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Multiscale modelling of transport in clays from the molecular to the sample scale

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A B S T R A C T

We report some recent applications of multiscale modelling to the transport of ions, water and CO_2 in clays. On the one hand, simulations on different scales allow us to investigate the physicochemical processes underlying the geochemical and transport behaviour of these fluids in the interparticle pores and at the surface of clay minerals. We discuss more specifically the insights gained from molecular simulations into the acidity of surface edge sites, ion exchange and the behaviour of clay interlayers in contact with a CO_2 reservoir. On the other hand, upscaling the descriptions from the molecular level to the macroscopic scale without forgetting the fundamental role of interfaces on the mesoscopic scale provides a means to capture complex phenomena such as electrokinetic couplings. We illustrate the complementarity of molecular dynamics, lattice-based mesoscopic simulations and Pore Network Models to address this issue.

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1. Introduction

Understanding the transport of water, ions, gas or oil through clay barriers is essential in the contexts of hydrology, petroleum and gas reservoir engineering, as well as the geological disposal of radioactive waste (ANDRA, 2005; Bradbury and Baeyens, 2003) or CO_2 sequestration (DePaolo and Cole, 2013; Gaus, 2010). Clay rocks display a complex multiscale structure, from the regular stacking of aluminosilicate lamellae on the microscopic scale to their disordered assembly into particles on mesoscopic scales (10^{-9} to 10^{-6} nm) with corresponding interlayer and interparticle porosities, up to the macroscopic assembly of clays with other minerals (e.g., carbonates or quartz). To

this hierarchy of length scales correspond a variety of physicochemical phenomena occurring over times spanning several orders of magnitude, many of them being associated with the structural charge of the mineral surface: chemical reactivity of surface sites, electrostatic interactions between the surface and ions in the interstitial solution, specific ion effects, wetting, swelling, electrokinetic couplings, etc. The electromagnetic signature of materials, in response to applied electromagnetic or acoustic waves, is at the basis of many logging tools and of seismo-electric exploration (see, e.g., Pride, 1994).

From the modelling point of view, this challenge set by multiple length and time scales can only be addressed within the framework of a multiscale strategy. On the one hand, this means adopting various complementary descriptions of the same system to capture different types of complexities. The reorganization of electrons around nuclei during chemical reactions requires using quantum descriptions, but their computational cost limits their use

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to a few hundred atoms (Boek and Sprik, 2003; Liu et al., 2013; Suter et al., 2008). Molecular simulations allow us to accurately describe clay layers and interlayers as well as the interface between clay particles and solutions over a few nanometres (Boek et al., 1995; Ferrage et al., 2011; Greathouse and Cygan, 2006; Hensen and Smit, 2002; Marry et al., 2002; Michot et al., 2012; Rotenberg et al., 2010a; Sposito et al., 1999). Mesoscopic simulations are then needed to model phenomena in pores with sizes in the range 10–100 nm (Boek and Venturoli, 2010; Rotenberg et al., 2010b; Stukan et al., 2010). On the other hand, one should make the link explicit between the various levels of description, exploiting more accurate models to calibrate coarser ones retaining the relevant information on larger scales. This "bottom-up" strategy includes, for example, using ab initio calculations to parameterize force fields (Cygan et al., 2004), or molecular simulation to derive simple kinetic models (Carof et al., 2014; Dufrêche et al., 2010; Rotenberg et al., 2007a,b). Even though all the references cited above are applications to clay minerals, this strategy is of course very general and has been successful in many other contexts.

In the present work, we review some recent theoretical and numerical developments in our group, using molecular and mesoscale simulations to address a number of issues related to the transport of ions, water and other fluids in clays. In Section 2, we first illustrate the interest of various simulation techniques to gain insight into geochemistry problems: ab initio molecular dynamics (MD) to predict the acidity of clay edge sites, classical MD to understand the thermodynamics of ion exchange, and Grand-Canonical Monte Carlo (GCMC) to investigate the interaction of clay interlayers with CO_2 reservoirs. In Section 3, we then show the interest of a multiscale simulation strategy to describe the transport of water and ions in clays, including electrokinetic couplings, from the molecular to the macroscopic sample scale, using a combination of molecular simulation, lattice-based mesoscopic simulation (Lattice Boltzmann Electrokinetics) and Pore Network Models.

2. Geochemistry: insights from simulation on the molecular scale

In order to predict the transport and retention of mobile species in complex, interfacial materials such as clays, one first needs to understand the underlying microscopic mechanisms. Here we examine three examples of such processes for which molecular simulation proved very useful in complementing experimental approaches.

2.1. Acidity of clay edges

Lateral surfaces of clay particles may provide sorption sites contributing significantly to the retention of heavy metal cations. This sorption depends largely on the protonation state of the various edge sites, which is controlled by their pK_a and the pH of the solution (Tournassat et al., 2013). Fig. 1 illustrates silanol SiOH and aluminol AlOH and $AlOH_2$ sites on the (0 1 0) surface of a dioctahedral TOT clay. Titration experiments only provide a global measure of the surface state and do not allow one to assess the state of individual sites (which however matters for cation sorption) (Bourg et al., 2007). In practice, an efficient strategy consists in introducing a priori or experimental structural information in semi-empirical models such as MUSIC (Hiemstra et al., 1996; Machesky et al., 2008) in order to reproduce the titration curve (Tournassat et al., 2004).

In this context, molecular simulation is an attractive alternative for evaluating the acidity of individual sites. The pK_a is related to the reaction free energy for the transfer of the surface proton to a water molecule, e.g., for a silanol group:

$$-SiOH + H_2O_{aq} \rightarrow -SiO^- + H_3O^+_{aq}. \tag{1}$$
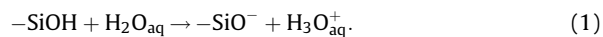
This involves the breaking and formation of chemical bonds so that DFT-based simulations are necessary (even though reactive force fields are now available, they remain less accurate, in particular for proton transfer reactions). Since the relaxation of bond lengths on edge surfaces plays an important role on the acid–base properties (White and Zelazny, 1988), it has first been proposed to introduce
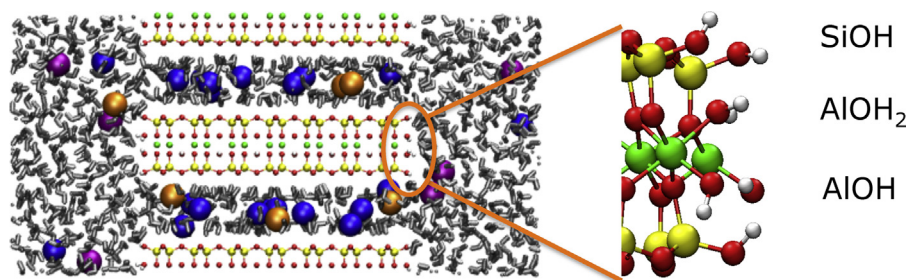
Fig. 1. Lateral surfaces of clay particles display edge sites arising from the reaction of broken Si–O and Al–O bonds with water molecules. The resulting groups, here silanol and aluminol on the (0 1 0) surface of a dioctahedral TOT clay such as montmorillonite, may protonate or deprotonate depending on the pH of the interstitial solution. The pK_a of each site can be determined separately from ab initio simulations, whereas experimental titration data can only provide global information. Colour code: yellow = Si, green = Al, red = O, white = H. In the left part water molecules are in grey and the spheres represent Na^+ (blue), Cs^+ (orange) and Cl^- (pink) ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)