

## Research paper

## Anion diffusion in clay-rich sedimentary rocks – A pore network modelling

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## ABSTRACT

Mass transport in compacted clays is predominantly by diffusion, making them preferred candidates for barriers to radionuclide transport in future repositories for nuclear waste. Diffusivity of species depends on a number of factors: (1) the physical and chemical properties of the clay, such as the geometry and topology of the pore space and the functional groups on the surface; (2) the environmental system, e.g. pH, ionic strength, temperature and organic matter; (3) the nature of species, e.g. charges, sizes and their interactions. Existing models do not consider these characteristics integrally in diffusion simulations and analysis. In this work, a developed pore network model is used to study the diffusion behaviour of  $\text{Cl}^-$  with different ionic strengths. The network is constructed based on experimental pore space information and mineral compositions, and captures the anisotropy and heterogeneity of clays. Opalinus clay is selected for testing the model. The effects of pore size distribution, porosity, cation exchange capacity and surface area on the transport behaviour of anions with different ionic strength are analysed. This improves the understanding of the effects of different factors on the species transport in Opalinus clay. The ionic strength of the pore water is varied between 0.01 and 5 M to evaluate its effect on the diffusion of  $\text{Cl}^-$  in clays. It is shown that the model predictions are in good agreement with measured experimental data of Opalinus clay. The agreement demonstrated, both qualitatively and quantitatively, suggests that the proposed approach for integrating known effects on diffusivity is reliable and efficient.

## 1. Introduction

Clays are considered as the ideal materials of disposing high level radioactive waste in various countries due to their low permeability, high structural charge, strong adsorption of radionuclides and surface area associated with the clay minerals (Altmann et al., 2012; Nagra, 2002; Nwmo, 2015; Xiong and Jivkov, 2015; Xiong et al., 2014). A comprehensive study of the mobility of species in clays is thus necessary to assess the safety of the geological disposal. A number of factors affect the mass transport through clays:

- (1) The physical and chemical properties of the clay;
- (2) The environmental system, e.g. pH and temperature;
- (3) The nature of species, e.g. charges, sizes and their interactions.

For instance, the pore size distribution has significant effect on the transport behaviour, because if the thickness of the electrical double layer (EDL) is greater than one half of the pore width, the overlapping of EDL makes the pore not accessible by anions. Thus the smaller the pore sizes, the greater percentages of pores not accessible by the anions. In addition, some species adsorbed onto the pore walls block smaller pores. Further, the charge of the species may change due to the pH and

temperature.

A number of methods at various length-scales have been proposed to study the impacts of different factors on the transport of species in clay and the interaction between the clay surface and the solutes (Appelo et al., 2010; Tinnacher et al., 2016; Tourmassat et al., 2009; Xiong et al., 2014). A class of microscopic models operating at a pore scale, including molecular dynamics (MD) and Monte Carlo, have the advantage of giving accurate representations of the water, anion and cation diffusivities and concentration profiles. In contrast, macroscopic models are more computation efficient, enable analysis of larger systems and provide direct access to transport properties. Macroscopic models include the continuum hydro-geo-chemical transport model, PHREEQC, and the discrete pore network models (PNM). PHREEQC has been developed to simulate cations, anions and neutral species in clays. It is implemented by obtaining the accessible porosities of different species firstly, and based on these simulating the diffusion of other species. The disadvantage of this method is that it cannot analyse the impacts of pore size distribution on the transport properties of species.

In contrast to PHREEQC, which is an indirect method that only considers one dimensional homogeneous porous media (Appelo et al., 2010; Appelo and Wersin, 2007), the 3D pore network models can take into account the heterogeneity and anisotropy of the porous media.

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PNMs have been widely used to simulate the relative permeation, dissolution and precipitation, diffusion and adsorption and biomass growth in different porous materials. PNMs which have been applied to shale and gas extraction, waste disposal and microbial enhanced oil recovery etc. (Xiong et al., 2016a). The model proposed here directly characterises the realistic pore size distribution of porous materials based on the measured data.

When species travel through the pores in clays they interact with the pore walls. In general, the cations diffusivity is enhanced, and that of anions inhibited, compared to a neutral tracer such as tritiated water (HTO) in charged pores (Appelo and Wersin, 2007; Glaus et al., 2015; Van Loon and Mibus, 2015; Van Loon et al., 2003a). The models used to simulate this interaction can be divided into two categories: (1) Traditional empirical models, e.g. Freundlich model, Langmuir model and Brunauer-Emmett-Teller (BET) model; (2) Models based on thermodynamic mechanisms including ion exchange model and surface complexation models (Bradl, 2004).

The empirical models only consider the chemical interaction but cannot explain the mechanism of solid-solution interaction on the solid-water interface. While the models based on thermodynamics consider both the chemical and electrostatic effects. The surface complexation models include constant capacitance model (CCM), diffuse layer model (DLM), triple layer model (TLM) and basic stern model (BSM). In the surface complexation models, the Gouy–Chapman model or modified Gouy–Chapman is usually used to describe the electrostatic interactions between the species, e.g. cations and anions, and the excess of charges of the clay minerals (Chapman, 1913; Gouy, 1910). The Poisson–Boltzmann equation and Navier–Stokes equation are then used to characterize the effects of the electrical charges on ionic and water fluxes (Coelho et al., 1996; Leroy and Revil, 2004). Another method is to average the exponential distribution of the ions in the EDL over a Donnan volume (Appelo and Wersin, 2007). This is computationally faster and gives equivalent results compared with MGC by integrating the Boltzmann equation (Hedström and Karnland, 2012; Tournassat and Appelo, 2011).

While PNMs have been used to simulate transport of species with traditional empirical models (Xiong et al., 2014; Xiong et al., 2015), PNMs based on the thermodynamic models have not been explored yet to the authors' knowledge. This work is intended to fill the existing gap. The effects of different pore size distribution and ionic strength are analysed. The reason to study the effects of ionic strength is that there is a lack of information about diffusion in porous clays with different pore space properties at different ionic strengths. It is known that an electric double layer (EDL) arises from the screening of the negative surface charge of clay minerals by accumulating cations, and that EDL is compressed at high ionic strength (Glaus et al., 2010; Tournassat and Appelo, 2011; Wigger and Van Loon, 2017). At high ionic strength a lower volume of the diffuse layer is necessary to compensate the negative charge on the surface, see Fig. 1 (Appelo et al., 2010; Glaus et al., 2010; Van Loon et al., 2007; Wigger and Van Loon, 2017). Thus, the ionic strength of the pore water has significant effects on the mass transport in clays.

The pore network proposed here is constructed based on

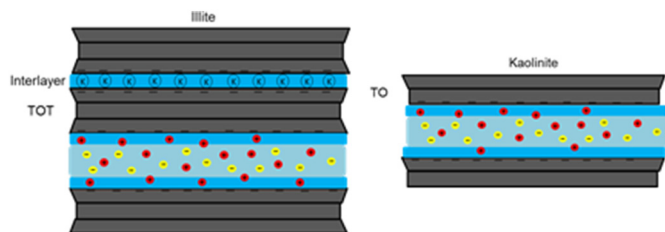


Fig. 1. Schematic representation of the structures of the clay minerals in OPA. The small horizontal lines denote the negative charges present in the clay systems (González Sánchez et al., 2008).

experimental pore space information and mineral characterisation, i.e. pore size distribution, connectivity and surface area. The constructed pore network can represent the anisotropy and heterogeneity of the clays by using different length parameters and percentage of pores in different directions. Then in each single pore, the pore space is divided into free pore water space, stern layer and a diffuse double layer as the clay surface is negatively charged. The stern layer completely excludes the anions. In the free pore water space, the diffusion is similar to diffusion in pure water. In the diffuse double layer, there is excess of cations and deficit of anions relative to these species in the free pore water. This results in the enhanced diffusion for cations and reduced diffusion for anions. The thickness of the diffuse double layer and the ionic concentration in the diffuse double layer are determined by electrochemical mechanisms taking into account the cation exchange capacity (CEC), surface area and ionic strength.

The geometric and physic-chemical information is embedded in a 3D network to solve the diffusion problems. This model is used to perform a systematic investigation of the anion transport behaviour in natural clay rocks. The anion diffusion behaviour and the anion exclusion effect in clay rocks with different porosity, pore size distribution, cation exchange capacity and specific surface area studied to understand better the relationship between the ionic strength of the pore water, the properties of the rock, and the anion diffusion in these clay rocks. This enables us to assess accurately the anion accessible porosity with respect to the estimation of the pore water composition. In addition, the developed PNM in this work can be easily coupled with lattice model for mechanical behaviour to investigate the effects of micro-crack generation, competition, and coalescence (Zhang and Jivkov, 2014) on transport, which is a difficult and attractive topic in assessing the performance of clays.

## 2. Experimental data and geometric modelling

### 2.1. Notes on clays microstructures

In Opalinus Clay, diffusion of cations is enhanced, and that of anions suppressed, relative to a neutral tracer such as tritiated water (HTO). This is suggested by results from many diffusion experiments with clayrock, bentonite or pure montmorillonite (Appelo et al., 2010; Descostes et al., 2008; Kozaki et al., 2008; Van Loon et al., 2007; Wersin et al., 2008; Xiong et al., 2016b). The effect can be explained by the negatively charged clay surface. An excess of cations and a deficit of anions are required to neutralize the remaining charge at the outer surface of the clays. When all charges on the surface are neutralized, the transport of species is similar to transport in pure water, but the flux is less because the tortuous path in the pores is longer than the straight-line distance used for the concentration gradient in Fick's laws (Appelo et al., 2010; Appelo and Wersin, 2007; Glaus et al., 2007; Jougnot et al., 2009; Nagra, 2002; Ohlsson and Neretnieks, 1998).

The negative surface charge can be explained at the microscopic scale as caused by the isomorphic substitutions in the crystal lattices. For example, the isomorphic substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the silica tetrahedra and  $\text{Al}^{3+}$  by  $\text{Fe}^{2+}$  and/or  $\text{Mg}^{2+}$  in the octahedral layer of the crystal lattice in smectite particles. Meanwhile, different clay minerals have different microscopic structures, e.g. smectite and illite are built of a succession of dioctahedral (TOT) layers (2:1) while kaolinite particles are built by a series of TO layers (1:1) (Hassan et al., 2006; Leroy and Revil, 2004). This influences the cation exchange capacity (CEC) of illite, kaolinite and smectite, which is around 0.22 equiv./kg, 0.03–0.04 equiv./kg and about 0.01 equiv./kg, respectively (Baeyens and Bradbury, 2004; Tinnacher et al., 2016). There are some K cations in illite particles and the interlayer porosity is not accessible for diffusive transport in illite (Meunier et al., 2004).

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