EUROPEAN
COMMISSION
Community research

CROCK

(Contract Number: 269658)

DELIVERABLE (D-N°:4.1)

Conceptualisation, modelling, and up-scaling of radionuclide transport in the crystalline host-rock far-field

Author(s): **James Crawford (KEMAKTA)**
Cristina Domènech (AMPHOS 21)
Thorsten Schaefer (KIT-INE)
Markus Olin (VTT)

Reporting period: e.g. 01/01/11 – 01/06/12

Date of issue of this report: **December 1st, 2011**

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

CROCK

EURATOM

DISTRIBUTION LIST

Name	Number of copies	Comments
Mr. Christophe Davies (European Commission)	One electronic copy submitted via participant portal	
All consortium members and European Commission	One electronic copy available on the restricted area of the CROCK webportal	

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	
CO	Confidential, only for partners of the CROCK project	

Objective:

The objective of this deliverable is to summarise the work that has been carried out in the period from the start date (month 6) to the current milestone (month 12). Given that the modelling work to be carried out in this work-package (WP4) is dependent upon future inputs from WP2, a significant portion of the work being done involves 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:

The present work being carried out involves the initialisation of molecular modelling, revisiting the experimental data and modelling from FUNMIG project, and first attempts to implement the surface complexation model within the COMSOL Multiphysics platform.

The goal in the molecular level modelling is a model for surface reactive behaviour of some relevant radionuclide on biotite surfaces. While the surface has been chosen, VTT will decide which radionuclide to focus on after communication with WP5. The most effort in the molecular level modelling has been reserved for year 2012.

VTT aims to develop a surface complexation model, e.g., nickel and europium on biotite. In addition to the biotite system VTT is also interested in extending the workto some other surfaces. VTT will also search open literature to find suitable sorption data for some other radionuclide on biotite. This far the work has mainly involved revisiting old data and planning of how to make some supplementary (in addition to FITEQL) parameter fitting exercises using the COMSOL Multiphysics software.

A reactive sorption model for some interesting system is the first major goal of VTT's work, and the major goal is the conclusion derived from comparison between the results of this model the PA-based model in WP5. The modelling will be done in defined geometrical setups (matrix diffusion and fracture water), although the setup is still being planned and VTT will request suitable and realistic data from other CROCK partners. Sorption will be modelled by surface complexation and ion-exchange reactions, and these models will be implemented within the COMSOL Multiphysics platform, which will enable very accurate geometry for transport modelling (say at least tens of millions degrees of freedom). However, the COMSOL program is not very well suited for chemical reactions, and even less suitable for modelling typical equilibrium reactions of surface complexation and ion-exchange. Therefore, VTT has started the implementation work and first results were presented in MRS Meeting in Argentina (Pulkkanen et al., 2011). In this case, two surface complexation reactions and one ion exchange reaction were modelled non-electrostatically (NEM) in a batch reactor with PHREEQC as well as with COMSOL Multiphysics and the results were compared. The COMSOL model was written such that it can be coupled with diffusive and advective transport. The coupling will be the next step in our model development.

K_d-values and SCM-models in the literature will be evaluated and modelled in different scales if possible (includes uncertainties), but this work has not yet started effectively.

Status of work being performed by KIT-INE:

The work conducted so far by KIT-INE has 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 channelling 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.

The velocity distribution obtained by CFD modelling of the real fracture geometry serves as information of the residence time variation and will be combined in a next step with the sorption/desorption rates/redox kinetics obtained under WP 2 to predict the radionuclide mobility on a microscale and compare these results with real column migration experiments. Matrix diffusion will possibly incorporated in further step. A second activity in close collaboration with AMPHOS 21 will focus on the application of a particle tracking code and reactive transport modelling (e.g. ion exchange/surface complexation) along these flow path realizations.

Status of work being performed by KEMAKTA:

The present work being carried out involves the reinterpretation of laboratory sorption data derived for crushed and monolithic granitic materials that were previously the focus of the Forsmark and Laxemar site investigations (SDM-Site) made by SKB in the Swedish national programme for geological storage of spent nuclear fuel, as well as similar data generated in two separate projects (TRUE and LTDE-SD) carried out at the Äspö Hard Rock laboratory (Äspö-HRL), also by SKB. The sorption data are for a number of different elements and redox states broadly representative of particular chemical groupings amongst nuclides typically prioritised in safety assessment. The intention is that the previous data sets should serve as a test base for the conceptualization and parameterisation of mechanistic models of radionuclide sorption in the rock matrix.

The sorption data are available for a number of different size fractions and an approximately geometric progression of contact times (1, 7, 31, 90, and 186 days in most cases). The data for monolithic samples consist of time series data related to aqueous phase concentrations as well as averaged depth profiles in the samples measured at the conclusion of sorption experiments. The data for monolithic samples are particularly valuable in that a phenomenologically consistent description of both sorption and matrix diffusion must be applied simultaneously to obtain agreement between the temporal and spatially resolved data sets.

Work is being carried out to understand the dynamics of the uptake process to both the granular and monolithic materials. Cesium (Cs) has been chosen as the main solute of interest in the preliminary modelling work as it is considered to be a good probe of rock matrix microstructure (this on account of its sorptive behaviour being relatively insensitive to pH, presence of ligands promoting aqueous phase complexation, and its ability to access the interlayer porosity of biotite). It is clear from the time series data for different size fractions that uptake of Cs cannot be effectively modelled (in a large number of cases) as a simple, single rate diffusive process. Based on theoretical reasoning and the observed macroscopic characteristics of Cs sorption, attempts are being made to model the time dependent uptake as a bi-porous process involving primary (grain boundary and microfracture) and secondary porosity (biotite interlayers). The model for bi-porous diffusion is based on an analytical Laplace space solution coupled with numerical inversion to the time plane. The sorption of ion-exchanging solutes including Cs is also being modelled using an ion-exchange modelling approach previously used to calculate chemical transfer factors in the recently completed SR-Site safety assessment (SKB, 2011). This work is on-going and will be shortly documented in the form of an interim technical report.

Assessment of the equilibrium sorptive behaviour of surface complexing solutes is being approached from two different directions with the aid of surface complexation modelling. The first using a pseudo “bottom up” approach whereby sorptivity is modelled as a linear combination of contributions from binding sites with properties derived from analogue mineral phases (essentially, stoichiometric combinations of SiO_2, α-Al_2O_3, and $Fe(OH)_3$ binding sites), while the second “top down” approach involves fitting reaction constants for generic binding sites to macroscopic sorption data.

Both the ion-exchange and surface complexation models are being developed for deployment in batch and flow system (i.e. field-scale) configurations using some well-known reactive transport codes with coupling of chemistry and matrix diffusive uptake. At the present time a number of potential candidate models have been formulated, although it is not yet possible to derive a consistent set of parameters for surface complexing solutes owing to significant ambiguities in the underlying sorption data. This is largely due to existence of sufficient statistical dispersion in the estimated (measured) macroscopic sorption properties that no clear chemical trends can be identified. Since the surface complexation models attempt to correlate changes in sorptivity as a function of chemical variables such as pH and pCO_2, the current data appear to be insufficient to properly constrain model parameters. Work is ongoing to identify possible reasons for the large statistical dispersion of the underlying data sets and to evaluate confounding factors that may not have been sufficiently well-characterised in previous studies of sorption in granitic rock. This work is also on-going and will be documented in the abovementioned interim technical report.

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 tool to minimise the uncertainty of the K_d values commonly used in geochemical 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 surface complexation models instead of K_d approaches reduces geochemical uncertainties, but increases the numerical complexitiy of the model.

The aim of AMPHOS 21 is to find how K_d values can be estimated from a surface complexation model taking into account the geochemical properties of the system where K_d approach is going to be applied.

Up to this moment, the work done by AMPHOS 21 has been:

- Compilation of the K_d values used in different PA studies, and the reasons of their selection;
- Literature research of experimental data concerning adsorption experiments of Cs, Eu and U on fracture filling materials (Iron oxyhydroxides, calcite, illite, SiO_2), and granitic materials.

Currently AMPHOS 21 is studying experimental data of Cs sorption. It is expected that it will be possible to reproduce experimental data with a common surface complexation model, from which K_d values will be derived.

References:

Pulkkanen V.-M.S, Itälä, A.P. and Muurinen, A.K. 2011. Buffering of pH conditions in sodium bentonite. A poster presented MRS 2011 Meeting in Argentina. To be published in conference proceedings.

SKB, 2011. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main Report of the SR-Site project. SKB TR-11-01, Swedish Nuclear Fuel and Waste Management Company (SKB), Stockholm, Sweden.