Applied Clay Science 96 (2014) 36–44

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Resolving diffusion in clay minerals at different time scales: Combination of experimental and modeling approaches

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ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 23 April 2014
Accepted 25 April 2014
Available online 16 May 2014

Keywords:
Restricted water diffusion
QENS
Molecular dynamics
2D confinement
Montmorillonite

ABSTRACT

Since no single experimental or modeling technique provides data that allow a description of transport processes in clays and clay minerals at all relevant scales, several complementary approaches have to be combined to understand and explain the interplay between transport relevant phenomena. In this paper molecular dynamics simulations (MD) were used to investigate the mobility of water in the interlayer of montmorillonite (Mt), and to estimate the influence of mineral surfaces and interlayer ions on the water diffusion. Random Walk (RW) simulations based on a simplified representation of pore space in Mt were used to estimate and understand the effect of the arrangement of Mt particles on the meso- to macroscopic diffusivity of water. These theoretical calculations were complemented with quasielastic neutron scattering (QENS) measurements of aqueous diffusion in Mt with two pseudo-layers of water performed at four significantly different energy resolutions (i.e. observation times).

The size of the interlayer and the size of Mt particles are two characteristic dimensions which determine the time dependent behavior of water diffusion in Mt. MD simulations show that at very short time scales water dynamics has the characteristic features of an oscillatory motion in the cage formed by neighbors in the first coordination shell. At longer time scales, the interaction of water with the surface determines the water dynamics, and the effect of confinement on the overall water mobility within the interlayer becomes evident. At time scales corresponding to an average water displacement equivalent to the average size of Mt particles, the effects of tortuosity are observed in the meso- to macroscopic pore scale simulations. Consistent with the picture obtained in the simulations, the QENS data can be described using a (local) 3D diffusion at short observation times, whereas at sufficiently long observation times a 2D diffusive motion is clearly observed. The effects of tortuosity measured in macroscopic tracer diffusion experiments are in qualitative agreement with RW simulations. By using experimental data to calibrate molecular and mesoscopic theoretical models, a consistent description of water mobility in clay minerals from the molecular to the macroscopic scale can be achieved. In turn, simulations help in choosing optimal conditions for the experimental measurements and the data interpretation.

1. Introduction

Due to extremely low hydraulic conductivity and their swelling capacity, compacted smectites are commonly utilized as backfill for the protection of the environment at waste disposal sites (NAGRA, 2002). The prediction of the long term performance of such engineered barriers requires understanding the water and ion transport mechanisms in clays and clay minerals. This has been proven to be challenging due to a tangled hierarchy of transport pathways and complex interactions between water, the surface of clay minerals, and aqueous cations.

Smectites have unique hydro-mechanical properties. These clay minerals form particles composed of stacks of quasi two-dimensional TOT-layers, which themselves are formed by a sheet of octahedrally coordinated cations (octahedral sheet) confined by two sheets of tetrahedrally coordinated cations (tetrahedral sheet) (Brigatti et al., 2006). The TOT layers carry permanent negative charge, which results from substitutions occurring in the octahedral and tetrahedral sheets (Fig. 1). The interlayer space between TOT layers is occupied by hydrated cations which compensate excess charge in the TOT layer. The interlayer space is typically varying from one to three water pseudo-layers depending on the TOT layer charge, the composition of the interlayer cations, the water chemical potential and the water to solid ratio.

In compacted rocks, montmorillonite (Mt) forms aggregates (particles) with 5–20 TOT layers (Segad et al., 2010). A typical radial size of

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http://dx.doi.org/10.1016/j.clay.2014.04.030
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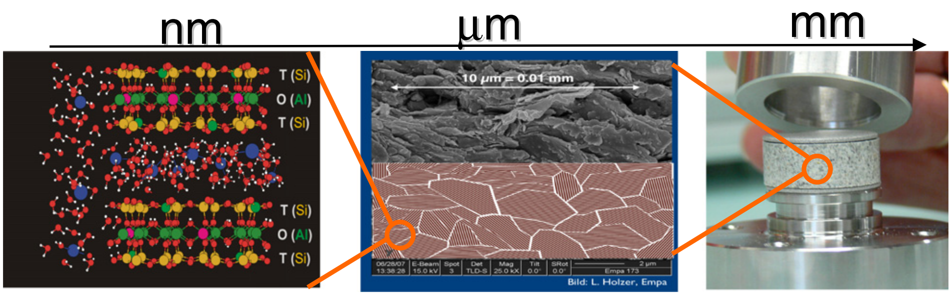

Fig. 1. Essential elements of clay structure at different scales. Left: atomistic representation of TOT-layers and interlayer porosity filled with water. Oxygen atoms are red, hydrogen atoms white, Al atoms green and Si atoms yellow. Blue spheres represent cations in the interlayer and external pores. Pink spheres illustrate divalent cations substituting for Al in the octahedral sheet. Middle: SEM image of compacted Mt and a model based representation of Mt by particles with interlayer porosity and larger inter-particle pores. Right: compacted Mt used in a macroscopic diffusion experiment.

these particles is of the order of 0.01 to 1 µm. The pore space between Mt particles is referred to as interparticle porosity. Depending on the degree of compaction, the interparticle porosity contributes 10 to 30% of the total water accessible pore space in Mt (Holmboe et al., 2012; Kozaki et al., 2001). Water in the central part of large interparticle pores may have bulk-like properties. However, close to the mineral surface water mobility is influenced by the interaction with the surface, similarly as in the interlayer space. The electrolyte ions in the diffuse double layer, which compensate the Coulomb potential of the charged mineral surface, substantially modify the water transport in the near surface film (Botan et al., 2011). The extent of these surface effects depends on the pore water composition and the charge density in the TOT layer, and is often of the order of a nanometer outward of the mineral surface (Churakov, 2013; Kosakowski et al., 2008; Marry and Turq, 2003; Wang et al., 2005).

Due to disparity of the transport scales in different types of porosity (Fig. 1) distinct numerical simulation techniques and experimental methods have to be applied to describe water mobility in clay minerals at different levels of details. Molecular dynamics (MD) simulations describe dynamics of atoms in the system based on inter-atomic interaction parameters. Such a detailed description is applicable for systems up to several thousand atoms and a time scale of several tens of nanoseconds. Thus, it is appropriate for a description of the water mobility in an idealized interlayer space or an external macropore, for which the water diffusion coefficients along the surface can be obtained by analyzing the mean square displacement (MSD) of water molecules. An atomistic description of the system at the scale of interparticle pores is not feasible. At this scale the molecular pore solution has to be approximated by an effective medium. A number of approaches have been considered based on Lattice-Boltzmann, Fokker–Planck and random walk equations (Churakov and Gimmi, 2011; Pagonabarraga et al., 2010; Rotenberg et al., 2007). An essential component of the modeling at this scale is the efficient representation of the connectivity of the pore space, which determines the geometrical effects on the water mobility (Tyagi et al., 2013).

Different experimental techniques are available to measure water diffusion, and each of them can be attributed to a particular time and space scale, too. In simple fluids, the measured diffusion coefficients do not depend on the accessed scales and are related to the molecular mobility (e.g. Einstein relationship, Allen and Tildesley, 1987). Contrarily, in complex liquids confined in hierarchical porous materials, like Mt, the measured diffusion coefficient may differ in magnitudes depending on the observation scales (González-Sánchez et al., 2009). On one end, quasielastic neutron scattering (QENS) can be used to derive local diffusional properties, whereas on the other end tracer diffusion provides values over macroscopic scales, which are relevant for large scale transport simulations.

QENS measures time- and space-correlation functions in the reciprocal space. The probed time scale is inversely proportional to the energy resolution of the instrument, while the length scale is inversely proportional to the probed range of momentum transfer. Depending on the type of the instrument and the experimental setup chosen, the accessed time scales can vary between 1 and 1000 ps (Bordallo et al., 2008; Gates et al., 2012; Skipper et al., 2006). Although the typical sample size used in QENS experiments is 0.1–1 cm, the accessible length scales are comparable with the one probed by MD simulations. The measured signal in QENS is averaged over the sample volume, however. In tracer diffusion experiments, the length scale is determined by the sample size, and the characteristic time scale depends on the local diffusion coefficient and the pore geometry. Here centimeter-sized samples are considered and the characteristic time scale of diffusion corresponds to several days.

A combination of several complementary approaches has to be applied to obtain a consistent description of transport processes at all relevant scales. Simulations, in particular, can help to understand and to explain the interplay between transport relevant phenomena at different scales and thus assist in the interpretation of experimental data. In the following, it is demonstrated how theoretical simulations of diffusion in clay minerals at atomistic and pore scales can be used to plan and correctly analyze experimental measurements of water mobility in Mt at different scales. The influence of the instrumental resolution on the interpretation of QENS data is further discussed. The experimental data, in turn, provide then input for multi-scale simulations.

2. Experimental

QENS measurements were performed using different energy resolutions (observation times) spreading over almost two orders of magnitude at SINQ, Paul Scherrer Institut in Villigen, Switzerland, at the hybrid time-of-flight spectrometer FOCUS (energy resolution, FWHM of 250 and 45 µeV), and at the FRM II in Garching, Germany, on the chopper time-of-flight instrument TOFTOF (ΔE, FWHM of 13 and 4 µeV). The experimental settings are summarized in Table 1. Mt from Milos Island (Decher, 1997) was converted into the homoionic Na-form, compacted to a bulk dry density of 1850 kg m^{-3} and hydrated to the desired water/solid ratio of 0.16, as described in Gonzalez-Sanchez et al. (2008). The sample was encapsulated in a watertight rectangular aluminum sample holder (15 mm × 50 mm × 1 mm) and placed at 45° (transmission geometry) into the beam. The measurements were performed at 300 K. Vanadium was used for detector efficiency calibration and to determine the energy resolution function of the instruments. The scattering from the empty sample holder was subtracted as background. The scattering from the dry Mt sample

Table 1
Instrumental parameters of QENS experiments.

Instrument	FOCUS	FOCUS	TOFTOF	TOFTOF
Incident wavelength, [λ]	3.65	5.75	10	14
Energy resolution (FWHM), [µeV]	250	45	13	4
Corresponding observation time, [ps]	3	15	50	160
Momentum transfer, Q[$Å^{-1}$]	0.36–2.65	0.26–1.65	0.22–1.12	0.14–0.78