

## Metal Attenuation Processes at Mining Sites

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### Background

The EPA Regional Ground Water Forum is a group of EPA scientists representing Regional Superfund and Resource Conservation and Recovery Act Offices (RCRA). The Forum is focused on exchanging information related to ground-water characterization, monitoring, and remediation. The application of monitored natural attenuation (MNA) for inorganic contaminants in ground water is a topic of concern to the Forum. The purpose of this Issue Paper is to provide scientists and engineers responsible for assessing remediation technologies with background information on MNA processes at mining-impacted sites. Some of the key issues concerning the application of natural attenuation for inorganic contaminants are discussed, such as the geochemical mechanisms responsible for attenuation, attenuation capacity, monitoring parameters, and evaluating whether attenuated metal and metalloid contaminants will remain immobile.

### Introduction

Acid mine drainage (AMD) is a major source of water contamination in metal-mining and coal-mining districts worldwide. The causes of AMD are well known. They relate to the natural weathering of mine wastes and rocks enriched in metal sulfide minerals. Environmental impacts include the destruction of aquatic life and habitats and contamination of drinking water resources. The most common reactions that lead to the production of AMD involve the chemical and biological oxidation of metal sulfides contained in mine waste heaps, active or abandoned mine workings, or in tailings piles left over from the processing of sulfide ores. The iron sulfides: pyrite, marcasite and pyrrhotite, are perhaps the most common sources of AMD production, because they are ubiquitous in metal sulfide ores and because they generally are not the target of ore beneficiation processes. Numerous variables factor into the assessment of potential

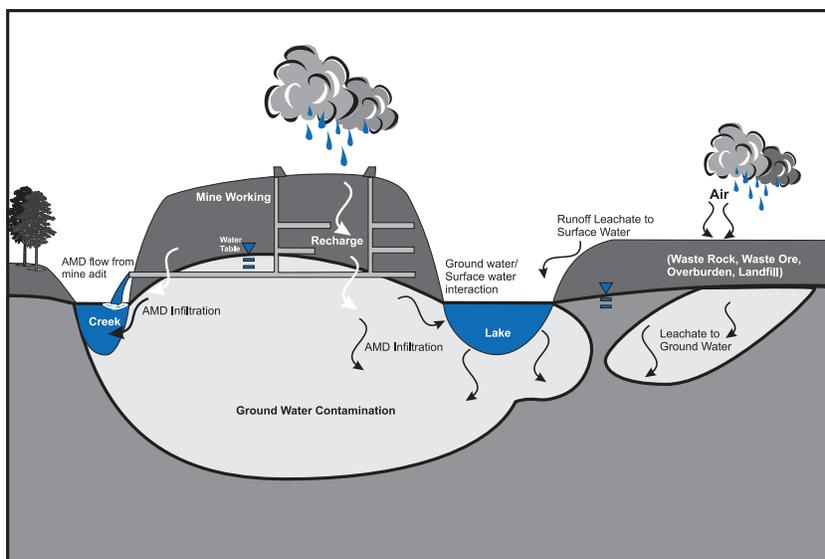
AMD releases, including the quantity of reactive sulfides, grain size distribution and grain morphology, bacterial activity, moisture content, and the availability of dissolved oxygen or other oxidants (e.g., Jambor et al., 2000; Lowson, 1982; Nordstrom and Southam, 1997; Rigby et al., 2006; Williamson and Rimstidt, 1994).

Acid mine drainage may form via the interaction of surface water or ground water with materials enriched in metal sulfides, such as tailings piles or the underground workings of deep mines (Figure 1). Production of AMD may occur during mine operations and may continue for many years after mines are closed and tailings dams are decommissioned from operation; consequently, evaluation of AMD is often a long-term proposition which usually adds up to high costs for site characterization, monitoring and cleanup. Estimates of the number of sites in the United States affected by AMD vary widely from 200,000 to over 550,000 (U.S. Environmental Protection Agency, 2004). Estimated costs to cleanup contamination at AMD sites are equally difficult to assess. One hundred and fifty-six hardrock mining sites were on or had the potential to be on the National Priorities List (NPL) for cleanup under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), with potential cleanup costs of up to \$24 billion dollars (U.S. Environmental Protection Agency, 2004). Mine sites are frequently remotely located, which further adds to the costs of site characterization, remediation, and monitoring.

In some cases, especially where ore host rock is capable of reacting with acidic drainage, metal concentrations may attenuate over time and space. A primary control on the process of metal attenuation at mining-impacted sites is acid neutralization (Al et al., 2000; Berger et al., 2000). Neutralizing capacity in sulfide ore tailings is predominantly from carbonate minerals (calcite and dolomite) because most non-carbonate minerals associated with metalliferous deposits are extremely slow to react and affect pH (e.g., Jambor et al., 2000). As pH increases, aqueous metal species tend to precipitate as hydroxide, oxyhydroxide, or hydroxysulfate minerals (Nordstrom, 1982). In addition, as pH increases dissolved metals may adsorb onto surfaces of these newly formed minerals and/or other surfaces present in the environment, such as organic matter due to decreasing competition with protons, decreased surface potential, and increased hydrolysis of metal ions at circum-neutral pH.

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**Figure 1.** Impacts of mine workings and mine wastes on ground water and surface water. As oxygenated waters interact with sulfide minerals, pH decreases and metals are mobilized in the absence of acid-neutralizing rocks and overburden.

In the context of mining sites, natural attenuation refers to the observed reduction of contaminant concentrations and/or contaminant mass flow rates as contaminants are transported downgradient from their source. At many mining sites that require cleanup of contaminated ground water, monitored natural attenuation is not expected to be relied upon as a sole remedy. The global magnitude of the acid drainage problem is clear evidence that in most cases natural processes are incapable of ameliorating the acidity and metal contamination produced by oxidizing sulfide minerals. However, monitored natural attenuation may be an effective strategy to augment more active approaches of remediation (summarized below). In addition, natural attenuation processes often tend to spread contaminants out in space away from source zones via various mineral-water reactions. Therefore, it is important to recognize natural attenuation processes from the perspective of tracking contaminant transport and fate in the environment. This Issue Paper provides remedial project managers and other state or private remediation managers and their technical support personnel with background information on the various physical, chemical, and biological processes of natural attenuation that may occur at mining sites. This background information is necessary for preparing sampling plans to support site characterization, remedy selection, and post-remedial monitoring efforts.

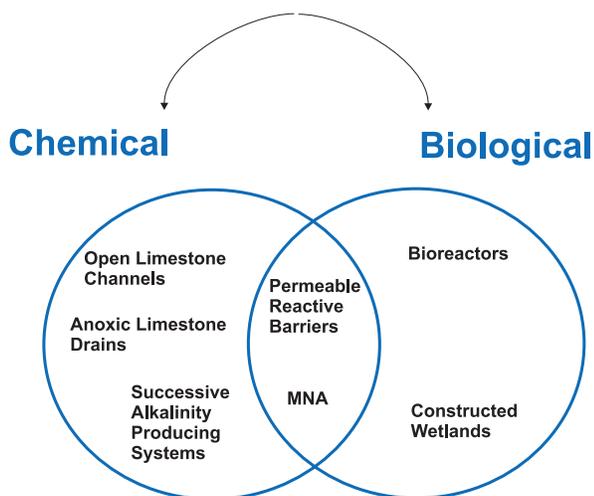
### Treatment Strategies for AMD

Strategies for dealing with AMD include source control and chemical or biological treatment of contaminated ground water. Preventing the formation or the migration of AMD from source zones is generally a favorable option, but is often difficult to accomplish effectively due to the large aerial extent of tailings areas and the large volumes of materials involved. Consequently, cleanup efforts are

usually focused on directly treating impacted ground water and surface water (U.S. Environmental Protection Agency, 2006). Remediation methods at mining sites can be generally divided into “active” and “passive” approaches (Johnson and Hallberg, 2005). Perhaps the most straightforward and common active approach to treat acidic effluents is through addition of alkaline materials to raise pH, increase the rate of ferrous iron oxidation, and cause the removal of metals and metalloids present in solution via mineral precipitation or surface adsorption processes. A number of alkaline materials have been used for active treatment, including lime, calcium carbonate, sodium carbonate, sodium hydroxide, and magnesium oxide. Use of these materials can lead to effective controls on the release of acidic drainage and dissolved metals. The cost of maintaining direct treatment facilities is often high. Large volumes of a low-density sludge result from the reaction between alkaline compounds and acidic effluents. Moreover, the sludge itself becomes an environmental concern, both in terms of disposal and the potential release of contaminants through subsequent leaching (Jambor et al., 2000).

Figure 2 presents a general classification of passive AMD treatment systems, which can be broadly grouped into chemical and biological systems (Neculita et al., 2007). Treatment systems that rely largely on abiotic chemical processes include open limestone channels, anoxic limestone drains, and successive alkalinity-producing systems. In open limestone channels, acidic water flows over crushed limestone or some other alkaline agent. The goals of such applications are to generate alkalinity, neutralize pH, and remove soluble aluminum, iron, and manganese via mineral precipitation (Mukhopadhyay et al., 2007; Ziemkiewicz et al., 1997). The treatment strategy with anoxic limestone drains is to neutralize acid-mine drainage using limestone while maintaining iron in a reduced state (as ferrous iron)

## AMD Passive Treatment Systems



**Figure 2.** Treatment systems for acid mine drainage.

to avoid iron oxidation and the consequent precipitation of hydrous ferric oxides on the limestone surfaces. Such surface precipitation or armoring by iron and aluminum precipitates greatly reduces the effectiveness of the neutralizing material. In its simplest form, an anoxic limestone drain (ALD) is a buried, limestone-filled trench that intercepts AMD before it is exposed to atmospheric  $O_2$  (Cravotta and Trahan, 1999; Hedin et al., 1994). ALD designs are enclosed to minimize gas flux in contrast to systems such as limestone channels that are open to the atmosphere. In this way  $CO_2$  gas is retained in the subsurface channel which leads to enhanced calcium carbonate dissolution and alkalinity production. After acidic waters pass through the ALD, effluents are exposed to the atmosphere and hydrous ferric oxides are produced by the oxidation of ferrous iron to ferric iron. In successive alkalinity-producing systems, both limestone and organic matter are used in vertical flow systems to provide alkalinity production, sulfate reduction, and metal removal (Keplar and McCleary, 1994).

Biological passive treatment systems for AMD include bioreactors and constructed wetlands (Figure 2). Sulfate-reducing passive bioreactors have received recent attention as promising technologies for AMD treatment (e.g., Alvarez et al., 2007; Annachatre and Suktrakoolvait, 2001; Costa and Duarte, 2005; Drury, 1999; Dvorak et al., 1992; Johnson and Hallberg, 2005; Neculita et al., 2007; Steed et al., 2000). The advantages of this technology are high metal removal capacity, stable sludge, and low operation costs. The chemical basis for treatment of AMD by sulfate reducing bacteria involves microbially-mediated sulfate reduction coupled to organic matter oxidation. Sulfide precipitation is the desired mechanism of contaminant removal, but other mechanisms including adsorption and precipitation of metal hydroxides occur in passive bioreactors (Neculita et

al., 2007). The efficiency of sulfate-reducing bioreactors is primarily controlled by the organic carbon source (Coester et al., 2006; Gibert et al., 2004; Prasad et al., 1999; Zamzow et al., 2006). Solid-phase testing suggests that organic substrates with high protein contents or low lignin contents (e.g., manure) are better capable of supporting bacterial activity and sustaining contaminant removal (Coester et al., 2006; Gibert et al., 2004).

Artificial wetlands and biological treatment systems have been used since the mid-1980s for the treatment of AMD. The effectiveness of these applications has been variable and generally difficult to predict (Barton and Karathanasis, 1999; Wieder, 1989; Wildeman and Updegraff, 1997), although recent process-based modeling efforts are beginning to provide insight into the functioning of these systems that feedback into system design refinements and operational improvements (Whitehead et al., 2005). Both aerobic and anaerobic processes contribute to contaminant removal in constructed wetland systems. The oxidation of ferrous iron to ferric iron and the subsequent precipitation of hydrous ferric oxides is a dominant process that is effective in removing iron and other metals from AMD (Brenner, 2001). Metal accumulation in these systems also occurs through precipitation of metal sulfides via the activity of sulfate reducing bacteria that consume natural organic matter and sulfate and produce reactive sulfide for metal removal (Webb et al., 1998).

Permeable reactive barriers (PRBs) and monitored natural attenuation (MNA) for treatment of ground water impacted by AMD can be classified either as chemical or biological passive treatment systems based on process function (Figure 2). The application of PRBs involves the excavation of a trench or pit in the flow path of contaminated ground water. The excavated volume is then filled with reactive materials that are permeable to allow flow of contaminated ground water and reaction to remove dissolved contaminants via chemical or biological processes. Reactive materials that have been shown to be effective in increasing pH and removing metals include mixtures of organic carbon, limestone, and zero-valent iron (Benner et al., 1999; Gibert et al., 2003; Ludwig et al., 2002; Shokes and Möller, 1999; Waybrant et al., 1998; Wilkin and McNeil, 2003). Organic carbon-based PRB systems take advantage of anaerobic microbiological processes within the PRB to generate alkalinity and remove metals as sulfides. In zero-valent iron PRB systems, a variety of abiotic and biotic metal uptake processes are important in neutralizing acidity and removing metals from solution. Similarly, MNA involves both biologically mediated processes and abiotic geochemical processes that are presented in the following sections. Note that many of the documented natural attenuation processes are actually strategically enhanced in designed remediation systems, such as bioreactors.

### Background on MNA for Inorganic Contaminants

The term "monitored natural attenuation" refers to the long-term examination of natural processes with the objective that such processes will reach site-specific remedial objectives. MNA can be applied in conjunction with other cleanup

approaches, such as source removal, source control, or plume control (Rügner et al., 2006). To be considered as an acceptable option, MNA would be expected to achieve site remedial objectives within a time frame that is reasonable compared to that possible by using other more active remediation technologies as described above. Natural attenuation processes include a variety of physical, chemical, and biological processes that can act to reduce the mass, mobility, volume, or concentration of contaminants in ground water. Attenuation processes important at mining sites include pH buffering and acid neutralization, adsorption at the mineral-water interface, mineral precipitation, and dilution/dispersion (Figure 3).



**Figure 3.** Processes of natural attenuation at mine-impacted sites.

EPA's Office of Research and Development is preparing a technical resource document for the application of MNA to inorganic contaminants in ground water (see Reisinger et al., 2005; U.S. Environmental Protection Agency, 2007). The technical resource document presents a four-tiered assessment of MNA as a viable remediation option for selected metal, metalloid, and radionuclide contaminants encountered in ground water. Components of the tiered approach include 1) demonstrating contaminant sequestration mechanisms, 2) estimating attenuation rates and the 3) attenuation capacity of aquifer solids, and 4) evaluating potential reversibility issues. The technical resource document is intended to provide a tiered decision-making approach for determining whether MNA is likely to be an effective remedial approach for inorganic contaminants in ground water at a particular location. EPA expects that users of this document will include EPA and State cleanup programs and their contractors, especially those individuals responsible for evaluating alternative cleanup methods for a given site or facility. A decision-making approach is provided for evaluating MNA as a possible cleanup method for contaminated ground water. Emphasis is placed on developing a more complete understanding of the site through development of a conceptual site model that includes an understanding of the attenuation mechanisms, the geochemical conditions governing these mechanisms, and indicators that can be used to monitor attenuation progress (U.S. Environmental Protection Agency, 2007).

A tiered decision-making approach is an appropriate and cost-effective way to screen out sites unsuitable for MNA while collecting the most relevant data at sites that might be amenable to this technology. Conceptually a tiered assess-

ment of MNA seeks to progressively reduce site uncertainty as MNA-specific data is collected. MNA for inorganics and radionuclides is most effectively implemented through four tiers that require progressively greater information on which to assess the reasonableness of MNA:

- Tier I. The plume is not threatening public health, is stable, and some direct evidence of contaminant attenuation exists.
- Tier II. The attenuation capacity of the site exceeds the estimated mass of contaminant at the site.
- Tier III. There is strong evidence that attenuation mechanism(s) will prevail over long periods of time.
- Tier IV. A record of decision including a long-term monitoring plan and other site closure considerations is developed.

### MNA Processes at Mining Sites

Based upon the tiered approach presented above, assessments of MNA at mining sites must demonstrate that chemical, physical, or biological processes are occurring to mitigate migration of contaminants, that the capacity of the MNA process exceeds the mass of contaminants in the source, and that the attenuation processes are sustainable over long periods of time. As noted previously, these conditions are frequently not met at mining sites. Although research findings clearly show that attenuation of contaminants does indeed occur at mining sites (Table 1), the documented mechanisms of attenuation are either rate- or capacity-limited so that contaminants are only partially attenuated or attenuation occurs over longer flow paths than are acceptable from a site cleanup perspective. It is equally clear, however, that many of the attenuation processes important at mining sites are long-lived, so that a sound understanding of the factors that control transport and fate of metals in ground water and across the ground water/surface water interface can benefit site cleanup efforts.

### Acid Neutralization

A primary control on the process of metal attenuation at mining sites is acid neutralization. Many factors affect the acid neutralization capacity of a system, including the type, abundance and reactivity of metal-bearing sulfides in the ore and waste rock, permeability of the mine workings or mine tailings, and the ability of the host or surrounding rocks to consume acidity. Methods are available to predict whether or not materials will be acid-generating (e.g., U.S. Environmental Protection Agency, 1994). These methods provide a numerical accounting with respect to prediction of acid production and neutralization potential. In general, materials containing elevated concentrations of carbonate minerals or that have elevated inorganic carbon to total sulfur ratios are the most effective in neutralizing acidity.

Mixing of mine effluents with ambient ground water and surface water dilutes the dissolved contaminants and can result in pH increases. In surface waters, dilution and neutralization can occur over spans of meters to many kilometers. Dilution and neutralization are often tied to seasonal

variations in flow patterns and volumes. Field studies have documented more effective attenuation of mine effluents in dry seasons compared to wet seasons (Webster et al., 1994). In addition, field studies and laboratory column testing results indicate that mineral assemblages present in tailings piles, underlying aquifers, and receiving surface waters play a pivotal role in controlling pH (Blowes and Ptacek, 1994; Jurjovec et al., 2002; Morin et al., 1988; Sánchez-España et al., 2005). Mineral phases important in buffering pH are calcite/siderite, aluminum hydroxides, iron hydroxides, and aluminosilicates.

### Role of Secondary Minerals

The oxidation of iron sulfides in mine wastes results in the release of iron, sulfate, acidity, and metals to solution. High aluminum and silica concentrations are also commonly encountered in mine effluents and are the result of weathering

of aluminosilicate minerals at low pH. Oxidation and hydrolysis reactions can subsequently lead to the precipitation of a wide array of hydroxide, sulfate, and/or hydroxysulfate minerals depending on geochemical and biogeochemical conditions (Nordstrom and Alpers, 1999). These secondary minerals play important roles in attenuating contaminants from mine effluents (e.g., Accornero et al., 2005; Casiot et al., 2005; Fukushi et al., 2003; Gault et al., 2005; Jamieson et al., 1999; Lee et al., 2002; Lee et al., 2005; Levy et al., 1997; McCarty et al., 1998; McGregor et al., 1998; Moncur et al., 2005; Munk et al., 2002; Sánchez-España et al., 2005; Sidenko and Sherriff, 2005; Webster et al., 1998; Zänker et al., 2002). Some of the common secondary minerals found in association with the weathering of mine wastes, their typical pH range of formation, and documented contaminant associations are listed in Table 1.

**Table 1.** Secondary Minerals Formed from Acid Mine Waters and Contaminant Associations

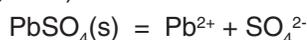
Mineral Phase	Formula	Typical pH range of formation	Examples of contaminant associations at mine-impacted settings	Reference
<i>Hydroxides</i>				
Goethite	FeOOH	2-4	Sorption/coprecipitation of Pb (up to 21 wt%), As (up to 7.7 wt%), Zn (up to 4.6 wt%), and Cu (up to 2.5 wt%)	Lee et al. (2005)
HFO, hydrous ferric oxide	~Fe <sub>5</sub> HO <sub>8</sub> •4H <sub>2</sub> O	>5	Sorption/coprecipitation of As-rich ferrihydrite; As/Fe=0.02-0.1, with 10-30% As(III)	Casiot et al. (2005)
Gibbsite	Al(OH) <sub>3</sub>	>5-6	Sorption in the general order of Pb>Cu>Zn>Ni with increasing pH	Munk et al. (2002)
<i>Hydroxysulfates</i>				
Alunite	KAl <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	4-6	Precipitation of Al	Accornero et al. (2005)
Jarosite	KFe <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	2-5	Coprecipitation with As(V) replacing sulfate in the jarosite structure	Gault et al. (2005)
Schwertmannite	Fe <sub>8</sub> O <sub>8</sub> (OH) <sub>6</sub> (SO <sub>4</sub> )	2-4	Coprecipitation of Cu, Ni and Zn	Sidenko and Sherriff (2005)
<i>Sulfates</i>				
Gypsum	CaSO <sub>4</sub> •2H <sub>2</sub> O	>3	“Hardpan” precipitate	Moncur et al. (2005)
Anglesite	PbSO <sub>4</sub>	>3-4	Precipitation at pH ~3; nanoparticles	Zänker et al. (2002)
Melanterite	FeSO <sub>4</sub> •7H <sub>2</sub> O	<2	Coprecipitation with Zn and Cu; temporary metal removal in a highly soluble phase	Jamieson et al. (1999)

Secondary precipitates can remove contaminants from impacted waters through adsorption and/or coprecipitation reactions. Adsorption processes are typically categorized by the relative “strength” of interaction between the adsorbate (species in solution) and the surface or adsorbent. If solvating water molecules are positioned between the cation or anion and the surface, the adsorption complex is referred to as outer sphere and is considered to be weak. Conversely, if upon adsorption the adsorbate loses waters of hydration such that there are no water molecules positioned between the cation or anion and the surface, the adsorption complex is referred to as inner sphere and is considered to be strong. The extent to which dissolved contaminants will sorb to secondary precipitates as outer sphere or inner sphere complexes will vary as a function of the contaminant species, the secondary precipitate, pH, particle size and surface area, and presence of other sorbing species that may compete for adsorption sites.

Inorganic contaminants may be removed from solution due to precipitation of an insoluble phase in which the contaminant represents a major or minor component within the solid. Examples of secondary precipitates that form in mine-impacted sites include oxyhydroxides [e.g., FeOOH(s)], hydroxysulfates [e.g., Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)(s)], sulfates [e.g., PbSO<sub>4</sub>(s)], and sulfides [e.g., ZnS(s)]. For each of these minerals there will be a limited compositional range of ground-water chemistry over which precipitation could occur and formation of these precipitates may compete with other removal processes such as adsorption (Table 1).

Characterization of secondary precipitates is carried out by using a variety of tools. Mineralogical identification is typically made by using powder x-ray diffraction techniques (XRD). The characterization of particle morphology and semi-quantitative composition are accomplished using scanning electron microscopy (SEM) and x-ray energy-dispersive spectrometry (EDX). Analysis of element partitioning to well-crystalline and poorly-crystalline components of the solid phase is typically accomplished using selective chemical extraction procedures. Used in combination, these methods allow for the identification of attenuation mechanisms involving secondary minerals (see U.S. Environmental Protection Agency, 2007). Knowledge about the types of mineral phases helps to understand the long-term stability of attenuated metals.

One can also evaluate whether there is a potential for contaminant precipitation by evaluating the saturation state of the ground water with respect to possible precipitate phases using a saturation state modeling approach. In order to evaluate whether a ground water is oversaturated, undersaturated, or at equilibrium with a particular phase, computer geochemical speciation models are of practical use. As an example, consider the solubility expression for lead sulfate (anglesite):



The mass-action expression that applies to the equilibrium is:

$$K_r = \frac{a_{\text{Pb}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{PbSO}_4(\text{s})}} = 10^{-7.8}$$

A natural water may or may not be at saturation with respect to anglesite, depending on whether the phase is indeed present, available surface area, residence time of water, and kinetic factors that may impede dissolution and/or precipitation. If we assume equilibrium between water and anglesite, then the ion activity product,  $Q$ , should be the same as the equilibrium constant,  $K_r$ , i.e.,

$$Q = a_{\text{Pb}^{2+}} a_{\text{SO}_4^{2-}} = K_r = 10^{-7.8}$$

where the activity ( $a$ ) of PbSO<sub>4</sub>(s) is taken to be 1. Because ion activity products may vary by orders of magnitude, it is often more convenient to take the logarithm of the ratio, that is, to compute the saturation index,  $SI$ :

$$SI = \log \frac{Q}{K_r} = 0 \quad \text{at equilibrium}$$

If a water is oversaturated in a particular phase, then the  $SI$  is positive, and there is a thermodynamic driving force for precipitation to occur. If the water is undersaturated, then the  $SI$  is negative, and the mineral, if present, will tend to dissolve:

$$SI > 0 \quad \text{if oversaturated}$$

and

$$SI < 0 \quad \text{if undersaturated.}$$

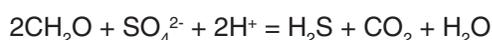
As previously indicated the stability of a precipitate will be dictated by the ground-water chemistry. Contaminant remobilization will occur as a result of dissolution of the precipitate phase, for example, when  $\log Q/K_r < 0$ . Precipitate dissolution may occur due to ground water acidification, oxidation/reduction of precipitate components, dilution, or complexation of the precipitate component(s) with dissolved species that form more stable compounds. Thus, it must be recognized that attenuation processes involving inorganic contaminants are reversible (e.g., Casiot et al., 2005; Gault et al., 2005; Moncur et al., 2005). Metals taken up at the mineral-water interface can be released back into solution. Geochemical modeling of mineral stability and contaminant adsorption/desorption behavior can provide insight into contaminant remobilization potential due to future changes in geochemical conditions. However, it must be noted that thermodynamic databases are often incomplete and thermodynamic constants for specific compounds may vary from database to database. Thus, results from geochemical models must be carefully reviewed. In addition, the method outlined above ignores rates of mineral dissolution and precipitation. Again data are often lacking on the kinetics of biogeochemical processes responsible for contaminant uptake and remobilization, especially data that can be applied in field systems to predict the long-term behavior of contaminants.

### Role of Biological Processes

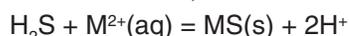
Microbial processes can play a role in both mobilizing and attenuating inorganic contaminants at mining sites. For example, Macur et al. (2001) showed that microbial reduction of arsenate [As(V)] to arsenite [As(III)] occurred over relatively short time scales and resulted in enhanced arsenic mobilization in mine tailings pore water. In addition, iron-

reducing bacteria may cause contaminant dissociation from aquifer solids as a consequence of iron oxide dissolution. Metals and metalloid species associated with secondary iron-bearing precipitates may be released via the activity of bacteria under certain conditions (Herbel and Fendorf, 2006; Langer and Inskeep, 2000).

Sulfate-reducing bacteria (SRB), however, have the ability to reverse the reactions causing acid mine drainage, by attenuating the movement of metals through the precipitation of sulfide minerals (e.g., Gammons et al., 2005), and by raising the pH of the water (Tuttle et al., 1969). This process is recognized in *ex situ* treatment of acid mine drainage as previously noted and also in the natural environment (Church et al., 2007; Kimura et al., 2006; Koschorreck et al., 2003; Labrenz et al., 2000; Paktunc and Davé, 2002). The overall sulfate-reduction process can be described by the reaction:



where  $\text{CH}_2\text{O}$  represents organic matter, either in the solid or aqueous phase. The resulting dissolved hydrogen sulfide can precipitate with divalent metals in AMD, for example (M = Cd, Cu, Fe, Ni, Pb, or Zn):



The mass concentration of reactants involved in sulfate reduction is usually much larger than the mass concentration of metals involved in secondary precipitation reactions, hence these combined reactions can lead to an increase in alkalinity and the pH of the water, while simultaneously attenuating divalent metals. Alkalinity produced during the sulfate reduction process can also drive the precipitation of carbonate minerals, such as calcite and siderite (Paktunc and Davé, 2002), and can help neutralize acidity in the receiving water body.

Most sulfate-reducing bacteria have been considered to be inactive at low pH (Johnson, 2003). More recent studies of acid mine drainage systems (both engineered and natural) have noted that there is some potential for low-pH sulfidogenesis. For example, in laboratory studies, sulfate reduction has been shown to occur in solutions as low as pH 3 in bioreactors using ethanol, methanol, or glycerol (alone or in various combinations) as an organic substrate (Kolmert and Johnson, 2001). In addition, in-situ remediation by sulfate reduction has been shown to occur in acidic pit lakes and sediments after the pH was raised to 5–6 by amendment with organic carbon plus lime (Wendt-Potthoff et al., 2002). In natural AMD systems the reduction of sulfate to sulfide has been reported at pH values as low as 2–3 (Koschorreck et al., 2003), but there are few reports of the isolation and/or characterization of acidophilic SRB from these environments. In a recent study, sediments recovered from the flooded mine workings of the Penn Mine, a Cu-Zn mine abandoned since the early 1960s, were cultured for anaerobic bacteria over a range of pH from 4.0 to 7.5 (Church et al., 2007). Phospholipid fatty acid (PLFA) analyses of Penn Mine sediment showed a high biomass level with a moderately diverse microbial community structure composed primarily of iron- and sulfate-reducing bacteria. Cultures of sediment from the mine produced dissolved sulfide at pH

values near 7 and near 4, forming precipitates of either iron sulfide or elemental sulfur. Phylogenetic sequences of Penn Mine sediment and laboratory cultures were closely aligned to the sulfate-reducing organisms *Desulfosporosinus* and *Desulfitobacterium* (Church et al., 2007). At this site, sulfate-reducing bacteria play a role in attenuating metals at moderately low pH. Precipitates of zinc sulfide were identified in the reducing mine sediments. In the absence of the bacterial activity, zinc and other metals could be transported into nearby surface waters.

Characterization of microbiological impacts on natural attenuation processes involves additional tools that can be used during site characterization efforts. Largely within the last decade, genetic analyses have been used to identify microbial communities in environmental samples. Many of these molecular biological methods rely on 16S rDNA sequences, such as denaturing gradient gel electrophoresis (DGGE). DGGE can be used for simultaneous analysis of multiple samples obtained at various time intervals to detect microbial community changes, which is an advantageous feature in studying microbial ecology and MNA (U.S. Environmental Protection Agency, 2007). Examples of the use of molecular techniques in relation to examinations of microbiological influences of contaminant behavior at mine sites are presented in Macur et al. (2001), Druschel et al. (2004), and Church et al. (2007).

### Monitoring Parameters

In order to evaluate whether or not natural attenuation processes can play a role in achieving site remediation goals, detailed site investigations are required. Generally, the necessary investment in site characterization for evaluating the applicability of natural attenuation is at least or is more expensive and time consuming than for other site remediation technologies. On the other hand, where MNA is applicable, long-term monitoring costs may be less than for other more active remedial technologies.

The evaluation of natural attenuation in a ground water system involves studies to determine the location, concentration, and movement of contaminants in the subsurface. Thus natural attenuation assessments typically focus on developing site hydrologic and conceptual models that can be simulated with a computer geochemical model (see U.S. Environmental Protection Agency, 2007). Evaluation of natural attenuation usually involves not only the determination of processes of attenuation that are currently occurring, but also projects the sustainability of these processes into the future. Table 2 lists attenuation reactions of selected contaminants and appropriate parameters that could be examined during site investigations. Table 3 lists examples of solid-phase analyses that would likely support MNA assessments. The use of MNA as part of a site remedial plan will necessarily require that a long-term monitoring plan be established. Such plans will be developed to enable decisions regarding whether or not site remedial objectives are being met, and to verify that site conditions are not changing in such a way as to impact the major natural attenuation processes for contaminants of concern. Long-term monitoring plans should be developed with well defined triggers that would initiate

**Table 2.** Attenuation Reactions and Capacity Parameters for Selected Contaminants

Contaminant	Possible Attenuation Reactions	Relevant parameters
As	Sorption in aerobic environments Sorption/Precipitation in anaerobic environments	<ul style="list-style-type: none"> <li>Abundance/stability of hosts; typically Fe and Al (hydr)oxides</li> <li>Solid-phase sulfide accumulation; redox buffer capacity, sulfate reducing activity</li> </ul>
Cd	Sorption in aerobic environments Sorption/Coprecipitation carbonates Sorption/Precipitation in anaerobic environments	<ul style="list-style-type: none"> <li>Abundance/stability of hosts; typically Fe and Al (hydr)oxides</li> <li>Abundance/stability of hosts; may require consideration of pH buffer capacity</li> <li>Solid-phase sulfide accumulation; redox buffer capacity, sulfate reducing activity</li> </ul>
Cu	Sorption in aerobic environments Sorption/Coprecipitation carbonates Sorption/Precipitation in anaerobic environments	<ul style="list-style-type: none"> <li>Abundance/stability of hosts; typically Fe and Al (hydr)oxides</li> <li>Abundance/stability of hosts; may require consideration of pH buffer capacity</li> <li>Solid-phase sulfide accumulation; redox buffer capacity, sulfate reducing activity</li> </ul>
Pb	Sorption/Coprecipitation in aerobic environments Precipitation as hydroxycarbonate or sulfate Sorption/Precipitation in anaerobic environments	<ul style="list-style-type: none"> <li>Abundance/stability of hosts; typically Fe and Al (hydr)oxides</li> <li>Aquifer pH buffer capacity</li> <li>Solid-phase sulfide accumulation; redox buffer capacity, sulfate reducing activity</li> </ul>
U	Reductive Precipitation Sorption	<ul style="list-style-type: none"> <li>Abundance/reactivity of electron donors</li> <li>Abundance of hosts; typically metal (hydr)oxides</li> </ul>
Ni	Sorption in aerobic environments Sorption Sorption/Precipitation in anaerobic environments	<ul style="list-style-type: none"> <li>Abundance/stability of hosts; typically Fe and Al (hydr)oxides</li> <li>Abundance of hosts (clays)</li> <li>Solid-phase sulfide accumulation; redox buffer capacity, sulfate reducing activity</li> </ul>

**Note:** Measurement objectives and methodologies to support MNA investigations are documented in U.S. Environmental Protection Agency (2007). MNA assessments focus on both the aqueous phase and the solid phase in order to identify attenuation pathways.

the implementation of contingency remedial technologies if natural attenuation processes fail to fulfill expectations.

### Conclusions

At most mining sites that require cleanup of contaminated ground water, MNA is not expected to be a sole remedy. The magnitude of the acid drainage problem is clear evidence that in most cases natural processes are incapable of ameliorating the acidity and metal contamination produced by oxidizing sulfide minerals. Nevertheless, at nearly all mining sites, natural processes are contributing to varying degrees and in some cases may contribute significantly to site remedial goals. Biogeochemical processes can be particularly important for natural attenuation of some metal and metalloid contaminants, under specific environmental conditions.

Cleanup of mining sites, in particular Megasites, is currently being viewed as a long-term process. This is partly due to the enormous size, the complexity of contaminants and sources, and the large volumes of materials encountered at many mining sites. It is also recognized that the long-term outcomes of site cleanup programs are extremely difficult to predict (Gustavson et al., 2007). Effective management of these sites over long periods of time requires complex organization of site characterization, technology selection and utilization, and long-term monitoring. Given that cleanup expectations at many mining sites are long-term, it may be appropriate to include an examination of natural attenuation processes and the role that such processes play in removing, repartitioning, or otherwise affecting the fate of contaminants in the environment.

**Table 3.** Examples of Solid-phase Analyses to Support MNA Assessments

Method	Data Objectives
Powder x-ray diffraction	Identification of mineral forms
Microbeam analysis	Analysis of micro-scale distribution and association of contaminants
Wet chemical extractions	Evaluation of contaminant associations in the solid-phase
Bulk elemental analysis	Evaluation of total concentrations of contaminants and other major and minor elements
Batch sorption/column testing	Evaluation of contaminant uptake capacity
Oxidation/reduction capacity	Evaluation of redox conditions/buffering capacity
Biological assays of 16S rDNA sequences	Molecular characterization of microbial populations
Most Probable Number (MPN) counts	Bacterial enumeration

### Notice

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### Quality Assurance Statement

All research projects making conclusions or recommendations based on environmentally-related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance (QA) program. This project did not involve the collection or use of environmental data and, as such, did not require a Quality Assurance Project Plan.

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