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Reviews in Engineering Geology 2007;17;25-45
doi: 10.1130/2007.4017(03)

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Reviews in Engineering Geology, Volume XVII
2007

Strategies to predict metal mobility in surficial mining environments

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ABSTRACT

This report presents some strategies to predict metal mobility at mining sites. These strategies are based on chemical, physical, and geochemical information about metals and their interactions with the environment. An overview of conceptual models, metal sources, and relative mobility of metals under different geochemical conditions is presented, followed by a discussion of some important physical and chemical properties of metals that affect their mobility, bioavailability, and toxicity. The physical and chemical properties lead into a discussion of the importance of the chemical speciation of metals. Finally, environmental and geochemical processes and geochemical barriers that affect metal speciation are discussed. Some additional concepts and applications are briefly presented at the end of this report.

Keywords: metals, transport, speciation, prediction, bioavailability

INTRODUCTION

The purpose of this report is to present some strategies to predict metal mobility at mining sites. Some metals found in mining-influenced waters include Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Tl, V, and Zn. Metals are different from regulated organic substances because they cannot be destroyed by biological or chemical processes. Instead, metals can only be reduced by physical removal (e.g., leaching, biological uptake). Hence, once released, metals persist in the environment. However, factors such as metal speciation can influence metal distribution and bioavailability within the environment. Consequently, the forms, transformations, and geochemical environment of metals need to be considered when evaluating potential effects of metals on the environment. In addition to the forms and concentrations of metals themselves, many synergisms or antagonisms involve interaction of other chemical elements and environmental factors with the metals. Once these other elements and factors are recognized and addressed, a more accurate assessment of metal mobility can be made. This report discusses some of the chemical and physical factors of metals and the geochemical processes that can influence metal mobility, distribution, and bioavailability in surficial mining environments. Understanding the ways that these factors and processes can influence metals can aid in forecasting the potential ecological effects of metals. Figure 1 illustrates some geochemical processes and conditions that can redistribute dissolved metals in the environment.

Spatial and Temporal Scales

In this report, chemical and physical properties and processes are discussed for a variety of scales, both spatial and temporal. Success in forecasting metal behavior in surficial environments depends on using an appropriate spatial scale (Fig. 2A), which can range from atomic scale to regional scale or larger. At a regional scale, generalizations often can be used to understand broad trends in metal mobility (e.g., Wanty et al., 2001). As the scale becomes increasingly finer, however, estimating metal behavior at an appropriate scale becomes increasingly difficult (e.g., Smith et al., 2000).

Figure 2B illustrates the rates of several types of reactions. The rates of geochemical and biological reactions can affect

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Smith, K.S., 2007, Strategies to predict metal mobility in surficial mining environments, *in* DeGraff, J.V., ed., Understanding and Responding to Hazardous Substances at Mine Sites in the Western United States: Geological Society of America Reviews in Engineering Geology, v. XVII, p. 25–45, doi: 10.1130/2007.4017(03). For permission to copy, contact editing@geosociety.org. All rights reserved.

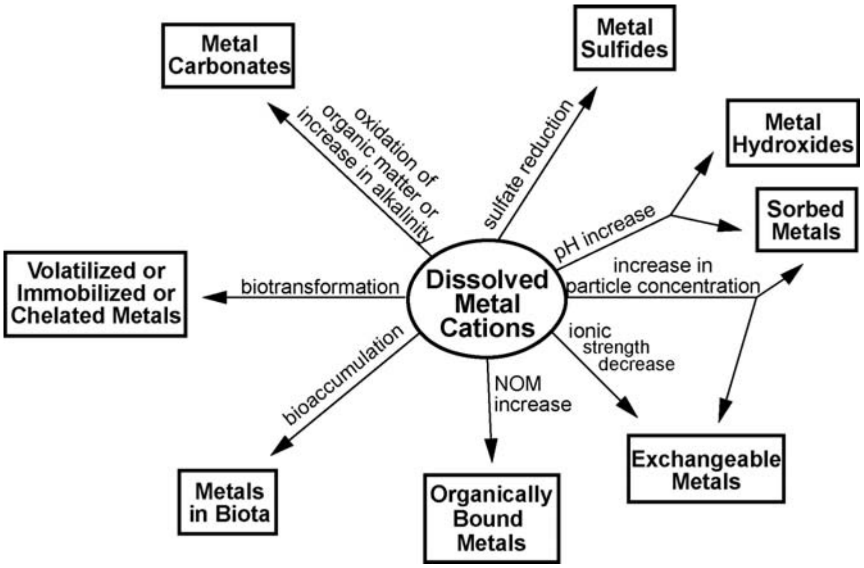

Figure 1. Diagram of some processes and geochemical conditions that can redistribute cationic dissolved metals in oxidizing, circumneutral-pH systems. Metals in each of the reservoirs (boxes) also can be redistributed by geochemical or biological processes or by changing geochemical conditions. NOM refers to natural organic matter (reprinted from Smith and Huyck, 1999, with permission).

metal mobility, and many reactions involving metals are kinetically controlled or biologically mediated. This rate dependence makes reactions extremely difficult to model (e.g., Langmuir and Mahoney, 1984). Some of the chemical reactions take place quickly (e.g., solute-water reactions), and other reactions take place more slowly (e.g., mineral recrystallization). In mining-influenced waters where many initial precipitates are amorphous or metastable, it is not likely that the residence time of the precipitates is long enough for the system to have reached equilibrium. Therefore, when modeling these systems, it is important to consider the solid phases that are actually present in the system instead of relying upon thermodynamically stable phases (Nordstrom and Alpers, 1999). Ritchie (1994) discusses some of the rates of processes in mine-waste systems.

Terminology and Scope

The term *mining-influenced waters* (MIW), introduced by Schmiermund and Drozd (1997), will be used in this report. MIW are affected by the weathering of rocks and minerals exposed by mining activities and may exhibit one or more of the characteristics of low pH, high sulfate, high Fe and Al, high noniron metals, and high turbidity (Schmiermund and Drozd, 1997). This report focuses on the behavior of metals, metalloids, and their inorganic compounds in areas that have been subjected to mining activities. The term *metal* is used in a general sense to mean a chemical element that, in aqueous solution, displays cationic behavior or that has an oxide that is soluble in acids (Parish, 1977). By this definition, elements that are nonmetals include H, the rare gases, B, C, Si, N, P, As, O, S, Se, Te, Po, F, Cl, Br, I, and At. A *metalloid* is an element with properties intermediate between those of metals and nonmetals. Metalloids include As, B, Ge, Po, Sb, Si, and Te. A *cation* is a positively charged ion; an *anion* is a negatively charged ion; and an *oxyanion* is an element that combines with oxygen to form an anionic species in aquatic systems (e.g., SO_4^{2-}, MoO_4^{2-}). A *ligand* is an anion or neutral molecule that can combine with a cation to form a complex. Common ligands in aquatic systems include hydroxyl (OH^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), sulfide (S^{2-}), hydrogen sulfide ion (HS^-), carboxyl (COOH), and dissolved organic carbon (DOC).

Many metals can be both essential and toxic, and their effects on organisms depend on concentration, speciation, and bioavailability. Some metals essential to plants or animals include Co, Cr, Cu, Fe, Mn, Mo, Ni, and Zn. Essential metals can exert toxic effects by being either too high in concentration or too low in concentration (deficient). Metals that are nonessential to biological functioning (e.g., Cd, Hg, and Pb) can be toxic at relatively low concentrations.

STRATEGIES TO PREDICT METAL MOBILITY AT MINING SITES

This section presents overall strategies to predict metal mobility at mining sites. The first topic is developing a conceptual model of a mining site, and the second topic is ways to estimate metal mobility. Guidelines to determine generalized relative mobility of metals under different environmental conditions are presented. Detailed information used to develop these guidelines is discussed in later sections of this report.

Conceptual Models

It is important to have an accurate conceptual model when assessing the potential effects of metals at a mining site. Metal speciation and transformations in the environment can be very

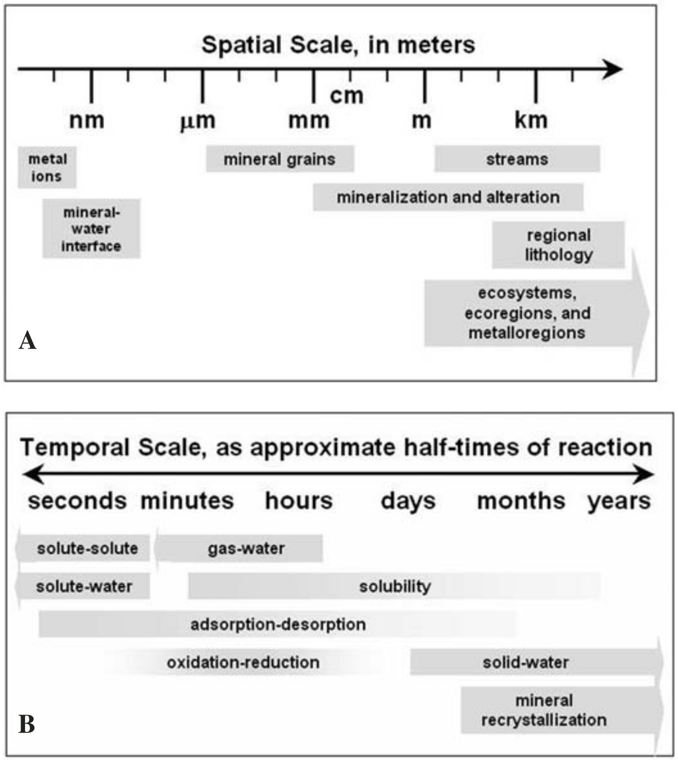

Figure 2. (A) Examples of differences in spatial scales of some factors that are influenced by geochemical processes. Note the wide spatial range of these factors. (B) Examples of differences in rates of some types of reactions that influence environmental geochemical conditions.

complicated, and a conceptual model will help focus on the most important factors to consider. Such a model should include relationships between the source, transport, and fate of the metals and should incorporate the mineralogical, hydrological, geological, and geochemical conditions at the site that might affect these factors. Conditions generally are site specific and are tied to receptor organisms of concern. Lefebvre et al. (2001) present an example of a conceptual model for mine-waste-rock piles. In the subsections that follow, some tools that aid in developing a conceptual model are briefly discussed.

Metal Source Characterization

When investigating metal mobility and bioavailability at a mining site, it is crucial to first consider and characterize the possible sources of metals in the environment. This is an important first step in developing a conceptual model. Numerous manuals and articles describe how to sample and characterize various potential metal sources (e.g., Al-Abed et al., 2006; Chao, 1984; Church et al., 2007; Cravotta and Kirby, 2004; Crock et al., 1999; Davis et al., 1993; Diehl et al., 2006; Ficklin and Mosier, 1999; Hageman, 2005; Hammarstrom and Smith, 2002; Jambor and Blowes, 1994; Jambor et al., 2003; Jenne and Luoma, 1977; Jordan and D'Alessandro, 2004; Macalady and Ranville, 1998; McLemore et al., 2007; MEND Manual, 2001; Mills and Robertson, 2006; Nimick et al., 2005; Plumlee and Ziegler, 2003; Plumlee et al., 2006; Price, 1997, 2005; Ranville et al., 2006; Sauvé, 2002; Smith et al., 2002, 2003; Tessier et al., 1979; U.S. EPA, 2001, 2004; U.S. Geological Survey; Wildeman et al., 2007). Maest et al. (2005a, b) provide a useful geochemical characterization toolbox that lists methods, references, and advantages and disadvantages of tools applicable to mining sites.

Geoenvironmental Models of Mineral Deposits

When developing a conceptual model of a mining site, it is important to consider geological aspects that resulted in the mineral deposit. Plumlee (1999), Plumlee et al. (1999), and Seal and Hammarstrom (2003) discuss how mineral deposits are classified according to similarities in their geologic characteristics and geologic setting and how this classification system may be extended to incorporate potential environmental effects of mineral deposits. This extended classification is termed *geoenvironmental models of mineral deposits* (du Bray, 1995). Geoenvironmental models can distinguish characteristics of various mineral deposits that may affect the geochemistry of aquatic systems. Geoenvironmental models provide information about natural geochemical variations associated with a particular type of mineral deposit and geochemical variations associated with its effluents, wastes, and mineral-processing facilities (Seal and Foley, 2002). Based on geoenvironmental models, potential metal sources and their likely concentration ranges can be determined for a given deposit type to provide an estimation of metal sources at a mining site.

Geoavailability

Once the important metal sources are identified, then considerations need to be turned to factors that will influence the mobility and bioavailability of metals at the site and away from the site. These factors are discussed in detail in later sections of this report.

The release of metals from solid phases is related to *geoavailability.* Geoavailability is that portion of a chemical element's or a compound's total content in an earth material that can be liberated to the surficial or near-surface environment (or biosphere) through mechanical, chemical, or biological processes. The geoavailability of a chemical element or a compound is related to the susceptibility and availability of its resident mineral phase(s) to these mechanical, chemical, or biological processes (Smith and Huyck, 1999; Smith, 1999a).

Figure 3 illustrates pathways and relationships between total metal content in an earth material and potential toxicity to an organism. Total metal is the abundance of a given metal in an earth material, and geoavailability is a function of the total metal content, access to weathering, and susceptibility to weathering. The definition for *bioavailability,* which is based upon Newman and Jagoe (1994), is the degree to which a contaminant in a potential source is free for uptake (movement into or onto an

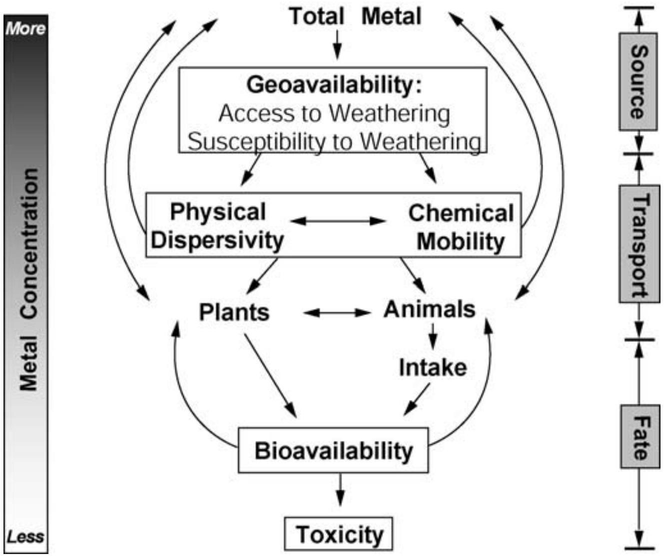

Figure 3. Diagram showing pathways and relationships between total metal in an earth material and toxicity. Geoavailability is that portion of a chemical element's or a compound's total content in an earth material that can be liberated to the surficial or near-surface environment (or biosphere) through mechanical, chemical, or biological processes. The gray scale on the left depicts that as a metal moves from one stage to another, generally less than 100% is transferred (modified from Smith and Huyck, 1999).

organism). In Figure 3, a distinction is made between plants and animals because bioavailability is generally a prerequisite for uptake in plants, whereas animals may intake (ingest, inhale, etc.) toxicants that subsequently pass through their bodies without any systemic uptake.

Each stage from total metal content in an earth material through toxicity in the surficial environment in Figure 3 is a reservoir with a distinct half-life. As a metal moves from one stage to another, generally less than 100% is transferred. Therefore, not all of the total metal content in an earth material is usually geoavailable, bioavailable, or toxic, and the gray scale in Figure 3 portrays this concept. Total metal content and geoavailability constitute the source factors; dispersivity and mobility comprise the transport factors; and uptake/intake, bioavailability, and toxicity represent the fate factors. Bioaccumulation links the fate and transport segments of the diagram.

Box Models

Box models can be a useful way to present a conceptual model of a mining site. Figure 4 shows an example of a simple box model developed to describe dissolved zinc concentrations in Lake Coeur d'Alene, Idaho (Balistrieri et al., 2002). Box models consist of reservoirs with inputs and outputs. Mass transfer between boxes is a function of residence time in the reservoir within each box. Box models use a mass-balance approach to represent processes that influence the element of interest. It is likely that not all of the processes considered in a box model are significant, but the action of creating and testing a box model helps develop an understanding of the important processes at the site.

Estimating Metal Mobility

Mobility refers to the capacity of an element to move within fluids after dissolution. It is difficult to predict element mobility quantitatively in surficial environments. Rather, mobility should be considered in a relative sense by empirically comparing the behavior of elements under changing environmental conditions, such as at geochemical barriers (which are discussed in a later section of this report). Table 1 lists the generalized relative mobility of elements expected under a variety of geochemical conditions. Factors controlling mobility include pH, solubility reactions, sorption reactions, and redox conditions (these factors are discussed in more detail in later sections of this report). Table 1 takes into account the tendency of the elements to sorb onto hydrous oxides or to precipitate (these processes are discussed in more detail in later sections of this report). Criteria for mobility distinctions are scaled by element abundance rather than being based on absolute solubility; no quantitative information can be inferred from Table 1. By comparing the different rows of Table 1, it is possible to make qualitative statements about the behavior of a given element under changing geochemical conditions. Data for Table 1 are derived from the author's personal experience with mine-drainage systems as well as from Vlasov (1966), Fuller (1977), Parish (1977), Perel'man (1977, 1986), Callahan et al. (1979), Lindsay (1979), Rose et al. (1979), Levinson (1980), Greenwood and Earnshaw (1984), Luka-

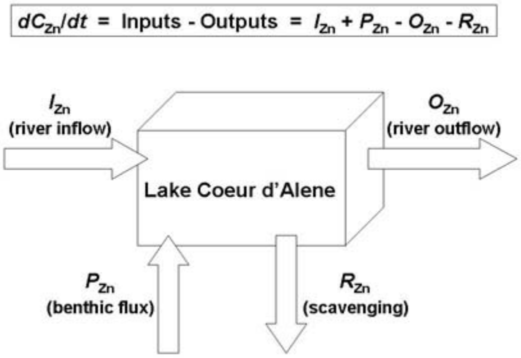

Figure 4. Simple box model to describe dissolved Zn concentrations in Lake Coeur d'Alene, Idaho. The lake is treated as a completely mixed system; dC_{Zn}/dt represents changes in dissolved Zn concentrations in the lake as a function of time; I_{Zn} represents the external inputs of dissolved Zn to the lake; P_{Zn} represents the internal sources of dissolved Zn to the lake water; O_{Zn} represents fluxes of dissolved Zn out of the lake; and R_{Zn} represents internal removal of dissolved Zn from the lake water (all as mg/L per day; modified from Balistrieri et al., 2002).

TABLE 1. GENERALIZED RELATIVE MOBILITY OF CHEMICAL ELEMENTS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

Environmental Conditions	Very Mobile	Mobile	Somewhat Mobile	Scarcely Mobile to Immobile
Oxidizing with pH < 3	Br, Cd, Cl, Co, Cu, F, I, Ni, Rn, S, Zn	Al, As, Ca, Fe, Hg, K, Mg, Mn, Na, P, Ra, REE, Se, Si, Sr, U, V	Ag, Ba, Be, Bi, Cr, Cs, Ga, Ge, Li, Mo, Pb, Rb, Sb, Th, Ti, Tl, W	Sc, Sn, Y, Zr
Oxidizing with pH > 5 to circumneutral, no iron substrates	Br, Cd, Cl, F, I, Rn, S, Zn	Ca, Mg, Mo, Na, Se, Sr, U, V	As, Ba, Bi, Co, Cr, Cs, Cu, Ge, Hg, K, Li, Mn, Ni, P, Ra, Rb, REE, Sb, Si, Tl	Ag, Al, Be, Fe, Ga, Sc, Sn, Th, Ti, W, Y, Zr
Oxidizing with pH > 5 to circumneutral, with abundant iron substrates	Br, Cl, F, I, Rn, S	Ca, Cd, Mg, Na, Sr, Zn	Ba, Bi, Co, Cs, Ge, Hg, K, Li, Mn, Ni, Rb, Sb, Se, Si, Tl	Ag, Al, As, Be, Cr, Cu, Fe, Ga, Mo, P, Pb, Ra, REE, Sc, Sn, Th, Ti, U, V, W, Y, Zr
Reducing with pH > 5 to circumneutral, no hydrogen sulfide	Br, Cl, F, I, Rn	Ca, Cd, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Sr, Zn	As, Ba, Co, Cr, Cs, Hg, K, Li, P, Ra, Rb, Si, Tl	Ag, Al, Be, Bi, Ga, Ge, Mo, REE, Sb, Sc, Se, Sn, Th, Ti, U, V, W, Y, Zr
Reducing with pH > 5 to circumneutral, with hydrogen sulfide	Br, Cl, F, I, Rn	Ca, Mg, Mn, Na, Sr	Ba, Cs, K, Li, P, Ra, Rb, Si, Tl	Ag, Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, Mo, Ni, Pb, REE, S, Sb, Sc, Se, Sn, Th, Ti, U, V, W, Y, Zn, Zr

Note: See text for details; information from Smith and Hyuck, 1999. REE = Rare-Earth Elements (which are treated here as a group, but individually can have somewhat different mobility behaviors).

shev (1984, 1986), Adriano (1986), Cotton and Wilkinson (1988), Hem (1989), and Kabata-Pendias and Pendias (1992).

Table 1 provides a general guide to predict metal behavior in surficial environments. This approach does not substitute for in-depth field studies and topical research; there is no reliable "cookbook" approach. The information in Table 1 may help to determine which elements could be mobile in a given environment and to anticipate the effects of various geochemical barriers. To use this approach in a natural setting, it is necessary to know something about the geochemical conditions. It is also necessary to have a good grasp of underlying chemical and geochemical principles (e.g., Garrels and Christ, 1965; Nordstrom and Munoz, 1994; Stumm and Morgan, 1996). Table 1 should be used only in a relative sense and does not provide any information about absolute concentrations or quantitative data.

CHEMICAL AND PHYSICAL PROPERTIES OF ELEMENTS

In order to understand the reasoning behind Table 1, it is necessary to drill down to the atomic scale to discuss some chemical and physical properties of chemical elements. This is because the behavior of a metal is determined largely by the chemical and physical characteristics of the metal. In order to generalize about the behavior of metals in the environment, it is important to understand the properties of a particular metal in addition to its geochemical environment.

Oxidation State

The oxidation state (also referred to as oxidation number or valence) of an element is important because it can have a significant effect on the mobility and interactions of the element. The oxidation state represents the charge that an atom appears to have when electrons are counted and may be either positive or negative. Oxidation states are used to track electrons in oxidation-reduction (redox) reactions. Table 2 lists the oxidation states of some chemical elements in aquatic systems.

Many elements can occur in more than one oxidation state in natural environments. Redox-sensitive elements include C, S, N, Fe, Mn, As, Cu, Cr, Hg, Mo, Sb, Se, U, V, and W.

Size

The size of an ion primarily depends on its oxidation state. Table 2 lists the oxidation states and effective ionic radii of some elements in aquatic systems. Note that an increase in the oxidation state results in a shrinkage in size. The ionic radius of an element is important in determining if it can take part in particular chemical and biochemical reactions. Also, elements with similar ionic radii and oxidation states can sometimes substitute for one another. For example, Cd^{2+} can substitute for Ca^{2+} in many geochemical and biological systems.

Electronegativity and Bonding

Electronegativity (EN) is the power of an atom in a molecule to attract electrons to itself (Pauling, 1960). Hence, EN is indicative of the types of compounds and the types of chemical bonds that a given element will form. In the periodic table of the elements, EN values increase in the direction of fluorine, which is the most electronegative element and is located in the upper right-hand corner. The Pauling scale is commonly used to quantify EN. In this scale fluorine is assigned a value of 4, and other elements have values ranging down to 0.7, which is the value for cesium, the least electronegative element. EN values for a variety of elements and complex ligands are listed in Table 3. Elements with high EN values (~2 or greater) are mainly nonmetals or potential ligands, whereas elements with low EN values (less than ~2) generally are metal cations.

EN relates to the type and strength of bonding between a metal and a ligand. A *covalent bond* is a type of chemical bond formed when an electron pair is shared between a metal and a ligand. Covalent bonds are relatively strong and tend to occur between elements with similar EN values. An *ionic bond* is a type of chemical bond based on electrostatic forces between two oppositely charged ions. Ionic bonds are commonly formed between metals and nonmetals, because metals tend to have low EN values and nonmetals tend to have high EN values. In reality, most metal-ligand bonds exhibit properties of both covalent and ionic bonding. However, two generalizations can be made:

1. A small difference in metal and ligand EN values leads to a predominantly covalent bond.
2. A large difference in metal and ligand EN values leads to a predominantly ionic bond.

Ionic Potential

Ionic potential (the ratio of oxidation number to ionic radius) of elements has been related to their mobility (Rose et al., 1979). As illustrated in Figure 5, elements with low ionic potential are generally mobile in the aquatic environment as simple cations (e.g., Na^+, Ca^{2+}), and elements with high ionic potential are generally mobile as oxyanions (e.g., sulfur in SO_4^{2-}, molybdenum in MoO_4^{2-}). Elements with high ionic potential tend to form covalent bonds rather than ionic bonds. Elements with intermediate ionic potential have a tendency to strongly sorb or hydrolyze and exhibit low solubility (see discussion in later sections); therefore, these elements are fairly immobile (Rose et al., 1979). The concept of ionic potential is useful in explaining how elements with apparently different chemical properties behave similarly during migration in the environment.

Classification of Chemical Elements

Inorganic-chemistry fundamentals can be useful in understanding metal behavior in the environment. Metals can be classified into groups based on their capacity for binding to different ligands. Several classification systems have developed through the years (e.g., Whitfield and Turner, 1983). One of the most useful classification systems was developed by Pearson (1963, 1968a, 1968b), who introduced hard and soft acid and base (HSAB) concepts to describe metals and ligands. Table 4 lists hard and soft acids and bases and their characteristics. Complexes are formed between metals (acids) and ligands (bases) in aqueous solutions and at interfaces (such as mineral or biological sur-

TABLE 2. OXIDATION STATES, EFFECTIVE IONIC RADII, AND THERMOCHEMICAL RADII OF SOME IONS IN AQUATIC SYSTEMS

Element	Chemical Symbol	Oxidation State	Radius (pm)(1)(2)
Aluminum	Al	+3	67.5
Antimony	Sb	+3	90
		+5	74
Arsenic	As	+3	72
		+5	60
Barium	Ba	+2	149
Beryllium	Be	+2	59
Bismuth	Bi	+3	117
Cadmium	Cd	+2	109
Calcium	Ca	+2	114
Cerium	Ce	+3	115
Cesium	Cs	+1	181
Chromium	Cr	+3	75.5
		+6	58
Cobalt	Co	+2	79
Copper	Cu	+1	91
		+2	87
Iron	Fe	+2	92
		+3	78.5
Lanthanum	La	+3	117.2
Lead	Pb	+2	133
Lithium	Li	+1	90
Lutetium	Lu	+3	100.1
Magnesium	Mg	+2	86
Manganese	Mn	+2	97
Mercury	Hg	+1	133
		+2	116
Molybdenum	Mo	+4	79
		+6	73
Nickel	Ni	+2	83
Phosphorus	P	+5	52
Potassium	K	+1	152
Radium	Ra	+2	162(3)
Selenium	Se	+4	64
		+6	56
Silicon	Si	+4	54
Silver	Ag	+1	129
Sodium	Na	+1	116
Strontium	Sr	+2	132
Thallium	Tl	+1	164
		+3	102.5
Thorium	Th	+4	108
Tin	Sn	+4	83
Titanium	Ti	+4	74.5
Tungsten	W	+6	74
Uranium	U	+4	103
		+6	87
Vanadium	V	+3	78
		+4	72
		+5	68
Zinc	Zn	+2	88

Polyatomic Ion	Radius (pm)(4)(2)
OH^-	119
NO_3^-	165
CO_3^{2-}	164
HCO_3^-	142
HS^-	193
SO_4^{2-}	244
NH_4^+	151

Note: Data from Huheey et al. (1993); pm = picometer (1×10^{-12} m).
(1) Effective ionic radius for six-fold coordination
(2) 100 pm = 1 angstrom (Å) = 0.1 nm
(3) For eight-fold coordination
(4) Thermochemical radius of polyatomic ions.

TABLE 3. PAULING ELECTRONEGATIVITY (EN) VALUES FOR A VARIETY OF CHEMICAL SPECIES IN AQUATIC SYSTEMS

Element	Species	EN
Aluminum	Al^{3+}	1.61
Antimony	Sb^{3+}	**2.05**
Arsenic	As^{3+}	**2.0**
	As^{5+}	**2.2**
Barium	Ba^{2+}	0.89
Beryllium	Be^{2+}	1.57
Bismuth	Bi^{3+}	**2.02**
Bromine	Br^{-}	**2.96**
Cadmium	Cd^{2+}	1.69
Calcium	Ca^{2+}	1.00
Carbon	C^{4+}	**2.55**
Cerium	Ce^{3+}	1.12
Cesium	Cs^{+}	0.79
Chlorine	Cl^{-}	**3.16**
Chromium	Cr^{3+}	1.6
	Cr^{6+}	**2.1**
Cobalt	Co^{2+}	1.88
Copper	Cu^{+}	1.8
	Cu^{2+}	**2.0**
Fluorine	F^{-}	**3.98**
Gold	Au^{+}	**2.54**
	Au^{3+}	**2.9**
Hydrogen	H^{+}	**2.20**
Iron	Fe^{2+}	1.7
	Fe^{3+}	1.8
Lanthanum	La^{3+}	1.10
Lead	Pb^{2+}	1.6
Lithium	Li^{+}	0.98
Lutetium	Lu^{3+}	1.27
Magnesium	Mg^{2+}	1.31
Manganese	Mn^{2+}	1.4
Mercury	Hg^{+}	1.8
	Hg^{2+}	**2.00**
Molybdenum	Mo^{4+}	1.6
	Mo^{6+}	**2.1**
Nickel	Ni^{2+}	1.91
Oxygen	O^{2-}	**3.44**
Potassium	K^{+}	0.82
Radium	Ra^{2+}	(0.83)
Selenium		**2.55**
Silicon	Si^{4+}	1.90
Silver	Ag^{+}	1.93
Sodium	Na^{+}	0.93
Strontium	Sr^{2+}	0.95
Thallium	Tl^{+}	1.5
	Tl^{3+}	**2.04**
Thorium	Th^{4+}	1.1
Tin	Sn^{4+}	1.96
Titanium	Ti^{4+}	1.54
Tungsten	W(II)	**2.36**
Uranium	U^{4+}	1.3
	U^{6+}	1.9
Vanadium	V^{3+}	1.35
	V^{4+}	1.6
	V^{5+}	1.8
Zinc	Zn^{2+}	1.65

Complex Ligand	Coord. Number	EN
OH^{-}	1	**3.1**
	2	**2.75**
	3 and 4	**2.15**
NO_3^{-}		**3.5**
$H_2PO_4^{-}$		**3.15**
HPO_4^{2-}		**2.8**
CO_3^{2-}		**(2.5)**
HCO_3^{-}		**(~4)**
HS^{-}		**(2.33)**
SO_4^{2-}		**3.7**

Note: Data from Huheey et al. (1993); Langmuir (1997); EN = electronegativity (in Pauling Scale units); values in parentheses are estimates; bold values are ≥2 (see text for details).

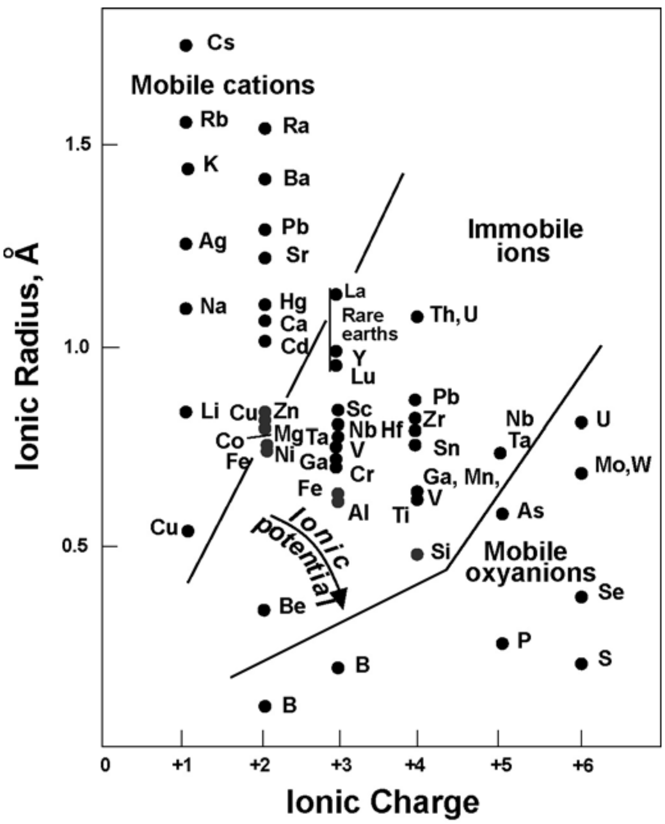

Figure 5. Mobility of elements in the surficial environment as a function of ionic potential (reprinted from Rose et al., 1979, with permission of the author).

faces). Hard-metal cations preferentially form complexes with F (the most electronegative element) and with ligands having O as the electron donor (e.g., COOH and PO_4^{3-}). Water is strongly attracted to these metals, and they do not form sulfides (complexes or precipitates). Hard-metal cations tend to form relatively insoluble precipitates with OH^{-}, CO_3^{2-}, and PO_4^{3-} (Stumm and Morgan, 1996). Soft-metal cations preferentially form complexes with ligands containing I, S, or N. Soft-metal cations form insoluble sulfides and soluble complexes with S^{2-} and HS^{-} (Stumm and Morgan, 1996).

The HSAB classification is a useful concept to help explain the strength of metal complexing and metal toxicity. According to this concept, cations are Lewis acids and act as an electron acceptor, and anions are Lewis bases and act as an electron donor. The term *soft* refers to an electron cloud that is readily deformable so that the electrons are relatively mobile (i.e., polarizable). The term *hard* refers to an electron cloud that is relatively rigid so that the electrons are relatively immobile (i.e., nonpolarizable). Soft species prefer to participate in covalent bonds, and hard species prefer to participate in ionic bonds (Langmuir, 1997). Hard acids tend to bind to hard bases, and soft acids tend to bind to soft bases. The terms *hard* and *soft* are relative, and there are borderline cases between hard and soft for both acids and bases. Generalizations about the speciation, behavior, and mobility of elements in aquatic

TABLE 4. HARD AND SOFT ACIDS AND BASES, AND THEIR CHARACTERISTICS

Hard (Class A)		Soft (Class B)
Often macronutrients Ionic bonding Binding preference is with oxygen Prefers F > O > N = Cl > Br > I > S $OH^- > RO^- > RCO_2^-$ $CO_3^{2-} >> NO_3^-$ $PO_4^{3-} >> SO_4^{2-} >> ClO_4^-$ pH sensitive		Often toxic Covalent bonding (more irreversible) Binding preference is with sulfur and nitrogen Prefers S > I > Br > Cl = N > O > F
Hard Acids	Borderline Acids	Soft Acids
Al^{3+}, As^{3+}, Be^{2+}, Ca^{2+}, Ce^{4+}, Co^{3+}, CO_2, Cr^{3+}, Cr^{6+}, Fe^{3+}, H^+, K^+, La^{3+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Sc^{3+}, Si^{4+}, Sn^{4+}, SO_3, Sr^{2+}, Th^{4+}, Ti^{4+}, U^{4+}, UO_2^{2+}, VO^{2+}, Zr^{4+}	Bi^{3+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Sb^{3+}, Sn^{2+}, SO_2, Zn^{2+}	Ag^+, Au^+, Cd^{2+}, Cu^+, Hg^{2+}, Hg_2^{2+}, Tl^+
Hard Bases	Borderline Bases	Soft Bases
NH_3, RNH_2, N_2H_4 H_2O, OH^-, O^{2-}, ROH, RO^-, R_2O CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^- F^-, (Cl^-)	$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2 NO_2^-, SO_3^{2-} Br^-	H^- R^-, C_2H_4, C_6H_6, CN^-, RNC, CO SCN^-, R_3P, $(RO)_3P$, R_3As R_2S, RSH, RS^-, $S_2O_3^{2-}$ I^-

Note: Information from Huheey et al. (1993); Langmuir (1997); Stumm and Morgan (1996); R = organic molecule.

systems can be made based on this type of HSAB classification system.

Using HSAB to Estimate Bioavailability

Nieboer and Richardson (1980) modified existing metal-classification systems to make them more applicable to biological systems. According to Nieboer and Richardson's classification, Class A (hard) metals, which tend to seek oxygen-containing ligands, comprise all the macronutrient metals (such as K and Ca). Class B (soft) metals, which tend to seek nitrogen- and sulfur-containing groups, comprise many of the more toxic metals. Borderline metals, which have intermediate properties, include most of the common metals. As shown in Figure 6, there is a distinct break between Class A metals and the borderline group, but there is little distinction between the borderline group and Class B metals. This type of approach can provide a general set of criteria by which the actions of different metals can be compared. For example, Class B metals may displace borderline metals, such as Zn or Cu, from enzymes. The toxicity of a borderline metal depends on its Class B character; it will be able to displace many Class A metals and, depending upon their relative affinities, other borderline metals. Nieboer and Fletcher (1996) discuss several chemical and physical factors of metals that relate to their reactivity and toxicity.

Walker et al. (2003) provide a review of reported correlations between physical and chemical properties of cations and toxicity to mammalian and nonmammalian species using in vitro and in vivo assays. They conclude that certain useful cor-

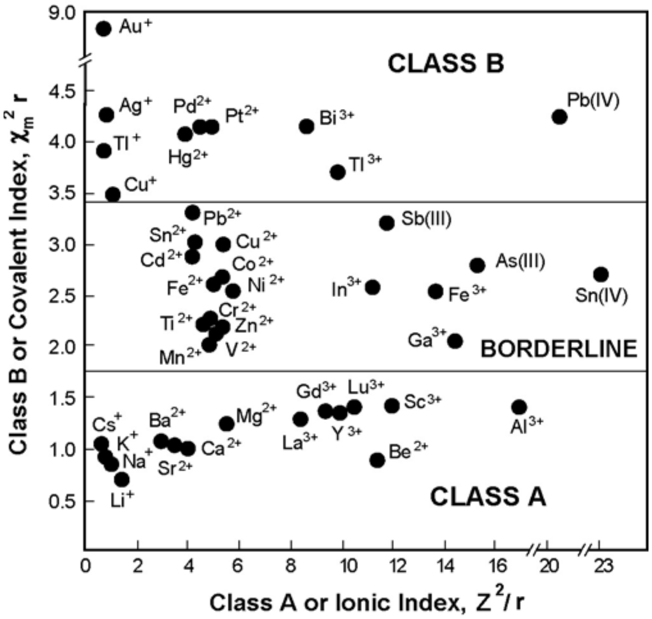

Figure 6. Chemical classification of metal ions according to Nieboer and Richardson (1980). χ_m is the metal-ion electronegativity, r is the metal ionic radius, and Z is the formal charge of the metal ion. Oxidation states given by Roman numerals imply that simple cations do not exist (modified from Nieboer and Richardson, 1980).

relations can be made between several physical and chemical properties of ions (mostly cations) and toxicity of metals. McKinney et al. (2000) provide a review of qualitative and quantitative modeling methods that relate chemical structure to biological activity. These structure-activity relationships (SARs) are being applied to the prediction and characterization of chemical toxicity. Quantitative ion character-activity relationships (QICARs) that use metal-ligand binding characteristics to predict metal toxicity are currently under development (Newman et al., 1998; Ownby and Newman, 2003). The QICAR work demonstrates the feasibility of predicting metal toxicity from metal-ion characteristics.

CHEMICAL SPECIATION

An understanding of metal speciation is key to understanding metal mobility, bioavailability, and toxicity. Different chemical species of a given metal often have different mobility behavior and toxicological effects. The terms *species* and *speciation* are used in the literature in a variety of ways. For the purposes of this report, distinct chemical species are "chemical compounds that differ in isotopic composition, conformation, oxidation or electronic state, or in the nature of their complexed or covalently bound substituents," and speciation is the "distribution of an element amongst defined chemical species in a system" (Templeton et al., 2000).

The general formula for metal cations is usually written as M^{n+}. This is a bit misleading because metal ions dissolved in water are not present as bare cations but, rather, are complexed with water molecules. When a metal binds to a ligand other than water, the ligand must substitute for the complexed water molecules. This substitution is faster for some metals than for others. Rules of thumb for this rate of substitution are:

1. For metal ions of the same charge, substitution rates for the same ligand will increase with increasing metal-ion size (e.g., $Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$).
2. For metal ions of about the same size, substitution rates will increase with decreasing metal-cation charge (e.g., $Mg^{2+} < Li^{+}$).

These rules of thumb can help determine why some metals readily bind with various ligands whereas other metals do not. This behavior is related to some of the same principles behind HSAB behavior.

Aqueous metal species occur as free ions (which are actually complexed with water molecules as discussed above) or as metal complexes. The formation of metal complexes in solution tends to increase metal mobility. Total metal concentration does not distinguish between the various species. For many metals, the free ion is thought to be the primary species that causes toxicity to aquatic organisms. Therefore, to achieve a reliable estimate of metal bioavailability, it is necessary to determine metal species. However, it should be noted that total metal concentration can provide an upper limit for estimation of metal bioavailability and toxicity.

There is ongoing research to find analytical and computational approaches to determine metal speciation. D'Amore et al. (2005) provide a recent review of speciation methods for metals in soils, and Buffle and Horvai (2000) and Ure and Davidson (2002) provide information on speciation methods for a variety of applications.

Factors that can influence metal speciation include pH, redox conditions, inorganic ligands, organic ligands (DOC), and competition from other ions. Several books provide detailed explanations about factors that influence metal speciation (e.g., Cotton and Wilkinson, 1988; Drever, 1997; Garrels and Christ, 1965; Greenwood and Earnshaw, 1984; Hem, 1989; Huheey et al., 1993; Langmuir, 1997; Morel and Herring, 1993; Nordstrom and Munoz, 1994; Parish, 1977; Stumm and Morgan, 1996). The relationship between metal speciation, mobility, and bioavailability has been reviewed by several authors (e.g., Allen, 2002; Allen et al., 1980; Bourg, 1988; Forstner, 1987; Luoma, 1983; Luoma and Carter, 1993; Nieboer and Fletcher, 1996; Pagenkopf, 1983; Tessier and Turner, 1995). Smith and Huyck (1999) provide a discussion of the links between metal abundance, mobility, bioavailability, and toxicity in mining environments.

Transition Metals

The transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) are in the center of the periodic table of the elements. Transition metals have unusual properties that affect their environmental chemistry. One important property is that they tend to have multiple oxidation states. Also, transition metals tend to form a variety of complexes and have a reasonably well-established rule for the sequence of complex stability based on empirical observation. According to this rule (the Irving-Williams order), the stability of complexes follows the order:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

Organometallic Transformations

Some metals can be transformed, either biotically or abiotically, into organometallic compounds, which are compounds that have a metal-carbon bond. Methylation, when a methyl group (CH_3) combines with a metal, is an example of the formation of an organometallic compound and is favored by anoxic, high-temperature environments. Mercury is perhaps the best-known example of a metal that undergoes organometallic transformations, but As, Pb, Se, and Sn may also be transformed into organometallic compounds (Craig, 2003). Organometallic transformations can affect metal mobility and toxicity. For the example of Hg, methylmercury (CH_3Hg) is the most bioavailable and toxic form of Hg (Gerould, 2000).

The Role of pH

Most metals found in MIW are cations (e.g., Cd, Cu, Ni, Pb, Zn), and the predominant charge on most of the cations is +2. For this reason, mobility and bioavailability are determined primarily by pH and are enhanced under acidic conditions. Figure 7 is an example of a Ficklin diagram, in which total concentrations of base metals are plotted against pH. This diagram clearly demonstrates the inverse relationship between high cationic metal concentrations and low-pH values. Zinc tends to dominate the base-metal concentrations in these types of plots, but individual-element plots exhibit similar behavior. Therefore, metal cations tend to be more mobile under low-pH conditions.

Some metals and metalloids (e.g., As, Cr, Mo, Se, Te, V) can combine with oxygen to form a stable, negatively charged (anionic) species called an oxyanion. As discussed above, elements with high ionic potential have a tendency to form oxyanions (e.g., MoO_4^{2-}). Because of their negative charge, oxyanions have very different mobility characteristics than do cationic species. Table 5 identifies elements that are anionic or cationic in aquatic systems. Cationic species tend to be more mobile under low-pH conditions and less mobile under high-pH conditions, whereas the opposite is true for anionic species. There are also distinct differences in bioavailability characteristics between cationic and anionic species. For example, oxyanions can be transported through living-cell membranes by diffusion-controlled processes (Wood, 1988). Arsenate may replace phosphate, and Se may replace S in many biological systems.

The pH of a system can also control which ligands are available for binding. Aqueous species of the carbonate system change with changing pH. At low pH, minimal CO_3^{2-} is available for metal binding, but at $pH > 8$, CO_3^{2-} can become a predominant ligand for many metals. The same is true for OH^-, which becomes more abundant with increasing pH.

The Role of Redox Chemistry

Table 5 lists some redox-sensitive elements in aquatic systems. A redox-sensitive element will generally undergo a change in mobility under different oxidizing or reducing conditions. For example, chromium dissolves as it is oxidized to chromium (VI) and precipitates upon reduction to chromium (III); this is important because chromium (VI) is much more toxic than is chromium (III). Similarly, uranium is immobile under reducing conditions but can be mobile under oxidizing conditions. Conversely, iron and manganese may be soluble under reducing conditions; consequently, metals sorbed onto iron oxides and manganese oxides can be released under reducing conditions.

It is very difficult to measure redox conditions in natural environments. Also, disequilibrium between redox couples (e.g., Fe^{2+} and Fe^{3+}) is common. Therefore, it is good practice to directly measure redox-sensitive species of interest whenever possible (Nordstrom, 2002).

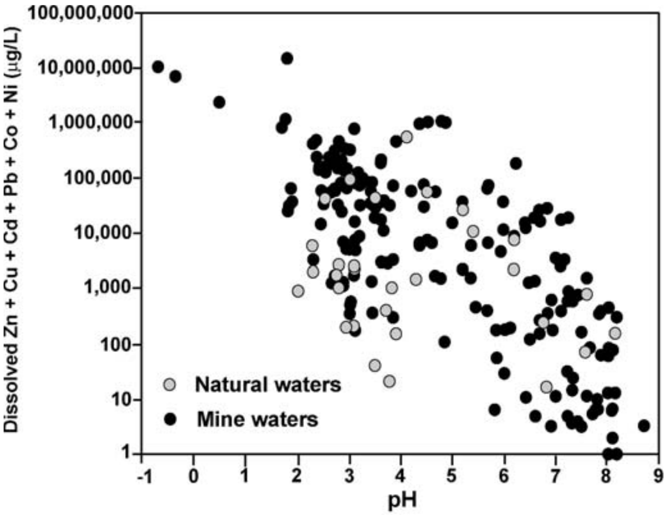

Figure 7. Ficklin diagram showing how the sum of dissolved base metals (Zn, Cu, Cd, Pb, Co, and Ni) varies with pH in natural (gray circles) and mine (black circles) waters draining diverse mineral-deposit types. Note that the trend is for lower-pH waters to contain higher concentrations of metals; however, higher-pH waters may still contain significant metal concentrations. For the diagram, ppb and µg/L are assumed to be equivalent (modified from Plumlee et al., 1999).

CHARACTERISTICS OF MINING-INFLUENCED WATERS AND IMPORTANT GEOCHEMICAL PROCESSES

Mining-influenced waters (MIW) generally have low-pH values, high concentrations of SO_4^{2-}, and high concentrations of Fe, Al, Mn, and several other metals. This unusual composition makes these systems somewhat unique when defining geochemical processes, reactants, and phases that control metal mobility. Discussion of the formation and composition of MIW can be found in Alpers and Blowes (1994), Ficklin et al. (1992), Nordstrom and Alpers (1999), Plumlee et al. (1999), Schmiermund and Drozd (1997), and Smith (2005a).

Solubility Reactions

In this report, the term *solubility* refers to the amount of a substance that can be dissolved in water at a given temperature and pressure. This parameter is used in environmental studies to help determine the fate of substances. Solubility in water is described by a solubility product (K_{sp}), which is the equilibrium constant for a solubility reaction. The tendency for a metal to form a solid compound is related to the chemical and physical properties previously discussed. Some metals can make extremely insoluble compounds (very low K_{sp} values; e.g., Pb), so these metals tend to precipitate as solids and have limited mobility. Other metals (e.g., Zn) tend to be relatively mobile

TABLE 5. GENERAL CHARACTERISTICS OF SOME CHEMICAL ELEMENTS IN SIMPLE SURFACE OR NEAR-SURFACE AQUATIC SYSTEMS(1)(2)

Element	Chemical Symbol	Anionic(3)	Cationic	Redox-Sensitive(4)	Commonly Forms Sulfides
Aluminum	Al		X		
Antimony	Sb	X		X	X
Arsenic	As	X		X	X
Barium	Ba		X		
Beryllium	Be		X		
Cadmium	Cd		X		X
Chromium	Cr	X	X	X	
Cobalt	Co		X		X
Copper	Cu		X	X	X
Iron	Fe		X	X	X
Lead	Pb		X	(X(6))	X
Lithium	Li		X		
Manganese	Mn		X	X	
Mercury	Hg		X	X	X
Molybdenum	Mo	X	X(5)	X	X
Nickel	Ni		X		X
Selenium	Se	X		X	
Silver	Ag		X		X
Thallium	Tl		X	X	X
Thorium	Th		X	(X(6))	
Uranium	U	X	X	X	
Vanadium	V	X	X	X	
Zinc	Zn		X		X

Note: Modified from Smith and Huyck (1999).

(1) This table is meant as a simple guide for element behavior under normal surface or near-surface aqueous conditions.

(2) This table does not include complexes with other elements.

(3) Anionic species exist as oxyanions.

(4) Elements that change oxidation state and oftentimes behavior under different redox conditions.

(5) Cationic species exist for Mo but are rare in aquatic systems.

(6) Some of the elements, such as Pb and Th, are redox-sensitive only under extreme conditions.

because they don't readily form insoluble solids. Due to the high SO_4^{2-} concentrations in MIW, metals that form strong bonds (and relatively insoluble precipitates) with SO_4^{2-} would be expected to precipitate and be relatively immobile. Examples of relatively insoluble sulfate minerals are anglesite ($PbSO_4$) and barite ($BaSO_4$). Table 5 lists chemical elements that form sulfide precipitates under reducing conditions. Nordstrom and Alpers (1999) provide a detailed discussion of the solid phases that may form from MIW.

Metal complexation can affect the concentration and transport of metal ions. Anions, such as SO_4^{2-}, are commonly elevated in MIW. Metal complexation with these anions can increase dissolved metal concentrations above what is usually observed for solubility reactions. Cravotta (2006) examined data for 140 water samples from abandoned Pennsylvania coal mines, with pH values ranging from 2.7 to 7.3. He found that formation of aluminum-sulfate complexes greatly increased total dissolved Al concentrations at equilibrium with aluminum hydroxide and hydroxysulfate minerals. Similarly, ferric-iron-sulfate complexes increased dissolved Fe^{3+} concentrations in equilibrium with iron hydroxide or hydroxysulfate minerals.

The pH is a major control on the solubility of most metal compounds. The solubility of many metals is amphoteric, which means that the metals have a tendency to dissolve and form cations at low pH and anions at high pH, with minimal solubility at intermediate pH. For example, $Al(OH)_3$ has its minimal solubility between pH 6 and 7 (Bigham and Nordstrom, 2000; Nordstrom and Ball, 1986). The pH value of minimal solubility is different for different metals. This concept is illustrated in Figure 8. Note that gibbsite (aluminum hydroxide) and ferrihydrite (iron oxyhydroxide) have minimal solubility between pH 6 and 8, and that hydroxides of Cd, Fe(II), Zn, and Cu have minimal

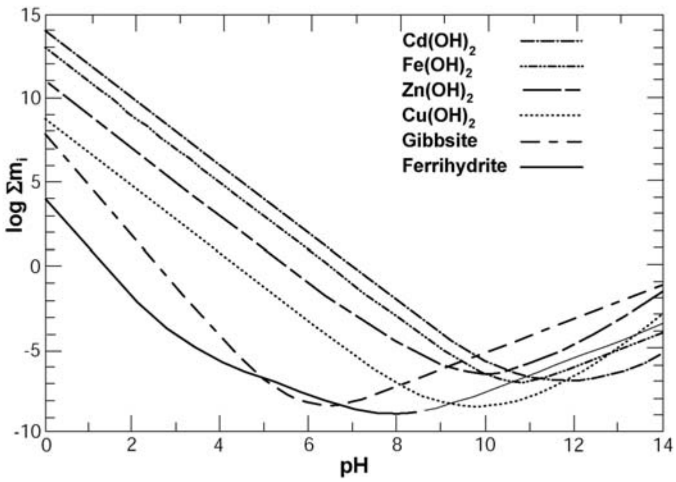

Figure 8. Solubility curves for hydroxides of Al, Fe^{3+}, Fe^{2+}, Cu, Zn, and Cd (reprinted from Nordstrom and Alpers, 1999, with permission).

solubility at much higher pH values (above pH 9). Also note that for a given pH value in Figure 8 the solubility is different for the different metals.

Aluminum mobility at mining sites is related to pH and SO_4^{2-} concentration. Nordstrom (1982) found that in MIW, aluminum-sulfate and aluminum-hydroxysulfate minerals are more stable than are more common aluminum minerals found in soil. In water with pH $<$ 4.5 or 5, dissolved Al tends to remain in solution, but in water with pH $>$ 5, Al tends to precipitate as a solid (Nordstrom and Ball, 1986). It is common to observe white aluminum-hydroxysulfate precipitates at mining sites where the water pH has risen to a value above pH 5. Also, Al solubility influences its bioavailability. Aluminum can be fairly toxic to aquatic life, but at circumneutral pH values Al is relatively insoluble and, hence, not very bioavailable to aquatic life.

Iron mobility at mining sites is also related to pH and SO_4^{2-} concentration. Saturation of iron-hydroxysulfate minerals generally occurs around pH 4. So, at pH $>$ 4, Fe precipitates as a solid and is no longer mobile. These iron precipitates form the yellow-orange-red precipitates that form on streambeds at many mining sites. Photoreduction of Fe in acidic streams also can play a role in the mobility of iron (McKnight et al., 2001). Solid-iron phases are known to strongly sorb many metals. The role of iron precipitates in controlling aqueous metal concentrations by sorption processes is discussed in the following section.

Nordstrom and Alpers (1999) compiled a list of minerals that likely would control metal concentrations in MIW. Generally, these minerals are either relatively insoluble or have components that are common in MIW (such as SO_4^{2-}). The minerals include alunogen, anglesite, barite, basaluminite, calcite, cerussite, chalcanthite, epsomite, ferrihydrite, gibbsite, goslarite, gypsum, halotrichite-pickeringite, manganese oxides, melanterite, otavite, rhodochrosite, schwertmannite, scorodite, siderite, microcrystalline silica, smithsonite, and witherite.

Sorption Reactions

Sorption reactions, involving both inorganic and organic particulates, largely control the fate of many trace elements in natural systems. Metal sorption is strongly pH-dependent and a function of metal-complex formation and ionic strength (Dzombak and Morel, 1987). At many mining sites there are abundant iron- and aluminum-oxide precipitates. These precipitates can act as effective sorbents for a variety of metals (Smith, 1999b; Smith et al., 1998).

The term *sorption* is a general term that describes removal of a solute from solution to a contiguous solid phase and is used when the specific removal mechanism is not known. *Sorbate,* or *adsorbate,* refers to the solute that sorbs on the solid phase. *Sorbent,* or *adsorbent,* is the solid phase on which the sorbate sorbs. *Adsorption* refers to the two-dimensional accumulation of an adsorbate at a solid surface. The term *absorption* is used when there is diffusion of the sorbate into the solid phase. Absorption processes usually show a significant time dependency. Sposito (1986) provides a more detailed description of these terms.

The formation and dissolution of iron-hydroxysulfate minerals such as jarosite and schwertmannite can influence the mobility of metals in the environment. Jarosite [$KFe_3(SO_4)_2(OH)_6$] is a ferric sulfate mineral that forms under acidic conditions. It can incorporate Pb, Hg, Cu, Zn, Ag, and Ra by substitution for structural K or Fe, and it can incorporate anions such as chromate, arsenate, and selenate by substitution for SO_4^{2-} (Dutrizac and Jambor, 1987). Schwertmannite [$Fe_8O_8(OH)_6(SO_4)$], informally known as yellowboy, is a poorly crystalline mineral with high specific surface area. It occurs as a precipitate from acidic, sulfate-rich waters (Bigham et al., 1996), such as acidic mine-drainage environments. Schwertmannite may accumulate metals, such as Cu, Zn, Ni, Se, and As, by substitution into the crystalline structure or sorption (Smith et al., 1998; Smith, 1999b). Although metals may be immobilized by coprecipitation or sorption with iron hydroxysulfate minerals, transport or burial of the materials or changes in the local redox environment could lead to conditions favoring remobilization by dissolution or desorption.

Trace elements partition between dissolved and particulate phases, and this partitioning can influence their transport and bioavailability (Luoma and Davis, 1983; Jenne and Zachara, 1987). In fact, sorption processes appear to control metal partitioning in most natural aquatic systems (Jenne, 1968; Hem, 1989). Partitioning of a metal between solid and solution phases is influenced by several factors. Generally, conditions that cause metals to be present in the solution phase include low-pH conditions, reducing conditions, low particulate loads, and/or high dissolved concentrations of a strong complexing agent.

For sorption of metals on oxide minerals, solution pH is the primary variable. Typically, cation adsorption increases with increasing pH from near zero to nearly 100% over a critical-pH range of 1–2 units (James and Healy, 1972; Kinniburgh and Jackson, 1981; Davis and Hayes, 1986). This critical-pH range is termed the *adsorption edge,* and its placement seems to be char-

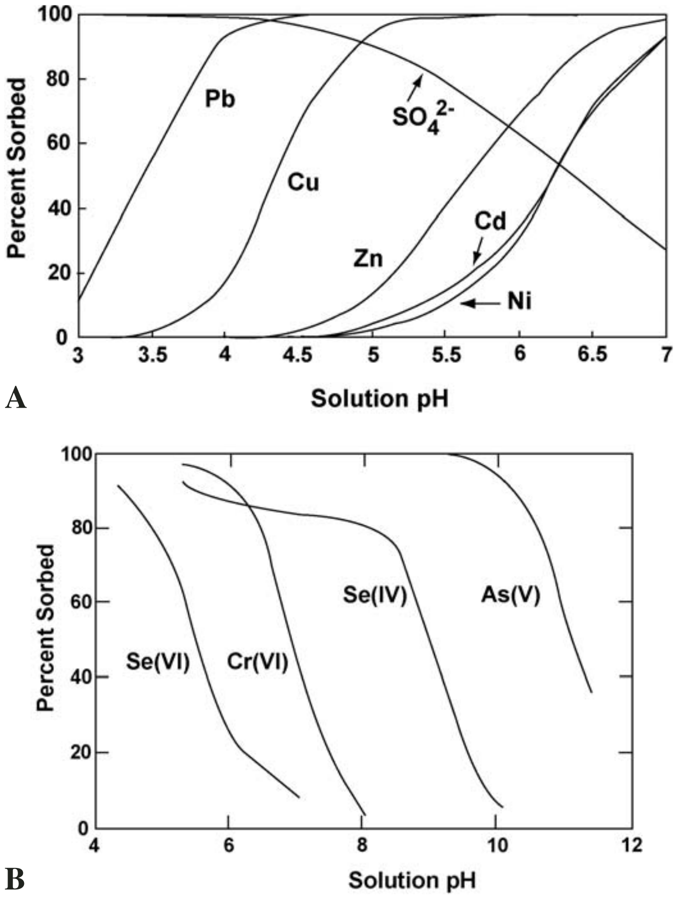

Figure 9. (A) Sorption curves showing the relative placement of the critical-pH range of metals and sulfate on hydrous iron oxide (modified from Smith and Macalady, 1991). (B) Sorption curves showing the relative placement of the critical-pH range of selected oxyanions on hydrous ferric oxide (modified from Davis and Kent, 1990).

acteristic of the particular adsorbate and, to a lesser extent, to the particular adsorbent (Spark et al., 1995). The critical-pH range (adsorption edge) is illustrated in Figure 9. Anion adsorption (Fig. 9B) is the mirror image of cation adsorption (Fig. 9A) in that anion adsorption tends to decrease with increasing pH. For a given sorbate concentration, increasing the amount of adsorbent material will shift down the pH of the adsorption edge for cations and shift up the pH of the adsorption edge for anions. Table 6 lists the critical pH ranges for metal sorption onto oxide sorbent materials.

The distribution of a metal between aqueous and solid phases can be described by a partition coefficient (K_d), which is the ratio between the metal on the solid phase and the metal in solution. Partition coefficients are commonly used in computer transport models. It is important to keep in mind that K_d values are not constants and that they vary across different conditions, such as type of solid material, pH, and oxidation state of the metal. Soil and sediment with high K_d values have a high sorption or buffering capacity for added metals.

TABLE 6. CRITICAL pH RANGES FOR SORPTION OF DIVALENT METAL CATIONS ON HYDROUS IRON AND ALUMINUM OXIDES

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

Note: After Kinniburgh and Jackson, 1981; generally, the critical pH range for a given cation is higher for silica and lower for manganese oxides.

Another approach that incorporates sorption into computer models is surface-complexation (Stumm et al., 1970, 1976; Schindler and Gamsjager, 1972; Schindler et al., 1976). In this approach, sorption of ions on surfaces of oxide minerals is treated as analogous to the formation of aqueous complexes. Unlike partition coefficients, surface-complexation models have predictive capabilities beyond the measured conditions.

IMPORTANT ENVIRONMENTAL CONDITIONS

When metals are introduced into a stream, interactions such as dilution, chemical transformations, degradation, settling, resuspension, and other processes take place. Conditions in the stream are also a factor (e.g., pH, organic content, suspended solids, and numerous other factors) and can significantly affect how a metal will behave. Factors affecting the chemical composition of most surface waters are climate, lithology, geoavailability of elements, vegetation, topography, flow rates, biological activity, and time. The composition of water is controlled by interactions with earth materials through which the water flows. It is possible to make generalizations about some of the environmental factors that control metal chemistry, which allows for estimates of metal behavior, mobility, and fate.

Geochemical Gradients and Barriers

Perel'man (1977) discusses the importance of geochemical gradients, which describe gradual changes of a landscape, and of geochemical barriers, which describe abrupt changes. An example of a geochemical gradient might be the vertical and horizontal distribution of certain elements away from a mineral deposit within a constant lithology; for a given element, an anomalous concentration eventually declines to a background concentration at some distance away from the deposit. Another example of a geochemical gradient is the concentration plume for some elements downwind from a smelter. Perel'man (1986) defines geochemical barriers as zones of the Earth's crust with sharp physical or chemical gradients that are commonly associated with accumulation of elements. Geochemical barriers comprise abrupt changes in physical or chemical environments in the path of migration of elements causing the precipitation of certain elements from solution. Geochemical barriers include mechanical, physicochemical, biochemical, and anthropogenic (or technogenic) types. Complex barriers may be created when two or more barrier types are superimposed. Complex barriers are a common occurrence because geochemical processes are often linked and result in changing geochemical conditions. Perel'man (1977, 1986) gives a more in-depth discussion of geochemical barriers. This concept can help to forecast element distributions in the surficial environment and explain metal transport and mobility.

pH Barriers

Acidic barriers develop when pH values decrease. Under these conditions, elements that form oxyanions, such as Mo, as well as certain complexes, generally become less mobile, whereas many cationic metals, such as Cu, generally become more mobile. Solubility relationships can play an important role. For example, Al is usually fairly mobile below a pH of ~4, but will gradually precipitate between a pH of ~5 and 9. On the other hand, Si (as SiO_2) is relatively insoluble at low pH and becomes more soluble at high pH. One of the most important effects of developing low-pH environments is the destruction of the carbonate-bicarbonate buffering system, a feedback mechanism that controls the extent of pH change in an aquatic system. Below a pH of ~4.5, carbonate and bicarbonate are converted to carbonic acid. Upon such acidification, the water loses its capacity to buffer changes in pH, and many photosynthetic organisms that use bicarbonate as their inorganic carbon source become stressed or die. Once damaged, the alkalinity of a natural system may take significant time to recover, even if no further acid is added to the system. The carbonate-bicarbonate system may have both a direct and an indirect effect on the mobility of several elements.

Alkaline barriers develop where acidic waters encounter alkaline conditions over a short distance (e.g., oxidation zones of pyrite in limestone host rock). This type of barrier mostly retains those elements that migrate easily under acidic conditions and precipitate as hydroxides or carbonates under alkaline conditions (such as Fe, Al, Cu, Ni, and Co). During the shift to alkaline conditions, hydrous iron, aluminum, and manganese oxides may sorb trace metals and create an alkaline/adsorption complex barrier.

Redox Barriers

In most surficial aquatic systems, atmospheric oxygen is the primary oxidant, and organic matter is the primary reductant. At mining sites, other reductants may include FeS, FeS_2, Fe^{2+}, Mn^{2+}, or H_2S. There is a redox balance that depends upon the rate of oxygen depletion versus the rate of oxygen replenishment. If the rate of oxygen depletion is greater, redox-sensitive elements may undergo transformations from one chemical species to another. At circumneutral pH values, some redox reactions that may take place are listed below in order of increasingly reducing conditions:

$NO_3^- \rightarrow N_{2\,(g)}$
$MnO_{2\,(s)} \rightarrow Mn^{2+}$
$NO_3^- \rightarrow NO_2^-$
$NO_2^- \rightarrow NH_4^+$
$Fe(OH)_{3\,(s)} \rightarrow Fe^{2+}$
$SO_4^{2-} \rightarrow H_2S$
$HCO_3^- \rightarrow CH_4$
$HCO_3^- \rightarrow CH_2O$

Reducing barriers can be divided into those that contain hydrogen sulfide and those that do not (referred to as reducing gley environments; Perel'man, 1986). Berner (1981) proposed a simple redox classification based on the presence or absence of dissolved oxygen (DO) and sulfide. Under this scheme, oxic conditions exist where DO > 30 μM. Anoxic systems are divided into those with and without measurable sulfide (sulfidic and nonsulfidic, respectively). In sulfidic systems, many metals may precipitate as sulfide minerals.

Reducing hydrogen sulfide barriers develop where oxidizing waters come into contact with a reducing hydrogen sulfide environment or with sulfide minerals, or where deoxygenated sulfate-rich water encounters an accumulation of organic matter. Insoluble sulfides of elements such as Fe, Cu, Zn, Pb, Co, Ni, and Ag may precipitate at reducing barriers that contain hydrogen sulfide. Reducing gley barriers can form where water infiltrates soil and the weathering crust, and where free oxygen is lost or consumed. Depending on the pH, reducing gley waters are usually favorable for the transport of many ore-forming elements; additionally, elements such as Se, Cu, U, Mo, V, Cr, Ag, and As are known to accumulate at some reducing gley barriers (Perel'man, 1986). For example, roll-front-type uranium deposits may form under such conditions. Both manganese and iron oxides may undergo dissolution in reducing environments. These oxides provide important substrates for metal sorption and coprecipitation, so dissolution of these oxides may result in release of associated metals in reducing environments.

Oxidizing barriers occur where oxygen is introduced into anoxic waters or where anoxic ground water is discharged to the surficial environment. Iron, and possibly manganese, may precipitate at these barriers. Because hydrous iron and manganese oxides are good sorbents for metals (such as Cu and Co), a complex barrier may form by combining an oxidizing barrier with an adsorption barrier.

Evaporation Barriers

Evaporation barriers are often indicated by the presence of salt crusts or efflorescent salts, and Na, Mg, Ca, Cl, S, and CO_3^{2-}

salts may precipitate at these barriers. Evaporation barriers may be temporary and related to changing climatic conditions. For example, in some mine-waste-rock piles, efflorescent salts, enriched in elements such as Fe, Al, Cu, and S, may form during the dry season. These salts will be flushed from the system during a subsequent wet period and may cause a brief spike in metal content and acidity of the storm-water runoff (Nordstrom and Alpers, 1999).

Adsorption Barriers

Adsorption barriers are typically part of complex barriers. The most common sorbents (e.g., hydrous iron, aluminum, and manganese oxides, organic matter, and clay minerals) have different affinities for elements under different geochemical conditions. Adsorption reactions are known to control trace-metal concentrations in many natural systems.

Temperature/Pressure Barriers

Temperature/pressure (thermodynamic) barriers are formed in areas with temperature and pressure variations. One example of such a barrier is the degassing of carbon-dioxide-rich ground water as pressure drops and the subsequent deposition of carbonate minerals. Trace elements, such as Pb and Cd, can precipitate as carbonate minerals or coprecipitate with $CaCO_3$.

CONSIDERATIONS AND POSSIBLE APPLICATIONS

Understanding the chemical and physical factors of metals and geochemical processes that can influence metal mobility, distribution, and bioavailability can aid in forecasting the potential ecological effects of metals in surficial mining environments. The following sections briefly describe some of the applications where incorporating information about metal mobility is useful.

Risk Assessment

Ecological risk assessments are becoming increasingly important in evaluating the effects of historical mining as well as in predicting the potential effects of present and future mining. The U.S. Environmental Protection Agency (U.S. EPA) adopted a framework for ecological risk assessment (U.S. EPA, 1998) that includes planning, problem formulation, analysis, interpretation and risk characterization, communicating results, and risk management. This approach has been applied to the U.S. EPA Framework for Metals Assessment (U.S. EPA, 2007b). Most risk-assessment approaches have been developed for synthetic organic compounds. Because of the differences in environmental behavior between metals and organic compounds, it is generally becoming accepted that risk assessments for metals should be designed differently than those for organic compounds (Lee and Allen, 1998).

Environmental chemistry can be used to determine metal speciation for use in risk assessments and to assess the mobility of metals in the environment. In risk assessments involving metals, it is essential to identify factors that control metal transformations between bioavailable and nonbioavailable forms (Campbell et al., 2006; U.S. EPA, 2007b; Waeterschoot et al., 2003). The unit-world model, which is under development, will provide a quantitative method to assess risks posed by metals from their source of contamination, through transport in the aquatic environment, to uptake by biological receptors (Allen et al., 2000). Risk assessments can be performed at various scales from site-specific to watershed to regional. Approaches for regional risk assessments are still in development (e.g., Landis and Wiegers, 1997).

Water-Quality Criteria: Approaches to Determine the Bioavailable Metal Fraction

Ambient water-quality criteria have been developed by the U.S. EPA in support of the Clean Water Act. The goal of the criteria is to protect the physical, chemical, and biological integrity of waters of the United States. Several accommodations have evolved in the criteria to account for site-specific differences in metal bioavailability. For example, dissolved concentrations replaced total concentrations in some of the criteria. Also, criteria for several metals have been expressed as a function of water hardness to account for the protective effects of Ca and Mg on aquatic metal toxicity. The water effect ratio (WER) is an empirical approach that was developed to account for site-specific conditions where the water chemistry can alter metal bioavailability and toxicity (U.S. EPA, 1994). In this approach, toxicity tests are performed with site-specific water and compared with results from tests performed with laboratory water. The water-quality criterion is then adjusted to reflect the influence of the site-specific water.

Recently, the U.S. EPA has adopted a computational approach to address aquatic metal toxicity. The biotic ligand model (BLM) is a computer model that mathematically estimates the effects of water chemistry on the speciation and bioavailability of metals and on their acute toxicity to aquatic biota (Di Toro et al., 2001; Gorsuch et al., 2002; Niyogi and Wood, 2004; Paquin et al., 2002; Santore et al., 2001; Slaveykova and Wilkinson, 2005; Villavicencio et al., 2005). It is being used to develop site-specific water-quality criteria and to assess aquatic risk for metal exposure. The BLM has been incorporated into the 2007 update of the ambient water-quality criteria for Cu (U.S. EPA, 2007a) and is being used to determine regulatory site-specific concentration criteria for Cu. Given site-specific water chemistry, a chosen metal, and a chosen organism, the BLM predicts the LC_{50} (lethal concentration 50, which is the metal concentration that results in the death of 50% of a group of test organisms) for the chosen metal and organism. The BLM also can be used for predictive ecological risk assessments (Smith, 2005b; Smith et al., 2006). Collection of dissolved organic carbon data is imperative for use of the BLM.

Baseline Metal Concentrations

The term *baseline* has various meanings, especially when used in an environmental context. An environmental baseline is a summary of existing conditions over some time frame for some environmental system or material of interest (Lee and Helsel, 2005). Baselines can take human influences into account. In contrast, an environmental background describes the natural tendency of an environmental system or material in the absence of human influences (Lee and Helsel, 2005). Determination of an environmental background is very difficult, if not impossible. Determination of an environmental baseline also can present some difficulties because baseline concentrations may be below or near analytical detection limits. Methods to handle data with less-than values are available in the literature (e.g., Helsel, 2005).

Metals in the environment may result from natural geologic processes as well as from mining activities. Therefore, both the environmental baseline and background of metals can be elevated in mineralized areas. Baseline concentrations of elements are important determinants for risk assessment because organisms may adapt to elevated concentrations (Chapman et al., 1998). Consequently, metal-toxicity thresholds for organisms in environments with elevated metal concentrations may be greater than those for organisms adapted to low-concentration conditions (McLaughlin and Smolders, 2001).

Because metals are naturally occurring substances, biota have evolved in the presence of metals. It is important to identify environmental controlling factors, such as pH, organic matter, iron, and redox conditions, and their effect on metal concentration and exposure to biota. For site-specific assessments, the key aspect is to identify the biota most likely to be susceptible to metals. For regional assessments, the approach is often taken to protect highly sensitive species with limited distributions, which results in criteria that are overprotective for the larger area. One interesting approach is the concept of metalloregions, or metal-related ecoregions (McLaughlin and Smolders, 2001). This approach considers conditions within each type of metal-controlling environment. A series of fact sheets published by the International Council on Mining and Metals (ICMM; available at http://www.icmm.com) discusses relationships between metals, baseline conditions, bioavailability, and risk assessment.

Landscape Geochemistry

Landscape geochemistry can help define metal distributions in the environment. Landscape geochemistry focuses on the interaction of the lithosphere with the hydrosphere, biosphere, and atmosphere, and links exploration geochemistry with environmental science (Fortescue, 1980). Landscape geochemistry is a holistic approach to the study of the geochemistry of the environment in that it involves element cycles and may involve local, regional, and global studies. Fortescue (1992) reviews the development of landscape geochemistry and provides the foundation of how it relates to environmental science.

Fortescue (1992) proposes the establishment of a discipline of global landscape geochemistry (GLG), which may provide the foundation for future developments in applied and environmental geochemistry and which is necessary to adequately address current geoenvironmental problems. GLG regional geochemical mapping can be used to delineate geochemical provinces, identify local geochemical enrichments in mineral deposits, determine baseline environmental geochemistry, monitor environmental changes in soil and water geochemistry in response to human activities, evaluate the nutritional status of plants and animals, and study human health. Fortescue (1992) notes that there is a need to map geochemical landscapes as an essential preliminary step to the study of environmental geochemistry. Geochemical maps based on the analysis of rocks, soils, sediments, waters, and vegetation, originally compiled for mineral exploration purposes, may be extended to multipurpose geochemical surveys that have applications in agriculture, pollution studies, and human health (Webb, 1964). However, geochemical analyses for mineral exploration purposes have generally been designed to be cost effective; consequently, the quality of the geochemical data often is inadequate for many environmental applications.

SUMMARY

The purpose of this report is to present some strategies to predict metal mobility at mining sites. Metals occur naturally in the environment. Some metals are essential or beneficial to living organisms, but many metals are potentially toxic. In mineralized environments, metal concentrations tend to be elevated compared with natural abundance. Mining activities can increase metal concentrations in the environment. Once introduced, metals persist in the environment and can only be reduced by physical removal. However, metal speciation can influence metal distribution, transport, and bioavailability within the environment. Consequently, the forms, transformations, and geochemical environments of metals need to be considered when evaluating potential metal mobility at mining sites. Understanding the factors that influence metal mobility can aid in forecasting potential ecological effects of metals in mining environments.

Physical and chemical properties of metals at the atomic level are responsible for differences in their environmental behavior. Some important properties include oxidation state, size, and electronegativity. Metals can be classified into groups based on their capacity for binding to different ligands. The hard and soft acid and base classification is a useful concept to help explain the strength of metal complexation, metal behavior, and bioavailability. Qualitative and quantitative modeling methods are being developed that relate the chemistry of metals to biological activity.

Different chemical species of a given metal generally have different mobility and bioavailability behavior and toxicological effects. Factors that can influence speciation include pH, redox conditions, availability of inorganic and organic ligands, and competition from other ions. Most metals exist as cations, although some metals exist as oxyanions. Cationic species tend to be more mobile under low-pH conditions and less mobile under high-pH conditions, whereas the opposite is true for anionic species. The pH of a system also can control which ligands are available for binding. For redox-sensitive elements, such as Cr, As, and Se, a change in mobility will occur under different redox conditions.

Mining-influenced waters generally have low-pH values, high concentrations of sulfate, and high concentrations of Fe, Al, Mn, and several other metals. This unusual composition makes these systems somewhat unique when defining the geochemical processes, reactants, and phases that control metal mobility. Solubility reactions generally control Fe and Al concentrations, as well as some other metal concentrations. The pH is important in controlling the solubility of most metal compounds. Sorption reactions, involving both inorganic and organic particulates, largely control the fate of many trace elements in natural systems. Metal sorption is strongly pH-dependent and is influenced by metal-complex formation and ionic strength. At many mining sites there are abundant iron- and aluminum-oxide precipitates that can act as effective sorbents for a variety of metals.

A conceptual model can help integrate and prioritize the importance of metal speciation and changing geochemical environments at a mining site. Such a model should include relationships and pathways between the sources, transport mechanisms, and fate of the metals, and should incorporate the mineralogical, hydrological, geological, and geochemical conditions at the site that might affect these pathways. An important aspect of a conceptual model is source characterization.

It is difficult to quantitatively predict metal mobility in surficial environments; however, mobility can be considered in a relative sense by comparing metal behavior under changing environmental conditions that control metal mobility (e.g., pH conditions, redox conditions, solubility reactions, and sorption reactions). Knowledge of how metal speciation responds to changing environmental conditions can be used to predict metal mobility. Hence, it is possible to make generalizations about relative metal mobility under different conditions.

There are several applications where incorporating information about metal mobility is useful. The U.S. EPA has developed an ecological risk assessment framework for metals to specifically address the speciation characteristics of metals. Also, water-quality criteria are being rewritten to address metal speciation using the biotic ligand model. Finally, considerations of metal-baseline conditions are being used to understand the potential effects of metals introduced to the environment.

ACKNOWLEDGMENTS

The author would like to thank Andrew Archuleta, Lopaka (Rob) Lee, and Carol Russell for their helpful reviews. Preparation of this report was funded by the U.S. Geological Survey Mineral Resources Program and the U.S. Geological Survey Toxic Substances Hydrology Program.

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