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Contaminant Attenuation Processes at Mine Sites

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Abstract The global imprint of acid drainage problems at mine sites is a clear reminder that generally, natural processes do not adequately ameliorate the acidity and metal contamination produced by oxidizing sulfide minerals. Yet at nearly all such sites, natural attenuation processes occur and may contribute to site remediation. Biogeochemical processes can be particularly important in controlling the transport and fate of certain metal and metalloid contaminants, under specific environmental conditions. This paper identifies the major natural attenuation processes that have been documented at mine sites around the world and discusses how monitored natural attenuation is sometimes used in combination with active treatment technologies to achieve site-specific remediation objectives.

Keywords Ground water · Metals · Natural attenuation · Remediation

Introduction

The term “monitored natural attenuation” (MNA) refers to the long-term examination of natural processes with the objective that such processes will reach site-specific remedial targets. MNA is best applied in conjunction with other cleanup approaches, such as source removal, source control, or plume control (e.g. Rügner et al. 2006). To be considered an acceptable treatment option, MNA is expected to achieve site remedial objectives within a time frame that is reasonable compared to that possible by using other more active remediation methods. 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, for example, in ground water. Attenuation processes important at mine sites include pH buffering and acid neutralization, adsorption at the mineral-water interface, and mineral precipitation.

The US Environmental Protection Agency (EPA) Office of Research and Development has recently prepared technical resource documents for the application of MNA to inorganic contaminants in ground water (US Environmental Protection Agency 2007a, b). The documents present a four-tiered assessment of MNA as a viable remediation option for selected metal, metalloid, and radionuclide contaminants in ground water. Components of the tiered approach include: (1) demonstrating contaminant sequestration mechanisms, (2) estimating attenuation rates, (3) estimating the attenuation capacity of aquifer solids, and (4) evaluating potential reversibility issues. The technical framework outlines a tiered decision-making approach for determining whether MNA is likely to be an effective remedial approach at a particular location for inorganic contaminants in ground water. Emphasis is placed on developing a 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.

Acid mine drainage (AMD) is a major source of water contamination in metal- and coal-mining districts worldwide. The causes of AMD are well known. AMD may form

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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. Environmental impacts include the destruction of aquatic life and habitats and contamination of drinking water resources. 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 are generally 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).

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. Estimates of the number of sites in the US affected by AMD vary widely from 200,000 to over 550,000 (US Environmental Protection Agency 2004). Costs to clean up contamination at AMD sites are equally difficult to estimate. One hundred and fifty six hardrock mine sites were on or had the potential to be on the national priorities list (NPL) for clean up under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), with potential clean up costs of up to $24 billion dollars (US 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; Stollenwerk 1994; Zhu et al. 2001). Neutralizing capacity of sulfide ore tailings is predominantly from carbonate minerals (calcite, dolomite, siderite) 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; Nordstrom and Ball 1984). In addition, as pH increases, dissolved metals may adsorb onto the 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.

Natural attenuation refers to the observed reduction of contaminant concentrations and/or contaminant mass flow rates as contaminants are transported down-gradient from their source. MNA is not expected to be relied on as a sole remedy at mine sites that require cleanup of contaminated ground water. The global magnitude of the acid drainage problem is clear evidence that natural processes are incapable of adequately ameliorating the acidity and metal contamination produced by oxidizing sulfide minerals. However, MNA may be an effective strategy to augment more active approaches of remediation. In addition, natural attenuation processes often tend to spread contaminants out in space away from source zones via various mineral-water reactions (Malmström et al. 2008). Therefore, it is important to recognize natural attenuation processes from the perspective of tracking contaminant transport and fate in the environment.

MNA Processes at Mine Sites

Assessments of MNA at mine sites must evaluate the chemical, physical, and/or biological processes that occur to mitigate migration of contaminants, the capacity of the MNA process in comparison to the mass of contaminants in the source, and whether the attenuation processes are sustainable over long periods of time. As noted previously, a favorable demonstration of these factors is frequently challenging at mine sites. Although research findings clearly show that attenuation of contaminants does indeed occur at mine sites, 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 mine 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 (Gandy et al. 2007).

Acid Neutralization

A primary control on the process of metal attenuation at mine 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, the 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. US 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 and surface water dilutes dissolved contaminants and can increase pH. In surface waters, dilution and neutralization can occur over spans of meters to many kilometers (e.g. Da Silva et al. 2006). 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). Furthermore, warmer temperatures appear to favor attenuation processes (Parker et al. 2007). 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; España et al. 2005a; Gunsinger et al. 2006; Jurjovec et al. 2002; Morin et al. 1988; Walter et al. 1994). 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; Dousova et al. 2005; España et al. 2005a; b; Fukushi et al. 2003; Gault et al. 2005; Hewlett et al. 2005; Jamieson et al. 1999; Jonsson et al. 2006; Lee et al. 2002; 2005; Levy et al. 1997; McCarty et al. 1998; McGregor et al. 1998; Moncur et al. 2005; Munk et al. 2002; Parker et al. 2007; 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.

Secondary precipitates can remove contaminants from impacted waters through adsorption and/or co-precipitation 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 (España et al. 2006).

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. $Fe_8O_8(OH)_6(SO_4)(s)$], sulfates [e.g., $PbSO_4(s)$], and sulfides [e.g., ZnS(s)]. For each of these minerals, there will be a limited compositional range of water chemistry over which precipitation could occur and formation of these precipitates may compete with other removal processes such as adsorption (Table 1). In some environments, comparatively unusual phases may form and control the aqueous concentrations of contaminants, such as lead and arsenic in beudantite $[PbFe_3(AsO_4)(SO_4)(OH)_6]$ (e.g. Romero et al. 2007). Mineral transformation may also be important over long time frames. For example, aged schwertmannite can transform to goethite, but the transformation pathway does not result in the release of co-precipitated arsenic (Courtin-Nomade et al. 2005).

Secondary precipitates are characterized using a variety of analytical tools. Mineralogical identification is typically accomplished using powder x-ray diffraction techniques (XRD). The characterization of particle morphology and semi-quantitative composition are accomplished using microbeam techniques such as scanning electron microscopy (SEM) coupled with x-ray energy-dispersive spectrometry (EDX). Analysis of element partitioning to well-crystalline and poorly-crystalline components of the solid phase is typically carried out using selective chemical extraction procedures. Advanced spectroscopic methods such as X-ray absorption spectroscopy can be used to identify contaminant oxidation states and bonding environments in the solid phase. Used in combination, these methods allow for the identification of attenuation mechanisms involving secondary minerals. Knowledge about the types of mineral phases present is an important aspect of developing conceptual site models that predict the long-term stability of attenuated metals.

As previously indicated, the stability of a precipitate will be dictated by water chemistry. Geochemical modeling of the aqueous phase can be helpful in understanding observed

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
Hydroxides				
Goethite	FeOOH	2–4	Sorption/coprecipitation of Pb ($\leq$21 wt%), As ($\leq$7.7 wt%), Zn ($\leq$4.6 wt%), and Cu ($\leq$2.5 wt%)	Lee et al. (2005)
HFO, hydrous ferric oxide	$\approx Fe_5HO_8 \cdot 4H_2O$	>5	Sorption/coprecipitation of As-rich ferrihydrite; As/Fe = 0.02–0.1, with 10–30% As(III)	Casiot et al. (2005)
Gibbsite	$Al(OH)_3$	>5–6	Sorption in the general order of Pb > Cu > Zn > Ni with increasing pH	Munk et al. (2002)
Hydroxysulfates				
Alunite	$KAl_3(OH)_6(SO_4)_2$	4–6	Precipitation of Al	Accornero et al. (2005)
Jarosite	$KFe_3(OH)_6(SO_4)_2$	2–5	Coprecipitation with As(V), replacing sulfate in the jarosite structure	Gault et al. (2005)
Schwertmannite	$Fe_8O_8(OH)_6(SO_4)$	2–4	Coprecipitation of Cu, Ni, and Zn	Sidenko and Sherriff (2005)
Tooelite	$Fe_6(AsO_3)_4(SO_4)(OH)_4 \cdot 4H_2O$	2.5–4	Precipitation of As(V)	Morin et al. (2003)
Sulfates				
Gypsum	$CaSO_4 \cdot 2H_2O$	>3	“Hardpan” precipitate	Moncur et al. (2005)
Anglesite	$PbSO_4$	>3–4	Precipitation at pH $\approx$ 3; nanoparticles	Zänker et al. (2002)
Melanterite	$FeSO_4 \cdot 7H_2O$	<2	Coprecipitation with Zn and Cu; temporary removal in highly soluble phase	Jamieson et al. (1999)

mineral assemblages and for evaluating mineral stability. 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 possible future changes in geochemical conditions. However, 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, equilibrium modeling ignores rates of mineral dissolution and precipitation. Again appropriate 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 mine 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, producing alkalinity, attenuating the movement of metals by the precipitation of sulfide minerals (e.g. Gammons and Frandsen 2001; Gammons et al. 2005), and raising the pH of the water (Tuttle et al. 1969). These processes are exploited in ex situ treatment of acid mine drainage and they are recognized in the natural environment (Church et al. 2007; Kimura et al. 2006; Koschorreck 2008;

Koschorreck et al. 2003; Labrenz et al. 2000; Paktunc and Davé 2002). The overall sulfate-reduction process can be described by the reaction:

$$2CH_2O + SO_4^{2-} + 2H^+ = H_2S + CO_2 + H_2O \quad (1)$$

where CH_2O represents organic matter, either in the solid or aqueous phase. The resulting dissolved hydrogen sulfide can precipitate with divalent metals in AMD, as shown in equation 2 (M = Cd, Cu, Fe, Ni, Pb, or Zn):

$$H_2S + M^{2+}(aq) = MS(s) + 2H^+ \quad (2)$$

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), thus helping to neutralize acidity in receiving water bodies.

Sulfate-reducing bacteria have been considered to be inactive at low pH (Johnson 2003). But studies of acid mine drainage systems have noted that there is some promise for low-pH sulfidogenesis (Koschorreck 2008). Laboratory studies have shown sulfate reduction in solutions as low as pH 3 in bioreactors using ethanol, methanol, or glycerol as organic substrates (Kolmert and Johnson 2001). Also, in situ remediation by sulfate reduction was demonstrated 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 on the characterization of acidophillic 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 iron sulfide and elemental sulfur. Phylogenetic sequences of Penn Mine sediment and laboratory cultures were closely aligned to the sulfate-reducing organisms *Desulfosporosinus* and *Desulfitobacterium*. 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, this zinc (and other metals) would 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. Examples of the use of molecular techniques in relation to examinations of microbiological influences of contaminant behavior at mine sites are presented in Church et al. (2007), Druschel et al. (2004), and Macur et al. (2001).

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 investments in site characterization for evaluating the applicability of natural attenuation is at least as, or even 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 approaches.

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

Table 2 Attenuation reactions and capacity parameters for selected contaminants

Contaminant	Possible attenuation reactions	Relevant parameters
As	Sorption in aerobic environments	• Abundance/stability of hosts, typically Fe and Al (hydr)oxides
	Sorption/precipitation in anaerobic environments	• Solid-phase sulfide accumulation, redox buffer capacity, sulfate reducing activity
Cd	Sorption in aerobic environments	• Abundance/stability of hosts; typically Fe and Al (hydr)oxides
	Sorption/co-precipitation carbonates	• Abundance/stability of hosts; may require consideration of pH buffer capacity
	Sorption/precipitation in anaerobic environments	• Solid-phase sulfide accumulation, redox buffer capacity, sulfate reducing activity
Pb	Sorption/co-precipitation in aerobic environments	• Abundance/stability of hosts, typically Fe and Al (hydr)oxides
	Precipitation as hydroxycarbonate or sulfate	• Aquifer pH buffer capacity, sulfate concentration
	Sorption/precipitation in anaerobic environments	• Solid-phase sulfide accumulation, redox buffer capacity, sulfate reducing activity
U	Reductive precipitation	• Abundance/reactivity of electron donors
	Sorption	• Abundance of hosts; typically metal (hydr)oxides

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
X-ray absorption spectroscopy	Identification of contaminant bonding environments; oxidation state
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

Concluding Remarks

Clean up of mine sites, and in particular, mega-sites, 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 mine sites. In addition, 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 site characterization, technology selection and utilization, and long-term monitoring. Given that cleanup expectations at many mine 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.

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