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Review and definition of modelling approaches: scale of analysis, physico-chemical processes, software, HPC resources

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ABSTRACT

This report gives details of the definition of the modelling approaches to be followed by each of the participants of Work Package 3, related to Modelling and Interpretation of the Experiments to be carried out in Work Package 1. The written descriptions reported here have been provided by the project partners, which are listed below as contributors. These contributions were reviewed and compiled by the WP3 leader, as editor of this deliverable.

Keywords: modelling, numerical methods, software, time and length scales, input and output data

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1. Introduction

The goal of WP3 is to model and interpret the experimental results obtained within Work Package 1 (WP1), with focus on physical and chemical processes leading to changes in transport properties, both in the cementitious matrix and the cement-host rock interface. Work Package 3 activities have started right after the Kick-Off of the CEBAMA project. However, an important basis for WP3 is the outcome of the experiments and their characterization performed in WP1 and the information on radionuclide retentions from WP2. These experimental results will not be available until much later in the project. Therefore, each WP3 is using an existing set of experimental data, which is relevant to their objectives within the project, in order to test and verify their modelling approaches. The overall objectives of WP3 are:

- Modelling of physical and chemical processes related with WP1 and WP2:
 - Calibration and test of reactive transport models, transport properties, and their coupling to chemical reaction schemes and databases.
 - Derivation by means of reactive transport modelling, of solute transport data and uptake of radionuclides from experiments with non-sorbing and sorbing tracers in both unaltered and altered cementitious systems, and interfaces with different host-rocks and bentonite.
 - Model development
 - Improvement and development of reactive transport models thermo-hydro-mechanical-chemical (THMC) models and codes for modelling the cement-clay interactions: chemical, mechanical, and hydrodynamic couplings, including temporal evolution of porosity, permeability and diffusion coefficients, effects of low-crystal size mineral phases, retention of anionic species, and solid deformations.
 - Multi-scale models covering the gap between a description of microstructural processes and the observations from laboratory experiments and describing the physico-chemical
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processes at the mineral/water interface, in the bulk pore water, and their influence on the transport properties of concrete.

- Electrostatic surface complexation models to describe the concrete/pore water interface, and electrically coupled multi-species transport.
- Up-scaling
 - Simulation of multi-scale coupled reactive transport processes and modelling of radionuclide transport through (aged) concrete materials and concrete/host rock interfaces in the repository environment.
 - Validation macro-scale (continuum) transport predictions by experimental and modelling information at the micro-scale.
 - Validation of micro-scale flow and transport models for predicting macroscopic transport properties based on microstructural information.

This deliverable summarizes the definition of the modelling approaches to be followed by each participant to Work Package 3 (WP3) on Modelling and Interpretation of the CEBAMA project. A description of the planned work for each of the participants of Work Package 3 can be found in the deliverable D3.01. The different modelling approaches, software and hardware, systems under study, scales of analyses, and input/output data are summarized.

2 Modelling approaches to be followed by each partner

2.1 KIT-INE modelling approach

2.1.1 System to be modelled

KIT-INE will perform reactive transport simulations consisting of a 2D fully saturated isothermal (298 K) problem representing a laboratory through-diffusion experiment of HTO, Cl^- and I^- . Diffusion occurs across the interface between bentonite porewater and low-pH cement, taking into account the coupling between porosity changes due to dissolution/precipitation reactions and transport properties.

The results of the simulations will be compared to experimental results. A schematic representation of the diffusion experiments is presented in Fig. 2.1.1.

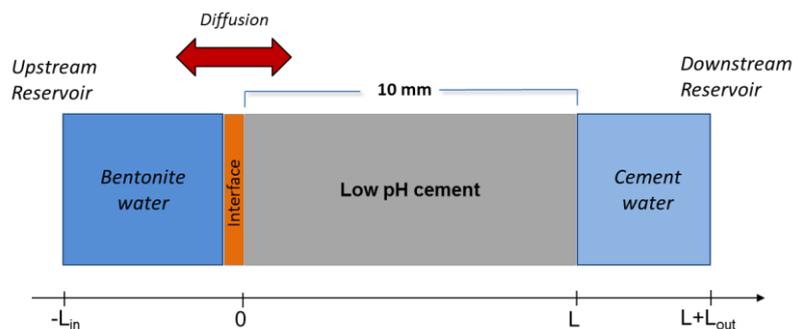


Fig. 2.1.1. Schematic representation of the diffusion experiments.

Different assumptions/cases will be tested with increasing complexity of the geochemical processes and geometry. The selection of the two modelling cases is summarized in Table 2.1.1 and details are provided below.

Table 2.1.1. Short Summary of two different cases to be modelled.

CASES	GEOMETRY	CHEMISTRY	TRANSPORT
1	2D	Thermodynamic	diffusion
2	2D	Kinetics	diffusion

2.1.2 Description of the software

The system under study is implemented in a newly developed code/interface called iCP (Nardi et al., 2014), which couples two different codes: the Finite Element code COMSOL Multiphysics V.5 (COMSOL, 2014) and the geochemical simulator PHREEQC v.3.1.7. (Parkhurst and Appelo, 2013). iCP is developed in Java® and input files are written in a JSON format. One of the features of iCP is that it does not perform the numerical calculations, but is only used as an interface to couple and maximize the synergies between COMSOL and PHREEQC. This interface provides a numerical platform that can efficiently simulate a wide number of multiphysics problems coupled to geochemistry (i.e. liquid flow, solute and heat transport, elastic and plastic mechanical deformations and geochemical reactions).

2.1.3 Geometry and physical processes

Geometrical and transport parameters including the discretization of the system will be initially implemented in 2D in COMSOL Multiphysics. The cementitious solid phase is represented by a block of 10 mm in contact with a bentonite porewater (see Fig. 2.1.1). The mesh size will be set to ensure a satisfactory compromise between computation time and sufficient spatial resolution of the expected geochemical and transport processes, especially at the interface between the bentonite porewater and the low-pH cement phase.

Considering the very low permeability of low-pH hydrated cement paste, mass transport will be dominated by diffusion, following Fick's law.

$$J = -D \frac{\partial C}{\partial x} \quad (2.1.1)$$

where J is the substance flux ($\text{kg}/\text{m}^2 \cdot \text{s}^{-1}$); $\partial C/\partial x$ is the concentration gradient (kg/m^4); and D is the diffusion coefficient (m^2/s) that in porous media depends on the properties of the diffusing chemical species, the pore fluid, and the porous medium.

In this work, the transport behaviour of HTO, I^- and Cl^- will be modelled. Porosity changes due to mineral precipitation/dissolution and feedback on transport will also be taken into account.

2.1.4 Mineralogical and chemical conditions

The (geo-) chemical conceptual model is implemented in the code PHREEQC v.3.1.7. (Parkhurst and Appelo, 2013). The mineralogical composition of the cement considered is representative of a low-pH cement ($\text{pH} \sim 11.0$). C-S-H phases with low Ca/Si ratio will be the main solid phases incorporated in the model. The porewater composition of the low-pH cement will be defined as the porewater in equilibrium with the solid phases present. The porewater composition of the clay is representative of the MX-80 bentonite described in the literature.

2.1.4.1 Chemical reactions and Thermodynamic database

As a first approximation, chemical reactions at equilibrium will be simulated using the thermodynamic database ThermoChimie v.9 (Giffaut et al., 2014), available in PHREEQC format. Precipitation of secondary phases to be formed in the cement/clay interface and dissolution of the major components of the low-pH cement will be taken into account. Although ThermoChimie v.9 includes the Specific Ion Interaction Theory (SIT) parameters for the activity correction, at present status the Davies equation will be preferred to save computational time, which is valid for the ionic strength of the studied system (<0.5 M).

ThermoChimie v.9. database includes thermodynamic data for 50 major, radioactive and toxic elements. A significant data set is also available for the stability of cement hydrates, clay minerals (Blanc et al., 2015) and other aluminium-silicate phases, such as zeolites, although no thermodynamic data are currently available for C-S-H phases with low Ca/Si expected to be present in our system. For this reason, thermodynamic data available in recent studies will be integrated in ThermoChimie database if needed (Walker et al., 2016).

2.1.4.2 Kinetic rates

Rate equations of precipitation/dissolution of secondary/primary phases will be provided directly in the input files of PHREEQC only as a second modelling approximation if local equilibrium does not provide a good representation of the experimental results.

ThermoChimie v.9 (Marty et al., 2015) contains a compilation of kinetic parameters for different minerals (albite, biotite, calcite, celestite, chlorite, CSH, dolomite, gibbsite, illite, kaolinite, portlandite, quartz, siderite and smectite) but probably this will need to be extended after a literature review of precipitation/dissolution kinetic parameters of C-S-H phases.

2.1.4.3 Sorption

The sorption reactions of Cl^- and I^- in low-pH cements will be considered in the model as a K_d value. Observations described in the recent review of Ochs et al. (2016) will be considered to select the most appropriate data.

2.2 Amphos 21 modelling approach

2.2.1 Modelled system

Amphos 21 will be involved in two different modelling activities:

1. Pore-scale reactive transport modelling at the micro-scale, in collaboration with FZJ (see FZJ modelling approach), and
2. Development of hydro-chemo-mechanical (HCM) models at the macro-scale (laboratory scale)

Only the second activity is described here. The focus of the work related with the HCM models will be on the chemical degradation of matrices of cementitious systems (cement paste, mortar, concrete samples) at the laboratory scale. Until WP1 experimental results are available, Amphos 21 is working with an existing experimental dataset that has been recently obtained at Chalmers University in Sweden (Babaahmadi et al., 2015a,b), in collaboration with SKB. They developed a new acceleration method enhancing calcium leaching processes in cementitious materials applying a combination of an aggressive solution (ammonium nitrate) and an external current. The method was applied successfully on a number of samples made of a mixture of Swedish structural Portland cement for

civil engineering (CEM I 42.5N SR3/MH/LA) and deionized water and with different water-cement ratios. The samples used had dimensions ranging from 5 to 10 cm in diameter and 2 to 7.5 cm in length. Water saturated conditions were considered. The characterization of the samples included hydro-chemo-mechanical parameters such as: pore size distribution, tensile and compressive strength, elastic modulus, gas and water (in some case) permeability, water sorptivity, diffusion coefficients of cations and chloride, sorption properties, qualitative mineral phase assemblages (portlandite depletion and partial C-S-H decalcification), and profiles of the Ca/Si ratio in the solid phase.

The model will include a detailed microstructural representation of the cementitious system to study the effect of changes in the microstructure on physical properties. The goal is to study under which circumstances the microstructure and chemical composition of the degraded samples obtained using an accelerated test method could be representative of a natural leaching process under repository conditions.

2.2.2 Equations and physical and chemical processes to be studied

The model that is used for the modelling of the experiments by Babaahmadi et al. (2015a,b) is based on a continuum-scale approach, i.e. solving the governing processes at the macroscopic scale, where cementitious materials are considered homogeneous. The model encompasses the following processes:

- Solute transport
- Chemical reactions at thermodynamic equilibrium using the CEMDATA database (Lothenbach et al., 2008)
- Fluid flow (even though diffusion-driven experiments are simulated here, the option of considering advective transport is relevant for upscaling to repository conditions of relevance to SKB)
- Mechanical damage due to external loads and the coupling of chemical degradation with an additional chemical damage (similar to e.g. Gérard et al., 1998)
- Multi-scale homogenization models (Bary, 2008, Stora et al., 2009, Bary et al., 2014) to predict the elastic properties of the cementitious system (cement paste, mortar, or concrete) at intact and aged states

The formulation for solute transport, fluid flow, and coupling to chemical reactions under thermodynamic equilibrium conditions is relatively standard and is not described here. For details, see e.g. Nardi et al. (2014) and Idiart et al. (2016).

The mechanical damage model is based on the well-known Mazars model (Mazars and Pijaudier-Cabot, 1996). This popular damage model has been specifically designed for cementitious materials, introducing two damage variables for compression and tension, respectively. These variables evolve as a function of an equivalent strain, which are calculated based on the principal strains. In turn, chemical damage is also considered through the following equation:

$$\sigma = (1 - d_m) \cdot (1 - d_c) E_0 \cdot \varepsilon \quad (2.2.1)$$

where σ (MPa) is the stress tensor, d_m and d_c are the mechanical (i.e. due to external loads) and chemical damage, respectively, E_0 (MPa) is the stiffness tensor, and ε is the strain tensor. Chemical damage may appear as a result of dissolution processes, which in the present case are driven by calcium leaching out of the system. It is well known that calcium leaching can negatively affect the mechanical properties of concrete to a significant extent (e.g. Nguyen et al., 2007).

To calculate the chemical damage, the following expression may be considered:

$$d_c = 1 - \frac{E_c}{E_0} \quad (2.2.2)$$

where E_c (MPa) is the chemically degraded Young modulus. This is calculated using homogenization theory. The Generalized Self-Consistent scheme (GSCS) and the Mori Tanaka (MT) scheme (Stora et al., 2009) are used to calculate the elastic properties of cement paste, mortar, and concrete based on the elastic parameters of the constituents (cement hydrates, porosity, sand, and gravel).

The evolution of permeability and effective diffusion coefficient with chemical degradation has been preliminarily considered using empirical relations between these parameters and porosity. A Kozeny-Carman type of relation has been used for permeability, whereas an Archie's law type of relation was implemented for diffusivity. The experimental results obtained for the initial (intact) state and after aging in their test setup will be used to verify whether these empirical relations are valid for cement system under study. Thereafter, if needed, the possibility of extending the homogenization methods described above for elastic parameters to the estimation of effective diffusion coefficient will be explored.

2.2.3 Numerical method and software

The software to be used is iCP (Nardi et al., 2014), an interface between the finite element software COMSOL Multiphysics (COMSOL, 2014), and IPhreeqc (Charlton and Parkhurst, 2011), a library that incorporates all the capabilities of PHREEQC (Parkhurst and Appelo, 2013). The result is a modelling platform that can be used to model non-isothermal unsaturated flow, heat transport, solid mechanics, and reactive solute transport. The interface is based on the operator splitting approach to solve for chemical reactions. Reactive transport models encompassing fluid flow, solute transport and chemical reactions of cementitious systems have already been implemented in iCP (Idiart et al., 2016). The implementation of the homogenization methods in iCP is currently under development.

2.2.4 Scale of analysis

The time scale of the simulations will be in the range from few months for the accelerated leaching experiments to several years for the natural leaching tests. The length-scale of the simulations covers a range from the microscopic level (using homogenization models) to the cm scale for the lab samples. The same model could then be used at the macro-scale (metre scale) for long-term predictions.

2.2.5 Output data

The intention of this modelling work is to develop reactive transport models of cement and concrete degradation at the continuum cm-scale in order to model different experimental setups. The goal is to verify the numerical approach used at larger scales (metre scale) with experimental data. In particular, microstructural aspects such as distribution of phases and porosity will result from the model. In addition, the validity of different relations between permeability/diffusivity and porosity will be explored. Finally, mechanical properties as a function of chemical degradation will also be obtained with the model and compared to experimental data.

2.3 BRGM modelling approach

2.3.1 Introduction

Cement materials are used for the storage of high-level and long-lived nuclear wastes in deep geological formations because of their very low permeability and high specific surface area that retain radionuclides in porous media (Marty et al., 2015). Transport of radionuclides in cementitious materials is mainly diffusive and is influenced by the electric field and surface complexation reactions at the mineral/water interface (Elakneswaran et al., 2010; Samson and Marchand, 2007). Nevertheless, the surface electrical properties such as the zeta potential of low-pH cements are not exactly known because of the difficulty to interpret correctly electrokinetic experiments (Labbez et al., 2006; Labbez et al., 2011). Furthermore, it is also very difficult to measure the low permeability of cement characterized by a connected microporosity and low water flow in the pores (Picandet et al., 2011). Therefore, there is a need for innovative methods that can be used to estimate the surface and transport properties of cement.

Electrical methods such as the streaming potential and low-frequency complex conductivity can be performed to non-intrusively describe the surface and transport properties of microporous media such as clays and cement-based materials (Okay et al., 2014; Revil et al., 2005). The streaming potential method consists in measuring the electrical potential difference due to the pore water flow resulting from the imposed water pressure difference. The streaming potential gives access to the zeta potential, which is a physico-chemical parameter of paramount importance to get information on the electrical potential and on complexation reactions at the surface of the minerals immersed in water (Hunter, 1981). The zeta potential is defined as the electrical potential located at the shear plane where the liquid velocity relative to the solid velocity is equal to zero (Hunter, 1981; Lyklema, 1995). The low-frequency complex conductivity method consists in measuring the electrical potential difference due to conduction and polarization phenomena occurring in the porous medium submitted to an alternative current, in the frequency range typically Hz to MHz (Chelidze et al., 1999). Low-frequency complex conductivity gives information on the surface electrical properties of the porous medium, but also on the grain/pore size distribution, surface area of the pores, and permeability (Bücker and Hördt, 2013b; Leroy et al., 2008; Revil and Florsch, 2010).

Zeta potentials estimation from streaming potential data is not straightforward, in particular when the ionic strength of the pore water is low (typically ≤ 0.1 M) because of the effects of the surface conductivity of the particles on the measured electrical potential difference, the streaming potential (Revil et al., 1999). Surface conductivity decreases the magnitude of the streaming potential and apparent zeta potential deduced from Helmholtz-Smoluchowski equation (Li et al., 2016). The ionic strength of low-pH cements (pH ~ 11) can be relatively low (≤ 0.1 M) (Calvo et al., 2010). Furthermore, calcium-silicate-hydrate (C-S-H) is the major phase of cement (weight fraction typically between 50 and 80% (Cao et al., 1997)). C-S-H form lamellar particles containing in average 2-4 unit layers, of nanometric dimension typically $30 \times 60 \times 5$ nm³ (Labbez et al., 2006), their specific surface area is very large (> 100 m² g⁻¹ (Jennings, 2008)) and they carry a negative surface charge associated with silanols surface sites when the Ca/Si ratio is low (typically < 1 (Labbez et al., 2006)). Regarding the high surface charge and specific surface area of α -C-S-H (Ca/Si ratio < 1 (Haas and Nonat, 2015)) and the low ionic strength of the pore water of low-pH cements, one may expect a strong influence of surface conductivity of C-S-H particles on streaming potential and zeta potential measurements of low-pH cements. Low-frequency complex conductivity measurements in relatively saline pore waters (ionic strengths typically $> 10^{-2}$ M) are challenging because of the polarization of the potential electrodes and of the small measured phase shift between injected current and measured electrical potential difference (Okay et al., 2014). Furthermore, complex conductivity models must consider

the presence of different types of ions (calcium, sodium, potassium, chloride, hydroxide, sulfate ions, etc...) in the pore water of cement and the presence of highly charged micropores presenting a complex connectivity (Calvo et al., 2010; Elakneswaran et al., 2010).

Streaming potential and electrical conductivity measurements will be combined and interpreted in WP3 of CEBAMA project to get information on the zeta potential of low-pH cement and complex conductivity measurements and models will be performed to get information on the pore size distribution and connectivity and on the permeability of low-pH cement. The chemical composition of the low-pH cement, and the methodology applied to interpret streaming potential and electrical conductivity measurements will be described briefly below.

2.3.2 System to be modelled: low-pH cement

CEBAMA reference mix design consists in ternary binder composition with CEM I (Anlåggningscement from CEMENTA, Table 2.3.1), Granulated silica fume (Parmix silica from Finnsementti), and Blast furnace slag (from Finnsementti, Table 2.3.1). The materials are easily available for VTT laboratories in Finland, where the samples will be casted. The binder composition is presented at Table 2.3.2.

Table 2.3.1. Chemical composition of Anlåggningscement cement from CEMENTA of Blast furnace slag (BSF) from Finnsementti. The exact chemical composition will be available during the project.

	CEMENT	BSF
CaO	65%	36-42%
SiO ₂	22%	36-40%
Al ₂ O ₃	3.5%	8-10%
Fe ₂ O ₃	4.5%	-
K ₂ O	0.6%	0.5-1.0%
Na ₂ O	0.1%	0.5-1.0%
MgO	1.0%	10-12%
SO ₃	2.0%	1.5-2%
Ti	-	0.9-1.3%
Cl	<0.01%	-

Table 2.3.2. Binder composition of CEBAMA reference mix design.

MIX PROPORTIONS	AMOUNT
TOTAL BINDER CONTENT	280 kg/m ³
CEM I	105 kg/m ³
SILICA FUME	110 kg/m ³
BLAST FURNACE SLAG	65 kg/m ³
CaO/SiO ₂ -RATIO	0.61

2.3.3 Proposed methodology

2.3.3.1 Zeta potential of low-pH cement

Laboratory streaming potential and direct current (DC) electrical conductivity measurements on low-pH cements and α -C-S-H will be combined to correct the apparent zeta potentials of low-pH cement inferred from Helmholtz-Smoluchowski eq. (2.3.1) from surface conductivity effects, following the approach developed recently by Li et al. (2016) for calcite powders assuming a thin electrical diffuse layer at the surface of C-S-H particles.

$$\frac{\zeta_a}{\zeta} = \frac{\sigma_w}{F\sigma(1+Re)} \quad (2.3.1)$$

where ζ_a and ζ are the apparent and corrected zeta potentials (in V), respectively, F is the electrical formation factor inferred from electrical conductivity measurements at different ionic strengths or using the measured connected porosity ϕ and cement exponent m associated with the C-S-H particles shape ($F = \phi^{-m}$, Archie first law), σ_w is the water electrical conductivity (in $S\ m^{-1}$), which can be estimated from the water chemical composition using PHREEQC or be measured, σ is the measured electrical conductivity of the low-pH cement, and Re is the Reynolds number deduced from the experimental conditions (sample length, measured water pressure). The calculation of the zeta potentials will be performed using an in-house tool that has been already developed by Shuai Li during his post-doc fellowship at BRGM and written in Matlab (Fig. 2.3.1).

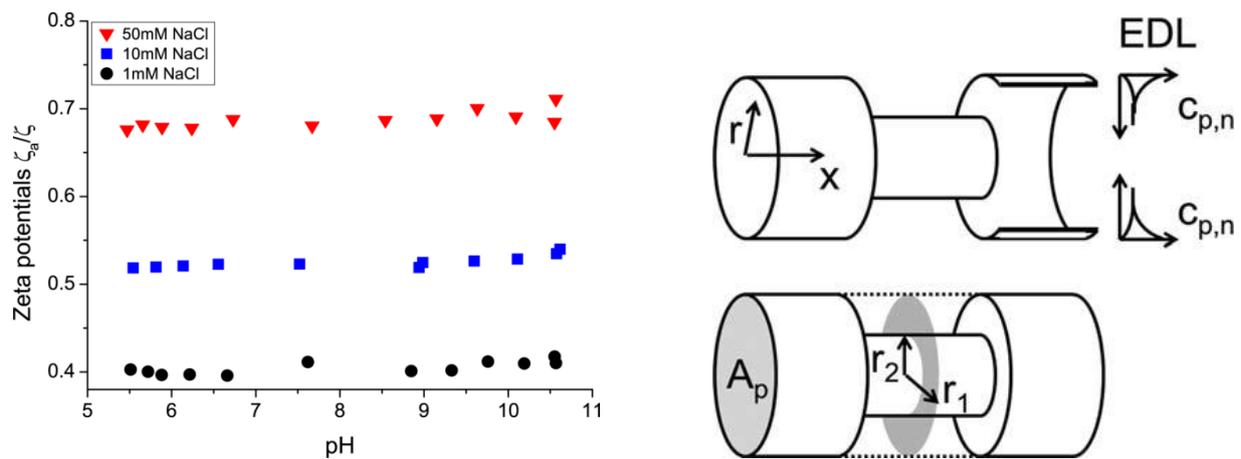


Fig. 2.3.1. (Left) Ratios of the apparent to corrected zeta potential versus pH at different salinities (0.001, 0.01 and 0.05 M NaCl) for calcite (Li et al., 2016). (Right) Sketch of the membrane polarization model used by Bückner and Hördt (2013a).

The corrected zeta potentials will be compared to those computed by an electrostatic surface complexation model assuming that the zeta potential is located at the beginning of the diffuse layer. The parameters of the electrostatic surface complexation model (sorption equilibrium constants, capacitances) will be adjusted according to the measured zeta potential data. Two surface complexation models will be tested (Elakneswaran et al., 2009 and Haas and Nonat, 2015) using the PHREEQC geochemical code (Parkhurst and Appelo, 2013) combined with the optimization code PEST (available at <http://www.pesthomepage.org/>).

2.3.3.2 Laboratory low-frequency complex conductivity of low-pH cement

Complex conductivity spectra of low-pH cement paste will be inverted to obtain relaxation time distribution using an available Matlab code (Florsch et al., 2014). Florsch et al. (2014) used generalized relaxation basis functions (such as the generalized Cole–Cole function) and the L-curve approach to optimize the damping parameter required to get smooth and realistic inverse solutions. Pore size distribution and permeability of low-pH cement paste will be estimated accordingly (Revil et al., 2015; Revil and Florsch, 2010).

Membrane polarization model (Bückner and Hördt, 2013a) will also be developed and applied to interpret low-frequency complex conductivity spectra of low-pH cement paste (Fig. 2.3.1). A membrane polarization code can be shared with researchers working at Braunschweig University (Germany, Prof. Andreas Hördt). A particular attention will be focused towards considering the

calculation of the charges at the C-S-H/water interface using the surface complexation model developed according to zeta potential measurements and considering interacting diffuse layers in cement micro- and nano-pores using the softwares PHREEQC, MATLAB, and COMSOL Multiphysics.

2.4 FZJ Modelling approach, in collaboration with Amphos 21

2.4.1 Introduction and modelled systems

Physical and chemical heterogeneities exist in a range of length scales (nm to cm) in cementitious systems. The macroscale physical and chemical properties in concrete strongly depend on the pore structure evolution during hydration and long-term degradation processes. Therefore, pore-scale models can be regarded as an appealing tool to describe the pore space structure and non-uniform distribution of chemical species in a realistic manner. The use of pore-scale models in other disciplines, such as oil and gas, is relatively well established for natural rocks (Shafei et al., 2013, Huber et al., 2014, Kang et al., 2014). However, pore-scale models of cement-based materials are only starting to be developed (Raouf et al., 2012, Patel et al., 2014a,b). The advantage of these models over traditional meso- and macro-scale models is that they allow to explicitly capturing microscopic effects of chemical reactions on the physical properties in a mechanistic way. This is the focus of this work, which is in line with the objectives of the CEBAMA project. In order to study the mass transport behaviour and the impact of the chemical degradation of cement pastes (e.g. due to calcium leaching and/or carbonation) on its transport properties, a pore-scale reactive transport model will be developed and validated in this work. For this purpose, a three dimensional (3D) advection-diffusion solver based on Lattice Boltzmann Method (LBM) will be coupled to a geochemical software.

In this work, focus will be on the reactive transport modelling at the pore-scale of cementitious matrices. No work on interfaces with host rocks or bentonite is envisaged. Processes of interest are the chemical degradation due to calcium leaching and carbonation of cementitious materials and its impact on physical properties, such as diffusivity, permeability, porosity, and pore size distribution.

2.4.2 Modelling approach

The Lattice Boltzmann Method simulates the microscopic behaviour of particles in a fluid in a discrete way. Space, time, and velocity vectors are discretized. By choosing proper discretization steps, mesoscopic and macroscopic properties can be recovered (Mohamad, 2011; Succi, 2001). The fundamental Lattice Boltzmann Equation (LBE) is:

$$f_i(r + e_i \Delta t, t + \Delta t) = f_i(r, t) + \Omega \quad (2.4.1)$$

In eq. (2.4.1), f_i is the particle distribution function at a particular discrete velocity direction i , r is the spatial vector and t is the time. The left-hand side of the equation represents the particle probability distribution at the neighbouring cell and next time step. On the right-hand side, the current local flow in the particular direction is corrected by a collision operator, Ω . The collision operator is the location in which the physical processes take place. By properly choosing collision terms and discretization magnitudes the macroscopic Navier-Stokes equation for fluid flow can be derived. The literature provides various modelling solutions for the collision operator. The most frequently-used collision term is the Bhatnagar-Gross-Krook (BGK) model, which contains a single relaxation time (SRT) operator (Bhatnagar et al., 1954).

Macroscopic properties such as fluid density, mass flux (J) and flow velocity (u_a) can be recovered from the sum of the probability functions and product of probability functions and local velocities, respectively:

$$\rho(r, t)(r + e_i \Delta t, t + \Delta t) = \sum_{i=0}^n f_i(r, t) \quad (2.4.2)$$

$$J(r, t) = \rho(r, t) \cdot u_a(r, t) = \sum_{i=0}^n e_i \cdot f_i(r, t) \quad (2.4.3)$$

$$u_a(r, t) = \frac{J(r, t)}{\rho(r, t)} \quad (2.4.4)$$

While the equations above describe advection mechanisms, diffusion processes can be calculated in a similar manner. In case of calculating diffusion processes, which are typically dominant in cementitious systems, it is sufficient to recover the species concentration. Therefore, the equilibrium function can be simplified to:

$$g_i^{eq}(r, t) = \omega_i C \left(1 + \frac{e_i \cdot u_a(r, t)}{c_s^2} \right) \quad (2.4.5)$$

Note that u_a in eq. (2.4.5) corresponds to the imposed macroscopic advection velocity instead of mass flow velocity of the species. Therefore, advection and diffusion are simulated in different steps. In order to simulate chemical reactions such as dissolution and precipitation and their effect on porosity changes the collision operation has to be extended (Patel et al., 2014):

$$\Omega = \Omega_{\text{BGK}} + \Omega_P + \Omega_{\text{rxn}} \quad (2.4.6)$$

$$\Omega_P = (1 - \theta(r, t)) \frac{C(r, t) - C(r, t - \Delta t)}{\Delta t} + C(r, t) \frac{\theta(r, t) - \theta(r, t - \Delta t)}{\Delta t} \quad (2.4.7)$$

Ω_P denotes the porosity collision operator. It can be seen in eq. (2.4.7) that the value is depending on the porosity of the local cell (θ) and the macroscopic species concentration (C). Ω_{rxn} is the source term for the species concentration and represents the coupling interface to the chemical module. Dissolution and precipitation reactions and consequent porous media geometry evolution are updated in the reaction term.

2.4.3 Numerical methods and software

To couple a pore-scale model with a geochemical simulator, a dedicated interface will be developed within the framework of CEBAMA. The coupling code (interface) manages the advective-diffusive flow calculation by a Lattice Boltzmann transport code. After the transport calculation, the new species concentrations are transferred to the chemical reactions code, which will calculate the resulting chemical species concentrations and the saturation indices for each compound. The solid phase composition and the abundance of the various solid phases, as well as the porosity values are updated after the chemical step (see Fig. 2.4.1). The interface will couple the codes Palabos (FlowKit, 2011, <http://www.palabos.org/>), for LBM pore-scale modelling, and PhreeqcRM (Parkhurst and Wissmeier, 2015), which are both open access software. If required in the future it is feasible to extend

the interface code for other chemical and transport codes such as GEMS (Kulik et al., 2013) and Sailfish (Januszewski and Kostur, 2014).

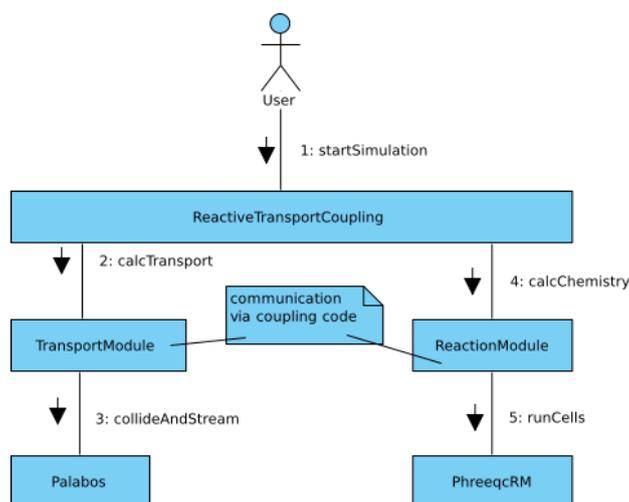


Fig. 2.4.1. Data flow chart of coupling code runtime. The interface will couple the LBM code Palabos (<http://www.palabos.org/>) with PhreeqcRM (Parkhurst and Wissmeier, 2015).

Palabos has already shared and distributed memory multi CPU capabilities, i.e. OpenMP and MPI. A modified version of PHREEQC will be used, named as PhreeqcRM (Parkhurst and Wissmeier, 2015), which is more suitable for coupling with external codes. PHREEQC is based on the law of mass action (LMA) approach to solve the chemical system of equations. PhreeqcRM implements a C++ interface to the PHREEQC core which can be used programmatically in order to prevent most of the overhead due to parsing text based input files. Another advantage is the possibility to use multi-CPU capabilities via multi-threading or MPI to reduce computing time.

It is planned to use the ThermoChimie thermodynamic database (Giffaut et al., 2014) implemented in PHREEQC format, containing relevant data on cement phases, e.g. from (Blanc et al., 2010). As an alternative, the database CEMDATA 14/01 could be used (Lothenbach et al., 2008, available at Empa's website (<https://www.empa.ch/web/s308/downloads>)).

2.4.4 Scale of model simulations, upscaling, and output data

The length scale of the model simulations at pore-scale will be in the micrometre to millimetre scale, to study processes at the microscopic level. Larger (micrometre sized) pores will be discretized explicitly in the LBM approach, while smaller (nano-scale) pores will be modelled as a porous continuum (e.g. C-S-H gels). The time scales will be in the range of days-years to match experimental setup.

The goal of the pore-scale reactive transport simulations is to obtain output parameters such as porosity, diffusivity, or permeability under different levels of chemical degradation, that can be up-scaled and ultimately used in continuum scale models, e.g. using iCP (interface Comsol PHREEQC, Nardi et al., 2014). To this end, the provided effective diffusion and permeability coefficients from the micro-scale calculations will be used as input data for mesoscopic and macroscopic continuum-based calculations.

2.4.5 Computational resources

Due to the nature of dynamic locality of the LBM algorithm it is possible to develop an interface, which is easily parallelizable on multiple CPUs. This assures good scalability with increasing number of calculation units as CPU cores or GPU computing units.

The development and testing of the coupling end extension of the LBM code will be done on a local office workstation. Shared memory computations will be performed to test and validate the code based on test problems assuming simple geometries. Thereafter, scalability tests with increased geometrical and/or chemical complexity will be done with help of the in-house cluster at Jülich (274 cores, 868 GB memory). Depending on the problem size, further calculations will be performed using HPC (High Performance Computing) resources of the Jülich Supercomputing Centre (JSC), employing either the JURECA cluster (Jülich Research on Exascale Cluster Architectures; 271 TB memory, 45000 CPU cores, 1.8 PFLOPS) or the IBM BlueGene/Q supercomputer JUQUEEN (448 TB memory, 5.9 PFLOPS).

2.4.6 Input data

In an initial phase, various benchmark calculations will be performed to validate the code. The benchmark cases should be simple enough to be either solvable analytically or well known by other benchmarking experiments. The cases are including but not limited to simple diffusion-only problems, coupled advection-diffusion problems, coupled diffusion-reaction problems (dissolution and precipitation) and reactive transport benchmarks of flow through material involving porosity effects. The distribution of porosity and cement phases will be obtained both numerically, e.g. by using CEMHYD3D (Bentz, 2005), and by 2D/3D imaging techniques (μ CT) and SEM measurements, that are planned to be used by several partners within CEBAMA WP1. Once the implementation and verification phases are complete, laboratory data produced in CEBAMA will be simulated.

2.5 NRG Modelling approach

2.5.1 Introduction

NRG will, in collaboration with TU-delft, develop a numerical model that describes reactive transport of macro and trace elements at a concrete-clay interface. This model development is a continuation of work on radionuclide migration processes in cementitious barriers (Marty et al., 2015).

2.5.2 Modelled system and equations solved

The model will be used to describe reaction-diffusion processes within a 1D Concrete-Boom Clay system. The equations that need to be solved for this system are a combination of (local) chemical equilibrium conditions with diffusion of mobile species. The chemistry part is solved by iterative (Newton Raphson) solving the set of mass-action mass-balance equations.

2.5.3 Numerical methods and software

The transport part is solved by a simple explicit finite-differences method with a series of well-mixed cells as elementary volumes. The open source code ORCHESTRA (Meeussen, 2003) will be used to set up the reaction-diffusion model. This code has been applied successfully to very

similar types of reactive porous media, concrete as well as soil/rock matrices, see e.g. (Sarkar et al., 2010, Dijkstra et al., 2009). A special feature of this software is that all chemical and physical model equations are accessible by end users and can be changed or extended.

Within this project, the effect of electric potentials on diffusion as a means to speed up the diffusion process will be studied. In order to simulate this the current model (diffusion module) has to be extended with the possibility to include the electric potential gradient as a driving force for diffusion.

2.5.4 Scale of model simulations

The scale of the model simulations is in agreement with the experimental set up and covers a range of ca. 0.1 to 20 cm. The time scales will be in the range of days-years to match experimental setup. However, the same model approach can be used to scale the model predictions up to larger time and length scales.

2.5.5 Input parameters and output of simulations

As input for the model predictions a chemical equilibrium description is required for the cementitious part of the matrix as well as for the Boom Clay zone. In both cases, literature databases will be used (Lothenbach et al., 2008, Dijkstra et al., 2009), in combination with specific parameters on the composition of the materials used in the experiments.

The model calculates local chemical conditions (total element concentrations, distribution of elements over different physical chemical forms e.g. minerals, solid solutions, adsorbed species, etc.) and fluxes within the diffusion system. Output for all chemical parameters is available as a function of time and space over the duration of the simulations (pH, redox and element concentration profiles as a function of time, etc.).

2.5.6 Computational resources

Reactive transport calculations are known to be computationally intensive. The ORCHESTRA code is written in Java and is able to run on desktop computers as well as on mainframe machines. The code is fully parallelized and makes efficient use of multiprocessor hardware. For this work, a dedicated server with 16 processor cores will be used.

2.5.7 Up-scaling

Although the focus of the model is the simulation of an experimental system at the mm-to-cm scale within this project, the same processes can be used to adapt the model to larger scales. At NRG, the ORCHESTRA modelling framework is used in this way to perform PA calculations at scales of hundreds of meters and at time scales up to 10 million years.

2.6 RWMC modelling approach

2.6.1 Introduction and system to be modelled

RWMC is developing a numerical strategy based on a coupled hydro-chemo-mechanical (HMC) approach, which has been so far mainly applied in bentonite (Ishii et al., 2013; Kobayashi et al.,

2015). The main interests of RWMC are how to model mass transport at the cement-clay interface and how to couple a geochemical–mass transport code with a clay –hydraulic-mechanical code.

The system to be modelled is the interface between cement-based materials and bentonite. The reference bentonite material is Kunigel V1, while cementitious materials to be considered in Japan are OPC and Low alkalinity cement. However, other cementitious materials, such as fly-ash mixed cement are also under study. It is planned to use the results of WP1 experiments as input for this work, although RWMC has also conducted experiments of cement-bentonite interaction (Negishi, 2013) and cement degradation (Kurumisawa et al., 2013). In addition, RWMC is also studying a natural analogue in the Philippines of alkaline alteration (pH~11) of bentonite formation.

2.6.2 Main processes modelled and modelling approach

RWMC will perform 2D simulations with and without the coupling between mechanical and chemical processes to confirm the effectiveness and necessity of such HMC coupling scheme. The final application of these models will be on the concept and cross-section of the Japanese TRU disposal facility.

The goal is to study the reciprocal influences between changes of (1) mechanical and hydraulic properties due to chemical evolution, and (2) changes in the chemical alteration patterns due to modifications in the hydraulic properties. The outcome of the work could be useful for evaluating the long-term performance of the engineered barrier system including cement-clay systems.

2.6.2.1 Data

An important parameter in this type of models is the dissolution rate of montmorillonite under compacted condition, which is an essential input data for the long-term predictions of mineralogical changes in a cement-clay interface. RWMC will provide data on this issue (Sato et al., 2013). The changes of mechanical and hydraulic properties of bentonite can then be modelled as a function of the “effective montmorillonite density”, which is used for the M-C coupled simulations of RWMC.

2.6.3 Numerical methods and software

The method proposed couples a geochemical, a mass transport, and a mechanical code. The mechanical code has been developed is based on the Finite Element Method code DACSAR, which can update the mechanical properties with changes in the mineralogy due to mass transport and chemical degradation. DACSAR has been developed by Tokyo Institute of Technology and Kobe university (Iizuka and Ohta, 1987).

In CEBAMA, RWMC will work on the development of the FEM code DACSAR regarding the calculation of changes in the mechanical properties and density of bentonitic clay and cementitious materials. Modification of DACSAR regarding M-C couplings is a collaborative work between Kobe Univ. (Prof. Iizuka) and RWMC. DACSAR will be coupled to the geochemical-mass transport simulation code PHREEQC (Parkhurst and Appelo, 2013). Part of the geochemical calculations will be performed by Hokkaido Univ. (Prof. Sato) in collaboration with RWMC.

2.7 SCK modelling approach

2.7.1 System to be modelled

SCK will study the interaction between high-pH cementitious materials and Boom Clay, the clayey host rock in the Belgium concept for the repository of nuclear waste. The focus will be on the chemical-physical alterations within concrete. The overall objectives are (i) to validate the prediction of macroscopic variables using experimental information on the microstructure, and (ii) to apply a coupled reactive transport model for simulating the relations between chemical degradation, microstructural changes and macroscopic transport properties at the micro-scale, explicitly taking into account the spatial arrangement of different phases (e.g. liquid, portlandite, C-S-H gels, clinker), at the interface between concrete and the host rock.

2.7.2 Main processes modelled and modelling approach

SCK will work on the prediction of macroscopic variables from microstructural information, starting from 3D geometries of concrete phases (input from FIB-SEM, WP1), deriving 3D geometries from 2D SEM images or using microstructures from integrated kinetic models (such as HYMOSTRUC (Breugel, 1991) and CEMHYD3D (Bentz, 2005)). A reactive coupled micro-scale model for simulating the spatial-temporal evolution of chemical changes will be applied to simulate influence of clay water on cement paste microstructure. In addition, a screening of important parameter of the cement affecting macroscopic transport properties will be conducted based on virtual 3D geometries generated using hydration models. Finally, changes in physical properties resulting from geochemical alteration will be predicted starting from 3D geometries of concrete phases (WP1) and applying the reactive-coupled lattice Boltzmann model. Additional analysis on obtaining effective properties from FIB-SEM images will be carried out and results will be compared with experiments from (WP1).

The goal is to validate if the modelling approach is able to predict macro-scale (continuum) transport properties (few hundreds of μm^3 to mm^3) using experimental information at the micro-scale (mainly spatial distribution of different concrete phases at μm scale). Moreover, the most critical processes and parameters affecting the microstructure and macroscopic transport properties will be investigated.

2.7.3 Numerical methods and software

A three-dimensional (3D) coupled reactive transport model based on a lattice Boltzmann approach to solve the water flow and solute transport equations and IPhreeqc (Charlton and Parkhurst, 2011) as the geochemical solver will be used. Alternatively, the lattice Boltzmann approach can also be linked with simplified reaction models pre-computed as look-up tables. The lattice Boltzmann approach allows incorporating the spatial distribution of different relevant phases in a discrete manner enabling to simulate alterations of micro-scale properties and features and the macroscopic transport variables. This allows simulating the interface processes starting from basic principles. SCK•CEN has developed this 3D code and demonstrated its versatility for cementitious materials (Patel et al., 2014a,b; Patel, 2016) including explicitly C-S-H transport properties.

2.7.4 Input and output data

The reactive transport model, within a lattice-Boltzmann framework, uses micro-scale information from WP1 as an input to the water flow and solute transport solvers: chemical composition, spatial-temporal information of phases. The model is then validated against micro-scale experimental data and macro-scale (continuum scale) measurements of transport properties such as porosity, tortuosity, and permeability. The main challenge is to link the estimated transport properties to the measurements

between which a scale-discrepancy exists. This may result in the use of additional upscaling techniques. For simulating reactive transport processes, input geometry would be either taken from 3D FIB-SEM analysis or virtual microstructures generated using integrated kinetic models. A feasibility analysis will also be performed for deriving 3D geometries from 2D SEM images.

The geochemical models for the cement-based material and for the Boom clay (percolation tests or samples for HADES) are based on previous work on concrete degradation (e.g., Jacques et al., 2010, Jacques et al., 2013, Phung et al., 2013) and experience within SCK•CEN.

2.8 UDC modelling approach

2.8.1 Modelled system

Models of the thermo-hydro- mechanical-chemical (THMC) behaviour of cement-clay interfaces developed by UDC will be applied on two different sets of experiments:

1. Six heating and hydration experiments performed on concrete-bentonite interfaces. These six cells (named HB cells: HB1 to HB6) were performed to study the interactions between concrete and bentonite porewaters at the conditions prevailing in the EBS during the early hydration stage. The cells were mounted at CIEMAT facilities on May 2006. Three of them were dismantled during the NF-PRO project after 196, 347 and 568 days (cells HB1 to HB3). Cell HB4 was dismantled during the PEBS project after 1610 days of heating and hydration. Cells HB5 and HB6 have been running for 2550 and 3650 days, respectively. HB6 will be dismantled in the course of the CEBAMA project, after 10 years. HB tests were performed on medium-size cells containing a 7.15 cm thick bentonite sample in contact with a 3 cm thick concrete sample. The cells are cylindrical with an internal diameter of 7 cm and an inner length of 10 cm. They were placed in a Teflon cover to prevent the lateral heat conduction and the swelling of bentonite. The cell was hydrated at a constant pressure and 25 °C at the top of the cell through the concrete while the temperature was maintained constant at 100 °C at the bottom of the cell. Sulphate-resistant ordinary Portland cement (CEM I-SR) was used. The dry density of the concrete and FEBEX bentonite was 2.22 and 1.65 g/cm³, respectively, and the initial water content was 2.6% and 13.3%, respectively. The cells were hydrated with the synthetic Spanish Reference Clay porewater at a constant injection pressure of 600 kPa applied on the top of the cell.
 2. The 2nd set of experiments consists of six heating and hydration tests performed on mortar-bentonite and bentonite-magnetite interfaces. These cells, named 2I cells, were designed to reproduce the repository conditions prevailing at 1000 to 3000 years after emplacement of the waste when the bentonite is fully saturated (Cuevas et al., 2013). The six double interface cells were performed by CIEMAT with mortar, bentonite and magnetite powder within the PEBS project. They started on May 2012 and were dismantled after 540 days on September 2013. The 2I cells were cylindrical with an internal diameter of 7 cm and an inner length of 2.5 cm. The cells were placed in a Teflon cylinder to prevent the lateral heat conduction and the swelling of bentonite. They were hydrated with synthetic argillaceous water and heated at 60 °C. A lime mortar was used as a surrogate of the product of concrete degradation. The dry density and the initial water content of the concrete and FEBEX bentonite were 1.7 and 1.65 g/cm³, and 2% and 13.3%, respectively. The initial water content of the magnetite was 3.2%. The 2I cells were hydrated using the same procedure as the first set of tests.
-

2.8.2 Equations solved and physical and chemical processes studied

Following the formulation by Navarro and Alonso (2000), water mass balance is given by:

$$\frac{D_s m^w}{Dt} + m^w \nabla \cdot v^s + \nabla \cdot (\rho^l X_l^w q^l + \rho^g X_g^v q^g + j_v) = 0 \quad (2.8.1)$$

where $\frac{D_s}{Dt}$ is the material derivative with respect to the solid particles which move with a velocity vector v^s (m/s), ρ^l and ρ^g are the bulk densities of the liquid and gaseous phases (kg/m^3), respectively, X_l^w is the mass fraction of water in the liquid phase, X_g^v the mass fraction of the vapour in the gas phase, q^l is the vector of volumetric liquid flux (m/s) given by eq. (2.8.15), q^g is the vector of volumetric gas flux (m/s) given by eq. (2.8.16), j_v is the dispersive mass flux of vapour with respect to the mean gas velocity ($\text{kg/m}^2/\text{s}$) given by eq. (2.8.17), and m^w is the mass of water per unit volume of porous medium (kg/m^3) given by

$$m^w = \emptyset [\rho^l X_l^w S_l + \rho^g X_g^v (1 - S_l)] \quad (2.8.2)$$

where \emptyset is the porosity and S_l is the liquid saturation degree. Air mass balance equation is given by:

$$\frac{D_s m^a}{Dt} + m^a \nabla \cdot v^s + \nabla \cdot (\rho^g X_g^a q^g + \rho^l X_l^a q^l) = 0 \quad (2.8.3)$$

where X_g^a is the mass fraction of air in the gaseous phase, X_l^a is the mass fraction of air in the liquid phase, and m^a is the mass of air per unit volume of porous medium (kg/m^3) which is given by:

$$m^a = \emptyset [\rho^g X_g^a (1 - S_l) + \rho^l X_l^a S_l] \quad (2.8.4)$$

The solid mass balance is given by:

$$\frac{D_s \rho^d}{Dt} + \rho^d \nabla \cdot v^s = 0 \quad (2.8.5)$$

where ρ^d is the dry density of the medium, equal to $\rho^s(1 - \emptyset)$, where ρ^s is the density of the solid particles (kg/m^3). Considering the coefficient of thermal expansion of the solid, C_T^s ($1/^\circ\text{C}$), and disregarding mechanical compressibility of the particles, eq. (2.8.5) becomes:

$$\frac{D_s \emptyset}{Dt} = (1 - \emptyset) \left[\nabla \cdot v^s - C_T^s \frac{D_s T}{Dt} \right] \quad (2.8.6)$$

where T is the temperature ($^\circ\text{C}$). The formulation assumes that all phases are at local thermal equilibrium and therefore they are all at the same temperature. Hence, the energy balance is described in terms of an equation of internal energy:

$$\frac{D_s h}{Dt} + h \nabla \cdot v^s + \nabla \cdot (-\Lambda \cdot \nabla T + I^e) = 0 \quad (2.8.7)$$

where h is the average specific enthalpy of the soil (J/kg) which in turn is given by:

$$h = \rho^l X_l^w \emptyset S_l h^w + \rho^l X_l^a \emptyset S_l h^a + \rho^g X_g^v \emptyset (1 - S_l) h^v + \rho^g X_g^a \emptyset (1 - S_l) h^a + \rho^l X_l^a \emptyset S_l h^a + \rho^s (1 - \emptyset) h^s \quad (2.8.8)$$

where h^w , h^v , h^a and h^s are the specific enthalpies of free water, vapour, air and solid particles, respectively, which are assumed to depend linearly on temperature and specific heat, and I^e is the vector of convective energy flux, given by:

$$I^e = \rho^l X_l^w h^w q^l + \rho^g X_g^v h^v q^v + \rho^g X_g^a h^a q^g \quad (2.8.9)$$

where q^g is the vector of volumetric vapour flux (m/s) which is given by the last terms of eq. (2.8.1), that is, $q^v = \rho^g X_g^v q^g + j^v$, and Λ is the bulk thermal conductivity tensor ($\text{W/m}^\circ\text{C}$) which for

unsaturated bentonite can be computed as a volume-weighted average of the conductivities of the components according to:

$$\Lambda = \phi S_l \Lambda^w + X_l^a \phi S_l \Lambda^a + \phi(1 - S_l)(\Lambda^v + \Lambda^s) + (1 - \phi)\Lambda^s \quad (2.8.10)$$

where Λ^w , Λ^v , Λ^a and Λ^s are the thermal conductivities of water, vapour, air and solid, respectively. This equation, according to Tang et al. (2008), provides the best fit to measured thermal conductivity data for several bentonites, including FEBEX bentonite.

The following incremental formulation of the equilibrium equation is used:

$$\nabla \cdot (\Delta\sigma' + \Delta P^g \delta) + \Delta\rho g k = 0 \quad (2.8.11)$$

where $\Delta\rho$ is the increment of the average soil density, g is the gravitational acceleration (m/s^2), k is the unit vector in the gravity direction, δ is the vector expression of Kronecker's delta, ΔP^g is the increment in gas pressure (Pa) which for saturated conditions should be replaced by the increment in the liquid pressure (Pa), ΔP^l , and $\Delta\sigma'$ is the vector of increments of effective stress (Pa) which is related to the vector of increments of total stress $\Delta\sigma$ (Pa) in unsaturated conditions through:

$$\Delta\sigma' = \Delta\sigma - \Delta P^g \delta \quad (2.8.12)$$

while for saturated conditions the previous equation is replaced by (Fredlund and Rahardjo, 1993): $\Delta\sigma' = \Delta\sigma - \Delta P^l \delta$.

Solute transport processes include advection, molecular diffusion, and mechanical dispersion. Each of them produces a solute flux per unit surface and unit time. There are as many transport equations as primary chemical species in the system. The mass balance equation for the j^{th} primary species is given by (Zheng and Samper, 2008a):

$$m_l^w \frac{\partial C_j}{\partial t} + \frac{\partial(m_l^w P_j)}{\partial t} + \frac{\partial(m_l^w W_j)}{\partial t} + \frac{\partial(m_l^w Y_j)}{\partial t} = L^*(C_j) + r_i(C_j^0 - C_j), j = 1, 2, \dots, N_c \quad (2.8.13)$$

C_j is the total dissolved concentration of the j^{th} species (mol/L), m_l^w is the mass of liquid water per unit volume of medium (kg/m^3) which is equal to $\rho^l X_l^w \theta$, where $\theta = S_l \phi$ is the volumetric watercontent (m^3/m^3), P_j , Y_j and W_j are the total precipitated, sorbed and exchanged concentrations (mol/L), respectively, of the j^{th} primary species, r_i is the sink term ($\text{kg/m}^2/\text{s}$), C_j^0 is the dissolved concentration of j^{th} species (mol/L) in the sink term r_i , N_c is the number of primary species. $L^*(\cdot)$ is the following transport operator:

$$L^*(\cdot) = \nabla \cdot [m_l^w D^j \cdot \nabla(\cdot)] - m_l^w q^l \cdot \nabla(\cdot) + (r_e - r_c)(\cdot) \quad (2.8.14)$$

where D^j is the dispersion coefficient (m^2/s), and r_c and r_e are the condensation and evaporation rates ($\text{kg/m}^2/\text{s}$), respectively. Coupled transport phenomena such as thermal and chemical osmosis may be important for compacted bentonites (Keijzer et al., 1999; Soler, 2001). The volumetric liquid flux, q^l , includes the classical Darcian term together with the chemical and thermal osmotic terms:

$$q^l = -\frac{K^{il} k^{rl}}{\mu^l} (\nabla p^l + \rho^l g \nabla z) - k_T \nabla T + \sigma \frac{K^{il} k^{rl}}{\mu^l} \nabla \pi_h \quad (2.8.15)$$

where p^l is the liquid pressure (Pa), K^{il} is the intrinsic permeability tensor of the liquid (m^2), k^{rl} is the relative permeability of the liquid, μ^l is the viscosity of the liquid (kg/m/s), z is the elevation, k_T is the thermal-osmotic permeability ($\text{m}^2/\text{K/s}$), π_h is the osmotic pressure (Pa), and σ is a dimensionless reflection coefficient for chemical osmosis which measures the non-ideality of a membrane and is defined as the ratio of the applied osmotic pressure to the developed hydraulic pressure at equilibrium. An ideal membrane has a reflection coefficient of 1 whereas it varies between 0 and 1 for non-ideal membranes. The volumetric gas flux, q^g , is given by:

$$q^g = -\frac{K^{ig}k^{rg}}{\mu^g}(\nabla p^g + \rho^g g \nabla z) \quad (2.8.16)$$

where K^{ig} is the intrinsic permeability tensor of the gas (m^2), k^{rg} is the relative permeability of gas, μ^g and is the viscosity of the gas phase (kg/m/s). The dispersive mass flux of vapour, j^v , is calculated by Fick's law:

$$j^v = -\rho^g D^v \nabla X_g^v \quad (2.8.17)$$

where D^v is the hydrodynamic dispersion tensor for vapour (m^2/s) which includes the effects of mechanical dispersion and molecular diffusion. The effective molecular diffusion coefficient for the vapour, D_e^v , (m^2/s) is calculated from (Pollock, 1986):

$$D_e^v = \frac{5.9 \cdot 10^{-6} \tau^v (T + 273.15)^{2.3}}{p^g} \quad (2.8.18)$$

where τ^v is the vapour tortuosity (dimensionless). The mechanical law is given by:

$$d\varepsilon = C d\sigma' + \beta d\Psi + \alpha dT \quad (2.8.19)$$

where ε is the strain vector, C is the elastic matrix (1/Pa), β is a vector of coefficients (1/Pa) which account for the deformation caused by changes in suction $\Psi = (p^l - p^g)$, and α is a vector of thermal expansion coefficients (1/°C). Nguyen et al. (2005) used successfully the state-surface approach to interpret a swelling pressure test. The following state-surface expression of Lloret and Alonso (1995) is adopted here to model bentonite swelling:

$$e = A + B \ln \sigma' + C \ln(\Psi + p^a) + D \ln \sigma' \ln(\Psi + p^a) \quad (2.8.20)$$

where e is the void ratio which is equal to the volume of voids divided by the volume of the solids; p^a is the atmospheric pressure (Pa), σ' is the mean effective stress (Pa), and A , B , C and D are empirical constants (see Nguyen et al., 2005).

The chemical model for compacted bentonite accounts for the following reactions: aqueous complexation, acid/base, cation exchange, surface complexation, and dissolution/precipitation of minerals. The chemical system is defined in terms of the concentrations of the following primary species: H_2O , H^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , $SiO_2(aq)$, Al^{3+} and Fe^{2+} . A detailed description of calculations of chemical reactions can be found in Xu et al. (1999). The database EQ3/6 (Wolery, 1992) is used, together with the Gaines–Thomas convention for cation exchange. Surface complexation is modelled using three types of protonation/deprotonation sites, SSOH, SW₁OH and SW₂OH (Bradbury and Baeyens, 1997). Temperature-dependent equilibrium constants of EQ3/6 are valid for temperatures between 0 and 300 °C.

2.8.3 Numerical method and software

The software to be used is INVERS-FADES-CORE, a finite element code for modelling non-isothermal multiphase flow, heat transport and multicomponent reactive solute transport under both chemical equilibrium and kinetics conditions. The code takes into account the mass balance of water, air, solid and energy; the transport of solids and mechanical equilibrium. INVERSE-FADES-CORE solves both forward and inverse multiphase flow and multicomponent reactive transport problems in 1-, 2- and 3-D axisymmetric porous and fractured media (Zheng and Samper, 2004, 2005). This code is the result of integrating the capabilities of FADES (Navarro, 1997), CORE2D (Samper et al., 2003), FADES-CORE (ENRESA 2000a) and INVERSE-CORE (Dai and Samper, 2004). State variables of the forward model include liquid and gas pressures and temperature, which are solved by a Newton–Raphson method. A sequential iteration method is used to solve reactive transport equations. The inverse problem is solved by minimizing a generalized least-squares

criterion with a Gauss-Newton–Levenberg–Marquardt method (Dai and Samper, 2004). The forward routines of INVERSE-FADES-CORE have been widely verified with analytical solutions and tested with THM and THC problems (Navarro and Alonso, 2000; ENRESA, 2000a; Samper et al., 2008a) as well as with THMC processes (Zheng, 2006; Zheng and Samper, 2004).

Codes of CORE2D series have been developed by the UDC. Most of them have been used to model FEBEX laboratory tests (Samper et al., 2006, 2008b; Zheng et al., 2010), in situ tests (Zhang et al., 2008; Zheng et al., 2011), field case studies (Molinero et al., 2004; Dai and Samper, 2004; Molinero and Samper, 2006; Dai and Samper, 2006; Dai et al., 2006), evaluate the long-term geochemical evolution of radioactive waste repositories in clay (Yang et al., 2008) and granite (Yang et al., 2007), analyse stochastic transport and multicomponent competitive cation exchange in aquifers (Samper and Yang, 2006), and study concrete degradation (Galíndez et al., 2006).

The code INVERSE-FADES-CORE will be used to model the laboratory experiments (HB and 2I cells) as well as the long-term simulations of the deep geological disposal of a HLW in a clay formation. This code has already been used in: (1) The THC model of the FEBEX in situ test (Samper et al., 2008a), (2) The THCM model of the FEBEX in situ test (Zheng et al., 2011), (3) The THCM model of the FEBEX mock up test (Zheng and Samper, 2008), (4) The THCM model of a heating and hydration lab experiment performed on compacted FEBEX bentonite (Zheng et al., 2010), (5) The THC model of the Ventilation experiment on Opalinus Clay (Zheng et al., 2008b), and (6) THCM models within PEBS Project such as heating and hydration tests on 60 cm long cell, heating and hydration corrosion tests and heating and hydration tests with concrete and bentonite.

Within the CEBAMA project UDC is working in the development of code improvements including: (1) Incorporating mechanical and geochemical couplings to account for porosity changes caused by swelling phenomena. This leads to fully coupled THMC models.

(2) Improvements in the chemistry of gaseous species such as $O_2(g)$, $CO_2(g)$ and $H_2(g)$.

Ordinary desktop computers are planned to be used for this work.

2.8.4 Scale of analysis

The time scale of analysis range from 0.5 to 11 years for the HB lab tests or 542 days for the 2I lab cells to 1Ma for the long-term performance of the engineered barrier system of a high-level radioactive waste repository. The space macro-scale of analysis is 2.5 cm for the 2I tests, 10 cm for the HB tests, and several meters for the long-term predictions.

2.8.5 Description of the input and output data

INVERSE-FADES-CORE needs the following input data (parameters) for: (1) water flow, (2) thermal properties, (3) mechanical properties, (4) solute transport, and (5) geochemical. Water flow parameters are intrinsic permeability of the liquid as a function of porosity, liquid relative permeability as a function of liquid saturation, retention curve, liquid viscosity ($kg/m \cdot s$) as a function of temperature, liquid density as a function of liquid pressure and temperature, gas intrinsic and relative permeabilities, vapour tortuosity, gas viscosity, solid density and thermo-osmotic permeability. Thermal parameters are specific heats and thermal conductivities (of the liquid, solid, vapour, and air), and vaporization enthalpy. Solute transport parameters are molecular diffusion coefficient in water as a function of T, longitudinal dispersivity, and solute tortuosity as a function of volumetric water content and porosity. Mechanical parameters are water mechanical compressibility and water and solid thermal expansion. Geochemical parameters are the initial and boundary water content, porosity, mineral composition, CEC, and sorption sites.

Output data of INVERSE-FADES-CORE are water inflow, water content, saturation degree, temperature and porosity temporal and spatial evolution, concentration of the mineral an aqueous phases, pH temporal and spatial evolution, porosity changes with mineral precipitation/dissolution, cation exchange concentration and sorbed species concentration.

2.8.6 Upscaling of results

UDC will test coupled THMC model improvements and evaluate time-scale effects from concrete-bentonite test data measured after times ranging from 0.5 to 7 years. UDC will also perform long-term reactive transport models of the concrete and bentonite barrier system of a high-level radioactive waste repository in a clay formation.

2.9 Czech Technical Univ. (CTU), Dep. Nuclear Chemistry (DNC) – modelling approach

2.9.1 Modelling of diffusion experiments

In the context of previous laboratory work and experiments proposed to be conducted in our laboratory within the CEBAMA project, the first goal of the modelling work in CTU-DNC is the improvement of evaluation methods of diffusion experiments. These experiments are planned to be performed in co-operating Czech laboratories (UJV and CTU-CEG).

The experiments consist of initially through-diffusion experiments with non-interacting species, with an arrangement with limited volume of working reservoirs in which concentrations will be monitored, but not kept constant, during the experiment. This type of experiment can be operated in a simple way, but its evaluation needs a modification of the broadly used *time-lag* method of evaluation of through-diffusion experiments.

For the evaluation of such experiments in blocks of compacted bentonite we developed a tool in GoldSim software (Vopalka et al., 2006) that also enables to model diffusion through the sandwich layers consisted of layers of different character (e.g. separating filters and studied layer in case of compacted bentonite). The model was thoroughly tested in numerous studies that showed for simply initial and boundary conditions the agreement between modeled solutions of 1D diffusion equation and corresponding analytical solutions. The model also proved to be consistent with theory in case of retardation of concentration signal due to the sorption described by linear isotherms (K_d model). The model is able to describe and evaluate numerous types of diffusion experiments, also above mentioned experiments with small volumes of working containers. The characteristic parameters of the diffusion, namely effective diffusion coefficient D_e and apparent diffusion coefficient D_a , could be obtained with the use of the proposed program. This characterization is not limited to experiments that reach stationary conditions, characterized by a constant mass flow in and out the studied layer, but also for experiments terminated sooner, i.e. during the transient regime. This capability enables to shorten the duration of diffusion experiments.

In the last year, we extended this older model with the aim to prepare methods for evaluation of diffusion experiments within the CEBAMA project, in two respects: (i) the non-linear sorption isotherm (Freundlich and Langmuir) can be now used for the description of interaction of studied species with the solid phase, and (ii) the Box method implemented in GoldSim software is used to fit the model parameters to experimental results. The first development enables to study for one species the influence of the shape of the interaction isotherm on the retardation of this species in the diffusion transport in a homogeneous porous layer. Sorption isotherm can be determined experimentally or obtained as a result of a multicomponent equilibrium modelling by a speciation code. For instance,

we have used an ion-exchange model implemented in PHREEQC for the description of Cs sorption on bentonite (Vopalka et al., 2015). The second development enables to determine the unknown parameters of the studied system (diffusion coefficients, parameters of sorption isotherm, porosity) more rigorously, avoiding the use of a trial and error approach. Three sets of data can be taken into account: concentration changes in (1) input and (2) output containers, and (3) concentration profile at the time of termination of the experiment. The application of the χ^2 test to the comparison of experimental and modelled results enables to assess the goodness-of-fit and helps to determine which set of fitted parameters is optimal, e.g. by the choice between linear and non-linear interaction model.

With the use of the developed model of diffusion experiments (based on 1st Fick's law), a simple tool for their evaluation was prepared, which allows to take into account the concentration changes in the containers during the through-diffusion experiment. The necessary data at experiment termination are: concentrations of studied species in both containers, mass flows in and out the studied porous layer, and total concentration in the studied layer. The model, implemented in Excel, supplies values of D_e and D_a and an assessment of uncertainties in both parameters. The tool is more complex than the *time lag* method and will help in the evaluation of diffusion experiments performed within CEBAMA.

2.9.2 Modelling of cement-bentonite combined barriers

The second goal of the modelling work at CTU-DNC is more theoretical and intends to help in the interpretation of diffusion experiments performed within CEBAMA, e.g. with a different formulation of the interaction isotherm applicable in simple transport modelling.

In a first step, two processes will be modelled separately: (1) the hydration of cement-based materials (and resulting precipitation and chemical changes in the leach) and (2) the physical and chemical changes of bentonite due to the equilibration with the leach from cement-based materials. The altered phase composition, structure and physical and chemical properties will be studied assuming both thermodynamic equilibrium and reaction kinetics simulations. The idea is to follow existing approaches for cement hydration modelling (Lothenbach et al., 2008). As a second step, these two processes will be modelled simultaneously.

In a third step, the retention of radionuclides will be studied (Sr, Ca, Se, I, Ra, and U), including their speciation. There are several ways to model this complex system, starting from isolated to simultaneous description of the processes mentioned above. The modelling of transport/migration of radionuclides of interest through combined barriers will follow with the use of the codes PHREEQC, GoldSim, and possibly GEMS-PSI; some subroutines will be modified by ourselves in Matlab or Wolfram Mathematica – e.g. instead of the generalized Debye-Hückel model, the Specific Ion Interaction Theory (SIT) will be used here for ionic strength corrections. The dependence of chemical reactions on temperature will also be analysed, as some of the experiments to be modelled will be performed at elevated temperatures.

Modelling work will start by using a reasonable range of input data available from published literature, until the necessary data from the experimental work within CEBAMA is obtained. The analysis will cover the meso- and macro-scales and will be tailored for the kinetic studies with a temporal range between hours to at least some hundreds of years. The thermodynamic data ($\Delta H^\circ(T)$, $\Delta G^\circ(T)$, $\Delta S^\circ(T)$, $C_p(T)$, SIT coefficients $\varepsilon(i,j,T)$), transport parameters (e.g. diffusion / dispersion coefficients) and kinetic parameters (reaction rates, activation energies) for the modelling will be obtained from the experimental work, and published literature (both experimental and theoretical values). Missing values will be estimated based on expert judgement and/or on the base of quantum chemical/molecular dynamical calculations (e.g. using Turbomole, Gaussian, or DIRAC software).

Finally, a sensitivity analysis will be carried out to estimate uncertainties in the determined parameters.

The modelling work will be done on both desktop computers and possibly also at clusters of the MetaCentrum organization (<https://www.metacentrum.cz/cs/>).

2.10 VTT Modelling approach

2.10.1 Introduction

The experimental work of VTT consists of two lines: (1) kinetic studies of low-pH concrete/ groundwater/ clay (bentonite focus) system with various leaching volumes and solid compositions; and (2) equilibrium studies of low-pH concrete/ groundwater/ clay -compositions.

The first one defines the rates of pozzolanic reaction, leaching effect, and groundwater interaction compared to each other in incongruent dissolution. Kinetic studies enable mass balance calculations for individual effects and give quantitative information of leaching hydroxyl ions in various scenarios. The goal of the second line is to determine congruent dissolution composition of various binders, C-S-H, and leachate compositions in various leaching groundwater. Equilibrium studies will be performed for selected material and groundwater compositions. Interaction between cementitious materials and clay/bentonite will be through the groundwater chemistry. Synthetic groundwater as well as real groundwater from long-term site investigations will be used in these investigations. Some of the above-mentioned experiments are ready while some are about to be started or are ongoing.

2.10.2 Modelling approach

VTT will develop numerical models to predict time-dependent effects of the interaction between low-pH concrete, groundwater, and clay on the formation of an alkaline plume. The evolution of the solid composition and the external solution will be modelled. Modelling is divided into two tasks: (1) modelling compositions at equilibrium and C-S-H degradation in batch systems using geochemical simulations and verify the results against the experiments of VTT within WP1; and (2) development of the time-dependent model. All the experiments are batch reactions with different chemical compositions. The models are thus going to be simple mass balance reactions. In some of the experiments kinetic rate equations are going to be used according to the experiments. The time scale of the analyses is going to be from days to months.

Simulations of batch systems will be performed using PHREEQC (Parkhurst and Appelo, 2013). Geochemist's Workbench, and GEMS (Kulik et al., 2013) might also be used. Simulations will be used to estimate the equilibrium composition and concentrations in various leaching volumes. In addition, the uncertainties in C-S-H degradation and ion replacement will be dealt individually, enabling further corrections in the time-dependent model.

Time-dependent effects of the interaction between low-pH concrete, groundwater, and clay will be modelled using the same software and existing thermodynamic databases, such as ThermoChimie (Giffaut et al., 2014), Thermoddem (Blanc et al., 2012), or CEMDATA (Lothenbach et al., 2008). Particular attention will be paid to model the solid solution behaviour of C-S-H. Time dependency of the pozzolanic reaction and groundwater leaching will be included in the model. Final corrections to the model will be made on the basis of information gained from batch simulations from the previous task.

The modelling work have just started, since the experimental research started autumn 2015 and the first set of results are coming out now. Experiments of the batch reactions have partially been made and some cement-pozzolana mixes have been started for ageing. The experiments with CaOH batch reactions at anoxic conditions have yet to be started since VTT's laboratories are moving to new building during next months (after the glove boxes have been moved during summer).

These batch experiments are going to be modelled using PHREEQC to see the equilibrium pH and to be able to see when these batch reactions reach equilibrium. In addition, existing results on low-pH concrete from the DOPAS project (2014, <http://www.posiva.fi/dopas>) will be modelled using the same methodology.

Concrete samples are ageing and low-pH concretes have been made using silica with different particle size. The experiments for the rate of pozzolanic reactions are continuing and Arrhenius equation is going to be used to fit the experimental data for PHREEQC models and to develop the time-dependent model.

$$k = Ae^{-E_a/RT} \quad (2.10.1)$$

where k is the rate constant, E_a is the activation energy, R is the universal gas constant, and T (K) is the temperature. The thermodynamic database used is going to be the CEMDATA (Lothenbach et al., 2008), available at Empa's website (<https://www.empa.ch/web/s308/downloads>). GEMS might be used together with PHREEQC to confirm the results.

2.10.3 Numerical methods and software

The tools to be used are existing tools (PHREEQC, GEMS3, Geochemist's Workbench) and no additional code developments are foreseen. On the other hand, some modifications to the used thermodynamic databases may be needed. A basic description of each software is given below:

- 1) PHREEQC (Parkhurst and Appelo, 2013) is a computer program designed for aqueous geochemical calculations in batch and 1D reactive transport environments. It is based on the law of mass action (LMA) approach. It includes speciation and saturation-index calculations. The reaction types include for example aqueous, mineral, gas, solid-solution, inverse modelling, surface-complexation and ion-exchange equilibria through equilibrium or kinetics. PHREEQC is intended for simulation of chemical reactions and transport processes in natural or polluted water, in laboratory conditions or in industrial processes. It is based on equilibrium chemistry, so-called pH-Redox-Equilibrium. PHREEQC uses a modification of the Newton-Raphson method to iterate the values of the master unknowns until solution to the equations has been found.
 - 2) GEMS3 (Kulik et al., 2013) is similar to PHREEQC, except that it is based on Gibbs Energy Minimization (GEM) approach. Otherwise the capabilities of GEMS are of the same kind as PHREEQC. One difference is that GEMS also includes graphical user interface with a nice context-sensitive help system. The Gibbs Energy Minimization is implemented as an Interior Points Method (IPM) algorithm.
 - 3) Geochemist's Workbench (GWB) is computer program similar to PHREEQC with graphical user interface including also 2-D models. However, databases might need to be modified to be fit for GWB. GWB is a set of software tools for manipulating chemical reactions, calculating diagrams and equilibrium states and plotting these results.
-

2.11 LML modelling approach

2.11.1 A micromechanics-based model for cement-based materials submitted to chemical degradation

A micromechanical model is presented for cement-based materials subjected to leaching and/or carbonation. This model will serve as a basis for describing the mechanical behaviour of the low pH concrete used in the CEMABA project. In recent studies carried out in the Laboratory of Mechanics of Lille, the development of micro-macro models has been a major research topic. Several micro-macro models were developed in order to describe the mechanical behaviour of cement-based materials subjected to chemical attacks such as carbonation and leaching. The use of these models is essential in case of chemical attacks, since they can directly link the macroscopic behaviour with changes in the microstructure. Amongst those models, developed for different specific materials and engineering applications, a quite general micro-mechanical model is presented here, which can take into account the effects of changes in porosity and of two populations of inclusions. This model can be easily applied to the case of cement paste, mortar, and concrete subjected to carbonation and leaching.

2.11.2 Microstructure of carbonated concrete

Concrete is a composite material consisting of cement paste, aggregates (sand, gravel) and an area called interfacial transition zone (ITZ), between aggregates and cement matrix. This zone, caused by the presence of aggregates, has a higher porosity than the cement paste. As a first approximation, concrete may be considered herein as a four-phase composite in the case of carbonated concrete: (1) a solid phase representing the hydrated cement; (2) micro inclusions ($\sim\mu\text{m}$) representing calcite grains, which are formed during the carbonation process; (3) mesoscopic pores (μm -mm); and (4) meso-inclusions (mm-cm) representing aggregates. As shown in Fig. 2.11.1 (top-left), at the micro-scale, the cement matrix is composed of an assembly of continuous cement particles (solid phase), which are reinforced by small inclusions (calcite grains) formed during the carbonation process. At the meso-scale, concrete is a porous medium reinforced by big inclusions representing aggregates.

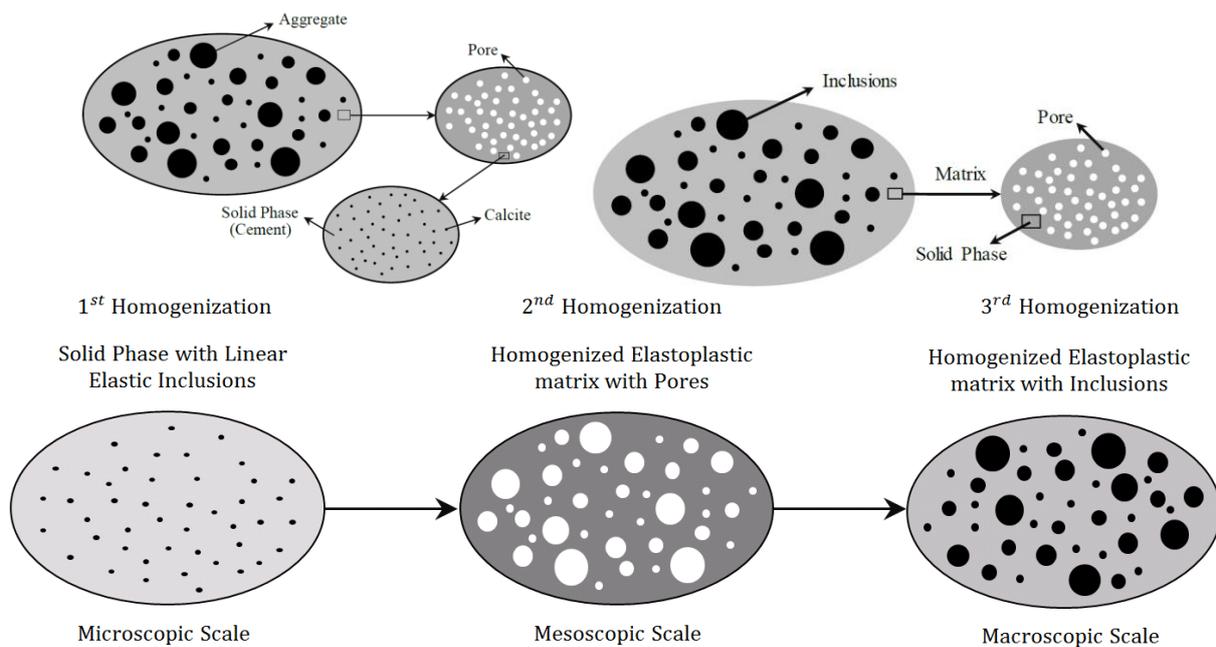


Fig. 2.11.1: Representative volume element (RVE) of (top-left) carbonated concrete and (top-right) of concrete. (Bottom) Schematics of the homogenization procedure.

It is assumed that pores and inclusions are randomly distributed in space so that the macroscopic behaviour remains isotropic. For the sake of simplicity, calcite grains, pores and aggregates are all assumed to be spherical. The cement matrix is supposed to obey a plasticity-based Drucker-Prager type criterion, and inclusions are assumed to be rigid and have a perfect bounding with the surrounding matrix.

The macroscopic criterion (1) of carbonated concrete is formulated from three homogenization steps (see Fig. 2.11.1 bottom) using the modified secant method. The 1st homogenization from the micro- to meso-scales is for the influence of calcite grains generated during carbonation. The effects of pores and aggregates are taken into account in the 2nd and 3rd homogenization steps, respectively, from the meso- to macro-scales.

$$F_c = \frac{1 + \frac{2}{3}f}{\tilde{T}^2 + \frac{2}{3}\rho_a \left(\frac{3f}{2\tilde{T}^2} - 1 \right)} \Sigma_d^2 + \left(\frac{3f}{2\tilde{T}^2} - 1 \right) \Sigma_m^2 + 2(1-f)h\Sigma_m - \left(\frac{3f\rho_a}{3+2f} + 1 \right) (1-f)^2 h^2 = 0 \quad (2.11.1)$$

In order to consider the transition from volumetric compaction to dilatation generally observed in concrete, a non-associated plastic potential is proposed (2) at the macro-scale, by keeping a similar form as the macroscopic plastic criterion.

$$G_c = \frac{1 + \frac{2}{3}f}{\tilde{T}\tilde{t} + \frac{2}{3}\rho_a \left(\frac{3f}{2\tilde{T}\tilde{t}} - 1 \right)} \Sigma_d^2 + \left(\frac{3f}{2\tilde{T}\tilde{t}} - 1 \right) \Sigma_m^2 + 2(1-f)h\Sigma_m - \left(\frac{3f\rho_a}{3+2f} + 1 \right) (1-f)^2 h^2 \quad (2.11.2)$$

where

$$\tilde{T} = T \sqrt{1 + \frac{3}{2}\rho_c} \sqrt{1 - \frac{2}{3}\rho_c t^2} / \left(1 - \frac{2}{3}\rho_c tT \right); \quad \tilde{t} = t \sqrt{\left(1 + \frac{3}{2}\rho_c \right)} / \left(1 - \frac{2}{3}\rho_c tT \right) \quad (2.11.3)$$

T and t are the frictional and dilatant coefficients of the solid phase, respectively, \tilde{T} and \tilde{t} are the initial frictional and dilatant coefficients affected by the presence of small rigid inclusions (calcite) during the 1st homogenization step f , ρ_c and ρ_a are respectively the porosity, calcite, and aggregates volume fraction, and h is the hydrostatic tensile strength of the solid phase at the microscopic level.

Fig. 2.11.2 shows a simulation of concrete carbonation. The only model parameters that were changed in the different simulations were the porosity and calcite volume fraction, which were provided by the authors.

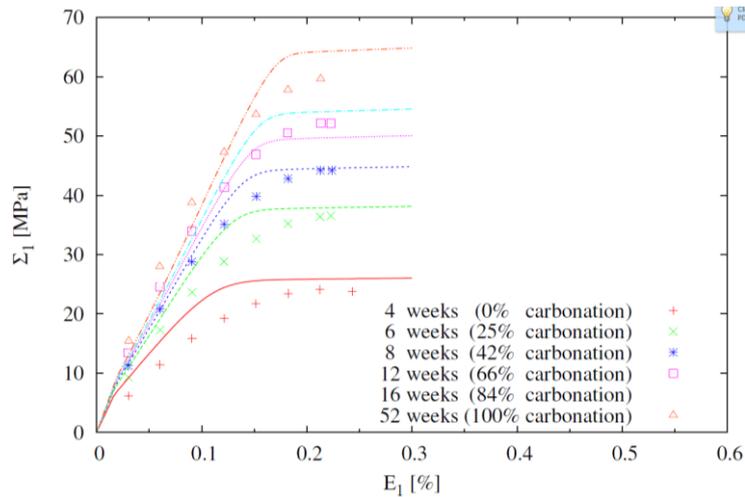


Fig. 2.11.2. Comparison between experimental data (Chang and Chen 2005) and numerical simulations on uniaxial compression tests at different levels of carbonation.

2.11.3 Case of chemical leaching

The main effect of leaching in concrete is to increase porosity by dissolution of calcium-bearing phases in cement paste hydrates. Considering the RVE in Fig. 2.11.1 (top-right) and the effect of lixiviation on it, the same criterion introduced in eq. (2.11.1) can be used by eliminating small inclusions of calcite that reinforce the hydrated matrix ($\rho_c = 0$). In this case, the criterion obtained coincides exactly with the criterion obtained by Shen et al. (2013) for a porous medium reinforced by rigid inclusions.

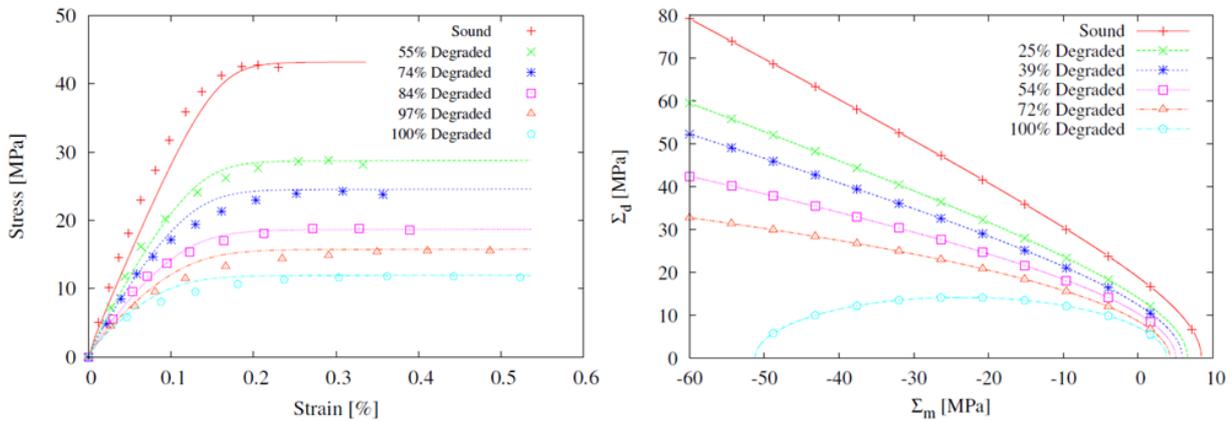


Fig. 2.11.3. Numerical simulations on sound and degraded concrete. Data from (Nguyen 2005).

2.11.4 Case of cement carbonation

The criterion in eq. (2.11.1) can also be used in case of cement paste carbonation. For this purpose, the effect of aggregates is disabled ($\rho_a = 0$). This new criterion coincides with the one obtained by (Ghorbanbeigi et al., 2016) in case of a porous medium reinforced by small rigid inclusions. The cement paste microstructure evolves during carbonation. There is a decrease in porosity as well as an increase in calcite volume fractions which is taken into consideration in the criterion.

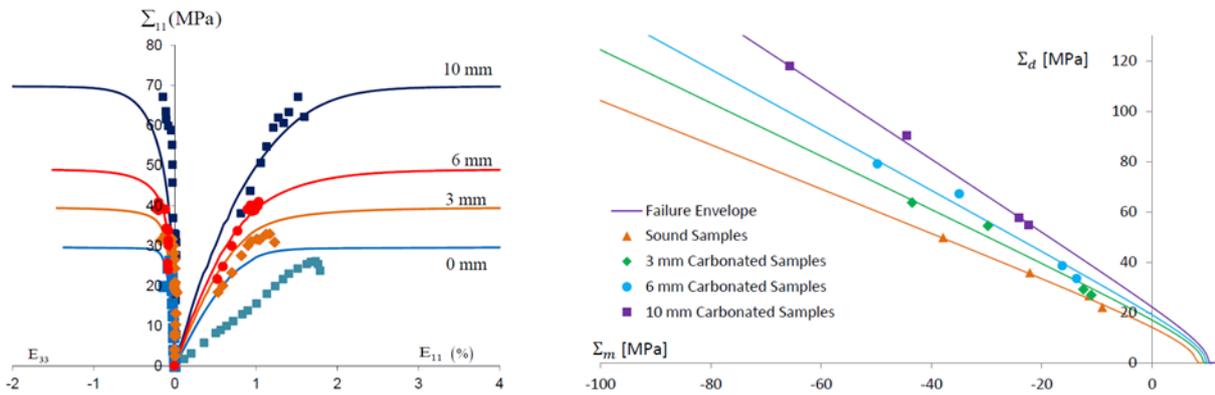


Fig. 2.11.4. Comparison between model predictions and data of cement on different states of carbonation (data from Takla et al., 2011).

2.11.5 Case of cement leaching

As mentioned above, calcium leaching induces an increase in porosity and therefore decreases the mechanical properties of the cement paste. In the case of a micro-macro approach, cement paste can be considered as a porous medium made of a solid phase (matrix) and pores (Fig. 2.11.5). Since there are no aggregates or calcite grains in this case ($\rho_a = 0, \rho_c = 0$), the criterion in eq. (2.11.1) turns out to be exactly the same as the one obtained by (Maghous et al., 2009). Fig. 2.11.5 shows the numerical simulations made on uniaxial compression tests (Carde et al., 1996) from sound to totally leached samples.

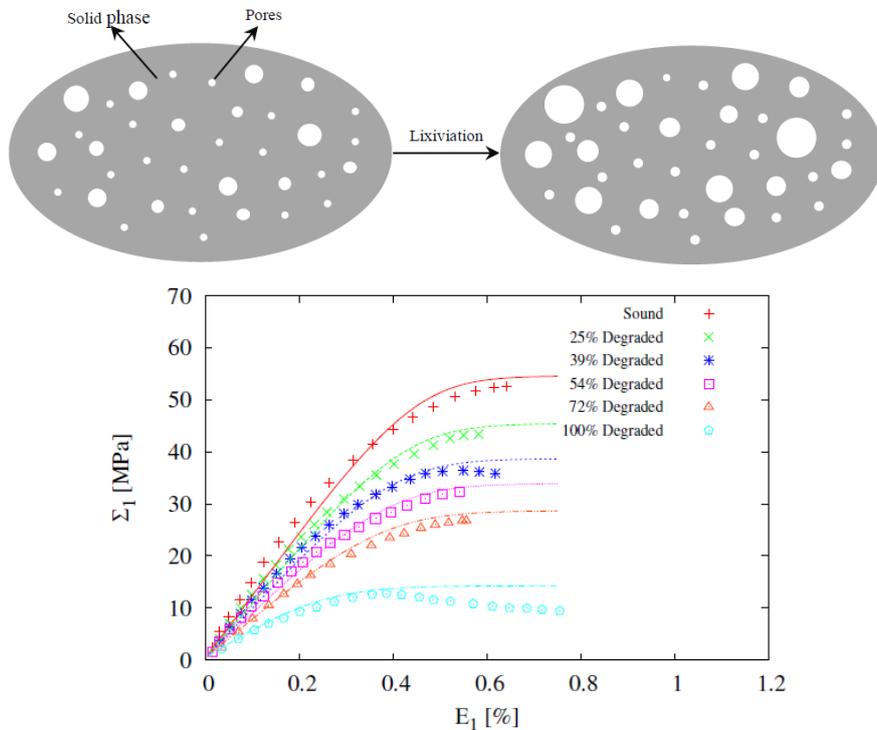


Fig. 2.11.5. (Top) Schematic evolution of cement matrix during leaching. (Bottom) Uniaxial compression tests of cement paste from sound state completely leached samples state (data from (Carde et al., 1996)).

2.12 Andra modelling approach

2.12.1 Design to be modelled

In the framework of CEBAMA, Andra aims to model THC evolution of two high scale components of an underground radioactive waste disposal: a seal, located in a drift (Fig. 2.12.1), and an intermediate long-lived waste disposal cell (ILL).

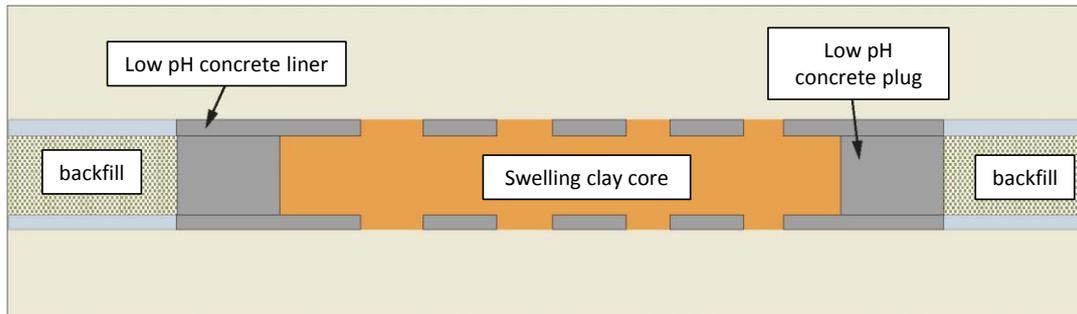


Fig. 2.12.1. Schematic diagram of a drift seal.

The seal of a drift is intended to be composed of a central swelling clay core surrounded by two supports (plug) made of low-pH concrete. The low-pH concrete is also used for the liner, which is maintained in place after closure. The material of the backfill surrounding the seal is based on reworked clay.

The ILL waste disposal cell consists of a concrete tunnel, which composition (CEMV, low-pH) depends on the type of ILL waste considered.

Thus, Andra aims to model the H(M)CR evolution of different components principally composed by clay and low-pH materials. The spatial scale of these components is of pluri-metric order and the considered time scale covers a few tens of thousands of years.

2.12.2 Main processes modelled

Andra will develop an approach combining:

- A change of spatial and time scales: from experiment to host rock, and from months to thousands of years
- and a change in representation: from phenomenological processes to performance assessment (PA).

This approach is divided into three steps:

- analysis of the data acquired in WP1 and WP2 on low-pH concrete and radionuclide behaviour characterization;
 - integration of the up-scaled data/model in H(M)CR modelling of ILL waste cell and drift seal evolution (reactive-transport approach);
 - large scale modelling through a PA approach (simplified chemistry).
-

2.12.2.1 WP1 and WP2 data

The modelling conducted as part of WP3 will integrate as much as possible the data acquired in WP1 and WP2. Andra does not intend to deduce these different data from WP1 and WP2 experiments (model development) but to integrate the acquired and formatted data.

The expected input data to be assessed are (i) diffusion properties of low-pH materials (porosity, diffusion coefficient...), (ii) mineralogy evolution due to chemical degradation progress, (iii) retention properties of low-pH concrete (molybdenum...). The high-scale evaluations will mainly consider diffusive transport of solutes. Thus, permeability data are, at this stage, of second order of importance for Andra's WP3 work.

2.12.2.2 Reactive transport modelling

The modelling strategy is based on a progressive increase in complexity of the integrated processes.

First the models will consider the chemical reactivity of the materials (concrete and clay). This reactivity is rendered by different chemical processes such as dissolution/precipitation of minerals at thermodynamic equilibrium or through kinetics reactivity, ionic exchange especially for clay or surface complexation for radionuclides. The system will be considered at water saturated conditions and solute transport will be limited diffusive processes. According to the evolution of the numerical tools, the transient resaturation period will be modelled, as boundary or environmental conditions.

The impact of thermal processes (transient phase of temperature increase) on the dissolution/precipitation processes and diffusion parameters will be considered, thanks to preliminary thermal detailed evaluations.

As a complement to the acquired data, the reactivity between the different chemical species will be modelled with the thermodynamic database ThermoChimie v9 (Duro et al., 2012).

2.12.2.3 Performance assessment modelling

The PA modelling will start from the reactive transport modelling of the ILL waste disposal cell and of the seal evolutions by applying some simplifications at the representation of the different phenomenological processes. For example, chemical processes will be modelled through simple properties varying in time and space.

2.12.3 Results

2.12.3.1 Reactive transport modelling

Main expected results are mineral evolution of the different materials, especially the low-pH concrete minerals (C-S-H, C-A-S-H, magnesium-bearing phases...). Other kinds of data will be produced such as the distribution of cations in the ionic exchanger of the swelling clay. Specific focus will be made on radionuclide speciation in cementitious environment linked with redox conditions.

To refine the understanding of the studied systems evolution, a sensitivity analysis will be performed on variability of the acquired data. This sensitivity analysis will be first mono-parametric on parameter values of the variation range.

According to the formalism of data acquired in WP1 and WP2, sensitivity could be conducted on retention processes (e.g. K_d approach vs. deterministic model).

2.12.3.2 Performance assessment modelling

Performance assessment modelling will allow us to model radionuclide transfer at a larger spatial scale, combining repository components and surrounding claystone, by using macroscopic geochemical approach (K_d , solubility limit) deduced from reactive transport modelling.

2.12.4 Numerical tools

Different numerical tools are intended to be used for the modelling according to the complexity of the processes modelled. For the reactive transport modelling, Phast (Parkhurst and Appelo, 2013), Crunchflow (Steefel and Yabusaki, 1996), MIN3P (Mayer et al., 2002), or iCP (interface Comsol-Phreeqc, Nardi et al., 2014) could be used. These reactive transport codes are recognized by the international community (Marty et al., 2014; Marty et al., 2015). These codes have different schemes for the resolution of the reactive transport equations. Phast and iCP work according to a sequential non-iterative approach, whereas Crunchflow and MIN3P use global implicit methods. The choice of a type of method instead of another will also be guided by the type of problem to solve.

Especially, iCP should be used for the non-saturated hydraulic part. For the PA approach, Andra will use Porflow (www.acricfd.com/software/porflow/).

2.12.5 Hardware

The computational resources will be adapted to the specificities of the retained reactive-transport tool. Crunchflow will be run in a 64bits-Windows environment of a computer based on Intel Core i7 processors. Phast, iCP, MIN3P, and Porflow have high performance computing capacities and may be launched on Andra's cluster disposing of 22 calculation nodes for a total of 528 cores on AMD processors.

2.13 PSI modelling approach

2.13.1 Introduction

The temporal and spatial evolution of alterations at interfaces between clay and cement-based materials in deep geological repositories for radioactive waste is a very active area of research (e.g. Gaucher and Blanc, 2006; Gaboreau et al., 2011; Jenni et al., 2014; Kosakowski et al., 2014; Marty et al., 2015). The mineral reactions taking place at such material interfaces may alter porosity, diffusion coefficients and other material properties (Gaucher and Blanc, 2006). The geochemical gradients between materials drive the diffusive transport of solutes, which is the primary cause of the reactions (Rübel et al., 2002). The most common way to model the diffusive transport is to use the same average diffusion coefficient for all species dissolved in the liquid phase.

Many clays and cement minerals exhibit charged mineral surfaces which are not only responsible for favourable sorption properties of many radionuclides (and other ions/cations), but also cause the formation of external or internal surface water layers that have different composition and transport properties compared to the water in macroscopic pores. Fig. 2.13.1 represents the diffusion in clays from two perspectives: a) in a local scale detailing the pore and surface diffusion and b) in a sample scale where a stack of clays are combined to represent the diffusion through pores and surface regions. The diffusive fluxes in these compartments have to be considered especially in clay-rich materials (see e.g. Tournassat and Appelo, 2011).

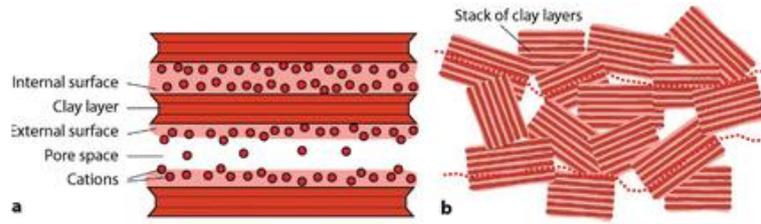


Fig. 2.13.1. Schematic representation of diffusion pathways in clays (a) in a local scale detailing the pore and surface diffusion, and (b) in a sample scale where clay stacks are combined to represent the diffusion through pores and surface regions (from Gimmi and Kosakowski, 2011).

2.13.2 Modelling approach and equations to be solved

A reactive transport model of charged ions in the presence of charged mineral surfaces will be implemented adopting a continuum scale approach, i.e. using the average system properties to represent the physical and chemical processes that take place at the pore scale.

A conceptual and numerical approach that splits the problem into two parts will be adopted: **(1) a transport solver** responsible for describing the movement of ions in the presence of an electric field, and **(2) a chemical solver module**, which divides the liquid phase into multiple compartments. These several compartments are in different degrees influenced by mineral surface charges.

For **the transport solver (1)**, the approach to be followed, as implemented for example in Crunchflow (Steefel and Maher, 2009), FLOTRAN (Hammond et al., 2007), or described in Samson and Marchand (2007), is to solve the Nernst-Planck equation:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot \left[-D_i \nabla C_i - \frac{z_i F}{R T} C_i \nabla \Phi \right] \quad (2.13.1)$$

where D_i is the diffusion coefficient for species i , C_i is the concentration, ∇ is the gradient symbol, z_i is the charge of the ion/species, F is the Faraday constant, R is the gas constant, T is the temperature and Φ is the electric potential. The first term on the right side of the equation is the Fickian diffusion term and the second one is the electrochemical migration term. The Nernst-Planck equation allows the possibility to simulate a domain with or without external electric field imposed or taking into account only the current generated by the motion of charged species. The electric field is defined by:

$$E = -\nabla \Phi - \frac{\partial A}{\partial t} \quad (2.13.2)$$

E is the electric field, and A is the magnetic vector potential.

For **the chemical solver module (2)**, total water (including charged and neutral dissolved species) will be separated into compartments that are influenced by surface charges.

2.13.3 Numerical method and software

For typical chemical system setups for clay/cement interactions, the number of species in solution might be very high. Therefore, it is proposed here to reduce the number of transport equations (2.13.1) by reformulating the transport in terms of chemical components as described e.g. in Liu et al. (2011). The system of coupled transport equations is then solved by Newton method to find the final concentrations of each species and, therefore, the total fluxes.

First, the Nernst-Planck equations will be implemented in FEniCS (Maddison and Farrell, 2014). FEniCS is an open source finite element library for rapid development of solver for partial differential equations. The use of FEniCS has the advantage that it allows to focus the work on the model equation itself. It provides the possibility to use different numerical methods like Continuous and Discontinuous Galerkin or Lagrange Finite Element methods. This provides a flexible environment to overcome difficulties, like numerical oscillations due to steep gradients or singularities, commonly encountered with reactive transport codes based on standard Finite Element methods. FEniCS is suited to implement desktop versions, as well as code suitable to run on workstations and high-performance computers, as FEniCS supports natively parallel computing via PETSc and multithreading via Boost library.

In a later stage, it is planned to add the FEniCS implementation as an external module to the reactive transport code OpenGeoSys-GEM (Kosakowski and Watanabe, 2014). OpenGeoSys (www.opengeosys.com) is a finite element based modular numerical code for the simulation of hydro-thermo-mechanical-chemical coupled problems in porous or fractured porous medium (Kolditz et al., 2012).

For the chemical solver module, a Donnan approach will be implemented, as described in Alt-Epping et al. (2014) for effects of charged external mineral surfaces/interlayers on pore water composition, and a solid-solution approach for cation exchange and interlayer hydration of clay minerals (Berner et al., 2013), into the TsolMod Class of the GEMS3K chemical solver (Wagner et al., 2012). GEMS3K is the numerical kernel of the GEM-Selektor geochemical modelling package (gems.web.psi.ch) which has been developed at PSI during the last 15 years (Kulik et al., 2013). Currently, the GEMS4R framework is being developed, which alternatively to GEMS3K allows using the Reaktoro geochemical solver (<https://bitbucket.org/reaktoro/>), see Leal et al. (2014; 2015). Both geochemical solvers, GEMS3K and Reaktoro, can be coupled via GEMS4R to FEniCS and OpenGeoSys.

2.13.4 Computational resources

The solution of reactive electrochemical transport is very computation- and time-consuming due to two main reasons:

(1) Large-scale and complex models based on the finite element or finite volume methods consist of a considerable number of non-linear coupled transport equations (PDE), which results in a large system of equations with the possibly very large number of unknowns ($>10E2$). For parallelized calculations of large problems, we use a domain-decomposition technique implemented with PETSc.

(2) Coupling to a chemical solver is done on node or volume level, which means that for each node or volume a complex system of equations, has to be solved. To speed up chemical calculations, multi-threading strategies will be used (Kosakowski et al., 2012).

The combined use of multi-threading and PETSc allows to solve effectively not only small 1D problems but also larger 3D repository models are within reach.

3 References

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