



## Modelling coupled chemico-osmotic and advective–diffusive transport of nitrate salts in the Callovo-Oxfordian Clay

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### ABSTRACT

Chemico-osmosis is a recognized phenomenon taking place in clay mineral-rich sedimentary formations and a number of questions have been raised concerning its potential effects on pressure fields in and around underground radioactive waste repositories installed in such formations. Certain radioactive waste packages contain large quantities of nitrate salts whose release might result in the presence of highly concentrated salt solutions in the disposal cells, during their resaturation after closure of the facility. This would lead to large solute concentration gradients within the formation's porewater which could then potentially induce significant chemico-osmotic fluxes. In this paper, we assess the impact of chemico-osmotic fluxes on the water pressure during the post-closure period of a typical disposal cell for intermediate-level, long-lived bituminised radioactive waste in the Callovo-Oxfordian Clay formation. A numerical model of chemico-osmotic water flow and solute transport has been developed based on the work of Bader and Kooi (2005) [5], and including Bresler's dependence of osmotic efficiency on concentration and compaction state [9]. Model validity has been extended to highly concentrated solutions by incorporating a concentration-dependent activity coefficient, based on the Pitzer's equations. Results show that due to the strong dependence of the osmotic coefficient on concentration, the impact of chemico-osmosis on water flow and on the pressure field around the disposal cell is relatively low. A maximum overpressure of the order of 1 MPa was obtained. No difference in the simulation results were noticed for disposal cell solutions having concentrations higher than 1 M NaNO<sub>3</sub>. Differences between simulations were found to be almost entirely due to Bresler's relationship i.e., the model of the dependence between osmotic efficiency and concentration, and only slightly on the activity coefficient correction. Questions remain regarding the appropriate function to use for describing the dependence of osmotic efficiency on salt concentration.

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### 1. Introduction

Over the past few decades a number of experimental and theoretical/numerical investigations have focused on understanding solute and solvent transport in low-permeability clay-rich rocks or geomaterials (e.g. shales, bentonite, geosynthetic clay liners) because of the interest in their use as natural and/or engineered clay barrier systems for waste disposal facilities [5,17,28]. The highly compacted, low permeability clay-rich materials of interest contain a significant amount (30–50%) of permanent negatively charged clay minerals (smectite, illite, ...) and characteristically have very small pore dimensions. An electrostatic field, called the diffuse double layer [28], is developed at the clay surfaces and extends out into the contacting pore solution. Electrostatic repulsion of anionic solutes from the clay surfaces surrounding a pore can

result in closing the pore volume to anion passage. These materials can therefore act as semi-permeable membranes when placed between two solutions of differing solute concentrations, hindering dissolved anion (and also cation, because of the need to insure electroneutrality) transport while allowing the solvent, H<sub>2</sub>O, to pass. This ability to limit solute transport is what makes these materials so attractive in waste confinement applications. Clay-rich formations are, for example, envisaged by several countries as hosts for installation of long-term deep geological disposal facilities for long-lived radioactive waste (see for example [2,24,38]), and many disposal concepts rely upon compacted bentonite materials to act as engineered barriers [2,31].

Research on these materials shows that chemico-osmosis can be an important phenomenon affecting both transport and pressure fields in clay-rich rocks [33]. Chemico-osmosis is a transient phenomenon driven by solute concentration gradients within a fine-grained saturated porous medium capable of acting as a semi-permeable membrane and leads to water flux towards the higher concentration zone, i.e., opposite to the solute flux direction.

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Flux magnitude is proportional to the solute activity gradient [14,15,37] and is strongly dependent on the ability of the membrane to limit or retard solute molecule transfer rates relative to water transfer [21]. The efficiency of the membrane to retard ions transfer, parameterized as the osmotic efficiency, or reflection coefficient, in mathematical models, is dependent on the thickness of the electrical double layer, itself dependent on solution ionic strength [9,23].

Clay-rich rocks and bentonite have been shown to act as non-ideal semi-permeable membranes for solutes and, as a result, to be subject to the chemico-osmosis phenomenon [22,28]. In the case of borehole drilling or exploitation in shales, solution concentration gradients between drilling fluid and a clay-rich formation-fluid can lead to an instability of the wellbore and to borehole failure [10,39]. Chemico-osmosis is also suggested to be the cause for anomalous fluid overpressures observed in indurate clay rocks [18,20,33]. Chemico-osmosis is also a plausible phenomenon in certain types of waste cells included in the French project for disposal of intermediate and high-level long-lived radioactive waste in the Callovo-Oxfordian Clay formation in eastern France [2]. Some types of intermediate-level waste contain high contents of sodium nitrate ( $\text{NaNO}_3$ ) and other highly soluble salts. After the operational phase, the disposal cell containing the waste packages will be sealed with bentonite and formation water will progressively fill the cell, coming into contact with the waste packages and dissolving the contained salts. The salt concentration in the solution could theoretically reach very high levels, the maximum being the saturation limit of  $\text{NaNO}_3$  ( $\sim 11$  M). The solutes would then migrate into the surrounding formation, mainly by diffusion due to the very low permeability of the clay. This would induce a strong concentration gradient between disposal cell solution and the much more dilute formation pore water, which could lead to significant osmosis-driven fluxes and overpressures in and around the cell. Theoretical considerations based on Van't Hoff's equation equilibrium and the osmotic potential indicates that these overpressures could potentially reach several MPa if a high osmotic efficiency is assumed.

Several models have been developed for the simulation of chemico-osmotically driven coupled water-solute flow [5,9,16,19,29,32,34] and successful simulations of experimental data have been shown in Bader et al. [5], Cruchaudet et al. [12], Garavito et al. [16] and Sherwood and Craster [39]. Even though an important part of the models available in the literature can simulate steady-state or transient chemico-osmotic transport, few of them integrate the strong dependence of the osmotic efficiency of the membrane on concentration [5] such as the one presented by Bresler [9]. The integration of this dependence is presented by Neuzil [32], in the context of the Pierre Shale (South Dakota, USA) and by Garavito et al. [16] in the context of the Boom Clay in Belgium.

The purpose of the present research was to develop a simulation code for assessing the impact of chemico-osmosis on the resaturation time, pressure evolution and solute transport in, and around, a waste disposal cell containing  $\text{NaNO}_3$  rich wastes, in the Callovo-Oxfordian Clay formation mentioned previously. The chemico-osmotic solute and water transport model is based on the one developed by Bader and Kooi [5] and is implemented in a numerical code using the FlexPDE-finite element library [13]. In order to be able to study cell concentrations extending up to the solubility limit of  $\text{NaNO}_3$  (11 M under standard conditions [3]), the model has been adapted to extend its validity to solutions exceeding 1 M by implementing an activity correction, based on a polynomial regression of the variation of activity as a function of concentration obtained using Pitzer's equation [35]. The osmotic efficiency is estimated through an analytical function which reproduces Bresler's relation [4,9]. In order to assess the impact

of osmotic flow on the resaturation time, the model was also designed to allow water unsaturated flow modelling.

## 2. Theory of chemico-osmotic flow and model development

### 2.1. Coupled flow and transport equations for solute-water transport

The work presented here follows that of Bader and Kooi [5], which was mainly inspired by the work of Malusis and Shackelford [28] and Katchalsky and Curran [21]. The basic flux equations expressed in pressure  $p$  [Pa] and  $\mu$  [J/mol] the chemical potential of the solute are:

$$\vec{J}_v = L_{11} \nabla(-p) + L_{12} \nabla(-\mu_s) \quad (1)$$

$$\vec{J}_s^d = L_{21} \nabla(-p) + L_{22} \nabla(-\mu_s) \quad (2)$$

where  $\vec{J}_v$  [m/s] is the volumetric flux of solution (water + solute), which is in fact the modified Darcy flux or the specific discharge  $\vec{q}$  [m/s],  $\vec{J}_s^d$  [mol/m<sup>2</sup> s] is the diffusive molar flux of solute relative to the solvent (water in our case) and  $L_{ij}$  are the Onsager's phenomenological coupling coefficients relating flux  $i$  to gradient type  $j$ . The system is considered to be isotropic and in which case Onsager's reciprocal relations require that  $L_{ij} = L_{ji}$  [6].

The advective-diffusive molar  $\vec{J}_s$  flux relative to the porous media is defined by:

$$\vec{J}_s = \vec{J}_s^d + c_s \vec{q} \quad (3)$$

where  $C_s$  [mol/m<sup>3</sup>] is the molar concentration of the solute. This concentration is equal to  $c_s = \frac{\rho_j \omega}{M_s}$  where  $\rho_j$  [kg/m<sup>3</sup>], is the density of the solution,  $\omega$  [-] the solute mass fraction and  $M_s$  [kg/mol] the molar mass of the solute. The chemical potential of the solute  $\mu_s$  [J/mol] is defined by the following equation [5,40]:

$$\mu_s = \mu_s^0 + \nu RT \ln a_s \quad (4)$$

with  $\mu_s^0$  [J/mol] being the constant standard potential of the solute,  $\nu$  [-] the dissociation factor for the solute (number of ions produced by  $\text{NaNO}_3$  dissociation: 2 ions),  $R$  [J/mol/K] the universal gas constant,  $T$  [K], the absolute temperature and  $a_s$  [-] the activity of the solute. As  $a_s = \gamma \frac{m}{m^0} = \gamma \omega \frac{1}{M_s}$ , where  $\gamma$  is the activity coefficient of the solute [-],  $m$  [mol/kg solvent (water)] is the molality of the solute and  $m^0 = 1$  mol/kg solvent (water) the standard concentration in the molal scale [40], the chemical potential gradient gives:

$$\nabla \mu_s = \nu RT \frac{1}{a_s} \nabla a_s = \nu RT \frac{1}{\gamma \omega} \nabla \gamma \omega \quad (5)$$

In the case of non-ideally dilute solutions, the activity coefficient  $\gamma$  is no longer constant and shows a non-linear behaviour relative to concentration [7]. Thus,  $\gamma$  cannot be factored out of the gradient as was the case in Bader and Kooi [5]. The way the activity coefficient variation was taken into account based on Pitzer's equations is discussed in Section 2.3.

After following the mathematical development of Bader and Kooi [5] with the assumption of activity coefficients which are variable in time and space, we obtain the following modified flux equations written in terms of freshwater head  $h = z + \frac{p}{\rho_0 g}$  with  $z$  [m] the elevation,  $g$  [m/s<sup>2</sup>] the gravitational acceleration and  $\rho_0$  [kg/m<sup>3</sup>] the density of freshwater under standard conditions:

$$\vec{q} = -\frac{k}{\mu} \rho_0 g \nabla h + \lambda \rho_f \frac{\nabla \gamma \omega}{\gamma} = -\frac{k}{\mu} (\rho_0 g \nabla h - \sigma \nabla \pi) \quad (6)$$

$$\vec{J}_s^d = -\sigma \rho_f \omega \vec{q} - D \rho_f \frac{\nabla \gamma \omega}{\gamma} \quad (7)$$

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