EUROPEAN COMMISSION
Community research

CROCK

(Contract Number: 269658)

DELIVERABLE (D-N°:5.1)
Calculation of effective Kd values for the migration of selected radionuclides through crystalline media (UPDATE)

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Reporting period: e.g. 01/07/12 – 30/06/13

Date of issue of this report: **March 31st, 2013**

Start date of project: **01/01/11** Duration: 30 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities (2007-2011)		
Dissemination Level		
PU	Public	X
RE	Restricted to a group specified by the partners of the CROCK project	
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Objective:

The objective of WP 5 is to apply the outcome of other WPs to the application in the Safety Assessment, thereby decreasing the PA uncertainty and providing improvements for future site characterizations.

To this end, a benchmark exercise has been set-up aimed at assessing the potential release, fate and transport of a set of radionuclides over the very large spatial and temporal scales typically involved in a Safety Assessment study. The results of this benchmark exercise will be used to infer **effective K_d/K_a values** upscaled over these very large scales (i.e. tens/hundreds of kilometres). A crucial point of this study is related to the need of a rigorous and exhaustive treatment of the underlying epistemic uncertainties, which will be handled in different ways by the different modelling teams.

Benchmark exercise

This benchmark exercise aims at assessing the potential release of a set of radionuclides at repository depth and the related migration and discharge at the surface.

It is worthwhile stressing that the different partners of this WP will focus on the evaluation of different retention processes. In fact, if on the one hand Amphos 21 will provide effective K_a values representative of the fracture-matrix interaction processes, the modelling work of KEMAKTA will be focused on the evaluation of the matrix retardation processes while the focal point of VTT will be to provide effective sorption properties based on the results of the molecular models performed in WP4.

1. Streamline delineation

The conceptual model assumes the release of the set of radionuclides from a number of deposition holes located in a deep geological repository.

First, a set of discharge streamlines (from the canister to the repository) has been delineated. This has been done as follows

- The Darcy's velocity field has been borrowed from the regional hydrogeological model of Olkiluoto (Löfman et al., 2010). A random component has been added to the velocity vector in order to make the exercise absolutely general and to avoid any implicit reference to the case of Olkiluoto.

- 3959 particles are injected in correspondence of the hypothetical location of a same number of deposition holes.
- The particles are tracked to the surface using the random walk particle tracking code RW3D-MT (Fernández-García et al. 2005).

The ensemble of streamlines is shown in Figure 1 and the related travel time histogram is shown in Figure 2.

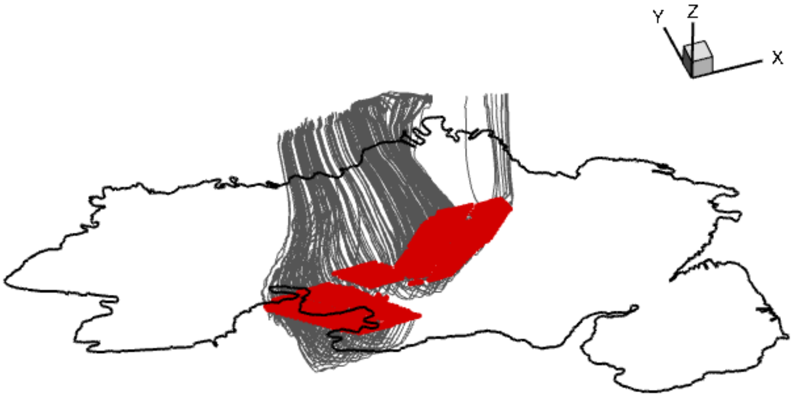


Figure 1 set of 3960 particles that delineates streamlines from the repository to the surface

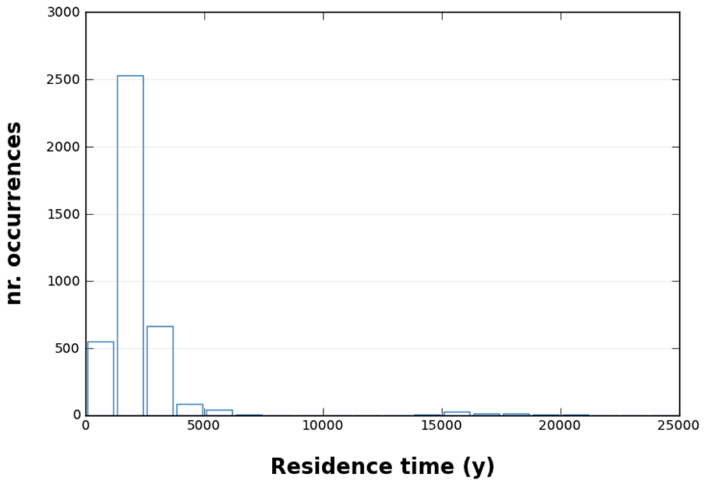


Figure 2 Histogram of travel times for the 3960 injected particles.

2. Geochemical conditions

The capacity of the subsurface system to retain radionuclides, mainly via sorption or precipitation, strongly depends on the pH and redox state of the groundwater. Both parameters, together with the water composition, control the speciation of the radionuclides and the stability of the mineral phases that are able to retain them. Nevertheless, in this model set-up, no specification is provided about the redox control system. In fact, the goal of the exercise is precisely to leave liberty to each modelling team and then to test the implications of the different assumptions made by each of them.

A representative groundwater composition has been chosen (Table 1). This proposed groundwater is a mildly reducing water representative of the average hydrochemical conditions that are found at repository depth in a typical Fennoscandian site.

Table 1 Initial geochemical coditions

	Initial porewater
pH	6.83
Eh (mV/l)	-2.63
$[Cl]_{total}$	$1.01\text{x}10^{-1}$
$[S]_{total}$	$2.21\text{x}10^{-3}$
$[Si]_{total}$	$5.63\text{x}10^{-4}$
$[PO_4^{3-}]_{total}$	$6.46\text{x}10^{-8}$
$[Na]_{total}$	$6.13\text{x}10^{-2}$
$[K]_{total}$	$8.00\text{x}10^{-4}$
$[Ca]_{total}$	$1.83\text{x}10^{-2}$
$[Mg]_{total}$	$1.83\text{x}10^{-2}$
$[Sr]_{total}$	$6.95\text{x}10^{-5}$
$[Ba]_{total}$	$4.36\text{x}10^{-7}$
$[C]_{total}$	$4.82\text{x}10^{-3}$
$[Fe]_{total}$	$5.80\text{x}10^{-5}$
$[U]_{total}$	$3.90\text{x}10^{-9}$
$[Cs]_{total}$	$3.65 \text{ x}10^{-9}$
$[NH_4^+]_{total}$	$7.28 \text{ x}10^{-5}$

It is assumed that the open fractures of this synthetic system are mainly populated by Calcite, Hematite and Clay Minerals and that they have been observed in 32%, 24% and 11% of the mapped fractures. The average mineral thickness is specified in **Table 2**.

Table 2 Average mineral thickness

Mineral	**Average thickness (mm)**
Calcite	$3.40\text{x}10^{-2}$
Clay minerals	$8.20\text{x}10^{-2}$
Hematite	$1.00\text{x}10^{-2}$

The average fracture aperture as well as the parameters related to matrix diffusion is summarized in Figure 3 and Table 3.

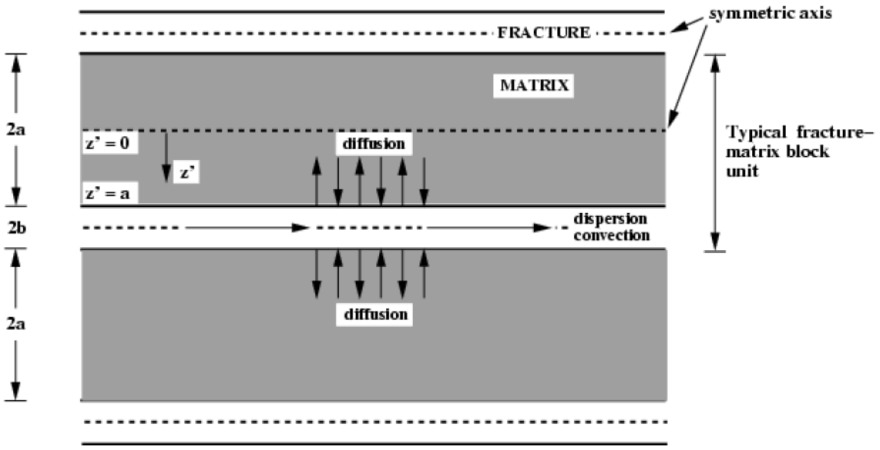


Figure 3 Parallel fracture model used to described the fractured system (modified from Löfman et al., 2010).

Table 3 Parameters and values used for the DP model parameterization.

Symbol	Parameter	Value
a	Half matrix thickness	4.15 m
b	Half fracture aperture	$1.83 \cdot 10^{-4}$ m
D_0	Molecular diffusion coefficient in the water	$1.0 \cdot 10^{-9}$ m^2/s
ϕ_{im}	Matrix porosity	$1.0 \cdot 10^{-4}$ (-)

It is worthwhile pointing out that all the processes involved in this modelling work and the underlying parameters are affected by large epistemic uncertainty. As one of the goal of the project is precisely “decreasing the PA uncertainty and providing improvements for future site characterizations”, the different teams will use tailored and alternative approaches to quantify and reduce these uncertainties.

Status of work being performed by Amphos 21:

1. Stremline-based reactive transport simulations over the whole set of streamlines

1.1 FASTREACT methodology

Amphos 21 is running the different cases of the benchmark exercise using the methodology called FASTREACT (FrAmework for Stochastic REACtive Transport). The methodology consists in coupling a set of 1D reactive transport simulations with one or multiple random-walk particle tracking realizations (see Figure 4; for the details of the methodology the reader is referred to Trinchero et al., 2013).

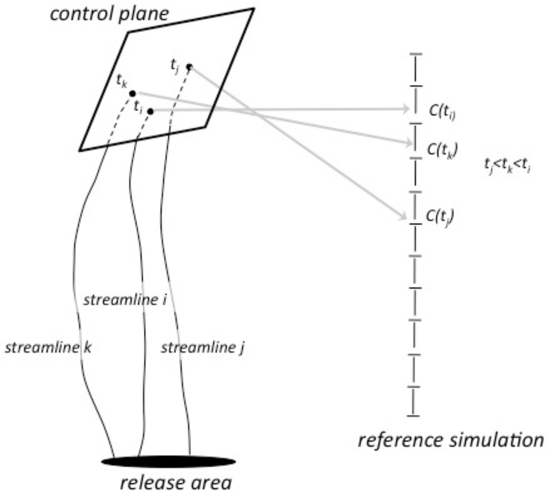


Figure 4 Illustrative sketch of the FASTREACT methodology

The results of the Base Case simulation are summarized in the next section whereas the full set of sensitivity simulations (i.e. sensitivity simulations to different sorption properties such as the Cation Exchange Capacity, CEC) will be summarized in the scientific and technical contribution (S&T) to be presented in the next CROCK workshop. These simulations focus on the evaluation of the transport of three radionuclides (strontium, caesium, and uranium) as well as a conservative tracer (here assimilated to HTO).

1.2 Results of the Base Case

For the sake of brevity, in this chapter we summarize the results of the Base Case simulations of radionuclide transport carried out by Amphos 21. An exhaustive discussion on the different modelling results (sensitivity simulations) will be presented in the final workshop of the CROCK project that will be held in Karlsruhe, next May 2013.

As mentioned above, these calculations, which have been carried out using the methodology FASTREACT (see previous section) have focused on the evaluation of the transport of three radionuclides, namely strontium, caesium, and uranium as well as a conservative tracer (here assimilated to HTO). A pulse-like release of these four radionuclides is assumed to occur at repository depth.

The different retention processes used in the modelling work are summarized next.

Strontium

For the case of strontium, the two main processes considered as possible retention mechanisms are the co-precipitation of Sr with calcite, forming a solid solution, and the sorption of Sr onto clays.

In the numerical modelling, the co-precipitation of strontium with calcite will take place as long as saturation is reached. Sr sorption onto clays is modelled using the thermodynamic constants reported for illite. In other words, illite has been selected as a proxy mineral phase to represent the behaviour of the clay minerals in the model.

Caesium

Similarly to Strontium, clay minerals are strong sinks for caesium. Therefore, in the numerical model, the sorption of caesium onto illite is the only retention process considered. In this case too illite is selected as a mineral phase representing the behaviour of all clay minerals in the fractures.

Uranium

In the reactive transport simulations, a set of minerals has been selected as possible solubility-limiting phases of aqueous uranium. For U(VI), a hydrated amorphous phase ($UO_2 \cdot 2H_2O$) has been used instead of a crystalline phase (e.g. uraninite). Also, schoepite and uranophane are allowed to precipitate if the solution becomes oversaturated with any of these phases.

The thermodynamic database used for aqueous speciation is the SKB-TDB (Hummel et al. 2002) with substantial modifications as reported in Duro et al. (2006), Grivé et al. (2008) and Arcos and Piqué (2009).

Bradbury and Baeyens (2000) proposed a model of cation exchange for illite which is here considered as representative for all the clay minerals, considering three types of sites (“planar”, “type II” and “Frayed Edge Sites”). The total concentration of sites in illite, the model clay mineral in this study, is kept constant during the reactive transport simulations since it is assumed that this mineral phase does not dissolve nor precipitate in the environmental conditions considered in the model. The initial amount of exchange sites has been defined based on the average values for clay minerals (as a group) thickness provided by Löfgren and Sidborn (2009). Since the aforementioned report does not provide further distinctions about the distribution of the different clay minerals, we have arbitrarily assumed that only 40% of the clay minerals are reactive and they have been modelled as illite. An equivalent cation exchange capacity (CEC) value of 225 meq/kg has been considered for illite (Baeyens and Bradbury, 2004), and according to this CEC, the concentration of cation exchange sites (CES) in the fracture-filling is set as follows:

- CEC = 225 meq/kg = 0.225 eq/kg = 0.225 mol/kg (exchange species is a monovalent X^-)
- [CES] = 0.225 mol/kg CEC x 0.02 kg/L_{water} = 0.0045 mol/L_{water}
-

The initial exchanger composition has been considered to be in equilibrium with the reference groundwater.

Table 4 Cation exchange reactions and their corresponding Gaines-Thomas selectivity coefficients for illite

Reaction	**Log K (25ºC)**	**Reference**
Planar sites		
$X^- + Na^+ \leftrightarrow NaX$	0.0	(1)
$X^- + K^+ \leftrightarrow KX$	1.1	(1)
$X^- + Cs^+ \leftrightarrow CsX$	1.6	(1)
$2X^- + Sr^{2+} \leftrightarrow SrX_2$	1.13	(2)
$2X^- + Ca^{2+} \leftrightarrow CaX_2$	1.13	(2)
$2X^- + Ba^{2+} \leftrightarrow BaX_2$	1.13	(2)
$2X^- + Mg^{2+} \leftrightarrow MgX_2$	1.13 (a)	
$2X^- + Ra^{2+} \leftrightarrow RaX_2$	1.13 (a)	
$2X^- + UO_2^{2+} \leftrightarrow UO_2X_2$	0.65	(3)
Type II sites		
$X^{II-} + Na^+ \leftrightarrow NaX^{II}$	0.0	(1)
$X^{II-} + K^+ \leftrightarrow KX^{II}$	2.1	(1)
$X^{II-} + Cs^+ \leftrightarrow CsX^{II}$	3.6	(1)
FES		
$X^{FES-} + Na^+ \leftrightarrow NaX^{FES}$	0.0	(1)
$X^{FES-} + K^+ \leftrightarrow KX^{FES}$	2.4	(1)
$X^{FES-} + Cs^+ \leftrightarrow CsX^{FES}$	7	(1)
$X^{FES-} + NH_4^+ \leftrightarrow NH_4X^{FES}$	3.5	(1)

(1) /Bradbury and Baeyens 2000/. (2) /Brouwer et al. 1983/. (3) /Bradbury and Baeyens 2009/.

(a) Value assumed, considering an equal sorption behaviour for all the alkaline earth elements.

Table 5 Calculated initial composition of the cation exchange sites in illite

Site	$mol \cdot L_{water}^{-1}$
Planar sites	
CaX_2	1.19×10^{-3}
NaX	4.72×10^{-4}
MgX_2	3.29×10^{-4}
KX	7.54×10^{-5}
SrX_2	3.76×10^{-15}
BaX_2	$2.62 x 10^{-8}$
CsX	$2.95 x 10^{-14}$
RaX_2	$5.89 x 10^{-15}$
UO_2X_2	$1.17 x 10^{-15}$
Type II sites	
KX^{II}	5.53×10^{-4}
NaX^{II}	3.47×10^{-4}
CsX^{II}	2.16×10^{-12}
FES	
NH_4X^{FES}	4.96×10^{-6}
KX^{FES}	4.21×10^{-6}
NaX^{FES}	1.32×10^{-6}
CsX^{FES}	2.07×10^{-11}

The calculations have been carried out using both a single and a dual porosity approach. In the former (denoted as Model A), transport and reactions occurs only in the fractures while in the latter (denoted as Model B) mass exchange occurs between the mobile domain (the fractures) and the matrix. The dual porosity approach has been implemented using a first-order exchange approximation (van Genuchten and Nielsen 1985) and the matrix has been considered as non-reactive.

Figure 5 shows the normalized breakthrough curves of HTO for the two considered models. It is worthwhile noting that in model A the breakthrough curve reflects the distribution of the ensemble of trajectories (Figure 2), with a sharp arrival peak followed by a fast decrease of concentration. In model B, the effect of the matrix is evident as the breakthrough curve shows a lower peak value and a long tail.

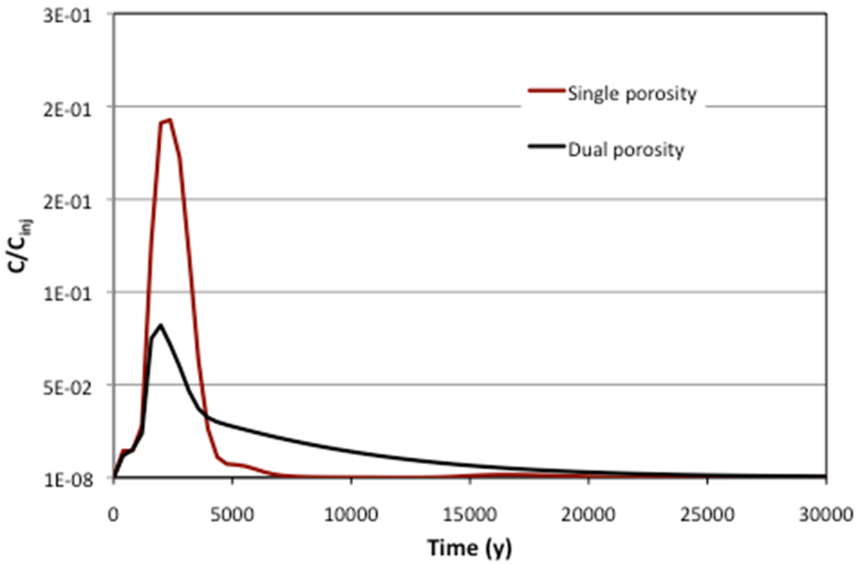


Figure 5 Breakthrough curve of HTO for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

Figure 6 and 7 show the breakthrough curves of uranium and strontium respectively. Their qualitative shapes are similar to those of the conservative simulations although the different retention processes implemented in the model result in an average retardation factor of 2.4 and 2.0 respectively.

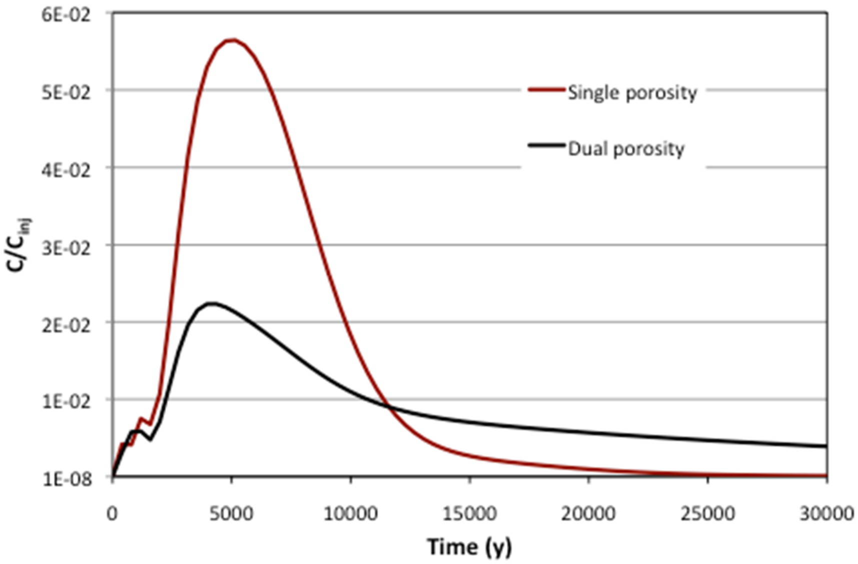


Figure 6 Breakthrough curve of uranium for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

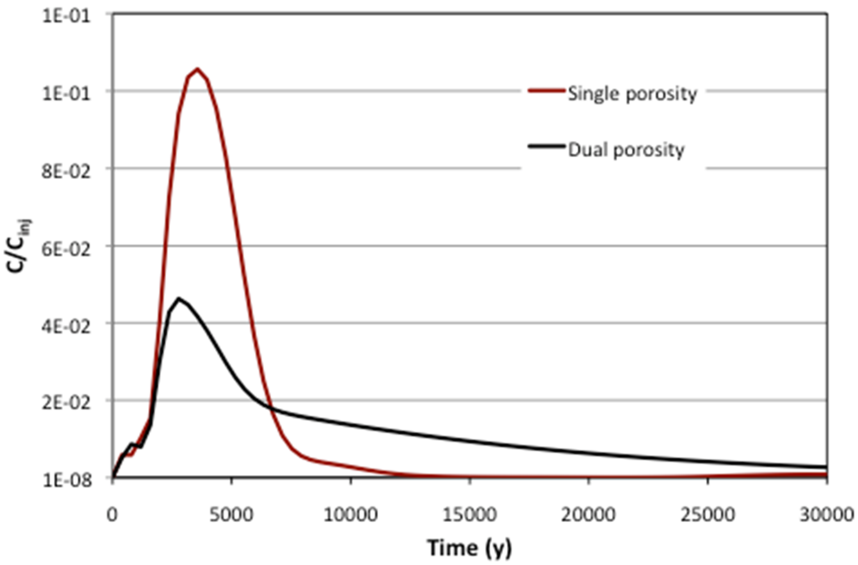


Figure 7 Breakthrough curve of Strontium for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

Figure 8 shows the breakthrough curve of caesium. Due to convergence problems, only the results of the single porosity model are available, so far. It is evident that the isotope is strongly sorbed onto the available clay minerals (in particular, illite) and the rise of concentration is extremely slow during the considered time frame.

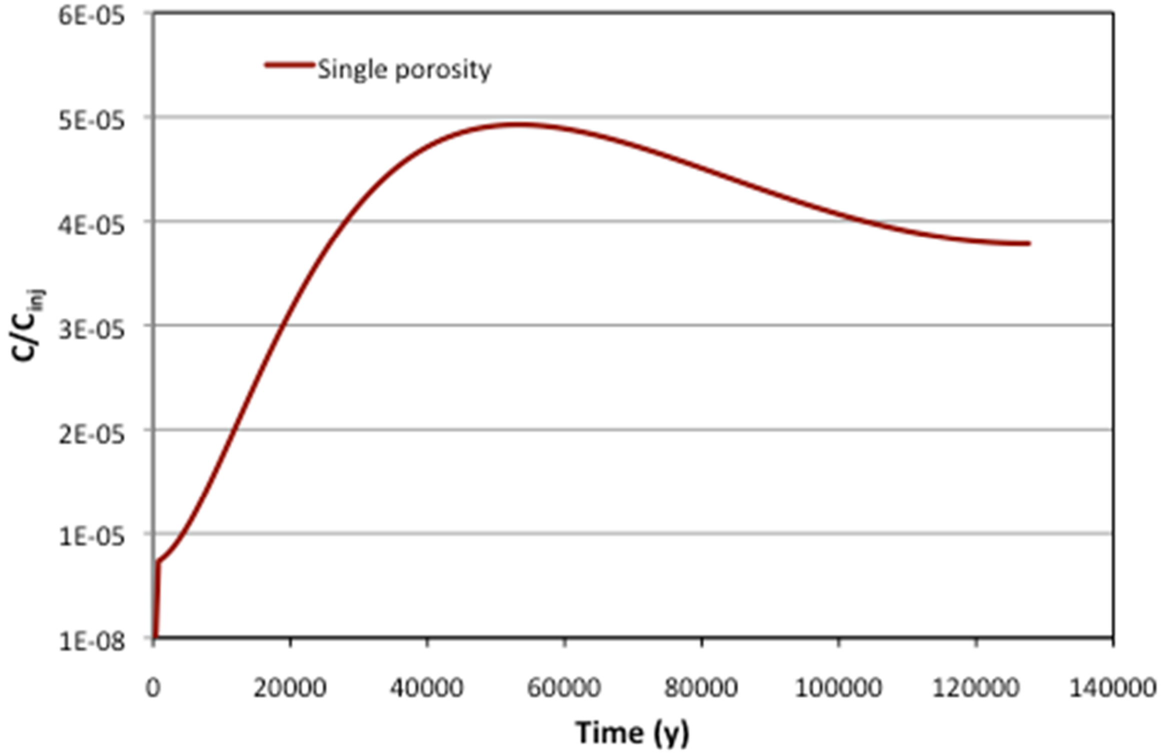


Figure 8 Breakthrough curve of caesium for the single porosity model. The curve is normalized by the injection concentration.

1.2 Effective Ka values for the Base Case

As shown by Wels et al. (1996), the K_a value for a given radionuclide can be computed as:

$$K_a = (R_a - 1)/a_w$$

where R_a is the surface retardation factor and a_w is the specific surface area defined as $a_w = 1/b$. From Figure 6, 7 and 8 one can see that the retardation factor for uranium, strontium and cesium is 2, 1.4 and 25 respectively. The related Ka values are summarized in

Table 6.

Table 6 FASTREACT -Computed K_a values for the three selected radionuclides

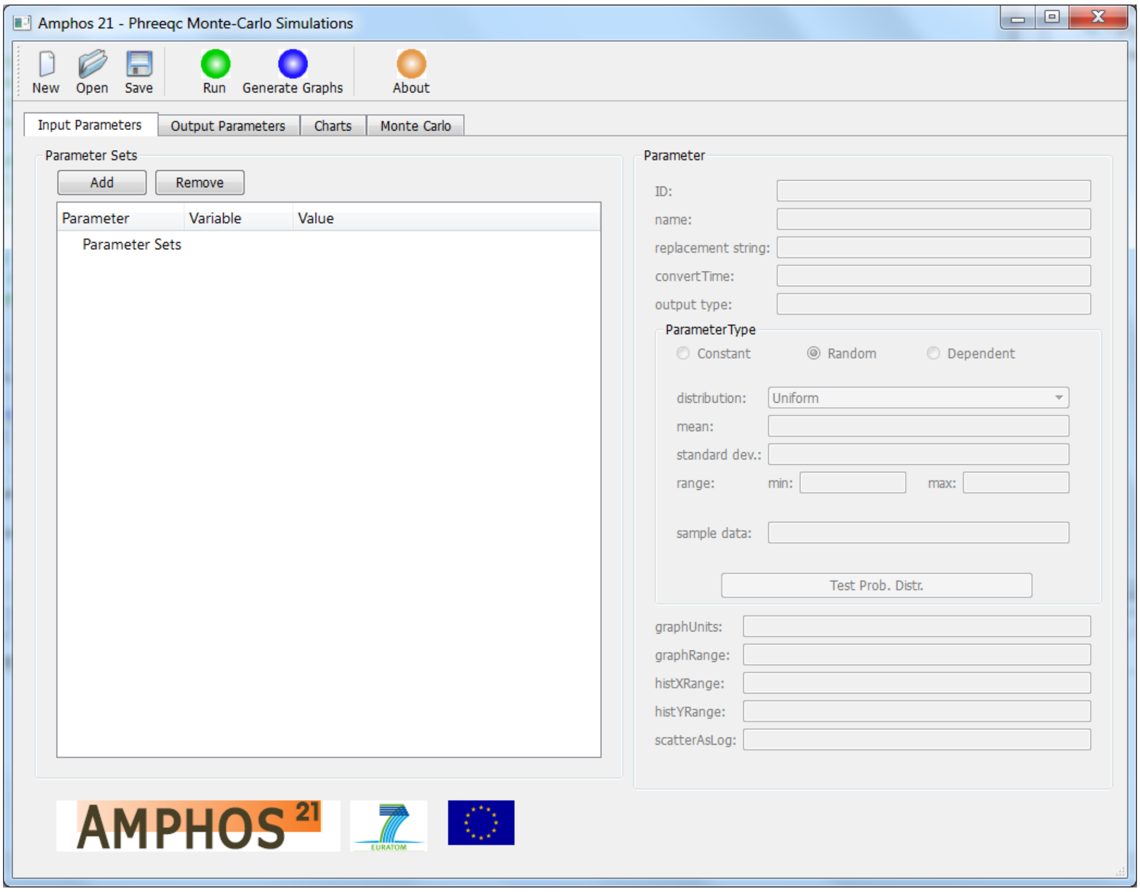
Radionuclide	K_a (m^3/m^2)
Uranium	1.83×10^{-4}
Strontium	7.21×10^{-5}
Cesium	4.63×10^{-3}

Uncertainty analysis:

1. Methodology (MCPhreeqc)

Geochemical processes can be modelled with many different types of software. These processes all have in common the uncertainty about the exact value of the used parameters. The classical approach is to do direct modelling combined with calibration to find the "correct" parameter values. A limited trial-and-error sensitivity analysis is often applied afterwards. In the framework of WP5 of the Crock project, we have developed a tool, called MCPhreeqc (de Vries et al., 2012), to apply Monte-Carlo simulations automatically to the PHREEQC geochemical models.

The software MCPhreeqc provides a way to do Monte-Carlo simulations automatically. As input it uses a Phreeqc input file, a PDF for each of the uncertain parameters and the settings for the Monte Carlo simulation. It comes with a graphical user interface (see Figure 9) to enter the configuration of the simulations that need to be run. In addition it can automatically generate histograms and scatter plots from the results. Simulations can be run in parallel to benefit from all the processor cores in the machine



ParameterType: ○ Constant ● Random ○ Dependent

distribution: Uniform

Figure 9 Screenshot of MCPhreeqc graphical user interface

It is written in the programming language Python and is released under an open source license (LGPL). The software can be freely downloaded form the following link:

http://www.amphos21.com/software/

In the aforementioned web page, explicit reference is made to the CROCK project.

2. Uncertainty assessment of the effective Ka values

In the considered geological system (i.e. a typical Fennoscandian fractured medium), cation exchange onto fracture filling clay minerals is one of the key retention processes that govern the sorption and related retardation of relevant radionuclides such as Cesium and Strontium. Thus, Monte Carlo simulations have been carried out to assess the impact of the geochemical heterogeneity of the fractures on the computed Ka values.

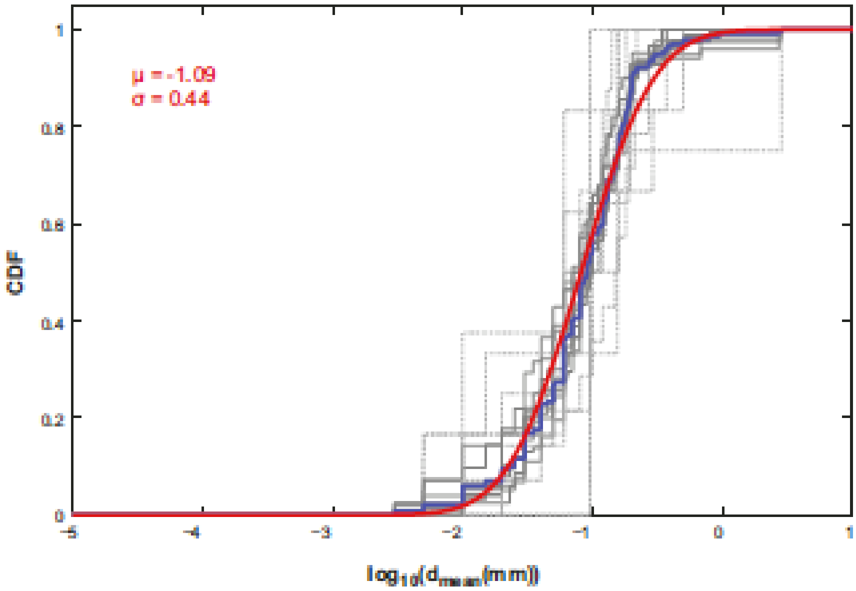
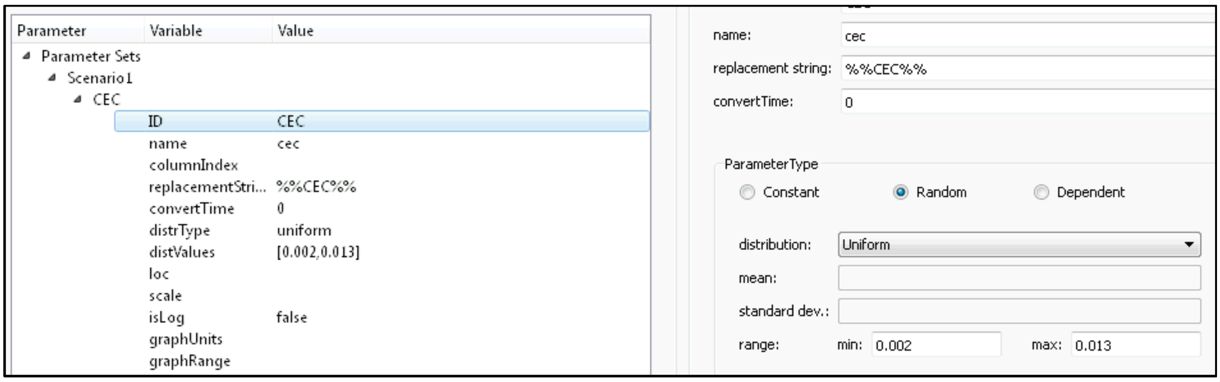


Figure 10 Suggested cumulative density function (CDF) of clay minerals thickness at the Forsmark site (Löfgren and Sidborn (2009))

The quantitative information provided by Löfgren and Sidborn (2009) (i.e. cumulative density functions of clay minerals thickness at the Forsmark site – see Figure 10) has been used to infer plausible ranges of Cation Exchange Sites (CEC). More specifically the sampling distribution of the average thickness of Clay minerals was represented by a uniform distribution with minimum and maximum values equal to $1.3 \cdot 10^{-2}$ and $2 \cdot 10^{-3}$ mol/Lwater respectively (see Trinchero et al, 2010 for further details) as shown in Figure 11 and 12.



Parameter	Variable	Value
◢ Parameter Sets		
◢ Scenario1		
◢ CEC		
	ID	CEC
	name	cec
	columnIndex	
	replacementStri...	%%CEC%%
	convertTime	0
	distrType	uniform
	distValues	[0.002,0.013]
	loc	
	scale	
	isLog	false
	graphUnits	
	graphRange	

name: cec

replacement string: %%CEC%%

convertTime: 0

ParameterType

○ Constant ● Random ○ Dependent

distribution: Uniform

mean:

standard dev.:

range: min: 0.002 max: 0.013

Figure 11 Screenshot showing the input file (i.e. PDF of CES) in the MCPhreeqc GUI.

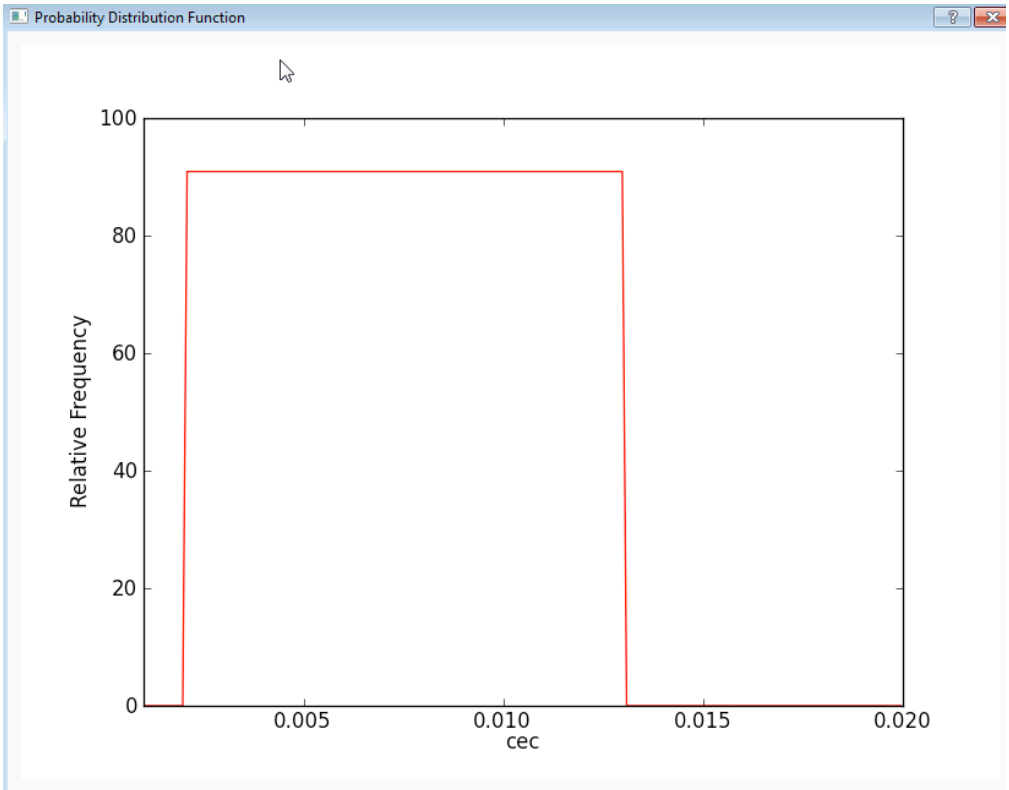


Figure 12 Uniform PDF used in the modelling exercise.

The MonteCarlo simulation is carried out over a single streamline among the set presented before and 100 realizations are computed. The simulations appeared to require very long computation times and thus only preliminary results are presented in this deliverable. A full account of the results will be presented in the next CROCK workshop and summarized in the related S&T contribution.

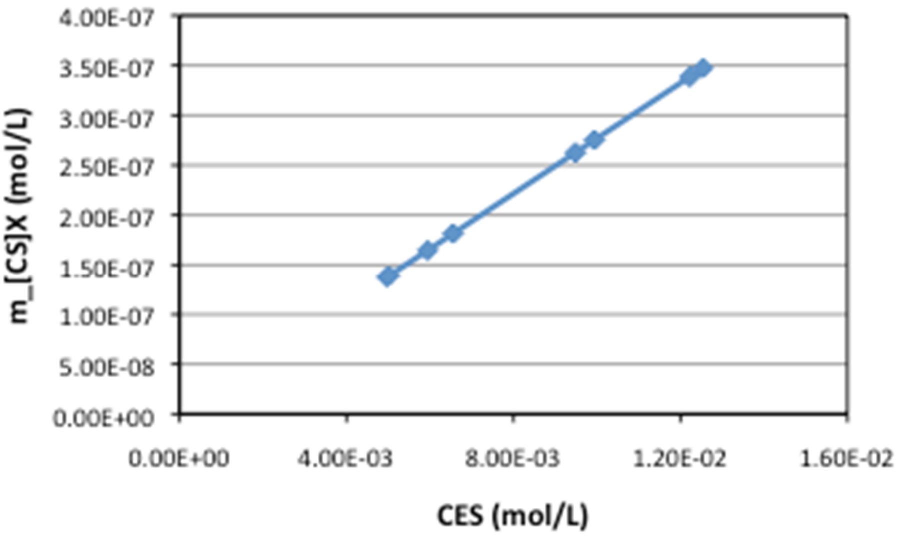


Figure 13 amount of Cesium in the exchanger as a function of the Cation Exchance Sites for 8 random realizations. The simulations are performed using MCPhreeqc.

Figure 13 shows the amount of Cesium in the exchanger as a function of the Cation Exchange Sites (CES) for 8 random realizations. The simulations have been performed using MCPhreeqc. The linear behaviour is attributable to the cation exchange capacity of the set of simulations, which is significantly higher than the concentrations of migrating trace components and thus no intrinsic non-linear behaviour (Langmuirian saturation of sites) was expected for this particular case study.

Status of work being performed by KEMAKTA:

The main focus of Kemakta's efforts in Work package 5 during the present reporting period has been the development of a template for use together with the CrunchFlow program (Steefel, 2009) to simulate 2D reactive transport problems involving advective transport of reactive components along a flowpath coupled with matrix diffusion and sorption on rock matrix microsurfaces. A helper program written in Matlab then facilitates the automatic generation of input files for different grid discretisation structures, hydrodynamic, and physicochemical boundary conditions directly from the template, circumventing the necessity to code multiple input files by hand. The template is structured in such a way that it can be used to generate input files for generalised 2D transport problems involving arbitrary sets of primary and secondary species together with ion-exchange, surface complexation, and mineral dissolution and precipitation reactions. Using the template, fully coupled reactive transport simulations have been made of the migration of the ion-exchanging solutes Rb, Sr, Cs, Ba, and Ra along a flowpath.

Preliminary test simulations have been made of the WP 5 benchmark as defined in the previous WP5.2 Deliverable ("Results of the benchmark exercise"). In order to ensure consistency between independent batch chemical modelling performed using the PhreeqC program (Parkhurst and Appelo, 1999) and that using CrunchFlow, some effort has been made to translate relevant parts of the official SKB thermodynamic database (Duro et al. 2006) into a CrunchFlow compatible format. This is to ensure that exactly the same thermodynamic data are used in simulations made with both programs. In spite of this there are still some small residual differences found between calculation results (simulated batch Kd values) obtained using CrunchFlow and PhreeqC which appear to be due to minor differences in the aqueous activity models and calculation procedures used by the programs.

CrunchFlow simulations have been made in a three step procedure going from the (0D) batch system considering only chemical equilibrium, to a 1D transport model incorporating equilibrium sorption, flow and hydrodynamic dispersion, and finally to a fully coupled 2D transport model incorporating matrix interactions as outlined above. Sorption of the ion exchanging solutes is modelled using the single site cation-exchange model for Finnsjön granite described by Byegård et al. (1995). In addition to selectivity coefficients for cation exchange of Rb+, Sr2+, Cs+, and Ba2+ (Ra2+ is assumed to be geochemically analogous to Ba2+), this model includes selectivity coefficients for the major groundwater constituents Na+, K+, Ca2+, Mg2+ thereby providing a natural coupling between the variation of major groundwater constituents and the non-linear sorption of the trace solutes.

Since the cation exchange capacity in the model is significantly higher than the concentrations of migrating trace components, no intrinsic non-linear behaviour (Langmuirian saturation of sites) was expected for this particular case study. Furthermore, since the bulk groundwater composition in the WP5 benchmark exercise is defined to be static, no extrinsic non-linear behaviour was expected to occur (i.e. changes in sorptivity due to varying bulk groundwater composition). The simulation results of the simplified 1D flow case and the more complex 2D case were compared with analytical solutions using conditionally constant Kd values derived from the batch simulations. In both cases, the CrunchFlow simulated results were found to agree with the analytical solutions to a sufficient number of significant figures that the results may be considered, for all practical purposes, identical. The results thereby confirm sorption linearity in the case study as expected.

The 2D simulations were made assuming an F-factor (hydrodynamic transport resistance) of 104 y/m corresponding to a fast flowpath with relatively poor retardation properties in order that well resolved breakthrough curves could be obtained within a reasonable simulation time frame (≈40 hours of CPU time for a 104 year simulated breakthrough curve). It may be noted that this F-factor is about 1.5 orders of magnitude less than that implied by the low end of the particle tracking ensemble delivered by the WP5 leader for the WP5.2 task together with the specified transport aperture of the fracture. The much higher F-factors implied by the particle tracking ensemble would have required significantly longer simulation times since the breakthrough time is known to scale with the square of the F-factor. The connected porosity of the rock matrix was also assumed to be 0.1% in these simulations rather than the 0.01% defined in WP5.2 deliverable (“Results of the benchmark exercise”) since this was deemed more appropriate for typical granitic bedrock types found in Sweden. Since the main focus of the benchmark exercise, however, is to demonstrate continuity between the different scales of problem abstraction from the (0D) batch system to a (1D) simplified flow system, and further to (2D) application-scale models these differences are not considered to be of great significance for the main outcome of the work.

Current work in WP5 is aimed at using the developed CrunchFlow model to reproduce the breakthrough curves for the cation exchanging solutes obtained previously using the simplified modelling approach incorporated in the PATHTRAC program. 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 Kd modelling approach. Results from this previous modelling exercise were documented in the S&T from the first annual workshop proceedings (Crawford, 2012). The simulation of trace solute breakthrough for the boundary condition of a temporally variable bulk groundwater composition appears to require longer CPU times than for the same breakthrough time assuming a static groundwater composition. Preliminary CrunchFlow verification simulations are currently underway, although we have encountered some practical issues related to restart of the program with altered boundary conditions that may take some time to fully resolve. Based on the current simulation performance trajectory it is expected that it will take at least 1-2 additional months to obtain representative breakthrough curves corresponding to the two PATHTRAC simulated cases at which point a comparative evaluation can be made.

Status of work being performed by VTT:

The bedrock in Finland is fractured, and therefore, radionuclides migrate via the fracture network consisting of fractures of varying apertures and other properties. Two major retarding mechanisms in these fractures are sorption on surfaces and matrix diffusion into intact rock. In a simple model a fracture of constant aperture is modelled by Darcy's law for flow, K_d approach for sorption and Fickian diffusion into intact rock. In our work we are applying basically three different spatial levels (Figure 1): molecular level, surface complexation and fracture transport modelling.

Our main results obtained this far are in the application of molecular level modelling to support surface complexation modelling and modelling of nickel and europium sorption onto biotite surface. Non-electrostatic models gave best fitting both for nickel and europium, and this observation is assumed to follow from inconsistent surface charging model of biotite surface. Reactive transport modelling based on surface complexation models is still going on, as is the comparison of reactive transport and PA models.

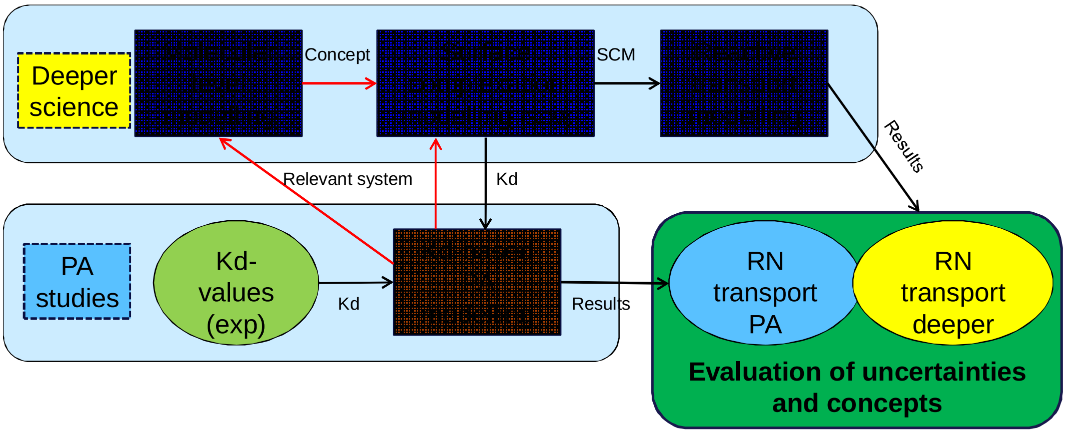


Figure 14. Overall concept of our approach.

1. Methods

1.1 Molecular level modelling

Density functional calculations were performed with the CASTEP code implemented into Materials Studio versions 6.0 (Accelrys, 2011).

1.2 Surface complexation modelling

In the surface complexation model previous experimental data were re-fitted, but the new work includes also 2-p*K* model and models without electrostatic corrections (NEM, non-electrostatics model). The fitting were done by using FITEQL 4.0-program (Herbelin & Westall, 1999).

1.3 Reactive transport modelling and PA calculations

Reactive transport modelling serving as a link between surface complexation and PA modelling, a stepwise approach between these two ends is taken by implementing models with varying level of details of the surface reactions. The models from the simplest (closest to PA models, can be compared to them) to the most realistic one are the following:

1. K_d approach
2. Surface complexation with surface sites divided to a volume of bedrock
3. Surface complexation with surfate sites divided to an area of fracture surface

The software used here is COMSOL Multiphysics.

2. Results

2.1 Molecular level modelling

Biotite, which ideal chemical formula can be expressed as $K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$, has a sheet-like structure, where the sheets are connected to each other by potassium cation layer (Accelrys, 2011). Construction of surface models to molecular modelling studies revealed that the smallest meaningful models are very atomic-rich. In order to simplify model structures, it can be used end-members of biotite: annite and phlogopite. In this study, annite, was utilized. The unit cell of annite is about half of that of biotite.

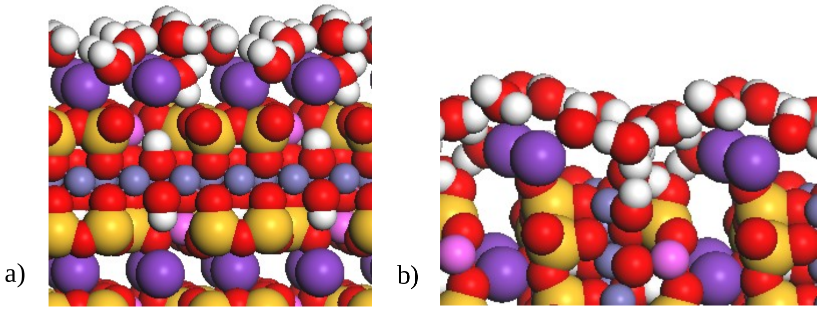


Figure 15. The first water molecular layer on the annite surfaces: a) (001) and b (110).

It was supposed that the cation exchange sites are basal surfaces like the (001) surface, and surface complexation sites are terminal surfaces like the (110) surface.On the ideal basal (001) surface of annite, there are no hydroxyl groups, and water dissociation does not happen on this surface. On the surface, there are 4.4 K^+ ions/nm^2 and 11 bridged O atoms/nm^2. The water molecular layer formed above this ideal basal surface consists of 11 H_2O molecules/nm^2 (Fig. 2a). On the ideal terminal (110) surface, there are 1.9 K^+ ions/nm^2 and 6.6 H^+ sites/nm^2. On the first water molecular layer, there are 10 H_2O molecules/nm^2 (Fig. 2b). Based on the calculated results, surface reactions are different on the basal and terminal surfaces on biotite and its end-members (annite and phlogopite). Cation exchange reactions between K^+ and Ni^{2+} take place on the basal surfaces, and surface complexation reactions on the terminal surfaces.

2.2 Surface complexation modelling

Surface complexation modelling was done in two steps (to be reported in detail elsewhere by

Olin et al. (2013b) and Itälä et al. (2013)):

1. In the first step, the number of surface sites and equilibrium constants for surface protonation reactions were fitted separately for 1-p*K* and in 2-p*K* models. Two electrostatic models (CCM, and DLM) and no NEM, were tested
2. The models and parameter form first step were used to fit the sorption data of
   a. nickel on three different biotite samples (Luumäki A and B, and Olkiluoto) and two different Olkiluoto rocks and
   b. europium on biotite.

The one and only reaction for 1-p*K*-model is

$$\equiv SOH^{(1/2)+} = \equiv SO^{(1/2)-} + H^{+} \tag{1}$$

and the log *K* for this reaction was fitted to be 5.4 together with site density 7 sites/nm^2 by DLM.

For 2-p*K* model the two reactions are

$$SOH + H^{+} = SOH_2^{+} \tag{2}$$

and

$$SOH = SO^{-} + H^{+} \tag{3}$$

and the log *K*= 3.6 and -6.2, respectively, and site density 9 sites/nm by DLM

In Olkiluoto biotites and rocks the results show that better fit can be obtained without using the log *K* values of Luumäki fits (see Figures 4 and 5) The awkward results for Europium results (see Figure 7) are result from properties of FITEQL, which can produce results only with 3-decimals , while some of the values are so near hundred per cent that FITEQL cannot make a difference between them.

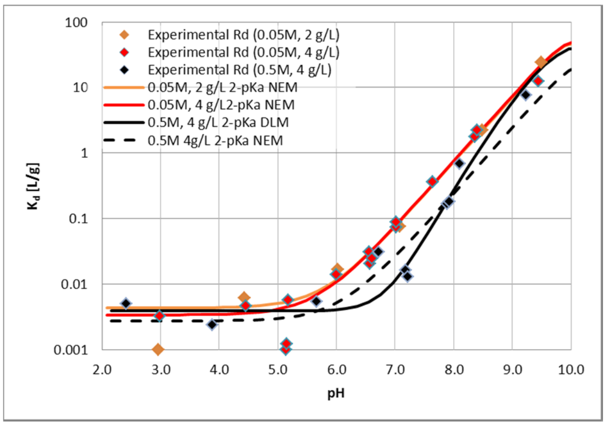


Figure 16. *K_d fits of nickel sorption on Luumäki biotite 2 and 4 g/L, 0.05 and 0.5M.The T_{SOH}-values for 2g/L and 4g/L are 1.4e-4 and 2.8e-4 respectively.*

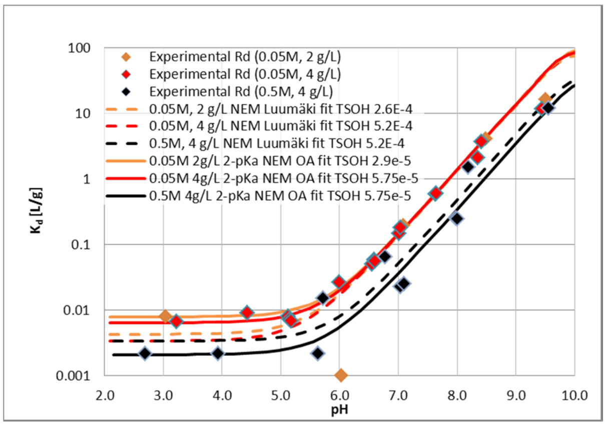


Figure 17. *K_d fits for nickel sorption on Olkiluoto A biotite 2-4 g/L, 0.05-0.5M.*

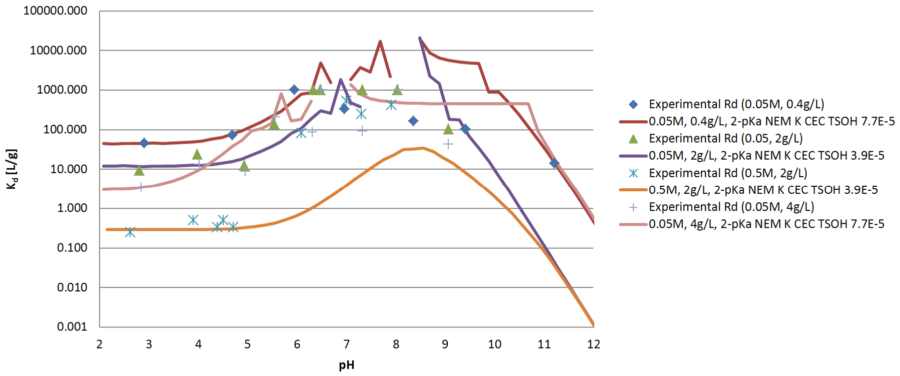


Figure 18. K_d fits for Europium sorption on Olkiluoto B biotite 0.4-4 g/L, 0.05-0.5M.

2.3 Reactive transport modelling and PA calculations

NEM surface complexation model giving the best fit for sorption of nickel on biotite was chosen for the reactive transport calculations. The PA-type of model handles sorption linearly with K_d values. This means solving the soluble nickel concentration c from equation

$$(\phi + \rho_{\mathrm{rock}} K_{\mathrm{d}})\frac{\partial c}{\partial t} + \nabla\cdot(-D_{\mathrm{e}} \nabla c) + \mathbf{u}\cdot\nabla c = 0$$

in a fracture geometry. Here ϕ is the porosity, D_{e} the effective diffusion coefficient and $\mathbf{u}$ the velocity of water which is solved from the Stokes equations.

In the surface complexation reactive transport model, the sorption is described with kinetic equilibrium reactions. Also, the number of variables increases from one to three: $c_{\mathrm{Ni2+}}$

(soluble nickel concentration), $c_{\mathrm{sONi}^{+}}$ (moles of sorped nickel per volume) and c_{sOH} (moles of free surface sites per volume). The equations that have to be solved simultaneously

$$\phi \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{j}_i = \phi R$$

where the subscript i stands for $c_{\mathrm{Ni2+}}$, $c_{\mathrm{sONi}^{+}}$ or c_{sOH}. The flux $\mathbf{j}_i$ is set to zero for the stationary surface variables. The reaction terms are of form $R = k\left(c_{\mathrm{Ni}^{2+}} c_{\mathrm{sOH}} - \frac{1}{K} c_{\mathrm{sONi}^{+}} c_{\mathrm{H}^{+}} \right)$ with altering sign depending on the variable. K is the equilibrium constant from the fits to the experiments and k is the reaction rate.

In the surface complexation reactive transport model, the surface sites are presented as surface variables $c_{\mathrm{s,sONi}^{+}}$ (moles of sorped nickel per area) and $c_{\mathrm{s,sOH}}$ (moles of free surface sites per area) which exist only on the fracture surfaces of the model. The transport equation for the soluble nickel in the fracture becomes

$$\phi \frac{\partial c_{\mathrm{Ni}^{2+}}}{\partial t} + \nabla \cdot \left(-D_{\mathrm{e}} \nabla c_{\mathrm{Ni}^{2+}} \right) + \mathbf{u} \cdot \nabla c_{\mathrm{Ni}^{2+}} = 0$$

and the surface reaction for soluble nickel is presented as a boundary condition

$$\mathbf{j} \cdot \mathbf{n} = R$$

on the fracture surfaces. The reactions term R is of the same form as for volumetric reactions but now the surface variables are used instead of volume variables. The equations for the surface variables are of form

$$\frac{\partial c_i}{\partial t} = \pm R$$

and they are defined only on the fracture surfaces.

Sorption can be implemented in reactive transport models as PA type of linear sorption or directly with kinetic surface complexation equilibrium reactions using either volumetric or surface variables. The different models have been implemented into COMSOL Multiphysics and tested. The final results and comparison between the models will be presented and discussed in Pulkkanen et al. (2013).

3. Discussion

Adsorption of radionuclides onto mineral surfaces is an essential retardation mechanism in granitic bed rocks. Sorption is typically given a as sorption distribution factor K_d measured for a certain rock sample, in given conditions (pH, salinity, carbon dioxide) and after crushing and possible purifying samples in different ways. Therefore, the uncertainties start to accumulate in sampling and sample preparation.

Our modelling concept was based on multiscale approach (starting from smallest scale):

1. MLM – molecular level modelling, about nanometre scale
2. SCM – surface complexation modelling in lab scale mainly
3. RTM – reactive transport modelling, in parts of a final repository
4. PA – performance analysis, which have to handle the entire repository

The most important information that MLM may offer to SCM studies is the existence and nature of surface sites. Second, the MLM studies may give valuable information about surface reactions and nowadays also about behaviour of water molecules near surface and near sorbing ions (hydration).

The developed surface complexation models have two different ways of application,

1. SCM model into RTM: sorption is modelled mechanistically as a part of transport model and in our approach (detailed geometry) sorption model is a kind of boundary condition in the RTM.
2. SCM based K_d's into PA: sorption is handled traditionally in PA, but instead of direct experimental values, their fit into SCM is applied to produce values.

Uncertainties in sorption modelling

Major goals in our work and especially in WP5 are:

- Evaluate uncertainties of K_d values
- Evaluate uncertainties of whole K_d based sorption model approach used in PA

Uncertainties are connected to scaling and extrapolation of the K_d values from the experimental conditions to the PA calculations and conditions.

Sorption is usually given by experimental K_d values, but the experimental results are "supported" by surface complexation modelling. Typical steps (not all included) for developing a SCM for radionuclide on some common bedrock in the repository

1. Identification and selection of the most important sorbing minerals and their occurrence in rock types (e.g., Olin et al., 2008)
2. Rock and mineral samples
3. Selection and preparation of water solutions
4. Titration to obtain surface acidity model
5. K_d measurements as function of pH, salinity, solid-water ratio, etc.
6. Model fitting to data
7. Prediction or interpolation to not measured systems

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