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Modelling of cation concentrations in the outflow of $NaNO_3$ percolation experiments through Boom Clay cores

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ABSTRACT

A laboratory percolation experiment was performed to study the effect of a $NaNO_3$ plume on the Boom Clay. In this experiment, Boom Clay cores were consecutively percolated with Boom Clay pore water and Boom Clay pore water to which $NaNO_3$ was added. The concentration of $NaNO_3$ in the pore water was increased stepwise (0.1, 0.5, and 1 M $NaNO_3$). The concentrations of Na, K, Ca, Mg and Sr in the eluted water were measured. After every switch of the $NaNO_3$ concentration, the concentration profiles of K, Ca, Mg, and Sr showed a sharp rise, followed by a slow decrease. It was hypothesised that the cation elution curves are mainly determined by cation exchange processes.

Reactive coupled transport modelling with the PHREEQC-2 code was used to describe the experimentally observed elution curves for the cations. Solute transport and water–clay interaction mechanisms, namely cation exchange, were accounted for in the model. Cation exchange parameters (cation exchange capacity and selectivity coefficients) previously determined on non-perturbed Boom Clay (De Craen et al., 2004) were used. A sensitivity analysis was performed to assess the influence of these parameter values on the goodness of the model to describe the experimental data. The model could fairly well describe the experimentally observed cation concentrations in the eluted water, confirming that cation exchange is indeed the dominant mechanism regulating the cation elution in the percolation experiments.

1. Introduction

In Europe, clay formations are intensively studied as potential geological formations for the deep disposal of high-level and intermediate-level radioactive waste. In Belgium, the Boom Clay is considered as a reference host formation for phenomenological studies (De Preter, 2007). The Boom Clay is a good barrier to radionuclide migration because of its low permeability and high sorption capacity (De Craen et al., 2004). However, disposal of radioactive waste in an underground repository may perturb the original properties of the Boom Clay. Excavation may cause oxidation of the Boom Clay (De Craen et al., 2008) and the use of cementitious materials in the construction of a repository may lead to the migration of an alkaline plume into the host rock (Gaucher and Blanc, 2006; Wang et al., 2010). Heat producing high-level radioactive waste may induce a temperature-perturbed zone (Weetjens and Sillen, 2005). The presence of large amounts of $NaNO_3$ in for instance Eurobitum bituminized intermediate-level radioactive waste will result in a $NaNO_3$ plume (Valcke et al., 2010). Since the clay rock formation is considered to be the main barrier against radionuclide transport, the impact of these perturbations on the performance of the host rock with respect to retarding contaminant migration, which is an important safety function of the Boom Clay (De Preter, 2007), needs to be evaluated.

This paper focuses on the geochemical perturbations caused by a $NaNO_3$ plume. Experimental data was acquired on the elution of exchangeable cations from Boom Clay by consequence of the injection of $NaNO_3$ contained in the Boom Clay pore water. Reactive coupled transport modelling was used to explain the observed elution curves for the main cations. The principal objective was to test the applicability of a cation exchange model with selectivity coefficients that were independently determined on undisturbed Boom Clay (De Craen et al., 2004), to predict the results of a percolation experiment.

2. Experimental set-up and data

Four undisturbed and saturated Boom Clay cores (0.030 m length and 0.038 m diameter), sandwiched between two 0.002 m thick stainless steel filters, were loaded to a total stress of 2.75 MPa in oedometer cells. The total mass was around 0.07 kg of wet clay in each test, being the initial dry density and water content of 2650 kg/m^3 and 18%, respectively. For two of the four cores (H2 and H4), the stratification of the clay core was parallel to the percolation direction ('horizontal cores'); whereas for the two

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other cores (V5 and V6), the stratification was perpendicular to the percolation direction ('vertical cores'). Cations were measured in the eluted water of cores H2 and V5; anions were measured in the eluted water of cores H4 and V6. As the focus of this paper was on the breakthrough curves of the cations, only the results from cores H2 and V5 were discussed here.

Real Boom Clay pore Water (RBCW) collected from the Extension Gallery Bottom Shaft (EG/BS) piezometer in the underground research laboratory in Mol (Belgium) and RBCW with additional $NaNO_3$ with concentrations up to 1 M were injected in four steps into the clay cores. After an initial percolation of the cores with RBCW, inlet solutions were switched to RBCW with 0.1, 0.5, and 1 M $NaNO_3$ solutions after respectively 527, 1782 and 3220 days of percolation. The composition of the inlet solutions is given in Table 1. The percolation solutions were supplied at a pressure between 0.65 and 1 MPa. The pH and the concentrations of the cations in the percolated water were measured at regular time intervals. After every switch of the $NaNO_3$ concentration, the cation concentration profiles showed a sharp rise, followed by a slow and gradual decrease, except for sodium (Fig. 1). Only small pH changes were observed. Just after a switch to a higher $NaNO_3$ concentration, the pH in the percolate decreased rapidly, with 0.5 pH units at most, and then returned slowly to the initial value. More experimental results are given in Aertsens et al. (2009).

Table 1
Composition of the different inlet solutions.

Element	Concentration (mmol/L)			
	RBCW	RBCW + 0.1 M $NaNO_3$	RBCW + 0.5 M $NaNO_3$	RBCW + 1 M $NaNO_3$
Al	0.001	0.001	<0.0074	0.001
Ca	0.09	0.13	0.09	0.09
K	0.24	0.27	0.28	0.24
Mg	0.12	0.16	0.12	0.12
Na	17.66	120.31	482.82	1017.66
Sr	1.32×10^{-3}	1.32×10^{-3}	1.32×10^{-3}	1.32×10^{-3}
Si	0.09	0.17	0.06	0.09
Total C	13.93	16.32	16.48	13.93
Cl	0.71	0.74	0.71	0.71
N	<0.01	100	498.48	1000
SO_4^{2-}	<0.01	<0.01	<0.003	<0.01
pH	9.59	9.21	8.83	9.59
pe	−4.8	−4.8	−4.8	−4.8
Temperature (°C)	25	25	25	25

Note: pe and temperature were the values used in PHREEQC-2. A pe value of −4.8 agrees with a redox potential E_{SHE} −274 mV, which is a typical value for Boom Clay pore water (De Craen et al., 2004); RBCW: Real of Boom Clay pore Water.

3. Model description

3.1. Computer code and database

Model simulations were performed with the geochemical computer code PHREEQC-2 version 2.15 (Parkhurst and Appelo, 1999). The thermodynamic database used was the llnl.dat database (Lawrence Livermore National Laboratory database), provided with the PHREEQC-2 code. However, the cation exchange selectivity coefficients were specifically determined for Boom Clay (De Craen et al., 2004). In a sensitivity analysis other cation exchange parameters were tested as well (see further).

3.2. Model domain, parameters and initial values

A one-dimensional transport model was built. The flow domain was discretisized in 17 grid cells of 0.002 m which is equal to the thickness of the filter plate. The amount of water in each cell was arbitrarily chosen as 0.025 kg. Note that the quantity of water in each cell does not affect the result of the modelling as solutes were given as concentration, not total mass. A constant pore water velocity was assigned to the inflowing Boom Clay pore water and $NaNO_3$ solutions for each injection step in the experiment. The effect of stratification was taken into account by assigning different water velocity in the modelling. The applied water velocity values were based on the average measured flow rates, which are given in Table 2. Values for the pore water diffusion coefficient (D_p) and dispersivity (λ) were taken from Aertsens et al. (1999) and are given in Table 3. The porosity (η) of the Boom Clay was set at 0.37 (De Craen et al., 2004) and the initial composition of the pore water in the clay cores is given in Table 4 (taken from De Craen et al., 2004).

3.3. Processes

The only processes considered for modelling the influence of sodium on the concentrations of the eluting cations (K, Ca, Mg, and Sr) was cation exchange and transport by diffusion. This was supported by a previous experiment (Wang et al., 2010), which demonstrated that in case of percolation with concrete water with high sodium and potassium concentrations, the elution curves of these cations showed a chromatographic pattern typical of cation exchange processes. Modelling of those results showed that these elution curves could be mainly described by a cation exchange model. Sodium is known to react with clay only via cation exchange, without important precipitation reactions (Hem, 1985). This was confirmed by the percolation experiments, where the inlet and the outlet concentrations of sodium were identical (Fig. 1), which suggested that no sparingly soluble Na-minerals were formed.

An average cation exchange capacity (CEC) of 18.5 meq/100 g for Boom Clay was used (this was the value used in the modelling of the Boom Clay pore water composition in De Craen et al., 2004). To convert the CEC in PHREEQC-2 units (*i.e.*, eq/L), a water content of 18 wt% was used. The cation exchange selectivity coefficients were experimentally determined on undisturbed Boom Clay and were reported in De Craen et al. (2004). Note that these values were determined independently. For strontium, no selectivity coefficient was determined for Boom Clay and therefore, due to the selectivity difference of strontium and calcium is quite small, the same selectivity coefficient as for calcium was used. Indeed, Juo and Barber (1969) refer to investigations of the adsorption of such cations on 63 Indiana soils in which the strontium to calcium selectivity coefficient (Gaines and Thomas formulation) varied between 0.61 and 1.51. The correlation between the selectivity coefficient and the organic matter content of the soils was negative, pointing to a preferential adsorption of calcium relative to strontium on organic matter. The results of Juo and Barber (1969) were corroborated by Baes and Bloom (1988). Tournassat et al. (2009) showed that the selectivity coefficients of calcium and strontium on MX-80 smectite were close to each other. The values of the selectivity coefficients for exchange reactions used are given in Table 5.

4. Results and discussion

Fig. 1 shows the experimental and modelled cation concentrations in the percolate as a function of time for the horizontal (H2) and vertical (V5) clay cores. For the horizontal clay core, there is an acceptable agreement between the experimental data and simulations during the first injection step (0.1 M $NaNO_3$), except the modelled calcium and strontium concentrations, which are too high during this first injection step. A possible reason for the high calcium concentration is the precipitation of $CaCO_3$ (not