Chapter 5

Molecular Models of Radionuclide Interaction with Soil Minerals

Randall T. Cygan

Geochemistry Department
Sandia National Laboratories
Albuquerque, New Mexico 87185-0750, U.S.A.
rtcygan@sandia.gov

INTRODUCTION

Experimental attempts to develop a fundamental understanding of the physiochemical processes that control the interactions of radionuclide species with soil minerals are often fraught with difficulties. Soil phases, including clays and other hydrous compounds, are typically characterized by sub-micron grain size, complex and multicomponent compositions, isomorphic substitutions, heterogeneous structures, large unit cells, low symmetry, site disorder, defects, lack of long-range order, variable hydration states, and complex surface speciation. It is therefore not surprising that these phases are far from the ideal state needed to provide quality and unambiguous results from standard characterization and spectroscopic methods. Fortunately, molecular modeling methods, in recent years, have matured to an extent where they can provide significant benefit to the soil scientist and geochemist in the evaluation of sorption and interactions of radionuclides with soil phases.

Molecular simulation techniques provide controlled procedures to discriminate among various competing models to explain the macroscopic observations of experiment and field studies. Computer modeling allows the soil chemist to reduce the complex nature of a sorption process to several possible structural models that can be tested using several molecular modeling tools to evaluate the local geometry, binding energy, potential reactions, transition states, and even produce diffraction patterns, and vibrational and other spectra. Results of the various structural models can then be compared with each other and with the results from experimental observations to form a more detailed conceptual model of sorption. Assuming a valid and accurate molecular model, it is even possible to model the behavior of soil phases at conditions that are not achievable by experimental means or are not observable in the field. Ultimately, any

success in applying molecular modeling in these research areas must rely on a thorough understanding of the theory and knowledge of the limits of each method. Furthermore, the modeler must provide suitable validation of the models through numerous tests and applications. It is important to remember that a model may be right or wrong, but it might also be irrelevant.

This chapter provides an overview of the theory and methods of molecular modeling and molecular simulation, and reviews applications involving soil minerals. The first section includes a review of the basic theory and then describes the molecular modeling methods that are in common use today. The second part of the chapter presents a review and discussion of several examples in which molecular models were used to evaluate the interactions of various radionuclides with commonly-occurring soil phases. Although a detailed review of molecular modeling methods is beyond the scope of this chapter, the reader is directed to the comprehensive and thorough reviews provided by Clark (1985) and Allen and Tildesley (Allen and Tildesley, 1987), and the excellent books by Frenkel and Smit (1996) and Leach (1996). The recent volume by Cygan and Kubicki (Cygan and Kubicki, 2001) is of particular interest in presenting a broad review of molecular modeling methods and providing numerous examples relating to mineralogical and geochemical processes.

THEORETICAL METHODS AND MODELING TOOLS

Molecular modeling methods rely on an accurate description of the potential energy of a chemical system. The energy forcefield may involve an empirical parameterization based on either experimental observables or on the results of quantum mechanical calculations. An analytical description of potential energy as a function of geometry typically requires the input of atomic structure and physical properties to be used to parameterize the coefficients of the energy expression. Alternatively, the energy forcefield may rely solely on the explicit calculation of energy through quantum calculations performed throughout a dynamics simulation. The latter approach, often referred to as quantum dynamics, or Carr-Parinello approach, is extremely costly and practical only in applications of limited size systems (see Hass et al., 1998 for a successful simulation of an unusually large system). However, molecular modeling of the complex nature of soil phases, especially clay minerals, requires models of bulk structures or representative surfaces that often incorporate hundreds if not thousands of atoms. In these cases, and even with access to some of the most advanced supercomputers, first principles quantum methods are impractical. Therefore, almost all molecular modeling studies of soil minerals to date involve the use of energy forcefields to describe the potential energy of the system.

Potential Energy

The total potential energy of a chemical system is typically represented by the following energy components:

$$E_{Total} = E_{Coul} + E_{VDW} + E_{Bond\ Stretch} + E_{Angle\ Bend} + E_{Torsion} \qquad [1]$$

where E_{Coul} and E_{VDW} represent the Coulombic and van der Waals energy and collectively are referred to as the nonbonded energy of the system. The last three terms represent the bonded

energy components associated with bond stretching, angle bending, and dihedral torsion, respectively. The Coulombic energy, or electrostatics energy, is described by the classical description of interacting charged particles and varies inversely with the distance r_{ij}:

$$E_{Coul} = \frac{e^2}{4\pi\varepsilon_o} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \qquad [2]$$

Here, q_i and q_j represent the charge on the two ions, e is the electron charge, and ε_o is the permittivity of a vacuum. The summation ensures that all atom-atom interactions are counted while avoiding duplication. As expected, Eqn. [2] provides negative energies for the attraction of atoms (ions) of opposite charge, and positive energy for repulsion of atoms (ions) having charges of like sign. Atoms are effectively treated as single point charges, which in practice is equivalent to having the atoms behave as spherical-shaped and rigid bodies.

Due to the long-range nature of Eqn. [2], the electrostatics contribution to the total energy must be properly determined to provide convergence for the case of materials having long-range order. This is problematic for crystalline compounds where the $1/r$ term is nonconvergent except for the most simple and highly symmetric crystals. Typically, molecular modeling techniques employ the Ewald method (Ewald, 1921; Tosi, 1964) for periodic systems in which the inverse function is replaced by a Laplace transform that is decomposed into real space and reciprocal space components which combined provide rapid convergence of the Coulombic energy. The need for an accurate determination of the Coulombic energy component is paramount in the analysis of radionuclide-substrate interactions due to the dominant role of electrostatics in controlling sorption processes. The covalent bonding associated with most molecules such as organic compounds—as opposed to the predominantly ionic bonding of minerals—requires the evaluation of the electrostatics as some partial charge character is maintained on atom centers.

This is especially important for the proper evaluation of molecule-molecule interactions in liquid, solution, or even within the interlayer of a clay. In these cases, the Coulombic energy can be evaluated by direct summation using Eqn. [2] without resorting to an Ewald summation.

The second nonbonded energy term involves the van der Waals interactions as represented by the Lennard-Jones expression:

$$E_{VDW} = \sum_{i \neq j} D_o \left[\left(\frac{R_o}{r_{ij}} \right)^{12} - 2 \left(\frac{R_o}{r_{ij}} \right)^6 \right]$$ [3]

where D_o and R_o are empirically-derived parameters that relate to the dissociation energy and the equilibrium distance, respectively. This function includes the short-range repulsion that occurs as two atoms approach each other ($1/r^{12}$ term), and the attractive force (London dispersion) associated with the fluctuations in electron density on adjacent atoms ($-1/r^6$ term). Several equivalent forms of Eqn. [3] are used in the molecular modeling literature based on the choice of fitting parameters. Additionally, other functional forms for the short-range interactions exist including the 9-6 function (two parameter) and the exponential-6 function (three parameter). Fundamentally, the exact form of these short-range energy functions are not critical as long as the resulting energy accurately describes the atomic interactions. An excellent discussion of the various forms of the van der Waals energy expression is provided by Halgren (1992).

A further refinement of the nonbonded energy terms that is often implemented in the modeling of ionic solids—where the first two terms of Eqn. [1] are sufficient for describing the total energy—is the incorporation of a shell model (Dick and Overhauser, 1958). This approach introduces a polarization energy term to account for the shift in the electronic cloud of an ion as induced by the local electrostatic field. The shell model uses two point charges joined by a harmonic spring to represent the polarization as a negatively-charged shell is shifted away from a

positively-charged core. This refinement dramatically helps to improve the modeling of the

structures and properties of various oxides and silicate phases having significant covalent

character (e.g., Lewis and Catlow, 1986), and is useful for the evaluation of certain surface

structures, and elastic, dielectric, defect, and diffusion properties of materials.

The addition of bonded energy terms to the total potential energy is important for

molecular models of compounds characterized by strong covalent bonds. Models of organic

compounds typically incorporate one of several functions to describe the energy as a bond

compresses or stretches about an equilibrium distance. A simple quadratic expression is

typically used:

$$E_{Bond\ Stretch} = k_1(r - r_o)^2 \tag{4}$$

where r is the atom-atom separation distance, r_o is the equilibrium bond distance, and k_1 is an

empirical force constant. The potential well also describes the energy constraints associated with

the vibration of atoms about the equilibrium bond distance, and often vibrational spectra are used

to derive the force constant. More refined models for bond stretching interactions include the

Morse potential in which the physical dissociation of a bond is allowed at large separation

distances:

$$E_{Morse} = D_o \left[1 - \exp\{1 - \alpha(r - r_o)\} \right]^2 \tag{5}$$

D_o is the equilibrium dissociation energy and α is a parameter related to the vibrational force

constant. The bond stretch energy will also be important in periodic systems in which covalent

bonds occur, for example, organic solids or inorganic compounds involving molecular anions

such carbonate, nitrate, or phosphate phases. In addition, soil minerals where water or hydroxyl

groups exist will often require Eqn. [4] or Eqn. [5] to accurately describe O-H behavior. To date,

only a few studies have modeled water behavior in soil minerals. These include the analysis of the bulk structure and swelling of clay minerals (Cygan et al., 2001) and the sorption and swelling of layered hydroxides including hydrotalcite (Kalinichev et al., 2000; Wang et al., 2001).

Additional bonded terms for the total energy include expressions for angle bend and torsion to assist in controlling the geometries for, respectively, three-body and four-body interactions:

$$E_{Angle\ Bend} = k_2 (\theta - \theta_o)^2 \qquad [6]$$

$$E_{Torsion} = k_3 (1 + \cos 3\varphi) \qquad [7]$$

Here, θ is the bond angle for a triad of sequentially-bonded atoms, θ_o is the equilibrium bond angle, ϕ is the dihedral angle for a quartet of sequentially-bonded atoms, ϕ_o is the equilibrium dihedral angle, and k_2 and k_3 are empirical force constants. These two terms effectively maintain bond geometries for various atom hybridization such as tetrahedral sp^3 carbons in alkanes, or planar sp^2 carbons in alkenes. Additionally, these terms are often used to describe angle bending for metal hydroxyl groups or out-of-plane torsion for carbonate groups. More complex potential energy expressions, often incorporating cross-term coupling of the bonded terms, can be incorporated into the total potential energy expression (e.g., Dauber-Osguthorpe et al., 1988). The functionality of these forcefields will only be limited by the quality and accuracy of the data used to parameterize the potential functions, which however often is lacking for the more complex nature of soil phases.

An important part of the potential energy forcefield is the assignment of partial charges for each atom type. Purely ionic models incorporate the formal charge of the atom as would be

expected for the localization of charge on the atom center. However, most chemical systems are non-ionic and require the partitioning of charges among the constituents. There are various schemes available to assign partial charges, one of the more common being the charge equilibration scheme of Rappé and Goddard (1992). This approach incorporates bond geometry, ionization potentials, electron affinities, and radii of the component atoms to derive partial charges, and can be applied in a dynamic fashion throughout a molecular simulation. Other simpler empirical schemes involve coordination, connectivity, and bond order to assign partial charges. Deformation electron densities derived from high-resolution X-ray diffraction analysis (e.g., Coppens, 1992; Spasojevicde-Bire and Kiat, 1997) can provide accurate partial charge assignments for inorganic solids. However, one of the most convenient approaches is to use quantum mechanics to derive Mulliken (Mulliken, 1955) or electrostatic potential (ESP) charges (Breneman and Wiberg, 1990; Chirlian and Francl, 1987). The significance of partial charge assignments cannot be overstated; accurate charges are critical in the evaluation of sorption processes where electrostatic dominate and control the behavior of radionuclides interactions with soil minerals.

Forcefields

Although the scientific literature has several general energy forcefields available for the molecular simulation of organic molecules (e.g., Dauber-Osguthorpe et al., 1988; Maple et al., 1994; Sprague et al., 1987; Weiner et al., 1984), only a few of the forcefields have been parameterized to model inorganic compounds, mostly aluminosilicate zeolite materials used in catalysis applications (e.g., Hill et al., 1994; Hill and Sauer, 1995; Rappé et al., 1992). Unfortunately, of the latter, none of the energy forcefields are satisfactory for the molecular

simulation of complex oxides such as clays and associated soil minerals. The structures and physical properties of layered compounds are not included in the database used in the parameterization scheme for the forcefield. Furthermore, clays and other layered soil phases are unique in having aluminum in octahedral coordination. Their low symmetry and anisotropic electrostatic fields are not necessarily compatible with the forcefields derived for the more symmetric structures of the zeolite materials. For example, most theoretical studies of clay mineral structures and interlayer dynamics to date rely on maintaining a fixed or rigid clay layers during the simulation (Chang et al., 1995; Greathouse and Sposito, 1998; Karaborni et al., 1996; Skipper et al., 1995a; Skipper et al., 1995b; Smith, 1998). Unfortunately, these molecular models are unable to allow full relaxation of all atoms and conserve the energy and momentum during dynamical simulations.

Recently, Teppen et al (1997), recognizing the failings of previous forcefields for simulating clays, developed a set of potentials suitable for the simulation of dioctahedral clay minerals and related compounds. Based on the valence format (bonded model) originally developed by Hill and Sauer (1994; 1995), Teppen et al. (1997) reparameterized nonbonded terms, and developed a unique O-Al-O angle bend potential, based on the experimental refinements of representative clay minerals. In addition, improved partial charge assignments were derived from ESP charges of quantum mechanic calculations of cluster models, and from deformation electron densities derived from X-ray diffraction studies of oxide compounds. The modified forcefield provided accurate models of the heavy element structure of various phyllosilicate phases, and, using molecular dynamics techniques, produced an excellent model of the sorption of hexadecyltrimethylammonium ions (HDTMA$^+$) in the interlayer of the dioctahedral clay beidellite (Teppen et al., 1997).

A more recent forcefield designed for application to clays and other hydrous phases was developed by Cygan et al. (2001) to simulate the bulk and surface structures and dynamics of hydroxides, oxyhydroxides, layered double hydroxides, and clays. The forcefield was designed specifically for the large-scale simulation of large simulation cells (up to tens of thousands of atoms), and therefore was based on a nonbonded interatomic potential (Eqn. [2] and Eqn. [3]) for the interaction of heavy atoms. The simplified nonbonded forcefield provides a computationally-efficient means for evaluating a significant number of configurational energies during large-scale simulations. Water and hydroxyl potentials from previous bonded and flexible potentials (Berendsen et al., 1981; Teleman et al., 1987) were used to provide a general and fully flexible hydrous forcefield. The forcefield provides similar structures of clays compared to the Teppen et al. (1997) that are in very good agreement with experimental structures. There is improvement in the disposition and behavior of hydroxyls in the clay structures compared to the previous clay forcefield.

Molecular Mechanics

The classical-based modeling methods are most attractive due to their relative efficiency in calculating total energies for various molecular configurations, especially in comparison to more sophisticated quantum chemical methods. The energetics and relative stabilities of various compounds can be assessed in this manner. Molecular mechanics includes those modeling methods that evaluate the energies through classical energy forcefield descriptions.

Conformational analysis

Conformers represent various arrangements of a particular molecular geometry that can be converted from one to another by rotation about a single bond, typically with energy barriers between stable and metastable configurations. Typical applications include the analysis of organic molecules and rotations about single carbon-carbon bonds. Cygan (2001b) discusses conformational analysis in detail and presents an example for the energy contributions for the various conformers of dichloroethane. More complex configurations for large organic molecules and large periodic systems can be easily examined using this technique.

Energy minimization

Geometry optimizations of molecules and periodic systems are achieved through the use of efficient energy minimization techniques. The procedure involves the repeated sampling of the potential energy surface for various system configurations until the potential energy minimum is obtained corresponding to a geometry where the forces on all atoms are zero. The energy of an initial configuration is first determined then the atoms and cell parameters (for periodic systems) are adjusted using derivatives of the potential energy to obtain a lower energy configuration. This procedure is repeated until suitable tolerances are obtained for the energy differences and derivatives between successive steps of the minimization. Repeated optimizations based on different initial configurations helps to ensure the identification of a global minimum configuration rather than a structure for a local minimum. An excellent description of the various minimization methods and algorithms is provided by Leach (1996).

An illustrative example of an energy minimum configuration is provided in Fig. 1 for the simple interaction of two rigid ions A and B of opposite charge. The plot presents the potential

energy of the system as a function of bond distance r_{AB} based on an interaction potential described by a Buckingham potential (Lewis and Catlow, 1986):

$$E_{AB} = \frac{q_A q_B}{r_{AB}} + A \exp(-r_{AB}/\rho) - \frac{C}{r_{AB}^6} \qquad [8]$$

The A, ρ, and C are empirical parameters and the ions are assigned two electron charges each. The short-range contribution to the potential energy is positive and rapidly increases at short distances; the dispersion term is ignored (C=0) for this example and therefore does not contribute to the total interaction energy. In contrast, the attractive Coulombic energy for the oppositely charged ions is negative and leads to stabilization as the two ions approach each other. The summation of the two energy terms leads to an energy minimum in the total potential curve that corresponds to the equilibrium separation distance (1.48 Å) for the ions. Alternatively, a Lennard-Jones expression (Eq. [3]) could be used to describe the short-range interactions.

This simple example demonstrates the approach used in more sophisticated methods to derive an energy-minimized configuration. However, rather than just examine two interacting atoms the optimization procedure will require tens to hundreds to perhaps thousands of interacting atoms. Special constraints can be imposed during the energy optimization. Molecular and crystallographic symmetry can be constrained or the atomic positions fixed. Periodic systems can have all cell parameters vary to simulate constant pressure conditions so that no net force occurs on the cell boundaries. Energy minimization procedures are also used in quantum mechanics to obtain optimized configurations. The algorithms are similar to those used discussed above but rather than obtain system energies using analytical forcefield methods the energies are obtained through one of several quantum-based calculations.

Monte Carlo methods

Stochastic analysis in molecular modeling usually entail the application of Monte Carlo methods to the analysis of the relative energies of a large number of possible structural configurations. Typically, a random sampling of the potential energy surface is performed in order to obtain a more practical selection of possible energy configurations. Energy-based criteria are used to sample in the sampling process and includes an option to accept configurations that might still might lead to a reasonable configuration for further analysis. The so-called Metropolis Monte Carlo method (Metropolis et al., 1953) has been successfully used in a variety of applications including the disposition of various species in zeolites: cation sites (Newsam et al., 1996), small organic molecules (Freeman et al., 1991), and inorganic gases (Douguet et al., 1996; Shen et al., 1999). There has also been substantial use of Monte Carlo methods to examine the interlayer of clay minerals. Much of this effort has been used to derive the structure and dynamics of interlayer water molecules and solvated cations due to the difficulty in obtaining this information through conventional experimental methods (e.g., Bridgeman and Skipper, 1997; Chang et al., 1995; Chang et al., 1997; Delville, 1991; Delville, 1992; Greathouse and Sposito, 1998; Skipper et al., 1991; Sposito et al., 1999).

Molecular dynamics

Molecular dynamics (MD) simulations provide a deterministic approach for evaluating the equilibrium and transport properties of a chemical system based on a classical description of the atomic interactions. Newton's equations of motion involving forces and velocities are iteratively solved to provide an evolving description of a large number of interacting atoms. A Boltzman distribution of velocities is imparted onto all or some of the atoms, and then velocities are scaled

to provide the mean kinetic energy for the system to meet the target temperature for the simulation. Forces are calculated based on the implemented forcefield, and then the motion equations are integrated over the selected time interval, usually one femtosecond or less. A Verlet algorithm (Verlet, 1967), or similar method, is used to calculate the new atomic positions and velocities that are then use to loop through the integration for the next time step. This procedure is then repeated for many interactions, typically on the order of several hundred thousand steps (tens to hundreds of picoseconds of simulation time), to obtain an equilibrium configuration. Allen and Tildsley (1987) and Frenkel and Smit (1996) provide details of the various approaches used in MD simulations. Quantum dynamics, or *ab initio* MD, methods are becoming increasingly common in the literature due to advances in computer platforms and faster supercomputers. Rather than use a classical forcefield, quantum dynamics incorporates, as the name implies, a quantum method to directly obtain the energy of the system (Car and Parrinello, 1985; Car and Parrinello, 1987; Tuckerman and Martyna, 2000). The high computation cost involved in these methods restricts their use to short simulation times, usually less than several picoseconds.

There are several excellent theoretical studies of clays that have used MD methods to examine the structure and dynamics of water, interlayer cations, and environmental contaminants (e.g., Greathouse et al., 2000; Hartzell et al., 1998; Kawamura et al., 1999; Miller et al., 2000; Shroll and Smith, 1999; Smith, 1998; Teppen et al., 1998a; Teppen et al., 1997; Yu et al., 2000). The agreement of theoretical swelling curves for various clay compositions with the results of experimental studies provides significant validation for the use of the simulations as predictive tools (Cygan, 2001b; Smith, 1998). Molecular dynamics simulations of double layered hydroxide materials have also been successfully completed to quantify the dynamic behavior of

interlayer water and anions (Aicken et al., 1997; Kalinichev et al., 2000; Wang et al., 2001) and sorbed species on external surfaces (Kalinichev et al., 2000). These latter studies are of special interest in evaluating a variety of candidate anion-sorbing materials being considered for isolating radionuclide species such as the pertechnetate anion ($^{99}TcO_4^-$), or for the treatment of arsenic in drinking water where it typically occurs as the arsenate anion (AsO_4^{3-}).

Quantum Mechanics

Quantum methods attempt to solve the Schrödinger equation by approximate means in order to evaluate the electronic structure of large and complex systems. These methods provide a fundamental approach that surpasses the limitations imposed by a classical description of atomic interactions involving the ball and spring model of molecular mechanics. Quantum calculations can provide a first principles determinations of energies, molecular and periodic structures and properties, electrostatic potentials, spectroscopic and thermodynamic values, details of reaction mechanisms, kinetic parameters, and even evaluate non-equilibrium structures. Electronic structure calculations also provide a useful means to examine chemical reactivity by providing molecular orbitals that map out the redistribution of electrons among the system atoms. The Schrödinger eigenfunction equation ($H\Psi = E\Psi$) includes the Hamiltonian differential operator H, the wavefunction Ψ, and the total energy of the chemical system E. The time-independent form of this relation is evaluated for a Hamiltonian comprised of kinetic and potential energy components. The solution to the Schrödinger equation ultimately relies on the methods used to obtain appropriate wavefunctions that successfully describe the molecular orbitals for the distribution of electrons in the compound.

Among the more common quantum approaches are the *ab initio* Hartree-Fock methods and their correlated extensions (see Hehre et al., 1986), density functional theory (DFT) methods (see Jones and Gunnarsson, 1989), and semi-empirical methods (see Pople and Beveridge, 1970). Briefly, Hartree-Fock methods use an antisymmetric determinant of one-electron orbitals to define the total wavefunction. Electrons are treated individually assuming the distribution of other electrons is frozen and represented by their average distribution as part of the potential. The wavefunction orbitals and their coefficients are refined through an iterative process until the calculation reaches a steady result know as a self-consistent field. The correlated Hartree-Fock methods introduce a term in the Hamiltonian that corrects for local distortion of an orbital in the vicinity of another electron. Standard Hartree-Fock methods provide favorable equilibrium geometries compared to correlated or DFT methods, but the lack of electron correlation typically produces inaccurate spatial distributions of electrons and therefore erroneous force constants and vibrational frequencies. DFT methods incorporate exchange and correlation functionals of the electron density based on a homogeneous electron gas, and evaluated for the local density of the molecule or crystal. The density of the electrons rather than the wavefunction is used in the DFT methods to describe the energy of the system. DFT methods are efficient and convenient to use in the calculation of electronic structures for large periodic systems. Semi-empirical methods, as the name implies, incorporate empirical or experimentally-derived parameters to reduce the computational cost of evaluating all components of the *ab initio* methods. Because of the recent success of DFT methods and the improvements in computer power, plus the inaccuracies associated with the approach, semi-empirical methods are no longer as common as they were twenty years ago.

Excellent discussions of quantum theory and the methods used to obtain solutions to the Schrödinger equation are available in several review articles and texts. Noteworthy of these for applications relating to inorganic and crystalline materials are the books by Hehre et al. (1986), Labanowski and Andzelm (1991), Springborg (1997), and Cook (Cook, 1998). Gibbs (1982) and Lasaga (1992) provide helpful discussions on the use of Hartree-Fock methods for mineralogical applications, while the recent review of Milman et al. (2000) covers the use of DFT methods to examine large periodic systems and includes several examples of calculations on minerals.

The use of quantum mechanics in the analysis of the structure and energetics of complex soil phases is a nontrivial task and often involve several ambiguous interpretations of the results. There are, however, a handful of studies that have successfully applied quantum methods to the analysis of layered aluminosilicate phases. Among the more useful of these quantum studies involving periodic calculations are those of Hess and Saunders (1992) and Hobbs et al. (Hobbs et al., 1997) of kaolinite, Bridgman et al. (Bridgeman et al., 1996) of talc and pyrophyllite, and Rosso et al. (2001) of muscovite (also see next section below). Often small cluster models representative of the clay structure are evaluated to assess site energies and particular coordinations (e.g., Chatterjee et al., 1998; Teppen et al., 1998b). As with classical forcefield methods, quantum methods can provide a single point energy for these structure or can be used to obtain a partial- or fully-relaxed optimized geometry.

MODELS OF RADIONUCLIDE SORPTION

Unfortunately, the soil science and mineralogical literature have few examples of the use of molecular simulation for modeling the mechanisms of radionuclide sorption on soil minerals. In part, this is due to the relatively recent advances in molecular modeling software and advanced hardware needed to examine the large and complex systems associated with soil and mineral systems. Although the published models may not accurately represent the true process for radionuclide-mineral interactions, the simulations often provide an opportunity to examine candidate mechanisms and allow the modeler, in concert with the experimentalist, to make comparisons of the possible structures and energies that may exist. In this fashion, molecular modeling provides a relatively inexpensive means to assess competitive mechanisms. This leads to further refinements of the candidate models that ultimately must survive further scrutiny and validation to be accepted as an accurate model. In this section, we examine several recent studies that have sought to develop models for metal sorption on the selected surfaces of an oxyhydroxide and exchange of metals in the interlayer of a layered aluminosilicate phase. First, however, is an example of a relatively simple modeling approach for identifying preferred sites for metal sorption.

Surface Sorption Maps

The computer simulation of clay minerals or other complex soil phases is often limited by the large unit cells and supercells required to properly represent the bulk or surface structure of the sorbing material. Furthermore, multicomponent substitutions in the structure, especially for clay minerals, lead to complex disordered systems that are not amenable to molecular simulation based on a simple unit cell to represent the system. Recently, Cygan and Kirkpatrick (2001)

determined the sorption sites of several complex clay phases based on the forcefield method of Pattabiraman et al. (1985). This approach allows for the evaluation of the fundamental atomistic properties that control the sorption of molecules, metals, and anions onto the internal or external surface of clays. It is possible to evaluate the influence of crystallography, cleavage surface, composition, isomorphic substitution, and surface protonation state on the relative sorption energy.

Forcefield methods, as noted above, can employ various functional forms to describe the energy of interatomic interactions. One of the most convenient forms is that based on a nonbonded model in which all of the interatomic interactions are incorporated in the long-range electrostatics term and short-range van der Waals term:

$$E_{nonbond} = \sum_{i>j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{i>j}^{N} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right) \qquad [6]$$

Here, the first term is the usual Coulomb description of interacting charges and the second summation includes a different, yet equivalent, description of the van der Waals interactions (compare with Eqn. [1]). The A_{ij} and B_{ij} terms represent the Lennard-Jones parameters for short-range interactions between atoms i and j. For sorption process, the electrostatics term dominates whereas the short-range energy term typically represents less than 20 % of the total energy. The Pattabiraman et al. (1985) recognized that computational costs for the evaluation of sorption energies could be substantially reduced if the energy components of a large molecule were defined separate of the smaller sorbate molecule (or metal cation). The van der Waals interaction parameters needed to be defined as geometric means of the values for the individual atoms:

$$A_{ij} = (A_i A_j)^{1/2} \qquad [7]$$

$$B_{ij} = (B_i B_j)^{1/2} \tag{8}$$

This approach effectively removes all of the energy parameters for the substrate component from the first summation and leads to a one-time calculation to fully evaluate the substrate material. Eqn. [6] can be rewritten with the j molecule (sorbate) removed from the inner summation:

$$E_{nonbond} = \sum_j q_j \sum_i q_i / r_{ij} + \sum_j \sqrt{A_j} \sum_i \sqrt{A_i} / r_{ij}^{12} - \sum_j \sqrt{B_j} \sum_i \sqrt{B_i} / r_{ij}^6 \tag{9}$$

Although originally employed for the analysis of drug receptor sites on macromolecules for pharmaceutical applications (Pattabiraman et al., 1985), this approach is applicable to the evaluation of sorbate-substrate interactions such as the sorption of a metal cation onto a mineral surface. The energy component for the large substrate molecule is initially evaluated over a large grid volume and the smaller sorbate or metal cation is moved to possible sorption sites where the energy is evaluated in real time. It is necessary to incorporate general or universal forcefields that are parameterized with geometric means and combination rules to describe the diagonal van der Waals energies. The CVFF (Dauber-Osguthorpe et al., 1988), UFF (Rappé et al., 1992), and CFF (Maple et al., 1994) forcefields represent several common forcefields that incorporate this convention.

A cluster model (non-periodic) of illite was developed by Cygan and Kirkpatrick (2001) based on the structural refinement of Lin and Bailey (1984). The cluster is comprised of about 660 atoms or about 12 unit cells. The size of the cluster was optimized so as to provide suitably-sized cleavage surfaces and minimize edge effects. Cleavage was chosen to occur along the (100), (010), and (001) crystal planes with termination designed to preserve complete metal coordination by oxygens. Potassium ions were positioned on two external basal surfaces and within the interlayer. Aluminum is substituted for silicon in the tetrahedral sheet allowing for a

disordered structure with aluminum avoidance and to provide the appropriate Si/Al composition. Only aluminum occupies the dioctahedral sheet. Protonation of the illite surfaces was designed to represent surface species expected to exist at pH values of 6, 8, and 10. The CVFF forcefield (Dauber-Osguthorpe et al., 1988) was used to assign interaction parameters for all atoms and to obtain a geometry optimization of the surface hydrogens. All heavy atoms were kept constrained to positions based on the observed crystallographic structure. A sorption energy grid of 42,000 points covering the extents of the illite cluster with an additional 3 Å border zone was then generated based on the evaluation of Eqn. [9]. Assuming a test sorbate characterized by unit values for the interactions parameters (i.e., fictive univalent metal cation) provides a means to compare the relative energies of the illite sorption sites.

The results of the sorption energy calculations for illite are presented in Fig. 2. The sorption energy map provides a convenient means to assess the relative variation in energy as a function of the illite crystallography, cleavage, pH, and local composition. Three-dimensional contours indicate the most energetically-favored sites for metal sorption. The increase in sorption energy (more negative energy values) with pH is related to the increased negative surface charge that occurs with deprotonation. The optimum sorption sites for the pH 6 cluster are clearly controlled by the coordinated location of tetrahedral aluminum sites. The aluminums on the left hand side of the (010) surface are opposite each other across the interlayer region where the contour is most prominent. Similar energy contours occur on the same surface for the deprotonated aluminol sites associated with the octahedral aluminums. The right hand (010) surface of the same cluster model does not have the concerted tetrahedral aluminums nor is there any effect of a local octahedral vacancy. Small localized sorption sites are visible near the aluminum vacancy on both illite layers for the (100) surface. The sorption map for pH 8

indicates enhanced sorption at the same sites as that for pH 6 but the right hand (010) cleavage now has enhanced sorption capability. Deprotonated silanol groups are able to contribute to the sorption energy and help to stabilize the interlayer sorption site. This sorption site is analogous to the frayed site model originally suggested by Jackson (1963) to describe the initial sorption site of a metal cation prior to incorporation of the metal into the clay interlayer. The fully-deprotonated illite cluster at pH 10 is characterized by an interlayer that is the dominant sorption site. Tetrahedral aluminol sites are now able to coordinate to the sorbing metal. A similar analysis of sorption on kaolinite surfaces is presented by Cygan and Kirkpatrick (2001).

The sorption energy maps provide a unique insight into identifying the optimal sites for sorption on the external surfaces of clays. Notwithstanding the simple assumptions of the model, the sorption energy maps provide a relatively cost-effective means to gauge the relative importance of various surface sites given the complex nature of clays with their low symmetry, order-disorder behavior, varied composition, stacking disorder, and protonation state (function of pH). Modeling approaches involving both metal cation sorbate and the external surface of the phyllosilicate (Cygan et al., 1998; Purton et al., 1997) provide a more detailed description of the relative binding energy and surface geometry associated with the sorbed metals or radionuclides such as cesium-137.

Sorption of Radium on Goethite

Iron oxide and iron oxyhydroxide minerals are commonly found in a variety of soils, various geological environments, and in numerous industrial applications (Tan, 1994). Due to the relatively high specific surface areas (greater than 200 m^2/g for goethite), these phases represent a large fraction of available surface area even when they are volumetrically minor

phases. Hydrous oxides, in particular, can sorb a host of chemical species and are the dominant

sorbents in nature due to their tendency to occur as finely dispersed phases and as coatings on

various mineral substrates. Metal sorption on these phases, especially onto goethite (FeOOH) or

the amorphous ferrihydrite (FeOOH·H$_2$O), is an important process that needs to be critically

evaluated for the safe isolation of radioactive waste materials (Lu et al., 1998; Moyes et al., 2000;

Turner and Sassman, 1996). In this effort, it is desirable to use molecular modeling methods as a

way to effectively evaluate the mechanisms of radionuclide sorption. The models not only offer

a fundamental perspective on the controlling factors of radionuclide sorption, but also provide a

convenient and relatively inexpensive means to complement direct experimental analyses that are

often costly, inexact, and potentially dangerous when dealing with selected radioisotopes.

Molecular dynamics methods are particularly attractive in the analysis of radionuclide

sorption mechanisms where the dynamical behavior of aqueous solution and solvated species

will be important in the analysis of the substrate-fluid interface. There have been few

applications of such techniques to soil phases, these being mostly for the analysis of the structure

and intercalation of clay mineral systems (e.g. Cygan, 2001a; Hartzell et al., 1998; Teppen et al.,

1997). Models of hydrous iron oxide phases—being similar to clay minerals having fine grain

sizes, the existence of hydroxyl groups, and extensive hydrogen bonding—have been modeled in

a few studies (Felmy and Rustad, 1998; Jones et al., 2000; Rustad et al., 1996a; Rustad et al.,

1996b). Rustad et al. (1996a) demonstrated the significance of using molecular modeling tools

to derive an improved model of the solvated (110) surface of goethite in which the surface

hydroxylation reactions can occur. Also of significance is the recent study of Randall et al.

(1999) in which the sorption of cadmium to various surfaces of iron oxyhydroxide phases was

examined by synchrotron-based spectroscopy combined with quantum DFT calculations on

molecular clusters designed to represent the mineral surface. In general, these studies provide an atomistic perspective on surface speciation and metal sorption that can be linked to the macroscopic description associated with using a surface complexation model approach (see Dzombak and Morel, 1990).

The following section presents an example of using a MD approach to examine the possible mechanisms of radium-226 interaction with goethite surfaces based on the recent work of Liang and Cygan (2001). Radium-226, with a half-life of 1600 years, is the decay product of uranium and thorium, either through natural decay processes or by discharge from uranium processing facilities (Wang et al., 1993). Unfortunately, except for a few limited bulk studies of radium sorption in soils (Nathwani and Phillips, 1979a; Nathwani and Phillips, 1979b), the mechanisms of the interactions between radium and soil minerals are unknown. The Liang and Cygan (2001) model involves the simulation of barium, as an analog of the radioactive radium, in order to correspond with a recent experimental and synchrotron study of barium sorption on goethite (Westrich et al., 2000).

The interaction potentials for the goethite-water system were modified from the forcefield parameters developed for the simulation of clay minerals (Cygan et al., 2001). A non-dissociative, but flexible, water model (Berendsen et al., 1981; Teleman et al., 1987) allows for the full dynamic behavior of the water molecules in the solution and for the solvation of the barium cation. The water model includes partial charge assignments appropriate for the dipole moment of water, a harmonic bond stretch term, and a harmonic angle bend term. Nonbonded interactions are described by a Lennard-Jones 12-6 potential as described in a previous section. In order to compare the common cleavage surfaces of goethite, four substrate surfaces were generated, each with single protonation of the dangling oxygens formed during the cleavage of

the bulk goethite crystal based on the refinement of Szytula et al. (1986). The (020) and (110)

surfaces of goethite represent the common columnar surfaces of the needle-shaped growth

morphologies, while the (101) and (021) surfaces occur as terminal faces. The termination of the

goethite surface with hydroxyls represents an acidic environment (approximately pH = 4)

corresponding to conditions moderately below the point of zero charge for goethite (Hayes and

Leckie, 1987). Any excess positive charge created by the protonation scheme was balanced by

appropriately reducing the partial charges on the iron atoms located in the central part of the

goethite slab. This procedure allowed the goethite substrate to remain charge neutral but yet

provide the appropriate localized charges on the exposed cleavage surface.

The simulation cell incorporates a goethite substrate combined with a previously

equilibrated barium solution corresponding to a concentration of approximately 0.01 molal.

Molecular dynamics simulations were completed at constant particle, volume, and temperature

conditions (NVT canonical ensemble) using the thermal bath method of Hoover (Hoover, 1985)

to maintain a temperature of 300K. All atoms of the cell were allowed to freely translate during

the MD simulations except for the central region of the goethite slab; goethite atoms within 5 Å

of the interface were allowed to relax. This procedure allowed for MD simulations to be run up

to 100 psec with 1 fsec time steps. Depending on the surface being simulated, the simulation

cells comprised anywhere from 2700 atoms to 3100 atoms.

An analysis of the energy and dynamics of barium sorption on each of the four major

goethite surfaces provided a comparison of the various geometries and relative binding strengths

for sorption. Fig. 3 presents three simulation cells examined for barium interacting on the

columnar (110) surface as an inner sphere complex, outer sphere complex, or fully solvated by

waters. Energies were obtained for each case after full equilibration of the system, and binding

enthalpies were calculated as the energy difference between the sorbed and water solvated states. The results indicate the preference of a strongly bound inner surface complex for each of the four surfaces having no intermediate solvating waters between the barium and the goethite substrate. The (101) and (110) surfaces exhibit the greatest sorbing capacity for barium as an inner sphere, whereas none of the four surfaces show a statistical energy gain while sorbed as an outer sphere complex. The equilibrated energies for the outer sphere complexes fall within the variation of the total energy for the fully solvated cases. No transition between outer sphere and inner sphere complexes was observed on the time scale of the molecular dynamics simulations suggesting some kinetic limitation on this process.

The (101) goethite surface exhibits a greater affinity for barium than the other surfaces. The sorption energy is about five times larger than that observed for the (110) surface. Barium sorption as an inner sphere complex on the (020) and (021) surfaces is relatively weak compared to the other two surfaces. In part, this comparison of binding strengths is related to the local geometry of the barium on each of the surfaces. Liang and Cygan (2001) suggest that the relatively strong (101) binding is related to barium being coordinated to 9.7 oxygens while bound to the surface, of which 3.0 of the oxygens are from the goethite and 6.7 are associated with the solvating waters. The fractional number of oxygens reflects the dynamical behavior of the sorption process on the time scale of the MD simulations—water molecules come and go while coordinating to the barium from above while the barium exhibits some movement on the goethite surface coordinating to various surface oxygens. Additionally, the (101) surface has both hydroxyls and bridging oxygens that coordinate to the inner sphere barium complex. In contrast, the (020) surface is dominated by hydroxyls that have less influence on the binding of the barium.

Cesium-Potassium Exchange in Muscovite

The isolation of radioactive cesium-137 in layered silicate minerals is of considerable environmental importance, especially in the ability of selected clay minerals to remove cesium preferentially from contaminated subsurface fluids and prevent further transport of it through the environment (Comans and Hockley, 1992; Koivula and Lehto, 1998). Recently, Rosso et al. (2001) investigated the structure and energetics of exchanging cesium ion for potassium ion in the interlayer of muscovite using a DFT quantum approach. Muscovite $(KAl_2(AlSi)_3O_{10}(OH)_2)$ provides a relatively simple and well-characterized layered structure that is representative of the more complex smectite and illite clay phases. This work is significant in that the authors performed fully-relaxed optimizations of the primitive unit cell of muscovite in which all 42 atoms and cell parameters were allowed to vary. A plane wave pseudopotential method (Payne et al., 1992) with a generalized gradient approach (Perdew and Wang, 1992) was used in the study. The authors chose several competing structural models for the $2M_1$ polytype of muscovite based on whether hydrogens (hydroxyls) were present, and on the aluminum-silicon substitution in the tetrahedral site relative to the two possible potassium exchange sites in the interlayer. The choice of models led to three different charge states for the 2:1 layers of the mica. The DFT approach provided a systematic means to determine the charge distribution, structural changes, and energetics of this system as a function of layer charge, tetrahedral substitution, and the interlayer structure. This modeling approach is fundamentally different from the previously described molecular mechanics simulations. The quantum-based DFT method evaluates the electronic structure of the chemical system rather than the atomic interactions described by

classical mechanics, and therefore incorporates any potential for reaction and the movement of electrons among atoms.

The exchange reaction was simulated by setting up several DFT calculations for the initial and final states of the exchange process: an initial state with potassium in the interlayer of the muscovite and hydrated cesium at infinite separation, and a final state with interlayer cesium and hydrated potassium at infinite separation (see Fig. 4). Experimental hydration enthalpies and ionization potentials were incorporated to obtain the appropriate energies for the designated states. The results of this exchange model (Rosso et al., 2001) indicate the cesium-potassium exchange reaction to be fairly isoenergetic and that the incorporation of cesium is favored by increasing layer charge of the model structure. The calculated exchange energies vary from -9.9 to 5.8 kJ/mol (per primitive unit cell) for, respectively, the doubly-charged and neutral simulation cells. Corresponding increases in the interlayer spacing with the incorporation of the cesium vary from 0.06 Å for the neutral cell to 0.42 Å for the doubly-charged model. The simulations also suggest that Al/Si substitution in the muscovite leads to local tetrahedral rotations and a reduction in the size of the interlayer cavity, and therefore less favored exchange for cesium. The authors conclude that the driving force for the exchange reaction is therefore quite small and that the exchange will be controlled by diffusion kinetics rather than thermodynamics. The modeling supports the frayed edge model of clays (Jackson, 1963; Sawhney, 1966; Tamura and Jacobs, 1960) where unsaturated charges and large interlayer spacings are available to promote cesium sorption.

CONCLUSION

Although not all the fundamental aspects associated with understanding the interactions of radionuclides with soil minerals are known, molecular modeling methods provide a convenient tool for evaluating the significance of various interaction mechanisms. Theoretical methods complement recent advances in materials characterization based on X-ray and neutron diffraction studies, surface spectroscopies, and synchrotron-based X-ray absorption and fluorescence methods. In combination with experiment and spectroscopic methods, molecular modeling methods can be used to develop new insights into the mechanisms of radionuclide sorption, intercalation, and reactivity with soil minerals. If properly validated and supported by experimental observation, the molecular models may ultimately be used to predict the interaction of radioactive wastes with selected soils phases that may not be amenable to experimental technique. This is especially significant if unique properties of a soil-like compound are required for specific radionuclide retention or isolation, and that may lead to the synthesis of an engineered compound to provide a solution for an important environmental waste problem.

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FIGURE CAPTIONS

Fig. 1. Potential energy as a function of distance described by a Buckingham potential for the interaction of A-B ions. The total energy curve exhibits an energy minimum corresponding to the equilibrium separation distance.

Fig. 2. Sorption energy maps of a molecular cluster representation of illite as a function of pH. The contour surface represents an energy value above the minimum interaction energy for the calculation (E_{min} + 335 kJ/mol). Modified from Cygan and Kirkpatrick (Cygan and Kirkpatrick, 2001).

Fig. 3. Simulation cells used in the molecular dynamics analysis of the sorption of barium to various goethite surfaces. Configurations represent barium sorbed on the (110) goethite surface as an inner sphere complex, outer sphere complex, and fully solvated solution species. Modified from Liang and Cygan (2001).

Fig. 4. Primitive unit cell of muscovite (doubly-charged layer model) and a schematic representation of energy calculations required to model the cesium-potassium exchange reaction. Modified from Rosso et al. (2001).
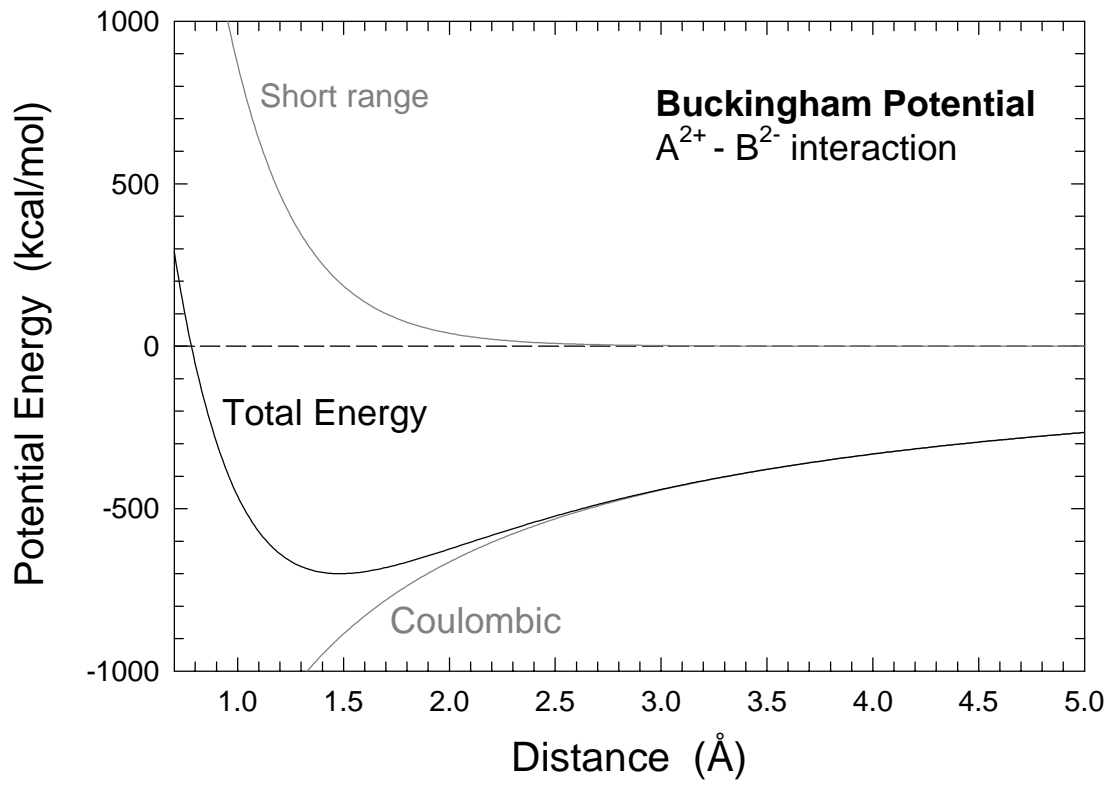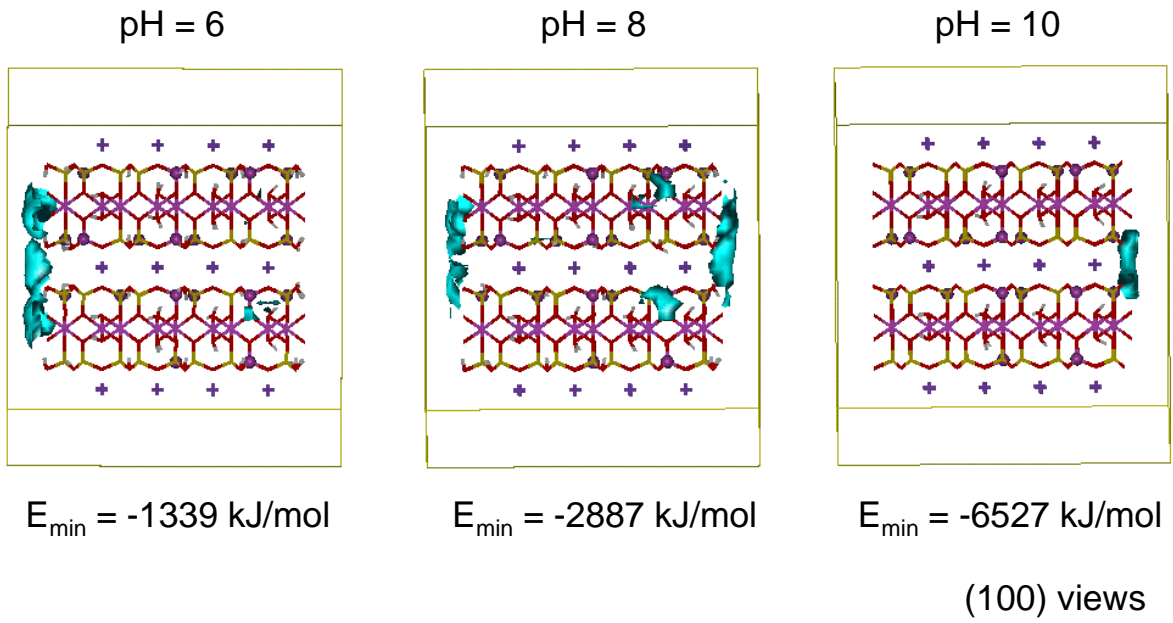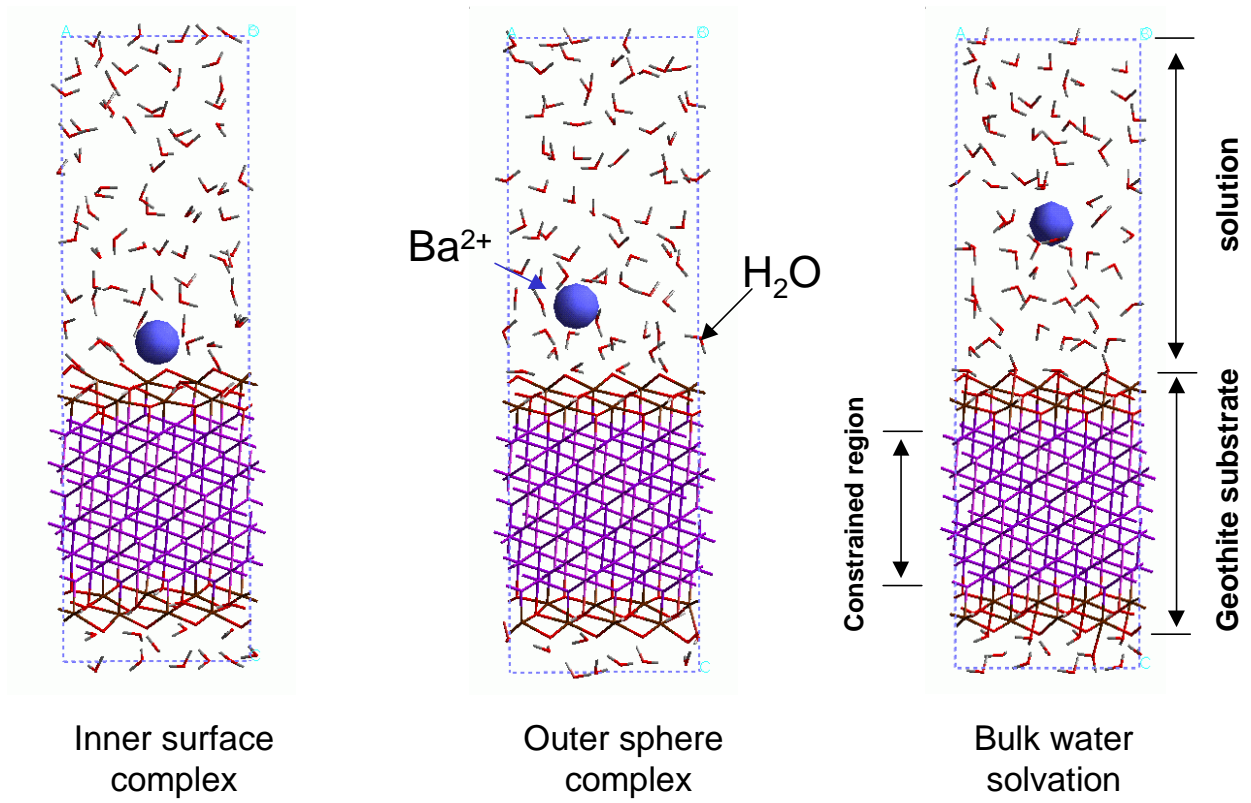
Figure 1

Figure 2

pH = 6   pH = 8   pH = 10

E_{min} = -1339 kJ/mol E_{min} = -2887 kJ/mol E_{min} = -6527 kJ/mol

(100) views

Figure 3

Ba^{2+} H$_2$O

solution

Constrained region

Geothite substrate

Inner surface
complex

Outer sphere
complex

Bulk water
solvation

Figure 4

$$X(K) \; + \; Cs^+_{(aq)} \rightarrow X(Cs) \; + \; K^+_{(aq)}$$