

## Molecular Dynamics study of unsaturated clay pore

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Numerous experimental and theoretical studies have focused on predicting the performances of clay minerals as barrier materials in the containment of high-level radioactive waste by evaluating the diffusion of mobile species in compacted, water-saturated Na-bentonites. However, storage conditions are sometimes unsaturated as in the ANDRA's Cigéo<sup>[1]</sup> deep storage center. Calculation codes used to study the reactive transport of species at the scale of the storage structures are based on data obtained experimentally or theoretically and because of the amount of data available, they describe rather well the saturated clay pore systems. On the other hand, available data becomes more sparse in the case of unsaturated pores. Yet, the unsaturation can deeply modify properties such as species distributions and diffusion coefficients. Thus, microscopic studies of unsaturated pores are necessary in order to implement the unsaturated case in reactive transport codes<sup>[2]</sup>.

Here, we choose to study unsaturated pores of Namontmorillonite and Na-illite, which have a negative structural charge and thereby have particular interactions with the ions. These interactions are more or less well described in the case of the saturated pore with the double layer model but have been little studied in the unsaturated case. Therefore, we explore the impact of the unsaturation on the structure of the mobile species at the solid/liquid interface and on their mobility. These properties are calculated at the microscopic scale by Molecular Dynamics simulations in order to validate macroscopic laws or propose new ones that could be integrated in a mesoscopic code. Finally, because the system presents two interfaces, a solid-liquid interface and a liquid-gas interface, we are comparing the results between a reference non-polarizable force field, CLAYFF<sup>[3]</sup>, and a polarizable force field PIM<sup>[4]</sup> currently in development at the PHENIX laboratory.

[1] ANDRA. (2005), Tome 2; Report CRPADS040022\_B. [2] Tinnacher et al. (2015) *Geochim. Cosmochim. Acta*. [3] Cygan T. et al. (2004) *J. Phys. Chem. B*, 108 (4) : 1255-1266. [4] Tesson, S. et al. (2015) *J. Phys. Chem. C*.