CHAPTER 16. PASSIVE AND ACTIVE TREATMENT OF MINE DRAINAGE

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INTRODUCTION

Extraction of mineral resources generates economic revenue, raw materials for industry and energy production, and liquid and solid waste that must be managed to prevent environmental degradation. Solid waste associated with mineral extraction includes mine waste-rock piles and tailings. Liquid waste comprises drainage from inactive mines, seepage and runoff associated with waste-rock piles and tailings, and effluent from processing activities associated with mineral extraction. Acidic drainage derived from solid mine wastes is termed acid mine drainage (AMD). Mine drainage that is not acidic is termed net alkaline mine drainage (NAMD) (Hedin *et al.* 1994a). Herein, the term mine drainage is used to denote either AMD or NAMD unless otherwise specified. Treatment for mine drainage falls into two general categories: passive and active (or conventional). In the past two or three decades there has been increased interest in the development of passive treatment because it is thought to be more cost-effective than conventional treatment at some sites (Baker *et al.* 1991, Brodie 1993, Sanders *et al.* 1999). Conventional treatment has also seen recent innovations regarding the breadth of chemical constituents that is amenable to treatment, and through incorporation of anaerobic treatment steps.

Passive treatment has been defined as "*the deliberate improvement of water quality using only naturally-available energy sources (e.g., gravity, microbial metabolic energy, photosynthesis), in systems which require only infrequent (albeit regular) maintenance in order to operate effectively over the entire system design life*" (Younger *et al.* 2002). Passive treatment systems were first designed to look like and mimic the chemical processes that occur in natural wetlands because observation of water-quality improvement in natural wetlands had sparked the initial interest in these systems (Walton-Day 1999). The thought that passive "wetland" systems offered a low-cost, low-maintenance alternative to conventional treatment drove research and experimentation into the use of wetland systems (Brodie 1993). Application was initially confined to drainage from coal mines in the eastern U.S., but use of the technology has since spread to treat drainage from coal mines in other regions (Younger 2000), drainage from metal mines and metal-mining operations (Machemer *et al.* 1993, Wildeman & Updegraff 1998, Eger *et al.* 2000, O'Sullivan *et al.* 2001, Gusek & Wildeman 2002), and even drainage associated with uranium mines (Noller *et al.* 1994). Although early systems resembled wetlands, systems currently being installed typically consist of a number of stages or cells, each designed to treat specific aspects of influent chemistry. Some types of treatment cells visually resemble wetlands, however others bear no visual or process relation to wetlands. The cells may operate in series, in parallel, or both. Among the different components that are utilized in treatment systems are reducing and alkalinity-producing systems (RAPS), also called vertical-flow wetlands (VFW); successive alkalinity-producing systems (SAPS); aerobic wetland cells; anoxic limestone drains (ALD); settling ponds; and cascade aeration steps. Some advantages of the passive systems include low operating costs, use of nonhazardous materials, and low maintenance requirements. Some disadvantages are a lack of standard design and construction guidelines; an inability to precisely control effluent quality; problems achieving water-quality standards for multiple metal-waste streams; large land requirements that make passive treatment impractical for some locations; and large capital (construction) costs (Younger *et al.* 2002).

In contrast, active treatment is "*the improvement of water quality by methods which require ongoing inputs of artificial energy and/or (bio)chemical reagents*" (Younger *et al.* 2002). Active treatment typically takes place in a treatment plant located on a minesite. Plants consist of a number of tanks, vats, and associated plumbing that treat mine drainage using proven technologies. Advantages of active treatment systems are that, because they utilize technologies used in conventional wastewater treatment, designs are readily adapted from that industry. As well, these treatment systems are precisely controlled, which allows for control of effluent quality even as influent quality fluctuates. Moreover, the land requirement for these systems is typically much smaller than for passive treatment systems because precise control allows for maximization of the efficiency of the chemical processes. Disadvantages of the systems are high and perpetual operation and maintenance costs; the handling of hazardous materials that are used in some systems; problems with dewatering sludge produced by treatment, and with disposal of the sludge; and problems achieving water-quality standards for multiple metal-waste streams (Karthikeyan *et al.* 1995, Fan & Anderson 1995, Younger *et al.* 2002).

Environmental Aspects of Mine Wastes (J.L. Jambor, D.W. Blowes, A.I.M. Ritchie, eds.).
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The objective of this chapter is to provide an overview of the chemical, geochemical, and biological processes that are utilized in both active and passive treatment systems; present case studies where each type of system has been used; highlight some of the difficulties encountered with treatment systems; and present some unique and evolving designs of treatment systems. A process-based understanding of treatment systems is necessary to enable design and construction of systems that will achieve water-quality goals. This review draws on an earlier review by the author (Walton-Day 1999), updates the references from that paper regarding passive treatment, and addresses active treatment mechanisms. This review does not consider the use of reactive barriers, which are the subject of Chapter 17 in this Volume. Throughout, the basic principles are illustrated using case studies compiled from the literature. Any errors in interpretation are the responsibility of the author.

CHEMISTRY OF MINE-DRAINAGE GENERATION

Treatment of mine drainage in passive or active systems involves reversing some of the chemical reactions that cause mine drainage, or using other physical/chemical/biological methods to limit the solubility of the constituents in mine drainage that compromise water quality. Consequently, it is worth reviewing the major processes involved in the generation of mine drainage to understand which processes mine-drainage treatment seeks to reverse.

AMD is typically generated from the weathering of pyrite in the presence of oxygen and water, a process that generates sulfuric acid in the overall reaction:

$$FeS_{2(s)} + 15/4\ O_{2(aq)} + 7/2\ H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\ H_2SO_{4(aq)} \qquad (1)$$

where one mole of ferric hydroxide and two moles of sulfuric acid are produced for every mole of pyrite oxidized (Nordstrom & Alpers 1999). This overall reaction involves at least 15 electron transfers and comprises many reaction steps. Some of the important subreactions involved in the formation of mine drainage include:

$$FeS_{2(s)} + 7/2\ O_{2(g)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2\ SO_4^{2-}{}_{(aq)} + 2\ H^+_{(aq)} \qquad (2)$$

$$Fe^{2+}_{(aq)} + ¼\ O_{2(g)} + H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + ½\ H_2O_{(l)} \qquad (3)$$

$$Fe^{3+}_{(aq)} + 3\ H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 3\ H^+_{(aq)} \qquad (4)$$

$$FeS_{2(s)} + 14\ Fe^{3+}_{(aq)} + 8\ H_2O_{(l)} \rightarrow 15\ Fe^{2+}_{(aq)} + 2\ SO_4^{2-}{}_{(aq)} \qquad (5)$$

where Reaction (2) represents the oxidation of pyrite to form aqueous ferrous iron and sulfuric acid; Reaction (3) describes the oxidation of ferrous to ferric iron; Reaction (4) represents the hydrolysis of ferric iron to form solid ferric hydroxide (note that this reaction produces acidity in the form of hydrogen ions); and reaction (5) describes the oxidation of pyrite by ferric iron, which is faster than Reaction (2) but only occurs at low pH values when ferric iron is soluble (Stumm & Morgan 1996, Nordstrom & Alpers 1999). NAMD generally forms through the interaction of AMD with rocks containing abundant carbonate material. The enrichment of other dissolved constituents in mine drainage (*e.g.,* Al, Si, K, Ca, Mg, Mn, Na, Cu, Pb, Zn, As) occurs through oxidation and acid dissolution of carbonate, silicate, sulfide, and other minerals contained in materials through and over which the mine drainage flows.

In light of these reactions, viable treatment processes include those that increase pH and thus limit the mobility of acid-soluble constituents; oxidation that enhances the formation of some metal hydroxides (*e.g.,* those of Fe and Mn); reducing reactions that reverse the mineral oxidation that occurs during mine-drainage formation; and a host of other reactions and processes that limit the solubility of constituents of concern, including but not limited to cation exchange, sorption, formation of metal–organic complexes, and active uptake of metals by plants and microorganisms. Treatment of mine drainage may emphasize one process, or it may constitute a number of processes that sequentially address different aspects of the drainage.

MINE-DRAINAGE TREATMENT PROCESSES

Many aspects of the treatment of mine drainage depend on altering the pH or the redox environment of the water to limit solubility of undesirable water-quality constituents, thereby improving water quality. Undesirable constituents in mine drainage are those that are toxic to aquatic organisms or humans, and those that cause taste, odor, and fouling problems in water supplies used for domestic or agricultural purposes. These constituents include multivalent metals such as Fe^{2+} and Fe^{3+}, Al^{3+}, Mn^{2+} and Mn^{4+}, Zn^{2+}, Cd^{2+}, and Cu^{2+}; excess hydrogen ion; and excess dissolved sulfur, usually as sulfate. Additional constituents of concern because of their toxicity include As, Se, and cyanide. This chapter contains limited discussion of the treatment of these constituents, and focuses primarily on treatment of trace metals, pH, and sulfate.

Treatment processes are examined herein in light of the geochemical rationale for using the processes to treat mine drainage; how the process is generally implemented; and the limitations on implementation and effectiveness of the processes. Case studies are presented as evidence of the use, effectiveness, and limitations of a particular process. Processes discussed include acid neutralization and alkalinity generation, adsorption and ion exchange, oxidation, formation of Fe and Mn minerals, anoxic processes including sulfate reduction and denitrifiation, metal-organic complexation, and active uptake of metals by plants and microorganisms. There is some overlap among the processes (*e.g.,* acid neutralization, adsorption, and formation of Fe and Mn minerals) because multiple processes can occur under similar pH and redox conditions. A discussion of the complex controls on metal solubility is beyond the scope of this chapter, and only an overview of the most important aspects of pH and redox control is given here. The reader is referred to reviews relevant to mine-drainage chemistry (Nordstrom & Alpers 1999, Younger *et al.* 2002) and general geochemistry (Stumm & Morgan 1996, Drever 1997), and to references cited herein for additional detail.

Acid neutralization and alkalinity addition or generation

The pH controls metal mobility and speciation through formation of hydroxide minerals and sorption of metals to mineral and substrate surfaces. Many of the metals in mine drainage are amphoteric, that is, they are soluble both at high and low pH conditions, and are relatively insoluble at near-neutral pH, where their solid hydroxide form is stable and controls solubility. Solubility curves for representative metal hydroxides (Fig. 1) illustrate this amphoteric property and the pH range where minimum solubility is obtained. As the pH of mine drainage is increased, metals will precipitate from solution in their hydroxide form from left to right in Figure 1. Note that, as pH increases to levels at which Zn and Cd hydroxide are least soluble, other hydroxides become more soluble. This pH separation of the minimum solubilities of metal hydroxides requires staged treatment systems in which precipitate containing one metal is separated before other metals are precipitated. The pH also controls sorption of dissolved metals. Treatment processes that use alkalinity addition affect sorption as well as mineral precipitation, and sorption is discussed in a following section "*Adsorption and ion exchange*".

Treatment increases the alkalinity and pH through addition of acid-neutralizing compounds or alkalinity, or both, to the mine drainage. The increase in pH must be sufficient to neutralize the acidity present in the water, to cause precipitation or sorption of the metals of concern for a particular mine drainage, and to counteract the production of protons, or acidity, that occurs during the hydrolysis of metal ions (Reaction 4).

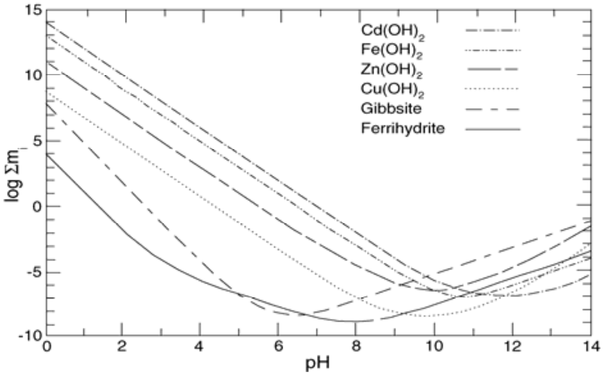


FIG. 1. Solubility curves for gibbsite (Al hydroxide), ferrihydrite (Fe hydroxide), and the hydroxides of Cu, Zn, Fe(II), and Cd shown as a function of pH (Nordstrom & Alpers 1999; reprinted with permission of The Society of Economic Geologists, Inc.).

Alkalinity is defined as the acid-neutralizing capacity of a water sample. It is measured by titrating a water sample with a strong acid. Total alkalinity (ALK_T) is the sum of the bases that can be titrated with a strong acid:

$$ALK_T = m_{HCO_3^-} + 2\,m_{CO_3^{2-}} + m_{B(OH)_4^-} + m_{H_3SiO_4^-} + m_{HS^-} + m_{\text{organic anions}} + m_{OH^-} - m_{H^+} \qquad (6)$$

where m is the molarity of the chemical constituents. In most natural waters the last six variables in Equation (6) are negligible compared to concentrations of carbonate and bicarbonate; thus, the equation reduces to:

$$ALK_T = m_{HCO_3^-} + 2\,m_{CO_3^{2-}} \qquad (7)$$

Acidity in mine drainage is most commonly neutralized by reaction with hydroxyl ion:

$$H^+ + OH^- = H_2O \qquad (8)$$

or by reaction with dissolved carbonate species:

$$H^+ + HCO_3^- = H_2O + CO_2 \qquad (9)$$

$$2\,H^+ + CO_3^{2-} = H_2O + CO_2 \qquad (10)$$

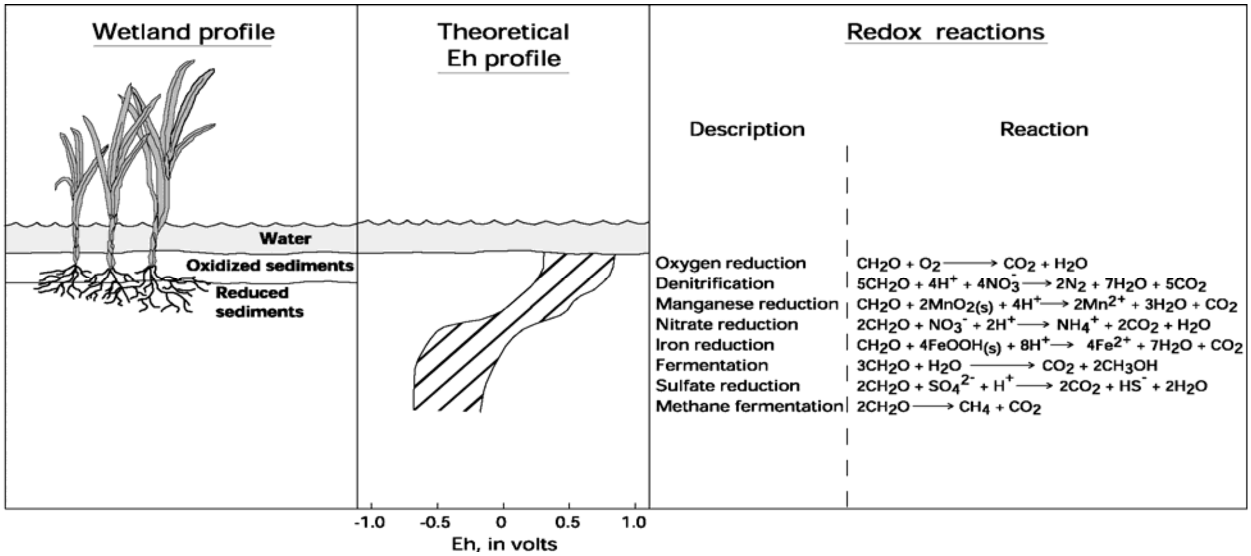
The behavior of CO_2 in treatment systems influences the amount of acidity that can be neutralized. In systems open to gas exchange, CO_2 exsolution will drive Reactions (9) and (10) to the right, which can result in more acid neutralization than in closed systems.

The dissolution of calcite:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (11)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2\,HCO_3^- \qquad (12)$$

is a common reaction used to neutralize acidity and generate alkalinity primarily in passive mine-drainage treatment systems. The behavior of CO_2 in a treatment system, the amount of CO_2 in the mine drainage, and the chemistry of the mine drainage, particularly with respect to calcite saturation, will affect the amount of



Description	Reaction
Oxygen reduction	$CH_2O + O_2 \longrightarrow CO_2 + H_2O$
Denitrification	$5CH_2O + 4H^+ + 4NO_3^- \longrightarrow 2N_2 + 7H_2O + 5CO_2$
Manganese reduction	$CH_2O + 2MnO_{2(s)} + 4H^+ \longrightarrow 2Mn^{2+} + 3H_2O + CO_2$
Nitrate reduction	$2CH_2O + NO_3^- + 2H^+ \longrightarrow NH_4^+ + 2CO_2 + H_2O$
Iron reduction	$CH_2O + 4FeOOH_{(s)} + 8H^+ \longrightarrow 4Fe^{2+} + 7H_2O + CO_2$
Fermentation	$3CH_2O + H_2O \longrightarrow CO_2 + 2CH_3OH$
Sulfate reduction	$2CH_2O + SO_4^{2-} + H^+ \longrightarrow 2CO_2 + HS^- + 2H_2O$
Methane fermentation	$2CH_2O \longrightarrow CH_4 + CO_2$

FIG. 2. Generalized profile of wetland soil, some soil chemical parameters, and redox reactions (from Walton-Day 1999; reprinted with permission of The Society of Economic Geologists, Inc.).

alkalinity generated by calcite dissolution, and dictate the dominant calcite-dissolution reaction (Hedin *et al.* 1994b, Rose & Cravotta 1998, Rose 1999). The kinetics of calcite dissolution are important; as calcite saturation is approached, the dissolution rate of calcite decreases (Berner & Morse 1974, cited in Hedin *et al.* 1994b). Specifically, the rate of calcite dissolution decreases as pH, Ca, HCO_3^- and CO_3^{2-} increase and as $P(CO_2)$ decreases (Plummer *et al.* 1979, Cravotta & Watzlaf 2002).

Another reaction that affects alkalinity is photosynthesis (Wildeman & Updegraff 1998):

$$6\ HCO_{3\ (aq)}^- + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2 + 6\ OH^- \qquad (13)$$

The reaction consumes carbonic acid and bicarbonate and produces oxygen and hydroxyl ions. Although there is no change in alkalinity with the reaction, the different chemical form of alkalinity may be important and the reaction increases pH. The reaction may help oxidize some aqueous constituents and promote their precipitation (Wildeman & Updegraff 1998).

Some metabolic reactions that occur in reducing environments produce alkalinity. Denitrification, Fe and Mn reduction, nitrate reduction, and sulfate reduction all consume protons (Fig. 2). In these reactions, acid consumption is associated with the consumption of organic matter by microbes. Some passive treatment systems utilize these reactions for alkalinity generation. A subsequent section in this chapter *"Anoxic (anaerobic) processes"* and Walton-Day (1999) describe in more detail the conditions that support reducing environments.

Alkalinity generation in passive treatment systems. Passive treatment systems add alkalinity to mine drainage by using biological reduction of organic matter and reaction of the mine drainage with alkalinity-producing materials. Consequently, in wetland treatment systems, constructed substrates contain alkalinity-generating material such as limestone (Sexstone *et al.* 1999), lime, spent mushroom compost, fly ash (Mercer & Nairn 1999, Nairn *et al.* 1999), or other amendments. Some passive treatment systems use ALDs as a discrete step to add alkalinity to mine drainage before allowing oxidation to occur (Brodie *et al.* 1993). In its most basic form, an ALD consists of a covered trench filled with crushed limestone. ALDs are closed to the atmosphere. Consequently, pH and alkalinity can increase to greater levels than in an open system (Younger *et al.* 2002). ALDs are sometimes difficult to operate, or are only minimally effective when they become coated with Fe^{3+}-hydroxide precipitates from oxidized mine drainage or with Al-hydroxide precipitates. In addition, understanding the specific calcite dissolution reactions occurring in treatment systems and their reaction kinetics is important. For example, Hedin *et al.* (1994b) noted that Reaction (12) generated more alkalinity than Reaction (11) in ALDs for one mine drainage that had higher $P(CO_2)$ and a lower calcite saturation index than another mine drainage that was used for comparison. Comparison of performance of 13 ALDs indicated that effectiveness of treatment depended on influent chemistry, detention time, and limestone purity (Cravotta & Watzlaf 2002). In addition, ALDs treating mine drainage having dissolved Al concentrations greater than 5 mg L^{-1} had performance difficulties. In some systems, high flow rates were used to flush particulate matter from ALDs (Cravotta & Waltzlaf 2002). Design criteria are conservative and indicate influent concentrations of dissolved O_2, Fe^{3+}, and Al^{3+} be less than 1 mg L^{-1} for successful operation of ALDs (Hedin *et al.* 1994a). Benchtop tests that consider influent chemistry, limestone dissolution chemistry, and kinetics are used to enhance ALD design and predict the mass of limestone needed to treat a particular mine drainage (Cravotta in press).

Oxic limestone drains (OLDs) are used in some systems to generate alkalinity. An OLD consists of an open channel lined with crushed limestone (Skousen *et al.* 1998). Armoring of the limestone by Fe minerals in an OLD apparently does not prevent alkalinity generation (Skousen *et al.* 1998, Gusek & Wildeman 2002). Similar to ALDs, considerations of the chemistry of limestone dissolution and reaction rates are important in understanding the design and operation of OLDs. However, on the basis of the frequency of citations in the literature, it seems there are more ALDs than OLDs in operation.

The successive alkalinity-producing system (SAPS) is a relatively recent innovation (Kepler & McCleary 1994) that has increased the amount of alkalinity that can be added through passive treatment. In SAPS (Fig. 3), the mine drainage flows first through an organic layer, and thence through a layer of limestone. This configuration uses microbial metabolic reactions to strip oxygen from the water before it reacts with the limestone, thus preventing the accumulations of the Fe^{3+} precipitates that often impose an operational difficulty with ALDs (Gusek & Wildeman 2002). The SAPS therefore surmount the main difficulty of ALDs, which is their inability to accept oxygenated water containing ferric iron. SAPS also are sometimes referred to as reducing- and alkalinity-producing systems (RAPS), or vertical-flow wetlands (VFW).

There are still problems with generating sufficient alkalinity in passive treatment systems. As mentioned previously, ALDs can clog with Al or Fe precipitates, and SAPS can clog with Al precipitates. The rate of alkalinity generation from the dissolution of limestone is limited by the kinetics of calcite dissolution, and additional research is required to utilize calcite dissolution rates in the design of passive treatment systems (Rose 1999).

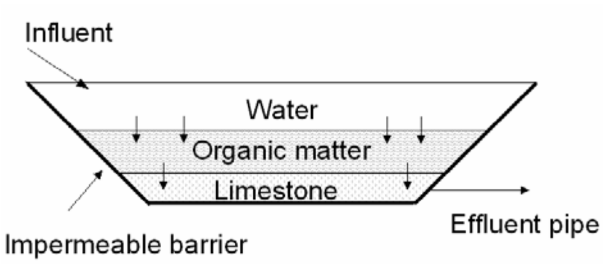


FIG. 3. Typical cross-sectional view of a successive alkalinity-producing system (SAPS) treatment component (after Kepler & McCleary 1994 and Skousen *et al.* 1998).

Alkalinity generation in active treatment systems. In active treatment systems, acidity is neutralized and alkalinity is generated by adding caustic or alkali compounds such as $Ca(OH)_2$, CaO, NaOH, Na_2CO_3, or NH_3 (Younger *et al.* 2002, Skousen 2002). Calcium hydroxide reacts to neutralize acidity and promote ferric hydroxide precipitation in the following reaction (Younger *et al.* 2002):

$$2\,Fe^{3+} + 2\,H^{+} + 4\,Ca(OH)_2 \rightarrow 2\,Fe(OH)_3 + 4\,Ca^{2+} + 2\,H_2O \qquad (14)$$

Ammonia gas consumes protons through formation of ammonium ion (Younger *et al.* 2002):

$$NH_{3(g)} + H^{+}_{(aq)} \Leftrightarrow NH^{+}_{4(aq)} \qquad (15)$$

Reaction (15) can increase pH to about 8.5 (Younger *et al.* 2002). The amount of pH increase needed to precipitate the metals of concern affects reagent choice. For instance, mine drainage that contains Zn, Mn, Cu, or Cd requires a higher pH to precipitate the metals as hydroxides (Fig. 1) than does one containing only Fe and Al. Thus, a reagent such as NaOH might be used because it can increase pH to higher values than hydrated lime can (calcium hydroxide; Younger *et al.* 2002). The choice of reagent also depends on cost. Skousen (2002) reported that at low flow all of the chemicals listed above are cost effective except $Ca(OH)_2$; in contrast, $Ca(OH)_2$ and CaO are most cost effective at high flow. Reagent choice also depends on ease of handling and reactivity.

Adsorption and ion exchange

Adsorption and ion exchange contribute to the removal of trace elements from solution in many natural aqueous systems, particularly in streams affected by mine drainage (Webster *et al.* 1998; Runkel *et al.* 1999). Similarly, adsorption and ion exchange contribute to metal immobilization in passive and active treatment systems, but most case studies have indicated that the contribution of adsorption and ion exchange is minor compared to other processes. Detailed geochemical discussions of adsorption have been given by Kinniburgh & Jackson (1981), Evans (1989), Davis & Kent (1990), Stumm & Morgan (1996), Smith (1999), and Koretsky (2000). This section provides an overview of adsorption and presents case studies showing its application in passive and active treatment systems.

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 involve the attachment of dissolved ions or molecules to a pre-existing solid (Drever 1997). Ion exchange (also referred to as nonspecific adsorption) is a relatively weak interaction between particle surfaces and ions. The process is rapid and usually reversible so that most ions can be easily removed from the surface under appropriate conditions. In ion exchange, a hydrated ion is held against the particle surface primarily by electrostatic attraction. The ions will readily exchange for other ions that form similar complexes with the surface. In contrast, in adsorption (also referred to as specific adsorption), a covalent bond forms between the mineral surface and the adsorbing ion. In this interaction, the adsorbing ion is not readily replaced but can desorb. 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 As, Cr, Mo, and Se, bond to variably charged particle surfaces through the process of ligand exchange. Cations also can bond to variably charged surfaces in which a hydrolyzed cation bonds with a negatively charged, deprotonated surface (Evans 1989, Stumm & Morgan 1996). Consequently, pH controls sorption of dissolved metals onto hydroxides and other minerals. For metal cations, as pH increases, the amount of metal sorbed on hydroxides increases (Fig. 4). For constituents that are oxyanions in solution, sorption is promoted by decreasing pH (Fig. 5). Note that sorption of some constituents in Figure 4 occurs at lower pH than formation of the metal hydroxide in Figure 1. In addition, increasing amounts of sorbent will shift the curves in Figure 4 to the left so that sorption occurs at lower pH values. Similarly, decreased amounts of sorbent will shift the curves to the right so that sorption occurs at greater pH values (Smith 1999). In passive and active treatment systems, hydrous Fe oxides and organic matter are probably the two most important substrates for adsorption.

Models for sorption are used to understand better the adsorption mechanisms, that is, the interaction between the sorbate and sorbent. Available models include empirical models and surface-complexation models. Empirical approaches to adsorption include partition coefficients and sorption isotherms (including Langmuir & Freundlich isotherms), which are relatively easy to employ and are most useful in cases where pH is uniform. Models for surface complexation are based on electrostatic theory and are more useful in situations where pH varies spatially and temporally (Dzomback & Morel 1990, Runkel *et al.* 1999, Smith 1999, Koretsky 2000).

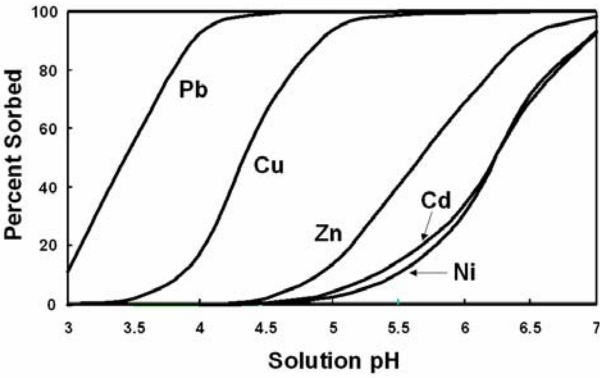


FIG. 4. Model sorption curves showing relative placement of adsorption edges of selected metals on hydrous ferric oxide (modified from Smith 1999).

Adsorption in passive treatment systems. Several studies have reported that ion exchange and adsorption contribute to metal retention in passive treatment systems (Wieder & Lang 1986, Tarutis & Unz 1990, Karathanasis & Thompson 1991, Machemer & Wildeman 1992). For some metals, such as Mn, ion exchange may be the dominant retention process, but it 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 (such as an acid shock to a treatment system caused by a major runoff event, or an underground collapse in the mine workings) 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 period of operation of a constructed wetland (Kleinmann 1990, Machemer & Wildeman 1992). However, wetland and substrate volume limit the amount of metal removed by these processes.

A few studies have used the high ion-exchange capacity of naturally occurring zeolite minerals to improve mine drainage quality. Sodium in zeolite readily exchanges for metal cations. Experiments using natural zeolite minerals to sorb metals from metal-rich solutions and mine drainage have demonstrated metal removal (Desborough 1992, Skousen *et al.* 1998, Gilbert *et al.* 1999). However, pilot-scale systems have not been established. One operational difficulty with ion exchange using zeolite is that, to avoid disposal of the metal-saturated zeolite, the metals may be removed from the zeolite and the zeolite recycled for treatment of additional mine drainage; however, the regeneration of the zeolite also creates a metal-rich solution that requires disposal or additional treatment.

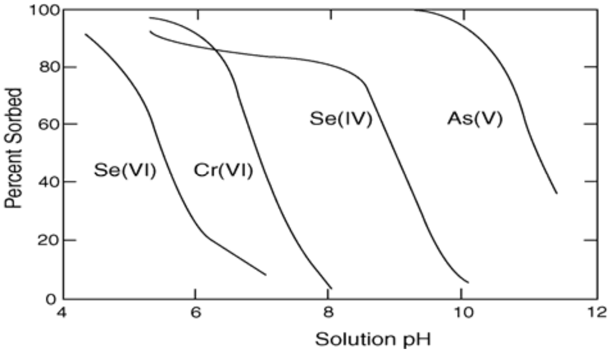


FIG. 5. Sorption curves showing relative placement of adsorption edges of selected oxyanions on hydrous ferric oxide (from Smith 1999; reprinted with permission of The Society of Economic Geologists, Inc.).

Adsorption in active treatment systems. The use of adsorption in active treatment systems is illustrated in several case studies. Metal sorption on composite adsorbents (granular activated carbon coated with Fe oxides and Mn oxides) indicated that the composites had a greater removal capacity for Cu(II) than the individual adsorbent materials (Fan & Anderson 1995, Wang & Anderson 1995). Another study investigated the feasibility of using bone char as an adsorbent to treat dissolved Cd in wastewater treatment systems (Cheung *et al.* 2001). Although this study described processes in a conventional wastewater treatment system, the results have obvious applications to treatment of mine drainage. Experiments with muskeg sediments indicated that adsorption was one process that removed As and Ni from mine drainage exposed to the sediments (Fyson *et al.* 1998).

As described previously, the pH at which most metals adsorb to Fe and Al hydroxides is generally lower than the pH at which most metals form their own hydroxide precipitates. This premise was used to investigate the feasibility of adding coagulant (hydrous Al and Fe oxides) to wastewater to enhance metal removal by sorption to the coagulant at a pH lower than required for precipitation of metal hydroxides (Karthikeyan *et al.* 1995). Metal removal was demonstrated and was a function of coagulent type and dosage and the particular heavy metal(s) present in the waste water. Adsorption has been identified as a removal process in a high-rate algal ponding system, which was part of an active treatment process (Rose *et al.* 1998).

There has been limited application of models to sorption in active treatment systems. Wang & Anderson (1995) applied equilibrium models to describe sorption of metals onto granular activated carbon coated with Fe oxide. Aside from this research, however, little work has been done on sorption modelling to improve the understanding of sorption in treatment systems and thereby enhance the systems. This is an area where treatment-system design could benefit from more research.

Oxidation

Treatment by oxidation simply involves increasing the oxidation state of solutes, *e.g.*, Fe in Reaction (3), to help facilitate precipitation of the metal, usually as a hydroxide. In passive treatment systems, oxidation is generally achieved in subaereal ponds, although some systems have utilized cascade aeration (Younger *et al.* 2002). Oxidation is achieved in active treatment systems by a variety of mechanisms that includes cascade aeration, trickle filter aeration, in-line venturi aeration, mechanical aeration, and less frequently, chemical aeration using hydrogen peroxide or sodium hypochlorite (NaOCl) (Younger *et al.* 2002).

Formation of Fe and Mn hydroxides, oxides, and hydroxysulfate minerals

The oxidation and hydrolysis of Fe to form Fe hydroxide can be written as a net reaction (Bigham *et al.* 1990):

$$Fe^{2+} + \frac{1}{4} O_2 + 5/2\ H_2O \rightarrow Fe(OH)_{3(s)} + 2H^+ \quad (16)$$

In aerated solutions at pH >5, ferrous iron autooxidizes to ferric iron. At lower pH values, however, bacteria such as *Acidithiobacillus ferrooxidans* catalyze Fe oxidation. Because *A. ferrooxidans* is acidophilic (acid-loving), Fe oxidation is optimal at pH 3 to 3.6 (Ehrlich 1981). Although Reaction (16) removes Fe from solution, the reaction produces hydrogen ions and decreases pH if alkalinity is not available to buffer the production of hydrogen ions.

The Fe hydroxides that form from mine drainage are complex; some consist of a poorly crystallized oxyhydroxysulfate (Bigham *et al.* 1990) called schwertmannite (Murad *et al.* 1994). In addition, the types of Fe-hydroxide minerals that form in mine drainage are a function of pH and sulfate content of the mine drainage (Bigham *et al.* 1992, 1996, Bigham 1994). At low pH values (1.5–3.0) and elevated concentrations of sulfate (>3000 mg L^{-1}), precipitation of jarosite [$(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6$] is favored; pH values from 3 to 4 and sulfate concentrations ranging from 1000 to 3000 mg L^{-1} favor schwertmannite [$Fe_8O_8(OH)_6SO_4$]; and pH values greater than 5 and elevated concentrations of Fe favor formation of ferrihydrite [nominally $5Fe_2O_3 \cdot 9H_2O$]. Goethite [α-FeOOH] forms as jarosite, schwertmannite, and ferrihydrite recrystallize and dehydrate, and can form directly at low pH and low sulfate concentrations, and at higher pH in bicarbonate-rich water (Bigham 1994, Bigham *et al.* 1992, 1996). These results indicate that precipitation of Fe oxides at high pH values and low sulfate concentrations is the most desirable scenario because it produces the most stable precipitate. In addition, recrystallization and dehydration of jarosite, schwertmannite, or ferrihydrite to goethite could release metals sorbed to the original mineral. In many of the case studies cited herein, authors did not make precise determinations of the mineralogy or stoichiometry of the oxidized Fe mineral forming in their treatment systems. Thus, the terms Fe oxides, Fe hydroxides, Fe oxyhydroxides, and hydrous Fe oxides are employed without benefit of analytical confirmation. Herein, citations of references attempt to accurately report the Fe mineral name used in the reference. In most cases, it was not possible to verify whether the authors used the terms correctly.

The oxidation of ferrous iron (Reaction 3) can involve soluble Fe species or sorbed Fe. If the reaction uses soluble Fe as the reactant, it is referred to as a homogeneous oxidation. If Fe(II) that is sorbed to a substrate or mineral phase is the reactant, the reaction is termed heterogeneous iron oxidation. There is evidence that the heterogeneous reaction is catalytically favored over the homogeneous reaction (Dietz & Dempsey 2001, Younger *et al.* 2002). Thus, some active and passive treatment processes recirculate Fe-hydroxide sludge to take advantage of the heterogeneous reaction and thereby maximize rates of Fe removal (Dietz & Dempsey 2001, Jarvis & Younger 2001).

As with Fe, the oxidation of Mn and its precipitation as Mn oxides in treament systems can reduce the levels of Mn in mine drainage. The oxidation and hydrolysis of Mn can occur by (Ehrlich 1981, Younger *et al.* 2002):

$$Mn^{2+} + \frac{1}{2} O_2 + 2 H^+ \rightarrow Mn^{4+} + H_2O \qquad (17)$$

$$Mn^{4+} + 2 H_2O \rightarrow MnO_2 + 4 H^+ \qquad (18)$$

These reactions occur at greater Eh and pH values than the oxidation and precipitation of Fe hydroxides by Reaction (16). As in the equivalent reactions for Fe, Reaction (18) produces acidity and can be catalyzed by bacteria. Formation of rhodochrosite [$MnCO_3$] or carbonates containing Mn in solid solution may be important under reducing conditions and high $P(CO_2)$ (Tarutis & Unz 1996), but has not been reported in passive treatment systems and is not described further herein.

Fe and Mn removal in passive treatment systems. Many case studies of natural, constructed, and laboratory-scale microcosm wetlands have indicated that the formation of Fe oxides or accumulation of Fe in oxic zones is an important Fe-removal process in passive treatment systems (Faulkner & Richardson 1990, Wieder *et al.* 1990, Tarutis *et al.* 1992, Tarutis 1993, Hedin *et al.* 1994a, Reed *et al.* 1995, Sexstone *et al.* 1999, Rees *et al.* 2001). In most of these systems, Fe removal occurs as mine drainage travels through an oxic wetland cell that contains a substrate consisting of organic and alkalinity-producing material populated with wetland vegetation. For many of these studies the amount of Fe removal is the principal objective, whereas the mineralogical form of the Fe removed is of secondary consideration and typically is not determined. One study explored the importance of crystallinity on the longevity of Fe removal in these systems; it was determined that, under reducing conditions, retention of the Fe originally removed from solution as oxides was increased as the crystallinity of the Fe-oxide material also increased (Tarutis 1993).

The removal of Mn by oxidative processes in passive treatment systems is generally less effective than the removal of Fe (Gerber *et al.* 1985, Wieder & Lang 1986, Henrot & Wieder 1990). Although Mn-oxidizing bacteria have been identified in wetlands (Batal *et al.* 1989), failure of wetland treatment systems to remove significant quantities of Mn by oxidative processes has been attributed to low pH values in the wetlands (Henrot & Wieder 1990, Wildeman *et al.* 1990). Manganese auto-oxidizes at pH values of 8.5 or greater. Limited research indicates that Mn-oxidizing bacteria are not active at low pH (Henrot & Wieder 1990). The failure of passive treatment systems to remove Mn was attributed by Hedin *et al.* (1994a) to the intolerance of the necessary catalytic microbes to pH values of less than 6, to a reaction path involving formation of Mn oxides from a $MnCO_3$ precursor that is not stable at low pH, to thermodynamic instability of Mn oxides at low pH, and to reduction of Mn oxides by ferrous iron.

In spite of the failure of many passive treatment systems to remove Mn through oxidative mechanisms, there have been some notable successes. In Pennsylvania, a passive treatment system alters influent concentrations of 25 mg L^{-1} Mn to an effluent containing less than 2 mg L^{-1} Mn. A consortium of bacteria, cyanobacteria, diatoms, green algae, and fungi oxidized the Mn within two cells composed of beds of limestone cobbles (Robbins *et al.* 1999). Removal of Mn in algae-rich systems (Wildeman & Updegraff 1998) was attributed to Mn oxidation promoted by increases in pH and enrichment of dissolved oxygen associated with photosysthesis by the algae (Reaction 13). Limestone in the systems did not enhance alkalinity, but served as a substrate for adsorption of Mn oxides, and these sites then provided autocatalysis for further oxidation of Mn. Stark *et al.* (1996) reported that Mn-oxide removal was possible on limestone beds as long as the influent mine drainage was Fe-free and had neutral pH.

Understanding attenuation of Mn in natural systems may help enhance treatment processes for excess Mn concentrations. Scott *et al.* (2002) reported that light promoted oxidation and removal of Mn from the water column of a stream affected by AMD, presumably through photosynthetically enhanced oxidation of Mn. The role of light in the oxidation of Mn in treatment systems had not been addressed previously, but may in part account for the observation that, in one study of wetland mesocosm, 88 percent of the Mn had been retained at the surface of the wetlands (Stark *et al.* 1996).

In another natural system, at Pinal Creek, Arizona, a groundwater plume affected by mine drainage emerges onto the streambed over the first 2 km of a 7-km perennial reach of the stream. Oxidation of Mn occurs both during mixing of this groundwater with oxygenated surface water in the hyporheic zone (over the first 2 km) and during hyporheic exchange downstream of the contaminated-groundwater input. The result is the formation of abundant Mn-oxide crusts in the streambed sediments. Precipitation of Mn has removed approximately 20 percent of the Mn load in the plume, and has reduced instream Mn concentrations from 1.2 to 0.9 m*M*. Conditions promoting Mn precipitation in Pinal Creek are (1) increased pH, from 6.0 to 7.8, over the perennial reach of the stream because of the re-equilibration of the elevated-$P(CO_2)$ groundwater with atmospheric levels of CO_2, (2) increased oxygenation of the suboxic groundwater through interaction with the atmosphere, and (3) bacterial catalysis of Mn oxidation and precipitation (Harvey & Fuller 1998, Fuller & Harvey 2000, Marble *et al.* 1999). These results are consistent with others, cited above, that indicate an elevated pH, dissolved oxygen, and bacterial catalysis enhance Mn removal.

Fe and Mn removal in active treatment systems. Active treatment systems achieve removal of metals as hydroxides through oxidation and addition of alkali (if necessary). The removal typically occurs in large mixing tanks. Various coagulants (*e.g.,* common starch, proprietary “poly electrolyte” compounds, and reactive liquids such as Al sulfate) are added in the mixing tank to catalyze precipitation of the metal hydroxides. The sediment-rich water is then passed to a sediment pond or to a clarifier to allow settling of the metal-hydroxide sludge. A sediment pond requires more space, but may be less costly than a clarifier. A clarifier is a conical tank within which the alkali dosing, oxidation, mixing, and sedimentation of flocculent material can occur. Agitation in the clarifier encourages flocculation. The accumulated sludge is removed periodically from settling ponds, and can be removed by piping from the bottom of a clarifier. Vacuum filtration, continuous pressure dewatering, frame-and-plate pressing, or centrifuge separation can increase sludge density. Problems with this type of conventional treatment include the high reagent cost necessary to achieve the high pH needed to remove some metals; equipment maintenance costs caused by fouling associated with the sludge and reagents; residual concentrations of some metals and sulfate that still impair water quality; and the chemical complexity and low density of sludges, which limit the ability to reuse the sludge and also increase the disposal costs (Younger *et al.* 2002).

The mineralogical composition of sludge affects sludge handling and disposal. Some facilities use a high-density sludge process that converts metal hydroxides to metal oxides. The resulting sludge is denser, settles faster, and dewaters more readily than hydroxide-dominated sludge (Zick *et al.* 1999). In addition, oxic forms of Fe (such as hematite Fe_2O_3) are more marketable than the hydroxide forms and may be economically recovered (Younger *et al.* 2002).

Depending on local regulations and because of the elevated pH necessary to remove some metals, the effluent from active treatment systems may require pH adjustment before discharge to the environment. In the United States, a pH between 6 and 9 is required for discharge. In systems where pH after metal removal is greater than 9, acid addition is used to bring the effluent into pH compliance. This addition increases cost and is one reason why alternative treatment techniques are still being sought for mine drainage containing Mn.

Anoxic (anaerobic) processes

Many of the metals that are constituents of concern in mine drainage are redox-sensitive. That is, their speciation or oxidation state changes as the oxidation state of their surroundings changes. Changes in oxidation state affect the solubility of many metals. For example, Fe can exist in its reduced ferrous state (oxidation state II, with the free ion having a charge of +2) or in its oxidized ferric state (oxidation state III, with the free ion having a charge of +3). In general, reduced Fe is more mobile than oxidized Fe. Similarly, Mn can exist in its reduced form having a +2 charge, or in the oxidized form that has a +4 charge. Similar to Fe, reduced Mn is generally more mobile than oxidized Mn. Dissolved sulfur is also redox-sensitive. Sulfate (SO_4^{2-}) is the most oxic form, wherein the oxidation state of sulfur is +6, and variations are to an oxidation state of –1, as in hydrogen sulfide (HS^-), and –2, as in sulfide (S^{2-}).

The oxidation state of the environment changes from oxidized to reduced as microbial respiration depletes the electron acceptors that yield the greatest amount of energy on a molar basis, thence proceeding down the redox ladder to the next most energetically favorable sequence of reactions (Fig. 2). Most organisms oxidize organic matter as a source of energy (aerobic respiration), but some organisms obtain energy by oxidizing reduced inorganic compounds (anaerobic respiration) (Mills 1999, Stanier *et al.* 1986). Oxidation releases electrons that must be incorporated into other compounds, known as terminal electron acceptors. Oxygen is the optimum 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. The sequence of reduction reactions proceeds on the basis of decreasing energy yield, from oxygen reduction to denitrification, Mn reduction, nitrate reduction, Fe reduction, fermentation, sulfate reduction, and methane fermentation (Fig. 2).

Changes in the oxidation state of the environment also depend on the demand for oxygen and other electron acceptors versus their resupply. In saturated sediments and stagnant water, oxygen replenishment is limited by the aqueous diffusion of dissolved oxygen into the sediments, which is four orders of magnitude slower than gaseous diffusion (Greenwood 1961). As aerobic and facultative anaerobic microorganisms deplete oxygen in flooded soils or stagnant water, 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 (such as ferric iron, nitrate, or sulfate – Fig. 2) are the terminal electron acceptors for oxidation of organic matter in anaerobic respiration. Generally, a redox zonation develops in saturated soils, stagnant water, and wetlands (Fig. 2) 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. In addition, most of these redox reactions generate alkalinity, which can cause pH and alkalinity to increase as the oxidation state decreases.

Some treatment systems use anoxic processes, particularly sulfate reduction, to add alkalinity, strip oxygen from the water, and promote formation of metal-sulfide minerals. Anoxic processes have been used to help improve water quality in passive treatment systems in which mine drainage contains trace metals, such as Cu, Ni, Pb, and Zn. Active treatment systems employ anoxic processes on a limited basis.

Sulfate reduction. Microbially mediated reduction of sulfate improves 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. Third, sulfate reduction promotes the formation of volatile, reduced organic and inorganic sulfur species that can diffuse from the substrate to the atmosphere. Fourth, sulfate reduction may incorporate reduced sulfur into organic sulfur species, a process that decreases the concentration of sulfate and may consume protons, depending on the stoichiometry of the organic sulfur compound. For the process to operate efficiently, transmission of water down to and through the reducing layers of the substrate must be large relative to the total amount of mine drainage in a system. Many case studies have documented the presence of sulfate-reducing bacteria in wetlands and the water-quality improvements attributed to some of these processes. In addition, some active treatment systems utilize these processes.

Sulfate reduction increases pH, but may not generate alkalinity, as indicated in Figure 2, unless the pH is greater than about 4.5. In assimilatory sulfate reduction, microorganisms incorporate the reduced sulfur into biochemical compounds; no extracellular sulfide is produced. In dissimilatory sulfate reduction, microorganisms use sulfate as a terminal electron acceptor and produce sulfide (Ehrlich 1981). In the net reaction:

$$2\ CH_2O + SO_4^{2-} + 2\ H^+ \rightarrow 2\ CO_2 + H_2S + 2\ H_2O \quad (19)$$

or

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^- \quad (20)$$

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 (20), the carbonic acid – bicarbonate equilibrium has been included to show the generation of bicarbonate alkalinity, which is equivalent to the consumption of protons that occurs as Reaction (19) proceeds to the right. At pH values less than about 4.5, sulfate reduction causes an increase in pH without generating bicarbonate (Reaction 19). At higher pH values, sulfate reduction also increases bicarbonate concentrations (Reaction 20). Sulfate-reducing bacteria are reported to be inactive at pH values of less than about 4.2 (Trudinger 1979). Consequently, the process may have no effect until higher pH is achieved either through other redox reactions (Fig. 2) or through addition of acid-consuming material.

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

$$Fe^{2+} + H_2S \rightarrow FeS + 2\ H^+ \quad (21)$$

Two protons are produced; thus, when Reactions (19) and (21) are combined:

$$2\ CH_2O + SO_4^{2-} + Fe^{2+} \rightarrow 2\ CO_2 + FeS + 2\ H_2O \qquad (22)$$

there is no net change in the proton budget. Similarly, protons are not consumed when other metals are present as free dissolved cations, such as Zn, and precipitate as sulfides (Anderson & Schiff 1987). If oxidized Fe in Fe-oxyhydroxide minerals is dissolved and reduced, however, then in the net reactions:

$$9\ CH_2O + 4\ FeOOH + 4\ SO_4^{2-} + 8\ H^+ \rightarrow 9\ CO_2 + 4\ FeS + 15\ H_2O \qquad (23)$$

and

$$15\ CH_2O + 8\ SO_4^{2-} + 4\ FeOOH + 16\ H^+ \rightarrow 4\ FeS_2 + 15\ CO_2 + 25\ H_2O \qquad (24)$$

protons are consumed where either Fe monosulfide or disulfide (pyrite) is formed. Reactions (23) and (24) transfer alkalinity from the solid Fe oxyhydroxides to the aqueous phase (Anderson & Schiff 1987). Therefore, if the reduction of a metal and the formation of its sulfide consumes protons, the net result will be an increase in alkalinity and pH. However, if reduction of sulfate and the formation of a metal sulfide does not consume protons (*e.g.,* Reaction 22), there is no net change in alkalinity and pH.

Reactions (19) and (20) indicate 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 reoxidization, it can escape to 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. Similarly, if gas can be vented from an active anaerobic treatment system, formation and exsolution of H_2S gas can improve water quality. The formation and exsolution of organic sulfur gases, such as methyl and dimethyl sulfide, also could contribute to the loss of sulfur from mine drainage in treatment systems.

Only limited research has been conducted on the role of H_2S loss in improving water quality in passive wetland treatment systems. Studies indicate that a maximum of 2% of sulfur removal in sulfate-reducing systems occurred as H_2S or S^{2-} loss from the systems (Wieder 1992, Machemer *et al.* 1993). On the basis of these case studies, loss of H_2S is not a major process contributing to loss of sulfur and acidity in wetlands. No references were identified that cited the importance of the process in active treatment systems, so it is not discussed further in this chapter.

Reduced organic sulfur compounds are formed through assimilatory sulfate reduction and during diagenesis through reactions between organic matter and H_2S (Anderson & Schiff 1987). These reactions indicate consumption of protons:

$$ROH + H^+ + SO_4^{2-} \rightarrow RO - SO_3^- + H_2O \qquad (25)$$

where ROH is an alcohol, and $RO\text{–}SO_3^-$ is a sulfate ester. Although there is some evidence that accumulation of organic sulfur is important in natural wetlands that receive elevated sulfur loadings (*e.g.,* Wieder & Lang 1986), other studies indicate that organic sulfur is unimportant compared to the formation of inorganic sulfur compounds in lake sediments and wetlands affected by mine drainage (Herlihy *et al.* 1988, Wieder & 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). Overall, the process does not seem important for treatment of mine drainage, and is not further discussed in this chapter.

Sulfate reduction in passive treatment systems. Water-quality improvements in lakes, wetlands, and passive treatment systems have been attributed to sulfate reduction, or the formation of metal sulfides, or both (Herlihy *et al.* 1987, Hedin *et al.* 1988, Kleinmann 1990, McIntyre & Edenborn 1990, Wildeman *et al.* 1990, Machemer & Wildeman 1992, Gusek & Wildeman 1995, 2002, Gusek *et al.* 1998, 1999). 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, that are more common in metal-mine drainage than in coal-mine drainage (*e.g.,* Wildeman *et al.* 1990, Machemer & 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, 1992). An anaerobic passive treatment system has reduced Pb and Zn concentrations in effluent from a Pb–Zn mine in Missouri, USA since 1996 (Gusek *et al.* 1998, 1999, Gusek & Wildeman 2002). The system consists of a settling pond followed by two anaerobic cells that operate in parallel, followed by an algae-filled rock filter and aeration pond (Fig. 6). Oxidation that occurs in the algae-filled rock filter and aeration pond helps lower the biological oxygen demand (BOD) from reduced sulfur compounds before discharge to the receiving stream (Fig. 6). The system covers 2 ha (5 acres) and successfully treats drainage whose reported flow rate of 272 $m^3\ h^{-1}$ (1200 gal min^{-1}) is larger than that of any other passive treatment system (Gusek & Wildeman 2002).

Detailed textural, petrographic, and geochemical studies of a vertical-flow system treating low-pH (<2.5) Fe(III)-dominated mine drainage indicated that sulfate reduction was initially important in removing Fe from

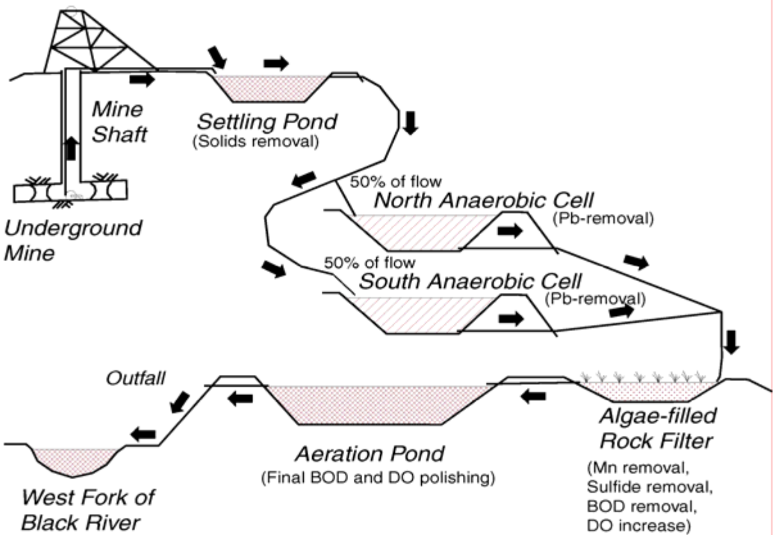


FIG. 6. Configuration of passive treatment system (at Doe Run mine, Missouri) that successfully treats Pb and Zn in mine drainage with a flow rate of 272 m^3 h^{-1}. Modified from Gusek *et al.* (1998) with permission from J. Gusek.

solution, but that longer term removal was achieved from oxidation and hydrolysis that produced Fe-oxyhydroxide minerals (Thomas & Romanek 2002a,b). A unique passive-treatment wetland design used floating cattail islands to provide a continuous supply of organic carbon for decomposition by anaerobic bacteria in a treatment system for metal-mine drainage at Sudbury, Ontario. The system removed 77–98% of the Cu, 80–87% of the Ni, and 10–20% of the S loadings. Sulfate reduction and complexation, and settling out of metal-organic complexes, promoted metal removal in the system (Berezowsky 1995, 1997). Sulfate reduction and precipitation of metal sulfides contributed to removal of Fe, Pb, and Zn in a passive system constructed to treat NAMD from a Pb–Zn mine. In this system, sulfate reduction occurred in constructed wetland substrates that were vegetated and where permanent water cover helped maintain reducing conditions. Alteration of the redox status of the substrate caused significant seasonal variation in metal removal rates and was attributed to plant rhizomes (O'Sullivan *et al.* 2000, 2001).

Performance problems have been noted for some passive anaerobic treatment systems. The failure of treatment systems dominated by sulfate reduction to remove Mn sulfide has been attributed to the higher solubility of MnS compared to that of other metal sulfides, and to the fact that MnS requires a greater pH to precipitate in anaerobic conditions than do other metal sulfides (Klusman & Machemer 1991). The failure of treatment systems to remove Mn as MnS is not surprising considering that MnS has a limited field of stability and is a rare mineral (Garrels & Christ 1965). The inability of sulfate reduction to become established in some passive treatment systems, or the reduced performance of sulfate reduction in some systems, 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, Eger & Wagner 2001), and insufficient flow of water through the substrate (Hedin *et al.* 1989).

Sulfate reduction in active treatment systems. There is interest in using sulfate reduction in active treatment systems. Active treatment using sulfate-reducing bacteria has been constrained by reactor size and cost, and by the availability and cost of a reliable carbon source for the bacteria (Rose *et al.* 1998). However, some case studies have indicated success using sulfate reduction in active treatment systems. One study demonstrated an active anaerobic approach that utilized a waste-stabilization ponding process and provided an established reactor technology for the treatment of large water volumes (Rose *et al.* 1998). The study indicated removal of 65 to almost 100% of influent Cd, Cr, Co, Fe, Ni, Pb, and Zn. In another study (Glombitza 2001), a minesite utilized a bioreactor that increased pH from 3.0 to 6.9 and removed almost 100% of influent Al, Fe, Ni, and Zn. The bioreactor contained sulfate-reducing bacteria that were fixed on an immobile porous material, with methanol provided

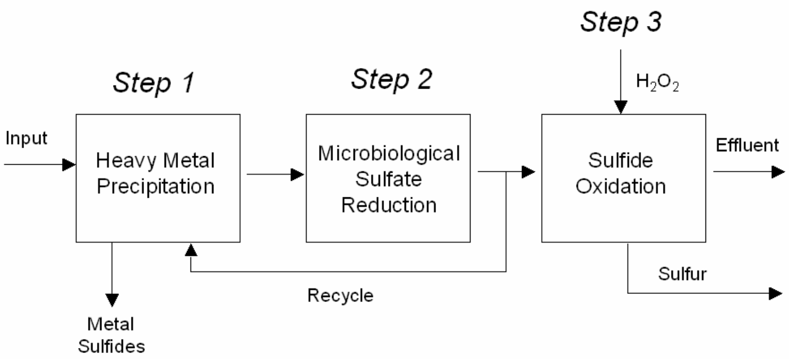


FIG. 7. Basic flowsheet of the microbial sulfate reduction process for the decrease of sulfate and the separation of heavy metals of mine water (modified from Glombitza 2001).

as a carbon source (step 2, Fig. 7). Recycling of sulfide-containing effluent from the bioreactor assisted heavy-metal removal via precipitation of sulfides (step 1, Fig. 7). Excess sulfur was precipitated as elemental sulfur in an oxidizing tank in series with the reducing system (step 3, Fig. 7). Mn removal was not possible with the system; however, the amount of heavy-metal sludge was less than would have formed in processes that utilize lime to increase pH and remove metals via oxic processes because no reagents were added in the sulfate reduction steps (Glombitza 2001). The composition of the aluminum precipitate is also not presented, but it is likely that Al-hydroxides precipitated as the pH increased. Other studies have reported more limited success with sulfate reduction in active treatment systems (Al-Ani *et al.* 1995, Younger *et al.* 2002).

Denitrification. Denitrification has been used in active treatment systems to remove dissolved nitrate associated with blasting activity. Anoxic biotreatment cells (ABC) were used to remove nitrate from water through denitrification which converted nitrate to N_2 gas:

$$4\,NO_3^- + 2\,H_2O \rightarrow 2\,N_2 + 5\,O_2 + 4\,OH^- \qquad (26)$$

It was reported (Reinsel & Botz 1999) that the same bacterial consortium that reduced nitrate also reduced selenate and selenite to elemental Se. The ABC also allowed the growth of sulfate-reducing bacteria to remove low concentrations of S and metals.

Metal–organic complexation

The complexation of metal ions with organic matter may be an important metal-removal process in some passive treatment systems that receive mine drainage. The process, however, can increase metal mobility in certain situations, and it has been cited as a reason for incomplete removal of metals in wetland systems. Metal–organic complexation is generally not a process that has been utilized to facilitate metal removal in active treatment systems.

Interactions between metal ions and organic matter help control the mobilities of some metals in organic-rich environments (Fraser 1961, Theis & Singer 1974). Metal–organic interactions include ion exchange, surface sorption, complexation and chelation, coagulation, and peptization. Because of the complexity of natural organic matter (the widely varied and sometimes unknown composition of natural organic matter) and the likelihood that many different types of organic molecules may interact with a metal ion, identifying the type of interaction taking place may be difficult. This section generally discusses complexation of metals by organic matter, which is the same as the specific adsorption to mineral surfaces discussed previously. Many of the specific details of metal–organic interactions are complex, poorly understood, or controversial (Thurman 1985, Hering & Kraemer 1998, Macalady & Ranville 1998); detailed discussion is beyond the scope of this chapter.

The formation of a metal–organic complex may increase or decrease mobility of a metal, depending on the solubility of the complex. For instance, Fe–humic-acid complexes are soluble if the pH ranges from 3 to 9, but they are insoluble at lower pH (Elder 1988). This behavior mimics the behavior of humic acids that are insoluble at low pH, but are soluble at higher pH. Metal–fulvic-acid complexes and fulvic acids are generally more soluble over a greater pH range (Kabata-Pendias & Pendias 2001). Hydroxyl and carboxyl functional groups on organic matter are probably the most important sites for complexation.

The stabilities of metal–organic complexes vary with metal and complexing substance. The Irving–Williams order indicates that the stability of divalent-metal–organic complexes decreases as follows (Irving

& Williams 1948):

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

Studies of interactions between metals and soil humic material (Schnitzer & Kahn 1978) have generally confirmed the Irving–Williams order. Studies of aquatic humic material (Mantoura *et al.* 1978) indicated a slightly different stability order:

Cu > Ni > Zn > Co > 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.

Case studies have indicated a variable importance of metal–organic interactions for metal removal in wetland and treatment systems, and have revealed some of the conditions that facilitate retention of organic-bound metals. Studies of wetlands that receive AMD indicated that organic binding of metals accounted for 20–90% of the Fe and Al accumulating in wetland sediments (Wieder & Lang 1986, Wieder *et al.* 1988, Henrot & Wieder 1990, Karathanasis & Thompson 1991). In wetlands that removed up to 90% of influent Ni, up to 60 % of the Ni was organically bound (Eger *et al.* 1994). Metal–organic interaction reportedly enhanced metal removal in a constructed wetland system, wherein floating cattail islands released organic acids to the water column, and the acids complexed metals, converting them to particulates that settled to the sediment (Berezowsky 1997). One study indicated that maintenance of anaerobic conditions facilitates the retention of organic-bound metals in engineered passive wetland-treatment systems (Michelutti & Wiseman 1995). Maintenance of oxygen-free conditions slows the decay of organic matter, thus preventing the release of organic-bound metals. 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 treatment systems that are rich in organic material, it is important to consider that organic complexation of metals can enhance metal precipitation, but it can also enhance metal mobility under some circumstances and for some metals. For example, Redman *et al.* (2002) indicated that interactions between As (a metalloid) and dissolved natural organic matter (NOM) increase the mobility of As in aqueous systems in two ways. First, NOM and As form complexes that increase As mobility in the presence of NOM. Second, the As and NOM compete for sorption sites on hematite so that As sorption to hematite is reduced in the presence of NOM. These results indicate that introduction of organic-rich water into a treatment system where As was sorbed to Fe-oxide material could cause release of As. In addition, attempts to treat As concentrations through sorption in systems that also contain organic matter could fail because of these interactions between NOM and As (Redman *et al.* 2002). Indeed, some studies have attributed poor performance of wetland treatment systems to the formation of metal–organic complexes that increased metal mobility (Lapakko & Eger 1988, Karathanasis & Thompson 1991).

Active uptake by plants

Microbially mediated sulfate reduction and the concomitant precipitation of metal sulfides are perhaps the most significant ways that biota contribute to treatment of mine drainage. However, plants also immobilize mine-drainage components by accumulating metals within their structures. The general mechanisms and controls on this process are fairly well understood (Mulligan 2002). Several case studies have indicated that elevated metal concentrations are present in plants from wetlands that treat mine drainage. In most cases, however, plant assimilation of metals does not significantly contribute to metal removal. Uptake of metals by plants is generally not employed in active treatment systems.

Many studies have described plant-assisted trace-metal removal in passive treatment systems, primarily in species of cattail and bryophytes (moss) (Kleinmann *et al.* 1983, Burris *et al.* 1984, Lee *et al.* 1984, Snyder & Aharrah 1984, Howard *et al.* 1989, Qian *et al.* 1999, Batty & Younger 2002). Algae and other aquatic organisms also contribute to metal removal in some passive treatment systems (Gale & Wixson 1979, Wildeman & Updegraff 1998, Robbins *et al.* 1999, O'Sullivan *et al.* 2001). Macrophytes may be of critical importance in removing residual amounts of Fe from mine water in constructed waste-treatment systems. In a system where influent Fe concentration was approximately 1 mg L^{-1}, almost 100% of the Fe was reported to have been taken up by plant tissues (Batty & Younger 2002). Storage of metal in and around roots is the most commonly reported mechanism for plant-assisted metal removal in passive treatment systems (Lan *et al.* 1990, Dunbabin & Bowmer 1992, Batty & Younger 2002), but translocation to leaves can be important (Powicki 1997). Plant uptake of metals has been identified as an important removal process for some contaminants associated with mine drainage, among which are As (Ashley & Lottermoser 1999), Pb, and Zn (O'Sullivan *et al.* 2000, 2001). Copper uptake by the macrophyte *Nelumbo lutea* (American lotus) was modelled using WASP (a program for water-quality analysis simulation) in a natural wetland along the shore of Lake Erie (Lung & Light 1996). Ambient concentrations of Cu in the wetland inflow were dilute (0.001 to 0.030 mg L^{-1}) relative to concentrations that occur in mine drainage. Nevertheless, the results indicate that plant uptake can be used as a polishing step to cleanse mine drainage and other waste streams that have recalcitrant but low levels of metal contamination.

In most wetlands, the absolute amount of metals removed by the plants is insignificant compared to the amounts that accumulate in the substrate (Sencindiver & Bhumbla 1988, Howard *et al.* 1989). However, researchers have hypothesized that wetland plants help support the ecological system that functions to remove metals in the substrate (Samuel *et al.* 1988, Sencindiver & Bhumbla 1988, Powicki 1997).

In summary, vegetative uptake rates and importance differ from site to site. Even when vegetative uptake is not an essential mechanism of metal removal, plants assist removal processes by increasing the retention time of the water, providing organic matter for microorganisms, increasing the surface area of the aerobic–anaerobic interface in the rhizosphere, and creating an oxidized rhizosphere where metals concentrate and bacteria can facilitate metal uptake by plants (Dunbabin & Bowmer 1992, Noller *et al.* 1994, Powicki 1997).

Microbial uptake

Microorganisms indirectly contribute to treatment of mine drainage in oxic systems by facilitating precipitation of Fe and Mn minerals and altering the redox state of the environment, which may promote metal removal through sulfide-mineral precipitation. In addition, some studies indicate a more direct role for microorganisms in the direct uptake of metals by microbes, and the sorption of metals to microorganisms and their exudates. Robbins *et al.* (1999) reported that microorganisms and algae play an active role in the removal of Mn in a passive treatment system. Ledin & Pedersen (1996) reviewed the variety of active and passive mechanisms through which microorganisms influence metal mobility, and cited numerous published examples of metal accumulations on and in microorganisms.

Biological treatment processes have been developed to treat cyanide-rich waste associated with some mining operations (Botz 2001). An active treatment plant that utilizes an aerobic, attached-growth biological process to remove cyanide compounds, ammonia, and metals has been operating successfully at Homestake Lead (South Dakota, USA) for more than 15 years (Botz 2001). Biological treatment for cyanide is limited to continuous solution flows with temperatures greater than 10 °C (Botz 2001).

INNOVATIVE PROCESSES AND DESIGN

Recent innovations in passive treatment include methods to add alkalinity to enhance metal precipitation, the use of filters to enhance Fe precipitation, treatment of waste containing unusual components, use of Fe-hydroxide sludge as raw material for industrial purposes, and incorporating reaction kinetics into the design of passive treatment systems. Innovations in active treatment include processes that extend treatment to include unusual contaminants, such as Se, As, and N-bearing compounds, the use of novel adsorbents or coagulants to maximize constituent removal, and processes to maximize sludge density and recovery.

Passive treatment

Simmons *et al.* (2002) added leach beds of steel slag in series below limestone-lined settling beds as a means of adding alkalinity. The leach beds successfully neutralized all of the acidity in the influent. One complication was that the leach beds added soluble Cr to the effluent, but removal rates of other metals were acceptable.

Some of the effluent in a staged passive treatment system that was used to treat acidic coal-mine drainage was recirculated to the detention pond at the beginning of the system (Fig. 8; Garrett *et al.* 2002). The recirculation increased the alkalinity entering a RAPS below the retention pond. The result was greater metal-removal rates and an increased ability of the system to deal with high loadings associated with storm events (Garrett *et al.* 2002). The system was not completely passive because the recirculation required energy.

The use of high-surface-area trickling filter media caused rapid accretion of Fe and some removal of Mn from NAMD (Jarvis & Younger 2001). Two towers containing two sizes of plastic filter media (lumps of plastic) comprise the high-surface-area trickling filters. The authors propose these filters as an alternative to aerobic wetlands because the systems may be an order of magnitude more efficient and require much less space than aerobic wetlands.

A pilot-scale passive-leach field system was constructed in Nevada (U.S.A.) to treat waste from heap-leach operations that contain sulfate, nitrate, and Se (Harrington *et al.* 1999). The leach fields combined two soil layers and an organic amendment constructed to overlie a 65-m-thick vadose zone. Column tests prior to construction showed removal of sulfate, nitrate, and Se. Groundwater is being monitored at the site to determine the effectiveness of treatment. The use of this method might be restricted to areas whose climate and depth to the water table are similar to those at the pilot site.

Iron oxides recovered from coal-mine drainage have been used as a feed for pigment production (Hedin 2002). Although there were some problems with purity of the Fe-oxide product and dewatering, the report

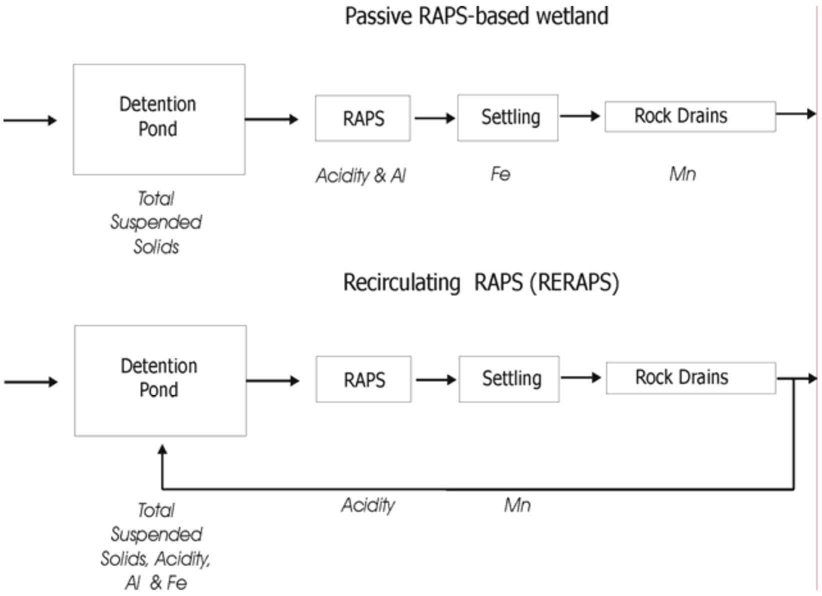


FIG. 8. Primary environment of pollutant deposition or consumption in a passive RAPS-based wetland and in a semipassive RERAPS wetland. Constituents listed below each treatment step are those removed by that step (modified from Garret *et al.* 2002).

indicated that there is potential to develop mine-drainage treatment systems where cost recovery from the Fe-oxide product can be used to reduce long-term operation and maintenance costs.

Among other findings, the issue of sludge reuse was addressed by Dietz & Dempsey (2001, 2002). They reported that recirculation of Fe sludge into cells in which the Fe is actively precipitating offers several improvements over typical passive treatment systems. Sludge recirculation (1) utilizes the faster heterogeneous precipitation of Fe; (2) can result in faster Fe-removal rates than those of typical passive treatment systems; and (3) can produce a purer sludge that may be more amenable to reuse than sludge produced by conventional treatment systems or typical passive treatment systems. The system was set up in tanks and required pumping for the recirculation, so the system was primarily one of active treatment.

In passive treatment, the concepts of treatment efficiency, area-adjusted removal rates, and first-order removal have been used to compare the performances of different systems and to apply an understanding of metal-removal rates to treatment-system design (Girts & Kleinmann 1986, Weider 1989, Hedin & Nairn 1990, Stark & Williams 1995, Tarutis *et al.* 1999). The most recent report indicated that first-order removal best described loss of Fe and Mn in wetlands. That is, the rate of metal removal is a function of metal concentration in the influent. However, more data are needed to develop accurate first-order removal rate constants that are a function of influent chemistry and ecosystem characteristics before a model with first-order removal can be used to design wetland treatment systems that are more effective (Tarutis *et al.* 1999).

Active treatment

In active treatment, there has been increased experimentation with innovative adsorbent and coagulant materials. A process called cost-efficient sulfate removal (CESR) attenuates sulfate and metals through precipitation of gypsum and ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$]. Ettringite precipitation occurs after addition of a proprietary reagent (Reinsel 1999). Apatite and hydroxylapatite promote formation of metal-phosphate minerals in acid solutions (Xu & Schwartz 1994, Choi *et al.* 1997) and may be useful in active or passive treatment systems. However, the use of apatite as a pH buffer and source of phosphate for metal precipitation is limited by its solubility (Choi *et al.* 1997). Bone char is a potential adsorbent for Cd in wastewater treatment systems (Cheung *et al.* 2001) and thus has potential for use in mine-water treatment systems. Magnetite employed in fixed-bed reactors removed metals and As from waste streams through adsorption and magnetic filtration (Navritil 2001). Recycled iron fines derived from manufacturing of cast iron have been used as an adsorbent for removing Cd, Pb, and Zn from wastewater (Smith 1995).

In active treatment, novel system designs allow treatment of metals and substances that are not typical in most mine drainages. Reinsel & Santina (1999) reported As removal by contact with an iron/sulfur slurry. They postulated that As removal occurred through direct precipitation of As onto "sponge" iron or through coprecipitation with Fe hydroxides. Reinsel & Botz (1999) reported removal of nitrate and Se in anoxic biotreatment cells (see "*Denitrification*" section).

Sludge management is one of the greatest difficulties encountered in active treatment systems that utilize oxidation and alkalinity addition to remove metals. Sludge typically has a high water content, and large volumes of sludge are generated in many treatment operations. It is difficult and costly to handle and dispose of sludge. Attempts to improve sludge management have included recycling of sludge during treatment, which improves the efficiency of metal removal, requires less chemical amendment, and increases the density of the final sludge product (Keefer & Sack 1983, Younger 2000). Addition of reagents such as fly ash or cement have been used to increase sludge density (Hustwit 1995). Research to improve sludge composition to make it a suitable feed for industrial processes was described by Dietz & Dempsey (2001, 2002) and Hedin (2002).

Design

The design of active and passive treatment systems continues to evolve. Passive treatment systems have evolved from single-cell constructed wetlands to designs that incorporate multiple components including aerobic and anaerobic wetlands, SAPS, and ALDs (Nairn 2001). Basic design guidelines consider influent pH, dissolved metal and oxygen concentrations, and flow rates (Hedin *et al.* 1994a, Skousen *et al.* 1998). Some newer designs incorporate an understanding of contaminant-removal rates to determine wetland size and the supply rates of carbon needed to sustain biogeochemical reactions (Kalin 2000). Hybrid systems using components of passive and active treatment have been described, and such systems may become more popular if recirculation of sludge or effluent is necessary to improve metal-removal efficiency. Design of passive and active treatment systems is site specific and depends on mine drainage chemistry, flow rate, site characteristics, and regulatory requirements. In addition, as innovative treatment processes are proven and become accepted in the remediation community, they are incorporated into new designs. Consequently, it is not surprising that there is not an accepted single set of consistent design guidelines.

SUMMARY

Processes exploited in passive and active treatment systems include equilibrium precipitation of metal-mineral phases, sorption of metals onto organic and inorganic material, and active and passive immobilization of metals by microbial and plant species. The processes occur over the redox ladder, extending from fully oxidized systems to anaerobic systems dominated by sulfate-reducing bacteria. Research into kinetic control of reaction mechanisms is helping to define rate-limiting steps in some treatment processes (*e.g.*, calcite dissolution), and to identify faster reaction mechanisms (*e.g.*, heterogeneous Fe oxidation). Research is also being conducted to increase the types of metals and other constituents that can be treated in these systems, to increase the amount of alkalinity that can be added in passive treatment systems, and to improve sludge management in active treatment.

Currently (2003), an understanding of the processes that remove metals from water, and the designs that can be implemented to maximize those processes, are expanding as the number of installed systems also expands. The new designs incorporate features ascertained from a greater understanding of the complex chemistry of the liquid waste that is treated, and of the processes available to treat the waste. Hybrid systems that borrow technology from passive and active treatment are successfully improving the water quality of mine drainage, and are becoming more common as design experimentation continues.

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