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CHAPTER 5

J. A. DAVIS AND D. B. KENT

SURFACE COMPLEXATION MODELING IN AQUEOUS GEOCHEMISTRY

INTRODUCTION

The quantitative description of *adsorption* as a purely macroscopic phenonmenon is achieved through the concept of *relative surface excess* (see chapter by Sposito, this volume). For accumulation of solute i at the mineral-water interface, the relative surface excess, Γ_i, or adsorption density of solute i, may be defined as:

$$\Gamma_i = \frac{n_i}{\mathcal{A}} \quad , \tag{1}$$

where n_i is the moles of surface excess of solute i per unit mass of the mineral phase, and $\mathcal{A}$ is the specific surface area of the mineral phase. This definition assumes that solute i does not enter the structure of the mineral phase. The term, *sorption*, is used in a more general sense to include processes such as surface precipitation or diffusion of solutes into porous materials (Sposito, 1986).

While Equation 1 appears simple, thermodynamic definition and measurement of the quantities n_i and $\mathcal{A}$, especially for soils, sediments, and rock surfaces, are complex topics. The surfaces of minerals are *loci* of a large suite of chemical reactions, including adsorption, ion exchange, electron transfer reactions, precipitation, dissolution, solid solution formation, hydrolysis, and polymerization (Davis and Hayes, 1986; Stumm, 1987). A thorough, mechanistic understanding of adsorption-desorption reactions is needed to understand their role as preliminary steps in various geochemical processes (Stone, 1986; Davis et al.,1987; and see chapter by Stumm, this volume). Soil scientists and analytical chemists have recognized for many decades that mineral surfaces and precipitates can adsorb a large number of ions and molecules (Bolt, 1982). However, the interest in adsorption processes now extends to many other fields, including geochemistry, hydrogeology, chemical oceanography, aquatic toxicology, water and wastewater treatment, and chemical, metallurgical, and mining engineering. As a result, there has been an explosive growth in experimental data describing the adsorption of ions on mineral surfaces in the last 30 years. Simultaneously, there have been significant advances in understanding the fundamental mechanisms involved in adsorption-desorption equilibria.

Experimental sorption data are described by various empirical means, including partition coefficients, iostherm equations, and conditional binding constants (Honeyman and Leckie, 1986). Because these relationships and empirical parameters are highly dependent on the chemical composition of aqueous solutions, empirical approaches to describing adsorption equilibria in aqueous geochemistry are considered unsatisfactory by many scientists (Davis et al., 1990; Honeyman and Santschi, 1988; Kent et al., 1986). Instead, it is envisioned that *surface complexation theory*, which describes adsorption in terms of chemical reactions between surface functional groups and dissolved chemical species, can be coupled with aqueous speciation models to describe adsorption equilibria within a general geochemical framework. While this approach has been adopted in computer models developed by experimental aquatic chemists (e.g., MINEQL, MINTEQ and HYDRAQL; Westall et al., 1976; Brown and Allison, 1987; Papelis et al., 1988), it has not been included in models used widely within the geochemical community (e.g., PHREEQE and EQ3/EQ6; Parkhurst et al., 1980; Wolery, 1983). A recent modification of the PHREEQE code that includes surface complexation equilibria has been published by Brown et al. (1990).

One of the reasons for the lack of acceptance of the surface complexation approach by geochemical modelers has been the development of several competing models, each with its own set of thermodynamic data and other model parameters. In addition to this problem, most of the apparent equilibrium constants for adsorption equilibria that are published in the literature are not self-consistent. Hopefully, this situation will soon improve. Dzombak and Morel (1990) recently published an excellent treatise on one of the surface complexation models (the diffuse double layer model) that included a critically reviewed and self-consistent thermodynamic database for use of the model with ferrihydrite. The extensive data sets in the literature at present should make it possible to compile databases for other mineral phases and each of the surface complexation models. In this chapter we argue that each of the models has advantages and disadvantages when evaluated in terms of model applicability to various geochemical environments. Thus, the existence of several adaptations of surface complexation theory should be viewed optimistically, since it provides modelers with several ways to approach the extremely complex interactions of natural systems.

Extensive experience has shown that the each of the models is extremely successful in simulating adsorption data from laboratory experiments with well-characterized synthetic minerals (Dzombak and Morel, 1987). Guidelines for the use of surface complexation models in geochemical applications are slowly developing (Fuller and Davis, 1987; Charlet and Sposito, 1987, 1989; Zachara et al., 1989b; Payne and Waite, 1990). However, application of the modeling approach to natural systems is considerably more difficult than when applied in simple mineral-water systems (Luoma and Davis, 1983; Bolt and van Riemsdijk, 1987; McCarthy and Zachara, 1989). In particular, there are severe difficulties associated with describing the reactive functional groups of soil, sediment, and rock surfaces and the electrical double layer properties of mixtures of mineral phases and their surface coatings. A realistic appraisal of these problems can lead to a pessimistic view of the future of surface complexation modeling in aqueous geochemistry (e.g., Bolt and van Riemsdijk, 1987).

In this chapter we review fundamental aspects of electrical double layer theory and the adsorption of inorganic ions at mineral-water interfaces. An important prerequisite for applying surface complexation theory is a detailed knowledge of surface functional groups, surface area, and the porosity of adsorbing mineral phases. Accordingly, we have discussed these topics in some detail. Both surface complexation and empirical approaches to adsorption modeling in natural systems are reviewed. The surface complexation models are compared in terms of their capabilities to simulate data and applicability to natural systems. Practical issues involving parameter estimation and experimental techniques applied to soils and sediments are discussed. Finally, guidelines for the application of surface complexation theory to natural systems are formulated based on the current state of knowledge.

SURFACE FUNCTIONAL GROUPS

Surface functional groups and mineral types

In surface complexation theory, adsorption is described in terms of a set of complex formation reactions between dissolved solutes and surface functional groups (Sposito, 1984). The free energies of the reactions can be divided into chemical and electrostatic contributions for modeling purposes. Surface functional groups influence both terms. The nature of the surface functional groups controls the *stoichiometry* of the adsorption reaction, and hence the variation in adsorption with solution chemistry. Surface functional groups also influence the electrical properites of the interface, and their density controls the adsorption capacity. Accordingly, the definition of *surface functional groups* represents the most basic concept of surface complexation theory.

A variety of materials are of interest as adsorbents in the field of aqueous geochemistry. For the purposes of this discussion, these materials are classified in terms of the nature of the surface functional groups that they possess (Kent et al., 1986). Hydrous oxide minerals and natural organic particulate matter possess proton-bearing surface functional groups. Consequently, adsorption onto these solid phases is pH dependent. Aluminosilicate minerals are divided into those that possess a permanent structural charge and those that do not.

Aluminosilicate minerals without permanent charge have proton-bearing surface functional groups, hence they are discussed along with hydrous oxides. Minerals with permanent structural charge, such as clay minerals, micas, zeolites and most Mn oxides, have ion-bearing *exchange* sites in addition to proton-bearing surface functional groups. The surface functional groups of *salt-type* minerals bear the cation or anion of the salt, e.g., Ca^{2+} or CO_3^{2-} on the calcite surface. Sulfide minerals are potentially important in many reducing environments. These minerals possess both proton-bearing and salt-type surface functional groups; however, metal ion sorption by sulfides may be controlled primarily by surface precipitation reactions.

Oxides and aluminosilicates without permanent charge

Surface hydroxyl groups constitute the complexation sites on oxide and aluminosilicate minerals that do not possess a fixed charge (James and Parks, 1982; Bolt and van Riemsdijk, 1987). Various types of surface hydroxyl groups are illustrated in Figure 1. M and O moieties present at the surface suffer from an imbalance of chemical forces relative to the bulk. This imbalance is satisfied by "chemisorbing" water to form surface hydroxyl groups (see Parks, this volume). Hydrogen bonding between surface hydroxyl groups and either water vapor or liquid water gives rise to layers of physically adsorbed water (Fig. 1).

Types of surface hydroxyl groups. Analyses of the crystal structures of oxide and aluminosilicate minerals indicate that the different types of surface hydroxyls have different reactivities (James and Parks, 1982; Sposito, 1984). Goethite (α-FeOOH), for example, has four types of surface hydroxyls whose reactivities depend upon the coordination environment of the O in the FeOH group (Fig. 2). The FeOH sites are designated A-, B-, or C-type sites, depending on whether the O is coordinated with 1, 3, or 2 adjacent Fe(III) ions. A fourth type of site, designated a Lewis-acid site, results from chemisorption of a water molecule on a "bare" Fe(III) ion. Sposito (1984) argues that only A-type sites are basic, i.e., can from a surface complex with H+, while both A-type and Lewis acid sites can release a proton. B- and C-type sites are considered unreactive. Thus, A-type sites can act as either a proton acceptor or a proton donor (i.e., are *amphoteric*). The water coordinated with Lewis-acid sites may act only as a proton donor site (i.e., an acidic site). Aluminosilicates posses both *aluminol* ($\equiv$ AlOH) and *silanol* ($\equiv$ SiOH) groups. Thus kaolinite has three types of surface hydroxyl groups: aluminol, silanol, and water adsorbed to Lewis acid sites (Fig. 3).

Spectroscopic studies have confirmed the presence of different types of surface hydroxyl groups on oxide minerals. IR (Infra-red) spectra of silica and aluminosilicate catalysts show bands corresponding to two different types of surface OH groups (James and Parks, 1982). Oxides of Al, Fe, Ti, and other metals show more bands, indicating the presence of several types of surface OH groups (James and Parks, 1982). Parfitt and Rochester (1976) discuss the relationship between IR spectra of molecules adsorbed at surface OH groups and the acidity of the surface OH groups. Application of Si-29 cross-polarization magic angle spinning NMR spectroscopy (CP MAS NMR) has confirmed the presence of surface hydroxyl groups with different chemical environments on amorphous silica (am-SiO_2). Cross-polarization is a method by which the spin from the ^1H (proton) spin system is transfered to nearby ^{29}Si centers (Pines et al., 1973). This technique eliminates spectral contributions from framework ^{29}Si centers and reduces complications arising from the presence of adsorbed water, which hamper the interpretation of spectral contributions of surface OH groups. ^{29}Si CP MAS spectra of am-SiO_2 samples show three peaks that correspond to O_4Si, $O_3Si(OH)$, and $O_2Si(OH)_2$ (Maciel and Sindorf, 1980; Sindorf and Maciel, 1981, 1983).

Density of surface hydroxyl groups. James and Parks (1982) offer a thorough review of the various methods used to quantify the density of surface hydroxyl groups. Analysis of the densities of groups that outcrop on the various crystal and cleavage faces of a mineral are possible if the crystal structure and habit are known (James and Parks, 1982; Sposito, 1984; Davis and Hem, 1989). This type of analysis yields insight as to the reactivity of most surface functional groups but does not take into account surface defects, which can be

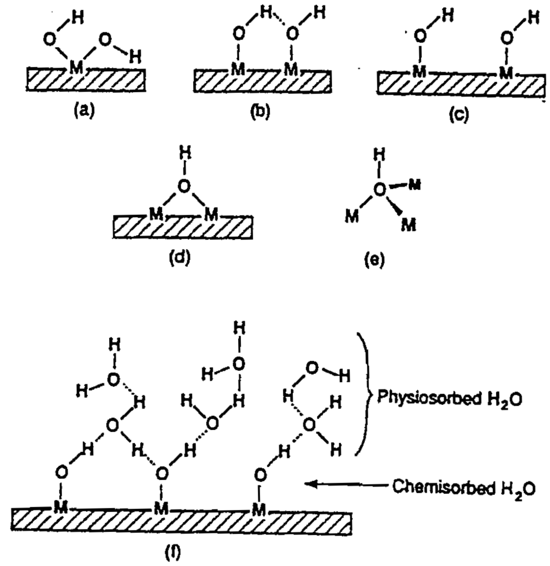


Figure 1. Different types of surface hydroxyl groups found on hydrous oxide surfaces: (a) Geminal hydroxyl groups, (b) vicinal groups, H-bonded, (c) isolated hydroxyls, (d) doubly coordinated hydroxyl, (e) triply coordinated hydroxyl, (f) idealized relationship between surface hydroxyls (= chemisorbed H_2O) and two layers of physiosorbed H_2O.

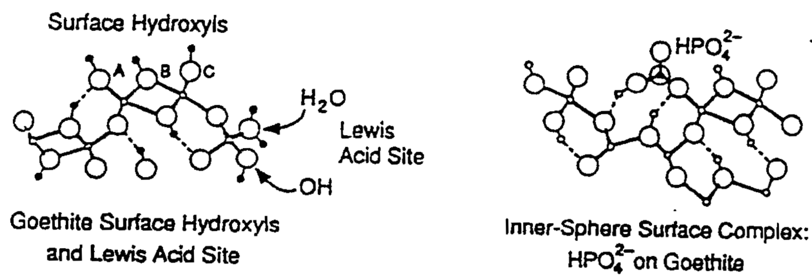


Figure 2. (a) Types of surface hydroxyl groups on goethite. Type A, B, and C groups are singly, triply, and doubly coordinated to Fe(III) ions (one Fe-O bond not represented for type B and C groups), and a Lewis acid site. (b) Phosphate adsorbed onto a Type A site. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

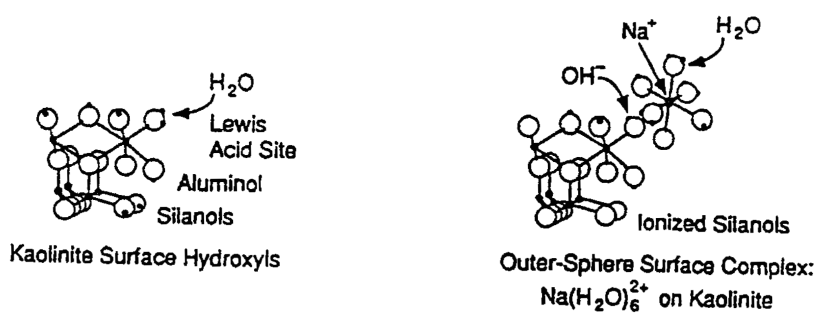


Figure 3. (a) Surface hydroxyl groups on kaolinite. Besides the OH groups on the basal plane, there are aluminol groups, Lewis acid sites (at which H_2O is adsorbed), and silanol groups, all associated with ruptured bonds along the edges of the crystallites. (b) Outer sphere surface complex between Na^+ and singly ionized H_2O (at a Lewis acid site) and ionized silanols. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

important sites for reactions at mineral-water interfaces. The tritium exchange method has been applied to a large number of oxide minerals to determine the density of surface hydroxyl groups (Berube and de Bruyn, 1968; Yates and Healy, 1976; Yates et al., 1980). A mineral is equilibrated in a solution containing tritiated water, dried to remove physically adsorbed tritiated water, and reequilibrated with water to assay for tritium rapidly released by the surface, which is assumed to be present as ≡MeOH groups. Another method involves drying the mineral to remove physically adsorbed water, reacting the mineral with an -OH labile compound, such as a CH_3-Mg-I, and determining the amount of reagent consumed (Boehm, 1971). Other methods that have been applied include themogravimetric analysis and water vapor adsorption. Attempts have been made to combine IR spectroscopy with either isotopic exchange, thermogravimetric anlysis, or reaction with methylating agents, to distinguish between the different types of surface hydroxyls (see James and Parks, 1982).

Ranges for the total densities of surface functional groups for several oxide minerals are collected in Table 1. Except for ferrihydrite, the ranges of total site densities were obtained using the methods described in the previous paragraph. For the crystalline solids, the breadth of the ranges reflects not only differences in the techniques used to obtain total site densities but also actual differences in the solids. It is important to consider that solid surfaces retain a partial memory of the history of the sample. Processes such as nucleation and crystal growth, grinding, heating, evacuating, and exposure to solutions containing stongly adsorbing solutes can leave their mark at the surfaces of solids. Synthetic minerals used in adsorption studies are often pretreated in an attempt to erase as much of this memory as possible. To the extent that this memory cannot be erased, one must expect variations in important surface properties between samples of different origin and history.

For ferrihydrite, (poorly crystalline hydrous ferric oxide), *microporosity* can be another source of variation in total site density. Micropores are pores of molecular dimensions (less than 2 nm; see section on "Surface Area and Porosity", below). Natural and synthetic ferrihydrites typically are formed by aqueous polymerization reactions at meteoric temperatures (Flynn, 1984; Schwertmann, 1988). Microporosity arises from incomplete cross-linking of the coalesced hydroxy polymer strands that comprise the primarly particles of the sample. Microporosity in ferrihydrite can extend well into the bulk of the solid (Yates, 1975; Cornejo, 1987). Because of this, the total density of surface sites for ferrihydrite is usually normalized to the Fe content rather than the surface area (Davis and Leckie, 1978; Dzomback and Morel, 1990). The site densities for ferrihydrite in Table 1 come from maximum extents of adsorption of various solutes as well as from tritium exchange experiments (see Dzomback and Morel, 1990) for an exhaustive review). Likewise, the variations reported for the total site density of synthetic amorphous silica (am-SiO_2) primarily reflect variations in the extent of microporosity between samples (Yates and Healy, 1976; Iler, 1979). Microporosity occurs in many natural materials, including biogenic amorphous silica, weathered aluminosilicate minerals and allophanes (Kent, 1983; and see chapter by Casey and Brunker, this volume).

Densities of proton donor and proton acceptor sites for goethite, rutile, gibbsite, and kaolinite, calculated from crystallographic considerations, are presented on the right hand side of Table 1. Clearly these sites represent a subset of the array of all types of surface hydroxyl groups. The density of proton donor sites exceeds that for proton acceptor sites because groups such as $\equiv MOH_2$, which result from attachment of water at Lewis acid sites, cannot accept protons (Sposito, 1984). Since silica sols do not acquire a detectable positive charge in aqueous suspensions, even at low pH (Iler, 1979), it has been suggested that silica may lack proton acceptor groups. This hypothesis is supported by observations that selenite ions do not adsorb on amorphous silica at pH values as low as 5 (Anderson and Benjamin, 1990). Evidence to the contrary can be found in the study of Dalas and Koutsoukos (1990), who have recently shown that orthophosphate ions adsorb on silica at pH 2.

Table 1. Density of Surface Functional Groups on Oxide and Hydrous Oxide Minerals

Mineral Phase	Range of Site Densities (sites/nm^2)	Reference	Proton Acceptor Groups (sites/nm^2)	Proton Donor Groups (sites/nm^2)	Reference
α-FeOOH	2.6-16.8	James and Parks (1982) Sposito (1984)	4.4	6.7	Sposito (1984)
$\alpha-Fe_2O_3$	5-22	James and Parks (1982)	-	-	-
Ferrihydrite	0.1-0.9 moles per mole of Fe	Dzombak and Morel (1990)	-	-	-
TiO_2 (rutile)	12.2	James and Parks (1982)	2.6	4.2	James and Parks (1982)
TiO_2 (rutile and anatase)	2-12	James and Parks (1982)	-	-	-
α-$Al(OH)_3$	2-12	Davis and Hem (1989)	2.8	5.6	Sposito (1984)
$\gamma-Al_2O_3$	6-9	Davis and Hem (1989)	-	-	-
SiO_2 (am)	4.5-12	James and Parks (1982)	0	all	James and Parks (1982)
Kaolinite	1.3-3.4	Fripiat (1964)	0.35	1.0	Sposito (1984)

Table 2. Estimates of Site Densities for α-FeOOH from Adsorption Measurements

Ion	Adsorption maximum (sites/nm^2)	Method	Reference
OH^-/H^+	4.0	a	f
OH^-	2.6	a	g
F^-	5.2	b	h
F^-	7.3	c	f
SeO_3^{2-}	1.5	d	i
PO_4^{3-}	0.8	d	i
Oxalate	2.3	b	j
Pb^{2+}	2.6	b	k
Pb^{2+}	7.0	e	k

Methods:
- a) Acid-base titration
- b) Adsorption isotherms
- c) Excess F^- at pH 5.5
- d) Adsorption isotherm at pH_{IEP}
- e) Fit with model

References:
- f) Sigg and Stumm (1981)
- g) Balistrieri and Murray (1981)
- h) Hingston et al. (1968)
- i) Hansmann and Anderson (1985)
- j) Parfitt et al. (1977)
- k) Hayes (1987)

<u>Site density determined by adsorption.</u> It is instructive to compare the site densities assembled in Table 1 to the maximum densities of adsorbed solutes. The maximum extent to which a solute adsorbs onto a mineral is controlled by the affinity of the adsorbing species for the surface sites as mitigated by steric and electrostatic effects. Thus, maximum site occupancy by an adsorbing species is favored when the species forms strong surface complexes that are not bulky and do not lead to an accumulation of charge. Adsorption is sometimes normalized per unit of surface area, in which case it is referred to as an *adsorption density*, Γ. "Maximum" adsorption densities (Γ_{max}) for various solutes adsorbing onto goethite are presented in Table 2. For F^- and oxalate, the Γ_{max} values are derived from plateaus in plots of Γ versus the aqueous concentration of the adsorbing solute, called *adsorption isotherms*. The isotherms were measured at the pH of maximum adsorption (see section on "Adsorption of anions", below). The Γ_{max} for F^- greatly exceeds that for oxalate. Hingston and coworkers found that F^- adsorption densities greatly exceeded those for other anions studied, including Cl^-, selenite, arsenate, phosphate, and silicate. F^- adsorption onto goethite is consistent with a two-step ligand exchange pathway (Sposito, 1984; Sigg and Stumm; 1981):

$$\equiv FeOH + H^+ \leftrightarrow \ \equiv FeOH_2^+ \quad , \tag{2}$$

$$\equiv FeOH_2^+ + F^- \leftrightarrow \ \equiv FeF + H_2O \quad , \tag{3}$$

which gives the net reaction:

$$\equiv FeOH + H^+ + F^- \leftrightarrow \ \equiv FeF + H_2O \quad , \tag{4}$$

where $\equiv FeOH_2^+$ and $\equiv FeOH^o$ represent positively charged and uncharged surface sites, respectively, on the oxide surface, and $\equiv FeF$ is a fluoride ion bound by ligand exchange to a surface iron atom. Extensive adsorption of F^- is promoted by the strength of the resulting Fe-F bond, small size of F^-, its strong nucleophilic character, and the lack of increase in surface charge resulting from F^- adsorption. The Γ_{max} for F^- lends support to the density of reactive surface sites calculated by Sposito (Table 1) as compared to the higher estimates represented by the upper end of the range of values in the second column of Table 1. The fact that the Γ_{max} for F^- exceeds the density of proton acceptor sites suggests that it may react with Lewis acid sites in addition to proton acceptor sites.

Hansmann and Anderson (1985) determined Γ_{max} values from selenite and phosphate adsorption isotherms on goethite, obtained at the pH of the isoelectric point (pH_{IEP}, see section on "The Electrified Mineral-Water Interface", below). The relatively low Γ_{max} values obtained indicate that for selenite and phosphate adsortion at the pH_{IEP}, steric factors limit the maximum amount adsorbed. The Γ_{max} for OH^- and H^+ were derived from acid-base titrations at high ionic strength. Goethite titration curves continue to rise at higher pH values, so it is not surprising that this value is much lower than the density of proton donor sites calculated by Sposito (Table 1). Two Γ_{max} were derived from the Pb^{2+} adsorption data of Hayes (1987). Hayes performed several experiments in which there was an excess in moles of Pb^{2+} in comparison to the moles of surface sites in the suspension. The lower value for the site density (2.6 sites/nm^2) represents the largest density of adsorbed Pb^{2+} measured experimentally. The higher value (7 sites/nm^2) was derived from an optimization of the fit between model simulations and experimental data collected over a wide range of conditions. The maximum molar ratio of Pb^{2+} to surface sites in Hayes' experiments was about 2, based on the 7 sites/nm^2 value for the total functional group density. The general agreement between the adsorption densities shown in Table 2 with the densities of proton donor and acceptor sites in Table 1 lends support to the hypothesis that only a portion of the hydroxyl groups present at oxide surfaces are active in surface complexation reactions.

Chang et al. (1987) measured a Γ_{Zn} of 5 sites/nm^2 for a TiO_2 sample by decreasing the solid-water ratio to low values (2 mg/liter) in solutions containing 1 µM Zn. This site density was somewhat lower than that estimated by tritium exchange (12.2 sites/nm^2; James and Parks, 1982). The maximum Zn/surface site molar ratio was only about 0.4, based on 12.2 sites/nm^2, suggesting that Γ_{max} for Zn^{2+} was possibly not reached.

Organic matter

A variety of functional groups are present in organic compounds that polymerize to form the humic substances commonly found in soils and sediments, e.g., carboxyl, carbonyl, amino, imidazole, phenylhydroxyl, and sulfhydryl groups (Sposito, 1984; Hayes and Swift, 1978). Dissolved natural organic material typically contains 6 to 12 millimoles/g of weakly acidic functional groups, primarily carboxylic and phenolic groups (Perdue et al., 1980). The stabilities of complexes between these groups and protons range from weak to very strong, and thus, a considerable range of functional group reactivity with dissolved constitutents in water can be expected. Organic material may contribute important surface functional groups for metal complexation (Sigg, 1987; Davis, 1984), either in the form of live organisms, detrital organic particulates, or organic coatings adsorbed on mineral surfaces (Davis, 1982; Tipping, 1981).

The importance of organic matter on the chemical properties of oxide surfaces is most simply evidenced by the negative charge observed on particles suspended in natural waters that would normally be positively charged at neutral pH values (Davis and Gloor, 1981; Hunter, 1980). Synthetic alumina particles suspended in a filtered lakewater with a dissolved organic carbon concentration of 2.3 mg/l attained a high surface coverage of adsorbed organic matter within a few minutes (Davis, 1982). Luoma and Davis (1983) reviewed the literature on the quantities of functional groups of organic particulate material in sediments and estimated a total functional group density of about 0.001 moles/g, based on the results of metal complexation studies.

The bulk of particulate matter settling in the open oceans is produced by biological processes (Whitfield and Turner, 1987), and a large percentage of suspended particulate matter in lakes is composed of biological material (Sigg, 1987). The capacities of these materials for binding metal ions is not well known. Morel and Hudson (1985) estimated that a representative phytoplankton cell contains 10^7 to 10^8 high-affinity sites for metal coordination. Sigg (1987) estimated the average dry weight of a diatom cell in Lake Zurich as 560 picograms, and applying this weight to the above site concentration yields a high-affinity site density of 0.03 to 0.3 µmoles/g. Fisher et al. (1983) concluded that the adsorption of transuranic elements on algal cells was similar, regardless of whether the cells were viable or dead.

Minerals with permanent structural charge

Phyllosilicate minerals. Clay minerals are important adsorbents in many systems of interest in aqueous geochemistry (Sposito, 1984; Bolt and van Riemsdijk, 1987). Kaolinite and minerals in the smectite, vermiculite, and illitic mica groups are especially important because they often occur as extremely small particles with high surface areas and they are widespread. In addition to surface hydroxyl groups, these minerals have rings of siloxane groups, $\equiv Si_2O$, which occur on the basal planes and interlayer regions that dominate the surface area of these minerals. In many phyllosilicate minerals these groups are not hydroxylated because the coordination environments of these bridging oxygen ions are satisfied by the two Si(IV) ions with which they are coordinated. The importance of the siloxane rings as surface functional groups is enhanced by the magnitude of the permanent charge of the crystal lattice of clay minerals, which is due to isomorphic cationic substitutions.

Most clay minerals are comprised of composite sheets consisting of layers of $M^{z+}O_6$ octahedra and SiO_4 tetrahedra (Figs. 4a,b). In the mineral kaolinite, each Al(III)-containing octahedral layer is linked to a Si(IV)-containing tetrahedral layer (Fig. 4c). In the smectite, vermiculite, and illitic mica groups, each octahedral layer is sandwiched in between two tetrahedral layers (Fig. 4d). Linkage of SiO_4 tetrahedra to form the tetrahedral layer gives rise to hexagonal cavities bounded by siloxane groups (Fig. 4a). Joining of the tetrahedral and octahedral layers causes distortion of these cavaties from hexagonal to ditrigonal symmetry (Fig. 5). Substitution of divalent cations for trivalent cations in the octahedral layer and trivalent cations for Si(IV) in the tetrahedral layers gives rise to the permanent structural charge on the composite layer that is compensated by complexation of mono- or divalent cations at the ditrigonal cavities between the sheets.

Kaolinite. Kaolinite has five types of surface functional groups: ditrigonal siloxane cavities on the face of tetrahedral sheets (Fig. 4c), aluminols on the face of octahedral sheets (Fig. 4c), silanols and aluminols exposed at the edge of the sheets (Fig. 3), and Lewis-acid sites at the edge (Fig. 3). The oxygen ions of the face aluminols are coordinated with two Al ions, hence are considered unreactive (Figs. 4b, c). The degree of ionic substitution in kaolinite is very low, less than 0.01 ion per unit cell (Sposito, 1984). The resulting low permanent charge renders the ditrigonal cavities along the tetrahedral sides of the sheets unreactive. The principal surface complexation sites are therefore the silanols, aluminols, and Lewis acid sites located along the edge of the sheets (Fig. 3). All three site types are proton donor groups, which can form complexes with metal ions. Only the aluminols are proton acceptor groups (Table 1), and these groups can complex anions.

Smectites, vermiculites, and illitic micas. These minerals all have significant permanent charges resulting from isomorphic cation substitutions. The permanent charge in the smectite group results from substitution of divalent cations (e.g., Mg^{2+} and Fe^{2+}) for trivalent cations in the octahedral sheet (e.g., Al^{3+} and Fe^{3+}). The degree of substitution in smectites imparts a permanent charge of 1-2 μequiv./m^2, where the denominator refers to the total sheet area (Bolt and van Riemsdijk, 1987). The charge resulting from the substitution of a single cation in the octahedral layer is distributed among the 10 surface oxygens of the 4 tetrahedra linked to the site (Sposito, 1984). The diffuse nature of the charge distribution in the ditrigonal cavities leads to the formation of outer sphere complexes between the exchangeable cation and the ditrigonal cavity. An outer sphere complex is one in which there is at least one layer of solvent between the complexing ion and the functional group. This is illustrated for the smectite mineral montmorillonite in Figure 6. The permanent charge in illitic micas results largely from the substitution of Al or Fe(III) for Si(IV) in the tetrahedral layer. A larger degree of substitution leads to a higher permanent charge, viz., about 3 μequiv./m^2 (Bolt and van Riemsdijk, 1987). The resulting negative charge is much less diffuse. Substitution in the tetrahedral layer leads to distribution of the resulting negative charge over the 3 surface oxygens of the tetrahedron, hence the charge on the ditrigonal cavity is much less diffuse. Higher permanent charge and higher density of charge on ditrigonal cavities favor the formation of inner sphere complexes between interlayer cations and ditrigonal cavities, i.e., complexes lacking solvent molecules between cation and site (Fig. 6). The ionic radius of K^+ corresponds almost exactly to that of the ditrigonal cavity, which enhances the strength of the resulting surface complex. Vermiculites resemble illitic micas in the mode of substitution, but often show lower degrees of substitution, and hence, lower permanent charges. As a result, both inner sphere and outer sphere complexes may occur in vermiculites.

Sposito (1984) has discussed methods of quantifying ditrigonal siloxane cavities. In order to form complexes with solutes, ditrigonal siloxane cavities need to be accessible to cations in solution. Clay minerals that form outer sphere complexes between interlayer cations and ditrigonal cavities fulfill this criterion. Thus, the interlayer cations of smectite minerals are exchangeable. The nature of the complexes formed in the interlayer region suggest that ditrigonal cavities in the interlayer region will react primarily with the major cations in solution, i.e., those present at the highest concentration.

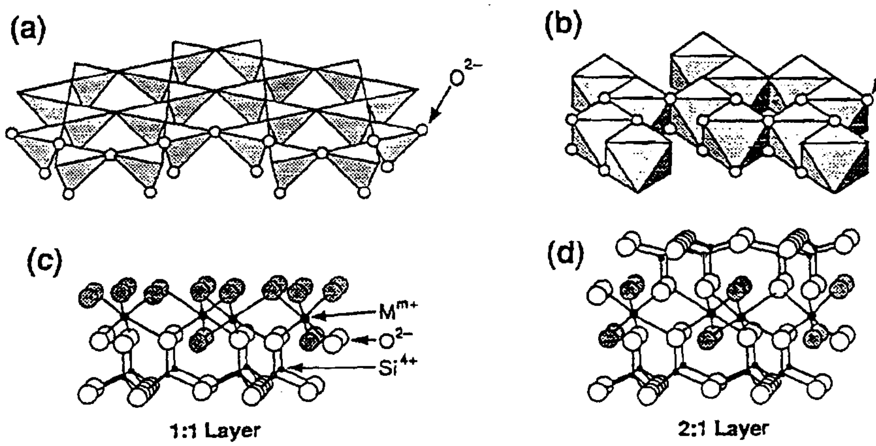


Figure 4. Structural elements of phyllosilicate minerals. (a) SiO_4 tetrahedra linked to form the tetrahedral sheet. (b) MO_6 octahedra linked to form the octahedral sheet. Note that only two of the three possible sites in the octahedral sheet shown are occupied, hence this is a *dioctahedral* sheet. (c) Tetrahedral and octahedral sheets linked to form a 1:1 layer structure (e.g., kaolinite). Shaded circles represent OH groups. (d) Tetrahedral and octahedral sheets linked to form a 2:1 layer structure. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

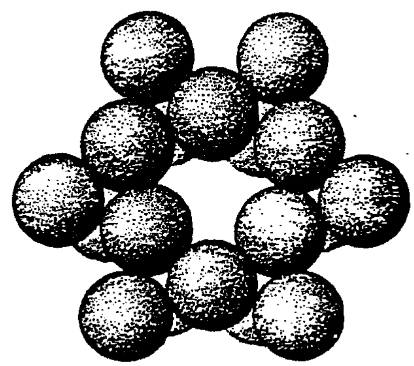


Figure 5. The siloxane ditrigonal cavity. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

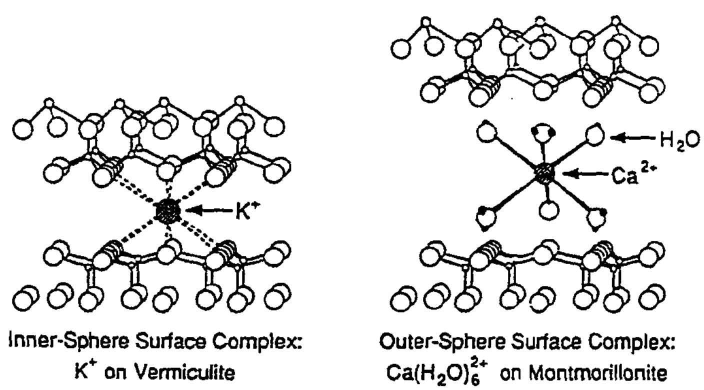


Figure 6. Surface complexes between cations and siloxane ditrigonal cavities on 2:1 phyllosilicates, shown in exploded view. Outer sphere complex between Ca^{2+} and ditrigonal siloxane cavities in the smectite mineral montmorillonite and inner sphere complex between K^+ and ditrigonal siloxane cavities in illite or vermiculite. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

The relative importance of ditrigonal cavities and surface hydroxyl groups depends on the system under investigation. Binding at ditrigonal cavities is predominantly electrostatic and the majority of ditrigonal cavities are located in the interlayer region. Consequently, these are the sites at which the major cations in natural waters bind. Anion binding on clay minerals occurs predominantly at surface hydroxyl groups along the *edges* of clay crystallites (Honeyman, 1984; Bar-Yosef and Meek, 1987; Zachara et al., 1989b; Neal et al., 1987a,b). Intuitively, one would expect that hydrolyzable cations present at trace concentrations would react primarily with edge sites. Electrostatic and hydration forces dominate the interaction between ditrigonal cavities and cations hence these sites should be populated by the dominant multivalent cations in the solution (e.g., for many natural water systems, Ca^{2+}). The proton stoichiometry of Cd^{2+} adsorption onto montmorillonite is much lower than that onto pure oxides, but increases sharply with increasing pH (Honeyman, 1984). This observation suggests that Cd^{2+} binds to both surface hydroxyls, releasing protons, and ditrigonal cavities, releasing exchangeable cations, *and* that the relative importance of surface hydroxyls increases with increasing pH. This is consistent with the results of Ziper et al. (1988) on adsorption of Cd^{2+} onto a variety of phyllosilicates at low pH. The site density of the edges of montmorillonite is believed to be similar to that of kaolinite (Bar-Yosef and Meek, 1987).

Manganese oxides. Hydrous Mn oxides that are important in natural systems are complex minerals characterized by poor crystallinity, structural defects, domain intergrowths, cation vacancies, and solid solutions (Burns and Burns, 1979; Sposito, 1984). These minerals consist of chains of $Mn(IV)O_6$ octahedra linked to form tunnels or sheets (Burns and Burns, 1979; Turner and Buseck, 1981; Turner et al., 1982). Mn(IV) vacancies and substituion of Mn(II) and Mn(III) for Mn(IV) in the structure give rise to a permanent structural charge that is compensated by loosely bound cations that occupy a range of interstitial positions. These cations are exchangeble, as are some of the Mn(II) ions in the structure. Clearly, Mn oxides can exhibit a large variety of types of adsorption sites. Considering the complexity of Mn oxide minerals, it is interesting to note the success of Balistrieri and Murray (1982) in applying a surface complexation model with homogeneous sites to describe the adsorption properties of a synthetic δ-MnO_2 in major ion sea water. Studies of adsorption onto Mn oxides confirm that these minerals have large capacities for metal ion adsorption because of their high surface area (James and MacNaughton, 1977; Dempsey and Singer, 1980; McKenzie, 1980; Catts and Langmuir, 1986; Zasoski and Burau, 1988). Zasoski and Burau (1988) observed a site density of 2.2 sites/nm^2 at Γ_{max} for Zn^{2+} and Cd^{2+}, similar to the values for goethite reported in Table 2.

Carbonate minerals

Interfaces between aqueous solutions and carbonate minerals are dynamic. Dissolution and precipitation reactions driven by differences in particle sizes (Ostwald ripening), surface dislocations, and, in some cases, phase transformations lead to a persistent flux of cations and carbonate ions across the interface (e.g., Lahann and Siebert, 1982). The interface consists of an array of sites that form surface complexes with cations and anions (herein designated $\equiv S_c$ and $\equiv S_a$, respectively). For salt-type minerals, these cation and anion sites are generally considered to be completely occupied with adsorbed cations, anions, or their hydrolysis products (Parks, 1975). The relative concentrations of cation surface complexes (e.g., $\equiv S_c$–Ca^{2+}) and anion (carbonate) surface complexes (e.g., $\equiv S_a$–CO_3^{2-}, $\equiv S_a$–HCO_3^-), varies with the relative concentrations of Ca^{2+} and CO_3^{2-} in solution (Somasundaran and Agar, 1967; Parks, 1975).

Studies of the interaction of Cd(II) (Davis et al., 1987) and Zn(II) (Zachara et al., 1988, 1989a) with calcite have illustrated the complexity of sorption behavior on carbonate minerals. Both of these cations form sparingly soluble carbonates. Cation uptake occurs in two steps. A relatively rapid step, which reaches completion within one day, is followed by a slow step, whereby the uptake rate appears to be constant over a long period of time (at least several days). The rapid step results from sorption onto a hydrated $CaCO_3$ layer. For Cd, the slow step results from incorporation into calcite as a $(Cd,Ca)CO_3$ solid solution during recrystallization. The adsorption step is consistent with the exchange of Cd or Zn with Ca in the hydrated $CaCO_3$ layer. Reactions with different types of sites or with different stoichiometries may also occur (Zachara et al., 1988), as has been observed with cation adsorption onto hydrous oxides. The importance of the slow step depends on the properties of the solid, adsorbing solute, and the solution chemistry. The calcite sample used by Zachara et al. had a much slower recrystallization rate than that used by Davis et al. The ionic radius and relative ease of dehydration of Cd favored incorporation into a $(Cd,Ca)CO_3$ solid solution. The ionic radius and relative difficulty of dehydration of Zn helped retard the rate of solid solution formation. Inhibition of the recrystallization rate by solutes such as Mg^{2+} also affect the rate of solid solution formation (Davis et al., 1987). Other cations appear to behave similarly (e.g., Mn^{2+}, McBride, 1979; see also references in Davis et al, 1987, and Zachara et al., 1988). Interpretation of the results of many sorption studies is difficult because the experiments were conducted in solutions supersaturated with respect to metal carbonate phases.

For cation adsorption on calcite, it appears of interest to determine the density of $\equiv S_c{-}Ca^{2+}$ groups. By analogy, for anion adsorption on carbonates it is of interest to determine the density of $\equiv S_a{-}CO_3^{2-}$ and $\equiv S_a{-}HCO_3^-$ groups. The density of Ca^{2+} (and CO_3^{2-}) lattice positions exposed on the $(10\bar{1}4)$ cleavage face of calcite is 5 sites/nm^2 (8.3 μmole/m^2, Moeller and Sastri, 1974). ^{45}Ca isotopic exchange studies with the calcite surface have shown that the density of exchangeable Ca is consistent with this value, but decreases with decreasing excess of dissolved Ca^{2+} over CO_3^{2-} or increasing Mg^{2+} concentrations (Moeller and Sastri, 1974; Davis et al., 1987). Under similar solution conditions, isotherms of Γ_{Zn} versus Zn^{2+} concentration reached a plateau at about 0.6 μmole/m^2 (0.33 sites/nm^2; Zachara et al., 1988). Surface irregularities such as dislocations and etch pits are potentially important sites for adsorption but their role has not been investigated.

Wersin et al. (1989) have studied the adsorption of Mn^{2+} on the surface of siderite ($FeCO_3$). Like the investigations of the calcite surface, the results exhibited complex kinetics, which were interpreted in terms of an adsorption step followed by incorporation of Mn^{2+} as a $(Mn,Fe)CO_3$ solid solution at the surface. The co-precipitation hypothesis was supported by electron spin resonance spectroscopy. Adsorption of Mn^{2+} was proportional to dissolved Mn^{2+} until the surface carbonate sites were filled (9.3 atoms Mn^{2+}/nm^2). The site density of siderite (11 sites/nm^2) estimated from crystallographic data (Lippmann, 1980) was in good agreement with the observed adsorption maximum.

Knowledge of the solution chemistry is an essential aspect of interpreting sorption behavior on carbonates. Chemical equilibrium cannot be assumed because long periods of time are required to attain equilibrium in some systems (especially those in which CO_2 gas must be exchanged between the gas and solution phases, Somasundaran and Agar, 1967), and equilibrium will not be achieved without considerable effort expended to pretreat the solid phase (Plummer and Busenberg, 1982). Crushing carbonate minerals should be avoided, since it can lead to production of high energy surfaces that can produce irreversible effects (e.g., Goujon and Mutaftshiev, 1976).

Sulfide minerals

Chemical interaction with sulfide minerals is likely to have a major impact on the transport and fate of trace metals in sulfidic environments (Berner, 1981; Raiswell and Plant, 1980; Emerson et al, 1983, see chapter by Bancroft and Hyland, this volume). The iron sulfide minerals, mackinawite, greigite, and pyrite (Berner, 1964; 1970), are especially important because of their widespread occurrence (e.g., Goldhaber and Kaplan, 1974; Raiswell and Plant, 1980). Removal of metal ions from solution by iron sulfide minerals can be extensive (Caletka et al., 1975; Framson and Leckie, 1978; Brown et al., 1979).

Systematic studies of sorption onto sulfide minerals are lacking. Previous investigations have identified two pathways by which metal ions are taken up by sulfide minerals: the metathetical reaction and adsorption. These pathways are discussed below. Experimental investigations have been hampered by the ease of oxidation of surface layers of sulfide minerals; strict anaerobic conditions must be maintained (Wolf et al.,1977; Framson and Leckie, 1978; Park and Huang, 1987).

The metathetical reaction between sulfide minerals and dissolved metals has been widely documented (Gaudin et al., 1957, 1959; Phillips and Kraus, 1963, 1965):

$$A_xS(s) + yB^{n+} = B_yS(s) + xA^{m+} \quad , \tag{5}$$

where $x=2/m$ and $y=2/n$. The reaction is driven by the lower solubility of $B_yS(s)$ in comparison to $A_xS(s)$. Replacement of the first two or three layers of $A_xS(s)$ proceeds rapidly, during which the reaction can be reversed by, for example, adding a complexing agent that has a much higher affinity for B^{n+} than A^{m+}. Extensive replacement of $A_xS(s)$ by $B_yS(s)$ can occur over short periods of time at room temperature. The metathetical pathway could be extremely important in natural systems because mackinawite is more soluble than the sulfides of most transition metals (Caletka et al., 1975; Framson and Leckie, 1978).

Adsorption onto sulfide minerals has been studied in systems where the dissolved metal forms a sulfide that is more soluble than the adsorbent (Gaudin and Charles, 1953; Iwasaki and deBruyn, 1958; James and Parks, 1975; James and MacNaughton, 1977; Wolf et al., 1977; Park and Huang, 1987; Park and Huang, 1989). The results support the hypothesis that the operative surface functional groups are ≡MOH and ≡SH (sulfhydryl or thiol) groups. The availability of both oxygen and sulfur donor ligands adds an interesting dimension to the adsorption properties of sulfide minerals. The relative abundance of these groups is controlled by the concentration of M^{n+}, $[M^{n+}]$. At high $[M^{n+}]$, ≡MOH groups are in excess, whereas at low $[M^{n+}]$, ≡SH groups dominate (Iwasaki and deBruyn, 1958; Park and Huang, 1987). As with hydrous oxides, the crystal structure of the particular sulfide mineral will dictate the types of groups that are available, their reactivities, and their densities. Some authors suggest that the sulfhydryl groups are inactive on some sulfide minerals, thus the surface chemistry is controlled by ≡MOH groups (e.g., Horzempa and Helz, 1979; Williams and Labib, 1985). Oxidation of surface layers could explain this behavior (Park and Huang, 1987). A complete understanding of the surface chemistry of sulfide minerals awaits the results of systematic studies of cation and anion adsorption over a wide range of solution conditions.

SURFACE AREA AND POROSITY

In this section, we will discuss methods for determining $\mathcal{A}$, the *specific surface area*, which is the amount of reactive surface area available for adsorbing solutes per unit weight of the material. The SI units for $\mathcal{A}$ are m^2/kg or cm^2/g, but herein we will use m^2/g for convenience. Knowledge of the amount of reactive surface area enables normalization of solute adsorption data to surface area, and is required for applying electrical double layer models (see section on "The Electrified Mineral-water Interface"). More importantly, it allows an estimation of the quantity of surface functional groups per unit mass of solids, if the group density per unit area is already known.

Physical Methods

The surface area of a solid phase is related to the size and morphology of the particles that make up the sample For example, a sample that consists of uniform spherical particles has a *geometric surface area* (A'), in m^2/g, given by:

$$A' = \frac{6 \times 10^{-4}}{\rho d} \quad , \tag{6}$$

where ρ is the density (g/cm^3) and d is the diameter (cm). Formulae for obtaining A' from particle size distributions and for other particle geometries can be found in Gregg and Sing (1982). Particle size and morphology of solids of interest to adsorption studies are usually determined using electron microscopy (EM).

Natural and synthetic materials often have much larger $\mathcal{A}$ values than the geometrical surface areas determined from particle size and morphology (White and Peterson, 1990). Crystalline solids often possess surface roughness caused by fractures and defects on cleavage and crystal faces. Materials with high surface areas usually consist of very small *primary* particles linked together to form larger *secondary* particles. The secondary particles are called *aggregates* if the primary particles are loosely held together and *agglomerates* if they are rigidly held together (Gregg and Sing, 1982; note that this terminology is not universal). Surface functional groups within the aggregates or agglomerates are accessible to solutes through the contiguous pore structure within the secondary particles.

Discussion of the characterization of pore structures of materials is beyond the scope of this chapter (see Gregg and Sing, 1982). It is useful, however, to introduce the standard operational definitions of pore sizes. Pores with diameters less than 2 nm, i.e., pores of molecular dimensions, are called *micropores*. Pores with diameters between 2 and 50 nm are called *mesopores*; capillary forces are important for pores in this size range. Pores with diameters in excess of 50 nm are called *macropores*. Macropores grade into *voids*, i.e., interparticle space. Porosity primarily affects the *rates* of adsorption and desorption reactions. Microporosity, however, is an important consideration in the determination of $\mathcal{A}$ and the density of adsorption sites. Amorphous and poorly crystalline hydrous oxides of Fe, Al, and Si that result from low-temperature polymerization reactions in solution usually possess extensive microporosity. Meso- and macroporosity in natural materials can result from agglomeration of colloidal-sized particles during polymerization, precipitation reactions, and low-temperature weathering reactions.

The $\mathcal{A}$ of phyllosilicates can by calculated from the unit cell dimensions and the chemical composition (van Olphen, 1977; Sposito, 1984). These calculations are most reliable for montmorillonite because (1) the unit cell dimensions are accessible from X-ray diffraction data, (2) the relationship between chemical composition and structure of the *quasicrystal* (the result of stacking phyllosilicate layers along the crystallographic c axis) is fairly well known (van Olphen, 1977), (3) the region between phyllosilicate layers of unit cell thickness is occupied by hydrated cations and accessible to solutes, and (4) the lateral dimensions of crystals often greatly exceed their thicknesses (Sposito, 1984). Crystallographic $\mathcal{A}$'s of montmorillonites lie in the range 600-800 m^2/g, most of which is accounted for by the interlayer region (van Olphen, 1977).

Clearly these physical methods are of limited application. It is therefore necessary to measure $\mathcal{A}$. Because we are interested in determining $\mathcal{A}$ on a molecular level, most methods involve determining the extent of adsorption of either a gas or solute and relating the amount adsorbed to the area occupied. Aspects of the most common used methods are described in the following sections and in Appendix A.

Gas adsorption

Adsorption isotherms on minerals. The most widely used non-polar adsorptives are N_2 and Kr, although Ar is used occasionally. Isotherms are collected by measuring the amount of gas adsorbed at the boiling temperature of liquid N_2 at atmospheric pressure (viz., 77 °K or -196 °C) as a function of the *relative pressure*, p/p^0, where p is the partial pressure of the adsorptive and p^0 is its equilibrium vapor pressure. The isotherm for N_2 on goethite shown in Figure 7 illustrates some basic features of gas adsorption isotherms. The goethite was synthesized in our laboratory using the method of Atkinson et al. (1972), rinsed with base, acid, and water, and then freeze-dried. The isotherm rises rapidly at low pressures, bends over near p/p^0 0.05, which gives rise to a "knee" in the isotherm, increases linearly over a short range of relative pressures (about 0.1 to 0.25 for this sample), has positive curvature above the linear region (above p/p^0 of 0.25 for this sample), and rises rapidly as p^0 is approached. For nonporous materials, the rapid rise at low relative pressure is due to build

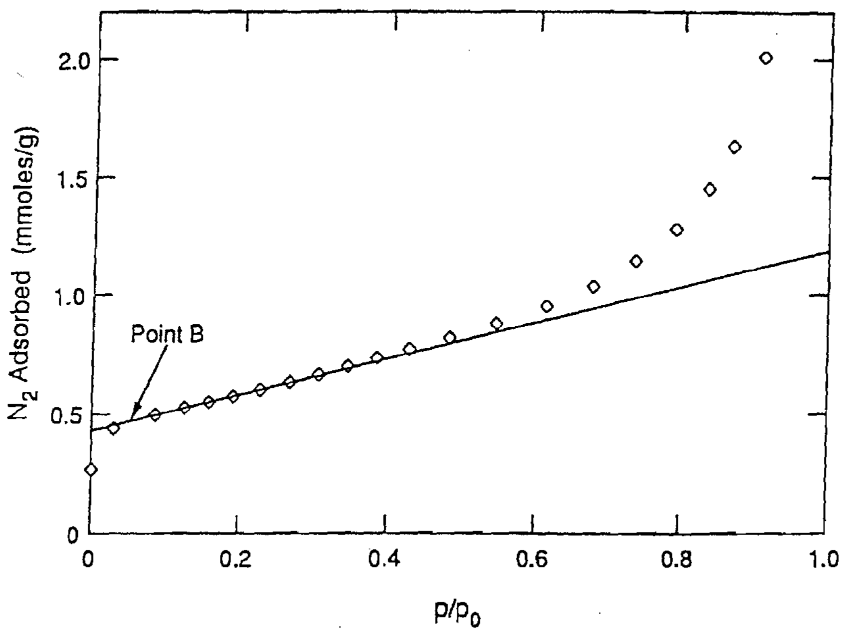


Figure 7. Adsorption isotherm for N_2 gas, at 77.4°K, on synthetic α-FeOOH (goethite). Point B is the point at which the line extending through the linear portion of the isotherm in the multilayer region departs from the isotherm. Point B corresponds to 0.48 μmoles/g for this sample. The sample was outgassed at 110°C for 36 hours, after which the pressure was below 10^{-4} torr.

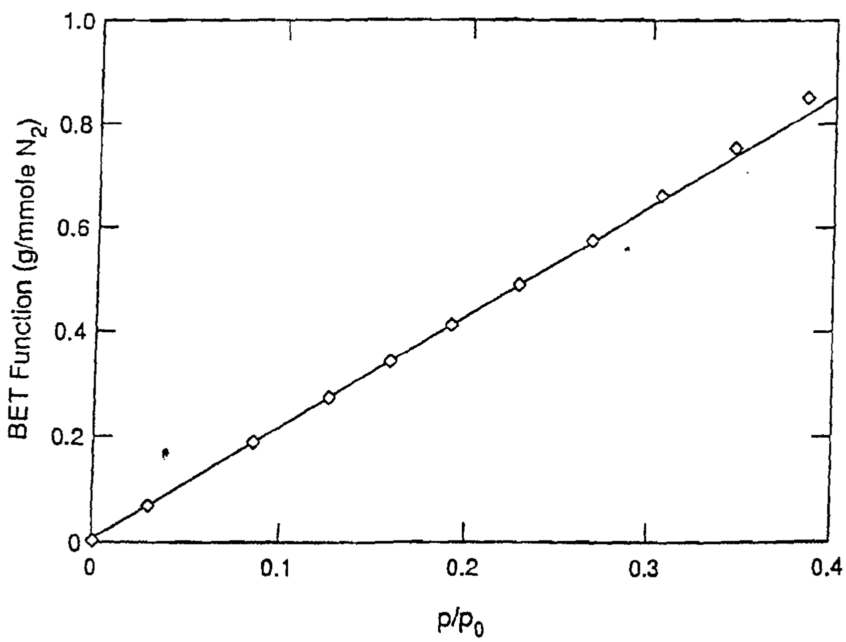


Figure 8. BET plot from the data in Figure 7. Plotted along the ordinate is the right hand side of Equation 7. The regression line of the data across the domain 0.08 to 0.23 is shown. Note that the intercept is near zero.

up of a monolayer of the adsorptive. Above the knee, multilayer adsorption occurs. The rapid increase at high relative pressure is due to the onset of condensation of liquid N_2 on the solid. Monolayer coverage is thought to correspond to "point B' (Fig. 7), which is where the line through the linear portion of the isotherm diverges from the isotherm on the low pressure side (Gregg and Sing, 1982). $\mathcal{A}$ is usually determined either by applying the BET model to the data in the multilayer region or by comparing the isotherm to that of a nonporous material with known $\mathcal{A}$. Mesoporous materials exhibit enhanced adsorption above relative pressures of about 0.4, which results from capillary condensation of liquid N_2 in mesopores. Microporous materials exhibit enhanced adsorption at extremely low relative pressures, which results in a sharp knee and flattening of the linear portion of the isotherm.

BET analysis. The most popular method for deriving $\mathcal{A}$ from gas adsorption isotherms is the BET method (Brunauer, et al., 1938). The BET model, whose derivation is presented elsewhere (Gregg and Sing, 1982), is based on generalization of the Langmuir isotherm to an inifinite number of layers of adsorptive. Several critical assumptions are embodied in the model. First, the number of adsorbed layers approaches infinity as p approaches p^0. This is a good assumption except for samples with a high density of very small pores. Second, all adsorption sites are identical, which is to say that adsorption occurs uniformly across the surface rather than in clumps. Third, for all layers except the first, the heat of adsorption equals the molar heat of condensation. Fourth, for all layers except the first, the tendency for a molecule to adsorb and desorb is independent of how many layers underlie its adsorption site. The BET equation, in linear form, is

$$\frac{p/p^0}{n(1-p/p^0)}=\frac{1}{C_{BET}n_1}+\frac{(C_{BET}-1)}{C_{BET}n_1}\frac{p}{p^0} \quad , \qquad (7)$$

where n is the amount adsorbed (e.g., moles/g), n_1 is the monolayer capacity (same dimensions as n), and C_{BET} is a dimensionless parameter related to the difference between the heat of adsorption onto the first layer and the heat of condensation, which should equal the heat of adsorption onto all layers except the first. A linear regression of the left hand side of the BET equation against p/p^0 yields a slope m and intercept b from which n_1 and C_{BET} are computed according to:

$$n_1=\frac{1}{m+b} \qquad\qquad C_{BET}=\frac{m}{b}+1 \quad .$$

$\mathcal{A}$ is calculated from n_1:

$$\mathcal{A}=n_1 a_m L \quad , \qquad (8)$$

where a_m is the average area of an adsorbate molecule in a completed monolayer and L is a conversion factor, which equals 6.02×10^5 for a_m in nm^2 and n_1 in moles per unit mass of solid. According to the original paper, the range of relative pressures over which the BET equation is valid is 0.05 to 0.30. Many solids, however, have more restricted BET ranges. A BET plot derived from the data shown in Figure 7 is shown in Figure 8; the regression line has also been plotted. The BET range for this sample is between 0.04 and 0.25. The n_1 and C_{BET} are 472 µmole/g and 305, respectively. Note that n_1 calculated from the BET equation is in good agreement with the estimated position of point B (Fig. 7). The $\mathcal{A}$ calculated from n_1 using Equation 8 is 46.0 m^2/g, based on the widely accepted value of 0.162 nm^2 for a_m for N_2 (Gregg and Sing, 1982).

Problems caused by microporosity. The assumptions of the BET model appear to be valid for a wide variety of solids, especially for N_2 as the adsorptive (Gregg and Sing, 1984). Major problems arise for microporous materials, however. Most adsorptives have a very high affinity for micropores, which results in clumping of the adsorptive in and around micropores (Gregg and Sing, 1982). This violates the assumptions of the BET model. The C_{BET} provides a means of assessing the validity of the BET model. The C_{BET} is related to the difference between the heat of adsorption on the surface of the solid and the heat of adsorption onto any of the layers except the first (which is assumed to be the heat of condensation). Materials with extensive microporosity have high C_{BET} values. Extremely low values of C_{BET} imply that multilayer adsorption occurs before monolayer coverage nears completion; the knee of the isotherm is diminished for such samples. Gregg and Sing (1982) suggest that BET theory is valid for materials with C_{BET} values in the range 50 to 150. Our experience suggests that, for N_2 as the adsorptive, samples with C_{BET} values as high as 475 showed no evidence of microporosity; microporous samples had C_{BET} values in excess of 700. BET plots for hydrous oxides tend to intercepts that are near zero (Fig. 8). The intercept is critical in calculating C_{BET}. Our experience indicates that it is important to have at least four points in the BET range to obtain a reliable value for C_{BET}. Negative values for the intercept yield negative C_{BET} values, which are meaningless. Usually, negative intercepts result from including points that are outside the linear BET range.

Low surface area materials. N_2 cannot be used with low $\mathcal{A}$ samples (i.e., below about 1 m^2/g) because of the non-ideal gas behavior of N_2 or buoyancy problems. Kr adsorption is usually used for these types of samples because it is an ideal gas under the conditions required for isotherm building. However, it has a number of disadvantages as an adsorptive (see Gregg and Sing, 1982). First, -196 °C is below the triple point so that there is disagreement over whether to use the vapor pressure of solid Kr or of the super cooled liquid for p^0. Usually, the vapor pressure of the super-cooled liquid is used (viz., about 2.5 torr). Second, BET plots of Kr adsorption isotherms often have smaller linear ranges than those for N_2. Third, Kr is *larger* and more polarizable than N_2. Consequently, a_m values reported for Kr (0.202 ±0.026 nm^2; McClellan and Harnsberger, 1967) vary over a wider range than those for N_2, and a_m for Kr has a much greater dependency on the nature of the solid than does the a_m of N_2. Gregg and Sing (1982) recommend that, if working with a solid for which a_m has not already been determined, it should be determined on a sample for which $\mathcal{A}$ is known (e.g., from N_2 adsorption); otherwise an uncertainty of ± 20% should be assigned to $\mathcal{A}$. Another consequence of the polarizability is that step-like isotherms are much more common for Kr than for N_2. In some cases, step-like isotherms are due to extreme regularity of the surface of the sample (Gregg and Sing, 1982). In other cases, they occur on highly disturbed samples.

Partial isotherms for N_2 and Kr adsorption onto a highly disturbed calcite sample are shown in Figure 9. The sample had been ground, rinsed briefly with dilute HCl and then with distilled water, and dried. The Kr adsorption isotherm exhibits a step near a relative pressure of 0.15. The high pressure branch of the isotherm is parallel to the isotherm for N_2, indicating that multilayer adsorption does not occur on this sample until the relative pressure exceeds 0.15. The high pressure arms of the isotherms for N_2 and Kr do not coincide because Kr has a larger a_m than N_2. A BET plot of the N_2 data yields an $\mathcal{A}$ of 4.5 m^2/g, but the C_{BET} is 776, indicating clumping of N_2 on regions of the surface. BET analysis yields an n_1 value of 38.2. Disagreement between the n_1 value from BET analysis (38.2 μmoles/g) and that from point B (50.4 μmoles/g; Fig. 9) also suggests problems with the BET $\mathcal{A}$. Experience with other calcite samples, both synthetic and commercial, shows that many calcites have similar steps in their Kr adsorption isotherms. Aging the calcites using the method of Plummer and Busenberg (1982) greatly reduces the magnitude of the step. Synthetic aragonites tested yield "normal" isotherms: linear BET ranges from 0.05 to 0.2, C_{BET} values around 60, and n_1 values from the BET equation in good agreement with point B.

Evaluation of microporosity. Comparison plots (t- and α_s-plots, see Appendix A) facilitate identification of micro- and mesoporosity; an estimate of the micorpore volume can also be obtained. t-plots for our goethite sample and a commercial amorphous SiO_2 sample (BDH precipitated silica) are presented in Figure 10. For goethite, the linear branch extrapolates through zero, indicating the lack of microporosity. The small deviations from linearity along the high pressure branch indicate the presence of a small degree of mesoporosity in the sample. The slope of the linear branch yields a value for $\mathcal{A}$ of 47.1 m^2/g, which agrees quite well with the BET $\mathcal{A}$ (Table 3). For BDH precipitated am-SiO_2, the large intercept of the extrapolated linear branch of the t-plot indicates extensive microporosity.

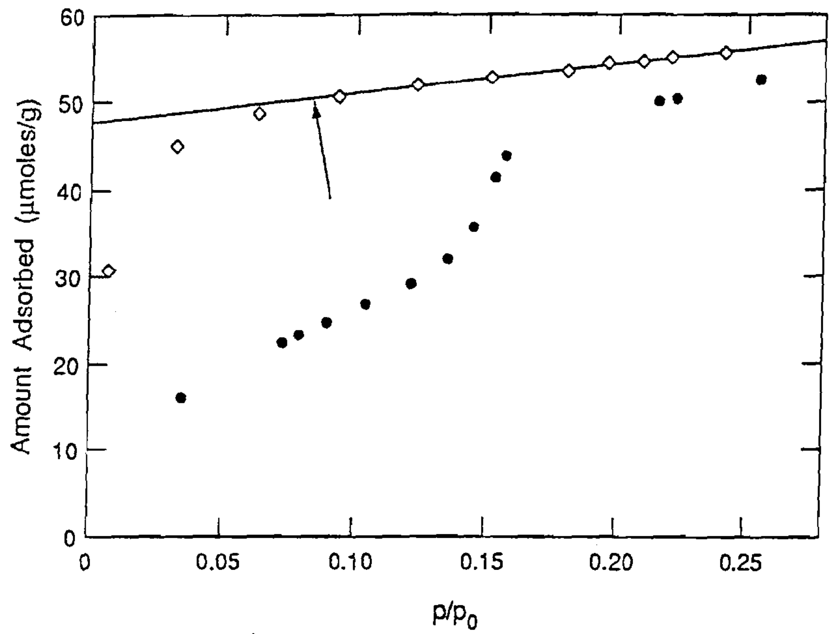


Figure 9. Partial adsorption isotherms for N_2 (open diamonds) and Kr (filled circles) at 77.4°K, on a highly disturbed calcite powder (see text). Point B is shown for the N_2 isotherm. The sample was outgassed at room temperature for 2 days (N_2 isotherm) or overnight at 70°C (Kr isotherm), but the results were independent of outgassing conditions.

Table 3. Specific Surface Areas by BET and t-plot Methods

Solid Phase	Outgassing Temperature (°C)	BET Area (m^2/g)	C_{BET}	BET Range (p/p^o)	t-plot area (m^2/g)	t-plot V_μ (mm^3/g)
α-FeOOH	110	46.0	305	0.03-0.23	47.1	0
SiO_2 (am) BDH precipitated	115	292	1070	0.01-0.17	53.4	102
Linde $\alpha-Al_2O_3$	60, 120	15.8	475	0.02-0.30	16.6	0
Linde $\alpha-Al_2O_3$	180	13.0	1450	0.05-0.20	10.0	1.35
Linde $\alpha-Al_2O_3$; Treated (see text)	100	16.0	275	0.03-0.24	16.0	0
Linde $\alpha-Al_2O_3$; Treated (see text)	195	16.3	467	0.01-0.21	15.6	0

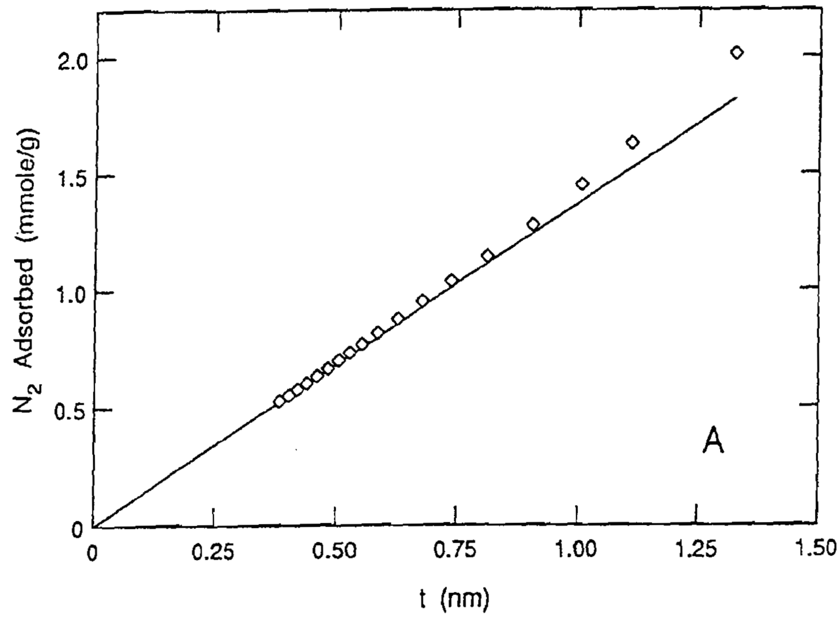
An estimate of the micropore volume can be obtained from the intercept (Table 3; see Appendix A). Yates and Healy (1976) present an α_s plot for a silica sample from the same source, which also reveals the presence of micropores. The slope of the linear branch yields an $\mathcal{A}$ of 53.4 m^2/g. BET analysis yields an $\mathcal{A}$ of 292 m^2/g and a C_{BET} of 1070 (Table 3). The disagreement between t-plot and BET $\mathcal{A}$, the high C_{BET}, and the large intercept of the t-plot ali corroborate that this am-SiO_2 sample is highly microporous.

The $\mathcal{A}$ of nonmicroporous materials does not depend on outgassing conditions as long as they are sufficient to desorb physically adsorbed water. The $\mathcal{A}$ of microporous materials, however, may vary with outgassing conditions. An example of this is shown in Table 3 for a synthetic corundum sample (i.e., α-Al_2O_3). The untreated sample shows no evidence of microporosity after being outgassed at 60 or 120°C. After outgassing at 180°C, evidence of microporosity is revealed by both BET and t-plot analyses. Treating the sample by washing with dilute acid, dilute base, water, and freeze-drying removes the microporous fraction (Table 3). Similar observations have been made for other oxides and aluminosilicates (e.g., Aldcroft et al., 1968; Yates, 1975; Gregg and Sing, 1982), although some apparently microporous materials do not show this effect (e.g., Pyman and Posner, 1978). Outgassing at temperatures above 200°C, however, may lead to a reduction in density of surface functional groups for some hydrous oxides (e.g., Aldcroft et al, 1968; Bye and Howard, 1971; Iler, 1979).

Surface area of clay minerals and soils. The evaluation of the $\mathcal{A}$ of clay minerals by gas adsorption is confounded by the microporosity of the interlayer regions. Murray and Quirk (1990) discuss the assumptions necessary and empirical methods for obtaining $\mathcal{A}$ for various clay minerals from adsorption and desorption isotherms of N_2.

Empirical methods based on the retention of polar organic compounds have been applied to measuring $\mathcal{A}$. The adsorptives include glycerol (1,2,3-trihydroxypropane; van Olphen, 1970), ethylene glycol (EG, 1,2-dihydroxyethane; Dyal and Henricks, 1950; Rawson, 1969), and ethylene glycol monoethyl ether (EGME, 2-ethoxyethanol; Bower and Goertzen, 1959; Carter et al., 1965; Eltantawy and Arnold, 1973). Each of these adsorptives can penetrate the interlayer region of expandable clays. Retention rather than adsorption of the molecules is measured because adsorption from the vapor phase is extremely slow (Hajek and Dixon, 1966). $\mathcal{A}$ is calculated from a calibration curve of surface area versus sample weight obtained from a reference material with known $\mathcal{A}$. A montmorillonite for which $\mathcal{A}$ can be calculated from crystallographic considerations is a convenient reference material for samples dominated by expandable clays. EGME has the distinct advantage that it volatizes much more rapidly than the other adsorptives. Desorption isotherms for glycerol on kaolinite, montmorillonite, and vermiculite samples indicate that adsorption is quasi-Langmuirian for the expandable clayes but multilayer adsorption appears to occur on kaolinite (Hajeck and Dixon, 1966). Pyman and Posner (1978) found that $\mathcal{A}$ values for hydroxypolymers of Fe(III), Al, and Si were much greater than those determined from water and N_2 adsorption if montmorillonite was used as the reference material. Agreement was much better if hydrous ferric oxide, whose $\mathcal{A}$ had been determined by water and N_2 adsorption, was used instead. Their results provide additional evidence that multilayer adsorption occurs on the external surfaces of minerals. The nature of interaction between these adsorptives and microporous materials is unknown. Steric considerations would suggest that they would be excluded from microporous regions that cannot expand to accomodate these bulky molecules. These methods appear to be most useful for determining $\mathcal{A}$ of phyllosilicate minerals whose $\mathcal{A}$ is dominated by the interlayer region.

EGME retention has been extended to determining the $\mathcal{A}$ of clay-dominated soils (Heilman et al., 1965; Cihacek and Bremner, 1979; Ratner-Zohar et al., 1983). It is difficult to achieve good precision for samples with $\mathcal{A}$ below about 50 m^2/g (Ball et al., 1990). Considering the results for single minerals, an accurate measurement of $\mathcal{A}$ requires an understanding of whether the reactive surface area is dominated by interlayer regions of phyllosilicate minerals or the external surfaces of hydrous oxides.



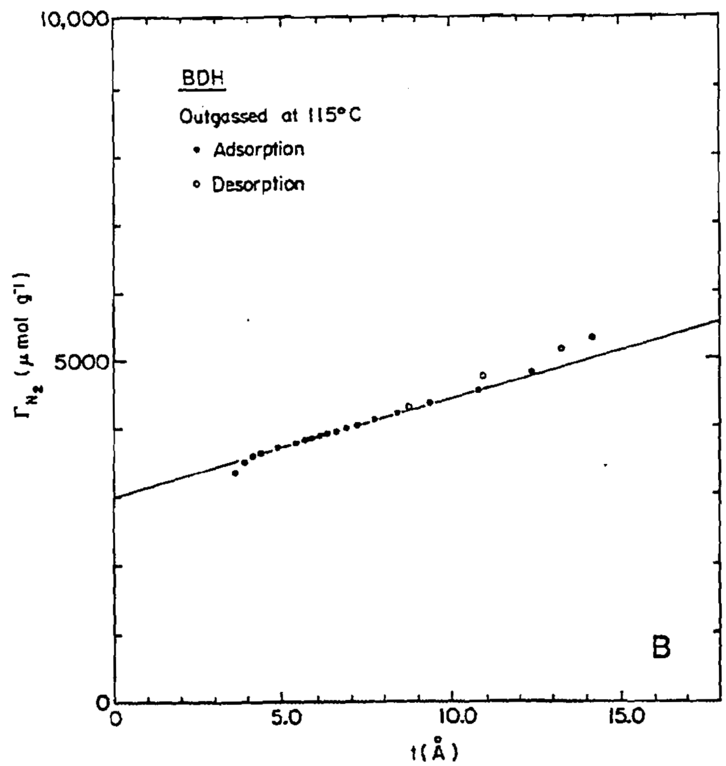


Figure 10. Plots of N_2 adsorbed versus the thickness of the statistical multilayer (*t* plots, see Appendix A). (a) Goethite sample from Figure 7. The zero intercept indicates lack of microporosity and the deviation from the regression line at high relative pressure (i.e., high *t* values) indicates the presence of mesoporosity. (b) A microporous synthetic amorphous silica sample (BDH precipitated silica), which was outgassed at 115°C overnight to a pressure of less than 10^{-4} torr.

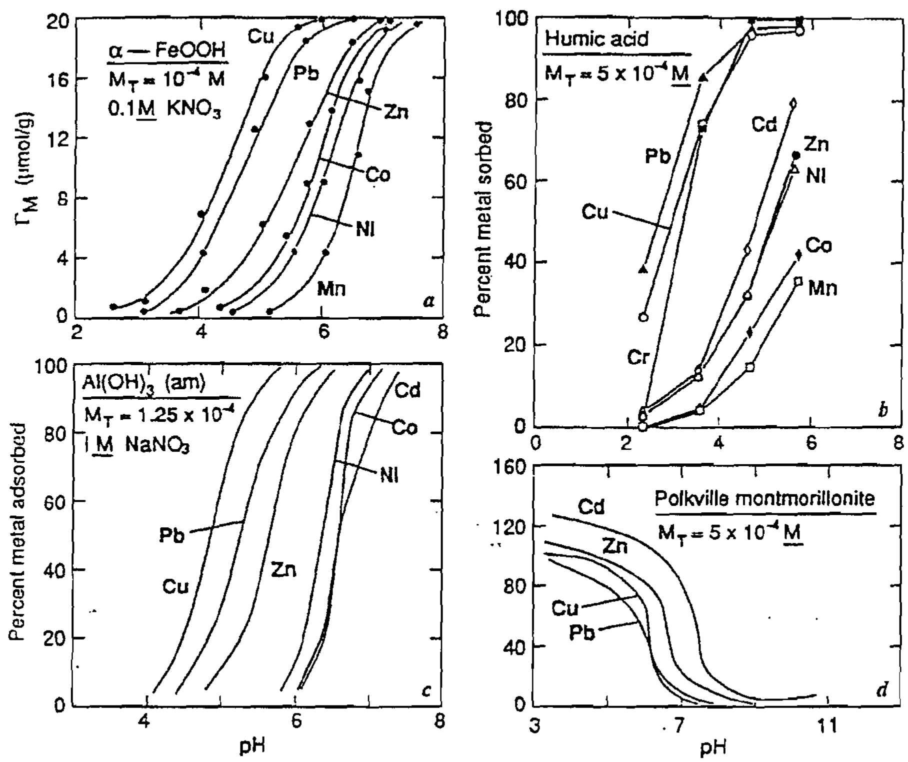


Figure 11. The effect of pH on the adsorption of metal cations by constituents of soils and sediments. (a) Adsorption on goethite from McKenzie (1980); (b) Adsorption on humic acids, from Kerndorf and Schnitzer (1980); (c) Adsorption on freshly precipitated aluminum hydroxide, from Kinniburgh et al. (1975); (d) Adsorption on montmorillonite (*note that metal concentrations [μmoles/dm3] remaining in solution are plotted*), from Farrah and Pickering (1977). Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

ADSORPTION OF IONS AT HYDROUS OXIDE SURFACES IN WATER

The following material presents a brief review of some important characteristics of the adsorption of ionic solutes on oxide minerals commonly found in soils, sediments, aquifers and other geological formations. Much of the material comes from the comprehensive reviews by Dzombak and Morel (1987) and Hayes (1987). The surface chemistry of hydrous aluminum oxides was reviewed recently by Davis and Hem (1989).

Adsorption of cations

Metal cations that form strong complexes with OH^- in water also bind strongly to hydrous oxides (Dzombak and Morel, 1987). Figure 11 illustrates the pH dependence of cation adsorption on various soil components with oxygen-containing functional groups as a function of pH. For most transition metal cations, adsorption typically increases from near zero to nearly complete (>99%) removal from water within a narrow pH range (Benjamin and Leckie, 1981a). It is known that cation adsorption on oxides is generally accompanied by the release of protons (or adsorption of OH^-) by the surface (James and Healy, 1972a; Hohl and Stumm, 1976; Kinniburgh, 1983), but the actual net stoichiometry of the adsorption process is still poorly understood (Hayes and Leckie, 1986; Fokkink et al., 1987). Cations and anions adsorb onto oxide surfaces in response to both chemical and electrostatic forces (James and Healy, 1972b). However, transition metal cations can be strongly adsorbed

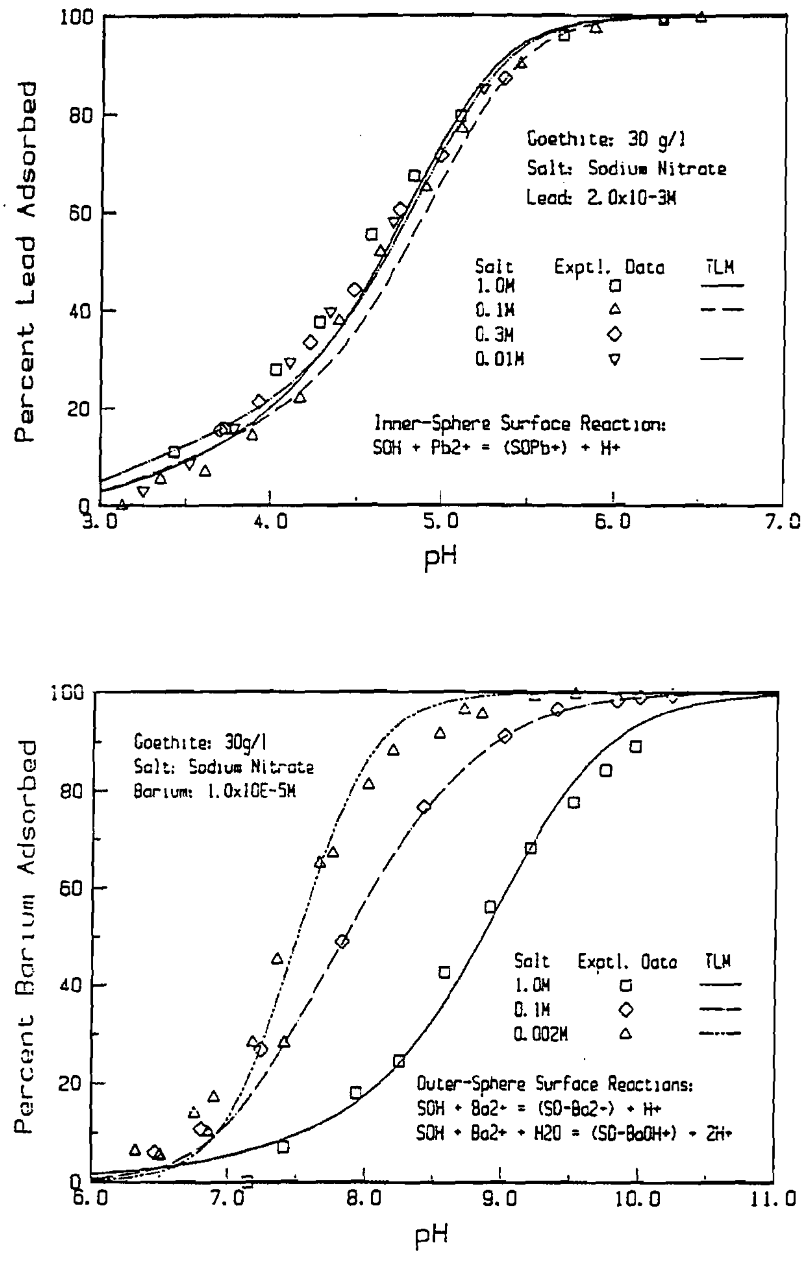


Figure 12. The effect of pH and $NaNO_3$ concentration on dilute Pb^{2+} and Ba^{2+} adsorption by goethite. Points denote experimental data. Curves denote triple layer model simulations (section "Triple layer model"). (a) Model simulations with Pb^{2+} coordinated as an inner-sphere complex; (b) Model simulations with Ba^{2+} coordinated as an outer-sphere complex. Reprinted from Hayes (1987). Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide/aqueous interface. Ph.D., Stanford University.

against electrostatic repulsion (Davis and Leckie, 1978a; Hohl and Stumm, 1976), demonstrating that it is the coordination chemistry of metal ion reactions with surface hydroxyls that is most significant (Stumm et al., 1976; Schindler, 1981). These ions are soft acids (Pearson, 1968) that tend to react with the least basic hydroxyl groups on the surface (Hayes, 1987). Adsorption of these cations by hydrous iron oxides (Fig. 12a) has been found to be nearly independent of ionic strength (Swallow et al., 1980; Hayes and Leckie, 1986), although adsorption on other hydrous oxides (quartz, titania) and some clay minerals does exhibit some ionic strength dependence (Vuceta, 1976; Chang et al., 1987, Hirsch et al., 1989). Weakly adsorbing cations (hard acids) like the alkaline earth ions (Ca^{2+}, Mg^{2+}, Ba^{2+}) do not generally form covalent bonds, and adsorption of these ions (Fig. 12b) has been shown to be influenced by electrostatic forces, via its dependence on ionic strength (Kinniburgh et al., 1975; Kent and Kastner, 1985; Hayes, 1987; Cowan et al., 1990). An emerging area of research is the investigation of cation adsorption by calorimetry (Fokkink, 1987) and as a function of temperature (Johnson, 1990; Bruemmer et al, 1988). Generally it has been found that cation adsorption increases with increasing temperature, but further studies of this type are needed.

Adsorption of anions

Anion adsorption on oxide surfaces is also dependent on pH, but in contrast to cations, adsorption is generally greater at lower pH values and decreases with increasing pH (Hayes et al., 1988; Zachara et al., 1987; Balistrieri and Chao, 1987; Sigg and Stumm, 1981; Hingston, 1981). Figure 13 shows the adsorption of some anions on ferrihydrite, (i.e., poorly crystalline hydrous ferric oxide) as a function of pH, oxidation state, and ionic strength. Anion adsorption on oxides is usually accompanied by an uptake of protons by the surface (or release of OH^-) (Hingston et al., 1972; Sigg and Stumm, 1981; Davis, 1982). The importance of the oxidation state in the adsorptive reactivity of anions is illustrated in Figures 13b and 13c. Some anions, e.g., phosphate, selenite (Fig. 13c), are strongly adsorbed in a manner that is independent of ionic strength (Hayes et al., 1988; Barrow et al., 1980; Ryden et al., 1977; Hingston et al., 1968). Like strongly bound cations, it is believed that this is caused by the formation of coordinative complexes at the surface. Adsorption of weakly bound anions, e.g., chromate, sulfate, selenate (Fig. 13c), is more dependent on ionic strength (Hayes et al., 1988; Rai et al., 1986; Davis and Leckie, 1980), suggesting a greater dependence on electrostatic energy contributions to the free energy of adsorption. The results of EXAFS spectroscopic studies indicate that selenite binds to goethite via an inner-sphere complex like structure (c) in Figure 14; structures (a) and (b) could be eliminated based on the EXAFS analysis (Hayes et al., 1987). The coordinative complex formation involves a two-step ligand exchange reaction in which a protonated surface hydroxyl is exchanged for the adsorbing anion. On the other hand, selenate does not lose its primary hydration sheath during adsorption, and it binds as an outer-sphere complex (Hayes, 1987). This interpretation of the differences between strongly and weakly adsorbed anions is supported by a unique kinetic study (Yates and Healy, 1975) and infrared adsorption results (Cornell and Schindler, 1980; Sposito, 1984). The chapter by Brown (this volume) contains a more detailed review of surface spectroscopic investigations. Investigations of anion adsorption by calorimetry have been published by Machesky et al. (1989) and Zeltner et al. (1986). It was postulated by these authors that the free energies of anion adsorption on hydrous oxides are dominated by large favorable entropies, with enthalpic contributions of minor importance.

Surface site heterogeneity and competitive adsorption of ions

As was noted in Figure 11, adsorption of cations on hydrous oxides increases rapidly over a narrow pH range, sometimes referred to as an *adsorption edge*. It is typically observed that an adsorption edge will shift to greater pH values in such experiments when the molar ratio of aqueous metal ion/surface site concentrations is increased (Kurbatov et al., 1951; Benjamin and Leckie, 1981a; Dzombak and Morel, 1986). In order for the adsorption edge to remain within a fixed pH range, the metal ion adsorption must be proportional to the metal ion concentration. The shift of the adsorption edge can be caused by surface site saturation when the metal ion to site concentration ratio is high, but such shifts are observed in cation adsorption experiments even when the site concentrations are in excess. Benjamin and Leckie (1981a) and Kinniburgh et al. (1983) interpreted the phenomenon as evidence

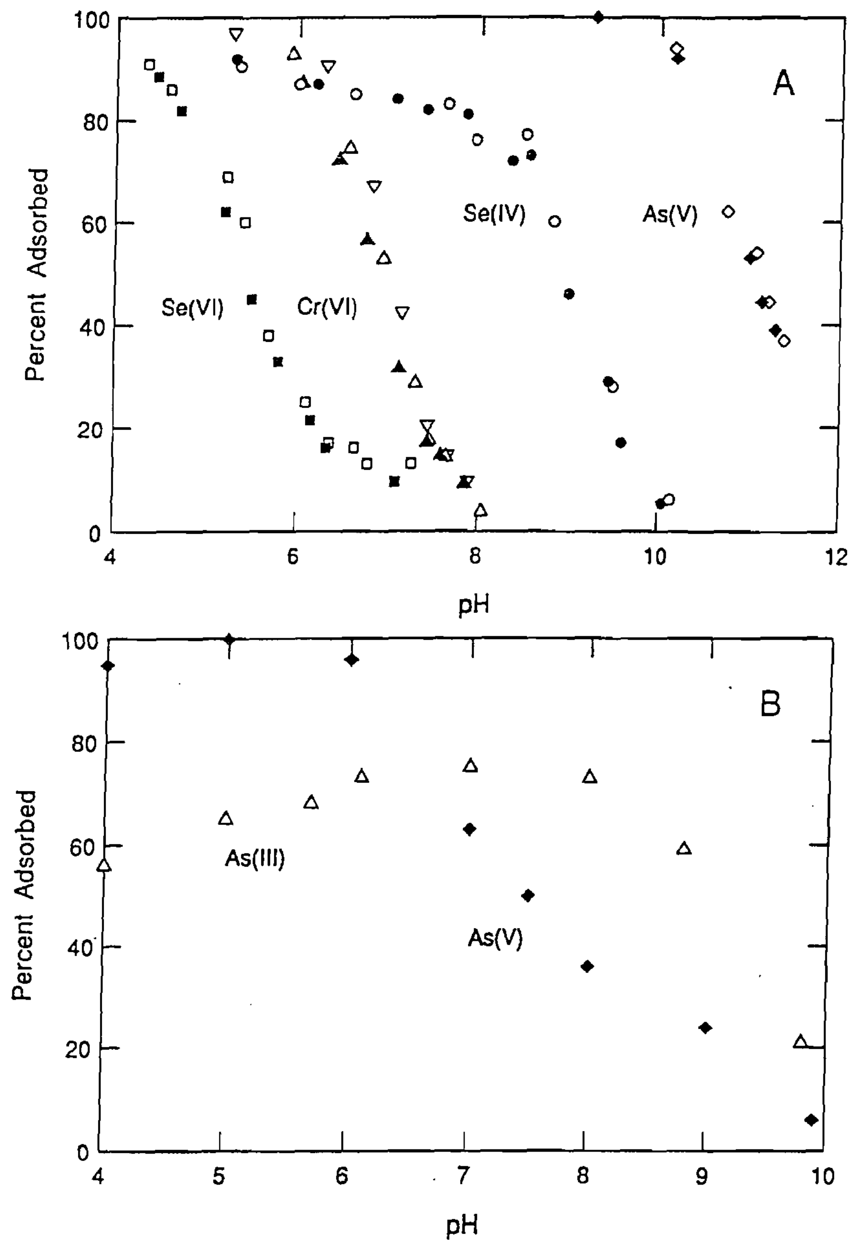
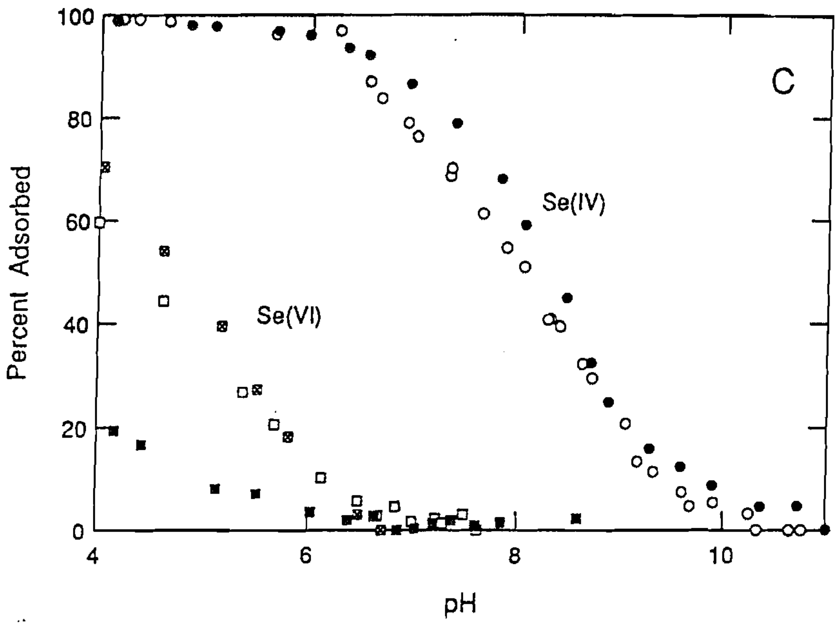


Figure 13. The effect of pH, ionic strength, oxidation state, and trace anion concentrations on the adsorption of oxyanions by ferrihydrite.

(a) Data for various anions adsorbed on 0.001 M Fe (as ferrihydrite) suspended in 0.1M $NaNO_3$:
Se(VI): open squares, 0.2 µM Se; filled squares, 10 µM Se; data from avis and Leckie (1980).
Se(IV): open circles, 0.5 µM Se; filled circles, 5.0 µM Se; data from Leckie et al. (1980).
Cr(VI): open upward triangles, 0.12 µM Cr; open downward triangles, 1.0 µM Cr; filled triangles, 5.0 µM; data from Honeyman (1984).
As(V): open diamonds, 0.5 µM As; filled diamonds, 5.0 µM As; data from Leckie et al. (1980).

(b) Adsorption of As(V) (filled diamonds) and As(III) (open triangles) on 42 µM Fe (as ferrihydrite), total As = 1.33 µM in each experiment; data from Pierce and Moore (1980, 1982).



(c) Effect of pH and $NaNO_3$ concentration on Se(VI) and Se(IV) adsorption by 0.001 M Fe (as ferrihydrite), total Se = 100 μM in each experiment; data from Hayes et al. (1988).
Se(VI): x-box, 0.013 M $NaNO_3$; open squares, 0.1 M $NaNO_3$; filled squares, 1.0 M $NaNO_3$.
Se(IV): open circles, 0.013 M $NaNO_3$; filled circles, 1.0 M $NaNO_3$.

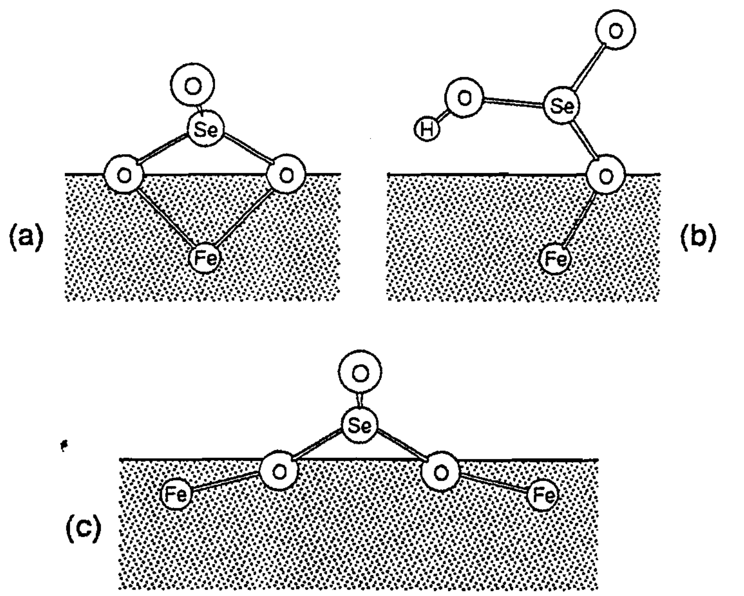


Figure 14. Possible molecular structures for selenite anion, SeO_3^{2-}, coordinated with Fe atoms at the goethite surface. It is possible to distinguish among these model structures for surface complexes using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, see Hayes et al. (1987). Reprinted from Hayes (1987), Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide/aqueous interface. Ph.D., Stanford University.

of the heterogeneity of surface hydroxyl groups, as was mentioned in the section on "Types of surface hydroxyl groups". This results in a lack of adherence of the adsorption data to the Langmuir isotherm (see section on "Empirical adsorption models," below). Although it is likely that several types (or a continous distribution) of nonequivalent surface hydroxyl groups exist on oxide surfaces (van Riemsdijk et al., 1986; 1987), adsorption data can usually be modeled with an assumption of only two nonequivalent sites (Loganathan and Burau, 1973; Kinniburgh, 1986; Dzombak and Morel, 1990). In two-site models, these are usually referred to as high and low energy sites or strong and weak complexation sites. Anion adsorption is usually modeled with a single site model, with some exceptions, e.g., phosphate (Sposito, 1982).

Site heterogeneity is also revealed in competitive adsorption experiments. Competitive effects among metal ions can be quite specific and concentration-dependent (Benjamin and Leckie, 1980; 1981b; Balistrieri and Murray, 1982; Zasoski and Burau, 1988). A small proportion of functional groups on hydrous oxides bind metal ions more strongly than others, and competition among metal ions for these high-energy sites occurs at very low adsorption densities (Benjamin and Leckie, 1981b; Zasoski and Burau, 1988). The specific effects are exhibited as different degrees of competition, e.g., Zn^{2+} having more effect on Cd^{2+} adsorption than Cu^{2+} or Pb^{2+}, which could not be explained in terms of the free energies of adsorption. Benjamin and Leckie (1981b) proposed that each metal ion was preferentially adsorbed at different high-energy sites that represent small fractions of the total site density. At high adsorption densities, the specific nature of the competitive effects is diminished, since most metal ions are bound to low energy sites. Cd^{2+} adsorption onto iron oxides is reduced by high concentrations of weakly-adsorbing alkaline earth cations (Cowan et al., 1990; Balistrieri and Murray, 1982), and Zn^{2+} competes with Ca^{2+} for adsorption sites on Mn oxides (Dempsey and Singer, 1980). Studies of strongly-bound anions also exhibit specific effects at low adsorption density (Hingston et al., 1971). Weakly-binding anions typically do not show these effects in competition experiments (Davis and Leckie, 1980; Leckie et al., 1984; Zachara et al., 1987). Competition among adsorbing anions may be important in regulating the concentration of phosphate in natural systems, especially the competitive interactions of organic acids and silicate (Davis, 1982; Sigg and Stumm, 1981). Competitive effects between cations and anions appear to be absent on ferrihydrite (Benjamin and Bloom, 1981; Benjamin, 1983). Synergistic effects have been observed in these types of experiments, and these effects have been attributed to surface precipitation or the formation of ternary complexes.

Kinetics of sorption reactions

The mechanisms that control the rates of adsorption reactions are poorly understood and require further study. In general, sorption of inorganic ions on mineral surfaces is a two-step process consisting of a short period of rapid initial uptake of adsorbate followed by a slower process(es) (van Riemsdijk and Lyklema, 1980; Dzombak and Morel, 1986; Davis et al., 1987; Fuller and Davis, 1987). The rapid step is usually assumed to be a diffusion-controlled adsorption reaction that takes minutes to reach equilibrium when mass transport in the bulk solution is not limiting. The slow step has been attributed to various processes, such as surface precipitation or solid solution formation, micropore diffusion, formation of aggregates via coagulation, or structural rearrangment of surface species, and these processes can take weeks to months to attain equilibrium. The relative importance of the second step appears to increase with increasing ionic strength or with an increasing molar ratio of adsorbate/surface site concentrations (Dzombak and Morel, 1990). The study by Dzombak and Morel (1986) demonstrated clearly that the rate-limiting process can change as adsorption density increases.

Recently the kinetics of the fast adsorption processes have been studied by pressure and temperature jump relaxation techniques; reviews of this work have been given by Yasunaga and Ikeda (1986) and Hayes (1987). Much of the following is taken from Hayes (1987). The kinetics of proton and hydroxide ion adsorption on hydrous oxides exhibit a single relaxation process (Ashida et al., 1980), which can be attributed to the rate-limiting desorption step. The relative acidities of the surface hydroxyl groups on iron oxides was found to be related to the magnitude of the desorption rate constant (Astumian et al., 1981).

Although the adsorption of protons is fast, proton transfer reactions can continue for weeks or months (Onoda and de Bruyn, 1966; Berube and de Bruyn, 1968) due to structural rearrangements at the surface (Yates, 1975) or micropore diffusion (Kent, 1983). Sasaki et al. (1983) studied the binding of weak binding electrolyte anions (e.g., ClO_4^-) and found that the adsorption was a two-step process, with the first step being a fast bulk diffusion step that was followed by a slower surface reaction, involving surface diffusion and ion pair formation. The relaxation time of the slower process observed was of the order of microseconds. Mehr et al. (1989) have shown that hysteresis occurs in calorimetric measurements of the enthalpy of proton adsorption by TiO_2 during acid-base titrations. The hysteresis is due to the slow release of weakly bound cations present as ion pairs at the surface, and the degree of hysteresis varies considerably among univalent cations (Mehr et al., 1990).

The mechanisms of adsorption and desorption of stongly-binding cations and anions have also been investigated by these techniques. Double relaxations are typically observed in these experiments (Mikami et al., 1983a; 1983b; Hachiya et al., 1984a,b), but the interpretation of the mechanisms that contribute to these relaxations is not as straightforward (Hayes, 1987). Hachiya et al. (1984a,b) postulated that the faster relaxation process was due to an adsorption/desorption reaction involving the release of a water molecule and a proton. The data were consistent with the rate-limiting step involving the removal of water from the hydration sheath of the metal ion to form an inner-sphere complex. The slower process was attributed to parallel adsorption/desorption reactions at heterogeneous sites with different adsorption energies. However, Hayes (1987) has shown that the slow relaxation process observed during the adsorption of Pb^{2+} is dependent on the ionic strength, suggesting that the slow process may be due to the adsorption/desorption of metal ions at surface hydroxyl groups that have formed an ion pair with a weakly binding anion.

Rates of adsorption onto aggergated and agglomerated solids are, in some cases, controlled by diffusion through the pore structure (Hansmann and Anderson, 1985; Kent, 1983; Smit, 1981; Smit et al., 1978). The rate of adsorption depends on the nature of the pore structure. For macroporous and mesoporous materials, the rate is proportional to the concentration of adsorbate in solution, the inverse square of the radius of the agglomerates, and the radius of the pores that comprise the structure (Kent, 1983; Helfferich, 1965). For Na^+ and OH^- adsorption on porous silicas, equilibrium was achieved in minutes to a few hours (Kent, 1983). Adsorption onto microporous materials can be much slower (Kent, 1983; Helfferich, 1965). The rate of cation adsorption is controlled primarily by the *acidity* of the functional groups in the microporous region (Helfferich, 1965; Smit et al., 1978; Smit, 1981; Kent, 1983). This results from the fact that adsorption involves interdiffusion of cations and protons in the microporous region; only free protons can diffuse and their concentration is controlled by the acidity of the functional groups (Helfferich, 1965). For example, adsorption of Na^+ onto microporous silica required several hours to reach equilibrium by this mechanism (Kent, 1983).

Reversibility of sorption processes. Hysteresis between adsorption and desorption of strongly-bound ions is frequently observed, with desorption taking more time than adsorption to attain equilibrium. Padmanabham (1983a,b) investigated the desorption of various transition metal cations from geothite and found that the desorption rate and extent of desorption was dependent on pH and the time of reaction allowed before initiating desorption. The effects were attributed to the formation of bidentate surface complexes at higher pH values and longer reaction times; such complexes would be expected to have greater activation energies for dissociation. Similar results have been obtained for anions like phosphate (Hingston, 1981). In some cases, the extent of reversibility has been used to estimate relative adsorption affinities of ions (Hayes, 1987, and references therein), however, this correlation does not generally apply because other processes may cause hysteresis. For example, when porous materials or aggregated particles are used as adsorbents, ions may diffuse into pore or void spaces and then diffuse out slowly after solution conditions are changed (Fuller and Davis, 1989). The formation of solid solutions or surface precipitates on mineral surfaces may also cause the slow release of sorbed ions (Davis et al., 1987).

Effect of solution speciation on ion adsorption

Complexation of metal ions by ligands can significantly alter their adsorption by mineral surfaces (Bourg and Schindler, 1978; Davis and Leckie, 1978b; Vuceta and Morgan, 1978; Schindler, 1981). Chloride and sulfate complexes of Cd(II) are weakly adsorbed by ferrihydrite in comparison to Cd^{2+} (Benjamin and Leckie, 1982), and metal-EDTA and metal-fulvate complexes are generally not adsorbed by the surfaces of silica, manganese oxides, calcite, or aluminosilicate minerals (van den Berg, 1982; Bowers and Huang, 1986; Davis, 1984; Davis et al., 1987; Hunter et al., 1988). In these cases, the mineral surface sites and dissolved ligands compete thermodynamically for coordination of metal ions, and the net adsorption of the metal ion at equilibrium can be estimated from straightforward equilibrium calculations (Benjamin and Leckie, 1982; Fuller and Davis, 1987). However, relatively basic oxides, e.g., hydrous aluminum oxide, may adsorb metal-EDTA, metal-fulvate, or metal-thiosulfate complexes in acidic solutions, resulting in a complicated pattern of increasing metal adsorption at low pH and decreasing metal adsorption at high pH (Bowers and Huang, 1986; Davis, 1984; Davis and Leckie, 1978b). Such complexes are called ternary surface complexes and their formation is reviewed in the chapter by Schindler (this volume). The pH dependence of ferrihydrite solubility can also introduce complex interactive effects in these systems (Bowers and Huang, 1987). Thus, it is difficult to generalize about the adsorption of complexes that form in solution between cations and ligands. For modeling, one hopes in general that adsorption equilibria can be formulated based on the activities of free (hydrated) cations and anions. This is often the case, but such an assumption must always be verified by experiment or other evidence.

Adsorption of hydrophobic molecules.

Detailed consideration of this topic is outside the scope of this chapter, and the reader is referred to the reviews of Karickhoff (1984) and Curtis et al. (1986) for more detailed information. Sorption of hydrophobic compounds can be considered as a solvent extraction process in which the hydrophobic solute partitions into organic particulate matter to avoid molecular interactions with the solvent, water. The process is driven by the incompatability of nonpolar compounds with water, not by the attraction of these compounds to the organic sorbent (Westall, 1987). Previous research has demonstrated that sorption of hydrophobic compounds by soils and sediments can be estimated with a small number of parameters, such as the solute's octanol/water partition coefficient and the mass fraction of organic carbon found in the sediment. Curtis et al. (1986) have considered the conditions under which mineral surfaces may influence the sorption of hydrophobic solutes on low-organic sandy aquifer materials. Westall (1987) reviewed the important molecular interactions involved in the sorption of hydrophobic compounds with ionizable or ionic moieties.

THE ELECTRIFIED MINERAL-WATER INTERFACE

The creation of an interface between mineral and liquid phases induces fundamental dissymmetry in the molecular environment of the interfacial region. The net effect on the molecular constituents of the two phases is a structural reorganization at the interface that reflects a compromise among competing interactions originating in the bulk phases (Sposito, 1984). These perturbations of the molecular environment invariably lead to a separation of electrical charge and the establishment of an electrical potential relative to the bulk solution phase.

Definitions of mineral surface charge

Surface charge can be classified into three types: (1) *permananent* structural charge, (2) *coordinative* surface charge, and (3) *dissociated* surface charge. Permanent structural charge is associated with the charge due to isomorphic substitutions in minerals, such as that due to substitution of Al^{3+} for Si^{4+} in tetrahedral sites of the crystal lattice of phyllosilicate minerals. Although in principle the permanent structural charge may be positive or negative charge, it is almost always negative among minerals commonly found in soils and sediments. Methods of estimating this component of charge in soils and sediments are given in Sposito (1984). The coordinative surface charge is the charge associated with the reactions of *potential-determining ions* with surface functional groups. For oxides, such reactions include the adsorption of H^+ or OH^- by the surface, but also include coordination reactions of other ions with surface functional groups. The coordinative surface charge may be negative or positive, and as will be shown below, may be subdivided into other subcategories in electrical double layer models.

The charge on particles is usually expressed as a *surface density*, σ_p, in units of charge per unit area (C m^{-2}). The net particle surface charge is defined as the sum of the surface densities of permanent structural charge, σ_s, and coordinative surface charge, σ_o, i.e.,

$$\sigma_p = \sigma_s + \sigma_o \quad . \tag{9}$$

In general, this sum will not be equal to zero, and to preserve electroneutrality, a counterion charge must accumulate near the particle surface. The counterion charge may accumulate as dissociated charge, σ_d, a diffuse atmosphere of counterions fully dissociated from the surface, or the counterion charge may take the form of a compact layer of bound counterions in addition to the diffuse atmosphere. In this case, the portion of the counterion charge that is present only as dissociated charge in the diffuse atmosphere is referred to as σ_d. The surface, compact, and diffuse layer charges are referred to collectively as an electrical double layer (EDL).

Classical electrical double layer models

The separation of charges in the EDL results in an electrical potential difference across the particle-water interface. Gouy (1910) and Chapman (1913) derived equations to describe the distribution of counterions in a diffuse swarm formed at a charged planar surface. The distribution of charge and potential within the EDL in the Gouy-Chapman theory are given by solutions of the Poisson-Boltzmann equation derived for a planar double layer. Detailed derivations and discussions of this equation are given in Bolt (1982) and Sposito (1984). In the model, all counterion charge is present as dissociated charge, σ_d, and the electroneutrality condition is given by:

$$\sigma_p + \sigma_d = \sigma_o + \sigma_s + \sigma_d = 0 \quad , \tag{10}$$

and σ_d, for a symmetical electrolyte with ions of charge z at 25°C, is derived from the Poisson-Boltzmann equation as:

$$\sigma_d = -0.1174\sqrt{I}\sinh\frac{ze\psi_o}{2kT} \quad , \tag{11}$$

where ψ_o is called the electrical potential at the surface. In the case of an asymmetrical electrolyte, a different charge-potential relationship is involved (Hunter, 1987). The calculated potential decays exponentially with distance from the surface (Fig. 15).

The Gouy-Chapman theory was in poor agreement with measurements made on charged mercury electrodes, because the predictions of electrical capacity greatly exceeded experimental observations. The theory was refined by Stern (1924) and Grahame (1947) to recognize the limitations imposed on electrical capacity by the finite size of ions and the likelihood that counterions may only approach the surface within some finite distance, probably close to the ionic radii of anions and the hydrated radii of cations. These authors introduced the concept of "specific adsorption", by which ions could bond chemically to the surface, and proposed that specifically adsorbed ions were located close to the surface, in essentially the same plane as the closest counterions (Fig. 15). With these modifications, Grahame (1947) was able to calculate EDL charges and electrical potentials that were in reasonable agreement with measured values for the mercury surface. In addition, the model provided a good description of the EDL properties of reversible electrodes (such as AgI and Ag_2S) at low ionic strength (Hunter, 1987). In the Stern-Grahame EDL model, the particle surface charge is now balanced by the charge in the Stern layer (referred to as the β plane charge) plus that of the dissociated charge, i.e.,

$$\sigma_p + \sigma_\beta + \sigma_d = 0 \quad . \tag{12}$$

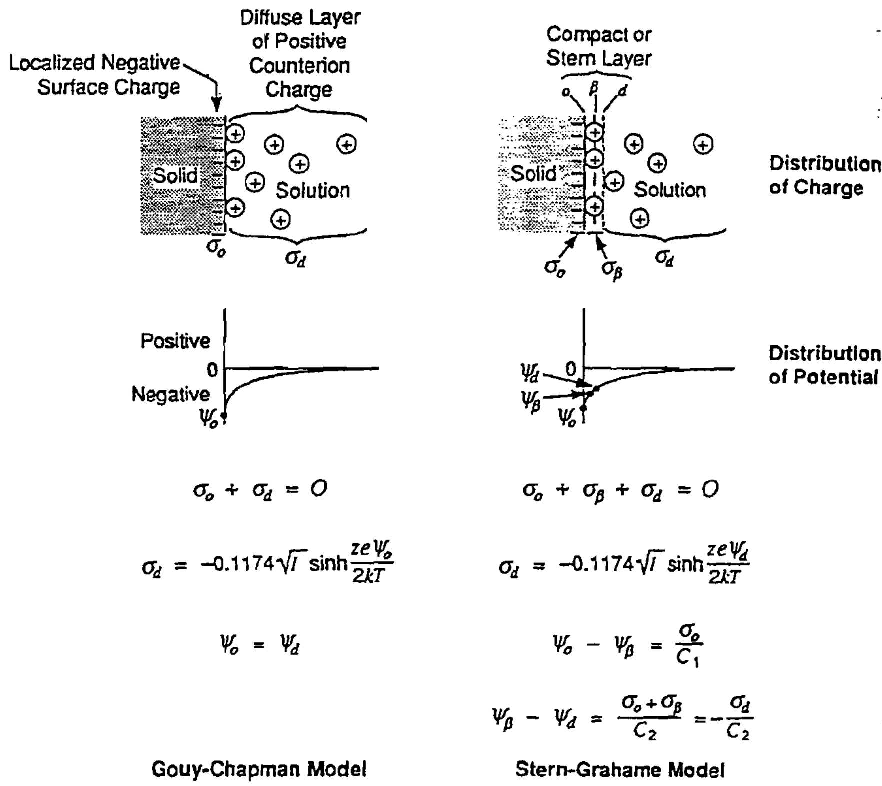


Figure 15. Schematic drawings of the electrical double layer in the classical Gouy-Chapman and Stern-Grahame models. Charge-potential relationships assumed for each model are shown below the diagrams. The relationships shown assume that σ_s equals zero. Reprinted from James and Parks (1982), in Surface and Colloid Science, v. 12, Plenum Press.

The Stern-Grahame model of the EDL also assumes that the electrical potential decays linearly with distance between the charged planes, leading to the following charge-potential relationships:

$$\Psi_o - \Psi_\beta = \frac{\sigma_o}{C_1} \quad , \tag{13}$$

$$\Psi_\beta - \Psi_d = \frac{\sigma_o + \sigma_\beta}{C_2} = -\frac{\sigma_d}{C_2} \quad , \tag{14}$$

where C_1 and C_2 are the integral capacitances of the interfacial layers. The Gouy-Chapman charge-potential relationship (Eqn. 11) is used to describe the decay of electrical potential away from the d-plane toward bulk solution (Fig. 15).

<u>The Electrical Double Layer at Oxide Surfaces</u>

<u>The Nernst equation and proton surface charge.</u> In applying the model to the reversible AgI electrode, it was noted that coordinative surface charge is acquired by nonstoichiometric transfer of the potential-determining ions, Ag^+ and I^-, from the solution phase to the electrode surface. As explained in more detail by James and Parks (1982), the coordinative surface charge can then be defined in terms of the adsorption densities of the potential-determining ions:

$$\sigma_o = F(\Gamma_{Ag^+} - \Gamma_{I^-}) \quad , \tag{15}$$

where F is the Faraday constant. The surface charge was shown to vary as a smooth function of the solution concentration of Ag^+, $[Ag^+]$. At one unique value of $[Ag^+]$, the surface charge equals zero, because Γ_{Ag} equals Γ_I, and this condition was called the *point-of-zero charge* (or PZC). Differences in the surface potential, ψ_o, as a function of potential-determining ions can then be expressed via a modified form of the Nernst equation (James and Parks, 1982), i.e.,

$$\psi_o = \frac{2.3RT}{F}(pAg_{pzc} - pAg) \quad , \tag{16}$$

where pAg is the negative log of $[Ag^+]$.

The success of the Stern-Grahame model in describing these EDL properties on reversible electrodes led other research groups to use this approach in modeling the surface of oxides, with H^+ and OH^- as the potential-determining ions. Parks and de Bruyn (1962) studied the formation of surface charge on hematite (α-Fe_2O_3) particles suspended in KNO_3 solutions by acid-base titration as a function of ionic strength. They argued that coordinative surface charge developed via proton transfer reactions of surface hydroxyl groups that formed when the virgin surface became hydrated (Fig. 1).

$$\equiv FeOH^o \leftrightarrow \; \equiv FeO^- + H^+ \quad , \tag{17}$$

$$\equiv FeOH^o + H^+ \leftrightarrow \; \equiv FeOH_2^+ \quad , \tag{18}$$

where $\equiv FeOH_2^+$, $\equiv FeOH^o$, and $\equiv FeO^-$ represent positively charged, uncharged, and negatively charged hydroxyl groups, respectively, on the oxide surface. To distinguish this type of coordinative surface charge from other types, we shall define the term, *proton surface charge*, or σ_H, i.e.,

$$\sigma_H = \Gamma_{H^+} - \Gamma_{OH^-} \quad . \tag{19}$$

The most common method of measuring the proton surface charge is by potentiometric acid-base titration of a mineral suspension in solutions of variable ionic strength (Bolt, 1957; Yates and Healy, 1980; James and Parks, 1982; Dzombak and Morel, 1990). If CO_2(g) and all other acids and bases (other than the mineral surface) are absent, the net consumption of H^+ or OH^- can be calculated with the expression:

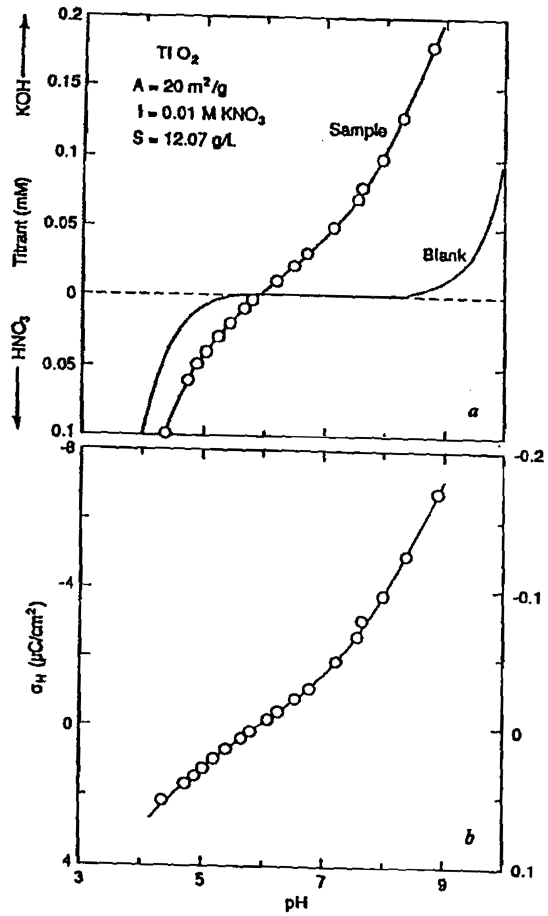
$$\Gamma_{H^+} - \Gamma_{OH^-} = (c_A - c_B - [H^+] + \frac{[OH^-])}{\mathcal{A}W} \quad , \tag{20}$$

where c_A and c_B are the molar concentrations of added acid and base, $\mathcal{A}$ is the specific surface area per unit weight of the mineral, and W is the weight of mineral in suspension per unit weight of water. The molar concentrations of H^+ and OH^- are calculated from the pH measurements. The mineral must be highly insoluble, so that the uptake or release of H^+ or OH^- by dissolved constituents of the solid are negligible (Parker et al., 1979). Proton surface charge may also be calculated by subtracting the titration curve of the background electrolyte (in the absence of the mineral) from the titration curve of the mineral suspension (Fig. 16) to yield the excess acid, q, defined as:

$$q = c_A - c_B - [H^+] + [OH^-] \quad . \tag{21}$$

Excess acid can then be plotted as a function of pH as shown in Figure 16b. The value of the proton surface charge is arbitrary until a value for zero charge is established for the given system. As will be discussed below, the pH at which the proton surface charge is assigned a value of zero is usually determined by a unique intersection point of q for a family of titration curves as a function of ionic strength (Fig. 17).

In the model of Parks and de Bruyn (1962), the proton surface charge forms via the reactions in Equations 17 and 18, and is defined as:



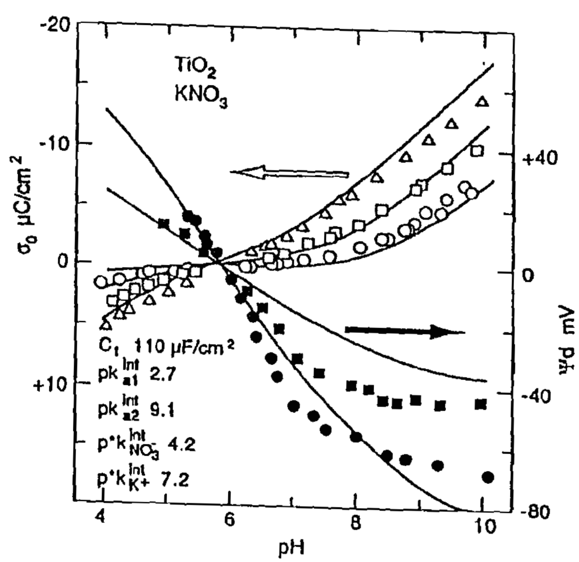


Figure 16 (left). Different methods of presenting data for acid-base titrations of oxide surface functional groups. (a) raw data (moles of protons in the titrant versus pH) for titration of a rutile (TiO_2) suspension in 0.01 M KNO_3 solution (data from Yates, 1975). (b) Proton charge density (σ_H), in units of $\mu C/cm^2$ as a function of pH. σ_H is computed from the excess acid, q (defined in Eqn. 21), which is derived from the raw data in part (a). Reprinted from Dzombak and Morel (1990), Surface Complexation Modeling: Hydrous Ferric Oxide, John Wiley & Sons.

Figure 17 (above). Proton charge density and zeta potential of rutile (TiO_2) in KNO_3 solutions as a function of pH and electrolyte concentration at 25°C. Data are taken from Yates(1975) and Wiese and Healy (1975a). Points denote experimental data: circles, 0.001 M; squares, 0.01 M; triangles, 0.1 M. Solid lines represent triple layer model (section "Triple layer model") simulations of the data using the model parameters shown in the figure. Reprinted from James and Parks (1982), in Surface and Colloid Science, v. 12, Plenum Press.

$$\sigma_H = [\equiv FeOH_2^+] - [\equiv FeO^-] \quad . \tag{22}$$

Parks and de Bruyn (1962) observed a unique pH at which σ_H was equal to zero at all ionic strengths, analogous to the behavior of the AgI electrode.

Despite this analogy, Li and de Bruyn (1966) and Hunter and Wright (1971) found that the Nernst equation was invalid in describing the surface potential of oxides in conjunction with the Stern-Grahame model. The lack of applicability of the Nernst equation to oxides, as opposed to reversible electrodes, has now been examined in great detail in many studies (Levine and Smith, 1971; Lyklema, 1971; Healy and White, 1978; Bousse and Meindl, 1986), with most authors concluding that oxides do not behave as reversible electrodes because (1) H^+ is not a constituent of the oxide lattice and the ionization of surface hydroxyl groups (Eqns. 17 and 18) is controlled by chemical reactions, and (2) a wide variety of ions may participate in coordination reactions with surface hydroxyl groups and thus become potential-determining ions (Dzombak and Morel, 1990).

The zero surface charge condition. The unique pH at which σ_H equals zero has been referred to as the *point-of-zero charge*, or pH_{PZC}, by most authors. Other authors have referred to the unique intersection point of a family of titration curves at different ionic strengths as the *point-of-zero-salt-effect*, or pH_{PZSE} (Parker et al., 1979; Pyman et al., 1979; Sposito, 1984). As mentioned above, many ions may participate in coordination reactions with surface hydroxyl groups. Thus, the coordinative surface charge, σ_o, can be divided into two sub-groups, the proton surface charge, σ_H, and the coordinative complex surface charge, σ_{CC}, i.e.,

$$\sigma_o = \sigma_H + \sigma_{CC} \quad . \tag{23}$$

The technique for determining σ_H measures a mass balance of moles of protons and hydroxide ions that are "bound" in some manner by the mineral surface (Eqn. 19), and as such it is not actually a measurement of surface charge. The pH_{PZC} has been defined as a pH value at which σ_H is zero. However, according to Equation 23, it is not necessary for the coordinative surface charge, σ_o, to be equal to zero when σ_H is zero. Thus, the pH_{PZC} may occur at a pH value at which σ_o is not equal to zero, and under these conditions, the term point-of-zero charge, no longer seems appropriate. Therefore, we shall refer to the pH value at which the proton surface charge, σ_H, equals zero as the *point-of-zero-net-proton charge*, or pH_{PZNPC}.

The observation above led to the definition of the *pristine point-of-zero charge* (pH_{PPZC}) of oxides (Bolt and van Riemsdijk, 1982). When an oxide surface is suspended in a solution in which H^+ and OH^- are the only potential-determining ions, then σ_{CC} equals zero, and $\sigma_o = \sigma_H$. The pH_{PPZC} distinguishes the pH_{PZNPC} of such a system from that in which coordination reactions of other ions take place. Surface coordination reactions of strongly adsorbing ions may shift the pH_{PZNPC} of an oxide to a new value. For example, in a system containing colloidal oxide particles suspended in a $Pb(NO_3)_2$ solution, the proton surface charge could be defined as in Equation 19. Since Pb^{2+} may also form coordinative complexes with the surface, the coordinative surface charge could be defined as follows:

$$\sigma_o = \Gamma_{H^+} + 2\Gamma_{Pb^{2+}} - \Gamma_{OH^-} \quad . \tag{24}$$

A specific pH value may exist in this system (defined by a particular Pb^{2+} concentration) at which the proton surface charge is zero, thus meeting the definition of pH_{PZNPC}. However, this pH_{PZNPC} will differ from the one found in a system in which Pb^{2+} is absent (Fig. 18), because the adsorption of H^+ is influenced by the adsorption of Pb^{2+} (Hohl and Stumm, 1976). The value of the pH_{PPZC} is indicative of the intrinsic acidity of the mineral surface alone in its reaction with pure water. A compilation of these values is given in Table 4. The more general term, pH_{PZNPC}, is indicative of a specific system defined by the mineral phase and solution composition. Little is known about the temperature dependence of σ_H and the pH_{PZNPC}; comprehensive studies on this topic have only recently been completed (Fokkink et al., 1989).

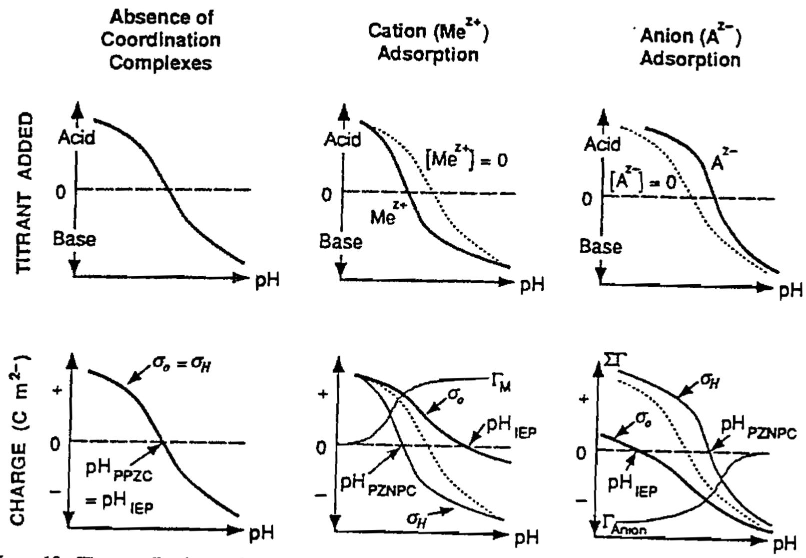


Figure 18. The coordinative surface charge (σ_o) on an oxide surface is established by proton transfer reactions and specific adsorption of anions and cations. Upper graphs show the way in which cation and anion adsorption affect acid-base titration curves. Lower graphs illustrate the effect of cation and anion adsorption on the coordinative surface charge (σ_o) and the proton surface charge (σ_H). Note the separation of the isoelectric point, pH_{IEP}, and point of zero net proton charge, pH_{PZNPC}, when cations or anions are specifically adsorbed. Modified from Hohl et al. (1980).

Table 4. Estimates of the pH_{PPZC} for various minerals

Mineral	pH_{PPZC}	Reference
$\gamma-Al_2O_3$	8.5	a
Anatase (TiO_2)	5.8	b
Birnessite ($\delta-MnO_2$)	2.2	c
Calcite ($CaCO_3$)	9.5	d
Corundum ($\alpha-Al_2O_3$)	9.1	e
Goethite ($\alpha-FeOOH$)	7.3	f
Hematite ($\alpha-Fe_2O_3$)	8.5	g
Hydroxyapatite ($Ca_5(PO_4)_3OH$)	7.6	h
Magnetite ($\alpha-Fe_3O_4$)	6.6	i
Rutile (TiO_2)	5.8	j
Quartz ($\alpha-SiO_2$)	2.9	e

References:

a) Huang and Stumm (1973)
b) Berube and de Bruyn (1968)
c) Balistrieri and Murray (1982)
d) Parks (1975)
e) Sposito (1984)
f) Atkinson et al. (1967)
g) Breeuwsma and Lyklema (1973)
h) Bell et al. (1973)
i) Tewari and McLean (1972)
j) Yates (1975)

Zeta potential. The electrical potential difference across a portion of the mineral-water interface can be estimated from electrokinetic methods such as electrophoresis or streaming potential measurements (Hunter, 1981; James, 1979). For electrophoresis, data are reported in terms of the electrophoretic mobility, the average, steady-state velocity of charged particles moving in response to an applied, constant electric field. Water near the particle surfaces has a greater viscosity than bulk water, and thus, some water molecules move along with the particles in the electric field. The zeta potential correponds to the electrical potential at the effective shear (or slipping) plane between the moving and stationary phases. The zeta potential can be calculated from the electrophoretic mobility for particles of simple geometry (Hunter, 1981; James and Parks, 1982, and references therein). The Gouy-Chapman theory can then be used to estimate the dissociated counterion charge in the diffuse atmosphere that is located on the solution side of the slipping plane.

The location of the slipping plane is not known with certainty. It is known that the distribution of dissociated charge on the solution side of the slipping plane is well described by Gouy-Chapman theory (Li and de Bruyn, 1966). It has been proposed that the approximation be made that the slipping plane lies near the distance of closest approach of dissociated counterion charge (Hunter, 1987; Lyklema, 1977). Thus, all dissociated counterion charge would be located outside the slipping plane and the zeta potential could be used to estimate σ_d. Probably the most important measurement that can be made by electrophoresis is that of the isoelectric point, or pH_{IEP}. For oxides, it is usually found that a suspension of colloidal particles in a solution of defined composition will have a unique pH value (or values) at which the electrophoretic mobility is zero. These pH values are referred to as isoelectric points (Breeuwsma and Lyklema, 1973), and the measurement defines conditions under which particles have no dissociated counterion charge, i.e., $\sigma_d = 0$. In oxide systems in which H^+ and OH^- are the only potential-determining ions, the pH at which there is zero counterion charge (the pH_{IEP}) is also the pristine point-of-zero charge (pH_{PPZC}), and,

$$pH_{IEP} = pH_{PPZC} = pH_{PZNPC} \quad . \tag{25}$$

However, as was the case with the pH_{PZNPC}, surface coordination reactions of strongly adsorbing ions shift the pH_{IEP} of an oxide to a new value (Fig. 18). For example, in a system containing colloidal oxide particles suspended in a $Pb(NO_3)_2$ solution, the coordinative surface charge is defined by Equation 24. At the pH_{IEP} of the system (defined by a particular Pb^{2+} concentration), the dissociated surface charge, σ_d, is equal to zero. Assuming that σ_s is zero, then by Equation 10, the coordinative surface charge, σ_o, must also be equal to zero (assumes the Gouy-Chapman model; in the Stern-Grahame model this condition also requires that σ_β be equal to zero). In this case, the zero value for coordinative surface charge represents a balance of positive and negative charges contributed by all ions coordinated at the surface plane. However, the pH_{IEP} in this system will differ from one in a system in which Pb^{2+} is absent, because of the influence of Γ_{Pb} on Equation 24 (Fig. 18).

In the Gouy-Chapman and Stern-Grahame models, electrical charge and potential are assumed uniform in any particular plane. It is recognized, however, that the physical discreteness-of-charge on the surface sites means that the actual surface potential cannot be equated with ψ_o, because the actual potential is expected to be much larger in the vicinity of the sites (Healy and White, 1978). Instead, it is assumed that the surface potential includes another term, the micropotential (Levine and Smith, 1971), which is insensitive to the values of surface charge or ionic strength, and thus, can be included within the values of acidity constants. The discreteness-of-charge is known to have a significant effect on the predictions of electrical potential at the beginning of the diffuse layer, Ψ_d (Hunter, 1987; Healy and White, 1978).

Interpretation of electrophoretic mobility measurements is complicated by the complex relationships between mobility and zeta potential that exist for complex particle geometries and the dependence of the relationships on ionic strength. Because of this, some authors have questioned the usefulness of zeta potential measurements in understanding EDL properties (e.g., Dzombak and Morel, 1987; 1990; Westall and Hohl, 1980). While it is true that the absolute value of the zeta potential will generally not be known unambiguously, measurement of the pH_{IEP} is not subject to these errors, and this measurement provides

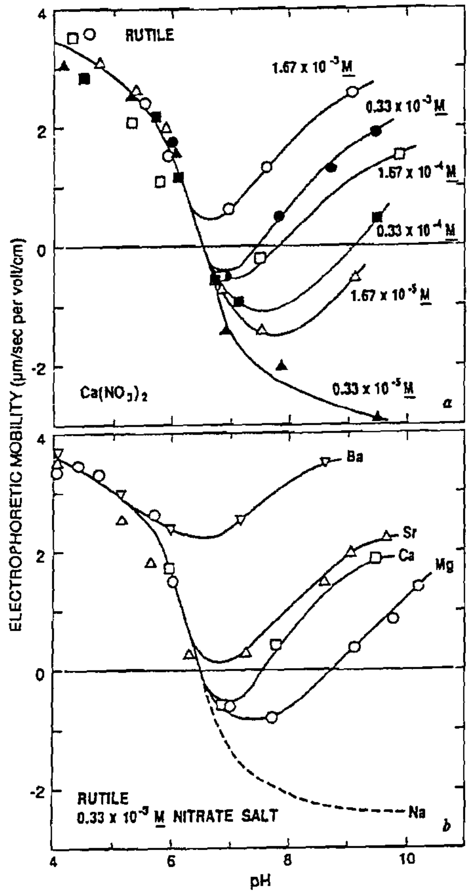


Figure 19. Dependence of the electrophoretic mobility of rutile particles on pH and electrolyte concentration in solutions containing alkaline earth cations. (a) Mobility at various concentrations of $Ca(NO_3)_2$; (b) Mobility at an electrolyte concentration of 0.330 mM in various alkaline earth nitrate solutions. Reprinted from Fuerstenau et al. (1981), in Adsorption from Aqueous Solutions, Plenum Press.

interesting additional information about the EDL that can be included in tests of EDL models. For example, Fuerstenau et al. (1981) and James et al. (1981) have investigated detailed effects of cation adsorption on the electrophoretic mobility of rutile suspensions in solutions with variable concentrations of metal and alkaline earth ions (Fig. 19). Wiese and Healy (1975a,b) have shown that measurement of the zeta potential is extremely effective in estimating the coagulation rates of colloidal suspensions. The establishment of pH_{IEP} is extremely important in many applications of EDL models, in particular for the flotation of minerals (Hornsby and Leja, 1982; de Bruyn and Agar, 1962) and in the optimization of drinking water and wastewater treatment by oxide precipitates (Dempsey et al., 1988; Benjamin et al., 1982; Sorg, 1979; 1978).

Early developments of surface coordination theory

As noted by Dzombak and Morel (1990), while the differences between the EDL properties of oxides and classical reversible electrodes were being discovered, other groups were emphasizing the importance of chemical reactions in describing the adsorption of ions by oxide surfaces. Kurbatov et al. (1951) studied the adsorption of cobalt ions by ferric hydroxide and considered the adsorption equilibria to be controlled by chemical reactions with specific surface sites. These equilibria were described in terms of mass law equations involving the exchange of protons for metal ions. Other groups (Ahrland et al., 1960; Dugger et al., 1964) applied this approach to describe the adsorption of many metal ions on the surface of silica. Long-range electrostatic interactions were not evaluated in these studies, but Dugger et al. noted that the equilibrium "constants" derived from the mass law expressions were only apparent constants that needed correction for the activities of the surface species. These developments were an important step toward the surface complexation models developed several years later.

Parks and de Bruyn (1962) noted that the titration procedure and analysis of the pH_{PZNPC} for hematite was essentially the same as that used commonly in characterizing proteins (Tanford, 1961), and that proton surface charge formation as a function of pH and ionic strength on the oxide was similar to that observed for colloidal proteins. The electrical charge on molecular and colloidal proteins arises from the ionization of carboxylate and amine functional groups, e.g.,

$$\equiv COOH \leftrightarrow \ \equiv COO^- + H^+ \quad , \tag{26}$$

$$\equiv NH_2 + H^+ \leftrightarrow \ \equiv NH_3^+ \quad . \tag{27}$$

Unlike monomeric solutes in water, however, the ionization constants for the reactions of Equations 26 and 27 are not invariant with solution composition, but are observed to depend on surface charge (Steinhardt and Reynolds, 1969).

An important development of this research, which was to be applied later to hydrous oxide minerals, was that charge and electrical potential developed as a result of chemical reactions at specific surface sites. As explained by James and Parks (1982), what distinguishes the protein surface reactions from analogous reactions in homogeneous solution is the variable electrostatic energy of interaction caused by the variable charge on the surface. An invariant acidity constant results when the activity of H^+ at the surface, $\{H^+\}_s$, is used in the equilibrium expression, for example, of Equation 26, i.e.,

$$K^{intr}_{Eq\,26} = \frac{\{\equiv COO^-\}\,\{H^+\}_s}{\{\equiv COOH\}} \quad , \tag{28}$$

and $\{H^+\}_s$ is related to $\{H^+\}_{aq}$ through a function of surface charge or potential. A considerable degree of success has been achieved in modeling the pH and ionic strength dependence of surface charge of colloidal proteins by applying a coulombic correction factor, derived from either Gouy-Chapman or Stern-Grahame theory, to the mass law equations for Equations 26 and 27 (Tanford, 1961; Steinhardt and Reynolds, 1969; King, 1965).

MODELS FOR ADSORPTION-DESORPTION EQUILIBRIUM

Two types of models for describing the equilibria of adsorption-desorption reactions at mineral surfaces can be distinguished: (1) empirical partitioning relationships, and (2) conceptual models for surface complexation that use the formalism of ion association reactions in solution as a representation of surface reactions (Hayes, 1987). Because of the complexity of natural systems, the empirical approach has been widely used in describing the partitioning of solutes between mineral and water phases in geochemical applications, especially in transport models and engineering applications. Surface complexation models, on the other hand, have been used primarily by aquatic scientists interested in developing a thermodynamic understanding of the coordinative properties of mineral surface ligand groups via laboratory investigations. It must be emphasized that the adsorption models discussed here are ***equilibrium*** models, and an assumption of adsorptive equilibrium should be justified before they are applied to laboratory or field observations. Attempts to apply the models to natural systems and typical problems encountered are discussed in the next section.

Empirical adsorption models

Distribution coefficients. Adsorption is often described in terms of equations or partitioning relationships that relate the activity of a solute in water to the amount of the solute adsorbed at constant temperature. The simplest of these expressions is the distribution coefficient derived from the association reaction:

$$J_{aq} \leftrightarrow J_{ads} \ , \tag{29}$$

where J is an adsorbing solute, J_{aq} represents solute J dissolved in the aqueous phase, and J_{ads} is solute J adsorbed. The amount of solute adsorbed is frequently expressed as an adsorption density parameter, Γ, in units of adsorbed solute per unit area or weight of adsorbent. The distribution coefficient, K_d, is usually defined as:

$$K_d = \Gamma_J/[J_{aq}] \ . \tag{30}$$

Usually $[J_{aq}]$ represents the concentration of all dissolved species of J, although a distribution coefficient for a specific species has been defined (Tessier et al., 1989). For inorganic ions, the distribution coefficient is highly dependent on the conditions under which it is measured, e.g., pH, background salt composition, concentration of dissolved carbonate, concentrations of competing adsorbates, etc. The calculation usually assumes that all aqueous species of solute J (including all complexes) have equal affinity for the surface and that all exposed surfaces of the adsorbent (even a complex mineral assemblage) have equal affinity for J. The value of K_d is often very strongly influenced by pH. Thus, the distribution coefficient has little value in predicting the response of solute adsorptive behavior that may result from changes in either the aqueous or mineralogical composition of a system. Applications of the distribution coefficient to natural systems are discussed in the section on "Applications in Aqueous Geochemistry".

Langmuir isotherm. Langmuir (1918) derived an equation to describe adsorption by considering the reaction:

$$\equiv S + J \leftrightarrow \equiv SJ \ , \tag{31}$$

where J is an adsorbing solute, $\equiv S$ is an adsorptive surface site, and $\equiv SJ$ represents the species of adsorbed solute J. Assuming that all surface sites have the same affinity for solute J, a mass law equation can be written for the equation above as follows:

$$K_L = \frac{\Gamma_J}{[J_{aq}]\Gamma_S} \ , \tag{32}$$

where Γ_S is the surface density of uncomplexed adsorptive sites and K_L is the conditional Langmuir equilibrium constant. Making the further assumption that the density of all adsorptive sites on the surface, S_T, is fixed and that J is the only adsorbing solute, the mass law can be combined with the mass balance for surface sites:

$$S_T = \Gamma_S + \Gamma_J \ , \tag{33}$$

to yield the expression commonly known as the Langmuir isotherm:

$$\Gamma_J = S_T\left[\frac{K_L[J_{aq}]}{1 + K_L[J_{aq}]}\right] \ . \tag{34}$$

The generalized shape of the Langmuir isotherm on a log-log plot is shown in Figure 20, where the x-axis represents $[J_{aq}]$ (shown as C). A useful method of evaluating whether data are consistent with the Langmuir isotherm is to plot the distribution coefficient, K_d, as a function of Γ_J (Veith and Sposito, 1977a). Multiplying both sides of the Langmuir isotherm by $\frac{1}{[J_{aq}]} + K_L$, and solving for K_d yields the following linearized form of the Langmuir equation:

$$K_d = S_T K_L - K_L \Gamma_J \ . \tag{35}$$

Graphical procedures can then be utilized to estimate the values of S_T and K_L if the Langmuir equation is applicable to experimental data. However, as discussed by Kinniburgh (1986), other linearizations of the Langmuir isotherm can be made, and each of the transformations has deficiencies with respect to parameter determination by linear regression, even when data are properly weighted for error. The parameters are best determined by nonlinear regression, which also allows testing and comparison with description by other isotherms (Kinniburgh, 1986).

The adherence of data to an adsorption isotherm provides no evidence as to the actual mechanism for the association of a solute with a mineral phase (Sposito, 1986). It has been shown that special cases of precipitation reactions may also exhibit data that conform to the Langmuir isotherm (Veith and Sposito, 1977b). Like the distribution coefficient, K_L is dependent on strictly constant solution conditions and is very sensitive to changes in pH. Thus, it cannot be applied in a straightforward manner under highly variable conditions.

Freundlich and other isotherms. For inorganic ions, it is frequently observed that a plot of K_d versus Γ_J results in a curve that is convex to the Γ_J axis instead of the straight line expected from the homogeneous site Langmuir expression. In these cases, the data must be fitted to a multiple-site Langmuir expression or a generalized exponential. isotherm (Kinniburgh, 1986), such as the Freundlich isotherm (Fig. 20). Isotherms for cation adsorption on hydrous oxides typically exhibit slopes of less than one on a log-log plot of adsorption density versus pH (Benjamin and Leckie, 1981a; Kinniburgh and Jackson, 1982; Honeyman and Leckie, 1986). The two-site Langmuir isotherm assumes that there are two types of surface sites that may participate in adsorption reactions, and this isotherm is frequently suitable for describing adsorption data on mineral surfaces with heterogeneous sites (Sposito, 1982; Sposito, 1984; Kinniburgh, 1986; Dzombak and Morel, 1990).

Other isotherms that exhibit a wide range of applicability to minerals are the Toth and the modified Dubinin-Radushkevich. One of the frequently mentioned drawbacks of empirical expressions is that they are applicable only to a specific set of conditions. In particular, the dependence of adsorption equilibria on pH is significant, and an empirical expression that is valid only for a single pH value would usually be of limited use in modeling the migration of inorganic contaminants in a groundwater system (Honeyman and Leckie, 1986). However, Kinniburgh (1986) has shown that generalized, pH-independent versions of the two-site Langmuir, Toth, and modified Dubinin-Radushkevich isotherms can be derived and successfully applied to problems such as phosphate adsorption by soils or zinc adsorption by ferrihydrite. If linked with geochemical aqueous speciation models, such generalized empirical expressions for adsorption could prove as useful for certain practical applications as the more elegant (but data intensive) surface complexation models. The migration of hydrophobic organic contaminants may be satisfactorily accomplished with distribution coefficients or isotherm relationships (McCarthy and Zachara, 1989).

General partitioning equation. Because adsorption of many inorganic ions is highly dependent on the concentration of H^+, it is important that an adsorption model be capable of predicting adsorptive behavior as a function of pH. The empirical relationships that relate adsorption density to adsorbate concentration are valid only for constant conditions, and thus, these models are generally insufficient for modeling in environmental geochemistry. Honeyman and Leckie (1986) have considered a modified form of the distribution coefficient which describes the adsorption of ion J in terms of the macroscopic observations of proton (or hydroxyl) exchange:

$$\equiv S + J \leftrightarrow \ \equiv SJ + \chi H^+ \quad , \tag{36}$$

and,

$$K_{part} = \frac{\Gamma_J [H^+]^\chi}{\Gamma_S [J]} \quad , \tag{37}$$

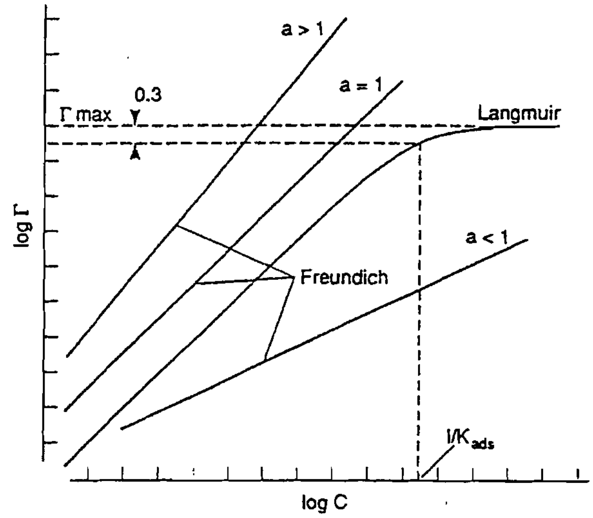


Figure 20. Characteristic shapes of Langmuir and Freundlich adsorption isotherms. Reprinted from Morel (1983), Principles of Aquatic Chemistry, John Wiley & Sons.

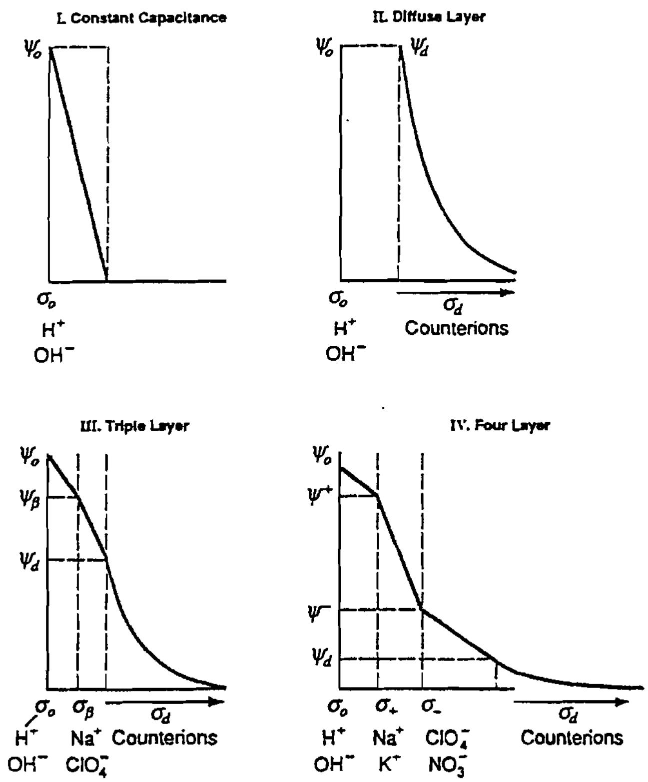


Figure 21. Idealized schematic drawing illustrating the decay of electrical potential with distance from the surface for the constant capacitance, diffuse double layer, triple layer, and four-layer models. Diagram assumes conditions typical of an oxide surface bathed in a simple electrolyte (e.g., NaCl) at a pH value different than the pH_{PZC}.

where χ is the apparent ratio of moles of protons released per mole of solute J adsorbed. Since the relationship described in Equation 37 corresponds to macroscopic observations of all surface reactions involving H^+, no information is provided about the source of protons in the adsorption process other than the generic relationship between adsorption and changes in the activity of H^+. In particular, it does not reveal stoichiometric information about microscopic adsorption reactions at the surface (Honeyman and Leckie, 1986), although some investigators continue to relate the macroscopic parameter to the stoichiometry of microscopic reactions (Belzile and Tessier, 1990; Tessier et al., 1989). The objective in using such a model should be to "calibrate" the values of χ and K_{part} for a range of system compositions of interest to specific applications. Since the speciation of J is usually not considered, the modeling approach is only useful for systems of constant composition. Despite the conditional nature of such constants, the approach has been useful in examining specific issues of adsorptive behavior (Balistrieri and Murray, 1983). Applications of this approach are discussed in the section on "Applications to Aqueous Geochemistry" (below).

Surface complexation models

An alternative to the empirical modeling approaches are the surface complexation models (SCM), which extend the ion-association model of aqueous solution chemistry to include chemical species on surfaces (Hayes, 1987). The concepts used in modeling the ionization of protein surface groups (see section on "Early developments of surface complexation theory," above) were extended by other research groups, particularly those of Schindler and Stumm (reviewed below), to the consideration of adsorption reactions on hydrous oxides. These concepts form the basic tenets of all surface complexation models:

1. The surface is composed of specific functional groups that react with dissolved solutes to form surface complexes (coordinative complexes or ion pairs) in a manner analogous to complexation reactions in homogeneous solution.

2. The equilibria of surface complexation and ionization reactions can be described via mass law equations, with correction factors applied for variable electrostatic energy using EDL theory.

3. Surface charge and surface electrical potential are treated as necessary consequences of chemical reactions of the surface functional groups. Unlike the Gouy-Chapman and Stern-Grahame models for polarizable and reversible electrodes, the specific chemical interactions of protein (and oxide) functional groups dominate the EDL properties; the electric field and electrostatic effects are secondary factors that result from the surface coordination reactions themselves.

4. The apparent binding constants determined for the mass law equations are empirical parameters related to thermodynamic constants via the rational activity coefficients of the surface species (Sposito, 1983).

A number of different surface complexation models have been proposed in the last two decades. The models are distinguished by differences in their respective molecular hypotheses. Each model assumes a particular interfacial structure (Fig. 21), resulting in the consideration of various kinds of surface reactions and electrostatic correction factors to mass law equations. While the models differ in their consideration of interfacial structure, all the models reduce to a set of simultaneous equations that can be solved numerically (Dzombak and Morel, 1987). These equations include: (1) mass law equations for all surface reactions under consideration, (2) a mole balance equation for surface sites, (3) an equation for computation of surface charge, and (4) a set of equations representing the constraints imposed by the model of interfacial structure. The models are illustrated below as applied to the surfaces of hydrous oxides, but the treatment could be extended in a straightforward manner to other minerals that develop amphoteric surface charge. Some common features of the models are presented first before explaining the differences that distinguish the models.

Properties of solvent water at the interface. Water molecules near mineral surfaces have distinct properties (Mulla, 1986). In surface complexation models it is assumed that the dielectric constant of the solvent remains constant at the value of the bulk electrolyte solution up to the outer adsorption plane of the model. Mulla's theoretical calculations suggest that the dielectric constant should be much lower close to a mineral surface, and the predictions suggest that the value decays gradually between the surface and bulk water. Pashley and others (Pashley and Quirk, 1989; Pashley and Israelachvili, 1984a; 1984b) have shown that oscillatory forces of hydration exist when two mica plates are forced together. The forces are a function of the separation distance, and the oscillations indicate density variations and the layering of water on the order of molecular dimensions. Regardless of the interfacial model used, the low dielectric constant of solvent water molecules in the interfacial region should enhance the formation of uncharged surface complexes (Davis and Leckie, 1979). Because of this, the hydrolysis of adsorbed metal ions and protolysis of adsorbed anions at oxide surfaces may occur more readily and at different pH values than occurs in bulk water.

Surface acidity of hydrous oxides. The acidity of a surface hydroxyl group depends on numerous factors, e.g., acidity and coordination number of the metal atom to which it is bonded, electrostatic field strength and induction effects of the mineral, structural ordering of water molecules in the vicinity of the surface, and the local surface structure (face, edge, dislocation, etc.) (Huang, 1981; Westall, 1986; also see chapter by Parks, this volume). Strong acid-base titrations of colloidal oxide suspensions in univalent electrolyte solutions exhibit no clear inflection points, indicating that surface acidity is a function of the degree of surface protonation. The existence of various types of surface functional groups was reviewed earlier, and the titration results are consistent with a distribution of surface site acidities (van Riemsdijk et al., 1986). Nonetheless, to simplify the modeling, the variation in surface acidity with surface charge is usually treated as a consequence of electrostatic perturbations on identical diprotic surface sites, rather than considering heterogeneity among surface sites (Hayes, 1987).

Following the observations of Parks and de Bruyn (1962) and the approach used for modeling polyelectrolytes (Tanford, 1961; King, 1965), a series of papers appeared applying this approach to oxide surfaces (Schindler and Kamber, 1968; Stumm et al., 1970; Schindler and Gamsjager, 1972). Two mass law equations for hydroxyl ionization reactions were written to describe the amphoteric behavior of oxide surfaces (a generalization of Eqns. 17 and 18):

$$\equiv SOH_2^+ \leftrightarrow \ \equiv SOH + H^+ \quad , \tag{38}$$

$$\equiv SOH \leftrightarrow \ \equiv SO^- + H^+ \quad . \tag{39}$$

Following the theoretical arguments of Chan et al. (1975), the chemical potential of species i is written as follows:

$$\mu_i = \mu_i^o + kT \ln C_i + kT \ln \gamma_i \quad , \tag{40}$$

where the terms containing $kTln_i$ represent the concentration-dependent part of the free energy of interaction of species i with its environment. All concentration-independent terms are included in the constant, μ_i^o. This equation defines the activity coefficient, γ_i. Thus, the thermodynamic equilibrium constant for Equation 38, defined for standard state conditions, K_{a1}^o, is given by:

$$K_{a1}^o = \frac{[\equiv SOH]\,[H^+]}{[\equiv SOH_2^+]} \frac{\gamma_{SOH}\gamma_{H^+}}{\gamma_{SOH_2^+}} \quad , \tag{41}$$

where the terms in square brackets are concentrations and the term, γ_i, is the activity coefficient of species i.

To apply the surface ionization model, Schindler and Stumm defined conditional equilibrium constants (called "intrinsic" constants) in the following manner:

$$K^{intr} = \frac{x_{SOH}[H^+]}{x_{SOH_2^+}} \quad , \tag{42}$$

where x_i refers to the mole fraction of species i among all surface sites. As explained in detail by Sposito (1983), in calculating K^{intr}, the authors assumed a Standard State for the species $\equiv SOH_2^+$ wherein $\equiv SOH_2^+$ exists in a chargeless environment. The conditional constant for Equation 42 derived in this manner differs from the true thermodynamic constant by the mean interaction energy per adsorbed proton. Most definitions of equilibrium constants in surface complexation models have used analogous unconventional definitions of the Standard State for surface species.

Following this approach, operational acidity quotients were derived that varied smoothly with surface charge, and by extrapolating the values to zero surface charge (Huang and Stumm, 1973; Huang 1981), conditional acidity constants were obtained that are dependent on ionic strength (Davis et al., 1978). The graphical procedures described in these papers assumed a complete dominance of positive or negative sites on either side of the pH_{PPZC}, but this assumption has been shown to result in systematic errors in estimating the apparent acidity constants (Dzombak and Morel, 1987). While the diprotic acid representation of the oxide surface has been widely accepted, other models for surface acidity have been used. Westall (1986) and van Riemsdijk et al. (1986) have described surface ionization in terms of one acidity constant. Healy and White (1978) and James and Parks (1982) have considered zwitterionic surfaces containing two separate acidic and basic monoprotic surface groups.

Surface coordination reactions. Following Sposito (1984), the general reactions that describe surface coordination are as follows:

$$a(\equiv \mathrm{SOH}) + p\mathrm{M}^{m+} + q\mathrm{L}^{l-} + x\mathrm{H}^+ + y\mathrm{OH}^- \leftrightarrow \equiv(\mathrm{SO})_a\mathrm{M}_p(\mathrm{OH})_y\mathrm{H}_x\mathrm{L}_q^{\delta} + a\mathrm{H}^+ \tag{43}$$

$$b(\equiv \mathrm{SOH}) + q\mathrm{L}^{l-} + x\mathrm{H}^+ \leftrightarrow \equiv \mathrm{S}_b\mathrm{H}_x\mathrm{L}_q^{\zeta} + b\mathrm{OH}^- \quad , \tag{44}$$

where $\delta = pm + x - a - ql - y$ and $\zeta = x + b - ql$ are valences of the surface complexes formed (hence are *whole numbers*). These valences contribute to the coordinative surface charge, σ_o. At the present stage of model evolution, all surface complexation models treat the adsorption of strongly-bound ions in accordance with Equations 43 and 44. Differences between the models are based on the interfacial structure of the EDL and the manner in which weakly-bound ions are treated. Mass law equations are defined for each coordination reaction (following the approach taken in Eqn. 41), but each model applies different terms for electrostatic correction factors that are consistent with the interfacial structure of the model.

The Constant Capacitance Model (CCM). The original development of the model can be found in Schindler and Kamber (1968) and Hohl and Stumm (1976), and it has been reviewed by Sposito (1984) and Schindler and Stumm (1987). The CCM is a special case of the diffuse double layer (DDL) model (reviewed below), applicable in theory only to systems at high, constant ionic strength. At high ionic strength, the EDL, consisting of the coordinative surface charge and dissociated counterion charge, can be approximated as a parallel plate capacitor (Fig. 21). The molecular hypotheses of this model are as follows (Hayes, 1987):

1. Amphoteric surface hydroxyl groups form ionized surface sites as described in Equations 38 and 39. Two apparent equilibrium constants, K_+^{CCM} and K_-^{CCM} describe these reactions, but the values are valid only for a particular ionic strength (Davis et al., 1978).

2. Only one plane in the interfacial region is considered: a surface plane for adsorption of H^+, OH^-, and all specifically adsorbed solutes. Only inner-sphere complexes are formed, via the surface coordination reactions (Eqns. 43 and 44). Certain ions, e.g., Na^+, K^+, Cl^-, NO_3^-, are assumed to be inert with respect to the surface.

3. The charge-potential relationship used in the model is $\sigma_o = C^{ccm}\Psi_o$, where C^{ccm} is the capacitance of the mineral-water interface.

4. The constant ionic medium Reference State is used for aqueous species; a zero charge Reference State is used for surface species.

In summary, for fitting acid-base titration data in a mineral bathed in a simple 1:1 electrolyte, the model has three adjustable parameters (K_+^{CCM}, K_-^{CCM}, and C^{ccm}) for each ionic strength.

The CCM has been widely applied in modeling the adsorption of dilute ions by hydrous oxides (Schindler and Stumm, 1987). Schindler et al. (1976) described the adsorption of transition metal cations by silica, and Hohl and Stumm (1976) applied the model to describe Pb^{2+} adsorption by γ-Al_2O_3. Adsorption of strongly binding anions has also been modeled with the CCM (Stumm et al., 1980; Sigg and Stumm, 1981; Goldberg and Sposito, 1984a,b; Goldberg, 1985).

The Diffuse Double Layer Model (DDLM). In the DDLM, introduced by Stumm et al. (1970) and Huang and Stumm (1973), all ions are adsorbed as coordination complexes within the surface plane, except the dissociated counterions present in the diffuse layer (Fig. 21). The model accounts for the ionic strength effects on ion adsorption through the explicit dependence of the diffuse-layer charge, σ_d, on ionic strength (Eqn. 11). A finite number of sites is designated, thus limiting σ_o to reasonable values, unlike the original Gouy-Chapman theory. Like the CCM, the model describes surface reactions in terms of amphoteric hydroxyl groups that form ionized sites and only inner-sphere complexes are formed in coordination reactions. However, the molecular hypotheses of the DDLM differ in the following ways:

1. There are two planes in the interfacial region: (1) a surface plane for adsorption of H^+, OH^-, and all specifically adsorbed solutes, and (2) a diffuse layer plane, representing the closest distance of approach for all counterions.

2. The Gouy-Chapman theory is applied for the charge-potential relationship (Eqn. 11) in the diffuse layer. The electrical potential at the beginning of the diffuse layer (the d-plane) is equal to the surface potential (see Fig. 21). Unlike the CCM, this model should be applicable at variable ionic strengths. Westall and Hohl (1980) have shown proton surface charge of rutile as a function of pH is well described at $I < 0.1$, in the absence of specifically adsorbing ions.

3. The infinite dilution Reference State is used for aqueous species; a zero surface charge Reference State is used for surface species.

For fitting acid-base titration data in a mineral bathed in a simple 1:1 electrolyte, the model has two adjustable parameters, K_+^{DDL} and K_-^{DDL}, that are applied uniformly to variable (but low) ionic strength solutions.

Until recently, the DDLM was not widely applied in modeling the adsorption of dilute ions from solution. Its first application was by Huang and Stumm (1973), who modeled the adsorption of alkaline earth cations by γ-Al_2O_3. The model was used by Harding and Healy (1985a,b) and Dzombak and Morel (1986) to model cadmium adsorption on amphoteric polymeric latex particles and ferrihydrite. The excellent treatise recently published by Dzombak and Morel (1990) describes an improved version of the DDLM in detail, provides a reviewed database for its use with ferrihydrite, and compares the model characteristics with other surface complexation models. The improved model uses the two-site Langmuir approach with strong and weak coordinative sites to simulate site heterogeneity and the lack of proportionality between metal ion adsorption density and aqueous metal ion concentrations. Example calculations using the DDLM of Dzombak and Morel (1990) to describe the adsorption of Cr(VI) and Zn^{2+} by ferrihydrite are shown in Figures 22 and 23.

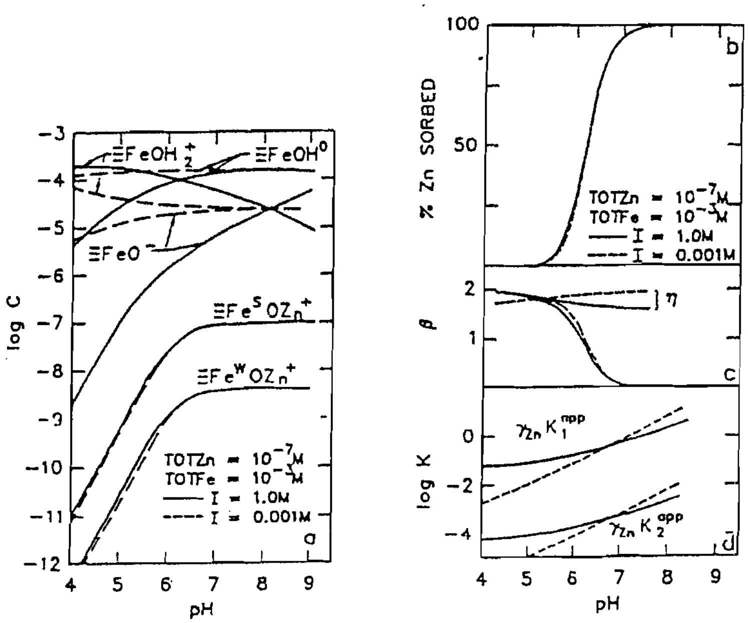


Figure 22. Variations of surface parameters in the two-site DDLM of Dzombak and Morel (1990) as a function of pH and ionic strength in the presence of low adsorbing cation (Zn^{2+}) concentration. (a) Concentrations of surface species, (b) pH adsorption edge for Zn^{2+}, (c) slope of $\log\Gamma_{Zn}$ versus pH (β) and stoichiometry of proton release (η), (d) apparent adsorption constants, i.e., conditional equilibrium constants corrected for electrostatic terms. Reprinted from Dzombak and Morel (1990), Surface Complexation Modeling: Hydrous Ferric Oxide, John Wiley & Sons.

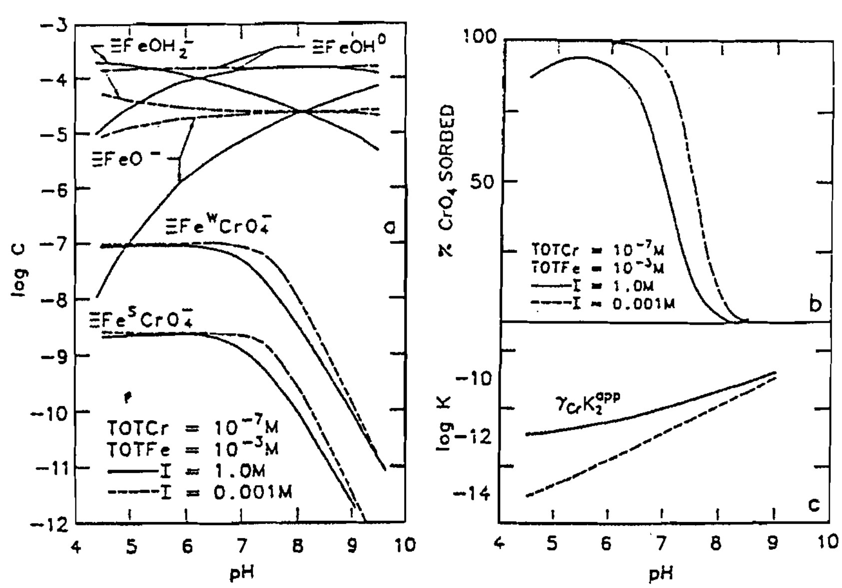


Figure 23. Variations of surface parameters in the two-site DDLM of Dzombak and Morel (1990) as a function of pH and ionic strength in the presence of low adsorbing anion concentration, [Cr(VI)]. (a) Concentrations of surface species, (b) pH adsorption edge for Cr(VI), (c) apparent adsorption constants, i.e., conditional equilibrium constants corrected for electrostatic terms. Reprinted from Dzombak and Morel (1990), Surface Complexation Modeling: Hydrous Ferric Oxide, John Wiley & Sons.

Triple Layer Model (TLM). Because the CCM and DDLM discussed above have only one adsorption plane in the interfacial structure, they are limited in their ability to distinguish between weakly and strongly bound ions (Hayes, 1987). Stern (1924) recognized this limitation and proposed the first three-plane model for the EDL (Westall, 1986). In this model, there was a surface plane, for adsorption of potential-determining ions, and a second adsorption plane for weakly bound counterions (the inner Helmholtz plane (IHP), also called the β plane). The capacitance of the layer between the IHP and the plane of closest approach of dissociated counterions (the outer Helmholtz plane, or OHP) was ignored (Westall, 1986). A significant problem in applying the DDLM to hydrous oxides was that the dissociated counterion charge was usually a small fraction of the proton surface charge, suggesting either specific adsorption of counterions or a microporous "gel" layer (Yates et al., 1974). Yates and others subsequently discounted the possibility of a gel layer for most crystalline minerals based on experimental evidence (Yates and Healy, 1976; Yates et al., 1980; Smit et al., 1978a; 1978b; Smit and Holten, 1980). The three-plane model with specific counterion binding was proposed for the oxide-water interface by Yates et al. (1974), but in this model the capacitance between the IHP and OHP was evaluated based on classical EDL studies, resulting in a decrease in potential between the β and d planes (Fig. 21). Quantitative application of the TLM to EDL data for hydrous oxides was subsequently developed by Davis et al. (1978).

A large body of literature now supports the hypothesis that essentially all electrolyte ions form complexes with surface hydroxyls on oxides (Smit el al., 1978a,b; Smit and Holten, 1980; Foissy et al., 1982; Sprycha, 1983; Sprycha, 1984; Sprycha and Szczypa, 1984; Jafferzic-Renault et al., 1986; Sprycha, 1989a,b; Sprycha et al., 1989; Mehr et al., 1990). It is likely that weakly adsorbed ions, e.g., alkali cations, alkaline earth cations, halides, have at least one layer of water separating them from surface oxygen or metal atoms, i.e., they form ion-pairs or outer-sphere complexes (Hayes, 1987; Hayes et al, 1987). These conclusions are also supported by reaction kinetic studies (see section on "Kinetics of sorption reactions," above).

In the EDL of the TLM applied by Davis et al. (1978), counterion binding in the β layer is incorporated directly into the model structure, allowing ion-pair complexes to form with charged surface hydroxyl groups, e.g.,

$$\equiv SOH + Na^+ + H_2O \;\leftrightarrow\; \equiv SO^-(H_2O)Na^+ + H^+ \quad , \tag{45}$$

$$\equiv SOH + NO_3^- + H^+ \;\leftrightarrow\; \equiv SOH_2^+NO_3^- \quad . \tag{46}$$

The counterions present as ion-pair complexes are included in σ_β in the TLM. Assuming that there is no permanant structural charge, the charge balance is derived from Equations 9 and 12, i.e.,

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad . \tag{47}$$

This allows an explanation of the increase in σ_o as a function of ionic strength as a simple consequence of an increase in counterion binding (Fig. 17).

The molecular hypotheses of the TLM model as implemented by Hayes (1987) are as follows:

1. Amphoteric surface hydroxyl groups form ionized surface sites as described in Equations 38 and 39.

2. There are three planes in the interfacial region: (1) a surface plane for adsorption of H^+, OH^-, and strongly-adsorbed ions, (2) a near-surface plane (the β-plane) for weakly adsorbed ions, and (3) a diffuse layer plane, representing the closest distance of approach of dissociated charge.

3. The Stern-Grahame interfacial model is applied for the charge-potential relationships for the two regions between the three layers (Eqns. 13 and 14). The Gouy-Chapman theory is applied for the relationship in the diffuse layer (Eqn. 11).

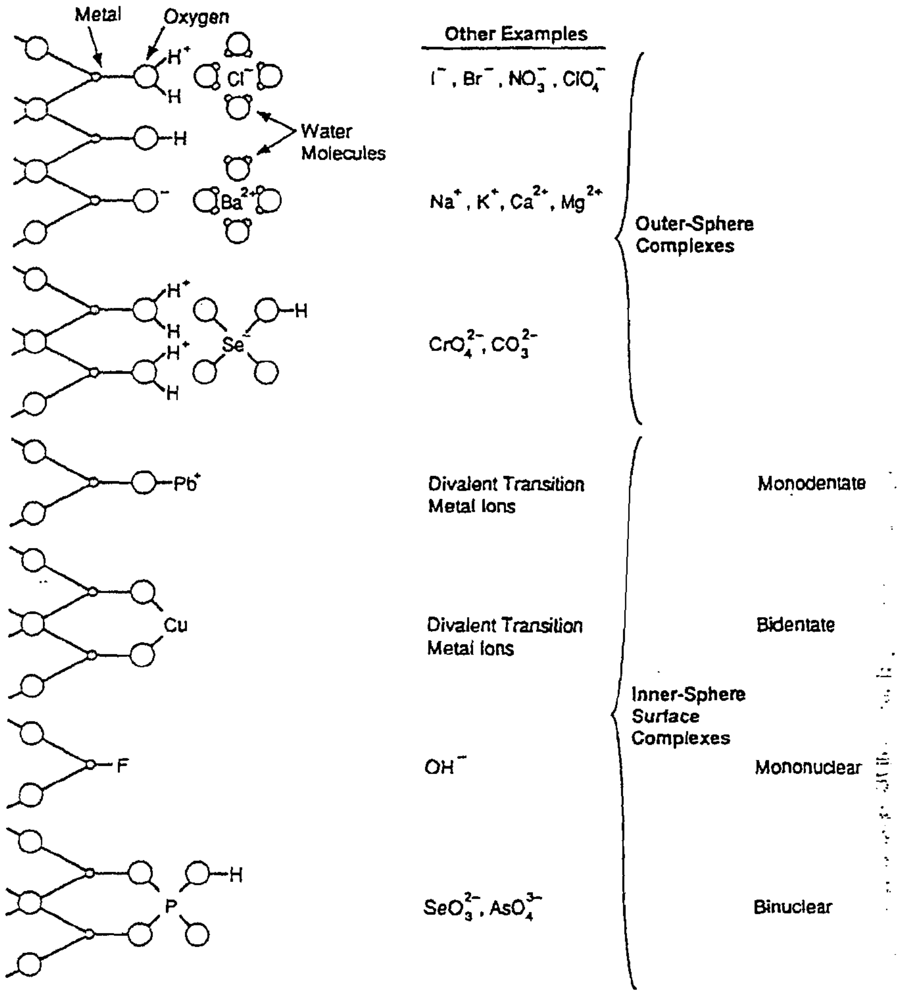


Figure 24. Schematic representation of coordinative surface complexes and ion pairs formed between inorganic ions and hydroxyl groups of an oxide surface in the triple layer model. Reprinted from Hayes (1987). Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide/aqueous interface. Ph.D., Stanford University.

4. Different Reference States have been applied in the model. These are discussed below.

In fitting acid-base titration data, the model has five adjustable parameters, K_{+}^{TLM}, K_{-}^{TLM}, C^{TLM}, and the apparent equilibrium constants for the ion-pair formation reactions (Eqns. 45 and 46).

Although the DDLM also predicts an increase in σ_o with ionic strength, it does so via an increase in σ_d and its dependence on ionic strength. In the triple layer model, σ_d is evaluated as the dissociated counterion charge only (not in ion-pair complexes), making it possible to estimate the electrical potential at the OHP. In the model simulations of Davis et al. (1978), these estimates compared favorably with experimental measurements of the zeta potential (Fig. 17), although no effort has been made to optimize TLM performance in this regard. The value of capacitance between the β plane and the OHP is usually given the constant value of 0.2 F/m^2; however, this value could be adjusted to achieve better agreement with zeta potential measurements. The TLM allows the introduction of specificity in describing the development of proton surface charge in different electrolyte solutions. For example, the charge of rutile in KNO_3 solutions is quite different than that found in $LiNO_3$ solutions (Yates and Healy, 1980). No attempt has been made to explain this phenomena with the DDLM.

Use of the TLM to model the adsorption of dilute cations and anions by hydrous oxides was first reported by Davis and Leckie (1978a, 1980). Since then the model has been widely applied (e.g., Balistrieri and Murray, 1982; Hsi and Langmuir, 1985; Catts and Langmuir, 1986; LaFlamme and Murray, 1987; Zachara et al., 1987; Hunter et al., 1988; Zachara et al, 1989b; Payne and Waite, 1990); earlier reviews were published by James and Parks (1982) and Sposito (1984). In the application of the model by Davis and Leckie, only charge from ionized surface hydroxyls contributed to the coordinative surface charge; all specifically-adsorbed ions were placed in the β plane as outer-sphere complexes. This implementation was largely based on the expectation that adsorption of cations was somewhat dependent on ionic strength, as had been reported by Vuceta (1976) for Cu^{2+} and Pb^{2+} adsorption on quartz. Hayes and co-workers (Hayes and Leckie, 1986; 1987; Hayes et al., 1988) recently completed a comprehensive study of the ionic strength dependence of cation and anion coordination by the goethite surface. The results demonstrate that the TLM overestimates the effects of ionic strength when cations or anions that are strongly-bound on goethite are assumed to occupy positions in the β plane of the EDL (Hayes and Leckie, 1986; Hayes et al., 1988). For such strongly-bound ions, the TLM simulates the experimental behavior more accurately (Fig. 12a) when the adsorbing ions are placed in the surface plane, thus contributing directly to the coordinative surface charge, σ_o. Weakly-bound ions, like Ca^{2+} or SO_4^{2-}, are significantly affected by ionic strength; in this case adsorption is best described as an outer-sphere complex in the TLM (Fig. 12b). Figure 24 illustrates the various types of surface species proposed in the more recent implementation of the TLM.

The original implementation and subsequent applications of the TLM (except Hayes and co-workers) used the infinite dilution Reference State for aqueous species and the zero charge Reference State for surface species (Davis et al., 1978; Sposito, 1983). The activity coefficients of surface species were assumed to be equal, following the arguments of Chan et al. (1975), which results in cancellation of these terms in evaluating surface stability constants (Hayes and Leckie, 1986, 1987). Hayes and co-workers adopted a different approach in defining activity coefficients. The Standard State for both solution and surface species was defined as 1 mole/liter at zero surface charge and no ionic interaction. The Reference State was chosen for all species as infinite dilution relative to the aqueous phase and zero surface charge (Hayes, 1987). Equation 40 was then redefined such that the activity coefficient term is replaced by an electrochemical potential, representing the free energy required to bring a species from the reference state potential to a given potential, Φ. A possible problem with the thermodynamic development may arise from the manner in which the electrochemical potential term is defined, such that uncharged surface species, e.g., $\equiv$FeOH, $\equiv$FeF, behave ideally and require no activity correction. A critical review of the thermodynamic arguments of Hayes (1987) has not yet been published.

Generalization of the implementation of the TLM used by Hayes to minerals other than hydrous iron oxides seems likely; however, it should be noted that adsorption of strongly-bound cations on quartz, titania, and soils does exhibit some ionic strength dependence (Vuceta, 1976; Shuman, 1986; Chang et al., 1987). James and Parks (1982) developed an application of the TLM to clay minerals. An interesting application of the TLM was recently made by Zachara et al. (1990) in a study of aminonaphthalene and quinoline adsorption by silica. Adsorption of these organic compounds was modeled using outer-sphere surface species, and the simulations agreed well with experimental behavior as a function of ionic strength.

Four layer models. Bowden et al. (1980) introduced a four-plane model to allow strongly-bound ions to be placed closer to the surface than the β plane of the TLM without being in the surface plane of adsorption. Although the model can simulate experimental data quite well, we have not considered it here because the model is based on empirical constraint equations rather than mass action equilibrium principles (Hayes, 1987; Sposito, 1984).

The four-layer model of Bousse and Meindl (1986) introduced a second plane for the adsorption of outer-sphere complexes (Fig. 21). As has been noted by Sposito (1984), it is frequently observed that the capacitance of the interface at pH values less than the pH_{PPZC} (positive surface charge) is less than that observed when the surface is negatively charged. It is likely that outer-sphere cation complexes can approach the surface plane more closely than outer-sphere anion complexes, and this may explain the observed differences in interfacial capacitance (Davis and Leckie, 1979). The four-layer model of Bousse and Meindl (1986) can describe proton surface charge in this manner and may provide a more accurate representation of EDL structure.

The non-electrostatic surface complexation model. The simplest SCM approach is to ignore the electrical double layer by excluding electrostatic terms from the mass law equations for surface equilibria (Kurbatov et al., 1951; Ahrland et al., 1960; Dugger et al., 1964). When this approach is utilized in equilibrium models, surface functional groups are treated computationally in exactly the same manner as dissolved ligands (for cation adsorption) or complexing metal ions (for anion adsorption). This is justified by the observation that for moderately or strongly adsorbing ions, the chemical contribution to the free energy of adsorption dominates over the electrostatic contribution (see sections on "Adsorption of cations and anions", above). To apply the model, integral stoichiometries for reactions between the adsorbing species and surface sites are proposed and apparent equilibrium constants for the reactions are derived by fitting experimental data. James and Parks (1975) used this approach to describe Zn^{2+} adsorption on cinnabar (HgS) with the following reaction:

$$Zn^{2+} + \equiv SH \leftrightarrow \equiv S{-}Zn + H^{+} \quad , \qquad (48)$$

where $\equiv SH$ represents a functional group on the cinnabar surface. By including $\equiv S{-}Zn$ as a species in an equilibrium computation, they were able to describe Zn^{2+} adsorption over the entire range of pH and Zn^{2+} concentrations investigated. Davis et al. (1987) used an analogous approach in describing Cd^{2+} adsorption by calcite.

As described above, this approach appears the same as the partitioning equation approach (Eqn. 37) with χ equal to one. However, the conceptual basis of the SCM approach allows the description of competitive effects from other ions in the solution, by computing their adsorption simultaneously. Thus, new constants need not be derived for each solution composition if the adsorption of all aqueous species is adequately described. The SCM approach without electrostatic correction has not been used frequently to simulate ion adsorption in systems with well-characterized mineral phases. However, interest in this approach has recently been renewed because of the complexities involved in applying the SCM to natural materials (see section on "Applications to Aqueous Geochemistry", below). For example, Çowan et al. (1990) applied the non-electrostatic model to describe Cd-Ca adsorptive competition on the ferrihydrite surface. Interestingly, the performance of the non-electrostatic model for this data set appeared to be as good as the TLM. Krupka et al. (1988) used this modeling approach to develop a small database for the adsorption of H^{+}, Ca^{2+}, Cd^{2+}, $CrOH^{2+}$, Zn^{2+}, SO_4^{2-}, CrO_4^{2-} on ferrihydrite from experimental data of other investigators. The goodness-of-fit of model simulations to experimental data was poor in comparison to DDLM and TLM simulations of the same data sets published in the literature. On the other hand, it should be noted that the simple modeling approach was adopted in order to increase the computational efficiency of the FASTCHEM solute transport computer code (Krupka et al., 1988). It remains to be seen if the increased efficiency of this approach is worth the potential loss of accuracy in adsorption simulations.

Proton stoichiometry in surface complexation reactions

That protons are released by cation adsorption and consumed by anion adsorption is well documented and is consistent with the coordination reactions shown in Equations 43 and 44. Nonintegral proton exchange stoichiometries per ion adsorbed are typically observed (Fokkink et al., 1987; Kinniburgh, 1983), and some authors have attempted to relate these values directly to microscopic reaction stoichiometry. However, as discussed in detail by others (Hayes and Leckie, 1986; Hayes, 1987; Dzombak and Morel, 1990), the proton release observed in experimental systems is the net result of adsorption reactions plus the adjustment of surface ionization and ion pair reactions to a new equilibrium condition (Fig. 18). Thus, calculated values of net proton release/uptake are dependent on the interfacial model chosen for the EDL and should be performed in a self-consistent model-dependent analysis. This has rarely been done. Hayes (1987) showed that the simulated net proton release using the TLM was considerably different for inner-sphere lead complexes than outer-sphere lead complexes. The experimental measurements of proton released supported the inner-sphere complex formation of Pb^{2+} on the goethite surface (in agreement with spectroscopic and kinetic measurements) with a release of only one proton during the adsorption reaction, even though the predicted net release of protons was closer to two protons per adsorbed lead ion. Similar differences between microscopic reaction stoichiometry and macroscopic observations of proton release are predicted with the DDLM, and an excellent detailed analysis is given by Dzombak and Morel (1990). As shown in Figure 22, the stoichiometry of proton release is a function of pH and ionic strength, and it has noted by Honeyman and Leckie (1986) that the proton coefficient is dependent on adsorption density. Comprehensive studies of net proton exchange stoichiometry need to be conducted in the future to allow further refinement of surface complexation models and constraints on adsorption reaction stoichiometry.

Parameter estimation

Objective determination of parameters for surface complexation models is best accomplished with the use of numerical optimization techniques (Dzombak and Morel, 1990; Hayes et al., 1990). It must be emphasized that the values of parameters obtained are dependent on the model chosen for fitting experimental data. The model-dependent parameters have frequently been compared in an inappropriate manner in the literature, e.g., in comparing surface acidity (Huang, 1981). Despite the objective nature of such numerical techniques, however, the parameter estimation procedure also has inherent limitations, due to (1) the covariance of estimated parameters (Westall and Hohl, 1980; Hayes et al., 1990) and (2) non-unique solutions during optimization, i.e., the solution has been shown to be dependent on the initial conditions assumed for variables (Koopal et al., 1987). The practice of not reporting goodness-of-fit parameters in comparisons of different models of interfacial structure, reaction stoichiometries or surface speciation (e.g., Cowan et al., 1990) seems inappropriate, since this parameter should be compared with the lower limit of the parameter established by a rigorous error analysis. Although the fits of calculated curves can sometimes be optimized beyond the variation expected from errors involved in data collection, comparisons of model performance are only valid above this lower limit for the goodness-of-fit parameter (Koopal et al., 1987). Bousse and Meindl (1986) concluded that acid-base titration data were only useful for an evaluation of ion-pair formation constants; surface ionization (acidity) constants should be determined from measurements of surface potential or from zeta potentials (Sprycha, 1989a,b).

Recent studies have shown that the ability of surface complexation models to fit adsorption data is relatively insensitive to the value of the site density used (Kent et al., 1986; Hayes et al., 1990). Clearly, the absolute value of the binding constants that describe the adsorption reactions are dependent on the choice of the site density. However, Hayes et al. (1990) showed that the ability to fit experimental data over a wide range of conditions (with a consistent set of model parameters) is independent of the choice of the site density over two orders of magnitude. This is true as long as the molar ratio of adsorbate to surface sites is small, i.e., there is an excess of surface sites over adsorbate in the system. When the adsorbing solute is present in excess, the ability to fit adsorption data becomes more adsorptive equilibrium should be established by reversibility studies that approach the proposed equilibrium condition in several ways (adsorption and desorption by dilution, pH changes, etc.). In addition, isotopic exchange techniques can be applied effectively to demonstrate the maintenance of a constant equilibrium condition as a function of time.

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LIST OF TERMS AND SYMBOLS

a_m = cross sectional are of adsorbed gas molecule [m^2]

$\mathcal{A}$ = specific surface area [m^2/g]

A' = geometric surface area [m^2/g]

C_{BET} = parameter from BET gas adsorption analysis

CCM = constant capacitance model

C^{model} = interfacial capacitance of the near surface region for a particular SCM

DDLM = diffuse double layer model

e = unit of electronic charge [Coulombs]

EDL = electrical double layer

F = Faraday constant

$\{H^+\}_s$ = activity of the hydrated proton at the surface

I = ionic strength

IHP = Inner Helmholtz plane (= Stern or β plane)

[J] = aqueous concentration of solute or species J [$moles/dm^3$]

k = Boltzmann constant

K_d = distribution coefficient [dm^3/g]

K_L = conditional equilibrium constant evaluated from Langmuir isotherm [$dm^3/mole$]

K_{part} = conditional equilibrium constant of the partitioning mass law equation [Eqn. 37]

K_+^{model} = conditional equilibrium constant for protonation of a surface hydroxyl group for a particular SCM

K_-^{model} = conditional equilibrium constant for proton release from a surface hydroxyl group for a particular

n = amount of adsorbed gas [moles/g]

n_1 = monolayer capacity for gas adsorptives [moles/g]

n_i = surface excess (adsorption) of solute i per unit mass of adsorbent [moles/g]

OHP = Outer Helmholtz plane (= diffuse layer plane)

p = partial vapor pressure [torr]

p° = equilibrium vapor pressure [torr]

pH_{PZNC} = pH at which $\sigma_\beta + \sigma_d = 0$

pH_{PZNPC} = pH at which $\sigma_H = 0$

pH_{IEP} = pH at which $\sigma_d = 0$

pH_{PPZC} = pH value when $\sigma_\beta = 0$ *and* $\sigma_H = 0$

pH_{PZSE} = pH at which $\frac{\delta\sigma_H}{\delta I} = 0$

q = concentration of excess acid in acid-base titrations [moles/dm^3]
R = gas constant
SCM = surface complexation model(ing)
S_T = surface density of all surface functional groups [moles/m^2]
TLM = triple layer model
t = thickness of statistical multilayer (see Appendix)
T = temperature
W = mass concentration of particles per unit volume of aqueous solution [g/dm^3]
z = sign and magnitude of ionic charge
$\equiv S$ = general symbol for a surface functional group
$\equiv$MeOH = surface hydroxyl group coordinated to metal or metalloid atom, Me
$\equiv S_c$ = surface functional group for cation complexation on carbonate mineral
α_s = normalized extent of gas adsorption (see Appendix)
γ_i = activity coefficient of species i
Γ_i = adsorption density of solute i [moles/m^2]
Γ_S = surface density of uncomplexed surface functional groups [moles/m^2]
Γ_{max} = maximum adsorption density [moles/m^2]
μ_i = chemical potential of species i in water
μ_i^o = chemical potential of species i in a chosen standard state
ψ_o = averaged electrical potential in the surface plane [volts]
ψ_β = electrical potential at the Stern or β plane [volts]
ψ_d = electrical potential at the diffuse layer plane [volts]
σ_p = surface density of net particle charge [Coulombs/m^2]
σ_s = surface density of permanent structural charge [Coulombs/m^2]
σ_o = surface density of coordinative charge (ions adsorbed in the surface plane) [Coulombs/m^2]
σ_{CC} = surface density of coordinative complex charge (ions other than H^+ or OH^- adsorbed in the surface plane) [Coulombs/m^2]
σ_β = surface density of charge in the Stern or β plane (outer-sphere complexes) [Coulombs/m^2]
σ_d = surface density of dissociated counterion charge [Coulombs/m^2]
σ_H = surface density of net proton charge [Coulombs/m^2]
θ_j = solid phase concentration of solute or species J per unit weight [moles/g]
χ = apparent (macroscopic) quantity of protons released in moles per mole of adsorbate

Appendix A. DETAILS OF SURFACE AREA MEASUREMENT

Gas Adsorption

Sample drying. In order to apply gas adsorption methods to determining $\mathcal{A}$, a sample must be removed from aqueous suspension and dried. Simply allowing the water to evaporate is unsatisfactory for materials that have hydrophilic goups at the surface or consist of small particles. As water evaporates, *menisci* form between particles and the surface tension of water draws particles together as the *menisci* shrink. This leads to agglomeration of the particles. Agglomeration introduces porosity, reduces the surface area due to formation of isolated pores, and can create microporous zones near particle contacts (e.g., Tyler et al., 1969; Rousseaux and Warkentin, 1976). Organic solvents such as acetone are sometimes added to decrease the surface tension of water and speed up drying. Freeze-drying, whereby the aqueous supension is frozen and the ice is removed by sublimation under vacuum, minimizes agglomeration. For example, amorphous silica samples consisting of 2 to 80 μm particles (volume-averaged particle sizes ranged from 5 to 30 μm) exhibited minimal agglomeration upon freeze-drying and no increase in microporosity (Kent, 1983). Precautions such as maximizing the exposed area of ice and minimizing its thickness produced the best results; these precautions minimized the amount of melting that occurred during the freeze-drying process. Colloidal particles are difficult to remove from aqueous suspension without causing some agglomeration of the sample. Whenever it is necessary to remove a sample from aqueous suspension to determine $\mathcal{A}$, the results must be examined critically for artifacts introduced by the drying process.

t- and α_s plots. $\mathcal{A}$ can also be obtained by comparing the isotherm for a sample to that for a reference solid of known surface area. If the reference material is nonporous, information on the existence of microporosity and mesoporosity can also be obtained. Empirical isotherms for N_2 adsorption on nonporous silica and alumina are available in the literature (Gregg and Sing, 1982; Payne and Sing, 1969). The quantity adsorbed is plotted as a function of either t, the thickness of the statistical multilayer, or α_s, the quantity adsorbed at p/p^0 divided by that adsorbed at $p/p^0 = 0.4$. The multilayer thickness is calculated from:

$$t = \frac{n}{n_m} t_1 \quad , \tag{A1}$$

where t_1 is the average thickness of an adsorbed monolayer, (0.345 nm for N_2). t or α_s is obtained from the isotherm for the reference material (Gregg and Sing, 1982). It is advisable to use data for relative pressures *above* 0.35 since the shape of the isotherm below relative pressures of 0.35 is strongly affected by the nature of the solid (e.g., as reflected in the magnitude of the C_{BET}; Gregg and Sing, 1982; Lecloux et al., 1979, 1986). If the sample is nonmesoporous and nonmicroporous, the t or α_s plot yields a straight line through the origin. With microporous samples, the slope of the linear branch yields an estimate of the *external* surface area. The $\mathcal{A}$ is calculated from the slope of the linear branch of the t plot using

$$\mathcal{A} = a_m t_1 L m_t \quad , \tag{A2}$$

or,

$$\mathcal{A} = 3.45x10^5 m_t \quad , \tag{A3}$$

for $\mathcal{A}$ in m^2/g and N_2 as the adsorptive, where m_t is the slope of the t-plot. Similar equations can be derived to calculate $\mathcal{A}$ from α_s plots (see Gregg and Sing, 1982). Samples with mesopores show deviations from linearity along the high pressure branch of the t or α_s plot. For microporous samples, the linear branch does not extrapolate through the origin. An estimate of the micropore volume can be otained from the y intercept by multiplying by the molar volume of liquid N_2 at -196°C. This estimate should be used for comparative purposes only (Gregg and Sing, 1982). Comparison plots thus offer several advantages: the existence of porosity can be determined, $\mathcal{A}$ can be determined for samples with high C_{BET} values, and, for α_s plots, $\mathcal{A}$ can be determined for adsorptives other than N_2 without need of evaluating a_m (Gregg and Sing, 1982).

Adsorption from solution

Various methods for determining $\mathcal{A}$ based on adsorption from aqueous solution have been proposed. There are methods based on the measurement of negative adsorption (co-ion exclusion from the electrical double layer), the determination of adsorption isotherms for organic cations, and empirical correlations between titration data and $\mathcal{A}$. These methods share the obvious advantage over gas adsorption methods that the sample does not have to be removed from suspension and dried. On the other hand, there are serious limitations to their applicability to a wide variety of natural materials.

The negative adsorption method has been used to determine $\mathcal{A}$ of a variety of hydrosols (James and Parks, 1982; Sposito, 1984). It is based on the concept that the surface charge is compensated by both positive adsorption of counterions (ions of opposite charge to the surface) and negative adsorption (exclusion) of co-ions (ions of like charge to the surface). Diffuse double theory yields a relationship between the exclusion volume (see Sposito, 1984) or excess concentration of co-ion in solution (see van den Hul and Lyklema, 1968) and $C^{-1/2}$, where C is the concentration of electrolyte. The measurement must be made at low ionic strength because the fraction of the surface charge compensated by co-ion exclusion decreases with increasing ionic strength. At low ionic strength, the thickness of the electrical double layer is large; porosity on a smaller scale than the double layer thickness will not be detected by this method (van den Hul and Lyklema, 1968). For porous materials, the method probes the geometrical $\mathcal{A}$ of the aggregates or agglomerates rather than the $\mathcal{A}$ on the scale of surface functional groups. For natural materials that consist of mixtures of minerals with different surface properties, the theoretical basis of the method may be invalid.

Adsorption of N-cetylpyridinium bromide (CPB) and methylene blue, both of which are monovalent organic cations, have been used to determine the $\mathcal{A}$ of clay minerals. CPB, which consists of a cetyl group ($CH_3(CH_2)_{14}CH_2$-) attached to the N of a pyridine ring, forms complexes with negatively charged sites on basal surfaces of phyllosilicates and in interlayer regions of expandable clay minerals. CPB exhibits Langmuir-type adsorption (see section on "Langmuir isotherm"); the maximum adsorption density value is used to calculate $\mathcal{A}$ (Greenland and Quirk, 1964; Sposito, 1984). The a_m value has been determined from X-ray diffraction studies to be 0.27 nm^2 on basal surfaces and 0.54 nm^2 on interlayer sites. Free soil organic matter sorbs CPB strongly and therefore must be removed prior to the analysis. CPB has a low affinity for neutral surface functional groups on hydrous oxides and aluminosilicates without fixed charge (Greenland and Quirk, 1964; Aomine and Otsuba, 1968). The methylene blue adsorption method is based on the same principal and has similar limitations to the CPB method (Hang and Brindley, 1970; van Olphen, 1977).

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sensitive to the value of surface site density used (Hayes, 1987). Under these conditions, the site density can be derived by optimizing the fit between model simulations and experimental data.

Because the goodness-of-fit between model simulations and experimental data for *dilute* ion adsorption is insensitive to the value of functional group density, it has been argued that the site density can be used as an additional fitting parameter. Three comments can be made about this modeling strategem:

1. Surface complexation theory treats surface functional groups in the same fashion as dissolved ligands (or metals) in an equilibrium speciation framework. It would be unacceptable to compute metal complexation by chloride ions in solution by co-varying the chloride concentration and chloride complexation constants within the model. The geochemist requires an accurate analysis of water composition before computing aqueous speciation at equilibrium. Ideally, surface complexation modeling should be performed with an accurate determination of surface site density, which can be made experimentally or estimated from previous studies.

2. The fit of model simulations to experimental data is dependent on the value of site density chosen at high ion adsorption densities. While many modeling applications will involve only dilute solutes, problems involving high adsorption densities will also need to be solved, e.g., near contamination sources, or in estuaries. If the site density is used as a fitting parameter and derived from experiments with dilute ions in a swamping 1:1 electrolyte, its value may no longer be optimal when applied under variable conditions. Thus, a general view of applicability should be considered in deriving model parameters.

3. Other model parameters (especially binding constants) are dependent on the value chosen for the density of surface functional groups (Luoma and Davis, 1983). In addition to being dependent on the interfacial model, the apparent binding constants reported in the literature are usually not self-consistent, because varying values for the site densities of minerals have been applied to derive the constants. For example, the binding constant reported for Pb^{2+} complexation with goethite surface hydroxyls by Hayes (1987), i.e.,

$$\equiv FeOH + Pb^{2+} \leftrightarrow \equiv FeOPb^{+} + H^{+} \qquad \log K = 2.3 \quad ,$$

is self-consistent with a goethite site density of 7 sites/nm^2. That is to say, this apparent binding constant should not be applied elsewhere with a different value for goethite site density. A self-consistent thermodynamic database for surface complexation models can only be developed when values for the density of functional groups of minerals have been established and accepted by the general scientific community. Dzombak and Morel (1990) recognized this in developing their database for ferrihydrite and the DDLM. These authors rederived apparent binding constants from original data sets in the literature, using a single value for the surface functional group density.

In addition to the considerations above, a parsimonious modeling approach is needed in order to extend surface complexation theory to applications in natural systems. In complex mixtures of minerals it is often difficult to quantify the numbers of surface functional groups that are present from various minerals. *We recommend that binding constants for strongly-binding solutes be derived with a site density of 2.31 sites/nm^2* (3.84 µmoles/m^2) *for all minerals*; this recommendation is based on the review in the section on "Surface Functional Groups" (above). While the actual Γ_{max} may vary from 1 to 7 sites/nm^2, it is important that one value be selected to encourage the development of a self-consistent thermodynamic database that can be applied easily to soils and sediments (see section on "Applications to Aqueous Geochemistry," below). To encourage unanimity within the field, we have chosen the particular value of 2.31 sites/nm^2 because it is consistent with the value chosen by Dzombak and Morel (1990) to describe ferrihydrite (0.205 moles per mole of Fe), assuming a specific surface area of 600 m^2/g of $Fe_2O_3 \cdot H_2O$. The value recommended closely approximates the site densities found by adsorption on various minerals, including goethite (Table 2), manganese oxides (Zasoski and Burau, 1988), and the edge sites of clay minerals (Motta and Miranda, 1989; Bar-Yosef and Meek, 1987; Inskeep and Baham, 1983).

Eventually this site density may be subdivided into high and low energy site densities for specific minerals, as was done by Dzombak and Morel (1990); however, that is not possible for most minerals without further research investigations.

Comparison of the performance of surface complexation models

Only a few examples of useful and objective model comparisons in the literature can be cited. Westall and Hohl (1980) examined the ability of various models to simulate proton surface charge and found that all models could perform this task well. Morel et al. (1981) compared the models in describing adsorption of Pb^{2+} by γ-Al_2O_3, and found that all the models tested performed well for a single pH adsorption edge. These conclusions of the equality of model performance have been used by some authors to argue that differences between the models are insignificant. With the evolution of implementation of the TLM made by Hayes and co-workers (Hayes and Leckie, 1986, 1987; Hayes et al., 1988), differences between the surface complexation models in describing dilute cation and anion adsorption have diminished even further. As has been noted by Hunter (1987) and Hayes (1987), the models differ primarily in their predictions of diffuse layer potential and the ionic strength dependence of weakly adsorbed solutes. However, the differences between model simulations are not easily demonstrated with small data sets. For example, it would have been a more significant test of model performance if Westall and Hohl (1980) had compared the abilities of models to describe the proton surface charge of rutile in KNO_3 *and* $LiNO_3$ solutions, which are significantly different (Yates, 1975).

From a geochemical point of view, the primary distinction among the models, at their present stage of evolution, is in the way that interactions of major ions in natural waters with mineral surfaces are treated, e.g., the surface reactions of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, and SO_4^{2-}. Each of the models has a distinct set of assumptions for the interfacial structure of the EDL. Thus, differences in model simulations would be expected to be most obvious as the major ion composition of water is varied.

For example, differences in model simulations can be exhibited by either varying ionic strength or in competitive adsorption experiments. Figure 25 shows the effect of sulfate concentration on adsorption of Cr(VI) by ferrihydrite and the ability of the TLM and DDLM to simulate the data. Only outer-sphere species were assumed for sulfate and chromate in the TLM, using the modeling approach of Davis and Leckie (1980). The ionic strength dependence of Cr(VI) adsorption on ferrihydrite (Music et al., 1986; Rai et al., 1986) suggests that it may form an outer-sphere complex. For the DDLM, the constants of Dzombak and Morel (1990) were used without any attempt at further optimization of the fit. Only slight differences between the model performances can be seen, and it can be concluded that either model performs well in describing the competition of sulfate and chromate adsorption. It has already been stated that ions like Na^+, K^+, and Cl^- do not affect the adsorption of strongly-bound ions (Figs. 12a and 13c). Dempsey and Singer (1980) showed that Ca^{2+} had little effect on Zn^{2+} adsorption by ferrihydrite. Both the TLM and DDLM predict the observed negligible effects on trace cation adsorption. Cowan et al. (1990) illustrated that Ca^{2+} decreases Cd^{2+} adsorption on ferrihydrite, but only limited success was achieved in simulating the data with the TLM. A combination of inner-sphere and outer-sphere complexes for Ca^{2+} was used in the modeling. Interestingly, a comparable degree of success was achieved with the non-electrostatic surface complexation model. We have found that neither the TLM or DDLM was able to simulate well the data of Hayes (1987) for Ba^{2+} adsorption by ferrihydrite as a function of ionic strength (calculations not shown). Hayes (1987) was able to simulate the data with the TLM (curves shown in Fig. 12b), but only after significant manipulation of the ion pair formation constants of Na^+ and NO_3^-. This appears to be the first set of *dilute* cation adsorption data ever collected that would require the four-layer model (Fig. 21) for an accurate description of all experimental data with a single set of model parameters. The justification for such a model stems from the need to place outer-sphere cation complexes closer to the surface than outer-sphere anion complexes (see section on ""Four layer models," above).

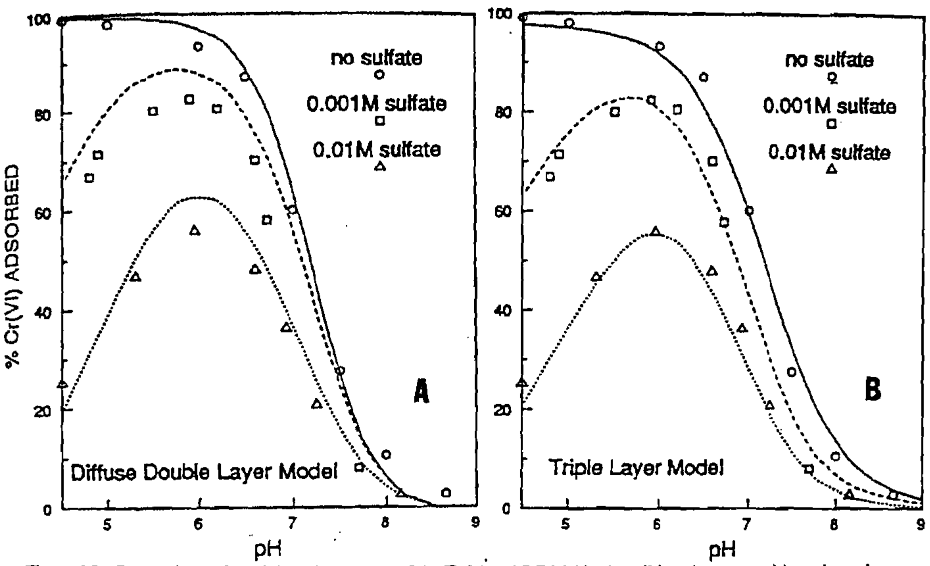

Figure 25. Comparison of model performances of the TLM and DDLM in describing the competitive adsorption of Cr(VI) and sulfate anions by 0.001 M Fe (as ferrihydrite) in 0.1 M $NaNO_3$ solution.

(a) DDLM parameters taken from Dzombak and Morel (1990).

(b) TLM: $\log K_{CrO_4^{2-}}$ 10.1; $\log K_{HCrO_4^-}$ 17.6; $\log K_{SO_4^{2-}}$ 9.4; $\log K_{HSO_4^-}$ 15.05; other model parameters taken from Davis and Leckie (1980), aqueous solution complex formation constants taken from Dzombak and Morel (1990).

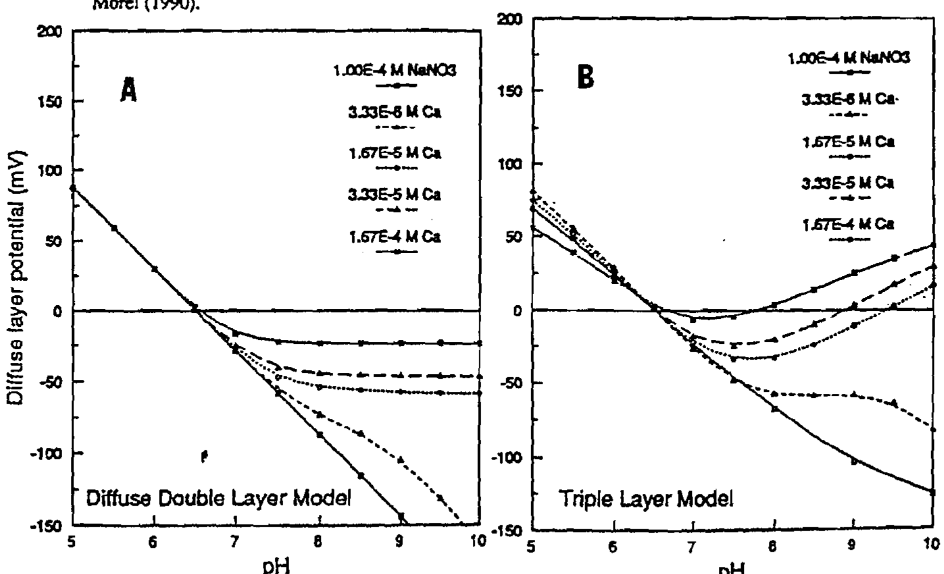

Figure 26. Comparison of model performances of the TLM and DDLM in describing the diffuse layer potential of rutile (TiO_2) suspensions in solutions of varying concentrations of $Ca(NO_3)_2$. Rutile properties in both models: $W = 100$ mg/dm^3; $\mathcal{A} = 26$ m^2/gm; $S_T = 4.96$ µmoles/m^2

(a) DDLM constants at I=0: $\log K_{+}$, 5.5; $\log K_{-}$, -7.5; $\log K_{Ca^{2+}}$, -4.5.

(b) TLM parameters at I=0: C_1, 1.05 F/m^2; $\log K_{+}$, 4.4; $\log K_{-}$, -8.6; $\log K_{Na^+}$, -6.9; $\log K_{NO_3^-}$, 6.1; $\log K_{CaOH^+}$, -11.2.

As was mentioned in the section on "Zeta potential" (above), accurate conversion between measurements of electrophoretic mobility and diffuse layer potential is made difficult by complex relationships involving particle geometry and viscoelectric effects (Dzombak and Morel, 1990; Hunter, 1987). It is generally acknowledged that the diffuse layer potential, Ψ_d, in the DDLM greatly overestimates measured values of zeta potential (Hunter, 1987). Dzombak and Morel (1987) argue that this problem can be overcome with the introduction of an empirical function describing the location of the shear plane in the DDL, and this approach was demonstrated for rutile suspended in KNO_3 solutions. However, it can easily be shown that such an empirical approach would be unsuccessful in $Ca(NO_3)_2$ solutions, which cause a reversal of charge (Fig. 19). Figure 26 illustrates the performance of the DDLM and TLM in simulating the diffuse layer potential of rutile suspended in calcium nitrate solutions of various concentrations. Ca^{2+} binding constants were derived from adsorption data. The TLM clearly performs better than the DDLM at simulating the pH_{IEP} as a function of pH (compare Fig. 26a with Fig. 19a).

It is widely recognized that the rate of coagulation of colloidal particles is dependent on surface charge (Hunter, 1987; Stumm, 1977; Stumm et al., 1970). Effective coagulation is of considerable significance in the settling of particles during waste treatment and in natural systems (Farley and Morel, 1986; O'Melia, 1987). Colloidal particles of hydrous aluminum and iron oxides are important adsorbents in the treatment of drinking water and wastewaters (Dempsey et al., 1988; Benjamin et al., 1982; Sorg, 1978, 1979). Manipulation of surface charge is of interest in the modeling of various engineering and industrial operations, such as ore processing and mineral flotation, secondary oil recovery from geological deposits, and the manufacture of ceramics, pigments, and other industrial products (Hunter, 1987; Hornsby and Leja, 1982; Fuerstenau, 1976; de Bruyn and Agar, 1962). Generally, the onset of rapid coagulation occurs when the absolute value of the diffuse layer potential decreases below about 14 mV (Wiese and Healy, 1975a,b). Thus, the prediction of diffuse layer potential, and more importantly, the pH_{IEP} is of considerable importance in these applications. One of the foremost objectives in the development of the TLM (Yates et al., 1974; Davis et al., 1978) was to create a model with more realistic simulations of σ_d and Ψ_d. The simulations shown in Figure 26 and the arguments of Hunter (1987) and James et al. (1981) support the view that the TLM better serves these objectives.

The primary objective of many applications of surface complexation models in aqueous geochemistry is to simulate the adsorption and transport of ions in natural systems. With the possible exception of the non-electrostatic model (Krupka et al., 1988), it can be stated that all surface complexation models simulate ion adsorption data adequately in simple mineral-water systems. It has frequently been argued that the DDLM and CCM models should be applied instead of the TLM, because of their simpler interfacial models. As noted by Dzombak and Morel (1987), the TLM in fact contains fewer model parameters than the CCM when applications involving variable solution compositions are considered. The few parameters required by the DDLM and its successful performance in complex solutions with single mineral phases (Fig. 25) are appealing features. The availability of the self-consistent, validated database and two-site model for ferrihydrite compiled by Dzombak and Morel (1990) is also an important development that will undoubtedly increase usage of the DDLM. However, the additional model parameters required by the TLM (two electrolyte binding constants in 1:1 electrolyte solutions and the inner layer capacitance) are of little consequence when incorporated in numerical computer algorithms, and electrolyte binding constants have now been determined for many hydrous oxides (Charlet and Sposito, 1987; James and Parks, 1982). Many difficult problems need to be addressed in order to apply surface complexation theory to soils and sediments. As will be shown in the next section, it is the ease of applicability that is most important in choosing a model for geochemical applications.

APPLICATIONS IN AQUEOUS GEOCHEMISTRY

Numerous field studies have demonstrated that sorption processes are important in natural systems. Sorption has been shown to be important for Zn and V in pristine rivers (Shiller and Boyle, 1985, 1987) and for Ni, Cu, Zn, Pb, and As in rivers contaminated by acid mine drainage and other industrial activities (Mouvet and Bourg, 1983; Johnson, 1986; Fuller and Davis, 1989). In rivers, sorption processes can control the dissolved concentrations of solutes, give rise to high concentrations of toxic metals in the bed load (Johnson, 1986; Fuller and Davis, 1989), and affect the discharge rates of solutes into estuarine and coastal marine systems (Shiller and Boyle, 1985; 1987). In lakes and the oceans, sorption processes are important in the flux of many elements from the water column to bed sediments (Belzile and Tessier, 1990; Tessier et al., 1989; Honeyman and Santchi, 1988; Sigg et al., 1987). Sorption may regulate the availability and toxicity of trace elements to phytoplankton (Kuwabara et al., 1986; Morel and Hudson, 1985), and the uptake of sorbed metals by filter feeding and burrowing organisms is a potential environmental risk in surface waters (Luoma and Davis, 1983). In soils and aquifers, sorption processes can retard the transport of solutes (Cherry et al., 1984; Lowson et al., 1986; Jacobs et al., 1988; Davis et al., 1990) and give rise to the formation of secondary repositories, i.e., regions where contaminants are accumulated downgradient from a source, from which they can be released in response to a change in the geochemical environment. Sorption processes have long been utilized in metallurgical processes (Robins et al., 1988; Bryson and te Reile, 1986; de Bruyn and Agar, 1962) and are important in the treatment of wastewaters and mining tailings (Khoe and Sinclair, 1990; Leckie et al., 1985; Benjamin et al., 1982).

In this section we discuss the problems typically encountered in the application of surface complexation theory to natural systems. Perhaps the most significant problem lies in the identification and quantification of surface functional groups in heterogeneous mixtures of mineral phases. The reactivity of functional groups among the minerals present may vary significantly, and the sorption of an ion may be controlled by interaction with the surface of a particular mineral that is present in minor or trace quantities or represents only a small fraction of the total surface area. Another problem is the definition of electrical properties and determination of model parameters for the electrical double layer. Interacting double layers of heterogeneous particles and the formation of organic coatings cause significant changes in the electrical properties of mineral-water interfaces; the techniques used in simple mineral-water systems to define surface charge densities cannot be applied in these complex systems. The determination of binding constants in laboratory experiments is complicated by variable solution compositions that may evolve from the dissolution of mineral phases and the desorption of ions. An accurate assessment of solution speciation is required to determine the binding constants and to apply them in natural systems. Guidelines for the resolution of some of these problems are presented.

Surface area and functional groups of soils and sediments

The solid phases involved in adsorption processes in natural systems are typically *composite* materials, that is, they consist of mixtures of various minerals and organic debris with a wide range of intrinsic chemical properties. Weathering reactions, diagenetic processes, and interactions with bacteria give rise to the leaching of surface layers of minerals (Casey and Brunker, this volume) and the deposition of extremely fine-grained, poorly crystalline minerals (Benson and Teague, 1982; Fritz and Mohr, 1984). These processes also lead to the formation of organic and hydroxypolymer (i.e., amorphous Al or Fe hydrous oxide) coatings on mineral grains (Jenne, 1977; Lion et al., 1982; Davis, 1984). Some important differences between well-characterized mineral phases typically used in laboratory studies and the composite materials of natural systems are illustrated in Figure 27. In many cases, the surface chemical properties of natural materials are dominated by secondary minerals and coatings, which usually constitute only a minor fraction of the whole sample (Jackson and Inch, 1989; Fuller and Davis, 1987; Davis, 1984; Fordham and Norrish, 1979). These surficial deposits are at least partly responsible for the differences observed between mineral dissolution rates in the laboratory and in natural systems (Velbel, 1986; White and Peterson, 1990).

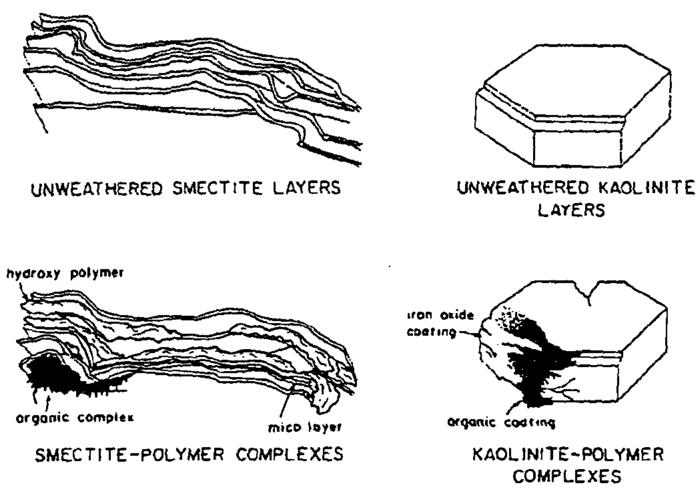

Figure 27. The unweathered smectite and kaolinite particles represent the idealized particles used in laboratory studies of adsorption reactions. Natural weathering processes can alter the surfaces of minerals, e.g., causing illitization of some smectitic layers and the acquisition of coatings of organic matter or poorly crystalline Fe and Al hydroxypolymers. Typical surfaces of natural materials are comprised of mixtures of functional groups with variable chemical properties. Reprinted from Sposito (1984), The Surface Chemistry of Soils, Oxford University Press.

The method selected for characterizing the surface area depends on the nature of the composite material and the types of interactions that give rise to the adsorptive process under investigation. For example, for samples abundant in smectites, the role of interlayer ditrigonal cavities in the adsorptive process needs to be assessed. Processes such as anion exclusion and the adsorption of major solution cations or various organic solutes respond to both external and interlayer sites on smectites. In this case, a method that evaluates interlayer as well as external surface area, such as EGME retention, is appropriate. Adsorption of anions and possibly trace cations, however, occurs primarily at external surface sites of clays (see section on "Smectites, vermiculites, and illitic micas," above). Thus, a method such as N_2 or Kr adsorption may provide a better estimate of *reactive* surface area. If the reactive surface area is dominated by potentially microporous components, such as allophane or hydroxypolymer coatings, measurements of $\mathcal{A}$ must be interpreted with caution. Analysis of gas adsorption isotherms using t- or α_s-plots is recommended for such samples, because these analyses yield estimates of the external surface area and micropore volume (Pyman and Posner, 1978; see section on "Surface Area and Porosity," above).

The solid phase-water ratios (W) in geochemical applications vary from a few $\mu g/dm^3$ in the deep oceans to several kg/dm^3 in sediments and aquifers. Given typical values for site density, this variation yields a range of 10^{-10} to approximately 0.5 Molar in the concentration of surface functional groups available for complexation with ions (Honeyman and Santschi, 1988). Ideally, the density of each type of surface functional group would be determined for surface complexation modeling. In practice, this information is usually not known for composite materials, and simplified approaches must be adopted. Balistrieri and Murray (1983) used tritium exchange (see section on "Density of surface hydroxyls," above) to estimate the total density of surface sites on some marine sediments. Later, they noted that the site densities estimated by tritium exchange agreed well with those from much simpler cation exchange measurements (Balistrieri and Murray, 1984), but the generality of this result has not been tested. As was discussed in the section on "Surface Functional Groups," these methods may overestimate the densities of *reactive* surface sites. Another method that has been used to estimate site densities of natural materials is acid-base titration (Mouvet and Bourg, 1983; Goncalves et al., 1987), but this approach is complicated by the possible dissolution of mineral phases or organic matter during the titration. Several investigators have estimated site densities directly from adsorption data, applying the Langmuir isotherm equation. Linearization of the Langmuir isotherm (Eqn. 35) has been used to obtain Γ_{max} values for phosphate adsorption on soils (Goldberg and Sposito, 1986), Na^+, K^+, Cl^-, and NO_3^- adsorption on soils (Charlet and Sposito, 1987), and Cr(VI) adsorption on subsurface earth materials (Zachara et al., 1989b). Determination of the density of surface functional groups by adsorption experiments, however, may be complicated by the low solubilities of many solutes and the release of ions from solid phases during batch experiments (Luoma and Davis, 1983). If the solubility is exceeded well before the surface sites are fully complexed, then the method cannot accurately estimate the site density.

An assessment of the predominant adsorbent(s) in a mineral assemblage often facilitates the estimate of site density for modeling purposes. For example, if hydroxypolymer coatings and poorly crystalline precipitates of hydrous iron oxides are assumed to dominate the adsorptive reactions of interest, then the site density for modeling purposes can be estimated from the abundance of these mineral phases in a sample of composite material (Payne and Waite, 1990; Belzile and Tessier, 1990; Tessier et al., 1989). Fuller and Davis (1987) identified incorporation into calcite in a sandy aquifer material as the most important sorptive process for Cd^{2+}. The site density for modeling was estimated from the weight abundance of $CaCO_3$ in the composite material and the density of $\equiv S_c$ sites on pure calcite.

If it cannot be shown that a specific mineral component dominates the adsorptive interactions of a composite material, a more general approach is needed. We believe the best approach is to multiply the measurement of *reactive* surface area by an average or typical value of site density for the major minerals present (Luoma and Davis, 1983). Based on the arguments given in the section on "Parameter estimation," we recommend a surface site density of 2.31 sites/nm^2 (3.84 μmoles/m^2) for general modeling of bulk composite materials. When applying apparent binding constants from the literature, it may be necessary to rederive the constants from the original data using a consistent value for the site density. Composite materials that have large abundances of minerals with permanent structural charge (e.g., smectites) require special consideration, both in terms of the definition and measurement of reactive surface area for the solute of interest and in the choice of surface site density.

<u>Observations of sorption phenomena in complex mineral-water systems</u>

The composite nature of mineral assemblages in soils and sediments and the variable aqueous speciation of solutes confront the researcher interested in describing sorption equilibria with a problem of considerable complexity. Experimental investigations in simple mineral-water systems have shown that there are three critical elements necessary for describing sorption phenomena (Kent et al., 1986). First, the range of aqueous speciation of the sorbing solute must be determined. Second, various chemical and physical properties of the composite materials are characterized. Third, sorption of the solute is determined experimentally for a relevent range of geochemical conditions. In the following paragraphs, we will illustrate that, in many cases, sorption of ions by soils and sediments can be understood with reference to the adsorption phenomena observed in simple mineral-water systems.

<u>Effect of aqueous composition.</u> Characterizing the speciation of solutes is central to understanding their adsorption from aqueous solutions. Identification of trends in adsorption with variations in solution composition should be established over the range of chemical conditions appropriate for the specific application. Important chemical variables include pH, ionic strength, concentration of the adsorbate, solid-water ratio, and concentrations of other solutes that either decrease or enhance the adsorption of the solute under investigation. In laboratory studies, aqueous speciation should be computed from a knowledge of the system composition and equilibrium constants for the array of complexes that can form. Monitoring the solution composition during laboratory experiments with soils and sediments is important, because elements such as Ca, Fe, Mn, Al, and Si and organic compounds can be released slowly by desorption and dissolution reactions, thereby affecting the experimental data (Goldberg and Glaubig, 1986a; Neal et al., 1987a; Davis et al., 1990). Accumulation of dissolved carbonate species can occur at high pH and have similar effects (Hsi

and Langmuir, 1985; Zachara et al., 1989b). In natural systems, thorough chemical analyses must be performed to determine the identity and concentrations of adsorbing species and potential complexing ligands, especially fulvic acids. Depending upon the nature of the application, it may be necessary to examine the influence of spatial or temporal variability in the composition of solutions or composite materials. The oxidation state of elements must also be considered, if variable. For example, Se(IV) forms strong coordinative complexes with the surface hydroxyl groups of ferrihydrite, while Se(VI) forms only weak complexes (Fig. 13). Similar observations have been made in experiments with soils (Neal et al., 1987a,b; Neal and Sposito, 1989).

The effects of solution composition on ion adsorption in simple mineral-water systems have general applicability to natural adsorbents. The importance of ionic strength on the adsorption of weakly-bound ions has been demonstrated for natural materials (Mayer and Schinck, 1981; Neal et al., 1987b; Charlet and Sposito, 1989). Unlike the findings for iron oxides, the adsorption of a strongly-bound cation, Zn^{2+}, on soils was found to depend on ionic strength (Shuman, 1986). The formation of dissolved complexes affects the adsorption of metal ions on sediments, soils, and suspended particles in the presence of natural organic material (Lion et al, 1982; Mouvet and Bourg, 1983; Davis, 1984). Studies with soils and suspended particulate matter from rivers have shown that proton dissociation reactions must be considered in characterizing the sorption of oxyanions and other weak acids (Goldberg and Sposito, 1984a,b; Goldberg and Glaubig, 1986; Shiller and Boyle, 1987; Zachara et al., 1989b).

Competitive effects need to be considered in the design of laboratory experiments and in modeling. Zachara et al. (1989b) showed that sulfate and carbonate anions compete with Cr(VI) for surface sites on subsurface soils. Neal et al. (1987b) found that Se(IV) adsorption was not affected by a large excess of sulfate, but was reduced significantly by equimolar concentrations of phosphate. Unusual synergistic effects were also observed, e.g., the enhancement of Se(IV) adsorption on soils in the presence of Ca^{2+}. Such synergistic effects of variable solution composition are difficult to predict *a priori*; these effects need to be identified in the course of characterizing adsorption trends with solution composition for specific applications.

<u>Identification of dominant sorptive mineral components in composite materials.</u> Various indirect methods have been developed to identify specific mineral components that dominate the sorption of ions on soil and sediment samples. Such studies may suggest dominant sorptive mechanisms and guide the modeling of sorption. Lion et al. (1982) studied Cd^{2+} and Pb^{2+} sorption on organic-rich sediments from San Francisco Bay (California). Chemical treatment targeted at removing organic matter had no effect on Pb^{2+} sorption behavior but reduced the sorption of Cd^{2+}. Amending the organic content of the treated sediments by adding humic material restored the Cd^{2+} sorption capacity. On the other hand, chemical treatment designed to leach Fe and Mn hydrous oxides had no effect on Cd^{2+} sorption, but reduced the extent of Pb^{2+} sorption. Based on a similar approach, Zachara et al. (1989b) suggested that Al-substituted goethite dominated the Cr(VI) sorption behavior of several subsurface soils comprised of clay minerals and hydrous Fe oxides. Aggett and Roberts (1986) observed a strong correlation of Fe and As released from As-contaminated sediments when leached with solutions containing EDTA, suggesting an association of these elements in the sediment.

The results of studies that utilize *selective extractions* must be interpreted with caution, because the chemical treatments employed are not completely selective (Lion et al., 1982; Gruebel et al., 1988). Attempts have been made to quantify the amount of trace elements associated with clay minerals, $CaCO_3$, Fe and Mn hydrous oxides, and organic matter using *sequential selective extractions* (Tessier et al., 1985). However, because the chemical treatments are not perfectly selective, and because they may allow trace elements to redistribute among other mineral phases or cause unintended redox reactions, such quantifications must be viewed with skepticism (Gruebel et al., 1988, and references therein). Such methods should be supported by isotopic confirmation that trace elements are fully desorbed during each extraction step (Belzile et al., 1989). In addition, multiple techniques and strategies should be applied to provide other evidence of particular element-mineral associations. For example, Fordham and Norrish (1979) used manual separation of minerals, autoradiography, and elemental analysis by electron microscope techniques to demonstrate a close association of As and Fe in soil samples. Lowson et al. (1986) and Waite and Payne (1990) demonstrated that the $^{234}U/^{238}U$ ratios in Tamm's oxalate extracts of subsurface profiles near uranium ore bodies were equal to the ratio of the isotopes found in the groundwater, while the U isotopic ratio of the bulk composite material was quite different. The authors concluded that dissolved U(VI) in the groundwater was in equilibrium with U(VI) adsorbed by poorly crystalline iron oxides in the composite material. Fuller and Davis (1987) showed that adsorption and coprecipitation on calcite dominated Cd^{2+} reactions with a calcareous aquifer material comprised of quartz, feldspars, calcite, and trace quantities of Fe and Mn oxides. Three methods were used in the study: selective extraction, manual separation of component minerals after sorption experiments employing a radioisotope of Cd^{2+}, and kinetic studies that determined that the rates of Cd^{2+} and Ca^{2+} sorption on the aquifer material were similar to those for pure calcite.

Trace element-mineral correlations do not prove that a mineral dominates the adsorption of a trace element in a composite material. The trace element may have been coprecipitated within a mineral and then released by dissolution of the mineral during the chemical extraction. Even when it can be demonstrated that a solute is probably at adsorptive equilibrium with a particular phase (Lowson et al., 1986), it does not mean that phase alone *dominates* adsorption by the bulk composite material. Sophisticated geochemical techniques should be applied to composite materials to provide the best understanding possible of their surface composition and quantities of surficial deposits. Hopefully, scanning Auger microscopy or other techniques can be developed for the purpose of estimating the types and quantities of surface functional groups of composite materials (see chapter on surface composition by Hochella, this volume).

Interactive effects of mineral phases. Honeyman (1984) compared adsorption measurements in experiments with binary mechanical mixtures of titania, alumina, ferrihydrite, and Na-montmorillonite to that of the individual minerals. Qualitatively, adsorption edges in mixtures were broader than those on single components, reflecting the presence of two or more sets of surface functional groups with different binding intensities. In most cases, adsorption in binary mixtures could not be predicted quantitatively by summing the adsorptive characteristics of the single components. Similar conclusions follow from the work of Altmann (1984) on Cu adsorption in binary mixtures of humic acid with geothite, rutile, or corundum. This phenomenon results from non-linear interactions between unlike particles that affect the stoichiometry and binding intensity of adsorption reactions. Simplified theoretical treatments of interacting electrical double layers of dissimilar surfaces suggest that substantially different surface potentials result from the interaction (Prieve and Ruckenstien, 1978). In addition, the work of Anderson and Benjamin (1990) gives evidence of chemical factors involved in changing surface chemical properties, based on studies of the adsorption of Ag^{+}, Zn^{2+}, Cd^{2+}, phosphate and Se(IV) on binary mixtures of Fe, Al and Si oxides. In mixtures containing Al oxides, surfaces of another mineral phase became enriched with Al, significantly altering surface chemical properties. Wiese and Healy (1975b) made similar observations in mixtures of titania and alumina.

Few conclusions can be drawn from this work at the present time for application to adsorption studies with soils and sediments. Adsorption on mixtures of minerals is likely to be somewhat less sharply dependent on pH than observed in experiments with single minerals, because of the heterogeneous surface functional groups available for complexation with ions. The relative importance of this effect is still the subject of some debate (Dzombak and Morel, 1990; Honeyman and Santschi, 1988), but the effects of adsorbed Al and Si on the surface chemistry of ferrihydrite and goethite seem significant (Anderson and Benjamin, 1990; Zachara et al., 1989b; Zachara et al., 1987). Component minerals in the assemblage will not necessarily have the same surface chemical properties in mineral assemblages that they possess in monomineralic systems. Thus, unless evidence can be given to the contrary, adsorption properties of composite materials should probably be characterized as a whole.

Special problems in sorption experiments with natural composite materials. Various physical and chemical properties of the mineral assemblage need to be considered in designing sorption experiments with soils and sediments. Most studies of sorption are conducted with batch reactors, which may allow the concentration of dissolved constituents to increase with time. A careful consideration of dissolution, precipitation and redox reactions of mineral phases over the range of pH and electrolyte concentrations used in the sorption experiments is required. At high pH, dissolution of soluble silicates can cause precipitation of metal silicates (Kent and Kastner, 1985). At low pH, dissolution of aluminum oxides can give rise to precipitation of phosphate (Veith and Sposito, 1977b; Goldberg and Sposito, 1984b). Carbonate minerals and ferrihydrite may have significant recrystallization rates, thus enhancing the formation of solid solutions at mineral surfaces via surface precipitation (Wersin et al., 1989; Davis et al., 1987; Dzombak and Morel, 1986). Characterization of the redox chemistry of the mineral phases is especially important in studies of the sorption of redox sensitive elements (White and Hochella, 1989; Eary and Rai, 1989; Rai et al., 1988).

Charlet and Sposito (1987, 1989) discussed the importance of pretreating samples to convert them to a form where all sites are populated by a particular cation or anion that can be later displaced by an adsorbing solute of interest. While the concept is of significance, it was not made clear how their procedure (saturation with $LiClO_4$) would displace strongly-adsorbed ions such as Al^{3+}. In some cases, the mineral assemblage may be contaminated with the solute whose adsorption behavior is to be determined. In these cases, it is necessary to pretreat the sample to remove the contaminant (Mouvet and Bourg, 1983) or account for the release of the contaminant in describing adsorption behavior (Goldberg and Glaubig, 1986b; Neal and Sposito, 1989). Isotopic exchange techniques can be effectively employed for this purpose (Davis et al., 1990; Payne and Waite, 1990).

A variety of sorptive mechanisms may be operative during experiments with soils and sediments. The mesoporous and microporous nature of reactive components in some materials can result in slow attainment of adsorption equilibrium (Fuller and Davis, 1989). When a strongly-bound ion diffuses into aggregated or agglomerated materials, its effective molecular diffusion coefficient may be orders of magnitude smaller than its diffusion coefficient in water (Berner, 1980), resulting in very slow equilibration. Quantification and comparison of the rates of sorption processes in laboratory and natural systems is not straightforward. Empirical rate laws have been proposed from laboratory studies (Honeyman and Santschi, 1988; Sparks, 1985), but these must be applied with caution since they have limited applicability outside the conditions under which they were determined (Helfferich, 1962). Rimstidt and Dove (1986) and Sparks (1985) discuss the importance of reactor design on the determination of rates for application to natural systems. In particular, it must be recognized that the rates of sorption processes may be limited by mass transfer in natural systems (Stollenwerk and Kipp, 1990), whereas that is often not the case in batch studies of simple mineral-water systems.

The electrical double layer of soils and sediments

Bolt and van Riemsdijk (1987) discuss the problems associated with the determination of the pH_{PZNPC} of composite materials. Acid-base titrations of soils and sediments are not expected to yield useful microscopic information as is the case in simple mineral-water systems. Kinetic effects and dissolution reactions during such titrations are expected to confound the interpretation of data; this includes the dissolution of organic matter throughout the entire pH range of titrations and dissolution of Al oxides and secondary minerals at low and high pH values (Parker et al., 1979). For didactic purposes, Bolt and van Riemsdijk (1987) simulated the titration curves that would result from combining various mineral types in mixtures, assuming no interaction. The results illustrate that the common intersection point found in acid-base titrations of simple mineral-water systems (Fig. 17) cannot be expected for many natural materials.

The determination of electrical double layer properties of composite materials was approached in a different manner by Charlet and Sposito (1987, 1989). They determined and modeled the properties of an oxisol consisting of kaolinite, gibbsite, and hematite. After a pretreatment to achieve saturation with $LiClO_4$, the adsorption of H^+ (or OH^-) and electrolyte ions was measured directly in 1:1 electrolytes (NaCl and KNO_3). The univalent electrolyte ions were assumed to be adsorbed either as outer-sphere complexes (thus contributing to σ_β in the triple layer model, TLM) or dissociated counterions (σ_d). The *point-of-zero-net-charge*, or pH_{PZNC}, is defined as the pH at which $\sigma_\beta + \sigma_d = 0$ (Sposito, 1984). The pH_{PZNC} was determined at several ionic strengths from the pH at which the adsorption densities of the electrolyte ions were equivalent. Because of the lack of minerals with permanent structural charge, $\sigma_s = 0$, and from Equation 47, the coordinative surface charge, σ_o, must also be zero at the pH_{PZNC}. The authors assumed that inner-sphere complexes were removed by the pretreatment, and hence, $\sigma_{CC} = 0$. It follows from Equation 23 that $\sigma_o = \sigma_H$, and thus, $\sigma_H = 0$ at the pH_{PZNC} given these assumptions. Thus, the pH_{PZNPC} must equal the pH_{PZNC} under these conditions.

In Charlet and Sposito's experiments, the adsorption of H^+ (or OH^-) and electrolyte ions were determined simultaneously, and curves for the variation of proton surface charge (σ_H) with pH and ionic strength could be determined once the values of the pH_{PZNPC} (= pH_{PZNC}) were known. For both the 1:1 and 2:1 electrolytes ($Ca(ClO_4)_2$, $Mg(ClO_4)_2$, and Li_2SO_4), significant adsorption of cations occurred at pH < pH_{PZNPC} and of anions at pH > pH_{PZNPC}, which attests to the heterogeneous nature of the adsorbent. For all ions except Ca^{2+}, increasing ionic strength increased the extent of adsorption; in most cases the effect was greater at pH > pH_{PZNPC} for cations and at pH < pH_{PZNPC} for anions. The authors applied the triple layer model (TLM) to the data, since this model is consistent with the observations of ion pair formation for univalent electrolyte ions at the pH_{PZNPC}. The authors used one "average amphoteric site" instead of attempting to consider the wide array of possible surface functional groups. Site density was determined by applying Equation 35 to the data. A good simulation of both the adsorption and surface charge data required that a combination of inner-sphere and outer-sphere complexes be used for the divalent ions.

The weak, but specific, interactions of electrolyte ions that are allowed within the interfacial structure of the TLM were useful for simulating the data of Charlet and Sposito (1987, 1989). It appears unlikely that simulations with the DDLM would have been as satisfactory in describing these data. Adsorption of weakly binding cations or anions occurs under conditions where the net charge on the composite material is positive or negative, respectively (Charlet and Sposito, 1987, 1989). This is consistent with the conclusion of Bousse and Meindl (1986) that proton surface charge data are only useful for the determination of ion pair formation constants. Surface acidity constants should be evaluated from measurements of surface electrical potentials or zeta potentials (Sprycha, 1989a,b). Given the interactive effects of minerals on surface potentials (Prieve and Ruckenstein, 1978), it is unlikely that the surface acidity constants can be meaningfully evaluated for composite materials. This means that the DDLM may be relatively ineffective in describing the electrical double layer properties of composite materials. Although it has not yet been tried, the TLM could be effectively used without surface ionization reactions (Eqns. 38 and 39), if estimates of the diffuse layer potential are not needed. This would effectively eliminate two of the five adjustable parameters in the interfacial model. This can be done because the proton surface charge and surface potential in the model are primarily controlled by the ion pair formation reactions (Eqns. 45 and 46).

Use of empirical adsorption models for soils and sediments

Distribution coefficients. Until the early 1980's, attempts to characterize sorption processes on natural materials focused on generating empirical parameters like distribution coefficients (K_d) or sorption ratios (R_d; e.g., Higgo and Rees, 1986; Kent et al., 1986; Duursma and Gross, 1971). The distribution coefficient (Eqn. 30) is usually determined in batch reactors by suspending a solid phase in a solution with a known concentration of solute and observing the amount of solute removed after a specified time (e.g., Higgo and Rees, 1986; Balistrieri and Murray, 1986; Nyffeller et al., 1984; Li et al., 1984). Although some authors have used a K_d value normalized for reactive surface area (e.g., Balistrieri and

Murray, 1984) or aqueous speciation (Tessier et al., 1989), in most cases, very little characterization of the solution speciation or chemical properties of the composite materials is performed. The approach involves collecting K_d values over the range of conditions encountered in the systems under investigation.

K_d values vary over several orders of magnitude with solution composition even in simple mineral-water systems. The pH is a primary variable (Tessier et al., 1989); cation and anion adsorption onto oxide minerals vary extensively with pH (Figs. 11-13). Variable concentrations of complexing ligands can cause large changes in K_d values for some metal ions (e.g., Hsi and Langmuir, 1985; Leckie and Tripathi, 1985; Tripathi 1983; Means et al., 1978). Changes in oxidation state of an adsorbing solute greatly influence K_d values, as has been shown for Pu sorption on marine sediments (Higgo and Rees, 1986). K_d values are affected by the concentrations of ions that compete for adsorption sites (Davis et al, 1990; Balistrieri and Chao, 1987) and other interactions between sorption sites and solution components (Honeyman and Santchi, 1988; Kent et al., 1986). The dependence on solution composition limits the usefulness of K_d values in systems of variable composition, such as estuaries or contaminated surface waters and groundwaters (Davis et al., 1990; Kent et al., 1986; Cederberg et al., 1985; Reardon, 1981).

Modeling based on the partitioning equation. The partitioning equation (Eqns. 36 and 37) has been applied to describe sorption processes in surface waters (Tessier et al., 1989; 1985; Honeyman and Santschi, 1988; Balistrieri and Murray, 1983). There are three parameters in the model: total site density (S_T), the apparent proton coefficient (χ), and the partitioning coefficient (K_{part}). S_T can be estimated by methods described earlier. K_{part} and χ, however, are empirical parameters. Even in simple mineral-water systems containing an oxide, one dilute solute (J), and a fixed background electrolyte, both parameters are functions of pH and adsorption density (Γ_J). These dependencies result from using a single reaction to describe the entire suite of surface ionization and complexation reactions (Honeyman and Leckie, 1986). Two methods have been used to evaluate K_{part} and χ: Kurbatov plots (Kurbatov et al., 1951) and isotherm subtraction (Perona and Leckie, 1985). Kurbatov plots are based on transforming Equation 37 to:

$$\log \frac{\Gamma_J}{\Gamma_S[J]} = \chi \cdot pH + \log K_{part} \quad . \tag{49}$$

K_{part} and χ are computed from the intercept and slope of a regression of the left hand side of Equation 48 against pH. Honeyman and Leckie (1986) have shown that Kurbatov plots are of limited applicability because the dependencies of K_{part} and χ on pH and Γ_J are not considered. The findings are significant because of a renewed interest in applying the Kurbatov method to natural systems (Belzile and Tessier, 1990; Tessier et al., 1989; 1985; Johnson, 1986; Davies-Colley et al., 1984). The better approach, isotherm subtraction, determines χ graphically using the equation:

$$\chi = \left(\frac{\Delta \log[J]}{\Delta pH} \right)_{\Gamma_J} \quad . \tag{50}$$

χ is evaluated as a function of pH and Γ_J; K_{part} can then be determined (Eqn. 37). Ignoring the variation in χ and K_{part} with pH and adsorption density can lead to large errors in the predicted adsorption of ions (Honeyman and Santschi, 1988). Adsorption data should be collected experimentally over the entire range of solution compositions and conditions of interest before this modeling approach is applied.

Johnson (1986) applied the partitioning approach in a study of Cu^{2+} and Zn^{2+} adsorption onto suspended particles in a river contaminated by acid-mine drainage. Adsorption was estimated in field samples, from determinations of dissolved and particulate Cu, Zn, and Fe, and in laboratory experiments using mixtures of acid-mine waters (pH 3) and sea water (pH 7.5). Concentrations of major and minor solutes were used to compute the speciation of Cu^{2+} and Zn^{2+}. Reactive surface area was assumed to be proportional to particulate Fe concentration. Good agreement was obtained between adsorption determined in the experimental mixtures and those in the field samples over a wide range of solution conditions (pH 3 to 7.5; water composition ranging from river water to sea water).

The partitioning approach is most appropriate for systems where the concentrations of the components of the background electrolyte are nearly invariant, such as sea water (Balistrieri and Murray, 1983) or some lakes (Tessier et al., 1989). Typically, the speciation of the dissolved solute is ignored (Honeyman and Santschi, 1988), although Tessier et al. (1989) considered the *inorganic* speciation of Zn in their analysis. Inclusion of speciation in the model enhances its applicability, especially in systems where changes in speciation occur as a function of pH.

Use of surface complexation models with soils and sediments

The use of empirical modeling approaches has been rationalized by the complexities associated with understanding sorption mechanisms in natural systems (Higgo and Rees, 1986), and until recently, only these approaches were used for applications in aqueous geochemistry. For example, when adsorption has been considered within solute transport models, distribution coefficients or isotherm equations were typically used to describe adsorption equilibria (Bencala, 1984; Grove and Stollenwerk, 1987). The advancement of surface complexation models, however, has greatly enhanced the understanding of adsorption processes, and an extension of this approach to natural systems is now beginning. The consideration of specific site-binding models that include aqueous speciation have been included in some recent solute transport models (Cederberg et al., 1985; Lewis et al., 1987; Krupka et al., 1988).

The surface complexation modeling (SCM) approach has advantages over empirical ones, even if employed in a semi-empirical manner. The advantages arise from a consideration of aqueous speciation and the sorptive reactivity of all aqueous species. As in the empirical approaches, adsorption must still be determined over the range of solution compositions expected in a field application, but the smaller number of model parameters can be incorporated within geochemical equilibrium computer codes to facilitate *interpolation* of adsorption behavior in natural systems. Clearly, *extrapolation* of adsorption behavior is not appropriate.

Modeling with the non-electrostatic SCM. Koβ (1988) used the SCM approach without EDL correction in modeling U(VI) adsorption in groundwater systems, using an average surface site for the composite aquifer materials, with site density estimated from the cation exchange capacity. Adsorption was described with a single equation, i.e.,

$$\equiv SOH + UO_2^{2+} \leftrightarrow \equiv SOUO_2^+ + H^+ \quad . \tag{51}$$

Mouvet and Bourg (1983) carried this simplified SCM approach a step further by considering two types of surface functional groups for suspended particulate matter in a contaminated river system. The authors compared laboratory determinations of Zn^{2+}, Cu^{2+} and Cd^{2+} sorption on suspended particles collected from the river with field measurements. Estimates of adsorption in the field were made by measuring dissolved and particulate concentrations of the metals. The concentrations of major dissolved cations and anions, as well as humic acid, were determined. Aqueous speciation computations accounted for complexation of the metals with carbonate, sulfate, chloride and humic acid ligands. Surface site density and apparent binding constants were adjusted to fit the laboratory data. Good agreement between predicted and measured adsorption for Zn^{2+} was obtained without further manipulation. Successful simulations of Cu^{2+} adsorption, however, required adjustment of the complex formation constant of the dissolved Cu-humate complex and introducing an additional equation for formation of a ternary complex involving Cu, humate, and surface hydroxyl groups. A similar modeling approach was used by Davis (1984), who found that the Cu complexation by adsorbed fulvate ligands had essentially the same stability constants (and pH dependence) as Cu-fulvate complexes in solution.

Fuller and Davis (1987) described the sorption of Cd^{2+} by a calcareous aquifer material suspended in artificial groundwater, with or without added EDTA, using the SCM approach without EDL correction. In the absence of EDTA, Cd^{2+} sorbed extensively on the aquifer material. Cd-EDTA complexes, however, did not sorb. Adsorption, at the early stage of the sorption process, was described by the reaction:

$$Cd^{2+} + \equiv S_c \leftrightarrow \equiv S\text{–}Cd^{2+} \quad , \tag{52}$$

where $\equiv S_c$ denotes a calcite surface site. Sorption of Cd^{2+} varied with pH due to dissociation of Cd-EDTA complexes. Inclusion of a pH-independent binding constant for Equation 52 in a computation of Cd speciation in the presence of the aquifer material, artificial groundwater, and EDTA gave good agreement with the adsorption data throughout the pH range studied. Site density was estimated from calcite content and the calcite surface site density. The binding constant found for the composite material using Equation 52 had the same value as that found for Cd^{2+} adsorption on pure calcite (Davis et al., 1987).

Modeling with electrical double layer corrections. The constant capacitance model (CCM) has been applied by Goldberg and coworkers (Goldberg and Sposito, 1984b; Goldberg and Glaubig, 1986a) to simulate sorption of phosphate and borate on soils. For the phosphate sorption study, published investigations of phosphate sorption onto non-calcareous, non-allophanic soils were modeled. $\mathcal{A}$ and total site density from the original studies were used when reported, otherwise they were estimated from phosphate sorption data. Average values for K_+^{CCM}, K_-^{CCM}, and C^{CCM} had previously been determined for a variety of Fe and Al oxides over a range of ionic strengths (Goldberg and Sposito, 1984a). These values were used for modeling phosphate sorption on the soils. Following the same methods used to model phosphate adsorption onto hydrous oxides, apparent binding constants for three surface complexation reactions were derived by fitting experimental data for each soil (44 in all), i.e.,

$$\equiv SOH + H_3PO_4 \leftrightarrow \equiv SOPO_3H_2 + H_2O \tag{53}$$

$$\equiv SOH + H_3PO_4 \leftrightarrow \equiv SOPO_3H^- + H_2O + H^+ \tag{54}$$

$$\equiv SOH + H_3PO_4 \leftrightarrow \equiv SOPO_3^{2-} + H_2O + 2H^+ \quad . \tag{55}$$

Values for the apparent binding constants obtained for each soil were averaged to obtain a single value for each of the three binding constants. Model fits to the data were quite good. The lack of sensitivity of the values of the phosphate binding constants to the values of K_+^{CCM} and K_-^{CCM} had previously been established (Goldberg and Sposito, 1984a) and is consistent with the hypothesis that the electrostatic contribution to the free energy of adsorption for strongly-binding ions is small. Thus, it is possible that similar success could have been achieved with the non-electrostatic SCM.

A similar approach was used to simulate borate adsorption onto a variety of soils (Goldberg and Glaubig, 1986a). A single binding constant was used with stoichiometry analogous to that of Equation 53. For some soils, it was necessary to adjust K_+^{CCM} and K_-^{CCM} to optimize the fit. This is consistent with the hypothesis that, as a weakly adsorbing solute, the binding of borate is more sensitive to the electrostatic terms. Considering the variety of soil compositions and electrolyte compositions, it is encouraging that good model simulations could be obtained with a single type of binding site.

SCM modeling to dominant adsorptive components of composite materials. Some investigators have applied the SCM approach to a specific mineral phase of composite materials to simulate ion adsorption on soils or sediments. Payne and Waite (1990) applied this approach to describe the adsorption of U(VI) on ferrihydrite present in two subsurface samples derived from cores within the vicinity of U ore bodies. One sample (Koongarra) was a highly weathered schist composed of quartz, kaolinite, vermiculite, goethite, hematite, and aluminum oxides. The other (Ranger) contained smectite, kaolinite, quartz, mica, goethite, hematite, and anatase. Adsorptive equilibrium of U(VI) with ferrihydrite was suggested by equal $^{234}U/^{238}U$ ratios in the groundwaters and oxalate extracts of the composite materials, while the isotopic ratio of the bulk samples were quite different. Dominance of the adsorptive reactions by ferrihydrite was assumed. The authors applied the TLM, using the binding constants and EDL parameters derived in the study of Hsi and Langmuir (1985) without further manipulation. In that study, it was found that the adsorption of two U(VI) carbonate complexes, i.e., $UO_2(CO_3)_2^{2-}, UO_2(CO_3)_4^{4-}$, had to be considered to fit model simulations with experimental data. Differences in the aqueous conditions in the study by Payne and Waite resulted in some solution compositions in which $UO_2(CO_3)^0$ was the predominant dissolved species of U(VI). To describe their data fully, it was necessary to add an additional adsorption reaction for this species. The binding constant for this species was derived with data from the Ranger subsurface sample. Interestingly, the same set of binding constants described U(VI) adsorption by the Koongarra sample, even though the ferrihydrite abundances in these samples were substantially different. It is surprising (and encouraging) that surface complexation modeling could be applied to these composite materials with binding constants derived from experiments with synthetic ferrihydrite: It suggests that the limitations caused by the interactive effects of mineral phases (Anderson and Benjamin, 1990; Altmann, 1984; Honeyman, 1984) may not always be significant.

The most sophisticated application of surface complexation modeling to natural materials has been performed by Zachara et al. (1989b). Adsorption of Cr(VI) on three subsurface soils was modeled using the TLM, based on a companion study of Cr(VI) adsorption onto Al-substituted goethite (Ainsworth et al., 1989). The soils were primarily composed of clay minerals, micas, and hydrous oxides, with very low organic matter and carbonate contents. Cr(VI) adsorption edges were obtained over modest ranges of ionic strength, soil-water ratios (W), Cr(VI) concentration, and concentrations of competing anions (carbonate and sulfate). Modeling focused on the role of hydrous Fe and Al oxides, which were thought to dominate the adsorptive interactions of Cr(VI) with the subsurface soils. Adsorption on Al-substituted goethites was modeled with a two site model whereby Cr(VI) was allowed to adsorb on both $\equiv$FeOH and $\equiv$AlOH functional groups. Each group had its own set of surface ionization, electrolyte binding, and Cr(VI) binding constants. Cr(VI) adsorption on each site was modeled with two reactions, i.e.,

$$\equiv FeOH + CrO_4^{2-} + H^+ \leftrightarrow \ \equiv FeOH_2^+{-}CrO_4^{2-} \tag{56}$$

$$\equiv FeOH + CrO_4^{2-} + 2H^+ \leftrightarrow \ \equiv FeOH_2^+{-}HCrO_4^- \tag{57}$$

$$\equiv AlOH + CrO_4^{2-} + H^+ \leftrightarrow \ \equiv AlOH_2^+{-}CrO_4^{2-} \tag{58}$$

$$\equiv AlOH + CrO_4^{2-} + 2H^+ \leftrightarrow \ \equiv AlOH_2^+{-}HCrO_4^- \ . \tag{59}$$

Surface ionization and electrolyte binding constants were taken from previous investigations on pure Fe and Al hydrous oxides in the same background electrolyte ($NaNO_3$). Apparent binding constants for Cr(VI) adsorption on $\equiv$AlOH and $\equiv$FeOH sites were obtained by modeling adsorption data onto corundum and goethite, respectively. With the exception of Cr(VI) binding constants on $\equiv$AlOH sites, all the same parameters were used to model adsorption onto subsurface soils. The functional group density was varied to optimize the fit to Cr(VI) adsorption data at one Cr(VI) concentration and soil-water ratio (W). The model was then applied to other data sets by scaling the site density to the reactive surface area of Fe and Al oxides. The binding constants of Cr(VI) with $\equiv$AlOH were adjusted also. Simulated Cr(VI) adsorption agreed well with the experimental data over most of the range of pH, ionic strength, and solids concentrations studied. Deviations were confined to low pH, where the model simulations underestimated Cr(VI) adsorption because the site density was too small. Competition with sulfate and carbonate was modeled using previously derived binding constants for these ions on ferrihydrite (Zachara et al., 1987); site density was again used to optimize the fit. The model simulations matched the data closely in the pH range 6 to 9. At lower pH values, actual Cr(VI) and sulfate adsorption exceeded the site density used in the model. The results demonstrate the ability of a heterogeneous, two-site surface complexation model to broaden the range of model applicability. In addition, these studies illustrate how one can optimize model simulations to fit adsorption data in ranges of solution composition that are of highest priority for specific applications.

Guidelines for surface complexation modeling with natural composite materials

A review of the studies that have applied surface complexation theory to the complex mixtures of phases present in natural materials suggests that the most important aspect of the work is detailed characterization of the solid phases and their surface composition. The best model simulations of experimental data or predictions of adsorption coupled with transport will probably be performed when the solid phases that dominate adsorptive interactions are known. Identifying the dominant adsorptive phases facilitates evaluating the stoichiometry of the adsorption process (see section on "Surface Functional Groups," above). It is well accepted in aqueous geochemistry that a thorough analysis of water composition is required to compute aqueous speciation as part of solute transport or geochemical flowpath modeling. By analogy, in surface complexation theory, surface functional groups are the reactants with ions that determine surface speciation, and a thorough understanding of the concentration (surface density) and types of functional groups is needed to calculate the effects of adsorption equilibria on aqueous composition. Therefore, studies involving the adsorption of ions by composite materials should first focus on the surface composition of the bulk material and techniques that can be applied to identify particular components of the solid phases that may dominate adsorptive interactions. The significance of interactive effects of mineral phases is not well understood; in two cases involving strongly-binding ions (Fuller and Davis, 1987; Payne and Waite, 1990), the effects appeared minimal. On the other hand, the effects were more substantial in the study of weakly-binding Cr(VI) conducted by Zachara et al. (1989b). Thus, the question of the applicability of binding constants found in simple mineral-water systems to mineral components of composite materials needs further research. In addition, systems in which organic functional groups dominate surface complexation are still poorly understood and deserve special attention, because of their likely significance in many natural systems. In the absence of evidence of adsorptive dominance by a particular component, the bulk composite material can be modeled as a whole. In this case, particular attention needs to be paid to a determination of the *reactive* surface area for the adsorptive interactions of particular solutes.

Given the complexity of natural materials, it can be argued that the simplest surface complexation model should be applied for modeling purposes. The non-electrostatic surface complexation model is clearly the simplest; this is especially true given the difficulties involved in the determination of double layer model parameters for natural materials. However, this model has not been widely used and its performance and general applicability cannot be evaluated. Simulations with the non-electrostatic model in simple mineral-water systems exhibited less pH dependence than experimental adsorption data (Krupka et al., 1988). On the other hand, the pH dependence of ion adsorption on heterogeneous materials has been shown to be less dependent than found in simple mineral-water systems. The non-electrostatic model would be best applied to strongly-binding solutes, i.e., those solutes whose adsorptive interactions exhibit little ionic strength dependence. The approach could be enhanced by inclusion of a two-site Langmuir model to allow for site heterogeneity and consistency with observed Freundlich isotherms for metal ion adsorption.

Ideally, an electrical double layer model would be included in applications of surface complexation theory. For weakly-binding solutes, electrostatic correction factors to the mass law equations for adsorption equilibria appear necessary. However, an assessment of surface electrical potentials and other double layer properties of soils and sediments is extremely complex. For modeling bulk composite materials, the flexibility of the TLM model appears preferable because the proton surface charge is defined primarily by the adsorption of electrolyte ions, which can be determined experimentally (Charlet and Sposito, 1987; 1989). However, if a particular mineral phase dominates adsorptive interactions, then either the DDLM or TLM may be applied if binding constants from the literature are available.

A convenient modeling approach for seawater uses apparent binding constants that incorporate pH effects, ionic strength activity coefficients, and electrostatic corrections within the constant (Dzombak and Morel, 1987; Luoma and Davis, 1983; Balistrieri and Murray, 1983). If the speciation of dilute ions is to be considered (e.g., complexes with organic molecules), it can be argued that the constant capacitance model (CCM) is most appropriate for simulating dilute ion adsorption in marine systems. The constant ionic medium Reference State is used in this model, and thus, binding constants can be determined in laboratory experiments in artificial seawater without need for further activity corrections. However, for model simulations of trace element scavenging in the deep oceans, it may be necessary to derive binding constants from laboratory experiments conducted under unusual conditions, e.g., at very low solid-water ratios (Honeyman and Santschi, 1988; Chang et al., 1987) or with free metal concentrations buffered at low values (Hunter et al., 1988).

For some applications, it may be necessary to examine the spatial variability of the surface chemical properties of composite materials. Neal et al. (1987a,b) examined the role of adsorption processes on the mobility of Se(IV) in alluvial soils in the San Joaquin Valley (California), an area affected severly by Se contamination from agricultural drain waters. Soil samples from a variety of environments in the San Joaquin Valley were examined. In the acidic pH range, Se(IV) adsorption correlated with the amounts of readily soluble Fe, Mn, and Al, suggesting the importance of oxide and hydroxypolymer coatings in the adsorptive interactions. No differences were observed between various soils in the alkaline pH range. In contrast, Zachara et al. (1989b) showed that Cr(VI) adsorption on subsurface materials increased with increasing Fe and Al oxide content and decreasing soil pH. A sample with a soil pH of about 10.6 did not adsorb Cr(VI) even at low pH. Our research group is conducting an investigation of the transport of Zn, Ni, Cr, and Se in oxic and suboxic zones of a shallow, sewage-contaminated, sand and gravel aquifer (e.g., Davis et al., 1989; 1990; Kent et al., 1989). Under identical aqueous conditions, Cr(VI) adsorption differs on subsurface materials collected from oxic recharge and suboxic, sewage-contaminated zones. These trends correlate with differences in the abundance of Mn oxides and poorly-crystalline Fe oxides in the different zones.

CONCLUDING REMARKS

Surface complexation theory has become increasingly popular for describing ion adsorption in simple mineral-water systems. The attractive feature of the theory is that it adopts the formalism of ion association reactions in solution as a representation of adsorption reactions at the mineral-water interface. The nature of surface functional groups is of primary importance because it determines which ions are typically exchanged for an adsorbing ion, e.g., H^+ for cations on hydrous oxides, Ca^{2+} for cations on calcite, Na^+ and H^+ for cations on montmorillonite. This characteristic, in turn, governs the ways in which adsorption on various minerals varies as a function of solution composition. Ion adsorption on oxides is highly dependent on the pH, but in addition, the ionic strength of solutions has now been demonstrated as an important variable that characterizes adsorption. Those ions whose adsorption is independent of ionic strength are strongly-bound ions that form inner-sphere coordination complexes with surface functional groups. Like complex formation in aqueous solution, the free energies of adsorption of these ions is dominated by covalent bonding rather than electrostatic attraction. Conversely, those ions that exhibit a dependence of adsorption on ionic strength are weakly-bound ions that form outer-sphere complexes with surface functional groups. Adsorption of these ions is more dependent on electrostatic attraction, which is revealed by the relationship between ionic strength and electrical potentials in the EDL. The major ions in natural waters are typically weakly-bound ions, whereas trace elements and many inorganic contaminants are strongly-bound ions. Although the effects of many variables on adsorption equilibria are now well documented, the stoichiometry of H^+ in surface complexation reactions and the temperature dependence of adsorption equilibria are still poorly understood.

A governing paradigm for the application of surface complexation theory to natural systems has not yet been fully developed. Two approaches have been used: (1) treatment of composite materials as an integrated whole with adsorption described as complexation with average surface functional groups or (2) consideration of a specific mineral surface in composite materials that is proposed to dominate adsorptive interactions. More experience is needed with each of these approaches before either can be accepted or rejected as expedient methods. Application of the second approach appears preferable, but this will require the development of more sophisticated techniques for characterizing surface composition and a greater understanding of how particle-particle interactions in heterogeneous systems affect adsorption behavior. Ideally, the results of such techniques could be interpreted in terms of the quantities of various types of surface functional groups. Based on experience with simple systems, it can be concluded that models with at least two types of sites (high and low energy) will probably need to be applied, because of the general observations of Freundlich isotherms for strongly-bound cations.

Considerable research effort has been expended by various groups to demonstrate the superior performance of particular interfacial models. Evolution of model implementations has narrowed their differences. Experience with simulating experimental data suggests that comparisons of model performance in simple mineral-water systems is a secondary consideration in evaluating model applicability to natural systems. Each of the models appears to have specific strengths and weaknesses when evaluated in terms of applicability to various geochemical environments. Given the complexities involved in describing the electrical double layer properties of soils and sediments, it is not surprising that interest in the non-electrostatic surface complexation model has been revived. This simplified description of surface complexation equilibria can be more easily incorporated in computationally intensive megamodels, e.g., solute transport models that are coupled with geochemical equilibrium speciation models. As a first approximation, it is certainly preferable that adsorption reactions be considered in this manner rather than lumped into empirical parameters as has been done previously.

Many of the experimental techniques that are used to characterize adsorption and electrical double layer properties in simple mineral-water systems cannot be applied in a straightforward manner to soils and sediments. For example, the methods commonly used to estimate surface functional group densities (tritium exchange, acid-base titration, and adsorption isotherms) may suffer from experimental artifacts when applied to natural materials. Based on a review of the important adsorbing mineral phases and arguments for a parsimonious modeling approach, a value of 3.84 μmoles/m^2 for total site density is recommended for future modeling applications. Because the fit of model simulations to experimental data is relatively insensitive to the value chosen, it is more important that a universal value be adopted for modeling than it is that accurate site densities be used for each mineral surface in a composite sample. The acceptance of a general value for the site density will aid the intercomparison of future studies and allow the development of a self-consistent database of apparent binding constants for specimen minerals. It is emphasized that the values of binding constants in surface complexation models are dependent on the value chosen for total site density, as well as the interfacial model. To apply this value for total site density, it is necessary to measure the reactive surface area. A review of literature on this subject suggests that gas adsorption techniques yield the most useful information when applied carefully, including estimates of external surface area and an evaluation of the extent of microporosity.

The experimental techniques employed to determine apparent binding constants may also be subject to artifacts when applied to natural materials. Complex and unpredictable interactive effects have been observed even in simple mineral-water systems as the solution composition was varied. Precipitation reactions, slow kinetics, and organic materials may confound the interpretation of adsorptive equilibrium in laboratory experiments conducted with soils and sediments. Adsorption may be only the first of a series of reactions that remove an ion from water. Subsequent reactions, e.g., redox reactions and surface precipitation, may occur on time scales only slightly longer than adsorption, thereby invalidating an assumed equality of sorption and adsorption in the experiment. Whenever possible,