



Fundamentals of Mine-Drainage Formation and Chemistry

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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



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



Oxidation Reactions

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

Initiator Reaction:

Propagation Cycle: $Fe^{2+} + 0.25 O_2 + H^+ \xrightarrow{Bacteria} 0.5 H_2O + Fe^{3+}$ $14 Fe^{3+} + FeS_2 + 8 H_2O \xrightarrow{}$ $15 Fe^{2+} + 2 SO_4^{2-} + 16 H^+$ Acidity





Pyrite oxidation by ferric iron (Fe³⁺): $FeS_2 + 14 Fe^{3+} + 8 H_2O \longrightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^+$

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

Pyrite oxidation by oxygen:



Oxidation Reactions Pyrite (FeS₂)



Oxidation Reactions Enargite (Cu₃AsS₄)



Enargite oxidation by oxygen:

 $Cu_{3}AsS_{4} + 8.75O_{2} + 2.5H_{2}O \longrightarrow$ 3 Cu²⁺ + HAsO₄²⁻ + 4 SO₄²⁻ + 4 H⁺

Enargite oxidation by ferric iron (Fe³⁺): Cu₃AsS₄ + 35 Fe³⁺ + 20 H₂O \longrightarrow 3 Cu²⁺ + 35 Fe²⁺ + HAsO₄²⁻ + 4 SO₄²⁻ + 39 H⁺



Sources of Fe³⁺

Microbially catalyzed oxidation of Fe(II)

- 10⁶ 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



Soluble Salts

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







Acid-Generating Reactions

Hydrolysis of metal cations $Fe^{3+} + 3 H_2O \longrightarrow Fe(OH)_3 + 3 H^+$ $AI^{3+} + 3 H_2O \longrightarrow AI(OH)_3 + 3 H^+$



Acid-Generating Reactions



Precipitation of hydrous metal-oxide minerals





Acid-Consuming Reactions

- Dissolution of carbonate minerals releases Ca, Mg, H₂CO₃° or HCO₃⁻ or CO₃²⁻
- Dissolution of aluminosilicate minerals releases AI, 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





Acid-Consuming Reactions

Most weathering reactions consume acid

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

calcite

 $\begin{array}{rcl} \mathsf{KAI}_3\mathsf{Si}_3\mathsf{O}_{10}(\mathsf{OH})_2 + \mathsf{H}^+ + 9 \,\mathsf{H}_2\mathsf{O} \longrightarrow \\ & \\ & \\ \mathsf{muscovite} & \mathsf{K}^+ + 3 \,\mathsf{H}_4\mathsf{SiO}_4 + 3 \,\mathsf{AI}(\mathsf{OH})_3 \end{array}$



The Carbonate System

$$CO_{2 (g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3 (aq)}$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$
$$> \text{ Important pH buffering system}$$
$$> \text{ Usually responsible for alkalinity}$$



Carbonate Buffering



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., Ca²⁺, Mg²⁺)
 - Water-quality criteria for some metals are hardness-dependent
 - In mining impacted systems, Ca²⁺, Mg²⁺, etc. can originate from the weathering of a variety of minerals







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



Geoavailability

"...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)





Trace Elements in Natural Waters

Regardless of their source, high concentrations of <u>dissolved</u> 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







Smith and Huyck (1999)