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DELIVERABLE (D-N°:4.1) **Conceptualisation, modelling, and up-scaling of radionuclide transport in the crystalline host-rock far-field**

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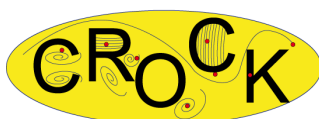
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PU	Public	X
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Objective:

The objective of this Deliverable is to summarise the work that has been carried out in the period from the submission of the first WP4.1 Deliverable (month 12) to the current milestone (month 27). Since much of the experimental data from WP2 was not available until a very late stage in the project, for some of the beneficiaries the work has focussed on revisiting data and modelling work carried out previously (i.e. data from project background). The work being carried out attempts to synthesise information over different spatial scales with the aim of deriving an internally consistent description of sorption processes encompassing all relevant spatial scales from the atomistic (VTT), to micro-scale domain (KIT-INE), macroscopic lab-scale (KEMAKTA/AMPHOS 21), to the site-scale domain (KEMAKTA/AMPHOS 21). The following sections summarise the main work that has been done and communicates some preliminary results from these efforts.

Status of work being performed by VTT:

In our work we are applying basically three different spatial levels; molecular level (less than 100 atoms), surface complexation (0-dimensional, laboratory scale) and fracture transport modelling (3D, scale about $100 \times 100 \times 1 \text{ m}^3$). A brief outline of the work performed follows below:

Molecular level modelling

Density functional calculations were performed with the CASTEP code implemented into Materials Studio versions 6.0 (Accelrys, 2011). The exchange-correlation was described with generalized gradient approximation GGA-PBE, and the ultrasoft pseudopotentials were used for each element. In the potential of iron, the semicore states were treated as a part of the core. The kinetic cut-off energy for a plane wave expansion of the wave function was 310 eV.

Surface complexation modelling

In the surface complexation model previous experimental data, of sorption of nickel on biotite and europium on biotite (Olin et al., 2008), were re-fitted, but this new work includes the extension of the fitting to be done also with 2-pK model and without electrostatic corrections (NEM, non-electrostatics model). The experimental data included titration data of Luumäki biotite, sorption data of nickel on Luumäki biotite and two different biotites from Olkiluoto (Olkiluoto A and Olkiluoto B), sorption data of nickel on two different rocks from Olkiluoto (Olkiluoto-Rock A and Olkiluoto Rock B, where in both, the amount of biotite in rock was 28.8%) and sorption of europium on Luumäki biotite and Olkiluoto A and Olkiluoto B biotites.

In the surface complexation modelling, one idea was to fit the experimental data of Luumäki biotite and after that test, if the values gained from Luumäki fit can be used to fit the experimental data of two other biotites (Olkiluoto A and Olkiluoto B) and two site specific rock samples (the analyses involving rock samples only consider nickel, since sorption of europium was not studied in the experiments). Model fitting was done using the FITEQL 4.0-program (Herbelin & Westall, 1999).

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 considered range in



complexity depending on how sorption is handled (i.e. K_d based approaches or surface complexation) and the conceptualisation of the sorptive surfaces (i.e. matrix diffusion and sorption on internal surface area of the rock matrix or equilibrium sorption on external fracture surfaces).

All the models consider sorption of nickel on biotite for which the exact surface complexation reactions with parameters and respective K_d -values have been obtained from the surface complexation modelling. The stationary Stokes equations for fluid flow are solved with a mixed finite element method, whereas the time-dependent diffusion-convection-reaction equations for the chemical components are discretised spatially using finite elements and integrated time-wise with numerical variable order, variable step size time integrators. The software used here is COMSOL Multiphysics.

Our main results obtained thus far are in the application of molecular level modelling to support surface complexation modelling and modelling of nickel and europium sorption onto biotite surfaces. 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: tested models were constant capacitance and diffuse layer models, because titrations this far were made only at one ionic strength, therefore making the application of three layer or basic Stern model impractical. Reactive transport modelling based on surface complexation models is still on going, as is the comparison of reactive transport and PA models.

Status of work being performed by KIT-INE:

The work conducted so far performed by KIT-INE focused on the comparison of conservative tracer (HTO) and colloid/nanoparticle transport by means of column migration experiments and comparison to 3D computational fluid dynamics (CFD) modelling. A natural single fracture from Äspö was scanned using micro computed tomography serving as direct input for the model generation. The 3D simulation does not incorporate so far any chemical processes besides the molecular diffusion coefficient solely reflecting the impact of fracture heterogeneity on mass transport. Complex fluid velocity distributions evolve as direct function of fracture geometry leading to flow channeling and flowpath heterogeneity. Both solute and colloidal breakthrough curves show heavy tailing (non-Fickian transport behaviour) in the experiments and the simulations, respectively. Experimental breakthrough of the nanoparticles always arrives faster than the solute tracer in line with the modelling results. Congruence of experimental and modelling results is better for the high flux experiments than for the low flux experiments. Besides processes like sorption or matrix diffusion, we show that fracture heterogeneity represents an additional retardation mechanism for solutes and colloidal phases.

In close collaboration with AMPHOS21 we focused on the application of a numerical framework called FASTREACT developed by Amphos21 for reactive transport modelling (sorption is the only retardation process considered in the work described below). The FASTREACT code is coupled to the geochemical code PHREEQC and the parameter estimation code PEST. This approach is applied to model experimental data on Np(V) migration through the natural fracture in the Äspö diorite drill core mentioned above. We tested different approaches with increasing complexity ranging from simplified sorption models (first order reversible sorption/desorption kinetics) to more complex, mechanistically based literature surface complexation models for sorption of NpO_2^+ onto one ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (HFO)), two (HFO and biotite (Bt)) and three (HFO, Bt and kaolinite) different mineral



phases. First results obtained so far show differences between the experimental breakthrough curve and the model results. Except the unknown total reactive surface area of the fracture no fitting has been applied in the modeling exercise. Thus, the simulations can be seen as simple blind predictions. Nevertheless, the applicability of the FASTREACT approach to model reactive transport in our system has been shown. A joint publication from KIT-INE and Amphos21 on the work described above is in preparation. Future work comprises the application of FASTREACT to HTO, Cl⁻ and Tc migration experiments on a new drill core obtained within CROCK.

Status of work being performed by KEMAKTA:

During the current reporting period efforts have been made to produce a surface complexation model (SCM) for granite that can be deployed either directly in reactive transport codes, or indirectly for estimation of groundwater specific, conditionally constant K_d values (often referred to as “smart” K_d ’s). The modelling work has considered two different, although related, approaches for the parameterisation of an SCM for granitic rock. The first, *top down* (generalised composite) modelling approach attempts to model the composite mineral system based on the assumption of one, or more generic binding site types without consideration of the detailed properties of the mineral surfaces upon which sorption is occurring. The second *bottom-up* (component additivity) approach involves careful consideration of the identity and proportion of total reactive surface area of individual minerals comprising the rock and combining separate SCM’s for pure mineral phases from the literature under the assumption of linear additivity of resultant sorption. A notable difference between the two approaches is that the first involves fitting of an assumed model to measurement data, whereas the second is largely predictive in nature since it is not conditioned on the actual measurement data. Each approach has advantages and disadvantages. The first approach is appealing owing to its relative simplicity and since a good fit can often be found which interpolates measurement data reasonably well, although it may not extrapolate well outside of its range of calibration. The second approach, on the other hand, is arguably more mechanistically correct and makes testable, although not always accurate, *de novo* predictions.

Since sorption measurements were not available for the Äspö materials characterised in WP2, we have elected to concentrate our efforts on understanding sorption data previously obtained during the site investigation carried out by SKB at Forsmark, Sweden. The modelling work has indicated that it may not be possible to use a single binding site type in a generalised composite model to simultaneously describe the sorption of all three solutes for which reliable sorption data are available (Am, Eu, Ni) in an internally consistent manner. It is also found that if a sub-optimal fit is made to the sorption data for any two of the solutes for a specific groundwater type, the resulting extrapolation to differing groundwater conditions can deviate considerably from measured values.

In the alternative component additivity approach, it was assumed that the sorption could be approximately modelled assuming a linear combination of three specific site types corresponding to quartz, biotite, and a smaller amount of hydrous ferric oxide. Binding constants for silica and hydrous ferric oxide were obtained from literature sources. Since appropriate binding constants were not available for biotite, literature data for illite were used under the assumption of a reasonably close geochemical analogy between illite and biotite. The main assumptions in the model are that the measured sorption can be described as a weighted sum of contributions from the three a priori assumed component minerals and that



literature data for experiments conducted on pristine mineral samples are also applicable for corresponding mineral phases comprising granite.

Given that the relative proportions of the different site types comprising the reactive surfaces of granite was not known to a sufficient level of accuracy for the samples in question, this has been treated as a fitting parameter in the modelling. The resulting model therefore is a hybrid with features reminiscent of both the top down and bottom up modelling philosophies and we refer to it as a *boot-strapped component additivity* modelling approach. It is found that the bootstrapped model conditioned to sorption data for Saline groundwater makes remarkably accurate extrapolative predictions of K_d for all three solutes when compared with actual measured values for the Fresh groundwater type (approximately on or within the studentised measurement error bounds of all three solutes). The resulting model also appears to very slightly underestimate the sorption of Ni under Fresh groundwater conditions, although this is consistent with the neglect of the contribution of ion exchange for Ni^{2+} at the lower ionic strength characteristic of the Fresh groundwater type.

Although the current modelling work is based on a limited data set that was never originally intended for this purpose, the results suggest possible strategies which might be used in future to improve the modelling of surface complexation on complex environmental substrates such as granitic rock with incomplete experimental data. The results also might be used to inform experimental design of sorption measurements to be carried out in detailed site investigation studies sometime in the near future. Further work will be needed to apply the modelling approach to other data sets including sorption data from the Laxemar site investigation and data derived from WP2. In addition, insights obtained during the work involving the generalised composite modelling approach suggest some simplifications for modelling of surface complexation involving pure mineral phases.

Status of work being performed by AMPHOS 21:

The work performed by Amphos 21 in the framework of this WP4 of the CROCK project is mainly focused on finding a reliable and easy approach to minimise the uncertainty of the K_d values commonly used in radionuclide transport modelling. K_d values generally have a very narrow field of validity and the uncertainty of the K_d outside this field significantly increases. The use of coupled geochemical models instead of K_d approaches reduces the uncertainties, but increases the numerical complexity of the model. As radionuclide transport calculations carried out in the context of performance assessment for a radioactive waste repository typically require a probabilistic approach (a large number of realisations), the application of such coupled models is currently prohibitively expensive numerically.

The aim of Amphos 21 work is to explore the possibility of deriving an “adaptable” K_d approach, where surface complexation and cation-exchange models are used to derive simplified analytical expression for K_d as a function of critical geochemical parameters. This approach is hoped to add some of the advantages of the coupled geochemical approach into K_d -based models (while at the same time allowing for fast probabilistic calculations).

In the following paragraphs a brief description of the work that Amphos 21 has been carrying out within the CROCK project is given. For the sake of conciseness only an outline of the conceptual approach is presented here. For further details on the work the reader is referred to the S&T contribution that Amphos 21 will present at the Final Workshop of the CROCK project to be held in Karlsruhe (Germany) May 2013.



The methodology that Amphos 21 has followed is based on following steps:

- Literature research of experimental data concerning adsorption experiments of some radionuclides (Cs, Eu and U) on fracture filling materials (Iron oxyhydroxides, calcite, illite, SiO₂), and granitic materials.
- Literature research of Surface Complexation Models (SCM) and/or cation exchange models, that aims for describing most of the datasets obtained in step 1.
- Development of geochemical models to reproduce experimental data with a common SCM, from which K_d values will be derived.
- Verification of the developed models based on data gathered within the CROCK project.

In the previous phase of the project we developed an analytic K_d model for Cs sorption onto magnetite (poster by García and Domènech, presented at the 1st CP CROCK Workshop held in Stockholm, Sweden, in May 2012). Figure 1 presents a comparison of the K_d values obtained using this model with the values calculated based on experimental data. It can be seen from the figure that the analytic K_d model is able to reproduce experimental data obtained under various geochemical conditions (i.e., pH, I, S/L ratio) with reasonable accuracy. A complete description of that work will be presented at the Final Workshop of the CP CROCK, to be held in Karlsruhe (Germany) May 2013.

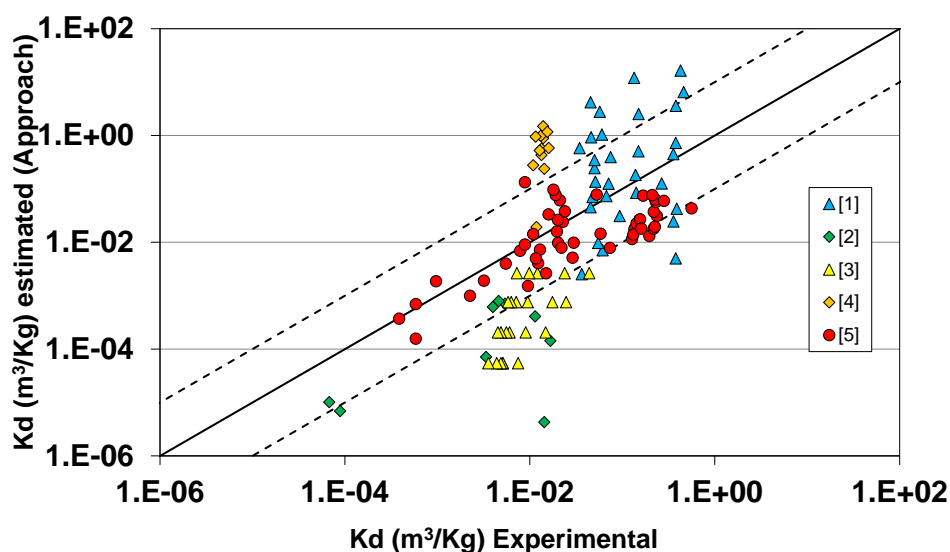


Figure 1. Relationship between experimental K_d values and estimated K_d values. Estimated K_d values were obtained by applying the simplified analytical model.

As a continuation of the work presented in the 1st CP CROCK workshop, Amphos 21 has recently been investigating the possibility of extending the simplified analytical K_d approach to the following systems:

- Cs exchange on illite,
- Eu sorption onto illite, and



- Eu sorption onto iron-hydroxide phases.

A complete description of that work will be presented at the Final Workshop of the CROCK project, to be held in Karlsruhe (Germany) May 2013. Nevertheless in the following just a short description of first results is provided.

The retention of Cs onto illite by cation-exchange has been studied by employing the Bradbury and Baeyens (2000) model. Based on this, a simplified algebraic K_d model was developed following an approach similar to that used for Cs sorption onto magnetite. Figure 2 shows a comparison of K_d values obtained experimentally, modelled using the geochemical simulator PhreeqC (Parkhurst and Appelo, 1999) and estimated using the developed K_d model.

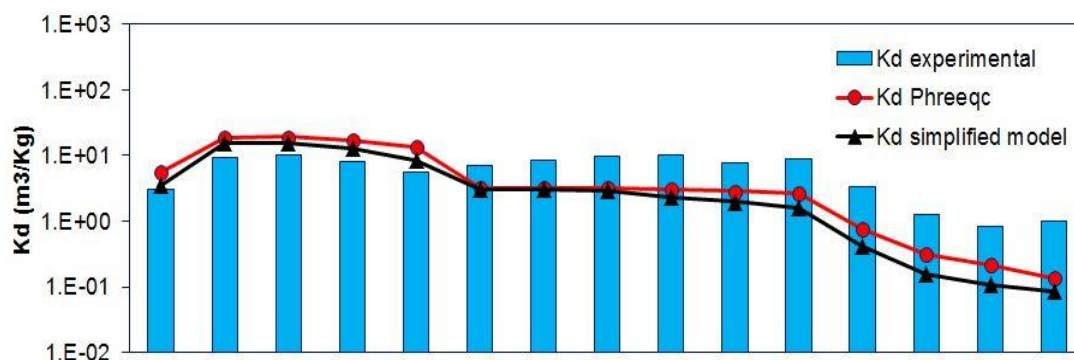


Figure 2. Comparison of K_d values calculated from experiments (Comans et al. 1991, Poinssot et al. 1999, and Staunton and Roubaud, 1997) with values obtained using the geochemical simulator PhreeqC and with values estimated using the simplified approach developed in this study for Cs-K exchange onto illite.

In the case of Eu sorption onto illite, a bottom-up K_d model has been developed based on the Bradbury and Baeyens (2004) model. Moreover a bottom-up K_d model accounting for sorption of Eu onto iron-hydroxide is under development following the Rabung et al. (1998) SCM.

In order to gain further insights as to the most important processes affecting Cs and/or Eu in a complex system (i.e. rock), we are currently developing a top-down approach (Davis et al., 1998) and comparing the results with the previously developed bottom-up approach. The comparison of results obtained from these complementary models will help to improve the reliability of the overall approach.

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