Modelling of radionuclides migration in the low pH cement / clay interface

Vanessa Montoya[1], Naila Ait Mouheb[1], Thorsten Schäfer[1,2]

[1] KIT-INE, Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (DE)
[2] Friedrich-Schiller-Universität Jena, Institute of Geosciences (DE)

* Corresponding author: vanessa.montoya@kit.edu

Abstract

Reactive transport modelling activities described in this work are focused on the definition of the conceptual model and the selection of the chemical and transport parameters to be applied on laboratory through diffusion experiments performed in KIT-INE (see contribution of Ait Mouheb et al., *this proceedings*). The model includes different coupled processes which are thought to play a role in a through diffusion experiment of HTO, $^{36}Cl^-$, $^{129}I^-$ and Be across the interface between bentonite porewater and low pH cement. One of these processes is the impact of porosity changes due to dissolution / precipitation reactions.

Introduction

Current deep geological repository concepts are based on the confinement of radioactive waste over a long period of time by multiple barriers. Many of the concepts developed internationally use concrete and clay as confinement barriers (ANDRA, 2005; ENRESA, 1995). During the prolonged post disposal period, cementitious materials can undergo alterations through evolution of the chemical and physical properties of the repository. One important process that could reduce the durability of a concrete barrier is the leaching / degradation of the solid due to the clay porewater in direct contact with the cementitious material.

In order to minimize the interaction between the "classical" high-pH cement materials and the bentonite, low-pH cements were developed within the nuclear waste disposal context in the late 90's. The main feature of these cements is the less alkaline pore solution (pH ~ 11) compared to what is observed in "classical" cements and the absence of portlandite as hydrated solid phase. The Ca/Si ratio in the hydrated low-pH cement paste is less than 1.0 and C-S-H phases are the main solids present.

The understanding of the evolution of the interface low pH cements / bentonite over geological time scales and the impact on radionuclide migration requires a detailed knowledge of a series of highly complex coupled processes. The conceptual understanding of the different processes and their integration in numerical models will increase the reliability and predictive capabilities of the simulations. By using small-scale laboratory experiments, under well-defined boundary conditions, reactive transport modelling can be used for their interpretation and provide valuable information for the repository design and predict radionuclide migration. Studies concerning the evolution of low-pH cementitious materials in clayey environment are scarce and the knowledge of their physicochemical evolution is very limited (Dauzeres et al., 2016). To the best of our knowledge the impact of these processes in radionuclide migration has never been studied.

This work includes modelling studies of interface processes between a low pH cement (50% CEM I 52.5N + 50 silica fume) and a MX-80 bentonite porewater and assesses the specific impact on HTO, $^{36}Cl^-$, $^{129}I^-$ and Be migration. The modelling work supports the interpretation of the experimental results performed in the CEBAMA project and helps to identify possible missing parameters and to the process understanding. The processes considered are diffusion transport in saturated media under isothermal conditions, sorption reactions, and both local equilibrium and kinetically controlled mineral dissolution-precipitation reactions. Update of the effective diffusion coefficient as a function of porosity changes is also considered. The reactive transport code where the model is implemented is PHREEQC v.3 (Parkhurst and Appelo, 2013).

Conceptual model and selected parameters

The reactive transport model consists of a one dimensional (1D) fully water saturated isothermal (298 K) problem representing a laboratory through diffusion experiment of HTO, Be, $^{36}Cl^-$, and $^{129}I^-$ across the interface bentonite porewater / low pH cement. Geometrical and transport parameters including the discretization of the system (water and solid domains) have been initially implemented (see Figure 1). The mesh size and the time steps have been selected 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 hydrated phases. A constant concentration and closed boundary condition have been imposed on the extremities of the upstream and downstream reservoir, respectively in order to reproduce the boundary conditions imposed in the experiments.

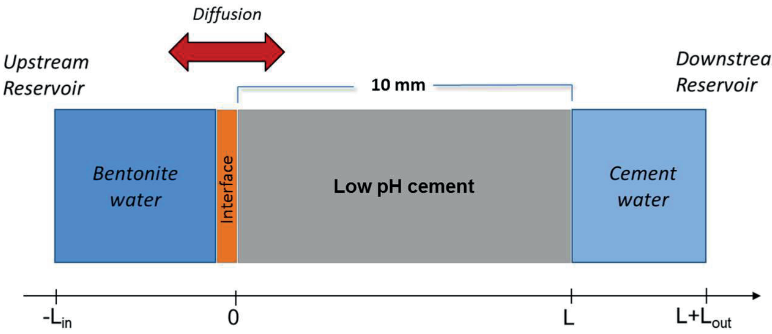


Figure 1: *Schematic representation of the through diffusion experiments.*

Considering the very low permeability of cement (10^{-10} - 10^{-14} m/s), mass transport will be considered diffusion-driven only, following Fick's law (Eq. 1).

$$J = -D\frac{\partial C}{\partial x} \qquad \textbf{\textit{Eq. 1}}$$

where J is the substance flux (kg/m^2·s); $\frac{\partial C}{\partial x}$ is the concentration gradient (kg/m^4); and D is the diffusion coefficient (m^2/s). In the absence of experimental data available concerning the effective diffusion in low-pH cements, a value of 10^{-10} m^2/s was tentatively selected as initial value taking into account the properties of the studied cement (Ait Mouheb et al., 2017). The effective diffusion coefficient evolution was then related to the porosity change according to Archie's law (Eq. 2) assuming n = 1.

$$D = D_w(porosity)^n \qquad \textit{Eq. 2}$$

Initial porosity of 35% has been determined experimentally by mercury intrusion porosimetry (MIP). Additionally, porosity changes due to mineral precipitation/dissolution and feedback on the effective diffusion coefficient are also taken into account in the model considering the molar volumes of the different solids formed or dissolved. Electrostatic surface interactions are not included, although they may influence the transport of the anionic tracers $^{36}Cl^-$, $^{129}I^-$ and $Be(OH)_3^-$ (Chagneau et al., 2015).

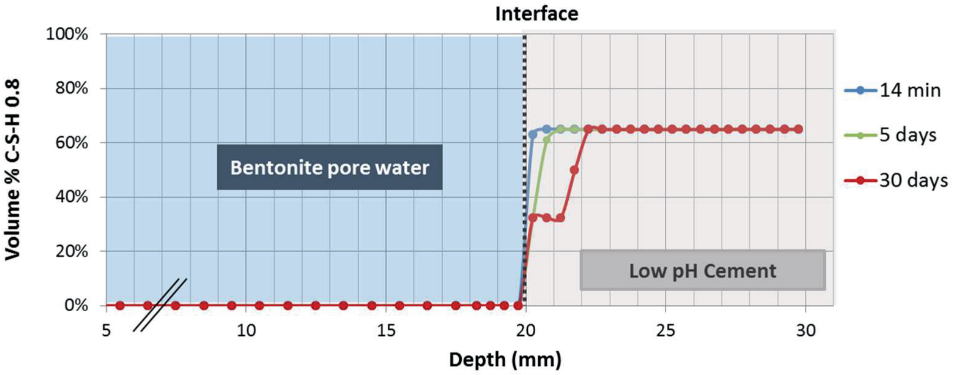
The system studied is implemented in the code PHREEQC v.3 (Parkhurst and Appelo, 2013) which can take into account geochemical and physical parameters variations due to mineralogical evolutions as a function of time. The initial mineralogical composition of the cement hydrated phases considered is representative of a full hydrated low-pH cement (pH ~ 11.0) with a 93 wt.% being formed by C-S-H phases with a Ca/Si ratio of 0.8. Mineralogical composition has been determined experimentally (Ait Mouheb et al., 2017) with a combination of different techniques (X-ray diffraction (XRD), thermogravimetric - differential thermal analysis (TG-DTA), ^{29}Si and ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (^{29}Si and ^{27}Al MAS NMR) and Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy (SEM-EDX) At this moment, it has not been possible to experimentally identify the solid phase containing iron and for this reason we have assumed that iron phases are in the form of Fe-ettringite. The initial porewater composition of the low-pH cement is defined in equilibrium with the hydrated solid phases present in the system and compares well with the measured concentrations. The porewater composition of the clay is representative of the MX-80 bentonite described in the literature (Wersin et al., 2003) and has been synthetized and measured in the laboratory.

Chemical reactions at equilibrium and kinetically controlled have been simulated using the thermodynamic database Cemdata07 available in PHREEQC format (Lothenbach and Winnefeld, 2006). Debye-Hückel equation, valid for the ionic strength of the studied system (< 0.3 M) is preferred to save computational time as it has been observed that calculations performed with SIT (Specific ion Interaction Theory) equation needs more computational effort. Cemdata07 includes hydrates commonly encountered in Portland cement systems in the temperature range 0 - 100°C. Rate equations of precipitation/dissolution of secondary / primary phases are provided directly in the input files of PHREEQC. Kinetic parameters for C-S-H phases and ettringite have been selected from Marty et al. (2015) and Baur et al. (2004).

In the present status, sorption of the tracers in the cement matrix is not included in the model. Sorption reactions of $^{36}Cl^-$, $^{129}I^-$ and Be tracers into the low pH cement matrix will be considered as a thermodynamic mechanistic sorption model to be implemented in PHREEQC. Observations described in the recent review of Ochs et al. (2016) will be considered to select the most appropriate data, as well as data generated in the Cebama project, consisting of batch experiments of the studied radionuclides on the same solid materials (Ait Mouheb et al., 2017).

Results and discussion

The simulations were carried out for different times of interaction (14 min, 5 and 30 days) predicting that the low-pH cement in contact with the bentonite pore water will have a degraded area of ~ 2 mm after one month of alteration. No significantly changes can be appreciated in the cement solid after 5 days (Figure 2). The alteration of the low-pH cement paste is mainly due to the partial dissolution of C-S-H phases controlled by kinetic rates resulting in an increase of the porosity due to the difference of the molar volumes between the initial solids and the final products of the alteration process in the interface. Carbonation is linked to the precipitation of calcite and thus the decalcification of C-S-H phases (Jenni et al., 2014). Magnesium enrichment in the decalcification area has been reported in the literature (Jenni et al., 2014; Dauzères et al., 2016). In our system, brucite is undersaturated and attempts to model the magnesium perturbation using available thermodynamic data suggested the formation of hydrotalcite. However, the recent determination of solubility data for M-S-H phases will make it possible to account for the potential formation of M-S-H phases (Dauzères et al., 2016) and will be considered in the future. Finally, no attempts have been done to model the iron evolution and the diffusion of HTO in the system will reach steady-state after 5 days of interaction.



$$(CaO)_2(SiO_2)_{2.4}(H_2O)_{3.2} + 1.2\ H_2O = 2\ Ca^{2+} + 2.4\ SiO(OH)_3^- + 1.6OH^-$$

Figure 2: *Simulation of the low-pH cement alteration at different periods of time. The main process identified is the partial dissolution of C-S-H phases resulting in an increase in porosity at few millimeters close to the interface bentonite / cement.*

Conclusion and Future work

We have developed and implemented a 1D model to simulate the interaction between a low pH cement and bentonite porewater. The model considered a low-pH cement paste (pH ~ 11.0) synthesized in the CEBAMA project with a 93 wt.% of the initial mineralogy being C-S-H phases with a Ca:Si ratio of 0.8. The simulations predict the formation of a degraded area in the cement phase of ~ 2 mm after one month of alteration. The alteration of the low-pH cement paste is mainly due to the partial kinetic dissolution of C-S-H phases resulting in an increase of the porosity. The carbonation of the cement is linked to the precipitation of calcite and thus the additional decalcification of the C-S-H phases.

The model will be improved including the iron and M-S-H solid phases in the system and the sorption properties of the cement to the selected radionuclides and toxic elements. Additionally, the model will be implemented in the iCP interface (Nardi et al., 2014) and compared with the results obtained with PHREQC.

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References

Ait Mouheb, N., Montoya, V., Schild, D., Soballa, E., Adam, C., Geyer, F., Schäfer, T. (2017). Characterization and sorption properties of low pH cements. Proceedings of the 2nd CEBAMA Annual Workshop (*this document*).