Project Final Report

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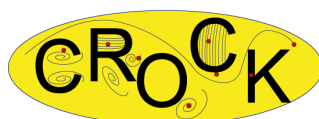Herrmann-von-Helmholtz-Platz 1
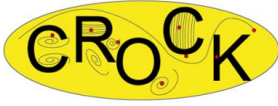
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1. Final publishable summary report

1.1 Executive Summary

The Collaborative Project Crystalline ROCK retention processes (CP CROCK) is funded by the European Commission under the 7th Framework Programme of the European Atomic Energy Community (EURATOM). CROCK was established with the overall objective to develop a methodology for decreasing the uncertainty in the long-term prediction of the radionuclide migration in the crystalline rock repository far-field. The project started in January 2011 and lasted 30 months until June 2013. CP CROCK is implemented by a consortium of 10 beneficiaries consisting on 5 large European Research Institutions, 2 Universities and 3 small and medium enterprises from six different countries with dedicated crystalline host-rock disposal programs and particular competence in this field. National Waste Management organizations as well as National Regulators, participate as end-user consulting group (EUG) with co-funding to beneficiaries, infrastructures, knowledge, work program review and guidance with respect to application of the project to the disposal Safety Case. The scientific-technical work program of the project is structured along six RTD (Research and Technological Development) workpackages (WP1-6) designed to cover the whole range of scales of interest of the project. Moreover, WP related with the knowledge management, dissemination and training (WP7), and with the project management itself (WP8) are also included in the work programme.

The key activities of the project are the presentation and discussion of the scientific and technical project achievements in the two project workshops organized within CROCK, at which 14 poster and 46 oral presentations were presented. From the aforementioned workshops two Proceedings were generated and published as KIT Scientific Reports including 36 reviewed S&T contributions. In association with the workshops, two Topical Sessions on "Reactive Transport Modelling" and "In situ URL experiments" were organized with presentations from several experts on those fields. The CROCK project itself and the work performed within CROCK has been presented in more than 10 international and national conferences, workshops and seminars. At the end of the project there are no published publications in peer-reviewed journals available but are under preparation. 10 PhD students as well as 6 Post-Doc researchers were involved in CROCK. No patent applications have been made and no Exploitable Foreground is reported.

The CROCK project, besides the provision of new non-oxidized Äspö rock samples, has provided key process understanding, especially for the redox sensitive radionuclides, for which a higher retardation has been demonstrated with a positive impact to the safety case. Furthermore no additional processes or observations have been recognized within the project which leads to an enhanced radionuclide migration. Additional topics for future studies have also be identified through the guidance of the EUG group.

CROCK has set up a project webpage at www.crockproject.eu where further information is made available.

1.2 Summary Project Description

CROCK, Crystalline ROCK retention processes, is a Collaborative Project based on the desire to improve the safety statement for the crystalline rock far-field as a radionuclide migration barrier. The project is funded by the European Commission under the 7th Framework Programme of the European Atomic Energy Community (EURATOM).

The key driver for the initiation of the Collaborative Project, identified by national Waste Management Organizations, is the undesired high uncertainty and the associated conservatism with respect to the radionuclide transport in the crystalline host-rock far-field around geological disposal of high-level radioactive wastes. The uncertainty may be divided into three categories: conceptual, modeling and experimental (Figure 1). Experimental uncertainties can be lowered by straightforward approaches. Contrary to this, conceptual uncertainties include lack in principle understanding on how scavenging processes in nature actually take place, including to which extent such processes can be considered to be in equilibrium, steady-state or under transient conditions. From a practical point of view, irrespective of the reasons for the large deviations in retention data for different radionuclides, the basic problem is that the large discrepancies cannot yet be related to specific processes and thus reduction in uncertainties is not defendable.
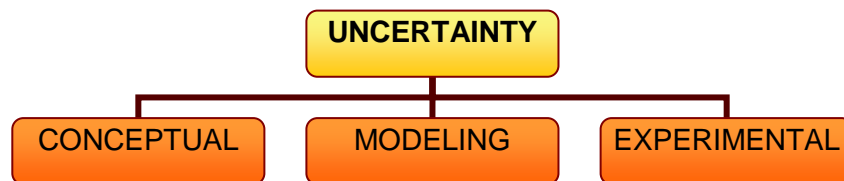

Figure 1. Sketch showing different issues in which uncertainty can be divided.

In response to this, the CROCK project has been established with the overall objective to develop a methodology for decreasing the uncertainty in the long-term prediction of the radionuclide migration in the crystalline rock repository far-field and to show how the outcome of the project can be used in future Safety Assessments and forthcoming site investigations programs. Below the list of strategic and scientific objectives is provided:

- The CROCK project will significantly contribute in increasing the process understanding in the transport simulations used to support Performance Assessment (PA) exercises with the purpose of increasing confidence in the safety of nuclear waste disposal.

- To show how the outcome of the project can be used in the Safety Assessment, and

- To propose how the developed approach can be successfully used in forthcoming site investigation programs.

- To investigate to which extent the recent uncertainty with respect to the radionuclide transport in the crystalline host-rock far-filed can be lowered by the methodology generated within the project.

In addition to the strategic and scientific objectives, communication and dissemination objectives are also present to ensure that all interested parties are informed about the project and its outcome.

The CROCK project is implemented by a Consortium of 10 beneficiaries (Table 1) consisting on 5 large European Research Institutions, 2 Universities and 3 small and medium enterprises from six different countries (Figure 2 and Table 1) with dedicated crystalline host-rock disposal programs and particular competence in this field.

Table 1. List of project beneficiaries

| No.	Beneficiary name	Short name	Country
1	KARLSRUHER INSTITUT FUER TECHNOLOGIE	KIT	Germany
2	AMPHOS 21 CONSULTING SL	AMPHOS	Spain
3	CENTRO DE INVESTIGACIONES ENERGETICAS, MEDIOAMBIENTALES Y TECNOLOGICAS-CIEMAT	CIEMAT	Spain
4	HELMHOLTZ-ZENTRUM DRESDEN-ROSSENDORF E.V.	HZDR *(formerly FZD)*	Germany
5	CHALMERS TEKNISKA HOEGSKOLA AB	CTH	Sweden
6	USTAV JADERNEHO VYZKUMU REZ A.S.	UJV *(formerly NRI)*	Czech Republic
7	CONTERRA AKTIEBOLOG	CONTERRA	Sweden
8	M V LOMONOSOV MOSCOW STATE UNIVERSITY	MSU	Russian Federation
9	TEKNOLOGIAN TUTKIMUSKESKUS VTT	VTT	Finland
10	KEMAKTA KONSULT AB	KEMAKTA	Sweden
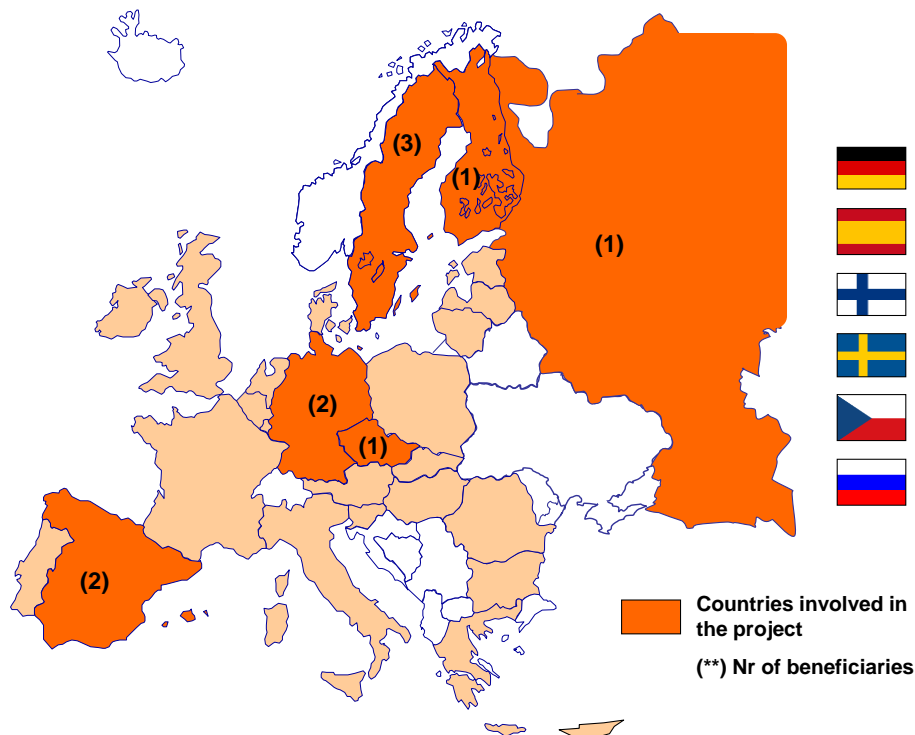
Figure 2. Geographical map highlighting the countries involved in the project.

Management structures and procedures are established in order to provide for adequate implementation, communication within the project, reporting, and dissemination and communication of the outcome of the project to different interested parties. In this context the roles and responsibilities of different bodies and partners within the project are defined:

- The *Coordination Team* (CT) consisted of two organizations, namely KIT-INE and AMPHOS. In addition to work program planning and project management, the CT was also implementing activities on management and dissemination of knowledge.

- The *Executive Committee* (ExCom) consisted of the respective workpackages (WP) leaders, ensuring adequate operation of the project.

- The *End-User Group* (EUG) which is based on Waste Management Organizations (SKB, POSIVA and RAWRA) and Regulators (SSM and STUK), and represents the interest of the end users to the project in view of ensuring usefulness of the project work for application to the Safety Case and review of scientific-technical reporting in this respect.

The project makes use of the broad set of existing analytical approaches, methodologies, and general knowledge from decades of past investigations. It builds on the output and main conclusions of the 6th FP IP FUNMIG project (www.funmig.com) and the Swedish site selection program. The experimental program reaches from the nano-resolution to the Performance Assessment (PA) relevant real site scale, delineating physical and chemical retention processes. Existing and new analytical information provided within the project is used to set up step-wise methodologies for up-scaling of processes from the nano-scale through to the PA relevant km-scale.

The scientific-technical work program of CROCK was established to reflect all the above discussed objectives. The project is structured along six RTD (Research and Technological Development) workpackages (WP1-6), there is also one workpackage on knowledge management, dissemination and training (WP7) and the last workpackage is on administrative and financial project management (WP8) (Figure 3).
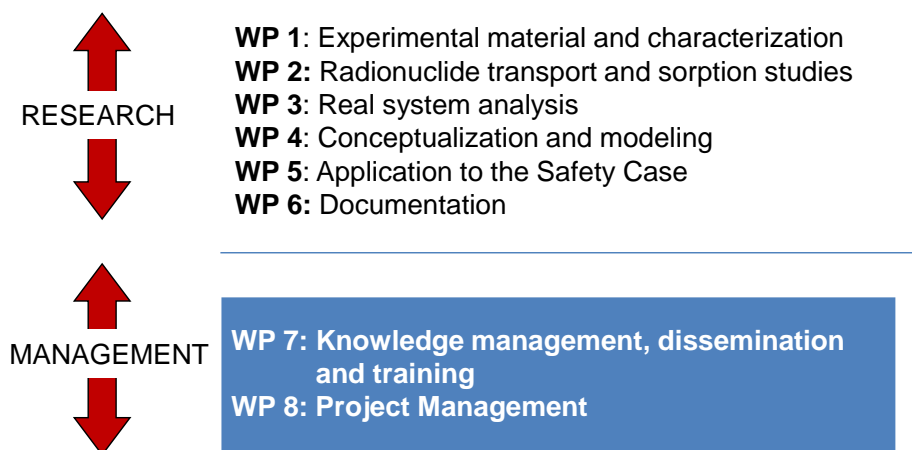

RESEARCH

WP 1: Experimental material and characterization
WP 2: Radionuclide transport and sorption studies
WP 3: Real system analysis
WP 4: Conceptualization and modeling
WP 5: Application to the Safety Case
WP 6: Documentation

MANAGEMENT

WP 7: Knowledge management, dissemination and training
WP 8: Project Management

Figure 3. List of workpackages established for the performance of the CROCK project.

The RTD workpackages cover different activities and are designed to cover the whole range of scales of interest in the overall objective of the project. The modeling efforts cover the entire spatial range of the project from the nano-resolution to the Performance Assessment (PA) relevant large scale.
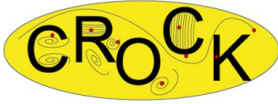
Workpackage 1, led by KIT-INE, started at the beginning of the project providing new drill core fracture samples, sampled and handled under anoxic conditions. A thorough characterization of the experimental materials was also done. CIEMAT led workpackage 2 which focused on radionuclide transport and sorption studies. Workpackage 3 dealt with matrix diffusion and natural chemical homologue analysis and was led by CONTERRA. The general objective of workpackage 4, led by KEMAKTA, was to conceptualize and model radionuclide transport processes on systems at different scales. AMPHOS led workpackage 5 integrating and describing how the outcome of the other WPs can contribute to decrease the uncertainty in Performance Assessment (PA). Workpackage 6, also led by AMPHOS, was a cornerstone of the project, since its first objective was to establish a state-of-the-art of the current knowledge on retention processes in crystalline rocks, then to continuously collect the results obtained in the other workpackages, and finally to deliver a report summarizing the major advances which have been accomplished at the end of the project.

Key activities on a project level have been the Kick-off meeting and two annual project workshops. The scientific and technical program and the results of the project were presented and discussed during the Kick-off meeting and the two Workshop meetings, held in Stockholm (Sweden) on May 2012 and Karlsruhe (Germany) on May 2013. In association with the workshops, and as a part of the training activities organized within CROCK, two Topical Sessions on "Reactive Transport Modelling" and "In situ URL experiments" were organized with presentations from several experts on those fields. The two Workshops are summarized in the Workshop proceedings. The key purpose of the proceedings is to document and make available the outcome of the CROCK project to a broad scientific community. Additional purposes of the proceedings were to ensure on-going documentation of the project outcome, promote systematic scientific-technical development throughout the project, and to allow thorough review of the project progress. In order to ensure the successfully progression and dissemination of the project the proceedings have been published as publicly available KIT Scientific Reports (Rabung et al. 2012, KIT Scientific Report No. 7629; Rabung et al. 2013, in preparation) issued via the Karlsruhe Institute of Technology.

1.3 Main Scientific and Technical results

CROCK has been a highly successful project with numerous scientific results being generated. Below a detailed summary of the published S&T contributions is provided and a more general overview of the results from the respective beneficiaries obtained for each RTD workpackage (Table 2) is provided.

Table 2. List of RTD workpackages within CROCK project and lead organization.

List of workpackages (WP)	
WP title	Lead organization
Experimental material and characterization	KIT-INE
Radionuclide transport and sorption studies	CIEMAT
Real system analysis	CONTERRA
Conceptualization and modeling	KEMAKTA

Application to the Safety Case	AMPHOS
Documentation	AMPHOS

It is worth to mention that the project results have been published in the Proceedings of the two project Workshops, namely as S&T contributions reviewed by EUG members. A total of 36 S&T contributions to the project Workshops are available from the respective Workshop Proceedings (Rabung et al., 2012, 2013), which are publicly available at the project website (www.crockproject.eu). Additionally, in the aforementioned Workshops 14 posters were presented by the different beneficiaries. Table 3 includes a detailed list which includes both, all S&T and posters contributions, presented at the two project Workshops.

Additionally, the CROCK project and the results gathered within the framework of the project have been presented by the different beneficiaries at several international and national conferences (Table 4). Finally, it must be remarked that results gathered within the CROCK project will be presented in the forthcoming conferences:

- Goldschmidt 2013, Florence (Italy) August 2013.

    o Alonso, U., Missana, T., Patelli, A., García-Gutiérrez, M., Rigato, V. and Ceccato, D: Se(IV) uptake by Äspö diorite: microscale distribution.

    o Schmeide, K., Gürtler, S., Müller, K., Steudtner, R., Joseph, C., Bok, F., Brendler, V.: Sorption of uranium and neptunium onto diorite from Äspö HRL.

- Migration 2013 - 14th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the geosphere, Brighton (UK) September 2013.

    o Alonso, U., Missana, T., Patelli, A., Ceccato, D., García-Gutiérrez, M. and Rigato, V. U(VI) surface distribution on Äspö diorite under anoxic conditions.

    o Rabung, Th., García, D., and Molinero, J. CP CROCK Crystalline Rock Retention Processes.

- EURADWASTE'13, Vilnius (Lithuania) October 2013

    o Rabung, Th., García, D., Montoya, V. and Molinero, J. CP CROCK Crystalline Rock Retention Processes.

The knowledge generated by the CROCK project thus has been successfully disseminated to the international scientific community. No patent applications have been made within CROCK and no Exploitable Foreground is reported.

Table 3. List of S&T contributions and posters presented at the two CROCK project Workshops. The works are listed in alphabetical order of the first author.

Author	Title	Year	Type
U. Alonso, T. Missana, A. Patelli, V. Rigato and D. Ceccato	Uranium retention under anoxic conditions on Äspö diorite: First micro-scale analyses	2012	S&T

Author	Title	Year	Type
U. Alonso, T. Missana, A. Patelli, V. Rigato and D. Ceccato	Uranium retention under anoxic conditions on Äspö diorite: First micro-scale analyses	2012	Poster
J. Crawford	Decreasing uncertainty of radionuclide migration predictions in safety assessment modelling	2012	S&T
J. Crawford	A simplified approach for reactive transport modelling involving strongly non-linear sorption and solute remobilisation	2013	S&T
J. Crawford	A simplified PA model for reactive transport featuring non-linear sorption processes	2013	Poster
J. Crawford	Approaches to modelling surface complexation sorption on complex geological mateials with limited data	2013	S&T
J. Crawford	What might K_d ratios be able to tell us about surface complexation sorption mechanism?	2013	Poster
D. García and C. Domènech	Cs sorption onto crystalline rock. From mechanistic sorption models to K_d	2012	Poster
D. García, M. Pękala and C. Domènech	Decreasing K_d uncertainties through the application of mechanistic retention models	2013	S&T
V. Havlova and P. Vecernik	Diffusion of species through Äspö diorite	2013	Poster
S. Holgersson	Characterisation of rock samples from Äspö using gas adsorption	2012	S&T
S. Holgersson	Characterisation of rock samples from Äspö using gas adsorption	2013	S&T
S. Holgersson	CROCK at Chalmers - Experimental program and results	2013	Poster
F. Huber, P. Trinchero, J. Molinero and Th. Schäfer	RN migration in a single fracture from Äspö, Sweden: Experiments and reactive transport modelling	2013	S&T
F. Huber, S. Heck and Th. Schäfer	RN sorption experiments using Äspö diorite, fined granite and Ävrö granite	2013	Poster
A. Idiart and M. Pekala	Work Package 6 – Documentation. Evaluation of treatment of radionuclide transport and retention phenomena in recent performance assessments	2013	S&T
A. Idiart, M. Pekala and M. Grivé	Status of Work package 6 – state-of-the-art of retention processes	2012	S&T

Author	Title	Year	Type
A. Itälä, M. Tanhua-Tyrkkö, E. Puukko and M. Olin	K_d-values and surface complexation modelling for biotite	2012	Poster
A. Itälä, M. Tanhua-Tyrkkö and M. Olin	Surface complexation modelling of biotite: Nickel and europium	2013	S&T
E. Krawczyk-Bärsch, K. Schmeide and F. Bok	Retention of U(VI) and Np(V) in bacteriogenic iron oxide-producing biofilms from Äspö HRL (Sweden)	2013	S&T
N. Kuzmenkova, V. Petrov, I. Vlasova, V. Petrov, V. Poluektov and S. Kalmykov	Uranium(VI) sorption onto rock samples from areas of the proposed HLW SNF repository in Russia (Nizhnekansky massive)	2013	S&T
T. Missana and M. García-Gutiérrez	Analysis of the cesium sorption behavior on biotites of different origins	2012	S&T
T. Missana and M. García-Gutiérrez	Analysis of the cesium sorption behaviour on biotites of different origins	2012	Poster
T. Missana and M. García-Gutiérrez	Analysis of sorption onto granites and granite minerals: The case of caesium	2013	S&T
T. Missana and M. García-Gutiérrez	Comparison of the cesium adsorption on different crystalline rocks	2012	S&T
H. Nordman	Snapshots of importance of geosphere parameters	2012	S&T
M. Olin, E. Puhakka, A. Itälä, M. Tanhua-Tyrkkö, V.-M. Pulkkanen, H. Nordman, K. Kajanto, E. Puukko and L. Koskinen	Radionuclide transport modelling by molecular chemistry, surface complexation and reactive transport modelling	2012	S&T
M. Olin, A. Poteri, V.-M. Pulkkanen and L. Koskinen	Possible causes of uncertainty in the sorption data for PA studies	2013	S&T
V.G. Petrov, I.E. Vlasova, N.V. Kuzmenkova, V.A. Petrov, V.V. Poluektov, A. Grivot and S.N. Kalmykov	Characterization of rock samples from areas of the proposed HLW and SNF repository in Russia (Nizhnekansky massive) and first sorption studies	2012	S&T
E. Puhakka and M. Olin	Molecular modelling approach for the formation of water molecular layer onto biotite surfaces	2012	Poster
E. Puhakka and M. Olin	*AB INITIO* studies on cation-exchange and surface complexation reactions on biotite surface	2013	S&T
V.-M. Pulkkanen, A. Seppälä and M. Olin	Reactive transport modelling of nickel in fractures bedrock	2013	S&T

Author	Title	Year	Type
Th. Schäfer, E. Stage, S. Büchner, F. Huber and H. Drake	Characterization of new crystalline material for investigations within CP CROCK	2012	S&T
K. Schmeide, S. Gürtler, F. Bok and V. Brendler	Interaction of uranium(VI) and neptunium(V) with Äspö diorite under anoxic conditions	2013	S&T
K. Schmeide, S. Gürtler, K. Müller, R. Steudtner, C. Joseph, F. Bok and V. Brendler	Interaction of uranium(VI) and neptunium(V) with Äspö diorite under anoxic conditions	2013	Poster
K. Schmeide, S. Gürtler, K. Müller, R. Steudtner, C. Joseph, F. Bok and V. Brendler	Sorption of U(VI) and Np(V) onto Diorite from Äspö HRL	2012	S&T
K. Schmeide, S. Gürtler, K. Müller, R. Steudtner, C. Joseph, F. Bok and V. Brendler	Sorption of U(VI) and Np(V) onto Diorite from Äspö HRL	2012	Poster
J. Smellie	Real system analysis	2012	S&T
J. Smellie	Real system analysis	2013	S&T
E. Stage, F. Huber, S. Heck and Th. Schäfer	Sorption/Desorption of ^{137}Cs(I), ^{152}Eu(III) and ^{233}U(VI) onto new CROCK derived Äspö diorite – A Batch type study	2012	S&T
Y. Totskiy, H. Geckeis and Th. Schäfer	Sorption of Tc(VII) on Äspö Diorite (ÄD)	2012	S&T
Y. Totskiy, Th. Schäfer, F. Huber, D. Schild, H. Geckeis and S. Kalmykov	Tc(VII) sorption natural granitic rocks and synthetic magnetite	2013	S&T
P. Trinchero, J. Molinero and L.M. de Vries	Radionuclide migration in crystalline media: From effective K_d distributions to reactive transport modelling	2013	S&T
P. Trinchero, L.M. de Vries, À. Piqué, L. Duro and J. Molinero	Radionuclide retention in fractured media: coping with uncertainty in PA studies	2012	S&T
P. Vecernik, V. Havlova and M. Löfgren	Determination of Rock migration parameters (F_f, D_e): Application of electromigration method on samples of different length	2012	S&T
P. Vecernik, V. Havlova and M. Löfgren	Application of electromigration method on long rock samples: Determination of migration parameters (F_f, D_e)	2013	S&T

Author	Title	Year	Type
K. Videnská, V. Havlová, M. Vašinová Galiová and P. Sajdl	Study of selenium sorption on Äspö diorite surface using spectroscopic methods	2013	S&T
K. Videnská, V. Havlova and J. Vejsadů	Speciation of Selenium in Äspö synthetic groundwater	2012	S&T
K. Videnská, V. Havlova and J. Vejsadů	Study of selenium sorption on Äspö diorite	2013	S&T
L.M. de Vries, P. Trinchero and J. Molinero	MCPHREEQC: Automatic stochastic simulations for geochemical modelling	2013	Poster

Table 4. List of complete references of the presentations performed by the beneficiaries at several national and international conferences. The works are listed in alphabetical order of the first author.

Author	Title	Conference / Year
U. Alonso, T. Missana, M. Garcia Gutierrez, A. Patelli, V. Rigato and D. Ceccato	Ion beam analyses of radionuclide migration in nuclear waste repositories	ENERGY 12: Modification and Analyses of Materials for Future Energy Sources / 2012
U. Alonso, T. Missana, M. Garcia Gutierrez, A. Patelli, V. Rigato and D. Ceccato	Ion beam analyses of radionuclide migration in heterogeneous rocks.	Ion Beams'12: Multidisciplinary Applications of Nuclear Physics with ions beams Conference / 2012
U. Alonso, T. Missana, A. Patelli, D. Ceccato, M. Garcia Gutierrez and V. Rigato	Micro-scale study of uranium retention on granite	Interface Against Pollution Conference / 2012
U. Alonso, Q. Lemasson, T. Missana, B. Moignard, L. Pichon and A. Zucchiatti	Detection of actinides and rare earths in natural matrices with AGLAE new high sensitivity detection set-up	IBA 2013- 21st Conference on Ion Beam Analyses / 2013
T. Missana, M. Garcia-Gutierrez, and U. Alonso	Adsorption processes in heterogeneous rock: top-down vs bottom-up modelling approach in modelling experimental data	Interface Against Pollution Conference / 2012
V.G. Petrov, I.E. Vlasova, N.V. Kuzmenkova, V.A. Petrov, V.V. Poluektov, A. Grivot and S. Kalmykov	Microdistribution of U(VI) onto granite minerals (Nizhnekansky massive) due to the sorption	Radiochemistry-2012 - 7th Russian Conference on Radiochemistry / 2012
V.-M. Pulkkanen, A. Italä and A. Muurinen	Buffering of pH conditions in sodium bentonite	XXXV International Symposium Scientific Basis for Nuclear Waste Management / 2011

Author	Title	Conference / Year
Th. Rabung	Crystalline Rock Retention Processes. A 7th Framework Programme Collaborative Project	NRC 8: EuCheMS – 8th International Conference on Nuclear and Radiochemistry / 2012
Th. Rabung	Crystalline Rock Retention Processes. A 7th Framework Programme Collaborative Project	EURADISS conference / 2012
Th. Rabung, V. Montoya and J. Molinero	Crystalline Rock Retention Processes. A 7th Framework Programme Collaborative Project (2011-2013)	13th International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere / 2011
Y. Totskiy, E. Stage, H. Geckeis, Th. Schäfer and S. Kalmykov	Sorption of Tc(VII), Cs(I), Eu(III), U(VI) and Am(III) on crystalline rock material from Äspö (Sweden) and Nizhnekansk massif (Russia)	Radiochemistry-2012 - 7th Russian Conference on Radiochemistry / 2012

In the following sections, the research results performed within CROCK on a workpackage level are summarizied. It is further reported which beneficiaries have contributed to the respective workpackages.

WP1. Experimental material and characterization

The main objective of WP1 was to organize new drill-core samples from Äspö URL, sampled and handled under anoxic conditions (Figure 4). Previous investigations were based on crystalline rock material that was drilled under the use of oxidizing surface water and/or where the drill cores have subsequently been treated, handled, transported and stored in contact with air. The usage – for the first time – of un-oxidized material in subsequent sorption studies is of special importance for redox-sensitive radionuclides and reflects the conditions in a repository after closure. Besides bore core sections also disks and crushed material of different size fractions have been provided to the beneficiaries.

Figure 4. Drilling campaign in Äspö.

The new experimental material has been characterized for its chemical/mineralogical composition, including structure and properties of accessible fluid systems (porosity, hydraulic conductivity etc.). In addition, BET surface area was determined for different size fractions of crushed material and a special focus should lie on the natural chemical homologue behaviour.

In addition to this new experimental material it was ensured in the project to have the access to experimental samples from previous studies.

In this context, the different participants of this workpackage were working on different issues:

Äspö HRL samples organization and characterization

KIT was responsible for organizing the new drill-core samples from Äspö. The drilling campaign was done in the first week of May 2011 including MIRO, a local drilling company (Figure 4). Two boreholes were drilled, one from tunnel surface parallel to water conducting feature, the other from a niche parallel to tunnel surface in a distance of approx. 7 m slightly dipping (~5°) perpendicular to structural features. In total, 71 bore-cores have been collected. In addition to bore-cores also natural groundwater was collected as well as samples from the drilling water. A special attention was drawn on a widely exclusion of oxygen during sampling, storage and transportation. Detailed characterization of the different water and solid samples was done.

Äspö diorite samples (discs, crushed material and cores) were prepared in an argon glove box (equipped with a diamond saw) for the partners CIEMAT, UJV, HZDR and KIT-INE as requested and shipped to the partners in autoclaves under argon atmosphere. Chemical and mineralogical characterization of the Äspö samples was mainly performed on the crushed material (CM) and included also BET surface area determination of different size fractions, XRF and SEM-EDX measurements. Determination of the iron content was done with a special focus on $Fe(II)$ concentration, as the $Fe(II)$ content should have an important impact on sorption of redox-sensitive elements studied in WP2. Furthermore, the measured $Fe(II)$ concentrations point to the fact that due to the sampling and preparation procedure at least a part of the ferrous iron pool in the rock material could be preserved. Sample characterizations based on Computed Tomography (CT) techniques were also performed for obtaining valuable geometrical information on sample fractures. The data

gathered by this technique can be used directly in numerical codes to carry out computational fluid dynamics (CFD) simulations, conservative solute transport as well as reactive transport calculations for radionuclide migration for comparison to experimentally measured data.

CTH was also involved in the sampling of new Äspö bore-cores within the sampling campaign in May 2011. CTH drill core samples have been sawed in sections of 3 cm, using a water-cooled low-speed saw. The work was made in an inert gas atmosphere glove-box. As a consequence, some delay in performing the subsequent sample characterization occurred. Drill-core sections were crushed and sieved into four different size fractions for later characterization with a) Kr-BET gas adsorption measurements for specific surface area and with b) N_2-BJH gas adsorption/desorption for specific pore volume. The measured porosity of the intact material is found to be much larger than predicted by a model. This is interpreted as a macroporosity which contributes very much to the porosity of the intact samples but contributes very little to their BET areas.

HZDR prepared various grain size fractions of the Äspö diorite material for the sorption studies and characterized the material.

From the provided grain size fractions of KIT of $0.5 - 1$ mm and $1 - 2$ mm as well as from provided bore cores additional grain size fractions were prepared by crushing and sieving: the grain size fractions $0.063 - 0.2$ mm and < 0.063 mm (required for spectroscopic studies) were prepared as well as additional material of the grain size fraction $1 - 2$ mm. The grain size fractions were characterized by determining Kr-BET surface areas. Furthermore, the mineralogical composition of the diorite was investigated. Sampling and characterization of site-specific biofilms from Äspö HRL (Figure 5) for subsequent U(VI) and Np(V) sorption studies was also done by HZDR. The characterization covered the analysis of the ultrastructure and elemental composition of the organic matter by EF-TEM (Energy-filtered Transmission Electron Microscopy), electron energy loss spectroscopy (EELS) as well as ICP-MS (Inductively coupled plasma mass spectrometry) and Powder X-ray diffraction of the cryo-dried BIOS (bacteriogenic iron oxides) biofilms. Mössbauer investigations have also be performed to study the bacterial ferrihydrite in BIOS biofilms.

Figure 5. Biofilm picture in Äspö environment.

Block scale experiment and comparison of granites from different origin

CIEMAT documented the progress of results obtained in the block-scale diffusion experiment started at CIEMAT in 2007 simulating a high level radioactive waste repository in granite (including compacted bentonite) after 5 years of experiment.

Figure 6. Block-scale experiment picture.

The evolution of the activity of Cs, Cl and HTO in the tracer reservoir (within the bentonite) has been analysed and modelled. The evolution of the activity of the conservative tracers Cl and HTO has been periodically measured in 11 different boreholes placed in granite at different distances from the source. Additionally a comparison of sorption properties of granites from different origin (Spain, Switzerland, Finland and Sweden) has been done.

Russian material samples characterization

MSU provided and characterized sample material from disposal sites in Russia, including rock samples from the proposed international repository of spent nuclear fuel in Nizhnekansky rock massive.

Core materials (Figure 7) from two areas (area Kamenny, drilling depth down to 700 m, and area Itatsky, drilling depth down to 500 m) were studied in terms of petrographic and mineralogical characterization; definition of filtration, elastic, petro-physical and strength properties; estimation of hydrothermal-metasomatic transformation of rocks. It was established that the most part of the core material from the area Kamenny is presented by granites and leucogranites, while the core material from the area Itatsky is mostly diorites and quartz diorites.
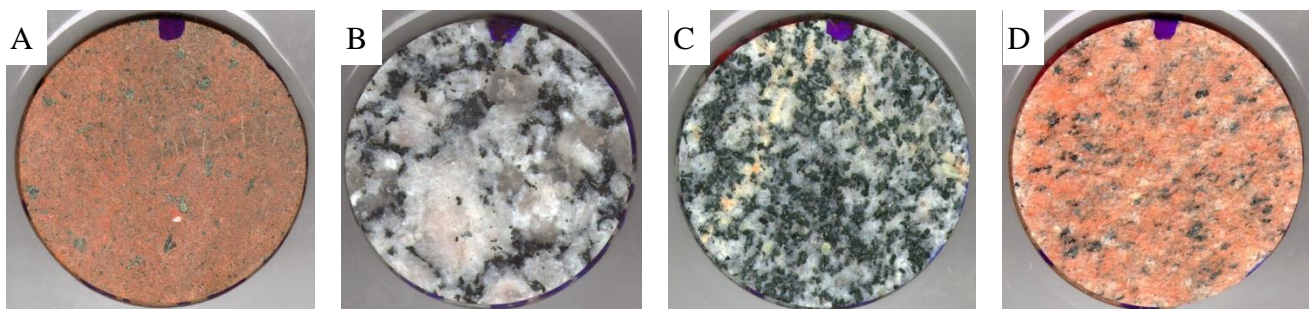

Figure 7. Rock slices for sorption experiments from Kamenny (A, B) and Itatsky (C, D) areas.

WP2. Radionuclide transport and sorption studies

The main objective of WP2 was to decrease the degree of uncertainty on retention parameters in crystalline rocks by providing sound experimental methodologies and improving the knowledge on retention processes in such heterogeneous materials. The existing uncertainties are related both to conceptual aspects and experimental problems (i.e. data gathered under conditions not fully representative of the scenario of interest or using samples not correctly handled or conserved) which need to be minimized. The effects of pH, ionic strength and radionuclide concentration were analyzed with the ultimate objective of developing sorption models for a more mechanistic description of retention in heterogeneous rocks.

For this aim, granites from different sites were used in sorption experiments, and a special emphasis was made on freshly sampled Äspö diorite. Studies were focused on different radionuclides: an ion-exchangeable dominated element (Cs), a strongly sorbing surface complexation dominated element (Eu), redox sensitive elements (U, Np, Tc, Se) and conservative non-sorbing tracers (HTO, Cl), as agreed by all the partners at the CROCK kick-off meeting. Micro-scale sorption studies onto non crushed rocks provided surface distribution coefficients (K_a) directly measured on intact rocks and single minerals and evidenced which are the more important minerals for the retention of different radionuclides.

Specifically, the overall aspects studied by the different beneficiaries were:

Differences between sorption onto granite and granite minerals

Sorption of cesium, uranium and europium onto granite and granite minerals (biotite, muscovite, K-feldspar, quartz) of different origin (Spain, Switzerland, Sweden) was analysed by **CIEMAT** under similar experimental conditions to reduce the experimental uncertainties and to evidence the role of several parameters on retention (mineral content, BET area, composition of the water, competitive ions in solution, etc.).

Cesium adsorption was found non-linear, in all analysed materials, indicating the existence of more than one sorption site. Batch sorption experiments were also complemented with tests on granite coupons combining different experimental techniques. In particular, detailed analyses of uranium and selenium adsorption in Äspö diorite were carried out by micro-Particle induced X-ray Emission (μPIXE).
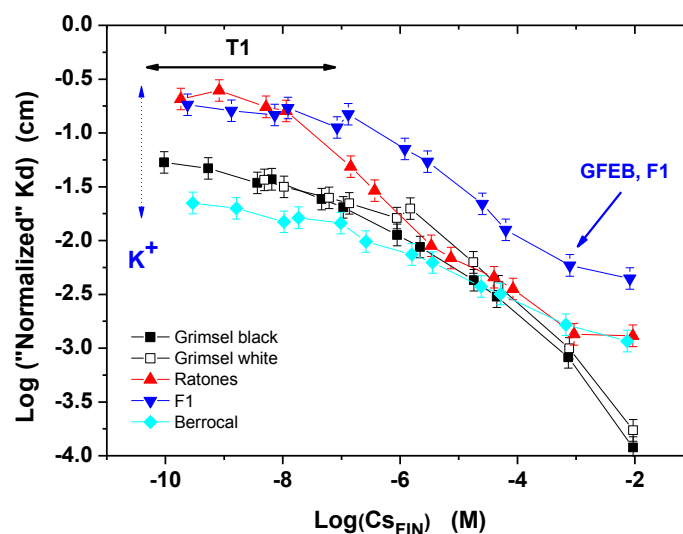
Figure 8. Cesium isotherms in different granites. K_d data normalized to the BET surface area.

Redox sensitive radionuclides

For redox sensitive radionuclides, the analysis of sorption on well-preserved materials, compared to sorption onto oxidized solids, clearly showed the importance of using fresh and well-preserved rock for obtaining valid distribution coefficients. For example, in the case of technetium (Figure 9), which was used originally as Tc(VII) in the sorption experiments by **KIT-INE**, a much stronger retention on the un-oxidized material was observed and could be explained by a reduction to Tc(IV) due to the presence of Fe(II) in the rock.
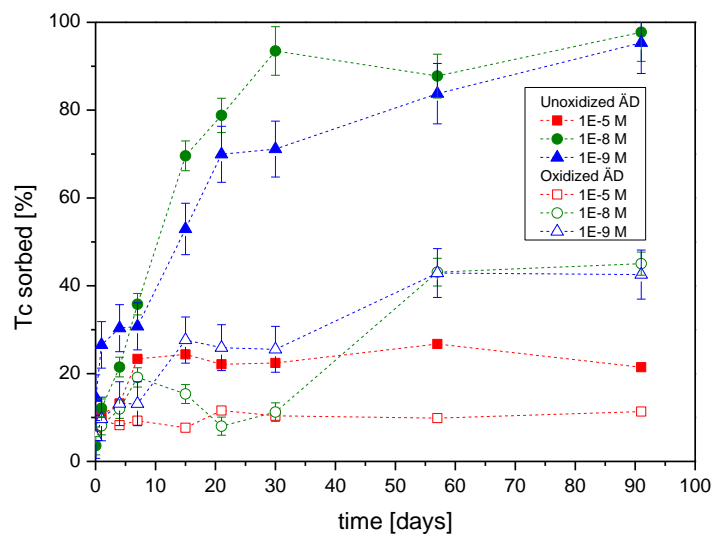
Figure 9. Tc sorption kinetics at different initial Tc concentrations on oxidized and un-oxidized Äspö diorite.

Sorption experiments with Se(IV) and Se(VI) on Äspö rock samples in Äspö groundwater were performed by **UJV** under aerobic and anaerobic conditions. It was found that the sorption of Se(VI) was almost negligible. Sorption of Se(IV) was detectable, however still very low (below 10 ml/g). Moreover, sorption experiments with Se(IV) / Se(VI) and Äspö granitic coupons were performed in order to determine Se distribution and oxidation state in the rock surface. By using ICP-LA and ESCA techniques it was observed that Fe bearing phases are the most important Se sorbents within the rock forming minerals.

Uranium(VI) and neptunium(V) interactions with Äspö diorite were studied by **HZDR** under anoxic conditions. Batch sorption experiments under N_2 were performed to study the interaction of U(VI) and Np(V) with crushed diorite ($1 - 2$ mm fraction, 200 g/L) in synthetic Äspö groundwater (pH 7.8, $I = 0.18$ M) as a function of contact time (5 to 108 days).

The speciation of uranium(VI) in solution and consequently, its sorption onto diorite was found to be strongly influenced by the groundwater composition. Calcium and carbonate ions have the strongest influence by forming the weakly sorbing $Ca_2UO_2(CO_3)_3(aq)$ complex. This complex was verified to be the dominating uranium species in Äspö groundwater at pH 7.8 by time-resolved laser-induced fluorescence spectroscopy. For the uranium(VI) sorption onto the $1 - 2$ mm diorite fraction, a K_d value of 3.8 ± 0.6 L/kg was determined. This value shows a low sorption affinity of uranium(VI) to diorite. Sorption equilibrium was reached relatively fast (after 10 to 20 d). In the case of

neptunium(V), the effect of the groundwater composition on its solution speciation and sorption behavior is weak. Np interaction with diorite is mainly determined by iron(II) at the diorite surface which induces a reduction of neptunium(V) to the sparingly soluble neptunium(IV) under anoxic conditions. The reduction of radionuclides to sparingly soluble mineral phases reduces migration risks. It was concluded that due to the different solution speciation and especially redox speciation at the diorite surface, sorption and mobility of the two actinides in a diorite environment under anoxic conditions are not comparable. The retention capacity of anoxic diorite towards neptunium is much higher than towards uranium. Consequently, a higher migration risk is expected for uranium(VI).

Electromigration experiments

UJV performed electromigration experiments, using ^{3}H and ^{36}Cl. The comparison of a conservative tracer (^{3}H) diffusion towards and anionic one (^{36}Cl) allows the study of potential anionic exclusion for Äspö diorite.

Formation factor F_f and effective diffusion coefficient D_e for iodine (used as a tracer) were also measured over samples with different length. The results confirmed that a modified electromigration method (Figure 10) can be applied for samples of different lengths and can speed up gaining the migration parameter data. The measurement revealed the results, consistent with previous results for Swedish samples.
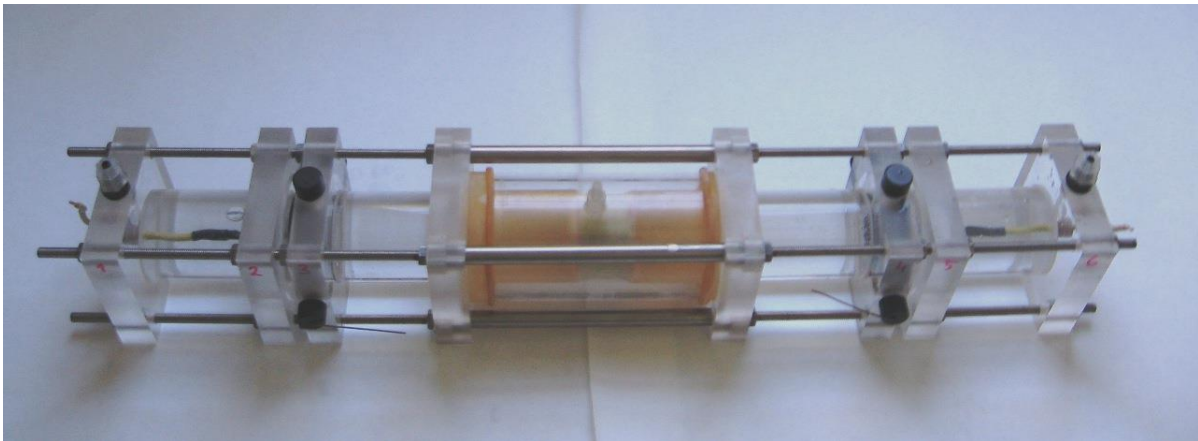

Figure 10. Photo of modified electromigration cell, enabling to use the samples of variable length (30 – 100 mm; UJV Rez, a. s. concept).

Sorption onto Russian samples material

MSU studied the sorption of U, Cs and Eu onto rock samples from areas of the proposed Russian HLW and SNF repository (Nizhnekansky rock massive).

It was observed that all investigated samples have low metasomatic transformations and that sorption of U(VI) have similar time- and pH-dependencies with low deviations at pH values > 8 for all samples from Itatsky area. Additionally, in case of Kamenny area samples, sorption does not decrease significantly until pH 10.

It should be mentioned here that HTO, Cs, Ra and U sorption on and diffusion in rock samples from Äspö were studied by **CTH**. Unfortunately due to an experimental shortcoming, an important delay affected the experiments and at present results are still unavailable.

WP3. Real system analysis

Real systems analysis is used specifically for identification of matrix diffusion on real time and spatial scales. The matrix diffusion process is identified by real system analysis making use of findings from the past Swedish site selection programme.

In Workpackage 3, **CONTERRA AB** has supplied the project beneficiaries all relevant background sources of the analytical and field porewater data, together with interpretations, from the recent Swedish site characterisation programme with a focus on matrix diffusion. All data are from the Forsmark (Figure 11) and Laxemar (Figure 12) sites with the majority collected from the period 2003-2008. Some additional data from Forsmark were taken more recently in 2011.

Generally, and to varying degrees, both sites (Forsmark and Laxemar) have been subjected to the same palaeoclimatic conditions following the last glaciation, i.e. since the last deglaciation (18,000-8000 BC). Porewater that resides in the connected pore space of crystalline rock cannot be sampled by conventional techniques and therefore are extracted by indirect methods based on rock material. This approach has been successfully carried out and porewater can be characterised by out-diffusion and diffusive isotope exchange techniques. Petrophysical parameters, such as measured water content, bulk density, and water-loss porosity determined by both gravity and isotope exchange, are also determined.

Solute transport in the intact rock matrix at both sites appears to be dominated by diffusion, and matrix diffusion has been identified to occur into the rock matrix. At Forsmark, experimentally derived average pore diffusion coefficients of Cl^- for the major rock types at a temperature of 25 °C are: metagranite to granodiorite = 1.2×10^{-10} $m^2/s \pm 0.40 \times 10^{-10}$ m^2/s (n = 21), granodiorite to tonalite = 8.1×10^{-11} m^2/s (n = 1), aplitic granite = 9.4×10^{-11} $m^2/s \pm 4.2 \times 10^{-12}$ m^2/s (n = 5) and fine-grained granite = 1.1×10^{-10} $m^2/s \pm 0.38 \times 10^{-10}$ m^2/s (n = 3). At Laxemar, the average pore diffusion coefficients of Cl^- for the major rock types at a temperature of 25 °C are: Ävrö granite = 6.3×10^{-11} $m^2/s \pm 2.9 \times 10^{-11}$ m^2/s (n = 9), quartz monzodiorite = 8.4×10^{-11} $m^2/s \pm 5.5 \times 10^{-11}$ m^2/s (n = 3), diorite = 3.8×10^{-11} $m^2/s \pm 4.1 \times 10^{-12}$ m^2/s (n = 2).
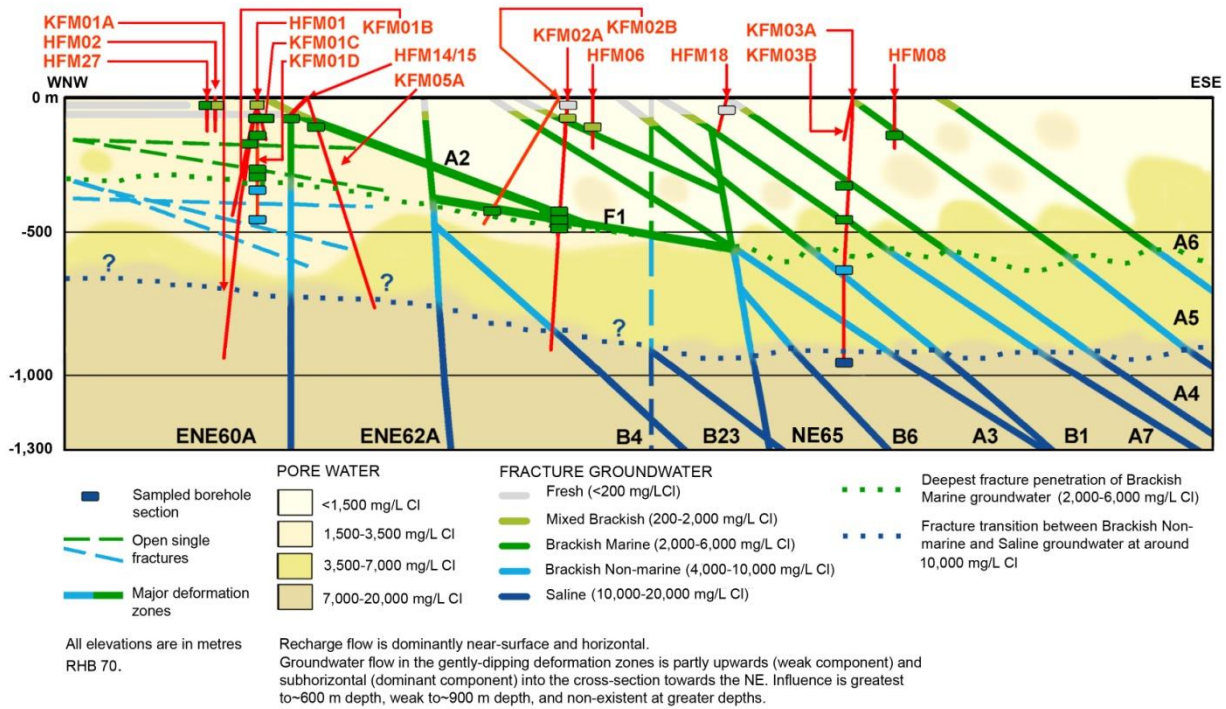
Figure 11. Forsmark site visualisation of the hydrochemical data along cross-section WNW-ESE. Shown are: a) the location of the boreholes and the sections which have undergone hydrochemical sampling, b) the main colour coded fracture groundwater types which characterise the site, c) the chloride distribution with depth along the major deformation zones and minor single open fractures, and d) the chloride subdivisions of the rock matrix porewater. The groundwater flow directions are explained in the legend. The dotted lines in different colours crossing the section represent the approximate penetration depths of (or extrapolation of) the various groundwater types along hydraulically-active deformation zones. (Cross-section length = 6,790 metres).

AMPHOS developed an improved method for correcting the measurement data to remove the theoretical bias introduced by surface conduction. The method is based on the use of an empirical power law relation describing how surface conduction varies as a function of the true geometric formation factor as ascertained in independent laboratory experiments made using core samples saturated with water of differing ionic strengths. Then, the corrected formation factors have been used to derive upscaled values of diffusion length, porosity and diffusion coefficients, which are key parameters required for the quantitative models of workpackage 5.
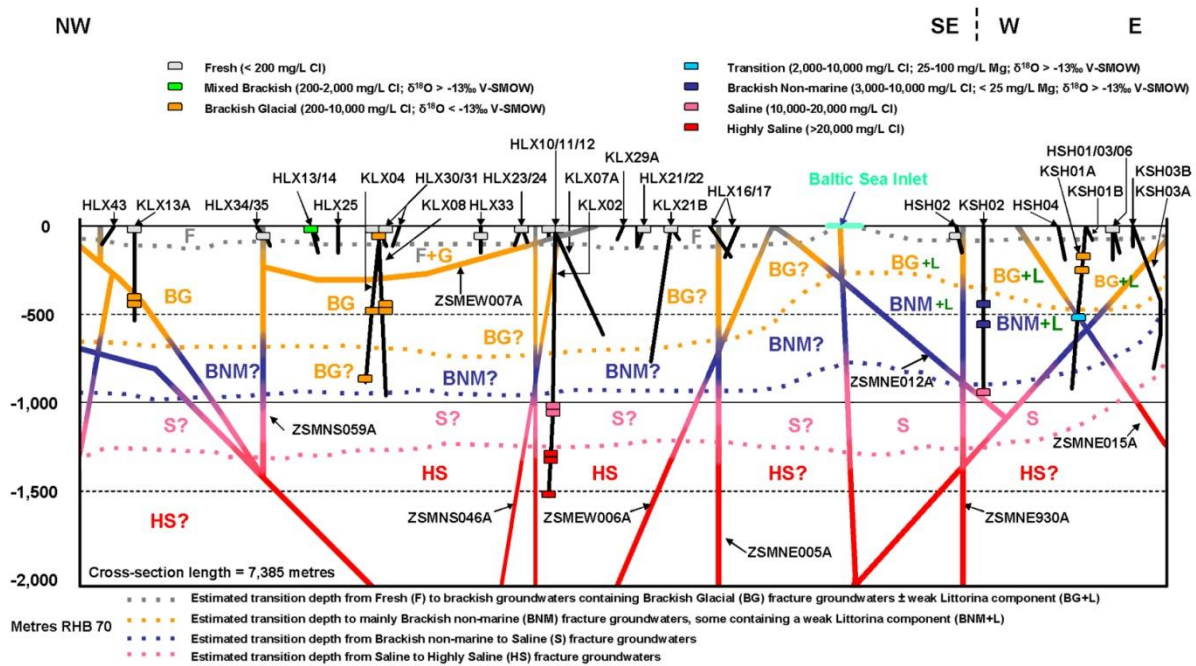
Figure 12. Approximately NW-SE/W-E cross-section through the Laxemar-Simpevarp area (Laaksoharju et al., 2009). Shown are: a) the location of the boreholes and the sections which have undergone hydrochemical sampling, b) the main fracture groundwater types (colour coded) which characterise the site, and c) the chloride distribution with depth along the major deformation zones. The dotted lines in different colours represent the approximate depths of penetration of the various fracture groundwater types along hydraulically active deformation zones. The main regional groundwater flow direction is from the west (recharge) to the east (discharge), approximately parallel to the section. (Cross-section length = 7,385 metres).

As part of the Geophysical programme in the recently completed SKB site investigations at Forsmark (SKB, 2008), a large number of measurements were made of *in-situ* formation factors using a downhole electrical resistivity probe technique. The formation factor is obtained as the ratio of the electrical conductivity of the rock divided by that of the pore water in the rock matrix. The accuracy of the method is strongly determined by, among other things, the accuracy with which the porewater conductivity can be estimated and the bias introduced by the effect of charge conduction in the electrical double layer in the constrictive pores of the rock matrix. Since the porewater ionic strength is uncertain and frequently too low to be able to discount this effect, a significant bias can be introduced which may result in an overestimation of the formation factor when interpreting data obtained using the *in-situ* geophysical technique.

In workpackage 3 **KEMAKTA** have demonstrated an improved method for correcting the measurement data to remove the theoretical bias introduced by surface conduction.. The method is based on the use of an empirical power law relation describing how surface conduction varies as a function of the true geometric formation factor as ascertained in independent laboratory experiments made using core samples saturated with water of differing ionic strengths (Figure 13).
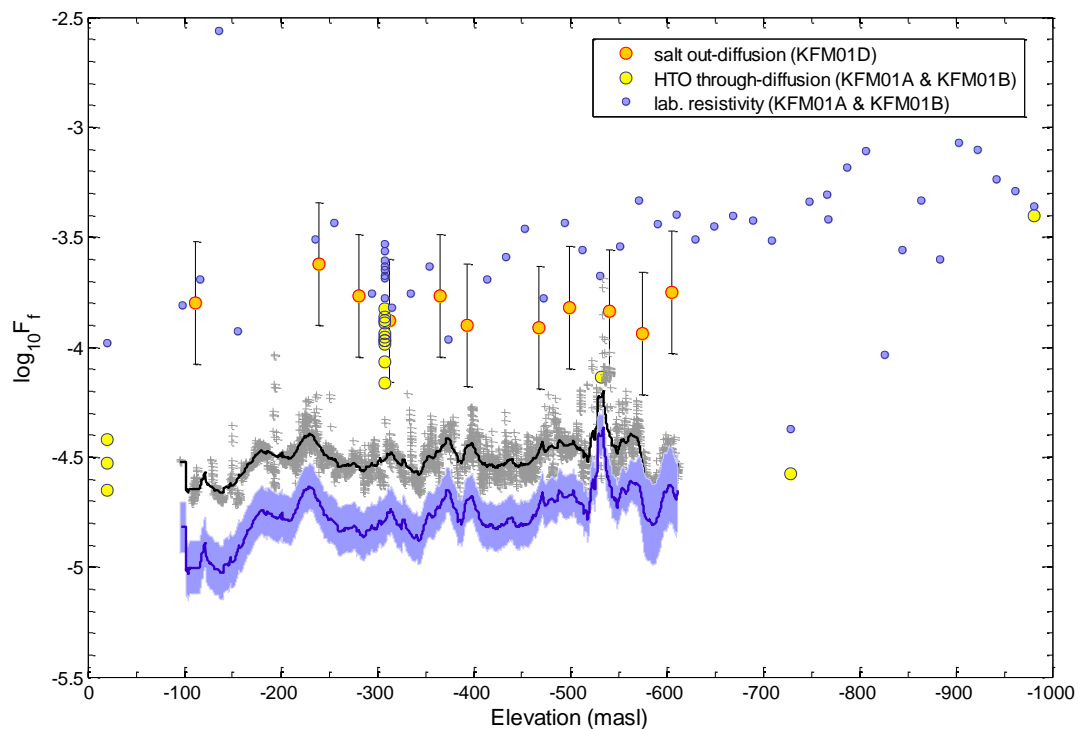
Figure 13. Best estimate geometric formation factor ($\log_{10}$ values) as a function of borehole elevation for rock surrounding Forsmark borehole KFM01D as determined by the in-situ measurement technique shown as a 10m running average (blue curve). The shaded region represents the corresponding 1-σ error of the estimate as determined by the Monte-Carlo calculations. The black curve shows the 10m running average of the apparent formation factor which is not corrected for surface conduction bias while the grey symbols indicate associated point values. Circular markers show laboratory estimated values derived from various measurement techniques as indicated in the legend (1-σ error bars shown where available).

WP4. Conceptualization and modelling

Crock WP4 has focused on minimizing uncertainties in performance assessment (PA) by developing and evaluating approaches for generating reliable data, improving the understanding of controls over radionuclide migration and evaluating modeling approaches.

One of the outcomes of this work has been the diverse range of approaches adopted by the different modelling teams to attack these various issues. **AMPHOS** approached the problem of K_d estimation in PA through the use of a semi-empirical spreadsheet tool based on a simplified representation of surface complexation and ion exchange. **KEMAKTA**, on the other hand, studied the K_d estimation problem by framing the issue in terms of generalised empirical relations describing binding constants in surface complexation models through the use of geochemical analogies. **VTT** looked at the problem on both a microscopic level using quantum chemistry computational approaches in parallel to more traditional approaches involving fitting of surface complexation binding constants to macroscopic sorption measurement data for biotite; a mineral thought to dominate sorption on site specific rocks within the Finnish national program for storage of spent nuclear fuel.

While **AMPHOS**, **KEMAKTA** and **VTT** studied K_d selection issues in PA involving batch measurement data, the **KIT-INE** team instead studied the simultaneous flow and reactive transport of radionuclides in laboratory tracer migration experiments involving a confined fracture sample. By looking at the dynamics of the coupled transport processes, additional insights were obtained that

would not have been apparent when considering only batch data in isolation. The following paragraphs detail the detailed work that has been performed by each of the beneficiaries in this challenging workpackage.

The lack of site-specific data for K_d-based transport and surface complexation modeling was identified as an important area of uncertainty in PA. Therefore, a significant effort was made to develop and evaluate methods for generating these kinds of data. **AMPHOS** evaluated a spreadsheet-based surface complexation and cation-exchange model for deriving K_d values for specific water phase conditions (pH, ionic strength, dissolved ligand concentrations etc) and rock properties (amount of mineral in the host rock, porosity and density). Data were calculated for three systems (Cs – Illite, Eu – Illite, Cs – Magnetite (Figure 14), Eu – Fe(III) hydroxide) that each involved one radionuclide and one mineral, with a long term aim of using an additive approach.
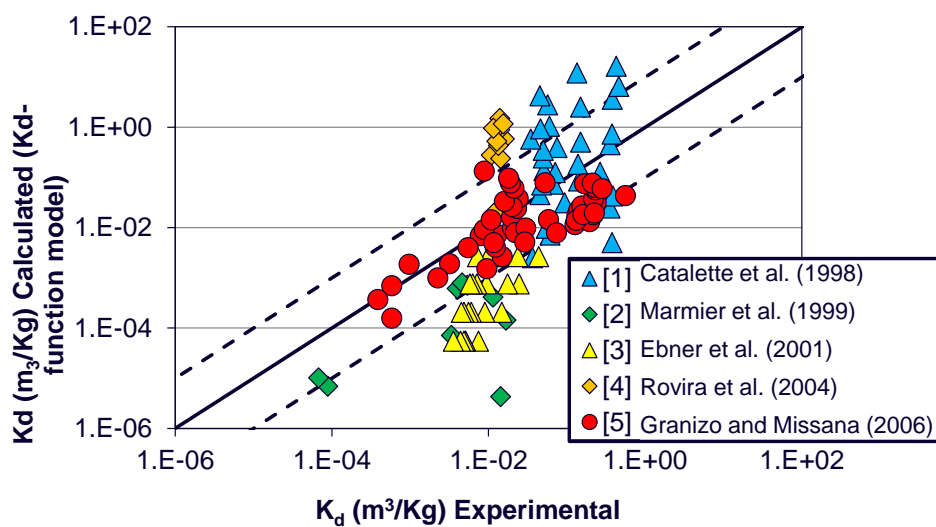

Figure 14. K_d calculated by using the analytical K_d model vs experimental K_d values for the Cs-magnetite system. Dotted lines indicates a K_d deviation of $\pm$ 1 log unit. The error bars of each value are within data point symbols.

The K_d values calculated were generally within one order of magnitude of experimental data from a number of studies, which themselves spanned up to 5 orders of magnitude. Evaluation of the K_d values against more complex PhreeqC calculations showed that the simplifications applied in the model introduced some additional data scatter, but the overall agreement was reasonable.

KEMAKTA explored the application of linear free energy relationships (LFER) to overcoming the scarcity of experimental data for surface complexation modeling in the *boot-strapped component additivity* approach (Figure 15). This assumes that the binding constants of dissolved metals to a mineral phase show a linear relationship with the hydrolysis constants of the metals when plotted on a log-log scale. Therefore each mineral has its own LFER with a characteristic intercept and slope which is supported in the literature for several minerals. Theoretical analyses suggested that the slope of the relation has overwhelming importance for describing the relative variation of sorption with pH, whereas the intercept can be treated as a normalisable parameter in a similar fashion to binding site density or mineral surface area. Site-specific data for Am, Eu and Ni sorption to Forsmark metagranite in saline and fresh groundwater were used to evaluate the approach. First, the speciation of the radionuclides in the saline water was calculated in PhreeqC, and then parameter fitting was used to identify weighting factors that incorporated both the intercept of the LFER and availability of

sites for the three key minerals present: quartz, illite (an assumed analogue for biotite) and hydrous ferric oxide. These minerals also encompass a wide range of LFER gradients. The weighting factors were then applied to predict sorption of the radionuclide species calculated to be present in the fresh Forsmark groundwater, and the results showed good agreement with the experimental data. It will be evaluated further using site specific data from Laxemar and Äspö Hard Rock Laboratory and appears to be a promising method for making predictions with sparse measurement data.
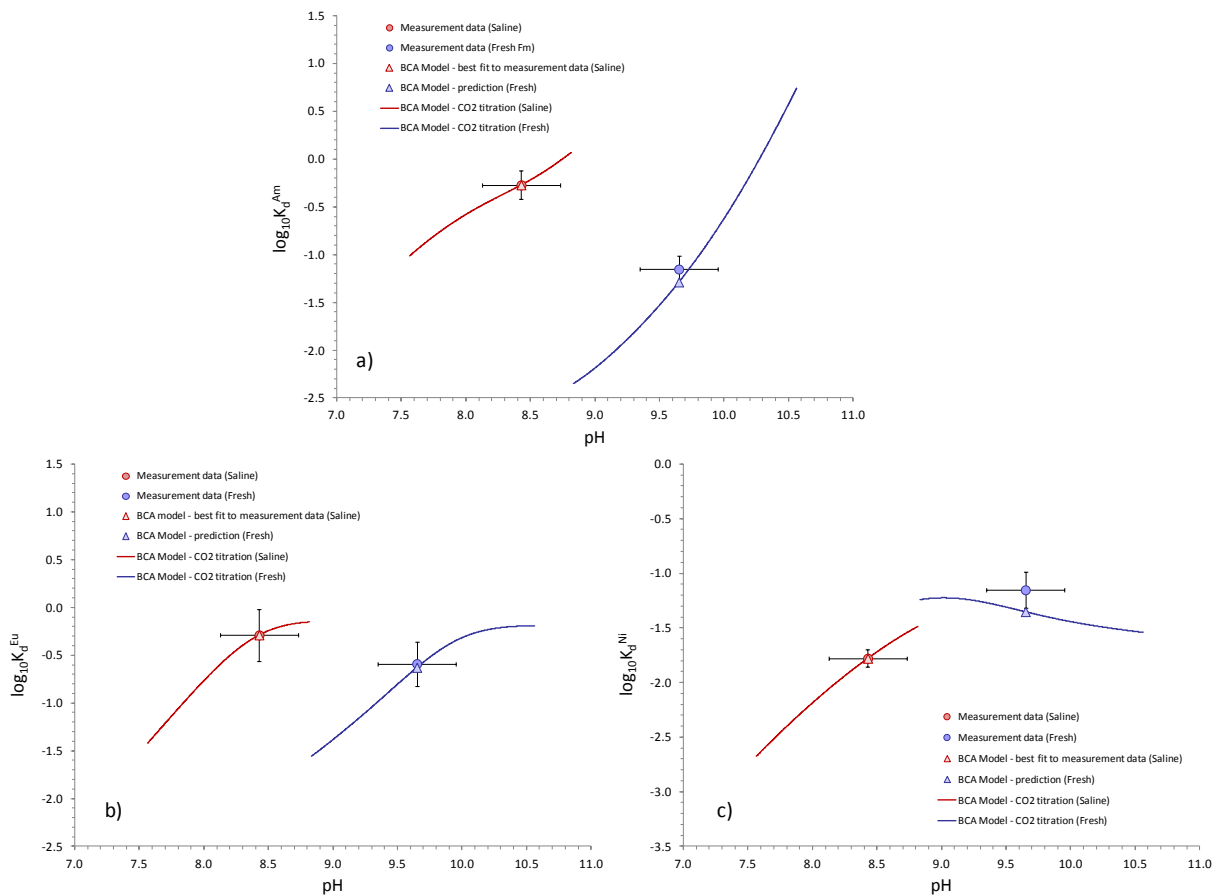

Figure 15. Boot-strapped component additivity model (BCA) predictions of K_d for a) Am, b) Eu, and c) Ni on Forsmark metagranite in contact with the Fresh groundwater (blue triangular markers) as compared with measured values (blue circular markers). The values for Saline groundwater (red markers) are calibrated to give an exact fit to the measured data. Solid lines indicate the simulated sorption edge for each groundwater where pH is adjusted by alteration of CO_2 partial pressure.

Biotite is an important reactive mineral phase at the Finnish Olkiluoto repository site, and was the focus of two studies by **VTT**-Finland. First, a quantum chemistry approach was used to calculate the molecular interactions of water and hydrated Ni^{2+} sorption to annite (Figure), the Fe-end member of the biotite series. The study identified two distinct surface environments: basal surfaces, with a reactivity controlled by surface bound K^+ ions; and terminal surfaces, which react readily with water to give a hydroxylated surface structure. On the basal sites, sorption of $Ni(H_2O)^{2+}$ involved ion exchange with surface bound K^+, while on the terminal sites, $Ni(H_2O)^{2+}$ formed a surface complex with the water molecule layer. Therefore, when the ratio of the two sites is known, each reaction can be calculated for the relevant proportion of the total surface.
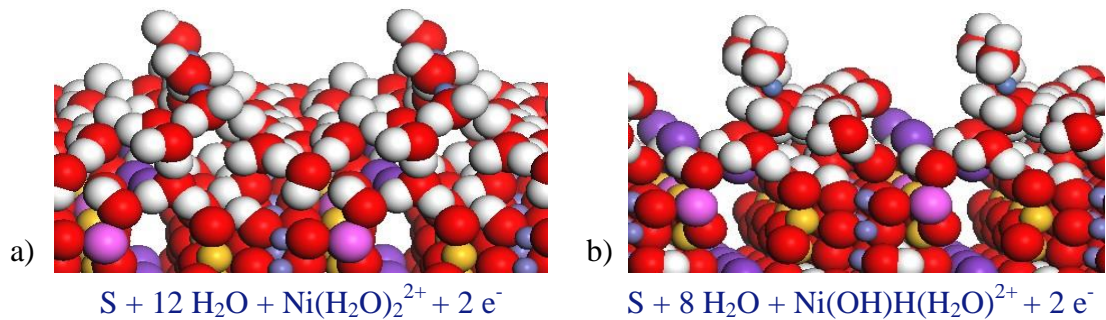
$$S + 12\ H_2O + Ni(H_2O)_2{}^{2+} + 2\ e^-$$

$$S + 8\ H_2O + Ni(OH)H(H_2O)^{2+} + 2\ e^-$$

Figure 16. The annite (110) surface: a) $Ni(H_2O)_2{}^{2+}$ above the first water molecule layer, and b) surface complexed $Ni(H_2O)_2{}^{2+}$.

Secondly, three surface complexation models (non electrostatic, diffuse layer and constant capacitance) were tested for their ability to fit Ni and Eu sorption data to 3 biotite and 2 rock samples (Ni only) over a pH range of 2-10 (7). Titration curves were available for one biotite sample (Luumäki), and these were fitted to generate stability constants for protonation/deprotonation reactions at the surface sites and sorption site density data. Although this data was used in the surface complexation modeling of Ni and Eu to Luumäki biotie, it did not improve the model fits to the other data sets. Therefore, each material needed to be parameterized independently. The non electrostatic model gave better fits to the data than the diffuse layer or constant capacitance models, and it was able to model Ni better than Eu, due to the very high Eu sorption observed at high pH.
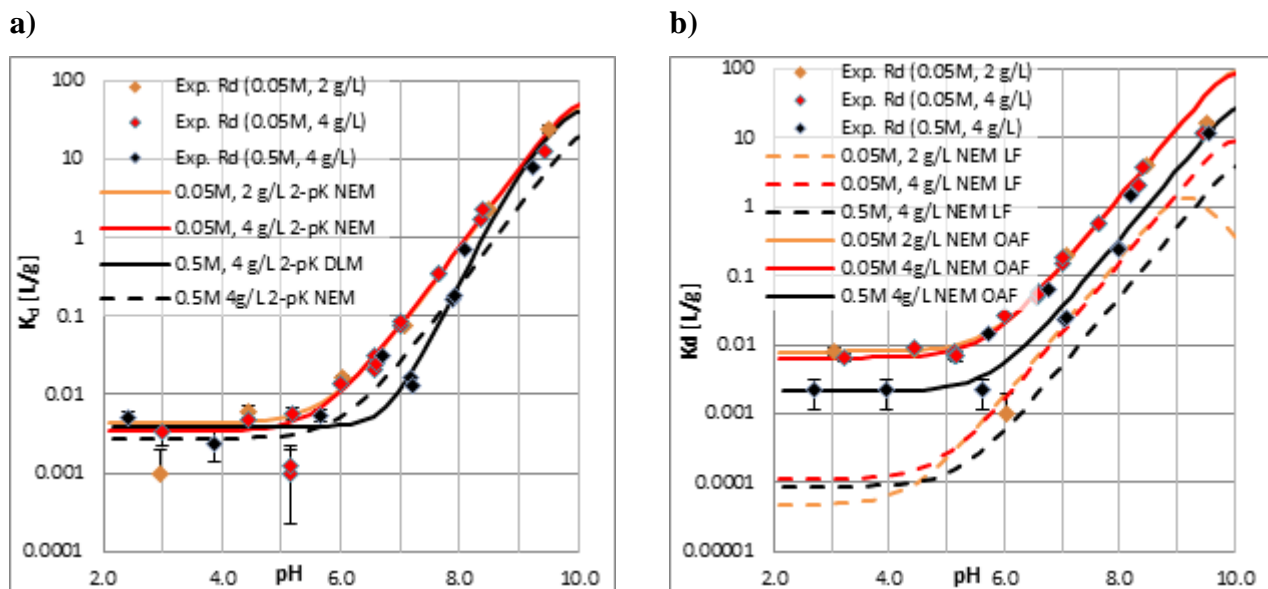
a)

b)

Figure 7. a) K_d fits of nickel on Luumäki biotite 2 and 4 g/L, 0.05 and 0.5M, and b) K_d fits for nickel on Olkiluoto A biotite (OAB) 2-4 g/L, 0.05-0.5M.

Finally, the FASTREACT reactive transport model has been coupled to PhreeqC in an attempt to describe Np transport through a fractured drill core from the Äspö Hard Rock Laboratory by **KIT-INE** in collaboration with AMPHOS. The streamtube modelling approach in FASTREACT assumes steady state flow with no mass exchange between adjacent streamlines in the fracture flow field. Sorption of the reactive tracer [237]Np was modelled using a number of different sorption modelling techniques ranging from simple K_d based sorption models (first order reversible sorption/desorption kinetics) to more complex, mechanistically based surface complexation models involving up to three separate mineral sorbing phases (hydrous ferric oxide, biotite, and kaolinite).

Assuming that sorption occurs primarily on the flow exposed fracture surface, the retardation factor for [237]Np transport could be estimated directly as the ratio of the central moments of the [237]Np and Hto tracer breakthrough curves. From the 3D model of the flowspace obtained by tomographic techniques, the specific surface area (i.e. flow wetted surface to flow volume ratio) could also be computed and the surface area normalised sorption partitioning coefficient, K_a calculated directly given the previously estimated retardation factor. By using this model Np breakthrough elution time can be reasonably well fitted, but not the peak concentration nor the pronounced tailing in the elution profile (Figure 17). It was proposed that for future studies this should be addressed by coupling the model to a code that can describe kinetically controlled surface complexation reactions.
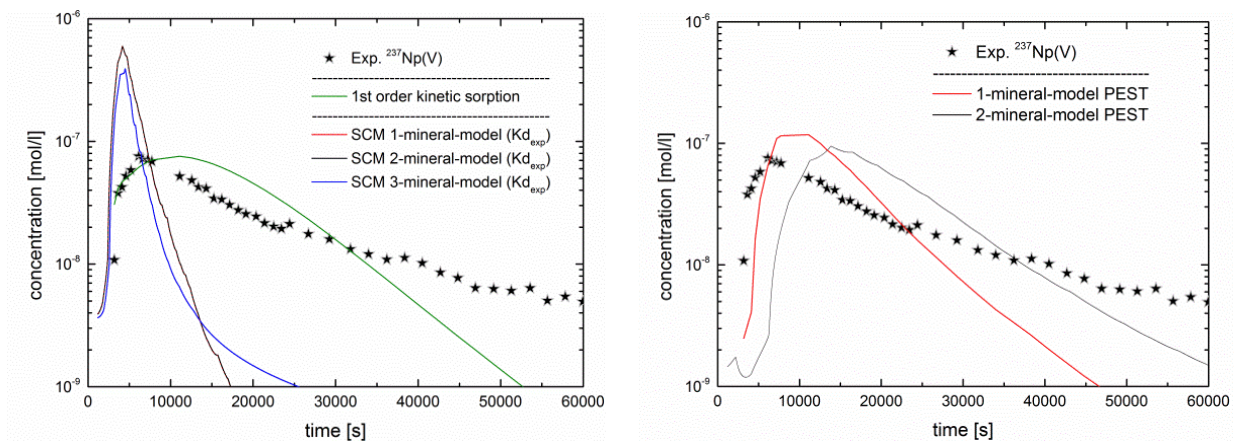

Figure 17. Left: Comparison between experimental Np breakthrough curve and model results on basis of the experimentally derived Kd. Note that the 1-mineral-model and the 2-mineral model are giving the same results. Right: Results of the FASTREACT/PEST fitting for the 1- and 2-mineral-model, respectively.

WP5. Application to the safety case

When dealing with safety assessment calculations, the prior information related to radionuclide retention processes is usually "wrapped" in a single lumped parameter, the distribution coefficient (K_d), which relates the radionuclide mass retained in the solid phase to its aqueous concentration. Although this modelling strategy is computationally appealing, it fails in describing the underlying nonlinearities of the system, especially when geochemical conditions are expected to change dramatically over the considered time frame (e.g. the transition from temperate to glacial conditions). This introduces further uncertainties to a problem that is intrinsically highly uncertain.

The work of this WP has focused on assessing different modelling approaches that, on the one hand allow nonlinearities to be properly accounted for and, on the other hand, try to circumvent the

computational limitations of "standard" fully coupled models. The different methodologies have been tested against a synthetic benchmark exercise that describes the migration of a set of radionuclides from the repository to the surface.

The CrunchFlow program was used by **KEMAKTA** to reproduce the breakthrough curves for the cation exchanging solutes obtained previously using the simplified modelling approach incorporated in the PATHTRAC program (Figure 18). These previous simulations were made for a sequence of alternating fresh and saline groundwater pulses intended to provoke clearly non-linear remobilisation behaviour which cannot be captured by a traditional constant K_d modelling approach. It was found that although remobilization of cation exchanging radionuclides could be modeled approximately using the decoupled major ion chemistry modeling approach, the breakthrough curves did not fully match those of the fully coupled simulations owing to the inability of the simplified method to capture transient chromatographic separation of base cation reaction fronts which influence radionuclide sorption.
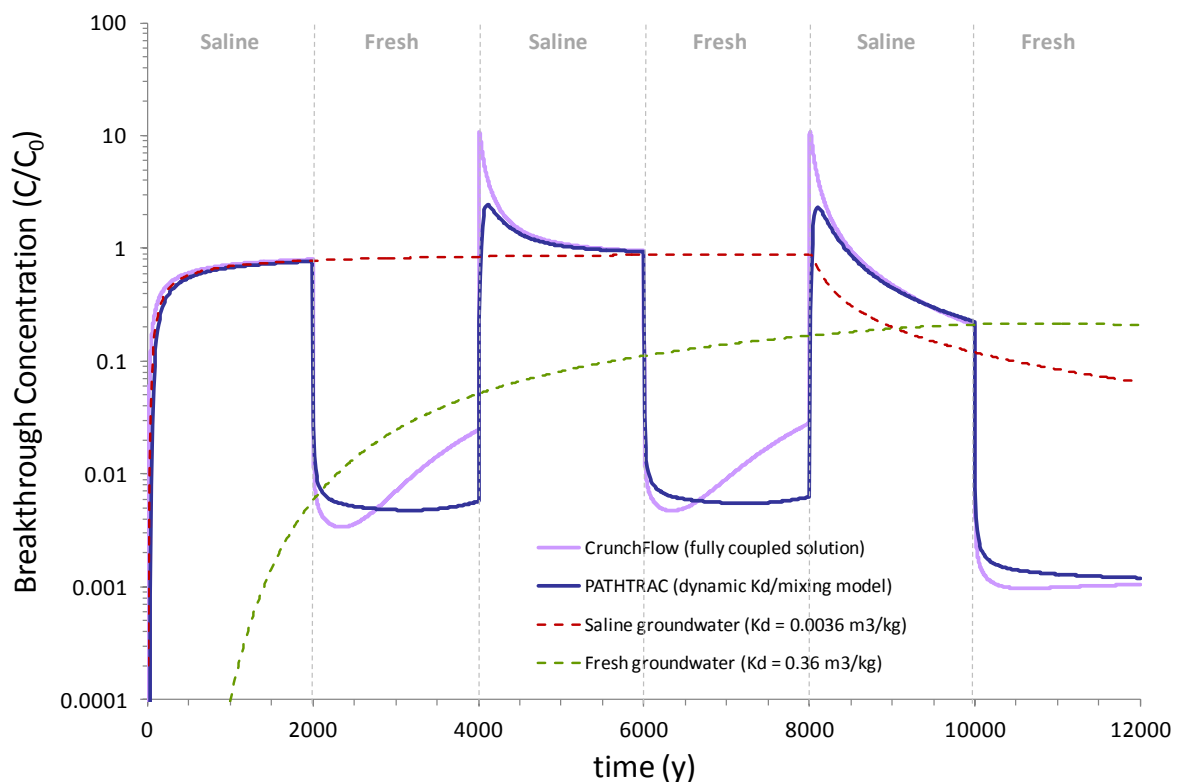

Figure 18. Comparison of breakthrough curves for Ra^{2+} migration simulated using PATHTRAC and a fully coupled reactive transport simulation using CrunchFlow for the temporally variable boundary conditions (as indicated by the fresh/saline labelled intervals in the figure). Breakthrough data are normalised relative to the constant inlet concentration boundary condition (10^{-12} mol/kgw).

In parallel, the FASTREACT methodology was used by **AMPHOS** to carry out mechanistic reactive transport simulations over the set of proposed flow paths of the benchmark exercise (Figure 19). The results of the simulations have shown that, when matrix diffusion is neglected, the breakthrough curves of the considered radionuclides (i.e. Sr, Ra and Cs) reflect the distribution of the ensemble of trajectories with a sharp arrival peak followed by a fast decrease of concentration. Furthermore, cesium appears to be strongly sorbed onto the available clay minerals (in particular, illite) and the

rise of concentration is extremely slow during the considered time frame (i.e. 90 Ky). The resulting retardation factor (i.e. 316 for the Base Case) is very sensitive to the heterogeneous distribution of the fracture filling minerals.
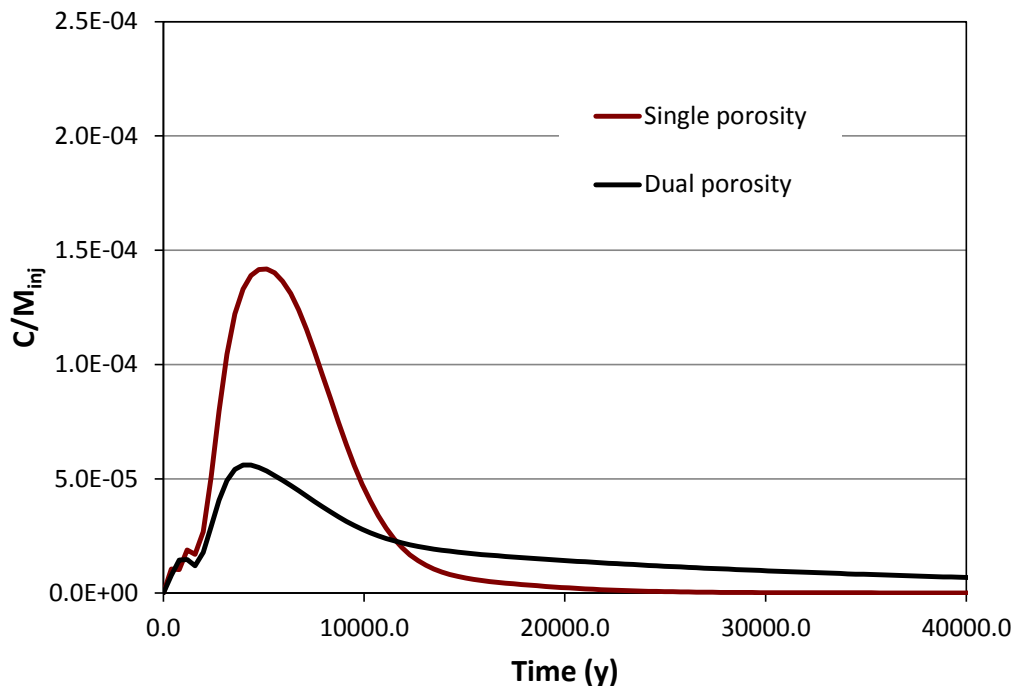

Figure 19. Breakthrough curve of uranium for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

The aforementioned numerical exercises have demonstrated the great potentiality of a number of "new" methodological approaches that, allowing non-linearities to be explicitly and efficiently accounted for, could help in reducing the intrinsic conservatism of safety assessment calculations. Nevertheless, in these type of applications one has always to deal with the epistemicity related to the different processes and the related variables. Thus, a rigorous stochastic framework is needed to quantify the uncertainty associated to the results of the calculations. To this end, in the framework of this WP, a tool, denoted as MCPhreeqc, has been developed by **AMPHOS** to apply Monte Carlo simulations automatically to the PhreeqC geochemical models. The software has been used to infer effective distribution coefficients related to cesium sorption in a typical Fennoscandian crystalline medium. The main conclusions of this numerical study highlight that the uncertainties related to the heterogeneous mineralogy of the medium along with nonlinearities arising from competition and depletion of sorption sites result in a large variation of the computed K_d values, which span more than seven orders of magnitudes (Figure 20). The linear isotherm computed using the average amount of cation exchange sites agrees well with recent laboratory experiments focused on cesium sorption on biotite.
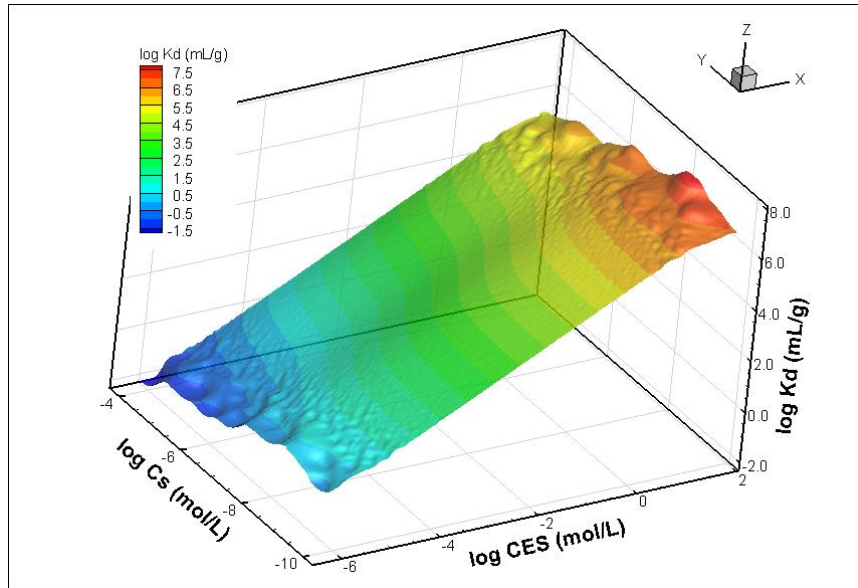
Figure 20. Results of the Monte Carlo simulation: cesium distribution coefficient (K_d) as a function of the aqueous concentration of cesium and the number of exchange sites (CES).

The focus of the **VTT**'s work was to facilitate the assessment of the K_d values to different conditions and different scales and to evaluate uncertainties that are connected to the assessment of the K_d values. The work was done for radionuclides and conditions that are relevant for the KBS3 type repository in the crystalline rock. Main objective of VTT's work within the framework of this WP is on the upscaling process. The modelling was based on upscaled sorption properties for three different scales: molecular level (less than 100 atoms), surface complexation and a single fracture scale (partial flow paths of the benchmarking exercise). Finally, transport properties were also applied in the PA modelling over the entire length of the flow paths in the benchmark exercise (Figure 21).
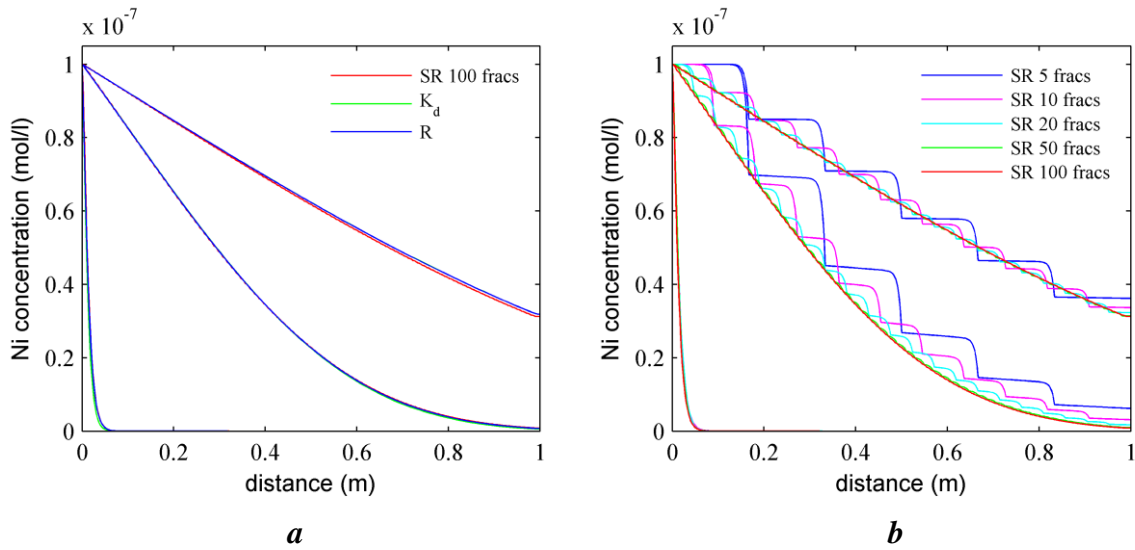
Figure 21. Soluble Ni^{2+} concentration profile at the midline of the fracture at times 0 years (lowest set of lines), 0.2 years (middle) and 1 year (top). The graphs in figure **a** are from the K_d-model, volumetric reaction model (R) and surface coverage model (SR) with 100 transverse fractures. In figure **b**, the number of transverse fractures varies.

WP6. Documentation

Workpackage 6 of the CROCK European collaborative project focus on the review of those processes which exert a major influence on the transport and retention of radionuclides in the far-field, as well as on the main conceptual models describing these processes available in the scientific literature.

Based on the results of a questionnaire distributed among different international organisations (Table 5), an analysis of how these retention processes are taken into account and modelled in the different Performance Assessments (PAs) currently being carried out by radioactive waste management organisations was conducted. The focus was on the evaluation of the long-term safety of deep geological disposal facilities for radioactive waste in crystalline rocks.

Table 5. List of participants in the questionnaire exercise

Host organization for a responder participating in the questionnaire	Performance Assessment activities in which the responder has been involved	Year
Kemakta Konsult AB	SR-Site (2011)	2011
Nuclear Research Institute Řež plc.	Initial safety report study (2010); C2 Long-term safety evaluation of GDR	2010
KIT-INE	First long-term Safety Assessment for a generic German SF repository in granite; KOLLORADO-1 (Colloid and nano-particle formation and mobility in the concept of a deep GDF)	
CIEMAT	Enresa 2000	2000
Lomonosov Moscow State University		
Technical Research Centre of Finland (VTT)	TILA-99	1999
Japan Atomic Energy Agency (JAEA)	H12 performance assessment	1999
Gesellschaft für Anlagen- und Reaktorsicherheit (GRS)		

The results have pointed out a number of issues in the PA that need further treatment with regard to transport and retention processes and having potentially high impact on radionuclide transport in the geosphere including:

- Bentonite erosion and formation of colloids as a result of intrusion of low-salinity waters into the near-field;

- Mixing and dilution during advective transport;

- Radionuclide re-mobilization;

- The effect of degradation of cementitious materials due to interactions with groundwater: the formation of hyper-alkaline plume and its impact on physical and chemical properties of the affected rock;

- Microbial activity. In particular microbial-mediated remobilization processes that may be characterized by slow kinetics;

- Modelling of solute transport: PA exercises could be improved by considering more detailed transport models than the simple models currently used

Most experts agree that the main challenges in modelling of radionuclide transport within Performance Assessment lie in the areas of:

- Sufficient conceptual understanding of relevant processes that control the transport and retention of radionuclides

- Adequate implementation of conceptual models into Performance Assessment codes

- Acquisition of reliable data for model parameterization

A general view of how are these processes included in PA exercises has been produced taking into account the following aspects:

- Relative importance of processes assumed to have a strong impact on transport and retention phenomena

- Main assumptions and simplifications of current PAs

- Main limitations of current PAs

- Processes not considered in current PAs deserving special attention

In addition, a second questionnaire was distributed among the different participants to inquire on the scientific activities carried out within the CROCK framework, to elaborate a precise picture of what are the main fields of research in the project and the potential impact on future PA exercises. The results of this questionnaire indicated that the contribution of the project to impact future PA exercises is potentially very high.

1.4 Potential Project impacts

The main objective of the project was to decrease the uncertainty with respect to the radionuclide transport in the crystalline host-rock far-field using the methodology generated within the project and to apply the outcome of the project to the Safety Assessment, leading to increased confidence in the associated Safety Case. This was done e.g. by using unaltered material and performing sorption experiments under anoxic conditions.

Nevertheless, due to strong limitations in time not all aspects of radionuclide interaction and transport in the far field of a repository located in a granitic host rock could be studied. Additional topics for future studies have also be identified as, e.g., the role and the mechanistic understanding of anion diffusion, pore-water characterization and chemistry, relevance and accurate description of large scale experiments, behavior of spent nuclear fuel under in-situ repository conditions etc.

Potential impacts

The key impact from the project is the application and implementation of the knowledge generated during the 2 and ½ years of CROCK in the associated Safety Case. The CROCK project, besides the provision of new non-oxidized Äspö rock samples, has provided key process understanding, at least for the redox sensitive radionuclide; for which higher retardation have be demonstrated with a positive impact to the safety case. Furthermore no additional processes or observations have been recognized within the project which could lead to an enhanced radionuclide migration.

The integration of an End-User Group (EUG) within the CROCK project, established with three representatives from Waste Management Organizations (from Sweden, Finland, Czech Republic) and two organizations with National Regulatory Functions (from Sweden and Finland), has been a decisive factor of ensuring usefulness of the CROCK project work for application to the disposal Safety Case. This was further assured by reviewing the scientific-technical reports published in the two workshop proceedings by members of the End-User-Group.

Specific questions and key achievements obtained in the different workpackages are:

- Acquisition and characterization of un-altered Äspö rock samples under anoxic conditions.

- *Impact:* The usage – for the first time – of un-oxidized material in subsequent sorption studies is of special importance for redox-sensitive radionuclides and reflects the conditions in a repository after closure.

- Sampling and characterization of biofilms in crystalline host-rock environments.

    - *Impact:* The biological material creates an abundant surface area for radionuclide adsorption that can affect radionuclide migration in deep disposal conditions. Detailed knowledge of this kind of material and its behaviour is of utmost importance for gaining trust on the Safety Case.

- New data for radionuclide sorption on granite and granite materials.

    - *Impact:* The provision of new and updated data increases the confidence in experimental data and helps to increase the process understanding. In addition it also helps the modellers with the conceptualisation of retention processes for being included in the Safety Case.

- Redox sensitive radionuclides retardation.

    - *Impact:* The results gathered within CROCK have demonstrated a higher retardation for redox sensitive radionuclides (i.e. Tc) with a positive impact to the Safety Case. This was only possible by using unaltered material sampled and handled under anoxic conditions.

- Development of approaches for conceptualizations and models for radionuclide retention processes.

    - *Impact:* Long-term predictions for the associated Safety Case could be improved through the use of the developed methodologies.

- Analysis and detection of issues for which further investigations and research are required for improving future PA.

    - *Impact:* Key points for future Safety Case studies have been detected and pointed out.

Societal impacts

The project has a direct impact on the European nuclear power community, including authorities representing public safety interests. The research results gathered within the CP CROCK are essential to maintain a high level of safety in the long-term management of radioactive wastes and to implement a safe geological disposal. It is thus directly related to long-term improvement in European competitiveness, employment, environmental quality and quality of life.

Another impact from implementing the work program is that the Consortium members become aware of the respective complementary competencies and thus can jointly tackle follow-up problems in the future. In addition, the project keeps up the knowledge and the expertise achieved in the past in an international environment of cooperation, helping European researchers to work together. This could also be useful for other countries with emerging interest on granitic host rock for nuclear disposal.

Dissemination activities

A significant part of the dissemination activities within CROCK is the o establishment of a public project website, www.crockproject.eu, where all the project advances and latest news are documented.
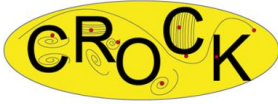
During the CROCK project a Kick-off meeting as well as two project workshops have been organized which were open to interested people from outside the project Below a description of main objectives of these meetings are detailed.

The Kick-Off meeting was held in Barcelona (Spain) on February, 10th-11th 2011, with the aim of:

- Ensuring that all project consortium members were aware of the project objectives, structure, work program and reporting obligations,

- Providing for detailed agreements on the work program described in the *"Annex I-description of work"* including specification of the systems under study, selecting of radionuclides and their homologues used, discussing and deciding joint and training activities,

- Ensuring that all consortium members were aware of the different scheduled meetings, giving importance to the two scheduled project workshops and the documentation of the outcome in the project workshop proceedings,

- Supervising that all bodies were established (Coordination Team (CT), Executive Committee (ExCom members), End User group (EUG) and beneficiaries) in accordance with the Consortium Agreement,

In association with the Kick off meeting specific ExCom (restricted to ExCom members) and EUG (restricted to EUG members and CT) meetings were held the first day of the Kick off meeting. The specific agenda of the meeting can be downloaded from the project website.

The objectives were achieved and the outcome of the Kick-Off meeting is documented in the minutes (available in the project Intranet) and the presentations are available on the project webpage (www.crockproject.eu).

The 1st CP CROCK workshop was held in Stockholm (Sweden) on May, 22nd-24th, 2012 in association with the second ExCom and EUG meetings. Additionally, a Topical session on "Reactive Transport Modelling" and a poster session were organized at the first day of the workshop. The specific agenda of the meeting can be downloaded from the project website (www.crockproject.eu).

The aims of the workshop were the same listed under the Kick-Off meeting, and in addition:

- The status of the different project activities was communicated between all the project consortium members,

- The work program status was presented in the form of workpackage plenary presentations and decisions were taken for the next steps until the end of the project. If necessary, deviations from original work planning was also discussed, and

- Finally, instruction for preparing the periodic reporting and the workshop proceedings was explained, for effective documentation and communication of the project achievements. The scientific-technical contributions included in the workshop were reviewed by the EUG members.

The objectives of the Workshop were achieved and the outcome is documented in the minutes (available in the project Intranet, www.crockproject.eu), the oral presentations (available on the project website, www.crockproject.eu) and in the workshop proceedings published on October 2012 as KIT Scientific Report No. 7629.

The Final CP CROCK workshop was held in Karlsruhe (Germany) on May, 14th-16th, 2013 in association with the third EUG meeting. Additionally, a Topical session on "In situ URL experiments" and a poster session were organized at the first day of the workshop. The specific agenda of the meeting can be downloaded from the project website (www.crockproject.eu).
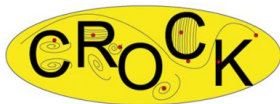
The aims of the workshop were the same listed under the Kick-Off meeting and 1st Workshop, and in addition:

- Instruction for preparing the final reporting and the workshop proceedings was explained, for effective documentation and communication of the project achievements. As for the 1st Workshop, the scientific-technical contributions included in the workshop proceedings were reviewed by the EUG members.

The objectives of the Final Workshop were achieved and the outcome is documented in the minutes (www.crockproject.eu), the oral presentations (www.crockproject.eu) and in the workshop proceedings to be printed as KIT scientific report (in preparation and scheduled to be available by the end of October 2013).

It is worth to mention that the generic poster of the project has been presented at several conferences:

- The 13th and 14th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (MIGRATION'11 and MIGRATION'13), held in Beijing, China in September 2011 and in Brighton, UK on September 2013,

- The EuCheMS International Conference on Nuclear and Radiochemistry (NRC-8) – held in Como, Italy in September 2012, and

- The EURADISS conference held in Montpellier, France in October, 2012.

Additionally, research performed within the project has been presented in several International and National conferences like:

- the Ion Beams'12: Multidisciplinary Applications of Nuclear Physics with Ion Beams (Italy, June 2012),

- ENERGY 12: Modification and Analyses of Materials for Future Energy Sources, (Madrid, September 2012),

- 7th Russian Conference on Radiochemistry "Radiochemistry-2012" (Russia, October, 2012),

- 21st Conference on Ion Beam Analyses "IBA 2013", (USA, June, 2013),

- Goldschmidt 2013, (Italy, August, 2013),

- 14th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the geosphere "Migration 2013" (UK, September, 2013).

1.5 Project website

The project website (www.crockproject.eu) was set up at the beginning of the project and has been continuously updated (Figure 22) by AMPHOS (Amphos 21, Passeig de Garcia i Faria, 49-51, 1-1, 08019 Barcelona, Spain. Contact: Dr. Jorge Molinero jorge.molinero@amphos21.com and Mr. David García david.garcia@amphos21.com).

The website includes two parts: one open to public and one restricted ("intranet") to the members of the Consortium and European Commission.
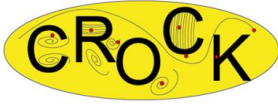
Figure 22. Project website home (www.crockproject.eu).