



Chapter 7

METAL SORPTION ON MINERAL SURFACES: AN OVERVIEW WITH EXAMPLES RELATING TO MINERAL DEPOSITS

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INTRODUCTION

Sorption reactions, involving both inorganic and organic particulates, are an important control on the transport and fate of many trace elements in natural systems. Understanding the controls on trace-element concentrations in waters is critical for a number of applications including the transport of contaminants and nutrients, geochemical prospecting, agriculture, municipal and industrial water treatment, and bioavailability to name a few. This chapter provides an overview of metal sorption on mineral surfaces and gives examples of predictive modeling of metal-sorption reactions in mine-drainage systems.

The word “sorption” is a general term that describes removal of a solute from solution to a contiguous solid phase and is used when the specific removal mechanism is not known. “Sorbate” or “adsorbate” refers to the solute that sorbs on the solid phase. “Sorbent” or “adsorbent” is the solid phase or substrate onto which the sorbate sorbs. “Adsorption” refers to the two-dimensional accumulation of an adsorbate at a solid surface. In the case of “surface precipitation,” there is a three-dimensional accumulation of sorbate at the solid surface. The term “absorption” is used when there is diffusion of the sorbate into the solid phase. Absorption processes usually show a significant time dependency. Sposito (1986) and Jenne (1998) provide a more detailed description of these terms. In this chapter, the term adsorption is used when describing laboratory studies with simple, well-characterized systems, and when discussing models that have been developed to describe adsorption phenomena.

PRINCIPLES OF SORPTION REACTIONS

Trace elements partition between dissolved and particulate phases and this partitioning can influence their transport and bioavailability (Luoma and Davis, 1983; Jenne and Zachara, 1987). Sorption processes probably limit metal mobility in most natural aqueous systems (Jenne, 1968; Hem, 1985). Partitioning of a metal between solid and solution phases is influenced by several factors. Generally, low-pH conditions, reducing conditions, low particulate loads, and/or high dissolved concentrations of a strong complexing agent cause metals to be present in the solution phase. Typically, pH is the most important control of metal partitioning. In general, sorption reactions depend on solution pH, sorbate identity and concentration, presence of competing sorbates, formation of solution complexes, sorbent composition, and the concentration of surface-binding sites on the sorbent.

Properties of important sorbent materials

Often, the most effective sorbent materials are secondary minerals that form from the weathering of primary minerals. Jenne (1968) noted that hydrous oxides of manganese and iron, as well as reactive particulate carbon, appear to be the principal controls on metal sorption in soils and fresh-water sediments. In addition, hydrous oxides of aluminum and silicon, and clay and zeolite minerals may contribute to the sorption potential of a soil or sediment (Jenne, 1977). Hydrous metal oxides and organic matter are ubiquitous in most natural systems and often exist as coatings on clay-size minerals in soils and sediments. These coatings likely give rise to the high metal sorption potential commonly observed for clay-size fractions. Consequently, because clay-size minerals often are coated in natural systems, it is difficult to assess their actual contribution to the metal-sorption potential of soils and sediments. Surface area is another consideration that will be discussed later.

The process of sorption involves interactions between a sorbate and a sorbent at the surface-water interface. Hence, surface properties of the sorbent(s) play an important role in the sorption process. Some earth materials are much better sorbents than others. This is related both to their capacity to bind metals and to the intensity with which they bind metals. A sorbent’s capacity to bind metals depends both on the number of metal-binding sites present, “binding-site density,” and on the amount of metal-accessible surface, “specific surface area.” The metal-binding intensity is related to the strength of interaction between the sorbate and sorbent, and can be expressed as a binding constant. The relative importance of various earth materials in sorption reactions is also dependent on their abundance.

Surface functional groups

Functional groups on mineral surfaces are the binding sites for sorption reactions. A surface functional group is “a chemically reactive molecular unit bound into the structure of a solid at its periphery such that the reactive components of the unit can be bathed by a fluid” (Sposito, 1989). Figure 7.1 illustrates the surface layer of a metal-oxide mineral. Metal-oxide minerals comprise some of the most important sorbent minerals in natural systems. Surface molecules have fewer nearest neighbors than bulk molecules and are not fully coordinated. When a metal-oxide mineral comes into contact with water, hydroxyl functional groups (OH⁻) form on the surface. This is due to the chemisorption (Fig. 7.1b) and subsequent hydrolysis (Fig. 7.1c) of water molecules at

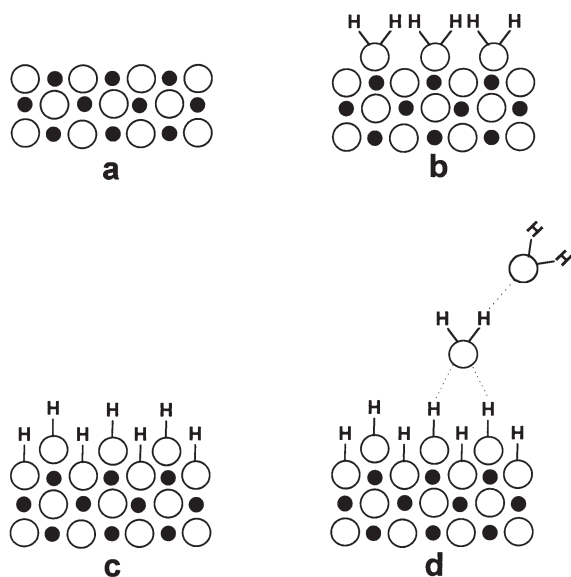


FIGURE 7.1—Cross section of the surface layer of a metal-oxide mineral. Filled circles are structural metal ions, open circles are oxide ions. (a) Unhydrated surface. (b) Surface metal ions coordinated with H₂O molecules. (c) Hydroxylated surface formed from the dissociation of protons from sorbed H₂O molecules. (d) Water sorption on the hydroxylated surface. Modified from Schindler (1981) and Dzombak and Morel (1990).

the mineral surface. Additional water can sorb on the hydroxylated surface. Figure 7.1d shows a hypothetical mechanism to form structured water at the oxide-water interface (McCafferty and Zettlemoyer, 1971). A variety of functional groups may be present on organic compounds including carboxyl (-COO⁻), amine (NH₃⁺), and sulfhydryl (-SH) groups (Macalady and Ranville, 1998).

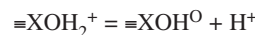
Surface-charge development

Interfacial regions between different phases have unique properties. Forces acting at solid-solution interfaces are extensions of forces within the individual phases. Solid surfaces acquire an electrical charge when in contact with an aqueous phase. This surface charge produces a microenvironment of electrical potential imbalance at the solid-solution interface that influences the distribution of neighboring ions. The charged surface attracts ions of opposite charge, “counterions,” and repels ions of like charge, “coions.” Macroscopically, there must be charge balance between the total net charge of the solid surface and solution to preserve electroneutrality.

Stumm and Morgan (1996) describe three principal origins of surface charge including: (1) chemical reactions at the surface of the particle; (2) crystalline imperfections, broken bonds, and isomorphous replacements within the crystal lattice; and, (3) sorption of a surface-active ion. There are two idealized end members for the origins of surface charge: (1) “variable surface charge” (e.g., hydrous metal oxides, organic matter, edges of clay minerals), where the surface charge is dependent on the composition of the surrounding solution, but the magnitude of the surface potential is not affected by the presence of indifferent electrolytes; and, (2)

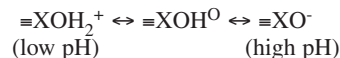
“constant surface charge,” which is approached by layer clay minerals such as smectite, where the surface charge is independent of the surrounding solution composition (van Olphen, 1977; Stumm and Morgan, 1996; Langmuir, 1997). Many minerals exhibit combinations of these idealized end-member types of charge distribution. The type of particulate surface (i.e., variable charge or constant charge) affects the environmental behavior of the particulates. For example, the cation exchange capacity (CEC) of a soil containing variable-charge surfaces increases with increasing pH. Consequently, liming the soil will increase both pH and CEC. However, it is difficult to raise the pH of a variable charge soil above 6.5 because H⁺ ions are released from the hydroxylated soil surfaces, which in turn will neutralize OH⁻ (Singh and Uehara, 1986). The type of surface also influences the stability of suspended particulates (flocculation status). See Ranville and Schmiermund (1999) for discussion of particle stability.

Variable surface charge—Many hydrous metal oxides and organic materials contain ionizable functional groups at their surfaces. Surface charge can develop as a result of the dissociation of these functional groups. The charge on particles is usually expressed as a surface density (units of charge per unit area). Proton exchange reactions for surface functional groups of metal-oxide minerals are expressed as:



where $\equiv\text{XOH}^0$ is a surface-binding site, and $\equiv\text{XOH}_2^+$ and $\equiv\text{XO}^-$ are proton-exchange surface complexes.

The charge at the surface is dependent on the pH of the surrounding water. Neutral or alkaline pH conditions generally will result in a net negatively charged surface. Conversely, under acidic conditions, excess protons generally are retained at the surface yielding a net positively charged surface as illustrated below:



(Parks, 1990). It is important to keep in mind that at almost any pH there is a distribution of positively, negatively, and neutrally charged species at mineral surfaces. At some intermediate pH, termed the “point of zero charge (PZC),” the net surface charge will be equal to zero such that:

$$[\equiv\text{XOH}_2^+] = [\equiv\text{XO}^-]$$

(Lewis-Russ, 1991; Sverjensky, 1994). Table 7.1 lists the PZC for several minerals. The surface charge may have an effect on the distribution of neighboring solutes in that decreasing the pH (more acidic) of the surrounding water will attract anionic species from solution. Conversely, increasing pH (less acidic) will attract cationic species from solution.

Constant surface charge—The constant surface charge or permanent charge case is most applicable to clay minerals that have lattice imperfections and(or) nonstoichiometric isomorphous substitution of cations within their lattice. These clay minerals

possess a net-negative charge deficiency. Sorption of interlayer cations may compensate for this deficiency. Owing to the fact that one ion may be replaced by another ion to compensate for charge imbalances, the term “cation exchange” often is used instead of sorption when speaking of constant surface charge situations.

TABLE 7.1—Point of zero charge (PZC) for a variety of minerals.

Mineral	pH _{PZC} ⁽¹⁾
Fe ₂ O ₃ •H ₂ O (amorphous) (hydrous ferric oxide)	8.1
α - FeOOH (goethite)	6–7
α - Fe ₂ O ₃ (hematite)	4.2–6.9
α - Al(OH) ₃ (gibbsite)	10
δ - MnO ₂ (birnessite)	1.5–2.8
SiO ₂ (amorphous)	3.5
Kaolinite	4.6
Montmorillonite	2.5

⁽¹⁾These values were determined by different researchers often using different methods and electrolyte solutions.

Physicochemical properties

Knowledge of sorbent properties such as particle size and shape, particle-size distribution, crystallinity, chemical composition, surface area, porosity, and numbers and types of surface functional groups is necessary for the interpretation and mechanistic modeling of sorption data. James and Parks (1982) review experimental methods and data for the physicochemical characterization of minerals. It is important to keep in mind that the chemical and physical properties of a bulk material are different from the chemical and physical properties of its surface (Hochella, 1990).

Composition and crystallinity—X-ray diffraction, microscopic, and spectroscopic techniques commonly are used to examine the composition and crystallinity of sorbent materials. Generally, the more crystalline a sorbent material, the less sorption capacity it has for metals. Recent advances in several spectroscopic techniques provide opportunities to gain a better understanding of surface composition and microtopography of sorbent materials (Hochella, 1990).

Surface area—Metal sorption by soils and sediments generally increases with decreasing grain size; this relationship is due to increasing surface area with decreasing grain size (Sposito, 1984; Ranville and Schmiermund, 1999). Horowitz and Elrick (1987) report a correlation between sediment surface area and trace-element content indicating that trace element incorporation into sediments may be primarily due to sorption.

Specific surface area is the amount of reactive surface area available for sorbing solutes per unit weight of the sorbent (Davis and Kent, 1990). Knowledge of the specific surface area is necessary for calculation of layer charges and potentials in many surface-complexation models. It can be determined by a number of techniques including gas adsorption, negative adsorption, adsorption from solution, and theoretical calculations (Gregg and Sing, 1982). Surface area measurements frequently are used to estimate adsorption binding site densities of minerals, but there are several potential limitations to this approach (White and Peterson, 1990; Chiou and Rutherford, 1993).

Influence of solution composition

The solution composition can influence sorption reactions on adjacent solid surfaces. For example, dissolved constituents can compete with the solid surface for sorbate ions, compete with sorbate ions for surface-binding sites, and bind to different surface sites and alter the surface properties. Consequently, it is essential to perform thorough chemical analyses to characterize the system and determine the presence and concentration of sorbate solutes and potential complexing species.

pH

For surface-binding reactions of metals on oxide minerals, solution pH is a master variable. Typically, cation adsorption increases with increasing pH from near zero to nearly 100% over a pH range of 1 to 2 units (James and Healy, 1972c; Kinniburgh and Jackson, 1981; Davis and Hayes, 1986). This pH region is termed the “adsorption edge” and its placement seems to be characteristic of the particular adsorbate and, to a lesser extent, to the particular adsorbent as well as to the concentrations of surface binding sites and adsorbate (Spark et al., 1995). The adsorption edge is illustrated on Figure 7.2. Anion adsorption is the mirror image of cation adsorption in that anion adsorption tends to decrease with increasing pH. For a given adsorbate concentration, increasing the amount of adsorbent material will shift down the pH of the adsorption edge for cations and shift up the pH of the adsorption edge for anions (see Fig. 7.2). Conversely, increasing the concentration of a cationic adsorbate for a given amount of adsorbent will shift the adsorption edge to higher pH values. This phenomenon is termed the “loading effect.” The loading effect may be an artifact of diffusion processes and disequilibrium (Axe and Anderson, 1998).

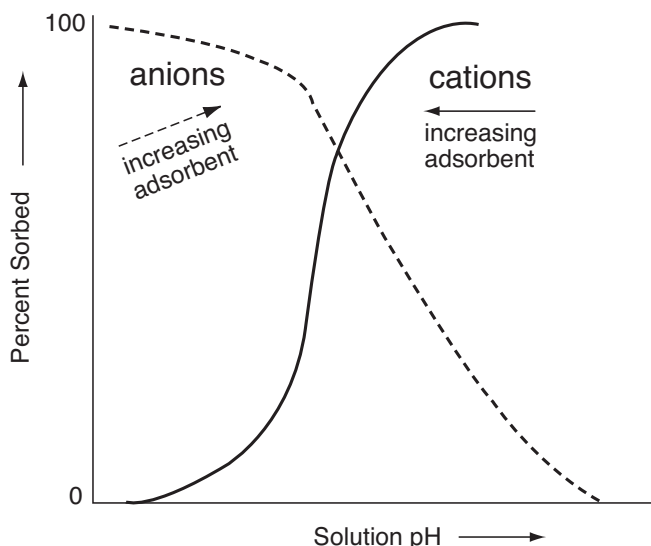


FIGURE 7.2—Generalized adsorption edge for cation (solid curve) and anion (dashed curve) adsorption on a metal-oxide mineral. For a given solute concentration, the adsorption edge will shift in the direction of the arrows with increasing adsorbent content.

Solute speciation

Complexation of metals by dissolved ligands can either enhance or inhibit sorption reactions (Davis and Leckie, 1978a). Generally, metal complexation with inorganic ligands tends to inhibit metal sorption. Zachara et al. (1989) report that surfaces and aqueous carbonate compete for Cr(VI) in soils. Smith and Langmuir (1987) and Smith (1986) observed similar competition between goethite surfaces and aqueous carbonate complexes for Cu and Pb, and Hsi and Langmuir (1985) for uranyl ion. Metal complexation by organic ligands with more than one functional group or by some inorganic ligands (such as SCN^- and $\text{S}_2\text{O}_3^{2-}$) often enhances metal sorption due to bonding of the other functional groups to the solid surface (Benjamin and Leckie, 1982).

Competition effects for surface-binding sites can be important in sorption reactions. Often, competition effects are not observed until one of the sorbates is in large excess (Benjamin et al., 1982). Hence, competition effects are most often noted when the surface-binding sites are nearly saturated.

Different redox states of a metal have different sorption affinities (e.g., As(III) versus As(V) and Se(IV) versus Se(VI)). For example, Bowell (1994) notes that reduction of As(V) to As(III) in mine tailings can lead to greater leaching of As due to a reduction in sorption on iron-oxide minerals. Balistrieri and Chao (1990) report stronger sorption of Se(IV) than Se(VI) on amorphous iron oxyhydroxide and manganese dioxide. Consequently, Se(VI) generally is more mobile in natural systems. Davis et al. (1993) discuss redox states and sorption affinities of metals in ground water.

Temperature

Most sorption studies are conducted at room temperature or carefully regulated at 20 or 25°C. Therefore, few studies address the temperature dependence of sorption reactions. Several factors can affect the temperature-dependence of sorption reactions. First, aqueous speciation of the sorbate solutes is temperature dependent, which will in turn affect sorption reactions. Also, the surface charge of the sorbent material is temperature dependent and the point of zero charge of metal-oxide minerals appears to increase as temperature decreases (Machesky, 1990). This has the effect of allowing more positively charged surface-binding sites to be present at a given pH. The degree of hydration of sorbent minerals may change with temperature (Avotins, 1975; Harter, 1991). Observations show that specific sorption of anions tends to increase and that of cations tends to decrease with decreasing temperature (Machesky, 1990). Based on this information, seasonal temperature fluctuations could impact sorption reactions in natural systems. Therefore, sorption studies should be performed over the temperature range of interest.

Sorption on oxide minerals

In addition to surface ionization reactions described previously for variable surface charge systems, there can also be complexation reactions between ions in solution and the ionized surface functional groups. Sorption of cations and anions on oxide minerals is strongly pH dependent. Cations and anions sorb with opposite pH dependence in that sorption of cations increases with increasing pH whereas sorption of anions decreases with increasing pH. An example of predicted relative placements of several

metal-adsorption edges on hydrous ferric oxide is given on Figure 7.3a for conditions at a stream that receives mine drainage. In-depth discussions of the sorption of ions on oxide minerals are provided by Hem (1977), Kinniburgh and Jackson (1981), Sposito (1984), Dzombak and Morel (1987), Schindler and Stumm (1987), Parks (1990), and Davis and Kent (1990).

Several generalizations can be made about metal-cation sorption on oxide surfaces:

- 1) Sorption is strongly pH-dependent, increases with increasing pH, and usually occurs over a narrow pH range.
- 2) The pH region of the adsorption edge is usually more characteristic of the sorbing cation than of the sorbent material.
- 3) The relative placement of the adsorption edge for different metals is similar to that for formation of hydrolysis species.
- 4) Protons are released (or OH^- consumed) as a result of sorption reactions.

The mechanism of metal sorption on hydrous ferric oxide has been demonstrated by Gadde and Laitinen (1974) and Hildebrand and Blum (1974) from the example of Pb^{2+} interactions under a variety of conditions. Dzombak and Morel (1990) present some generalizations about cation sorption on hydrous ferric oxide. They state that the larger the cation charge, the more strongly the cation is sorbed. Also, the stronger the tendency of the cation to hydrolyze, the more strongly it is sorbed. Leckie and coworkers have studied metal sorption on hydrous ferric oxide (Davis, 1977; Davis and Leckie, 1978b; Benjamin, 1979; Leckie et al., 1980; Benjamin and Leckie, 1981a, 1981c, 1982; Benjamin et al., 1982; Benjamin, 1983). Benjamin and Leckie (1981c) report that oxide surfaces consist of sites of varying energy and that metals preferentially bind to high-energy sites. Also, Benjamin and Leckie (1981a, b) found that there is little competition among metals for binding sites on hydrous ferric oxide. This indicates that many of the high-energy metal-binding sites on hydrous ferric oxide may be metal specific.

Reviews covering anion sorption include Parfitt (1978), Hingston (1981), Mott (1981), and Barrow (1985). Generally, maximum sorption of anions occurs at pH values near their acidity constants ($\text{p}K_a$) (Hingston et al., 1967). An example of placements of several anion-adsorption edges is given on Figure 7.3b. Smith and Huyck (1999, Table 2.13) list the tendency for various metals to be cationic, anionic, and redox-sensitive in aqueous systems.

Specific and non-specific sorption

Sorption of ions on oxide minerals can involve predominantly electrostatic (non-specific) or predominantly chemical (specific) interactions with the oxide surface. These two types of interactions result in very different sorption behaviors about which some generalizations can be made.

Non-specific sorption:

- 1) Sorption takes place on surfaces of opposite charge, but little sorption takes place on surfaces of neutral or similar charge.
- 2) Sorption density decreases with increasing ionic strength.

Specific sorption:

- 1) Sorption is insensitive to surface charge.
- 2) Sorption is insensitive to ionic strength.

In the case of non-specific sorption, the surface charge of the mineral controls the sorption process and the identity of the sorbate is relatively unimportant. Non-specific sorption takes place

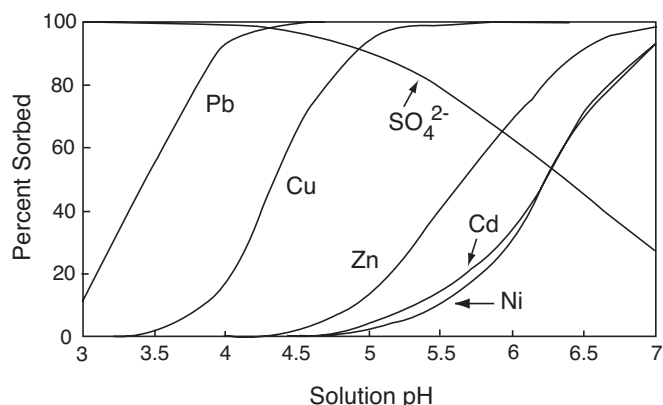


FIGURE 7.3a—Model sorption curves showing relative placement of adsorption edges of selected metals and sulfate on hydrous ferric oxide. Model input was for geochemical conditions from a stream receiving acid-mine drainage. Modified from Smith and Macalady (1991).

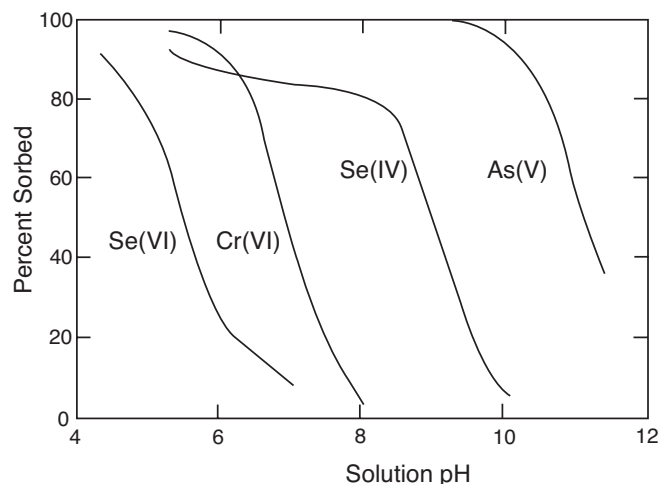


FIGURE 7.3b—Sorption curves showing relative placement of adsorption edges of selected oxyanions on hydrous ferric oxide. Modified from Davis and Kent (1990).

through coulombic attraction between the charged surface and the oppositely charged sorbate ion. Non-specific sorption is also referred to as physical adsorption, and the sorbates form outer-sphere complexes with the mineral surface.

Specific sorption involves chemical bonding of a particular sorbate to the mineral surface and the identity of the sorbate is often very important. Specific sorption can result in a reversal of surface charge, which implies that specifically sorbed ions are able to overcome electrostatic repulsion. Specific sorption is also referred to as chemical adsorption, and the sorbates form inner-sphere complexes with the mineral surface.

Sorption selectivity

Many studies have demonstrated that pH is a master variable for metal sorption reactions on oxides (Kinniburgh and Jackson, 1981, and references therein). Selectivity is a measure of the relative affinity of a particular ion for a given sorbent. The lower the pH that a cation sorbs on a sorbent, the higher the selectivity. Because sorption of monovalent ions (not including H⁺) is usually non-specific, selectivity differences between monovalent ions is usually small, and monovalent-ion selectivity is generally much lower than that for multivalent ions. Divalent transition-metal cations typically have much higher selectivities than do alkaline-earth cations. It has been noted that there appears to be a broad relationship between selectivity of metal cations and the onset of hydrolysis (James and Healy, 1972c). For alkali and alkaline earth cations, the sorption selectivity increases with the ionic radius of the ion:

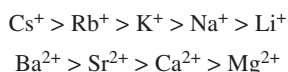


Table 7.2 lists sorption selectivity sequences determined by various researchers for divalent metal cations on a variety of metal-oxide minerals and organic matter. There is general agree-

ment for selectivity sequences of a given metal oxide, although some differences between phases exist. Several of the sequences are similar between different metal-oxide minerals, but there are some distinct differences (such as the preference of MnO₂ for Co). With few exceptions, the sorption selectivity on most metal-oxide minerals follows the sequence Cr ≥ Pb ≥ Cu > Co ≥ Zn and Ni ≥ Cd (Schultz et al., 1987).

The pH at which metal sorption becomes significant varies with the particular metal cation, the particular sorbent, the solid:solution ratio, the specific surface area of the sorbent, the total metal-cation concentration, and the concentration of other competing or interacting species. Consequently, it is very difficult to make generalizations about metal sorption on different oxide minerals. However, based on synthesis of results from numerous studies reported in the literature, there appears to be specific pH ranges in which adsorption edges occur for metal-cation sorption on oxide minerals. This is discussed in detail in Kinniburgh and Jackson (1981).

Table 7.3 lists the pH ranges that usually approximate observed adsorption edges for divalent metal sorption on iron- and aluminum-oxide minerals. Adsorption edges for metal sorption on silica tend to be at higher pH values than those listed, and edges for sorption on manganese-oxide minerals tend to be at lower pH values (Kinniburgh and Jackson, 1981). Therefore, manganese-oxide minerals generally have higher selectivities, and silica has lower selectivities than do aluminum- and iron-oxide minerals for divalent metal cations. A comparison of metal-binding constants for sorption on iron- and manganese-oxide minerals is given in Smith and Jenne (1991) in the context of a sorption model. In a study by Kinniburgh et al. (1976), it appears that metal cations are more strongly sorbed by iron gel than by aluminum gel.

Sorption rates

The importance of sorption reactions in controlling trace-element concentrations in natural systems is partly due to the initial rapid equilibration of most sorption reactions (Ahmed and

TABLE 7.2—Sorption selectivity sequences for divalent metal cations on a variety of metal-oxide minerals and organic matter. (Some data in this table are from Sparks, 1995.)

Cu > Pb > Zn > Ni > Co > Cd	Al gel	Kinniburgh et al., 1976
Cu > Zn > Co > Cd	α -alumina	Spark et al., 1995
Pb >> Cu > Mn > Zn, Cd	natural Al/Fe precipitate	Paulson, 1997
Pb > Cu > Zn > Ni > Cd > Co	Fe gel	Kinniburgh et al., 1976
Zn > Cd > Hg	Fe gel	Brunnix, 1975
Pb > Zn > Cd	Fe gel	Gadde and Laitinen, 1974
Pb > Cu > Zn > Cd	amorphous Fe oxyhydroxide	Benjamin, 1979
Pb > Cu > Zn > Cd ~ Ni	natural Fe precipitate	Smith, 1991
Cu > Zn > Mn	natural Fe-rich sediment	Davis et al., 1991
Pb > Cu > Zn, Cd	natural Fe-rich sediment	Sanden, 1991
Cu > Pb > Zn > Co > Cd	α -FeOOH	Forbes et al., 1976
Cu > Zn > Co > Mn > Cd	α -FeOOH	Grimme, 1968
Cu > Zn > Cd > Co	α -FeOOH	Spark et al., 1995
Cu > Zn > Ni > Mn	Fe ₃ O ₄	Venkataramani et al., 1978
Co \geq Mn > Zn > Ni	MnO ₂	Murray, 1975b
Pb > Zn > Cd	MnO ₂	Gadde and Laitinen, 1974
Co > Cu > Ni	MnO ₂	Murray et al., 1968
Cu > Co > Zn > Ni	MnO ₂	Kozawa, 1959
Co > Cu > Mn	MnO ₂	Traina and Doner, 1985
Co > Zn	δ -MnO ₂	Loganathan and Burau, 1973
Co > Cu > Zn > Ni	α -MnO ₃	McKenzie, 1972
Cu > Zn > Co > Ni	δ -MnOOH	McKenzie, 1972
Pb > Cu > Mn > Zn > Ni	natural MnO ₂	Eley and Nicholson, 1994
Pb > Cu > Zn	natural MnO ₂	Catts and Langmuir, 1986
Zn > Cu > Ni > Co > Mn	Si gel	Taniguchi et al., 1970
Zn > Cu > Co > Mn > Ni	Si gel	Vydra and Galba, 1969
Cu > Zn > Cd > Co	silica	Spark et al., 1995
Cu > Zn > Co > Fe > Ni > Mn	SnO ₂	Donaldson and Fuller, 1968
Ni > Co > Pb > Cu > Zn	Soil fulvic acid	Schnitzer and Hanson, 1970
Cu > Fe ²⁺ > Ni > Pb > Co > Zn > Mn at pH 3.5	Soil fulvic acid	Schnitzer and Skinner, 1966, 1967
Cu > Pb > Fe ²⁺ > Ni > Mn ~ Co > Zn at pH 5.0	Soil fulvic acid	Schnitzer and Skinner, 1966, 1967
Fe ³⁺ > Al > Cu > Zn > Ni > Co > Mn	Soil humic acid	Khan, 1969

Maksimov, 1968) in contrast to the often longer periods of time required for precipitation reactions. Mechanisms that control the rate of sorption reactions are poorly understood. Sorption appears to be a two-step process. In the first step, metals sorb to external surface sites and rapidly equilibrate with the surrounding solution. With sufficient mixing, the rates of this reaction are quite fast (generally seconds to minutes; Hachiya et al., 1984; Hayes and Leckie, 1986). In the second step, the metal slowly diffuses to interior sites (e.g., Coughlin and Stone, 1995; Papelis et al., 1995; Axe and Anderson, 1998). This fraction can become isolated from the bulk solution. It is important to recognize that sorption processes may be limited by mass transfer in natural systems (e.g., Stollenwerk and Kipp, 1990; Weber et al., 1991).

TABLE 7.3—Critical pH ranges for sorption of divalent metal cations on hydrous iron and aluminum oxides (after Kinniburgh and Jackson, 1981). Generally, the critical pH range is higher for silica and lower for manganese oxides.

Cation	Critical pH Range
Cu, Pb, Hg	3 - 5
Zn, Co, Ni, Cd	5 - 6.5
Mn	6.5 - 7.5
Mg, Ca, Sr	6.5 - 9

Desorption

Desorption processes can be extremely important in understanding the mobility, bioavailability, and fate of metals in natural systems. The sorbent mineral acts as a sink for sorbed metals. When the metals desorb, the sorbent mineral can act as a constant source of metals to the surrounding solution (e.g., Wanty et al., 1999; Axe and Anderson, 1998). There are relatively few studies of metal desorption from natural materials. It is often observed that sorbed metals are not readily or completely desorbed (i.e., sorption reactions are partially irreversible; e.g., McKenzie, 1967; Gadde and Laitinen, 1974; McLaren et al., 1983, 1986; Padmanabham, 1983; Schultz et al., 1987; Backes et al., 1995). However, completely reversible sorption also has been observed (e.g., Gadde and Laitinen, 1974). Desorption also can be induced by dissolved species.

Barrow (1986) and Hogg et al. (1993) observed that increasing the contact time between soil and sorbed trace metals decreases the desorption of the metals. This may be due to diffusion of the metals into interior sites of the sorbent mineral (Axe and Anderson, 1998).

The reversibility of metal sorption in iron-rich systems can be influenced by the transformation or aging of metastable sorbent phases to more thermodynamically stable phases. Upon aging of metastable sorbent phases, some sorbed metals may be incorporated into the structure and other metals may be excluded from the structure (e.g., Ford et al., 1997).

DESCRIPTION OF SORPTION REACTIONS

Several empirical, semi-empirical, and mechanistic approaches are used to describe sorption reactions. The following brief discussion of several approaches is intended to provide an overview of how sorption reactions are described. More detailed discussions can be found in Sposito (1984), Stumm and Morgan (1996), and Jenne (1998).

Partition coefficients

The partition coefficient or distribution coefficient, K_d , is the ratio of the amount of adsorbate adsorbed per mass of adsorbent solid to the amount of the adsorbate remaining in solution per solution volume. The K_d can be expressed as:

$$K_d = q / C$$

where C is the adsorbate concentration remaining in solution and q is the amount of adsorbate adsorbed on the adsorbent solid. It is generally assumed that available adsorption sites are in ample excess compared with C .

The K_d is valid only under the conditions it is measured and cannot be extrapolated to other adsorbents, adsorbates, or aqueous conditions (e.g., pH, electrolyte concentrations, etc.; Reardon, 1981). Some researchers have normalized K_d values for variables such as surface area (Balistreri and Murray, 1984) and aqueous speciation (Tessier et al., 1989).

Tabulations of K_d values have been made for use in contaminant transport models. For example, Thibault et al. (1990) tabulate K_d values for soils based on soil texture.

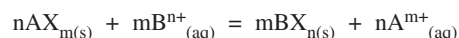
Particle concentration effect

It is commonly observed that K_d decreases with increasing total suspended solids. This effect, termed the particle concentration effect (PCE) or solids concentration effect, can have a substantial influence on solid-solution partitioning (O'Connor and Connolly, 1980; DiToro, 1985; Honeyman and Santschi, 1988). There is some controversy about what causes the PCE. Some possible explanations of the PCE include kinetics, irreversible adsorption, incomplete desorption, variations in surface chemistry, filtration artifacts, particle-particle interactions, and the presence of colloids in the filtrate. Morel and Gschwend (1987) and Benoit (1995) present data indicating that the PCE is due to metals associated with colloidal particles included in the "dissolved" fraction. McKinley and Jenne (1991) found that the PCE could often be attributed to experimental or data interpretation artifacts.

Ion exchange reactions

There are several meanings of ion exchange. The most general meaning is any replacement of an ion in a solid phase in contact with a liquid by another ion. In soil science the term ion exchange often means the replacement of one readily exchangeable ion by another ion. This implies surface phenomena involving outer-sphere complexes or ions in the diffuse layer (Sposito, 1984, 1989).

An ion-exchange reaction on a clay between cations A and B with valences of m and n , respectively, can be expressed as



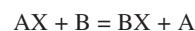
where X is the exchanger surface, $AX_{m(s)}$ and $BX_{n(s)}$ represent the exchanger surface with exchangeable cation A of valence m and exchangeable cation B of valence n , respectively, and $B^{n+}_{(aq)}$ and $A^{m+}_{(aq)}$ are aqueous cations.

As previously mentioned, most clay minerals have a permanently negative charge. This negative charge is compensated for by interlayer cations or accumulation of counterions. Clay minerals generally favor polyvalent cations over monovalent cations. Among the monovalent cations, they prefer the larger, less hydrated cations such as Cs^+ . Usually, clay minerals do not show much selectivity among multivalent cations of the same charge.

Thomas (1977) gives a good overview of historical developments concerning ion exchange in soil chemistry and Dzombak and Hudson (1995) and Mahoney and Langmuir (1991) provide a detailed discussion of electrostatic contributions to ion exchange. The understanding of exchange reactions is a starting point for understanding soil sorption phenomena in general.

Power exchange function

For the exchange reaction



the general power-exchange function can be written as

$$K_{ex} = \frac{[A]}{[B]} \left(\frac{BX}{AX} \right)^n$$

where the ratio of sorbed cation mole fractions is raised to the nth power (Langmuir, 1981, 1997). When $n \neq 1$ and $K_{ex} \neq 1$, the power exchange function can model trace element adsorption behavior on variable-charge surfaces.

Adsorption isotherms

Adsorption reactions are often described in terms of isotherms that relate the amount of an adsorbate in solution to the amount of adsorbate adsorbed at constant temperature. Adsorption isotherms are empirical and can be used to describe data but cannot be used to define adsorption mechanisms (Veith and Sposito, 1977).

Langmuir isotherm

The Langmuir isotherm can be written as:

$$q = kCb / (1 + kC)$$

where q is the amount of adsorbate adsorbed per unit mass of adsorbent, C is the adsorbate concentration remaining in solution

at equilibrium, b is the maximum adsorption capacity of the adsorbent (monolayer coverage), and k is a constant related to the binding strength. The Langmuir isotherm assumes (1) a finite number of surface sites, (2) no electrostatic or chemical interactions, (3) constant binding energy for all surface sites, (4) that binding energy is independent of the adsorption density, and (5) that maximum amount of adsorption is limited to a monolayer coverage of the surface sites (Adamson, 1990).

When the above equation is rearranged, a plot of C/q against C results in a linear representation of adsorption data with a slope of $1/b$ and an intercept of $1/kb$. In many cases, sorption in natural systems deviates from this linear representation.

Freundlich isotherm

The Freundlich isotherm can be written as:

$$q = KC^{1/n}$$

where q and C are previously defined, and K and n are positive empirical constants. The value of n is generally ≥ 1 ; in dilute solutions $n = 1$ but as the adsorption density increases $n > 1$.

When the above equation is rearranged to the linear form, a plot of $\log q$ against $1/n \log C + \log K$ results in a slope of $1/n$ and an intercept of $\log K$. One drawback of the Freundlich isotherm is that it does not predict an adsorption maximum (Sposito, 1980).

Affinity distributions

Affinity spectrum and log- K models are semi-empirical models to describe metal partitioning reactions in complex systems. For each site i for a one-dimensional case:

$$[C] [X_i] K_{MX_i} = [CX_i]$$

$$T_{X_i} = [X_i] + [CX_i]$$

where $[C]$ is the dissolved metal concentration, $[X_i]$ is the concentration of free binding sites of type i , $[CX_i]$ is the concentration of the bound metal, K_{MX_i} is the stability constant, and T_{X_i} is the total analytical concentration of binding sites of type i . Constants for the model are determined by setting values of K_{MX_i} equal to integral values that span the range of $[C]$ in solution, and then calculating corresponding values for T_{X_i} using a nonlinear least squares optimization procedure (Westall, 1994). A binding curve can be simulated by a distribution of values and thought of as a linear superposition of Langmuir isotherms (Borkovec et al., 1996).

Using empirically derived affinity distribution models, it is possible to quantitatively describe metal-partitioning reactions. This type of an approach may represent a preferred alternative to mechanistic sorption modeling in some heterogeneous natural systems (Westall et al., 1995). These models have interpolative abilities and may have some extrapolative abilities (Westall, 1994; Westall et al., 1995; Cernik et al., 1995, 1996; Borkovec et al., 1996).

Surface-complexation models

A surface complex can be defined as the stable molecular unit formed out of the reaction between a chemical species in aqueous solution and a functional group exposed at the surface of a solid (Sposito, 1995). Table 7.4 illustrates some types of surface complexes that can form on metal-oxide mineral surfaces. In the surface-complexation approach (Stumm et al., 1970, 1976; Schindler and Gamsjager, 1972; Schindler et al., 1976) sorption of ions on surfaces of oxide minerals is treated as analogous to the formation of aqueous complexes. Hence, these surface-complexation reactions can be described by mass-law equations. Surface-complexation reactions have an additional coulombic-correction term incorporated into their mass-law equations that takes into account electrostatic effects due to variable surface charge.

Several surface-complexation models (SCM) exist and have been reviewed and evaluated by Westall and Hohl (1980), Morel et al. (1981), Westall (1986), Davis and Kent (1990), Dzombak and Morel (1990), and Goldberg (1992). Table 7.5 lists some SCM and gives the main references for each model. The models differ in their description of the structure of the electrical double layer, specifically in the number of planes within the interface, the relationships between charge and potential, and the location of surface complexes relative to the surface. These models require knowledge of concentrations of various adsorbing species, intrinsic constants that define the interaction between surface sites and each adsorbing species, and characteristics of the adsorbent surface such as capacitances, specific surface areas, and surface hydroxyl site densities.

The following criteria characterize all surface complexation models (Dzombak and Morel, 1990; Langmuir, 1997):

- 1) Sorption takes place at specific surface coordination sites.
- 2) Sorption reactions can be described by mass law equations.

TABLE 7.4—Surface complexes between metal-oxide functional groups and solutes. X represents a binding site on an oxide-mineral surface, M represents a cationic metal solute, and L represents an anionic solute.

Proton Exchange:	
$XOH_2^+ = XOH + H^+$	
$XOH = XO^- + H^+$	
Cation Complexes:	
$XOH + M^{2+} = XOM^+ + H^+$	
$2XOH + M^{2+} = (XO)_2M + 2H^+$	
Anion Complexes:	
$XOH + L^{2-} + H^+ = XL^- + H_2O$	
$XOH + L^{2-} + 2H^+ = XHL + H_2O$	
Outer-Sphere Complexes:	
$XOH + M^{2+} + H_2O = XO^-(H_2O)M^{2+} + H^+$	

TABLE 7.5—Some types of surface-complexation models with brief descriptions and references. Information from Davis and Kent (1990); Goldberg (1992); and Sposito (1995).

Model	Comments	References
Diffuse Double-Layer Model (DDLMM)	Two interfacial planes; surface plane contains H^+ , OH^- , and inner-sphere complexes; diffuse-layer plane contains outer-sphere complexes	Stumm et al., 1970; Huang and Stumm, 1973
Constant Capacitance Model (CCM)	Special case of DDLMM; all surface complexes are inner sphere; linear relationship between surface charge and surface potential	Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976
Generalized Two-Layer Model (GTLMM)	Based on DDLMM with additional features; two binding-site types for cations; all surface complexes are inner sphere	Dzombak and Morel, 1990
Triple-Layer Model (TLM)	Two capacitance layers and a diffuse layer; three layers relate potential to charge; H^+ and OH^- are inner sphere; metals and ligands are outer-sphere	Davis and Leckie, 1978b, 1980
Modified Triple-Layer Model (TLM)	Enhancement of original TLM; allows metals and ligands to be inner-sphere	Hayes and Leckie, 1986, 1987
Four-Layer Model (FLM) (a.k.a. Stern Variable Surface Charge-Variable Surface Potential Model (VSC-VSP))	Combines CCM and TLM; H^+ , OH^- , and strongly sorbed ions are inner-sphere; weakly sorbed ions are outer-sphere	Bowden et al., 1977, 1980; Barrow et al., 1980, 1981
One-pK Stern Model	H^+ and OH^- are inner-sphere; metals and ligands are outer-sphere	Bolt and van Riemsdijk, 1982; van Riemsdijk et al., 1986, 1987; Hiemstra et al., 1987

- 3) Surface charge results from the sorption reaction itself.
- 4) The effect of surface charge on sorption can be taken into account by applying a correction factor derived from electric double-layer theory to the mass law constants for surface reactions.

SCM can describe data over a broad range of conditions such as varying pH, ionic strength, adsorbate concentrations, adsorbent concentrations, and solution conditions.

Electrical double-layer theory

The distribution of electrical potential at the solid-solution interface has been envisioned as a double layer of charge, the electrical double layer (EDL), in which one layer of charge is localized next to the surface and the other layer is developed in a diffuse region extending out into the solution (Adamson, 1990; Stumm and Morgan, 1996). Many of the SCM that describe sorption behavior are based on EDL theory developed by Gouy (1910) and Chapman (1913) who mathematically describe the diffuse distribution of ions adjacent to a charged surface. Stern later modified the Gouy-Chapman model to include a layer of counterions (ions of opposite charge to the surface charge) nearest the charged surface. James and Healy (1972a, b), Adamson (1990), Shaw (1980), Stumm and Morgan (1996), and Singh and Uehara (1986) provide a detailed discussion of EDL theory.

Figure 7.4 shows the Gouy-Chapman model of the diffuse double layer (DDL), which illustrates a negatively charged surface and the distribution of cations and anions with distance from the surface. The counterions are most concentrated nearest the surface and decrease exponentially with distance away from the surface. The coions (ions having the same charge as the surface) are depleted nearest the charged surface. Calculations show that for a counterion concentration of 1 mmol/dm³, the thickness of the double layer will be 10 nm for monovalent counterions and 5 nm for divalent counterions (van Olphen, 1977).

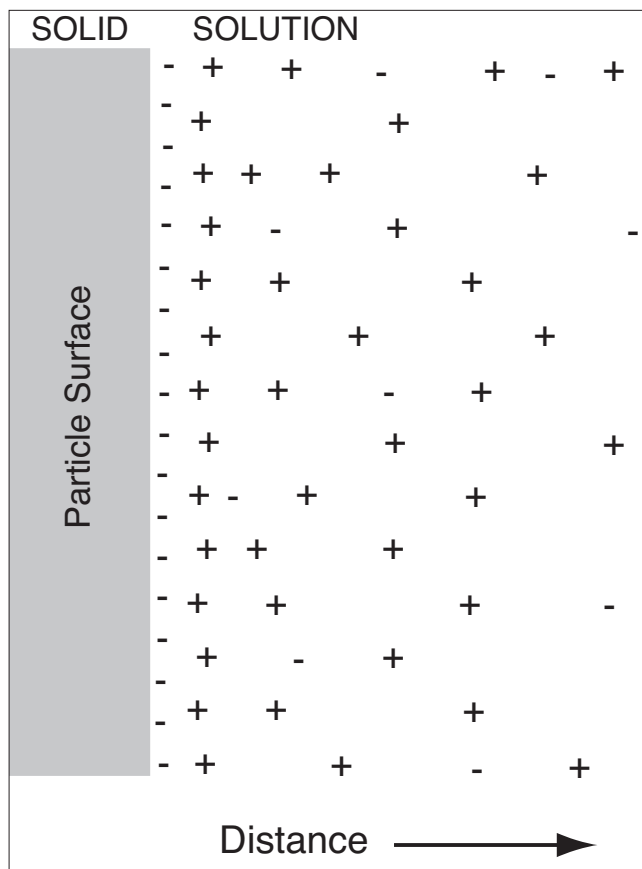


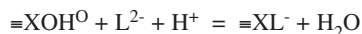
FIGURE 7.4—Cartoon of the diffuse double layer adjacent to a negatively charged surface. Positively charged counterions are most concentrated near the surface with decreasing concentration away from the surface. Modified from van Olphen (1977).

Inner-sphere and outer-sphere complexes

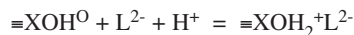
SCM refer to specific and non-specific ion binding on an oxide surface as inner-sphere and outer-sphere complexes, respectively. In the formation of inner-sphere complexes, a largely covalent bond between the surface and the ion is formed. Inner-sphere complexes can affect the reactivity of a surface (Sposito, 1984; Stumm, 1992, 1995, 1998). In the case of an outer-sphere complex, an ion of opposite charge approaches the surface, and the ion and the surface are separated by one or more water molecules (see Table 7.4). These types of bonds are largely electrostatic. Outer-sphere complexation is usually a rapid, reversible process. In contrast, inner-sphere complexation tends to be somewhat slower, and not completely reversible. Adsorption of inner-sphere complexes can occur on a surface regardless of surface charge. The distinction between inner- and outer-sphere is important because the bound species have different chemical properties depending upon how they are bound to the surface.

The presence of inner-sphere complexes has been confirmed by the use of spectroscopy (Hayes et al., 1987; Chisholm-Brause et al., 1990; Roe et al., 1991). Brown (1990) provides an overview of spectroscopic studies. Another method used to distinguish inner-sphere and outer-sphere complexes is to assess the effect of ionic strength on the surface complex. Outer-sphere complexes typically have a strong dependence on ionic strength (Hayes and Leckie, 1987; Hayes et al., 1988).

Ligand exchange: Strongly binding anions sorb on metal-oxide minerals by a ligand exchange mechanism (Stumm et al., 1980; Harrison and Berkheiser, 1982). This mechanism involves the exchange of an anion for a surface hydroxyl group:



where $\equiv\text{XOH}^{\text{O}}$ is a surface binding site, L^{2-} is a divalent anion, and $\equiv\text{XHL}^{\text{O}}$ and $\equiv\text{XL}^-$ are surface complexes. This results in the formation of an inner-sphere complex. In contrast, weaker binding anions sorb through electrostatic interactions with the oxide surface and a water molecule remains between the surface site and the sorbed anion (Hayes et al., 1987):



which results in an outer-sphere complex.

Model parameters

Different surface complexation models require different parameters. The following tabulation lists parameters required for three of the models (Sparks, 1995; Langmuir, 1997).

<u>Diffuse</u>	<u>Constant Capacitance</u>	<u>Triple Layer</u>
<u>Double-Layer</u>		
Specific surface area	Specific surface area	Specific surface area
Total site concentration	Total site concentration	Total site concentration
pK for proton gain	pK for proton gain	pK for proton gain
pK for proton loss	pK for proton loss	pK for proton loss
pK for metal binding	pK for metal binding	pK for metal binding
	1 capacitance	pK for electrolyte
		2 capacitances

These parameters represent fitted or separately determined values. Generally, fitted parameters are determined with the use of numerical optimization techniques. Each of the models contain different parameters or different parameter values because each of the models assumes different geometric features of the oxide-water interface. Westall and Hohl (1980) demonstrated that five different SCM could fit proton adsorption data on Al_2O_3 equally well despite their mutually contradictory underlying molecular hypotheses. This is because of the adjustable parameters that can be employed to fit the data (Dzombak and Morel, 1987).

Literature sorption data have been interpreted with a variety of SCM. Because the parameters for these SCM are different, literature sorption parameter values and surface-complexation constants are not consistent. Parameter values and sorption constants are not interchangeable between SCM.

MODELING METAL-SORPTION REACTIONS IN NATURAL SYSTEMS

Knowing the distribution of metals between dissolved and particulate phases is important in understanding their ecological impact, transport and fate, and infiltration into ground-water systems. Particulates in natural systems consist of mixtures of different organic and inorganic materials, which makes predictive sorption modeling a formidable task. Some attempts have been made to characterize the metal-binding properties of naturally occurring particulates (Vuceta and Morgan, 1978; Balistrieri et al., 1981; Luoma and Bryan, 1981; Lion et al., 1982; Balistrieri and Murray, 1983, 1984; Mouvet and Bourg, 1983; Tessier et al., 1985; Muller and Sigg, 1990; Ali and Dzombak, 1996; Tessier et al., 1996; Wang et al., 1997; Payne et al., 1998; Smith et al., 1998; and Wen et al., 1998).

Although many of the empirical approaches to sorption reactions (e.g., isotherms) are descriptive, they are not predictive, especially beyond the conditions measured. This discussion will emphasize surface-complexation models (SCM) because they have predictive capabilities beyond the measured conditions. Surface complexation reactions and other descriptions of sorption reactions (such as K_d) have been incorporated into several speciation and transport modeling codes.

Modeling difficulties

When modeling sorption reactions in natural systems, an assumption often is made that most of the reactive metal-binding surfaces are natural organic matter, and hydrous oxides of iron, manganese, aluminum, and silica. Crystalline minerals and clay minerals generally are of lesser importance. In natural systems low in organic matter, metal sorption is commonly thought to be controlled by iron- and aluminum-oxide coatings on particle surfaces (Davis and Kent, 1990). Metal sorption by pure oxide phases can be successfully predicted by SCM (e.g., Dzombak and Morel, 1990). Application of SCM to natural systems necessitates detailed characterization of the solid phases and their surface composition. Many of the experimental techniques that are used to characterize sorption and EDL properties in simple mineral-water systems cannot be applied in a straightforward manner to soils and sediments. The real trick is determining the types and concentrations of important surface functional groups and their reactive surface areas.

Incorporation of metal binding on natural organic matter (NOM) into predictive sorption models presents a major challenge (Kinniburgh et al., 1998). Binding site concentrations and constants are not easily determined for NOM. Discussion of metal binding on NOM is beyond the scope of this paper. However, NOM may play an important role in many cases and there are some NOM metal-binding models and approaches that look promising (e.g., Wilson and Kinney, 1977; Cabaniss et al., 1984; Ephraim et al., 1986; de Wit et al., 1991; Bartschat et al., 1992; Tipping and Hurley, 1992; Benedetti et al., 1995; Tipping et al., 1995; and Westall et al., 1995). Future developments may allow incorporation of NOM into predictive sorption models. Metal sorption onto biological surfaces also has been considered (e.g., Beveridge and Murray, 1976; Hudson and Morel, 1990; Sigg, 1994; and Fein et al., 1997). Sorption of dissolved organic carbon onto oxide minerals can be an important mechanism in some systems (e.g., McKnight et al., 1992). Westall et al. (1995) suggest the use of semi-empirical models, instead of mechanistic models, for complex systems. This approach offers an alternative for many applications including the incorporation of metal-partitioning capabilities into transport models.

Langmuir (1997, p. 392–393) suggests several questions be asked when applying adsorption models to natural systems. Among those questions are: (1) when multiple sorbent phases are present, which are most likely to interact with the sorbate species of interest?; (2) when multiple sorbent phases are present, can we simplify the problem and limit our analysis to adsorption by a single sorbent?; (3) what are the absolute and relative abundances of important sorbent phases and what fraction of their surface areas is exposed to flowing water?; and (4) what is the chemical composition of the water?

Additivity and interactive effects between phases

There is an ongoing controversy about whether or not the sorptive properties of minerals are the same in mixtures as they are individually. Honeyman (1984) found differences in sorptive properties when certain minerals were present in mixtures. Anderson and Benjamin (1990) showed that aluminum hydroxide in a binary system altered the surface chemical properties of the other mineral phase. Meng and Letterman (1993) also noted altered sorptive properties due to interference by aluminum hydroxide. Davis (1984) reported that dissolved organic carbon was able to coat metal-oxide minerals in many natural systems. This organic coating interacted strongly with some metals, such as Cu, and did not seem to affect other metals, such as Cd.

On the other side of the sorption additivity controversy, Davies-Colley et al. (1984) found little difference in sorptive properties of a variety of minerals in mixtures. Siegel et al. (1992) successfully modeled sorption in a mixture of goethite and montmorillonite. The compilation of Vandergraaf et al. (1993) assumes additivity of the sorptive properties of minerals. Tessier et al. (1996) modeled sorption reactions in a natural system assuming additivity of sorptive properties.

It appears that some amorphous minerals and dissolved organic carbon are able to alter the sorptive properties of minerals in some mixed systems. Consequently, the assumption of sorptive additivity in natural systems should be made with caution. When possible, empirical observations of sorption reactions on natural materials should be made for the mixture as a whole.

Surface functional groups

As mentioned, one of the most difficult tasks in modeling is the identification and quantification of surface functional groups in heterogeneous mixtures of mineral phases. 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 (e.g., Davis, 1984). Techniques to measure these parameters must be chosen with care. Balistrieri and Murray (1983) used tritium exchange to estimate the total density of surface sites on marine sediments and noted that these data compared well with those from simpler cation exchange measurements (Balistrieri and Murray, 1984). Zachara et al. (1989) estimated site densities from sorption data by applying the Langmuir isotherm. If a particular mineral phase is thought to dominate sorption processes, site densities can be estimated from the abundance of the mineral phase in the bulk material (e.g., Smith, 1991).

For coatings, abundance can be estimated by partial chemical extractions (e.g., Chao and Zhou, 1983; Chao, 1984; Tessier et al., 1989). For example, Fuller et al. (1996) used partial chemical extractions combined with surface area measurements to estimate metal sorption in a sand and gravel aquifer. Jenne and Creclius (1988) used partial chemical extractions to estimate the quantities of amorphous iron- and manganese-oxide sorbents, reactive particulate organic carbon, and associated sorbed metals in fine-grained sediments.

Iron oxide minerals are generally the primary adsorbent for transition metals in oxic environments unless unusual amounts of other adsorbents exist (Jenne, 1998). In the absence of evidence of sorptive dominance by a particular component, the bulk can be modeled. Davis and Kent (1990) recommend that the reactive surface area be multiplied by an average value for site density of surface hydroxyl groups per unit surface area. They suggest a single value for total surface-site density of 2.31 sites/nm² (or 3.84 $\mu\text{moles}/\text{m}^2$; Dzombak and Morel, 1990). In this way a uniform value can be accepted for modeling site density and metal adsorption density.

Several spectroscopic and microscopic techniques, such as scanning Auger microscopy, show promise for the examination and determination of surface functional groups. For example, Hayes et al. (1987) examined surface complexes of SeO_3^{2-} on goethite. Hochella (1990) and Sposito (1995) discuss several of these techniques.

Reactive surface area

One of the most difficult parameters to estimate for model input is the reactive surface area of the various sorbent materials. Surface-area estimates are dependent on the analysis used to determine them. Warren and Zimmerman (1994) found that, in the case of mixed coatings on particulates, the exposed surface area for a given geochemical phase is not well represented by surface areas estimated from single component sediments or by calculated estimates using total surface area measurements and concentration data for suspended particulate matter. Wanty et al. (1991) suggest a method that involves calculating the minimum surface area of a model sorbent required to reduce the sorbate concentration to a value of the difference between the dissolved concentration in equilibrium with saturation indices and the observed value in

natural water. Davis and Kent (1990) state that gas adsorption techniques yield the most useful information, including estimates of external surface area and an evaluation of the extent of microporosity. Gas adsorption techniques can be problematic for porous sorbents (White and Peterson, 1990; Chiou and Rutherford, 1993).

Surface-complex data sets

A drawback of SCM is the lack of complete internally consistent data sets of surface complexes. Determining such complexes is cumbersome. Data for several different types of sorption models are in the literature, but surface complexation data are not interchangeable between models. Therefore, it is extremely important to stick with one type of surface complexation model when compiling a data set. Dzombak and Morel (1990) and Smith and Jenne (1991) have published internally consistent data sets for the GTLM and TLM, respectively, and Turner (1995) compiled a data set for radionuclide sorption using the TLM.

MODELING METAL-SORPTION REACTIONS IN MINE-DRAINAGE SYSTEMS

Mine-drainage systems offer a rather unique situation for metal-sorption modeling. Due to the often high levels of iron in these systems, they represent a case in which metal-sorption reactions usually are dominated by a single component, hydrous ferric oxide (HFO). Therefore, the types of functional groups are known, and the quantity of functional groups can be estimated from the bulk iron content.

Role of iron-oxide minerals

Iron-oxide minerals are ubiquitous in the near-surface environment and are common components of natural gossans, soils, and mine waste. Several different iron-oxide minerals have been identified in nature. Hydrous ferric oxide (a.k.a. amorphous ferric hydroxide, amorphous iron oxyhydroxide, and ferrihydrite) is the solid formed upon rapid hydrolysis of ferric Fe solutions at 20–30°C (Dzombak and Morel, 1990). HFO is usually amorphous or nearly amorphous as determined by X-ray diffraction. The stoichiometry is uncertain and is represented by the general formula $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Measurements and calculations of associated surface areas vary widely. Upon aging, HFO gradually transforms to a crystalline oxide, usually goethite ($\alpha\text{-FeOOH}$).

Dzombak and Morel (1990) defined properties of HFO in order to extract surface-complexation constants from experimental data using the GTLM. Table 7.6 lists some of those HFO properties. Dzombak and Morel (1990) developed an internally consistent database for metal sorption on HFO for the GTLM. Although the iron-rich precipitates in mine-drainage systems consist of a variety of iron-oxide minerals, it is possible to consider them in bulk and lump them under the “HFO definition.”

Previous studies of metal partitioning in mine-drainage systems

Downstream decreases in dissolved metal concentrations will occur due to oxidation, precipitation, sorption, and dilution pro-

cesses. Several researchers have studied metal dispersion and attenuation in acidic, metal-rich drainages. The following discussion covers some representative studies from the literature. There is a wide variety of data in the literature, but no clear-cut picture exists as to how to anticipate metal mobility in mine-drainage systems. Additional studies include Theobald et al. (1963), Collins (1973), Foster et al. (1978), Filipek et al. (1981), Robinson (1981, 1983), Kuwabara et al. (1984), Johnson (1986), Jones (1986), Andrews (1987), Bencala et al. (1987), Karlsson et al. (1987, 1988a, 1988b), Fuller and Davis (1989), Rampe and Runnells (1989), Axtmann and Luoma (1991), Sanden (1991), Winland et al. (1991), Howell (1994), Kimball et al. (1994, 1995), Webster et al. (1994), Benner et al. (1995), Broshears et al. (1996), Levy et al. (1997), and Paulson (1997).

TABLE 7.6—Properties of hydrous ferric oxide used in the extraction of surface-complexation constants from experimental data using the Generalized Two-Layer surface-complexation model (data from Dzombak and Morel, 1990).

Specific Surface Area	=	600 m ² /g
High-Affinity Site Density	=	0.005 moles sites / mole Fe
Low-Affinity Site Density	=	0.2 moles sites / mole Fe
Stoichiometry	=	Fe ₂ O ₃ • H ₂ O
Molecular Weight	=	89 g HFO/mole Fe
Pristine Point of Zero Charge	=	8.1

Chapman et al. (1983) found that a combination of sorption, precipitation, and dilution processes accounts for the decrease in concentration of dissolved elements in two streams (pH 2.7–3.2 and pH 3.1–6.8) in New South Wales, Australia. In the lower-pH stream, they report that Al, As, Fe, SiO₂, and SO₄²⁻ are reactive constituents resulting from the precipitation of Fe as amorphous ferric hydroxide and the subsequent sorption of Al, As, SiO₂, and SO₄²⁻. They attribute diminished concentrations of Cd, Cu, and Zn to dilution effects. In the higher-pH stream, Chapman and others found that Al, Cu, Fe, and Pb are reactive elements, and that Al, Cu and Fe probably precipitate. They attribute decreased Pb concentrations to sorption reactions and decreased concentrations of Cd, Mn, and Zn to dilution effects.

Filipek et al. (1987) studied confluences of acidic metal-rich waters with West Squaw Creek, California. They found that the ratios of sorbed Cu, Mn, and Zn concentrations to dissolved concentrations are a function of pH with the least amount of sorption taking place at lower pH. They observed that As is quickly scavenged from solution near its source. They calculate that both ferric hydroxides and jarosite are at saturation in these waters.

Davis et al. (1991) examined factors that affect element partitioning between water and suspended sediment in North Clear Creek (pH 5.8–7.4), Colorado. Based on mass balance calculations, they found that Al, Ca, Cl, F, and Zn (and perhaps Cd, K, Mg, and Na) behave conservatively whereas Cu, Fe, Mn, and SO₄²⁻ are reactive. They observed that Al, Cu, and Fe are mainly associated with the suspended sediment, and Cd, Mn, and Zn are present predominantly as dissolved species. They concluded that Al and Fe solubilities are controlled by precipitation and that dissolved Cu is controlled by sorption reactions. Based on batch laboratory desorption studies using sediment collected from North Clear Creek, Davis and others found the affinity sequence of metals for the sediment to be Al > Cu > Zn > Mn.

Webster et al. (1998) studied sorption of metals onto a natural iron(III) oxy hydroxy sulfate mineral precipitated in a mine-drainage system and compared those results with sorption studies using synthetic schwertmannite and pure hydrous iron(III) oxide. They found that Cu and Zn sorption onto the natural precipitate was greater than that onto synthetic schwertmannite, which was in turn greater than that onto hydrous iron oxide. Cadmium sorption was also enhanced onto the natural precipitate. Sorption modeling generally underestimated the degree of metal sorption onto the natural precipitate.

Predictive modeling of metal mobility in mine-drainage systems

Smith and colleagues (Smith et al., 1989, 1991, 1998; Smith and Macalady, 1991; Smith, 1991, 1996) studied metal-sorption reactions between stream water and streambed sediment from St. Kevin Gulch, Colorado, a subalpine stream impacted by mine drainage. They performed batch pH-dependent metal-partitioning experiments (see Smith, 1991 for details) using the natural stream water and streambed sediment, and observed that the metal-partitioning reactions follow previously observed trends (Kinniburgh et al., 1976; Benjamin, 1979) for sorption of metals by synthetic HFO. They successfully used the GTLM surface-complexation model to predictively model metal sorption reactions on natural iron-rich streambed sediment. This work demonstrates that predictive SCM can be used for modeling mine-drainage systems and provides a field validation for the GTLM coupled with the MINTEQA2 computer program (Allison et al., 1991).

The previous studies lay the groundwork for additional metal-sorption studies and predictive modeling in a variety of mine-drainage systems (Smith et al., 1992, 1993, 1994, 1998; Webster et al., 1994). The general approach is briefly outlined below.

General sorption-modeling approach

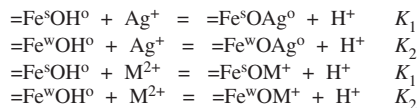
Computer simulations of sorption reactions employ the equilibrium speciation program MINTEQA2 (Allison et al., 1991) coupled with the GTLM and accompanying database of surface-complexation constants for HFO (Dzombak and Morel, 1990). MINTEQA2 computes sorption reactions and solution equilibria simultaneously in a self-consistent manner. The GTLM evokes a two-site model for cation sorption that includes a subset of high-affinity cation-binding sites. It is assumed that M^{2+} is the only metal species that sorbs on HFO. Table 7.7 lists some of the surface-complexation constants for metal sorption on HFO using the GTLM. It is important to note that the parameters and surface-complexation constants listed in Tables 7.6 and 7.7 are specific for HFO and for the GTLM. Consequently, use of these parameters and constants with other sorption models or for other sorbent surfaces is not valid.

Complete analytical data for water composition are input to MINTEQA2. The pH is fixed at desired values with the water in equilibrium with atmospheric carbon dioxide. Neither trace-metal hydroxide phases nor anglesite ($PbSO_4$) exceed saturation in the computer simulations. Only two solid phases, ferrihydrite and amorphous aluminum hydroxide, are allowed to precipitate in the simulations because they are the most likely solids to control Fe and Al solubilities during the 6-hour time frame of the batch experiments (6 hours were determined to be adequate from sorp-

tion-rate experiments; see Smith, 1991; Smith et al., 1998).

TABLE 7.7—Derived and estimated surface-complexation constants for metal-cation sorption on hydrous ferric oxide from the Generalized Two-Layer sorption model (data from Dzombak and Morel, 1990).

Cation	log K_1^{int}	log K_2^{int}
Ag ⁺	-0.72	-5.3
Ba ²⁺	5.46	-7.2
Be ²⁺	5.7	3.3
Cd ²⁺	0.47	-2.90
Co ²⁺	-0.46	-3.01
Cu ²⁺	2.89	0.6
Hg ²⁺	7.76	6.45
Mn ²⁺	-0.4	-3.5
Ni ²⁺	0.37	-2.5
Pb ²⁺	4.65	0.3
Sn ²⁺	8.0	5.9
UO ₂ ²⁺	5.2	2.8
Zn ²⁺	0.99	-1.99



HFO is the sole sorbent material in the model simulations. All of the Fe in the sediment is assumed to be present as HFO and calculations of binding-site concentrations and total amorphous Fe are based on this assumption. As suggested by Dzombak and Morel (1990), for conversions from g/l HFO to mole/l Fe, the stoichiometry $Fe_2O_3 \cdot H_2O$ (89 g HFO/mole Fe) was assumed. In the case of suspended sediment, the difference between filtered and unfiltered Fe values in water is assumed to be the concentration of Fe in the suspended sediment. All of that Fe is assumed to be present as HFO.

All of the model input is derived either from chemical analyses or from information and parameters provided by Dzombak and Morel (1990). None of the model parameters were modified and no fitting of parameters is involved in these model simulations. A similar modeling approach has been used by Loux et al. (1989) and Stollenwerk (1994).

Importance of suspended sediment in sorption reactions

Smith et al. (1992) compared field data with computer-model predictions for metal sorption at ten diverse mine-drainage sites. In the mine-drainage streams they observed that metal sorption on iron-rich suspended sediment appears to regulate dissolved metal concentrations, with bed sediment playing a decidedly lesser role. They achieved good agreement between computer-model predictions and field measurements in mine-drainage streams when they assumed that all metal sorption takes place only on suspended sediment (i.e., no sorption on bed sediment). Therefore, it appears that a limited amount of sorbent material is available for metal-sorption reactions in mine-drainage streams. Figure 7.5 illustrates the consequences of having a limited amount of sorbent available. When there is abundant sorbent material present (Fig. 7.5A), well-defined adsorption edges result. However, when the sorbent material becomes limited and competition for binding sites with major

cations becomes more important (Fig. 7.5B), as is usually the case with metal sorption on suspended sediment in mine-drainage systems, less-defined adsorption edges result, and Zn, Cd, and Ni tend not to sorb at all. Consequently, Zn, Cd, and Ni would be expected to be mobile in many mining areas, which is observed by Plumlee et al. (1999).

SELF-MITIGATING CAPACITY OF MINE WATERS

The self-mitigating capacity of a mine water is the inherent ability of the water to clean itself up by removing dissolved metals from solution. It is related to the amount of dissolved Fe in the water that can precipitate and consequently attenuate dissolved metals by sorption reactions. Dissolved Fe commonly precipitates in response to oxidation or neutralization of mine waters. Self-mitigating capacity depends on the amount of dissolved Fe, the concentration and identity of dissolved metals, and the ratio of precipitated Fe (available surface-binding sites) to dissolved metals at a given pH.

The self-mitigating capacity of a mine water is useful for predicting metal mobility, providing guidance in remediation and planning, estimating pH and optimal conditions for removal of a particular metal, and predicting metal-removal efficiency. Dissolved or particulate Fe in a metal-contaminated watershed can have a positive influence on the attenuation of metals. However, Smith et al. (1992, 1993) observed that it is important to maximize contact between the particulate Fe and dissolved metals.

Method to predict self-mitigating capacity

Computer-model simulations can predict the self-mitigating capacity of a mine water. Smith et al. (1993, 1998) discuss this approach, which is summarized here. The simulations employ the

equilibrium speciation program MINTEQA2 (Allison et al., 1991) coupled with the GTLM as described previously.

To determine the amount of sorbent for the computer simulations, the dissolved Fe is assumed to precipitate and the concentration is converted to HFO. Two site densities are used, 0.005 moles sites per mole Fe for the high-affinity site densities and 0.2 moles sites per mole Fe for the low-affinity site densities as described previously. HFO is the sole sorbent material in the simulations and sorption on HFO is the sole mechanism for removal of trace metals in the simulations.

Examples

We now look at some examples of the use of computer-model simulations to predict the self-mitigating capacity of mine waters. These examples use data from actual mine waters and illustrate several concepts that are important in the self-mitigating capacity of mine waters.

Example 1—Oxygen-deficient mine water from a collapsed adit

Water containing ferrous Fe at pH 5.8 emanates from the collapsed Rawley-12 adit near Bonanza, Colorado. Table 7.8 lists the composition of the mine water. Figure 7.6 shows results from a computer simulation in which the dissolved Fe in the water precipitates and is allowed to sorb metals in the mine water. HFO sorbs most of the As, Cu, and Pb between pH 6 and about 7.5. HFO sorbs little Zn, Cd, or Ni at any pH between 6 and 8. Removal efficiency of Cu and Pb decreases above pH 7.5 due to competition by dissolved hydroxo and carbonato species. Cadmium and Ni concentrations were too low to show on the figure.

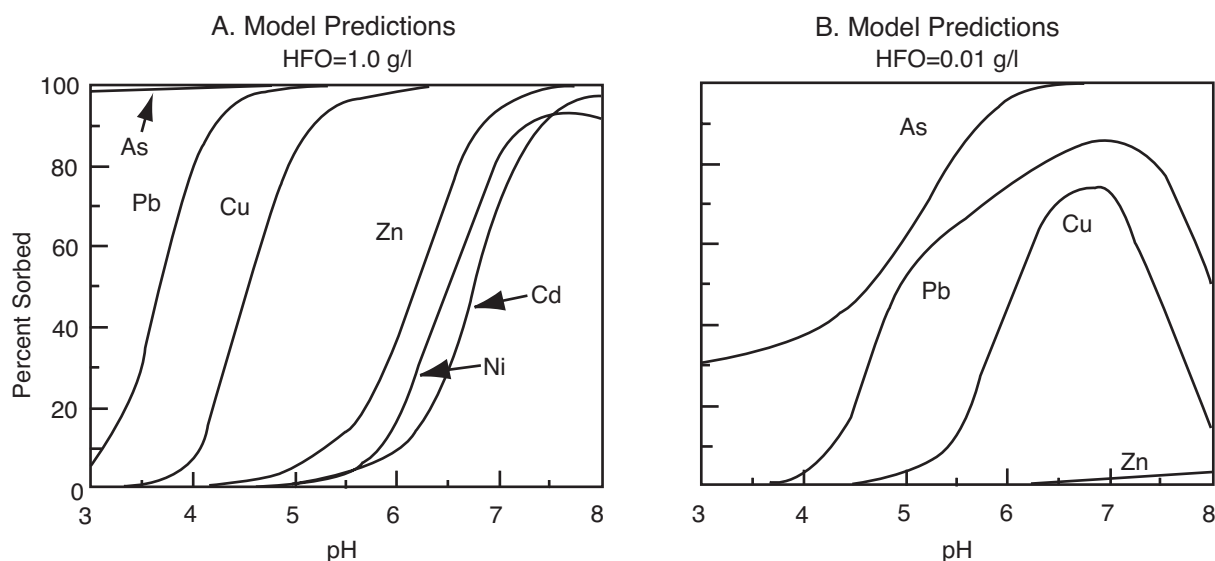


FIGURE 7.5—Model predictions of metal sorption on hydrous ferric oxide (HFO) as a function of pH for two different sorbent concentrations (A and B). After Smith et al. (1992).

This example illustrates that some oxygen-deficient waters can have a relatively good self-mitigating capacity once the Fe is oxidized and precipitated. Also, the computer simulation shows the importance of knowing an optimal pH range in order to maximize the removal efficiency of Cu.

TABLE 7.8—Chemical composition of filtered water from the Rawley-12 adit near Bonanza, Missionary East Seep at Summitville, and Tip Top adit adjacent to Gamble Gulch, Colorado. Samples were filtered through a 0.1 µm filter.

	Rawley-12 Adit	Missionary East Seep	Tip Top Adit
As (µg/l)	8.5	200	—
Pb (µg/l)	120	210	13
Cu (µg/l)	4,900	58,000	100
Zn (µg/l)	58,000	6,800	2,500
Cd (µg/l)	280	50	11
Ni (µg/l)	36	350	38
Fe (mg/l)	42	150	4.7
SO ₄ ²⁻ (mg/l)	700	1,540	300
pH (field)	5.7	3.8	3.8

Example 2—Low pH, high Fe and metals

The Missionary East Seep at Summitville, Colorado, discharges pH 3.8 water containing 150 mg/l of Fe and extremely high concentrations of some metals (see Table 7.8). Figure 7.7 shows computer-simulation results when this 150 mg/l dissolved Fe precipitates as HFO and sorbs dissolved trace metals over the pH range 4 to 8. Sorption of Ni over the pH range 4 to 8 was <1%, and sorption of Cd was <2% (curves not shown on Fig. 7.7). HFO sorbs most of the As and little of the Zn between pH 4 and 8. Removal efficiency of Cu never reaches values above about 40%.

This example illustrates that, even if it contains high Fe concentrations, a water may not have a particularly good self-mitigat-

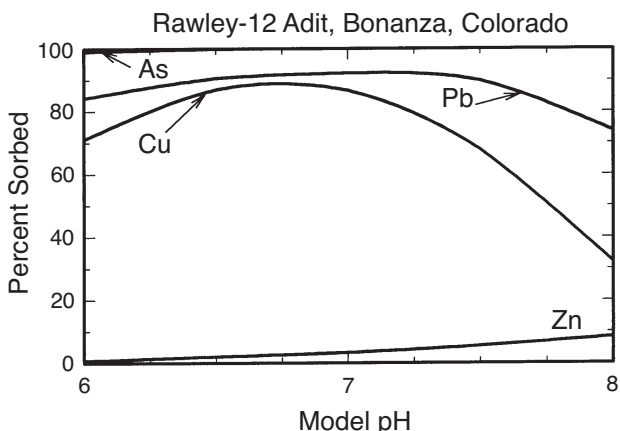


FIGURE 7.6—Computer simulation of metal sorption on hydrous ferric oxide (HFO) as a function of pH for drainage from the Rawley-12 adit, near Bonanza, Colorado. HFO concentration was derived from the precipitation of dissolved Fe originally present in the drainage.

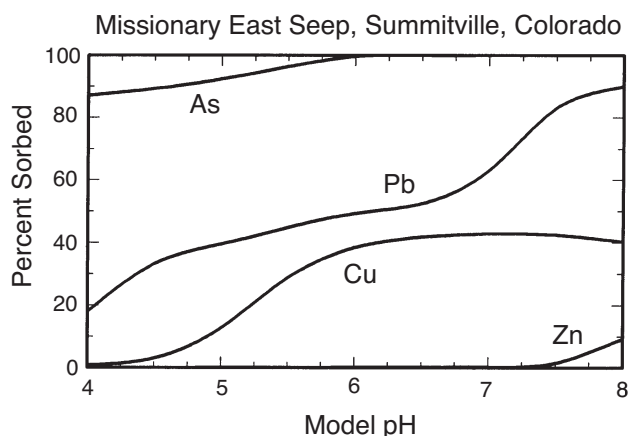


FIGURE 7.7—Computer simulation of metal sorption on hydrous ferric oxide (HFO) as a function of pH for drainage from the Missionary East Seep at Summitville, Colorado. HFO concentration was derived from the precipitation of dissolved Fe originally present in the drainage.

ing capacity. In this case, the extremely high concentration of Cu cannot be self-mitigated by more than about 40%. Dissolved Cu, Zn, Cd, and Ni can remain largely mobile in waters discharging from this site.

Example 3—Low pH, moderate Fe and metals

The Tip Top adit adjacent to Gamble Gulch, Colorado, discharges pH 3.8 water containing 4.7 mg/l of Fe and moderate concentrations of some metals (see Table 7.8). Figure 7.8 shows computer-simulation results when this 4.7 mg/l dissolved Fe precipitates as HFO and sorbs dissolved trace metals over the pH range 4 to 8. Sorption of Ni over the pH range 4 to 8 was <1%, and sorption of Cd was <2% (curves not shown in Fig. 7.8). HFO sorbs most of the Pb between pH 5.5 and 8 and little of the Zn between pH 4 and 8. Removal efficiency of Cu peaks at about 80% at pH values near 7. Removal efficiency of Cu decreases above pH 7.5 due to competition by dissolved hydroxo and carbonato species.

This example illustrates that, even though it contains only moderate Fe concentrations, a water may have a relatively good self-mitigating capacity at some pH values. In this case, HFO sorbs most of the Pb and Cu at around pH 7. However, dissolved Zn, Cd, and Ni can remain mobile in waters discharging from this site.

Applications

Some mine waters have the inherent ability to clean themselves up when discharged into the environment. Computer-model simulations can predict this self-mitigating capacity of mine waters. This approach could provide guidance in mine-drainage remediation and planning efforts.

Zinc, Cd, and Ni are difficult to self-mitigate in mine waters due to their relatively weak sorption on hydrous iron oxides. Consequently, these metals tend to remain mobile in waters discharging from mined lands. Elevated levels of Zn have been documented in numerous mine waters (e.g., Plumlee et al., 1999).

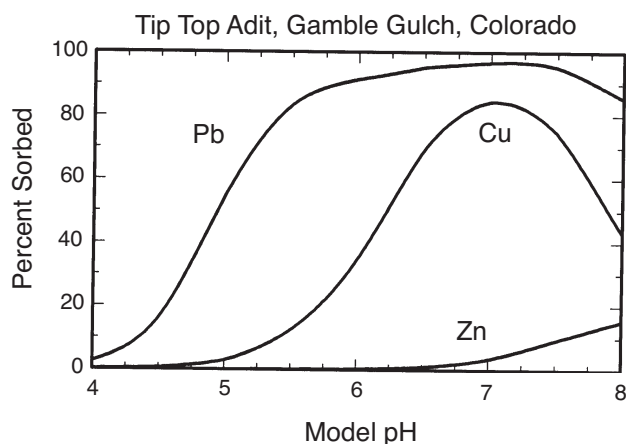
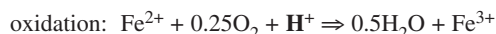


FIGURE 7.8—Computer simulation of metal sorption on hydrous ferric oxide (HFO) as a function of pH for drainage from the Tip Top adit adjacent to Gamble Gulch, Colorado. HFO concentration was derived from the precipitation of dissolved Fe originally present in the drainage.

The concept of self-mitigating capacity can be exploited in remediation activities. Addition of dissolved Fe to mine waters can enhance the eventual attenuation of dissolved metals. Computer simulations can predict the amount of additional Fe necessary to achieve the desired results. Iron and aluminum flocculants often are used in industry to clean up inorganic contaminants (e.g., Clifford et al., 1986).

An important factor to keep in mind with Fe-treatment systems is that, although the oxidation of Fe consumes acid, the precipitation of Fe generates acid as illustrated in the following equations:



When planning for pH adjustment, it is important to add enough base to counteract acidification by hydrolysis and precipitation reactions (not only for Fe but for all metals in the mine water).

Another important factor is that of desorption. Metal sorption may be transitory if conditions change to favor desorption. Change in factors such as pH, dissolved species, and temperature may trigger desorption reactions. Aging of sorbent material may also result in desorption of some metals.

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Volume 6A

THE ENVIRONMENTAL GEOCHEMISTRY OF MINERAL DEPOSITS

Part A: Processes, Techniques, and Health Issues

Volume Editors: Geoffrey S. Plumlee and Mark J. Logsdon

CONTENTS

INTRODUCTION

AN EARTH-SYSTEM SCIENCE TOOLKIT FOR ENVIRONMENTALLY FRIENDLY
MINERAL RESOURCE DEVELOPMENT

G.S. Plumlee and M.J. Logsdon

AN OVERVIEW OF THE ABUNDANCE, RELATIVE MOBILITY, BIOAVAILABILITY, AND HUMAN
TOXICITY OF METALS

Kathleen S. Smith and Holly L.O. Huyck

PROCESSES

THE ENVIRONMENTAL GEOLOGY OF MINERAL DEPOSITS

G.S. Plumlee

SOME FUNDAMENTALS OF AQUEOUS GEOCHEMISTRY

D. Kirk Nordstrom

THE ROLE OF BACTERIA IN ENVIRONMENTAL GEOCHEMISTRY

A.L. Mills

GEOCHEMISTRY OF ACID MINE WATERS

D. Kirk Nordstrom and C.N. Alpers

METAL SORPTION ON MINERAL SURFACES: AN OVERVIEW WITH EXAMPLES RELATING TO MINERAL DEPOSITS

Kathleen S. Smith

GENERAL ASPECTS OF AQUATIC COLLOIDS IN ENVIRONMENTAL GEOCHEMISTRY

J.F. Ranville and R.L. Schmiermund

GEOCHEMICAL PROCESSES CONTROLLING URANIUM MOBILITY IN
MINE DRAINAGES

R.B. Wanty, W.R. Miller, P.H. Briggs, and J.B. McHugh

GEOCHEMISTRY OF THE PROCESSES THAT ATTENUATE ACID MINE DRAINAGE IN WETLANDS

Katherine Walton-Day

THE ENVIRONMENTAL GEOCHEMISTRY OF CYANIDE

A.C.S. Smith and T.I. Mudder

TECHNIQUES

FIELD METHODS FOR SAMPLING AND ANALYSIS OF ENVIRONMENTAL SAMPLES FOR UNSTABLE AND
SELECTED STABLE CONSTITUENTS

W.H. Ficklin and E.L. Mosier

LABORATORY METHODS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

J.G. Crock, B.F. Arbogast, and P.J. Lamothe

GEOCHEMICAL MODELING OF WATER-ROCK INTERACTIONS IN MINING ENVIRONMENTS

C.N. Alpers and D. Kirk Nordstrom

STATIC-TEST METHODS MOST COMMONLY USED TO PREDICT ACID-MINE DRAINAGE:
PRACTICAL GUIDELINES FOR USE AND INTERPRETATION

W.W. White III, K.A. Lapakko, and R.L. Cox

HEALTH ISSUES

THE HEALTH EFFECTS OF MINERAL DUSTS

Malcolm Ross

BIOAVAILABILITY OF METALS IN THE ENVIRONMENT:
IMPLICATIONS FOR HEALTH RISK ASSESSMENT

G.R. Krieger, H.A. Hattemer-Frey, and J.E. Kester

EFFECTS OF HEAVY METALS ON THE AQUATIC BIOTA

M.G. Kelly

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