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A CRITICAL ASSESSMENT OF SORPTION-DESORPTION MECHANISMS AT THE SOIL MINERAL/WATER INTERFACE

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Sorption is one of the most important chemical processes in soil. It affects the fate and mobility of nutrients and contaminants in soils and waters greatly. This paper critically reviews the mechanisms of sorption/desorption phenomena at the mineral/water interface. A brief discussion of macroscopic, equilibrium approaches for describing sorption processes is provided. However, emphasis will be placed on the importance of understanding the rates of sorption/desorption processes and coupling the kinetic investigations with in-situ atomic/molecular resolution surface techniques. The use of X-ray absorption fine structure (XAFS) spectroscopy and scanning force microscopy (SFM) will be emphasized.

ADSORPTION has been one of the hallmarks in soil chemistry research, and because of environmental concerns, it will continue to be a major research emphasis. Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution. It is strictly a two-dimensional process and does not include three-dimensional processes such as surface precipitation, coprecipitation, and diffusion into the crystal. Adsorption, surface precipitation, coprecipitation and diffusion into the crystal would all be examples of sorption, a general term that should be used when the retention mechanism at a surface is unknown. Unfortunately, some scientists still use the term adsorption, rather than sorption, even when they have not definitively ruled out the possibility of precipitation and diffusion phenomena.

Adsorption is one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, radionuclides, pesticides, and other organic chemicals that are retained on soil surfaces and, therefore, is one of the primary processes that affects transport of nutrients and contaminants in soils. Sorption also affects the electrostatic properties of suspended particles and colloids. The electrostatic properties affect coagulation and settling (Stumm 1992; Sparks 1995).

The forces involved in adsorption can range from weak, physical, van der Waals forces (e.g., partitioning) and electrostatic outer-sphere complexes (e.g., ion exchange) to chemical interactions (Fig. 1). Chemical interactions can include inner-sphere complexation that involves a ligand exchange mechanism, covalent bonding, hydrophobic bonding, hydrogen bonding, hydrogen bridges, and steric or orientation effects (Stumm and Morgan 1981; Sparks 1995). Inner-sphere complexes can be either monodentate or bidentate (Fig. 1).

As the amount of a metal cation or anion sorbed on a surface (surface coverage) increases to a higher surface coverage, a surface precipitate can form (Fig. 1). When the precipitate consists of chemical species derived from both the aqueous solution and dissolution of the mineral, it is referred to as a coprecipitate.

There is a continuum between surface complexation (adsorption) and surface precipitation. At low surface coverages surface complexation tends to dominate. As surface coverage increases nucleation occurs and results in the formation of distinct entities or aggregates on the surface. As surface loading increases further, surface precipi-

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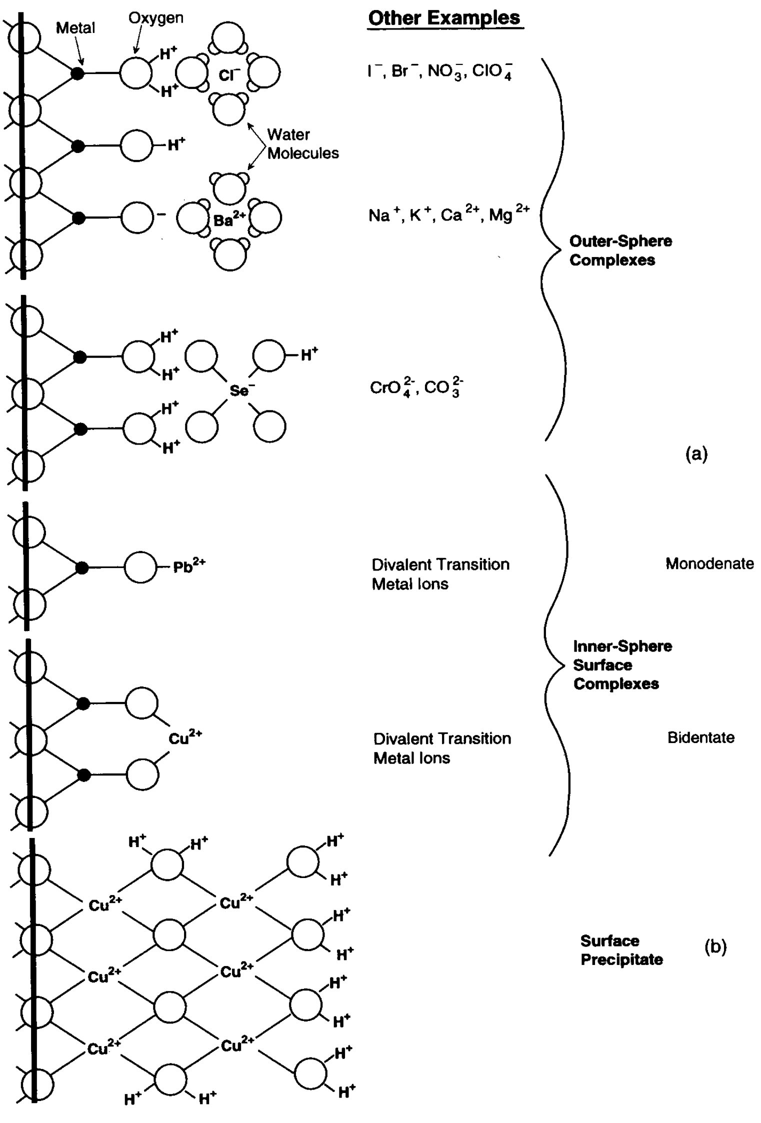

Fig. 1. Possible sorption complexes at the mineral/water interface. (a) surface complexes formed between inorganic ions and hydroxyl groups of an oxide surface (after Hayes 1987); (b) precipitation phenomena (after Brown et al. 1995).

tation becomes the dominant mechanism. Diffusion of molecules or ions through crystalline solids is extremely slow at 25°C so that the term solid diffusion should generally be interpreted to mean transfer through micropores, faults, or interfaces of the solid rather than through the lattice itself (McBride 1994).

DESORPTION

The release of adsorbed species is often referred to as desorption. While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils, the desorption process is also extremely important. This is particularly true for soils that are already contaminated. To predict the fate and mobility of contaminants in such soils and to develop sound and cost-effective remediation strategies, information on desorption is required. For example, if it is found that the contaminant is bound strongly to the soil and little if any desorption occurs, or if the desorption process is extremely slow, movement into groundwater may not be a problem. However, depending on the use of the soil, the "persistence" of the contaminant in the soil may present a problem for homesite construction or crop production. On the other hand, if desorption is effected easily, the contaminant could become mobile and contaminate water supplies. However, its ease of desorption could be an advantage in using remediation techniques such as leaching to decontaminate the soil. Without question, a great need in sorption research is more research on desorption phenomena.

It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed, i.e., the reactions appear to be irreversible. Such apparent irreversibility is commonly referred to as hysteresis or nonsingularity. In such cases, the adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide (Verburg and Baveye, 1994). Such hysteresis is often observed in both organic chemical and metal reactions with natural materials. There are a number of reasons that "non-real hysteresis" may be observed, including artifacts related to experimental conditions such as failure to attain an adsorption equilibrium (Sparks 1989) and to prewash the sorbent (to remove fine particles, etc.) before initiation of sorption and subsequent desorption studies, and chemical and microbial transformations that occur during a particular experiment.

However, it appears that "real hysteresis" can occur, and this is affected dramatically by the type of adsorbent, especially humic substances, and the time over which the adsorption process has occurred.

EQUILIBRIUM-BASED SORPTION MODELS

The scientific literature is replete with investigations on various aspects of adsorption and desorption of plant nutrients, metals, radionuclides, and organic chemicals. Many of these studies have used macroscopic approaches such as adsorption isotherms, empirical and semi-empirical equations (e.g., Freundlich, Langmuir), and surface complexation models (e.g., constant capacitance, triple layer) to describe adsorption. While these investigations have been useful, no real mechanistic information about sorbate retention/release can be gleaned.

It should be recognized that adsorption isotherms are purely descriptions of macroscopic data and do not definitely prove a reaction mechanism. For example, the conformity of experimental adsorption data to a particular isotherm does not indicate that this is a unique description of the experimental data, and that only adsorption is operational. Thus, one cannot differentiate between adsorption and other sorption processes, such as surface precipitation, and surface diffusion using an adsorption isotherm, even though this has been done in the soil chemistry literature.

Surface complexation models are chemical models that are based on molecular descriptions of the electric double layer using equilibrium derived adsorption data (Goldberg 1992). Thus, no mechanistic information on sorption can be obtained. Surface complexation models often describe sorption data over a broad range of experimental conditions such as varying pH and ionic strengths and have been used widely to describe metal cation and anion sorption reactions on oxides, clays, and soils and organic ligand and competitive sorption reactions on oxides. However, surface complexation models employ an array of adjustable parameters to fit experimental data, and it has been shown that often sorption data will equally well fit a number of the models (e.g., Westall and Hohl, 1980).

Another major disadvantage of the surface complexation models, and of most equilibrium-based models, is that three-dimensional surface complexes are not accounted for or differentiated. An exception is the research of Farley et al. (1985) and James and Healy (1972), who considered surface precipitation in successfully modeling sorption of hydrolyzable metal ions. In fact, Farley et al. (1985) include precipitation in a thermodynamic sorption model that is a surface complexation model. Arguably, one of the major needs in modeling sorption on soils and natural materials is to include surface precipitation and other non-adsorption phenomena as part of the model description and prediction. This is particularly important as recent research is definitively showing that multinuclear surface species occur on an array of natural surfaces at low surface coverages and over rapid time scales (Fendorf et al. 1994a; O'Day et al. 1994a and b; Papelis and Hayes 1996; Scheidegger et al. 1996a, b, c, and d).

To ascertain precise sorption/release mechanisms, one must employ approaches that yield atomic/molecular information. Such information can be obtained using surface spectroscopic/microscopic techniques. The rate of sorption/desorption reactions also provides significant information on possible mechanisms. Thus, a knowledge of the kinetics and mechanisms of sorption/release reactions is imperative in predicting the fate and mobility, speciation, and risk assessments of ions and molecules in soil and aqueous environments.

Accordingly, this critical review will focus on past and future research on nonequilibrium aspects of sorption/desorption and the confirmation of reaction mechanisms using in-situ atomic/molecular resolution surface techniques.

KINETICS OF SORPTION/DESORPTION REACTIONS

Without question, macroscopic sorption phenomena are exceedingly important in soils. However, most soils are seldom, if ever, at equilibrium. Moreover, while equilibrium sorption data can be used to propose reaction mechanisms, definitive mechanisms cannot be obtained and time-dependent or kinetics data are not determined.

Many soil chemical processes are time-dependent. To fully understand the dynamic interactions with soils of metals, radionuclides, pesticides, industrial chemicals, sludges and manures, and fertilizers, and to predict their fate with time, a knowledge of the kinetics of these reactions is important.

Certainly an important factor in controlling the rate of many soil chemical sorption reactions is the type and quantity of soil components. For example, ion exchange adsorption reactions are usually more rapid on clay minerals such as kaolinite and oxides than on clay surfaces such as vermiculite and mica. This is attributed to the readily available sites for adsorption on kaolinite compared with the multiple types of sites on vermiculite and micas. External planar, edge, and interlayer sites exist on the surfaces of vermiculite and micas, with some of the latter partially or totally collapsed. High rates of reaction are often observed for external sites, intermediate rates on edge sites, and low rates on interlayer sites (Jardine and Sparks 1984).

The type of surface complex, i.e., outer-sphere versus inner-sphere (monodentate vs. bidentate) also affects the rate and reversibility of sorption reactions. Outer-sphere complexation is usually rapid and reversible, whereas inner-sphere complexation is slower and may appear to be "irreversible" (Sparks 1995).

The kinetics of metal and organic sorption reactions on soils and soil components are often characterized by a rapid, followed by a slow, reaction (Fig. 2). The rapid reaction is most probably ascribable to chemical reaction and film-diffusion processes. For example, sorption reactions of certain metal cations such as Cu^{2+} and oxyanions such as borate, arsenate, molybdate, selenite, selenate, and chromate on goethite occur on millisecond times scales, as measured by pressure-jump relaxation (Zhang and Sparks 1989, 1990; Grossl et al. 1994). Sorption of metals on humics is also rapid. Half-lives for Pb^{2+}, Cu^{2+}, and Zn^{2+} sorption on peat ranged from 5 to 15 s (Bunzl et al. 1976), and film diffusion was assumed to be the rate-limiting step.

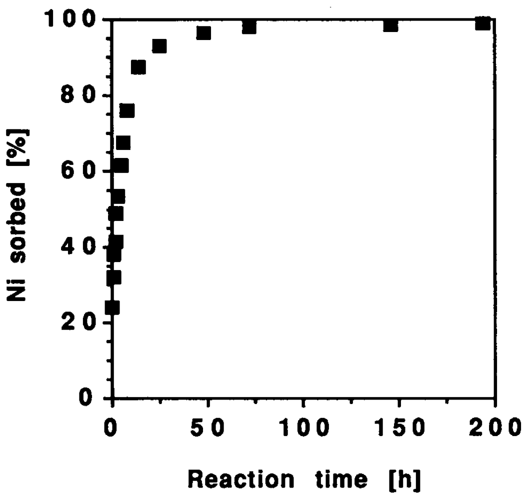

Fig. 2. Kinetics of Ni sorption on pyrophyllite from a 3 m*M* Ni solution at pH = 7.5 and an ionic strength I = 0.1 *M* ($NaNO_3$). (n) denotes the relative amount of sorbed Ni (%) (after Scheidegger et al. 1996b).

The slow sorption reaction (occurring over time scales of days and longer) has been attributed to diffusion into micropores of inorganic minerals and humic components, sites of lower reactivity, and surface precipitation (Sparks 1996a and b). However, the mechanism(s) is not clearly understood and must be confirmed via in-situ (viz., aqueous suspensions and the absence of high vacuums) surface spectroscopic/microscopic techniques.

An important factor affecting the degree of the slow sorption of metals and organics on natural materials is the time period the sorbate has been in contact with the sorbent (residence time). Ainsworth et al. (1994) studied the sorption of Co^{2+}, Cd^{2+}, and Pb^{2+} on hydrous ferric oxide (HFO) as a function of oxide aging and metal-oxide residence time or aging. Oxide aging did not cause hysteresis of metal cation sorption-desorption. Aging the oxide with the metal cations resulted in hysteresis with Cd^{2+} and Co^{2+}, but little hysteresis was observed with Pb^{2+}. With Pb^{2+}, there was slight hysteresis over a 21-week aging process between pH 3 and 5.5

(hysteresis varied from <2% difference between sorption and desorption to ≈ 10%). At pH 2.5, Pb desorption was complete within a 16-h desorption period and was not affected by aging time. However, with Cd and Co, extensive hysteresis was observed over a 16-week aging period, and the hysteresis increased with aging time. After 16 weeks of aging, 20% of the Cd and 53% of the Co was not desorbed, and hysteresis was even observed at pH 2.5. Ainsworth et al. (1994) attributed the hysteresis to Co and Cd incorporation into a recrystallizing solid (probably goethite) via isomorphic substitution and not to micropore diffusion.

Bruemmer et al. (1988) studied Ni^{2+}, Zn^{2+}, and Cd^{2+} adsorption on goethite, and found that as reaction time at pH 6 increased from 2 h to 42 days (at 293K) adsorbed Ni^{2+} increased from 12 to 70% of total adsorption, and total increases in Zn^{2+} and Cd^{2+} adsorption over this time increased 33 and 21%, respectively. Bruemmer et al. (1988) attributed the slow kinetics to diffusion-controlled reactions on external and internal surface sites.

A kinetic study on Ni sorption on pyrophyllite at pH = 7.5 (Fig. 2) has shown that Ni sorption is fast initially, occurring on times scales of minutes, and then the rates diminish gradually, over time scales of hours or days (Scheidegger et al. 1996b). Nickel detachment from the pyrophyllite surface was extremely slow. The detachment rate depended strongly on the pH and the experimental method. Under steady-state conditions, a constant Ni detachment rate was observed that was much slower than the dissolution of a crystalline $Ni(OH)_2$ reference compound. The slow Ni release kinetics was attributed to dissolution of Ni surface precipitates (Scheidegger et al. 1966b). In a subsequent study, Scheidegger et al. (1996a and d) observed, via extended X-ray absorption fine structure (EXAFS) spectroscopic analysis, the formation of mixed Ni-Al polynuclear hydroxides on the surface of an array of clay minerals and metal oxides. The formation of such polynuclear surface species could be a major factor in causing slow metal-natural material sorption and the subsequent hysteresis that is often observed.

Many investigations of organic chemical reactions with natural materials have shown that sorption/desorption is characterized by a rapid, reversible stage, which is followed by a much slower, nonreversible stage (Karickhoff et al. 1979; DiToro and Horzempa 1982; Karickhoff and Morris 1985) or biphasic kinetics. The rapid phase has been ascribed to retention of the organic chemical in a labile form that is easily desorbed. However, the much slower reaction phase involves the entrapment of the chemical in a nonlabile form that is difficult to desorb. This slower sorption/desorption reaction has been ascribed to diffusion of the chemical into micropores of organic matter and inorganic soil components (Wu and Gschwend 1986; Steinberg et al. 1987; Ball and Roberts 1991). The labile form of the chemical is available for microbial attack, whereas the nonlabile portion is resistant to biodegradation.

In a study of polychlorinated biphenyl (PCB) desorption from sediments, 55% of the labile PCBs were desorbed in a 24-h period, whereas little of the remaining 45% nonlabile fraction was desorbed in 170 h. Over an additional 1-yr period, about 50% of the remaining nonlabile fraction desorbed. In another study with volatile organic compounds (VOCS), Pavlostathis and Mathavan (1992) observed a biphasic desorption process for field soils contaminated with trichloroethylene (TCE), tetrachloroethylene (PCE), toluene (TOL), and xylene (XYL). A fast desorption reaction occurred in 24 h, followed by a much slower desorption reaction beyond 24 h. In 24 h, 9–29%, 14–48%, 9–40%, and 4–37% of the TCE, PCE, TOL, and XYL, respectively, were released.

A number of studies have also shown that with increased residence time, the nonlabile portion of the organic chemical in the soil/sediment becomes more resistant to release (McCall and Agin 1985; Steinberg et al. 1987; Pavlostathis and Mathavan 1992; Schribner et al. 1992; Pignatello et al. 1993). However, Connaughton et al. (1993) did not observe the nonlabile fraction increasing with age for naphthalene-contaminated soils.

One way to gauge the effect of time on organic contaminant retention in soils is to compare K_d (sorption distribution coefficient) values for "freshly aged" and "aged" soil samples. In most studies K_d values are measured based on a 24 h equilibration between the soil and the organic chemical. When these values are compared with K_d values for field soils previously reacted with the organic chemical ("aged" samples), the latter have much higher K_d values, indicating that much more of the organic chemical is in a sorbed state. For example, Pignatello and Huang (1991) measured K_d values in "freshly aged" (K_d) and "aged" soils (K_{app}, apparent sorption distribution coefficient) reacted with atrazine and metolachlor, two widely used herbicides. The "aged" soils had been treated with the herbicides 15 to 62 months before sampling. The K_{app} values ranged from 2.3 to 42 times higher than the K_d values.

Scribner et al. (1992), studying simazine (a widely used triazine herbicide for broadleaf and grass control in crops) desorption and bioavailability in "aged" soils found that K_{app} values were 15 times higher than K_d values. Scribner et al. (1992) also showed that 48% of the simazine added to the "freshly aged" soils was biodegradable over a 34-day incubation period, whereas none of the simazine in the "aged" soil was biodegraded.

One of the implications of the above results on slow metal/organic sorption reactions is that while many transport and degradation models for contaminants in soils and waters assume that the sorption process is an equilibrium phenomenon, the above studies show clearly that kinetic reactions must be considered when making predictions about the mobility and fate of metals and organics. Moreover, calculations of K_d values based on a 24-h equilibration period, which are used commonly in fate and risk assessment models, can be inaccurate because 24-h K_d values often overestimate the amount of pollutant in the solution phase.

CONFIRMATION OF REACTION MECHANISMS USING SPECTROSCOPIC AND MICROSCOPIC TECHNIQUES

In spite of many decades of intensive efforts by soil chemists to understand sorption processes, our understanding of the mechanisms of chemical reactions at the solid/liquid interface is still not definitive. One of the main reasons for this is that until quite recently, studies of the reactions between environmental particle surfaces and aqueous solutions have been limited to macroscopic studies. Although macroscopic equilibrium studies and models reveal some important information about sorption/desorption phenomena, no mechanistic or molecular information is revealed. Kinetic studies can reveal something about reaction mechanisms at the soil particle/solution interface, particularly if energies of activation are calculated and stopped-flow or interruption techniques are employed. However, molecular and/or atomic resolution surface techniques should be employed to corroborate the proposed mechanisms hypothesized from equilibrium and kinetic studies. These techniques can be used either separately or, preferably, simultaneously with kinetic investigations. Whereas the latter approach is preferable, only limited studies have been reported in the literature. Examples of both approaches will be cited in the following discussions. Additionally, we will present an overview of contemporary spectroscopic and microscopic techniques that are important for studying sorption processes on soils and soil minerals. Without question, the application of molecular and atomic resolution techniques to elucidation of sorption mechanisms should be a major research thrust in soil and environmental chemistry for decades to come.

There are two principal subdivisions in molecular spectroscopy: in-situ and non-in-situ methods (Johnston et al. 1993). The principal invasive non-in-situ techniques used for soil and aquatic systems are X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), and Secondary Mass Spectroscopy (SIMS). Each of these techniques yields detailed information about the structure and bonding of minerals and the chemical species present on the mineral surfaces. The disadvantage of invasive techniques is that they often must be performed under adverse experimental conditions, e.g., desiccation, high vacuum, heating, or particle bombardment. Such conditions may yield data that are misleading as a result of experimental artifacts (Perry et al. 1990; Fendorf et al. 1994b). XPS is the most widely used non-in-situ surface-sensitive technique. It has been used to study sorption mechanisms of inorganic cations and anions such as Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, selenite, and uranyl in soil and aquatic systems (Koppelmann et al. 1980; Dillard and Koppelmann 1982; Schenk and Dillard 1983; Hochella and Carim 1988; Davison and McWhinnie 1991; Stipp and Hochella 1991; Scheidegger et al. 1993; Junta and Hochella 1994; Wersin et al. 1994; Papelis 1995). Review articles on XPS, AES, and SIMS are available (Hochella 1988; Hochella 1990; Perry et al. 1990).

In-situ methods require little or no alteration of the sample from its natural state (Johnston et al. 1993). They can be applied to aqueous solutions or suspensions; most involve the input and detection of photons. Examples of in-situ techniques are electron spin resonance (ESR), Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray absorption (XAS), and Mössbauer spectroscopies. However, many other techniques are available (Brown 1990).

ESR spectroscopy [also called electron paramagnetic resonance (EPR)] is a technique for detecting paramagnetism. Electron paramagnetism occurs in all atoms, ions, organic free radicals, and molecules with an odd number of electrons. ESR is based upon the resonant absorption of microwaves by paramagnetic substances and describes the interaction between an electronic spin subjected to the influence of a crystal field and an external magnetic field (Calas 1988). The method is applicable to transition metals of Fe^{3+}, Cu^{2+}, Mn^{2+}, V^{4+}, and molybdenum (V) and has been used widely to study metal ion sorption on soil mineral components (McBride 1982; McBride et al. 1984; Bleam and McBride 1986; Wersin et al. 1989) and soil organic matter (Senesi and Sposito 1984; Senesi et al. 1985; Goodman and Cheshire 1987; Senesi and Calderoni 1988; Senesi et al. 1989; Neto et al. 1991). Several review articles on ESR are available (Calas 1988; Cheshire 1994; Senesi 1994).

The Mössbauer effect is based on the recoil-free emission and resonant absorption of γ-rays by specific atomic nuclei in a solid. γ-rays are used as a probe of nuclear energy levels which, in turn, are sensitive to the details of both local electron configuration and the electric and magnetic fields of the solid (Hawthorne 1988). In natural systems, Mössbauer effects specifically relate to iron (Cheshire 1994). Mössbauer spectroscopy is able to distinguish between high spin Fe^{2+} and Fe^{3+} without interference from any other element. It also provides information on the chemical nature of chemical entities bound to the iron. Application of Mössbauer spectroscopy in soil science is not common (Goodman and Cheshire 1979; Kallianou and Yassoglou 1985; Goodman and Cheshire 1987; Kodama et al. 1988; Goodman et al. 1991). There are some review articles available on application of Mössbauer spectroscopy to soil materials (Hawthorne 1988; Goodman 1990; Cheshire 1994).

Application of infrared (IR) spectroscopy to the study of sorbed species has a long history. The introduction of Fourier transform techniques has made a significant contribution to the development of new investigation techniques such as diffuse reflectance infrared Fourier transform (DRIFT) and attenuated total reflectance (ATR) spectroscopy. IR spectroscopy now extends far beyond classical chemical analysis and is applied successfully to study sorption processes of inorganic and organic soil components. These techniques, and other vibrational spectroscopies, such as Raman, are the subject of numerous reviews (Hair 1967; Bell 1980; McMillan and Hofmeister 1988; Johnston et al 1993; Piccolo 1994).

The use of NMR spectroscopy to study surfaces has a shorter history, and fewer applications than vibrational spectroscopies. The primary reason is that the sensitivity of NMR is much lower than that of IR. Properties that might be exploited are the chemical shift, NMR relaxation times, and magnetic couplings to nuclei that are characteristic of a surface (Wilson 1987). Most NMR studies in the field of soil science concentrate on the characterization of soil organic matter and soil humification processes and, therefore, involve ^{1}H, ^{13}C and ^{15}N NMR. Reviews on these and related topics are available (Wershaw and Mikita 1987; Wilson 1987; Johnston et al. 1993; Hatcher et al. 1994). In the past few years, ^{3}Li, ^{3}Na, ^{39}K, ^{111}Cd, and ^{113}Cs-NMR spectroscopy have been used increasingly as tools to elucidate cation exchange sites on clay mineral surfaces (Bank et al. 1989; Luca et al. 1989; Laperche et al. 1990; Weiss et al. 1990). Because it is virtually impossible to obtain any useful molecular information by observing the nucleus of a paramagnetic metal directly, studies of cation exchange have focused on diamagnetic metals, such as Cd^{2+}, which have a spin of 1/2 and an acceptable natural abundance (e.g., 12% and 13%, respectively, for the two NMR-active isotopes, ^{113}Cd and ^{111}Cd). NMR is essentially a bulk spectroscopic technique. The advent of high-resolution, solid-state NMR techniques, such as magic angle sample spinning (MAS) and cross-polarization (CP), along with more sensitive, high magnetic field, user-friendly, pulsed NMR spectrometers has brought increased applications to heterogeneous aqueous systems (Johnston et al. 1993). In particular, ^{27}Al and ^{29}Si NMR in zeolites and other minerals have proven valuable for the structural elucidation of samples whose disorder has prevented diffraction techniques from being very useful (Altaner et al. 1988; Herrero et al. 1989; Woessner 1989).

One of the most powerful noninvasive surface sensitive techniques is X-ray absorption spectroscopy (XAS). XAS is a powerful, element-specific in-situ technique that can be used to determine the local structure (bond distance, number and type of near neighbors) around a sorbing element, even when the element is at low concentration levels [depending on element and matrix as low as 0.03 to 0.05% per weight (Charlet and Manceau 1993)]. XAS can be used to probe most types of phases (crystalline or amorphous solids, liquids, gases) and at structural sites ranging from those in crystals and glasses to those at interfaces such as the mineral/water interface. Like other spectroscopic methods, XAS is not without limitations. It requires intense X-rays, and these are generated by electrons/positrons that circulate in a storage ring of a synchrotron facility at energies of 1 to 6 GeV in paths curved by a magnetic field. Synchrotron facilities are not readily accessible. In addition, in most cases studies are primarily limited to elements heavier than Sc. There are several reviews on XAS that the reader can consult. Particularly relevant to soil science are those by Brown et al. (1989), Brown (1990), Charlet and Manceau (1993), Fendorf et al. (1994b), and Schulze and Bertsch (1995).

By convention, XAS spectra (one scans near the X-ray absorption edge K, L, M of the element of concern) can be divided into two energy regions: (i) the X-ray absorption near edge structure (XANES) region and (ii) the extended edge X-ray absorption structure (EXAFS) region. The XANES region runs to about 50 eV above the absorption edge (Schulze and Bertsch 1995). It is usually characterized by intense resonance features arising from electron transitions to unoccupied bound state and continuum levels and from multiple scattering of the emitted photoelectrons by atoms surrounding the absorber. For many first row transition elements, the pre-edge resonances provide information on the site geometry of the absorber, which is commonly related to the oxidation state. For example, Cr oxidation states can be deduced from the presence or absence of a predominant pre-edge feature that is characteristic of Cr(VI), which is tetrahedrally coordinated, but is nearly absent for Cr(III), which is octahedrally coordinated (Bidoglio et al. 1993; Fendorf et al. 1994b; Schulze and Bertsch 1995). XANES was also used to determine oxidation states of Mn (Manceau et al. 1992a and b; Lytle et al. 1996); Se (Pickering et al. 1995); Ce (Bidoglio et al. 1992); Tl (Bidoglio et al. 1993), Tl (Bajt et al. 1994), and U (Bertsch et al. 1994) in natural environments. Although interatomic distances can be deduced from the XANES region (Waychunas et al. 1983; Petiau et al. 1987; Waychunas 1987), the main application of XANES is "fingerprinting." By comparing known spectra with unknown samples, important qualitative information on bonding environments can be deduced. This method has proven to be beneficial for investigating unknown heterogeneous samples such as soils (Manceau et al. 1996).

The EXAFS region that follows the XANES region in the XAS spectra runs up to about 800 eV beyond the edge (Charlet and Manceau 1993). The frequency oscillations in the region arise from constructive and destructive interference patterns between the outgoing and the returning photoelectronic wave that has been backscattered from first and sometimes second shell neighboring atoms. The frequency of the oscillation is related inversely to the bond distance between the absorber and neighboring atoms. The amplitude of these oscillations is related to both the identity and number of atoms surrounding the central absorber (Schulze and Bertsch 1995). EXAFS has long been applied to problems in physics, chemistry, biochemistry, and materials science (Sayers et al. 1971). It is also well established in earth and marine material research (Calas and Petiau 1983; Waychunas et al. 1983; Petiau and Calas 1985). One of the earliest uses of EXAFS to determine sorption mechanisms of ions on natural surfaces was in the research of Hayes et al. (1987), who studied selenate and selenite adsorption on goethite. They showed that selenate was absorbed as an outer-sphere complex and selenite was adsorbed as an inner-sphere complex (Hayes et al. 1987). This interpretation was later questioned by Manceau and Charlet (1994), who found that selenate ions form binuclear bidentate surface complexes on goethite. Recently, numerous studies have demonstrated the usefulness of EXAFS for providing specific chemical speciation information on contaminants associated with sorptive phases, including soils (Table 1).

Studies using EXAFS have shown that the adsorption of heavy metals on clay and oxide surfaces results in the formation of multinuclear or polynuclear surface complexes much more frequently than previously thought. Multinuclear metal hydroxides of Pb, Ni, Co, Cu, and Cr(III) on oxides and aluminosilicates have been discerned (Chisholm-Brause et al. 1990a and b; Roe et al. 1991; Charlet and Manceau 1992; Fendorf et al. 1994a and b; O'Day et al. 1994a and b; Bargar et al. 1995; Papelis and Hayes 1996; Scheidegger et al. 1996a and d). Such surfaces precipitates have been observed at metal surface loadings far below a theoretical monolayer coverage and in a pH-range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product (Fendorf et al. 1994a; O'Day et al. 1994a and b; Scheidegger et al. 1996a,b,c). This is demonstrated in Fig. 3 which shows the radial structure functions (RSFs) of Ni-treated pyrophyllite spectra compared with the spectrum of the crystalline $Ni(OH)_2(s)$ model compound. With increasing surface loading ($\boldsymbol{\Gamma} = 0.51$ µmol m^{-2}; Fig. 3) a peak appeared at R ≈ 2.7 Å and increased in intensity with further increased Ni uptake (Fig. 3). This peak, also present in $Ni(OH)_2$,

TABLE 1

Studies on sorption mechanisms of inorganic cations and anions using EXAFS

System	Reference
SeO_4^{2-}/α-FeOOH	Hayes et al. (1987)
SeO_4^{2-}/δ-$Al(OH)_3$	Papelis et al. (1996)
SeO_3^{2-}/α-FeOOH	Manceau & Charlet (1994)
SeO_3^{2-}/α-Al_2O_3	Papelis et al. (1995)
SeO_3^{2-}/α-Al_2O_3	Papelis et al. (1995)
SeO_3^{2-}/hydrous Fe oxides	Manceau & Charlet (1994)
SeO_3^{2-}/α-FeOOH	Hayes et al. (1987)
AsO_4^{3-}/ferrihydrite	Waychunas et al. (1993)
AsO_4^{3-}/α-FeOOH	Waychunas et al. (1993)
AsO_4^{3-}/β-FeOOH	Waychunas et al. (1993)
AsO_4^{3-}/γ-FeOOH	Waychunas et al. (1993)
U(VI)O_2^{2+}/ferrihydrite	Waite et al. (1994)
U(VI)O_2^{2+}/silica	Dent et al. (1992)
U(VI)O_2^{2+}/montmorillonite	Dent et al. (1992)
U(VI)O_2^{2+}/smectite	Chisholm-Brause et al. (1994)
Np(V)O_2^{2+}/α-FeOOH	Combes et al. (1992)
Co(II)γ-Al_2O_3	Chisholm-Brause et al. (1990a)
Co(II)/kaolinite	Chisholm-Brause et al. (1990a)
Co(II)/kaolinite	O'Day et al. (1994a,b)
Co(II)/silica	O'Day et al. (1996)
Co(II)/rutile	O'Day et al. (1996)
Co(II)/rutile	Chisholm-Brause et al. (1990a)
Co(II)/montmorillonite	Papelis & Hayes (1996)
Cu(II)/mica	Farquhar et al. (1996)
Cr(III) bentonite	Corker et al. (1991)
Ni(II)/pyrophyllite	Scheidegger et al. (1996a)
Ni(II)/montmorillonite	Scheidegger et al. (1996d)
Ni(II)/kaolinite	Scheidegger et al. (1996d)
Ni(II)/gibbsite	Scheidegger et al. (1996d)
Cr(III)/beidellite	Corker et al. (1991)
Cr(III)/laponite	Corker et al. (1991)
Cr(III)/HFO	Charlet and Manceau (1992)
Cr(III)/α-FeOOH	Charlet and Manceau (1992)
Cr(III)/silica	Fendorf et al. (1994a)
Cr(III)/birnessite	Manceau and Charlet (1994)
Pb(II)/α-FeOOH	Roe et al. (1991)
Pb(II)/γ-Al_2O_3	Chisholm-Brause et al. (1990b)
Pb(II)α-Al_2O_3	Bargar et al. (1995)
Pb(II)/gibbsite	Alcacio et al. (1995)
Pb(II)/pyrophyllite	Alcacio et al. (1995)
Pb(II)/soils	Manceau et al. (1996)
Cd(II)/α-FeOOH	Spadini et al. (1994)
Cd(II)/HFO	Spadini et al. (1994)

EXAFS = Extended X-ray absorption fine structure spectroscopy.

represents the second Ni shell and reflects backscattering among multinuclear Ni complexes. The presence of multinuclear surface complexes was depicted at low surface loading (<10%) and at reaction conditions undersaturated with respect to the formation of $Ni(OH)_2(s)$ (Scheiddegger et al. 1996a). In another study, Fendorf et al. (1994a) and Fendorf and Sparks (1994) used EXAFS, FTIR, and HRTEM to study Cr(III) sorption on Si-oxide. At low Cr(III) surface coverage (<20%), adsorption was the dominant process and Cr(III) formed an inner-sphere monodenate surface complex on Si. As Cr(III) surface coverage increased (>20%), surface precipitation occurred and became the dominant sorption mechanism at higher surface coverages. Surface clusters were observed at the high surface loadings. This EXAFS study, as well as others (O'Day et al. 1994a and b; Scheidegger et al. 1996a), demonstrates that the total coverage of surface sites is not necessary for the formation of multinuclear surface complexes and implies that the natural mineral surfaces promote hydrolysis and multinuclear complex formation.

While XAS provides local chemical information, it provides no information on spatial resolution of surface species. Such information can only be obtained by microscopic methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM or HRTEM-high resolution TEM) are well established methods for acquiring both chemical and micromorphological data on soils and soil materials. TEM can provide spatial resolution of surface alterations and the amorphous nature or degree of crystallinity of sorbed species (ordering). It can also be combined with electron spectroscopies to determine elemental analysis. In the last two decades, several books and review articles on microcharacterization of soils using electron microscopy have been published. A partial list of these includes the books edited by Smart and Tovey (1981), Bullock and Murphy (1983), and Douglas (1990), as well as review articles by Whalley (1985), Bisom et al. (1990), Tovey et al. (1992), and Chen (1994).

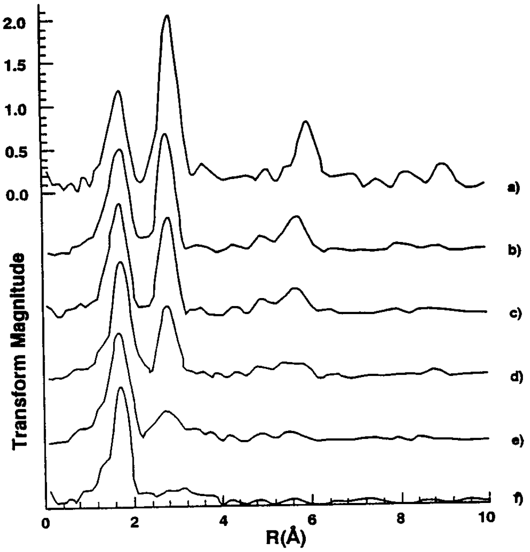

Fig. 3. Radial structure functions (RSFs) of Ni-treated pyrophyllite samples at surface sorption densities Γ of b.) 3.1, c.) 2.0, d.) 1.0,e.) 0.49, and f.) 0.27 μmol m^{-2} compared with the spectrum of the crystalline $Ni(OH)_2(s)$ model compound a.). The spectra are uncorrected for phase shift. Note the appearance of a peak at a R of about 2.7 Å with increasing sorption density (after Scheidegger et al. 1996a).

From the very inception of the scanning tunneling microscope (STM) in 1981, it was apparent that this technique would revolutionize the study of mineral surfaces and surface-related phenomena. Indeed, by the end of the 1980s, applications of STM were beginning to appear in the earth sciences literature (Hochella et al. 1989; Eggleston and Hochella 1990). However, the major event for the environmental science community came with the development of scanning force microscopy (SFM; also known as atomic force microscopy, AFM). SFM allows imaging of mineral surfaces in air or immersed in solution, at sub-nanometer scale resolution (Maurice 1996). Applications to date include: determining the molecular to atomic scale structure of mineral surfaces (Johnsson et al. 1991; Ohnesorge and Binning 1993); probing forces at the mineral/water interface (Ducker et al. 1991; Ducker et al. 1992); visualizing sorption of hemimicelles and macromolecular organic substances such as humic and fulvic acid (Manne et al. 1994; Maurice 1996); determining clay particle thicknesses and morphology of clay-sized particles (Hartman et al. 1990; Friedbacher et al. 1991; Lindgreen et al. 1991; Blum and Eberl 1992; Maurice et al. 1995); imaging soil bacteria (Grantham and Dove 1996); and measuring directly the kinetics of growth, dissolution, heterogenous nucleation and redox processes (see later discussion).

Nevertheless, one must realize that SFM imaging of soil samples presents a challenge for the microscopist because natural samples tend to be heterogeneous. SFM does not provide chemical data; hence, minerals must be identified primarily based on morphology. Yet, morphology alone can lead to ambiguous results. Even atomic-scale imaging may not be conclusive because the crystal structures of many soil minerals are similar. Maurice (1996) suggested the following approach to working with soil samples: (i) compile as many images as possible of well characterized minerals to use as a catalog for particle identification, (ii) characterize the soil samples as fully as possible by XRD and other chemical and physical analytical techniques, and (iii) simplify image interpretation through the use of techniques for isolating different components and fractions. Several review articles on SFM are available; particularly relevant to soil scientists are those by Hochella (1990), Vempati and Cocke (1994), and Maurice (1996).

USE OF KINETIC AND SPECTROSCOPIC APPROACHES TO ELUCIDATE SORPTION MECHANISMS

An ideal way to confirm sorption/desorption mechanisms is to combine kinetic investigations with surface spectroscopic/microscopic experiments. There are a few examples in the literature of studies where mechanisms of metal sorption reactions on soil components have been hypothesized via kinetic experiments and verified in separate spectroscopic investigations (Fuller et al. 1993; Waychunas et al. 1993). An example of this approach can be found in the recent research of Fuller et al. (1993) and Waychunas et al. (1993), who studied the kinetics and mechanisms of As(V) sorption on ferrihydrite. Adsorption was investigated during coprecipitation, in which As(V) was present in solution during the hydrolysis and precipitation of Fe, and after coprecipitation (post-synthesis adsorption). In the post-synthesis adsorption studies, As(V) uptake was rapid initially and then increased slowly for up to 8 days. The rapid uptake was ascribed to adsorption on surface sites near the outside of aggregates, and the slower adsorption was attributed to diffusion of As(V) to adsorption sites on ferrihydrite surfaces within aggregates of colloidal particles. The latter were caused by coagulation and crystallite growth processes. These processes resulted in a decrease in the number of adsorption sites, and as aggregates formed, adsorption sites were buried in large clusters of the particles (Fuller et al. 1993). In the coprecipitation studies, initial As(V) uptake was much greater than observed for the post-synthesis adsorption studies, and the uptake rate was not diffusion-controlled as As(V) was coordinated by surface sites before crystallite growth.

The mechanistic hypotheses, based on the kinetic studies, were verified with companion EXAFS studies (Waychunas et al. 1993). Analyses of the EXAFS data provided no evidence for surface precipitation, one possible mechanism that has been proposed for slow metal sorption processes. Arsenate retention in both the coprecipitation and post-synthesis adsorption studies involved primarily inner-sphere bidentate and monodentate binding on sites initially adsorbing arsenate. Waychunas et al. (1993) hypothesized that these defect sites probably adsorb As(V) as a bidentate complex first and then sorb as a monodentate complex. Monodentate complexes accounted for about 30% of all As-Fe correlations and occurred only at low As loading levels.

Ideally, one would prefer to study sorption reaction mechanisms by following reaction rates spectroscopically (time-resolved or real-time studies) using in-situ approaches. Such studies are scarce in the literature. The quick EXAFS technique, abbreviated (QEXAFS), depends on a constant monochromator scan rate and fast array defectors to obtain a full EXAFS spectrum in a fraction of a second compared to tens of minutes in a traditional EXAFS method. Thus, msec or µsec time scales could be monitored spectroscopically (Frahm 1991; Lytle and Greeger 1991; Dobson 1994; Schulze and Bertsch 1995). Such studies would be very useful for many rapid soil particle/solution reactions. Energy dispersive EXAFS, abbreviated (DEXAS), can also be used to determine a full EXAFS spectrum in a fraction of a second (Baker et al. 1991). However, detection can only be determined in the transmission mode.

A recent example of time-resolved in-situ spectroscopic analyses is the research of Hunter and Bertsch (1994). They employed attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to quantitatively measure the degradation kinetics of tetraphenylboron (TPB) on clay minerals. The mechanisms of degradation were ascribed to surface-facilitated oxidation at Lewis acid and Brönsted acid sites. First-order models based on these mechanisms described the time-dependent data quite well.

USE OF KINETIC AND MICROSCOPIC APPROACHES

Scanning force microscopy (SFM) has been used increasingly as an in-situ technique for imaging mineral surfaces immersed in aqueous solution, over the course of dissolution, precipitation, and heterogeneous nucleation reactions (Dove and Hochella 1993; Gratz and Hillner 1993; Bosbach and Rammense 1994; Junta and Hochella 1994; Stipp et al. 1994; Maurice et al. 1995; Fendorf et al. 1996). SFM permits a direct measure of surface-controlled growth and dissolution rates by providing 3-dimensional data on changes in microtopography. In-situ SFM has the unique ability to detect separate processes, such as dissolution and secondary phase formation, occurring simultaneously on a mineral surface (Maurice 1996). Some of the studies in which SFM has been used to study the kinetics of mineral reactions are reported in Table 2.

Recently, Fendorf et al. (1996) studied the kinetics of Cr(III) sorption reactions on single goethite and silica particles using a flow-cell mounted in a SFM. This procedure enabled one to study the reactions in-situ and to react the surface while imaging (real-time measurements).

TABLE 2

Studies on the kinetics of mineral reactions using SFM†

Dove et al. (1992)	Calcite precipitation
Hellman et al. (1992)	Albite dissolution
Hillner et al. (1992a, b)	Calcite growth and dissolution
Johnsson et al. (1992)	Muscovite dissolution
Dove and Hochella (1993)	Calcite precipitation mechanisms and inhibition by orthophosphate
Gratz and Hillner (1993)	Step dynamics and spiral growth on calcite
Bosbach and Rammensee (1994)	Gypsum growth and dissolution
Junta and Hochella (1994)	Mn(II) oxidation on hematite, goethite and albite
Stipp et al. (1994)	Calcite surface structure
Maurice et al. (1995)	Dissolution of hematite in organic acids
Fendorf et al. (1996)	Precipitation kinetics of chromium hydroxide on goethite and silica

†Studies are listed in chronological order.
SFM = scanning force microscopy.

Figure 4a shows an image of the unreacted silica in an aqueous environment. The surface is mostly flat and smooth with no island outcroppings. One hour after a 1 m*M* Cr(III) solution at pH 6 was introduced into the flow cell, one sees that the surface morphology of silica has changed dramatically (Fig. 4b). Surface clusters have formed on the surface, and within 2 h (figure not shown) the clusters have expanded in width and girth. The precipitates form as discrete surface clusters on the silica surface rather than distributing across the surface (Fendorf et al. 1996).

CONCLUSIONS AND FUTURE RESEARCH NEEDS

Research on the mechanisms of sorption/desorption reactions at the soil particle-solution interface will be a common theme in soil and environmental sciences for decades to come. This research emphasis is largely the result of the need to control more accurately the long-term fate and transport of contaminants in the subsurface environment. Without such data, economically sound decisions about soil remediation cannot be made, and risk assessment models are not complete. For further advancement to occur in the area of sorption/desorption, the following research is needed: long-term sorption/desorption rate studies, a better understanding of residence time effects on nutrient, radionuclide, metal, and organic retention/release mechanisms on soils and other natural materials, and increased use of time-resolved, in-situ spectroscopic and microscopic techniques to confirm sorption/desorption reaction mechanisms.

In just the last decade, major advances in surface spectroscopic and microscopic techniques have greatly enhanced our ability to study sorption phenomena at the solid/solution interface. One of the most important findings is the direct verification that the chemical properties of natural interfaces are highly heterogeneous (Hochella 1992). The microtopography of the natural mineral/water interface is invariably complex (micro-topography includes surface features on atomic and molecular scales such as steps, kinks, defect outcrops, microcracks, pits and so on). This results in compositional and structural heterogeneity, which is the largest obstacle and challenge to obtaining a better understanding of sorption processes at the mineral/water interface (Hochella 1992). The heterogeneity complicates evaluation of spectroscopic data and theoretical modeling, and it makes interface thermodynamic observations much harder to rationalize without resorting to oversimplification. Ironically, it is this very feature of natural surfaces that makes them so important geochemically and environmentally.

We must realize that our understanding of sorption processes is still in its infancy. One reason for this is that the physical and chemical characteristics of the first few layers of solid and fluid on either side of the interface are just starting to be explored. For example, Knight and Dvorkin (1992) obtained experimental evidence that the first three or four monolayers of water on a mineral surface are distinctly different from bulk water. With solids, it is known for a number of nonmineral crystalline solids that the first few atomic layers are structurally (and electronically) modified because of the termination of the bulk solution (Somorjai and van Hove 1989; Somorjai 1990). Therefore, the properties of the near surface of the mineral and the first few atomic layers

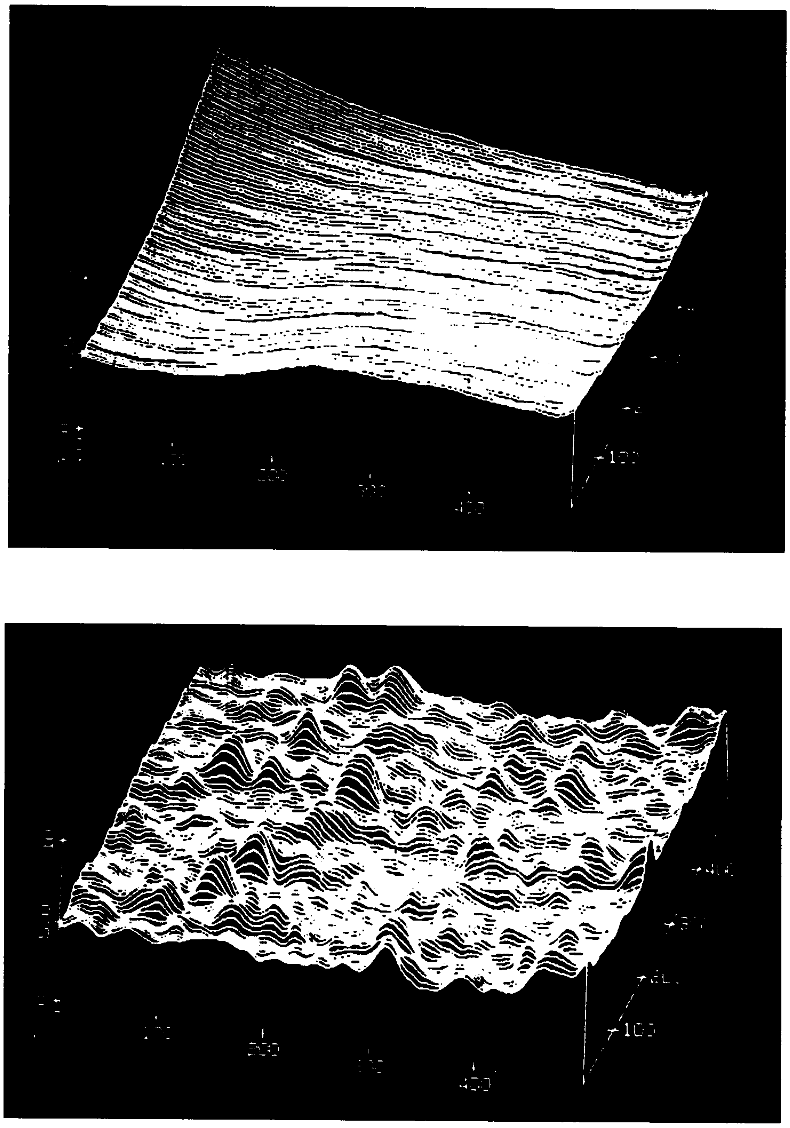

Fig. 4 Using a flow cell, a single-particle of silica was imaged in an aqueous environment. The unreacted silica (a) is relatively flat and smooth over the 500 × 500 nm scan region; no pronounced outcroppings from the surface are observed. After reacting with 1 m*M* Cr(III) for 1 h at pH 6.0 (b) a different surface morphology is apparent; distinct surface clusters have formed that protrude away from the silica surface. These clusters continue to expand away from the surface and fuse together after 2 h (not shown) of reacting with Cr(III). (after Fendorf et al. 1996).

of the fluid will be modified relative to their bulk phases.

Hochella (1992) demonstrated our lack in understanding sorption phenomena clearly by posing fundamental questions. For example, during the time that a species is attached to a specific surface site, how is the sorbed molecule, and the site on which it sits, electronically modified? As a result of this, what is the molecular orientation of the attachment, and what are the relative probabilities that this sorbed species will dissociate, migrate to another site, diffuse into the near-surface, or desorb back into solution? How and at what rate do surface species diffuse and combine with other species to form products?

Answering these questions will not be easy and will require detailed macroscopic, kinetic, microscopic, and spectroscopic data. If possible, the studies should include a multitude of advanced, complimentary surface characterization techniques because no single technique provides a complete depiction of most systems. Such studies will, however, be costly and will be possible only if soil scientists collaborate with chemists, physicists, biologists, engineers, and other professionals. This will mean that soil scientists must understand the "language" of other scientists and engineers and be well versed in fundamental analytical, physical, chemical, and biological principles.

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