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Chapter 10

GEOCHEMISTRY OF THE PROCESSES THAT ATTENUATE ACID MINE DRAINAGE IN WETLANDS

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INTRODUCTION

Because conventional treatment of acid-mine drainage (AMD) involves installation and maintenance of water treatment plants, regulators and mine operators have sought lower cost and lower maintenance technologies. One ecological engineering technology that has received increasing research attention is the use of natural and constructed wetlands for remediation of some of the water-quality problems associated with AMD. As surface water flows through a wetland, several processes can occur to decrease the elevated concentrations of sulfate, trace metals, arsenic, and hydrogen ions that characterize AMD. These processes range from precipitation of mineral phases to the active uptake of solutes by vegetation. The relative importance of these processes between different wetlands depends on the hydrologic and geochemical characteristics of the wetlands.

This paper describes the geochemistry of the processes that contribute to AMD attenuation in wetlands and presents some of the case studies that have identified these processes. The attenuation of AMD in wetlands has been studied in natural and in manmade (constructed) wetlands. In this paper, case studies of both are presented. A discussion of some of the general characteristics of wetlands is followed by more detailed discussions of the processes and geochemistry that contribute to the treatment of AMD in wetlands, relevant case studies, and a brief discussion of constructed wetland design. The physical, chemical, and hydrologic characteristics of a wetland that affect its potential for supporting specific types of reactions are also emphasized.

Although mine drainage can have pH values ranging from acid to alkaline (Hedin, personal commun., 1992; Ficklin et al., 1992; Plumlee et al., 1993; Smith et al., 1994; Plumlee et al., 1999), most wetlands that have been studied with respect to their effect on the water quality of mine drainage receive AMD, and the discussion in this paper, therefore, focuses on processes that occur where wetlands interact with AMD. Other recent summaries concerning wetland treatment of AMD are Kleinmann (1990) and Klusman and Machemer (1991). Nordstrom and Alpers (1999) review the formation of AMD.

GENERAL AND GEOCHEMICAL CHARACTERISTICS OF WETLANDS

Wetlands are transitional between terrestrial and aquatic ecosystems. They are characterized by one or more of the following conditions (Cowardin et al., 1979; Hammer and Bastian, 1989):

1) They contain hydrophytic vegetation (plants that are adapted to survive in waterlogged soils).
2) They contain hydric soils (soils that are wet enough for sufficient time to produce anaerobic conditions which, in turn, limit the types of plants that can grow).
3) They contain nonsoil substrate (such as rock or gravel) that is saturated or covered by shallow water at some time during the growing season.

A scientific classification of wetlands has been developed by the U.S. Fish and Wildlife Service (Cowardin et al., 1979) and is being used to map and inventory wetlands in the United States. Currently (as of late 1995), the definition of wetlands for jurisdictional purposes in the United States is a subject of controversy (Kusler, 1992). Studies of natural wetlands presented in this paper have not been examined to determine whether the study areas are scientific or jurisdictional wetlands, or both.

Comprehensive discussions of the geochemistry of wetlands are provided in several publications (Ponnamperuma, 1972; Gambrell and Patrick, 1978; Sikora and Keeney, 1983; Mitsch and Gosselink, 1986; Shotyk, 1988; Faulkner and Richardson, 1989). A general discussion derived from these references and others follows.

A generalized profile of a flooded wetland includes an oxidized water column and oxidized sediment layer that overlie a reduced sediment zone (Fig. 10.1). A relatively uniform level of oxygen exists in the water column and upper sediment layer because of

1) The rapid exchange of oxygen across the atmosphere/surface-water interface;
2) The limited population of oxygen-consuming organisms present;
3) Oxygen production by photosynthetic algae within the water column; and
4) Surface-water mixing by convection and wind action (Gambrell and Patrick, 1978).

In saturated sediments, the replenishment of oxygen is limited by the aqueous diffusion of dissolved oxygen into the sediments, which is four orders of magnitude slower than gaseous diffusion (Greenwood, 1961). Therefore, oxygen concentrations in the oxidized sediment zone decrease with depth, and anaerobic (anoxic) conditions develop in the underlying sediment zones (the reduced sediments) where microbial and chemical oxygen demand exceed the rate of resupply by aqueous diffusion. Within the reduced sediments, oxidized microenvironments can exist immediately adjacent to roots that transport oxygen from the atmosphere. The thickness and continuity of the oxidized and reduced soil zones are variable and depend on several factors, including soil permeability, duration and frequency of flooding, and supply of carbon avail-

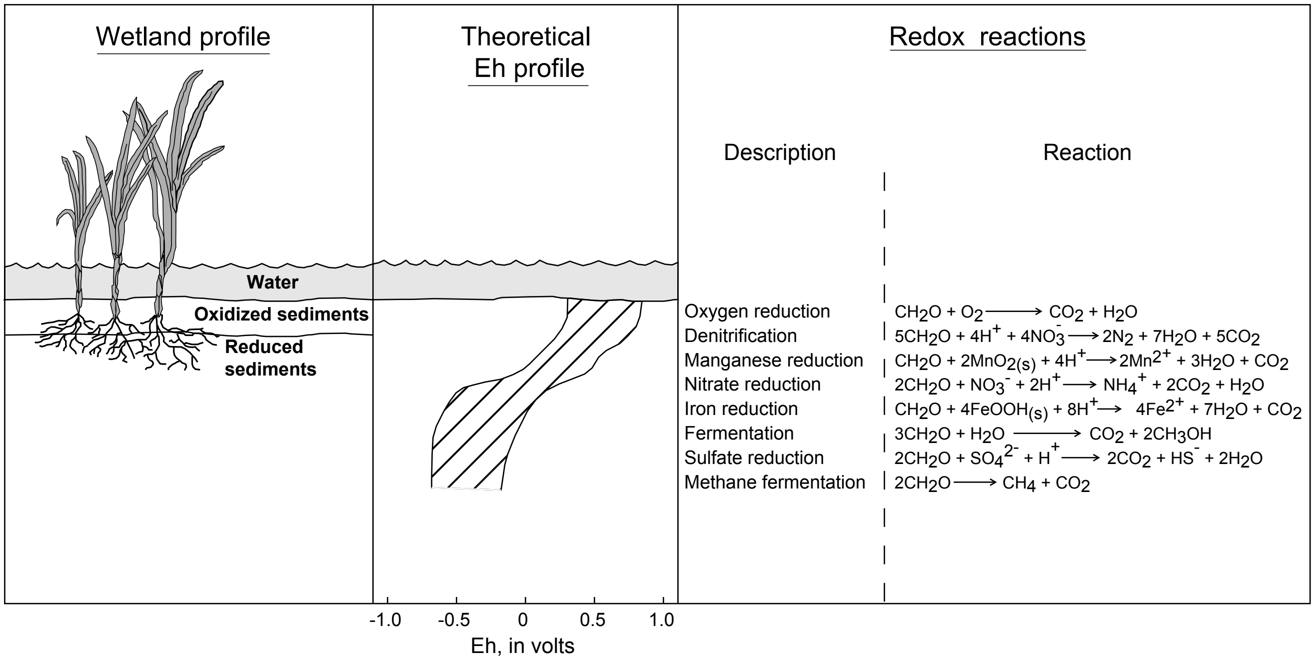

FIGURE 10.1—Generalized profile of wetland soil and some soil chemical parameters (adapted from Gambrell and Patrick, 1978; Stumm and Morgan, 1981).

able for microbial metabolism (Gambrell and Patrick, 1978). This typical wetland redox profile develops independent of wetland hydrology; that is, the profile can develop in flow-through wetlands, in wetlands that recharge adjacent and underlying ground-water systems, and in wetlands that receive discharge from adjacent ground-water systems.

The redox profile that develops in saturated soils results from a sequence of microbially mediated reactions that are thermodynamically controlled: the reactions yield less energy on a molar basis as the redox potential decreases. Respiration is the amalgam of biological processes whereby organisms oxidize organic and inorganic matter to obtain energy. Most organisms oxidize organic matter as a source of energy, but some specialized organisms known as chemoautotrophic bacteria obtain energy from the oxidation of reduced inorganic compounds (Stanier et al., 1986; Mills, 1999). Oxidation releases electrons that must be incorporated into another compound known as the terminal electron acceptor. Oxygen is the optimal terminal electron acceptor because the oxidation of organic matter by oxygen (known as aerobic respiration) yields more energy on a molar basis than any other common oxidant. As aerobic and facultative anaerobic microorganisms deplete oxygen in flooded soils, facultative and obligate anaerobes that use anaerobic respiration to obtain energy begin to dominate. Facultative anaerobes are organisms that can use aerobic or anaerobic respiration, whereas obligate anaerobes use only anaerobic respiration. Inorganic substances other than oxygen are the terminal electron acceptors for oxidation of organic matter in anaerobic respiration. The sequence of reduction reactions proceeds, based on decreasing energy yield, from oxygen reduction to denitrification, manganese reduction, nitrate reduction, iron reduction, fermentation, sulfate reduction, and methane fermentation (Fig. 10.1). Generally, a redox zonation develops in soils as the supply of an energetically favorable terminal electron acceptor is depleted, and as organisms that use the next most energetically favorable terminal electron acceptor begin to dominate. Most of these reactions generate alkalinity, so that the pH tends to increase with depth in a wetland. Values of pH in peat-dominated wetlands normally range from 4 to 8.5 (Shotyk, 1988).

The differences between aerobic and anaerobic respiration also account for the accumulation of organic matter in wetland soils. Aerobic respiration usually degrades organic materials faster than anaerobic respiration; hence, organic materials are more likely to accumulate in anaerobic settings (Gambrell and Patrick, 1978; Stanier et al., 1986).

PROCESSES THAT CONTRIBUTE TO ATTENUATION OF ACID MINE DRAINAGE IN WETLANDS

Water-quality improvement that occurs as AMD flows through wetlands is caused by the transformation of dissolved and particulate constituents to forms not available for waterborne transport. The constituents of AMD are transferred from the aqueous phase to other phases including inorganic solids, gases, and biomass within the wetland substrate. Specific processes in wetlands that are known to contribute to AMD attenuation are (Fig. 10.2):

1) Sedimentation of particulate material;
2) Oxidation and precipitation of iron and manganese oxyhydroxides;
3) Ion exchange and adsorption of dissolved constituents onto solid components of the wetland substrate;
4) Complexation of dissolved constituents with organic matter;
5) Sulfate reduction and precipitation of metal sulfides; and
6) Plant assimilation of metals.

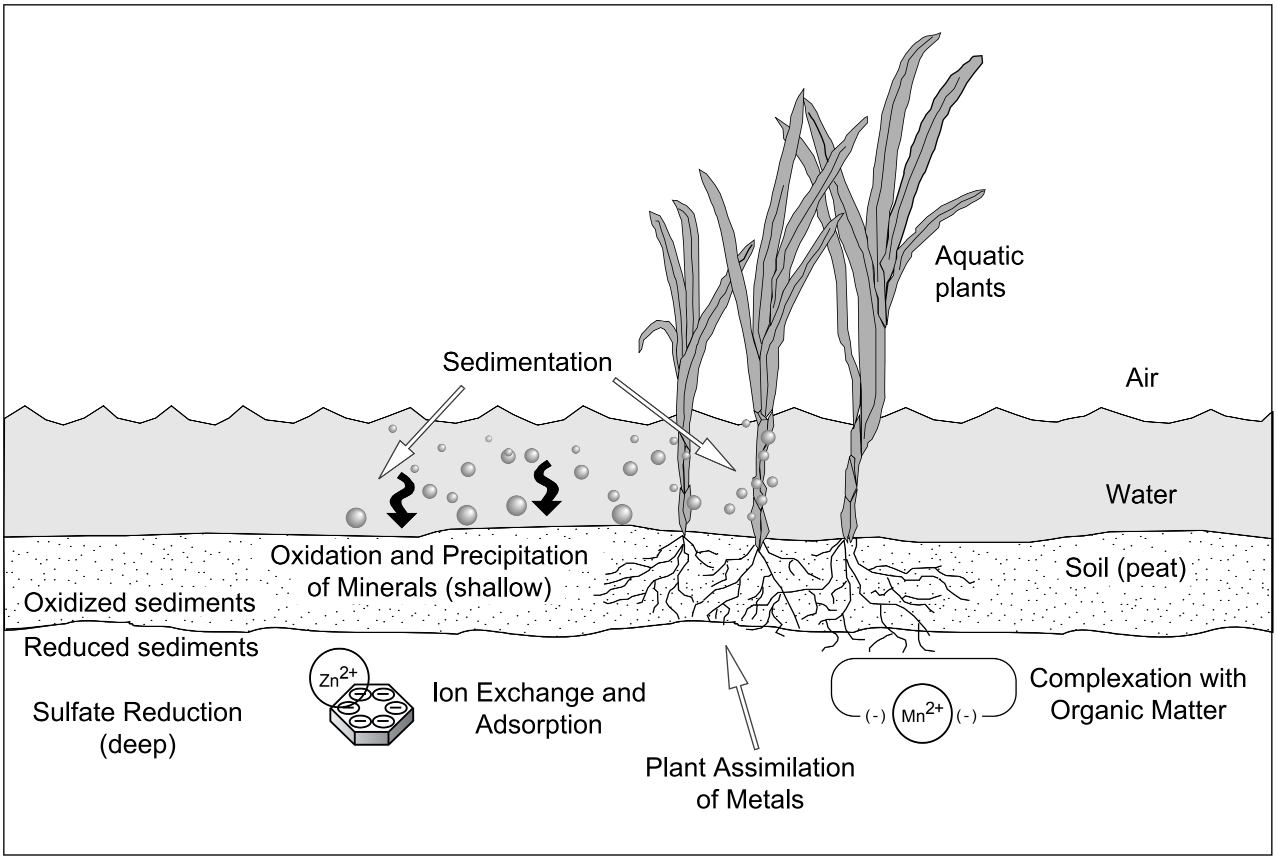

FIGURE 10.2—Geochemical and physical processes that contribute to metal retention in wetlands. Cartoons represent hydrated manganese ion complexing with organic molecule and zinc ion adsorbed to charged surface of a mineral.

Processes 1 and 2 occur primarily in the upper, oxidized zones of wetland sediments. Process 5 is restricted to the reduced zone of the sediment, whereas the other processes occur throughout the soil column or in the plants. The bacterial uptake of metals (Grappelli et al., 1992; Pradhan and Levine, 1992) is another process that may operate in wetlands, but has not been investigated with respect to AMD in wetlands and, therefore is not discussed further. The discussion in this paper of AMD attenuation by wetlands also does not consider the water-quality improvements that occur where additional water sources in the wetland (such as springs, tributary streams, or precipitation onto the wetland) dilute the concentrations of dissolved constituents. Instead, the discussion is concerned with reactions and processes that immobilize or otherwise remove the constituents from the water column so that not only the concentration, but also the mass rate of transport of dissolved constituents, is decreased as AMD flows through the wetland.

Investigators have used several different approaches to quantify constituent removal as water passes through wetland treatment systems. One method defines "treatment efficiency" (TE) as follows:

$$TE = (C_i - C_o)/C_i \qquad [1]$$

where C_i and C_o are the inflow and outflow concentrations of the constituent of interest (Girts and Kleinmann, 1986). This method is used most often because it employs concentrations that are the criteria used to determine if a facility has met its regulatory requirements. However TE does not account for wetland hydrology. Therefore, dilution from water sources in the wetlands, such as springs, could cause a positive TE value; whereas, evaporation from the wetland could cause a negative TE value. In addition, TE does not account for the magnitude of inflow versus outflow concentration. For instance, a wetland that has constituent inflow and outflow concentrations of 700 and 500 mg/l has the same TE as a wetland with constituent inflow and outflow concentrations of 7 and 5 mg/l. Obviously, the magnitude of the problem and treatment (200 mg/l removed compared to 2 mg/l removed) is very different in the two wetlands (Wieder, 1989). Finally, TE does not account for size variations between wetlands. In the previous example, the identical TE values are comparable only if the former wetland were 100 times larger than the latter.

Another variable that has been used to describe constituent removal efficiency is area adjusted constituent loading or removal expressed as mass of metal per time per area [e.g., grams day^{-1} m^{-2} or gdm (Hedin and Nairn, 1990)]. Calculation of this variable is more time consuming and costly than the calculation of TE because it requires measurement of influent and effluent concentrations and discharges or flux rates (Wieder, 1988; Wieder, 1989). This variable is superior to TE because it accounts for dilution and evaporation effects and the size of the wetland and, therefore, enables performance comparisons between wetlands. Unfortunately, hydrologic flux data are expensive to obtain and are often not available for a study site, so that this variable cannot readily be calculated (Wieder, 1989).

Sedimentation of particulate material

Primary sedimentation in wetlands can remove much of the influent sediment load and, consequently, can remove any chemical constituents associated with the sediments. Sheet flow of water through wetlands decreases the velocity of water and promotes the settling of suspended particles (Boto and Patrick, 1978; Mitsch and Gosselink, 1986). In addition, filtration of sediment by closely spaced plant stems contributes to sediment trapping in wetlands.

Some case studies have reported that sedimentation can be a major contributor to the treatment of AMD in wetlands. Results of a mass-balance study of iron in a constructed wetland that receives AMD indicated that most of the iron removal in the wetland was caused by sedimentation and precipitation of iron hydroxides (Fennessey and Mitsch, 1989). A mass-balance study of iron and trace metals in a subalpine wetland that receives AMD, showed that 60–70% of the iron removal that occurs in the wetland is due to physical settling of iron oxyhydroxide particles greater than 0.1 µm (Walton-Day, 1996).

Oxidation and precipitation of iron and manganese oxyhydroxides

The oxidation of iron and precipitation of iron oxyhydroxides is an important metal removal mechanism in wetlands. Many studies have reported iron removal from mine drainage as a result of this process, and many constructed wetlands have been designed to maximize this process. Theoretically, manganese also ought to precipitate in oxic zones of wetlands by this mechanism.

The oxidation of iron and precipitation of iron oxyhydroxides can be written as a net reaction (Bigham et al., 1990):

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_{3\ (s)} + 2H^+ \qquad [2]$$

In aerated solutions at pH >5, ferrous iron autooxidizes to ferric iron. However, at lower pH values, bacteria such as *Thiobacillus ferrooxidans* catalyze iron oxidation. Because *T. ferrooxidans* are acidophilic (acid-loving), iron oxidation is optimal at pH 3 to 3.6 (Ehrlich, 1981). Although reaction [2] removes iron from solution, the reaction also produces hydrogen ions. The decreased pH that results from this reaction if there is no buffering is undesirable and is one reason other wetland processes have been sought to remove iron from AMD.

The iron hydroxides that can form in AMD and oxic wetlands are complex. Some of the iron hydroxides that from in AMD are actually poorly crystallized oxyhydroxysulfates of iron (Bigham et al., 1990) that have recently been named schwertmannite (Murad et al., 1994). In addition, the types of iron hydroxide material that form in mine drainage can be classified on the basis of pH and sulfate content of the mine drainage (Bigham et al., 1992; Bigham, 1994): jarosite [$(K,Na)Fe_3(OH)_6(SO_4)_2$] precipitation is favored by very low pH values (1.5–3.0) and elevated sulfate concentrations (>3,000 mg/l); pH values from 3 to 4 and sulfate concentrations ranging from 1000–3000 mg/l favor schwertmannite [$Fe_8O_8(OH)_6SO_4$]; pH values greater than 5 and elevated concentrations of iron favor ferrihydrite [$Fe_5(OH)_8 \bullet 4H_2O$] formation. Goethite (Alpha FeO•OH) forms as an alteration product of jarosite, schwertmannite, and ferrihydrite, and can form directly at low pH and low sulfate concentrations and at higher pH in bicarbonate-rich water (Bigham et al., 1992; Bigham, 1994). The results of this classification have not yet been applied to precipitation of iron solids in wetlands, but seem to indicate that precipitation of iron oxides at high pH values and low sulfate concentrations is the most desirable scenario because it produces the most stable precipitate. In addition, alteration of jarosite, schwertmannite, or ferrihydrite to goethite could release metals sorbed to the original mineral phase.

Many case studies of natural, constructed, and laboratory-scale microcosm wetlands have indicated that the formation of iron oxides is an important iron-removal process in wetland treatment systems. Formation of iron oxides was responsible for 73–86% of iron retention that occurred in laboratory-scale constructed wetlands exposed to synthetic acid coal mine drainage (Wieder et al., 1990). Iron oxides accumulated in the oxic zone of a natural wetland (Pennsylvania, U.S.A.) exposed to AMD (Tarutis et al., 1992). Faulkner and Richardson (1990) reported that 80% of the iron accumulating in constructed wetlands in Alabama, U.S.A., was in an oxide form (goethite) and that biological or chemical oxidation, or both, was the dominant removal mechanism.

The acidity produced by oxidation and precipitation of iron hydroxides can exacerbate water-quality problems. In constructed wetlands that receive AMD containing extremely elevated iron concentrations (40–170 mg/l) and pH values less than or equal to 5.6, oxidation of iron and precipitation of iron hydroxides increases acidity and lowers pH in the wetlands necessitating additional water treatment to comply with regulations (Brodie, 1990).

The factors controlling iron mobility in natural systems are complex and include the pH and Eh of the system and the presence of certain types of bacteria, complexing agents, and ligands that combine with iron to form minerals. A process that affects iron speciation in acid streams is the photoreduction of iron. In daylight, sunlight striking an acid stream promotes reductive dissolution of iron hydroxides in the stream. This dissolution results in greater concentrations of dissolved ferrous iron during daylight versus darkness (McKnight et al., 1988). If iron photoreduction occurs in wetland treatment systems where precipitation of iron oxyhydroxides is a major treatment mechanism, the photoreduction could cause less effective removal of iron and dissolution of previously precipitated iron oxides during daylight. Henrot et al. (1989) initially attributed diurnal fluctuations in dissolved iron concentrations exiting a wetland treatment system to iron photoreduction. However, in a subsequent report, Henrot and Wieder (1990) reported that photoreduction caused insignificant iron remobilization in laboratory peat microcosms that were subjected to AMD. Similar results were reported for five pilot-scale constructed wetlands (Wieder, 1992). In addition, Wieder (1992) noted that iron retention effectiveness was greater during the daytime than at night, which he attributed to daytime oxygenation of surface waters by photosynthetic algae.

As with iron, the oxidation of manganese and precipitation of manganese oxides in wetlands can reduce manganese levels in AMD. The oxidation of manganese can occur as follows (Ehrlich, 1981):

$$Mn^{2+} + 1/2\ O_2 + H_2O \rightarrow MnO_2 + 2H^+ \qquad [3]$$

The oxidation of manganese and the precipitation of manganese oxides occurs at greater Eh and pH values than oxidation and precipitation of iron hydroxides (Fig. 10.3). As in the equivalent reactions for iron, reaction [3] produces acidity and can be catalyzed by bacteria.

The removal of manganese by oxidative processes in wetlands is generally less effective than the removal of iron (Gerber et al., 1985; Wieder and Lang, 1986; Henrot and Wieder, 1990). Although manganese-oxidizing bacteria have been identified in wetlands (Batal et al., 1989), failure of wetland treatment systems to remove significant quantities of manganese by oxidative processes has been attributed to low pH values in the wetlands (Henrot and Wieder, 1990; Wildeman et al., 1990). Manganese autooxidizes at pH values of 8.5 or greater. Limited research indicates that manganese-oxidizing bacteria are not active at low pH (Henrot and Wieder, 1990). Removal of manganese by formation of $MnCO_3$ should proceed at higher pH values (Sikora and Keeney, 1983). This removal process has not been reported in wetlands that receive AMD, but could be important if wetlands are used to remediate mine drainage that has circumneutral to alkaline pH.

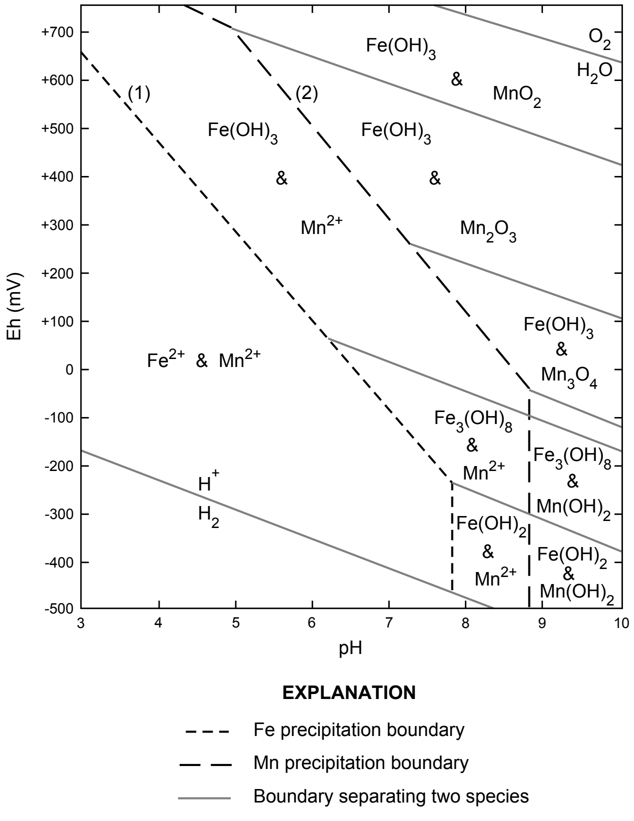

FIGURE 10.3—Eh-pH diagram for Mn and Fe (from Collins and Buol, 1970; Faulkner and Richardson, 1989; reprinted with permission).

In summary, oxidation and precipitation of oxides, hydroxides, or oxyhydroxides in wetlands remove iron from AMD. However, iron removal by these processes is incomplete and generates acidity. These processes do not seem to remove manganese at the acid to circumneutral pH values that predominate in wetland treatment systems. Other metals, such as copper and aluminum, can also oxidize and(or) form metal-oxide precipitates in the Eh and pH ranges where iron and manganese hydroxides and oxides form; however, no case studies of wetlands were found that examined if these processes remove other metals present in AMD. The role of sorption of trace metals to these minerals is described in the section "Ion exchange and adsorption." In addition, in circumneutral- to alkaline-pH mine-drainage/wetland systems, other minerals, such as carbonate minerals, could form and remove metals; however, only limited research has been reported on alkaline mine drainage/wetland systems.

Ion exchange and adsorption

Adsorption and ion exchange contribute to the removal of trace elements from solution in many natural aqueous systems. Similarly, they contribute to metal immobilization in wetlands, but most case studies indicate that their contribution is minor compared to other processes. Detailed geochemical discussions of adsorption are in Stumm and Morgan (1981), Evans (1989), Davis and Kent (1990), and Smith (1999).

Ion exchange and adsorption are processes that occur at the surface of particles in the substrate and between layers in the crystal structures of some clay minerals. Both processes attach dissolved ions or molecules to a pre-existing solid (Drever, 1988). Ion exchange (also referred to as nonspecific adsorption) is a relatively weak interaction between particle surfaces and ions, and most attached ions can be easily removed from the surface under appropriate conditions. It is rapid and usually reversible. In ion exchange a hydrated ion is held against the particle surface primarily by electrostatic attraction. The electrostatic bond is also known as an outer-sphere complex. The sorbed ions will readily exchange for other ions that similarly only form outer-sphere complexes with the surface. In contrast, in adsorption (also referred to as specific adsorption), a covalent bond (or inner-sphere complex) forms between the mineral surface and the adsorbing ion. In this interaction, the adsorbing ion is not readily replaced. The difference between the two processes results from a different degree of interaction between the particle surface and the ion.

In adsorption, elements that form oxyanions, such as arsenic, chromium, and molybdenum bond to variably charged particle surfaces through the process of ligand exchange. Cations also can bond to variably charged surfaces where a hydrolyzed cation forms an inner-sphere complex with a negatively charged, deprotonated surface (Stumm and Morgan, 1981; Evans, 1989).

In wetland systems, hydrous iron oxides and organic matter are probably the two most important substrates for adsorption. The zero point of charge (ZPC) for iron oxyhydroxides has been reported at values of pH ranging from 6.1 to 8.5 (Leckie and James, 1974; Stumm and Morgan, 1981). This result indicates that the net surface charge on iron oxyhydroxide minerals should be positive in the pH range of AMD and of wetlands affected by

AMD. Therefore, based on purely electrostatic considerations, sorption of anions would predominate in wetland treatment systems. Nevertheless, removal of trace-metal cations from AMD has been attributed to adsorption onto hydrous iron oxide minerals (K.S. Smith, U.S. Geological Survey, written commun., 1995). Specific adsorption of trace-metal cations would not be subject to the electrostatic constraints described. It is also possible that the surface charge of the minerals is modified by adsorption of organic or other anions, resulting in (nonspecific) adsorption of cations to the iron oxide surfaces as described by Tipping et al. (1983).

Several studies have cited ion exchange and adsorption as processes contributing to metal retention in wetland treatment systems (Wieder and Lang, 1986; Karathanasis and Thompson, 1991; Machemer and Wildeman, 1992). For some metals such as manganese, ion exchange may be the dominant retention process, but the process does not remove a sufficient amount of metal to be an efficient removal mechanism on its own. In addition, because ion exchange is readily reversible, it is not a reliable treatment process in long-term passive treatment systems; unforeseen changes in environmental conditions could release metals held in exchange positions. In general, ion exchange and adsorption may contribute to metal removal in mine drainage, particularly in the initial stages of a constructed wetland (Kleinmann, 1990; Machemer and Wildeman, 1992). However, the amount of metal removed by these processes in a wetland is limited by the volume of the wetland.

Complexation with organic matter

The complexation of metal ions with organic matter may be an important metal-removal process in wetlands that receive AMD. However, the process also can increase metal mobility in certain situations and has been cited as a reason for incomplete removal of metals in wetland treatment systems.

Organic matter in soils consists of plant and animal products in various stages of decomposition. This material can be divided into humic and nonhumic substances, which, depending on the substance and ambient conditions, can have varying degrees of solubility in water. Humic substances are the most stable compounds in soils and include humic acid, fulvic acid, and humin. Nonhumic substances include high- and low-molecular-weight organic acids, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons, and lignin fragments (Kabata-Pendias and Pendias, 1984). The source of organic matter in a wetland and its degree of decomposition will affect the properties of the organic matter. For instance, organic matter in a constructed wetland that has a manure substrate might have very different properties than organic matter in a natural wetland that has a substrate consisting primarily of decomposed plant material.

Interactions between metal ions and organic matter help control the mobilities of some metals in organic-rich environments (Fraser, 1961; Theis and Singer, 1974). Metal-organic interactions include ion exchange, surface sorption, complexation and chelation, coagulation, and peptization. Because of the complexity of natural organic matter and the possibility that more than one molecule may interact with a metal ion, identification of the specific process involved may be difficult. The discussion in this section is confined to complexation of metals by organic matter, which is essentially the same as specific adsorption to mineral surfaces that was discussed previously. The discussion is general in nature because many of the specific details of metal-organic interactions are complex, poorly understood, controversial, or all three, and a detailed discussion is beyond the scope of this presentation.

Metal-organic complexes may assume many forms. Two possible complex types are shown on Figure 10.4. The manganese-organic complex (Fig. 10.4a) is termed an outer sphere complex because the organic ligand does not interact directly with the hydrated manganese ion; the hydrated manganese ion is held within the ligand by electrostatic forces. In the inner sphere complex (Fig. 10.4b), the ligand donates electrons to the hydrated metal ion, and a covalent bond forms. The latter is a stronger interaction than the former and more strongly affects the solubility of the metal (Bloom, 1981). Hydroxyl and carboxyl functional groups on organic matter are probably the most important sites for complexation.

Formation of a metal-organic complex may result in increased or decreased mobility of the metal, depending on the solubility of the metal-organic complex. For instance, iron-humic-acid complexes are soluble if the pH ranges from 3 to 9, but precipitate at lower pH values (Elder, 1988); this behavior mimics the behavior of humic acids that are insoluble at low pH values, but soluble at

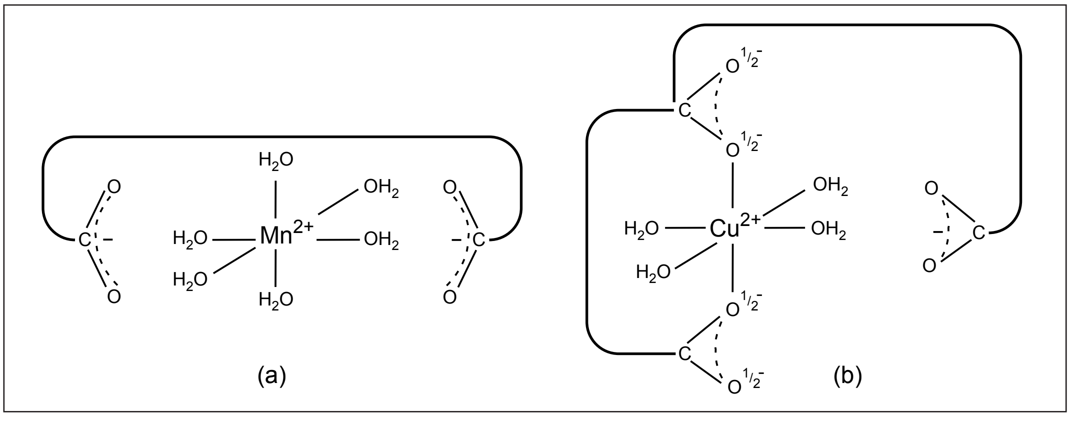

FIGURE 10.4—Generalized chemical structures of outer sphere (a) and inner sphere (b) metal-organic complexes (from Bloom, 1981; Salomons and Förstner, 1984; reprinted with permission).

greater values. In contrast, metal-fulvic-acid complexes and fulvic acids are generally more soluble over a greater pH range (Kabata-Pendias and Pendias, 1984).

The stabilities of metal-organic complexes vary. The Irving-Williams order is probably the most cited, and it indicates the stability of divalent-metal-organic complexes decreasing as follows (Irving and Williams, 1948):

$$Cu > Ni > Co > Zn > Cd > Fe > Mn$$

Wieder (1990) reported slightly different orders of stability for metal binding to *Sphagnum* peat and sawdust. As mentioned previously in this section, the study of metal-organic interactions is evolving, and more quantitative descriptions await advances in the science.

Many case studies have cited organic binding of metals as an important metal-retention process in wetland substrates that receive AMD. Wieder and Lang (1986) reported that most of the Al and Fe retained in four natural wetlands that received metal-rich inputs were bound to organic matter in the peat. About 40% of the Al accumulating in a constructed wetland receiving highway runoff was specifically adsorbed (complexed) to organic matter (Wieder et al., 1988). Twenty-two percent of iron retained in peat microcosms that were subjected to applications of synthetic AMD was organic-bound iron (Henrot and Wieder, 1990); however, 62% of the iron was contained in iron oxides. In a case study of metal retention in the substrate of a constructed wetland, Karathanasis and Thompson (1991) reported that Cu and Al were retained by association with organic matter more than other metals. From 20–40% of the two metals were bound to organic matter and the remainder was distributed between exchangeable, adsorbed, and residual forms. However, Karathanasis and Thompson (1991) did not report absolute metal concentrations in the extractions, or pretreatment-substrate-metal concentrations, so it is difficult to evaluate how much of the extracted metal had accumulated in the substrate since the onset of treatment. Other case studies also have indicated the importance of organic-bound metals (such as, Cu, Pb, and U) in wetlands that are metal-rich from sources other than AMD (Walton-Day et al., 1990; Ton et al., 1991; Owen et al., 1992).

In these case studies, the details of the metal-organic interactions are seldom described, and evidence for their existence is based on the results of sequential chemical extraction of sediment samples. In general, the specificity of extractions for sediment phases, such as a specific mineral or organic matter, is operationally defined, often controversial, and depends on:

1) The dominant matrix and chemical composition of the sample (Robinson, 1984; Martin et al., 1987);
2) The order in which the extractions are applied (Miller et al., 1986); and
3) Alteration by mineral dissolution and resorption of elements under certain extraction conditions (Rendell et al., 1980).

Therefore, although evidence gained through sequential chemical extraction of sediments has indicated the phases in which metals may be present in wetlands, much of this evidence has been accumulated using operationally defined, indirect techniques.

Some case studies have attributed poor performance of wetland treatment systems to the formation of metal-organic complexes that have increased metal mobility. For instance, Lapakko and Eger (1988) attributed limited metal removal observed at low inflow metal concentrations in batch and column experiments with peat and different mine drainage solutions to formation and leaching of dissolved-metal organic complexes. In one study where metal speciation was directly quantified, 40 and 99% of dissolved Al and Cu, respectively, were complexed with organic matter in the effluent of a constructed wetland that receives AMD (Karathanasis and Thompson, 1991). They described low and variable removal of Al in the wetland but did not report the extent of copper removal or the speciation of the metals in the wetland influent.

In summary, the formation of metal-organic complexes can retain metals in wetlands that receive AMD. However, most evidence for this process is somewhat indirect, and details have not been described. Additional research in AMD-wetland systems and in metal-organic interactions in general would remedy this situation.

Sulfate reduction and precipitation of metal sulfides

Microbially mediated reduction of sulfate affects improvement in several water quality parameters. First, sulfate reduction can increase the alkalinity and pH. Second, in the presence of reduced metal species, such as ferrous iron, the reduction of sulfate to sulfide promotes the precipitation of metal sulfide minerals that have low solubilities. This process decreases aqueous concentrations of metals and sulfate. Third, sulfate reduction promotes the formation of volatile, organic and inorganic reduced sulfur species that can diffuse to the atmosphere out of the wetland; through this process, sulfur is transferred from the water to the atmosphere. Fourth, sulfate reduction may result in the incorporation of reduced sulfur into organic sulfur species; this process decreases the concentration of sulfate and sometimes consumes protons depending on the stoichiometry of the organic sulfur compound. Transmission of water down to and through the reducing layers of the substrate must be large relative to the total amount of AMD in a system for the process to operate efficiently. Many case studies have documented the presence of sulfate-reducing bacteria in wetlands and the water-quality improvements attributed to some of these processes.

During microbially mediated sulfate reduction, facultative and obligate anaerobes oxidize organic matter using sulfate as a terminal electron acceptor. In assimilatory sulfate reduction, the microorganisms incorporate the reduced sulfur into biochemical compounds; no extracellular sulfide is produced. In dissimilatory sulfate reduction, the microorganisms use sulfate as a terminal electron acceptor and produce sulfide (Ehrlich, 1981). In the net reaction:

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O \qquad [4]$$

or

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad [5]$$

microorganisms oxidize organic matter (CH_2O) to CO_2 and water (or bicarbonate), and SO_4^{2-} is reduced to H_2S. The two reactions are equivalent except that, in reaction [5], the carbonic acid-bicarbonate equilibria has been included to show the generation of bicarbonate alkalinity, which is equivalent to the consumption of protons that occurs as reaction [4] proceeds to the right. At pH values less than about 4.5, sulfate reduction tends to cause an increase in pH without generating bicarbonate (reaction [4]). At greater pH values, sulfate reduction also increases bicarbonate concentrations (reaction [5]). In addition, the sulfate-reducing bacteria are reported to be inactive at pH values less than 4.2 (Trudinger, 1979); therefore, the process may have no effect until greater pH is achieved.

The net consumption of protons or the generation of bicarbonate alkalinity in this reaction depends on interactions of iron and other metals with sulfur in the system. If reduced iron and H_2S combine to form FeS:

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \qquad [6]$$

two protons are produced so that when reactions [4] and [6] are combined:

$$2CH_2O + SO_4^{2-} + Fe^{2+} \rightarrow 2CO_2 + FeS + 2H_2O \qquad [7]$$

there is no net change in the proton budget. Similarly, protons are not consumed when other metals that occur as free dissolved cations [such as Zn (II)] form sulfides following sulfate reduction (Anderson and Schiff, 1987). However, if oxidized iron in iron oxyhydroxide minerals is dissolved and reduced, then in the net reactions:

$$\begin{aligned}&9CH_2O + 4FeOOH + 4SO_4^{2-} + 8H^+\\ &\rightarrow 9CO_2 + 4FeS + 15H_2O \qquad [8]\end{aligned}$$

and

$$\begin{aligned}&15CH_2O + 8SO_4^{2-} + 4FeOOH + 16H^+\\ &\rightarrow 4FeS_2 + 15CO_2 + 25H_2O \qquad [9]\end{aligned}$$

protons are consumed where either iron monosulfide or pyrite is formed. The alkalinity in the iron oxyhydroxides is transferred from the solid to the aqueous phase using reactions [8] and [9] (Anderson and Schiff, 1987). Therefore, if the reduction of a metal and the formation of its sulfide involves consumption of protons, the net result will be an increase in alkalinity and pH. However, if reduction of the metal and the formation of its sulfide does not involve consumption of protons (e.g., reaction [7]), there is no net change in alkalinity and pH.

Reaction [5] indicates that H_2S gas can form during sulfate reduction. If this gas diffuses upward through the sediments and the water column in a wetland without being reoxidized, it can escape to the atmosphere. If the gas escapes, sulfate reduction results in a consumption of hydrogen and sulfate ions, and the loss of hydrogen and sulfur from the sediment/water system into the atmosphere. The evidence that this process occurs is obvious to anyone who has walked across a sulfur-rich wetland and smelled “swamp gas” rich in reduced sulfur compounds. Also, the formation and loss of organic sulfur gases such as methyl and dimethyl sulfide possibly could contribute to loss of sulfur from mine drainage in wetlands.

Reduced organic sulfur compounds can be formed through assimilatory sulfate reduction, and during diagenesis through reactions between organic matter and H_2S (Anderson and Schiff, 1987). Reactions can be written that indicate consumption of protons during this process:

$$ROH + H^+ + SO_4^{2-} \rightarrow RO\text{-}SO_3^- + H_2O \qquad [10]$$

where ROH is an alcohol, and $RO\text{-}SO_3$- is a sulfate ester. Some case studies have indicated that accumulation of organic sulfur is more important than accumulation of inorganic sulfur in natural wetlands that receive elevated sulfur loadings (e.g., Wieder and Lang, 1986). However, studies investigating the forms of sulfur in lakes and wetlands affected by AMD have shown that organic sulfur formation and accumulation is relatively unimportant compared to formation of inorganic sulfur compounds (Herlihy et al., 1988; Laudon, 1988; Wieder and Lang, 1988). With diagenesis, the fixation of sulfur in organic compounds possibly becomes more important, as evidenced by the amounts of organic sulfur in coal deposits (Davis, 1982; Casagrande, 1987).

Water-quality improvements in lakes and wetlands have been attributed to sulfate reduction and the formation of metal sulfides or both (Herlihy et al., 1987; Hedin et al., 1988; Kleinmann, 1990; McIntyre and Edenborn, 1990; Wildeman et al., 1990; Machemer and Wildeman, 1992). Sulfate reduction seems to be the only wetland process capable of removing significant quantities of some of the metals, such as dissolved Cu, Zn, and Cd, more common in metal-mine drainage than in coal-mine drainage (e.g., Wildeman et al., 1990; Machemer and Wildeman, 1992). Ninety-five percent removal of dissolved Fe, Zn, Mn, Ni, and Cd was attributed to sulfate reduction and precipitation of metal sulfides in pilot-scale bioreactors [barrels loaded with water-saturated mushroom compost (Dvorak et al., 1991)]. A failure of treatment systems dominated by sulfate reduction to remove manganese sulfide has been attributed to the higher solubility of MnS compared to other metal sulfides and to the fact that MnS requires a greater pH to precipitate in anaerobic wetlands than do other metal sulfides (Klusman, 1991). The inability of sulfate reduction to become established in some wetland systems or the reduced performance of sulfate reduction in some wetlands has been attributed to excess acidity (Kuyucak et al., 1991), metal toxicity (Kuyucak et al., 1991), lack of oxidizable organic matter (Dollhopf et al., 1988; Stark et al., 1991; Tarutis et al., 1992), and insufficient flow of water through the substrate (Hedin et al., 1989). In addition, there is some controversy about the source of alkalinity generated in these wetlands. As described previously in this section, sulfate reduction combined with the precipitation of metal sulfides has no net effect on the proton budget; therefore, alkalinity is not generated unless precipitation of sulfides is accompanied by reduction of metal oxyhydroxides. The alkalinity generated in some systems where sulfate reduction occurs may be from dissolution of $CaCO_3$ or other alkaline materials in the substrate (McIntyre and Edenborn, 1990; T. Wildeman, Colorado School of Mines, written commun., 1995) or from dissolution of ferric iron oxyhydroxides (Wieder, 1992; Vile and Wieder, 1993). However, Dvorak et al. (1992) demonstrated alkalinity generation in substrates where all carbonate alkalinity was removed by acid-leaching prior to the initiation of sulfate reduction. In addition, Kalin et al. (1991) demonstrated increases in alkalinity attributed to the activity of microorganisms, including sulfate-reducing bacteria.

Only limited research has been conducted on the role of H_2S loss in improving water-quality in wetland treatment systems. Effluent from pilot-scale sulfate-reducing systems that were constructed to treat mine drainage water contained S^{2-} and H_2S (Dvorak et al., 1991). Emission of H_2S accounted for up to only 2% of sulfur accumulation in five wetlands constructed to treat AMD (Wieder, 1992). Studies of a constructed wetland indicated that about 1% of total sulfur input escaped as H_2S gas and dissolved sulfide (Machemer et al., 1993). About 17% of the escaped sulfur, or less than 0.2% of the total sulfur input, escaped as H_2S gas. Based on these case studies, loss of H_2S is not a major process contributing to loss of sulfur and acidity in wetlands that treat AMD.

In summary, sulfate reduction and the precipitation of metal sulfides may have great potential to improve water quality in wetland treatment systems. In fact, treatment designs have been moving away from vegetated wetlands toward unvegetated bioreactors (Dvorak et al., 1991; Dvorak et al., 1992) in order to optimize sulfate reduction. There are, however, some details about the precise controls and mechanisms of the process that need to be clarified. Specifically, the alkalinity controversy and the reduced performance of sulfate-reducing wetlands caused by excess acidity, metal toxicity, lack of oxidizable organic matter, and insufficient flow of water through the wetland substrate need to be resolved to allow optimal performance of wetland treatment systems.

Plant assimilation of metals

Microbially mediated sulfate reduction and the concomitant precipitation of metal sulfides are perhaps the most significant ways that wetland biota contribute to treatment of mine drainage. However, plants also contribute to the immobilization of mine drainage components by accumulating metals within their structures. The general mechanisms and controls on this process are fairly well understood. Several case studies have indicated that elevated metal concentrations are present in plants from wetlands that treat mine drainage. However, plant assimilation of metals does not significantly contribute to metal immobilization in mine drainage and may be undesirable because assimilation makes some toxic metals available to consumers farther up the food chain (Kleinmann, 1990; Kelly, 1999).

Trace elements are termed micronutrients if small amounts are essential for plant nutrition. Macronutrients, such as carbon, sulfur, and nitrogen, are those required by the plant in copious amounts. Examples of micronutrient elements that are present in mine-drainage waters are aluminum, arsenic, cadmium, cobalt, copper, iron, manganese, mercury, molybdenum, nickel, silicon, and zinc. These elements are present in: structural materials (e.g., Fe and Si); small molecules, including antibiotics and porphyrins (e.g., As, Co, Cu, Fe, Hg, Si); large molecules (e.g., Co, Cu, Fe, Mn, Mo, and Zn); large molecules having storage, transport or unknown functions (e.g., Cd, Co, Cu, Fe, Hg, Mn, Ni, and Zn); and organelles or their parts (Cu, Fe, Mn, Mo, and Zn) (Kabata-Pendias and Pendias, 1984). Together, these elements participate in many important metabolic functions such as respiration, photosynthesis, and fixation and assimilation of other essential elements. Other trace metals that are present in plants, but that have no known physiological function (nonessential trace elements), include lead and silver. Many trace elements, both micronutrient and nonessential, can be toxic to plants where large quantities of the element are present in the environment of the plants.

Trace element uptake by plants can be either passive or active. In passive, or nonmetabolic, uptake, ions of an element diffuse along a chemical gradient from the external soil solution into the root endodermis. Active, or metabolic, uptake, requires metabolic energy and can occur against a chemical gradient (Kabata-Pendias and Pendias, 1984). If metabolic absorption of an element occurs faster than its arrival by mass flow from the soil solution, a concentration gradient develops, and diffusion then assists the absorption process (Loneragan, 1975).

Chemical speciation in the soil limits element availability to plants. Therefore, parameters that affect the speciation of an element and the sorptive capacity of a soil for an element such as pH, Eh, concentrations of complexing ions, organic-matter content of the soil, and clay content and mineralogy of the soil, will in turn affect the availability of an element to a plant. Freely dissolved ions, ions complexed with some forms of dissolved organic matter, and ions held in exchange positions on the surface of clay minerals are most readily available to plants (Kabata-Pendias and Pendias, 1984).

Specific molecular-scale descriptions of trace-element uptake by vegetation are difficult to locate. Kabata-Pendias and Pendias (1984) proposed three mechanisms of trace element uptake by roots: cation exchange by the roots, transport into cells with chelating agents or other carriers, and rhizosphere effects. Excretions of mucilaginous material, organic acids, amino acids, bicarbonate, and protons by the plant may mobilize trace elements (specifically trace metals) that are fixed in the soil, thereby enabling their uptake by the plant (Loneragan, 1975). Dejaegere et al. (1981) proposed a proton pump model wherein cation uptake by plants is promoted by proton extrusion by roots. They used the model to describe the mechanisms of K^+, NH_4^+ and Ca^{2+} absorption by plants, but the model also could be extended to account for absorption of trace cations.

Many case studies have described trace-metal accumulation by plants in natural and constructed wetlands affected by AMD. Vegetation in a constructed wetland in Colorado had as much as 1% metal content (Howard et al., 1989b). Heavy-metal removal potentials (in kilograms per hectare) have been reported for several types of submerged, emergent, and floating wetland aquatic vegetation (Chan et al., 1982). Concentration decreases of iron and manganese in water have been attributed to uptake of the metals by *Typha* (cattail) species in two wetland systems receiving mine drainage in Pennsylvania (Snyder and Aharrah, 1984). Algae and other aquatic organisms contributed to lead and zinc removal from mining and milling effluents in Missouri (Gale and Wixson, 1979). The ability of *Sphagnum* moss and other bryophytes to accumulate metals has been reported in several case studies (Kleinmann et al., 1983; Burris et al., 1984; Lee et al., 1984; Kelly, 1999). In addition, the U.S. Bureau of Mines developed a product manufactured from *Sphagnum* for use in metal-mine drainage treatment (Bennett et al., 1991).

In most wetlands, the absolute amount of metals removed by the plants is insignificant compared to the amounts accumulating in the substrate. In constructed wetlands in Colorado, plants accumulate metal concentrations of as much as 1%, but the amounts are insignificant compared to metal removal occurring in the substrate (Howard et al., 1989b). Uptake of iron by *Typha* accounted for less than 1% of the iron that was being removed from mine drainage by some natural West Virginia wetlands (Sencindiver and Bhumbla, 1988). However, researchers have hypothesized that the cattails help support the ecological system which functions to remove iron in the substrate (Sencindiver and Bhumbla, 1988; Samuel et al., 1988). Iron uptake by *Sphagnum* was minor in comparison to the binding of iron to organic matter and the formation of iron oxides that together can account for as much as 97% of iron retention in natural and constructed wetlands (Spratt and Wieder, 1988; Wieder, 1988).

The translocation of metals from soils to plants makes the metals available for ingestion by many higher organisms that graze or feed in the wetlands and, thus may be undesirable because the metals then move up the food chain and may cause toxicity problems in higher organisms. In addition, despite the ability of plants to accumulate metals, this process is usually insignificant compared to other accumulation mechanisms occurring in wetlands and may be undesirable from an ecological standpoint.

CONSTRUCTED WETLAND DESIGN

Although natural wetlands have been used to treat AMD either by chance or on purpose, constructed wetlands are becoming the preferred medium for AMD treatment because of the legal problems associated with using natural wetlands, the lack of natural wetlands at sites where treatment is needed, and the need to control and optimize hydraulic and chemical parameters in the treatment system. In addition, ecosystems have been destroyed or severely injured where AMD was introduced into natural wetlands (e.g., Wheeler et al., 1991). The brief discussion of constructed wetland design in this section is intended as a minimal introduction to the topic. The interested reader is referred to the references cited for more detailed information.

A basic design scheme for a constructed wetland includes an excavated or constructed, sealed, shallow pond that

1) Is filled with organic substrate (e.g., peat, manure, mushroom compost);
2) Supports natural wetland vegetation; and
3) Contains discrete, controlled inflow and outflow locations.

Several references describe some of the design criteria including sizing, choices of substrate and vegetation, and optimal pH, flow rates, and mineral loadings (Kleinmann et al., 1986; Howard et al., 1989a; Cohen and Staub, 1992).

Two basic constructed wetland designs have evolved to maximize the aerobic and anaerobic aspects of wetland geochemistry. In aerobic constructed wetlands, water flow is dominantly over the surface of the wetland substrate to maximize oxidation of the water column, and to take advantage of the geochemical processes that occur in the oxidized portions of wetlands. This design requires that sufficient alkalinity be added to the water or substrate to prevent pH from falling due to the precipitation of iron oxyhydroxide minerals. Aerobic constructed wetlands are most often used in coal mine drainage where concentrations of metals other than iron are low. Anaerobic constructed wetlands must be engineered to maximize water flow through the subsurface where anoxic conditions prevail. Typically, these wetlands are designed so that water flows vertically through the substrate. In these wetlands, sulfate reduction is used to precipitate metals as sulfide minerals. Anaerobic constructed wetlands are used to help remove heavy metals such as zinc and copper that are not efficiently removed in aerobic wetlands (Filipek et al., 1991). Constructed wetland design continues to evolve as the understanding of the dominant processes in wetland treatment systems evolves.

SUMMARY

The processes that occur in wetlands that can improve water quality of AMD with respect to trace metal and sulfate concentrations and pH include: sedimentation of particulate material, oxidation and precipitation of iron and manganese oxyhydroxides and oxides, complexation with organic matter, ion exchange and adsorption, sulfate reduction and formation of metal sulfides, and plant assimilation of metals. The most significant contributors to water-quality improvement are formation of iron hydroxides and metal sulfides. Sulfate reduction is particularly significant because it is the only process to date that is capable of removing significant quantities of trace metals common to metal-mine drainage. Other processes contribute to metal removal but are limited by surface area in the substrate (e.g., ion exchange and adsorption), and by biomass and uptake capacity of biomass (e.g., plant assimilation). In addition, the ability of a given wetland to remove metals by oxide or sulfide formation may be limited by hydrologic and geochemical characteristics of the wetland. For instance, limited residence time in the wetland, insufficient substrate permeability, low pH, or lack of organic material may limit the effectiveness of sulfate reduction. Therefore, the ability of wetlands to treat mine drainage varies between each site. Research continues to define optimal design characteristics for wetland treatment systems; however, some implementation continues on a pilot scale despite the limitations.

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