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### Radionuclide transport modelling by molecular chemistry, surface complexation and reactive transport modelling

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## Summary

Radionuclide transport calculations, usually done for set of radionuclides, in large systems, over long periods and variations of conditions, form an essential part of any safety study of final disposal of spent nuclear fuel. Therefore, simplified models are applied in these performance analysis (PA) calculations. However, in order to verify and validate the simplified models and data applied by PA models, some deeper scientific analysis has to be carried out. Accordingly, we approach the PA models from the scientific basis through three different spatial levels: 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: 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 going on, as is the comparison of reactive transport and PA models.

## Introduction

A final repository for spent nuclear fuel has a major demand to restrict the release and transport of radionuclides below the limits specifically given to different barriers and time scales by authorities. It is the duty of waste producer to design the repository in a way these limits and other possible demands are fulfilled in all time scales. Radionuclide transport calculations, usually done for set of radionuclides, in large systems, over long periods and variations of conditions, form an essential part of these studies. Therefore, simplified models are applied in these performance analysis (PA) calculations. In the KSB3 concept, the buffer material, bentonite, can be modelled as homogeneous system, but 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. However, in order to verify and validate the simplified models and data applied by PA models, some deeper scientific analysis based either on experimental work or modelling have to be carried out. In our work we are applying basically three different spatial levels (Figure 1): molecular level (less than 100 atoms), surface complexation (0-dimensional, laboratory scale) and fracture transport modelling (3D, scale about  $100 \times 100 \times 1 \text{ m}^3$ ).

The goals in WP4 work are



- Molecular level modelling - Model for surface behaviour of some relevant radionuclide on biotite surface by molecular level modelling tools
- Developing of sorption models - VTT develops surface complexation model, e.g., nickel and europium on biotite
- Reactive transport modelling
  - Different geometrical setups (fracture and bedrock or fracture with different reacting surfaces)
  - Sorption is modelled by surface complexation and ion-exchange reactions (surface sites are divided into a certain volume of rock or onto a certain area of a fracture surface in the transport model)
  - Surface reactions based on the developed sorption models (previous bullet)
  - Cooperation with WP5: Comparison between  $K_d$  and surface reaction approaches

The goals in WP5 work 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 conditions

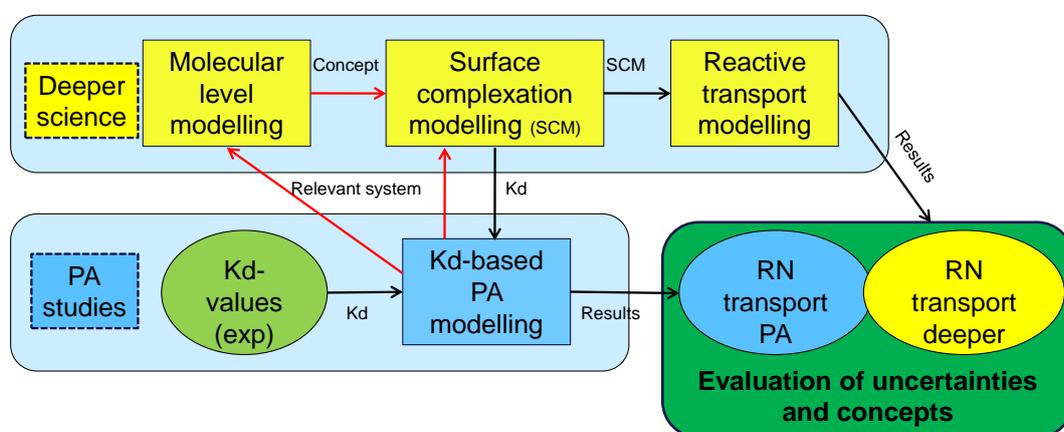


Figure 1. Overall concept of our approach.

Usually PA studies are based on experimentally defined  $K_d$  values, selection of which may be supported by surface complexation modelling (SCM). In principle, SCM can be applied in extrapolation of  $K_d$  values outside measured conditions, but the modelling must then be supported for example by molecular level modelling, which is not directly applying any macroscopic experimental data. In addition to producing experimental  $K_d$  values for PA purposes, the SCM can be applied to produce mechanistic sorption models to be applied in reactive transport modelling (RTM). All these approaches together can be used in evaluation of uncertainties and applied conceptual thinking (Figure 1).



## Methods

### 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 rocks (only in case of nickel, sorption of europium on these rocks were not included in the experiment).

The fitting were done by using 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 from the simplest (closest to PA models, can be compared to them) to the most realistic one are the following:

1.  $K_d$  approach
  - Fracture flow from Stokes equations (flow velocity is very low, no need for the inertia term in Navier-Stokes equations)
  - Diffusion into rock matrix
  - Sorption as linear sorption
2. Surface complexation with surface sites divided to a volume of bedrock
  - Fracture flow from Stokes equations
  - Diffusion into rock matrix
  - Sorption with kinetic equilibrium reactions with surface sites divided into a volume of bedrock
3. Surface complexation with surfate sites divided to an area of fracture surface



- Fracture flow from Stokes equations
- No diffusion into rock matrix or diffusion along very narrow fractures
- Sorption with kinetic equilibrium reactions with surface sites divided onto fracture surfaces in the model

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.

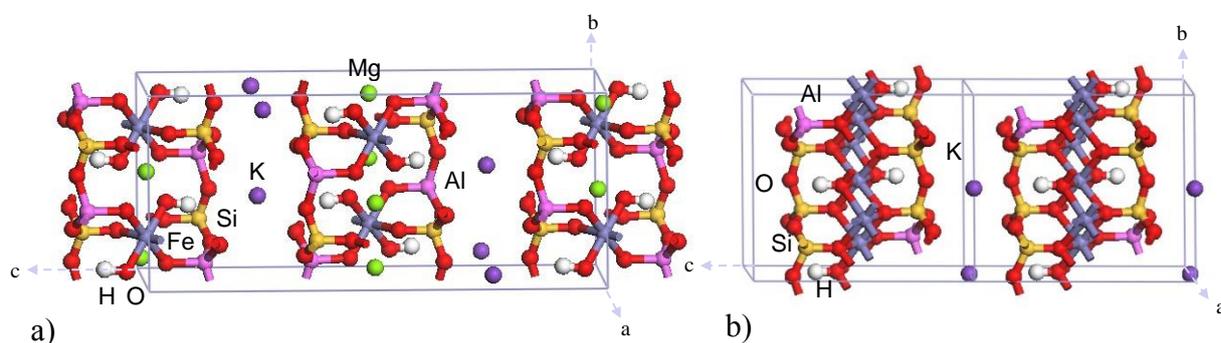
The stationary Stokes equations are solved with mixed finite element method, whereas the time-dependent diffusion-convection-reaction equations for the chemical components are discretized spatially with using finite element method and integrated time-wise with numerical variable order, variable step size time integrators. The software used here is COMSOL Multiphysics.

The comparison between PA and RTM models are planned to done later, when we have enough modelling results from our COMSOL applications.

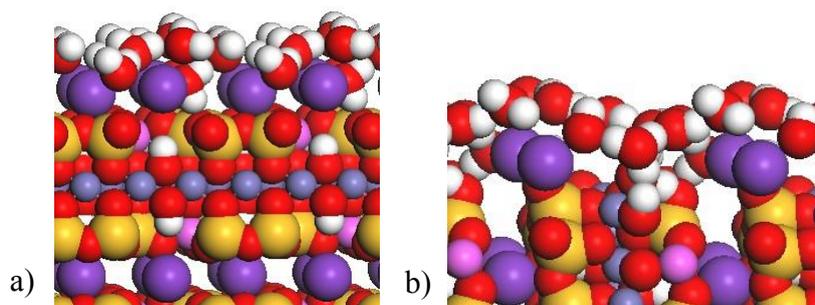
## Results

### 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). According to the density functional calculations, the optimized lattice parameters of the energetically stable biotite structure are  $a = 528.4$  pm,  $b = 916.2$  pm,  $c = 2077.3$  pm and  $c/a = 3.931$  (Fig 2a). Construction of surface models to molecular modelling studies revealed that the smallest meaningful models are very atomic-rich, which causes long calculation times. In order to simplify model structures, it can be used end-members of biotite: annite and phlogopite. In this study, annite (Accelrys, 2011), where all magnesium ions are substituted by iron ions, was utilized. The unit cell of annite is about half of that of biotite. The optimized lattice parameters are  $a = 513.1$  pm,  $b = 893.3$  pm,  $c = 1037.3$  pm, and  $c/a = 2.022$  (Fig. 2b), and the Si:Al ratio is 3:1.



**Figure 2.** Optimized unit cells for a) biotite, and b) annite.



**Figure 3.** The first water molecular layer on the annite surfaces: a) (001) and b) (110).

The aim of molecular modelling was to deepen understanding of sorption phenomena studied typically by mechanistic sorption modelling: surface complexation (SCM) and ion exchange. The molecular modelling approach was utilized to investigate formation of water molecular layer onto annite surfaces and reaction of  $\text{Ni}^{2+}$  species on cation exchange sites and surface complexation sites. 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.

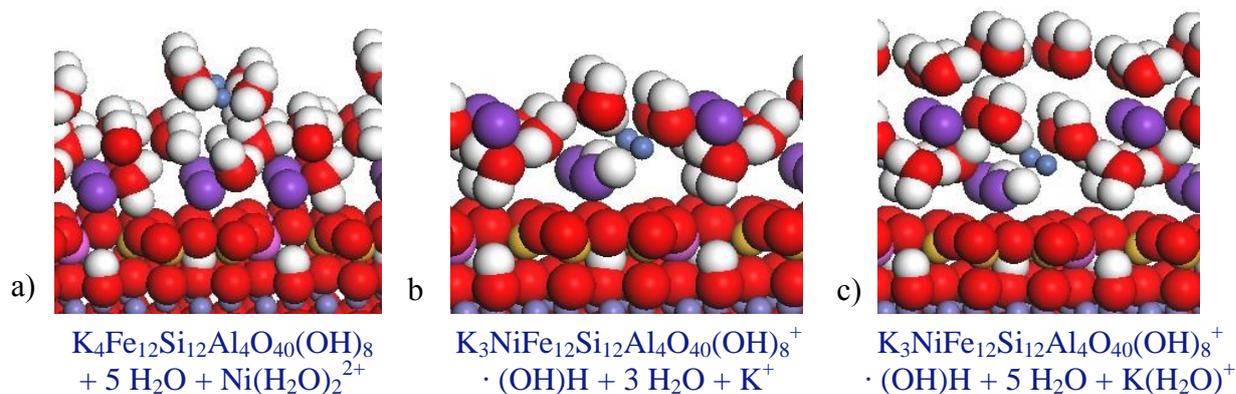
First, formation of water molecular layer was considered including both the adsorption and possible dissociation of water on the basal (001) and terminal (110) surfaces. On the basal surface, the reactivity of the surface depends on the existence of potassium ions on the surface. Otherwise, the surface structure is rather stable. On the terminal surface, there are no empty vacancies in the coordination sphere of aluminium and/or silicon atoms. However, this oxide surface can be very reactive with water forming hydroxylated surface structure. In the water adsorption studies, water molecules were adsorbed onto the surface one by one, and water molecules were allowed to find their energetically favourable positions on the surface. Also, dissociation of water molecules was allowed on the surfaces. As a result, the formation of the first water molecular layer was described.

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  $4.4 \text{ K}^+$  ions/ $\text{nm}^2$  and  $11$  bridged O atoms/ $\text{nm}^2$ . The water molecular layer formed above this ideal basal surface consists of  $11 \text{ H}_2\text{O}$  molecules/ $\text{nm}^2$  (Fig. 3a).

On the ideal terminal (110) surface, there are  $1.9 \text{ K}^+$  ions/ $\text{nm}^2$  and  $6.6 \text{ H}^+$  sites/ $\text{nm}^2$ . Based on the calculations, every sixth water molecule dissociates forming surface hydroxyl groups in the adsorption of water onto the surface. On the first water molecular layer, there are  $10 \text{ H}_2\text{O}$  molecules/ $\text{nm}^2$  (Fig. 3b).

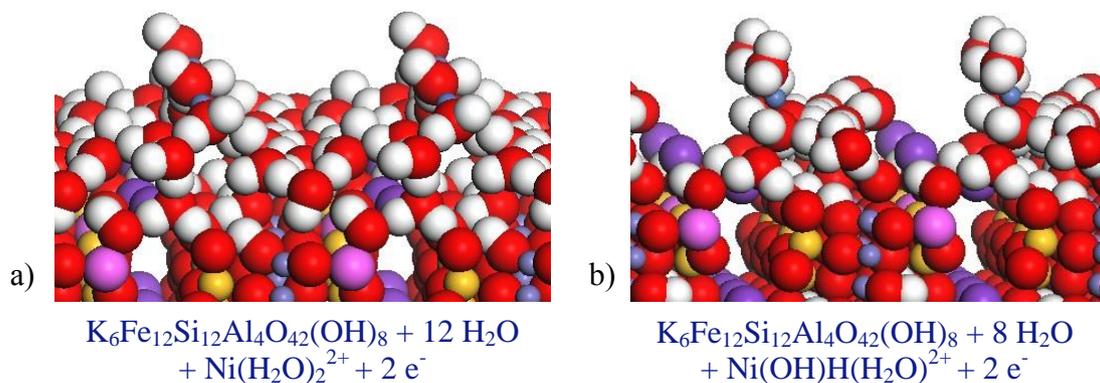
After the structure of water molecular layer was defined, then reaction of  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  species on cation exchange sites and surface complexation sites was considered. The aim was to define, if a difference between the sites can be detected. It was calculated step-by-step mechanism for the reaction path which consists of a) sorption of  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  above the first water molecule layer, b) desorption of water molecules from the surface, so that  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  can adsorb onto the surface, and c) re-formation of the water molecule layer.

Based on the molecular modelling results, cation exchange reaction between  $\text{Ni}^{2+}$  and  $\text{K}^+$  ions takes place on the basal (001) surface of annite. In Fig. 4a,  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  species is above the first water molecule layer, and after desorption of half of the water molecules, re-arrangement of  $\text{Ni}^{2+}$  and  $\text{K}^+$  ions is possible, which ensues the cation exchange reactions (Fig. 4b). When also re-formation of the water molecular layer (Fig. 4c) is included into the reaction path, the cation exchange reaction is spontaneous reaction, which releases energy -0.29 eV.



**Figure 4.** The annite (001) surface: a)  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  above the first water molecule layer, b)  $\text{Ni}^{2+}$  ion has replaced  $\text{K}^+$  ion (cation exchange), and c) the re-formed water molecule layer.

Possibility for the cation exchange reaction was also investigated on the terminal (110) surface. On this surface,  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  species forms a surface complex with the water molecule layer (Fig. 5a). This complex does not dissociate and move to other position on the surface, though desorption of water molecules reduces steric hindrance on the surface (Fig. 5b). Therefore, steric shielding around the  $\text{K}^+$  ions is minor, and  $\text{K}^+$  ions are susceptible for other reactions. Energy needed for this surface re-arrangement reaction is 1.57 eV.



**Figure 5.** The annite (110) surface: a)  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$  above the first water molecule layer, and b) surface complexed  $\text{Ni}(\text{H}_2\text{O})_2^{2+}$ .

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  $\text{K}^+$  and  $\text{Ni}^{2+}$  take place on the basal surfaces, and surface complexation reactions on the terminal surfaces. If the ratio between the basal and terminal surfaces can be determined,

then reactions needed in the surface complexation modelling can be restricted only essential reactions. A more detailed description will be given by Puhakka & Olin (2013).

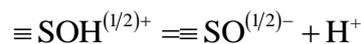
### Surface complexation modelling

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-pK and in 2-pK models. Two electrostatic models (Constant Capacitance, CCM, and Diffuse Layer, DLM) and non-electrostatic model, 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.

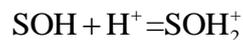
In the first phase there were experimental data for titration of Luumäki biotite with NaOH and HCl.

The one and only reaction for 1-pK-model is



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

For 2-pK model the two reactions are



and

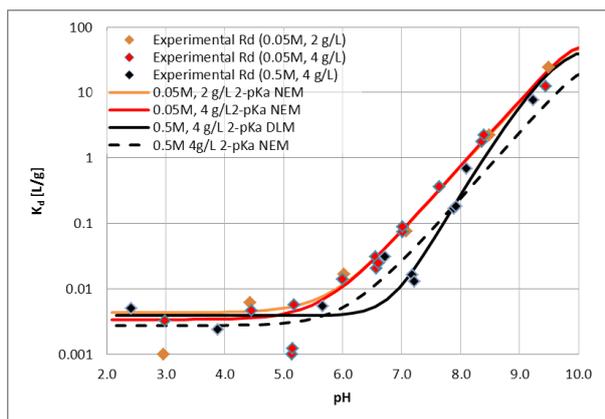


and the log  $K$ = 3.6 and -6.2, respectively, and site density 9 sites/nm<sup>2</sup> by DLM

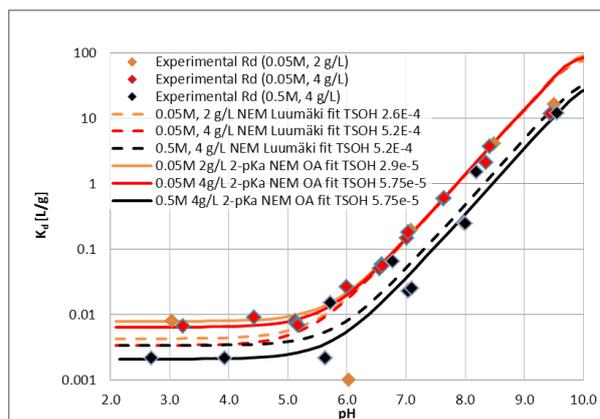
For step 2 the  $K_d$ -results from the fittings, for all cases, are presented in figures below. In Olkiluoto biotites and rocks the results show that better fit can be obtained, if the fitting is done without using the log  $K$  values of Luumäki fits, but the fit is done for Olkiluoto biotites separately (see Figures 6-10). If the Luumäki log  $K$  values were used we had to increase the amount of surface complexation sites (TSOH) from Luumäki case by a factor of 1.8. This is in contradiction to the experimental data where Olkiluoto biotites have actually smaller surface area and thus (by assumption) less surface complexation sites. Thus it was decided that the fitting has to be done independently to Olkiluoto samples.

The awkward results for europium results (see Figures 11 and 12) 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.

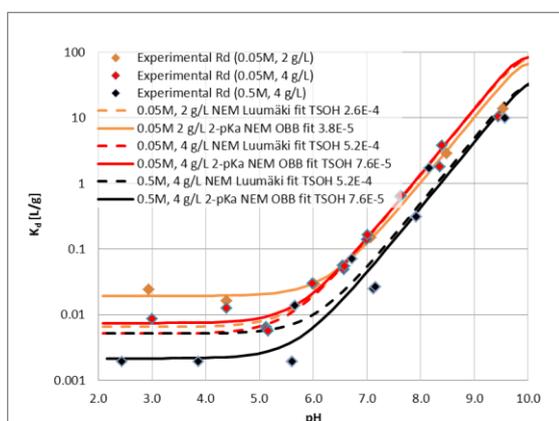




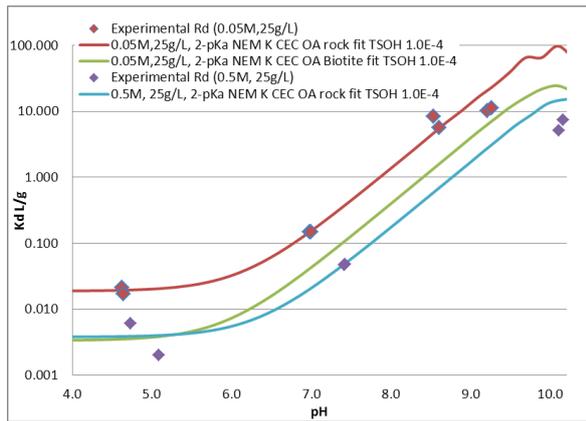
**Figure 6.**  $K_d$  fits of nickel sorption on Luumäki biotite 2 and 4 g/L, 0.05 and 0.5M. The  $T_{SOH}$ -values for 2g/L and 4g/L are  $1.4e-4$  and  $2.8e-4$  respectively.



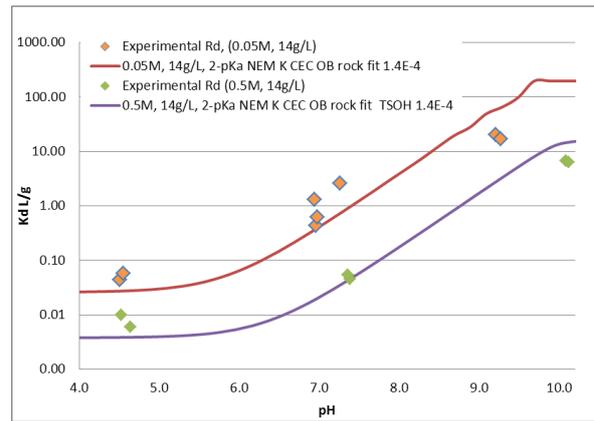
**Figure 7.**  $K_d$  fits for nickel sorption on Olkiluoto A biotite 2-4 g/L, 0.05-0.5M.



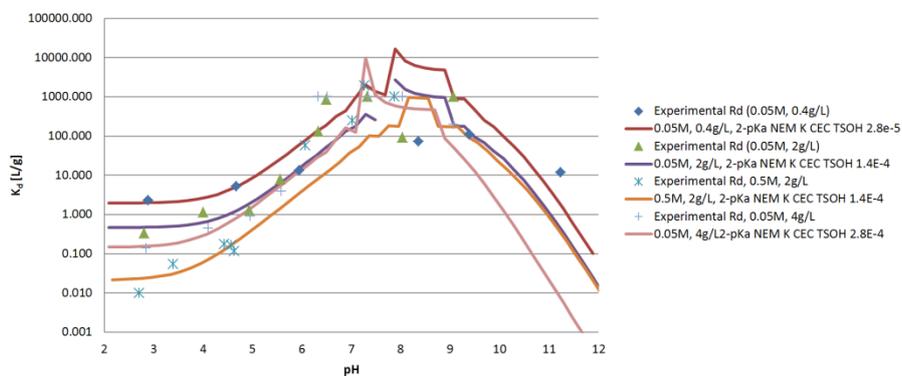
**Figure 8.**  $K_d$  fits for nickel sorption on Olkiluoto B biotite 2-4 g/L, 0.05-0.5M.



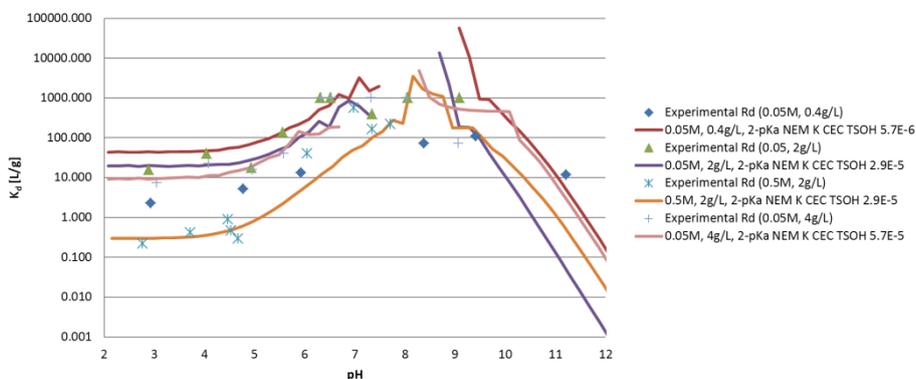
**Figure 9.**  $K_d$  fits of nickel sorption on Olkiluoto A Rock 25 g/L, 0.05-0.5M.



**Figure 10.**  $K_d$  fits for nickel sorption on Olkiluoto B rock 14 g/L, 0.05-0.5M.

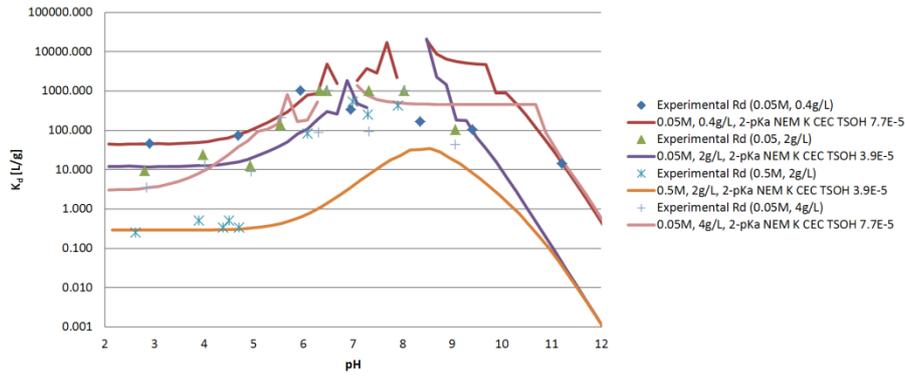


**Figure 11.**  $K_d$  fits of europium sorption on Luumäki biotite 0.4-4 g/L, 0.05-0.5M.



**Figure 12.**  $K_d$  fits for europium sorption on Olkiluoto A biotite 0.4-4 g/L, 0.05-0.5M.





**Figure 13.**  $K_d$  fits for europium sorption on Olkiluoto B biotite 0.4-4 g/L, 0.05-0.5M.

### Reactive transport modelling and PA calculations

Non-electrostatic surface complexation model giving the best fit for sorption of nickel on biotite, this surface reaction model was chosen for the reactive transport calculations. Cation exchange reactions were also considered early on in the reactive transport modelling but were omitted, since the surface reaction fits to experiments showed that their effect on the quality of the fits was negligible.

The simplest transport model, that is, the PA-type of model handles sorption linearly with  $K_d$  values obtained directly from the fits to the experiments. Mathematically expressed this means solving the soluble nickel concentration  $c$  from equation

$$(\phi + \rho_{\text{rock}} K_d) \frac{\partial c}{\partial t} + \nabla \cdot (-D_e \nabla c) + \mathbf{u} \cdot \nabla c = 0$$

in a fracture geometry. Here  $\phi$  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, where the surface sites have been divided in to a volume of rock, the sorption is described with kinetic equilibrium reactions. Also, the number of variables increases from one to three:  $c_{\text{Ni}^{2+}}$  (soluble nickel concentration),  $c_{\text{sONi}^+}$  (moles of sorped nickel per volume) and  $c_{\text{sOH}}$  (moles of free surface sites per volume). The concentration of  $\text{H}^+$  is high compared to the solved variables and can therefore be obtained directly from pH. The equations that have to be solved simultaneously take the form

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

where the subscript  $i$  stands for  $c_{\text{Ni}^{2+}}$ ,  $c_{\text{sONi}^+}$  or  $c_{\text{sOH}}$ . The flux  $\mathbf{j}_i$  is set to zero for the

stationary surface variables. The reaction terms are of form  $R = k \left( c_{\text{Ni}^{2+}} c_{\text{sOH}} - \frac{1}{K} c_{\text{sONi}^+} c_{\text{H}^+} \right)$

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, where the surface sites have been divided onto model surfaces, the sorption is also described with kinetic equilibrium reactions. In this case, however, the surface sites are presented as surface variables  $c_{s,\text{sONi}^+}$  (moles of sorped nickel per area) and  $c_{s,\text{sOH}}$  (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

$$\phi \frac{\partial c_{\text{Ni}^{2+}}}{\partial t} + \nabla \cdot (-D_e \nabla c_{\text{Ni}^{2+}}) + \mathbf{u} \cdot \nabla c_{\text{Ni}^{2+}} = 0$$

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 types of reactive transport 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).

## Discussion

The discussion starts by experimental work and modelling, after which uncertainties in sorption studies is discussed. This discussion is based mainly on the author's very long term experience on the subject, and the results shown above are used as examples of more general observations.

### Experimental work

Adsorption of radionuclides onto mineral surfaces is an essential retardation mechanism in granitic bed rocks. Sorption is typically given as a 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. All laboratory work includes uncertainties, which may vary from typical 10 per cent uncertainty to much higher ones especially at very low and very high  $K_d$  values. In order to fit the model over large enough condition space, the lab work must be carried out at least varying pH, solid to water ratio, salinity and other case specific parameters.



Experimentally obtained  $K_d$  values and modelling fittings based on them, will be applied in PA work and more detailed RTM work. In the PA analysis either experimentally results are used as such (after careful selection process) or via mechanistic sorption modelling (SCM and IE), which can produce values with varying uncertainty depending on many topics. In the RTM work, mechanistic models may be applied as such. However, the  $K_d$  values are needed both in fracture surfaces and in intact porous rock, where the solid to water ratio (even 10 000 kg/L) exceeds by several orders magnitude typically applied laboratory values (0.001 – 0.1 kg/L). Also there is problems related to reactive surface area and in the case of kiilemineraali like biotite also to orientation of minerals in the studied system.

No experimental work was carried out in present work, and the modelling was based on our experimental results from FUNMIG project (Olin et al., 2008).

### Modelling work

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

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

First, we have noticed a gap in our modelling between MLM and SCM, which should be coupled via molecular dynamics (MD) and possible even via some mesoscale model. MD is basically adding the statistical physics into molecular level studies and larger models are also more realistic (only fraction of surface sites may be occupied etc.). However, study times in MD are really short (nanoseconds) compared to equilibrium approach of MLM studies. About available mesoscale models, the authors of this report have no notice.

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 first class uncertainties in sorption studies is related to this basic question of surface sites and reactions, which are relatively easy to fit by macroscopic experimental data, but for which not much direct experimental nano-level data (EXAFS or other methods) or modelling is available.

PA studies are able to define the most relevant systems to be studied, and this means mainly radionuclides in our case, because in Olkiluoto conditions the biotite has appeared the most important sorbing mineral. The availability of data in MLM studies for other radionuclides except caesium, nickel and europium was studied very briefly, and data for strontium was found.



The developed surface complexation models have two different ways of application, which appear to have basic differences

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. This may extend the approach into conditions not measured and is in that content a kind of an extension instead on interpolation.

### 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 perimental 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)
  - a. may be done for example by applying autoradiography of the thin rock sections for a set of radionuclides together with optical analysis for mineral phases
  - b. uncertainties are coupled in sampling and laboratory work, of which first one probably causes bigger uncertainty
2. Rock and mineral samples
  - a. representative rock samples are needed for PA applicable results
  - b. sorbing mineral (biotite) separation from rock for SCM
    - i. in addition possible to apply pure natural (like Luumäki biotite in our case) or
    - ii. commercial mineral samples
  - c. purified mineral (biotite) characterisation: impurities, specific surface area, cation exchange capacity (*CEC*)
    - i. impurities are a common source for uncertainties: they may alter *CEC*, surface area, protonation and sorption properties



- ii. specific surface area is a complicated topic, which depends for example on crushing and grinding of samples, and is an important parameter in SCM development
- 3. Selection and preparation of water solutions
  - a. usually simple electrolyte solutions for SCM development
  - b. for more PA relevant cases groundwater simulants must be used, and often with real rock samples and not only with purified minerals
  - c. uncertainties here track back to site specific data, which increases rapidly during real construction phase of the repository
- 4. Titration to obtain surface acidity model
  - a. surface acidity model has been a very basic thing in SCM development
    - i. non-electrostatic models (NEM) have been however popular, but in principle they don't have need for surface protonation
    - ii. uncertainties here are coupled to consistent description of sorption and diffusion, because both diffusivity and porosity models for anions include often anion exclusion, which is interpreted commonly by an electrostatic interaction with negatively charged surfaces
  - b. basically two options 1-pK and 2-pK models, where the first one has only two parameters (one binding constant and surface site density) to fit in addition of electrostatic parameters
  - c. one big uncertainty here in surface sites
    - i. How many different types are needed?
    - ii. Distinction between surface site density and binding constants, which appear as a product in SCM, and may therefore need some additional information to be fitted properly
    - iii. Are these types and densities observable also by some other method than fitting of titration data?
- 5.  $K_d$  measurements as function of pH, salinity, solid-water ratio, etc.
  - a. SCM models are based on measured  $K_d$  values, which are however measured in different conditions
    - i. typically at least pH is varied, but especially very low and high pH may cause mineral dissolution to appear and therefore is a source of uncertainty
    - ii. salinity is varied both in electrolyte solutions and by groundwater simulants, but usually experimental work at low salinity (below say 10



mM) has appeared difficult, while the modelling is difficult in saline (over 500 mM) solutions to complex interaction of species

iii. solid-fluid ratio is often varied only little, which increases uncertainty when models are applied in PA conditions, where there is usually small amount of water surrounded by huge amount of rock

b. in order estimate experimental uncertainty, there is need for many repetitions under many conditions (e.g., varying contact time)

#### 6. Model fitting to data

a. SCM is a non-linear theory and addition of surface charging models and realistic groundwater conditions make it still more non-linear

b. fitting is often done against percentage sorbed,

i. which causes problems and uncertainties at high sorption

ii. commonly used programs like FITEQL have only percentage options

iii. in modern codes, like COMSOL Multiphysics, no such limitation exists, but this far we have not applied COMSOL in fitting of sorption data

#### 7. Prediction or interpolation to not measured systems

a. SCM model have aimed to be used

i. Either as predictive sorption models, which can effectively substitute direct measurements, or

ii. as a smart  $K_d$ , which has some explicit dependencies on pH, salinity and solid-fluid fraction.

b. Prediction outside measured conditions or materials, have appeared to be difficult like in this work (see SCM results for details).

## Conclusions

The chosen multiscale approach to extrapolate  $K_d$  values for conditions without measured data and evaluation of uncertainties in PA studies appears promising, but very tedious and time consuming work. We have results from molecular level and surface complexation modelling, but we are still working with reactive transport modelling. After having all these tasks completed, we can start fully extrapolation of  $K_d$  values and evaluation of uncertainties.

However, we have been able to identify by molecular methods surface complexation (proton) and cation exchange (permanent charge) sites on biotite structure. We have observed that both acid-base titration results and sorption of nickel and europium on biotite are better fitted by non-electrostatic models (NEM) than applying either diffuse layer or constant capacitance models. The reason behind this observation may be in wrong surface charging models



(compare with montmorillonite, which has layer structure, models developed recently, Bourg et al. (2007)).

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