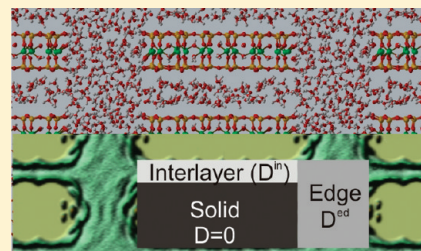


Up-Scaling of Molecular Diffusion Coefficients in Clays: A Two-Step Approach

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ABSTRACT: Materials with low permeability such as clays are major components in engineered or natural barriers in waste disposal sites. Diffusion of dissolved chemicals through such materials is a relatively slow process that can strongly limit the spreading of contaminants. The macroscopic diffusive transport of chemicals through barrier materials originates from Brownian motion of molecules and ions in the solution and their interaction with the surface of the solid medium. Up-scaling these molecular phenomena to the continuum scale, which is required for large-scale and long-time predictions, is particularly challenging because the considered scales differ by orders of magnitude. To address the up-scaling problem we developed a two-step simulation approach which enables us to derive macroscopic diffusion coefficients of water and ions for continuum equations from pore scale molecular diffusion coefficients. Our starting points for the up-scaling procedure were local pore diffusion coefficients derived in molecular dynamics simulations for specific local environments, such as the interlayer or edge regions of clay particles. We then assigned these local diffusion coefficients to different types of porosity of a model clay structure and obtained the structure-averaged diffusion coefficient of the sample by random walk simulations. We demonstrated the validity of the suggested approach by comparing the results of direct molecular simulations for a stack of pyrophyllite nanoparticles with the two-step up-scaling approach. We then investigated the effects of mineralogical heterogeneities and of anion exclusion on the larger-scale diffusion coefficients for a model clay structure which resembles a typical clay material. Our up-scaling concept is general and can be used for up-scaling molecular diffusion coefficients for porous materials with almost arbitrarily complex structures.



INTRODUCTION

Compacted smectite clays, such as bentonites, possess near zero hydraulic conductivity,¹ which makes molecular diffusion the dominant transport process for aqueous species. The diffusive mass transport of cationic species is further retarded by sorption on the surfaces of negatively charged clay particles. Due to such exceptional transport properties, clay-rich rocks are considered as a buffer and backfill material for high-level radioactive waste repositories worldwide.^{2–5} Clays are also used as sealing materials in landfill sites to prevent the spreading of toxic substances into the surroundings.^{6–8}

To predict diffusive migration of ions and water in a porous medium with porosity ε on a macroscopic scale, continuum models are used⁹

$$\varepsilon \frac{\partial C_i}{\partial t} = -\nabla \cdot J_i + R_i = \nabla \cdot (\varepsilon D_p^{\text{REV}} \nabla C_i) + R_i \quad (1)$$

In these models, solutes are transported according to the diffusive flux $J_i = -\varepsilon D_p^{\text{REV}} \nabla C_i$ and retarded or released by means of chemical reactions R_i due to precipitation/dissolution of solid phases and sorption/desorption on the surfaces of minerals. Such a separate description of diffusion and sorption (and/or precipitation) processes is possible due to an order of magnitude difference in the mobility of ions in aqueous and ab- or adsorbed states. The distribution of ions between mobile and immobile states, which is accounted for by the source/sink term in eq 1,

depends on the composition of the system. In typical applications, eq 1 is solved numerically on a grid. The smallest possible volume element of the grid is given by the representative elementary volume (REV). At the REV scale the porous medium is replaced by a conceptual macroscopic medium by means of some averaging over microscopic heterogeneities. The pore diffusion coefficient, D_p^{REV} , thus, represents average properties of the medium at the REV scale.¹⁰

Diffusion of ions and water in porous media is restricted to the porous space occupied by solvent, and thus the average macroscopic diffusion coefficient in porous media depends on the specific pore space topology in the sample and the strength of fluid–surface interaction. Numerous attempts have been undertaken to relate diffusion coefficients in porous media to those of the same solute in bulk solution D_0 . The bulk diffusion coefficients are typically reduced with a so-called formation factor F ¹¹

$$D_p^{\text{REV}} = \frac{1}{F} D_0 \quad (2)$$

For a “simple” porous medium with large pores, it has been suggested that the formation factor can be approximated by two geometric factors, one accounting for an increased length of the diffusion path (tortuosity τ^2) and the other accounting for the

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variation of the pore width along the diffusion path (geometric constrictivity δ)¹²

$$D_p^{\text{REV}} \approx \frac{\delta}{\tau^2} D_0 = \frac{1}{G} D_0 \quad (3)$$

Obviously the geometric parameters δ and τ are some average quantities that depend on the total porosity and the pore structure of the sample, which in turn depend on the mineralogical composition and the chemical-mechanical history of the rock. In practical applications, the exact meaning of the geometric parameters δ and τ is unclear, and they can rarely be obtained independently.¹³ They are therefore most often lumped together into a geometric factor or tortuosity term G and related to the average porosity by the empirical Archie's law, for instance.¹⁴

Smectite and illite minerals, which are major components of clays and shales, are composed of stacks of several basic clay layers with a typical size of the order of 0.01–1 μm .¹⁵ Due to isomorphic substitutions, smectite and illite particles carry permanent electrical charge, which is compensated by mono- and divalent cations occupying the interlayer and interparticle space. When brought into contact with aqueous solution, smectite particles absorb water which hydrates the interlayer cations. Typical thicknesses of the *interlayer pore space* in smectite minerals vary from one to three water layers, depending on the bulk density of the sample and the water activity in the external reservoir, the nature of the interlayer cations, and the charge of the clay particles.^{16–21} Transport properties of such thin molecular water films are influenced by the interaction with the surface. The *diffuse double layer pores* are found at the external interface of permanently charged mineral surfaces with the aqueous electrolyte. The inhomogeneous distribution of electrolyte ions in the diffuse double layer compensates the coulomb potential of the charged mineral surface. High ionic concentrations near the surface and electrostatic interactions with the surface potential influence the diffusion coefficients of water and ions in the diffuse double layer. The extent of the compositional heterogeneities at external surfaces depends on the pore water composition and the bulk density and is often of the order of a nanometer outward of the mineral surface. Finally, *bulk-type pore solution* can be found in macropores in which the effects of the surface interactions are negligible. In typical clays and shales, however, up to 50–70% of the porosity is attributed to the interlayer and diffuse double-layer porosity where the properties of the solution, namely, the mobility of ions and water, are strongly influenced by the mineral surfaces.^{22–28} In such cases, F as used in eq 2 is not a truly geometrical parameter anymore, and eq 3 has to be modified to account for these effects. Accordingly, Bourg et al.²⁹ and Gonzalez Sanchez et al.³⁰ introduced a surface constrictivity, δ_s , in addition to the tortuosity term G , to account for the fluid–surface interactions

$$D_p^{\text{REV}} = \frac{1}{F} D_0 = \frac{\delta_s}{G} D_0 \quad (4)$$

The formation factor F accounts for all processes affecting diffusion through the porous medium. The surface constrictivity δ_s is, as the geometrical tortuosity G , an average quantity, which depends on the specific structure of the sample. Both δ_s and G are mostly considered as empirical parameters, and eq 4 has therefore a limited predictive power.

Direct measurements of diffusion coefficients in clays are time-consuming and technically nontrivial. A promising, but challenging, approach is to derive the D_p^{REV} for water and ions in clays

based on more easily accessible macroscopic information about the structure of the sample such as porosity, mineral composition, particle size, orientation distributions, various structural correlations, and interlayer diffusion properties. Bourg et al.,³¹ for instance, modeled D_p^{REV} for water tracers based on the fraction of interlayer water, the interlayer diffusion coefficient, and an empirical geometric tortuosity parameter. Pore and particle size distributions and mineralogical information may also be used to infer a model of the pore structure. On the basis of such a model pore structure, the average D_p^{REV} could then in principle be estimated by various modeling techniques. Atomistic simulations such as molecular dynamics (MD) provide data on the diffusivity of interlayer water and ions as a function of the interparticle distance and the clay composition, as well as molecular diffusivities in the diffuse double layer. Due to the limitation of computer power such simulations cannot be performed on the scale of several clay particles. Stochastic particle-based simulations such as random walk (RW) or lattice Boltzmann techniques, on the other hand, do not capture all the details of the surface–molecule interaction but take into account the irregularities of the particle arrangements, that is, the geometrical structure of the porous medium.³²

Here we suggest an approach for up-scaling molecular diffusion coefficients in which we combine the advantages of deterministic molecular dynamics simulations and stochastic random walk-based methods. Suppose that the representative distribution of solids and voids of a clay rock is given as a map. We refer to this map as a pore or clay structure map. To every point x of such a clay structure map we can assign a local diffusion coefficient $D_1(x)$. This local diffusion coefficient is obtained from MD simulations of interacting fluid and solute atoms or molecules and atoms of the solid crystal surfaces in a given environment, such as, for instance, fluid confined between mineral surfaces

$$D_1^\Omega(x) = \frac{1}{2nt} \langle |R(t) - R(0)|^2 \rangle_{\Omega, \text{MD simulations}} \quad (5)$$

where Ω refers to the local environment; $R(0)$ is the position of the molecule of interest at time zero; $R(t)$ is the position at time t ; and n is the dimension of the diffusion process considered. Random walk simulations in the larger-scale, polymineral structure map, using noninteracting particles, will then provide an average pore diffusion coefficient D_p^{REV} for the given REV volume of the porous medium

$$D_p^{\text{REV}} = \frac{1}{2nt} \langle |R(t) - R(0)|^2 \rangle_{\text{REV, RW simulations}} \quad (6)$$

The MD simulations represented by eq 5 quantify mainly the local surface interactions, whereas the RW simulations represented by eq 6 quantify both the geometric restrictions as given by the pore connectivities as well as the average surface interactions given by the local $D_1^\Omega(x)$.

For this approach to be expedient, the following three conditions need to be fulfilled: (1) efficient algorithms are required to simulate diffusion in strongly heterogeneous domains, (2) the effort of compiling the local pore diffusion coefficients $D_1^\Omega(x)$ must be modest, and (3) pore structure maps must be available. Random walk simulations can easily deal with very complex heterogeneous structures and so meet the first requirement. Fortunately, clay particles maintain a limited set of hydration states, and the diffusion coefficients in a diffuse double layer are constrained within the limits of bulk solution diffusion coefficients and those of the interlayers. So the effort of the required

MD simulations is reduced to a compilation of a lookup table with diffusion coefficients for a set of hydration states of interlayers and diffuse double layers. Moreover, numerous simulation results are already available in the literature.^{33–38} Finally, model pore structure maps can be generated to match available macroscopic structural properties such as porosity, mineral composition, particle size, and orientation distributions. Depending on the sizes of the pores, information from 2D or 3D imaging methods may also be used.

In this paper, we validated the two-step up-scaling approach represented by eqs 5 and 6 against equivalent full-scale MD simulations. We tested the statistical uncertainty of the results for various simulation setups. As an application of the method, we investigated the influence of $D_i^\Omega(x)$ resulting from specific surface–solute or surface–solvent interactions on the D_p^{REV} based on a single reference pore structure map. This pore structure map mimics essential features of a typical composite clay material. The efficient generation of structure maps is a separate topic that was not addressed in this paper. We specifically tested the effect of local interlayer and edge diffusion coefficients, of mineralogical heterogeneities, and of anion exclusion on the macroscopic diffusion coefficient.

METHOD

MD Simulation. Molecular dynamics simulations were performed using the LAMMPS package³⁹ developed at Sandia National Laboratory. The interaction between atoms and molecules was taken into account using the CLAYFF force field.⁴⁰ The corresponding flexible SPC water model⁴⁰ has been used throughout the simulations. The simulations were performed in NVT ensemble with a time step of 1 fs. A Nose–Hoover chain of thermostats^{41,42} with the temperature dumping parameter equal to 1 ps was applied to keep average temperature at 300 K during the simulations. The parameters of the simulation box for NVT simulations were obtained from a set of NPT simulations at the pressure of 1 bar. The systems studied were equilibrated for 500 ps followed by a 110 ns long trajectory which was used for the analysis of the distribution of water molecules and their diffusivities. Diffusion coefficients of the water molecules along the direction of Cartesian coordinates were derived from the mean square displacement of the molecules using the Einstein relationship,⁴³ as indicated in eq 5.

RW Simulations. Random walk simulations in a heterogeneous domain were performed using the predictor-corrector scheme suggested by LaBolle et al.⁴⁴ to account correctly for heterogeneous local diffusion coefficients

$$\delta x = Z\sqrt{2D(x(t))\Delta t} \quad (7)$$

$$\mathbf{x}_k(t + \Delta t) = \mathbf{x}_k(t) + Z\sqrt{2D(\mathbf{x}_k(t) + \delta x)\Delta t} \quad (8)$$

In this algorithm, the random number Z is drawn to generate a predictor step δx according to eq 7. Then the particle is moved using the same random number Z but the diffusion coefficient $D(\mathbf{x}_k(t) + \delta x)$ obtained at the position $\mathbf{x}(t) + \delta x$ (eq 8). We used the Gaussian distribution to obtain Z , but other distributions can also be used. The appropriateness of this algorithm has been verified by La Bolle et al.^{44,45} and by ourselves through comparisons with analytical solutions for simple heterogeneous arrangements. A zero diffusion coefficient was attributed to impermeable regions, such that the system of eqs 7 and 8 also

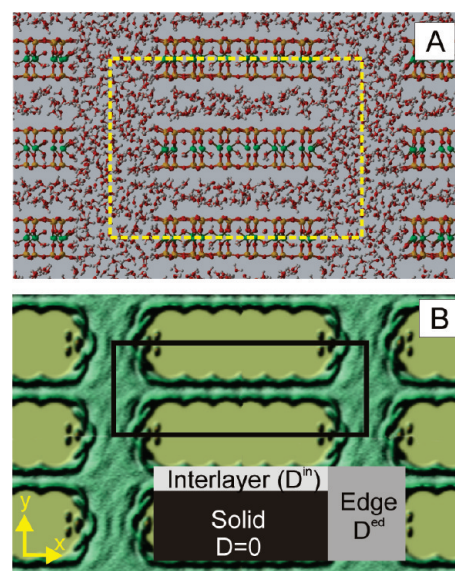


Figure 1. (A) Snapshot from MD simulations of pyrophyllite particles separated by two water layers. Oxygen, hydrogen, silica, and aluminum atoms are shown as red, gray, yellow, and green spheres, respectively. The simulation supercell is shown by the yellow dashed line. (B) A surface plot of the 2D probability density profile of water molecules from molecular dynamics simulations. Peak areas correspond to long residence times. In the overlay, light gray and gray areas indicate interlayer space and interparticle porosity, respectively, as assigned for the RW simulations. The diffusion coefficients D^{in} and D^{ed} for these pore spaces were obtained from short (200 ps) MD trajectories resident in the corresponding domains. The solid phase domain impenetrable for water is shown as a black area. The simulation cell for the RW simulations is shown by the solid black line.

restricted the positions of particles to the open pore space of the sample. A radius of 0.15 nm, representing a typical radius of a water molecule or anion, was attributed to the particles, to prevent nonphysical overlap of the particles with the solid structures. The time step Δt for the simulations was chosen according to the spatial resolution Δx_{map} of the structure map and the largest diffusion coefficient in the medium D_{max}

$$\Delta t = 10^{-3} \frac{\Delta x_{\text{map}}^2}{D_{\text{max}}} \quad (9)$$

Such a small time step ensures that particles sample correctly all local diffusion properties during their passage through the sample, without crossing over the slow diffusion areas, for instance. It also keeps the errors associated with the reflection at impermeable boundaries small. Finally the sample diffusion coefficient was estimated according to eq 6.

VALIDATION OF THE UP-SCALING APPROACH

The main purpose of this work was to validate the up-scaling strategy defined in eqs 5 and 6. To demonstrate the validity of the approach we compared full-scale MD simulations with the two-step up-scaling approach on an instance of one and the same simplified model of a porous medium (Figure 1). Two sets of 110 ns long MD simulations were performed for systems with two and three water layers (denoted as bilayer and trilayer system, respectively) confined between the planar sides of uncharged particles of pyrophyllite. The interlayer space was connected with the pores at the (010) edge surfaces of the clay particles. The

initial geometry of the edge sites was taken from our former ab initio simulations.^{46,47} Pyrophyllite is an uncharged, nonswelling clay. We did intentionally choose pyrophyllite for the validation of the up-scaling approach because it has a smaller number of system-controlling parameters (e.g., pure water in the pore solution, unique clay sheet composition) as compared to montmorillonite. This makes the comparison unambiguous.

A snapshot from MD simulations with the two-layer geometry of the interlayer space is shown in Figure 1a. The geometrical parameters of the simulation cell are summarized in Table 1. Due to periodic boundary conditions, clay sheets are infinite in the z -direction, and the diffusion path in this direction is nontortuous. The MD trajectories were analyzed in two different ways. First, we determined local diffusion coefficients of water molecules in the interlayers (D_{il}^{Ω}) and in the regions between edges of clay particles (D_{ed}^{Ω}) from short-time (200 ps) MD trajectories, which started and remained either in the interlayer or in the interedges domain, respectively. These local diffusion coefficients were later used as input for the RW simulations. Second, average diffusion coefficients D_p^{REV} of the simulation cell were obtained directly from long-time (110 ns) trajectories of the MD simulations. These diffusion coefficients were later compared with the outcome of the RW simulations. The local diffusion coefficients D_{il}^{Ω} and D_{ed}^{Ω} for the bi- and trilayer configurations are listed in Table 2. The basal plane of pyrophyllite shows a weak hydrophobic character which leads to faster diffusion of the interlayer water compared to charged clays like montmorillonite. Quasi-elastic neutron scattering experiments on pyrophyllite samples confirmed this behavior.⁴⁸ The hydrophobic surface properties explain also the faster diffusion of water in bilayer geometry compared to the trilayer system obtained in the simulations. The diffusion coefficient in the edge regions is slightly lower than that of bulk water.

Corresponding RW simulations were performed in a 3D setup with a single slice of the medium in the z -direction and periodic boundary conditions applied on all directions. The size of the RW simulation cell was fixed according to the parameters of the supercell in the MD simulations. Only half of the MD simulation supercell was considered in the RW modeling due to symmetry considerations. The structure map for the RW simulations was derived from the two-dimensional probability density profile of the positions of water molecules obtained by MD simulations (Figure 1b). The extent of the solid particle in the RW simulations was adjusted in such a way that the ratio of interlayer and edge porosity areas was equal to the ratio of the water molecules

resident in the interlayer to the number of water molecules in the pore space at the edges in MD simulations (Figure 1b). This was done to match mass balance between RW simulations with uniform water particle density and MD simulations, where water density variations occurred at interfaces. The width of the fluid accessible pore space between edges in the bi- and trilayer systems was chosen to be identical (Table 2). The local MD diffusion coefficients D_{il}^{Ω} and D_{ed}^{Ω} were then assigned to the corresponding pore areas (Figure 1 and Table 2). The structure map for the RW simulations was represented with a resolution of 0.01 nm. From 1000 to 10 000 particles were used in each run. MD simulations, for comparison, contain only 462 and 704 water molecules for bi- and trilayer simulations, respectively.

Results of the RW simulations (10 000 particles) are compared with the sample scale MD simulations in Figure 2. The agreement between the mean square displacement of the particles in the two-scale RW-MD simulations and the direct MD simulations is overall very good confirming the validity of the approach. To test the convergence of the simulations with respect to the particle number, we performed RW simulations

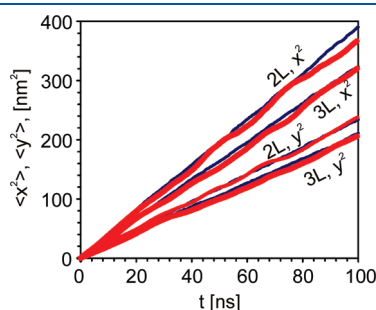


Figure 2. Comparison of the mean square displacement for water molecules obtained in direct MD simulations (red lines) and the results of the two-scale RW-MD simulations (blue lines) obtained with 10^4 particles.

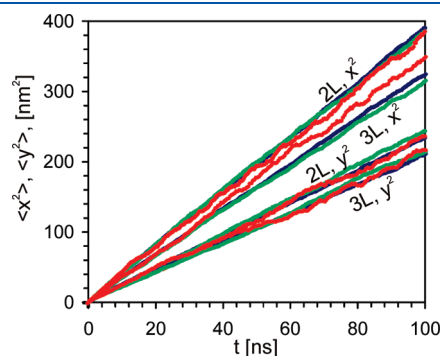


Figure 3. Comparison of the mean square displacement obtained in RW simulations using 1×10^3 , 5×10^3 , and 10×10^3 particles shown by red, green, and blue lines, respectively.

Table 1. Geometry of the Super Cell and the Number of Water Molecules in the Interlayer, n_W^{in} , and between Edges, n_W^{ed} , for the MD Simulations

interlayer	cell dimensions [nm $\times$ nm $\times$ nm]	n_W^{in}	n_W^{ed}
bilayer (2L)	20.83 $\times$ 41.13 $\times$ 29.65	201	259
trilayer (3L)	20.83 $\times$ 41.13 $\times$ 34.98	319	385

Table 2. Geometric Parameters of the Solid Pyrophyllite Particles and Diffusion Coefficients Derived from MD Simulations and Then Used in RW Simulations

interlayer	solid/cell [nm/nm]		diffusion coefficients D [10^{-9} , $m^2 s^{-1}$]	
	x	y	D_{il}^{Ω}	D_{ed}^{Ω}
bilayer (2L)	2.845/4.113	0.978/1.483	2.92	1.98
trilayer (3L)	2.845/4.113	1.113/1.749	2.25	1.83

in the same setup using $1 \times$, $5 \times$, and 10×10^3 particles. The results in Figure 3 indicate that already 5×10^3 particles provide an accurate representation of the mean square displacement and diffusion coefficients for the given system geometry.

■ SYSTEM SETUP AND STATISTICAL ASPECTS OF RW SIMULATIONS FOR COMPOSITE CLAY MATERIALS

Clay Structure Model. The structure of real clays and shales is much more complex than the simple test geometry (Figure 1b) used for the validation of the up-scaling approach. A direct visualization of the natural pore structure of clays with tomographic methods (X-ray, neutron, or MRI)⁴⁹ is at present impossible because of the typically small pore sizes in the range of nanometers and the limited spatial resolution of the various imaging techniques, even though some new developments,⁵⁰ e.g., FIB tomography, push the limits toward the desired range. Thus, our present understanding of clay pore structure and pore connectivity is based on indirect, macroscopic data such as total porosity, mineralogical composition of the sample, average interlayer distance between sheets of clay particles, particle size distribution, and rock texture.

To investigate the effect of variable local diffusion coefficients, as obtained from the MD simulations, as well as of the effect of anion exclusion on the macroscopic tortuosity and anisotropy of diffusion, we assembled a two-dimensional reference clay structure map (Figure 4) fulfilling average properties of the sample as summarized below. The structure was modeled as a domain of $200 \times 150 \times$

0.05 nm^3 with a 0.05 nm resolution. Smectite particles with a mean cross-sectional area (x, y) of about 480 nm^2 and infinite in z direction were arranged to occupy about 90% of the volume, which leaves about 10% external pore space. The equivalent diameters of the smectite particles range between about 8 and 40 nm (Figure 5a). Each smectite particle is composed of a stack of about 4–20 clay layers, separated by interlayers with an extent corresponding to two water layers. The two-layer hydration state of the smectite particles dominates for bulk dry densities of the clay material between about 1.5 and 1.9 Mg m^{-3} .^{30,51} The bulk dry density of our sample is 1.75 Mg m^{-3} . This bulk density was calculated using a montmorillonite solid density of 2.9 Mg m^{-3} ,³⁰ which leads to bulk dry densities of individual smectite particles of 1.9 Mg m^{-3} . The total porosity is $0.40 \text{ m}^3 \text{ m}^{-3}$ of which $0.30 \text{ m}^3 \text{ m}^{-3}$ are interlayer pores in clay stacks and $0.097 \text{ m}^3 \text{ m}^{-3}$ or 25% of all pores are external (interparticle) pores. The orientation of the clay layers was along the major axis of the particles and varied between -75° and $+89^\circ$ from the horizontal, with higher fractions around 0° and lower fractions around $\pm 90^\circ$ (Figure 5b, mean of about 9°). Real clay rocks typically have a preferred orientation of the clay particles along the bedding plane. Thus, the x direction can be considered as being parallel to the bedding plane and the y direction as perpendicular to the bedding plane.

The area-weighted distribution functions of the particle circularities, which are calculated as $4\pi AP^{-2}$, with A the area and P the perimeter of the particle, are shown in Figure 5c. The majority of the particles in the map have circularities in the range from 0.6 to 0.7. These dimensions correspond to values reported for real clay particles⁵² but to the upper limit for real clays rocks as inferred from clay micrographs,⁵³ which show the formation of elongated tactoids of several clay particles. We intentionally have chosen the larger circularities to allow simulations using a relatively small domain size. One has to keep in mind, though, that the definition of single particles is ambiguous for claystones, anyway. The specific surface area of our structure is about $790 \text{ m}^2 \text{ g}^{-1}$ (per dry weight), with $\sim 85 \text{ m}^2 \text{ g}^{-1}$ of external and $\sim 705 \text{ m}^2 \text{ g}^{-1}$ of internal surfaces. These values are typical for montmorillonites.^{30,54–56} A summary of the geometrical properties of this sample is given in Table 3.

We emphasize that the generated structure is a model which just mimics the microscopic arrangement of mineral phases and the pore space connectivity in a clay or shale. The model used is not unique, and numerous sets of other realizations might equally well reproduce the target macroscopic parameters of the rock. The used clay structure map does not represent a particular clay sample, but it serves as an example to demonstrate the upscaling approach. We investigate the ability of our simulation algorithm

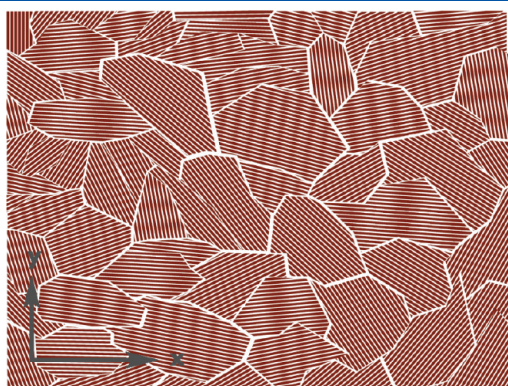


Figure 4. Clay structure map of the polymineral ensemble used for random walk simulations representing montmorillonite. Solid area is brown. Pore space is white.

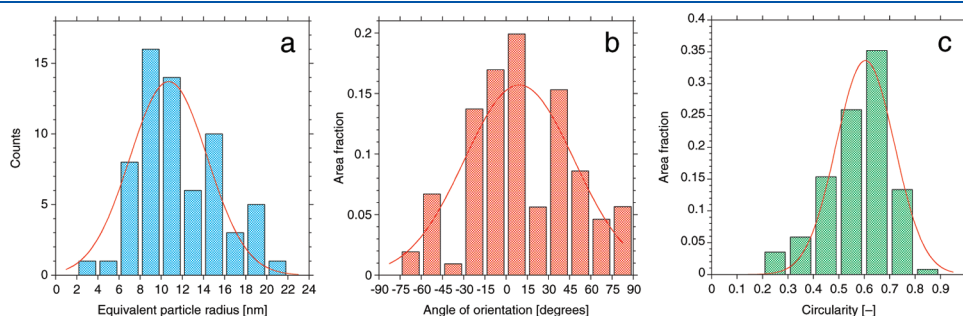


Figure 5. Structural characteristics of clay map shown in Figure 4. (a) Particle size distribution function. (b) Area-weighted distribution function of orientation (angle with respect to horizontal) of the clay layers. (c) Area-weighted distribution function of circularity ($4\pi AP^{-2}$, with A the area and P the perimeter of the particle) of single clay particles.

Table 3. Geometric Characteristics of the Structure Maps Used for the RW Simulations

unit	property	montmorillonite content [%]			
		100	73	27	0
sample	size [nm ³]	200 × 150 × 0.05			
	resolution [nm]	0.05			
	solid density montmorillonite [Mg m ⁻³]	2.9			
	solid density illite [Mg m ⁻³]	2.7			
	bulk dry density [Mg m ⁻³]	1.75	1.94	2.25	2.44
	total porosity [m ³ m ⁻³]	0.398	0.315	0.180	0.097
	external porosity [m ³ m ⁻³]	0.097			
	interlayer porosity [m ³ m ⁻³]	0.301	0.219	0.083	0.0
	interlayer pore fraction [–]	0.76	0.69	0.46	0
	edge porosity (external) [m ³ m ⁻³]	0.071			
	edge pore fraction [–]	0.18			
	external planar porosity [m ³ m ⁻³]	0.026			
	int. and ext. planar porosity [m ³ m ⁻³]	0.328			
	int. and ext. planar pore fraction [–]	0.82			
	anion exclusion distance [nm]	0.35			
	anion accessible porosity [m ³ m ⁻³]	0.039			
	anion accessible pore fraction [–]	0.10			
	total specific surface area [m ² g ⁻¹]	790	555	230	85
	[m ² m ⁻³]	1.4	1.07	0.519	0.202
	external specific surface area [m ² g ⁻¹]	85	90	80	85
	[m ² m ⁻³]	0.14	0.177	0.179	0.202
	internal specific surface area [m ² g ⁻¹]	705	460	150	0
	[m ² m ⁻³]	1.23	0.895	0.340	0
clay particles	mean size [nm ²]	480			
	mean circularity (area weighted) [–]	0.6			
	mean orientation (area weighted) [°]	9.0			
	mean number of interlayers [–]	ca. 10			
	bulk dry particle density [Mg m ⁻³]	1.9			
	particle porosity [m ³ m ⁻³]	0.334			

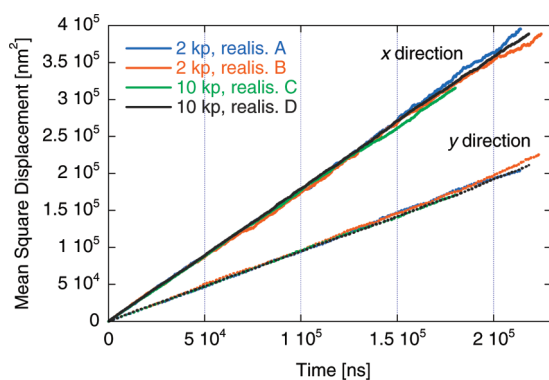


Figure 6. Mean square displacements in x (solid lines) and y directions (dashed lines) for the large heterogeneous structure, based on different initial particle distributions and either 2000 (2 kp) or 10 000 particles (10 kp).

to address the influence of pore connectivity and local diffusion properties on the average diffusive flux through the sample, and we focus on general relations between the accessibility of the pore space and transport properties.

Statistical Uncertainties of RW Simulations. In this section we investigate the statistical accuracy of the RW simulations for

our clay structure map. As long as homogeneous local diffusion coefficients are considered, the exact value of the $D_1^Q(x)$ is unimportant. Accordingly, we use the bulk diffusion coefficient of water ($2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) as a reference case parameter. All RW simulations were performed in a pseudo-3D setup with periodic boundary conditions. A single slice of elements was used in the z -direction. Since the transport in the z -direction is nontortuous and thus related to the pore diffusion coefficients in a trivial way, we only discuss the particle transport in x - and y -directions of the model clay structure.

To test the statistical uncertainties inherent in the RW approach, we performed simulations with different initial random particle distributions and using 2000 and 10 000 walker particles. Figure 6 shows the mean square displacements in x - and y -directions. The differences between realizations as well as the fluctuations around a linear relation are small when using 10 000 particles. The derived diffusion coefficients are given in Table 4. The variations in D_p^{REV} are below 5% for 2000 particles and below ~ 1 –3% for 10 000 particles for the simulation times of about 0.2 ms. All further simulations were performed using 10 000 walker particles and for simulation times of about 0.2 ms. We therefore estimate the relative uncertainty of all derived diffusion coefficients as $\pm 1.5\%$.

Figure 7 illustrates that the fluctuations of the calculated instantaneous D_p^{REV} around the constant asymptotes increase

Table 4. Input Parameters and Results of the Different Simulations for the Heterogeneous Clay Structure^a

run	particle number	$D_1^\Omega(x)$ [$10^{-9} \text{ m}^2 \text{ s}^{-1}$]	D_x [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	D_y [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	D_x/D_y	F_x	F_y	G_x	G_y
homog. local D	2 k	2.3	9.2 ± 0.0026	4.9 ± 0.0013	1.88				
homog. local D	2 k	2.3	8.8 ± 0.0029	4.9 ± 0.0015	1.78				
homog. local D	10 k	2.3	8.7 ± 0.0015	4.7 ± 0.00082	1.85	2.63	4.86	2.63	4.86
homog. local D	10 k	2.3	9.0 ± 0.0010	4.8 ± 0.00084	1.88	2.57	4.82	2.57	4.82
homog. local D	10 k ^b	2.3	8.8 ± 0.013	4.8 ± 0.0071	1.86 ± 0.021	2.60	4.84	2.60	4.84
heterog. local D pyrophyllite	10 k	$2.92D_{il}^\Omega$	9.2 ± 0.0008	5.0 ± 0.00050	1.84	2.50	4.60	2.99	5.51
		$1.98D_{ed}^\Omega$							
heterog. local D montmorillonite	10 k	$1.20D_{il}^\Omega$	5.4 ± 0.0006	3.2 ± 0.00018	1.69	4.26	7.19	2.48	4.18
		$1.90D_{ed}^\Omega$							
heterog. mineralogy, 30% illite	10 k	2.3	8.67 ± 0.0007	4.95 ± 0.00051	1.76	2.66	4.69	2.66	4.69
heterog. mineralogy, 70% illite	10 k	2.3	7.61 ± 0.0009	5.31 ± 0.00054	1.45	3.01	4.35	3.01	4.35
heterog. mineralogy, 100% illite	10 k	2.3	8.85 ± 0.0007	6.19 ± 0.00044	1.40	2.61	3.66	2.61	3.66
heterog. mineralogy, 100% illite	10 k	2.3	8.67 ± 0.0006	6.02 ± 0.00029	1.42	2.67	3.80	2.67	3.80
anions	10 k	1.9	4.09 ± 0.0003	2.63 ± 0.00038	1.55	5.62	8.74	4.63	7.17

^a D_x , D_y : Sample-scale diffusion coefficients parallel (x) and perpendicular (y) to bedding; F_x , F_y : Formation factors in x and y direction; G_x , G_y : Geometric tortuosities in x and y direction; ^b Means and errors estimated from the two runs with 10 k particles.

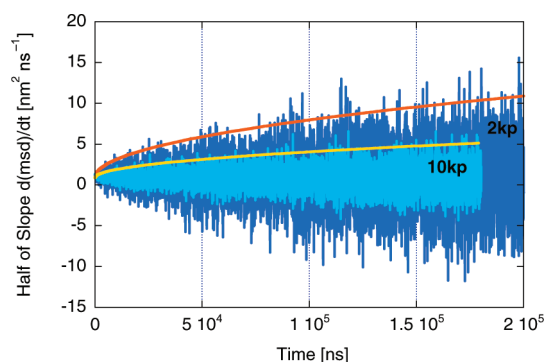


Figure 7. Variability of half of the local slope of the mean square displacement (x direction) with respect to time. The mean value corresponds to the average diffusion coefficient of the medium. The dark blue curve was obtained for 2000 walker particles and the light blue curve for 10 000 walker particles. The orange and the yellow curve illustrate the time dependence of the fluctuation amplitude according to eq 13.

with time. Such fluctuations can influence the determination of the diffusion coefficients. The effect is much more pronounced in the simulation with 2000 particles as compared to that with 10 000 particles. We interpret this as an effect of dilution of the particle density, that is, of the number of particles per reference volume, with the simulation time. Let us consider a simple case of a heterogeneous, but isotropic, medium. In such a system the initial coordinates of all particles can be placed in the center of the coordinate system without loss of generality. During the simulations the maximum of the particle density will be in a sphere around the origin. The surface area of this sphere will be proportional to the simulation time

$$4\pi\langle |R(t)|^2 \rangle \sim t \quad (10)$$

and the reference volume associated with the spherical shell of thickness ΔR will be

$$\Delta \tilde{V}(t) \sim 4\pi\Delta R \langle |R(t)|^2 \rangle \sim 4\pi\Delta R t \quad (11)$$

Because the number of particles N is constant during the

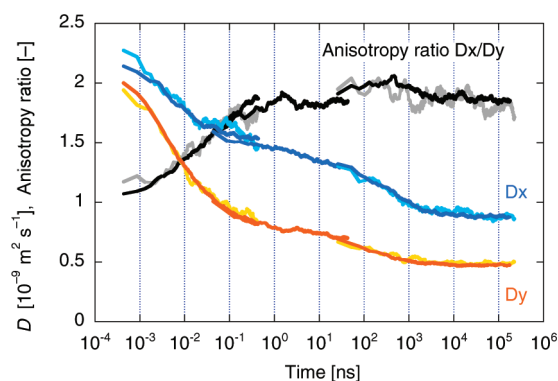


Figure 8. Development of average diffusion coefficients in horizontal (D_x) and vertical (D_y) directions and of anisotropy ratio with simulation time. The data were calculated from five simulations with different initial particle distributions and over different simulation times, using either 2000 particles (bright lines) or 10 000 particles (dark lines).

simulations, the “effective” particle density available for the mean square displacement calculations will decrease as

$$\Delta \tilde{\rho}(t) \sim \frac{N}{4\pi\Delta R t} \quad (12)$$

Accordingly, the fluctuation amplitude $\xi(t, N)$ will increase as square root of the time

$$\xi(t, N) \sim \frac{1}{\sqrt{\Delta \tilde{\rho}(t)}} \sim \sqrt{\frac{t}{N}} \quad (13)$$

as also shown by the yellow and orange lines in Figure 7. With respect to the above relations, it is thus more efficient to increase the number of particles but keep the simulation time short. Still, the simulation time should be long enough such that all statistical heterogeneities of the material can be sampled by the walker particles.

Time Dependence of Porous Medium Diffusion Coefficients. Figure 8 displays the development of the average diffusion coefficients as a function of the simulation time. The running average diffusion coefficients $D_p^{\text{REV}}(x)$ start from values close to

the local diffusion coefficients D_1^{Ω} ($2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), as is expected for very short times where the pore confinements are not yet encountered by the walkers. Then, they decrease within about 1 ns to intermediate values, before they reach the asymptotic values after about 10^3 – 10^4 ns. The plateau with intermediate values corresponds to root-mean-square distances equal to ~ 1 nm, whereas the asymptotic values are obtained after root-mean-square distances of ~ 100 and ~ 50 nm in horizontal and vertical directions, respectively. The latter distances represent about half or one-third of the size of the structure map (Table 3). The intermediate values after about 1 ns probably represent the state where the walkers were affected by the confinements perpendicular to the pores in which they started, but not yet by any confinement along the pores. For a two-dimensional random network in straight pores, one would then expect average diffusion coefficients about half of the local ones. The observed values are of this order; the differences are probably due to the fact that our pores are not completely randomly oriented. The anisotropy ratio shows some fluctuations at intermediate times, including a slight maximum, but converges to the asymptotic value more quickly than the individual diffusion coefficients. This may also be related mainly to the narrow interlayer pores with an extent of about 0.6 nm, where diffusion perpendicular to the layers is limited, and the fact that the clay particles are oriented mostly (sub)-horizontally.

The average asymptotic D_p^{REV} obtained from the two simulations with 10 000 particles for this sample are $(8.85 \pm 0.13) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the x direction and $(4.75 \pm 0.07) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the y direction, leading to an anisotropy ratio of 1.86 ± 0.04 . The errors of the diffusion coefficients were calculated from the relative errors of 0.015 given above; that of the anisotropy ratio was calculated to be $0.015\sqrt{2} = 0.021$ according to first-order error propagation. When comparing with the self-diffusion coefficient of bulk water of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, we calculate formation factors F of 2.6 (x direction) and 4.8 (y direction). These factors also equal the geometric tortuosities G because the surface constrictivity is equal to one in this case. The values are comparable to values found in the literature for illites or kaolinites⁵⁷ and lead to a mean principal value (average between directions parallel and perpendicular to bedding) of 4.1, which compares well with the value of 4.0 ± 1.6 found for bentonite at densities between about 1 and 1.6 Mg m^{-3} .²⁹ They are, however, somewhat lower than those of montmorillonites or bentonites at densities around 1.8 Mg m^{-3} .^{57–59} Also, the anisotropy ratio obtained from our simulations is somewhat lower than that obtained experimentally for similar densities,⁵⁸ but it is similar to that obtained for a lower bulk dry density of 1.35 Mg m^{-3} .⁵⁹ As mentioned, we used a generic structure map which was not tailored to a specific sample. Real montmorillonite particles have typically lower circularities than those of the used structure map and are more closely interlinked, which will lead to lower external pore space and thus to higher tortuosity and anisotropy of the media.

APPLICATION OF THE TWO-STEP APPROACH TO COMPOSITE CLAY MATERIALS

Influence of Heterogeneous Local Diffusion Properties. For the above simulations, the bulk water diffusion coefficient of $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was used in all pore areas. Local diffusion of water and ions in the pores of clay minerals is generally modified by interaction with the surface. From our atomistic simulations of pyrophyllite with two water layers between particles, we derive diffusion coefficients of $2.92 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the interlayers

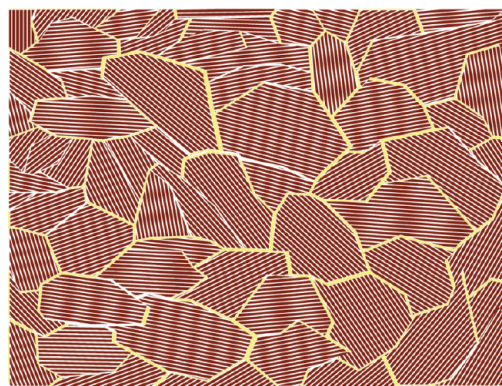


Figure 9. Clay structure map representing the locations of the edge (yellow) and the interlayer diffusion coefficients (white) for the simulations for pyrophyllite or montmorillonite with heterogeneous local diffusion coefficients.

and of $1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the edge regions (Table 2). For montmorillonite with two layers of water in the interlayer we adopt an interlayer diffusion coefficient of $1.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ from a previous study.³⁶ These data were used to investigate the effects of the heterogeneity in the local pore diffusion coefficient $D_1^{\Omega}(x)$ on D_p^{REV} .

We proceeded by assigning a value of $D_1^{\Omega}(x) = 2.92 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, representing pyrophyllite with two water layers, to the interlayer and a value of $D_1^{\Omega}(x) = 1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ to the edge regions (Figure 9) in the clay map. The latter regions account for about 18% only of the total porosity of 0.398 (edge porosity of 0.071). Simulations with these heterogeneous parameters led to D_p^{REV} of 9.2×10^{-10} and $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the x and y direction, respectively, or to formation factors F of 2.5 and 4.6.

In the homogeneous case, where a bulk diffusion coefficient of water was used in all pores (i.e., $\delta_s = 1$ everywhere), the formation factors could be interpreted as purely geometrical tortuosity G . Here, in the case of heterogeneous local diffusion coefficients, the formation factors are influenced by geometrical as well as by surface effects that affected the interlayer and edge diffusion coefficients. To separate the two effects, we assumed that an average surface constrictivity can be calculated from the area-weighted local edge and interlayer constrictivities. This assumption is supported by recent findings of Bourg and Sposito.⁶⁰ They calculated average constrictivities from values for interlayer nanopores and for bulk water in macropores and found that they compare well with experimental data. The average surface constrictivity for the pyrophyllite model δ_s of 1.20 is calculated from the fractional areas of the local δ_s of 1.27 (interlayers) and 0.86 (edges). Note that the obtained constrictivity is larger than unity due to enhanced mobility of water along the surface of pyrophyllite. From the average δ_s , we calculated geometrical tortuosities $G_{x,y}$ of 2.99 and 5.51, respectively. The obtained anisotropy ratio 1.84 ± 0.04 is similar to the value derived for the homogeneous local diffusion coefficients.

In our next simulation set, we assigned diffusion coefficients of $D_1^{\Omega}(x) = 1.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ to the interlayer regions, as obtained for montmorillonite with two water layers in the MD simulations by Kosakowski et al.³⁶ and $D_1^{\Omega}(x) = 1.90 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the edge regions (average value for the edge regions obtained in the MD simulation of pyrophyllite). The calculated area-weighted surface constrictivity δ_s is equal to 0.59, in agreement with the

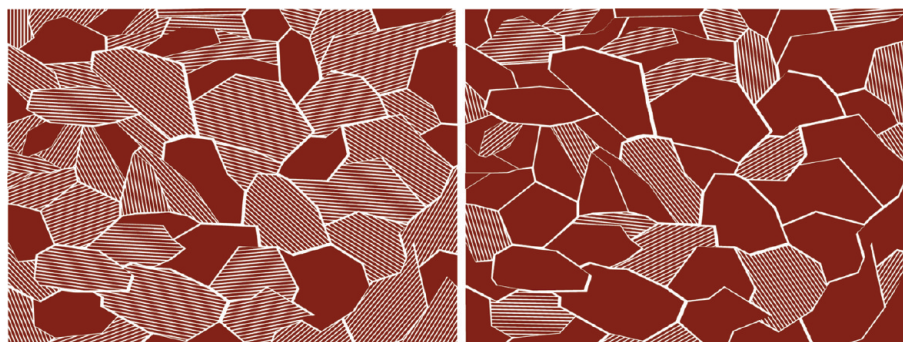


Figure 10. Clay structure maps for the simulations representing a heterogeneous mineralogical composition. Left: About 30% of the clay particles represent illites without interlayers. Right: The complementary 70% represent illite particles.

value of 0.5–0.6 obtained by Gonzalez et al.^{48,57} for montmorillonite at a similar density from a comparison of neutron scattering and macroscopic diffusion measurements. In this case, average D_p^{REV} equal to 5.4×10^{-10} and $3.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ were obtained for x and y directions, respectively. The anisotropy ratio of 1.69 ± 0.08 is lower than for the homogeneous diffusion coefficients. This can be explained by a combined effect of smaller diffusion coefficients in the interlayer compared to the edge regions and predominant orientation of the interlayers in the x direction. The faster diffusion along the edges in the y direction seems to compensate the effect of the slower diffusion in the interlayers in the x direction. The overall formation factors F are 4.26 and 7.19. Using the calculated average surface constrictivity for montmorillonite we derive the geometrical tortuosities G with values of 2.48 and 4.18.

It is worth mentioning that one and the same structure has been used for the simulations of pyrophyllite and montmorillonite with both homogeneous and heterogeneous local diffusion coefficients. Still the geometric tortuosity values derived from the simulations are different. This result illustrates a strong nonlinear coupling between the structure, local diffusivity in the pore space, and macroscopic diffusion in the media. The relations like eq 3 and eq 4 are too simplistic to hold generally for a complex structural environment.

Influence of Mineralogical Heterogeneities. In the previous simulations the clay structure map was composed of a single type of clay minerals, namely, either pyrophyllite or montmorillonite. In the next set of simulations, we considered the influence of heterogeneous mineralogy. We modified our reference structure map such that only a fraction of the clay particles are montmorillonites, while the rest are illites. Illites have no water-accessible interlayer space because the single layers are bound to each other by potassium ions. We mimicked illites by setting the interlayer diffusion coefficients of illite particles to zero. Such simulations allow assessing the contribution of the interlayers to the overall rate of transport. In addition to the previous series with 0% illites, we performed three sets of simulations with an illite fraction equal to ~30%, ~70%, and 100% of the particle area (Figure 10). Note that the change of montmorillonite particles with bulk dry densities of 1.9 Mg m^{-3} to illites with a density of 2.7 Mg m^{-3} leads to a reduction of the total porosity and an increase of the bulk dry density, as indicated in Table 3. To simplify the analysis of the results, we again assigned the diffusion coefficient of water $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ to all types of the porosity. We obtained sample-average diffusion coefficients $D_p^{\text{REV}} = 8.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the x direction and $D_p^{\text{REV}} = 5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in the y direc-

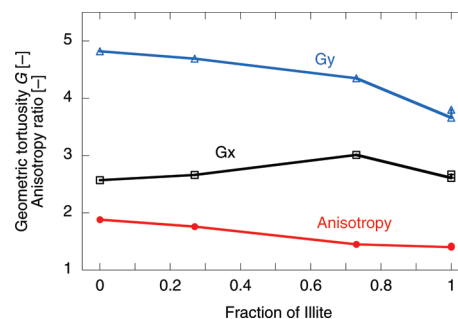


Figure 11. Geometrical tortuosities G as well as anisotropy ratios for varying fractions of illite without interlayers.

tion (30% illite), $D_p^{\text{REV}} = 7.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_p^{\text{REV}} = 5.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (70% illite), and $D_p^{\text{REV}} = 8.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_p^{\text{REV}} = 6.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (100% illite). From these coefficients, we calculated geometrical tortuosities G of 2.7 and 4.7 (30% illite), 3.0 and 4.4 (70% illite), and 2.6 and 3.7 (100% illite) in x and y direction, respectively. The latter values can be compared with the geometrical tortuosities G of 2.6 and 4.8 obtained for 0% illites and homogeneous local diffusion coefficients (Figure 11). We draw the following conclusions from the obtained results: (1) Increasing the fraction of illite and thus decreasing the interlayer porosity results in a decrease of the geometric tortuosity in the y direction. This is related to the mostly (sub)-horizontal orientation of the clay layers. Obviously, the interlayers slow the diffusion perpendicular to bedding in this case. (2) In polymineral illite–montmorillonite samples, the geometric tortuosity in x direction is slightly higher than in monomineral illite or montmorillonite samples. It seems that the mineralogical heterogeneity leads to a more complicated pore structure (including more dead-end pores) and thus to a larger tortuosity. (3) The anisotropy ratio increases steadily with the montmorillonite content or decreases with the illite content (Figure 11). This again is related to the mainly (sub)-horizontal bedding of the clay layers.

Anion Exclusion. So far, all simulations were done for water molecules that could access all open pores. Anions, in contrast, are partly rejected from the negatively charged clay surfaces. A more or less continuous decrease of the anion concentration is observed from an external electrolyte solution toward the charged surfaces. This function may be obtained from MD simulations in relation to the external solution composition and the bulk density of the sample or from other approximate solutions of the ion distributions around charged surfaces.⁶¹ We

simplified the continuous profile to a binary step function, where anions are completely excluded from regions within a given distance from the surface but can access the remaining pore space. We used an exclusion radius of 0.35 nm, which is consistent with the typically high salinities in natural clays. In this case, all interlayer pores of our montmorillonite clay structure model are effectively blocked for anions, in addition to a fringe of 0.35 nm around the external surfaces. The resulting anion-accessible porosity of 0.039 is smaller than the interparticle porosity. It is only 10% of the total porosity of 0.398, which is comparable with the values reported by van Loon et al.⁶² for chloride in montmorillonites at a density of 1.6 Mg m⁻³ and an intermediate ionic strength of the pore solution (0.1–0.4 M) or at a density of 1.9 Mg m⁻³ and a high ionic strength of the pore solution of 1 M.

We set the local pore diffusion coefficients equal to water diffusion along the edge $D_p^{\Omega}(x) = 1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (for a homogeneous local diffusion coefficient the results can be arbitrarily rescaled to match ion-specific $D_p^{\Omega}(x)$) and obtained sample-scale diffusion coefficients $D_p^{\text{REV}} = 4.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_p^{\text{REV}} = 2.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in x and y directions, respectively. This leads to the geometrical tortuosities G of 4.6 (x direction) and 7.2 (y direction) and the anisotropy ratio of 1.55. The diffusion coefficients are lower in both directions and the geometrical tortuosities G higher than those of a water tracer in the same sample (e.g., heterogeneous montmorillonite). This results from the inaccessibility of the interlayers and the partial exclusion of anions from the external pore space. When comparing the results of simulations for anions with the 100% illite sample, where only the interlayers were blocked, we see that the partial exclusion from the external pores has a significant effect on diffusion of the anions in both directions. In fact, the geometrical tortuosity G for anions perpendicular to bedding is clearly larger than that of a water tracer in montmorillonite, whereas just blocking of the interlayers (water tracer in 100% illite) had the opposite effect. Furthermore, the anisotropy ratio for anions is clearly smaller than that for a water tracer in the same montmorillonite sample. It is about similar to that in the samples of illite, which means that the partial exclusion from the external pores had about similar effects on diffusion in x and y direction.

The anion-accessible porosity in clays depends on the composition of the pore water solution and specific properties of the studied anion. As water salinity decreases, the diffuse double layer at the surface of clay minerals broadens, and the anion-accessible porosity gets reduced. Eventually some of the pore throats may become inaccessible for anions, and the pore network may lose the interconnection. In our RW simulations, the extent of the diffuse double layer is controlled by the size of the fringe, which has to be adjusted for specific anion properties, clay composition, and pore water chemistry. If the fringe size is such that the pore network is noncontinuous our random walk simulation will correctly predict zero-effective diffusion coefficient. Thus, tuning the structure map and fringe size to the system of interest the conditions for the diffusion percolation threshold can be determined.

SUMMARY AND CONCLUSIONS

We presented a two-step simulation approach which enables us to derive the average diffusion coefficient of water and ions in complex, heterogeneous porous media based on the results of molecular simulations performed in this study and reported in

the literature. The obtained average diffusion coefficients are ready to be used as input parameters for continuum diffusion equations. We have shown on an instance of a simplified system that the proposed approach produces results for a complex porous medium identical to those which would be obtained by direct molecular dynamics simulations. While the direct molecular simulations can handle systems with a size up to a few nanometers, our up-scaling approach is capable of treating systems in the micrometer scale or even larger with very complex structure.

We applied our simulation technique to an idealized poly-mineral structure map containing montmorillonite and/or illite particles. By varying the values of the diffusion coefficients in the pore space and modifying the accessible porosity, we investigated the effects of the structure of the pore space, and notably of mineralogical heterogeneities and type of tracer and fluid chemistry, on the macroscopic diffusion coefficients in the sample. We derived tortuosities, constrictivity, and anisotropy ratio for the given structure map. We observed that consistent with experimental evidence the interlayer diffusion in a sample with a preferred orientation of the clay layers along the bedding considerably slows diffusion perpendicular to bedding and thus is responsible for an increased anisotropy ratio compared to a sample without interlayers, as for instance illite. Finally, we showed that the diffusion of anions through the montmorillonite sample is strongly reduced by the partial exclusion from the external pores (in addition to the exclusion from the interlayers) and that the anisotropy ratio is lower as compared to a water tracer mainly because of complete exclusion from the interlayers.

We found that the clay structure map which we used in the present simulations leads to values in a range comparable to those measured but does not match exactly some transport properties of real media. The geometry factors G calculated for a montmorillonite structural map are similar to experimental values for illites or kaolinites and to experimental values for bentonites at somewhat smaller bulk densities but somewhat lower than experimental values for montmorillonites at the same densities. These discrepancies can be explained by the imperfection and the simplicity of the clay structure map used in the simulations. Some generally unknown details of the pore-scale structure such as the closeness of the contacts between different particles are important for the overall results. The sample map used in the simulations, $200 \times 150 \text{ nm}^2$, is small. For this size, larger circularities of the particles than for real samples had to be used, and the characteristic distribution functions (notably the particle sizes) had to remain relatively narrow. Real samples are likely to have larger structural heterogeneities and broader distributions of particle sizes and shapes, which will lead to larger tortuosities. These discrepancies will be addressed in the future by using a representative set of structure maps tailored to a specific sample.

The suggested up-scaling approach is very robust, versatile, and capable of unraveling the relation between structural and diffusion properties of very complex porous media. In the future we will focus on developing an algorithm for automated generation of structure maps, which will enable tailoring the simulation setup to specific clay samples. Investigating larger samples, possibly including heterogeneities on the next higher level, is a second direction for future development. Besides this, further work improving the high-resolution, pore-scale description will be required to strengthen this up-scaling approach.

So far we have considered the mobility of water in porous media or of aqueous ions at chemical equilibrium. To describe the relaxation of a nonequilibrium system toward the equilibrium state the immobilization of ions due to strong site-specific sorption and/or incorporation into the solid phase need to be considered at the continuum scale through the source/sink term in eq 1, which accounts for the equilibrium ion distribution between aqueous (mobile) and sorbed (immobile) states. Technically speaking, site-specific ion sorption on the surface of minerals can also be included in the pore-scale random walk simulation.⁶³ The practical efficiency of both approaches will depend on the system-specific questions to be answered. Considering general-purpose simulation of multispecies transport with chemical reactions the coarse-grain description of the system that combines molecular simulations according to eq 5, pore scale modeling according to eq 6, and continuum transport simulations will be most robust.

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