Interaction of Ions with Hydrated Clay Surfaces: Computational Molecular Modeling for Nuclear Waste Disposal Applications

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Interaction of ions with hydrated clay surfaces: Computational molecular modeling for nuclear waste disposal applications

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Abstract

The Callovo-Oxfordian clay formation (COx) is the potential host rock for long term nuclear waste repository in France. The clayey component of COx consists mostly of illite, smectite and interstratified illite/smectite (I/S) clay minerals. We performed a series of molecular dynamics (MD) computer simulations in order to quantify the molecular scale mechanisms responsible for the adsorption and transport of ions at the hydrated surfaces of illite, smectite, and I/S clays. New structural models of illite, smectite, and I/S allowed us to identify several structurally different adsorption sites at the basal surfaces of all three clay substrates. Adsorption free energy profiles above each individual adsorption site on each clay surface for a wide range of metal cations were then calculated and the metal sorption properties for the three clay surfaces are compared in terms of the preferable sorption sites and their surface distributions, most stable adsorption distances, and free energies of adsorption. The resulting equilibrium constants for surface adsorption and ion exchange were calculated and found in general agreement with available literature data. The observed discrepancies between the exchange energies obtained in the current MD simulations and the values obtained through the interpretation of recent X-ray reflectivity measurements can be attributed to the differences in the description of the exchange reaction equilibria between the experimental conditions and the simplified conditions of our simulations.

Keywords: mineral-water interfaces; clay; molecular dynamics simulations; nuclear waste disposal

1. Introduction

Safe and sustainable geological nuclear waste disposal poses major scientific challenges to the efforts to minimize the environmental footprint of nuclear energy for extremely long periods.[1,2] To that purpose, safety assessment models must account for radionuclides behavior over time- and distance- scales spanning many orders of magnitude

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in space and time. Complementary to substantial experimental work in this field,[3] significant efforts are made to develop numerical models that would allow to understand the interactions of radionuclides with natural and engineered barriers (consisting mostly of clay and cementitious materials) and to predict their behavior in the geosphere on various scales from the molecular-level adsorption and transport in clay nanopores to the larger scale geochemical mobility in macroscopically heterogeneous systems.[4] Computational molecular modeling can be especially effective in providing fundamental molecular level information on the energetics, structure, and dynamics of ions and water molecules in clay nanopores.[5] We used molecular dynamics (MD) computer simulations in order to quantify the molecular scale mechanisms responsible for the adsorption and transport of hydrated cations at the basal surfaces of illite, smectite, and interstratified illite/smectite clays and to clarify current macroscopic thermodynamic, geochemical and transport models. The MD simulations with the CLAYFF force field[6] were performed for a number of monovalent (Li^+, Na^+, K^+, Rb^+, Cs^+) and divalent (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ni^{2+}, UO_2^{2+}) cations, but our primary focus[7-10] is on the behavior of Cs^+ as one of the most important radionuclide in radioactive waste[3,11] which can also be unintentionally introduced in the environment in case of nuclear accidents.[12]

2. Models and methods

All three clay minerals studied belong to the so-called 2:1 clay family and represent layered structures made of several stacking T-O-T units in which one sheet of Al-cations (O) octahedrally coordinated by oxygens and hydroxyls is sandwiched between two sheets of tetrahedrally coordinated Si-cations (T). Isomorphic substitutions (typically, Mg for Al in the octahedral sheets and/or Al for Si in the tetrahedral sheets) give rise to a negative clay layer charge that is compensated by the presence of cations in the interlayer space and on the surface of clay particles.

The newly developed models allowed us to identify several structurally different energetically favorable adsorption sites at the basal surfaces of all three clay substrates. MD simulation results are quantitatively analyzed in terms of the adsorption free energy profiles above each individual adsorption site on each clay surface for each individual cation. For the most highly charged case of muscovite (illite) the tetragonal sheets of the model consisted of hexagonal (ditrigonal) rings of either Si_4Al_2 or Si_5Al composition in equal proportions randomly distributed within the structure and yielding 3 different types of adsorption sites for the charge compensating cations: *H2a* - two Al tetrahedra are symmetrically places across each other in the hexagonal ring and separated by the presence two Si tetrahedra in the same ring; *H2b* – two Al tetrahedra asymmetrically separated in the ring by one and three Si tetrahedra from each side, making them in closer proximity to each other than in the symmetric case; *H1* – a hexagonal ring containing only one Al substitution.[7] On the smectitic surfaces of montmorillonite and I/S (both having much lower structural charge than illite) five such types of sites can be identified: *H1* as above in muscovite, *H0* – a "normal" hexagonal ring without substitution; *T1* – above a tetrahedrally substituted Al; type *T0* – a "normal" tetrahedral Si site without a substitution next to it; and *T0a* – a "normal" tetrahedral Si site adjacent to a tetrahedrally substituted Al.[8] It is worth noting that the tetrahedral sites *T1*, *T0*, and *T0a* are also present on the illite surface, but they are not analyzed here because all MD simulations have demonstrated that due to the high illitic surface charge and high concentration of the charge-balancing cations these sites remain unoccupied and do not participate in adsorption processes. The molecular model of the interstratified I/S particles[10] was based on the concept of so-called fundamental particles,[13] which implies that the mixed-layer I/S particles are divided at the interlayer smectitic spaces, therefore the I/S surface sites are similar to the sites of montmorillonite smectite.

The adsorption free energy profiles of ions as function of their distance from the clay surface at thermodynamic equilibrium were determined using potential of mean force (PMF) calculations with the umbrella sampling algorithm, which are discussed in detail elsewhere.[7] The calculations were performed separately for each individual surface site defined above in order to provide quantitative information on their site-specific adsorption strength and to determine the ion exchange mechanisms on the surface.

3. Results and discussion

On the surface of muscovite mica (our model of illite), K^+ ions are naturally present as part of the muscovite composition, and can be exchanged for Cs^+ from the interfacial aqueous solution. Our MD simulations show that

irrespective of the surface site, inner-sphere adsorption represents the most stable surface complex for both K^+ and Cs^+ (Fig. 1). Such an adsorption structure is dictated primarily by the high structural charge and strong electrostatic attraction of the cations, which presents a very high energy barrier for the formation of outer-sphere surface complexes or for a complete desorption. Also, regardless of the cationic nature, the strength of the stable adsorption sites is ordered in a sequence of *H2a > H2b > H1*, which should be attributed to the nature of interaction potentials used in the simulation. In the CLAYFF parameterization, tetrahedrally coordinated Al atoms bear a partial positive charge that is ~30% lower compared to the tetrahedrally coordinated Si atoms.[6] In addition, the bridging oxygen atoms coordinating substituted Al tetrahedra are ~11% more negative than ordinary bridging oxygens around Si tetrahedra. Due to these relatively minor local charge inhomogeneities the short range cation-surface electrostatic interactions are significantly affected and lead to individual site-specific differences in the adsorption strength.
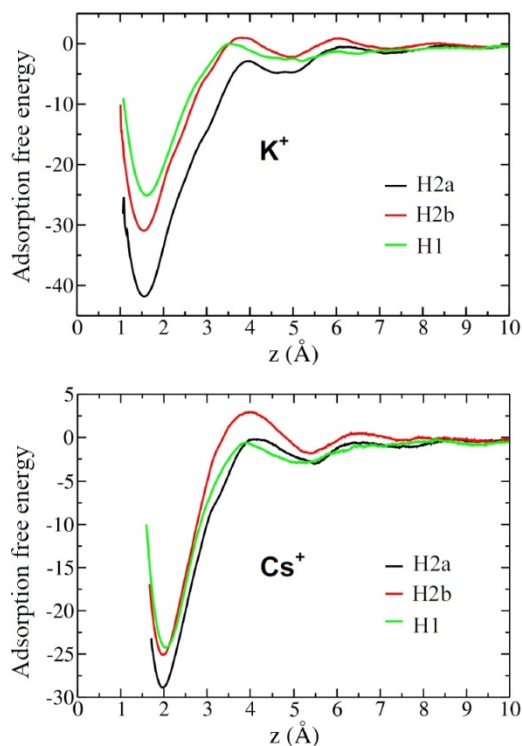

Fig. 1. Adsorption free energy profiles of K^+ and Cs^+ (in kJ/mol) as functions of their distance from the surface for 3 different adsorption sites on the muscovite basal surface.[7] The adsorption sites *H2a*, *H2b*, and *H1* are defined in the text.

The overall thermodynamic equilibrium of the Cs^+/K^+ ion exchange reaction can be represented by the equation $Cs^+_{(aq)} + K^+\text{-}X \rightleftharpoons Cs^+\text{-}X + K^+_{(aq)}$, where X indicates a specific surface adsorption site, and the differences of the hydration free energies of Cs^+ and K^+ in bulk aqueous solution are also taken into account. Since muscovite surface contains, on average, 1/6 of sites *H2a*, 1/3 of sites *H2b*, and 1/2 of sites *H1*, the total energy for the Cs^+/K^+ equilibrium exchange reactions is the weighted sum of the exchanges at all three sites. The final thermodynamic parameters of this exchange reaction are estimated to be $\Delta G_{Cs+/K+} = -4.6$ kJ/mol and and $K_{ex} = 0.7$, in reasonable agreement with the experimentally deduced energetics.[14] The discrepancies can be attributed to the differences in the description of exchange reaction equilibria between the experimental conditions and the simplified conditions of our simulations.[7]

For the adsorption of Cs^+ and Na^+ on the smectitic surface of I/S clay,[10] our simulations show that: (i) Cs^+ is improbable to be sorbed on the tetrahedral sites (*T1* and *T0*); (ii) Cs^+ on such sites is easily exchangeable by Na^+ existing in the system; (iii) Cs^+ and Na^+ can be present together on the I/S basal surface (at different adsorption sites); (iv) Cs^+/Na^+ cation exchange observed in experimental studies[11] should correspond to the Cs^+/Na^+ cation

exchange reaction on sites *H1* and *H0* only (Fig. 2), with sites *H0* being strongly predominant, due to the low structural charge and low concentration of *H1* sites on the surface of I/S particles. The free energy of the exchange reaction is estimated to be $\Delta G_{Cs+/Na+}$ = -2.73 kJ/mol.
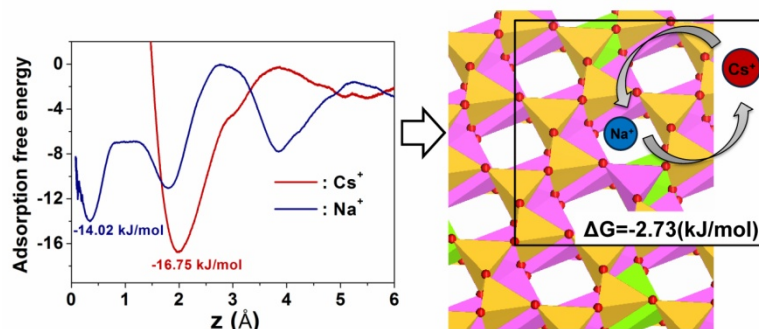

Fig. 2. Adsorption free energy profiles of Cs^+ and Na^+ (in kJ/mol) as functions of their distance from the surface of I/S clay and the mechanism of their exchange on the hexagonal adsorption site.[10]

Acknowledgements

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