Cs, Sr, AND Ba SORPTION ON CLAYS AND Fe-OXIDES

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ABSTRACT

Technical guidance for performance assessment (PA) of low-level radioactive waste (LLRW) sites is currently dependent upon experimental retardation factors (K_D's) to predict radionuclide transport. Accurate predictions of waste transport or retardation will require mechanistic models of radionuclide sorption so as to be applicable to a wide range of soil/groundwater environments. To that end, we have investigated Cs^+, Sr^{2+}, and Ba^{2+} sorption on several clay and Fe-oxide minerals. Relative metal binding strengths for montmorillonite clay decrease from Ba^{2+} to Sr^{2+}, which is similar to that sorption trend noticed for kaolinite. Molecular dynamics simulations for kaolinite suggest that Cs^+ is sorbed at aluminol (010) edge sites as an inner-sphere complex and weakly sorbed as an outer-sphere complex on (001) basal surfaces. Sorption is thought to occur on similar sites for smectite clays, however, the basal plane residual charge and its increased basal plane exposure should have a greater influence on metal sorption. On the other hand, phase transformation kinetics (e.g., ferrihydrite to goethite) is a very important control of metal sorption and desorption for Fe-oxides/hydroxides. These results provide a basis for understanding and predicting metal sorption on complex soil minerals.

INTRODUCTION

The Nuclear Regulatory Commission (NRC) and other State agencies have been charged with decommissioning of civilian nuclear facilities, as well as licensing and regulation of uranium mill tailings sites and commercial radioactive waste disposal facilities. NRC and state regulators must be able to evaluate the expected performance of a decommissioned site or a waste disposal site in accordance with federal or state regulations. Current performance assessment (PA) models of radionuclide transport in soil and groundwater use simplified conceptual models for radionuclide retardation that are based on linear and reversible partition coefficients (K_D s) measured for a specific set of experimental conditions. The K_D approach should be appropriate when the site is well characterized, both chemically and hydrologically and where groundwater chemistry does not change greatly across the site. Unfortunately, experience shows that this empirical approach often fails to correlate with field measurements of actual radionuclide transport. The reason is that experimental K_D s have localized application and are sometimes unrealistic when considering the range of nonlinear geochemical parameters that can significantly affect radionuclide transport mechanisms and kinetics (temperature, pH, fluid composition, ionic strength, mineral structure, substrate reactivity, organic complexation, etc.). To predict radionuclide retardation over a wide range of environmental conditions, it is critical to understand and model each of these effects, especially for common soil minerals. Since sorption and desorption phenomena often dominate radionuclide retardation in soils, they are probably the most important geochemical processes to model in PA codes. Once radionuclide sorption and desorption mechanisms are better understood, more appropriate retardation models can be incorporated into PA codes to allow for improved treatment of uncertainty when making estimates of dose to the public.

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Transport and attenuation of radionuclides in subsurface environments are largely controlled by the geochemical interactions of dissolved aqueous waste with common oxide and silicate minerals. These minerals, which range in complexity from quartz to smectite-like clays to poor and/or well-crystalline Fe-oxides/hydroxides, are found in soils and rocks adjacent to the waste site. An understanding of the surface structure and sorptive properties of soil minerals in contact with dissolved radionuclides is fundamental to modeling metal retardation. Hydrogeochemical transport codes can accurately predict the transport and retardation of dissolved radionuclides only when there is a mechanistic understanding of the adsorption and fixation behavior of metals in near-field soils. While theoretical models exist for modeling surface complexation, sorption, and desorption at mineral surfaces, experimental verification of those models lags, as does atomistic characterization of retardation mechanisms. This project is designed to provide mechanistic and kinetic data about the sorption behavior of metals with complex mineral surfaces. Unraveling the mechanistic controls on sorption under diverse geochemical conditions is necessary to predict metal transport and retardation in soils. These data will provide the technical confidence for regulatory decisions on radionuclide transport and retardation. The regulatory objectives of this project are to provide the NRC, state regulators, and disposal site operators with defensible models describing radionuclide retardation by soil-forming minerals.

We have emphasized complementary experimental, analytical, and theoretical investigation of the mechanism(s) of alkali and alkaline earth sorption onto the surfaces of clay and Fe-oxyhydroxide minerals. This research combines batch sorption, surface complexation, molecular modeling, and atomic force microscopy to characterize the mechanisms by which metals (Cs^+, Sr^{2+}, and Ba^{2+}) adhere to mineral surfaces. This study will provide the data to evaluate and quantify those critical mechanisms and geochemical parameters, including measurement of the kinetic data that control the retardation of radionuclides on common mineral phases in near-field soils. This study is an expansion of our previous work on metal sorption onto simple oxides and a simple clay mineral, kaolinite[1, 2], to sorption on more complex soil minerals, montmorillonite clay and Fe-oxides/hydroxides.

PROCEDURE

General analytical and experimental studies of cation sorption processes were performed using a natural montmorillonite (SWy-1, a smectite clay standard from Wyoming), and synthetic goethite and ferrihydrite (iron oxyhydroxides). Sorption isotherms for Sr^{2+} and Ba^{2+} (as an analog for Ra^{2+}) onto smectite clays and Fe-oxyhydroxides were measured at 25-50°C over a wide pH range (2-12) with $NaClO_4$, $SrCl_2$, or $BaCl_2$ or KNO_3 as background electrolytes (Cl^-, ClO^-_4 and $NO_3^=$ do not complex with these metals strongly). Measurement of Ba^{2+} sorption for Fe-oxyhydroxide minerals differed from that of clays in that ferrihydrite [$Fe_2O_3 \cdot H_2O$] transforms to goethite [FeO(OH)] over time. These tests were conducted at pH 12 and 50ºC because the conversion of ferrihydrite to more crystalline goethite is accelerated at these conditions. Solution aliquots were taken after pH stabilization and were analyzed for metals by directly coupled plasma (DCP) or inductively coupled plasma (ICP) spectroscopy using matrix-matched standards. Metal sorption was calculated by difference from starting solutions. The dissolved metal concentrations and pH data were regressed using the computer code FITEQL[3] to calculate best-fit values of pK_x and site density for Sr^{2+} and Ba^{2+} as a function of temperature. Characterizations of powdered minerals and reacted samples were made using standard analytical techniques, including X-ray diffractometry (XRD) and nitrogen BET adsorption measurements of surface area. Atomic force microscopy (AFM) studies of the clays were initiated because metal sorption is a function of the charge distribution on the surfaces and the absolute proportions of exposed basal and edge planes. Particle dimensions and step heights were measured for a few representative grains and were used to calculate relative amounts of edge and basal surface area.

Several computational models were utilized to simulate dissolved Cs sorption onto kaolinite surfaces. These models included lattice energy minimization and molecular dynamics (MD). By combining these techniques, we have developed a general approach for evaluating sorption sites, docking mechanisms, and van der Waals potentials. However, molecular-scale simulations of Cs^+ sorption onto kaolinite require an accurate atomistic description of clay structures and surfaces, based either on X-ray crystal cell refinements or quantum chemical structure calculations. An all-atom geometry optimization of kaolinite has been calculated using the local density approximation to density functional theory (DFT) in a Gaussian-based linear combination of atomic orbitals (LCAO) basis. The calculations were performed using the QUEST (Quantum Electronic Structure) code, which is designed for massively-parallel, distributed-memory computing architecture and were run on an 1824 processor Intel Paragon computer.

RESULTS

Sorption isotherms for Sr^{2+} and Ba^{2+} onto montmorillonite surfaces at 25°C have been measured for both untreated clays as well as prewashed SWy-1 clays (pretreated with NaCl to remove exchangable Ca^{2+}). The amount of Ba^{2+} exchanged onto prewashed montmorillonite clay as a function of pH and the Ca/Na ratio of the solution has been measured. Table 1 lists the calculated constant for Ba/Na exchange as a function of pH in 0.001*M* NaCl solutions. Note that the exchange constant is relatively independent of pH, suggesting that sorption onto edge sites is minor. Addition of Ca^{2+} to the solution decreases the amount of Ba^{2+} exchanged onto the clay. Millimolar levels of Ca^{2+} decrease Ba^{2+} retention by about 40%, and there is no clear pH dependence observed in its retention.

Table 1. Ba/Na Exchange Constants

pH	K_{Ba}
4.3	2.3
6.2	6.0
6.5	4.3
7.8	5.2
9.1	5.3

Figures 1 and 2 show Ba^{2+} and Sr^{2+} exchange onto SWy-1 that was not washed or presaturated with Na^+. Instead, the basal planes possessed both Ca^{2+} and Na^+ as opposed to just Na^+. The same trends are noted as in the Na-saturated case; that is, metal sorption (via ion exchange) is independent of pH and Ca^{2+} competed successfully for some sorption sites. The only exception to this behavior appears to be Sr^{2+} exchange at pH > 7, where appreciable desorption occurs.

The particle morphology of SWy-1 montmorillonite was measured by tapping mode AFM techniques. This sample of montmorillonite contains trace quartz and calcite and its BET surface area, measured using N_2(g), is 31.82 m^2/g. Montmorillonite particles range in diameter from a minimum of about 0.1 μm to a maximum of about 1 μm, and particle thickness ranges from about 2 to 45 nm. The thicker particles appear to be composed of overlapping thinner particles 20 to 30 nm thick. The thin particles are also extremely flat on their basal surfaces. Aspect ratio (thickness to diameter) ranges from about 0.02 to 0.45. Edge surface area ranges from 4 to 9%, much less than that observed for the KGa-1 kaolinite. This percentage of edge surface area is more in line with values typically estimated for clays. Most particles appear irregular in outline with minimal basal surface topography (i.e., rare unit-cell high steps). Although samples were sonicated for only 20-30 sec in an ultrasonic bath, it is possible that some cleavage and breakage occurred, particularly in the case of the smaller, thinner particles.

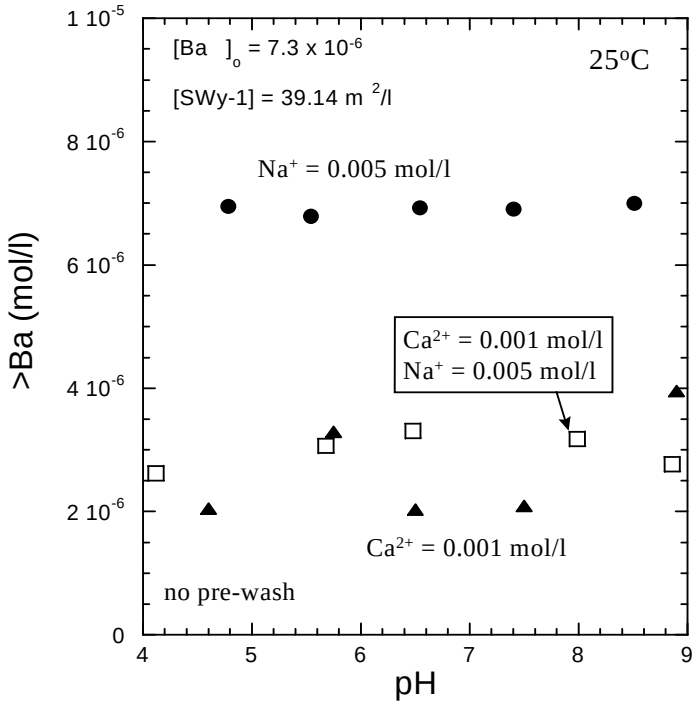

Figure 1. Ba exchange onto unwashed Swy-1.

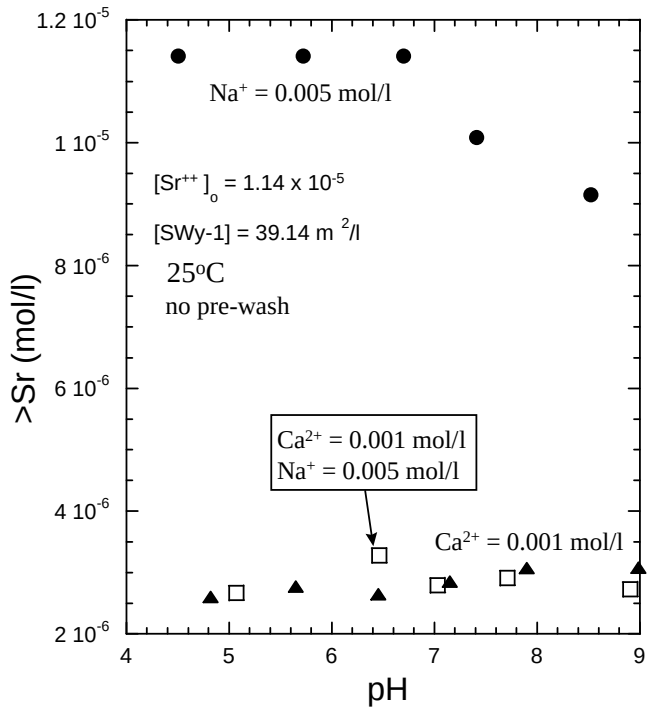

Figure 2. Sr exchange onto unwashed Swy-1.

Molecular electrostatic potential (MEP) calculations, which represent the net summation of the atomic partial charges at the mineral cluster surface, were performed using the observed crystallographic structure of kaolinite and DFT-calculated, energy minimized positions (including hydroxyl groups) on selected surfaces. The MEP surface (Figure 3) depicts the most favorable sites for ionic sorption on kaolinite by color mapping near-surface electrostatic potentials. MEP results show that there is a significant difference in the electrostatic potential of edge and basal surface sites. That is, siloxane and gibbsite basal planes (001) are not as negatively charged as edge silanol or aluminol edge sites, and are more reactive for cation sorption (greater electrostatic charge) than the edge silanol sites.

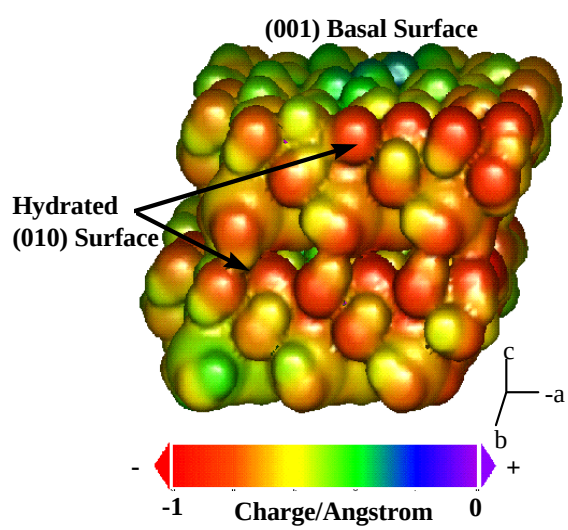

Figure 3. Molecular electrostatic potential surface of hydrated kaolinite crystal viewed along (010) edge; arrows point to areas of high negative charge.

Both energy minimization and molecular dynamics techniques were used to simulate the interactions of dissolved cesium with a kaolinite surface. One Cs^+ atom, along with its waters of hydration, was positioned adjacent to either the (010) edge or the (001) basal aluminol surface of kaolinite prior to energy minimization. Simulations indicate that Cs^+ sorbs directly to the aluminol ((010) edge) as an inner sphere complex. Solvating water molecules are not positioned between the Cs^+ and the (010) edge of kaolinite, but rather coordinate to silanol and other unreacted edge sites. Energy minimization results for

the (001) surface indicate that Cs^+ is coordinated to the basal aluminol plane as an outer sphere complex, with waters of hydration completely surrounding the Cs^+. This contrasts sharply with the inner sphere configuration of Cs^+ sorption at the (010) edge. However, shortly after equilibration of the water molecules on the (001) surface, Cs^+ (outer sphere complex) migrates toward the (010) edge and repositions itself as an inner sphere complex coordinated to an aluminol site. Clearly, these computer simulations suggest that the edge aluminol site is the preferred Cs^+ sorption site for kaolinite.

Ba^{2+} sorption data from the ferrihydrite transformation experiment at pH 12 and 50°C in 0.01 *M* KNO_3 with Ba^{2+} added are presented in Figure 4. Analyses of the suspension filtrate indicate that 100% of the Ba^{2+} added was retained by the iron oxide for at least 25.2 h of aging and that 4 and 7% of the Ba^{2+} was desorbed after 45.9 and 68.4 h of aging, respectively. Barium desorption began when ferrihydrite transformation to goethite was 92 to 94% complete. Consequently, the amount of Ba^{2+} sorbed by ferrihydrite (Ba_{FH}) began to decrease after 25.2 h of aging. The Ba^{2+} sorbed by goethite (Ba_G) increased at the beginning of the aging period (0.4 to 19.3 h) and then remained constant as ferrihydrite transformation neared completion. Transformation of ferrihydrite to goethite was compared to samples aged at 50 °C in 0.01 *M* KNO_3 with and without Ba^{2+}. There was a slight decrease in transformation rate in samples with Ba^{2+} added during the first 12.4 h of aging, although the decrease is not consistently greater than the standard error of the data. After 25.2 h of aging, there is no difference between the rate of ferrihydrite transformation with and without Ba^{2+}.

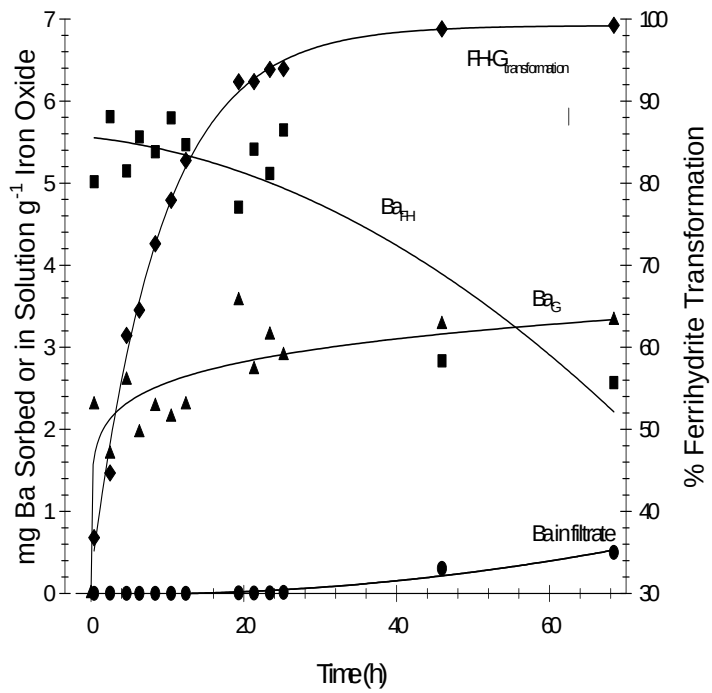

Figure 4. Ba sorption on ferrihydrite at pH 12 and 50°C; note the transformation of ferrihydrite to goethite with time and the associated drop in Ba sorption.

XRD patterns for subsamples taken during 68.4 h of aging without Ba^{2+} at 50°C in 0.01 M KNO_3 were compared to those patterns of subsamples aged with Ba^{2+} during the same time period. These data show a slight decrease in transformation rate in samples with Ba^{2+} added during the first 12.4 h of aging. No difference can be detected in this study between XRD patterns for samples aged with or without Ba^{2+} from 12.4 to 68.4 h. Some poorly crystalline goethite formed during the first 0.4 h of aging and that the goethite XRD peaks increase in intensity and decrease in width during the first 12.4 h of aging. This indicates an increase in the amount of goethite present and its crystallinity. Between 12.4 h and 25.2 h of aging, there are no further changes in XRD peak width and a slight increase in peak height, indicating an increase in the amount of crystalline goethite present. After 25.2 h of aging, when the transformation of ferrihydrite to goethite is 94 to 95% complete, there are no further changes in the XRD patterns of the samples. Figure 4 also shows that the amount of Ba^{2+} partitioned to goethite (Ba_G) appears to reach a constant level after about 25.2 h. The surface area of samples aged with and without Ba^{2+} decreased rapidly during the first 19.3 h of aging and then approached a constant level. The surface area decreased

rapidly until the transformation of ferrihydrite to goethite neared completion. Barium desorption may be caused by this decrease in surface area. The surface areas of samples aged without Ba^{2+} appear to be slightly lower than those of samples aged for the same time with Ba^{2+} during the first 19.3 h of the experiment.

DISCUSSION

One of the primary goals of this study is to identify specific sites and mechanisms for alkali or alkaline earth sorption and desorption on clay and Fe-oxyhydroxide minerals, as well as to quantify the kinetics of those processes. Metal sorption on mineral surfaces is a function of the charge distribution on the surfaces as well as the absolute proportions of exposed planes of differing surface charge. Although total surface areas can be measured using routine BET methods, the best way to determine proportions of edge and basal surfaces on clay minerals is to use an imaging technique in which all three dimensions can be determined on individual particles (e.g., AFM). Quantification by AFM of edge and basal surface areas for kaolinite showed that edges can comprise as much as 50% of the total BET surface area.[4] This is in contrast to untreated SWy-1 montmorillonite, where edge surface areas typically measure <10%. This percentage of edge surface area for smectite clays is more in line with values typically estimated for clays. It is apparent that the decreased grain size and thinner clay platelets of the montmorillonite sample result in increased surface area and available basal reactive sites. In addition, smectites have very reactive basal surface sites due to heterovalent octahedral and tetrahedral lattice substitutions (e.g., Na^{+} for Mg^{2+} or Al^{3+} for Si^{4+}), which induce a permanent charge to the (001) surfaces.

Potentiometric surface charge titrations of a simple tetrahedral-octahedral (TO) clay, kaolinite, have demonstrated that proton donor-acceptor reactions were found to occur simultaneously on the Si and Al sites exposed at basal planes and edges and that there is a pH dependence of multisite surface charge as a function of temperature.[4] Sorption isotherms for Cs^{+}, Sr^{2+} and Ba^{2+} onto kaolinite surfaces have also been measured[2]. Relative metal binding strengths over all kaolinite sites were found to decrease from Ba^{2+} to Sr^{2+} to Cs^{+}, where metals are sorbed on both kaolinite edges and basal surfaces. Some fraction of these metals also appears to be irreversibly sorbed (especially in acid solutions, pH<7) and are thought to be associated with the siloxane basal surface. The most likely explanation is that the basal siloxane layer has a small permanent and pH-independent charge arising from minor substitution of Al^{3+} and/or Fe^{3+} for tetrahedral Si^{4+}. Metal sorption on unwashed montmorillonite (more complex TOT clay with an expandable interlayer site) has similar trends to those found for kaolinite, where the relative binding strength for Ba^{2+} is slightly greater than that for Sr^{2+}. Also, sorption appears to occur via a simple ion exchange reaction and is independent of pH, although the presence of Ca^{2+} in solution seems to suppress cation exchange. The only exception to this pH-independent metal sorption behavior is for Sr^{2+} at pH > 7, where appreciable desorption from SWy-1 occurs. The Sr^{2+} behavior is anomalous, and we do not at present have an explanation for it. These results, however, are consistent with an interpretation of H^{+}/OH^{-} adsorption occurring primarily at charged edge sites, and by implication, with metal sorption also occurring at edge sites. However, multivalent octahedral and tetrahedral cationic substitutions that commonly give rise to the compositional and surface charge variability of expandable TOT layer clays (smectites) will probably complicate our understanding of metal sorption.

In order to simulate, at an atomistic level, specific site acidity at edge and basal plane sites in kaolinite and metal sorption reactions, clay structures for realistic compositions must be ascertained either from experimental diffraction, or ab initio simulation techniques. For the first time, the structural features of kaolinite have been accurately predicted by DFT molecular orbital methods, including bulk structural symmetry as well as hydroxyl orientations in the interlayer region. Calculated O-H bond lengths and hydrogen bonds also correlate well with observed single-crystal infrared spectra of kaolinite.[5] Empirical

MD simulations suggest that Cs^+ is sorbed on kaolinite at aluminol (010) edge sites as an inner-sphere complex and weakly sorbed as an outer-sphere complex on (001) basal surfaces.[4] These computer simulations are consistent with results of sorption and desorption isotherms as a function of ionic strength. MEP calculations also show that there is a significant difference in the electrostatic potential of kaolinite edge and basal surface sites, where siloxane and gibbsite basal planes (001) are not as negatively charged as edge silanol or aluminol sites (010), and aluminol edge sites have greater negative electrostatic charge than edge silanol sites. The combination of charge distributions calculated from potentiometric titrations, proportions of edge and basal plane areas measured from AFM images, and MEP surface charge densities calculated from atomistic simulations provides a consistent picture of distinct crystallographic sites that control kaolinite surface charge and reactivity. That is, aluminol edge sites are preferred metal sorption sites over edge silanol or basal Si- or Al-sites. It should be noted that a small permanent negative charge might exist on the basal planes due to ionic substitutions in the octahedral or tetrahedral layers.

Barium sorption and desorption on Fe-oxyhydroxides is directly linked to the transformation of ferrihydrite to goethite. Ba^{2+} rapidly sorbs onto poorly crystalline ferrihydrite, but partially desorbs during the recrystallization process to goethite. Other studies, however, have suggested that cation sorption may retard ferrihydrite transformation.[6, 7] However, addition of small amounts of Ba^{2+} (0.0005 *M*) was not sufficient to prevent ferrihydrite dissolution or goethite nucleation and crystal growth. Ba^{2+} is also known to sorb on ferrihydrite and sorbs more strongly at pH values above its zero point of charge (pH > 8). While goethite is thought to form from ferrihydrite by dissolution and reprecipitation[8], Ba^{2+} is too large to replace Fe(III) in the goethite structure. Ba^{2+} released after ferrihydrite dissolution may have been adsorbed and then occluded during rapid nucleation of goethite crystals. As the goethite crystals grew larger, surface area decreased and the number of sites for Ba^{2+} sorption and/or occlusion also decreased, causing some Ba^{2+} to be desorbed. Perhaps longer aging periods will determine whether Ba^{2+} desorption reaches a constant level or ceases with time. In particular, atomic force microscopy could be used to relate ferrihydrite aging with and without Ba^{2+} to changes in crystal size and morphology. Initial trends indicate that Ba^{2+} may slow the transformation of ferrihydrite to goethite.

CONCLUSIONS

A combination of analytical, experimental and theoretical techniques was used to characterize metal sorption mechanisms and kinetics onto common soil minerals, including kaolinite and montmorillonite clays as well as goethite and ferrihydrite Fe-oxyhydroxide phases. New efforts include measurements for Ba^{2+} and Sr^{2+} sorption on expandable interlayer smectite clays and aged Fe-oxyhydroxides, and AFM measurements of smectite clay particles. Computer simulations were devoted to a mechanistic understanding of Cs^+ sorption onto kaolinite, and provide a basis for understanding and predicting metal sorption onto simple clays and a general framework for characterizing the sorption of other metals onto more complex soil minerals. Sorption models describing surface complexation reactions are refined by comprehensive evaluation of adsorption isotherm measurements, bulk solution-mineral surface complexation reactions, topological measurements, and molecular or atomistic models of the mineral-solution interface. Care should be exercised when applying these preliminary models to contaminated sites because they are only a hypothetical interpretation of metal sorption in very complex systems.

ACKNOWLEDGMENTS

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