Transport for the Earth and Environmental Sciences in the 21st Century

October 2nd – October 5th

Chateau du Clos de Lucé

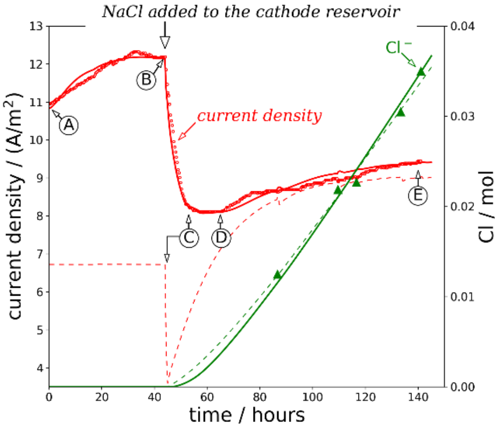
Amboise

Extracting the chemical and physical properties of concrete pores from electro-migration experiments

C.A.J. Appelo

appt@hydrochemistry.eu

An electrical potential gradient enhances the diffusion of charged species and facilitates the determination of the diffusion coefficient of Cl^-, a major factor for the corrosion of steel in concrete. However, to model both the measured Cl^--breakthrough and the current is a challenge, as illustrated in the figure with experimental results of Friedmann (2004, CCR 34, 1967). Concrete was cured with (Na,K)OH solution, and the same solution was placed in anode and cathode reservoirs at the column ends. A 3 Volt gradient was applied over the 1 cm sample, and, after 44 hours, NaCl was added to the cathode reservoir. The current falls when NaCl is added since Cl^-, with a smaller diffusion coefficient than OH^-, partly replaces OH^- in the column while the total anion concentration remains the same, because Na^+ must diffuse against the electric gradient. When Cl^- arrives at the anode, the current increases by slow Na^+ diffusion. The dashed lines show results of the Nernst-Planck equation (NP) as traditionally applied, with a good fit for Cl^-, but incorrect for the current density.



From points A to B, the current increases with time, but NP keeps it fixed at much too small value. At point C, Cl^- arrives at the anode and the current-fall stops. NP lets the current arrive 10 hours earlier and jump up sharply.

The model improves (full lines) when NP is extended with kinetic dissolution of cement minerals for the current increase from A to B; ion exchange of Cl^-/OH^- for the Cl^- retardation; stagnant and mobile water exchange for the current plateau from C to D; an electrical double layer in the pores that slows the diffusion of Na^+ and reduces the current increase rate from C to E.

Imaging and Modeling of Flow and Reactive Transport in Subsurface Rock and the Importance of Distribution Functions

Branko Bijeljic, Department of Earth Science and Engineering, Imperial College, London, UK

Understanding of flow, transport and reaction processes in the subsurface has been transformed by the advances in both X-ray imaging and pore-scale modeling. More accurate experimental description of solid and fluid(s) distributions in the pore space and the ability to study dynamics of multi-phase flow and reactive transport has helped better understand fundamental physics of these processes, and enabled new concepts for validation of theoretical models at the pore scale and using them for pore-to-core scale predictions and upscaling.

A digital rock analysis methodology based on probability distribution functions (PDFs) is demonstrated through determination of the signatures of flow, transport and reaction in subsurface rock. Pore-scale imaging and modeling on voxelised representation of pore space makes it natural to introduce the intrinsic functions characterizing flow, transport and reaction in the form of distributions, rather than average values. This concept is illustrated by the predictive modeling of flow and transport on micro-CT images of a beadpack, a sandstone, and a carbonate, representing porous media with an increasing degree of pore-scale complexity.

Furthermore, this concept is applied for highly complex processes such as coupling transport with fluid/fluid reaction or fluid/solid reaction in porous media. Modeling of fluid/fluid reactive transport on micro-CT images is validated with benchmark experiments starting from the reaction in homogeneous beadpacks and expanding it to study more complex pore structures under a range of flowrates and reaction rates in order to predict the coupled behaviour. Modeling of fluid/solid reactive transport on micro-CT images is validated by dynamic X-ray tomography experiments in which brine-equilibrated supercritical CO2 is injected in a limestone at reservoir conditions. The changes in porosity, permeability, velocity field and transport behaviour are characterized by PDFs. Using the concept of PDFs characterizing heterogeneity for each scale of interest, an upscaling methodology can be applied first from pore to core scale and then extended to the block and field scale.

The next level of complexity is studying reactive transport in chemically heterogeneous reservoir rocks, and combining reactive transport and multi-phase flow processes. New experimental and modelling methodologies can offer new insights into the physics of pore-scale processes and help develop predictive modeling of multi-phase flow and reactive transport.

Coupling reactive transport models with specific alteration models for engineered materials: the example of steel corrosion

O. Bildstein

CEA, DEN, DTN/SMTA/LMTE, 13108 Saint-Paul-lez-Durance, France

The predicting of the long term behavior of natural and engineered materials is largely based on reactive transport modeling (RTM). In the context of deep geological disposal of radioactive waste, a variety of materials will be introduced into the host-rock (claystone, granite) including glass, metallic components, bentonite, and concrete. In most cases, these materials can usually be dealt with in common RTM since they do not require any specific geochemical capabilities. This is also valid for complex materials such as glass, at least as long as the kinetic formulation can be cast into the existing ones (see presentation of P. Frugier). This approach is however limited with steel when the corrosion rate has to be calculated as a function of the local chemistry (Bildstein et al., 2016). In this case, the coupling between a RTM and a specific electrochemical model may be required.

For this purpose, the CEA has developed a model (Calipso) to simulate the corrosion of low alloy steel in reducing anoxic conditions using the “Diffusion Poisson Coupled Model”. In this model, iron corrosion is described as a series of electrochemical reactions occurring at the surface of the steel and/or a protective oxide layer, and the transfer of charge under electrical potential gradient in this latter layer (Bataillon et al., 2010). In the model, all the processes take place in the solid and the RT system is solved on a discretized domain with moving boundaries.

The coupling between Crunchflow and Calipso is presented in this session, showing the concept and the key interacting parameters, as well as the assumptions made to ensure the consistency between the two models. Preliminary results and specific points, such as charge balance, will also be discussed.

Bataillon, C., Bouchon, F., Chainais-Hillairet, C., Desgranges, C., Hoarau, E., Martin, F., Perrin, S., Tupin, M., Talandier, J. (2010) Corrosion modelling of iron based alloy in nuclear waste repository. Electrochim. Acta 55 (15), 4451-4467.

Bildstein O., Lartigue J.E., Schlegel M.L., Bataillon C., Cochepin B., Munier I., Michau N. (2016) Gaining insight into corrosion processes from numerical simulations of integrated iron-claystone experiments, Geological Society, London, Special Publications, 443

Reactive surface areas in 1D and 2D RT simulations of the interaction between sedimentary rocks and CO_2-rich waters

Jordi Cama

In the context of the geological sequestration of CO_2 we have performed a number of flow-through experiments (columns filled with crushed rock samples; Garcia-Rios et al., 2014; Davila et al., 2016a; Thaysen et al., 2016) and percolation experiments (artificially fractured cores; Garcia-Rios et al., 2015; Davila et al., 2016b, 2006c) in the laboratory. The rock samples were representative of the reservoir rocks (limestone and sandstone) and cap rocks (argillaceous limestone and marls) at the Hontomín site (Spain). In these experiments, acidic sulfate-rich solutions were injected into the columns. The composition of the outflowing solutions was continuously monitored and the reacted solids were analyzed after the end of the experiments. Different pCO_2 conditions were implemented.

The CrunchFlow code (Steefel et al., 2015) was used for the 1D and 2D reactive transport modeling of the experiments. Model fit to the experimental observations was performed by adjusting the values of mineral surface areas, using reaction rate laws from the literature. Additionally, in the 2D simulations (fractured cores), diffusion coefficients in the rock matrix also had to be adjusted. An important result from the calculations was the extent of mineral reaction and porosity changes inside the columns. In general, the calcite surface area had to be diminished with respect to initial geometric values, which may be explained by transport control of the fast calcite dissolution. Different flow conditions also resulted in different values of the calcite surface area, reflecting different degrees of transport limitation. In contrast, the values for aluminosilicates (illite, clinochlore, albite) had to be increased, possibly due to differences in size, shape and surface roughness.

Accurate values of reactive surface areas, including transport control of fast reacting minerals (e.g. calcite), are important factors to take into account when trying to predict mineralogical and porosity changes during CO_2 sequestration.

References

Davila et al., (2016a) Chem. Geol. 448, 26-42.
Davila et al., (2016b) Int. J. Green Gas Control 48, 105-119.
Davila et al., (2016c) Int. J. Green Gas Control 54, 145-159.
Garcia-Rios et al. (2014) Chem. Geol. 383, 107-122.
Garcia-Rios et al. (2015) Chem. Geol. 414, 95-108.
Steefel et al. (2015) Computat. Geosci. 19, 445-478.
Thaysen et al. (2016) Chem. Geol. 450, 31-43.

The role of interlayer cations in the montmorillonite dissolution kinetics: experimental data and RT modeling

Jordi Cama

The dissolution kinetics of K-montmorillonite was studied at 25 °C, acidic pH (2-4) and 0.01 M ionic strength by means of well-mixed flow-through experiments. The variations of Si, Al and Mg over time resulted in high releases of Si and Mg and Al deficit and also in long periods of incongruent dissolution before reaching stoichiometric steady state. This behavior was caused by simultaneous dissolution of nanoparticles and cation exchange between the interlayer K and released Ca, Mg and Al and H.

The effects of pH and the degree of undersaturation on the K-montmorillonite dissolution rate were determined using R_{Si}. Employing dissolution rates farthest from equilibrium, the catalytic pH effect on the K-montmorillonite dissolution rate was expressed as $R_{diss} = k \cdot a_H^{0.56 \pm 0.05}$ whereas using all dissolution rates, the ΔG_r effect was expressed as a non-linear $f(\Delta G_r)$ function

$$R_{diss} = k \cdot \left[1 - exp\left(-3.8 \times 10^{-4} \cdot \left(\frac{|\Delta G_r|}{RT}\right)^{2.13}\right)\right]$$

The functionality of this expression is similar to the equations reported for dissolution of Na-montmorillonite at pH 3 and 50 °C (Metz, 2001) and Na-K-Ca-smectite at pH 9 and 80 °C (Cama et al., 2000; Marty et al., 2011), which lends support to the use of a single f(ΔG_r) term to calculate the rate over the pH range 0-14. Thus, we propose a rate law that also accounts for the effect of pOH and temperature by using the pOH-rate dependence and the apparent activation energy proposed by Rozalen et al. (2008) and Amram and Ganor (2005), respectively, and normalizing the dissolution rate constant with the edge surface area of the K-montmorillonite.

1D reactive transport simulations of the experimental data were performed using the Crunchflow code (Steefel et al., 2015) to quantitatively interpret the evolution of the released cations and to elucidate the stoichiometry of the reaction. After the implementation of (i) the obtained f(ΔG_r) term in the K-montmorillonte dissolution rate law, (ii) a fraction of highly reactive nanoparticles and (iii) the cation exchange reactions between the interlayer K^+ and the released Al^{3+}, Mg^{2+}, Ca^{2+} and H^+, the simulations agreed with the experimental concentrations at the outlet. This match indicates that fast dissolution of nanoparticles and exchange between the interlayer K and dissolved structural cations (Al and Mg) and protons are responsible for the temporary incongruency of the K-montmorillonite dissolution reaction.

References

Amram K. and Ganor J. (2005). Geochim. Cosmochim. Acta 69, 2535-2546.
Cama et al. (2000). Geochim. Cosmochim. Acta 64, 2701-2717.
Marty et al. (2011) Geochim. Cosmochim. Acta 75, 5849-5864.
Metz (2001) PhD Thesis BGU of the Negev.

Rozalén et al. (2008). Geochim. Cosmochim. Acta 72, 4224-4253.
Steefel et al. (2015) Computat. Geosci. 19, 445-478.

Modelling of reactive transport, multiphase flow and double porosity in a concrete cell storing radioactive waste at El Cabril (Spain)

M. Carme Chaparro[a,c] and Maarten W. Saaltinkb[b,c]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Jordi Girona 18, 08034, Barcelona, Spain, e-mail: mcarme.chaparro@gmail.com
[b] Department of Civil and Environmental Engineering, Universtitat Politècnica de Catalunya (UPC), JordiGirona 1-3, 08034 Barcelona, Spain, e-mail: maarten.saaltink@upc.edu
[c] Associated Unit: Hydrogeology Group (UPC-CSIC), Spain

‘El Cabril’ is the low and intermediate level radioactive waste disposal facility of Spain. Water with high concentration of tritium is collected from a drain, which is situated at the centre of a concrete cell that stores radioactive waste, indicating flow of water within the cell. 2D numerical models have been made in order to develop a qualitative and partial quantitative understanding of the processes that causes this phenomenon. The conceptual model considers evaporation and condensation processes due to temperature gradients, matrix diffusion between a mobile zone (with advection, dispersion and diffusion) and an immobile zone (with only diffusion). The numerical model shows that this phenomenon is caused by capillary rise from the groundwater, evaporation and condensation within the cell produced by temperature gradients caused by seasonal temperature fluctuations outside (1,2). In addition to this model, a reactive transport model has been developed, in order to study qualitatively the changes in the mineralogy of the concrete due to the interaction between the groundwater and the concrete cell.

References:

[1] Chaparro, M. C. and Saaltink, M. W. (2016), Water, vapour and heat transport in the concrete cells for storing radioactive. Advances in Water Resources, 94:120-130.
[2] Chaparro, M. C. and Saaltink, M. W. (2017), Modelling tritium transport, matrix diffusion andmultiphase flow in a concrete cell used for storing radioactive waste at ’El Cabril’ (Spain), 9th Workshop of CODE_BRIGHT Users, Barcelona, Spain, p.1-6.

Sensitivity Analysis of Complex Biogeochemical Models using Bayesian Networks

Xingyuan Chen[1], Heng Dai1, Ming Ye[2], Xuehang Song[1], Glenn Hammond[3], and John M. Zachara[1]

[1]Pacific Northwest National Laboratory, Richland, WA 99352, USA.
[2]Department of Scientific Computing, Florida State University, Tallahassee, FL 32306, USA
[3]Sandia National Laboratories, Albuquerque, NM 87123, USA
*Corresponding Author, Email: Xingyuan.Chen@pnnl.gov, Phone: (509) 371-7510.

Abstract

Sensitivity analysis is a vital tool in numerical modeling to identify important parameters and processes that contribute to the overall uncertainty in model outputs. Conventional methods of sensitivity analysis are focused on identifying important individual model parameters, despite the complex dependence between uncertain model structures and parameters. We developed a new method of sensitivity analysis to quantify relative importance of model processes that consist of multiple parameters and implemented it to a real-world biogeochemical model at the groundwater-surface water interface at the Hanford Site's 300 Area. Our method is based on the concepts of Bayesian networks and hierarchical uncertainty structure. The uncertainty structure of a complex system model system is represented by a Bayesian network, which allows the inference on flexible combinations of different uncertain inputs given their characteristics and dependency structures. It also allows the hierarchical decomposition of uncertainty contribution using the Bayesian theory. The uncertainty of a biogeochemical product (i.e., carbon consumption) quantified by a biogeochemical model arise from three primary physical processes based on our understanding of the complex system — flow process, heat transport process and reactive transport process. Each physical process has uncertainty in its driving forces, properties, and parameters. In operator splitting style of process coupling, the velocity fields output from the flow process serves as inputs for both the heat and reactive transports and both velocity and temperature fields are inputs to the reactive transport process. A Bayesian network was built to represent this real system for hierarchical sensitivity analyses. The results demonstrate that the groundwater flow process is the most important source of uncertainty for carbon consumption predictions. Within the groundwater flow process, the structure of geological formations is more ,important than the permeability heterogeneity within a given geological formation. This new sensitivity analysis framework, based on the Bayesian networks, brings great flexibility in investigating the importance of combinations of uncertainty sources, and it is suited for a wide range of multi-physics models for complex systems.

Alkaline plume in the Aptian Sand Aquifer in the Context of Low- Level Radioactive Waste Surface Disposal

Benoit Cochepin, Isabelle Munier, Benoît Madé

The storage vaults for low and intermediate-level short-lived radioactive waste in the East of France are settled on the Aptian sand layer. In the context of the periodic examination by the nuclear regulators, it has been recommended to assess more precisely the chemical conditions for a potential release of radionuclides in the underlying water table. In particular, this study aims at assessing the eventuality of spreading an alkaline plume in the Aptian sand pore water by the chemical degradation of the vault cementitious materials.

The numerical approach developed for this purpose is supported by both experimental characterizations of tracers in the water table and results from preliminary numerical studies on the hydrology of the site and the hydraulic evolution of the storage. The results from these specific simulations were simplified in the reactive transport model to focus on the mechanistic description of the chemical processes taking place in the waste and vaults and on their consequences on the underlying water table.

During the operating period of the disposal, the reactive transport modelling shows that the low water saturation in the vaults material and in the vadose zone prevents the aquifer from a significant increase of the water pH under the cement-based vaults. These results are in reasonable agreement with the pH regularly measured in the underlying water table.

After storage closure, during the few hundred years of the monitoring period and furthermore beyond, the reactive transport modelling shows a noticeable release of hydroxyls and alkali ions under the disposal vaults and their spread downstream the storage site leading to pH values above 10. It is noteworthy that the pH is not buffered in the Aptian sands because of their low amount in clayey minerals. This effect is now considered for pH-sensitive radionuclide solutes in safety assessment calculations by weighting correspondingly their retention parameters.

Considering gases in reactive-transport codes

Jérôme Corvisier

Geochemical and coupled reactive-transport codes, CHESS and HYTEC respectively, improved recently their representation of the gas phase, of its interaction with water, salts and rock and even of its mobility.

The integration of analytically solved cubic equations of sate (such as Peng-Robinson) and of their appropriate parameters, and of adapted splited flow/transport solvers allow to reproduce nicely laboratory measurements as well as some CO_2 storage field observation with reasonable computing times. The obtained numerical results are very satisfactory when compared to both existing experimental data and numerical models. The relative simplicity of our approach (i.e. same EOS for each compound and limited parametrization) shall also be highlighted as it leads to comparable results.

CHESS/HYTEC are now able to handle non-ideal gas mixtures and then to simulate the injection/storage of high pressure complex gases into the undeground. They consequently offer important opportunities within various fields of applications such as CO_2 geological storage with impurities, or gas (CH_4, H_2…) storage in salt caverns.

Fracture evolution in multi-mineral systems: the role of mineral compositions, flow rate and geometric heterogeneity

Hang Deng, Carl Steefel, Sergi Molins, Donald DePaolo

Fractures are the preferential flow pathways in porous media, and are highly relevant to many geological applications. The hydraulic properties of fractures are largely dependent on heterogeneities in fracture apertures, and can be altered by the presence of reactive fluids and their interactions with the rock matrix. Geochemical reactions further complicate the characterization and prediction of fracture hydraulic properties because these reactions strongly depend on factors - such as mineral composition – that are highly heterogeneous as well. The role of mineral heterogeneity on fracture evolution, however, has been rarely investigated.

The objective the current study is to investigate fracture evolution in multi-mineral systems under different flow conditions and with different levels of geometric and mineralogical heterogeneities. This investigation is enabled by the recent development of a reduced dimension reactive transport model. The model was developed and tested based on experimental studies, and addresses the complex morphological and geochemical changes arise from multiple minerals of different reactivities. Sets of numerical experiments using the reduced dimension model were performed with controlled flow conditions, initial fracture geometries, and geochemical conditions like mineral compositions. Based on the results of the numerical experiments, a general framework following the concept of the Damkohler number was designed for the prediction of fracture evolution, fracture channelization in particular, in multi-mineral systems.

Isotopic reactive transport for improved simulation of subsurface biogeochemical dynamics in heterogeneous systems

Jennifer L. Druhan

Analysis of the partitioning of isotopes is widely recognized as a means of improving our understanding of processes at work in complex natural systems where the presence of multiple pathways may hinder the evaluation of bulk concentrations. Because isotopes effectively "trace" a wide array of processes, the incorporation of isotopes into RTM frameworks represents a development that can be applied across a broad diversity of diciplines. In practice, a wide range of models have been employed to describe the partitioning of stable isotopes between reactant and product species during dissolution, precipitation and biologically mediated reactions. These approaches vary in complexity and degree of parameterization from simple Rayleigh distillation to transition-state-theory and Monod descriptions of isotopic partitioning. Under carefully constructed laboratory conditions, the advantages of more rigorous models can be shown. The question remains, however: when faced with the need to quantify an observed isotope fractionation at the field scale, which model is appropriate? We will present examples of metal stable isotope fractionation during secondary mineral formation and biologically mediated reduction to study the conditions under which particular models are necessary to reproduce observed behavior. We demonstrate that for most conditions, numerical methods can accurately reproduce the observed trend in metal stable isotope fractionation, and indicate that this isotopic partitioning is highly sensitive to heterogeneity in fluid flow fields.

Variability in crystal surface reactivity: A critical constraint for reactive transport modeling

Cornelius Fischer

Helmholtz-Zentrum Dresden-Rossendorf, Reactive Transport Division, Leipzig, Germany

c.fischer@hzdr.de

Reactive transport modeling of fluid-solid interactions relies on (i) contrasts in fluid flow velocity and (ii) variability of surface reactivity. The first point is based on data from, e.g., PET and µCT techniques. The second point, however, is usually addressed by simple kinetic data only. Thus, it neglects information about the intrinsic variability of crystal surface reactivity that often results in a rate range of 2-3 orders of magnitude (1). Such variability is however an important constraint for the evolution of surface roughness and porosity pattern in crystalline matter (2). Here, we highlight important sources of the intrinsic variability of crystal surface reactivity and their impact on surface reaction rates. Rate maps (3) and rate spectra (4) provide critical information about the spatial and temporal variability of surface reactivity that is required to predict the evolution of porosity pattern in crystalline matter (5).

1. Luttge A, Arvidson RS, & Fischer C (2013) A Stochastic Treatment of Crystal Dissolution Kinetics. *Elements* 9(3):183-188.
2. Fischer C, Kurganskaya I, Schäfer T, & Luttge A (2014) Variability of Crystal Surface Reactivity: What do we know? (Review Article). *Applied Geochemistry* 43:132-157.
3. Fischer C & Luttge A (2017) Beyond the conventional understanding of water–rock reactivity. *Earth and Planetary Science Letters* 457:100-105.
4. Fischer C, Arvidson RS, & Luttge A (2012) How predictable are dissolution rates of crystalline material? *Geochimica et Cosmochimica Acta* 98:177-185.
5. Michaelis M, Fischer C, Colombi Ciacchi L, & Luttge A (2017) Variability of Zinc Oxide Dissolution Rates. *Environmental Science & Technology* 51(8):4297-4305.

Modeling passivation process in a reactive transport code.

P. Frugier

CEA, DEN, DE2D/SECT/LCLT, 30207 Bagnols-sur-Cèze, France

Affinity law is a corner stone of minerals dissolution rate laws used in reactive transport codes. Its formalism, r=k(1-Q/K), is justified by the existence of the backward precipitation of the dissolving mineral. However, for many multi-elemental minerals, glasses or metals, this reaction is largely questionable when placed far from their formation conditions, such as low temperature for a glass, or oxidizing conditions for a metal: only a fraction of the elements of the primary mineral can really condensate on the surface. This may justify the use of only this fraction of the elements in the affinity law. Sometimes, either from local condensation or bulk precipitation, a new secondary mineral is formed. This secondary mineral may exhibit so-called protective or passivating properties: the higher its thickness, the lower the dissolution rate of the primary mineral.

Taking into account such passivation process requires to model explicitly the nanometer scale transport phenomenon in the layer while still modeling centimeter scale diffusion and convection in the three dimensions of the fluid. Such a complexity is not mandatory for many purposes. Diffusion process can be simplified as what has been proposed for the glass dissolution model called GRAAL (Frugier, Gin et al. 2008, Jollivet, Frugier et al. 2012). Basic idea is to use the local concentration of the protective mineral to drive the primary mineral alteration rate: the higher the quantity of the protective mineral, the lower the dissolution rate of the primary mineral. Concepts, equations, and implementation feedbacks are shared in the hope it proves useful for other application fields.

Frugier, P., S. Gin et al. (2008). "SON68 Nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model." JNM **380**(1-3): 8-21.
Jollivet, P., P. Frugier et al. (2012). "Effect of clayey groundwater on the dissolution rate of the simulated nuclear waste glass SON68." JNM **420**: 508-518.

Reactive transport with emphasis on vadose zone applications - Overview of the HPx codes

D. Jacques[1*], J. Šimůnek[2]

[1]Engineered and Geosystems Analysis Unit, Belgian Nuclear Research Centre, 2400 Mol, Belgium; diederik.jacques@sckcen.be

[2]Department of Environmental Sciences, University of California Riverside, Riverside, CA 92521, USA; jsimunek@ucr.edu

Coupled multicomponent reactive transport models for the so-called critical zone are essential tools to analyse nonlinear interactions between hydrological, geochemical, and (micro)biological processes. Such codes provide excellent platforms for a flexible and extendible problem-solving environment, allowing users to incorporate a range of user-defined conceptual models to tackle their specific projects. Important elements of such codes include capabilities to describe the generic nature of the geochemistry for mixed equilibrium-kinetic reaction networks and to handle the coupling between different state variables (water saturations, temperatures, concentrations, and geochemical variables) and system properties, and corresponding parameters of the flow, transport, and geochemical models. One example is the HPx reactive transport model which couples HYDRUS-1D or HYDRUS (2D/3D) as the transport solvers (water flow, solute transport, and heat transport) and PHREEQC-3 as the geochemical solver. Coupling of these two codes resulted in a flexible and extendible coupled model that represent a powerful tool for simulating complex coupled processes in variably-saturated porous media. This code is specifically developed to tackle flow and transport in variable-saturated porous media such as soils. In this presentation, we illustrate some of the capabilities of the HPx codes, illustrating their versatility in studying complex processes such as long-term material evolution, organic matter dynamics, and colloid and colloid-facilitated solute transport. One example investigates the effects of flow interruption and ionic strength on the transport of surfactant-stabilized silver nanoparticles (AgNP). The model combines the DLVO theory with an extended colloid filtration theory and a colloid release model. The numerical model reproduced well the measured AgNP breakthrough curves and indicated that attachment to the air-water interface occurring during flow interruption was the process for AgNP retention.

Reactive transport modelling based on parameters obtained from GeoPET analysis of column leaching experiments

L. Karimzadeh[1], S. Schymura[1], J. Kulenkampff[1], S. Eichelbaum[1,2], J. Lippmann-Pipke[1] , C. Fischer[1]

[1]*Helmholtz-Zentrum Dresden-Rossendorf, Forschungsstelle Leipzig, Germany*
[2]*Nemtics Visualization, Leipzig, Germany*

E-mail: L.karimzadeh@hzdr.de

Abstract

GeoPET is the application of positron emission tomography (PET) for direct, non-destructive, quantitative spatiotemporal measurement and visualization of fluid transport in natural geological media on drill-core scale [1-5]. Here, we present new results that focus on reactive transport simulations on a drill core sample in 4D (3D+t) by using velocity fields (v_x, v_y, v_z) obtained from GeoPET measurements of a fractured rock sample in the context of BIOMOre[6] project.

For this, a mechanically induced fracture was obtained by a geomechanical shear test in a calciferous sandstone drill core sampled from the Permian Kupferschiefer ore formation (Rudna mine, Poland). Column leaching experiments using the core sample (D = 6 cm, L = 10 cm) were carried out in a plexiglas reaction cell in the laboratory at atmospheric pressure. The leaching solutions were injected with constant flow rate of 1 mL/h in three stages: irst, a moderately hard synthetic fresh water (pH = 8.5) was used as inflow solution for 22 days in order to remove the salts minerals. Second, an acidic solution with pH of 1.5 (H_2SO_4) was injected to reduce the carbonat content within another 23 days. In stage three, 0.17 mol/L concentrated ferric iron was added to the acidic inflow solution (pH 1.5, H_2SO_4) for 20 days in order to dissolve the Cu-sulfid minerals and increase the copper recovery from sample. The tracer transport in the sample was monitored by PET technique and the velocity fields were derived using an image analysis algorithm. The velocity fields were then imported into COMSOL Multyphisics to simulate and calibrate the fluid flow. Three dimensional modeling by means of iCP 1.3[7] (an interface coupling of the finite element based code COMSOL

Multiphysics® with the geochemical code PhreeqC[8]) was performed to predict the leaching process and solute transport through the core sample by using kinetic mineral dissolution and precipitation data (BRGM database). The reactive transport model results are compared to and refined using the results of the laboratory column leaching experiments.

References:
[1] Richter, M., et al. (2000) Z.angew.Geol. 46(2): 101-109.
[2] Gründig, M., et al. (2007) App.Geochem. 22: 2334-2343.
[3] Zakhnini, A., et al. (2013) Comp.Geosci. 57: 183-196.
[4] Kulenkampff, J., et al. (2008) Phys.Chem.Earth 33: 937-942.
[5] Kulenkampff, J., et al. (2015) Clay Min. 2015.
[6] http://www.biomore.info/home.
[7] Nardi, A. et al. (2014) Com. & Geosci. 69:10-21.
[8] Parkhurst, L.D. et al. (2013) U.S.G.S. Denver, Colorado p. 497.

Micro-Macro Models for Reactive Flow and Transport Problems in Porous Media

Peter Knabner

Department of Mathematics

Friedrich-Alexander University of Erlangen-Nürnberg

E-Mail: peter.knabner@math.fau.de

In porous media and other complex media with different length scales, (periodic) homogenization has been successfully applied for several decades to arrive at macroscopic, upscaled models, which only keep the microscopic information by means of a decoupled computation of “effective" parameters on a reference cell. On the other hand, if the interplay of processes becomes to complex, e.g. the scale seperation does not act in a proper way, the porous medium itself is evolving, ..., the upscaled models obtained may be *micro-macro* models in the sense, that the coupling of the macroscopic equations and the equations at the reference cell is both ways, i.e. at each macroscopic point a reference cell is attached and the solution in the reference cell depends on the macroscopic solution (at that point) and the macroscopic solution depends on the microscopic solutions in the reference cells. We will discuss various examples and in particular numerical approaches to keep the numerical complexity in the range of pure macroscopic models.

Reactive transport from academic research to industrial deployment: uranium ISR

Vincent Lagneau

MINES ParisTech, PSL Research University, Centre de Géosciences

In situ recovery involves the circulation of fluids to dissolve the target mineral within the deposit. The fluid is then produced and the metal extracted in a separation plant. The HYTEC code has been used for the past decade to address different problems around ISR, particularly exploitation, with a view to provide technical advice to the mine manager. Data from the mine has been invaluable to understand and quantify the system.

From the early stage of the project, the huge impact of the spatial variability has been recognized. The consequence is the need for a fine discretization of the system, in 3D, to correctly capture the heterogeneity. An accurate description of the chemical and physical processes at stake is also key, although a balance has to be found between more complexity (and increased CPU intensity) and operational targets. Finally, the number of fitting parameters has to be kept as low as possible to preserve the predictive capacity of the model. This tool is currently tested at operation scale for KATCO Mine in Kazakhstan: prediction of uranium recovery and reagent consumption over several years of exploitation for complete production areas (up to 300 production wells), test of optimization scenarios...

The industrial deployment brings whole new challenges: HYTEC is being completely encapsulated so that the users should only see information directly related to their usual line of work (GIS rather than mesh, acid content in the injection line rather than boundary conditions). Also, the outputs are presented so that the engineer gets the information needed (production curve, net present value).

The author acknowledges AREVA and KATCO for their support. The project is co-funded by AREVA and the ANR program *industrial chairs* for the period 2016-2020.

Impact of mixing processes on biogeochemical reactions

Tanguy Leborgne

Biogeochemical reactions, such as redox, dissolution, precipitation and microbial processes, are controlled by the concentrations of dissolved chemical species in fluids and their interactions with minerals. In porous and fractured media, flow and structural heterogeneities imply that solute concentrations are both spatially distributed and dynamic in time. While conventional dispersion theories capture relatively well the macroscopic distribution of solutes and their average concentrations, the prediction of the full spectrum of concentration statistics and their impact on reaction processes remains an outstanding challenge. Here I will present recent developments in mixing theories allowing for an accurate prediction of the temporal dynamics and spatial distributions of concentration statistics. I will discuss the consequences of these findings for reactive transport processes at scales ranging from pores to hillslopes

Hydrogeochemical coupling Drives Chemostatic Behavior in Stream Chemistry: a reactive transport perspective at the watershed scale

Li Li, Chen Bao, Pamela Sullivan, Yuning Shi, Susan Brantley, Chris Duffy
The Pennsylvania State University

Reactive transport models have been used for decades in understanding coupled flow, transport, and reaction processes mostly in subsurface environment. Recent model development integrating surface hydrological land surface processes and multi-component reactive transport modeling capabilities has led to new insights into long-standing questions in hydrogeochemistry. Here we use RT-Flux-PIHM, a newly developed code, to answer the question "Why do solute concentrations in streams remain largely constant while discharge varies over orders of magnitude?" for the non-reactive chloride (Cl) and geogenic magnesium (Mg) in the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) in central Pennsylvania, USA. The stream water comes from surface runoff subsurface lateral flow, and deeper groundwater with subsurface lateral flow contributing 80-90% of the stream flow. In the summer when high evapotranspiration (ET) dries up the watershed, Cl is trapped along planar hillslopes. Successive precipitation events in the fall and winter wet the watershed and mobilize trapped Cl, which mitigate the effect of dilution brought about by the infiltration of large amounts of precipitation and thus maintains a chemostatic behavior for Cl. Similarly, the synchronous response of clay dissolution rates and the subsurface lateral flow to hydrological conditions drives the chemostatic behavior of Mg in the stream by maintaining a relatively constant ratio between the wetted surface area (A_w) and soil water volume (V_w). Compared to clay dissolution, cation exchange plays a secondary role in determining the chemostatic behavior, although it stores an order-of-magnitude more Mg on exchange sites than soil water. Sensitivity analysis indicates that dilution (stream concentrations decrease with increasing discharge) occurs only when hydrologically unresponsive influxes from the deeper groundwater dominate the runoff. This work demonstrates the potential of process-based hydrogeochemical models in integrating and differentiating competing processes and in testing hypothesis at the interface of hydrology and geochemistry.

Reactive transport in evolving porous media – Challenges and opportunities

ULRICH MAYER

**University of British Columbia, Dept. of Earth, Ocean and Atmospheric Sciences,
Vancouver, BC, Canada, umayer@eoas.ubc.ca**

Many problems of relevance in the fields of the earth and environmental sciences are affected by evolving porous media properties, including reactivity, porosity, permeability, tortuosity and effective diffusion coefficients.

These problems include for example the weathering of mine waste rock and tailings. In this case, reactivity often declines over time due to mineral alteration, changes in reactive surface area and surface passivation. In extreme cases, the formation of hardpans may substantially inhibit the progress of weathering in the long term. Similarly, surface passivation can affect the effectiveness of carbon sequestration in ultra-mafic mine waste by limiting the release of Mg into solution. Surface passivation has also been shown to play an important role in engineered systems for water treatment such as permeable reactive barriers and limestone drains, reducing their long-term effectiveness to remove contaminants.

Evolving porous media properties are not restricted to evolving reactivity, mineral-dissolution precipitation reactions can also lead to significant changes in porosity and subsequently permeability, leading to either permeability increase or reduction. Reduction of permeability leads to well-fouling, associated with the precipitation of amorphous Fe- and Mn-oxide mineral phases, or can jeopardize well development in the oil and gas industry including hydraulic fracturing operations, for example due to the precipitation of barite.

In the case of interfaces in constructed waste disposal facilities, including cement-clay and cement-bentonite contacts, it is also important to understand the evolution of porosity, tortuosity, effective diffusion coefficients and reactivity to enable meaningful assessments of long-term evolution and waste containment.

This presentation will provide an overview on common formulations for evolving porous media based on selected case studies and will discuss existing challenges and possible future research directions.

Perspectives on reactive transport pore scale modeling

Sergi Molins

Understanding the formation of reaction rates in porous media is essential in many subsurface energy applications, including shale gas production, fracking, CO_2 sequestration, nuclear waste storage, or geothermal energy extraction. Conventional Darcy-scale models treat porous media as a continuum. This approach requires the assumption of well-mixed conditions inside the pore space as well as the use of mechanistic models for the bulk parameters of the porous medium (e.g. reactive surface area, porosity-permeability relationship). Along with advances in characterization techniques, pore-scale models –where reactive surface are considered explicitly– have allowed for accurate simulations of flow and reactive transport within individual pore spaces.

In this talk, I will review advances made over the last decade in the numerical simulation of reactive transport processes at the pore scale and discuss the contributions of pore scale modeling to advancing knowledge in relation to the themes proposed for this workshop including high resolution simulation, physical evolution of porous media, biogeochemical reactions and multiscale systems.

Pore scale modeling has proven particularly useful in quantifying the effect of transport limitations to reactive surfaces. Using the case of calcite dissolution as an example, I show that the nonuniformity in the flow field at the pore scale has the effect of decreasing the overall reactivity of the system. Transport-limited conditions at the grain-pack scale may result in unstable evolution, a situation in which dissolution is focused in a fast-flowing, fast-dissolving path. Simulation of dissolution in mineralogically heterogeneous media shows that non-uniform dissolution owing to heterogeneous reactivity leads to increasing transport limitations to reactive surface.

High-performance computational tools used in models have allowed for the simulation of the relevant processes in the physically and mineralogically complex media. Increasingly, experimental results also make it possible to improve model representation and improve our understanding of reactive transport processes in subsurface materials.

Coulombic interactions during advection-dominated transport of ions in porous media: Experiments and modeling

Muniruzzaman M.[1] and Rolle M.[2]

[1]Geological Survey of Finland
[2]Technical University of Denmark

Solute transport of charged species in porous media is significantly affected by the electrochemical migration term resulting from charge-induced interactions among dissolved ions. Therefore, the characterization of such Coulombic interactions and their effect on multicomponent ionic transport is of critical importance for assessing the fate of charged solutes in porous media. In this work we present a detailed investigation of the electrochemical effects during multicomponent ionic transport, under advection-dominated conditions, in homogeneous and heterogeneous domains by means of laboratory bench-scale experiments and numerical simulations. We show remarkable differences, caused by the electromigration term, on the propagation of diffusive/dispersive pH fronts during the advection-dominated transport of ionic admixtures [1]. We also report results showing the important role of Coulombic interactions in the lateral displacement of different ionic species for steady-state transport in heterogeneous porous media in which dilute electrolyte solutions are continuously injected through different portions of the flow-through chamber [2]. Successively, we focus our attention on transient transport and pulse injection of the electrolytes. In these experiments high-resolution spatial and temporal monitoring (600 samples; 1800 measurements), at closely spaced outlet ports (5 mm), allowed us resolving the effects of charge interactions on the temporal breakthrough and spatial profiles of the cations and anions [3].

The interpretation of the experimental results requires a multicomponent modeling approach with an accurate description of local hydrodynamic dispersion, as well as the explicit quantification of the cross-coupling between dispersive fluxes due to the Coulombic interactions of the charged species. A new 2-D simulator [4], coupling the solution of the multicomponent ionic transport problem with the geochemical code PHREEQC has been developed and used to quantitatively interpret the experimental results. Additionally, we show numerical simulation results revealing the significance of Coulombic cross-coupling during field-scale reactive transport in physically and geochemically heterogeneous domains.

References

[1] Muniruzzaman M. and Rolle M., (2015). *Water Resour. Res.* 51.
[2] Muniruzzaman M., Haberer C.M., Grathwohl P. and M. Rolle (2014). *Geochim. Cosmochim. Acta* 141, 656-669.
[3] Muniruzzaman M. and M. Rolle (2017). *Water Resour. Res.* 53.
[4] Muniruzzaman M. and M. Rolle (2016). *Adv. Water Resour.* 98, 1-15.

Challenging reactive transport modeling from pore scale observations

Catherine Noiriel

Precipitation or dissolution of carbonate and silicate minerals at the heart of porosity and pore geometry changes in rocks. The reactivity of minerals control the evolution of permeability, flow and transport properties of fluids in porous and/or fractured geological reservoirs by altering the shape, size and connectivity of the pores, the roughness of their surface, and by partial or complete alteration of flow in pore throats.

Developing a full understanding of the feedbacks between geochemical reactions and flow and transport characteristics at the reservoir scale requires investigations of geochemical mechanisms at the pore scale. Application of high-resolution and/or non-invasive imaging techniques like X-ray micro-tomography has considerably increased experimental capability by giving access to a spatio-temporal vision of the physical-chemical processes within the rocks. New information is now accessible, which provides a better understanding of the coupled thermo-hydro-mechano chemical processes and allows numerical models to be better constrained.

In my presentation, I will present some applications of 4D imaging related to reactive transport experiments and discuss the results and issues for reactive transport modelling. In particular, I would point out several processes that challenge the continuum description of porous media and assumptions required for reactive transport modeling at large scales [1]. Processes include heterogeneous and anisotropic reactivity of both individual minerals and rocks. The physical and chemical heterogeneities that develop in both minerals and rocks can also strongly impact the interplay between surface reaction kinetics and transport both near the fluid−mineral interface and along the flow paths. In particular, the growth of alteration layers at different scales, by preventing the contact between the dissolving solids and the pore fluid and slows the transport in the vicinity of the fluid-solid interface, potentially inhibits the dissolution/carbonation processes.

[1] Noiriel C. and Daval D. (2017) Pore-Scale Geochemical Reactivity Associated with CO_2 Storage: New Frontiers at the Fluid-Solid Interface. Accounts of Chemical Research, special Issue on Chemistry of Geologic Carbon Storage, DOI: 10.1021/acs.accounts.7b00019

DISSOLUTION-PRECIPITATION PROCESSES IN CONFINED MEDIA: EXPERIMENTAL BENCHMARKS FOR REACTIVE TRANSPORT MODELLING AT DIFFERENT SCALES

J. Poonoosamy(1), N. Prasianakis(2), C. Westerwalbesloh(3), G. Deissmann(1), M. Klinkenberg(1), F. Brandt(1), D. Kolheyer(3), D. Bosbach(1)

(1) *Institute of Energy and Climate Research (IEK-6) Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

(2) *Laboratory for Waste Management, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

(3) *Institute of Bio- and Geosciences (IBG-1) Biotechnology, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

The modification of the pore space due to mineral dissolution and precipitation and associated changes of transport properties of porous media are of major interest with regard to flow and solute transport in the subsurface. The implementation of such coupled processes into numerical codes for reactive transport simulations and the evaluation of porosity evolution and feedback on transport require a mechanistic understanding of the relevant precipitation/dissolution processes and validation with quantitative experiments. To investigate kinetically controlled dissolution/precipitation reactions causing porosity/permeability changes, we developed a set-up to perform 2D experiments at different scales in a reproducible manner. The first approach comprised an experiment using a quasi 2D Plexiglas tank of dimensions 10 × 10 × 1 cm filled with quartz sand [1]. In the middle of the tank a vertically oriented k reactive layer (thickness 1 cm) consisting of celestine ($SrSO_4$) crystals with a bimodal grain size distribution was placed. A $BaCl_2$ solution was injected into the tank causing an asymmetric flow field to develop that crossed the reactive layer. As the barium chloride reached the reactive layer, dissolution of celestite was initiated and barite precipitated. As a consequence of barite precipitation, the porosity – and thus also the permeability – of the porous medium decreased, due to the higher molar volume of barite compared to celestine. The changes of the flow field in space and time were monitored via the injection of conservative tracers, fluid pressure measurements and the analysis of the effluent composition. Moreover, an extensive post-mortem analysis of the reacted porous medium was conducted. We could successfully model the flow and the transport of conservative tracers with the (continuum scale) reactive transport code OpenGeosys-GEM. However, the prediction of the reactive experiments initially failed. Only the inclusion of information from post-mortem analysis led to a satisfactory match of observation and simulation. Hence, we refined the post-mortem analysis and focussed on investigating the dissolution/precipitation mechanisms at the pore scale [2], employing scanning electron microscopy and synchrotron X-ray micro-diffraction/micro-fluorescence, performed at the

XAS beamline (Swiss Light Source). The newly formed phases include barite micro-crystals epitaxially grown on large celestite crystals and a nano-crystalline barite phase (resulting from the dissolution of small celestite crystals) with residues of celestite crystals in the pore interstices (Figure3). Classical nucleation theory, using well-established and estimated parameters describing barite precipitation, was applied to explain the mineralogical changes occurring in our system. The results from mineralogical-microscopic investigations clearly show that effects related to the metastability of supersaturated solutions and distinct nucleation mechanisms are important with respect to precipitation kinetics. Besides, the nucleation mechanisms depend on the local supersaturation and affect the evolution of porosity, permeability and diffusivity. Our pore scale investigations revealed the limits of continuum-scale reactive transport models and indicate that such a parameterized model cannot be used for predictions of these kinds of coupled processes. Thus, appropriate upscaling of pore scale processes to the continuum scale is required. Pore scale models can be used to investigate physicochemical processes (e.g. nucleation, passivation of surfaces, creation of unconnected porosities, etc...) that cannot be resolved in continuum scale models. The results of these models can then be utilized to derive and parameterize constitutive equations to introduce pore-scale corrections into macroscopic (continuum-scale) reactive transport models. To follow this course of action, we propose a microfluidic approach [3] to investigate dissolution/precipitation processes at the pore scale. Therefore, we recently developed a miniaturised experimental set-up that will enable us to monitor and visualize precipitation/dissolution processes (e.g. of celestine crystals) in the pore space in real time. These experiments will be addressed by a pore scale model in future to aid in the development of appropriate upscaling approaches.

[1] Poonoosamy, J., Kosakowski G., Van Loon R. and Mäder U., (2015). Dissolution-precipitation processes in tank experiments for testing numerical models for reactive transport calculations: Experiments and modelling. Journal of Contaminant Hydrology, 177-178, 1-17.

[2] Poonoosamy, J., Curti, E., Kosakowski, G., Van Loon, L. R., Grolimund, D. and Mäder U., (2016) Barite precipitation following celestite dissolution in a porous medium: a SEM/BSE and micro XRF/XRD study. Geochimica et Cosmochimica Acta, 182, 131-144.

[3] Kohlheyer, D., Unnikrishnan, S., Besselink, G., Schlautmann, S., and Schasfoort, R., (2008) A microfluidic device for array patterning by perpendicular electrokinetic focusing. Microfluidics and Nanofluidics

Cross-scale modeling of precipitation processes

Dr. Nikolaos Prasianakis (Transport Mechanisms Group, Lab for Waste Management, PSI)

Precipitation and dissolution reactions in porous media dominate and control a large number of geochemical processes and industrial applications that span from geothermal energy and georesources to pharmaceutical products, batteries, catalysts and to long-term nuclear waste containment. The precipitation-dissolution of minerals from aqueous solutions alters the pore space and its connectivity in a way that has a complex feedback to the ion transport in aqueous phase itself. There are clear evidences that the macroscopic properties of the medium depend on the physical and chemical processes that occur at the micropore scale in a *strongly non-linear way*. It is the microscopic physics *per se* that ultimately control the macroscopic processes. Fundamental in-depth understanding and accurate prediction of the underlying processes can be enhanced by direct pore-scale modeling, supported by experimental investigations.

In our effort to increase the predictive capability of macroscopic filed scale codes we investigate processes that occur at the pore-level using the lattice Boltzmann modeling framework. This allows the modeling and simulation of transport phenomena in realistic complex geometries e.g. X-ray tomography output of porous media with resolution down to 10nm. The onset and evolution of precipitation at a sub-grid level is modelled via classical nucleation theory. Evolution of permeability and effective diffusivity can be measured exactly for upscaling purposes. Applications relevant to clogging of interfaces and radionuclide retention will be presented.

Nuclear glass alteration: bridging the gap from surface reactivity description to reactive transport at the scale of the fractured block

M.REPINA[1*], F.BOUYER[1], V.LAGNEAU[2]

[1] CEA, DE2D/SEVT, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France (*correspondance: maria.repina@cea.fr; frederic.bouyer@cea.fr)
[2] Mines ParisTech, 35 rue Saint Honore, 77305 Fontaine-bleau Cedex, France (vincent.lagneau@mines-paristech.fr)

The treatment of the long-lived high-level radioactive waste via its vitrification is a subject of prime importance for the nuclear industry. It requires an in-depth understanding of the behavior of the glass dissolution and the amorphous layers development at the micro scale, as well as the effect of the diffusion, the thermo convection and certain parameters of modeled systems that govern the kinetics of the glass dissolution.

The glass matrix being highly fractured, as a result of stress release generated during the glass cooling, the treatment of such a medium demands the application of both the discrete modelling and the homogenized modelling approaches.

This research starts with the study of the evolution of the amorphous layers by executing the reactive transport modelling (HYTEC transport code [1], [2]) in conjunction with the GRAAL geochemical model [3]. At the first step the behavior of fractures is described explicitly. The influence of such parameters as number of fractures, their length and aperture as well as the volume of water in contact and water diffusion coefficient is observed and explained with respect to the GRAAL model.

Following, the characterization of the fracture network by the tools of Morphological Mathematics is performed. Two entire blocks of vitrified glass are characterised by means of the analysis of the high quality 2D images that allows us to extract the network of fractures and describe its main parameters.

Next, the upscaling techniques are elaborated for flow, transport, and chemical behavior. Furthermore, their reliability is currently at the stage of verification; for instance, we are investigating whether the explicit fracture representation could be replaced by the geometrical representation by barycenters of crystals and if it would not have the undesirable consequences on the upscaled diffusion coefficient and equivalent permeability.

Eventually, we will carry out RTM at the scale of the fractured block and, to confirm the validity of the model, we plan to compare the results of modeling with the experimental data of the aqueous alteration of the full-scale SON68 nuclear glass block that has been altered for 7.5 years in a static reactor at LCLT laboratory.

[1] Lagneau, V. (2013) Géochimie Université ParisVI [2] van der Lee et al. (2002) Developments in Water Science 47, 599-606 [3] Frugier, P.et al.(2008) Journal of Nuclear Materials 380, 8-21

Theme: 2. Diversity of porous media and physical evolution
Topic: Fractured media and dual domain approaches

A new Time Domain Random Walk approach for modeling reactive transport processes in heterogeneous fractured porous media

D. Roubinet[1], A. Russian[1,2], M. Dentz[3], and P. Gouze[1]

[1] Géosciences Montpellier, UMR 5243, CNRS, University of Montpellier, France
[2] Now at Politecnico di Milano, Italy
[3] IDAEA, CSIC, Barcelona, Spain

Recent developments of time domain random walk (TDRW) methods focused on the modeling of advective-diffusive transport accounting for mass transfer between mobile and immobile regions and linear sorption-desorption reactions in highly heterogeneous porous media. The main advantages of these methods are that (i) they do not rely on standard Fickian modeling concepts that are often not adapted to reproduce the observed anomalous transport behaviors, (ii) they are well suited to take into account heterogeneous properties of the mobile and immobile regions (i.e., heterogeneous distributions of porosity, diffusion coefficient, and flow velocity), (iii) the method does not depend on the simulation scale (from Stokes to Darcy scale), and (iv) numerical simulations can be efficiently optimized by memory-shared massive parallelization. To the best of our knowledge, these methods have been applied only to single continuum approaches with simple (theoretical) reactions. Here, we extend the TDRW approach to dual-continuum representations considering a highly permeable fracture network embedded into a poorly permeable rock matrix and accounting for the occurrence of heterogeneous geochemical reactions in this matrix. This gives us the opportunity to noticeably extend the range of the modeled heterogeneity scales, while modeling accurately solute transport with no assumption on the process Fickianity. The model will be compared first to existing particle-based methods that are usually used to model reactive transport in fractured rocks assuming a homogeneous surrounding matrix. Then, using this modeling tool, numerical experiments will be run for investigating the impact of the matrix heterogeneity on the fate of reactive solute for different reactions and fracture network configurations.

Modelling pore-size-dependent kinetics in reactive transport codes

N. Seigneur, A. Rajyaguru, S. Savoye, V. Lagneau, A. Dauzères,

C. Wittebroodt, V. Detilleux

This poster presents experimental and numerical results to understand the precipitation of two sulfate alkali minerals namely Barite and Gypsum within similar chalk porous matrix. Experimental precipitation impact of these two minerals on chalk porosity and subsequently on water tracer diffusivity (HTO/HDO) was determined using classical through diffusion experimental setup. Where, a chalk sample is sandwiched in-between two reactive salt rich solution reservoirs. At the end of experiments, similar impact of Barite/Gypsum precipitation on overall chalk porosity was observed. However, both of these minerals lead to distinct impact on water tracer diffusivity. Thus, at the end of experiments Barite/Gypsum precipitated samples were subjected to Xray-mircotomography. These measurements revealed two distinct evolution of both of these minerals within similar chalk porous matrix. For Barite a thin precipitated zone was observed in the center of sample, however, isolated big spheres of Gypsum were in the sample center. Our observation lead us to conclude that locally, Barite blocked more diffusive pathways as compared to Gypsum. Thus, leading to higher impact on diffusivity.

To model this, we implemented a dedicated reactive transport simulation, describing a kinetic precipitation of the minerals. The innovative part of this simulation is that the amount of precipitation takes into account a given pore size distribution with partial kinetic rates. Based on experimental data, the code assigned higher kinetics for Gypsum in larger porosity; and higher kinetics within small pores for Barite. 2D simulation of this precipitation is shown on a approximation of a representative elementary volume of the chalk sample. Furthermore, 1D simulation are presented, coupled with an imagined methodology to incorporate these methods in existing reactive transport codes. Though consisting of some arbitrary parameters, this new method

Portland cement – rock interaction in the geological disposal of radioactive waste. Examples from modeling of laboratory/field experiments and natural/industrial analogues.

Josep M. Soler, IDAEA-CSIC, Barcelona, Catalonia, Spain

Several experimental and modeling studies of Portland cement – rock interaction have been performed within the HPF and LCS projects at the Grimsel Test Site (Switzerland). Within HPF, laboratory and in situ injection of high-pH solutions into fractured granite were performed. In LCS, pre-hardened cement was placed in a borehole intersecting a fracture. Modeling studies of a natural analogue (Eastern Springs at Maqarin, Jordan) and an industrial analogue (DM borehole at Tournemire, France) were also performed. The different rock structures (impermeable clay rock, fractured porous limestone, fractured tight granite) imposed very different transport regimes translating into very different spatial extents of alteration.

At Tournemire (concrete-mudstone interaction), transport control by diffusion resulted in a very small spatial extent of alteration. Porosity was clogged at the cement – rock interface (mm scale) due to the precipitation of C-A-S-H, calcite and ettringite, together with clay dissolution (source of Al and Si). Porosity of the concrete increased due to portlandite dissolution. At Maqarin, long term circulation of portlandite-saturated solutions along a fracture resulted in intense mineral alteration along the fracture and in the wall rock (cm scale), due to the porous nature of the rock (matrix diffusion). Primary aluminosilicate dissolution also provided Al and Si for C-S-H/C-A-S-H and ettringite precipitation. The relative magnitudes of fracture flow vs. rock matrix diffusion control the extent of fracture-rock interface clogging vs. fracture clogging.

In the Grimsel experiments (year scale), there is very limited mass transfer from the fracture to the rock matrix due to the very small granite porosity. pH buffering by reaction is limited and primary aluminosilicate dissolution (fault gouge) controls also C-S-H/C-A-S-H and ettringite precipitation in the rock fracture. Mineralogical changes are only minor. Fracture heterogeneity is an important control in the spatial distribution of alteration within the fracture.

Pore-scale simulation of reactive mass transfer with a micro-continuum approach

Cyprien Soulaine (csoulain@stanford.edu)

Stanford University

A micro-continuum approach is proposed to simulate the dissolution of solid minerals at the pore scale. The approach employs a Darcy–Brinkman–Stokes formulation and locally averaged conservation laws combined with immersed boundary conditions for the chemical reaction at the solid surface. The simulation framework is validated using an experimental microfluidic device to image the dissolution of a single calcite crystal. The evolution of the calcite crystal during the acidizing process is analyzed and related to the flow conditions. Macroscopic laws for the dissolution rate are proposed by upscaling the pore-scale simulations. Then, the emergence of wormholes during the injection of acid in a two-dimensional domain of calcite grains is discussed based on pore-scale simulations. Finally, the simulation framework is extended to two-phase reactive transport to investigate the effect of the production of gas during the injection of acid in a porous medium. In this case, the chemical reactions at the grain boundaries generate CO2 that form a separate phase. Some gas bubbles detach and flow out of the domain. Others occupy pores and continue to grow. When they filled the entire volume of the pore, bubbles from adjacent pores connect and coalesce forming larger clusters that are flow barriers that limit the distribution of the acid concentration in the domain.

Reactive Transport at the Crossroads

Carl Steefel
Lawrence Berkeley National Laboratory

Reactive transport in the Earth and Environmental Sciences is at a crossroads today. On the one hand, there is new evidence that the discipline has reached a level of maturity well beyond what could be said even 15 years ago. This is shown now by the successes in describing complex and in many cases coupled behavior in a range of natural Earth environments, ranging from radioactive Cs leaking into the vadose zone from corroding storage tanks (Steefel et al, 2005), to the successful prediction of mineral and pore solution profiles in a 226 ka chemical weathering profile (Maher et al, 2009), to the prediction of ion transport in compacted bentonite (Tournassat and Appelo, 2011) and natural clay rocks (Appelo et al., 2010). The list of successes is actually quite long. The maturity of the discipline is also shown by recent benchmarking activities that have shown that as many as ten different software packages can simulate complex natural reactive transport problems and achieve essentially the same results (Steefel, Yabusaki, & Mayer, 2015).

This is all good, but potentially it sets the stage for taking the developments and successes in reactive transport for granted, leading some to think that the “reactive transport problem” is solved. However, for those thinking deeply about Earth and Environmental Science problems impacted by reactive transport processes, it is also clear that many challenges remain. Arguably the most significant challenge is associated with the huge range of length scales that need to be addressed, since these range from the molecular to nanoscale to pore scale below the more conventional centimeter to meter scale all the way up to the watershed to continental scale. Beyond the range of scales, the constitutive equations and parameters that are used to describe the reactive transport processes may change as well across these scales. Another challenge is associated with partially saturated porous media in which capillary forces become important in terms of thermodynamics and transport properties. Charged porous media offers special challenges, since ion mobility can be strongly affected in some significant fraction of the porosity and can lead to such effects as anion exclusion. Where the charged porous media involves nanoscale porosity, off-diagonal coupling effects on transport between such master variables as fluid pressure, electrical current, chemical composition may become increasingly important. At the watershed and continental scales, reactive transport is further complicated by the coupling with diverse Earth surface processes, including subsurface and surface water, vegetation, and the atmosphere, all played out typically in highly heterogeneous settings. This can lead to “hot spots” and “hot moments” that may have an outsized effect on system function even though they represent a limited percentage of the total land surface area.

For all the past successes and new challenges, reactive transport in the Earth and Environmental sciences still operates largely in the shadows. We will use this presentation to explore some of the ways in which this might be changed for the better.

Diffusion in clays. Continuum and micro-continuum approaches

Christophe Tournassat [1], [2], Carl I. Steefel [2], Stéphane Gaboreau [3]

[1]ISTO, Orléans, France. c.tournassat@brgm.fr

[2]EESA, LBNL, Berkeley, California, USA. cisteefel@lbl.gov

[3]BRGM, Orléans, France. s.gaboreau@brgm.fr

The properties of clays have been the subject of longstanding study for several important subsurface energy-related applications. While the low permeability and high adsorption capacity of clay minerals are widely acknowledged, it is clear nonetheless that there is a need for an improved understanding of how the chemical and mineralogical properties of clay rocks impacts transport through them. It is at the pore-scale that the chemical properties of clay minerals become important since their electrostatic properties can play a large role. Numerical methods for modeling diffusion processes in clay media with the consideration of the presence of a diffuse layer have met a growing interest in diverse communities in the past years. Information on diffusivity has been sought at the molecular level for the smallest pore sizes, i.e. the interlayer nanopores, and this information has been used to draw a consistent picture of diffusion processes at the mesoscale using up-scaling approaches and pore-scale modeling techniques. These approaches are, however, not yet applicable to the modeling of “laboratory scale” experiments, or to large temporal and spatial scale modeling exercises where numerous coupling with the materials reactivity must also be taken into account. In this respect, reactive transport modeling approaches have the significant advantage to be able to handle complex geometries and chemistry, heterogeneities and transient conditions. In this presentation, we will highlights recent developments of reactive transport modeling that makes it possible to tackle problems on diffusion processes coupled to geochemical reactions at the continuum and the micro-continuum scale.

Hydrobiogeochemistry in the Plant-Soil Interactome

Steve Yabusaki
Yilin Fang

Rhizosphere hydrobiogeochemistry is an important control on plant performance and carbon cycling, but is in turn affected by plant uptake and rhizodeposition processes. A key need is to understand this plant-soil interactome and how future climate conditions will affect the dynamic interplay of plant and soil processes and conditions. Of interest are experimental and modeling capabilities that will lead to a better understanding of plant-soil interactions, including the spatiotemporal hydrobiogeochemistry in the rhizosphere and surrounding soil. We report on a plant-soil ecosystem model of *Brachypodium distachyon*, a genomics model bioenergy grass. In this case, a growing root system architecture, is explicitly embedded in the representation of the belowground model domain. Diel cycles of transpiration-driven water and nutrient-specific uptake rates are simulated resulting in corresponding cycles of local desaturation-saturation and increasing-decreasing concentrations of ions not taken up by the roots. The availability of nutrients that compete for exchange sites (e.g., K^+, NH_4^+) is a function of their changing concentrations, cation exchange capacity, and ion exchange reactions. Elucidation of the controlling processes and their interactions will contribute to a better basis for assessing the impact of drought on the exchange of water and nutrients in the plant-soil interactome.

Surface Complexation from the Grain to Plume Scale in a Gravel Aquifer Influenced by Surface Water Exchange: Considerations and Challenges for Predictability with Reactive Transport Models.

John M. Zachara[1] Xingyuan Chen[1], and Glenn Hammond[2]

[1] Pacific Northwest National Laboratory, Richland WA

[2]Sandia National Laboratory, Albuquerque, NM

We describe the results of a long term study to understand factors controlling the dynamic concentration trends of dissolved uranium in a persistent groundwater plume located near the shoreline of a major river system (Columbia River). The river experiences large seasonal stage fluctuations that cause water table vacillations, water compositional changes resulting from river water intrusion, and temporal groundwater flow reversals. Experimental, monitoring, and modeling studies were conducted from the grain to the plume scale to characterize reaction networks, physical and chemical properties distributions, and seasonal hydrologic dynamics influencing key system analytes (U_{aq}, pH, specific conductance, Ca, and HCO_3^-/CO_3^{2-}). A goal was to identify process dominance at each scale, facilitated by application of reactive transport models including PFLOTRAN for field calculations. At small scale (laboratory stirred reactors and columns), system parameters were primarily influenced by the kinetic surface complexation of U from surfaces and diffusion-limited intra-grain domains. At the intermediate scale, where a compact well field was sampled, system parameters in proximate wells were strongly influenced by the kinetic release of heterogeneously distributed, adsorbed U in the lower vadose zone during high water table events. In contrast, dynamic seasonal hydrology, and large scale hydrogeologic structures and depositional features (e.g., >10m) promoting groundwater-surface water exchange were found to be the most important factors controlling system parameters for wells distributed throughout the entirety of the plume, with little apparent influence of geochemical reaction. We discuss the implications of these findings to conceptual model development and identify future approaches and actions to improve system scale predictability.