DIFFUSION OF IONS IN UNSATURATED
CLAY-ROCKS: THEORY AND APPLICATION
TO THE CALLOVO-OXORDIAN ARGILLITE

D. Jougnol\textsuperscript{1,2} and A. Revil\textsuperscript{1,3}

1. CNRS-CEREGE, Dept. d'Hydrogéophysique et Milieux Poreux, Aix-en-Provence, France.
2. ANDRA, 1-7 rue Jean Monnet, 92298 Chatenay-Malabry, France.
3. Colorado School of Mines, Golden, CO.

INTRODUCTION
The intrinsic permeability of low-porosity clay-rocks is usually much below $10^{15}$ m$^2$ and therefore the dominant mechanism of transport of the ions in these media is by diffusion of the ionic species through the connected porosity. The problem of predicting the effective diffusion coefficient of ions in porous media is currently attracting attention, especially in clay-rich materials because of their application to nuclear waste storage. In this contribution, we extend the theoretical model of transport developed by Revil and Linde (2006) under saturated conditions to include the influence of unsaturated conditions upon diffusion of ionic species in clay-rocks. This theory provides a new way to predict the effect of the saturation on the diffusion coefficient and to make an application to the EDZ (Excavated Damaged Zone) matrix of the COx (Callovo-Oxfordian) argilite.

THEORY
In a salinity gradient, the diffusion of ions through the connected porosity of a clay-rock is influenced by the charged nature of the interface between the pore water and the clay minerals. This influence is exerted through the generation of a macroscopic electrical field called the diffusion or membrane potential. This electrical field depends on the excess of counterions located in the pore space to counterbalance the charge density of the surface of the clay minerals.

Revil and Leroy (2004) and Revil et al. (2005) derived recently a new set of constitutive equations to study the transport of ions in a water-saturated clay-rock. Their model was able to explain successfully the influence of the pore water chemistry and tortuosity of the pore space upon the diffusivity coefficient of a salt through a water-saturated clay-rock or a compacted bentonite.

In unsaturated clay-rocks, we have to consider (1) the effect of the charged nature of the air / water interface, (2) the increase of the counterions density as the counterions are packed in a smaller volume when the saturation of the non-wetting phase (air) increases (Figure 1), and (3) the influence of the water saturation upon the tortuosity of the water phase. In this contribution, we volume average the Nernst-Planck equation to determine the coupled constitutive equations for the diffusion flux and the current density of a multi-component electrolyte in unsaturated conditions with water being the wetting phase for the grains.

The work by Hunt and Ewing (2003) is a recent effort to include the influence of the water content upon diffusion in soils based on percolation theory. They have shown that the diffusion coefficient decreases with the desaturation and vanish at threshold moisture content. We include this observation in our theory.

APPLICATION TO THE COX
The material considered for the sensitivity analysis is the argillite clay-rock from the Callovo-Oxfordian geological formation under consideration in the eastern part of France for a deep geological disposal facility for radioactive wastes. We compute the effect of the water saturation upon the effective diffusion coefficient of a binary salt (like NaCl or KCl) in this clay-rock. The sensitivity analysis was made using the data provided by Leroy et al. (2007). The result shows a decrease of the diffusion coefficient by a factor four when relative water saturation decreases from 100% to 60% (Figure 2).
Figure 1: Distribution of the ionic species in pore space of a clay-rock. The Stern layer of adsorbed counterions is considered to be part of the solid. a. At high water saturations, the excess charge density of the pore water is relatively low. b. At low water saturations, the counterions are packed in a smaller volume and therefore the excess charge density of the pore water is higher.

Figure 2: Influence of the saturation $s_w$ upon the diffusion coefficient of NaCl of the Callovo-Oxfordian argillite. a. For different values of the partition coefficient $f_Q$ of the counterions between the Stern and the diffuse layers (for a salinity of 1 mol L$^{-1}$). b. For different values of the salinities $c_w$ (for a partition coefficient of 0.94).

Reference