

Overview of geochemistry, acid generation, and metal solubility



Spring Creek, 1974, pH =2.75

Acid/base

- Acid (mine/rock) drainage (pH < 1 to 6)
 - One of largest water quality problems at hardrock mine sites
 - Starts with pyrite/fools gold in mine sources
 - Need water and air
 - Leaches more metals in mine sources
 - Harms drinking water, aquatic biota and habitat (stream beds), vegetation
- Basic mine drainage (pH 8.5 to 12+)
 - Tailings; cyanide; weathering of rocks

Contaminants of concern

- Metals
- Acid
- Radionuclides
- Sulfate, nitrate
- Extraction/beneficiation reagents (e.g., cyanide)

Metals

- Cadmium, copper, lead, zinc
 - Copper mines
 - Gold mines
- Cobalt, nickel, chromium, uranium, vanadium, molybdenum, tungsten
- Mercury
- Lithium
- Iron, manganese, aluminum
 - Potential baseline issues
- Thallium, beryllium
 - “Rare” contaminants that are toxic in low concentrations
- Metalloids
 - Arsenic
 - Selenium
 - Antimony

Non-metal Anions

- Fluoride
 - Hydrothermal mineral deposits commonly contain fluorite
- Chloride
 - Saline waters associated with mineral deposits
- Sulfate
 - Often high from pyrite oxidation and gypsum dissolution

Relation of mineralogy to water chemistry

Aqueous Element	Most Common Mineral Source
F	fluorite
SO ₄	pyrite, gypsum
Fe	pyrite, hematite, goethite,
Mn	Mn-oxides, rhodochrosite
Al	clays, feldspars, micas
Cu	chalcopyrite, bornite, malachite
Zn	sphalerite, smithsonite
Cd	sphalerite, smithsonite
Pb	galena, anglesite, cerrusite
As	arsenian pyrite, arsenopyrite
Co, Ni	pyrite, pyrrhotite, sulfides
Cr	chromite, micas, chlorites

COMMON MINERALS

“REACTIVE”

Simple Stoichiometry

Halite
Gypsum
Calcite
Fluorite
Barite
Gibbsite
Ferrihydrite
Siderite
Rhodochrosite
Magnesite
Strontianite
Witherite
Celestine
Microcrystalline Silica
Melanterite
Pyrite
Sphalerite

Complex Stoichiometry

Equilibrium Possible

Kaolinite
Dolomite
Talc
Zeolites
Alunite
Jarosite
Smectites

“NON-REACTIVE”

Quartz
Rutile
Zircon
Magnetite
Spinel
Ilmenite
Kyanite
Olivines
Pyrophyllite

Titanite (Sphene)
Tourmaline
Garnets
Pyroxenes

Equilibrium Unlikely

Feldspar
Amphibole
Micas
Chlorites

Basic geochemical processes

- Mineral precipitation/dissolution



- Complexation



- Acid/base reactions



- Sorption



- Oxidation/reduction



Basic geochemical processes

- Mineral precipitation/dissolution, example with fluorite



In a high bicarbonate water calcium will precipitate as calcite:



(incongruent)

Complexation

In a water with ~~high~~ aluminum concentrations, the solubility of fluorite increases because of complexation:



Solubility-product, K_{sp}



When equilibrium solubility, or saturation, is reached
The ion-activity product becomes solubility-product
constant:

$$\text{IAP} = a_{\text{Ca}^{2+}} a_{\text{F}^-}^2 = K_{sp}$$

The ratio of the IAP to the K_{sp} is then unity and is
called the degree of saturation

THE SATURATION INDEX

IAP = ION ACTIVITY PRODUCT

K_{sp} = SOLUBILITY PRODUCT CONSTANT

THE DEGREE OF SATURATION, Ω

$$\Omega = \frac{IAP}{K_{sp}}$$

THE SATURATION RATIO, S (PREFERABLE)

$$S = \left(\frac{IAP}{K_{sp}}\right)^{\frac{1}{v}}$$

where v is the total number of ions
in the formula unit ($v = v_+ + v_-$)

THE SATURATION INDEX

$$SI = \log \Omega = \log\left(\frac{IAP}{K_{sp}}\right)$$

THE NORMALIZED SATURATION INDEX
(PREFERABLE)

$$\log S = \frac{SI}{v} = \frac{1}{v} \log\left(\frac{IAP}{K_{sp}}\right)$$

Acid/base reactions

Many minerals are more soluble in a strong acid or a strong base:



This behavior is readily apparent for metal hydroxides

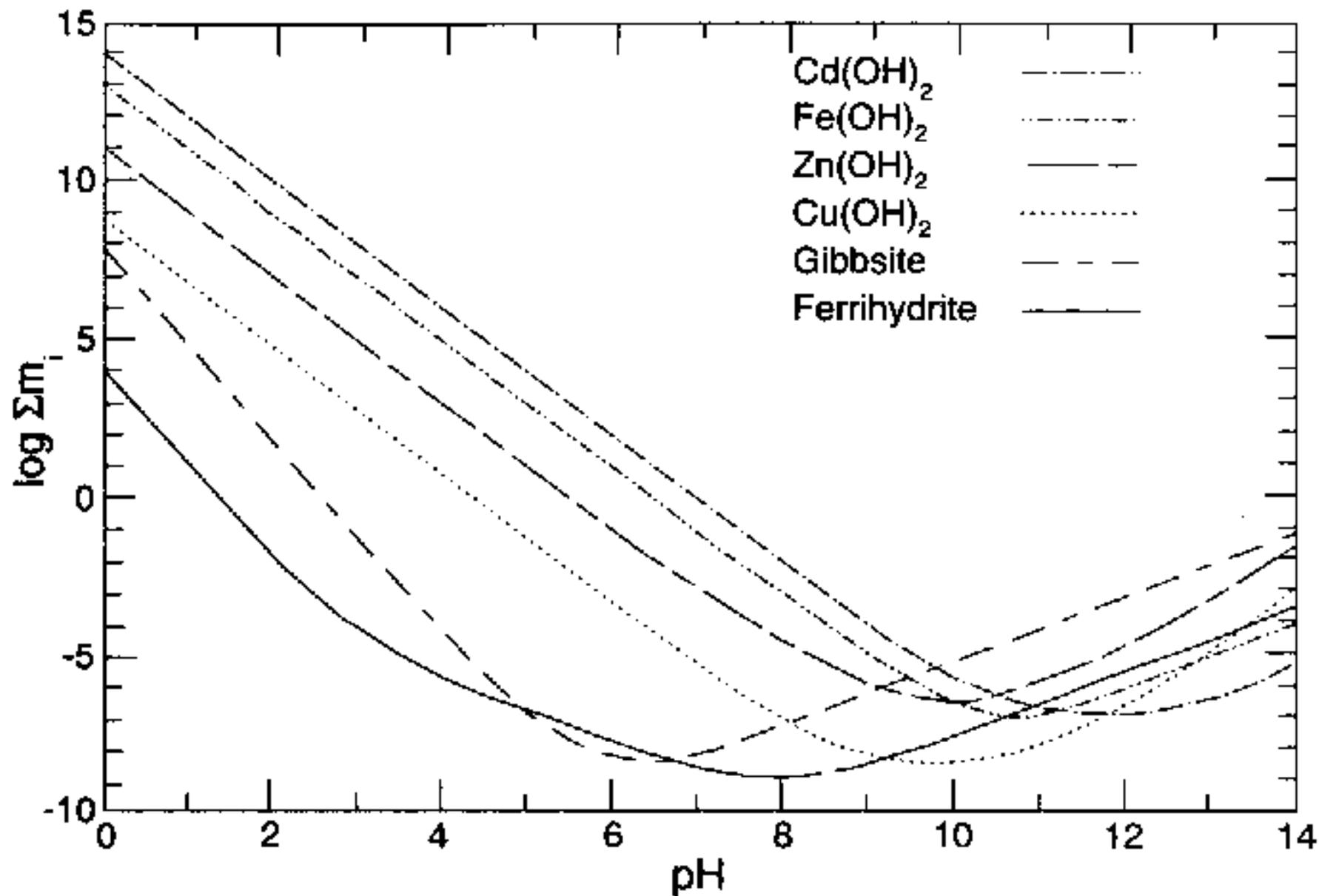


FIGURE 6.6—Solubility curves for gibbsite, ferrihydrite, and the hydroxides of Cu, Zn, Fe (II), and Cd shown as a function of pH.

Sorption – adsorption desorption

Binding of an aqueous species to a surface



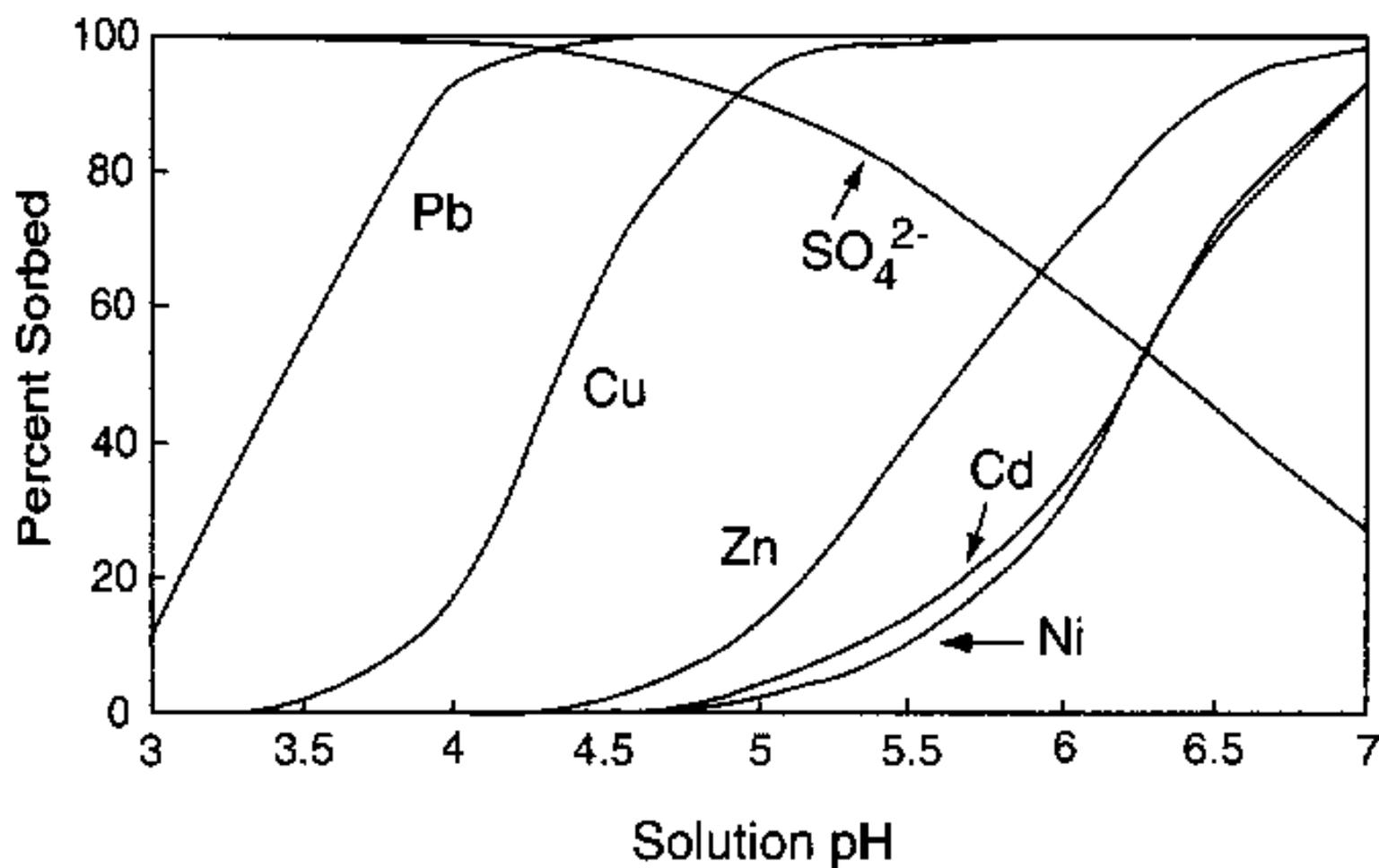


FIGURE 7.3a—Model sorption curves showing relative placement of adsorption edges of selected metals and sulfate on hydrous ferric oxide. Model input was for geochemical conditions from a stream receiving acid-mine drainage. Modified from Smith and Macalady (1991).

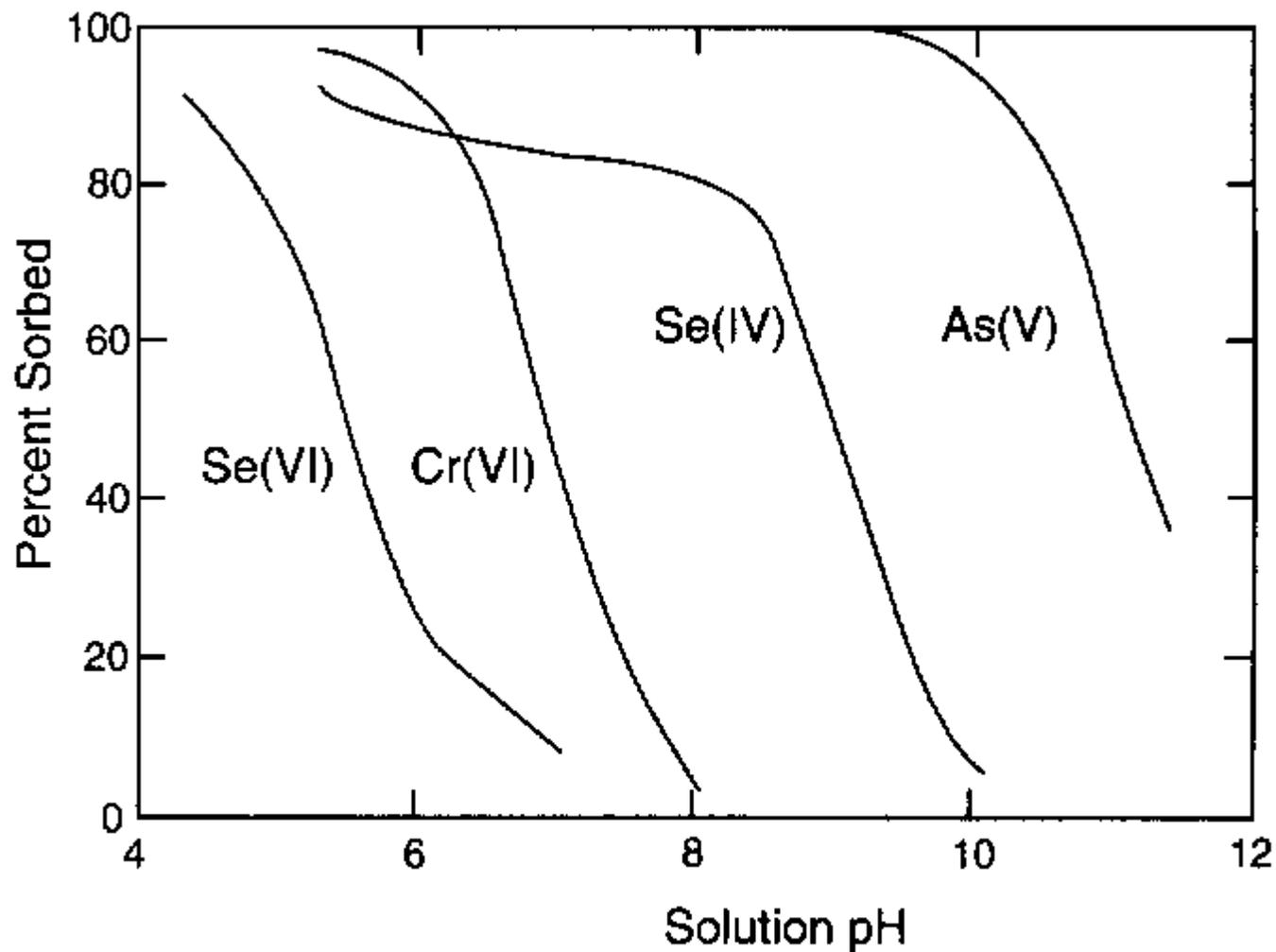
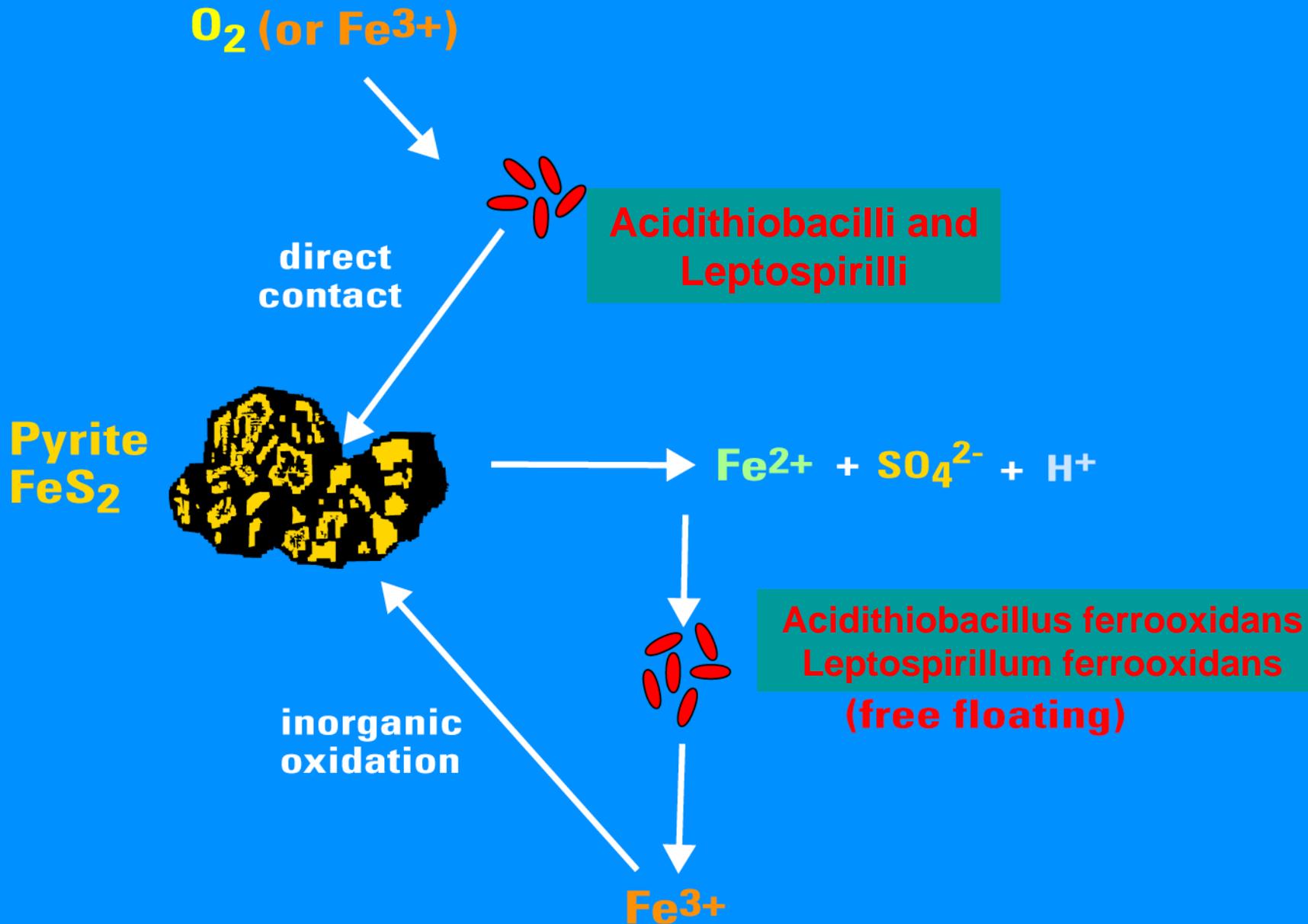


FIGURE 7.3b—Sorption curves showing relative placement of adsorption edges of selected oxyanions on hydrous ferric oxide. Modified from Davis and Kent (1990).



Pyrite oxidation



Pyrite + air + water acid ferrous sulfate soln



Oxidation rates from the literature

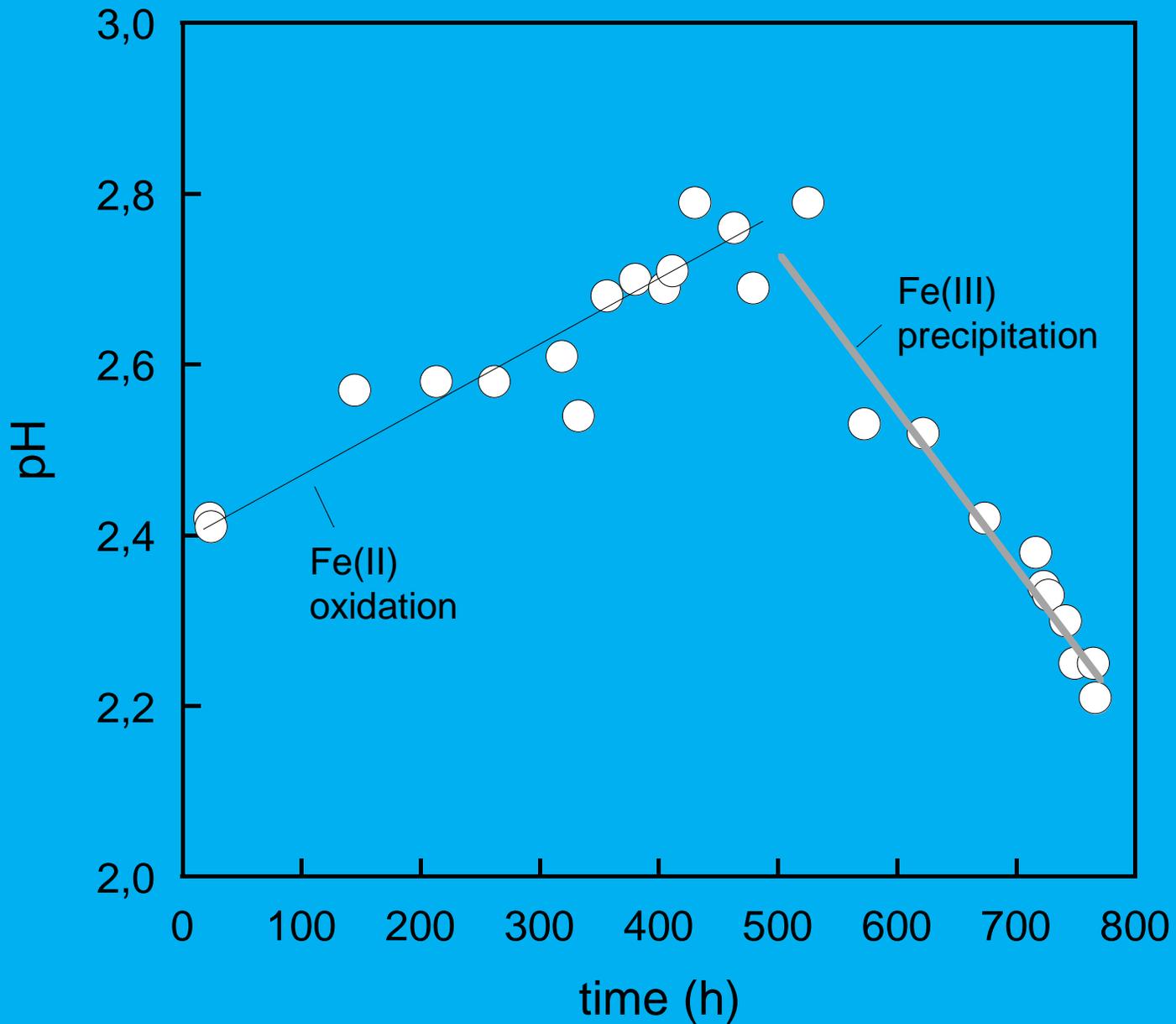
Mineral/Oxidant	Rate
Pyrite/O ₂ (abiotic)	1-5x10 ⁻¹⁰ mol m ⁻² s ⁻¹
Pyrite/Fe ³⁺ (abiotic)	1x10 ⁻⁸ mol m ⁻² s ⁻¹
Pyrite (biotic, <i>A. ferro.</i>)	9x10 ⁻⁸ mol m ⁻² s ⁻¹

show that ferric iron oxidizes pyrite more rapidly than oxygen by 2 orders of magnitude and with microbes it is another order of magnitude faster

Oxidation of aqueous Fe(II)

Abiotic rate	Microbial rate	Field Rate
$3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$	$5 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$	$5 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$

Nordstrom and Alpers (1999) estimated that the oxidation rate of pyrite by Fe(III) is slightly slower than the rate of Fe(II) oxidation by microbes; hence, pyrite oxidation will occur as fast as the microbes can grow.



Microbial oxidation

Microbial communities can be composed of a large number and diversity of bacteria, algae, and archaea. However, those most commonly encountered bacteria are:

- *Leptospirillum ferrooxidans*
 - *Acidithiobacillus ferrooxidans*
 - *Acidithiobacillus thiooxidans*
- and several strains of these.

Archaea have been found such as those of the *Ferroplasma* genus.

Table 1. Members of the Bacteria genera *Thiobacillus* (arranged alphabetically by species name), *Leptospirillum*, and *Sulfobacillus*, the inorganic substances they utilize (adapted from Kelly and Harrison 1984 and Barrett et al. 1993, except where otherwise indicated), and four additional Archaea spp. that are known to be associated with acid mine waters and pyrite oxidation. Acidophilic species are shown in bold type.

<i>Thiobacillus albertis</i>	H ₂ S, S ₂ O ₃ ²⁻
<i>Thiobacillus acidophilus</i> ¹	S ⁰ , S ₂ O ₃ ²⁻ , S ₃ O ₆ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus denitrificans</i>	H ₂ S, S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus delicatus</i>	S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus ferrooxidans</i>	H ₂ S, sulfide minerals, S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻ , Fe ²⁺
<i>Thiobacillus halophilus</i> ²	S ⁰
<i>Thiobacillus intermedius</i>	S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus neapolitanus</i>	H ₂ S, sulfide minerals, S ⁰ , S ₂ O ₃ ²⁻ , S ₃ O ₆ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus novellus</i>	S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus perometabolis</i>	S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus tepidarius</i>	H ₂ S, S ⁰ , S ₂ O ₃ ²⁻ , S ₃ O ₆ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus thermophila</i> ³	H ₂ S, sulfide minerals, S ⁰
<i>Thiobacillus thiooxidans</i>	S ⁰ , S ₂ O ₃ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus thioparus</i> ⁴	H ₂ S, sulfide minerals, S ⁰ , S ₂ O ₃ ²⁻ , S ₃ O ₆ ²⁻ , S ₄ O ₆ ²⁻
<i>Thiobacillus versutus</i>	H ₂ S, S ₂ O ₃ ²⁻
<i>Leptospirillum ferrooxidans</i>	Fe ²⁺ , sulfide minerals
<i>Leptospirillum thermoferrooxidans</i>	Fe ²⁺ , sulfide minerals
<i>Sulfobacillus thermosulfidooxidans</i>	Fe ²⁺ , S ⁰ , sulfide minerals
Archaea spp.	
<i>Acidianus brierleyi</i>	Fe ²⁺ , S ⁰ , sulfide minerals
<i>Sulfolobus solfataricus</i>	S ⁰
<i>Sulfolobus ambivalens</i>	S ⁰
<i>Sulfolobus acidocaldarius</i>	Fe ²⁺ , S ⁰

¹Also known as *T. organoparus*

²Wood and Kelly, 1991

³Egorova and Deryugina, 1963 (not a *Thiobacillus* sp.)

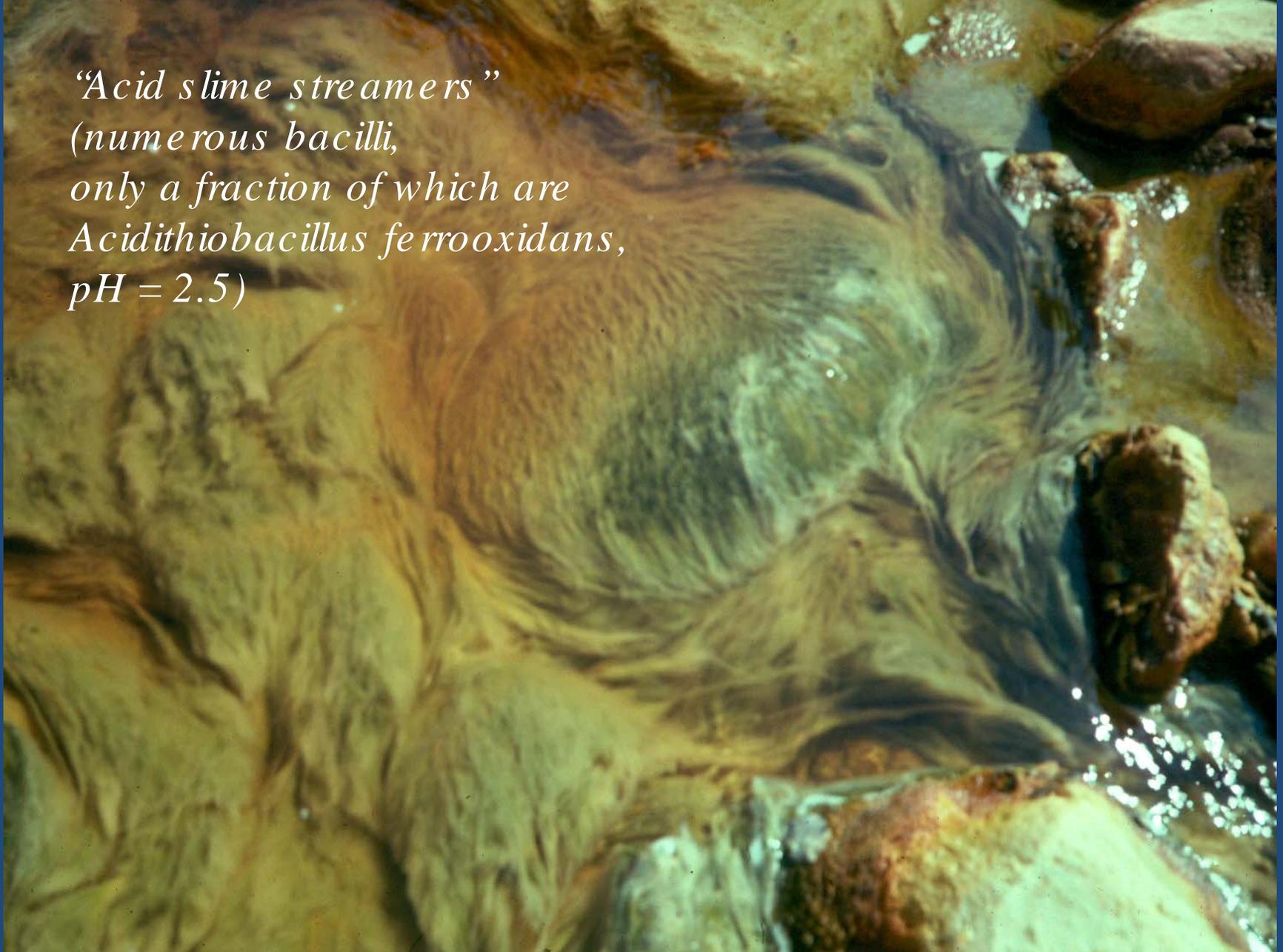
⁴Range of pH = 3 to 10

From Nordstrom
and Southam
(1997)



*Green filamentous algae in
pH 2.5 AMD*

“Acid slime streamers”
(numerous bacilli,
only a fraction of which are
Acidithiobacillus ferrooxidans,
pH = 2.5)



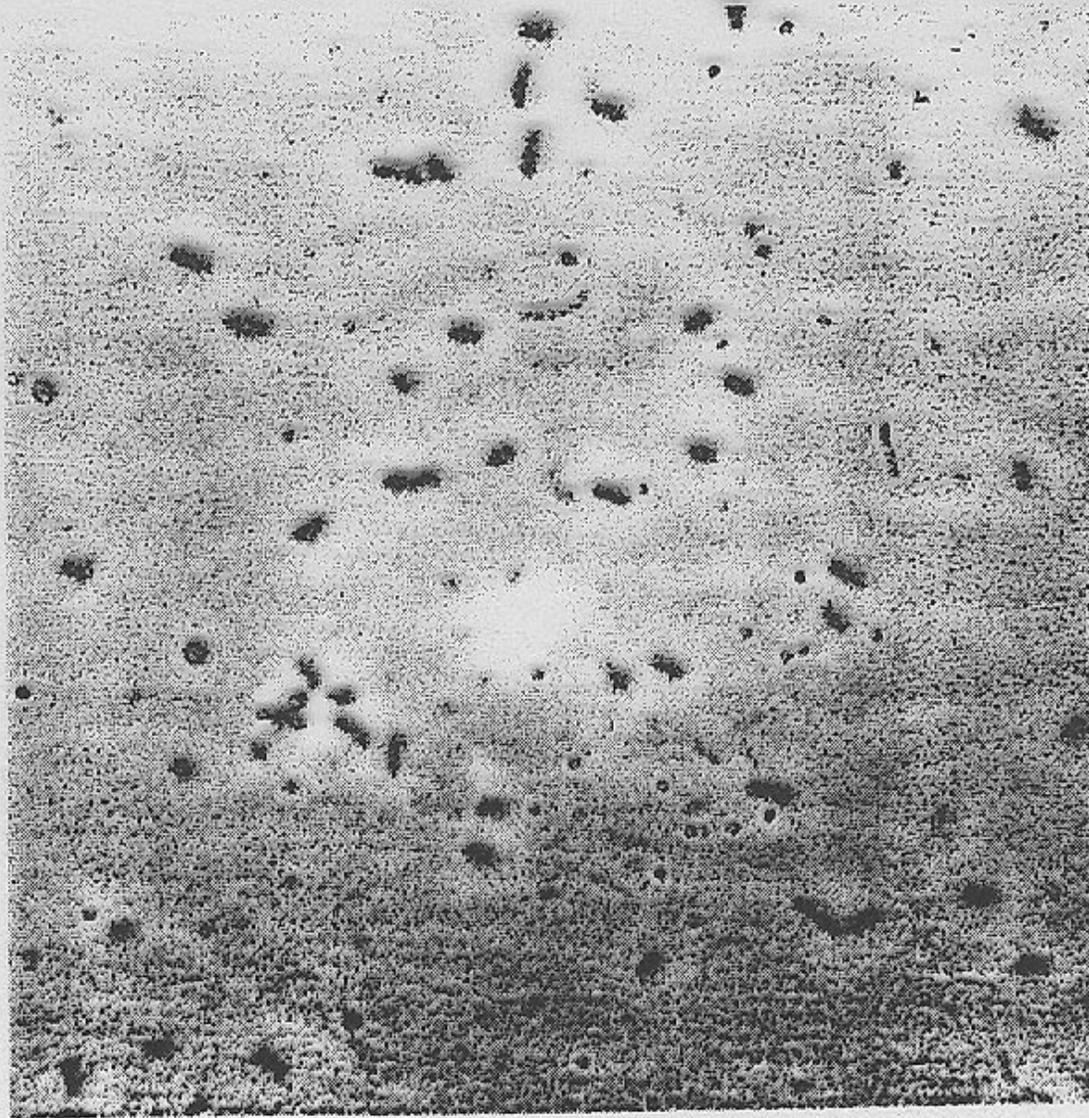


Figure 14.2 *Thiobacillus ferrooxidans* ($\times 5,170$). Cell suspension viewed by phase contrast.
(*Acidithiobacillus ferrooxidans*)



Figure 14.3 *Thiobacillus ferrooxidans* ($\times 30,000$). Electron photomicrograph of a thin section. (Courtesy of D. G. Lundgren.)

Remediation of mine sites by application of bacteriacides has been researched and tried.

There are two main problems:

- the application has to be continued in perpetuity; once it stops, the microbial community reestablishes itself
- bacteriacides can be harmful to aquatic ecosystems

Biological resources/risk assessment

- Aquatic biota
 - Periphyton, aquatic invertebrates, shellfish, fish
- Vegetation
 - Bacteria, algae, vascular plants, effects on crops
- Terrestrial wildlife and livestock
 - Mammals, birds, effects on livestock
- Human health

Impacts on the Environment: *Fate and Transport*

- Physical movement of chemical constituents from sources to receptors (water, aquatic life, people)
- Chemical changes and interactions along that pathway

