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Modeling diffusion and adsorption in compacted bentonite: a critical review

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Abstract

The current way of describing diffusive transport through compacted clays is a simple diffusion model coupled to a linear adsorption coefficient (K_d). To fit the observed results of cation diffusion, this model is usually extended with an adjustable "surface diffusion" coefficient. Description of the negative adsorption of anions calls for a further adjustment through the use of an "effective porosity". The final model thus includes many fitting parameters. This is inconvenient where predictive modeling is called for (e.g., for waste confinement using compacted clay liners).

The diffusion/adsorption models in current use have been derived from the common hydrogeological equation of advection/dispersion/adsorption. However, certain simplifications were also borrowed without questioning their applicability to the case of compacted clays. Among these simplifications, the assumption that the volume of the adsorbed phase is negligible should be discussed. We propose a modified diffusion/adsorption model that accounts for the volume of the adsorbed phase. It suggests that diffusion through highly compacted clay takes place through the interlayers (i.e., in the adsorbed phase). Quantitative prediction of the diffusive flux will necessitate more detailed descriptions of surface reactivity and of the mobility of interlayer species.

Keywords: Bentonite; Diffusion; Models; Mechanisms

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1. Introduction

Compacted clay engineered barriers are one of the serious options for the confinement of high-level toxic or radioactive waste (e.g., Nowak, 1980). The very low permeability of the clay barrier is expected to lengthen the lifetime of the waste packaging (canisters) and slow down the consequent release of contaminants. Low porosity, slow diffusive transport, high adsorption of cations, and plasticity/swelling (self-healing of fractures) are among the interesting properties of bentonite clays.

Any transport model to be used in performance assessment must be able to account for the results of small-scale diffusion experiments in the lab, but must also be grounded in the mechanisms of adsorption and diffusion so that the necessary extrapolation over time, distance (over 4 orders of magnitude in both), and environmental conditions (higher temperatures, near-saturation concentrations) can be meaningful. The following is a discussion on the modeling of diffusion through reactive pore networks, with the aim of devising a model better adapted to the particularities of highly compacted bentonite (at ca. 2 kg/l of bulk dry density).

2. State of the art diffusion through compacted bentonite

The current way of describing a diffusive flux F through a pore network is through Fick's law (with D_{free} as the diffusion coefficient in pure water), with corrections for porosity ε and tortuosity τ:

$$\varepsilon\frac{\partial C}{\partial t}=-\frac{\partial F}{\partial x_i}=\frac{\partial}{\partial x_i}\left[\frac{\varepsilon D_{\mathrm{free}}}{\tau^2}\frac{\partial C}{\partial x_i}\right] \tag{1}$$

If the diffusing species can be adsorb to the surface, a transient term $\rho_{\mathrm{b}}\partial q/\partial t$ (accumulation of adsorbed species) must be added to the left-hand side of the equation (ρ_{b} is the bulk dry density of the porous material). At low surface coverage, we can approximate q (moles adsorbed per mass of solid) as linearly related to C (moles in solution per volume of free liquid):

$$q=K_{\mathrm{d}}C \tag{2}$$

Combining the two, the classical diffusion/adsorption equation (e.g., Torstenfelt et al., 1985) can be written as:

$$[\varepsilon+\rho_{\mathrm{b}}K_{\mathrm{d}}]\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left[\frac{\varepsilon D_{\mathrm{free}}}{\tau^2}\frac{\partial C}{\partial x_i}\right] \tag{3}$$

When solid properties (ε, ρ_{b}, and τ) and adsorption coefficient K_{d} (a function of pH and concentration of main background ions) are constant in time and space, this equation can be solved analytically because the apparent diffusion coefficient D_{a} is constant:

$$\frac{\partial C}{\partial t}=D_{\mathrm{a}}\frac{\partial^2 C}{\partial x_i^2}\ \text{where}\ D_{\mathrm{a}}=\frac{D_{\mathrm{free}}}{\tau^2}\frac{\varepsilon}{\varepsilon+\rho_{\mathrm{b}}K_{\mathrm{d}}} \tag{4}$$

However, this model has been observed to underpredict the diffusion of cations, notably "hard" Lewis acids, e.g., Cs^+ or Sr^{2+} (e.g., Soudek et al., 1983). This is often interpreted as due to the diffusion of adsorbed species along the surface (e.g., Soudek et al., 1983; Muurinen and Lehikoinen, 1995). Using a semiempirical "surface diffusion" coefficient D_{surf}, the equation becomes:

$$[\varepsilon + \rho_{\mathrm{b}} K_{\mathrm{d}}] \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left[\frac{\varepsilon D_{\mathrm{free}}}{\tau^2} \frac{\partial C}{\partial x_i} + \frac{\rho_{\mathrm{b}} D_{\mathrm{surf}}}{\tau_{\mathrm{surf}}^2} \frac{\partial q}{\partial x_i} \right] = \frac{\partial}{\partial x_i} \left[\frac{\varepsilon D_{\mathrm{free}} + D_{\mathrm{surf}} \rho_{\mathrm{b}} K_{\mathrm{d}}}{\tau^2} \frac{\partial C}{\partial x_i} \right] \tag{5}$$

where by lack of a better description, the tortuosity of pore and surface paths are generally considered equal.

However, as pointed out by Van Schaik et al. (1966), only a fraction of the adsorbed species (those adsorbed through a diffuse-layer mechanism) should diffuse along the surface. The simple K_{d} linear adsorption model does not distinguish between diffuse-layer and specific adsorption (see e.g., Eriksen et al. (1999), in the light of the spectroscopic data of Chen and Hayes (1999)). This could account for the lack of predictive power of the surface diffusion model, with D_{surf} used as a free parameter for fitting results of apparent diffusion vs. K_{d}.

Negative adsorption of anions—electrostatic anion exclusion from the diffuse-layer due to the negative charge of the solid—calls for a further adjustment through the use of an "effective porosity" (defined by analogy with the concept of effective porosity in hydrogeology, where it accounts for the way that a fraction of the porosity does not participate in the advective transport). This treatment can be found, for example, in Muurinen et al. (1988):

$$\varepsilon_{\mathrm{eff}} \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left[\frac{\varepsilon_{\mathrm{eff}} D_{\mathrm{free}}}{\tau^2} \frac{\partial C}{\partial x_i} \right] \tag{6}$$

However, as pointed out by Muurinen et al. (1988), Oscarson et al. (1992), Whitworth and Fritz (1994), or Lehikoinen et al. (1995), anion exclusion should vary with ionic strength and the charge of the anion in question. This cannot be predicted using an adjusted effective porosity. Furthermore, it is curious that electrostatic attraction and repulsion from the diffuse-layer are modeled in completely different ways (a K_{d} coefficient with surface diffusion in one case, an effective porosity in the other) despite their common mechanism.

3. Discussion

3.1. Volume of the adsorbed phase

The porosity of compacted smectite is not as simple as that described by the classical diffusion/adsorption model. Smectite layers stack up to form particles (on the order of 10 layers per stack), where the interlayer space is available as porous volume (responsible for the swelling of smectites). Compacted smectite will then have two porosities: large pores between the clay particles, where diffusion can take place relatively unaffected by the surface, and very thin interlayer pores (two or three water molecules thick, e.g., Fripiat et al. (1982) and Torikai et al. (1996)), where diffusion will be very much affected by the surface (cations are attracted to the interlayers, anions are repulsed, the "ionic strength" of this interlayer solution is very high, much of the water present belongs to the solvation shell of the cations). Diffusion should take place differently in these two volumes, and compaction should have a different impact on them (the interlayer pores are difficult to "squeeze" further, so early compaction should affect mostly the "free" porosity). It seems logical to attempt to represent these two porosities separately. According to current understanding of the thickness of diffuse-layer and the extent (observed by spectroscopy) to which the interlayer is affected by the negative charge of the solid aluminosilicate layers, we can assign the interlayer volume to the adsorbed phase. The interlayer solution has properties (activity of the water molecules, density, viscosity, concentrations of cations and anions, etc.) distinct from that of the "free" solution in the larger pores. Here we will name this interlayer volume "adsorbed" or "diffuse-layer" porosity, the larger pores being then termed "free" porosity.

Note that we choose here to define adsorption not as a Gibbs surface excess, but according to location of the "adsorbed" species. This is practical for purposes of modeling the transport, and is possible here because the boundary between interlayers and free porosity is sufficiently clear.

Arguably, the interlayer volume does not make up the whole volume of the adsorbed phase. For montmorillonite particles, about 90% of the surface area are turned inward towards the interlayers. Of the remaining outer surface area, about 90% should be made-up of basal planes, whose diffuse-layers will become similar to interlayers upon compaction. We neglect the ca. 1% of edge surface area and its accompanying diffuse-layer.

Montmorillonite should have a specific surface of the order of 800 m^2/g, as in Papelis and Hayes (1996), and according to Madsen (1998), the MX-80 bentonite used in our experiments contains at least 75% montmorillonite. If the interlayer spacing of a compacted Na–montmorillonite is 0.58 nm (corresponding to the two-layer hydrate), as observed by Kozaki et al. (1997), above 1.4 kg/l of dry density, and even if we neglect approximately 10% of the total surface of the montmorillonite particles, which is not turned towards the interlayer volume, that volume would still be at least 160 mm^3/g of solid. The volume fraction occupied by the interlayer space can then be linked to the dry bulk density of the compacted bentonite:

$$\varepsilon_{\mathrm{ilayer}} \approx 0.16\rho_{\mathrm{b}} \tag{7}$$

Using the montmorillonite composition from Madsen (1998) for the MX-80 bentonite, we can also estimate the volume fractions occupied by the solid and the free phase (Fig. 1). Inserting this in the original diffusion/adsorption equation, and supposing the flux through the interlayers to be negligible, we reach the following expression:

$$[1 - 0.55\rho_{\mathrm{b}} + \rho_{\mathrm{b}}K_{\mathrm{d}}]\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left[\frac{D_{\mathrm{free}}(1 - 0.55\rho_{\mathrm{b}})}{\tau^2}\frac{\partial C}{\partial x_i}\right] \tag{8}$$

The free phase—and the diffusive flux—should then disappear as the dry density of compaction reaches approximately 1.8 kg/l. This is in good agreement with results of

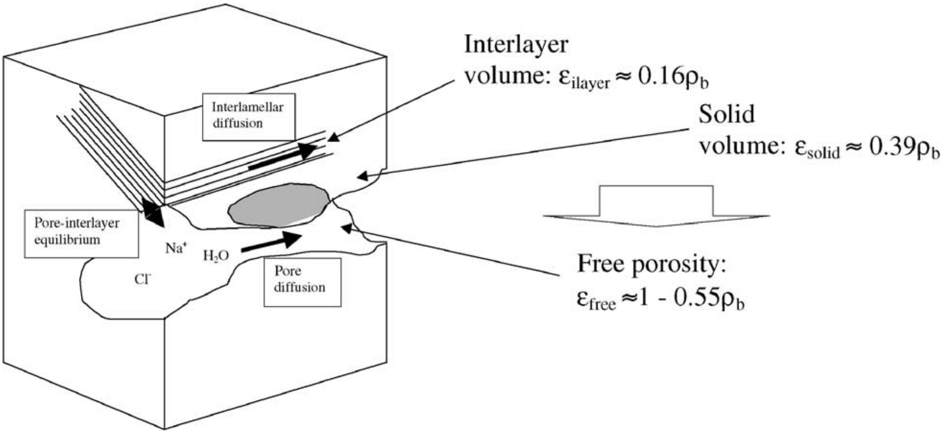

Fig. 1. Elementary volume of compacted bentonite, with estimates of the volume fractions of interlayer porosity, free porosity, and solid material.

apparent diffusivity vs. dry density of compaction from Kim et al. (1993) on the MX-80 bentonite (Fig. 2). The classical diffusion/adsorption model, which makes no difference between free and interlayer porosity, would use $\varepsilon \approx 1 - 0.39\ \rho_b$ (instead of $1 - 0.55\ \rho_b$), and thus fail to explain the clear change in the diffusion regime at 1.8 kg/l dry density. This leads its proponents to use τ as a fitting parameter that increases to very high values (up to 50) as the dry density approaches 1.8 kg/l (e.g., Ochs et al., 2001).

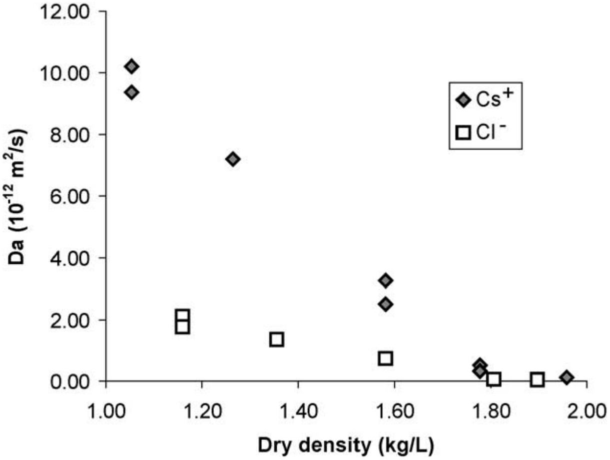

Fig. 2. Apparent diffusivity vs. dry density of compaction for Cs^+ and Cl^- diffusion through the MX-80 bentonite clay, from Kim et al. (1993).

Above 1.8 kg/l of bulk dry density, as the free porosity disappears, fluxes through the interlayer porosity will no longer be negligible. This meets comments by Pusch et al. (1990) and Madsen (1998), as well as experimental results from Okamoto et al. (1994), Torikai et al. (1996) and Kozaki et al. (1999). Kato et al. (1995) have built an interesting model based on diffusion only through the interlayers, although the lateral concentration profiles that they suggest in the interlayers do not fit spectroscopic or molecular modeling results (e.g., Boek et al., 1995). Finally, diffusion through the interlayers, from which anions are partly excluded, explains the membrane behavior of compacted clays (membrane potential, osmosis,. . .) observed by Elrick et al. (1976), Fritz (1986), or Keijzer et al. (1999).

In order to reach 2.0 kg/l of bulk dry density, the interlayers must be compacted to a width of less than 0.58 nm. Interlayer cations might then not form a full hydration sphere. Adsorption mechanisms should be affected (more outer- or inner-sphere adsorption, less diffuse-layer adsorption), as well as ion-exchange selectivity to the surface. Sodium, for example, does not compete well against cesium because the latter dehydrates more easily to form inner-sphere complexes, but if compaction forces a partial dehydration of the sodium, this handicap might be overcome (e.g., the results of Oscarson et al., 1994).

3.2. Mobility in the interlayer phase

Results from spectroscopy and molecular dynamics models show that ions adsorbed in the interlayers in a diffuse or outer-sphere position (hard to distinguish in this case because the interlayers are so thin) have diffusion coefficients not much lower than in a free solution, whereas species that loose some of their hydration sphere to form inner-sphere complexes (e.g., cesium) are temporarily immobilised (e.g., Chang et al., 1999; Sposito et al., 1999; Marry, 2001).

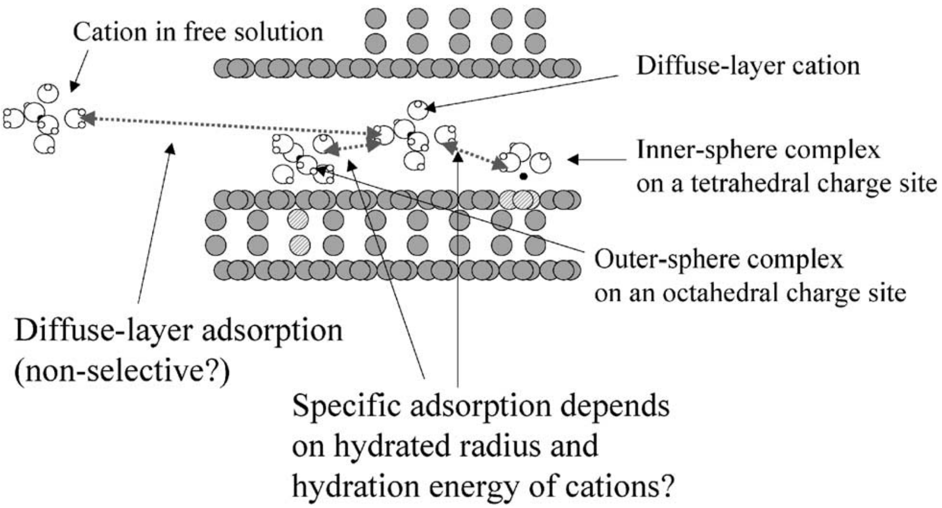

Fig. 3. Diffuse-layer, outer-sphere, and inner-sphere interlayer adsorption.

Accounting for a possible diffusion of species adsorbed in the interlayers according to a diffuse-layer mechanism (e.g., Van Schaik et al., 1966), we can extend the previous model:

$$\varepsilon_{\text{free}}\frac{\partial C}{\partial t}+\rho_{\text{b}}\frac{\partial q}{\partial t}=\frac{\partial}{\partial x_i}\left[\frac{D_{\text{free}}\varepsilon_{\text{free}}}{\tau^2}\frac{\partial C}{\partial x_i}+\frac{D_{\text{dl}}\varepsilon_{\text{ilayer}}}{\tau^2_{\text{ilayer}}}\frac{\partial C_{\text{dl}}}{\partial x_i}\right] \tag{9}$$

where C_{dl} is the concentration adsorbed in the interlayers by a diffuse-layer mechanism. As noted above, $\varepsilon_{\text{free}}$ should disappear above ca. 1.8 kg/l of dry density. This simplifies to:

$$\rho_{\text{b}}\frac{\partial q}{\partial t}=\frac{\partial}{\partial x_i}\left[\frac{D_{\text{dl}}\varepsilon_{\text{ilayer}}}{\tau^2_{\text{ilayer}}}\frac{\partial C_{\text{dl}}}{\partial x_i}\right] \tag{10}$$

Finally, if diffusion happens only through the interlayers, the clay should act as a semipermeable membrane due to the partial exclusion of anions. Variations in the electrostatic potential ψ_{clay} could develop across the clay barrier, affecting the flux according to the charge z of the species in question (a similar term is used by Olin et al., 1994). Revil (1999) also shows the theoretical importance of this effect. We can write as follows:

$$\rho_{\text{b}}\frac{\partial q}{\partial t}=\frac{\partial}{\partial x_i}\left[\frac{D_{\text{dl}}\varepsilon_{\text{ilayer}}}{\tau^2_{\text{ilayer}}}\left(\frac{\partial C_{\text{dl}}}{\partial x_i}+C_{\text{dl}}\frac{zF}{\text{RT}}\frac{\partial \psi_{\text{clay}}}{\partial x_i}\right)\right] \tag{11}$$

Such a model should approach the mechanisms that take place within a highly compacted clay membrane. There is hope that the various parameters can be determined independently and not by empirical fit:

τ_{ilayer}	Because the interlayers have a known shape, a theoretical evaluation of the tortuosity of interlayer paths might be possible—e.g., Kato et al. (1995).
C_{dl}	At a boundary where the compacted clay is in contact with a free solution, we can write an adsorption equilibrium between the concentration C in the bounding solution and the diffuse-layer concentration C_{dl} in the clay interlayers adjacent to the boundary. This could be described as a purely electrostatic phenomenon, as in Kraepiel et al. (1999): $C_{\text{dl}}=C\mathrm{e}^{-\frac{zF}{\text{RT}}(\psi_{\text{clay}}-\psi_{\text{free}})}$ (12) where $(\psi_{\text{clay}}-\psi_{\text{free}})$, the difference in electrostatic potential between the free solution and the clay interlayers, is such that charge balance is conserved across the boundary (i.e., it keeps anions from diffusing into the clay interlayer, and keeps cations from diffusing out). In this way, anion exclusion and the semipermeable properties of clay membranes are described at the boundary of the compacted clay.
ψ_{clay}	All the potential gradients $\partial\psi_{\text{clay}}/x_i$ must be such that no net flux of charge takes place. The model should adjust all the potential gradients during each time-step to fulfill this condition (through iterative calculation, probably). This would further allow the model to predict the evolution of a membrane potential between "upstream" and "downstream" free solutions, as observed by Elrick et al. (1976).

q	A more complete description of adsorption processes must be achieved so that total adsorbed quantities q can be linked to diffuse-layer concentrations C_{dl}. Progress has been made in distinguishing the various sites and mechanisms that contribute to the total adsorption onto smectites, thanks to progress in spectroscopic methods—e.g., Chisholm-Brause et al. (1994), Papelis and Hayes (1996), Kim et al. (1996), Di Leo and O'Brien (1999), Schlegel et al. (1999), Sylwester et al. (2000)—and molecular modeling—e.g., Delville (1991), Chang et al. (1999)—adsorption studies covering a wider range of conditions—e.g., Papelis and Hayes (1996), Turner et al. (1996), Baeyens and Bradbury (1997), Turner et al. (1998), Onodera et al. (1998)—and the development of mechanistic models—for recent works, see for example Stadler and Schindler (1993), Zachara and Smith (1994), Turner et al. (1996), and Kraepiel et al. (1999). These studies have mostly clarified the separation between edge and interlayer adsorption. Inside the interlayers, different adsorption mechanisms are difficult to distinguish. The conceptual difference between diffuse-layer species (mobile) and outer-sphere complexes (immobile) is not very pronounced (Fig. 3). Furthermore, none of the studies above addresses the effect of compaction upon the various adsorption processes.
D_{dl}	To some extent, the interlayer space of montmorillonite should be comparable to a solution of high ionic strength—e.g., Sposito et al. (1999). The properties of interlayer water are different from those of pure liquid water. What correlation should be used to account for this in assessing interlayer diffusion coefficients? Molecular dynamics simulations could be a useful tool to reconstruct the diffusion of these interlayer species.

4. Conclusion

The free porosity must be correctly determined, not forgetting to subtract the interlayer porosity. This eliminates the need to use tortuosity as a fitting parameter to describe results of diffusion at different degrees of compaction. It also explains the semipermeable membrane behaviour of bentonite at higher degrees of compaction. But the rapid diffusion of hard acids vs. soft ones at equivalent values of K_{d} cannot yet be interpreted; interlayer diffusion may be fast enough that it is not negligible compared to diffusion through the free porosity, or slow enough that adsorption into the interlayers is limited by interlayer diffusion kinetics (in both cases leading to an increased diffusive flux of cations that should adsorb by cation-exchange). The assessment of interlayer diffusion coefficients is problematic because the interlayer solution is very different from pure liquid water.

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