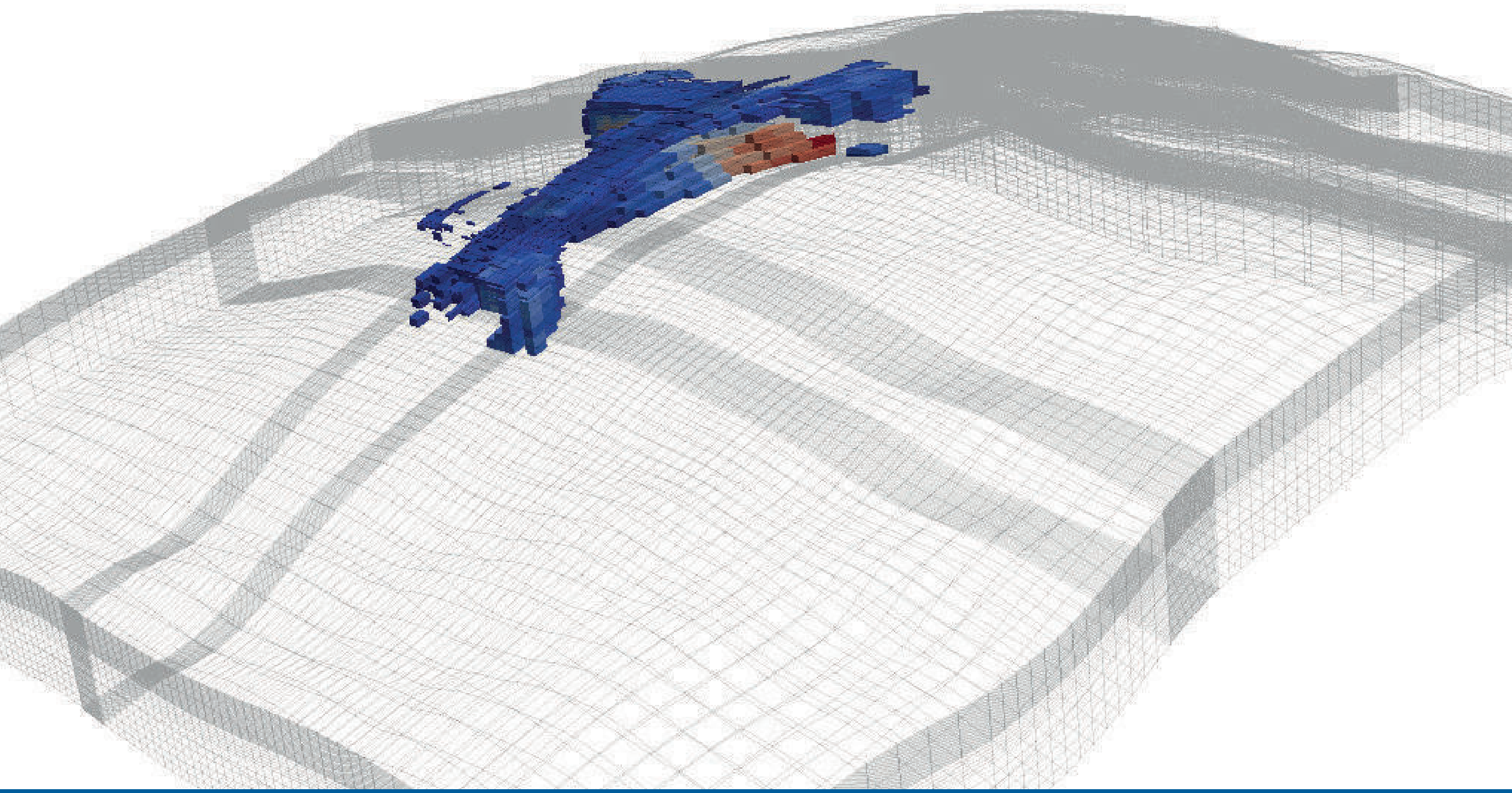
HZDR-111

International Workshop on

How to integrate geochemistry at affordable costs into reactive transport for large-scale systems

February 05 – 07, 2020



ABSTRACT BOOK

Wissenschaftlich-Technische Berichte
HZDR-111 · 2020 · ISSN 2191-8708

HELMHOLTZ ZENTRUM
DRESDEN ROSSENDORF

Wissenschaftlich-Technische Berichte
HZDR-111

International Workshop on

How to integrate geochemistry at affordable costs into reactive transport for large-scale systems

Abstract Book

February 05–07, 2020
HZDR – Helmholtz-Zentrum Dresden-Rossendorf
Dresden, Germany

Organized by
Institute of Resource Ecology
Helmholtz-Zentrum Dresden-Rossendorf e.V.

Editors:
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HELMHOLTZ ZENTRUM
DRESDEN ROSSENDORF

Impressum

Print edition: ISSN 2191-8708
Electronic edition: ISSN 2191-8716

https://www.hzdr.de/publications/Publ-30921
urn:nbn:de:bsz:d120-qucosa2-708102

Published by Helmholtz-Zentrum Dresden-Rossendorf e.V.

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Cover picture

The cover picture shows the reactive transport simulation of the potential spatial distribution of mineralized CO_2 in the anticline of the Ketzin pilot site after 10,000 years (Graphic provided by GFZ Potsdam).

Cover created by WERKSTATT X. Michael Voigt (www.werkstatt-x.de).

Contents

Preface

This international workshop entitled "How to integrate geochemistry at affordable costs into reactive transport for large-scale systems" was organized by the Institute of Resource Ecology of the Helmholtz-Zentrum Dresden Rossendorf in February 2020.

A mechanistic understanding and building on that an appropriate modelling of geochemical processes is essential for reliably predicting contaminant transport in groundwater systems, but also in many other cases where migration of hazardous substances is expected and consequently has to be assessed and limited. In case of already present contaminations, such modelling may help to quantify the threads and to support the development and application of suitable remediation measures.

Typical application areas are nuclear waste disposal, environmental remediation, mining and milling, carbon capture & storage, or geothermal energy production.

Experts from these fields were brought together to discuss large-scale reactive transport modelling (RTM) because the scales covered by such predictions may reach up to one million year and dozens of kilometers. Full-fledged incorporation of geochemical processes, e.g. sorption, precipitation, or redox reactions (to name just a few important basic processes) will thus create inacceptable long computing times.

As an effective way to integrate geochemistry at affordable costs into RTM different geochemical concepts (e.g. multidimensional look-up tables, surrogate functions, machine learning, utilization of uncertainty and sensitivity analysis etc.) exist and were extensively discussed throughout the workshop.
During the 3-day program of the workshop keynote and regular lectures from experts in the field, a poster session, and a radio lab tour had been offered. In total, 40 scientists from 28 research institutes and 8 countries participated.

The focus of the workshop was:

- ☐ To provide and discuss existing geochemical concepts in reactive transport modelling to describe sorption and related retardation processes of contaminants on a variety of sediments and rocks.
- ☐ To explicitly set focus on large-scale natural systems as experienced, e.g., in nuclear waste disposal, carbon capture & storage, environmental remediation, or geothermal applications.
- ☐ To explore how the discussed approaches can be integrated at affordable costs into current paradigms in THMC models and long-term safety assessments in general.
- ☐ To promote the exchange of scientific knowledge and practical experience between the workshop participants in an efficient way.

Based on the intensive discussions and very positive feedback on the workshop, a continuation is intended to bundle and strengthen the respective research activities and stipulate the international network that started to form during the conference days.

Finally, the organizers would like to thank the HZDR administration for their kind support and the German Federal Ministry for Economic Affairs and Energy (BMWi) for the partial funding under contract No. 02E 11668B.

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Haibing Shao
Helmholtz Centre for Environmental Research –
UFZ Leipzig (Germany)

Carl I. Steefel
Lawrence Berkeley National Laboratory (USA)

Paolo Trinchero
Amphos21 (Spain)

Scientific Program

Wednesday, February 05th

11:00 – 13:00 **Registration**

13:00 – 13:15 Welcome and introduction to HZDR – *Thorsten Stumpf (HZDR, Germany)*

13:15 – 13:35 Motivation and aims of the workshop – *Madlen Stockmann / Vinzenz Brendler (HZDR, Germany)*

13:35 – 14:10 **Keynote Talk 1:** Reactive Transport at the Crossroads: Progress and New Directions – *Carl Steefel (Lawrence Berkeley National Laboratory, USA)*

14:10 – 17:45 **Working Session 1:** Full coupling of reactive transport programs with geochemical codes, *Chair: Mavrik Zavarin (Lawrence Livermore National Laboratory, USA)*

TOUGHREACT, a simulation program embedded in the TOUGH suite of codes used in reactive transport modelling of the geological subsurface – *Dorothee Rebscher (BGR Hannover, Germany)*

Reactive Transport Modeling of Large-Scale Systems for Industrial Applications – *Erika Myers (UIT GmbH Dresden, Germany)*

Bounding Computation and Complexity for Reactive Transport on Supercomputers: A Perspective from Nuclear Waste Repository Performance Assessment – *Glenn Hammond (Sandia National Laboratories, USA)*

Cross-scale understanding and description of mineral precipitation processes in reactive transport models – *Jenna Poonoosamy (FZ Jülich, Germany)*

Hydrogeochemical modeling of mineral precipitation potentials in carbon capture and storage (CCS) – *Ulrich Maier (University of Göttingen, Germany)*

Joint discussion - Session 1

18:00 – 21:00 Get-together and Poster Session

Thursday, February 06th

09:00 – 9:35 **Keynote Talk 2:** *OpenGeoSys-6 development of reactive transport modeling with the application for radionuclides sorption processes – Haibing Shao (Helmholtz Centre for Environmental Research - UFZ Leipzig, Germany)*

9:35 – 12:30 **Working Session 2:** Sorption and diffusion processes in reactive transport simulations, *Chair: Glenn Hammond (Sandia National Laboratories, USA)*

Estimation of Radionuclide Partitioning in Agricultural Soils - Calculation of KD for Various Parameter Combinations – *Volker Hormann (University of Bremen)*

A Prediction of Uranium(VI) Diffusion in Montmorillonite at Various Chemical Solution Conditions – *Christophe Tournassat (BRGM, France)*

Modelling Cs migration through Opalinus clay: A benchmark for single- and multi-species sorption-diffusion models – *Vanessa Montoya (UFZ Leipzig, Germany)*

Joint discussion - Session 2

13:00 – 13:35 **Keynote Talk 3:** Radionuclide transport in fractured rock: overview and applications – *Paolo Trinchero (Amphos21, Spain)*

13:35 – 17:30 **Working Session 3:** Multidimensional look-up tables, surrogate functions and SA/UA exploitation for reactive transport modelling, *Chair: Gabriel Wittum (G-CSC University Frankfurt, Germany)*

Implementation of the Smart K_d-concept into the transport code d3f++ and application to PA relevant systems – *Ulrich Noseck (Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) gGmbH Braunschweig, Germany)*

Smart K_d-concept as efficient approach to improve geochemistry in reactive transport – *Madlen Stockmann (HZDR, Germany)*

Multiple complex reactive transport calculations to estimate the influence of uncertain Cs sorption parameters on Cs diffusion in clay and to construct a “new Cs K_d band” – *Wilfried Pfingsten (Paul Scherrer Institute, Switzerland)*

Advanced methods for sensitivity analysis: a means to improve robustness and reduce complexity of geochemical models – *Elmar Plischke (TU Clausthal, Germany)*

Parameter sensitivity and uncertainty of particle-based reactive transport: numerical analysis of pathogen transport at a riverbank filtration site – *Dustin Knabe (TU Berlin, Germany)*

Speeding up reactive transport simulations using statistical surrogate models and other algorithmical acceleration techniques – *Marco de Lucia (GFZ German Research Centre for Geosciences Potsdam, Germany)*

Joint discussion – Session 3

19:00 Workshop dinner in Restaurant e-VITRUM, Lennéstraße 1, Dresden

Friday, February 07th

09:00 – 9:35 **Keynote Talk 4:** Accelerating reactive transport simulations with on-demand machine learning *– Allan Leal (ETH Zurich, Switzerland)*

9:35 – 11:00 **Working Session 4:** Variable metrics, *Chair: Wilfried Pfingsten (Paul Scherrer Institute, Switzerland)*

Multiscale modelling and simulation of geochemical processes – *Gabriel Wittum (G-CSC University Frankfurt, Germany)*

Machine learning enhanced process coupling and parameter upscaling in reactive transport simulations – *Mohamed Mahrous (Paul Scherrer Institut / University of Bern, Switzerland)*

Implementation of mineral-water interface reactions in models for use in environmental management and nuclear waste repository performance assessment – *Mavrik Zavarin (Lawrence Livermore National Laboratory, USA)*

Joint discussion - Session 4

11:40 – 12:30 **Final discussions of the different approaches to integrate geochemistry in reactive transport modelling - Conclusions**

13:30 End of the workshop

14:00 – 16:00 Visit of the radiochemical laboratories of the Institute of Resource Ecology at HZDR

ORAL PRESENTATIONS

- Invited Talks
- Regular Presentations

Accelerating reactive transport simulations with on-demand machine learning algorithms

Allan M. M. Leal

Abstract

Geochemical reaction calculations in reactive transport simulations are extremely costly. These are chemical equilibrium and/or kinetics computations involving many fluid species and rock minerals, which are needed (at least once) in every mesh cell, at every time step of the simulation. As a result, they can account for over 99% of all computing costs in the simulation, especially when realistic chemical descriptions of fluids and rocks are considered in the model. It turns out, however, that many such geochemical calculations, during the course of a reactive transport simulation, have similar (*but not identical!*) input conditions; and these conditions might occur at different points in space and time (at distinct mesh cells and time-steps).

Let us represent a chemical equilibrium or chemical kinetics calculations using the following functional notation:

$$y = f(x), \tag{1}$$

where f is the function that performs the necessary steps to solve the problem; x is the input vector and y the output vector. In case of chemical equilibrium, x contains temperature, pressure, and element amounts, whereas y contains the amounts of each chemical species, distributed among one or more phase. In case of chemical kinetics, x comprises of temperature, pressure, the initial amounts of each chemical species and the time-interval that we let them react, and y has the final amounts of each chemical species.

In reactive transport simulations, f needs to be evaluated millions to billions of times, and we want to avoid this as much as possible by first trying an estimate for y using a first-order Taylor expansion (*the prediction step*):

$$\bar{y} = y^{\star} + \left(\frac{\partial f}{\partial x}\right)^{\star}(x - x^{\star}), \tag{2}$$

where x is a new input at which we want to evaluate f (corresponding to some mesh cell, at some time-step); $x^{\star}$ is an input previously evaluated (not necessarily at the same

current mesh cell), whose output is $y^\star$; and $(\partial f/\partial x)^\star$ is the *sensitivity matrix* of f at $x^\star$. Note that this Taylor prediction can be orders of magnitude faster than the actual evaluation of f, because the former is just a matrix-vector multiplication, whereas the latter requires an iterative process with several matrix equations to be solved, and computation of species activities and/or reaction rates.

We need now to determine whether $\bar{y}$ is sufficiently accurate (*the acceptance test*). This is to ensure $\bar{y}$ does not significantly deviate from exact $y = f(x)$. This needs to be done without actually evaluating f, and strategies are discussed in the presentation. If the estimate does not fulfill imposed acceptance criteria, then f is fully evaluated, followed by the computation of $\partial f/\partial x$. This process, after a failed prediction, constitutes the *training phase* of the on-demand machine learning algorithm (*thus, the training happens on the fly during the simulation*).

We show the use of this acceleration strategy in some reactive transport simulation problems, where speedups of orders of magnitude are achieved while maintaining significant accuracy. In addition, we present further work towards improving the algorithm and demonstrating it in extremely challenging chemical conditions.

OpenGeoSys-6 development of reactive transport modeling with the application for radionuclides sorption processes

Haibing Shao[1,2], Renchao Lu[1,3], Madlen Stockmann[4], Vanessa Montoya[1], Dmitri Naumov[1], Vinzenz Brendler[4], Olaf Kolditz[1,3]

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[4] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

This work presents the latest OpenGeoSys-6 development on the reactive transport modeling process. The robustness and efficiency of the implemented computational framework is examined with an application of radionuclide transport through a sedimentary rock sample. The common practice of performing reactive transport modeling is achieved by passing the aqueous geochemical calculations to an external third-party solver, e.g. Phreeqc, GEM, and Reaktoro. The data exchange between the multi-physics simulator and the geochemical solvers is either via the file system or via a string buffer. The data exchange constitutes a considerable overhead and thus slow down the computation. In particular, for waste repository simulations where the spatial scale is up to dozens of kilometers and required simulated time is millions of years long, the computational load becomes unaffordable. To reduce this overhead, the third-party geochemical solver is deeply integrated into OpenGeoSys at the source code functional level. The data exchange via files or streams is no longer needed. The saving on the data exchange overhead between the multi-physics simulator and the geochemical solver brings to about 20 times speed-up in benchmarks containing both equilibrium and kinetically controlled reactions. The speed-up effect becomes more significant with the increasing size of mesh nodes. In addition, accuracy of the reactive transport simulation has also been improved, as the precision truncation commonly seen in the file and stream based data exchange is now avoided. A well-defined test case for radionuclide transport through a typical sedimentary rock system in North Germany will be analyzed to demonstrate speed-up effect.

Radionuclide transport in fractured rock: overview and applications

Paolo Trinchero

Amphos21, Spain

In fractured crystalline rocks radionuclides are transported by fluid flow along open fractures and are retarded by a mechanism known as matrix diffusion. Other processes that might affect the fate and migration of radionuclides are sorption (onto both the fracture surface and the available mineral surfaces in the rock matrix), in-plane dispersion, diffusion into in-plane stagnant water, decay and ingrowth. All these processes are included in a particle-based computer code called MARFA (Migration Analysis of Radionuclides in the Far Field; Painter and Mancillas, 2013), which is used by the Finnish and Swedish nuclear waste management companies (POSIVA and SKB, respectively) to carry out radionuclide transport simulations for their respective safety assessment studies. Key advantages of MARFA, compared to other available software for radionuclide transport modelling, are that (i) it is based on a numerically efficient time-domain (TD) random walk scheme, (ii) it is free of numerical dispersion and (iii) it offers a great flexibility in the way complex processes are included in the calculation. In the first part of this talk we will give an overview of MARFA's capabilities and we will also discuss on-going developments focused on a tighter integration of MARFA into existing DFN-based groundwater flow simulators. We will also show an application case where MARFA has been used to analyse nickel transport for the safety evaluation of the Swedish repository concept for long-lived low- and intermediate-level waste (SFL). In this application case, changes in retention properties due to the evolution of background geochemical conditions are considered using a dynamic-K_d approach (Trinchero et al., 2016).

In the second part of the talk we will present a brief overview of the modelling activities that Amphos 21 is carrying out in the framework of Task 9B of the SKB GWFTS Task Force GroundWater Flow and Transport of Solutes, www.skb.se/taskforce, which is focused on the modelling and interpretation of an in-situ diffusion experiment. Using an Inter-Granular Network Model (IGN; Iraola et al., 2017), which is built in PFLOTRAN and run in a supercomputer, along with a detailed micro-characterisation data obtained using X-ray computed microtomography, we show that the sparse distribution of biotite grains leads to anomalous penetration profiles of cesium that are in agreement with experimental observations.

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Trinchero, Paolo, et al. "Modelling radionuclide transport in fractured media with a dynamic update of Kd values." Computers & geosciences 86 (2016): 55-63.

Speeding up reactive transport simulations using statistical surrogate models and other algorithmical acceleration techniques

Marco De Lucia, Theresa Hennig, Michael Kühn

GFZ German Research Centre for Geosciences, Section 3.4 Fluid Systems Modelling,
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Reactive transport simulations of interacting physical and chemical processes in the subsurface are characterized by high computational effort (CPU time) and hampered by numerical instabilities and non-convergence of the simulations. Their total computational cost is mainly controlled by geochemistry, which routinely accounts for up to 90 % of CPU time [1], and is therefore an important limiting factor for the wide application of this type of models. With the currently available tools, only reduced/simplified systems can be successfully investigated at a notably lower spatial and temporal resolution than, for example, pure hydrodynamics simulations. For these reasons, it is current practice to simplify both the geochemical system and the geometric and geological features of the investigated domain, thus limiting the coupled models to homogeneous, 2D or extremely coarse 3D models. Such models can thus achieve a qualitative description of ongoing processes, but are often not capable to provide quantitative predictions for use, i.e., in risk analysis or large scale reservoir simulations. Moreover, large uncertainties are associated with the heterogeneity of the investigated system and the parametrization of processes, which are especially significant for geochemical reactions. Paradigmatic examples are kinetic constants and measurements of reactive surfaces of minerals, whose values may span across several orders of magnitude. Thus, the computational effort of reactive transport simulations appears unjustified.

A promising strategy for speeding up the coupled simulations at price of acceptable losses in accuracy is to replace the *full physics* geochemical model with a data-driven statistical *emulator* or *surrogate*. A surrogate is an arbitrary statistical multivariate regressor which can be trained on a set of pre-calculated full physics simulations covering the whole parameter space of geochemistry or even directly at runtime during the coupled simulations. Recent advances in the theory and implementation of regressors by the machine learning community make readily available many different methods. To name a few among the most powerful: tree-based regressors (such as Random Forests or xgboost), Artificial Neural Networks, Gaussian Processes and Support Vector Machines. They all have different properties, performances and training times depending, i.e., on non-linearity of the dataset and amount of available data. Given the “black-box” nature of statistical surrogates, it is not always possible to obtain predictions honoring important physical constraints. We found out, that a runtime check of charge and mass balance on the surrogate predictions is necessary: those offending a given tolerance must be rejected and the full physics chemical simulations run instead. However, if the percentage of offending simulations is low throughout the coupled simulation, which means that the surrogate is trained enough, large scale simulations can achieve a speedup factor up to 10 or even 100 [2], and can be thus computed on common workstations instead of large clusters. In this contribution we show our R-based implementation of the whole workflow for training and evaluate surrogates and benchmark studies in a parallel sequential non iterative coupled reactive transport simulator.

A further acceleration technique which can be easily implemented in coupled reactive transport is the caching of geochemical simulation results in lookup tables for further reuse in subsequent time steps, under the premise that query and retrieval from such tables is much faster than the full geochemical calculation. We show how our implementation of Distributed Hash Tables enhances the speed of massively parallel large scale reactive transport simulations up to a factor of four, depending on initial heterogeneity, flow regime and memory allocated to the tables. The advantage of this approach is that it is completely deterministic up to the rounding of the variables stored in the lookup table, having thus virtually no loss of accuracy compared to surrogate models.

Benchmarks and exemplary “real life” case studies to illustrate the advantages and drawbacks of the proposed computational methods are taken from the subsurface utilization, e.g. CO_2 storage or sorption processes in the frame of nuclear waste disposal in claystones.

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Bounding Computation and Complexity for Reactive Transport on Supercomputers: A Perspective from the Nuclear Waste Repository Performance Assessment Community

Glenn Hammond[*], Peter Lichtner[+], Paul Mariner[*], David Sevougian[*], Emily Stein[*]

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Simulation of geologic repositories for nuclear waste pushes computational resources to their limits. To be effective and predictive, performance assessment (PA) calculations must couple multiple processes, such as thermal, hydrologic, mechanical, and chemical (THMC), over spatial scales ranging from pore to field scale. Large statistical ensembles of these million-year simulations are generally required to account for uncertainties in the available data, future scenarios and conceptual representation.

The US Department of Energy leverages a balance of mechanistic and reduced-order modeling (ROM) and high-performance computing (HPC) to address these demanding computational requirements for PA in its development of the GDSA (Geologic Disposal Safety Assessment) Framework. The use of reduced-order approximations to THMC process models can lessen computational burden by reducing memory and runtime requirements, while supercomputing can expand available memory and processing power, enabling increased complexity and sophistication. Both ROM and HPC make ensemble-based, large-scale, long-time performance assessment more tractable.

In developing simplified geochemical process models, it is advantageous to first delineate the HPC resources required to simulate mechanistic reactive transport on a large, realistic problem domain. Reduced-order geochemical process models can then be employed on the same problem domain with similar HPC resources in order to quantify the computational savings produced by using the simplified model. For instance, comparing the parallel performance (runtime and scalability) of solute transport with linear sorption (or even solute transport alone) to that of multicomponent reactive transport with aqueous speciation and surface complexation bounds the computational requirements for sorption processes. To this end, we present a comparison of computational performance for reactive transport modeling on a large HPC cluster – specifically, a comparison of PFLOTRAN performance for representations of the sorption process over a large spatial domain: equilibrium and multi-rate kinetic surface complexation vs. linear sorption.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2019-13626 A

Estimation of Radionuclide Partitioning in Agricultural Soils - Calculation of K_D for Various Parameter Combinations

Volker Hormann

Institute of Environmental Physics, University of Bremen, Germany

The contamination of agricultural soils with radionuclides like americium and plutonium and the subsequent uptake by plants is a scenario which will be relevant in the course of a radiological accident. The nuclides may be introduced by air deposition and subsequently move downward into the root zone. They may also enter the soil if the ground water is contaminated by leakage from a nuclear waste repository and be transported upwards. For the estimation of plant uptake, the solid/solution distribution coefficient (K_D) plays a crucial role. In general, K_D will not be constant, but is expected to depend on soil parameters like organic matter (OM) content and pH.

Recently, a model for the partitioning of Am and Pu has been developed, which is based on the UNiSeCs model described by Hormann (2015). This model has been successfully implemented into the well-known geochemical code PHREEQC and validated using studies from the literature. For each element, the most relevant soil parameters (OM, dissolved OM and, in the case of Pu, also clay content and redox potential) have been identified by modelling. For instance, the increase of dissolved OM concentration from 1 to 10 mg/L will decrease the K_D for Am by two orders of magnitude.

A special software has been developed for the manipulation of PHREEQC input files to vary these parameters sequentially and calculate the resulting K_D values. The resulting multidimensional K_D grid can be used by algorithms that calculate the transport of radionuclides with the soil water taking into account the retention by soil materials. This approach is similar to the ‘smart K_D’ concept.

This grid is being used within the German joint project Trans-LARA (funded by the German Federal ministry of Education and Research, Grant No. 02NUK051) where the environmental transport of these elements from contaminated ground water into edible plants will be predicted. We present the impact on K_D caused by parameter variations which may occur within the soil environment.

Literature:

Hormann, V.**:** Modelling Speciation and Distribution of Radionuclides in Agricultural Soils. 2015. In: C. Walther, D.K. Gupta (eds.), "Radionuclides in the Environment", pp. 81 - 99, Springer International Publishing Switzerland 2015

Reactive transport modelling issues in radioactive waste disposals safety assessment

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[1]Nuclear Safety Institute of the Russian Academy of Sciences

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Construction of radioactive waste (RW) disposals demands safety assessment in which groundwater flow and contaminants transport modelling usually plays the major role. The GeRa (Geomigration of Radionuclides) code is being developed for general purpose hydrogeological modelling with specific features for RW [1]. GeRa includes simple and more complicated transport models taking into account chemistry, such as:

1. Sorption governed by Henry, Langmuir and Freundlich isotherms;
2. Sorption governed by Henry isotherm with variable K_d, dependent on concentration of a major contaminant.
3. Coupled reactive transport model with geochemistry taken into account using the IPHREEQC interface to PHREEQC software [2]. Coupling may be done using sequential noniterative and iterative approaches.

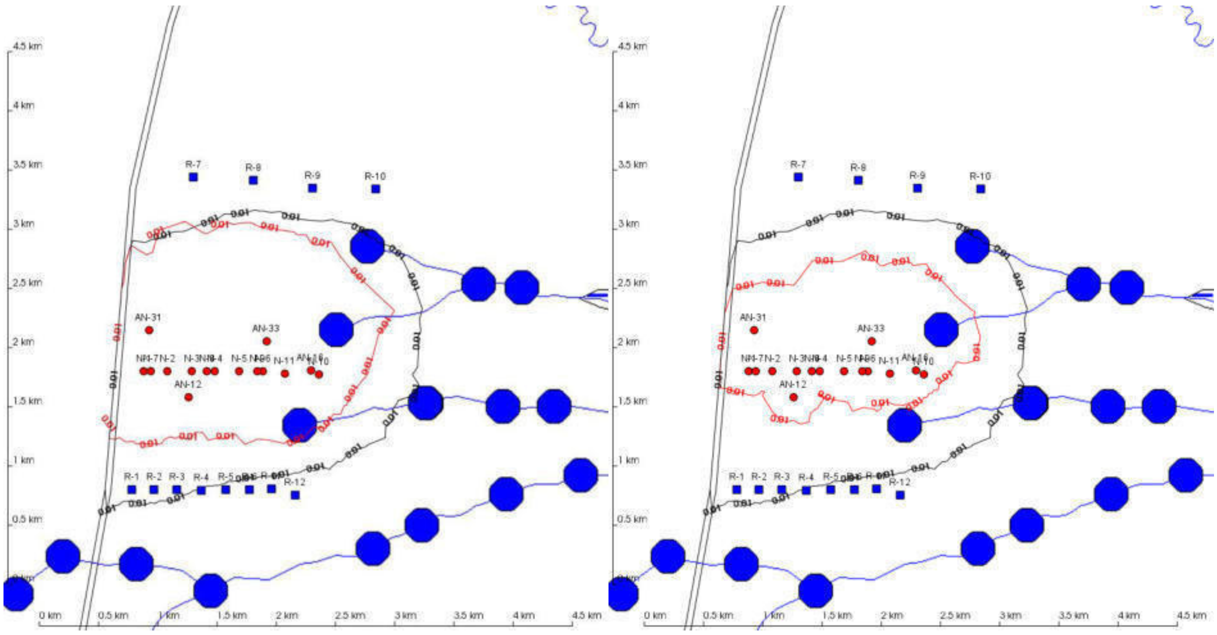

Figure 1 – Calculated plumes of NO_3^- in the aquifer lowest (left) and highest (right) possible nitroreduction rate. Black lines – basic calculation without nitroreduction, red – with nitroreduction.

Liquid RW deep injection disposals (LRW DID) [3] are a good example of sites with complicated chemistry. The injected RW besides radionuclides contains a large amount of sodium nitrate. The latter one strongly affects sorption of other contaminants. Its influence on strontium sorption was shown using variable K_d approach and coupled reactive transport model in [4].

One more effect to be taken into account for LWR DID is biological nitrate reduction. On figure 1 the influence of nitroreduction process on nitrate-ion contamination plume in an aquifer of LRW DID is shown. This process, first, reduces groundwater contamination by nitrate-ion with time. Second, due to the lower concentration of nitrate-ion one can expect stronger sorption of radionuclides.

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Parameter sensitivity and uncertainty of particle-based reactive transport: numerical analysis of pathogen transport at a riverbank filtration site

[1]Knabe, D., [2]Guadagnini, A., [2]Riva, M., [1]Engelhardt, I.

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Abstract

A reactive-transport model was developed to predict pathogen transport at a riverbank filtration site in Germany. Pathogens (bacteria and viruses) in surface waters origin from discharge of wastewater and surface run-off from agricultural fields. Pathogens can migrate from lakes and streams through the hyporheic zone into groundwater and can reach drinking water production wells. Especially, short subsurface travel times and specific physical and geochemical conditions can enhance the mobility of pathogens. Prediction and risk assessment of pathogen transport under natural hydraulic, hydrological, and geochemical conditions is challenging with respect to prevailing uncertainty of model input parameters, initial and boundary conditions as well as hydrogeological and geochemical heterogeneity.

Therefore, we developed a two-dimensional particle-based reactive transport model to simulate pathogen transport using PFLOTRAN, a massively parallel next-generation code. The reactive transport model simulates advective-dispersive transport including particle-driven transport using the colloid-filtration-theory coupled with the Maxwell approach to predict the collision efficiency of colloids based on the DLVO interaction energy. The model also includes the ability to mimic attachment and detachment of pathogens to and from the sediment, inactivation, straining and blocking of pathogens.

Model analysis and calibration employed long-term hydraulic, thermal, and chemical data (including concentration of E. coli and Coliforms) sampled in the river, within 3 observation wells with different depths and an active production well. Furthermore, the model considers subsurface heterogeneity by differentiating between an upper and lower aquifer and explicitly including the colmation layer at the interface between river and subsurface.

Due to the complexity of the investigated processes the reactive transport model is characterized by a high parametrization with a total of 59 parameters, where several are extremely difficult to obtain. These include 27 hydraulic and solute transport parameters (e.g., permeabilities, porosities and dispersivity), and 32 pathogen transport parameters (e.g., pathogen size, inactivation coefficients, and zeta potentials) for two pathogen species. A global sensitivity analysis was applied to identify the most relevant model parameters to target model outputs (piezometric pressure head, groundwater temperature, and concentrations of chloride, oxygen, Coliforms and E. coli), which are then further analysed in a stochastic model calibration to quantify the parameter uncertainty.

A parameter screening method was employed using globalized local sensitivity metrics via the Morris Indices based on 3,000 model runs to identify insensitive parameters to the target model outputs. The 26 most sensitive parameters were then used for a model calibration within a stochastic framework. The calibration utilized piezometric pressure head, groundwater temperature and concentrations of chloride, oxygen, E. coli and Coliforms at four spatial locations. We employed a machine learning technique called Particle Swarm Optimization to identify a single solution for the inverse problem. In this algorithm, a number of particles are initially randomly spread into the parameter space, each with a random initial velocity. Within each iteration the objective function to be minimized is evaluated for each particle. Afterwards the velocity of each particle is updated based on its previous velocity and the distance of its currents position in the parameter space to the position where the lowest value of the objective function has been found. Before the next iteration all particles are displaced by their updated velocities.

Based on this analysis we can highlight that pathogen transport parameters such as inactivation and straining coefficients as well as pathogen size were most sensitive for E. coli and Coliform transport. However, beside these parameters driving colloid transport, dispersivity and the permeability of the colmation layer were the most sensitive parameters for Coliform and E. coli migration. Additionally, we observed a correlation between temporal changes of sensitivity indices and the level of the river,

which can be explained by the influence of the river water level on the groundwater flow velocity. This indicates that the relevance of a process changes with the river level fluctuation. For the stochastic model calibration, we have obtained 50 solutions to the inverse problem using the Particle Swarm Optimization algorithm. The results show in general a higher model output uncertainty for E. coli and Coliform concentrations compared to other observed data (e.g. chloride and oxygen). This might be the result of a more complex subsurface (physical and geochemical heterogeneity) that has a higher impact on colloid transport than on flow and other transport (non-reactive and reactive) processes.

MACHINE LEARNING ENHANCED PROCESS COUPLING AND PARAMETER UPSCALING IN REACTIVE TRANSPORT SIMULATIONS

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Natural mass transport phenomena are driven by thermal, chemical, mechanical and hydraulic gradients. Simulation of complex systems require consideration of different physical and chemical processes in a coupled self-consistent approach. The implementation of process coupling is scale dependent. Effective phenomenological simulation parameters often rely on complementary simulations conceptualized at different, typically lower, scales. Although the scale specific models and experimental research tools are well established, an automated coupling between processes at different scales will remain to be challenging. Direct coupling between models at different scales is in general prohibitive from computational point of view. Alternative implementation of the process coupling and parameters transfer could be the use of data driven surrogate models. We show how process coupling and multiscale modelling can be enhanced with the use of neural networks.

Hydrogeochemical modeling of mineral precipitation potentials in carbon capture and storage (CCS)

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Capture and storage of CO_2 from power generation (CCS) has been under discussion for the last two decades as a potential measure to reduce greenhouse gas emissions to the atmosphere, and is under investigation with respect to its storage potentials as well as its energetic and economic costs. Of special importance, alterations of the mineral phase of deep reservoirs are desired as a process for long term carbon capture and storage, driven by changes in fluid composition and pressure due to CO_2 injection.

Storage of carbon dioxide in geological reservoirs is attributed to three different processes, *i)* filling of pore space within the reservoir by gaseous or supercritical CO2 (pore trapping), *ii)* dissolution of the CO_2 into the formation water (solubility trapping) and *iii)* precipitation of carbonate as mineral phase (mineral trapping). Whereas pore trapping and solubility trapping may utilize carbon storage on a relatively short time scale, mineral trapping has probably the most long-term potential of carbon sequestration in the subsurface, but is also the most susceptible to uncertainty and remains a matter of ongoing research. As an additional aspect, just as hydraulic fracturing, in contact with cap rocks CO_2 is expected lead to alterations of the mineral phase of overlying formations as well. Understanding of the relevant processes of mineral trapping is therefore a significant task.

Underlying concepts of geochemical equilibria computation have become available in a reliable manner during the last decade (e.g. Krupka et al., 2010, Appelo et al., 2014, Appelo, 2015) for the conditions of pressure and temperature in deep reservoirs up to 300°C and 1000 atmospheres. The geochemical codes Phreeqc and MIN3P have recently been upgraded for that purpose and were applied in the study.

Simulations were performed using field data from the Heletz sandstone formation (Israel), showing a shift of saturation index (SI) and dissolution/precipitation reactions of silicates and carbonates subsequent to injection of CO_2. The site had been exploited as an oil field over the previous decades, where oil was trapped in an anticline beneath a shale caprock (Niemi et al, 2016).

Alterations of the mineral phase over time become visible and potentials to precipitate were observed for the minerals Ankerite > Dolomite > Siderite ~ Calcite > Magnesite, and for the mineral Dawsonite during early stages when only the Na^+ ion is present in high ionic concentrations.

Uncertainty of mineral saturation is implied by variability of water chemistry and the thermodynamic database records. Analysis was performed by means of principal component analysis and sensitivity coefficients, and showed strongest variability of Dolomite presence due to salinity and a reversed dependency of total amount of carbon mineralization between Pitzer and Debye-Hückel/Davies based activity computation.

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Modelling Cs migration through Opalinus clay: A benchmark for single- and multi-species sorption-diffusion models

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This work presents a benchmark exercise related to a long term laboratory (cm)-scale diffusion experiment of Cs (representative moderately sorbing radiotracer) through Opalinus clay by using different codes: CORE^{2D}V5, Flotran, COMSOL Multiphysics, OpenGeosys-GEM, MCOTAC, PHREEQC v.3 and iCP 1.5 (interface COMSOL-PHREEQC). The benchmark exercise is divided into two different conceptual models, i) a single-species model by using a look-up table for a Cs sorption isotherm and ii) a multi-species diffusion model including a complex mechanistic Cs sorption model. The calculations were performed for three different Cs boundary concentrations (10^{-3}, 10^{-5}, 10^{-7} mol / L) including the non-linear sorption behaviour of Cs at different locations of the clay sample (x = 1, 5, 7 and 9 mm). Additionally, code specific properties have been investigated to show how different software's behave on their specific input parameters, and how a better agreement for the results of the different codes could be achieved.

All codes results show a general agreement for both single-species and multispecies benchmark cases, however, sometimes discrepancies have been identified, especially at 1 mm where a high spatial/time resolution is needed to obtain results in a reasonable computational time. In addition, the benchmark exercise yielded information on code performance, setup options, input output data management and post processing options. Finally, the comparison of single-species and multi-species model concepts shows that the single-species approach yields generally an earlier breakthrough than the multi-species approach. Main differences between both approaches, it is related with the computational time needed, with simulations at

least 25 times faster with the single species concept than with the multi-species one. Although this can be seen as clear advantage for the application of the single species concept in long term prediction of radionuclides migration in the environment, the multispecies approach can give information of the geochemistry and a deeper process understanding of the system can be analysed. It is, then worth mentioning that the two different conceptual approaches underline their applicability for modelling diffusion dominated systems and accounting for non-linear sorption processes and the selection of one concept or the other would depend mainly on the required output information.

Finally, it can be said that he difficulty of this benchmark has been related to i) the low concentration of the chemical species under study (Cs) and its numerical converge problems associated and ii) the high spatial resolution needed to solve the equations in sub-millimetre scale under high gradients of concentrations produced by sorption processes.

Reactive Transport Modeling of Large-Scale Systems for Industrial Applications

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UIT has 20 years of experience in modeling reactive transport processes in small- and large-scale systems: in-situ recovery (ISR) in sedimentary and fractured-rock deposits (as well as in permeability enhanced hard rock), post mining natural attenuation studies, sediment and solute transport in river systems, remediation of pit lakes from lignite mining, etc. For the projects we use (i) commercial software (e.g. FEFLOW), (ii) open-source packages (e.g. PHREEQC), (iii) in-house software, or (iv) combinations of them. For example, to describe the flooding of former uranium mines, case-specific compartment models have been developed from scratch.

From a mathematical point of view, these models are based on the same conservation laws (mass and charge balance), the same thermodynamic laws (mass action), and specific kinetic rate laws. The dynamics is described by a set of (partial) differential equations, which are solved by spatial and temporal discretization. Although all models are based on the *same* fundamental equations, each problem requires its own handling that is both *problem-* and *site-specific*.

The typical workflow of a reactive-transport project includes the following tasks:

1. Data compilation and review
2. Conceptual model
3. Model implementation
4. Input generation
5. Model calibration/Parameter studies
6. Simulations and interpretation of results

The "data compilation" is often the most time and cost intensive task of the entire project, especially for large-scale systems. This task includes the evaluation of the available field and lab data. The spatial and/or temporal resolution of field data is often low. In contrast, lab data can be generated with high accuracy, but is focused on a micro- or mesoscale. Therefore, an *upscaling* of lab data to field conditions is required, which is non-trivial.

The following input data/parameters should be extracted for a deterministic reactive transport model:

- Hydrogeological data for fluid flow: geography, geology, climate, hydrology (porosity, permeability, hydraulic head, sources/sinks)
- Mass transport: geochemistry, mineralogy, groundwater composition, sources/sinks
- Reactions: definition of observable (relevant) chemical processes, thermodynamic and kinetic data

The "conceptual model" should be focused on the *main* processes (ignoring higher-order effects). The conceptual model depends on the available data and its spatial-temporal discretization (1D, 2D, or 3D). Since the fluid-flow system is the basis of the mass transport, the former defines the model space including all of its heterogeneity (fracture networks, faults, permeability variations). This requires high-resolution input data and appropriate modeling techniques.

There are at least two challenges in 3D reactive transport: (i) the dual-porosity approach and (ii) the implementation of chemical reactions (via equilibrium thermodynamics or kinetic-rate laws). In the dual-porosity approach, the transport of dissolved species is considered in free-water (mobile) pores, while reactive minerals dissolve mainly in the stagnant-water (immobile) pores. The interplay between mobile and stagnant water can be described by a mass transfer rate (either species- or composition-dependent).

The distinction between *fast* and *slow* reactions is crucial for the application of equilibrium and/or kinetic approaches. The corresponding equilibrium data for aqueous, solid, and gaseous phases are taken from “standard” thermodynamic databases. Non-existing or low-quality data can be determined in batch and/or column tests. From a numerical point of view, the temporal discretization and kinetic rate approaches need to be considered to avoid numerical instabilities or negative concentrations/masses.

There is a compromise between the model size and model complexity. The computation time could be a killer argument for the success of the project. The more simulation runs (per day) that can be calculated, the better is the understanding of the system and the quality of the forecasts and predictions.

The above modeling principles will be demonstrated for several application cases including:

(1) In-situ recovery of technology metals from sedimentary formations and post-mining scenarios (natural attenuation)
(2) 3D-compartment model to simulate mine flooding

Implementation of the smart K_d-concept into the transport code d^3f++ and application to PA relevant systems

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The code d^3f++ (distributed density-driven flow) has been established and further developed during the last decades (Fein et al. 2004, Schneider 2016) to simulate density driven flow and contaminant transport in large heterogeneous areas with extensions of several kilometers and over long periods in time, namely one million years, as required in performance assessments (PA) for radioactive waste repositories. Sorption on mineral surfaces is one crucial mechanism retarding the transport of contaminants. Due to the large temporal and spatial scales considered, in recent safety assessment studies, sorption is usually described with temporally and spatially constant distribution coefficients, so-called K_d-values. Since sorption of many radionuclides strongly depends on the geochemical properties of solution and sediments, this approach is justified for constant geochemical conditions. However, within time frames of one million years, hydrogeological and chemical alterations are expected due to environmental variations caused by climatic or geological changes.

A straightforward approach to describe changing geochemical conditions and its impact on sorption is the direct coupling of a transport code with a geochemical code, capable of using thermodynamic sorption models. Such an approach, however, leads to unacceptably long computational times for the PA relevant systems described above. The challenge for any realistic geochemical modelling is the integration of the important basic processes at affordable costs into large-scale reactive transport modelling (RTM). As an effective way to integrate variable geochemistry in RTM, we developed the smart K_d-concept (www.smartkd-concept.de), based on a bottom-up approach of a competitive mineral-specific sorption of dissolved species on surfaces, combining surface complexation models with ion exchange and precipitation in a quasi-thermodynamic manner (see abstract Stockmann et al. 2020). The philosophy behind this approach is to compute a-priori multidimensional look-up tables with distribution coefficients (K_d-values) for a wide range of important environmental input parameters (e.g. pH, ionic strength, concentration of competing cations and complexing ligands such as calcium (Ca) and dissolved inorganic carbon (DIC)), to be accessed during subsequent reactive transport simulations. As a prerequisite the transport of all relevant environmental parameters needs to be considered in d^3f++.

Here, we will discuss the requirements for transport modelling on PA scale and present the fundamental strategy for implementation of the smart K_d-concept in the existing 3D reactive transport program d^3f++ (Noseck et al. 2012, 2018). Selected results from flow and transport calculations through a typical sedimentary rock system covering potential repository host rocks, namely salt and clay formations in Northern Germany, over very long time frames are shown. In general, the environmental parameters reflect well the interaction of the initial and boundary conditions as well as the mixing processes and thus the changes of the geochemical environment. The impact of the environmental parameters on the distribution coefficients of Cs and its impact on Cs retardation can be well retraced (see Fig. 1). Furthermore, changes in the environmental parameters and their impact on retardation of different radionuclides will be discussed in the presentation.

A comparison of CPU times needed for the transport simulations employing the conventional K_d-value with those for the new approach using the smart K_d-concept shows only an increase by a factor of 3 – 3.5, which is fully feasible for performance assessment calculations.

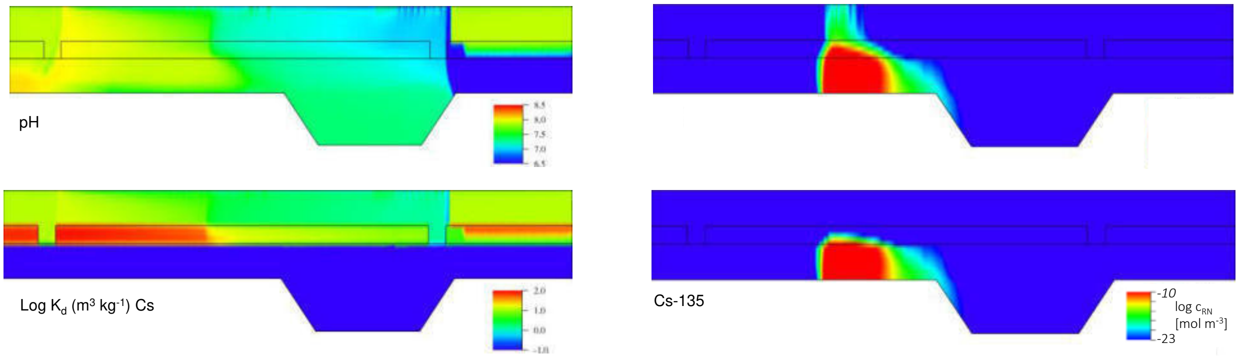

Fig. 1. Distribution of pH and log K_d-value for Cs (left) and distribution of Cs-135 concentration calculated in a 2D model area after 160,000 years transport time with d^3f++ using temporally constant K_d-values (top, right) and smart K_d-concept (bottom, right).

Acknowledgement:

This work is funded by the German Federal Ministry for Economic Affairs and Energy (BMWi) under contract Nos. 02 E 10518+02 E 10528, 02 E 11072A-B and 02E11668A-C.

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Multiple complex reactive transport calculations to estimate the influence of uncertain Cs sorption parameters on Cs diffusion in clay and to construct a "new Cs K_d band"

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The quantification of parameter uncertainty is of major interest for modelling radionuclide migration from nuclear waste repositories in performance assessment studies. Of special interest is the quantification of uncertainties of sorption parameters and its influence on the prediction of radionuclides' concentration levels, arrival times and migration distances in clays. Up to now, however, the parameter uncertainty for sorbing radionuclides was limited to simple k_d sorption approaches, with focus on the radionuclides' k_d values and diffusion coefficients (see e.g. [1, 2]). Depending on the uncertainty of these two parameters, a range of arrival times are calculated. Here, we use a complex three-site sorption model for Cs described in [3] within a multi-species reactive transport model (MCOTAC, [4]) in combination with a two-step sensitivity analysis, the Morris method [5] followed by an extensive Sobol sensitivity analysis [6]. The Morris analysis quantifies the average effect of a parameter on the output of interest, whereas the Sobol analysis quantifies the relative contribution of a parameter to the variance of the output, which yields a ranking of uncertain parameters' importance. The implementation of reactive transport calculations into a probabilistic framework allows the quantification and ranking of the sensitivity to sorption parameters of MCOTAC for Cs diffusion in clay using reference illite sorption parameters. These uncertain parameters can be divided into two groups of different origin. One group refers to the uncertainty of sorption model parameters for the specific equilibrium cation exchange reactions (constant in time); the second group refers to the uncertainty of major cations concentrations involved in the cation exchange reactions, whereas this porewater composition might be time dependent, when the geochemical system is evolving, especially for long-term radionuclide migration. Multiple realizations (>20000) of Cs breakthrough curves calculations are evaluated showing a variation of Cs arrival times for different diffusion distances due to sorption parameters and cation concentration uncertainties. From initially 12 assumed uncertain parameters, the analysis yields major influence of equilibrium sorption reaction constants of Cs on Type2 and FES sites, in addition to the concentrations of respective cations involved in these reactions (Na^+ and K^+) on the diffusion of Cs through the clay. Moreover, the multiple realisations of the Cs breakthrough curves, yield ratios of values for Cs sorbed and Cs in solution, i.e. a "complex Cs sorption model isotherm", which includes all the uncertainties of the considered sorption model parameters and major cations concentrations. These isotherms are state-of-the-art, more accurate, look-up table for modelling Cs sorption-diffusion in reference illite and can be applied for simple k_d approach calculations in performance assessment studies. Finally, the new approach presented here identifies a roadmap for how and what has to be done to quantify the importance of each uncertain parameter in reactive transport modelling. The developed knowledge can be used in other complex reactive transport problems with respect to parameter uncertainty and related influence on migration fronts of contaminants, precipitation or dissolution fronts etc. To this aim, if the computed breakthrough curves are affected by large uncertainty or variability, parameter uncertainty analysis can help in designing laboratory experiments with respect to geometrical (e.g. sample thickness), and geochemical set-up (major cation concentrations chosen) in order to produce informative data and reduce uncertainty.

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Advanced methods for sensitivity analysis: a means to improve robustness and reduce complexity of geochemical models

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Literature offers a variety of definitions for the term "sensitivity analysis" (SA). Hereinafter, we follow Saltelli (2006) by saying: "Sensitivity analysis is the study of how the variation on the output of a model (numerical or otherwise) can be apportioned, qualitatively or quantitatively, to different sources of variation, and of how the given model depends upon the information fed into it." More specifically, we refer to situations in which "[…] the problem setting is twofold: A description of input uncertainty is needed, as well as a simulation model representing physical properties. […] we understand by SA addressing both aspects and considering the input uncertainty given by probability distributions." (Kuhlmann et al. 2013). Thus, the uncertainty of the output of the physical model under consideration can also be described using a probability distribution. The investigation of this (a priori unknown) output distribution is commonly referred to as uncertainty analysis, while sensitivity analysis addresses input-output relationships by investigating the *joint* input/output distribution.

SA can support tasks like factor prioritization (i. e. identifying the most important model inputs) and factor fixing (i. e. identifying the least important model inputs). Moreover, there are tools to identify and describe so-called interactions, i. e. situations in which the *joint* influence of two or more inputs on the output is of interest. SA is being applied in a variety of very different fields such as economics or safety assessment.

Both factor prioritization and fixing might be used to support model simplifications: With respect to factor prioritization, SA methods enable not only to determine important factors but also to describe the type of their relationship to the output. Knowledge acquired by such methods could be used to simplify models. As for factor fixing, one could screen out input-output relationships which might considerably increase model complexity although the uncertainty of the input under scrutiny has only negligible impact on the output uncertainty. In the opinion of the authors, both might ease otherwise complex tasks such as the determination of smart K_d-values (Stockmann et al. 2017) using complex surface complexation / ion exchange models.

Over the decades, a variety of increasingly powerful and often sophisticated SA methods were developed. For the practitioner, it might sometimes be hard to get an overview, to choose suitable SA method(s) and, more generally, to decide on a strategy appropriate for the problem at hand. However, when having a closer look one is able to detect systematics in this variety of methods and it even turns out that certain methods are closely related to each other (Borgonovo, Hazen & Plischke 2016, Borgonovo & Plischke 2016). Attempts have been taken to develop guidance for applying SA to practical problems (Kuhlmann et al. 2013, Kuhlmann, Plischke & Röhlig 2015). Currently, an international initiative supported by the OECD/NEA is underway which strives for an improvement and broader acknowledgement of such guidance (Becker et al. 2019), taking advantage from recent developments and improvements of SA methods (Plischke 2010, Plischke & Borgonovo & Smith 2013, Borgonovo & Plischke 2016) and using several "real-life" data sets.

The OECD/NEA initiative could well benefit from further complex datasets, e.g. from thermodynamic modelling or lab experiments. As explained above, the authors believe that the benefit could be mutual since SA methods might contribute to reducing model complexity.

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Cross-scale understanding and description of mineral precipitation processes in reactive transport models

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Dissolution and precipitation of minerals and its impact on the transport of fluids and solutes in porous media is a key factor for the long-term behaviour of natural and engineered systems in the subsurface. The implementation of such coupled processes into numerical reactive transport codes requires a mechanistic process understanding and model validation with quantitative experiments. In this context, we conducted a series of flow-through column experiments (at the cm scale) to investigate the effect of supersaturation on barite (secondary mineral) precipitation mechanisms (e.g. nucleation) following celestine (primary mineral) dissolution and consequential permeability changes. These experiments were modelled using the reactive transport code OpenGeoSys-GEM. The supersaturation strongly affects the nucleation rates and consequently the morphology of the newly formed phase. This, in turn, led to diverging changes of the pore architecture and the connectivity of the pore network of the porous medium, which, in combination with the varying surface roughness of the precipitates, have a distinct impact on permeability. This phenomenon is not covered by simple porosity-permeability relationships as implemented in most current reactive transport codes (Xie et al., 2015, Cochepin et al., 2008, Poonoosamy et al., 2018). In contrast, the Verma and Pruess (1988) relationship, introducing the concept of a critical porosity, gave more satisfactory results. The introduction of a critical porosity term in porosity-permeability relationships could thus be an elegant way forward to introduce pore-scale corrections into macroscopic transport models (upscaling) (Poonoosamy et al. 2019). Nevertheless, the parameterization of such empirical relationships still remains a challenge and needs to be tested and validated for different systems, and the physical meaning of the critical porosity needs to be explored further. For this purpose, pore-scale modelling taking into account precipitation scenarios in different pore geometries are used to determine up-scaled parameters and parameterize power law equations of porosity-permeability relationships for usage at the continuum scale (cf. Prasianakis et al. 2017). Moreover, in co-dissolution and precipitation systems, the dynamic evolution of the passivation processes depends on two intertwined processes: i) the dissolution of the primary mineral that is needed for the subsequent precipitation, and ii) the suppression of the dissolution reaction as a result of secondary mineral precipitation. The description of evolving reactive surface areas to account for mineral passivation mechanisms in reactive transport models following Daval et al. (2009) showed several limitations, and prompt for an improved description of passivation processes that include the diffusive properties of secondary phases. For a better understanding of passivation processes, a micromodel (µm scale) combined with Raman spectroscopic techniques is currently being used to investigate the mineral transformation at the pore scale *in situ* (see Fig. 1). The results will provide new insights regarding application and extension of the description of surface passivation processes consideration in continuum scale descriptions of system evolution with co-dissolution and precipitation.

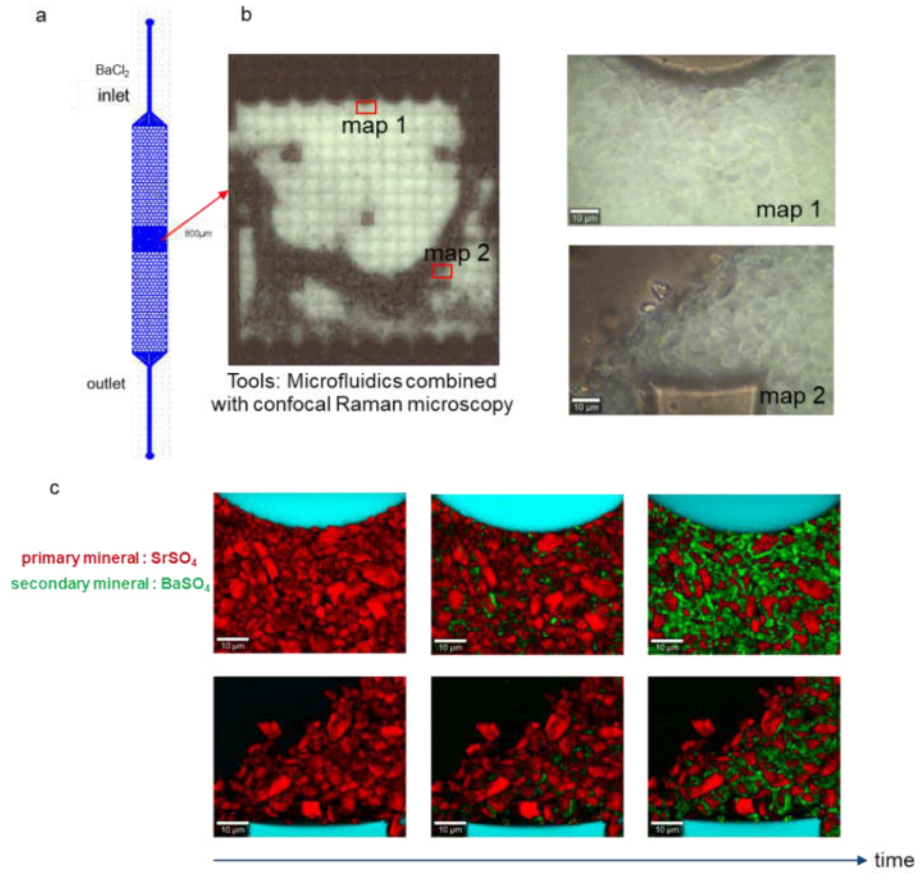

Fig. 1: a) A micronized flow-through experiment to understand dissolution/precipitation in porous media (micromodel), b) optical image of the porous media showing two regions map1 and map2, and c) Raman imaging of the evolution of map 1(top) and 2 (bottom)with time.

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TOUGHREACT, a simulation program embedded in the TOUGH suite of codes used in reactive transport modelling of the geological subsurface — some examples for large-scale systems

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A broad range of questions relevant for modern society regarding the potential and sustainability of the geological subsurface depend on reliable and validated numerical simulations. In many cases, the complexity of the problem, the vast number of model input parameters and their uncertainties, and the large scales in time and space that need to be considered require a careful approach in the generalization and formulation of the specific problem, as well as in the choice of appropriate numerical tools.
One of the established modelling software packages with worldwide use is the TOUGH suite of codes (Transport Of Unsaturated Groundwater and Heat) [LBNL, 2019]. Based on the integral finite difference method, TOUGH calculates nonisothermal multiphase flow in porous and fractured media in the geological subsurface. This simulator has been developed and enhanced continuously over four decades [e.g. Pruess, 1991; Pruess, 2004; Finsterle et al., 2014; Jung et al., 2017] and is accompanied by elaborate documentation [e.g. Pruess et al., 1999; Zhang et al., 2008; Jung et al., 2018]. Responding to and anticipating demands, various equation-of-state modules have been developed over the years, steadily enlarging the portfolio of the TOUGH software assets. The wide range of successful applications of this code has also been documented in numerous benchmarks [e.g. Pruess et al., 2004; Mukhopadhyay et al., 2015; Steefel et al. 2015, Marty et al., 2015, Arora et al., 2014].

The program TOUGHREACT is part of the TOUGH family, integrating reactive chemistry to the thermal and hydrological processes investigated using TOUGH2 [Xu et al., 2011, Sonnenthal et al, 2017]. Hence, this provides for modeling in a coupled manner multiphase fluid and heat flow, solute transport, and chemical reactions in the subsurface. Specific to the problem and the objectives to be considered, an optimization has to be found between, on one side computational cost and on the other side complexity, coverage, and resolution in space and time. The right balance between computing speed and accuracy is problem-specific and has to be found without compromising scientific results. These endeavors cover the range from basic and rather obvious approaches to more elaborate ones. Examples of applications will be presented in the fields of carbon capture and sequestration, geothermal use, and nuclear waste isolation, covering subjects such as parallelization and mesh optimization, spatial dimension reduction, taking advantage of symmetry, minimizing the number of geochemical variables, analytical solutions and superpositions, reduced-order models, and the integration of lookup tables in flow and transport simulations (references below).

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Smart K_d-concept as efficient approach to improve geochemistry in reactive transport modelling

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Understanding and appropriate modelling of geochemical processes is essential for predicting the contaminant transport in groundwater systems and, therefore, important in many application areas such as groundwater prediction, environmental remediation, or disposal of hazardous waste. One important natural retardation process is sorption on mineral surfaces of rocks or sediments. In order to treat the radionuclide sorption processes in natural systems more realistically, we developed the smart K_d-concept (www.smartkd-concept.de) to predict variations in sorption as consequence of changing physicochemical conditions which have to be considered in long-term safety assessments for radioactive waste repositories (Noseck et al., 2012, 2018; Stockmann et al., 2017).

In this presentation, we describe the fundamental strategy of the smart K_d-concept to calculate distribution coefficients (referred to as smart K_d-values) for a wide range of important environmental parameters. This mechanistic approach mainly based on surface complexation models and is combined with the "Component Additivity" approach to describe a natural system close to reality. This bottom-up approach based on the principle that the sorption of contaminants can be determined based on the competitive mineral-specific sorption of dissolved species on surfaces. Therefore, a full thermodynamic description of both the aqueous, solid and interface reactions is required. Using the geochemical speciation code PHREEQC (Parkhurst and Appelo, 2013), multidimensional smart K_d-matrices are computed as a function of varying (or uncertain) input parameters such as pH, ionic strength, concentration of competing cations and complexing ligands, e.g. calcium (Ca) and dissolved inorganic carbon (DIC). On the one hand, sensitivity and uncertainty statements for the distribution coefficients can be derived. On the other hand, smart K_d-matrices can be used in reactive transport codes (see abstract Noseck et al. 2020). This strategy has various benefits: (1) rapid computation of K_d-values for large numbers of environmental parameter combinations; (2) variable geochemistry is taken into account more realistically; (3) efficiency in computing time is ensured, and (4) uncertainty and sensitivity analysis are accessible. It is worth mentioning that the basic methodology described here can be transferred to any other transport code relying on conventional distribution coefficients as well as to any other complex natural site.

Results of a case study (serving as a comprehensive proof-of-concept) for a typical sedimentary rock system in Northern Germany as natural geological barrier for a deep geological repository site showed that the smart K_d-approach goes considerably beyond the conventional concepts. We can illustrate that constant K_d-values (see for U(VI) in Fig. 1, right, green line) previously used in transport simulations are a crude assumption, as in reality they rather range over several orders of magnitude. Moreover, with the results from the sensitivity analyses (SA) (Becker, 2016), the most important input parameters influencing the radionuclide retardation can be identified (key parameters of the model). The calculated sensitivity indices allowed us to assess the most and less sensitive parameters. From the visualized smart K_d-matrix for U(VI) (Fig. 1, left) it is obvious that mainly the pH value and the DIC influences the sorption of U(VI) under the given conditions. SA is a useful means for reducing the complexity of a geochemical model by focusing on the most important input parameters.

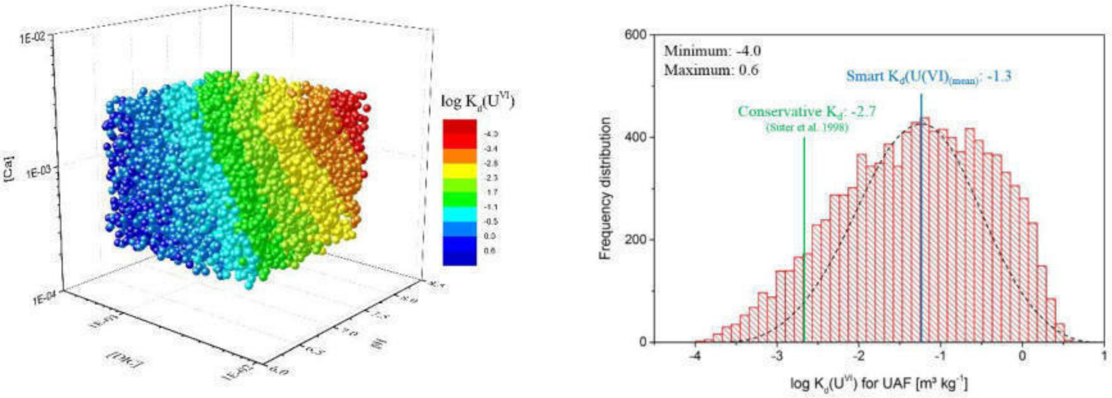

Fig. 1. Results for 10 000 pre-calculated smart K_d-values for U(VI) sorption in a sandy aquifer based on random sampling (K_d in m^3 kg^{-1}, logarithmic scale): Left: Multidimensional smart K_d-matrix as a function of pH, [DIC], and [Ca]. Right: Histogram with main statistical characteristics.

Acknowledgement:

This work is funded by the German Federal Ministry for Economic Affairs and Energy (BMWi) under contract Nos. 02 E 10518+02 E 10528, 02 E 11072A-B and 02E11668A-C.

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A Prediction of Uranium(VI) Diffusion in Montmorillonite at Various Chemical Solution Conditions

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Uranium (U) is the primary element in spent nuclear fuel, and a potential contaminant of water resources. Uranium sorption onto clay and its slow diffusive transport away from waste canisters are expected to limit U(VI) mobility, and possibly also control nuclear fuel degradation rates based on mass action considerations.

A prediction of U(VI) diffusion in these systems is complicated by two main factors: (1) the complex mineralogical structure of montmorillonite clay, leading to two types of clay porosities and surface sites, and (2) the dependence of U(VI) sorption on U(VI) solution speciation and the specific chemical system conditions. For instance, depending on pH and ionic strength, U(VI) may sorb onto montmorillonite due to weak ion exchange reactions or the formation of stable surface complexes. Furthermore, in contrast to conventional porous media, U(VI) diffusion in montmorillonite is not only limited by contaminant sorption, but also by a (potential) lack of access to the full clay porosity for some U(VI) solution species. For instance, at the high degrees of clay compaction expected in future barrier systems, the partial or full exclusion of U(VI) from negatively-charged clay interlayer spaces may substantially decrease U(VI) fluxes.

In this modeling study, we specifically investigated how the charge of U(VI) solution species affects U(VI) sorption and diffusion behavior. For this purpose, we first simplified complex *chemical* solution speciation diagrams to *charge* speciation diagrams. Then, we coupled an existing U(VI) surface complexation model (Tournassat et al., *Geochim. Cosmochim. Acta*, 2018) with an analytical solution of the diffusion equation to simulate U(VI) mobility in lab-scale through-diffusion experiments for various chemical conditions. Our results suggest that there are two important parameters that govern U(VI) diffusion in these systems. First, U(VI) surface complexation on clay edge surfaces leads to contaminant retardation. On the field scale, this will determine how early a plume may cross site boundaries and pose risks to drinking water resources. Second, the degree of access of U(VI) solution species to diffuse layers in clay interlayer spaces largely controls U(VI) diffusive fluxes. In the field, this parameter will govern the level of U(VI) concentrations that can be expected in contaminated waters.

Multiscale Modelling and Simulation of Geochemical Processes

Gabriel Wittum

Geochemical processes typically involve a lot of small scale events, i.e. intermediate steps, which do not deal with the quantities of interest on the final scale, but still are important for the outcome of the whole process. Topics like complex formation are highly relevant on the small scale and massively influence the final result. Modelling them as part of a long-range computation, however, causes serious complexity issues. Incorporating these effects into a large scale model is possible only by a strong reduction of the geochemical part of the model. Up to now, this is mainly done based on special Geochemical expertise. In this way, the Smart-Kd concept has been developed by Brändler and Noseck.

In Mathematics, however, there are several methods to formally achieve reduced models from known detailed ones. Homogenisation and coarse graining are well-known techniques mainly used for spatially strongly varying problems with periodicity. In Geochemistry, however, we are dealing with highly complex processes. Here, another approach from Mathematical Finance can be helpful. The method expands solutions of high dimensional problems by means of low dimensional ones. This can be very helpful for derving reduced models in Geochemistry. In the talk, these methods will be presented and applications will be shown.

Implementation of mineral-water interface reactions in models for use in environmental management and nuclear waste repository performance assessment

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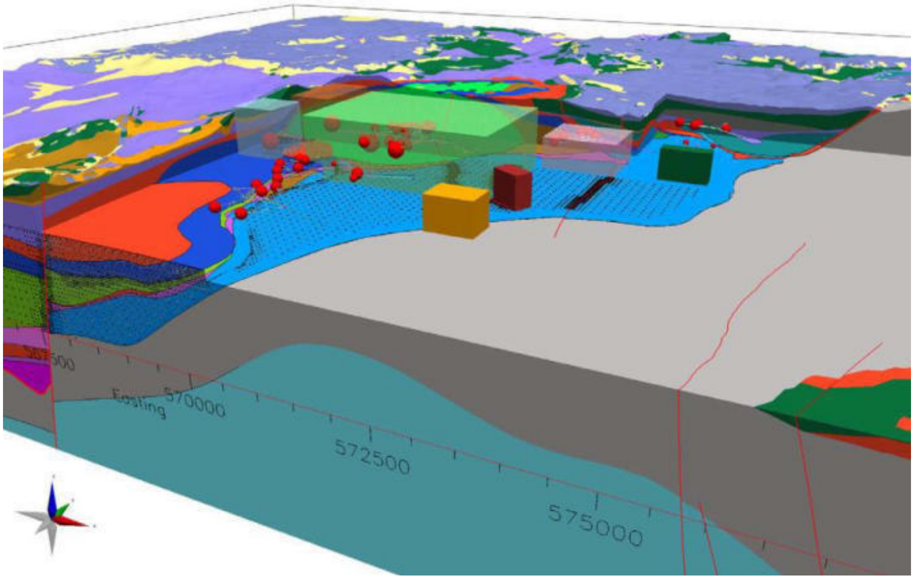
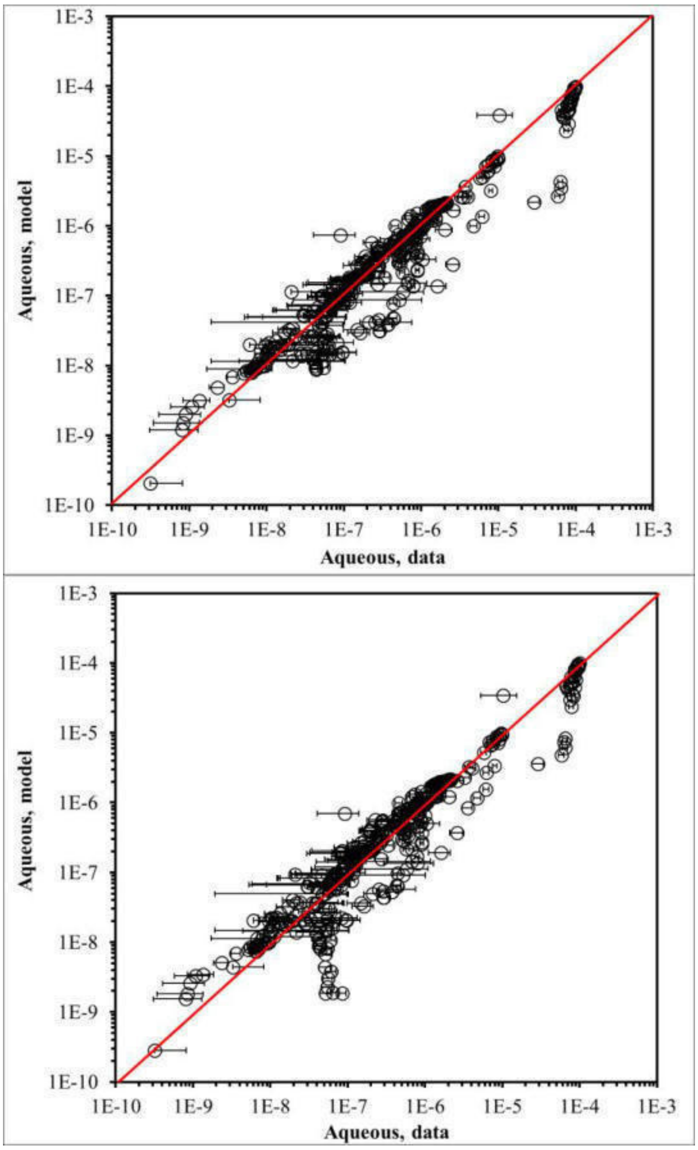
At the Nevada National Security Site (NNSS) in Nevada, USA, the Underground Test Area environmental management project has employed a number of reactive transport codes to simulate the migration of radionuclides in groundwater at the 1000 year timescale. Detailed reactive transport models (~1 km scale) have employed a combination of groundwater flow and mechanistic reactive chemical transport codes (e.g. OS3D/Gimrt; Crunch; CrunchFlow,[1] Parflow,[2] NUFT[3]) to simulate the migration behavior of radionuclides in groundwater away from underground source areas under thermally and geochemically transient conditions. The transport models explicitly included surface complexation and ion exchange reactions (along with mineral dissolution and precipitation) to address the effect of transient geochemical conditions and local formation variability on the reactive transport of radionuclides, especially at near-field scales near source areas. However, simplified geochemical models (i.e. Kd approaches) were employed to simulate transport at the larger spatial scales (>10 km). These simplifying assumptions were justified by the observation that transient geochemical conditions do not extend over these larger spatial and temporal scales. Thus, the Kd approach was deemed suitable. To integrate detailed reactive transport simulations with the (geochemically) simplified transport simulations used at larger scales, an upscaling approach was used to account for both uncertainty and variability in both the water chemistry and mineralogy along identified transport flow pathways and to incorporate those uncertainties into a bulk Kd parameter. This upscaling methodology proved to be an effective approach to address (1) geochemical complexities in the near field, (2) the need to simulate longterm (1000 year) transport over large spatial scales (>10 km), and (3) ensure consistency between models.



The NNSS Rainier Mesa testing area model domain and submodel domains embedded within the larger model (rectangular areas). From [11]

While the approach used at the NNSS was effective in helping resolve the regulatory requirements of this site, the cost of developing an effective surface complexation and ion exchange database for use in reactive transport modeling is very high. In addition, updating the surface complexation and ion exchange database proved to be very difficult and testing alternative approaches (e.g. various electrostatic models) proved to be intractable based on the manual data fitting approaches using adsorption data fitting routines such as FITEQL. The need for a more flexible surface complexation database development is clearly needed. Presently, this need is particularly prominent for nuclear waste repository performance assessment[4]. However, the best path for developing such databases remains an open question[5]. One approach, though somewhat painful, is to digitize raw sorption data available in the literature and develop models that capture sorption across the widest possible range of solution conditions in a comprehensive manner.

We have begun developing such an approach. References from the RES^{3}T database[10] are being digitized and data fitting routines developed using a combination of the (1) PHREEQC geochemical code [6], (2) PEST parameter estimation software [7], and (3) LLNL thermodynamic database [8]combined with the NEA Themchemical databases [9]. A critical component to this effort is the quantification of data uncertainty. At present, there are >5000 individual data points included in the database, focussed primarily on radionuclides and minerals relevant to the nuclear waste repository performance assessment needs in the United States. A test-case for U(VI) sorption to quartz demonstrates how a self-consistent set of surface complexation constants could be produced by simultaneously fitting ~500 batch sorption data digitized from the published literature (Figure 1). The approach provides a platform for testing various surface complexation models and assess their ability to capture available sorption data. This approach can provide a robust path forward for database development and testing. However, the upfront costs of sorption data digitization are quite large.



Comparison of simultaneous PHREEQC/PEST fit to >500 data of U(VI) sorption to quartz across a wide range of solution conditions using a non-electrostatic (top) and diffuse later (bottom) surface complexation models.

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POSTER PRESENTATIONS

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P2 Pharmaceuticals attenuation in groundwater bodies – *Laura Ceresa (Politecnico di Milano, Italy)*

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P4 Lab-Lysimeter Modelling – *Daniel Jara-Heredia (Friedrich Schiller University Jena, Germany)*

P5 Surrogate Modeling of Spatially Heterogeneous Source Terms for Probabilistic Assessment – *Paul Mariner (Sandia National Laboratories, USA)*

P6 The Up-scaling of Transport Phenomena in Groundwater and Soil as a Basis for Long-Term Considerations within Radioecological Modeling – *Veronika Ustohalova (Öko-Institut e.V. Darmstadt, Germany)*

P7 Preliminary safety assessments in the site selection procedure in Germany and the implications on the reactive transport modelling – *Johanna Wolf (Bundesgesellschaft für Endlagerung (BGE), Germany)*

P8 An efficient approach for modeling the reactive flow and transport processes in fractured porous media – *Tao Yuan (HZDR, Germany)*

THEREDA – Thermodynamic Reference Database

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The disposal of nuclear waste including the assessment of long-term safety is still an open question in Germany. Part of the process to assess the safety of disposal sites for radioactive or chemical-toxic waste is the predictive modeling of the solubility of hazardous components in a complex aqueous solution. In addition to the still pending decision about the repository host rock (salt, granite, or clay) the basic necessity of a consistent and obligatory thermodynamic reference database persists. Specific challenges are comprehensive datasets covering high temperatures and salinities. In response to deficiencies of other databases THEREDA, a joint project of institutions leading in the field of safety research for nuclear waste disposal in Germany and Switzerland, was started in 2006.

The core of THEREDA consists of a relational databank whose structure has been designed in a way that promotes the internal consistency of thermodynamic data. Data considered cover the needs of Gibbs Energy Minimizers and Law-of-Mass-Action programs alike. Pitzer coefficients to describe solute activity coefficients in high-saline solutions are considered. Both thermodynamic data and interaction coefficients can be described by temperature functions.

Ready-to-use parameter files are created from the databank in a variety of formats. Supported target codes are ChemApp, PHREEQC, EQ3/6, and Geochemist's Workbench. Data can also be downloaded in a generic JSON-type format to promote conversion for other geochemical codes Prior to their release all parameter files are submitted to internal test calculations – one essential element of the quality assurance scheme. The results are documented and provided to the users and accessible via internet through http://www.thereda.de.

Data are currently available to describe the solubility of the following radionuclides or fission elements: U(IV/VI), Th(IV), Np(IV/V), Pu(IV) Am(III), Nd(III), Cm(III), Tc(IV/ VII), Sr, Cs and the matrix elements (oceanic salt system, cement phases).

Future developments are thermodynamic data sets for Rubidium, Selenium and Oxygen in high saline solutions as well as the inclusion of low saline sorption data.

Pharmaceuticals attenuation in groundwater bodies

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Groundwater contamination by emerging micropollutants (EMPs) is a topic of increasing concern [5] due to potential threats caused by their accumulation in aquatic environments, which is conjectured even as these are usually found at trace concentration levels $[\frac{\mu g}{L} - \frac{mg}{L}]$. Pharmaceuticals (PhAs) constitute a highly monitored category of EMPs. These are characterized by an intrinsic chemical stability, which often results in their persistence in the environment, and capability to interact with biologically active substances, an element which might lead to bio-accumulation and bio-magnification. While documentation of experimental results on this subject is becoming increasingly frequent, albeit still scarce, robust interpretations of such results appear to be at times contradictory. Firm and systematic studies on Pharmaceuticals contamination in aquatic environments are then critical to broaden available information basis and embed it in a comprehensive theoretical framework leading to address attenuation mechanisms and degradation paths in groundwater and assist aquifer remediation and/or recovery for possible re-use. The approach which will be employed in this study is based on (a) grouping compounds belonging to the same PhAs categories (in terms of, e.g., structure and/or physical-chemical properties) and (b) focusing on representative compounds to document and quantify dominant transport mechanisms associated with these under specified environmental conditions.

The project will first focus on the RedOx sensitive, Non-Steroidal Anti-Inflammatory Drug (NSAID) Diclofenac (DCF) - commercially available as Sodium Diclofenac Salt (Na-DCF), $C_{14}H_{10}Cl_2NaNO_2$ - which is one of the most detected contaminants in European groundwater sources and is of high interest due to the peculiar behavior shown by its free acid ($C_{14}H_{11}Cl_2NO_2$) under anaerobic, denitrifying conditions in biotic environments. Indeed, microbial degradation of DCF has been documented to exhibit a partially reversible behaviour under anoxic denitrifying conditions [1], with temporary transformation products that are likely to be back-transformed to the parent compound when nitrate and nitrite have been depleted. In most aquifers characterized by wide RedOx zoning, the occurrence of this phenomenon is typically related to a decrease of RedOx potential below nitrate-reducing conductions, causing a switch from denitrifying to sulfate-reducing or even methanogenic conditions. As evidenced by Barbieri at al [1] [4], a similar behavior is exhibited also by the widely prescribed antibiotic Sulfamethoxazole (SMX). This is possibly correlated to the chemical structure of these molecules (i.e., DCF and SMX are primary and secondary aromatic amines undergoing nitrosation and desamination, respectively, under denitrifying conditions). Thus, a possible direction of investigation is to focus on microbial degradation of aromatic amines under the above-mentioned conditions, neglecting other attenuation mechanisms, such as, e.g., sorption. Indeed, according to several studies [2], Diclofenac sorption affinity to soils is only marginally relevant when compared to the extent of its metabolic and co-metabolic biodegradation in the presence of high Dissolved Organic Carbon (DOC) contents (which is a reducing agent in most aquifers under Managed Aquifer Recharge conditions). Despite this evidence, the precise mechanism governing DCF biodegradation is still poorly understood, also with specific reference to the reactions driving the reversible parent compound molecule drop and rebound in denitrifying conditions (i.e., only a possible microbial co-denitrication pathway has been proposed [3]). Nevertheless, the information available in the literature supports the possibility of the formation

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of specific transformation products (Figure 1).

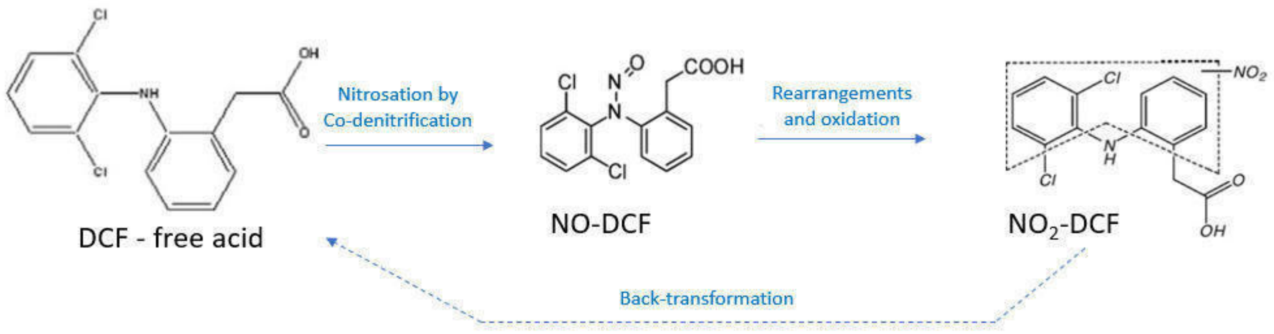

Figure 1: DCF free acid possible degradation pathway in the hyporheic regions of the aquifers.

These are often detected during batch-experiments, Nitro-Diclofenac derivative (NO_2-DCF) and N-Nitroso-Diclofenac derivative (NO-DCF) playing major roles in this context [1]. Here, a key goal of the investigation is to derive a robust geochemical model describing Diclofenac attenuation mechanisms and embed it in a transport framework, to simulate DCF fate along laboratory-scale porous media with a view to future transferability to field-scale groundwater bodies. The modeling goal will be achieved by incremental steps, i.e., starting from one-dimensional system to eventually move to more complex three-dimensional settings.

Once a firm and satisfactory modeling workflow is developed for the analgesics representative, it would be desirable to promote investigation efforts towards other classes of Pharmaceuticals (and the corresponding most detected representatives), such as antibiotics (Sulfamethoxazole (SMX)), anticonvulsants (Carbamazepine (CBZ)), lipid regulators (Gemfibrozil (GFZ)) and X-ray contrast agents (Iopamidol (IPD)), to provide a broader context to describe differing Pharmaceuticals attenuation processes in groundwater bodies.

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Numerical modelling of contaminant migration experiments in the crystalline single fracture models

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Migration of contaminants (radionuclides, heavy metals, nanoparticles) in crystalline rock environment is driven mainly by advective processes in fractures. The main goal of our project is to develop tools for evaluation of migration and retention of potential contaminants in the rock environment as the key input values for the safety assessment of anthropogenic activities. Since the naturally fractured environment is typically too complex to describe, it is common to mimic its behaviour by means of numerically simulated fracture network. The groundwork for applicable simulation of large-scale structures comes out from comprehension and verification of parameters for basic components such as a single fracture. For this reason, number of numerical simulations were performed to evaluate hydraulic and transport properties of an artificial and natural single fracture system by means of different modelling approaches.

Two granite blocks were split and reassembled to generate physical models with artificial fractures. Significant contribution to the exact model representation of the flow regime is the precise fracture topography description, derived from the method of the laser scanning. This allows the model resolution up to 100 μm for each of the two granite blocks used in the study and subsequently the identification of the preferential pathways of the contaminant spreading. Both blocks were customized for on-line measurement of the selected parameters (electric conductivity, concentration of ions, pressure), allowing performing of migration experiments with different conservative (NaCl, KCl, KI, HTO) and sorbing ($Pb(ClO_4)_2$, $Pb(NO_3)_2$) tracers. The focus of the numerical modelling effort is to fully describe the hydraulic and transport properties of the fractured granite environment based on the data from experimental tracer tests (Fig.1). Pressure field distribution across the fracture and breakthrough curves at the sampled positions were used for the fracture parameters calibration and evaluation of the model overall reliability (Fig. 2).

Radionuclide tracer (^{18}F) propagation in the fractured crystalline cores were studied in collaboration with HZDR (Leipzig, Germany). Spatiotemporal images of the tracer concentration during conservative transport were recorded with positron emission tomography (GeoPET), and the underlying fracture structure was characterized by μCT-imaging, which serves as a structural model for reactive transport modelling. First results indicate the opportunities in reactive transport analysis by using PET-μCT techniques, proving the existence of preferential migration pathways (Fig. 3).

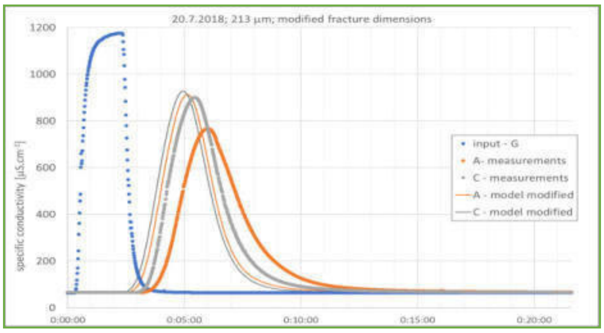

Fig. 1 Comparison of simulated and measured BTC with conservative tracer in the artificial fracture

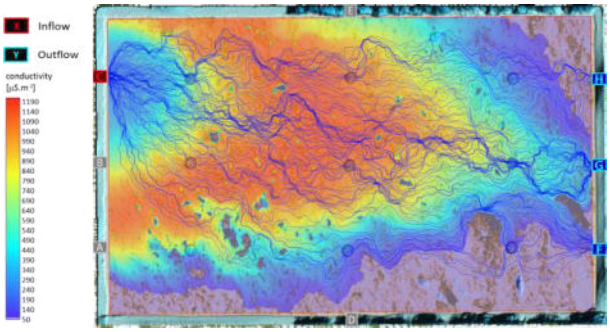

Fig. 2 Contamination cloud and particle trajectories simulation for multiple outflow experiment

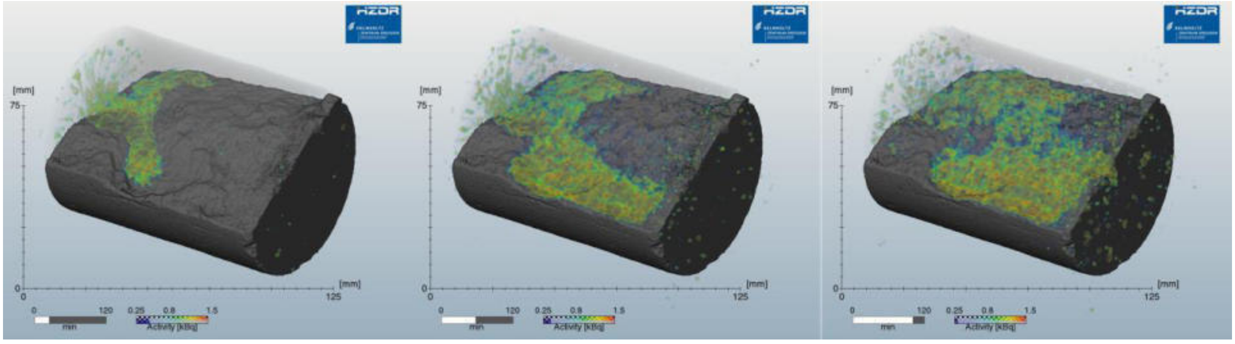

Fig. 3 GeoPET/µCT-imaging of the tracer propagation (^{18}F) in the natural fracture

The activities were funded by Czech Technological Agency under Project No. TH02030543 and NuWaMa project (Bundesministerium für Bildung und Forschung – BMBF)

LAB-LYSIMETER MODELLING

(TRANS-LARA PROJECT)

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High-level and long lived radioactive waste is planned to be stored for a safety assessment period of up to 1 Ma in deep geological repositories (POSIVA 2016; BGE). Although a safe multi-barrier system principle is generally accepted and conceptually designed, several accident scenarios should be assessed due to the uncertainties that arise from long time and large spatial scale.

The Trans-LARA project aims to clarify some of the factors that affect the transport of radionuclides from the saturated zone (groundwater) via the unsaturated zone to the biosphere overcoming the simplifications of transfer factors. Consequently, we set up four lab-lysimeter experiments using different types of soils representing various climatic evolutions (FraunhoferIME). Numerical simulations of the lysimeter column experiments will be carried out and compared against the outcome of the lysimeter column lab experiments, considering three main phenomena that take place: groundwater flow, vertical transport via the unsaturated zone and geochemistry.

The complex soil-liquid system is not trivial to model due to several reasons such as limited spatial resolution of data, lack of knowledge on the interplay between the different components (e.g. microbes), mathematical ill-conditioned systems, the difference heterogeneities among soils, etc. We approach such complex system by using a sorption component additive approach (Hormann 2015; Hormann and Fischer 2013), which is made up of illite as main active component in clay (Bradbury and Baeyens 2000; Bradbury and Baeyens 2009a, 2009b), hydrous ferric oxides (Dzombak and Morel 1990) and humic substances (Tipping, Lofts, and Sonke 2011; Marsac et al. 2017). Although, this chemical system can be solved within the classical reactive transport approach at the continuum scale where each representative element volume is in general treated as a batch reaction, the exploration of new techniques such as smart-Kd (Stockmann et al. 2017) or surrogate models (Jatnieks et al. 2016) is nowadays a must for two main reasons: 1) reduction of the computational time, since usually the computational time of chemistry is higher than the one of transport (van der Lee et al. 2003), 2) reduction of the complexity of the chemical system, e.g. Tipping model VII requires more than 50 mass action laws for each cation that interacts with the humic substance, making it prone to multiple assumptions.

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Surrogate Modeling of Spatially Heterogeneous Source Terms for Probabilistic Assessment of Repository Performance

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Process modeling of a waste package source term requires mechanistic simulation of coupled thermal-hydrological-chemical (THC) processes. Considerable computational time is needed for process modeling because a large set of nonlinear equations must be solved by iteration for each cell in the process model at each time step. For a repository performance assessment involving thousands of waste packages, thousands of time steps, and hundreds of realizations, the use of such a process model is prohibitively expensive.

Reducing the number of applications of a process model in a performance assessment by spatially and temporally homogenizing the source term to various extents is not a good solution. Spatial heterogeneity can be a dominant source of uncertainty in performance metrics. In fact, spatial heterogeneity is the dominant source of uncertainty in a generic reference case we are developing for a repository in crystalline rock with a stochastically-generated discrete fracture network (Chapter 8, Swiler et al. 2019). In that reference case, the mean waste package lifetime is on the order of 100,000 years, and the simulation time is one million years.

One way to dramatically reduce computational expense and to simulate each waste package individually is to develop surrogate models that can rapidly emulate the mechanistic process models. In 2018, a team of modelers and mathematicians at Sandia National Laboratories began exploring the potential value of developing a surrogate model for the Fuel Matrix Degradation (FMD) process model (Appendix A, Mariner et al. 2019). The surrogate model would be coupled to PFLOTRAN to permit emulation of the model in reference case repository simulations (pa.sandia.gov). The FMD process model is a complex mechanistic spent fuel dissolution model coded in Matlab and developed at Argonne National Laboratory and Pacific Northwest National Laboratory. The process model calculates spent fuel dissolution rates as a function of radiolysis, alteration layer growth, diffusion of reactants through the alteration layer, temperature, and interfacial corrosion potential. The model employs a one-dimensional reactive transport model to simulate diffusion and a set of aqueous and heterogeneous chemical reactions over time.

Three different types of surrogate models were developed to emulate the FMD process model: a polynomial regression surrogate, an artificial neural network regression surrogate, and a k-nearest neighbors regression (kNNr) surrogate. Results indicate that each of the surrogate models enables rapid and accurate prediction of spent fuel dissolution rates for each individual breached waste package in a probabilistic repository simulation, with the kNNr surrogate providing the highest accuracy at this point (Appendix A, Mariner et al. 2019).

The power of these surrogates is expected to be realized once we have them coupled to PFLOTRAN and we use them in probabilistic repository simulations. In such simulations, the coupled surrogate models will allow each source term across the repository to begin emulating the FMD process model as soon as its waste package breaches. This will allow assessment of the overall effects of these models and their input parameters on repository performance and will allow uncertainties in these inputs to be propagated and quantified as to their relative contributions to the uncertainties in output metrics. In addition, by simulating all waste packages individually, the coupled surrogates will allow spatial heterogeneity in the source term to be simulated with high resolution. Finally, on a practical level, two additional benefits of developing surrogate models are appreciated and expected: 1) the process of developing surrogate models provides an excellent test of the process model over the entire sampling space, and 2) surrogate models coupled to repository simulation codes are expected to have no trouble converging to solutions.

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The Up-scaling of Transport Phenomena in Groundwater and Soil as a Basis for Long-Term Considerations within Radioecological Modeling

Veronika Ustohalova, Manuel Claus, Christian Küppers

The proper consideration of radionuclide transport and retention in the geological formations and how they are affected by geochemical processes belong to the major radioactive waste disposal issues. The long-term safety assessment for the disposal of high-level radioactive waste shall demonstrate that the necessary permanent isolation of radioactive waste is ensured and that an unacceptable release of radionuclides into the biosphere is inhibited within a period of one million years. In the case of legacies or existent situations respectively (e.g. Asse mine), a consequence analysis must identify the possible burden to human in short as well as in long term under several possible scenarios of radionuclide release. The description of radionuclide migration through the engineer barriers and surrounding geological environment delivers the information about how far the ground water table and soil can be contaminated. This radioactive contamination is the initial condition for the assessment of radiological exposures where radionuclides are transferred along several exposure pathways. Radioecological modeling is a key element of such assessments whereby it identifies and quantifies processes taking place. Radioecological models deliver reliable estimates of possible radiological exposures by taking into account all the integral parameters playing role during radionuclide release in the surrounding rock layers and transport into the biosphere as well as by radionuclide transfer along exposition pathways to human. It must be fitted in dependence on the question: e.g. fast estimation of a radiological exposure in the case of a legacy where the results must be delivered in a relatively short term or a proper analysis within the long-term safety assessment of a planned repository. One of the main questions is how fare the investigated processes on the micro scale influence the macroscale transport and which simplifications/assumptions can be taken (up-scaling).

On behalf of the Federal Ministry of Environment we originally developed a radioecological model for estimating possible doses to human in long-term (e.g. thousands of years) that had to show which dose values could be relevant in the case of the Asse II mine collapse with an uncontrolled inflow of brine. Here, one dimensional transport was considered by using the analytical solution of the dispersion convection transport equation whereby the sorption, solubility limits and special aspects of decay chains migration had to be taken into account in a suitable way. For this reason, we discussed the microscale aspects of sorption and solubility with the Institute for Nuclear Waste Disposal at the Karlsruhe Institute of Technology (KIT-INE). They determined and suggested the value ranges of sorption coefficients K_d of the relevant radionuclides and solubility limits for the purposes of our model. In the next step the parameters of the radioecological modelling were tested for the meaningful possibility of variation with the Monte Carlo method. The corresponding distribution functions, parameter dependencies and correlations were identified. For the first time the radiological exposure along the relevant pathways was estimated under not equilibrated conditions for the case of short-time expositions. This model allowed the comparison of various possible exposition scenarios in order to find the worst case.

Currently, this model is a basis for the model development with the software ECOLEGO[1] within the research project Trans-Lara[2]. The aim of the Trans-Lara project is to gain deeper understanding of radionuclides behavior in the far field of a nuclear repository site (biosphere). The project results should contribute to the improvement of risk assessments for the exposure of the population over long time periods. A major step forward should be the understanding of the several absorption mechanisms of selected radionuclides (Pu, Tc, I, Se; also involved U, Cm, Am) in the soil and in the crop plants at the molecular level, a concept allowing for much better significance in comparison with “previous” transfer factors. Öko-Institut’s research in the project encompasses mainly aspects of soil genesis under long-term climatic changes and radioecological modeling. We consider radionuclide migration from the groundwater table via the soil into the plants under long-term climatic changes. Beside the modeling of transport processes in a soil in long term, a model for radionuclide uptake into the plant at the cellular level will be developed on our part.In this process we cooperate with our project partners on experiment design devel-

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[1] https://ecolego.facilia.se/

[2] https://www.trans-lara.de/; a joint project granted by German Federal Ministry of Education and Research (BMBF) in the field of "Basic R&D work in nuclear safety and disposal research to promote scientists and maintain competence" within the framework of the funding concept "Basic Energy Research 2020+". Project partner: Institute for Geosciences of the Friedrich Schiller University Jena (FSU AnGEO); Institute for Resource Ecology of Helmholtz-Zentrum-Dresden-Rossendorf (HZDR IRE), Institute for Environmental Physics, University of Bremen (UB IUP), Institute for Radioecology and Radiation Protection (LUH IRS – project lead) and Department of Cell Physiology and Biophysics of Leibniz University Hannover (LUH IfB)

opment and conducting experimental investigations as this is important for the agreement on which parameter values are to be experimentally investigated and used in the model. Figure 1 shows the link between experiments and modeling. The soil laboratory analysis on a microscale and soil experiments on a mezzoscale (lysimeter) provide the basic information on soil texture, sorption behavior and soil transport characteristics while plant experiments on a cellular scale investigate the radionuclide uptake of the plant. One of the key transport parameters is the K_d-coefficient. UP-IUP has derived the K_d-Matrix (smart-K_d similar concept) describing the radionuclide complexation at the soil surface (clay, sesquioxides, organic matter) in dependence on the values of pH/pe and redox potential with the PHREECQ model. The transport model of the FSU Jena uses this information and describes the transport in the lysimeter at the mezzoscale (Software iCP). The Öko-Insitut's model in ECOLEGO (Figure 2) takes into consideration the transport on the field scale in the vadose zone (tool Transport in Soil). In parallel, we test and compare model results of this tool with our project partners from FSU Jena. The investigated concentration in the capillary fringe nearby the root zone is the input for the plant uptake (tool Transfer in Plant) and finally for the human exposure due to plant ingestion (tool Exposition). The parameter variability is finally investigated by a Monte-Carlo analysis.

Within the workshop we are interested in a discussion on how to consider the results of the dedicated geochemical concepts in reactive transport modeling at the small space and time scale within the long-term safety assessment for a repository or within a consequence analysis and what the suitable averaging approaches are.

Figure 1: Interfaces Experiments-Modeling

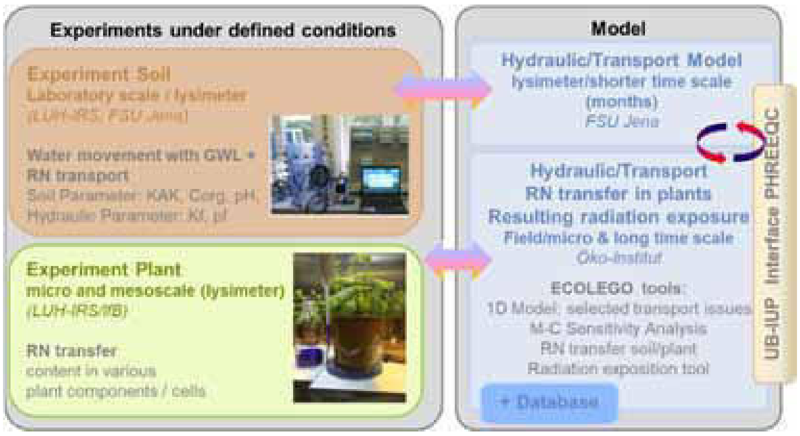
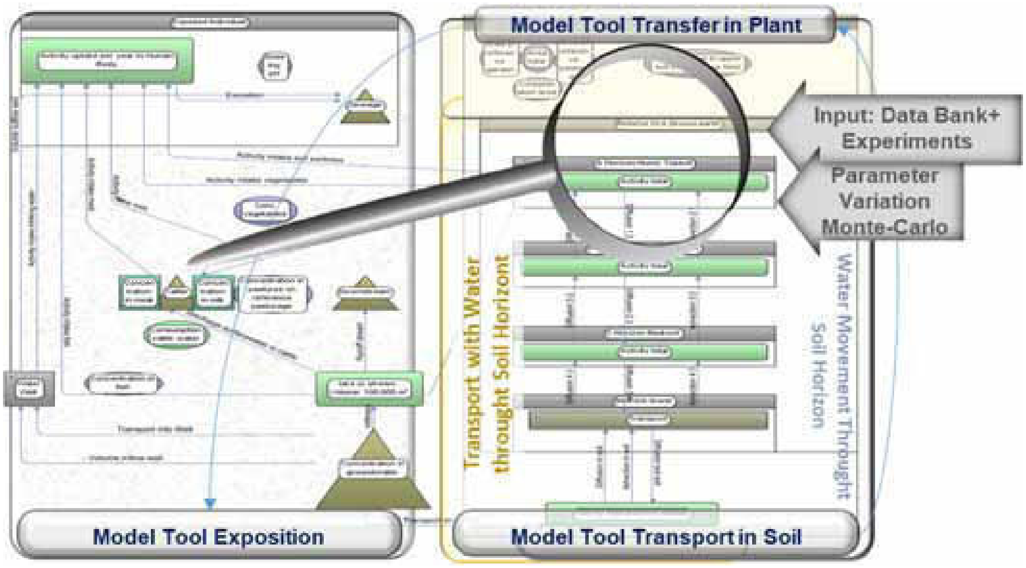


Figure 2: ECOLEGO Model Tools



Preliminary safety assessments in the site selection procedure in Germany and the implications on the reactive transport modelling

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In Germany, the site selection for a repository for high level radioactive waste in deep geological formations was restarted in 2017 with the Repository Site Selection Act[1] coming into force. The Site Selection Act envisages Preliminary Safety Assessments as a tool to account for the safety of a considered site. The Federal Ministry for Environment, Nature Conservation and Nuclear Safety provided a draft[2] for the legimate requirements on the Safety for the disposal of high level radioactive waste as well as the requirements on the Preliminary Safety Assessments in summer 2019.

In this contribution, the significance of the Preliminary Safety Assessments within the site selection process will be presented. In this context, the difference between Preliminary Safety Assessments and the actual Safety Case will be discussed. The main focus of the contribution will be the methodology of the Preliminary Safety Assessments as it is derived from the safety requirements. Concluding, the implications on modelling requirements, especially on the reactive transport modelling, will be pointed out.

[1] Standortauswahlgesetz vom 5. Mai 2017 (BGBl. I S. 1074), das zuletzt durch Artikel 3 des Gesetzes vom 12.Dezember 2019 (BGBl. I S. 2510) geändert worden ist

[2] Referentenentwurf, Verordnung über die sicherheitstechnischen Anforderungen an die Entsorgung hochradioaktiver Abfälle, Bearbeitungsstand: 11.07.2019 15:08 Uhr, Artikel 1:
Verordnung über Sicherheitsanforderungen an die Endlagerung hochradioaktiver Abfälle (Endlagersicherheitsanforderungsverordnung – EndlSiAnfV), Artikel 2: Verordnung über Anforderungen an die Durchführung der vorläufigen Sicherheitsuntersuchungen im Standortauswahlverfahren für die Endlagerung hochradioaktiver Abfälle (Endlagersicherheitsuntersuchungsverordnung – EndlSiUntV)

An efficient approach for modeling the reactive flow and transport processes in fractured porous media

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The coupled subsurface reactive flow and transport processes play an important role in fractured porous media like carbonate formations, which lead to dynamic changes in rock properties. These dynamic changes can cause the evolution of a natural fracture system and can eventually cause important issues such as limited hydrocarbon production in the petroleum reservoir as well as a failure of geological CO_2 sequestration. An efficient numerical model that can rigorously capture such coupled phenomena is thus essential to the optimized design of implementations for those addressed problems.

In this contribution, we present a 3D mathematical model that couples the Stokes-Brinkman equation and reactive transport model for modeling the coupled processes of reactive flow and transport in fractured porous media. Applying the Stokes-Brinkman equation for modeling reactive flow in fractured porous media is advantageous with a single set of equations over the entire domain, providing a feature that allows us to efficiently model the alterations of rock properties, such as porosity and permeability. The reactive transport model describes the coupled processes of solute transport and geochemical reactions in the geological subsurface. The proposed numerical model can be applied to describe both linear and radial flow for different scenarios. We then employ a decoupled approach to sequentially solve the Stokes-Brinkman equation and the reactive transport model. The numerical experiments show that the proposed model can efficiently simulate the coupled processes of fluid flow, reactive transport, and alterations of rock properties in fractured porous media under both linear and radial flow. The sensitivity case studies can provide valuable guidelines for designing the operation and treatment in oil and gas production.

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