Fundamentals of Mine-Drainage Formation and Chemistry

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Assessing the Toxicity Potential of Mine-Waste Piles Workshop

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U.S. Department of the Interior
U.S. Geological Survey

Colorado School of Mines

Acidity

pH is a function of:

- Balance between acid-generating and acid-consuming reactions
- Relative rates of these reactions
- Accessibility of minerals that contribute to these reactions

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Acid-Generating Reactions

- Oxidation of pyrite and some other sulfide minerals
- Hydrolysis of metal cations
  - especially Fe and Al
- Precipitation of hydrous metal-oxide minerals
  - such as iron and aluminum oxides

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Oxidation Reactions

(from Singer and Stumm, 1970; Forstner and Wittmann, 1979)

Initiator Reaction:

$$FeS_2 + 3.5\ O_2 + H_2O \longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

Pyrite — Acidity

Propagation Cycle:

$$Fe^{2+} + 0.25\ O_2 + H^+ \xrightarrow{\text{Bacteria}} 0.5\ H_2O + Fe^{3+}$$

$$14\ Fe^{3+} + FeS_2 + 8\ H_2O \longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

Acidity

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Oxidation Reactions

Pyrite (FeS_2)

$$FeS_2 + 3.5\ O_2 + H_2O \longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \longrightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

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Oxidation Reactions

Enargite (Cu_3AsS_4)

$$Cu_3AsS_4 + 8.75\ O_2 + 2.5\ H_2O \longrightarrow 3\ Cu^{2+} + HAsO_4^{2-} + 4\ SO_4^{2-} + 4\ H^+$$

$$Cu_3AsS_4 + 35\ Fe^{3+} + 20\ H_2O \longrightarrow 3\ Cu^{2+} + 35\ Fe^{2+} + HAsO_4^{2-} + 4\ SO_4^{2-} + 39\ H^+$$

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Sources of Fe^{3+}

- **Microbially catalyzed oxidation of Fe(II)**
  - **10^6 times faster than abiotic (Singer and Stumm, 1970)**
  - **See Schrenk et al., 1998**
- **Secondary iron-sulfate soluble salts**
  - **e.g., Coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$]**
  - **Form from acid mine drainage**

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Soluble Salts

- Soluble salts may form upon evaporation of acidic waters
- These salts store acid and metals until released by rainfall or snowmelt

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Acid-Generating Reactions

$$Fe^{3+} + 3\,H_2O \longrightarrow Fe(OH)_3 + 3\,H^+$$

$$Al^{3+} + 3\,H_2O \longrightarrow Al(OH)_3 + 3\,H^+$$

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Acid-Generating Reactions

Precipitation of hydrous metal-oxide minerals

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Acid-Consuming Reactions

- Dissolution of carbonate minerals releases Ca, Mg, $H_2CO_3^\circ$ or HCO_3^- or CO_3^{2-}
- Dissolution of aluminosilicate minerals releases Al, Ca, Fe, K, Mg, Mn, Na, Si
- Dissolution of hydrous Fe and Al oxide minerals releases Fe, Al, sorbed elements
- Sorption of H^+ onto mineral surfaces releases sorbed elements

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Acid-Consuming Reactions

$$CaCO_3 + 2\,H^+ \longrightarrow Ca^{2+} + H_2CO_3$$

calcite

$$KAl_3Si_3O_{10}(OH)_2 + H^+ + 9\,H_2O \longrightarrow K^+ + 3\,H_4SiO_4 + 3\,Al(OH)_3$$

muscovite

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The Carbonate System

$$CO_{2\,(g)} + H_2O_{\,(l)} \longleftrightarrow H_2CO_{3\,(aq)}$$

$$H_2CO_3 \longleftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+$$

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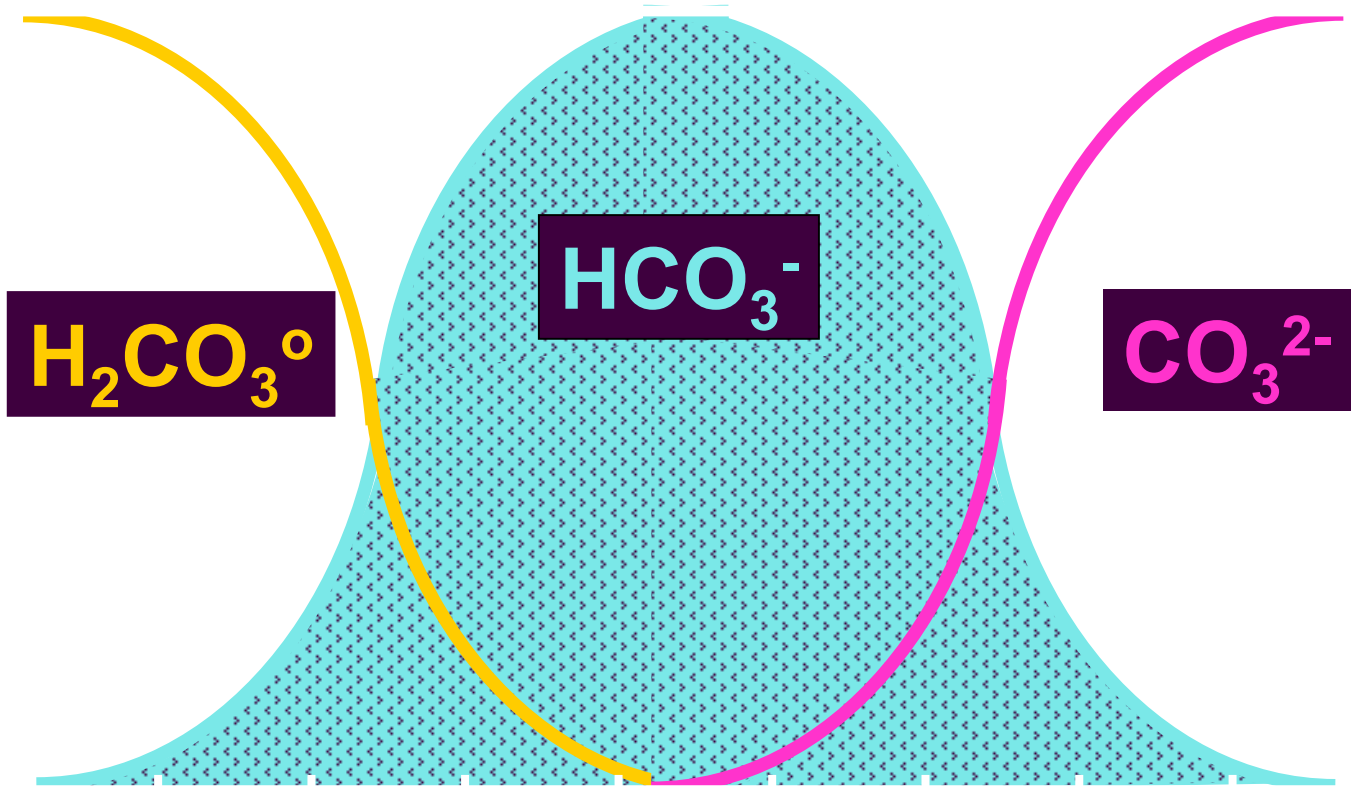
Carbonate Buffering



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Alkalinity

- Capability of water to neutralize acid
- Important to aquatic life
  - Buffers against rapid pH change
- Often related to hardness
  - Hardness is the concentration of divalent cations (e.g., Ca^{2+}, Mg^{2+})
  - Water-quality criteria for some metals are hardness-dependent
  - In mining impacted systems, Ca^{2+}, Mg^{2+}, etc. can originate from the weathering of a variety of minerals

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RIVER WATER
CONTAMINATED
BY HEAVY
METALS
DO NOT DRINK

Chemical Constituents

Concentration of a chemical element is a function of:

- **Presence and concentration of that element in the ore or host-rock minerals**
- **Accessibility of these minerals (mining method, porosity, grain size, climatic conditions, etc.)**
- **Susceptibility of these minerals to weathering**
- **Mobility of the element**

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"…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"

Smith and Huyck (1999)

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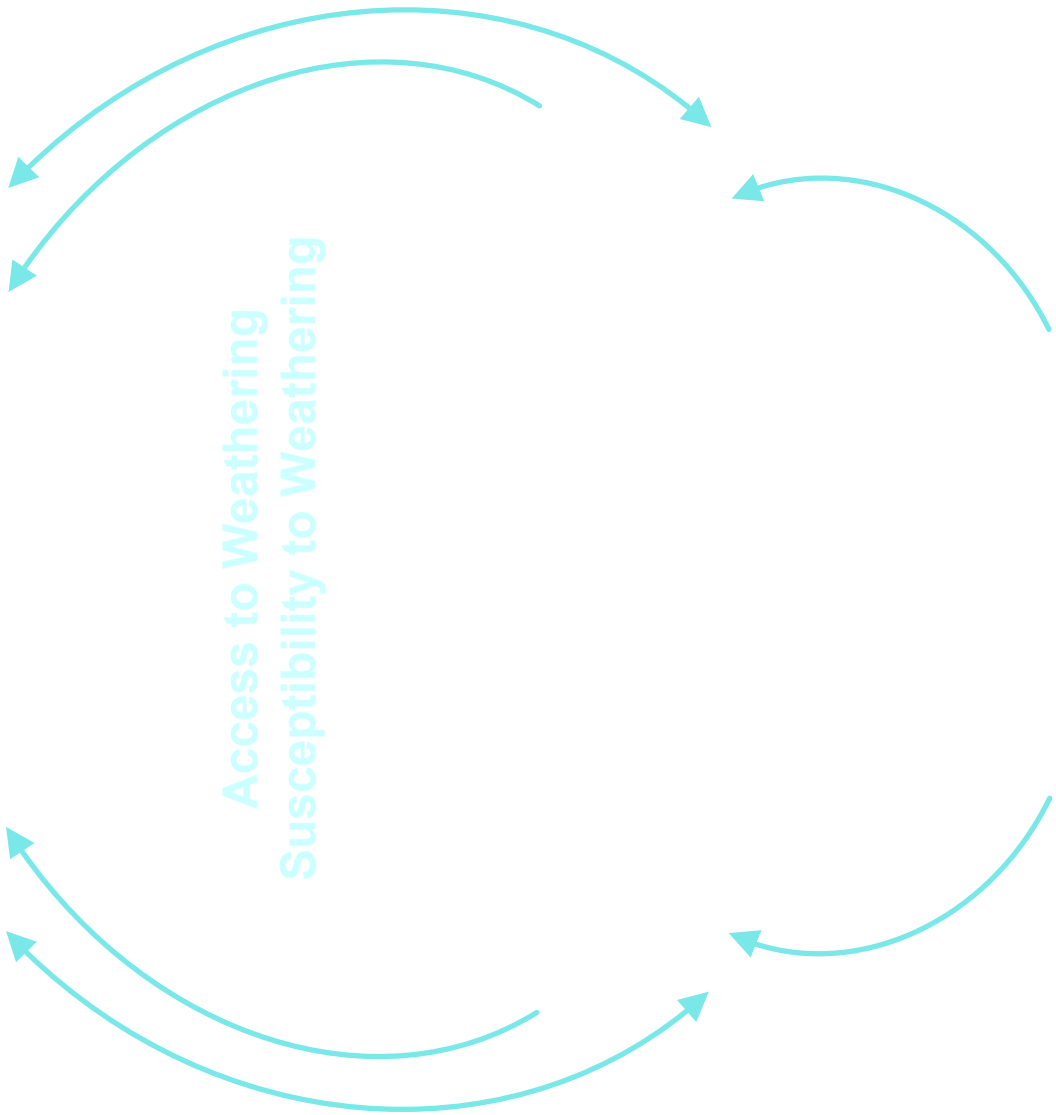
Source → Transport → Fate



after Smith and Huyck (1999)

Metal Concentration

Less

Regardless of their source, high concentrations of dissolved trace elements often do not persist as they are transported through aqueous systems due to:

- Precipitation reactions
- Sorption reactions
- Biological uptake and transformation
- Dilution
- Some exceptions include Mn and Zn

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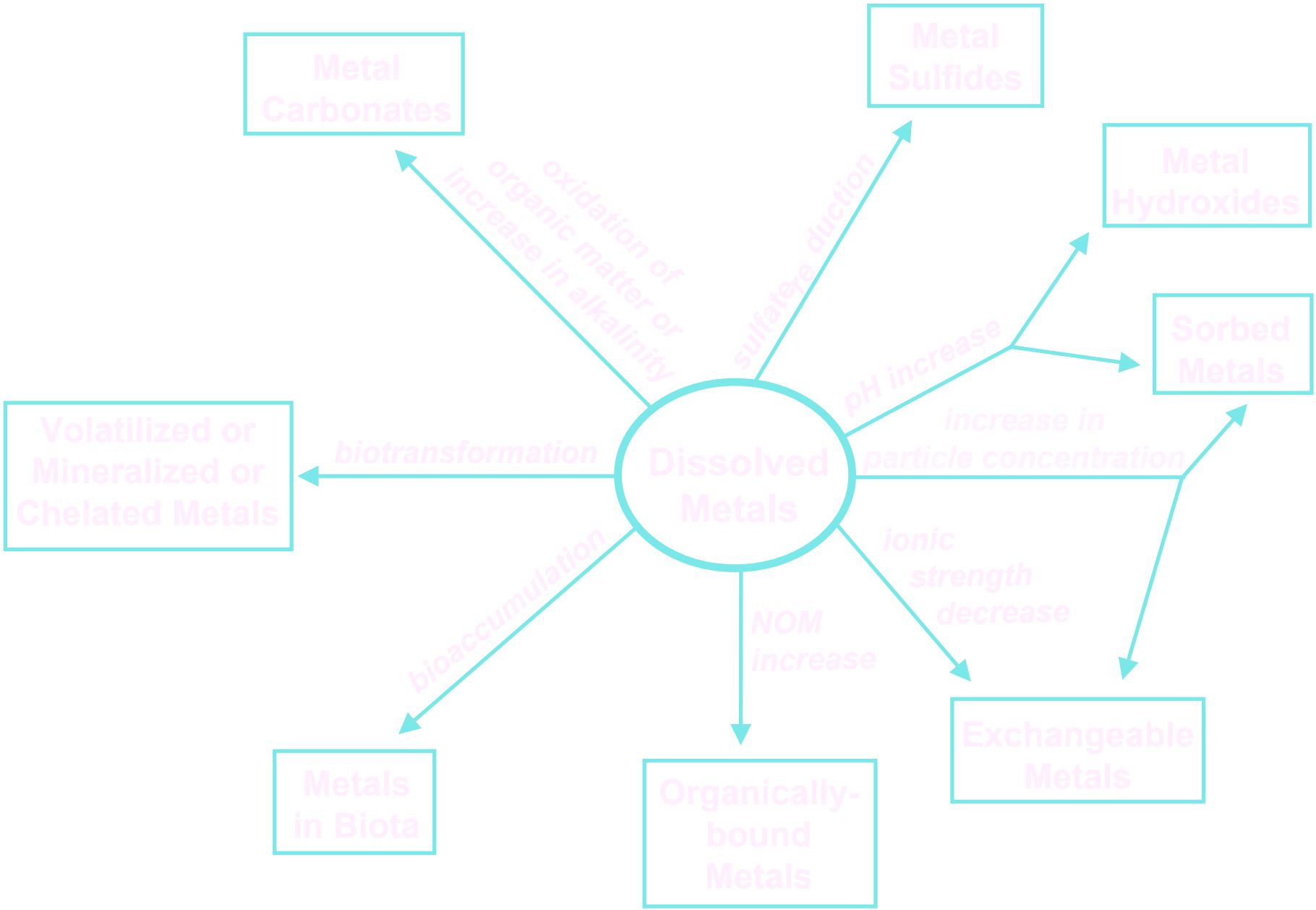

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Smith and Huyck (1999)