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State of the art on cation diffusion in clay mineral systems

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1 The problem of cation transfer in compacted clay materials

1.1 Main objectives

The purpose of this report is to provide a state of the art on the diffusive transport properties of cations in compacted or natural clays. Understanding cation transfer in clays is of primary importance in order to evaluate the capacity of natural host rocks and bentonite-based engineered barriers to constrain radionuclide migration. In the scientific literature, the study of cation transfer in clays is mainly focused on two topics (i) cation retention by sorption on clay minerals and its associated retardation effects on diffusive transfer and (ii) the higher mobility of cations compared to that of anions and neutral species.

For reasons of simplicity, cation retention on clays is preferably studied in dispersed (batch) systems rather than in compact or intact systems. Using batch systems, the retention behavior of various cations has been studied for many clay minerals or clay rocks for a large range of aqueous conditions. The mechanisms of cation retention can generally be explained in terms of the combined effect of ion exchange and surface complexation reactions with functional groups located on the clay surface (Bradbury and Baeyens, 2005, 2009). In the framework of Funmig project, the applicability of the batch approach for evaluating retention in compact systems was investigated for various species and clay systems. Taken together, the obtained results provide evidence that, for equivalent system conditions, a similar retention behavior would apply to both dispersed and compact states for Cs^+ , Na^+ and Sr^{+2} (Van Loon and al. 2005, 2009; Maes et al., 2008). This statement has not however been demonstrated for all cationic species and particularly for the most strongly interacting ones such as actinides (Wang et al., 2003).

Cation diffusion behavior is generally studied at the macroscopic scale (millimeter - centimeter size samples) using tracer diffusion experiments. The interpretation of these experiments is usually based on analytical solutions assuming homogeneous transport properties and linear sorption (constant K_d) (Garcia Gutierrez et al., 2006). Some studies highlight the limitations of this type of approach for modeling reactive transfer for moderate and strongly sorbing species (Van Loon et al., 2005, Wersin et al., 2008, Jakob et al., 2009). On the other hand, the effective diffusion coefficients measured in intact or compacted clay systems for various cations are generally higher than the ones predicted by a simple pore diffusion model (Melkior et al., 2007, Jakob et al., 2009, Glauss et al., 2010). This behavior is known to depend on the nature of the cations, the porewater conditions and the clay material properties (amount of clays, clay type, pore size...). Even if some authors attribute the highest cation mobility to the preferred migration of cations next to clay mineral surfaces, there is currently no scientific consensus regarding its origins. The mechanisms involved in cation diffusion are distributed from atomic to macroscopic scales and greatly complicate experimental studies and modeling.

In the framework of CatClay, retention and diffusion of specific cations (Sr^{2+} , Zn^{2+} and Eu^{3+}) will be studied in compacted illite material and in various clay rocks (Callovo-Oxfordian mudstone, Opalinus clay and Boom clay) in order to better understand and predict cation diffusion in such systems of interest to radioactive waste disposal concepts. This document aims to examine the problem of cation transfer in clay materials (briefly presented above). In this objective, this paper will present (i) a review of diffusion and retention behavior in clays (ii) a review of the various works dedicated to modeling diffusion-retention performed at

different scales (clay surface, pore and pore network and macroscale), and (iii) a discussion concerning the expectations and the position of CatClay according to the state of art of cation diffusion.

1.2 Clay materials

In CatClay, two categories of clay materials will be studied: natural clayrocks (Callovo-Oxfordian argillite, Opalinus Clay and Boom Clay) and a “pure clay” material (illite du Puy).

A clayrock can be defined as a sedimentary type rock containing a significant proportion of clay minerals (illite, smectite, and interlayered illite-smectite,...). In additions to clays, clayrocks contain variable amounts of carbonate minerals (calcite, dolomite), quartz, accessory minerals (pyrite, feldspar) and organic matter. In clay rocks, the clay minerals are organized in the form of more or less aggregated clay particles (stacks of 2 to 20 clay sheets). Clay aggregates or particles usually have a size of a few hundreds of nanometers. While non clay minerals generally have sizes ranging between 1 µm and a few hundreds of microns. The clayrock pore network consists of a combination of pores mainly ranging from 2 nm to a few hundreds of nanometers located between the clay particles or the clay aggregates. The microstructure (porosity and mineral spatial distribution) depends mainly on the size and the spatial distribution of non clay minerals.

Purified clay materials are made by eliminating the non clay minerals of a clayrock raw material having a high amount of a specific clay mineral. The clay aggregates are then mechanically compacted together to constitute a dense material. Clay minerals are present in compact clays in the form of individual clay particles and clay particle aggregates. The microstructure of this material can be considered as being homogeneous above a scale of several hundreds of microns.

1.3 Constitutive equations

Before reviewing the scientific literature on cation diffusive transfer in clays, and in order to avoid any confusion for the reader, we present here a simple representation of equations and parameters characterizing diffusive transport in porous materials. The diffusive flux of a solute subjected to a concentration gradient is provided by Fick's first equation:

$$J = -D_e \cdot \text{grad}(C_i) \quad \text{Equation 1}$$

where J is the diffusive flux (in mol.m⁻².s⁻¹), D_e the effective diffusion coefficient (in m².s⁻¹), C_{aq} the concentration of species i in pore water (in mol.m⁻³). Note that this equation is only valid for low solute concentrations; otherwise the equation must involve electrochemical potentials. The evolution of solute concentration for sorbing species is given by:

$$\omega \cdot \frac{\partial C_i}{\partial t} + (1 - \omega) \rho_s \cdot \frac{\partial S_i}{\partial t} = -\text{div}(J) \quad \text{Equation 2}$$

where S_i is the mass concentration of the sorbing species on the solid (in mol.kg⁻¹), ω the effective porosity (-) and ρ_s the solid mass volume (in g.cm⁻³).

The retention behavior of a chemical species onto clays is usually evaluated from batch experiments. In batch systems, a known quantity of specie(s) is put in contact with a mass of crushed and dispersed material. The simplest model describing the sorption behavior of a species is given at the equilibrium state by the ratio S_i/C_i known as the distribution coefficient K_d. For a given species, K_d values can depend strongly on the chemical composition of the

background electrolyte (species concentration, pH, ionic strength...) and the clay type (Bauer et al., 2005; Bradbury and Baeyens, 2001, Elzinga and Sparks, 2001, Maes et al., 2008). Analytical and numerical chemical models have been developed at various levels of complexity to describe sorption data. The chemical models based on multi cation exchange and surface complexation sites are currently considered to be the most efficient for describing and predicting cation retention on clay minerals and clayrock (Bradbury and Baeyens 2000, 2005).

Considering instantaneous linear K_d sorption ($\partial S_i/\partial t = K_d \times \partial C_i/\partial t$), the retention-diffusion equation (eq. 2) can be written as:

$$(\omega + (\rho \cdot K_d)) \cdot (\partial C_i/\partial t) = -div(-D_i e - grad(C_i t)) \quad \text{Equation 3}$$

with ρ the dry mass density (g/m^3), $\rho = \rho_g (1 - \omega)$, the $(\omega + \rho \cdot K_d)$ term being a dimensionless parameter known as the capacity factor α . For the one dimensional, homogenous case, eq. 3 is

written as follows:

$$\frac{\partial C_i}{\partial t} = D_a \frac{\partial^2 C_i}{\partial x^2} \quad \text{Equation 4}$$

with D_a being the apparent diffusion coefficient ($D_a = D_e/\alpha$).

In porous media, the effective diffusion coefficient of species i is related to its diffusion coefficient in free water D_w , the effective porosity ω and the geometry factor of the diffusion paths G (-) by:

$$D_i e = (\omega \times D_i w \times G) \quad \text{Equation 5}$$

G is classically expressed as a function of the diffusion path tortuosity τ [-] : $G = \tau^{-2}$ (Van Brakel and Heertjes, 1974, Ullman and Aller, 1982). The so-called “constrictivity” δ [-] is sometimes used in the following relationship $G = \delta \times \tau^{-2}$ (Van Brakel and Heertjes, 1974). Tortuosity is related to porosity using empirical relationships (Archie, 1942, Koponen et al., 1997, Boudreau, 1996).

1.4 Experimental studies of cation transfer in compacted clay materials

In clay materials, measurements of diffusion parameter values are usually performed on roughly cm-thick samples. Various experimental configurations and initial/boundary conditions can be used depending on the studied species, the most common being the *through*-diffusion and the *in*-diffusion methods. Species are generally kept as low as possible in order to minimize modifications of the porewater equilibrium. These experiences are generally interpreted using analytical solutions assuming homogenous properties and instantaneous linear sorption.

The *through*-diffusion experiment requires complete crossing of the sample by the tracer. It is mainly used to analyze the transport behavior of non-interacting or weakly sorbing species. The effective diffusion coefficient and the apparent diffusion coefficient are determined respectively from the study of steady and transient state flux in the outlet reservoir. For species having high K_d values, the tracer sorption will dominate diffusion-driven transfer and, consequently, these elements will move very slowly through clayrock. The *in*-diffusion method, which involves only partial crossing of the sample by the tracer, is therefore more suitable for sorbing species. While the apparent diffusion coefficient can be determined by evaluating the tracer profile in the sample along the concentration gradient, determination of the effective diffusion coefficient requires the coupled analysis of the tracer loss data and depth profile (Van Loon and Eikenberg, 2005). Recent improvements in tracer profiling and element mapping methods can measure tracer profiles over depths less than a few hundreds of microns (see the μ LIBS method Menut et al., 2006 and the high-resolution abrasive method Van Loon and Eikenberg, 2005) and allow the study of strong interacting species such as actinides or metals.

1.4.1 Data interpretation by analytical solutions

In many works, diffusion experiments are interpreted using analytical solutions assuming homogenous transport properties and linear sorption (a constant K_d). Even if this approach is widely used, it is questionable for moderate and strong sorbing cations.

Describing the cation retardation behavior using a linear K_d approach provides a restricted view of retention processes (Steeffel et al., 2005). The best example is given by Cs^+ transfer in natural systems; K_d measured for Cs^+ is known to depend strongly on the concentration of the tracer as well as on the composition of the background electrolyte (Melkior et al., 2005, Van Loon et al., 2009). This means that a simple linear sorption approach cannot be used to describe retardation behavior (Melkior et al., 2005). In batch systems, the Cs^+ retention on clays can be described by multi-site exchange and complexation models (Bradbury and Baeyens, 2005). Implementation of these models in a transport code improves description of Cs retardation in clay materials (Appelo et al., 2010, Jakob et al., 2009). The complete evaluation of the aqueous chemistry is sometimes also required to evaluate retardation and diffusion behavior due to the formation of aqueous complexes involving the studied species. Use of a complete geochemical model is thus recommended to interpret diffusion experiments involving cations (see Appelo et al., 2010).

Geochemical models are usually validated and calibrated against retention data measured in batch systems. The applicability of these data to compact systems has also been subject to question. Van Loon et al., (2009, 2005) and Montavon et al., (2006) have studied retention of various cations under similar aqueous conditions using both dispersed and compacted clayrock samples (Opalinus clay, Callovo-Oxfordien argilites). For both clayrocks, the K_d values for Na^+ , Sr^{+2} and Cs^+ were found to be similar (within a factor of 2) to those measured on crushed rock, with the intact rock values tending generally to be higher. This was attributed to the much longer equilibration times used for the compact material studies relative to batch experiments. The variation in Cs sorption as a function of total Cs concentration for intact Opalinus clay could be modeled using the same ion exchange plus surface complexation model developed for sorption on ground rock (Jakob et al., 2009;). The results for Co^{+2} sorption on intact Opalinus clay are also in good agreement with the corresponding K_d values measured in batch systems (Van Loon PID3.2.19). This statement needs to be also demonstrated for other species.

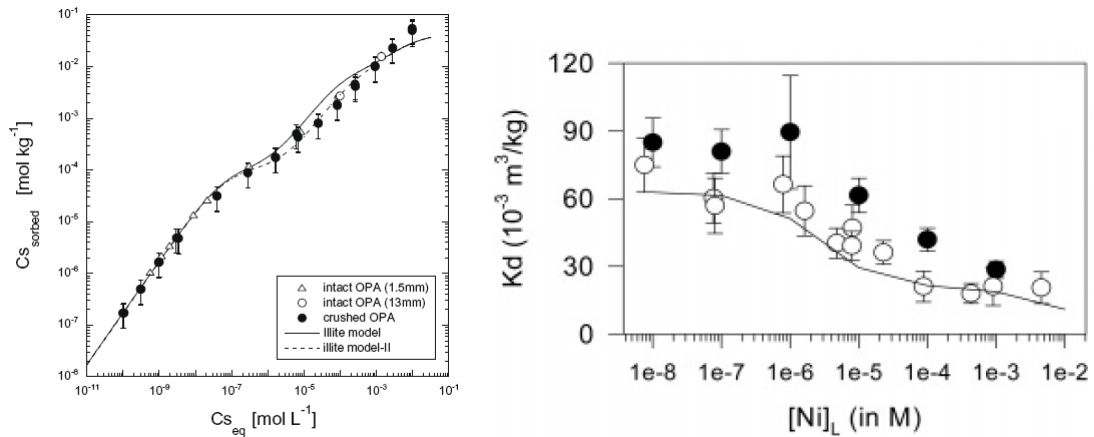


Figure 1 Comparison between sorption behavior measured on batch and intact (left) Cesium from Van Loon et al., (2009) (right) Nickel from Montavon et al., 2006

The validity of homogeneous transport mechanisms was also studied at small scales. In-diffusion of Co^{+2} and Eu^{+3} (strong sorbing species) into Opalinus Clay were quantified in terms of tracer loss over time from the source solution and determination of tracer depth profiles at the end of the experiment using the abrasive peeling method. The combined tracer loss data and depth profiles could not be fit using a single Fick's law model, and required the summed contributions of two simultaneous diffusion/retention processes represented by paired α and D_e values. This might be evidence for a dual-porosity system created by intrinsic rock structure at this scale. It also might be indicative of the existence of a zone near the sample surface having different diffusion-retention properties than the deeper clayrock. Evidence that the latter might be the case is provided by data obtained during a study of Cu(II) in-diffusion into Callovo-Oxfordian clayrock samples (Robinet, 2008).

1.4.2 The cation “acceleration” phenomena

Considering a pore diffusion model, the effective coefficients of two chemical species exploring the same porosity are linked by their free water diffusion coefficients. According to this model, effective diffusion coefficients of cations D_e^+ can be estimated from those of neutral species D_e^0 (HTO is used as a reference) by:

$$D_e^+ = \frac{D_e^0 \cdot D_w^+}{D_w^0} \quad \text{Equation 6}$$

In clay materials (natural or compacted clay), this relation is not verified. The diffusion of cations is generally observed to be higher than that predicted by Equation 6 that of anions lower (Janhke et Radke, 1985, Oscarson, 1994, Erikssen et Jansson, 1996, Melkior et al., 2007 among others), i.e.:

$$\frac{D_e^+}{D_w^+} > \frac{D_e^0}{D_w^0} \quad \text{and} \quad \frac{D_e^-}{D_w^-} < \frac{D_e^0}{D_w^0} \quad \text{Equation 7}$$

Since neutral species are hardly influenced by electrostatic interactions with the surfaces of clay minerals, their effective diffusivity depends only on the geometry of the pore space. The

acceleration of the cations relative to neutral species can be evaluated by the parameter A [-] defined by the following relationship:

$$A = \frac{D_g^+ \cdot D_w^0}{D_g^0 \cdot D_w^+} \quad \text{Equation 8}$$

An overview of variations of the A parameter as a function of various other parameters (nature of the cation, clay type, compaction state and water composition) are given in Table 1. In the framework of this document, it is important to keep in mind that the acceleration of cations (A) is controlled by:

- the nature of clay minerals or their charge density (A increases with the structural charge of the clays : kaolinite in comparison to illite),
- the mass density of the compacted clay which controls the pore size distribution: A increases as the pore diameter decreases,
- the nature of the cation (ionic charge, size and retention behavior on clays): A decreases as the size of the hydrated cation decreases. This effect is illustrated by the behavior of alkaline cations (Melkior and al., 2007).
- the pore water composition: A tends to decrease with increasing ionic strength.

For strongly sorbing species such as Eu^{3+} which interact mainly by surface complexation, the effective diffusion coefficient remains difficult to determine since through-diffusion experiments cannot be used due to the time required to reach steady state. *In*-diffusion experiments, although more suitable in terms of needed experimental time, require determination of both the tracer profile and the rate of tracer loss from the source solution in order to evaluate the effective diffusion coefficient. In addition, loss of Eu^{3+} tracer mass by sorption on different materials in the experimental set-up severely complicates its study. Note that Wang et al., (2003) have developed an in-diffusion method using a capillary system allowing indirect determination of the effective diffusion coefficient by measuring the apparent diffusion coefficient and retardation coefficient. They found that $A \approx 1$ for Eu^{3+} in bentonite.

Generally speaking, cation diffusion results from interactions between charged clay surfaces and ions in solution. The negative structural charge carried by clay minerals generates an electrostatic field in the proximity of their surface, consequently attracting cations and repelling anions. The spatial distribution of ions in the contacting pore solution is most frequently described in terms of the so-called electrical double layer (EDL) theory, which considers a first layer (the Stern layer) comprised of ions adsorbed directly onto the surface and a diffuse layer composed of ions attracted to the surface charge via the Coulomb force. The specific distribution of the different types of ions in the pore solution affects their mobility in the pore space. The electrostatic repulsion of anions from clay surfaces can block their passage through certain small pores thus increasing tortuosity and therefore the time it takes for anions to explore the volume accessible to them (although this volume is smaller than for neutral species that are not repelled from the surfaces) (Rotenberg et al., 2010). Several phenomena are cited to explain the higher mobility of cations, among which a preferential diffusion along the surface (in the Stern layer or interlayer space) or in the double layer.

Table 1 – Review of effective diffusion coefficient D_e and acceleration A (eq. 8) of cations in clay materials. The effective diffusion coefficients determined only by through-diffusion experiments (steady state conditions) on low swelling clays and clay rocks were selected.

Reference	Rock type	Ionic strength	Species	D_e	D_w	D_e/D_w	A
Apello, Van Loon, 2010	Opalinus Clay	Site water	HTO	6.3E-11	2.4E-09	0.026	-
			Na	9.6E-11	1.3E-09	0.072	2.8
			Sr	7.5E-11	7.9E-10	0.095	3.7
Van Loon and Müller, 2008	Opalinus Clay	Site water	HTO	1.4E-11	2.5E-09	0.006	1.0
			Co	4.0E-11	7.0E-10	0.057	10.0
Van Loon et al., 2005	Opalinus Clay (MT3)	Site water	HTO	1.2E-11	2.4E-09	0.005	-
			Na	1.4E-11	1.3E-09	0.011	2.1
			Sr	1.4E-11	7.9E-10	0.018	3.5
	Opalinus Clay (MT1)	Site water	HTO	1.5E-11	2.4E-09	0.006	1.0
			Na	1.6E-11	1.3E-09	0.012	2.0
			Sr	1.7E-11	7.9E-10	0.021	3.5
Melkior et al., 2007	Callovo-Oxfordian (R=1)	Site water	HTO	2.6E-11	2.3E-09	0.011	-
			Li	2.1E-11	9.8E-10	0.021	1.9
			Na	4.8E-11	1.3E-09	0.038	3.4
			K	1.1E-10	1.9E-09	0.059	5.3
			Rb	1.8E-10	2.0E-09	0.091	8.1
			Cs	2.0E-10	2.0E-09	0.102	9.1
Melkior et al., 2004	Callovo-Oxfordian (R=0)	0.001-1	HTO	3.5E-11	2.3E-09	0.015	-
		Site water	Ca	9.0E-11	7.9E-10	0.113	7.5
		Site water	K	7.4E-11	1.9E-09	0.040	2.6
		Site water	Sr	9.5E-11	7.9E-10	0.120	7.9
		Site water	Cs	2.5E-10	2.0E-09	0.125	8.2
		0.5 ¹	Cs	1.3E-10	2.0E-09	0.065	4.3
		1 ¹	Cs	9.5E-11	2.0E-09	0.048	3.1
	Callovo-Oxfordian (R=1)	Site water	HTO	3.0E-11	2.3E-09	0.013	-
		Site water	Ca	8.1E-11	7.9E-10	0.102	7.9
		Site water	K	6.4E-11	1.9E-09	0.034	2.7
Glauss et al., 2010	Illite	0.1-1 ²	HTO	1.3E-10	2.3E-09	0.056	-
		0.1 ²	Na+	3.9E-10	1.3E-09	0.293	5.3
		0.5 ²	Na+	2.3E-10	1.3E-09	0.173	3.1
		1 ²	Na+	1.3E-10	1.3E-09	0.098	1.8
	Kaolinite	0.1-1 ²	HTO	1.3E-10	2.3E-09	0.057	-
		0.1 ²	Na+	1.5E-10	1.3E-09	0.115	2.0
		0.5 ²	Na+	1.0E-10	1.3E-09	0.077	1.4
		1 ²	Na+	0.8E-10	1.3E-09	0.062	1.1

¹ site water + NaNO₃ (M) ² NaClO₄ (M)

2 Pore-scale modeling

Pore-scale modeling is based on the complementarities of two methods of modeling transport phenomena (Figure 2):

- Molecular modeling, wherein the interaction forces between atoms and polar molecules are described explicitly in order to determine their acceleration and subsequent trajectories, over very short time scales. These results can be time averaged in order to estimate, at very small space scales, the equivalent macroscopic parameters such as local concentration and fluid properties (density, viscosity...). These models can be classified into several types: ab-initio molecular dynamics, classical molecular dynamics, brownian dynamics.
- Continuous media modeling (also called mesoscopic hydrodynamics), wherein water and solute molecules are not defined explicitly, but their average concentrations and interaction properties are determined using classical fluid mechanics laws (such as Navier-Stokes). This method allows the pore network structure to be accounted for.

The ultimate objective of pore-scale modeling is to integrate small-scale model results in terms of local properties at the meso-scale, in order to solve macroscale hydrodynamics and solute transport properties.

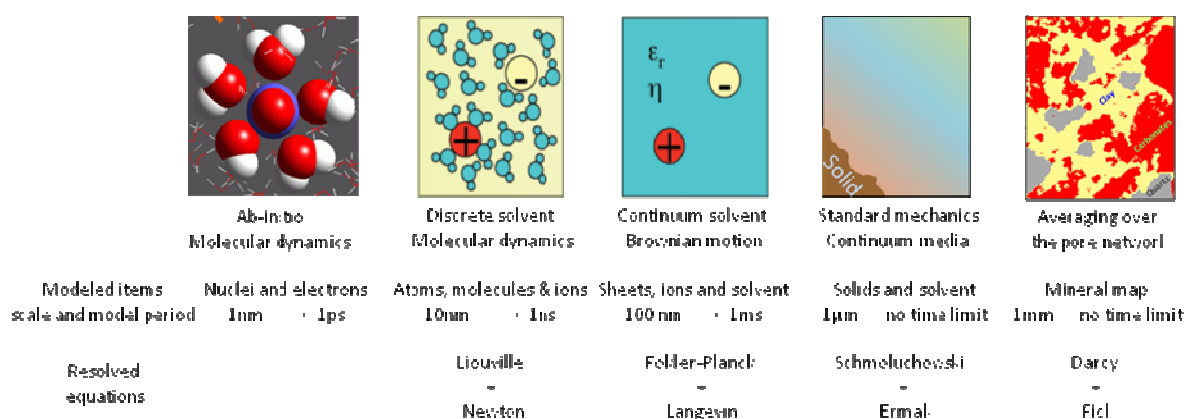


Figure 2 Modeling methods and corresponding scales

Several experimental techniques allow probing transport properties at various scales: neutron scattering, dielectric spectroscopy, NMR and tracer diffusion, among others, and their results can, in certain cases, be used to constrain the transport model operating at the corresponding scale (molecular dynamics, continuous solvent or diffusion-retention). Modeling and measurement of transport at these different scales in a single material can give a great deal of insight into overall transport phenomena without necessarily calling upon a detailed comprehension of the links between the representation scales (i.e. an explicit up-scaling method).

2.1 Microscale modeling: Molecular and brownian dynamics

Most microscale models resolve interaction forces between solute ions, water molecules and clay structural charges. Over the last decade, these models have allowed a description of solute and water behavior in clay interlayers (or in the vicinity of external basal surfaces) and the corresponding thermodynamic and kinetic properties.

Ab-initio models calculate interactions between atoms contained in solutes, water molecules and clay surfaces. The forces acting on the nuclei are determined by electronic structure calculations while the molecular dynamics trajectory is being generated. In this way, the electronic structure variables are not integrated out beforehand, but rather considered as active degrees of freedom. Ab-initio models are therefore classified as quantum mechanics based. Since these models have the ability to represent reactions that involve breaking or formation of covalent bonds, ab-initio models are particularly well adapted for studying the physical origin of the distinct behavior of cations, since they permit an accurate representation of the clay sheet border, an aspect that that might not be properly captured by the Lennard-Jones potential used in classical molecular dynamics. The main drawback of this method is the limited number of molecules which can be included in a calculation, tens of thousands with modern computers, which is somewhat inconsistent with the modeling objectives (transfer of radionuclides at trace concentrations through an ensemble of clay platelets).

In classical molecular dynamics, interactions between atoms in water molecules, ionic solutes and located on clay surfaces are classically accounted for by introducing two forces: Van-der-Waals repulsive forces between polar molecules (characterized by the dielectric constant ϵ) and electrostatic (Coulomb) forces between charged moieties (ions, localisations of charge deficit in clay surfaces) characterized by their electric charge q :

1. The short range Van-der-Waals attraction and steric repulsion between atoms i and j which can be characterized by the Lennard-Jones potential:

$$V_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \text{ with } \begin{cases} \sigma_{ij} = (\sigma_i + \sigma_j)/2 \\ \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \end{cases} \text{ Equation 9}$$

with r_{ij} the distance between atoms i,j . $\sigma_{i,j}$ and $\epsilon_{i,j}$ are the Lennard Jones parameters of atoms given by a specific model (Ex. SPC/E model).

2. The Electrostatic interaction between atoms i and j is described by the Coulombic potential:

$$V_{ij} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \text{ Equation 10}$$

where q_i and q_j are the effective atomic charges and ϵ_0 is the permittivity of free space. Molecular Dynamics (MD) and Monte-Carlo (MC) simulations are used to model systems containing n atoms interacting according to these forces.

- MD simulations consist of tracing the real time evolution of individual atomic positions or trajectories in the system. The time evolution of each atom is governed by the Newton's law of motion:

$$\sum_{j \neq i} F_{j \rightarrow i}(t) = ma_i(t) \quad \text{Equation 11}$$

With $\sum F_{j \rightarrow i}$ the sum of forces (electrostatic and Van der Waals) applied by the j particles on i , m being the particle's weight and a its acceleration.

- MC simulations are designed to determine the whole system minimum energy by stochastic sampling. Atoms are displaced randomly; these displacements being validated when the resulting energy variations are negative or lower than the prescribed by their activation energy potential.

MD and MC simulations can both be used to determine thermodynamic properties (from the positions and momenta of all atoms in the system), local structural properties (from static correlations between particles) and density profiles. Molecular dynamics also allow dynamic properties (diffusion coefficient, viscosity) to be calculated from the time evolutions of atomic positions and momenta or time-correlations between particles, but require a fairly large number (from a statistical point of view) of studied particles to be able to do this. MC models allow estimation of the hydrogen bond and cation hydration energy in free water and within inter-layers, allowing interpretation of clay swelling pressure. When applied to external clay surfaces, molecular dynamics have shown the water structuration caused by hydrogen bonding and confirmed cation internal/external sphere interaction modes (Kirkpatrick et al., 2005).

An example of the state of the art of research in this field is that conducted by the PECSA/UPMC team (V. Marry, N. Malikova and B. Rotenberg doctoral thesis : Marry, 2002; Malikova, 2005; Rotenberg, 2008 and associated published papers : Marry et al., 2002, 2003; Marry and Turq 2003; Dufrêche et al., 2001; Malikova et al., 2003, 2004a, 2004b; Rotenberg et al., 2007) which enabled linking the different scales of modeling ion dynamics, from molecular-scale to continuous solvent, and then to implement them in calculating diffusion / reaction processes, thereby offering a detailed understanding of structural, thermodynamic and dynamic properties of clay interlayers. These authors were able to determine the overall behavior of ions relative to clay interlayer and edge sites, including the exchange properties between interlayer and inter-particle pore volumes. Such exchanges can be studied both in thermodynamic (cationic exchange CEC, microcalorimetry experiments) and kinetic terms by determining the free energy profiles at the interface between particle and interlayer porosity according to the atomic scale "force fields", the latter method allowing evaluation of the transfer probabilities at the interface for each species (water, anions, cations) which may be introduced into continuous solvent models. These simulations showed differing behaviors for Na^+ and Cs^+ in clay interlayers and near basal surfaces, with Na^+ behavior being similar to that in bulk water while Cs^+ partly dehydrates and diffuses by jumping from site to site (Malikova et al., 2004).

MC and MD results can be directly interpreted or used as input parameters in higher scale models once time averaging is possible, thereby providing local fluid properties (permittivity, viscosity, density, ionic mobility). For instance, Tournassat et al. (2009) performed time integrations of ion trajectories in several zones located at different distances from a clay surface. The results are illustrated in Figure 3 which shows that the lateral mobilities of Na and HTO decrease as they approach of the surface. Their relative mobility can be compared, as for diffusion experiments, using the "acceleration" parameter, $A =$

$(D_s(\text{Na})/D_w)/(D_s(\text{H}_2\text{O})/D_w)$. Na^+ cations are “accelerated” only in part III where their concentration is the highest. To the best of our knowledge, this integration was never thoroughly extended to other state parameters such as permittivity, however some equations were proposed and introduced in modified Boltzmann laws (PBMHE, see next section).

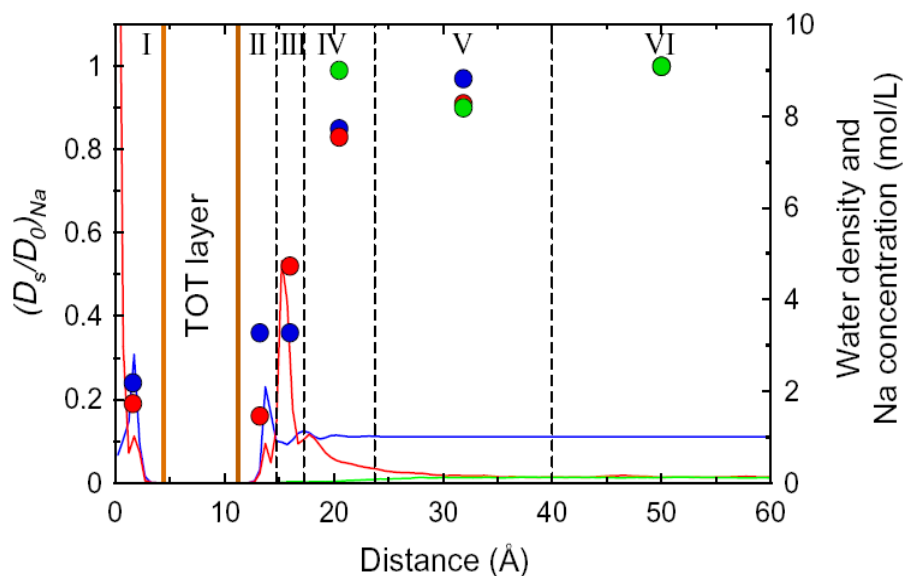


Figure 3 Comparison of $D_s(X)/D_0$ of water (blue circles), Na (red circles) and Cl (green circles) as a function of their distance from the surface of the clay. Lines: water density (blue), Na concentration (red) and Cl concentration (green). From Tournassat et al, (2009).

The main drawback of micro-scale modeling is the maximum simulation domain size and the length of time that can be modeled. In classical molecular dynamics, simulations can address about one million atoms which is quite constraining given that in a 0,1 M solution, about one atom in one thousand is an ion. Continuous solvent models have the advantage of not explicitly addressing the behavior of water molecules. However the presence of water must be taken into account for determining the interaction forces between ions.

This limitation justifies the introduction of Brownian dynamics-based modeling in which ions undergo Brownian motion in an implicit and continuous solvent. This motion is ruled by probability distribution functions that allow micro-scale interactions such as steric repulsion and Van der Waals attraction to be accounted for. In order to do this, Langevin dynamics are developed into Fokker-Planck equations. This method can integrate spatially varying properties, allowing surface and ionic interactions, as well as spatially varying fluid properties and a wide range of surface boundary conditions, to be taken into account. It is generally comparable to the Lattice Boltzmann method described in the next section.

2.2 Continuous media

2.2.1 Stokes – Poisson (Nernst Planck) equations

The diffusive and electro-osmotic behavior of finely-divided, charged porous media can be roughly predicted using homogenization methods (Revil et Leroy, 2004). These transport properties can also be calculated by performing numerical simulations in the pore space with the transport equations applied to the pore space generally being resolved in their continuous form, i.e. by solving the potential fields such as chemical potential or hydraulic pressure. These equations and the related field parameters are determined by measurements in homogeneous and continuous media. For instance, fluid viscosity and trace ion diffusivities are experimentally measured in water, for various temperatures and ionic strengths. These parameters should be representative of the results obtained by time and space averaging of the results of molecular dynamics models. In clay media however, the force fields are very sharp and fluid properties, such as viscosity, diffusivity and permittivity, are locally impacted. This can however be taken in account, as briefly developed in next paragraphs.

The main equations that govern transport in water-saturated porous media are:

- The Stokes equation $\eta\Delta\mathbf{v} + \mathbf{F} - \nabla p = \mathbf{0}$ (Equation 12) which governs solvent transport, where η is the water viscosity, Δ is the Laplace operator, ∇p is the hydraulic pressure gradient and \mathbf{F} represents other forces, among which electrical forces.
- The Poisson charge distribution function: $\Delta\Psi + \frac{\rho}{\epsilon} = 0$ (Equation 13) where Ψ is the electric potential, ρ is the charge density and ϵ is the fluid permittivity. It is commonly associated with the Boltzmann function $\rho = \sum e z_i c_i^0 \exp\left(-\frac{e\Psi}{kT}\right)$ (Equation 14)
- The conservation equation $\frac{\partial c}{\partial t} + \text{div}(\mathbf{J}_c + \mathbf{J}_d) = 0$ (Equation 15) which governs local ionic transport, with \mathbf{J}_c being the advective flux and \mathbf{J}_d being the diffusive flux. \mathbf{J}_d is given by the Fick relation $\mathbf{J}_d = -c \frac{D}{kT} (\text{grad}\mu - \mathbf{F}_{\text{ext}})$ (Equation 16) where μ is the ionic potential and \mathbf{F}_{ext} represents other forces, including Coulombian and Van der Waals forces.

The most challenging task for modeling ionic transport in charged porous media is the description of the boundary condition at the interfaces. Surface and border charges are not modeled explicitly, but they are accounted for by average surface charge densities or potentials. In most cases, knowledge of the pure mineral phases allows specification of the charge density in the clay layers. Part of this charge is however counterbalanced by charges sorbed on basal or surface sites, which for the latter can depend on solution pH. The potential can be measured at the interface between non-slipping inner sphere and slipping water using a zetameter. However this potential may not be the most accurate measurement of basal/edge/interlayer surface potential. Several models are proposed to represent the charge spatial distribution in the Solid (mineral) – Stern (sorbed) – Diffuse system (see Figure 4).

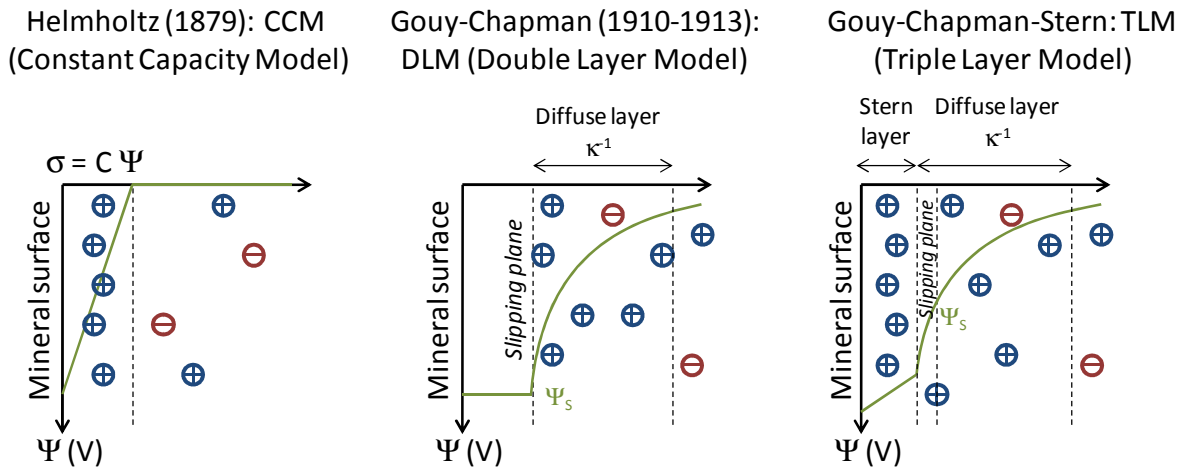


Figure 4 Schematic views of Helmholtz, Double and Triple layer models.

2.2.2 Double Layer Models

As a first approximation we will consider the Gouy-Chapman representation of the electrical double layer. One can consider that ions are at low concentration and have negligible volume and that only electrostatic forces need be considered, i.e. that steric constraints, Van-der-Waals forces and variations of the fluid state properties (permittivity, viscosity) can be neglected. Under these assumptions, the electrochemical potential can be expressed as:

$$\mu = \mu^0 + kT \cdot \ln C + Ze\psi \quad \text{Equation 17}$$

When equilibrium is reached, the electrochemical potential is uniform and the solute concentration C of ionic species is linked to the electric potential Ψ according to the Boltzmann distribution function.

$$C = C^0 \exp\left(-\frac{Ze\psi}{kT}\right) \quad \text{Equation 18}$$

where F is the Faraday constant (96485 J/V/eq), ψ_D the potential in the Donnan volume (V) and R the gas constant (8.314 J/K/mol). The resolution of the Poisson-Boltzmann equation can be greatly simplified by linearizing the exponential term using a Taylor series, which is a valid hypothesis for small surface potentials ($\Psi < 25\text{mV}$). This leads to an exponential decrease of the potential with distance to the surface and the Debye layer thickness:

$$\kappa^{-1} = \sqrt{\frac{\epsilon kT}{2N e^2 I}} \quad \text{Equation 19}$$

where ϵ is the permittivity, N is the Avogadro number, e is the electron charge and I is the ionic strength. This electric field is impacted by the introduction of a macroscopic gradient in the concentration or electric potentials. An ionic potential was introduced by O'Brien and White (1978) in order to solve ionic transport in porous media. This method was later used by Gupta et al. (2007) who solved the electrokinetic equations with a finite differences scheme

utilisable for any discretized porous media (e.g. packed spheres, reconstructed media). The introduction of dimensionless quantities such as the ratio between the thickness of the electrical double layer and the characteristic length of pores Λ , allow the results to be generalized.

$$\Lambda = 2 \frac{\iiint_{\text{pore}} E^2(\mathbf{r}) dV}{\iint_{\text{surf}} E^2(\mathbf{r}) dS} \quad \text{Equation 20}$$

This work allowed postulating that the electro-osmotic process and the related ionic transport are only functions of surface potentials and characteristic dimensions ($\kappa \cdot \Lambda$). However, this study doesn't account for surface-sorbed species and the resulting variable transport behavior of cationic species. At this stage, the model correctly represents the diffusion properties of non-sorbing species, such as Cl^- or Na^+ , but the Stern layer must be explicitly considered in order to account for the specific transport properties of sorbed species.

2.2.3 Model refinements

Gupta et al (2007b) have also introduced a Stern layer to assess its relative contribution to cation transport. The Stern layer is characterized by a capacitance, and sorbed ions have a non-zero mobility. Besides the fact that their model was not implemented with measured or calculated surface properties, their numerical results show that dilute media (suspensions) behave very differently relative to compact media, where the Stern layer is continuous. Further studies would allow the physical interpretation of these results and their application to clay rocks and multi-component fluids.

This approach has, however, many implicit approximations and assumptions:

- Electric charges are local (there is no steric problem)
- Ionic species are uniformly hydrated
- The surface potential (or charge density) is uniform
- The sorption model is oversimplified
- The solid (non clay minerals) do not participate in transport
- The density, viscosity and permittivity are uniform
- The forces applied to ions and water are only Coulombian (no VdW dipole force)
- No fluid slip velocity at the walls
- The concentration is sufficiently small everywhere so that activity coefficients can be neglected.

This raises the major drawback of continuous media methods that require state parameters - their local values cannot be easily addressed numerically, nor can they be assessed by experimental measurements. This difficulty can be bypassed by implementing correction factors or using a more flexible numerical approach.

The Boltzmann distribution, which links the ion concentration to the electrical potential, is only valid when interactions between particles are exclusively electrostatic (no interactions with water, no steric constraint, no VdW forces). However, it is possible to introduce corrective terms in the Poisson-Boltzmann equation to take these forces in account (Bolt, 1979, Neal and Cooper, 1983, Lehtikonen, 1998). This has been achieved by Nathalie Diaz (CEA Thesis, 2009), who added hydration and ion exclusion volume correction factors in the

Poisson-Boltzmann equation: (PBMHE). The corrected equation is detailed

$$\frac{\partial c_i}{\partial t} = \nabla \left[\underbrace{D \cdot \nabla c_i}_{\text{Chemical diffusion}} - D \cdot c_i \cdot \frac{z_i \cdot F}{R \cdot T} \cdot \nabla \left(\Psi + \frac{A_i}{z_i \cdot F} \frac{1}{\epsilon_r} - \frac{RT}{z_i \cdot F} \ln(1 - v \sum c_j) \right) \right]$$

Standard Nernst-Planck equation Corrective terms

hereafter: Electro-diffusion Variations of the hydration free enthalpy Ionic exclusion volume (Bikerman) Equation 21

By introducing an alteration of the fluid permittivity (ϵ_r decreases in an electric field of more than 10^8 V/m, which can affect the electric field as soon as the surface charge density is greater than 0.1 C/m^2), N. Diaz was able to differentiate the retention behavior (selectivity) of different alkaline cations (Figure 5) ($\text{Li}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$) and model the sorption properties of alkaline cations in illite (including basal and border surfaces), accurately reproducing the sorption isotherm of weakly hydrated cations such as Cs^+ , but not that of strongly hydrated ions as Na^+ . The differences between Na and Cs observed in compact clay (bentonite) and COx argillites with an ionic strength of 0.1 mol / kg also could not be explained. Figure 5 shows the concentration profiles of several alkaline cations against distance from the clay surface.

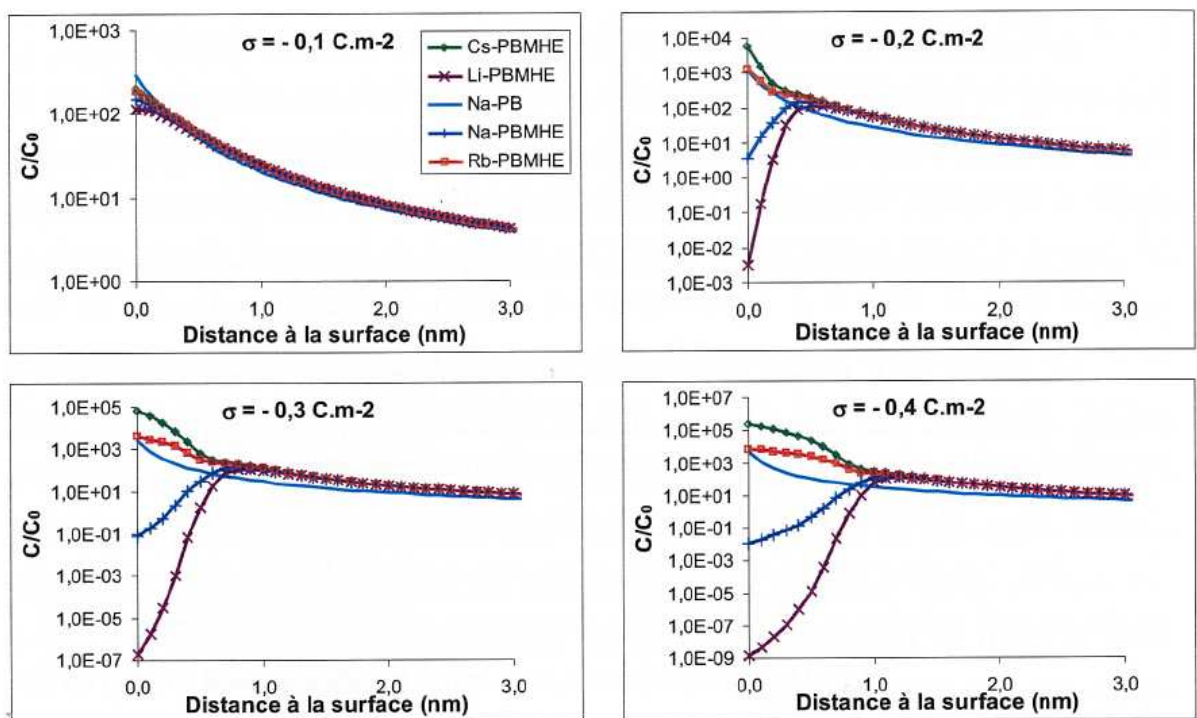


Figure 5 Concentration profiles of several alkaline cations (Li^+ , Na^+ , Rb^+ and Cs^+) at trace concentration (10^{-11} M) in KCl (10^{-2} M) for various surface charge densities ($\sigma = 0,1, 0,2, 0,3, 0,4 \text{ C.m}^{-2}$) against distance from the surface, from Diaz (2009)

2.2.4 Introducing Lattice Boltzmann Equations

The numerical resolution of transport equations is usually limited to linear physics with « simple » boundary conditions. An alternative implementation method was recently developed by Rotenberg et al., 2010 in order to explain the relationship between the effective diffusion coefficients measured through clay samples and the tracer diffusion paths in the clay interparticle porosity. The numerical method is based on the Lattice-Boltzmann network which has the advantage of not having to explicitly solve the equations that govern the transport. Transfers are represented by the probability of moving tracers from one node to another, whereas physical interactions and boundary conditions are determined by collision laws at the nodes. The authors used this method to calculate the time-dependent diffusion coefficient for ionic tracers in a planar channel and a more complex porous medium (e.g. centered cubic lattice of touching spheres). The authors calculated the effective diffusion coefficient (D_e) and the normalized relaxation time (τ) of neutral and charged tracers as a function of the fraction of counterions lying in the Stern layer ($1-f$). Results displayed in Figure 6 reveal the influence of the tracer's electric charge on the continuity/tortuosity of their transfer tracks. This study provided a insight into the mechanisms of "surface diffusion" and anion exclusion (at the pore scale, in addition to the Donnan effect), revealing the specific role of the electric potential field on the transfer rates in pore networks.

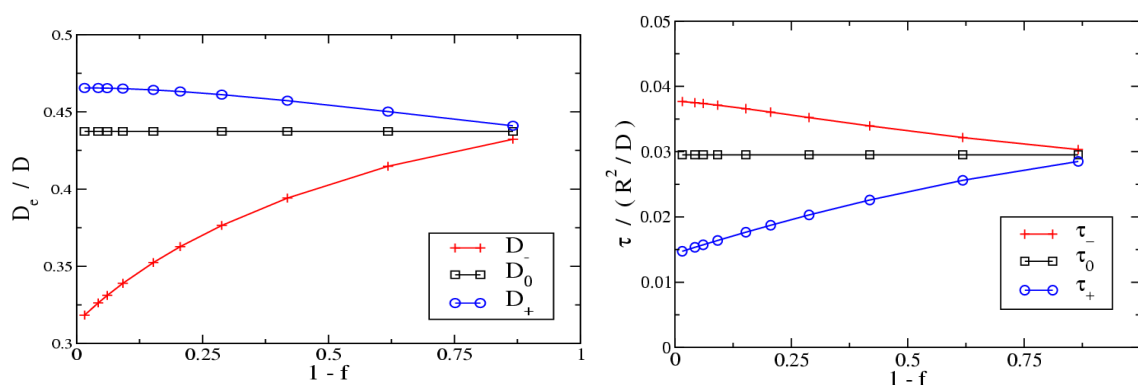


Figure 6 *Diffusion of ions in a centered cubic lattice of spheres, against the fraction of cations from the salt. Left: Effective diffusion coefficient. Right: Characteristic time to explore the accessible porosity for each species.*

This approach will be further developed in the ANR Simisol project in order to perform cation transfer modeling at mesoscopic scales, along the basal and edge surfaces of illite, as well as in more complex pore structures, inspired by the organization of compacted illite de Puy as visualized by actions in WP2 of the CatClay project. Local fluid properties will be provided by model results at smaller scales (e.g. molecular dynamics and Brownian dynamics calculations).

2.2.5 The effect of the mineral spatial distribution on diffusion

At the mesoscale (μm - mm), clayrocks are characterized by the spatial distribution of the clay matrix (composed of clay particles and inter-particle porosity) and the non-clay, mainly non-porous mineral grains (carbonates, tectosilicates, heavy minerals such as pyrite). The

effect of this structuration was investigated by Robinet (2008). The mesoscale structure of the Callovo-Oxfordian mudstone was first imaged 3D using X-ray synchrotron microtomography with a 0.7 μm resolution. The spatial distribution of major mineral phases (clay matrix, carbonates, tectosilicates and heavy minerals) was then extracted using an image analysis procedure (Figure 7a). The diffusion process based on Fick's equations was modeled for non-interacting species (or species interacting by linear sorption processes) over the tridimensionnal distribution of minerals using a particle tracking method (Figure 7b and 7c). The mesoscopic structure (the presence of non clay and porous minerals) modify the diffusion pathways by increasing the global tortuosity. At this scale the tortuosity of the diffusion pathways depends mainly on the fraction of non porous grains (Figure 7d).

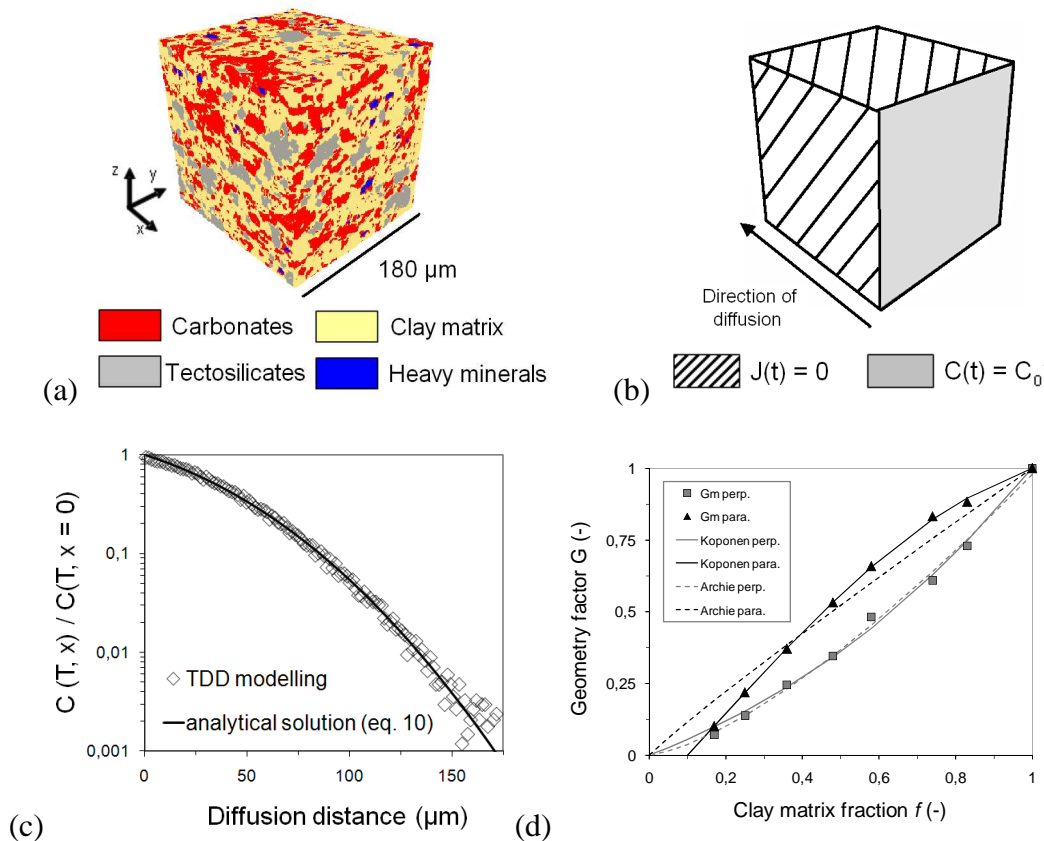


Figure 7

Summary of the methodology developed to model in-diffusion experiment from the actual tridimensionnal microstructure of clay-rock: (a) tridimensionnal spatial distribution of mineral groups obtained using X-ray synchrotron tomography; (b) boundary limits definition; (c) modeled diffusion profile (points) and computation and fitting of the profile by Crank (1975) equation (cf. eq. 10); Evolution of the geometry factor according to the fraction of clay matrix fraction in perpendicular and parallel direction to the bedding plane. The data are adjusted with Archie (1942) and Koponen et al. (1997) equations.

3 Macroscale modeling

3.1 Reactive transport models

As we have previously seen, the traditional linear K_d concept provides a limited description of cation retention behavior in clays. A better consideration of retention processes in transfer problems can be obtained by using reactive transport modeling. Reactive transport models can incorporate a large variability of geochemical processes. An overview of reactive transport modeling codes can be found in Steefel et al. (2005) and van der Lee and De Windt (2000). Considering solute transfer in clayey systems, the following phenomena might need to be taken into account: aqueous reactions, dissolution/precipitation of minerals, redox reactions, interface mechanisms (including ion exchange, ion complexation, co-precipitation and solid solution formation), multi species diffusion, porosity variations...

These models solve reactive transport on a grid where each cell is characterized by homogeneous properties (porosity, mineralogy, surface properties,...). According to the spatial distribution of the properties (heterogeneous systems) reactive transfer model grids can be constructed based on a local description of the medium up to the field scale. Classical applications of these models limits their use to scales above that of the pore network (i.e. pore network properties are treated in terms of parameters 'homogenized' at a higher scale: porosity, tortuosity, constrictivity, surface to volume ratio...).

Appelo and Wersin (2007) and Appelo et al. (2008, 2010) used the reactive transport model PHREEQC to simulate transfer of cations in clays. At present, PHREEQC is likely the most sophisticated model used to solve reactive transfers in rock, and especially in clays. PHREEQC successively solves step-by-step chemical interactions (thanks to equilibrium constants) and transfer equations. It uses chemical potential gradients in order to model the transfer of multiple species characterized by different diffusion coefficients. In order to model the transfer of cations in clays, Appelo and Wersin (2007) and Appelo et al. (2008, 2010) model the porous medium as a single pore channel divided along its length into a succession of paired cells: (i) a volume of free water where the totality of the charges are compensated ($\psi = 0$) and (ii) a volume representing a diffusive layer having an homogeneous charge deficit and resulting potential ($\psi = \psi_d$). The two cells are assumed to be in equilibrium via the Donnan relationship. The charge needed to compensate the diffusive layer is calculated by a surface complexation / ion exchange model based on the CEC, the specific surface area, the surface site densities and their respective thermodynamic constants for sorption of solute species. The up-scaling toward a macroscopic volume is based using a geometric factor G obtained from HTO diffusion experiments. The volume of the diffusive layer is determined using the anion accessible porosity. The model can also account for dead-end pores. Appelo et al., 2010 states that dead-end pores are needed to reproduce Cs^+ diffusion in Opalinus Clays. This model was applied to the diffusion of a cocktail of tracers (Appelo and Wersin: Opalinus Clay HTO, I^- , Na^+), single tracers (Appelo et al. 2010: Opalinus Clay Na^+ , Cs^+ , Sr^{2+}) and the diffusion of major cations (Appelo et al., 2008, Callovian-Oxfordian argillites).

3.2 Analytical models

Analytical and empirical models of cation diffusion have been developed since the 1990s mainly for interpreting the effective diffusion coefficient values obtained by diffusion experiments (which can be also derived from D_a and K_d) and cation acceleration A . These

models are based on various conceptual views of ion interactions with pore surfaces. Fick's equations constitute a common basis for these models, and integration of the interactions between ions and surface is thus performed based on an analytical development of these equations. Ultimately, the development of Fick's equations leads to an expression of the effective diffusion coefficient and the parameter A .

3.2.1 Surface diffusion based models

The first models developed used the concept of surface diffusion (Jahnke and Radke, 1985; Oscarson, 1994) to predict cation diffusion in clays. The total flux of cations (J) is considered as the sum of cations diffusing in bulk pore water, J_{pore} , and those moving by surface diffusion along the clay mineral surfaces J_{surface} . The totality of the cations sorbed on the solid (S) are assumed to move by surface diffusion. This statement leads to the following expression of the total flux:

$$J = -D_p \cdot \frac{\partial C}{\partial x} + D_s^* \cdot \frac{\partial S}{\partial x} \quad \text{Equation 22}$$

with D_p being the effective diffusion coefficient in the pore solution ($\text{m}^2 \cdot \text{s}^{-1}$) and D_s^* the effective diffusion coefficient along the surface ($\text{m}^2 \cdot \text{s}^{-1}$). Assuming the tortuosities τ and τ_s for diffusion pathways in pores and along pore surfaces respectively, and using a linear K_d model, the effective diffusion coefficient of cations is thus expressed as:

$$D_s^* = \left(\omega \cdot \frac{D_w^+}{\tau^2} + \rho \cdot K_d \cdot \frac{D_s}{\tau_s^2} \right) \quad \text{Equation 23}$$

Jahnke et Radke (1985) consider that surface diffusion occurs in the same pores as pore diffusion and thus assume $\tau_s = \tau$. Tortuosity τ being obtained from the effective diffusion coefficient of a neutral species (HTO), the acceleration of the cation can be written as follows:

$$A = \left(1 + \frac{\rho \cdot K_d}{\omega} \cdot \frac{D_s}{D_w^+} \right) \quad \text{Equation 24}$$

Molera and Erikssen (2002) interpret the ratio D_s/D_w as the partitioning coefficient f between species located in the diffusive layer and those located in the Stern layer. They determined f from A and K_d measured on batch systems for various cations diffusing through MX80 bentonite. For cations interacting by surface complexation mechanisms (such as Co^{2+}), K_d is high but $f \approx 0$ implying $A \approx 1$, the authors justify $f \approx 0$ due to the predominance of Co^{2+} in the form of immobile inner sphere complexes in clay systems. Na^+ is mainly present as mobile outer-sphere complexes, $f \approx 1$ but its K_d is relatively low leading to A higher than 1.

3.2.2 Electric constrictivity model

In contrast to the dual-flux approach previously described, single porosity models were developed to analyze both cation and anion behavior. The general concept of these models is to interpret the diffusion of anions and cations by introducing an identical ion-surface interaction mechanism. These models are based on a more complex conceptualization of the spatial distribution of ions in the pore space and the addition of a diffuse layer along the pore surface. Sato et al. (1995) have proposed accounting for the macroscopic effects of electrostatic interactions by introducing an electric constrictivity parameter δ_{el} (-). The effective diffusion coefficient is expressed as follows:

$$D_a^+ = \omega \times \frac{\delta_g \cdot \delta_{el}}{\tau^2} \cdot D_0^+ \quad \text{Equation 25}$$

The geometric constrictivity δ_g and the tortuosity τ are assumed to be identical for both ionic and neutral species; whereas $\delta_{el} = 1$ for neutral species, $\delta_{el} < 1$ for anions and $\delta_{el} > 1$ for cations. In this way, acceleration of cations A is equivalent to $\delta_{el} (-)$.

Starting from the assumption that the effect of the cation electric charge on diffusivity (i.e. electrical constrictivity) is strictly proportional to its impact on the cation average concentration, Ochs et al. (2001) defined the electrical constrictivity δ_{el} as the ratio of the cation average concentration in the diffusive layer C_{DL} to its concentration in the bulk water C_{bulk} (free of electric potential). The authors determined the average concentration in the diffusive layer by integrating and averaging the concentration profile of ions $C(x)$ from the surface of particles (0) to a distance equal to the average pore size of the material (d):

$$\delta_{el} = \frac{C_{DL}}{C_{free}} = \frac{1}{d \cdot C_{free}} \int_0^d C(x) \cdot dx \quad \text{Equation 26}$$

$C(x)$ is calculated by the numerical solution of the Poisson-Boltzmann equation in the vicinity of an infinite plane. This resolution requires however knowing the electrical potential at the interface between the Stern and diffuse layers, the concentration in free water and the average pore size (d). Note here that the up-scaling from pore surface to the macroscopic material is done by simply using average material parameters (i.e. porosity, geometrical tortuosity, etc.). The average pore size can be obtained by physical measurements such as nitrogen adsorption or mercury intrusion. The concentration of ions in the free water is computed from a chemical speciation model taking into account interactions with clay minerals (cation exchange and surface complexation model). The surface electric potential is more difficult to assess. This Dirichlet boundary condition can however be represented in terms of the Neumann surface charge density calculated at the outer boundary of the Stern layer. The authors propose to estimate it by the quantity of electrical charges compensated only in the diffuse double layer. To do this, the authors assume that the K_d measured in batch experiments is the result of complete structural charge compensation by the cations. The structural charge of the clay is assumed to be given by the Cation Exchange Capacity (CEC). In compact systems, only a fraction of the structural charge is compensated in the Stern layer, the other fraction being compensated by cations located in the diffuse layer (e.g. EDL theory) thus contributing to diffusive transport. The authors also performed in-diffusion experiments in order to obtain apparent diffusion coefficients D_a (see equation 4) that depend on D_e and K_d according to their model. These data allowed them to fit the fraction of cations that contribute to transport and thereby deduce the fraction of cations that remain in the Stern layer in the compact rock. They obtained $f=0.67$ in 0.4 kg.L^{-1} Kunipia-F bentonite.

From a theoretical point of view, the integration of phenomena occurring at small scales (the Poisson Boltzmann equation) in order to access macroscopic parameters was an innovative and useful means of evaluating the sensitivity of δ_{el} to various parameters such as surface potential, pore size and pore water composition. On the hand, its application is limited mainly due to the difficulties in determining the surface potential.

More recently, Jougnot et al. (2009) used the same theoretical basis but a different means of estimating the fraction of the structural charge compensated in the Stern layer in that they

expressed δ_{el} using the Donnan equilibrium between the reservoir concentration C_{free} and the concentration C_i in the REV porosity of rock in contact with the reservoir:

$$\delta_{el} = \frac{C_i}{C_{free}} = \exp\left(\frac{-q_i \cdot \varphi_m}{k_b \cdot T}\right) \quad \text{Equation 27}$$

where φ_m is the Donnan potential (i.e. the electric potential that accounts for the mean ionic concentrations in the diffuse layer, $q = (\pm e)z_i$ represents the charge of the ion i (in C) with z_i the charge number of the ion and e the elementary charge (1.6×10^{-19} C), and k_b the Boltzmann constant (1.381×10^{-23} J.K⁻¹). The authors propose estimating the Donnan potential from the CEC, the concentration of ions in solution and the partition coefficient (f_Q) of countercharges between the Stern and the diffuse layers. In this study, f_Q was calculated from the Triple Layer Model developed by Leroy and Revil (2004). δ_{el} is finally expressed according to:

$$\delta_{el} = \exp\left(\frac{-q \cdot \varphi_m}{k_b \cdot T}\right) = \frac{CEC \cdot \left(\frac{1-\omega}{\omega}\right) \cdot \rho_g \cdot (1-f_Q)}{\sum_{i=1}^Q q_i \cdot C_i} \quad \text{Equation 28}$$

where $CEC \times \rho_g \times (1-\omega)/\omega$ is the total charge density related to the cation exchange capacity of the material (CEC).

This model was successfully applied to Na⁺ diffusion through the Callovian-Oxfordian argillites (using $f_Q = 0.94$ estimated by Leroy et al., 2007). As Na⁺ is dominant in the Callovo-Oxfordian clayrock porewater, its partitioning between Stern and diffuse layers is correctly accounted for by f_Q and its diffusion is therefore well reproduced. However electric constrictivity models consider the cations as point charges and all ions having the same valence have the same electrical constrictivity. As a result, these approaches can only distinguish the diffusion of different cations by taking into account their charges.

3.2.3 Multi-porosity models

In order to better account for the structure of water and ions in pores, Bourg et al. (2003) divided the total porosity into sub-volumes. The flux of cations is therefore composed of the sum of individual fluxes acting in parallel:

$$J = -\frac{\delta_1 \cdot \omega_1}{\tau_1^2} \cdot D_w \cdot \frac{\partial C_1}{\partial x} - \frac{\delta_2 \cdot \omega_2}{\tau_2^2} \cdot D_w \cdot \frac{\partial C_2}{\partial x} - \dots - \frac{\delta_n \cdot \omega_n}{\tau_n^2} \cdot D_w \cdot \frac{\partial C_n}{\partial x} \quad \text{Equation 29}$$

with, ω_n , δ_n , τ_n and C_n , being respectively the porosity, the constrictivity, the tortuosity and the concentration of sub-volumes n , $\omega = \sum \omega_n$ and $D_{e,n} = D_w \times (\delta_n \times \omega_n) / \tau_n^2$.

Appelo and Wersin (2007), Glauss et al. (2010), and Appelo et al. (2008, 2010) use the general framework of this equation by dividing the pore space (ω_T) into three sub-volumes: the free water ($f_{free} = \omega_{free}/\omega_T$), the diffuse layer ($f_{DL} = \omega_{DL}/\omega_T$) and the interlayer space which includes the Stern layer ($f_{IL} = \omega_{IL}/\omega_T$):

$$J = -\omega_{free} \cdot \frac{1}{G_{free}} \cdot D_{w,free} \cdot \frac{\partial C_{free}}{\partial x} - \omega_{DL} \cdot \frac{1}{G_{DL}} \cdot D_{w,DL} \cdot \frac{\partial C_{DL}}{\partial x} - \omega_{IL} \cdot \frac{1}{G_{IL}} \cdot D_{w,IL} \cdot \frac{\partial C_{IL}}{\partial x} \quad \text{Equation 30}$$

Note that there are 9 unknowns in this equation. Appelo et al, (2010) propose reducing the number of unknown parameter as follows. First, the Donnan equilibrium is used to link the concentrations in free water and the diffusive layer.

$$C_{DL,i} = C_{free,i} \cdot \exp\left(\frac{-z_i F \psi_D}{RT}\right) \quad \text{Equation 31}$$

Considering the same geometrical factor for both the free water and the diffusive layer ($G_{free}=G_{DL}$) and eq. 30, the flux of cations in free water and the diffusive layer is expressed as follows:

$$J_{free} + J_{DL} = - \frac{\omega_T}{G_{free}} \cdot D_w \left(f_{free} + f_{DL} \cdot \exp\left(\frac{-z_i F \psi_D}{RT}\right) \right) \cdot \frac{\partial C_{free,i}}{\partial x} \quad \text{Equation 32}$$

From the effective diffusion coefficient of HTO, the acceleration parameter A is finally expressed:

$$A = f_{free} + (1 - f_{free}) \cdot \exp\left(\frac{-z_i F \psi_D}{RT}\right) \quad \text{Equation 33}$$

As for Jougnot et al. (2009), the Donnan potential is a key parameter in this model. Appelo et al. (2010) assessed the Donnan potential in another way, using anion porosity (ω_{Cl-}) and water porosity (ω_{HTO}), both determined from diffusion experiments:

$$\frac{\omega_{Cl-}}{\omega_{HTO}} = f_{free} + (1 - f_{free}) \exp\left(\frac{F \psi_D}{RT}\right) \quad \text{Equation 34}$$

Using this model, f_{free} is the only remaining unknown parameter for determining the flux of cations in free water and the diffusive layer ($J_{free} + J_{DL}$). Figure 8 illustrates the evolution of A according to f_{free} and the ionic charge for $\omega_{Cl-}/\omega_{HTO} = 0.5$ which is measured in Opalinus clay and Callovian-Oxfordian argillites.

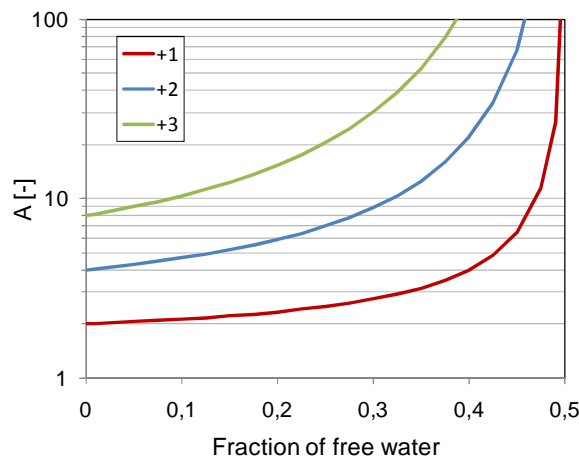


Figure 8 Evolution of acceleration factor A according to the ionic charge of cations and the fraction of free water ($\omega_{Cl-}/\omega_{HTO} = 0.5$) (from results of Appelo et al., 2010)

Finally, Appelo et al., (2010) estimated the fraction of free water from the charge density (CEC, specific surface area) and the exchange constants Na/K. $f_{\text{free}} = 0.117$ was obtained for the Opalinus clay.

The overall model was completed by adding a surface (Stern layer)/interlayer diffusion flux and a resulting diffusion coefficient expressed as follows (Appelo et al., 2010):

$$D_{\text{IL}} = -\omega_{\text{IL}} \cdot \frac{1}{G_{\text{IL}}} \cdot D_{\text{w,IL}} \cdot \frac{C_{\text{IL}}}{\beta_i} \cdot \frac{\partial \beta_i}{\partial C_i} \quad \text{Equation 35}$$

with C_{IL} , the concentration of the species i in the interlayer, β_i , the fraction of the CEC compensated by the species i in the interlayer space and Stern layer. β_i and $\partial \beta_i / \partial C_i$ are given by the surface complexation model but G_{IL} is estimated a priori and used as a fitting parameter. The integration of interlayer and Stern layer diffusion in the flux expression allows the specificity of cations having the same charge to be taken into account.

The model proposed by Appelo et al. (2010) allows differentiation of (i) the influence of the charge of the cation on the acceleration parameter A constrained by material properties (anion exclusion, CEC, specific surface area) and the values of selected surface complexation models (exchange constant) and (ii) the sorption characteristics of the tracer from the diffusion in the interlayer space/ Stern layer. This approach is used to interpret the effective diffusion coefficients of Na^+ , Cs^+ and Sr^{2+} in Opalinus Clay. Due to their identical charge, the difference of D_e for Cs^+ and Na^+ depends only on interlayer or Stern diffusion.

Since the geometrical factor of interlayer space G_{IL} is not accessible experimentally, it is poorly documented and no reliable value is proposed in the literature; G_{IL} can be optimized numerically and the model can be used as a blind approach. However some insights are available in Melkior et al (2009) who studied cation diffusion through compacted bentonites with various textures.

4 Discussion

The transfer of cations in clay materials is controlled by diverse phenomena acting at atomic to macroscopic scales. Various types of models have been developed at the different scales in order to improve description and prediction of the retardation and diffusion behavior of cations which are mainly observed at macroscopic scale by retention or diffusion experiments. In the light of the studies presented in this document, some comments can be expressed concerning the overall approach and the requirements for improving description/prediction of cation behavior in clay rocks.

✓ *Can these models provide tangible elements describing cation transfer in clays?*

At the atomic scale, classical molecular simulations have provided a large quantity of results regarding the dynamics of cation-interlayer exchange, distribution and mobility of ions and water adjacent to clay mineral surfaces and interlayer porosity. These studies have mainly been focused on monovalent cations. As regards the cation exchange, results for alkali cations are in good agreement with experimentally determined ion selectivity and K_d values. Molecular simulations have also been used to describe ion distribution profiles extending from the clay surface towards the pore centre, and continuous models representing surface interactions at same scale give reasonable fits to these results. Ion mobility in the vicinities of the clay basal surfaces have also been addressed by molecular dynamics modeling with different behavior being found for strongly and weakly hydrated cations. These results however do not allow drawing of clear conclusions about the mobility behavior of alkali cations in clays. The case of more complex cations (divalent metals, actinides) and the lateral edges of sheets has been little studied, showing the current limits of applications of the molecular simulation approach, thus our understanding of retention and transfer phenomena at small scales.

At the pore network scale, models based on Poisson-Nernst-Planck equations (solved by finite difference or using Brownian Motion or Lattice Boltzmann method) catch the overall effects of the porosity (the relationship between diffusion coefficient and porosity), the pore size, the ionic strength and surface potential on cation mobility. These models allow the higher mobility of cations relative to neutral species to be described. However, Poisson-Nernst-Planck equations are not capable of modeling complex electrolyte and chemical interactions with clays. Thus, these simulations predict a higher mobility of divalent cations than monovalent cations, which is not observed experimentally. Some developments (PBMHE or MGC2) introduce additional terms in order to take into account the behavior of different ions (hydration and size exclusion). Promising results have been obtained on the retention (qualitative behavior for alkali cations) and should be extended to cation mobility in pore network.

At the macroscopic scale, geochemical models can describe the behavior of major species in pore water and their retention on the solid using aqueous equilibrium and surface interactions model (ion exchange mechanisms and complexation) and thus predict cation retention behavior on clays. Coupling these models with transport codes allows the retardation behavior of cations in diffusion experiments to be modeled. At this scale, the mobility of cations in pore water can be described by a Donnan equilibrium and surface diffusion (interlayer or Stern layer diffusion).

The results of small scale studies tend to indicate that the mechanisms that underpin the phenomenological concepts used in macroscopic analytical models can be assumed to be valid, notably for the models based on ion structuring in pores (models of surface diffusion seem to be less adequate in the light of micro models). On the other hand, multiple porosity models such as the one recently proposed by Appelo et al. (2010) uses a simple up-scaling strategy considering the pores network as a pore channel with “mean” properties. Considering structural heterogeneities (the spatial distribution of mineral surfaces and pores) of purified clay and clay rock materials, this approach may seem not enough complex.

✓ *Is our theoretical understanding of small and very small scales sufficient?*

Molecular simulations (Molecular Dynamic and Monte Carlo) performed over the last twenty years have mainly studied the interactions and dynamics of monovalent cations in the vicinity of clay mineral basal surfaces and inside the interlayer space. Much work remains however to be done regarding di- or trivalent cations which interact with the basal and edge surfaces of clay minerals. Classical molecular simulations are based on the representation of interactions between components by a force field. Molecular simulations depend mainly on the force field which is used. Even relatively simple ones consisting of pair-wise additive interaction potentials (e.g. Lennard-Jones), calibrated against experimental data on bulk systems, are able to capture some specific effects in clays. However significant uncertainties subsist regarding the transferability of models used for monovalent cations to represent complex electrolytes containing divalent and trivalent cations. Few studies have been dedicated to interactions between cations and clay edge surfaces. In this regard, first-principles simulations are first required to provide suitable force fields. This work is in progress in the framework of the french ANR SIMISOL project (associated project in CatClay).

Mesoscale models (Brownian dynamics and Lattice Boltzmann model) are currently limited to the Poisson Nernst-Planck equations. New improvements of these models could consider specific ion-surface interactions, ion-solvent interactions, ion size, and the diffusion coefficients of ions contained in a complex electrolyte.

At the same scale, the continuous medium models go beyond the Poisson-Nernst-Planck equations and are presently able to consider specific interactions (chemical) with the pore surface (presence of a Stern layer) and interactions between the ions and the solvent as well as ion size. The integration of these developments within a unique model should be considered and applied to realistic pore networks of compact clay or clayrocks.

✓ *How to deal with the multi-scale structure of clay materials?*

In clay materials, the pores are distributed over several orders of magnitude (nm-microns) and are highly structured: the pores of larger sizes are interconnected by pores of smaller sizes and the pore walls are formed by clay edges, basal surfaces and the various surfaces of accessory minerals. Are the pore structure and its effects on diffusion sufficiently considered in macroscopic models? Macroscopic models take into account the geometry of the pore network considering the pore network as a single pore channel characterized by mean values (diameter, surface potential, fraction of double layer...). Geometric factors (e.g. the tortuosity determined by the HTO diffusion coefficient) are then used to upscale cation behavior inside a “mean” pore to the entire pore network.

The complexity of existing macroscopic models requires a great deal of data regarding the geometric features of pores such as the tortuosity of the double layer, the free porewater, the interlayer space. This means that, in the absence of specific data, the values for these parameters must be assumed. For instance, the double layer tortuosity is considered equal to that of the free pore water. Are these considerations correct? Possibly not given that it is well known that tortuosity depends on porosity or on the volume fraction, and the free porewater and double layer fractions have been estimated to be different in Opalinus Clay for example. This comment is also addressed towards the determination of the interlayer space tortuosity.

The pore structure could be integrated in macroscopic models using an up-scaling strategy based on a better knowledge (notably the visualization) of the pore structure and the pore surface properties, followed by development of corresponding mesoscopic models. Concerning the acquisition of pore structure, various approaches are conceivable. The first consists of imaging the pore structure (representative of in situ conditions) for scales ranging from nm to μm . In the framework of CatClay, this approach is planned; the pore structure will be imaged in 2D using TEM or HRTEM techniques on resin impregnated materials. The gray level images will be partitioned in various groups of elements (pores, clay sheets, clay particles, clay aggregates, accessory minerals...). The 2D resulting imaging must be “transformed” into a 3D volume in order to perform mesoscale simulations. Various methods exist for doing this (object generation using density probabilities, direct sampling...). Another approach for obtaining pore structure is to simulate a fictitious pore network (a network of links and nodes) to reproduce a set of macroscopic data related to fluid transfer (permeability, mercury intrusion curves) (this type of study is under investigation in the frame work of Andra scientific program). The 3D volumes must then be given appropriate physical properties (e.g. surface properties...). Mesoscopic models are then applied to these volumes in order to compute geometrical parameters such as tortuosity.

✓ *How to constrain or validate the models by experimental observations at small scales?*

Existing difficulties in the proposition of an integrated multi-scale transfer model of cations in clay materials originates partly from the lack of experimental control points at the different scales.

At pore scale, ion distribution and mobility across the pore are difficult to evaluate experimentally. The methods used at these scales (X-ray reflectometry, NMR, Quasi-Elastic Neutron Scattering, dielectric spectroscopy) are not applicable to the study of cation transfer in compact systems (non homoionic electrolyte, small size of surfaces, and presence of impurities ...).

At the pore network scale, quantification of cation distributions (and their chemical states) during and/or after a diffusion experiment could be used to evaluate local cation retention or diffusion coefficients. This kind of approach was initiated in FUNMIG. The distribution of cations was imaged after a diffusion experiment with a resolution of a few microns using EPMA and micro-LIBS characterization. These studies showed that for argillaceous rocks, the transfer of RN was limited to the clay matrix, the non-clay minerals being mainly non-porous. These methods cannot also provide chemical properties of diffusing cations (outer, inner sphere). Developments will be done in CatClay using in situ TRFLS-situ methods which acts with this level of resolution.

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