	Base for K_d & C_{sol}	Medium: Po, NDA, SKB, En Site-specific: En Demonstrating process understanding: SKB, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB	HU: No achievements No achievements. Suspended and resources allocated to task 4.5.1	Improvement of knowledge: n/a: Po, En, NDA Improvement of data influencing PA: n/a: Po, En, NDA Work was suspended, and no results were gathered.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.1						
Characterisation of geochemical conditions in crystalline host rock (continued)						
4.1.2	<i>Analysis of migration processes at the FEBEX site (GTS)</i>					
4.1.2a	Design of the experimental set-up for water chemistry and colloid analyses. Borehole drilling and water sampling.	R4a (boundary conditions for pore-water composition)	Base for K_d & C_{soil}	Medium: SKB, NDA, En, Po Demonstrating process understanding: SKB, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, En	ATEMIN, UPC and CIEMAT: Improvement of geochemical sampling quality. Experimental data obtained in an environment simulating a deep geological repository in granite and in "realistic" conditions.	Improvement of knowledge: Supporting: En, Po, SKB, NDA Improvement of data influencing PA: n/a: Po, En, NDA, SKB Improvement of water sampling will provide better data for host rock characterisation, but is not of direct application to PA.
4.1.2b	Study of solute migration mechanisms in crystalline host rocks influenced by the presence of the bentonite buffer. Experimental and modelling work.	R1, R2, R4a (boundary conditions for pore-water composition)			CIEMAT: Slight solute mass transfer from the near-field to the far field was observed. The effective diffusion coefficient for Cl ⁻ was obtained from geochemical modelling of the <i>in-situ</i> data. The in-situ estimation of diffusion coefficients can be useful also if the bentonite buffer is not present.	Improvement of knowledge: Supporting: En, NDA, SKB n/a: Po Improvement of data influencing PA: Supporting: En, NDA, SKB, Po This full scale experiment in relevant geology indicates process for further consideration. The study can provide useful data on mass transfer at the bentonite-granite interface.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.1	Characterisation of geochemical conditions in crystalline host rock (continued)					
4.1.2	<i>Analysis of migration processes at the FEBEX site (GTS) (continued)</i>					
4.1.2c	Modelling of mass transfer at the bentonite/granite interface	R1, R2, R4a (boundary conditions for porewater composition)			ENVIROS, CSIC, UPC: The mass transfer from near to far field is very dependent on the bentonite saturation and therefore, minor mass transfer is expected until full saturation of bentonite.	<p>Improvement of knowledge: Supporting: En, NDA, SKB n/a: Po</p> <p>Improvement of data influencing PA: Supporting: En n/a: Po, NDA, SKB Po: no decisive results. En: The results of the modelling should be presented together with data gathered in FEBEX gallery. NDA: modelling study appeared not to give predictive capability.</p>
4.1.2d	Analysis of bentonite colloid generation at the FEBEX site	R6	(Colloid concentrations)	High: SKB	CIEMAT and FZK-INE: After 10 years from the bentonite emplacement, and in a very favourable environment for the stability of bentonite as it is Grimsel water, the quantity of bentonite colloids in the groundwater at 30 cm far from the bentonite-granite interface is not higher than 1 ppm.	<p>Improvement of knowledge: Important: En, SKB</p> <p>Improvement of data influencing PA: Important: En, SKB Colloid concentrations are necessary to evaluate colloid-enhanced radionuclide transport.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.2 Fluid flow system characterisation in crystalline host rock						
<i>Matrix diffusion</i>						
4.2.1						
4.2.1a	Transport by matrix diffusion: development and validation of a novel experimental methodology to measure radionuclide diffusion coefficients in granite at a mineral scale	R3	$D_e+K_d (D_a)$	High: Po, NDA Medium: SKB, En Demonstrating process understanding: SKB Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, Po, NDA, En	CIEMAT, HU: The methodology allowed measuring apparent diffusion coefficients of radionuclides at a mineral scale accounting for heterogeneity of the material. Diffusion coefficients and porosity are simultaneously measured. Input data for transport modelling.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, NDA, En, SKB Useful process/methodology development. The methodology developed allows to measure apparent diffusion coefficients on granite at a mineral scale. Useful data on D_a for different granites have been generated. It has been found that Uranium diffusion coefficient increases with granite porosity.
4.2.1b	Experimental and modelling tool development for understanding the effect of heterogeneities on matrix diffusion. Transport by matrix diffusion: experimental work (quantification of spatial porosity distribution in crystalline rock)	R3			HU, HYDRASA, CIEMAT, OVIUNI, VTT: Improvement of process understanding concerning matrix diffusion from water flowing fractures.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Useful data on porosities and heterogeneities for different granites have been generated.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.2 Fluid flow system characterisation in crystalline host rock (continued)						
<i>Matrix diffusion (continued)</i>						
4.2.1						
4.2.1c	Quantification of spatial porosity distribution in crystalline rock	R3			UNIOVI and HU: Compared and optimised the microfractographic network characterisation techniques. Improvement of knowledge: Supporting: En, NDA, Po, SKB Improvement of data influencing PA: n/a: En, Po, NDA, SKB This task deals with the comparison of different techniques. Although it is useful to improve knowledge it is not of direct application to PA.	
<i>Application of new visualisation techniques as a support of transport experiments (with radionuclides and colloids) in crystalline rocks</i>						
4.2.2						
4.2.2a	Experimental and modelling work combining information based on laboratory migration experiment on fractured rock core samples from the Aspö granodiorite	R1, R2, R6			FZK-INE, JGUM: Improvement of process understanding on colloid retention mechanisms in real fractured rock systems.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB Matrix diffusion of colloids was not observed in these experiments of transport in a fracture. This result is consistent with the very low values of D_a for colloids in granite measured in Task 4.3.2.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.2 Fluid flow system characterisation in crystalline host rock (continued)						
<i>Application of new visualisation techniques as a support of transport experiments (with radionuclides and colloids) in crystalline rocks</i> (continued)						
4.2.2						
4.2.2b	New experimental method Positron Emission Tomography (PET) for spatial resolved studies of advective flow and matrix diffusion in crystalline rock drilled cores	R1, R3			IIF: A new experimental approach for non-destructive spatially resolved studies of fluid flow and colloid transport in fractured drilled rock cores with PET was developed, new data sets for transport modelling of heterogeneous transport processes in crystalline host rock were evaluated.	<p>Improvement of knowledge: Supporting: Po, NDA, En, SKB</p> <p>Improvement of data influencing PA: Supporting: Po, En, NDA</p> <p>A novel technique to study radionuclide and colloid transport in a fracture was successfully developed. Very graphical results are obtained and have allowed to identify the relevance of heterogeneous transport in a single fracture.</p>
4.2.2c	Development and application of combined X-ray microtomography and microfluorescence for spatial resolved analysis of crystalline host rock microstructure and composition	R3			NILPRP: A new experimental approach for non-destructive spatially resolved mapping of the mineral composition and the volumetric microstructure of the host rock samples was established. This can offer the possibility to study at a microscopic scale physical properties and composition and can be of help to understand the role heterogeneity on RN retention.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: En, Po, NDA, SKB</p> <p>Methodology and concept support.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.2 Fluid flow system characterisation in crystalline host rock (continued)						
<i>Hydrogeological and geophysical studies at the FEBEX gallery</i>						
4.2.3						
4.2.3a	Hydrogeological studies: hydraulic tests	R1		High: Po, En, NDA Medium: SKB Demonstrating process understanding: SKB Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, Po, En	UPC, ATEMIN, CIEMAT, CSIC: Improvement the knowledge fluid flow system in granite rocks near the bentonite-granite interface.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB Site-specific results, although the methodology can be of interest for site characterisation.
4.2.3b	Hydrogeological studies: Characterisation of the hydrogeological behaviour at the scale of the granite-bentonite contact within the FEBEX experiment	R1			UPC, ATEMIN, CIEMAT, CSIC, UNIOVI: Identifying the main structures and their connectivity is essential to identify potential paths suitable for the migration of contaminants.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: n/a: Po, En, NDA, SKB Hydrogeological characterisation of the granite around a disposal drift is important to model flows in the near field. Results obtained in this study are site-specific but the methodology can be applied to other granite formations.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.2 Fluid flow system characterisation in crystalline host rock (continued)						
<i>Hydrogeological and geophysical studies at the FEBEX gallery (continued)</i>						
4.2.3c	Geophysical studies. System characterisation: determination of the detailed internal structure of a granite rock body	R1			<p>CSIC: Detailed high resolution geophysical characterisation is mandatory in order to design realistic fluid flow models. The structural constraints provided by the geophysical imaging techniques are an asset for successful 3D model building.</p> <p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: En, NDA, Po, SKB</p> <p>Characterisation of the host rock close to the disposal drift is important to model flows around the drift. Results obtained in this study are site-specific but the methodology can be applied to other granite formations.</p>	

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.3						
<i>Generation, quantification, characterisation, stability and mobility of groundwater colloids</i>						
<i>4.3.1 Generation and characterisation of natural and bentonite colloids</i>						
4.3.1a	Study the nature of natural colloids generated from the fracture infill minerals in samples from the Grimsel test site. Laboratory tests on colloid release rates from compacted bentonite	R6c	Base for R	High: SKB, En Medium: Po, NDA Site-specific: Po Demonstrating process understanding: En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, Po, En	FZK-INE, CIEMAT: Improvement of knowledge on colloid generation from fracture filling material and compacted bentonite.	<p>Improvement of knowledge: Supporting: Po, NDA, En, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB Po: No decisive results yet.</p> <p>The study has found that erosion of fracture filling material can generate colloids. Parameters controlling the generation of colloids from bentonite have been identified: dry density, pH and ionic strength.</p>
4.3.1b	Study of the bentonite colloid generation source term in realistic conditions	R6c			CIEMAT, FZK-INE: Many parameters have been identified as relevant for colloid generation related to the clay nature and the chemistry of the groundwater. Another interesting parameters affecting colloid generation are the clay compaction density and the surface exposed to hydration (and consequent extrusion paths). Nevertheless to analyse the impact of colloid generation is necessary to account for mobility studies (see 4.3.2).	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, En, NDA, SKB Useful data on bentonite colloids concentration and generation rates have been generated.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.3	Generation, quantification, characterisation, stability and mobility of groundwater colloids					
4.3.2	<i>Colloid mobility and stability</i>					
4.3.2a	Analysis of colloid mobility in a fracture. Dynamic experiments	R6a,c,d	Base for R	High: SKB, En Medium: Po, NDA Site-specific: Po Demonstrating process understanding: En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, Po, En	CIEMAT: Even in conditions favourable for colloid stability and mobility (e.g Grimsel water) bentonite colloids are extensively filtered in the fractures when the water flow is low (mL/h).	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, NDA, SKB, En
4.3.2b	Development of a methodology to experimentally measure colloid diffusion coefficients in crystalline rocks	R6a,c,d	$D_e + "K_d"$ (D_a)	Medium: SKB Basis for deriving SA parameter values: SKB	Apparent diffusion coefficients for colloids experimentally measured are in the range of 10^{-17} m ² /s.	Improvement of knowledge: Important: En, SKB Improvement of data influencing PA: Important: SKB Supporting: En Apparent diffusion coefficients of colloids in granite have been measured and are very small ($<10^{-17}$ m ² /s). Colloid diffusion data are necessary to evaluate colloid-enhanced radionuclide transport.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.4	Radionuclide transport studies including the effects of inorganic/organic colloids					
4.4.1	<i>Laboratory migration studies</i>					
4.4.1a	Mock-up experiment. Transport of HTO, Cl and Cs from the bentonite to granite. Experiment design and first experimental results	R1, R2, R3, R4, R6		High: En Medium: SKB, Po, NDA Demonstrating process understanding: SKB, En Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, Po, En	CIEMAT, UDC: Determination of radionuclide diffusion coefficients under realistic conditions.	<p>Improvement of knowledge: Important: En (potentially) Supporting: Po, NDA</p> <p>Improvement of data influencing PA: Important: En (potentially) Supporting: Po n/a: NDA</p> <p>Promising large-scale migration experiment in presence of bentonite has been implemented. It is expected to provide (in the future) information about the relevance of bentonite colloids for transport.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.4	Radionuclide transport studies including the effects of inorganic/organic colloids (continued)					
4.4.1	<i>Laboratory migration studies (continued)</i>					
4.4.1b	Transport of Pu, Eu, Sr and U in granite fracture in the presence of bentonite colloids	R1, R2, R3, R4, R6		High: En Medium: SKB, Po, NDA Demonstrating process understanding: SKB, En Enhancing process understanding: Po, NDA basis for deriving SA param.values: SKB, Po, En	CIEMAT: Model calculation showed that the presence of colloids could increase significantly (a factor 100) the release rates from the near field for strongly sorbing RNs (Th, Pu). Calculation was made considering high concentration in water of bentonite colloids (0.1 g/L) and much higher sorption on colloids than in compacted bentonite (100 times). The effect of bentonite colloids on less sorbing elements (Cs) is much smaller (just a factor 2 of increase), and negligible for weakly sorbing or conservative RN. The irreversibility of sorption from colloids would increase the effects.	Improvement of knowledge: Supporting: En, SKB Improvement of data influencing PA: Supporting: En, SKB Colloidally enhanced transport of strongly sorbing radionuclides may be important, but these strongly sorbing radionuclides are not expected to diffuse through the bentonite buffer engineered barrier. RN transport experiments in granite fractures in the presence of bentonite colloids have given mixed results: it seems that Eu desorbs from the colloids while Pu does not.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.4 Radionuclide transport studies including the effects of inorganic/organic colloids (continued)						
<i>Laboratory migration studies (continued)</i>						
4.4.1c	Scoping calculation and modelling of the mock-up first results	R1, R2, R3, R4, R6		Medium: SKB Enhancing process understanding: SKB	UDC: 3D models of large-scale experiments provide reliable estimates of rock diffusion anisotropy. Numerical models overcome the limitations of analytical methods which cannot account for non-ideal effects such as sinter filters, gaps, and damaged zones. Interpretation of lab and in situ experiments and estimation with numerical models provides unbiased estimates of diffusion and retention parameters.	Improvement of knowledge: Supporting: SKB n/a: En Improvement of data influencing PA: n/a: En, SKB Modelling that will improve our process understanding. Confidence in the models relies on experimental data.
4.4.1d	Experimental programme to understand colloids-RN interactions and the effects of colloids on radionuclide migration	R1, R2, R3, R4, R6			FZK-INE, CIEMAT: Improvement of knowledge on reversibility of actinide – colloid interaction and colloid – rock interaction.	Improvement of knowledge: Supporting: Po, En, NDA, SKB Improvement of data influencing PA: Supporting: Po, En, NDA, SKB This task has the potential of providing very useful data for colloids, but the TAF contains little information on results.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.4	Radionuclide transport studies including the effects of inorganic/organic colloids (continued)					
4.4.2	<i>Batch retention studies</i>					
4.4.2.a	Kinetics of complexation/sorption of humic substances to cations	R1, R2, R3, R4			Royal Inst. of Technology: Sorption/complexation of humic substances to cations is very fast. The rates are or are near to being diffusion controlled. At low ionic strengths (no competing ions) the work shows that the sorption/complexation of cations to humic substances is very fast. The process is fast enough to neglect the kinetics. NRI-REZ: Advanced methodologies, studying microscale and medium scale radionuclide distribution, was invented for the Czech rock samples and groundwater.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, NDA, En, SKB Complexation/sorption of humic substances to cations is very fast.</p> <p>Improvement of knowledge: Supporting: Po, NDA, En, SKB</p> <p>Improvement of data influencing PA: n/a: NDA, Po, En, SKB Transport parameters have been measured in Czech granite. Results are site-specific but can serve as supporting data for other sites.</p>
4.4.2c	Study of the retention properties of the Czech granitic reference samples	R1, R2, R3, R4				

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 4.5	Process identification and verification by real system analysis					
4.5.1a	Process understanding under present hydrological and hydrogeochemical conditions	R1, R2, R3		High: Po Medium: En, NDA, SKB Site-specific: SKB, Po, En Enhancing process understanding: En	<p>GEOPINT: The collected values and the process understanding can be used for: 1) input parameter values in calculating long-term repository safety, and 2) to understand the present undisturbed hydrogeochemical conditions and how these conditions will change in the future. The data are site-specific but the performed analysis and modeling reflects the main processes common for all groundwater systems and can therefore be used for SA. It gives a unique reference to real system analysis.</p>	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: NDA, En, Po, SKB Data compilation is site-specific, but it can be used for other sites as supporting data.</p>
4.5.1b	Study of freezing processes in crystalline bedrock. Effect of recent glacial events on the naturally occurring uranium	R1, R2, R3			<p>HUT: Better understanding of the freezing processes of crystalline bedrock deep in the repository level.</p>	<p>Improvement of knowledge: Supporting: Po, NDA, SKB n/a: En</p> <p>Improvement of data influencing PA: Supporting: Po, NDA, SKB n/a: En Glacial conditions are not expected in the Spanish safety case.</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Process identification and verification by real system analysis (continued)						
WP 4.5	Process identification and verification by real system analysis (continued)					
4.5.1c	Development of integration of isotope methodology into groundwater flow modelling – utilisation of U isotopes	R1, R2, R3			HU, FZK-INE, GEOPOINT: Increased understanding of the behavior of U isotopes helps to develop models for simulating future groundwater system.	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: Po, NDA, En, SKB</p> <p>An analysis of the usefulness of the U234/U238 ratio to understand groundwater systems was done. This methodology can be applied to other granitic formations.</p>
WP 4.6	Upscaling of processes					
4.6.1	Matrix diffusion upscaling	R1, R2, R3		High: Po, En, NDA Medium: SKB Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, Po Improve SA modelling: En	VTT: Supports more realistic modelling of the geosphere retention in PA. Model will be tested against available laboratory scale tracer tests	<p>Improvement of knowledge: Supporting: Po, En, NDA, SKB</p> <p>Improvement of data influencing PA: n/a: NDA, Po, En, SKB</p> <p>A tool to include rock heterogeneities in PA has been developed.</p>
4.6.2	Sorption upscaling	R4	K_d	High: En, NDA Medium: SKB, Po Enhancing process understanding: Po, NDA, En Basis for deriving SA parameter values: SKB, Po, En	CIEMAT: K_d values determined in the material not previously crushed are more realistic. The effects of heterogeneity in K_d values can be accounted for.	<p>Improvement of knowledge: Supporting: En, NDA, Po, SKB</p> <p>Improvement of data influencing PA: Supporting: En, NDA, Po, SKB</p> <p>Would be an important topic but seems to be in an early stage (limited range of conditions).</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Upscaling of processes (continued)						
WP 4.5						
4.6.3a	Development of a model for implementation of multi-component reactive transport in PA. (upscaling and effective modeling of reactive transport in heterogeneous media)	R1, R2, R3, R4a (specification)		Medium: Po, En, NDA Low: SKB Enhancing process understanding: Po, NDA Basis for deriving SA parameter values: SKB, Po Improve SA modelling: En	UPC, CSIC: The quantification of effective reaction and transport in heterogeneous media is a prerequisite for the realistic large-scale modelling and thus prediction of the fate of radionuclides in geological media. The developed concepts and modelling frameworks are implemented in numerical PA tools.	Improvement of knowledge: Important: Po, SKB Supporting: En, NDA Improvement of data influencing PA: Supporting: Po, En, SKB n/a: NDA A computer code has been developed, with potential application to PA.
4.6.3b	Analysis of modelling methodologies for upscaling transport parameters in porous fracture system (abstraction of transport processes to performance assessment analysis)	R1, R2, R3, R4a (specification)			UPV: The upscaling methodology we developed provides an efficient tool to simplify the transport problem involved in the safety case. The advantages/limitations of using this method is shown through performance assessment exercises.	Improvement of knowledge: Supporting: Po, En, SKB n/a: NDA Improvement of data influencing PA: Supporting: Po, En, SKB n/a: NDA A new upscaling methodology has been developed. It can be applied to PA.

Tab. C-3: Task evaluation table for salt

Concerning "Importance of improvements for SA parameter uncertainty reduction":

- * The relevance of this parameter is site- and case-specific. If the examined radionuclide is dose-relevant for the specific site/case the higher rating applies.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.1	Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data					
1.1.1a	Determine the thermodynamic parameters related to the formation of the sulphate complexes $\text{UO}_2(\text{SO}_4)_i^{2-2i}$ ($i = 1 - 3$), and confirm the stability of the third complex $\text{UO}_2(\text{SO}_4)_3^{4-}$	3.2.2.1 3.2.5.1	Base for K_d & C_{sol}	High*/Medium Basis for deriving SA parameter values	CEA: In oxidative conditions, the influence of sulphate might be taken into account for their complexing properties toward U(VI) (and other radionuclides). The complex formation is even strengthened by increase of temperature.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.1.1b	Determination of thermodynamic data by TRLFS for the $\text{Eu(III)/U(VI)-SO}_4$ systems, and validation of the use of ESI-MS for quantitative analysis of species concentrations and for mixed complexes detection				CEA: Evaluation of analytical methods for speciation analysis of radionuclides in environmental conditions.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.1.2a	State of the art on the formation of silicate complexes of trivalent f-element cations and identify the needs of experimental work that could be done in a collaborative work between CEA and CTH. The few available studies have been reviewed for a better understanding in a thermodynamic point of view	3.2.2.1 3.2.5.1	Base for K_d & C_{sol}	High*/Medium Basis for deriving SA parameter values	CEA, CTH: Possible role of oligomeric and/or colloidal silicate species in the speciation (and migration) of trivalent radionuclides in groundwaters.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.1						
Ionic species/speciation, processes determining physico-chemical conditions and generation of missing thermodynamic data (continued)						
1.1.2b	Determination of stability constants Determination of missing key thermodynamic constants and their uncertainties for phosphate and silicate complexation in aqueous solutions with selected metals by solvent extraction					Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.1.2c	Determinations of thermodynamic data for relevant chemical species of Am(III), Cm(III), Eu(III) and U(VI) in the presence of carbonate and sulphate					Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
WP 1.2						
Ion exchange and surface complexation						
1.2.1	Batch sorption studies of Am, Cm, Th on apatite, quartz	3.2.3.1	K_d	High* /Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values		Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.2	Batch sorption studies of Ni, Eu, U(VI) on illite, OPA in the presence of carbonate	3.2.2.1 3.2.3.1 3.2.5.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	PSI: Extend the currently available thermodynamic sorption models for Ni(II), Eu(III) and U(VI) onto illite and Opalinus Clay for performance assessment purposes by including the influence of carbonate complexation on radionuclide sorption.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.2.3	Batch sorption studies of Tc, Se on pyrite, illite, Boom Clay	3.2.2.1 3.2.3.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	KULeu: Experimental results indicate that the long term Se speciation in Boom Clay will be governed by the presence of reduced Se phases, due to interaction with reducing minerals such as e.g. pyrite.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.2.4a	Batch sorption studies of Cm, Eu, U(VI) on various substrates	3.2.3.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	FZK-INE: A parameter estimation tool for treating multiple data sets was developed and its application within a non-electrostatic model framework was tested, where the non-electrostatic approach was found to be inferior compared to the respective benchmark electrostatic model.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.4b	Batch sorption studies of Cm, Eu, U(VI) on various substrates	3.2.3.1			FZK-INE: The bulk composition of a mineral phase does not necessarily reflect the properties of its surface when contacted with water and therefore the nature and the amount of the sorbed metal ion complex can be strongly affected.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
1.2.4c	Molecular scale mechanisms	3.2.3.1			CEA: These studies confirm that in near-neutral pH conditions, lanthanide (and, by analogy, actinide) retention on clay mineral occurs essentially by specific sorption at the layer edge, providing an additional mechanism of radionuclide retention.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
1.2.5	Very commonly found in clayey rocks, illite was chosen as material support for assessing eventual non-ideal behaviour of sorbed species in the framework of IXT2 – Another aim was cross-evaluation of SCM and IXT2 in the modelling of sorption properties of the same and often studied mineral, gibbsite	3.2.3.1	K _d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	CEA: Illite thermodynamic sorption data (IXT2 version) outcoming from this research are potentially useful for PA.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.2 Ion exchange and surface complexation (continued)						
1.2.6	Batch sorption studies of Ni, Eu on granitic rock materials	3.2.3.1		n/a	HU & VTT: Knowledge of sorption at molecular level and sorption models. Back-up sorption data for safety case calculations.	
1.2.7	Sorption studies of Th on magnetite and ferrihydrite	3.2.3.1		High*/Medium Site-specific Enhancing process understanding	UPC: In order to be included or considered the sorption process of thorium onto magnetite and ferrihydrite in PA, Kd values and surface complexation constants have been obtained from batch experiments and surface complexation modelling.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.2.8	Batch sorption experiment on clay minerals	3.2.3.1		High*/Medium Site-specific Enhancing process understanding	CIEMAT: The thorough analyses of sorption data, based on a quasi-mechanistic description of simplified systems is the basis for the understanding of mixed clay systems.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.2.9	Batch sorption studies of tetravalent & trivalent actinides on Boom Clay	3.2.3.1		n/a	SCK-CEN: 1. Site-specific sorption data for tri- and tetravalent RN are obtained which can be used for selection of retention data for PA 2. Increased process understanding (sorption, complexation, colloid mobility) in the interaction of trivalent RN with clays in presence of NOM.	

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.3						
Influence of organics on the retention of radionuclides by minerals						
1.3.1	Batch sorption studies of Am on clay minerals in the presence of humic acids	3.2.2.1 3.2.3.1 3.2.4.1 3.2.5.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	FZD: The presence of humic acid may affect the Am(III) migration under environmentally relevant conditions.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.3.2	Characterisation of goethite and soil surfaces, sorption of humics	3.2.2.1 3.2.3.1	Base for K_d & C_{sol}	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	WU: Improve prediction of ion adsorption to natural samples.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
1.3.3	Batch sorption studies of Ni, Eu, Cs, Cd, Fe on montmorillonite, kaolinite, goethite in the presence of various organics	3.2.3.1 3.2.5.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	Uni Lough: Whilst the simple organics do show interactions with mineral surfaces and radionuclides, their effect on PA is likely to be considerably less than the ubiquitous humic acids in the geosphere.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Influence of organics on the retention of radionuclides by minerals						
WP 1.3	Influence of organics on the retention of radionuclides by minerals					
1.3.4	Batch sorption studies of Np, U, Eu, Cu, Ag, Cd, Am on silica, magnetite, calcite, goethite in the presence of humics	3.2.3.1 3.2.5.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	Uni Man & Lough: Basically, kinetics leads to slower reversibility. A methodology has been developed that predicts the impact of humic colloid kinetics in field scale transport calculations, and parameters have been provided to allow the calculation of RN transport through ternary systems via either equilibrium and/or kinetic speciation. Damkohler numbers are used to decide when full kinetics should be included for an accurate transport prediction and when approximations may be used instead. All of the parameters have been provided to allow predictions to be made either by the exact (kinetic) method or via the approximations (including an equilibrium approach).	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.3.5	Batch sorption studies of Eu, Cm on smectite in the presence of organics	3.2.3.1	K_d	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	FZK-INE: New data on clay host rock (OPA, COx) sedimentary organic matter spatial distribution, functionality, kerogen reactivity and RN complexation is provided.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Formation of solid solutions and secondary phases, including retardation of anions						
WP 1.4	Formation of solid solutions and secondary phases, including retardation of anions					
1.4.1	Generation and characterisation of uranium reference minerals	3.2.2.1	C_{sol}	Low	FZD: Very small amounts of boltwoodite and com-preignacite are identifiable by TRLFS in complex geological samples. The identification of such uranium minerals contributes to a better understanding of the uranium chemistry and its migration behaviour around contaminated sites.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a
1.4.2a	Coprecipitation and sorption studies of Se on clay minerals Sorption of Se(IV) on compacted clay materials	3.2.2.1	C_{sob} , K_d	Medium	Armines, Leuven University: Sorption data between Se(IV) and clay materials are not affected by compaction ($600 - 1300 \text{ kg/m}^3$). High compactions are not possible with this methodology.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a
1.4.2.b	Incorporation of selenium into pyrite				SUBATECH: A full Se retention model for reducing repository near- and far field environments does not yet exist, but the clarification of the interaction of Se(-II) with pyrite is an important cornerstone for the creation of such a model. It is particularly important that both the interaction of Se(-II) and of Se(IV) (literature data) lead to the formation of Se(0).	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 1.4						
Formation of solid solutions and secondary phases, including retardation of anions (continued)						
1.4.3	Coprecipitation experiment of U, Np, Pu with calcite	3.2.2.1	C_{sol}	Low Site-specific	FZK-INE: Formation of a solid solution with calcite can lead to effective entrapment of NpO_2^{2+} in calcite particles.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
1.4.4.	Determine radionuclide sorption/incorporation by calcite	n/a			KU: New data for PA modelling: Lanthanide analogues allowed estimation of actinide uptake in calcite to be significant and low concentrations of nickel were observed to adsorb onto calcite and substitute as solid solution with a distribution coefficient near 1. The source of calcite in a PA framework is the secondary calcite that forms down gradient from concrete, or weathering of rock containing Ca.	
1.4.5	Theoretical expression of thermodynamics of solid solutions (co-precipitation)	3.2.2.1	C_{sol}	Low Site-specific	CEA: Modelling solubilities provides thermodynamics bases for validating predictions of the retention of radionuclides here by not-pure solids.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.1	Formation, migration and transport processes of inorganic colloids					
2.1.1	Inorganic colloid formation and RN interaction	3.2.4.1	R	Medium Site-specific Enhancing process understanding	TUM-RCM & FZK-INE: 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 > 0.015 M in the absence of humic substances.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.1.2	Backfill-derived clay colloid stability in far-field groundwater of crystalline host rocks	3.2.4.1	R	n/a	FZK-INE: Smectite colloid stability as a function of pH, ionic strength and cation composition; bentonite buffer erosion rates and RN smectite reversibility kinetics were determined.	
2.1.3	Colloid stability in far-field groundwater of crystalline host rocks	3.2.4.1	R	n/a	FZD: Improved knowledge on uranium mobility in strongly reducing environments was obtained; it refers to both the thermodynamic solubility of U(IV) and the formation of U(IV) colloids.	

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2 Inorganic colloid formation and RN interaction						
2.2.1.a	<p>Radionuclide interaction with clay formation derived natural organic matter</p> <p>Investigation of immobile organic matter from real site conditions (Ruprechtov site), its behaviour and influence on U migration. Selection of appropriate extraction technique.</p> <p>Characterisation and complexation of extracted humic substances with U(VI). Refers to overburden</p>	3.2.4.1	R	<p>Site-specific</p> <p>Enhancing process understanding</p> <p>Basis for deriving SA parameter values</p>	<p>NRI-RES: OM on the Ruprechtov site does not influence speciation of uranium directly as sorbing/complexing agent, but indirectly via maintaining reducing conditions and contributing to U(IV) immobilisation in secondary phases.</p>	<p>Improvement of knowledge: Supporting</p> <p>Improvement of data influencing PA: Supporting</p>
2.2.1.b	<p>Investigate the interaction of Se with mobile and immobile NOM derived from the Boom Clay (BC) formation, using batch experiments and spectroscopy to elucidate the interaction mechanism and reaction products</p>				<p>KULeuven: Se(VI) is unaffected by NOM. Se(IV) is reduced by BC NOM, resulting in Se⁰ precipitation. Final Se solution concentrations of 4.4×10^{-8} M (BC HS) and 1.3×10^{-7} M (Gorleben HS) were measured after six months observation.</p>	<p>Improvement of knowledge: n/a</p> <p>Improvement of data influencing PA: n/a</p>
2.2.1.c	<p>Investigation of RN interaction with both mobile and immobile NOM (Boom Clay NOM), aiming at a quantitative description</p>				<p>SCK-CEN: A quantitative description of the interaction of Eu and Boom Clay NOM for different size fractions is achieved which will help us in the selection of trustworthy maximum mobile concentrations (PA relevant solubility) for trivalent RN for PA.</p>	<p>Improvement of knowledge: n/a</p> <p>Improvement of data influencing PA: n/a</p>

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Inorganic colloid formation and RN interaction						
WP 2.2	Inorganic colloid formation Radionuclide interaction with natural organic matter (NOM) Within this task the redox behaviour of plutonium and neptunium in solutions containing humic substances (HS) is investigated and modelled by equilibrium thermodynamic. To elucidate reaction mechanism simple hydroquinones as model compounds are used beside the HS	3.2.4.1	R	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	FZK-INE: Plutonium can exist in trivalent oxidation state at low concentration of $< 10^{-8}$ M. At higher plutonium concentrations colloid formation dominates and only Pu(IV) is present at pH > 3 . At the end of the project thermodynamic constants are given that will update modelling of plutonium and neptunium.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.2.2b	Twofold: i) advance TRIFS methods as analytical tools for improved speciation of actinides and ii) increase/improve fundamental understanding of interaction processes between actinides (lanthanides were used as surrogates and luminescence probes!) and humic substances (HS)				UPPC: Improvement of spectroscopic-based speciation analysis and stressing importance of differentiation between FA and HA fractions for modelling approaches.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2 Inorganic colloid formation and RN interaction (continued)						
2.2.2c	Study of the competition between radionuclides – Co^{2+} , UO_2^{2+} , and Eu^{3+} – and major cations – Ca^{2+} and Mg^{2+} – for humic substances complexation				CEA & UPPC: Functionalised NOM can be generated by an alkaline fluid in clay media. The alkaline earth metals, Ca^{2+} and Mg^{2+} , are merely in competition with actinides and lanthanides for natural organic matter complexation: Fe^{3+} , Al^{3+} , and inter- Ln/An competition should be accounted.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.2.2d	Determination of stability constants for the complexation of plutonium(III) with humic substances.				FZD: The stability constants for the complexation of plutonium(III) with humic substances obtained within this study will improve the basic process understanding and contribute to the enhancement of the existing thermodynamic data base.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.2.2e	Development of new relativistic quantum-chemical methods for interpretation of NMR spectra of lanthanide complexes with humic acids and model ligands				SAS-IIC: Quantum-chemical predictions of paramagnetic NMR spectra of Gd with a model ligand (salicylic acid) in water solution were performed. The results of these calculations demonstrate that complexes formed via carboxyl group with monodentate coordination are preferable but fast exchange of ligand-coordinated water is expected.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.2						
Inorganic colloid formation and RN interaction (continued)						
2.2.2f	Consistency of tetravalent actinide humic acid complexation				CEA & NRIRR & Uni Lough: If no competition occurs, the humic complexation of tetravalent actinides can be obtained with a rather good approximation from Th(IV).	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.2.2g	Determination of the effect of ionic strength on complexation of Pu(IV) with humic acid				NRIRR: The present work contributes to providing interaction parameter of Pu(IV) humate that varies with ionic strength. This parameter can be applied in the geochemical modelling of the migration of Pu(IV) under the influence of humic substances.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.2.3a	Radionuclide interaction with natural organic matter (NOM) in the presence of mineral phases (ternary systems) Role of the adsorptive fractionation of natural organic matter on alumina, on the interaction with radionuclides	3.2.4.1	R	High*/Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	CEA & INE: The humic acid like structures obtained after micro-organism mediated oxidation in sedimentary formation are not comparable to surface extracts, but the complexation properties are similar. These extracts can only be obtained out of a normal evolution scenario.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
2.2.3b	Study of solubility of UO ₂ (OH) ₂ and UO ₂ CO ₃ as a function of the humic acid concentration				Uni Cyprus: The presence of humic acids may affect both solid phase stability and the solution chemistry and this has to be included in PA calculations.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide redox transformation on minerals						
WP 2.3	Radionuclide redox transformation on minerals, fracture infills Äspö, Grimsel Find out if redox reactions on the biotite surface influence the U immobilisation by reducing adsorbed U(VI) species to U(IV) species	3.2.2.1 3.2.3.1	K_d	Medium Site-specific Basis for deriving SA parameter values	FZD: It can be stated that U reduction during the U adsorption process on the Fe ²⁺ containing silicate minerals, biotite (typical for granitic host rocks) seems to play an insignificant role in the immobilisation behaviour of aqueous U(VI) under oxidising conditions. Note that the investigations performed in collaboration between FZK & KTH (task 2.3.1b) were conducted under inert gas (argon globe box) conditions and the samples were directly transferred to XPS for redox state analysis in an environmental chamber preserving oxygen free atmosphere (see PID 2.3.7). FZD work was conducted under atmospheric conditions (see PID 2.3.2).	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.3.1.b	Investigating the uptake of U(VI) on Fe(II) minerals in granite in presence of carbonate at near-neutral pH conditions				KTH & FZK-INE: Experimental results have shown reduction of U(VI) on Fe(II) minerals to potentially be important for the immobilisation of uranium in oxygen free granitic environments at near-neutral pH and in presence of carbonate.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.3	Radionuclide redox transformation on minerals (continued)					
2.3.1c	Investigation and quantification nonlinear sorption processes: Retention of redox sensitive actinides onto pristine and altered granite				FZK-INE: The retention of Np(V) occurs by redox transformation to Np(IV) forming a low soluble solid at iron phases in the granite.	
2.3.2a	Radionuclide redox transformation on minerals, pyrite, siderite Investigate the role of Fe(II) bearing minerals on the retention of Se in reducing conditions (reaction mechanism-formed Se species)	3.2.2.1 3.2.3.1	K_d	Medium Site-specific Basis for deriving SA parameter values	KULeuven: Proof was provided that Se^{VI} and $FeSe_x$ will be the solubility limiting phases in Boom Clay conditions.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
2.3.2b	Investigation of radionuclide -U(VI)- sorption/sorptive reduction on pyrite/siderite in presence/absence of Boom Clay NOM. <i>cf.</i> Clay				SCK-CEN: Confidence building with respect to the U speciation in the Boom Clay far field: dominant U speciation for Boom Clay conditions is the tetravalent state.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Radionuclide redox transformation on minerals (continued)						
WP 2.3	Radionuclide redox transformation on minerals, green rust, fracture infill Åspö	3.2.2.1 3.2.3.1	K_d	Medium Site-specific Basis for deriving SA parameter values	KU: Green rust (Fe(II),(III)-hydroxide) has been documented in groundwaters when little or no oxygen is present. Composition and structure for the sulphate, sodium phase are now known and thermodynamic constants are available. It was shown that it is highly reactive, especially in the presence of redox active species. Green rust forms colloidal particles that could be mobile in the near or far field, thus acting as vectors for contaminant transport.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a
WP 2.4	Impact of biogeochemical processes					
2.4.1a	Radionuclide mobility influenced by biofilms Time dependent sorption and desorption of selected radionuclides onto in-situ grown biofilms and assess the effect of microbially generated ligands on sorption	3.2.7.7	K_d	Low Site-specific Basis for deriving SA parameter values	CTH: The results indicate that the effect of biofilms in most cases is not vividly distinct but can be observed but the effect of different oxidation states and radionuclides on the sorption capacity appears to be significant and should be considered.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 2.4	Impact of biogeochemical processes (continued)					
2.4.1b	Determination of the structural components, e.g. exopolymeric substances (EPS) within biofilms and their influence on the actinide speciation and immobilisation of actinides (U) we used stable multi-species biofilms				FZD: The addition of uranium in ecologically relevant concentrations has a strong effect on the O ₂ concentration and consumption rates in biofilms due to a stimulation of the metabolism of the microbes and on their respiratory activity and oxygen consumption. This increased respiratory activity results in O ₂ depleted zones closer to the biofilm air interface which may trigger uranium redox processes, which may lead to precipitation of uranium (IV) solids and consequently to a removal of uranium from the aqueous phase.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
2.4.2	Radionuclide mobility influenced by microbes	3.2.7.7	K _d	Low Site-specific Basis for deriving SA parameter values	Uni Utrecht: In addition to be potentially involved in reduction of U(VI), dissolved Fe(II) and S(II) can affect 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 if the formation of crystalline uraninite is kinetically hindered.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Determination and characterisation of colloids under variation of geochemical conditions						
WP 5.1						
5.1.1	Geo-monitoring of groundwater under undisturbed conditions		Base for R	Medium	FZK-INE, GRS, NRI-REZ: This new method improves quality of and therefore confidence in in-situ colloid analyses to be used for site characterisation and field experiments in a safety case.	Improvement of knowledge: n/a Improvement of data influencing PA: n/a Comment: The methodology developed for geo-monitoring is of high importance and will be used in future investigations.
5.1.2	Interpretation of results with regard to colloid stability in natural systems	3.2.4.1	Base for R	Medium Basis for deriving SA parameter values	FZK-INE, NRI-REZ, GRS: These analyses complement information from various laboratory- and field-investigations on formation and stability of colloids in geochemically different natural systems.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
Geochemical behaviour of radionuclides in the natural host rock						
WP 5.2						
5.2.1	Natural sample characterisation by μ -spectroscopical multi method strategy	3.2.2.1 3.2.3.1	C_{sol}	Low Site-specific Enhancing process understanding	FZK-INE (M.A. Denecke): One of the processes leading to U immobilisation in the natural system on a long term scale was successfully identified.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting Comment: The methodology developed is of high importance and will be used in future investigations.

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
Geochemical behaviour of radionuclides in the natural host rock						
WP 5.2						
5.2.2	U(IV)/U(VI) separation	3.2.2.1 3.2.3.1	C_{sol}	Low Site-specific Enhancing process understanding	UH, GRS: The results contribute to the understanding of the behaviour of uranium in a complex natural system over very long time scales. NRI-Rez: The quantification and characterisation of uranium in different chemical forms in the sediment, contributes to the understanding of the main immobilisation processes of U in the complex natural system.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
5.2.3	Extraction experiments	3.2.2.1 3.2.3.1	C_{sol}	Low Site-specific Enhancing process understanding	NRI-Rez: The quantification and characterisation of uranium in different chemical forms in the sediment, contributes to the understanding of the main immobilisation processes of U in the complex natural system.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
5.2.4	Uranium desorption experiments	3.2.2.1 3.2.3.1	K_d, C_{sol}	Medium Site-specific Enhancing process understanding	NRI-REZ, CTU (AG): An independent method for determination of accessible uranium by ^{233}U was successfully verified by comparison with sequential extraction tests and showed that the amount of exchangeable U minerals in sedimentary samples increases with increasing content of clay minerals.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
5.2.5	Uranium adsorption experiments	3.2.2.1 3.2.3.1	K_d	Medium Site-specific Enhancing process understanding	CTU (AG), NRI-Rez: K_d values for U sorption on clay sediments was found to be directly dependent on V/m value and indirectly on U concentration in solution; the mineralogical composition of samples (granite, clay) also play a role in U uptake.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 5.3						
Real system analysis						
5.3.1	Isotope geochemical characterisation of Ruprechtov site	3.2.2.1 3.2.3.1 3.2.5.1		n/a	GRS, NRI-REZ, FZK-INE: This work shows the potential of isotope analyses for characterisation of a site to be used in a safety case building the basis for understanding of chemical reactions in particular the role of organic matter in a natural system.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
5.3.2	Inverse modelling	3.2.2.1 3.2.3.1 3.2.5.1		n/a	GRS, NRI-REZ: The modelling exercises illustrate the evolution of the geochemical conditions and contributes to the understanding of carbon chemistry and therewith the behaviour of organic matter in the natural system.	Improvement of knowledge: Supporting Improvement of data influencing PA: n/a
5.3.3	Description of behaviour of organic matter at Ruprechtov site	3.2.2.1 3.2.3.1 3.2.4.1 3.2.5.1	Base for K_d , C_{sol}	Medium Site-specific Enhancing process understanding Basis for deriving SA parameter values	NRI-REZ: Concerning U mobility degradation of natural organic matter at Ruprechtov site is/was important for establishing reducing conditions and phosphate release but do not cause high amounts of dissolved humic substances due to its low availability and sorption on clays.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting

Number	FUNMIG Tasks	Investigated processes	SA parameter	Importance of improvements for SA parameter uncertainty reduction	Achieved improvements within FUNMIG	
					Researcher's view	WMO's view
WP 5.3						
Real system analysis (continued)						
5.3.4	Application of geochemical models to the natural system at Ruprechtov site	3.2.2.1 3.2.3.1 3.2.5.1	K_d, C_{sol}	Medium Enhancing process understanding	GRS, NRI-REZ: This work contributes to the understanding of the geochemical evolution of the site and shows that uranium concentration, speciation and sorption can be described with existing thermodynamic models and data which increase confidence in both.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting
5.3.5	Description of behaviour of uranium in the natural system at Ruprechtov site	3.2.2.1 3.2.3.1 3.2.5.1	K_d, C_{sol}	Medium Enhancing process understanding	GRS, NRI-REZ, FZK-INE, UH: This work shows the strengths of the combination of microscopic and macroscopic methods to understand radionuclide behaviour in a complex natural system and illustrates the potential barrier effect of a sedimentary layer for uranium migration under specific boundary conditions.	Improvement of knowledge: Supporting Improvement of data influencing PA: Supporting