

Sorption Kinetics of Trace Elements in Soils and Soil Materials

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INTRODUCTION

Environmental contamination resulting from the extensive use of metals and semimetals in industry, agriculture, and in manufactured products has magnified the threat of toxicity for plants, animals, and society. Since soils and sediments have a large capacity for sorbing trace elements, an understanding of metal reaction mechanisms with natural materials is critical. Many studies have appeared in the literature on various aspects of metal sorption. Results from these studies have been used to develop government regulations, devise cleanup strategies, and develop models that predict the fate of trace elements in the environment. However, in conducting these studies researchers often overlook two important aspects: (1) the length of time soils are exposed to a contaminant (residence time) in the laboratory is relatively short compared with the much longer residence times that exist in field contaminated soils, and (2) the kinetics of metal sorption and desorption are often slow. These oversights lead to improper evaluation of contaminant behavior in the environment, resulting in regulations that may be improper, and models and remediation strategies that may be unsuccessful. This chapter will investigate the effects of residence time (aging) and slow kinetics on sorption and desorption reaction mechanisms of metals with soils and soil materials (e.g., clay minerals, metal oxides, and organic matter). Such information is important, and can be used in combination with transport models to predict the fate of trace metals through the vadose zone, and can provide information on metal bioavailability and speciation.

Trace elements exist in the soil as either aqueous species, as structural elements in solids, or sorbed onto the surfaces of soil materials. While many of these trace elements are present naturally in the environment, their indigenous levels are usually nonthreatening. The buildup of these elements to dangerous levels is a result of commercial use and disposal practices. The following are a few examples of common sources of contamination: disposal of batteries that contain Pb, Cd, and Hg; exhaust from automobiles that

burn gasoline with Pb additives; application of pesticides that contain Pb and As, e.g., $Pb_3(AsO_4)_2$; the use of Pb in paint; trace elements which are used in manufacturing that end up in waste disposal and the environment from either discarding the product or as a by-product of the manufacturing process; desiccation of agricultural runoff water in ponds which results in Se and As concentrating to dangerous levels; disposal of sewage which contains several trace elements, in particular heavy metals; and mine drainage which is often acidic and can increase the mobility of metals.

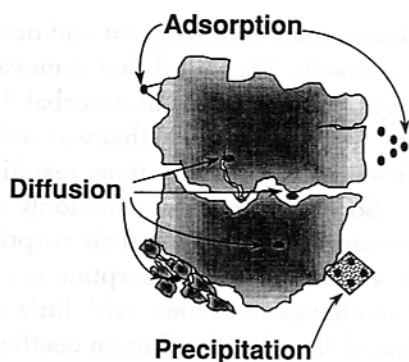
Scientific studies have clearly shown that exposure to metal contaminants at higher than natural levels is toxic. As a result, many past uses and disposal practices of metals are now illegal, and trace element contamination of the environment is now regulated more closely. However, due to the relatively low solubility of many trace metals, and often strong sorption to soils, environmental contamination persists, and the threat from contaminants remains a problem that merits continued scientific investigation.

While toxicity from trace elements, and their presence in the environment at dangerous levels are well-established facts, the questions remain: how does one remediate contaminated soils effectively, and how can significant risks be accurately evaluated? Finding effective answers to these questions hinges on a clear understanding of the behavior and interactions of trace elements with soils. In particular, an understanding of slow desorption and release kinetics from environmental settings which have been contaminated for long periods is critical. For example, Smith and Comans (1996) conducted sorption and desorption experiments on Cs contaminated sediments. They found that failure to include slow reactions in their model gave much lower estimates of the remobilization potential of the Cs. They concluded from model fits that sorption half-lives were between 50 and 125 days, and desorption half-lives were on the order of 10 years.

Many studies rely on an equilibrium approach to predict the retention of contaminants on natural materials and subsequent migration through the vadose zone. Researchers often focus on determining parameters such as distribution coefficients, and the maximum amount of sorption possible. These studies are often based on the contaminant-solid interactions over a short period (24 hours or less) because it is assumed that the reaction has reached completion (Griffin et al., 1986). However, field soils are seldom, if ever, at equilibrium, often laboratory studies are also far from equilibrium, and slow sorption may change the distribution between solid and solution over a period of time (Smith and Comans, 1996; Sparks, 1998). This is primarily due to slow metal sorption and desorption kinetics. The failure to account for the slow kinetics results in either underpredictions of the amount of contaminants retained by soils and minerals, or overpredictions of contaminant availability in the environment. A better approach is to base mobility estimates, remediation strategies, and risk assessments on the true availability of the contaminant, which is often controlled by a rate-limited sorption reaction.

Most soils are heterogeneous media that contain a host of different minerals, solids, and organic materials. Thus, the interaction of trace elements with soils is a heterogeneous process. Several possible sorption mechanisms have been proposed (Figure 1.1): diffusion into micropores and solids followed by subsequent sorption onto interior surfaces; sorption to sites of variable reactivity, including sites which involve different bonding mechanisms, i.e., inner-sphere vs. outer-sphere and monodentate vs. bidentate; and surface precipitation (Fuller et al., 1993; Loehr and Webster, 1996; Scheidegger and Sparks, 1996). Due to the heterogeneity of soil, these processes can occur simultaneously. A

Figure 1.1. Schematic of soil particles illustrating the different types of sorption that are possible. See text for definitions.



measured sorption or desorption rate often reflects a combination of all of the sorption mechanisms. However, it is possible that one mechanism may dominate at a particular time in the sorption reaction and the measured rate is primarily an expression of that reaction rate. For example, outer-sphere complexation can precede inner-sphere complexation, which can precede surface precipitation. The significance of this continuum in sorption is that while many sorption and desorption reactions may appear to have reached equilibrium, in fact the reaction can be continuous, and the slow process will not be measured if the experimentalist studies a short reaction time. In such cases, important secondary processes which are slower than the primary process may be completely overlooked. Thus, predictions on the fate of the contaminant may be inaccurate. This can cause increased threats of toxic exposure, improper evaluation of risks, and/or misappropriation of valuable cleanup and public safety funds.

To protect human health and the environment from overexposure there must exist effective cleanup strategies, accurate risk assessment technologies, and models that correctly predict the fate of trace elements. For these tasks to be accomplished, time dependent reactions of trace elements with soils must be taken into consideration. Thus, the goals of this chapter are to discuss the kinetics of trace element interactions with soil and soil components, including the importance of slow reactions and possible sorption mechanisms.

EVIDENCE FOR SLOW SORPTION AND DESORPTION REACTIONS

There are two separate phenomena associated with slow kinetic sorption processes: (1) a continuous slow removal of the sorptive from solution (sorption), and (2) a slow release of the sorbate from the sorbent (desorption). The second of these phenomena, desorption or release, may be influenced by the length of time in which the contaminant is in contact with the sorbent; i.e., there may be a decrease in the ability of the sorbate to be removed from the surface with increasing incubation or residence time. As mentioned above, several hypotheses for the cause of these two phenomena have been proposed (they are discussed in detail in later sections).

An early report on the effect of incubation time on desorption reactions of metals from soils was given by McKenzie (1967). It was observed that manganese nodules present in Australian soils accumulated a large amount of Co. To account for this selective accumulation, a continuous sorption reaction was hypothesized. To test this, McKenzie (1967)

determined both sorption and desorption kinetics of Co on manganese nodules isolated from soils. He found that removal of Co from solution slowed considerably after two days, but the extent of desorbability showed a continuous decrease with increasing aging periods. Thus, Co that was sorbed would become increasingly resistant to desorption from the nodule with time, resulting in an accumulation over time.

Sorption processes commonly come to a state of quasi-equilibrium rapidly, and many researchers terminate their sorption experiments at relatively short times. However, it has been shown that sorption is a continuous process, and that the sorption mechanism can change over time, with little additional uptake. For example, Nyffeler et al. (1984) found that the distribution coefficients for Be, Mn, Zn, Co, and Fe sorption on particulate matter from surface sediments and sediment traps increased over the entire time of observation, 108 days (Figure 1.2), suggesting that sorption is a slow process. Similarly Bruemmer et al. (1988) found that Ni, Zn, and Cd uptake by soils was continuous for times up to 42 days; e.g., Ni removal from solution at pH = 6 was 12% in two hours and 70% in 42 days. Bibak et al. (1995) studied the retention of Co by various goethite polymorphs and impure goethite. They found that Co sorption behavior varied between the different polymorphs and minerals, but in all samples the Co uptake increased with contact time (sorption kinetics measured from two hours to 504 hours). McBride (1982) found that sorption of Cu on noncrystalline aluminum oxide increased over periods of weeks, and proposed that different bonding mechanisms were responsible for the slow sorption process.

McLaren et al. (1983) studied the desorption of Cu from humic acid, ferro-manganese concretions, and montmorillonite. In the desorption procedure the sorptive solution was replaced by the electrolyte solution (no metal), the suspension was allowed to incubate for four hours, and then, new electrolyte solution was added. The repeated washing of the soil removed little of the Cu, demonstrating that Cu sorption was strong. Young et al. (1987) compared Cu sorption and desorption reactions on river sediments with Cr and Zn. They observed that sorption of Zn was complete in four hours, Cr sorption was far from complete after 48 hours, and Cu sorption kinetics were intermediate. In addition, Young et al. (1987) concluded that desorption was not irreversible as McLaren et al. (1983) found, but that the observed irreversibility was a result of the slow kinetics involved. This slow desorption phenomenon was also observed for phosphate by Lookman et al. (1995). They found that slow phosphate desorption from soils continued for up to 1,600 hours, and showed no signs of reaching a plateau. In fact, using a rate constant derived from a first-order fit of the slow reaction, they predicted that 500 days would be required for desorption of 90% of the phosphate.

Several researchers have noted that not only are trace elements strongly sorbed and exhibit slow desorption kinetics, but that the rate of desorption decreases with increasing residence times. Padmanabham (1983) conducted desorption experiments of Cu from goethite and concluded that Cu was sorbed in two different ways: a fraction was associated with low bonding energy and the rest was associated with high bonding energy. It was observed that a gradual interchange with increasing incubation time occurs between the readily desorbed fraction (low energy) and the less readily desorbed fraction (high energy). Similar results were found by Kuo and Mikkelsen (1980), Schultz et al. (1987), and Backes et al. (1995), who showed that the desorption rate of several transition metals (Zn, Co, and Cd) from soils and soil components decreased with increasing

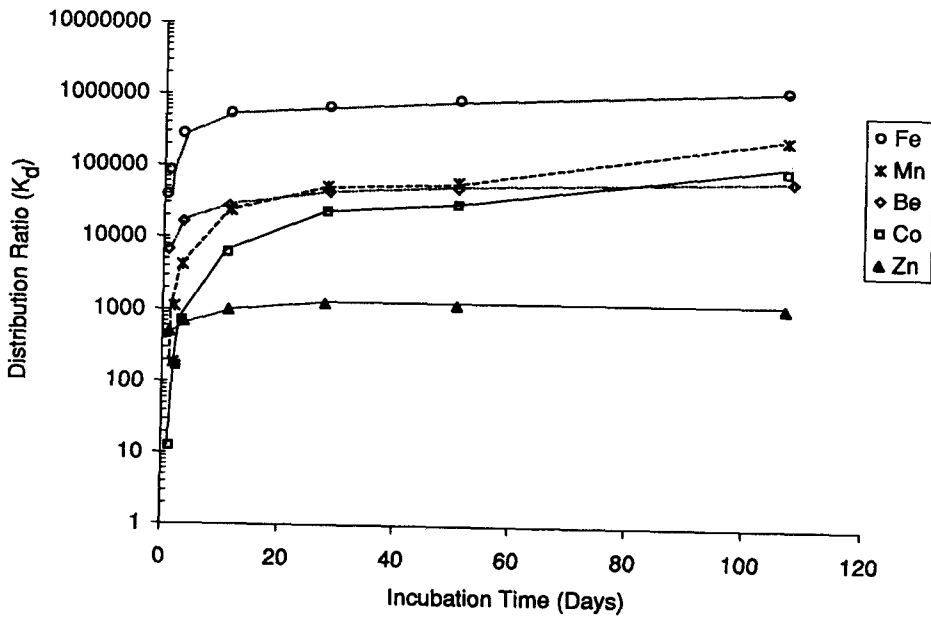


Figure 1.2. Effect of incubation time on the distribution coefficient (K_d) for the sorption of selected trace elements (radioactive tracers) on sediments. From Nyffeler et al. (1984), with permission.

aging time. Their findings further support the hypothesis that a slow process occurs between trace metals and soils that affects the availability of the metal. Smith and Comans (1996) observed an increase in the slowly desorbed fraction of sorbed Cs from sediments with increasing incubation time. Modeling of their data using a two-compartment model (Figure 1.3) suggests that there exists an exchangeable sorbed fraction and a "fixed" fraction. Slow transfer between the two fractions was responsible for slow kinetics of sorption and desorption.

Another method for determining the reversibility of sorption, or the effects of aging, is to measure the exchangeability of the sorbate using isotopic exchange. This approach was used by McLaren et al. (1986) who studied the sorption and desorption behavior of Co from soil components. For humic acid, a large proportion of the Co was isotopically exchangeable, even for sorption incubation times as long as 50 days. However, for a soil oxide (ferro-manganese concretions) and montmorillonite, the fraction of nonisotopically exchangeable Co increased continuously as sorption time increased. Comans (1987) determined that the isotopic exchangeability of Cd on illite was 100%, but required an equilibration time of seven to eight weeks. These results suggest that with increasing incubation time the association between the sorbate and the sorbent changes to that of a more stable complex, i.e., less readily desorbed.

Hysteresis, or nonsingularity, is a phenomenon in which the sorption and desorption isotherms do not coincide because of a shift in the equilibrium point. Pseudo-hysteresis is often observed in systems that have a slower desorption reaction than the sorption reaction (or vice versa), and is a result of not carrying the experiment out for a long enough period, i.e., the system has not reached equilibrium (McBride, 1994, p. 91). For example, Comans (1987) found that sorption and desorption isotherms of Co on illite are

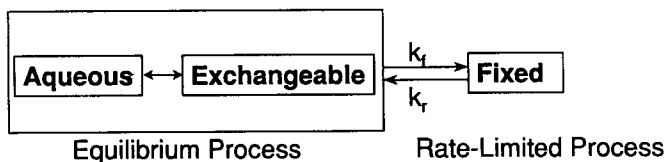


Figure 1.3. Schematic illustrating a modeling approach used to describe the slow transition of Cs from a mobile (exchangeable phase) to a fixed phase. From Smith and Comans (1996), with permission.

singular (nonhysteretic) only if the desorption reaction is allowed to come to equilibrium, which took 54 days.

Many researchers have found that the magnitude of hysteresis increases with longer sorption incubation periods. Ainsworth et al. (1994) found that despite increasing the desorption times from 16 hours to nine weeks, hysteresis persisted for Co and Cd sorbed on hydrous ferric oxide (HFO). They also found that Cd and Co displayed increasing hysteretic behavior upon aging from two weeks to 16 weeks (Figure 1.4, Cd data not shown), while Pb sorption/desorption behavior was reversible (Figure 1.5).

Oftentimes it is observed that the amount of sorbate able to be desorbed decreases with increasing incubation time. For example, the results of McKenzie (1980) suggest that Pb sorption on Fe-oxides is a slow process, and can affect the total amount of Pb able to be desorbed. McKenzie (1980) incubated Pb on hematite and goethite for periods from one day to 28 weeks, and then extracted the samples with 2.5% acetic acid until no additional Pb was removed. A comparison of the Pb removal from the different samples showed that increasing the incubation time from one day to 28 weeks increased Pb retention by 50% on hematite, and 100% on goethite. Similar experiments were conducted by Bibak et al. (1995) for Co sorbed on iron oxides; they used a strong acid extractant to measure the amount of Co released from iron oxides incubated for different periods. Their results indicated that the percentage of Co released decreased with increasing aging times. The results of McKenzie (1980) and Bibak et al. (1995) suggest that many adsorption reactions that appear to be at equilibrium are undergoing slow transformations that decrease the amount of sorbate able to be desorbed.

Hysteresis has also been observed in cation exchange reactions, where the exchange of one sorbed cation with another is not completely reversible, i.e., the forward and reverse exchange reactions do not result in the same isotherms. The hysteretic behavior of cation exchange is abundantly reported in the literature; an excellent critical review of this literature was published by Verburg and Baveye (1994). From a survey of the literature they were able to categorize several elements into three categories (Table 1.1). The elements in each category were found to show hysteretic exchange between groups, but not within groups. Verburg and Baveye (1994) proposed that exchange reactions are most likely a multistage kinetic process in which the later rate-limiting processes are a result of physical transformation in the system; e.g., surface heterogeneity, swelling hysteresis, and formation of quasi-crystals, rather than simply a slow kinetic exchange process where there exists a unique thermodynamic relationship for forward and reverse reactions. While this may be true in some circumstances, an apparent (pseudo) hysteresis also can result from slow sorption and desorption reactions, i.e., lack of equilibrium.

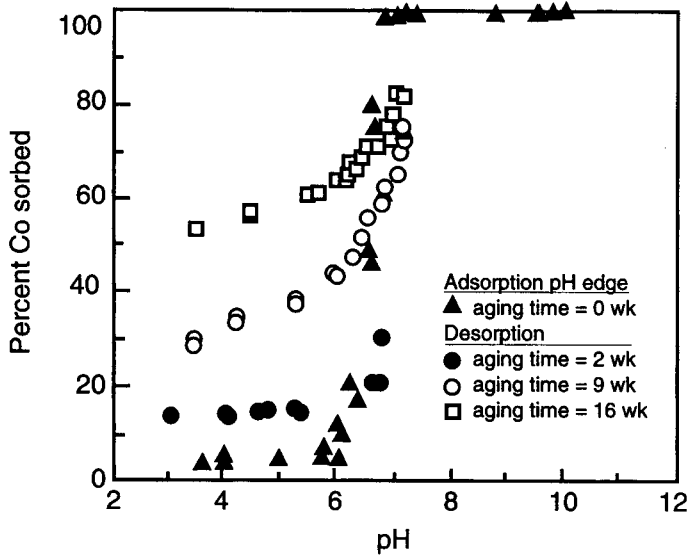


Figure 1.4. Effect of sorption incubation time on the desorption of Co from Fe oxide. From Ainsworth et al. (1994), with permission.

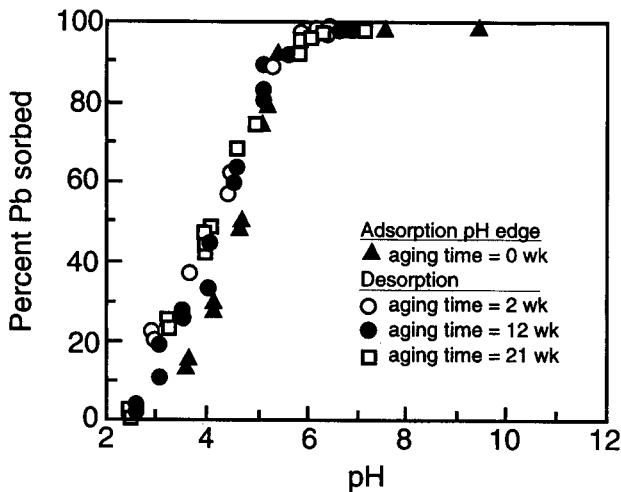


Figure 1.5. Effect of sorption incubation time on the desorption of Pb from Fe oxide. From Ainsworth et al. (1994), with permission.

Regardless of the different reasons for hysteresis, we agree with the proposal of Verburg and Baveye (1994) that to be of practical value, kinetic models need to be complemented by detailed information on the mechanism(s) responsible for the slow kinetic reaction(s).

The above discussion has presented many examples of slow kinetics for both sorption and desorption processes. Several of the researchers have speculated on the mechanism(s) that control slow reactions. However, these hypotheses are based primarily on macroscopic data, while sorption and desorption processes are microscopic phenomena. At

Table 1.1. Classification of Cations into Three Groups in Such a Way that Hysteresis Has Been Documented in the Literature for Binary Reactions Involving Cations from Different Groups^a

Group 1	Group 2	Group 3
Na ⁺	K ⁺	Ca ²⁺
Li ⁺	Rb ⁺	Ba ²⁺
	Cs ⁺	Sr ²⁺
	NH ₄ ⁺	Mg ²⁺
		Mn ²⁺
		Cu ²⁺
		Ni ²⁺

^a From Verburg and Baveye (1994), with permission.

best, macroscopic investigations suggest a particular mechanism may be occurring; they provide little evidence that other mechanisms are not involved (Sposito, 1986; Chisholm-Brause et al., 1990). Despite this problem, reasonable predictions of sorption mechanisms based on macroscopic observations are often made. However, the uncertainty becomes clear when one observes the discrepancies in predictions of mechanisms between published reports on similar systems. For example, Ainsworth et al. (1994) predicted that the similarities of the ionic radii between Co and Fe suggested a coprecipitation mechanism as responsible for aging. This hypothesis was supported by their observation that as ionic radius decreased, i.e., $Pb > Cd > Co$, hysteresis increased. However, Bibak et al. (1995) predicted that the mechanism responsible for the slow reaction of Co on various iron oxides was diffusion. This prediction was based on a good fit of the data to a diffusion model. An important point to note about comparing these two systems is that in the experiments of Ainsworth et al. (1994) the initial Fe-oxide was amorphous and underwent recrystallization, while the Fe-oxides used in the experiments of Bibak et al. (1995) were crystalline and did not undergo a solid phase transformation. Such differences can have important consequences on sorption mechanisms. Despite this discrepancy, one can conclude from these studies that in order to better predict the mechanisms responsible for the slow kinetic processes, microscopic as well as macroscopic data are necessary.

DIFFUSION-CONTROLLED KINETIC REACTIONS

Diffusion is an activated process driven by the necessity of a system to be at its lowest possible energy, i.e., uniformly distributed throughout space. Since soils are porous materials containing both macropores (>2 nm) and micropores (<2 nm) (Pignatello and Xing, 1996), diffusion is a mechanism that can control the rate of sorption of trace elements on soils. These pores can be interparticle (between aggregates) or intraparticle (within an individual particle). Intraparticle pores can form during weathering, upon solid formation, or may be partially collapsed interlayer space between mineral sheets; i.e., vermiculite and montmorillonite. The rate of diffusion through a pore is dependent on pore size, particle size, tortuosity, chemical interactions, chemical flux through the soil, and whether the pore is continuous or discontinuous. Besides pore diffusion, solid-

phase diffusion is also a transport-limited process. Solid phase diffusion is dependent on the characteristics and interactions of the diffusant and the solid (Pignatello and Xing, 1996). Since there exists a range of diffusion rates in the soil, it follows that with increasing exposure time the fraction of contaminants in the more remote areas of soil particles (accessible via slow diffusion) will increase. This slow sorption phenomenon is often the explanation researchers use to account for the slow continuous sorption and desorption observed between metals and soil (Sparks, 1989; Burgos et al., 1996).

Bruemmer et al. (1988) measured sorption and desorption of Cd, Zn, and Ni with goethite, a porous iron oxide known to have defects within the structure in which metals can be incorporated to satisfy charge imbalances. They found that the kinetics were described well with a solution to Fick's second law (a linear relation with the square root of time), and proposed that the uptake of the metal followed a three-step mechanism: "(i) adsorption of metals on external surfaces, (ii) solid-state diffusion of metals from external to internal sites,^o and (iii) metal binding and fixation at positions inside the goethite particle," suggesting that the second mechanism is responsible for the slow reaction (Bruemmer et al., 1988). Similar observations on sorption of divalent metal ions were made by Coughlin and Stone (1995). They suggested that the slow sorption and desorption could be a result of slow diffusion that occurred because their synthetic goethite may have had an unusually high level of pores and cavities. Axe and Anderson (1997) also found that sorption of Cd and Sr could be characterized by a model which included two steps: a rapid reversible sorption step followed by a slow, rate-limiting process involving the diffusion of the cations through small pores existing along the surface.

While the above examples have hypothesized that diffusion is the rate-limiting step based on good model fits to data and some speculation, macroscopic sorption experiments are not definitive proof of a mechanism (Sposito, 1989, p. 150). To give additional support to diffusion as a mechanism for sorption onto porous media, Papelis (1995) measured surface coverages of Cd and selenite on porous aluminum oxides using X-ray photoelectron spectroscopy (XPS). Papelis (1995) calculated the expected thickness of sorbed Cd and selenite from the total metal loss from solution using both external and internal surface areas. A good agreement was found between the calculated and the measured (using XPS) surface coverage thickness when the total surface area (i.e., internal and external surface area) was used. When the surface layer thickness was calculated without considering internal surface area, then the calculated thickness exceeds the thickness observed using XPS. Therefore, the most likely sorption mechanisms were sorption to external sites, diffusion of Cd into the internal structure, and subsequent sorption. While Papelis (1995) didn't measure the kinetics of the reaction, it seems probable that the sorption to the interior sites is slower than the exterior sites, and thus a slow kinetic sorption step would exist.

Fuller et al. (1993) combined kinetic sorption and desorption experiments with spectroscopic observations (Waychunas et al., 1993) to conclude that the rate-limiting process in arsenate sorption by ferrihydrite is diffusion into the solid structure. Using X-ray

^o Classical solid-state diffusion is a very slow process in crystalline structures, and usually only significant at very high temperatures (McBride, 1994, p. 28). In this case, solid state diffusion should be interpreted as diffusion processes through faults and micropores.

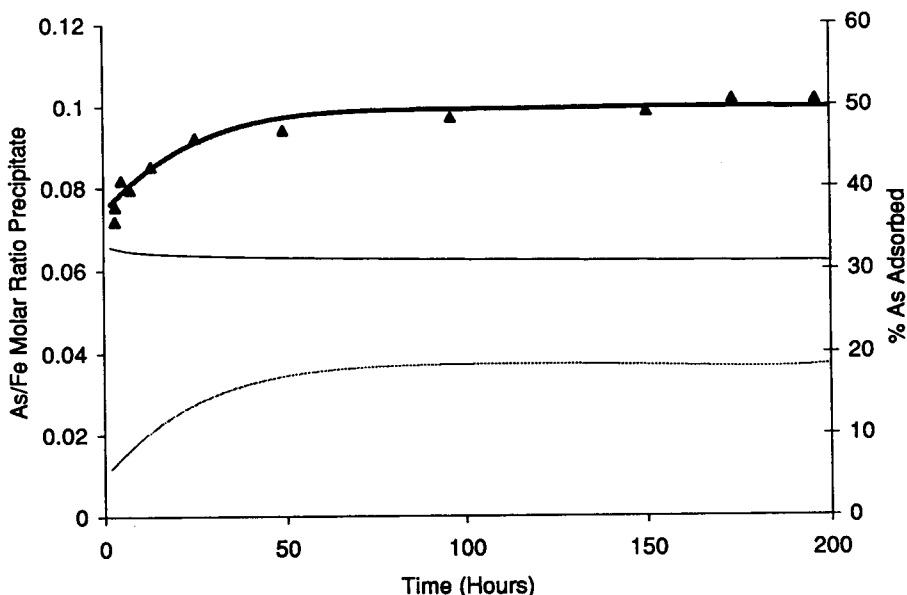


Figure 1.6. Pore-space diffusion fit of As(V) adsorption density as a function of time for total (dark line), diffusion-limited (dotted line) and exterior surface components of adsorption (thin solid line). The solid triangles represent the adsorption data. Exterior sites are modeled based on equilibrium. From Fuller et al. (1993), with permission.

absorption fine structure (XAFS) spectroscopy, Waychunas et al. (1993) found that arsenate is sorbed predominantly as inner-sphere bidentate complexes, regardless of whether the arsenate was adsorbed post-mineralization of the ferrihydrite, or present during precipitation. Thus, at the pH of their study (8.00), arsenate surface precipitates were not formed. Slow sorption and desorption were explained as slow diffusion of the arsenate to or from interior surface complexation sites that exist within disordered aggregates of crystallites. The arsenate sorption and desorption kinetics (Figure 1.6) were explained well using a model which included two types of sorption sites: those easily accessible were described assuming equilibrium (thin solid line), while the sites which had limited accessibility (dotted line) were well represented by an equation which is based on Fick's second law of diffusion.

Kinetics and Mechanisms of Adsorption Processes

Adsorption is a phenomenon in which matter accumulates at the interface between a solid phase and a solution phase; it is largely considered to be two-dimensional (Sposito, 1989, p. 132). Adsorption reactions are governed by the laws of thermodynamics: energy is conserved, and the entropy of a system increases to a maximum. These two concepts can be combined to create the Gibbs free energy (G) function. For a reaction to occur, the products must have a lower free energy than the reactants ($\Delta G < 0$). This can occur by either a decrease in enthalpy, an increase in entropy, or both. It is important to note that a change in enthalpy can dominate the free energy function creating a negative ΔG even when the entropy is decreased in the reaction, and vice versa. Therefore, an

adsorption process leads to an association between an ion and a surface, driven by the desire of the system to achieve an overall lower free energy.

While thermodynamics can be used to determine if a reaction is favorable, it does not indicate the rate of the reaction, nor the pathways involved in arriving at the state with the lowest free energy. This information can be gained by measuring reaction kinetics. In real systems, such as soils and sediments where there exist several different types of sorption sites, reaction mechanisms and kinetics can be heterogeneous. In these systems kinetics plays an important role in the fate of trace elements since such systems are not at equilibrium, but are continuously undergoing chemical changes as they seek to produce the most stable species (Steinfeld et al., 1989, p. 1). The change may be slow, resulting in the sorbate becoming less available with time (aging) (Koskinen and Harper, 1990), and can result in a change from one type of sorbed complex to another. This process is similar to the concept of the Ostwald-step rule: the first product in a precipitation reaction is that which has the highest solubility, followed by a slow continuous transformation to a more stable species (Stumm and Morgan, 1996, p. 807). An analogous process in adsorption would result in a multitude of adsorbed complexes, some of which may be in a metastable equilibrium state, undergoing continuous transformation to the most stable species.

Evidence for this slow, continuous change to a more stable species is commonly observed for solid materials. Upon initial precipitation the solid is in an *active* form that has a disordered lattice (amorphous), and exists in a metastable equilibrium with the solution (Stumm and Morgan, 1996, p. 356). With time the solid slowly converts to the more stable *inactive* form. The *inactive* form is more crystalline-like, and has a lower solubility. This slow kinetic phenomenon may continue for geological time spans. An example is aragonite (a polymorph of calcite), which is found in rocks < 300 million years old. Aragonite is not thermodynamically stable, but forms under surficial temperatures and pressures, and slowly reverts to the more stable calcite (Blackburn and Dennen, 1994, p. 102). Waychunas et al. (1993), using XAFS data fitting, found that aging and continued polymerization of ferrihydrite resulted in a transformation of the number of linkages and interatomic distances to those suggesting a progression to the more ordered polymorph goethite. The slow transformation of a solid to a state with a lower free energy is often observed as an aging mechanism for precipitates, but transformations between sorption mechanisms is more difficult to distinguish, and little direct evidence exists for such processes. However, it seems reasonable to suggest that the energetics of sorption and desorption reaction processes are analogous to those of precipitation; i.e., kinetically limited by a transformation to the most stable sorption configuration (lowest ΔG).

Adsorption reactions occur via three different mechanisms: inner-sphere complexes, outer-sphere complexes, and diffuse ion (Figure 1.7, diffuse ion not indicated) (Sposito, 1989, p. 132). Outer-sphere bonds consist of a solvated ion that forms a complex with a charged functional group; the primary bonding force is electrostatic. An inner-sphere complex is partially dehydrated; the ion forms a direct ionic or covalent bond with the surface functional groups. A diffuse ion exists in the water layers near the surface, and is held by electrostatic attraction from permanent charges that exist in the solid structure. A major difference between the outer-sphere complex and the diffuse ion complex is in the strength of the electrostatic force, which is directly correlated to the proximity of the ion to the surface (McBride, 1994, p. 73). The type of sorption and bonding mechanism

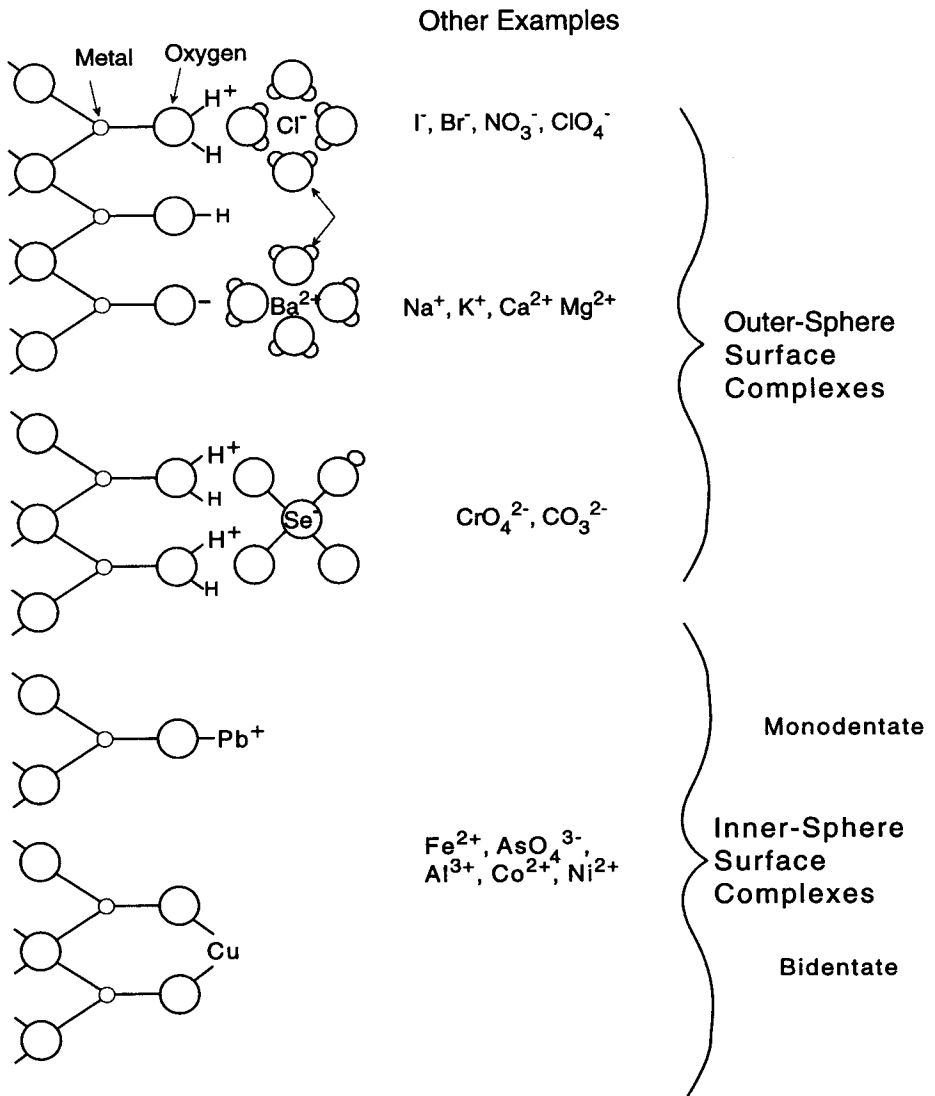


Figure 1.7. Schematic showing the different types of adsorption complexes that can occur on solid surfaces. See text for definitions. From Hayes (1987), with permission.

depends on several factors: (1) ionic radius, (2) electronegativity, (3) valence charge, (4) surface type, and (5) ionic strength of the sorptive solution. There are two major types of surface sites: variable charged sites, e.g., silanol and aluminol; and permanent charge sites that result from isomorphic substitution.

To model surface complexation and understand the controlling mechanisms, scientists often assign a hypothetical bonding mechanism between an ion and a given surface. However, ions can bond to surfaces via several different mechanisms, and can undergo a continuous transition between adsorption mechanisms (Stumm and Morgan, 1995, p. 586). Waychunas et al. (1993) found that arsenate adsorbed onto ferrihydrite by both monodentate (30%) and bidentate bonding mechanisms. Bargar et al. (1996) used X-ray

absorption spectroscopy (XAS) to distinguish between outer- and inner-sphere sorbed Pb on α - Al_2O_3 . They found that on the planar 0001 surface Pb-O-Al distances were consistent with an outer-sphere bond, while on the 1102 plane Pb was sorbed as an inner-sphere complex. Benjamin and Leckie (1981) conducted sorption experiments at several different loading levels and equilibrium pHs for Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. Their data suggested that there exist several types of bonding sites with variable bonding strengths, and that measured equilibrium constants are average values from these different types of sites. McBride (1982) found similar results on pure noncrystalline aluminum oxide using electron spin resonance (ESR) spectroscopy to study the change in Cu sorption mechanisms with time. He found that sorption involved sites of varying reactivity. The first reaction step was the rapid sorption of a low level of Cu; the second reaction occurred over several weeks and resulted in the uptake of a greater amount of Cu and ESR spectra distinct from the first reaction step. Such heterogeneity is enhanced in natural systems that contain materials with a variety of organic and inorganic surface sites.

Adsorption reactions are often considered to form the most stable bond immediately, but commonly there are intermediates which can be metastable for long times. In fact, adsorption may consist of a series of chemical and physical reactions that may limit the overall reaction rate; i.e., ion and surface dehydration, breaking of a strong bond, bond formation, and surface diffusion (Stumm and Morgan, 1996, p. 761; McBride, 1994, p. 135). Hayes and Leckie (1986) and Grossl et al. (1994) used pressure-jump relaxation to measure the kinetics of Pb sorption on aluminum oxide and Cu(II) sorption on goethite, respectively. They found that the best fit to the data was obtained by fitting a kinetic model that included a transformation from outer-sphere to inner-sphere complexation. Their results also suggested that sorption behavior was biphasic, which they explained by suggesting that the slower reaction was a result of sites with lower affinities. This concept is similar to the high and low affinity site model proposed by Dzombak and Morel (1990, p. 92). While the kinetics of these reactions are quite rapid (reactions considered on a millisecond time scale), the demonstration of a multiple step adsorption mechanism rationalizes the hypothesis that in some systems one step may be slow enough to be responsible for the slow adsorption and desorption reactions often observed in soils (Sposito, 1989, p. 150).

The kinetics of Pb sorption on γ - Al_2O_3 are shown in Figure 1.8. These data show a fast initial reaction followed by a slow sorption reaction continuing for several hours. Such biphasic behavior is likely a result of sorption to sites of variable reactivity and/or diffusion limited sorption. Slow surface precipitation reactions can be ruled out because analysis of the radial structure function obtained using XAFS (Figure 1.9) does not exhibit any major features (e.g., second peaks indicative of second shell neighbors) beyond the primary Pb-O structural peak at $\sim 1.9 \text{ \AA}$ (uncorrected for phase shifts) with long incubation times.

Biphasic sorption reactions have also been observed in soils. An example is the result of Lehman and Harter (1984) who measured the kinetics of chelate-promoted Cu release from a soil to assess the strength of the bond formed. Their sorption/desorption data were biphasic, which they attributed to high and low energy bonding sites. They also found that with increased residence time, 30 minutes to 24 hours, there was a transition of the Cu from low energy sites to high energy sites (as evaluated by release kinet-

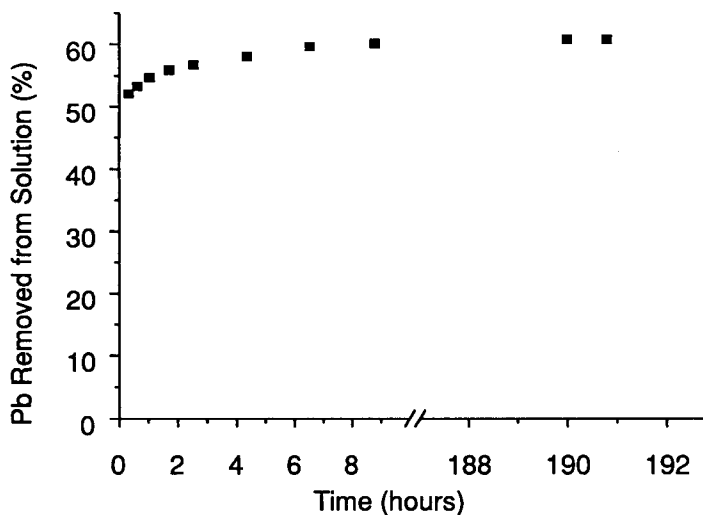


Figure 1.8. Kinetics of Pb removal from solution by $\gamma\text{-Al}_2\text{O}_3$. Ionic strength = 0.1, pH = 6.50, initial Pb concentration = 0.002 M.

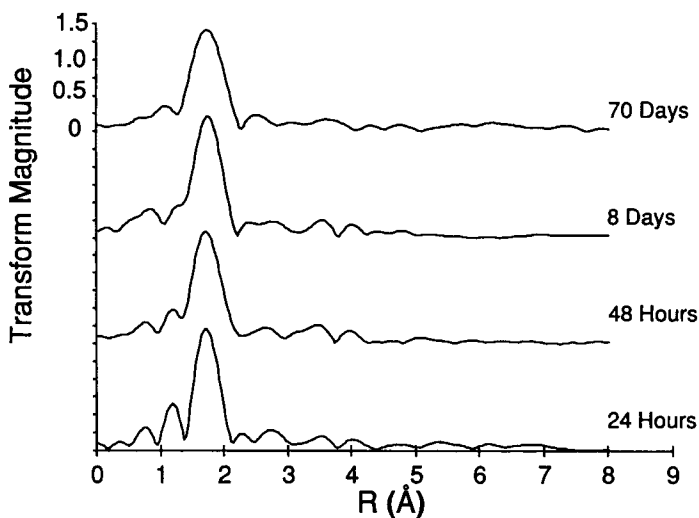


Figure 1.9. Radial distribution function (uncorrected for phase shifts) for Pb sorbed on $\gamma\text{-Al}_2\text{O}_3$ incubated for 24 hours to 70 days. Incubation conditions are the same as in Figure 1.8.

ics). Incubations for up to four days showed a continued uptake of Cu and a decrease in the fraction released within the first three minutes, which was referred to as the low energy adsorbed fraction. The results of Smith and Comans (1996), already mentioned, also showed that Cs sorption onto sediments is biphasic. They modeled exchange reactions assuming exchangeable and fixed fractions. The fixed fraction was assigned to Cs that was incorporated in the mineral lattice, i.e., predominantly specific exchange sites on illitic clay. The Cs adsorption mechanisms proposed by Smith and Comans (1996)

were based on kinetic experiments, i.e., macroscopic observations. Kim et al. (1996) used nuclear magnetic resonance (NMR) spectroscopy to make microscopic observations of Cs sorption mechanisms on kaolinite, boehmite, silica gel, and illite. Their experiments coincide with those of Smith and Comans (1996), suggesting that Cs formed two distinct types of complexes on the surfaces of the minerals: inner-sphere and outer-sphere.

The energy and stability of adsorbed species varies depending on the type of surface complex formed. It is generally accepted that surface complexes with more than one bond are more stable than complexes with a single bond (Stumm and Morgan, 1996, p. 276; McBride, 1994, p. 134), and likewise for inner-sphere vs. outer-sphere sorption (McBride, in Bolt, 1991, p. 168). One explanation for the increased stability of a multidentate bond over a monodentate bond may be the increased entropy gained from a more stable configuration (steric effect) (Steinfeld et al., 1989; McBride, 1994, p. 80). An analogous phenomenon is the *Chelate Effect*; for example, the ΔG for the ethylenediamine complex, a chelate ring with bidentate bonding to a cation, is lower than ΔG of the diamine complex, which forms monodentate complexes with cations (Stumm and Morgan, 1996, p. 279, from Schwarzenbach, 1961). The lower ΔG for the ethylenediamine complex means it is more stable. Since the enthalpies for the complexation of cations by the two chelates are similar, the lower ΔG is a result of an increased entropy for the bidentate ring complex; as mentioned above, this phenomenon is often referred to as a steric effect or configurational entropy (Steinfeld et al., 1989, p. 250; McBride, 1994, p. 80). Since the reactive sites on minerals (silanol and aluminol sites) and organic matter (carboxyls and phenolic-OH) are often considered to be analogous to ligand functional groups, the steric effect is likely to be an important consideration when determining mechanisms of trace element adsorption reactions in soil. Thus, it is reasonable to conclude that if the coordination environment is appropriate, multidentate bonding will be favored (thermodynamically) over monodentate bonding. However, the formation of multiple bonds may have intermediate products that have a higher activation energy than a complex with only a single bond. As discussed below, an increase in the activation energy may limit the kinetics of complex formation.

The formation of a surface complex, or conversion of an adsorbate from one bond type to another, may be thermodynamically favored but inhibited by an activation energy, which is the extra energy, beyond the difference in the free energy between the products and reactants (ΔG°), required to complete the reactions (Figure 1.10). The activation energy results from the energy required to form intermediate products not accounted for in the reaction stoichiometry (Noggle, 1989, p. 532). A large activation energy will result in slower adsorption and desorption kinetics compared to sorption processes which have a lower activation energy.

Since the strength of adsorption varies depending on the surface and adsorptive being considered, the adsorbate availability (via desorption) and kinetics are variable (Pignatello and Xing, 1996). For many adsorbed ions it is found that the rate of adsorption is faster than desorption (McBride, 1994, p. 134; Swift and McLaren, in Bolt, 1991, p. 285). A possible reason for the slower rate of desorption is an increase in the activation energy required to break the adsorption bonds. The activation energy for desorption can be quantified as follows: $\Delta G_{\text{desorption}}^\ddagger = \Delta G_{\text{adsorption}}^\ddagger + \Delta G_{\text{adsorption}}^\circ$, where $\Delta G_{\text{desorption}}^\ddagger$ = activation energy for desorption, $\Delta G_{\text{adsorption}}^\ddagger$ = activation energy for adsorption (≥ 0), and

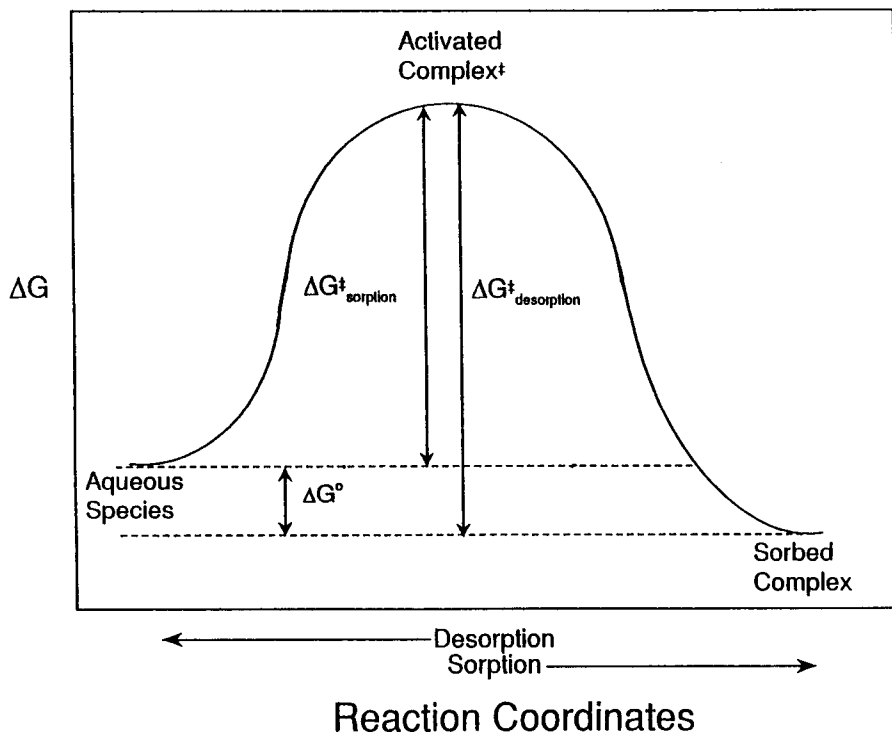


Figure 1.10. Schematic diagram of G vs. reaction coordinate for sorption and desorption processes. Adapted from Sparks and Jardine (1981), with permission.

$\Delta G^{\circ}_{\text{adsorption}}$ = energy of adsorption, see Figure 1.10 (McBride, in Bolt, 1991, p. 168). This equation indicates that desorption of chemisorbed ions yields a larger activation energy than adsorption reactions, causing desorption to be a slower process. This may be the cause of the pseudo-hysteresis that is commonly observed in sorption and desorption experiments; i.e., the forward and reverse isotherms do not overlap when given the same reaction time.

The experiments of McLaren et al. (1986) were discussed briefly in an earlier section; however, another look at their results is merited at this point to evaluate possible mechanisms. They found that Co sorbed by a soil oxide demonstrated a continuous decrease in isotopic exchangeability as sorption times increased (only 20% was exchangeable when sorption was carried out for 50 days) (Figure 1.11). For humic acid, the isotopic exchangeability of sorbed Co decreased only slightly with increased sorption incubation time (Figure 1.12) (the amount of Co that was isotopically exchangeable remained as high as 80% for 50 days of sorption incubation time). It is difficult to prescribe a particular mechanism as the cause for the aging observed in McLaren's studies; however, it is possible that a more stable complex is being formed on the oxide with increasing sorption incubation time, increasing the energy required for isotopic exchange. Eliminating diffusion as a slow exchange mechanism seems reasonable in this case since the humic acid fraction, a porous material, lacked a slow exchange portion. However, more detailed studies and measurements of the porosity of the two materials is needed for diffusion to be completely ruled out. Surface precipitation is difficult to eliminate; the authors

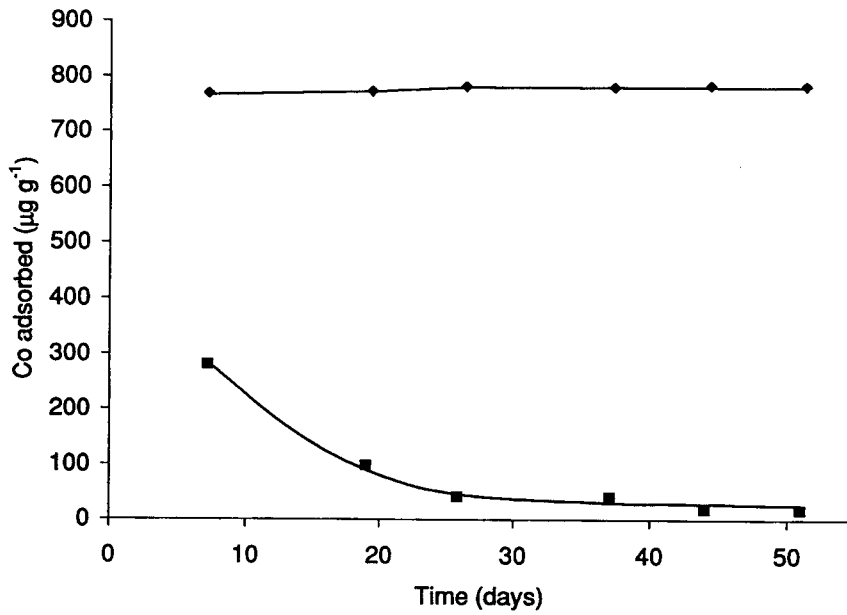


Figure 1.11. Isotopic exchangeability of Co sorbed by soil oxide: total Co sorbed (◆), and isotopic exchangeable (■). The space in between the two lines indicates the nonisotopic exchangeable fraction. From McLaren et al. (1986), with permission.

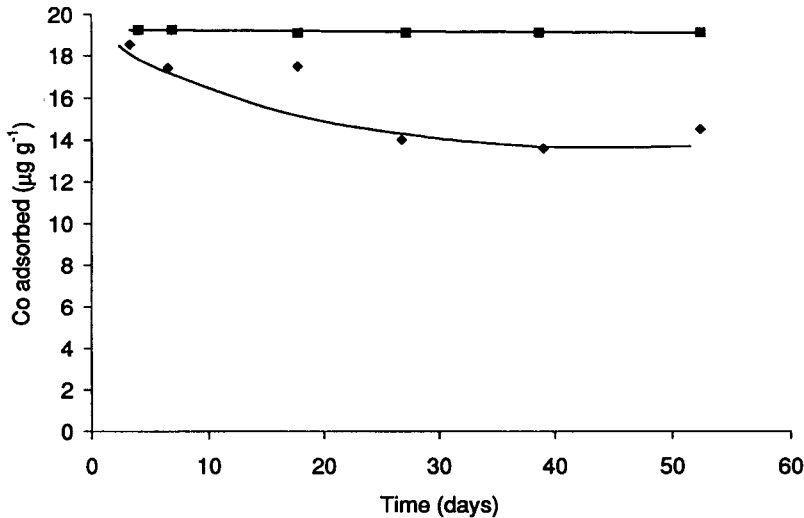


Figure 1.12. Isotopic exchangeability of Co sorbed by soil organic matter: total Co sorbed (■), and isotopic exchangeable (◆). The space in between the two lines indicates the nonisotopic exchangeable fraction. From McLaren et al. (1986), with permission.

discounted it as the predominant sorption mechanism since surface coverages were low. For more conclusive evidence, microscopic measurements are necessary.

In this section we have discussed adsorption and desorption kinetics and sorbate stability. The kinetics of sorption and stability of a surface complex is a factor of both entropy (steric factors) and enthalpy (bond energetics). However, the formation of the most stable adsorbed species may be limited by intermediate complexes. Thus, if a sorbate slowly converts from one sorption or bonding species to a more stable complex that has a lower free energy, the result is important toward controlling the rate of uptake and affecting the availability of trace metals.

Kinetics and Mechanisms of Surface Precipitation

In contrast to adsorption, surface precipitation is a 3-dimensional growth phenomenon that occurs on surfaces. Classical solution chemistry defines aqueous systems in three states: undersaturated, saturated, and supersaturated, with respect to the solubility of inorganic precipitates. A system saturated or supersaturated has a negative ΔG , indicating that the precipitation of a solid product is favored. Precipitation that occurs in a saturated system proceeds more slowly than a supersaturated system (Stumm and Morgan, 1996, p. 802). Surface precipitation during trace metal sorption has been observed in systems undersaturated with respect to the pure hydroxide, and below monolayer surface coverage (Fendorf et al., 1992; Fendorf and Sparks, 1994; O'Day et al., 1994a,b; Scheidegger et al., 1996). This means that the availability and transport of a cation or anion may be controlled by precipitation and dissolution mechanisms, as opposed to adsorption phenomena. Veith and Sposito (1977) showed that traditional sorption data are described equally well by both surface precipitate models and adsorption isotherms. In addition, it has been noted that solubility lines of many soil solutions (logarithm of metal activity plotted as a function of pH) reveal undersaturation with respect to common precipitates; however, they often have slopes paralleling those of pure precipitates (McBride, in Bolt et al., 1991, p. 171, from Lindsay, 1979). Such examples display the ambiguity of macroscopic models in describing microscopic processes; i.e., surface precipitation and adsorption models seem to describe sorption data equally well. Since precipitation and dissolution reactions exhibit slower kinetics than adsorption and desorption (Farley et al., 1985) they may be the mechanism responsible for aging and the slow kinetics of sorption and desorption often observed in experimental systems (Fendorf et al., 1992).

In this section we categorize surface precipitation into three different types that are commonly discussed in the literature. These include formation or sorption of metal polymers (dimers, trimers, etc.) on the surface (Chisholm-Brause et al., 1990); a solid solution or coprecipitate that involves coions dissolved from the sorbent; and a homogeneous precipitate formed on the surface composed of ions from the bulk solution, or their hydrolysis products (Farley et al., 1985). The continuum between surface precipitation and chemisorption is controlled by several factors, including (1) the ratio of the number of sites vs. the number of metal ions in solution, (2) the strength of the metal-oxide bond, and (3) the degree to which the bulk solution is undersaturated with respect to the metal hydroxide precipitate (McBride, in Bolt, 1991, p. 163). The different types of surface precipitation are explained in more detail below.

Polymeric metal complexes that form at the surface, and/or the sorption of aqueous polymers, may be a mechanism that typifies surface precipitate-like complexes (Fendorf

et al., 1992). Chisholm-Brause et al. (1990) interpreted the presence of Pb in the second coordination shell of a sorbed Pb (determined using XAS) as small clusters or polynuclear structures that are analogous with hydroxy metal complexes formed in water solution. The formation of complete surface precipitates was ruled out because the number of Pb atoms in the second shell was small (0.3 to 1.5). Bargar et al. (1997) observed similar polymer formation at high loading levels for Pb on Al-oxide surfaces. Fendorf and Sparks (1994) found that Cr polymerization, and eventually Cr-hydroxide surface clusters, began at surface coverages as low as 20%. It was proposed that when the structures of the sorbate and sorbent are dissimilar, epitaxial growth is energetically unfavorable and thus nucleation growth is away from the surface, i.e., surface clusters.

The formation of a homogeneous solid on a surface can occur when a solution becomes saturated and the surface acts as a nucleation site, or from a chemisorption-precipitation continuum, i.e., when adsorption reaches monolayer coverage sorption continues on the newly created sites resulting in a precipitate on the surface (multilayer surface coverage) (McBride, in Bolt et al., 1991, p. 171; Farley et al., 1985). This phenomenon is analogous to the assumptions used in the classical Brunauer-Emmett-Teller (BET) isotherm model of gas sorption onto surfaces (Borg and Dienes, 1992, p. 400). The distinction between a surface precipitate and a sorbed metal complex can be subtle, and somewhat confusing, especially since polymer sorption can lead to, or preface, surface precipitation. Adding to the difficulty of distinguishing surface precipitation from sorbed metal complexes is the fact that methods for distinguishing between the two phenomena are at present in their early development, and few studies exist on this subject matter.

The solid solution concept of surface precipitation was presented in detail by Farley et al. (1985); it is described as a process similar to homogeneous coprecipitation. The composition of the surface precipitate varies, "continuously between that of the original solid and a pure precipitate of the sorbing metal" (Farley et al., 1985). The solid solution concept differs from the multilayer precipitation concept in that it includes both desorption and/or dissolution of structural ions from the sorbent and the inclusion of ions from solution. The result of coprecipitation of the solution ions with ions dissolved from the surface is a solid with isomorphic substitution, or a stable mixture of two solids (Stumm and Morgan, 1996, p. 814). An important factor controlling which ions will form a solid solution is the ionic radius. For example, Ainsworth et al. (1994) found that the extent of reversibility with aging for Co, Cd, and Pb was inversely proportional to the ionic radius of the ions, where ionic radii increase in the order $\text{Co} < \text{Cd} < \text{Pb}$. Since the ionic radius of Co is the most similar to Fe, they concluded that the hysteresis was a result of the formation of a solid solution. Solid solution formation is probably limited by the rate of mineral dissolution, rather than a lack of thermodynamic favorability (McBride, 1994, p. 163; Scheidegger et al., 1998). O'Day et al. (1996) observed a small amount of Si backscattering from the XAFS spectra of Co sorption on quartz ($\alpha\text{-SiO}_2$). They explained this by proposing that Co was coordinated in Si tetrahedra, which occurred by either diffusion to defect sites, or a small amount of quartz dissolution and reprecipitation of a mixed Co/Si phase (solid solution).

Surface precipitation and dissolution are slower processes than adsorption and desorption. Farley et al. (1985) noted that the rate of Cd uptake by amorphous iron hydroxide was lower when the initial solution concentration exceeded that required for monolayer coverage. One possible reason for the slower precipitation reactions is that a

precipitated ion must form several bonds, which requires more activation energy than adsorption complexes which have fewer bonds. Likewise, surface precipitates may be more stable than adsorbed species because of the formation of high energy bonds and increased coordination. Another factor which makes surface precipitates more stable is that only the surface of the precipitate is accessible to the solution for dissolution to occur (for a 3-dimensional object only the exposed surfaces are surrounded by solution).

The formation of a surface precipitate involves several reactions, including (1) adsorption of the ion on the surface, (2) surface nucleation, and (3) crystal growth (Stumm and Morgan, 1996, p. 812). Each of these steps contains several independent reaction sequences, and the rate of precipitate formation is determined by the slowest reaction step. While the formation of surface precipitates is important for predicting the fate of trace elements in the environment, dissolution reactions are also important processes that may be the controlling mechanisms for trace element mobilization when a soil has been contaminated for long periods. For the dissolution of surface precipitates the reaction sequence is similar to the steps of dissolution of a pure solid: (1) transport of reactants from the bulk solution to the surface, (2) adsorption of solutes, (3) interlattice transfer of reacting species, (4) chemical reactions, (5) detachment of reactants from the surface, and (6) mass transport into the bulk solution (Stumm and Wollast, 1990). These steps can be summarized as transport and surface reaction mechanisms. The mechanism controlling the rate of dissolution is dependent on several factors; i.e., solution composition, pH, mixing, etc.

The kinetics of surface precipitate formation and dissolution has not been extensively studied. In a recent study by Scheidegger and Sparks (1996) the rate of release of Ni from a pyrophyllite surface known to have Ni precipitates showed both a fast and slow reaction. The fast reaction was attributed to desorption of specifically sorbed Ni. The slow reaction was attributed to the slow dissolution of polynuclear Ni complexes, which were found to dissolve more slowly than pure Ni(OH)₂. In another study, Scheidegger et al. (1998) monitored the kinetics of surface precipitate formation on pyrophyllite, montmorillonite, and gibbsite using XAFS. Surface precipitate formation was initially fast on pyrophyllite and gibbsite (within minutes), but did not occur until 48 hours on montmorillonite. Figure 1.13 shows that Ni uptake by pyrophyllite is initially rapid, with approximately 25% of the Ni being sorbed within the first 30 minutes. Then the reaction slowed considerably, but was continuous for times as long as 72 hours (97% of the Ni is removed from solution). Analysis of the radial structure function (Figure 1.14) derived from XAFS spectroscopic characterization of the samples after different sorption periods shows an increase in a second shell at ~2.75 Å (uncorrected for phase shifts). This suggests that the slow development of polynuclear Ni complexes is responsible for the slow sorption reaction. These complexes have been identified as mixed Ni-Al (takovite-like) hydroxide phases (Scheidegger et al., 1998).

O'Day et al. (1996) used XAS and kinetic experiments to hypothesize the mechanisms of surface precipitation on two different minerals. Their hypotheses were strengthened by comparing and contrasting the spectroscopic and kinetics results for different mineral surfaces. XAFS results for Co on rutile (TiO₂) showed an increase in the number of backscattering Co atoms for aging times of one day to 11 days, suggesting an increase in the size of multinuclear complexes formed on the surface. However, similar results were not seen for Co aging on quartz (α-SiO₂), which had Co(OH)₂ surface

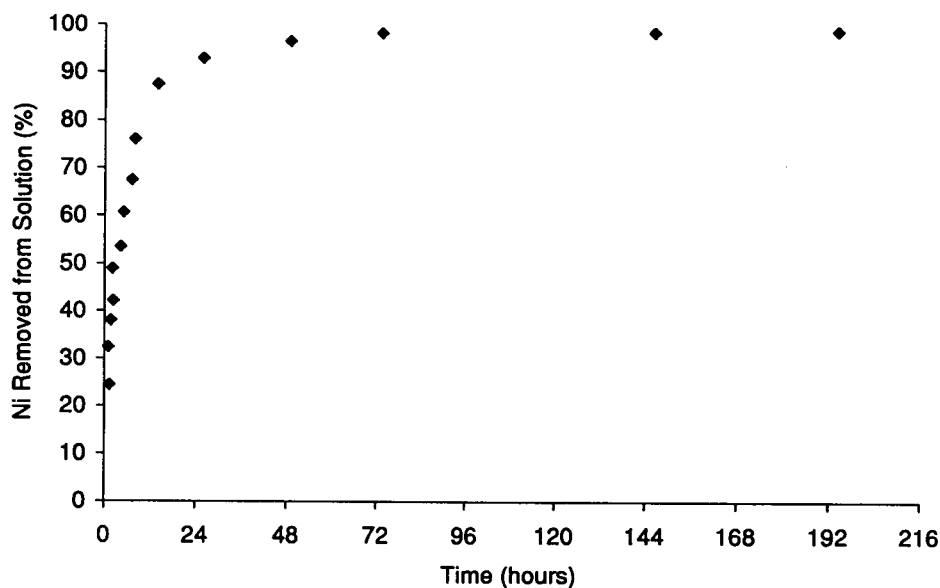


Figure 1.13. Kinetics of Ni removal from solution by pyrophyllite. From Scheidegger et al. (1997b), with permission.

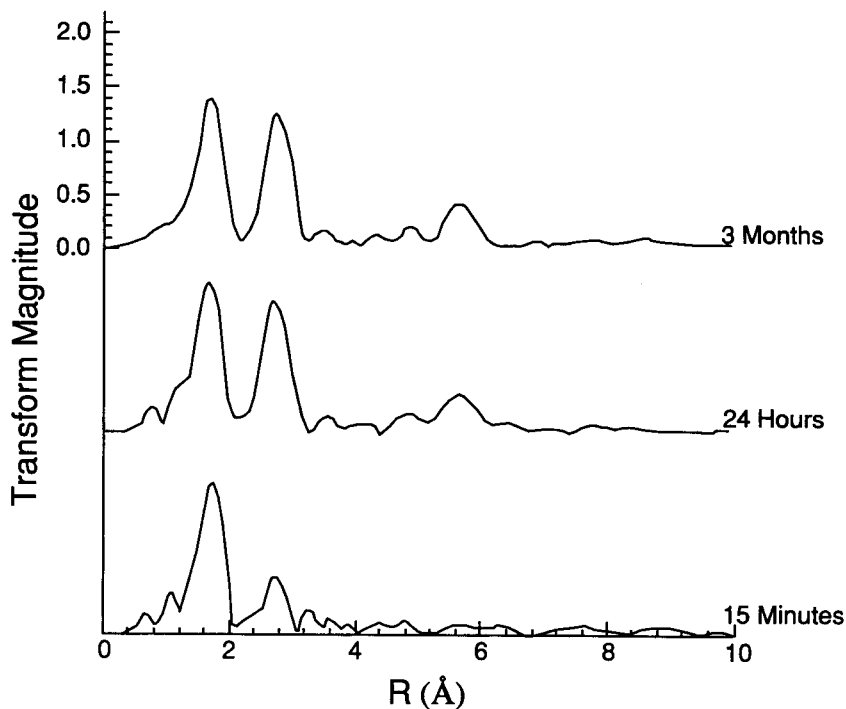


Figure 1.14. Radial distribution function (uncorrected for phase shifts) for Ni sorption on pyrophyllite incubated for 24 hours to 3 months. From Scheidegger et al. (1997b), with permission.

precipitates present. They hypothesized that the reason for the observed slow change in the multinuclear surface precipitate on the rutile and not on the quartz was a result of the similar radii between Co and Ti, while the radius of Si is larger than Co. As a result of this difference in atomic radii, the Co hydroxide-like precipitate formed on quartz was attached only to corners of select Si tetrahedra on the surface. However, Co sorption on the rutile was consistent with the formation of a precipitate that had similar lattice dimensions as the surface, effectively extending the lattice structure of the bulk solid; i.e., an epitaxial growth. The resulting Co surface precipitate was structurally strained due to charge imbalances and distortion of the CoO_6 octahedra. Thus, they proposed that the change with increasing equilibration times was due to the formation of an anatase-like structure (conclusion made based on similar octahedra bond distances between the anatase and the surface precipitate). The anatase structure, a TiO_2 polymorph, has favorable lattice dimensions for Co because of a more open structure which better accommodates the slightly larger Co ion.

There are several thermodynamic reasons for the formation of surface precipitates in unsaturated systems. For example, the solid surface may lower the energy of nucleation by providing sterically similar sites (McBride, in Bolt, 1991, p. 171), the activity of the surface precipitate is less than unity (Sposito, 1986), and the solubility of the surface precipitate is lowered because the dielectric constant of the solution near the surface is less than that of the bulk solution (O'Day et al., 1994a). It has not been established which one of these mechanisms predominates; however, it is possible that the three phenomena simultaneously influence precipitation reactions on surfaces. To ensure that precipitation is truly a surface-induced phenomenon, experimental systems should be run at conditions undersaturated with respect to known phases. However, the solubility products of many possible phases are unknown, making it difficult to determine if such phases will precipitate in a given system. This is particularly true for mixed cation hydroxides and coprecipitation reactions on surfaces (d'Espinose de la Caillerie et al., 1995; Towle et al., 1997; Scheidegger et al., 1998). The theories on the enhancement of surface precipitation by the three mechanisms mentioned above are discussed in more detail below.

As discussed above, Farley et al. (1985) presented a solid solution model to explain the continuum between precipitation and chemisorption onto solid surfaces. The model suggests that sorption is a process that includes solid dissolution, and then reprecipitation onto the surface. Thus, the formation of a surface complex involves the coprecipitation of both the ions dissolved from the sorbent, and the ions present in the bulk solution. Therefore, assuming the solid phase is a pure crystal and has unit activity (relative to the pure macrocrystal) is an inappropriate assumption, and invalidates solubility determinations based on the law of mass action, and ion activity products that do not account for surface activity. In addition, the resulting surface complex may not be compositionally homogeneous and completely free from inclusions, causing the activity of the solid phase to be even lower (Sposito, 1986). Sposito (1986) illustrated this idea by considering the dissolution of CdCO_3 :



$$\text{Ion Activity Product (IAP)} = [\text{Cd}][\text{CO}_3] = K_{\text{so}} [\text{CdCO}_3(\text{s})] \quad (2)$$

where the brackets indicate ion activity. The activity of a pure solid is often considered to be one; however, if Cd forms a mixed precipitate (coprecipitate) with another ion in solution, such as Ca, the result is not $[\text{CdCO}_3(\text{s})] = 1$, but $\text{Cd}_x\text{Ca}_y\text{CO}_3(\text{s})$ with activity < 1 . This means that the IAP (including Ca) at the surface of the precipitate is greater than the IAP of the bulk solution. Thus, $\text{Cd}_x\text{Ca}_y\text{CO}_3(\text{s})$ will precipitate at the surface before CdCO_3 . The actual IAP of a solid solution depends on the concentration of the foreign ion (Ca in the above case) in the solid mixture phase:

$$(\text{IAP})_i = g_i X_i K_i^{\text{so}} \quad (3)$$

where g_i is the activity coefficient of solid i , X_i is the mole fraction of solid i and K_i^{so} is the solubility product of the pure mineral i (Van Riemsdijk and Van der Zee, in Bolt, 1991, p. 251). From this equation one sees that a coprecipitate with one constituent present in minor amounts has a decreased solubility product with respect to the pure mineral.

The enhancement of precipitate formation on the surface may also be due to the reduction of the energy barrier necessary for nucleation processes to occur in an aqueous solution. This is a factor of the lattice dimensions of the solid, and those of the precipitate to be formed, i.e., a steric interaction (McBride, in Bolt et al., 1991, p. 171). The result of surface nucleation sites is that the extent of supersaturation required for precipitation is decreased. However, there may be other important factors contributing to surface nucleation interactions. For example, Fendorf et al. (1992) observed Al surface precipitates on MnO_2 using high resolution transmission electron microscopy (HRTEM), but not on TiO_2 under the same conditions (undersaturated with respect to the most likely Al hydroxide precipitates, and equivalent surface coverages). If promotion of surface precipitation below saturation was a result of the presence of nucleation sites, then one would expect to see precipitates on both surfaces. Thus, another factor inhibited surface precipitate formation on the TiO_2 , i.e., steric hindrances between the two surfaces.

The dielectric constant of the solution at the interface of a solid is much less than it would be in the bulk solution (Hiemenz, 1986, p. 725). This is a result of the surface charge aligning the dipoles of the water layers nearest the surface. This phenomenon is called dielectric saturation, and results in a dielectric constant an order of magnitude or less in the first few angstroms of the surface (McBride, 1994, p. 296). The activity of individual ions in solution is inversely proportional to the dielectric constant of water. Consequently, near the surface the lowered dielectric constant of the water causes an increased ion activity, and the IAP near the surface will exceed that of the bulk solution. O'Day et al. (1994a) used a more direct approach to this concept that calculates the change in the free energy near the surface as a function of the dielectric constant using the Born charging equation for a spherical ion. However, calculations for sorption of Co on kaolinite revealed that the average surface dielectric constant is not low enough to account for surface precipitation of a pure hydroxide phase as the predominant mechanism of sorption. Thus, if surface precipitation was the mechanism of sorption, then either the value of the dielectric constant near the surface was incorrect (possible, since dielectric constants near surfaces are difficult to determine), or precipitation was enhanced by one of the aforementioned mechanisms (O'Day et al., 1994a).

Regardless of the mechanism, surface precipitation is an important process affecting trace metal reactions with natural materials. Since surface precipitation kinetics can be

slow, the extent of precipitation and subsequent dissolution of surface precipitates are affected by residence time; thus, they are important slow kinetic mechanisms which can control the fate of trace elements in the environment.

SUMMARY

In this chapter we have presented evidence that slow kinetics are important when estimating the extent and reversibility of trace metal sorption on soils and soil materials. We have also discussed three possible mechanisms for such slow kinetics: diffusion, rate-limited adsorption processes, and precipitation reactions on surfaces. While evidence exists that suggests all three mechanisms occur, the slow sorption mechanism occurring in a particular system is highly dependent on the prevailing environmental conditions; e.g., solution pH, sorbent characteristics, ionic strength, trace metal physico-chemical characteristics, dissolution rate of the solid, and the microporosity of the solid.

In addition to a review of relevant studies in the literature, two examples from our own research were given that suggested different mechanisms as the rate controlling processes responsible for the slow sorption of metals on model soil components. In one case Pb sorption on γ - Al_2O_3 resulted in little change in the local chemical environment (determined using XAFS) with increased incubation time. In another example, Ni sorption on the clay mineral pyrophyllite resulted in increased polynuclear surface complexation with increasing reaction time. While it is difficult to make direct comparisons of the two metals since the surfaces present are different, we think it is justifiable since additional experiments (data not shown) for Pb on pyrophyllite (Alcacio, 1997) and Ni on gibbsite (a form of Al hydroxide) (Scheidegger et al., 1997a) showed similar sorption behavior to the systems being compared above. We propose that one reason for the different apparent bonding mechanisms is the difference in the ionic radius of the two metals (1.20 Å for Pb and 0.69 Å for Ni). The sorbents studied in these two cases have Al present as a structural component. Since Al can dissolve and has a similar radius as Ni they can form a coprecipitate, while the Pb ion is too large to form such a coprecipitate. Ainsworth et al. (1994) observed that the extent of sorption reversibility was positively correlated to the ionic radius of the sorbing metals. Coughlin and Stone (1995) also suggested that coprecipitation of metal ions with Fe is directly dependent on ionic radius. While these studies do not provide direct evidence on the formation of a coprecipitate, they agree well with our data; Ni (the smaller ion with an ionic radius similar to Al) forms a mixed precipitate, while Pb does not. This information can be used to improve predictions on the fate of these metals in the environment, and will allow for better simulations in the laboratory.

When predicting the transport of trace elements in the vadose zone, researchers must know the kinetics of sorption and desorption behavior. If slow kinetics are controlling these mechanisms then reaction-transport models should include such chemical processes. This will result in more accurate predictions and improved management of existing and potential risks. In addition, if the mechanism responsible for slow sorption or desorption is known, researchers can design remediation strategies more efficiently. This may include mobilizing or immobilizing contaminants based on the pH of the soil solution, treating the soil with chelating ligands, or creating treatments for specific exposure times based on the kinetics of the reactions.

To obtain complete sorption and desorption kinetic behavior, researchers should conduct experiments in the lab for extended time periods. When possible, mechanisms of slow kinetics should be determined to better predict the fate of trace elements in the environment. To ascertain the mechanisms, both macroscopic and microscopic experiments should be used. In this chapter we have presented several methods that have been used for the determination of mechanisms. With the rapid advancement of technology the future should bring an even better understanding of soil sorption mechanisms and kinetic processes. It is critical that researchers combine their efforts with those in related fields so that the most contemporary and valid models can be developed and employed to predict the fate of trace elements in the environment.

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