

New frontiers in elucidating the kinetics and mechanisms of metal and oxyanion sorption at the soil mineral/water interface[§]

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Summary – Zusammenfassung

An understanding of the kinetics and mechanisms of metal and oxyanion sorption on soil minerals and soils is fundamental in assessing the speciation, mobility, and bioavailability of metals and oxyanions in natural systems. Traditionally, sorption has been studied using macroscopic equilibrium approaches. It is now well recognized that the kinetics of metal and oxyanion sorption/release must be understood if accurate predictions are to be made about metal/oxyanion fate/mobility and soil remediation. This paper covers aspects of kinetic models and their applicability to heterogeneous systems and the rates and mechanisms of rapid and slow metal and oxyanion sorption reactions. With some metals (e.g. Co, Ni, Zn) residence time affects the rate of metal release while with other metals such as Pb, there is little effect of residence time. To definitively understand the dynamics of sorption mechanisms, one must employ molecular scale approaches. Over the past decade, with the advent of cutting-edge molecular-scale in-situ analytical techniques, significant advances have occurred in determining the speciation and sorption/release mechanisms of metals and oxyanions in the subsurface environment. These frontiers in environmental science have major impacts on: soil remediation strategies, development of predictive models, and contaminant/bioavailability assessments. Frontiers in metal sorption at the soil mineral/water interface are highlighted in this review.

Key words: metal sorption / oxyanion sorption / XAFS / kinetics / sorption mechanisms

Neue Ansätze zur Aufklärung der Kinetik und der Mechanismen der Sorption von Metallionen und Oxyanionen in der Mineralboden/Wasser-Grenzfläche

Zur Bewertung der Art, Mobilität und Pflanzenverfügbarkeit von Metallionen und Oxyanionen in Ökosystemen ist eine ausreichende Kenntnis ihrer Sorptionskinetik und -mechanismen im Boden bzw. Bodenmineralen vonnöten. Bisher wurde die Sorption vorwiegend unter dem Gesichtspunkt makroskopischer Gleichgewichtsbedingungen betrachtet. Mittlerweile hat man jedoch erkannt, dass man für genauere Voraussagen zur Bodensanierung d.h. zur Beweglichkeit und zum Schicksal von Metallen und Oxyanionen die Kinetik ihrer Sorption/Freisetzung kennen muss. In der vorliegenden Arbeit werden kinetische Modelle in ihrer Anwendbarkeit auf heterogene Systeme diskutiert sowie die Raten und Mechanismen rascher bzw. langsamer Sorptions-/Freisetzungsreaktionen für Metallionen und Oxyanionen betrachtet. Von besonderer Bedeutung hierbei scheint die Bildung von Präzipitaten an Oberflächen (z.B. Ni-Al-Hydroxid-Doppelschichten an Tonmineralen) zu haben. Dies trifft infolge des Ionenradius zu für Cu, Ni, Zn, deren Freisetzung infolgedessen von der Verweildauer (Alterung) im Substrat abhängig ist. Das Bleiion hingegen ist zu groß, um in die Struktur von Tonmineralen und Pyrophyllit zu passen. Für ein tieferes Verständnis der Sorptionsdynamik sind Forschungsansätze auf molekularer Ebene Voraussetzung. So konnten innerhalb der letzten Dekade anhand neuester Analysetechniken unter in-situ Bedingungen und gleichzeitig im molekularen Maßstab beträchtliche Erkenntnisfortschritte zur Spezifizierung und zu Sorptions-/Freisetzungs-Mechanismen von Metallen/Oxyanionen in Bereichen unter der Sorptionsoberfläche gemacht werden. Ein solch neues Grenzgebiet kann somit in den Umweltwissenschaften einen wesentlichen Beitrag zur Entwicklung von Sanierungsstrategien, von Prognosemodellen und zur Bewertung der Bioverfügbarkeit bzw. von Kontaminationen in Böden leisten.

1 Introduction

Since its inception in the mid 1850s, soil chemistry has focused on the macroscopic, equilibrium aspects of soil chemical reactions and processes. From these studies, much was learned about important soil chemical processes including sorption, desorption, precipitation, complexation, dissolution, and oxidation/reduction. However, such investigations do not convey information on reaction rates or reaction mechanisms. In the past two decades, as concerns and interests about soil and water quality have increased, soil

and environmental chemists, environmental and chemical engineers and geochemists have increasingly realized that reactions in subsurface environments are time dependent. Thus, to accurately predict the fate, mobility, speciation, and bioavailability of environmentally important plant nutrients, trace elements, radionuclides, and organic chemicals in soils, one must understand the kinetics and mechanisms of the reactions.

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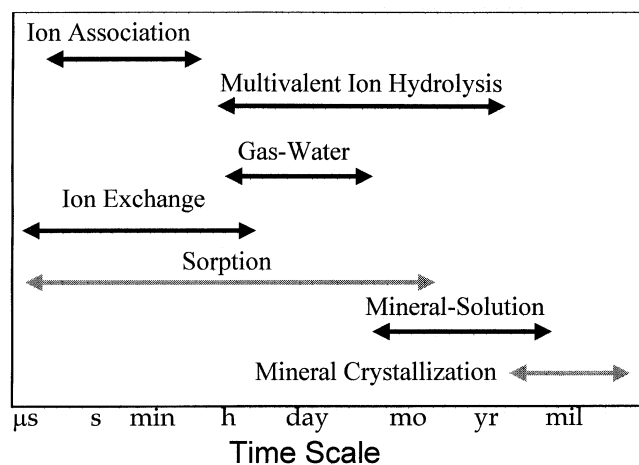


Figure 1: Time range required to attain equilibrium by different types of reactions in soil environments. From Amacher (1991).

Abbildung 1: Zeitbedarf zur Gleichgewichtseinstellung verschiedener Reaktionen in Böden.

While major progress has been made in better understanding the kinetics of soil chemical processes, much uncertainty remains. In part, this is due to the complex, heterogeneous nature of natural materials such as soils. However, with development of kinetic techniques that can be used to measure a wide range of time scales, time-dependent models that can describe both chemical reaction and mass transfer processes, and the employment of state-of-the-art *in situ* spectroscopic and microscopic surface techniques in combination with rate studies, major advances are being made in understanding the kinetics and mechanisms of soil chemical reactions. Arguably, this will be a major leitmotif in soil chemistry research for decades to come (Sparks, 1999b). In this paper, I wish to review some recent advances in understanding the kinetics and mechanisms of metal and oxyanion sorption/release on soils and soil components. Before discussing these, a brief discussion on application of chemical kinetics to heterogeneous soil systems will be covered, along with information on nonequilibrium sorption models.

A variety of chemical reactions occur in soils and often in combination with one another. Reaction time scales can vary from microseconds and milliseconds for many ion association and some ion exchange and sorption reactions to years for many mineral solution and mineral crystallization phenomena and for some sorption/release reactions (Fig. 1). Ion association reactions include ion pairing, inner- and outer-sphere complexation, and chelation in solution. Gas-water reactions involve gaseous exchange across the air-liquid interface. Ion exchange reactions occur when cations and anions are adsorbed (outer-sphere complexation) and desorbed from soil surfaces by electrostatic attractive forces. Ion exchange reactions are reversible and stoichiometric. Sorption reactions can involve adsorption processes including partitioning, outer-sphere and inner-sphere complexation, polymerization and precipitation (e.g., surface precipitation). Mineral-solution reactions include precipitation/dissolution of minerals, and coprecipitation reactions in

which small constituents become a part of mineral structures (Sparks, 1989; Amacher, 1991).

2 Application of chemical kinetics to heterogeneous soil systems

The study of chemical kinetics, even in homogeneous systems, is complex and often arduous. When one attempts to study the kinetics of reactions in heterogeneous systems such as soils, sediments, and even soil components such as clay minerals, hydrous oxides, and humic substances, the difficulties are greatly magnified. This is largely due to the complexity of soils which are made up of a mixture of inorganic and organic components. These components often interact with each other and display different types of sites with various reactivities for inorganic and organic sorptives. Moreover, the variety of particle sizes and porosities in soils and sediments further adds to their heterogeneity. In most cases, both chemical kinetics and multiple transport processes are occurring simultaneously. Thus, the determination of chemical kinetics, which can be defined as the investigation of rates of chemical reactions and of the molecular processes by which reactions occur where transport is not limiting (Gardiner, 1969) is extremely difficult, if not impossible, in heterogeneous systems. In these systems, one is studying kinetics, which is a generic term referring to time-dependent or nonequilibrium processes. Thus, apparent and non-mechanistic rate laws and rate parameters are determined (Skopp, 1986; Sparks, 1989).

The objectives of this review are: to provide a brief overview of models that can be used to describe rate processes in soils; and, to present some recent advances on the use of macroscopic- and molecular-scale techniques to elucidate mechanisms of metal and oxyanion sorption on soil minerals.

2.1 Rate-limiting steps and chemical kinetics models

Both transport and chemical reaction processes can affect the reaction rates in the subsurface environment. Transport include (Aharoni and Sparks, 1991): (1) transport in the solution phase; (2) transport across a liquid film at the particle/liquid interface (film diffusion [FD]); (3) transport in liquid filled macropores (>2 nm), all of which are nonactivated diffusion processes and occur in mobile regions; (4) diffusion of a sorbate at the surface of the solid; (5) diffusion of a sorbate occluded in micropores (<2 nm); and (6) diffusion processes in the bulk of the solid, all of which are activated diffusion processes (pore diffusion [PD]) (Fig. 2). Pore and surface diffusion within the immediate region can be referred to as interaggregate (interparticle) diffusion while that in the solid is intra-aggregate diffusion. The actual chemical reaction (CR) at the surface, for example, adsorption, is usually instantaneous. The slowest of the CR and transport processes is rate-limiting.

A number of chemical kinetics models including various ordered equations, e.g., zero-, first-, and second-order, have been employed in soil chemistry to describe reaction rates of inorganic and organic species in soils and soil components. Additionally, models that were originally developed to describe chemisorption of gases on solids and diffusion of ions in a cylinder, i.e., the Elovich and parabolic diffusion equations, respectively, have been used to describe an array of soil chemical processes (Sparks, 1989; 1995; 1998; 1999a, b). In many cases, the above models have often described rate data equally well, based on correlation coefficients and standard errors of the estimate (Sparks, 1999a).

2.1.1 Nonequilibrium kinetic models

However, simple chemical kinetics models such as ordered reaction and Elovich models may not be appropriate to describe reactions in heterogeneous systems such as soils, sediments, and soil components. In these systems, where there is a range of particle sizes and multiple retention sites, both chemical kinetics and transport phenomena are occurring

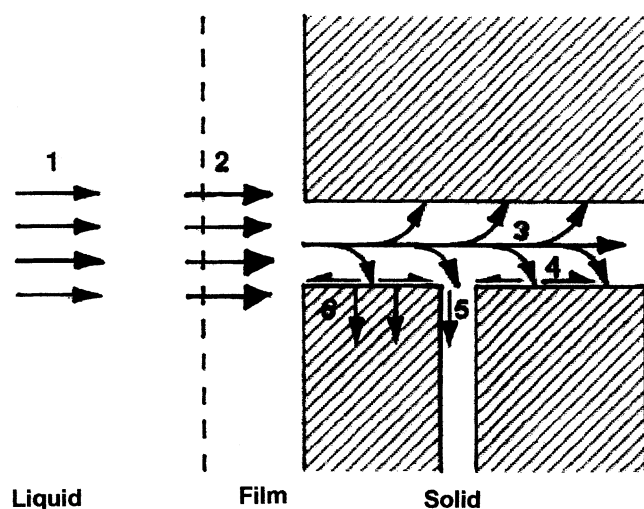


Figure 2: Transport processes in solid-liquid soil reactions. Nonactivated processes: (1) transport in the soil solution, (2) transport across a liquid film at the solid-liquid interface, (3) transport in a liquid-filled macropore; activated processes: (4) diffusion of a sorbate at the surface of the solid, (5) diffusion of a sorbate occluded in a micropore, (6) diffusion in the bulk of the solid. From Aharoni and Sparks (1991).

Abbildung 2: Transportprozesse in der Fest/Flüssig-Phase in Böden. Nichtaktivierte Prozesse: (1) Transport in der Bodenlösung, (2) Transport durch einen Flüssigkeitsfilm im Grenzbereich Fest/Flüssig, (3) Transport in Lösungs-gefüllten Makroporen. Aktivierte Prozesse: (4) Diffusion des Sorbats zur Oberfläche des Festkörpers, (5) Diffusion des Sorbats in einer Mikropore, (6) Diffusion im Festkörper.

simultaneously, and a fast reaction is often followed by (a) slower reaction(s). In such systems, nonequilibrium models that describe both chemical and physical nonequilibrium and that consider multiple components and sites are more appropriate. Physical nonequilibrium is ascribed to some rate-limiting transport mechanism such as FD or PD while chemical nonequilibrium is due to a rate-limiting mechanism at the particle surface (CR). Nonequilibrium models include two-site, multiple site, radial diffusion (pore diffusion), surface diffusion, and multiprocess models.

The term sites can have a number of meanings (Brusseau and Rao, 1989): (1) specific, molecular scale reaction sites; (2) sites of differing degrees of accessibility (external, internal); (3) sites of differing sorbent type (organic matter and inorganic mineral surfaces); and (4) sites with different sorption mechanisms. With chemical nonequilibrium sorption processes, the sorbate may undergo two or more types of sorption reactions, one of which is rate-limiting. For example, a metal cation may sorb to organic matter by one mechanism and to mineral surfaces by another mechanism, with one of the mechanisms being time-dependent.

Chemical nonequilibrium models describe time-dependent reactions at sorbent surfaces. The *one-site model* is a first-order approach that assumes that the reaction rate is limited by only one process or mechanism on a single class of sorbing sites and that all sites are of the time-dependent type. In many cases, this model appears to describe soil chemical reactions quite well. However, often it does not. This model would seem not appropriate for most heterogeneous soil systems since multiple sorption sites exist.

The *two-site* (two compartment, two box) or *bicontinuum model* has been widely used to describe chemical nonequilibrium and physical nonequilibrium. This model assumes that there are two reactions occurring, one that is fast and reaches equilibrium quickly and a slower reaction that can continue for long time periods. The former is described by an equilibrium isotherm equation while a first-order equation is usually employed for the latter. The reactions can occur either in series or in parallel (Brusseau and Rao, 1989).

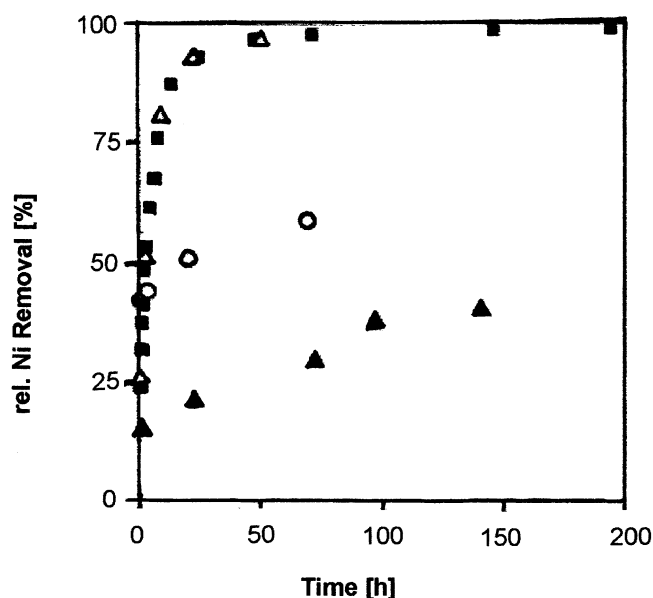


Figure 3: Kinetics of Ni sorption (%) on pyrophyllite (■), kaolinite (Δ), gibbsite (▲), and montmorillonite (○) from a 3 mM Ni solution at pH 7.5 and an ionic strength $I \approx 0.1$ M (NaNO_3). From Scheidegger et al. (1997). **Abbildung 3:** Kinetik der Ni-Sorption an Pyrophyllit, Kaolinit, Gibbsite und Montmorillonit aus einer 3 mM Ni-Lösung bei pH 7,5 und einer Ionenstärke von $I = 0,1$ M (NaNO_3).

With the two-site model, there are two adjustable or fitting parameters, the fraction of sites at local equilibrium (X_1) and the rate constant (k). A distribution (K_d) or partition coefficient (K_p) is determined independently from a sorption/desorption isotherm.

To account for the multiple sites that may exist in heterogeneous systems, Connaughton et al. (1993) developed a *multisite compartment* (continuum) model that incorporates a continuum of sites or compartments with a distribution of rate coefficients that can be described by a gamma density function. A fraction of the sorbed mass in each compartment is at equilibrium with a desorption rate coefficient or distribution coefficient for each compartment or site. The multisite model has two fitting parameters, α a shape parameter, and $1/\beta$, which is a scale parameter that determines the mean standard deviation of the rate coefficients.

2.2 Physical nonequilibrium models

A number of models can be used to describe physical nonequilibrium reactions. Since transport processes in the mobile phase are not usually rate-limiting, physical nonequilibrium models focus on diffusion in the immobile phase or interaggregate/diffusion processes such as pore and/or surface diffusion. The transport between mobile and immobile regions is accounted for in physical nonequilibrium models in three ways (Brusseau and Rao, 1989): (1) explicitly with Fick's law to describe the physical mechanism of diffusive transfer, (2) explicitly by using an empirical first-order mass transfer expression to approximate solute transfer, and (3) implicitly by using an effective or lumped dispersion coefficient that includes the effects of sink/source differences and hydrodynamic dispersion and axial diffusion.

A *pore diffusion model* has been used by a number of investigators to study sorption processes using batch systems (Wu and Gschwend, 1986; Steinberg et al., 1987; Ball and Roberts, 1991; Harmon et al., 1992; Pignatello et al., 1993). The sole fitting parameter in this model is the effective diffusion coefficient (D_e) which may be estimated *a priori* from chemical and colloidal properties. However, this estimation is only valid if the sorbent material has a narrow particle size distribution so that an

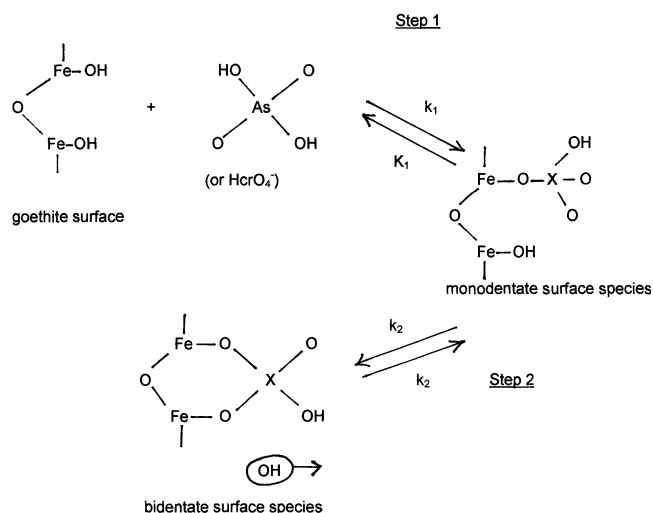


Figure 4: Proposed mechanism for arsenate/chromate adsorption/desorption on goethite. The x represents As(V) or Cr(VI). From Grossl et al. (1997).

Abbildung 4: Mechanismus der Arsenat/Chromat-Adsorption-Desorption von Goethit.

accurate, average particle size can be defined. Moreover, in the pore diffusion model, an average representative D_e is assumed, which means there is a continuum in properties across an entire pore size spectrum. This is not a valid assumption for micropores in which there are higher adsorption energies or sorbates causing increased sorption. The increased sorption reduces diffusive transport rates and results in nonlinear isotherms for sorbents with pores less than several sorbate diameters in size. Other factors can cause reduced transport rates in micropores including steric hindrance, which increases as the pore size approaches the solute size, and greatly increased surface area to pore volume ratios (which occurs as pore size decreases).

Another potential problem with the pore diffusion model is that sorption and desorption kinetics may have been measured over a narrow concentration range. This is a problem since a sorption/desorption mechanism in micropores at one concentration may be insignificant at another concentration.

Fuller et al. (1993) used a *pore space diffusion model* to describe arsenate adsorption on ferrihydrite that included a subset of sites whereby sorption was at equilibrium. A Freundlich model was used to describe sorption on these sites. Diffusion into the particle was described by Fick's second law of diffusion; homogeneous, spherical aggregates, and diffusion only in the aqueous phase were assumed. The fit was better when sites that had attained sorption equilibrium were included based on the assumption that there was an initial rapid sorption on external surface sites before intraaggregate diffusion.

Pedit and Miller (1995) have developed a general *multiple particle class pore diffusion model* that accounts for differences in physical and sorptive properties for each particle class. The model includes both instantaneous equilibrium sorption and time-dependent pore diffusion for each particle class. The pore diffusion portion of the model assumes that solute transfer between the intraparticle fluid and the solid phases is fast *vis-à-vis* interparticle pore diffusion processes.

Surface diffusion models, assuming a constant surface diffusion coefficient, have been used by a number of researchers (Weber and Miller, 1988; Miller and Pedit, 1992). The dual resistance model combines both pore and surface diffusion.

3 Metal/oxyanion sorption kinetics and mechanisms

The sorption of metals and oxyanions on soil minerals and soils is usually characterized by rapid sorption, occurring over time scales of milliseconds to hours, followed by a slow sorption process occurring over time scales of hours to days (Fig. 3). The rapid process has traditionally been ascribed to adsorption (outer- and inner-sphere complexation). However, as will be discussed later, surface precipitation, via metal hydroxide phase formation, can occur on relatively rapid time scales (minutes in some cases). Thus, the rapid sorption process can be due to both adsorption and surface precipitation in the case of certain metals such as Co, Ni, and Zn (Scheidegger et al., 1997; 1998; Towle et al., 1997; Roberts et al., 1999; Thompson et al., 1999). Accordingly, a continuum in sorption mechanisms is often occurring in soils.

As noted earlier, sorption of heavy metals and oxyanions on soil components via CR often involves a very rapid reaction, occurring on a millisecond time scale. For such rapid reactions, chemical techniques such as pressure jump (p-jump) relaxation must be employed (Hayes and Leckie, 1986; Sparks, 1989; Sparks and Zhang, 1991; Grossl and Sparks, 1995; Sparks et al., 1996).

The use of p-jump relaxation to measure the kinetics of ion sorption/desorption on metal oxide surfaces was pioneered by several Japanese chemists. Their research includes some of the following sorption/desorption kinetic studies: divalent metal ion (Hachiya et al., 1984), phosphate (Mikami et al., 1983a), chromate (Mikami et al., 1983c), and uranyl (Mikami et al., 1983b) sorption reactions on γ -Al₂O₃. Hayes and Leckie (1986) were the first to use p-jump relaxation to study sorption/desorption kinetics of a metal ion contami-

nant (Pb^{2+}) on goethite ($\alpha\text{-FeOOH}$). Other successive studies monitored the rapid sorption/desorption kinetics of molybdate (Zhang and Sparks, 1989), sulfate (Zhang and Sparks, 1990a), selenate and selenite (Zhang and Sparks, 1990b), Cu^{2+} (Grossl et al., 1994), and arsenate and chromate (Grossl et al., 1997) on goethite. Additionally, studies have investigated borate sorption/desorption kinetics on pyrophyllite (Keren et al., 1994) and on $\gamma\text{-Al}_2\text{O}_3$ (Toner and Sparks, 1995).

Details of many of these studies are summarized in Hayes and Leckie (1986), Sparks (1989; 1995), Sparks and Zhang (1991) and Sparks et al. (1996) and will not be detailed here. A recent study of Grossl et al. (1997) will be summarized to illustrate rapid CR rates of two environmentally important oxyanions, chromate and arsenate, on goethite. A double relaxation was observed for both arsenate and chromate sorption/desorption over a pH range of 6.5 to 7.5 for arsenate and 5.5 to 6.5 for chromate, respectively. Based on the double relaxations, a two-step process (Fig. 4), resulting in the formation of an inner-sphere bidentate surface complex was proposed and successfully described using linearized rate equations relating reciprocal relaxation time values (τ^{-1}) to the concentrations of reactive species. The first step involves an initial ligand exchange reaction of the aqueous oxyanion (H_2AsO_4^- or HCrO_4^-) with goethite, forming an inner-sphere monodentate surface complex. This first step produces the signals associated with the fast τ values. The succeeding step involves a second ligand exchange reaction, resulting in the formation of an inner-sphere bidentate surface complex. This step produces the signal associated with the slow τ values. These mechanisms are in agreement with spectroscopic data obtained from X-ray absorption fine structure (XAFS) analyses (Fendorf et al., 1997) which indicated a mixture of both monodentate and bidentate arsenate and chromate surface complexes; but at low surface coverage, a greater proportion of chromate is associated with the monodentate complex than the bidentate complex. The results from both kinetic and XAFS experiments suggest that arsenate is more likely to form an inner-sphere surface complex with goethite than chromate.

3.1 The role of surface precipitation in metal retention/release

The slow metal sorption process has been ascribed to (i) diffusion into micropores of solids, followed by sorption to interior sites, (ii) sorption to sites of lower reactivity (e.g., outer-sphere vs. inner-sphere complexes and monodentate vs. bidentate sites) and (iii) surface precipitation (Axe and Anderson, 1997; Brümmer et al., 1988; Fuller et al., 1993; Lehmann and Harter, 1984; Scheidegger et al., 1996; 1997).

I will briefly review some of the literature on diffusion-controlled sorption, but will primarily focus on some of the recent literature definitively showing the important role that surface precipitation has on the rate of both slow and fast metal sorption reactions. Certainly, the role of diffusion is paramount in causing slow sorption. For example, Brümmer et al. (1988) measured sorption and desorption of Cd, Zn, and Ni with goethite. They found that the kinetics were

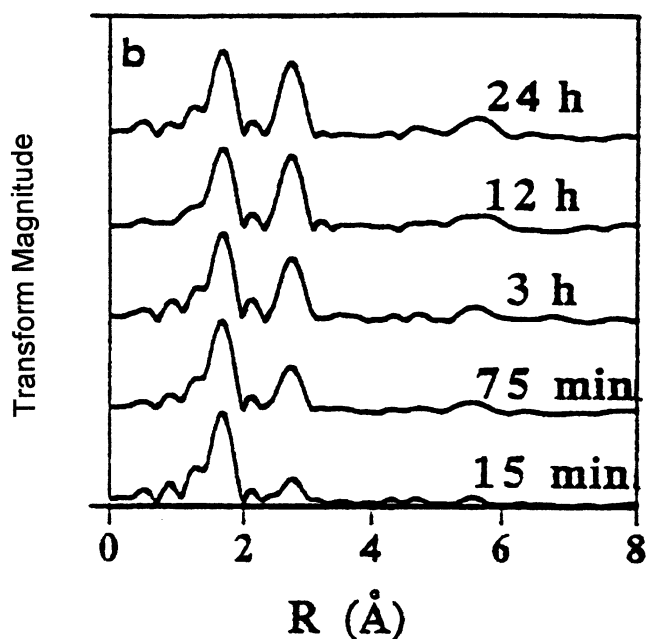


Figure 5: Fourier transforms (uncorrected for phase shift) of Ni sorbed [from a 3 mM Ni solution at pH 7.5 and an ionic strength $I \approx 0.1$ M (NaNO_3)] on pyrophyllite as a function of time. Note the growth of a peak at a R of about 2.8 Å with increasing reaction time. From Scheidegger et al. (1998).

Abbildung 5: Fourier-Transformation der Ni-Sorption an Pyrophyllit in Abhängigkeit von der Zeit. Man beachte die Zunahme des Peaks bei $R = 2,8$ Å mit zunehmender Reaktionsdauer.

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: (1) adsorption of metals on external surfaces, (2) solid-state diffusion of metals from external to internal sites, and (3) metal binding and fixation at positions inside the goethite particle. Brümmer et al. (1988) suggested that step 2 was the main reason for the slow sorption. 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 could have a large number of pores and cavities that could promote diffusion processes. Axe and Anderson (1997) also found that sorption of Cd and Cr 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. Strawn and Sparks (2000) ascribed slow Pb sorption on a soil to diffusion in interior soil organic matter sites.

Over the past five years, new frontiers in metal sorption mechanisms have convincingly demonstrated the extraordinary role that surface precipitation can play in metal speciation, mobility, and sequestration. These frontiers have resulted by combining macroscopic, kinetic studies with cutting-edge *in-situ* molecular-scale techniques.

Metal surface precipitates could be a significant cause of both fast (Scheidegger et al., 1998; Roberts et al., 1999) and slow (Scheidegger et al., 1998) metal sorption on soil sur-

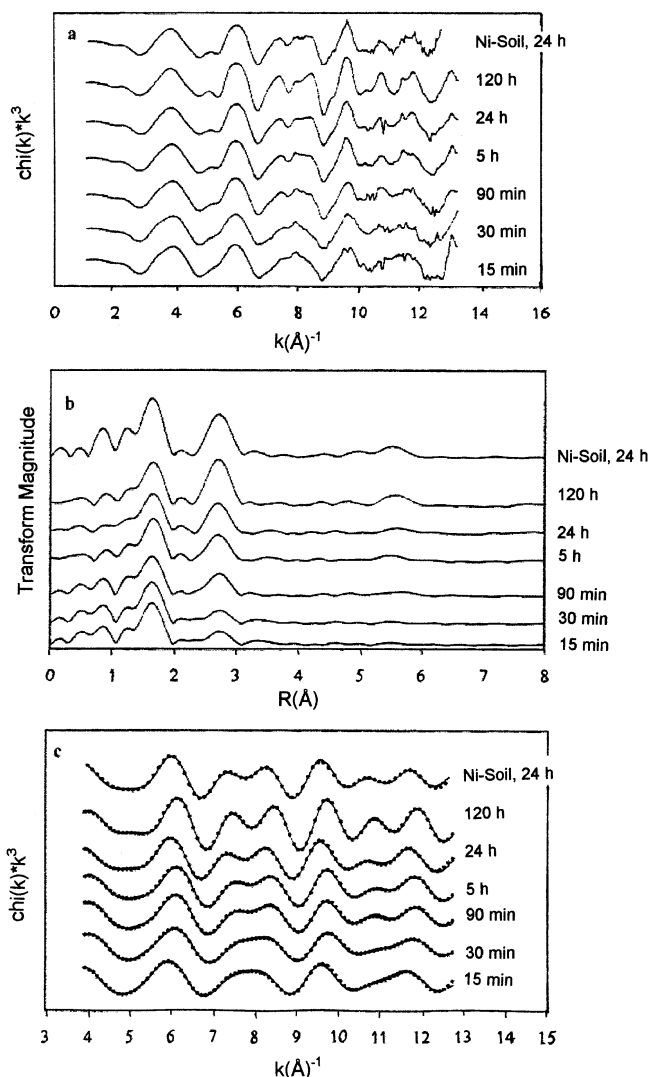


Figure 6: Results of XAFS experiments performed at pH 7.5 at the clay fraction of a Matapeake soil from Delaware, USA, and the whole soil (Ni soil) for different times (from Roberts et al., 1999)

a) χ -Funktion für sorbiertes Ni (hintergrund-korrigiert, normiert, k^3 -gewichtet)

b) Fourier-Transformation der χ -Funktion aus a); keine Korrektur der Phasenlage

c) k^3 -gewichtete XAFS-Daten der Fourier-rücktransformierten Spektren; Linie = experimentell; Punkte = theoretisch

Abbildung 6: Ergebnisse des XAFS-Experimentes bei pH 7.5 in den Tonfraktionen sowie im Gesamtboden („Ni soil“) des Matapeake-Bodens aus Delaware, USA, zu verschiedene Zeiten

faces (Scheidegger et al., 1997; 1998). Such surface species do not seem to occur with larger metals such as Pb^{2+} at surface loadings where such species have been observed with smaller metals such as Co^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} (Strawn and Sparks, 1999; 2000). This appears to be related to the mismatch in size between Pb^{2+} (1.19 Å), and Al^{3+} (0.535 Å) that is contained in the structure of the clay

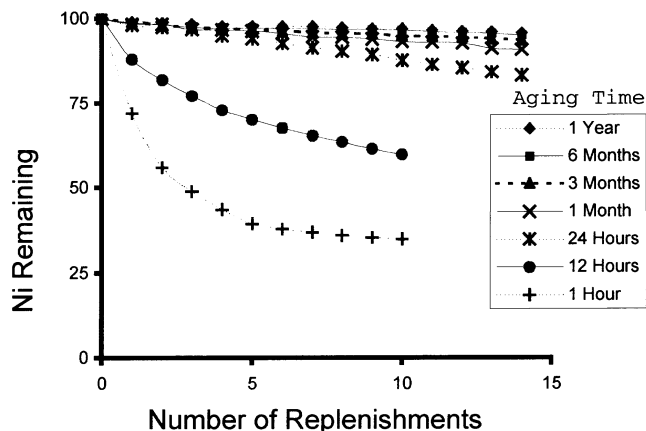


Figure 7: Kinetics of % Ni remaining on pyrophyllite as a function of aging of the surface precipitates. The numbers on the x axis represent the number of replenishments (each 24 hours) with HNO_3 at pH 4.0 to effect Ni dissolution. From Scheckel et al. (2000).

Abbildung 7: Kinetik des prozentualen Ni Verbleibs an Pyrophyllit als Funktion der Alterung des Oberflächenpräzipitates. Die Abszisse gibt die Anzahl Austauschvorgänge mit HNO_3 bei pH 4 zwecks Ni-Freisetzung an.

minerals and Al-oxides. The Pb^{2+} ion is too large to fit into the mineral structure, while ions such as Ni^{2+} (0.69 Å) and Co^{2+} (0.65 Å) can. For example, Ni-hydroxide surface precipitates formed on pyrophyllite (Scheidegger et al., 1998) and a Delaware soil in 15 minutes (Roberts et al., 1999), on talc in 7 hours (Scheinost et al., 1999), on montmorillonite in 48 hours (Scheidegger et al., 1998), and on amorphous silica in 3 days (Scheinost et al., 1999) at Ni concentrations of ≥ 1.5 mM and pH levels of ≥ 6.8 .

Scheidegger et al. (1997) were the first to show that sorption of metals such as Ni on Al-bearing clay minerals such as pyrophyllite and montmorillonite and gibbsite resulted in the formation of mixed Ni-Al hydroxide phases which were of the layered double hydroxide (LDH) type that were similar to the mineral takovite, $Ni_6Al_2(OH)_{16}CO_3 \cdot H_2O$. Using XAFS, Scheidegger et al. (1998) showed that the mixed Ni-Al hydroxide precipitate phases formed in 15 minutes on pyrophyllite (Fig. 5). Radial structure functions (RSFs) produced by forward Fourier transforms of the XAFS spectra represented in Fig. 5 show a peak at $R \approx 2.8$ Å (uncorrected for phase shifts). As reaction time proceeds, the peak at $R \approx 2.8$ Å in the RSFs increased in intensity. These data, along with calculated structural parameters (Table 2 in Scheidegger et al., 1998) suggests that in the first shell Ni is surrounded by 6 oxygen atoms, indicative of an octahedral environment. The Ni-O bond distance (≈ 2.05 Å) and coordination numbers were not affected by the reaction time. Data analysis of the second shell showed that the number of second-neighbor Ni atoms increased with increasing time (2.0–6.3 as time increased from 15 min to 3 months), and the presence of 1.7–4.0 second neighbor Al atoms. The results observed for the second coordination shell clearly showed the formation of mixed Ni-Al hydroxide (LDH) phases on the surface of pyrophyllite, which increased in size with time. Scheidegger et al. (1997; 1998) theorized that the Al^{3+} necessary for Ni-Al LDH formation was derived from weathering of the clay mineral surface. Roberts et al. (1999) have very recently also

shown the formation of mixed Ni-Al LDH precipitates on a Matapeake soil and its clay fraction (Fig. 6). At pH 7.5, the LDH phases formed within 15 minutes. At pH 6.8, it took 2 hours for the phases to form, while they did not form at pH 6.0 over a 72 hour period. Zinc LDH phases also form on clay minerals (Ford and Sparks, 2000) and soil clays (Roberts et al., 1999). Nickel hydroxide precipitates also form on non-Al bearing minerals such as talc and silica, but they are of the α -Ni(OH)₂ form (Scheinost et al., 1999).

The formation of metal hydroxide surface precipitates greatly affects metal stability. Ford et al. (1999) and Scheckel et al. (2000) have shown that Ni becomes increasingly resistant to dissolution as the surface precipitate ages (Fig. 7). For example, after 1 hour of Ni sorption, 65% of sorbed Ni is released, but after about 24 hours of aging Ni release greatly diminishes. After one year of aging, less than 15% of the sorbed Ni was released using HNO₃. The mechanism for this increased metal stability, using an array of spectroscopic (XAFS, DRS) and thermogravimetric (HRTGA) techniques, is the conversion of the Ni-Al LDH to a precursor Ni-Al phyllosilicate. This transformation proceeds as the silica and aluminum, that are released during mineral weathering, replace nitrate in the interlayer space of the LDH, creating Si-Al polymers that bind to the hydroxide layers (Ford et al., 1999; Scheckel et al., 2000). Recent NMR analyses of the interlayer spaces (unpublished data) further corroborates this mechanism.

4 Conclusion

In short, it would appear that with metals such as Co, Ni, and Zn, the formation of metal hydroxide surface precipitates could be an important way to sequester metals in the soil environment, (particularly in contaminated soils where metal concentrations can often be high), such that they are less mobile and less prone to leach and move in surface waters and groundwaters. Moreover, to properly model metal sorption/release in soils, one must include the role of surface precipitation. The majority of the currently used surface complexation models, such as the constant capacitance and triple layer models, assume only adsorption complexes are operational.

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