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METAL SULFIDE LEACHING POTENTIAL
IN THE DULUTH GABBRO COMPLEX

-A Literature Survey-

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Metal Sulfide Leaching Potential
in the Duluth Gabbro Complex

-A Literature Survey-

Prepared for the
Minnesota State Planning Agency
and
Cu-Ni Regional Study

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Introduction

Copper-nickel mining is fast becoming a reality in northeastern Minnesota where significant deposits of base metal sulfides comprise the Duluth Gabbro Complex. Prior to initiation of site-specific environmental impact statements, the State of Minnesota has authorized the preparation of perhaps one of the most scientifically meaningful regional environmental impact statements. One of the problems causing potential concern is the release of toxic heavy metals through the leaching of lean ore, tailings, waste rock and displaced overburden. A task force consisting of Professors Eisenreich, Bydalek, Iwasaki and Hoffmann were charged with surveying the literature relevant to environmental metal leaching. The following literature survey is the result of our efforts. The scientific literature in the areas of chemistry, biology, hydrology and mining as well as reports and unpublished data were consulted. Computer searches were initiated in Water Resources Abstracts, Pollution Abstracts, Ecological Abstracts, Mineralogical Abstracts, Engineering Index, Chemical Abstracts and Biological Abstracts. To our astonishment, surprisingly little research on metal leaching processes under environmental situations has been reported. Thus, the authors summarized the fundamental processes of metal sulfide leaching and subsequently applied, by inference and implication, this information to the mining of Cu-Ni in the Duluth Gabbro Complex.

Duluth Gabbro Complex-Geology and Mineralogy

Geology

Copper-nickel mineralization in the Duluth Gabbro of northeastern Minnesota has been known for more than 90 years with early estimates of six million tons of ore assaying at least 0.5% combined copper-nickel. Recent estimates (Bonnichsen, 1974) show that the deposits in the Ely-Hoyt Lakes region alone contain between 2 and 14 billion tons of mineralized rock having a combined nickel-copper content of 0.5 to 1.0%, and a 3:1, Cu:Ni ratio. Several reports outlining the geology and mineralogy of the Duluth Gabbro have been published and are summarized below (Boucher, 1975; Bonnichsen, 1972, 1975; Lawver et al., 1975; Sims, 1968; Weiblen, 1965, 1975; Phinney, 1972; Hardyman, 1969).

The Duluth Gabbro Complex is a large body of mafic and anorthositic plutonic rocks of Late Precambian age that underly nearly 2,500 square miles of northeastern Minnesota (Figure I). The large formation of various igneous rocks comprising the Gabbro stretches northwards from Duluth, Minnesota to about ten miles south of Ely, then northeastwards to about ten miles north of Grand Marais. The Duluth Complex has the general composition of a feldspar-rich (anorthositic) gabbro, but is made up of many intrusive units which differ in composition and internal structure. Principal segregations of copper and nickel presently known lie along the northwestern margin of the Gabbro near Hoyt Lakes, Babbitt and the Kawishiwi River, southeast of Ely. Significant open pit mining operations for taconite are presently active in the Mesabi Range to the west and north. Disseminated

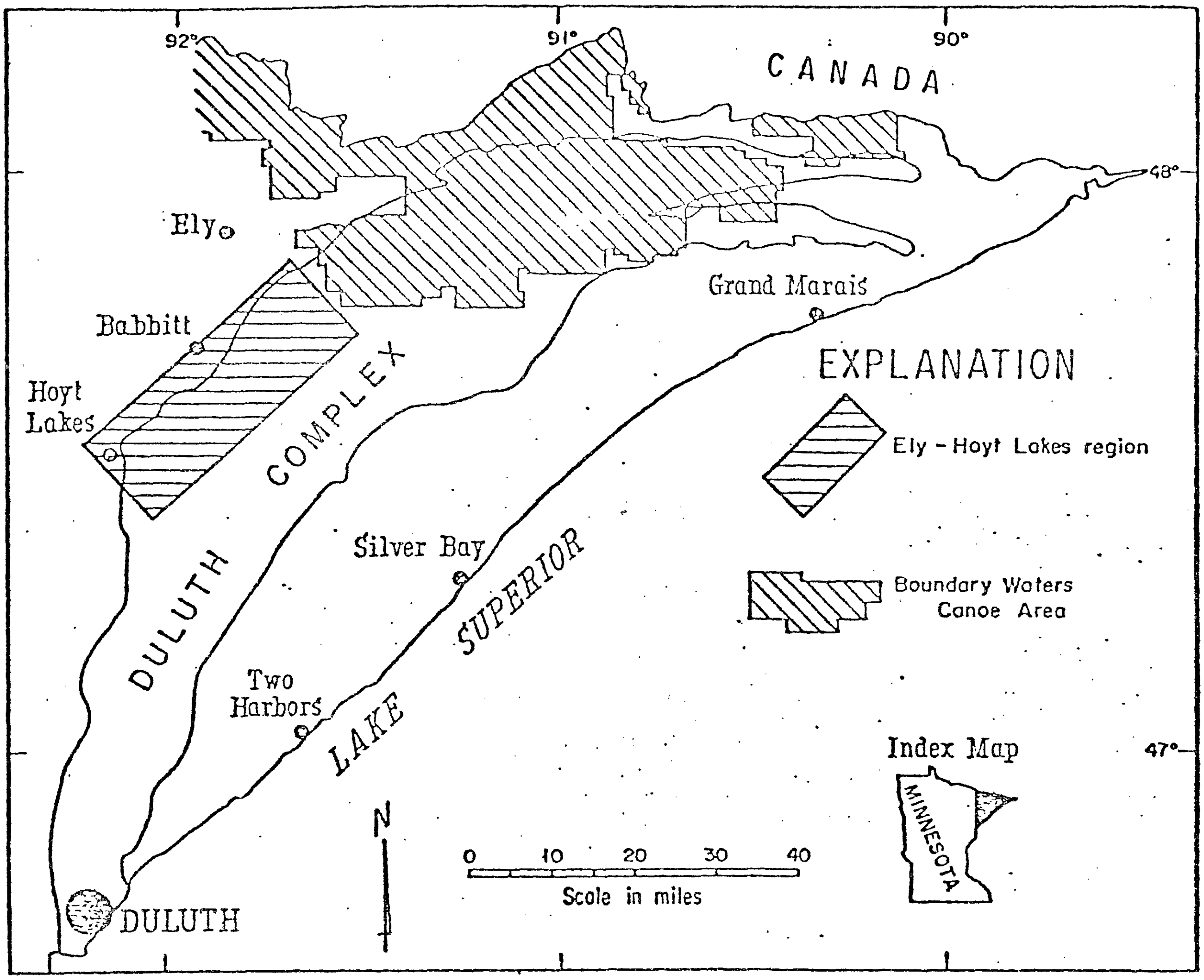


Figure 1. Map of northeastern Minnesota, showing the location of the Ely-Hoyt Lakes region relative to the Duluth Complex and to the Boundary Waters Canoe Area.

deposits of copper and nickel sulfide ore are mostly confined to the area near the base of the Duluth Complex and reported to be from 50 to 300 feet in aggregate thickness. Exploratory mine shafts have been sunk by INCO and AMAX along the contact zone. The economically-important copper-nickel deposits lie in an inclined zone several hundred feet thick and 30 to 35 miles long. Significant concentrations of copper-nickel sulfide ore have been traced to nearly one mile.

Mineralogy

The copper and nickel sulfides in the Duluth Gabbro are combined with iron and sulfur in a complex intergrowth. The major sulfide minerals in decreasing order of abundance are: pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$) and pentlandite $(Fe,Ni)_9S_8$). The proportions of these minerals differ widely from place to place in the Gabbro. Bornite (Cu_5FeS_4) and sphalerite (ZnS) are present in much lower concentrations. The metal sulfides are disseminated as small particles found in the interstices between silicates (plagioclase, olivine, pyroxene) or intimately intergrown with the silicates. Bonnichsen (1972) reported that the major zones of sulfide concentration "vary in shape, from lenses that are parallel to the base of the Gabbro, to lenses or very elongated bodies that are inclined to the base, to irregular lenses."

The copper-nickel ratio is about 3:1 in the mineralized parts of the basal intrusive unit but varies from 1:1 to 8:1 in bodies of underlying granite. For comparison purposes, the Cu:Ni ratio in the Sudbury, Ontario mining region is closer to 1:1. Other metals present as sulfides or other combined form which are present in potentially attractive concentrations economically include cobalt, silver, palladium, gold, platinum and rhodium. Careful mineralogical and chemical analysis of numerous drill cores have been reported in the last twenty years (Boucher, 1975; Bonnichsen, 1972; 1975; Grosh, et al., 1955).

A typical ore assayed from the contact area is approximately 1.0% combined copper-nickel dropping to 0.5% combined at depth. Average percentages for the copper and nickel concentration in ore are (0.45-1.0)% and (0.05-.35)% respectively. Chemical concentrations and relative abundance of major and minor minerals is discussed in the following section.

Composition of Gabbroic Materials

It may be useful for the non-geologists involved in the study of the chemical and biological properties of gabbro material to have working definitions of commonly encountered geological terms and some idea of the mineralogies and compositions of the gabbroic and contact zone rocks in the study area. To this end, the following sections are provided;

A. A list of most of the minerals found in the rocks of the Duluth complex and the contact zone defined in terms of chemical compositions and solid-solution relationships. The formula for a given mineral may be expressed in different forms in different references. Cation substitution in many minerals often makes exact representation implausible. Notations of the form (Mg,Fe) in the formulas indicates which cations may substitute in a given crystallographic site.

B. A minimal glossary containing a few geological terms commonly encountered in the literature bearing on the study. The definitions are taken, for the most part, from the A.G.I. Glossary of Geology

(Gary et al., 1972). While they may not be universally accepted, they do provide a frame of reference. The authors of the individual studies cited may more precisely define terms where they vary from generally accepted definitions or are by nature somewhat ambiguous.

C. Tables of average compositional characteristics of the gabbroic and related rocks from the Duluth complex and the basal contact zone compiled using data from several detailed petrographic studies. It should be noted that the averages are taken over series of related rocks and one for the troctolitic-gabbroic rocks of the complex). For detailed textural descriptions, the references cited are suggested (Anderson, 1956; Hardyman, 1969; Renner, 1969; Boucher, 1975; Phinney, 1972). An overall view of the geology of the entire study area is provided in papers by Bonnichsen (1972a, b, 1974) and Phinney (1969, 1972).

MINERALS

Below are listed most of the minerals occurring in the rocks of the Duluth complex and the contact zone in the study area.

Major minerals

plagioclase: [$(Na,Ca)AlSi_3O_8$]: a continuous solid-solution feldspar series with end members albite ($NaAlSi_3O_8$) to anorthite ($CaAlSi_3O_8$). Series members in order of increasing anorthite percent are: albite (An_0-An_{10}); oligoclase (An_{10}-An_{30}); andesine (An_{30}-An_{50}); labradorite (An_{50}-An_{70}); bytownite (An_{70}-An_{90}); anorthite (An_{90}-An_{100}).

olivine: [$(Mg,Fe)_2SiO_4$]: continuous solid-solution series with forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) as end members. Intermediate varieties are olivine.

pyroxene: a closely related group of mafic minerals commonly divided into two groups based on crystal structure.

orthopyroxenes: (orthorhombic crystal structure) enstatite ($MgSiO_3$) to hyperstehene [$(Mg,Fe)SiO_3$] forming a continuous series not extending to pure $FeSiO_3$.

clinopyroxenes: (monoclinic crystal structure) the main clinopyroxenes are clino-enstatite ($MgSiO_3$), clino-hypersthene $(Mg,Fe)SiO_3$, diopside ($CaMgSi_2O_6$), hedenbergite ($CaFeSi_2O_6$) augite (intermediate between diopside and hedenbergite), and pigeonite (intermediate between clino-enstatite and augite). The most common pyroxenes in the Duluth complex rocks are augite-pigeonite and slightly less hypersthene.

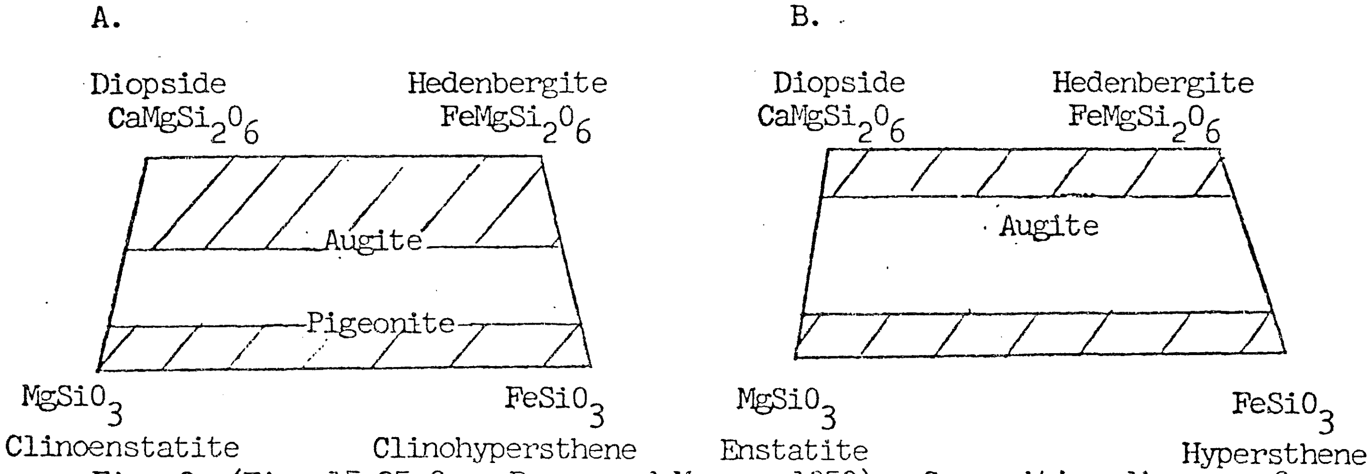


Fig. 2 (Fig. 15-35 from Berry and Mason, 1959). Composition diagrams for the common pyroxenes. (A.) at high temperatures (B.) at medium temps. The unshaded areas are miscibility gaps between the high- and low-calcic pyroxene series.

Accessory and minor minerals

biotite: $[K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2]_a$ a mica commonly occurring as an accessory mineral in these rocks.

sulfide minerals

chalcopyrite: [$CuFeS_2$]: the most common copper-sulfide phase in the mineralized zone.

cubanite: [$CuFe_2S_3$]: one of the two principal copperbearing sulfide phases.

pentlandite: [$(Fe,Ni)_9S_8$]: the iron/nickel ratio in pentlandite is somewhat variable but usually close to 1/1.

pyrrhotite: [$Fe_{1-x}S$]: x may vary from 0 to 0.2.

pyrite: [FeS_2]

bornite: [Cu_5FeS_4]

troilite: [FeS]

mackinawite: [FeS]

valleriite: [$CuFeS{:}Mg,Al,Fe(OH)_2$]

sphalerite: [(Zn,Fe)S]

violarite: [$(Ni,Fe)_3S_4$]

talnakhite: [$Cu_{10}(Fe,Ni)_{18}S_{32}$]

oxide minerals

magnetite: [Fe_3O_4]

ilmenite: [$FeTiO_3$]

spinel: [$(-,Mg)(-,Ti,Al)_2O_4$]: (-) are appropriate cations

serpentine: [$Mg_6Si_4O_{10}(OH)_8$]: an alteration product of olivine.

sericite: [$KAl_2(AlSi_3O_{10})(OH)_2$]: a fine-grained variation of muscovite. A common alteration product.

apatite: [$Ca_5(PO_4)_3(F,Cl,OH)$]

DEFINITIONS

gabbro:	"a group of dark-colored, basic intrusive igneous rocks composed principally of basic plagioclase (commonly labradorite or bytownite) and clinopyroxene (augite, generally diallage), with or without olivine and orthopyroxene; also, any member of that group. ..."
troctolite:	"a gabbro that is composed chiefly of calcic plagioclase (e.g. labradorite) and olivine with little or no pyroxene."
anorthosite:	a plutonic (formed at depth) igneous rock composed almost entirely of calcic plagioclase.
hornfels:	"a fine-grained rock composed of a mosaic of equi-dimensional grains without preferred orientation and typically formed by contact metamorphism." — (in the study area, the hornfels are thought to be derived from the Virginia Formation argillite

and the Ely Greenstones. They are composed of plagioclase and pyroxene ± olivine, biotite, and oxides.)

picrite: "a dark-colored, ... rock containing abundant olivine along with pyroxene, biotite, possibly amphibole, and less than 10 percent plagioclase. ..." (Boucher, however, uses this term for olivine-rich rocks with up to 45.7 percent plagioclase.)

pegmatite: "an exceptionally coarse-grained (most grains one cm or more in diameter) igneous rock, with interlocking crystals ..."

norite: "A coarse-grained plutonic rock containing basic plagioclase (labradorite) as the chief component and differs from gabbro by the presence of orthopyroxene (hypersthene) as the dominant mafic mineral."

granite: "a plutonic rock in which quartz constitutes 10 to 50 percent of the felsic "(feldspar plus quartz)" components and in which the alkali "(K-Na, orthoclase to albite series)" feldspar/total feldspar ratio is generally restricted to the range of 65 to 90 percent." (actually used much more loosely for quartz-alkali feldspar dominated rocks.

greenstone: ".. term applied to any compact dark-green altered basic to ultrabasic igneous rock (e.g., .. basalt, gabbro, diabase, ..) owing its color to the presence of chlorite, hornblende, and epidote.. ."

iron formation: "a chemical sedimentary rock, typically thin-bedded and/or finely laminated, containing at least 15% iron of sedimentary origin, and commonly but not necessarily containing layers of chert." - (this describes quite nicely the Biwabik Iron Formation which dips under the gabbro complex in the southern part of the study area.)

argillite: "a rock derived from clay and silt which has been compacted more highly than a shale and less highly than a slate."- (the Virginia Formation which underlies the Complex in part of the study area is thought to have provided much of the material now seen as hornfelses and xenoliths in the Duluth complex, is largely argillite.)

Table 1. Average modal composition of gabbroic rocks; in vol.%.

	1.		2.		3.		4.		5.
	ave.	range	ave.	range	ave.	range	ave.	range	range
plagioclase	60	40-79	60.2	20.8-82.7	58.8	6.1-95.1	76.4	65.6-88.0	55-80
olivine	14	0.34	24.9	0.0-76.3	21.1	0-53.9	7.7	tr-19.3	12-30
hypersthene (OPX)	6	0-45	1.1	0.0-15.9			4.9	0.6-23.9	2-14
augite (CPX)	7	0.40	5.4	0.0-27.9	6.0	0-47.7	5.5	2.6- 9.7	
biotite	2	0- 8	2.1	0.0- 5.9	.9	0- 5.2	1.5	.4- 3.5	1- 4
serpentine	3	tr-20	(1)	tr- 45.8	1.5	0-16.6			0- 5
chlorite	3	0- 5							0- 5
magnetite	2	0- 5							
ilmenite			3.5	0.0-18.4	4.1	0-50-7	2.3	1.3- 3.9	6-17
sulfides	2	0- 8							
other	3	0-12	1.4	0.0-34.2	4.8		1.1	0- 4.3	0- 5

1. Anderson. (average of 18 samples-nos.2-19 from Anderson-Table 2. Samples ranged from mineralized to normal to altered gabbros in rock type).
2. Handyman. (average of 49 samples from Table 1., app. 1 in Hardyman's thesis. Rock types range from troctolite to olivine-gabbro to picrite.)
3. Boucher. (ave. of 72 samples from U.S.B.M.- H-IA. excludes hornfels. includes anorthosite, troctolite and olivine gabbro to picrite.)
4. Phinney. (average based on Phinney's ave. data from 318 thin sections of anorthositic gabbro, troctolite and norite from the South Kawishiwi and contact zones.)
5. Vifian, Iwasaki and Bleifuss. 1967. (ranges given by the authors-p.2 for a bulk sample ranging from olivine gabbro to troctolite.)

"other" may include considerable sericite, apatite, amphibole (hydrous equivalents of the pyroxenes), symplecite, [talc $Mg_3Si_4O_{10}(OH)_2$],etc.

Table 2. Average modal composition of hornfels and contact rocks.

	1a.		2a.		3a.	
	ave.	range	ave.	range	ave.	range
plagioclase	54.4	45.7-65.8	48.8	10.3-75.8	44.6	40.6-48.7
olivine			8.0	0-17.0		
OPX (hyp.)	29.6	2.0-44.9	12.8	0-40.6	10.8	6.3-15.4
CPX (augite)	3.3+	.4-13.2	17.4	0-65.4		
biotite	1.9	.1- 7.4	.7	0- 2.2	17.6	13.6-20.6
opaques (ilm)	4.5	2.0-10.6	3.3	0- 8.5	13.9	4.3-23.5
(sulf)	.9+	.1- 9.6				
other	3.0	0-11.3	3.3	0-16.4	13.5	

1a. Renner, 1969. (ave. of 16 samples from "D-series" rocks from the Duluth complex-Virginia Fm. contact zone.)
2a. Boucher, 1975. (ave. of 9 samples from U.S.B.M.-DDH-IA. hornfels)
3a. Hardyman, 1969. (these averages are based only on 2 samples of hornfels and are thus rather poor as averages.)

Table 3. Opaque compositional distribution (vol. %).

	1b.	2b.*	3b.	4b.		
				Cu	Fe	S
chalcopyrite	31.5	44.8	22.7	34	33	35
cubanite	22.5	13.4	11.2	22	43	35
pyrrhotite	22.4	37.1	24.3	—	61	39
pyrite	2.3					
violarite	3.5					
pentlandite	4.9	5.7	3.4			
oxides	12.9	*	37.6			
other		tr	.8	(42	27	31)-bornite
ave. vol.% opaque in samples	—	10.6*	8.9			

1b. Anderson, 1956. (ave. vol.% for opaques from 10 samples.)
2b. Hardyman, 1969. (ave. vol.% for sulfides from 15 thin sections.)
3b. Boucher, 1975. (ave. vol.% for opaques from 16 thin sections.)
4b. Hardyman, 1969. (elemental compositions for chalco., cuban., pyrr., and bornite averaged from Hardyman's microprobe anal. on 7,5,4, and 2 grains of the respective sulfides.)
* these averages are based on total sulfides not total opaques.

Table 4. Average plagioclase and olivine compositions.

	1c.	2c.
plagioclase-mole % in An- $CaAlSi_3O_8$	57	51
olivine-mole % Fo- Mg_2SiO_4	53	39

1c. Hardyman, 1969. (plagioclase ave.-24 samples; olivine-35 samples)
2c. Renner, 1969. (plag. ave.-24 samples; olivine ave.-5 samples)

Table 5. Average pyroxene compositions.

	1d.		2d.	
	CPX	OPX	CPX	OPX
mole % enstatite $MgSiO_3$	40	62	38	51
mole % ferrosilite $FeSiO_3$	18	36	19	47
mole % wollastonite $CaSiO_3$	45	1	43	2

1d. Hardyman. (35 CPX (clinopyroxene) samples- 29 OPX samples.)
2d. Renner. (15 CPX camples - 22OPX samples.)

Chemical Leaching of Metal Sulfide Minerals

Little information is available on the chemical oxidation and leaching of metal sulfide minerals with regard to potential environmental contamination in the mineral mining industry. Examples of metal release from stockpiled lean ore, tailings and open pit operations associated with Cu-Ni mining in the Ontario, Canada region are documented by Hawley (1971). Yet understanding of the reactions responsible for metal leaching from metal sulfide deposits under environmental conditions is lacking.

The literature summarized in the following review is drawn from the chemical, hydrometallurgical and mining areas with the emphasis being necessarily on the latter two. A plethora of information is available on the formation of acid mine drainage resulting from pyrite oxidation by oxygen, ferric ion and bacterial-catalyzed reactions. Although not directly applicable to the Gabbro complex, added insight into the general behavior and mechanisms of leaching will be gained. The following review will elucidate 1) the factors responsible for leaching, 2) various leaching models as applied to dump or in-situ leaching, and 3) mechanisms of environmental leaching. Further discussions of base metal sulfide and iron pyrite leaching have been published (Wadsworth, 1972; McKay and Halpern, 1958; Gerlach et al, 1973; Dutrizac and MacDonald, 1974).

The major minerals comprising the Duluth Gabbro complex and considered in the following discussion are silica (Si)-based plagioclase, olivine and pyroxene. The major metal sulfide minerals of economic and environmental interest are chalcopyrite ($CuFeS_2$), cubanite ($CuFeS_2$), pentlandite ($(Fe,Ni)_9S_8$) and pyrrhotite ($(Fe_{1-x})S$) where x may vary from 0 to 0.2. Of lesser concentration are pyrite (FeS_2) and bornite (Cu_5FeS_4). For more detailed mineral analyses, refer to the previous section.

Thermodynamics and Kinetics

The dissolution of metal sulfides resulting in the release of heavy metals and sulfate or elemental sulfur is a chemical process, although thought to be catalyzed by microbial action. As a result, examination of the thermodynamics and kinetics of leaching processes will establish the framework within which leaching occurs.

The principle variables in thermodynamic considerations of mineral assemblages and stability are E_h (electrochemical potential) and pH(-log H^+ activity). Temperature and pressure have relatively small effects on leaching processes within the climatic constraints of the environment. The primary means of depicting thermodynamic considerations of chemical processes is the E_h-pH diagram or Pourbaix diagram (Pourbaix, 1966) whereby all reduction-oxidation reactions of interest are expressed as single electrode reactions in which pH is an important variable as well as concentration of reactants and products. Garrells and Christ (1967) have calculated and constructed numerous E_h-pH diagrams depicting stability regions of minerals and aqueous species. The E_h-pH diagram has been applied to leaching of metal sulfides as a means of predicting products of oxidation as a function of solution acidity. It should be understood that E_h-pH diagrams can depict which reactions are favored thermodynamically but not those which are determined by kinetics. Peters (1971), Garrells and Christ (1967) and Peters (1972) have discussed in great detail the use of E_h-pH diagrams and should be consulted for further details.

The oxidation of metal sulfide minerals is integrally related to the stable and metastable sulfur species in solid or aqueous form. Figure 3. illustrates the E_h-pH relationships of the sulfur-H_2O couple (Garrells and

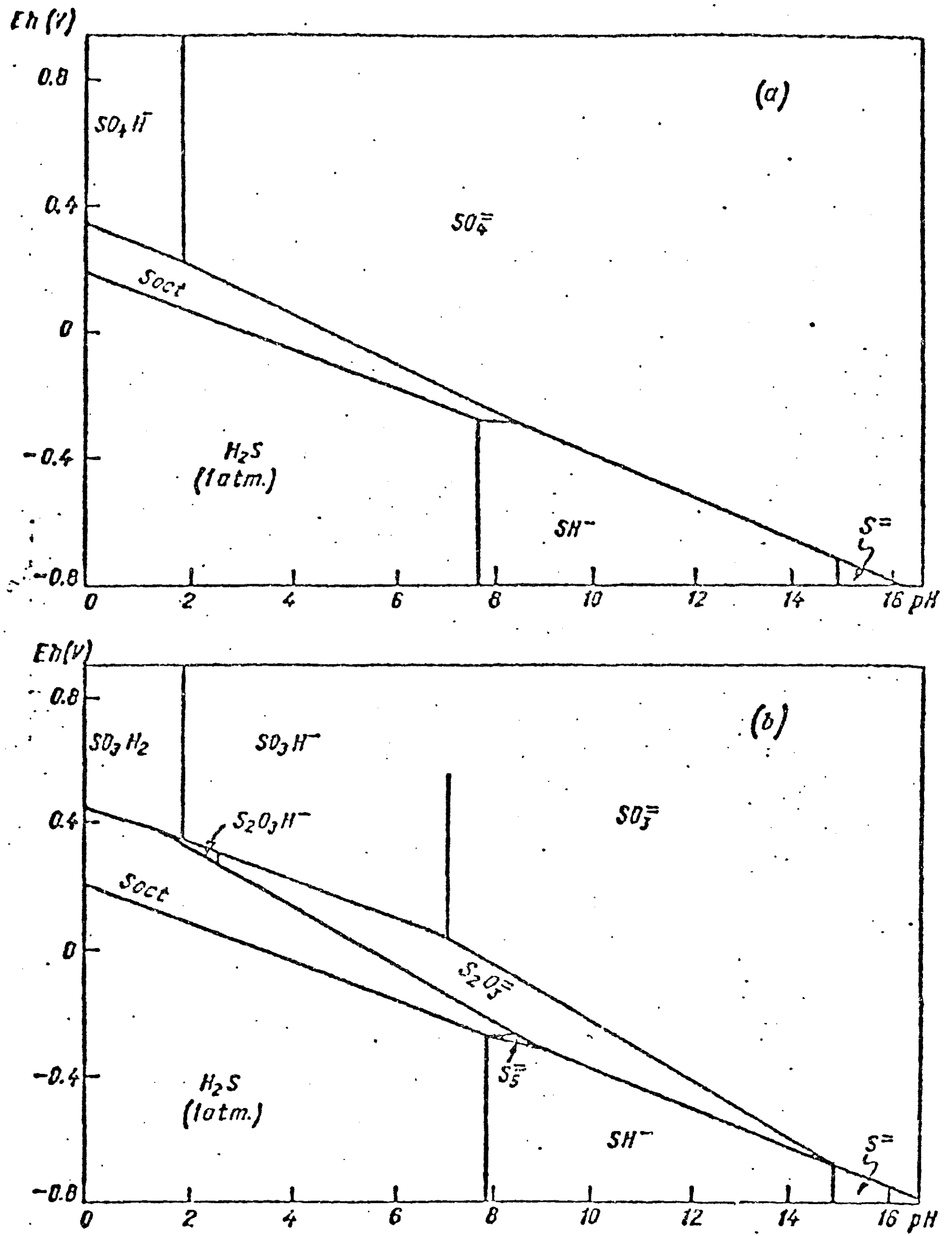


Figure 3. Potential-pH diagrams of the S-H_2O system at 25°C for activity = 1 (a) stable state and (b) metastable state. (From Peters, 1970).

Christ, 1967; Peters, 1970, 1973). The E_h-pH diagram would lead us to predict that the oxidation of reduced sulfur ($S^=$,HS^-,H_2S) would result mainly in $SO_4^=$ formation whereas metastable S species such as $S_2O_3^=$ and $S_5^{\equiv}$ are actually observed.

The E_h-pH diagram for chalcopyrite ($CuFeS_2$), the most prevalent Cu-bearing mineral in the Duluth Gabbro complex, is shown in Figure 4. The diagram predicts that chalcopyrite is stable under conditions of reducing potential and alkaline pH conditions. If chalcopyrite is placed in an acidic, oxidizing environment resulting potentially from the oxidation of pyrrhotite ($Fe_{1-x}S$), chalcopyrite would become unstable and form bornite, pyrite and hydrogen sulfide releasing additional acid. Further oxidation would lead to decomposition of bornite to chalcocite. In reality, the formation of pyrite is exceedingly slow and bornite and chalcocite are unstable under these conditions. Covellite (CuS), the product of $CuFeS_2$ destabilization, is rapidly oxidized by Fe^{+3} or O_2 to form Cu^{+2} and elemental sulfur or sulfate. Chemical oxidation tends to favor metastable S^o formation while bacterial-catalyzed oxidations favor sulfate formation. It is important to remember that E_h-pH diagrams predict reactions which are irreversible kinetically and therefore may not be environmentally accurate. Pyrite formation in the destabilization of $CuFeS_2$ is such an example. In addition, sulfate formation is predicted but in dump leaching situations, elemental sulfur is the principle oxidized sulfur product. In general, the leaching process can be viewed in a E_h-pH diagram as a movement of electrochemical conditions from the bottom lower right (alkaline pH, reducing E_h) to the top upper left (low pH, oxidizing conditions). The leaching process is favored thermodynamically by the introduction of acid and oxidants such as O_2 of Fe^{+3}.

Factors Affecting Leaching

The rate and extent of metal leaching (metal sulfide oxidation) are

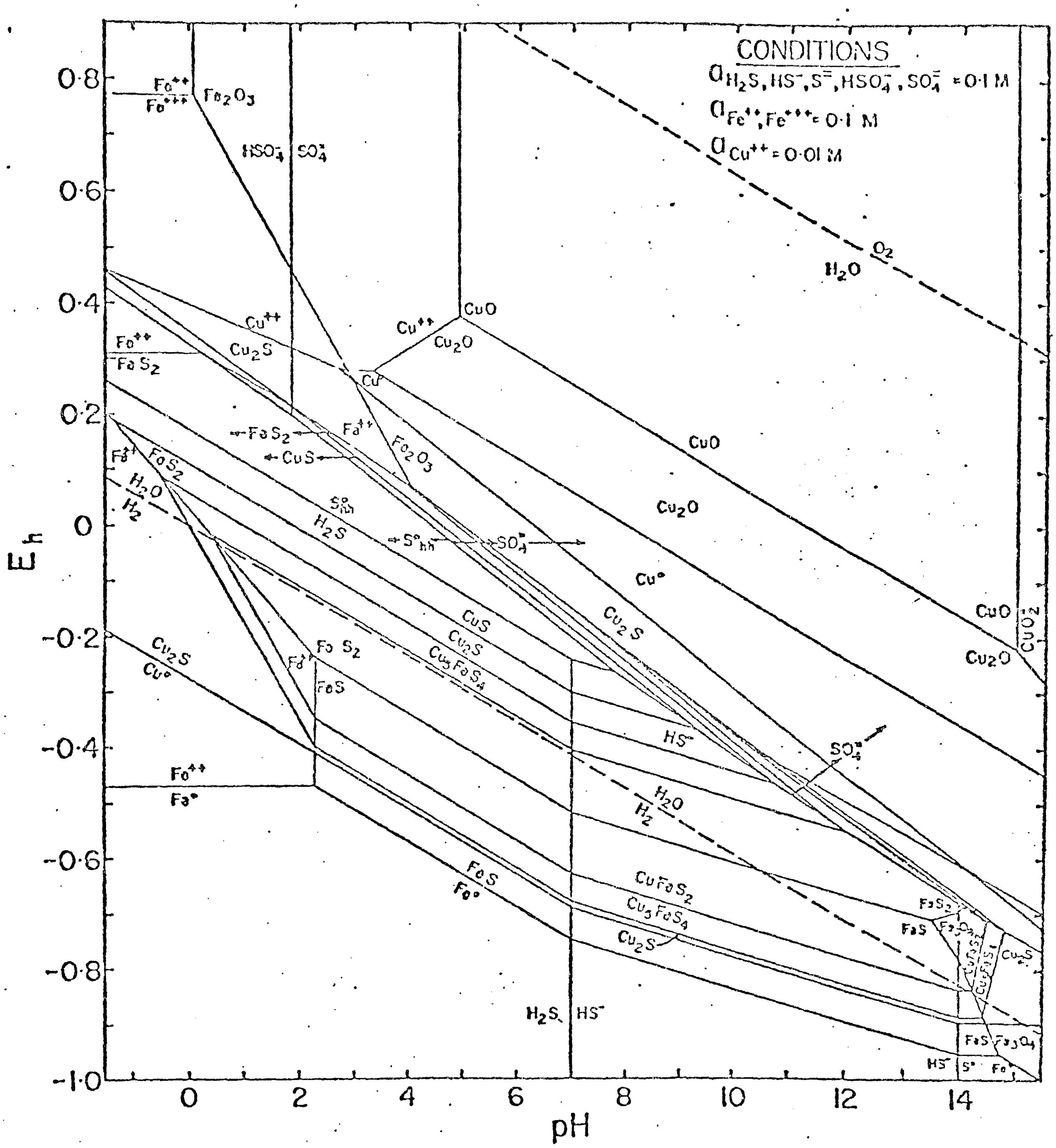


Figure 4. Eh-pH diagram for the Cu-Fe-S-H_2O system. (Peters, 1970).

controlled by availability of dissolved oxygen, temperature, degree of surface saturation by water, acidity (pH), particle size, presence of chemical and microbial catalysts and solution composition. The effect of inorganic and organic substances on the extent of leaching at equilibrium will be discussed in a later section.

The oxidation of pyrite (FeS_2) as a primary component responsible for acid mine drainage is thought to occur as follows (Smith and Shumate, 1971).

$$FeS_2(s) + 7/2\ O_2 \rightleftarrows 2SO_4^{-2} + Fe^{+2} + 2H^+$$

$$Fe^{+2} + 1/4\ O_2 + H^+ \rightleftarrows Fe^{+3} + 1/2\ H_2O$$

$$Fe^{+3} + 3H_2O \rightleftarrows Fe(OH)_3(s) + 3\ H^+$$

Pyrite is attacked by O_2 whereby sulfide is oxidized to SO_4^{-2}, releasing acid to solution and Fe^{+2} is oxidized to Fe^{+3} by oxygen. Ferric ion (Fe^{+3}) is likewise an effective oxidant for FeS_2 as follows:

$$FeS_2(s) + 14\ Fe^{+3} + 8\ H_2O \rightleftarrows 15\ Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+$$

The regeneration of Fe^{+3} is thought to be assisted by bacteria such as Thiobacillus ferrooxidans and Ferrobacillus ferrooxidans which are discussed in a later section.

The [illegible] equation above denotes the hydrolysis of ferric iron. At elevated concentrations of Fe^{+3}, formation of basic ferric sulfates and ferric hydroxides at $pH > 3$ is responsible for the characteristic yellowish-brown deposits known as "yellowboy" which coat acid waste discharges.

Summing the three equations above, we obtain:

$$FeS_2(s) + 15/4\ O_2 + 7/2\ H_2O \rightleftarrows 2H_2SO_4 + Fe(OH)_3(s)$$

The oxidation of pyrite and other iron-bearing minerals such as pyrrhotite ($Fe_{1-x}S$) where $x = 0$ to 0.2 and marcasite (FeS_2) by O_2 or Fe^{+3} result in low pH (high acidity) waters. The additional hydrolysis of Fe^{+3} to form insoluble substances also releases acid as shown below for reactions occurring in mine drainage to surface waters:

$$Fe_2(SO_4)_3 + 6\ H_2O \rightleftarrows 2\ Fe(OH)_3(s) + 3\ H_2SO_4$$
$$Fe_2(SO_4)_3 + 2\ H_2O \rightleftarrows 2\ Fe(OH)SO_4(s) + H_2SO_4$$

The acidity of acid mine drainage correlates well with the amount of pyrite or pyrrhotite available in the system (Stumm and Morgan, 1970). One mole of FeS_2 will give rise to four equivalents of hydrogen ion; two from the oxidation of FeS_2 and two from the oxidation of Fe^{++}.

In the absence of microorganisms, the oxidation of mineral sulfides likely occurs by a surface reaction in which oxygen diffuses through a thin surface film and reacts with the surface or reduced species in the interstices of the solid surface. As a result, conditions at the surface of the metal sulfide control leaching (Smith and Shumate, 1971). At constant pH and temperature, the rate of oxidation of pyrite and chalcopyrite is directly proportional to the oxygen concentration in the water (P_{O_2}). Conversely, dissolution of metal sulfides in the absence of O_2 is negligible. The rate of pyrite oxidation increases with increasing pH and decreases as the solution goes acidic, a situation analogous to the oxidation of S^{-2} by oxygen (Stumm and Morgan, 1970; Chen and Morris, 1972 a,b,c). The oxidation of metal sulfides is more efficient with Fe^{+3} than with O_2 (Woodcock, 1961) but there is disagreement on this point. Extremely acidic conditions are necessary to keep Fe^{+3} in solution.

Temperature may increase the rate of pyrite oxidation by a factor of two for every 10° C rise in temperature if the oxidation process is chemically controlled (Smith and Shumate, 1971; Stumm and Morgan, 1970). Diffusion or microbial controlled oxidation will be affected by temperature in a predictable manner.

The rate and extent of metal sulfide oxidation increases with decreasing particle size permitting surface reactions to occur over a greater surface area (Roman and Benner, 1973; Dutrizac and MacDonald, 1974). Smaller particle sizes not only increase the surface area but also decrease diffusion limitations and generate a greater number of reactive sites (Roman and Benner, 1973).

Water is important not only as a transport medium for removing oxidation products but also as a diffusion barrier to oxygen transfer. The rate of pyrite oxidation in a water-saturated metal sulfide environment is significantly less than that in which only the surface is in contact with humid air. In the former case, oxygen transport is limited.

There is considerable disagreement whether bacteria such as T. Ferrooxidans are important in the rate of metal sulfide oxidation. Smith and Shumate (1971) consider microbial catalysis unimportant in the rate of pyrite oxidation. They argue that the water in contact with reaction sites is small, and contains high concentrations of sulfate salts and sulfuric acid which are toxic to bacteria. However, bacteria do affect discharge water by oxidation of Fe^{+2} to Fe^{+3} in ponded water releasing acid. Others (Dutrizac and Mc Donald,1974) conclude that the rate and extent of oxidation of pyrite, chalcopyrite, pyrrhotite and chalcocite are significantly enhanced by bacteria, probably by the regeneration of additional oxidant, Fe^{+3}.

The effect of pH or acidity on the oxidation of metal sulfides is dependent upon the need to generate ferric ion as a chain oxidant in addition to oxygen. Highly acidic conditions are necessary to keep Fe^{+3} in solution. Figure 4 the E_h-pH diagram for chalcopyrite ($CuFeS_2$), suggests that fairly strong oxidizing potentials are necessary to effect dissolution of base metal sulfides in acid media.

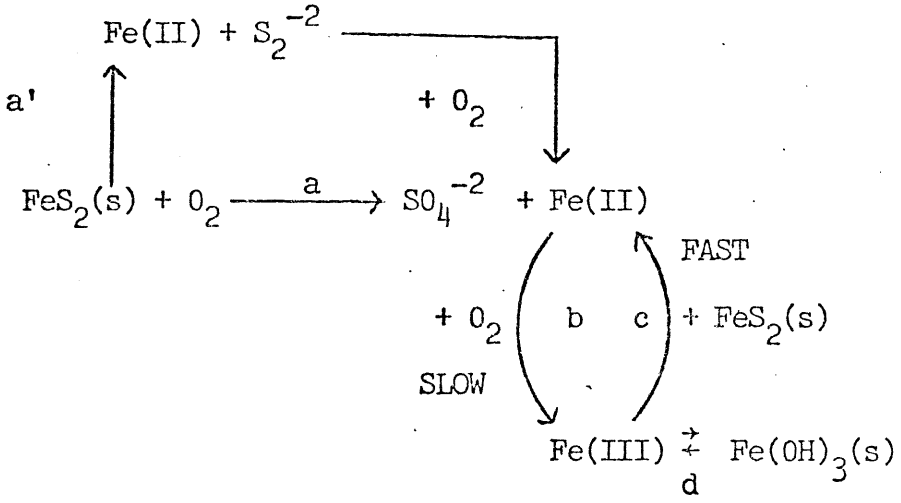
The dissolution of chalcopyrite by acidic ferric sulfate is thought to occur according to the following stoichiometry (Sullivan, 1933; Brown and Sullivan, 1934:

$$CuFeS_2 + 4\ Fe^{+3} \rightleftharpoons Cu^{+2} + 5\ Fe^{+2} + 2\ S^{o}$$

$$CuFeS_2 + 4\ Fe^{+3} + 2\ H_2O + 3O_2 \rightleftharpoons Cu^{+2} + 5\ Fe^{+2} + 2H_2SO_4$$

The induced in-situ leaching by added ferric sulfate is thought to follow the former stoichiometry while microbial-catalyzed oxidation the latter. Solutions of only 1 ppm Fe^{+3} (1 mg/l) have a potential of at least +0.4 v which is sufficient to attack metal sulfides. Dutrizac and MacDonald (1974) have concluded that chalcopyrite and pyrite dissolution occurs by direct attack of Fe^{+3} on exposed sulfide.

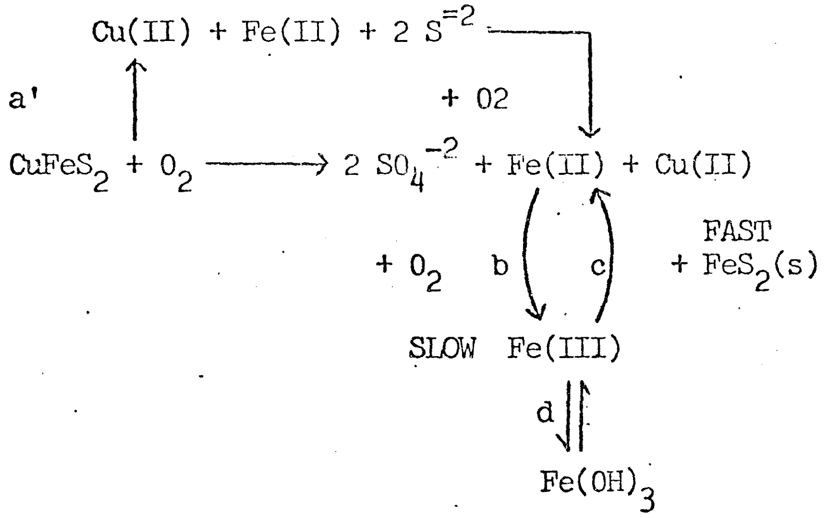
The effect of solution composition and an integration of previously discussed factors on the oxidation of metal sulfides can best be discussed by considering the following model of iron pyrite oxidation (Stumm and Morgan, 1970).



The rate-determining step is the slow oxidation of ferrous to ferric iron (b) exhibiting a half-life of ∿ 1000 days at pH 3 whereas the oxidation of FeS_2(s) by ferric ion (c) is very fast (half-life of 20 to 1000 minutes).

The sequence is initiated by the direct oxidation of pyrite by O_2(a) or by dissolution followed by oxidation (a'). The oxidation of S_2^{-2} can go to elemental sulfur (chemically-controlled) or to sulfate (microbial-assisted). The oxidation of ferrous iron proceeds slowly but ferric ion rapidly oxidizes pyrite. Once initiated, the reaction involves oxygen only indirectly through reaction (b).

An analogous model is proposed below for chalcopyrite dissolution:



The direct oxidation of chalcopyrite by O_2 as well as S^{-2} oxidation by O_2 following dissolution have been proposed as mechanisms of leaching. The release of heavy metals from base metal sulfides in the absence of Fe^{+3} has been found to be inversely proportional to solubility product lending support to reaction (a') (Torma, <u>et al</u>, 1974). Other aspects of the above model are similar to those presented for pyrite.

The above model suggests that factors controlling the oxidation of S^{-2} by oxygen likely control the rate and extent of chalcopyrite dissolution. The removal of S^{-2} by oxidation would shift the solubility equilibrium to the right favoring dissolution. Stumm (1970) has found that Cu (II), clays and fine charcoal powder catalyze the oxidation of pyrite by O_2. These factors also catalyze S^{-2} oxidation (Chen and Morris, 1972 a,b).

Chemical substances in solution can catalyze or inhibit oxidation rates. Inorganic and organic complexing agents can enhance oxidation by binding Cu(II) or Fe(II) increasing solubilization and are discussed in a later section. Chen and Morris (1972, a,b,c) have published a series of review and experimental papers on S^{-2} oxidation. They observed that the rate law was dependent on the oxygen partial pressure to the 0.56 power, that the oxidation rate of S^{-2} by O_2 increased with increasing pH (maximum, pH 8 to 8.5) and that S^{-2} oxidation occurred exceedingly slow at low pH where H_2S is the primary sulfide species. Chen and Morris (1972b) also reported that Ni^{+2} and Co^{+2} are extremely effective catalysts for the oxygenation of sulfide at low concentrations (10^{-4} M) in mildly alkaline solution. Organics such as phenols, hydroquinone and amines were found to be effective catalysts but octadecylamine, cyanide, EDTA, and others inhibited the rate of oxidation, apparently by a chain-breaking mechanism. Krebs (1929) also found that Mn^{+2}, Co^{+2}, Ni^{+2}, Fe^{+2} and Cu^{+2} enhanced the oxygenation rate of sulfide.

Kinetics of Metal Sulfide Oxidation

Burkin (1965) studied the dissolution of pyrite in the presence of O_2 (0 to 4 atm.) and at temperatures from 100 to 130° C in sulfuric acid media (0-0.15 M). The reaction and rate equation for dissolution of pyrite are:

$$FeS_2 + 2\ O_2 \rightleftarrows Fe^{+2} + SO_4^{-2} + S^0$$

$$\frac{-d[FeS_2]}{dt} = 0.125 \cdot 10^4\ A\ pO_2\ \exp\ (-13300/RT).$$

In this situation, a first order reaction order was observed for O_2 but acidity is not a factor in the rate law. Gerlach (1965) reported a similar study for pyrrhotite ($Fe_{1-x}S$) leaching at pO_2 = 1 to 5 atm., temp. = 30 to 80° C and $[H_2SO_4]$ = 0.4 to 1.4 m. The rate equation was similar to the above only pO_2 had a reaction order of 0.5. Other iron sulfide kinetic studies

(McKay and Halpern, 1958; Wadsworth, 1967; Dutrizac and MacDonald, 1974) show similar O_2 dependency.

Smith and Shumate (1971) found that the oxidation of pyrite was directly proportional to O_2 concentration in the water phase on the surface of pyrite and the rate of oxidation increased from 25 to 45° C (doubled for each 10° C rise in temperature). Acidity was reported to have an inverse effect on pyrite oxidation; i.e. oxidation rates increased with increasing pH, analogous to S^{-2} oxygenation (Chen and Morris, 1972a).

Roman and Benner (1973), Wadsworth (1972) and Dutrizac and MacDonald (1974) have reviewed extensively the hydrometallurgical literature on the kinetics of Cu, Ni sulfide dissolution. In general, acidity, oxygen, particle size, temperature and ferric iron are rate controlling factors in leaching. Dependence of oxygen partial pressure ranged from 0.3 to 1.0 reaction order. Acid ferric sulfate solutions were effective in copper sulfide mineral leaching:

$$CuFeS_2 + 2\ Fe_2(SO_4)_3 \rightarrow CuSO_4 + FeSO_4 + 2S^o$$

Acid is a dependent variable because of the need to maintain Fe^{+3} in solution. Temperature generally increases the rate of leaching by overcoming activation energies of individual steps. Rates of dissolution also increase with decreasing particle size and are directly correlatable to the weight of sulfide mineral present. It is important to note that metal sulfide leaching can occur in neutral and mildly alkaline solutions <u>if</u> the dominant reaction involves oxygenation.

Recently, Verhulst (1974) proposed a model for the dissolution of ZnS in acid ferric iron media:

$$ZnS + 2H^{+} \rightleftarrows Zn^{+2} + H_2S(aq)$$

$$H_2S(aq) + 2\ Fe^{+++} \rightleftarrows S^{o} + 2\ H^{+} + 2\ Fe^{+2}$$

The oxidation of $H_2S(aq)$ by Fe^{+++} was found to be dependent on $[H_2S]^{1.44}$, $[Fe^{+++}]^{1.68}$ and $[H_2SO_4]^{-2.49}$.

Burkstaller, et al (1975) studied the oxidation of cinnabar (HgS) by Fe(III) in conditions similar to acid mine waters. They found that the leaching rate increased with Fe(III) and (Cl^{-}) concentrations, quantity of HgS present and available surface area. Oxidation rates varied from 1.7 to 22.7 micromoles/ℓ-day at 0.3 to 33 g/ℓ HgS. Hg(II) solubilized by leaching was re-sorbed to a great extent on the cinnabar surface.

Sullivan (1933) and Brown and Sullivan (1934) found that 33% of the copper in a chalcopyrite crushed ore could be extracted in 57 days by a 1% Fe^{+3} solution as acid ferric sulfate. Dutrizac et al. (1969) and others found that chalcopyrite is leached according to:

$$CuFeS_2 + 4\ Fe^{+3} \rightleftarrows Cu^{+2} + 5\ Fe^{+2} + 2\ S^{o}.$$

They reported that at low Fe^{+3} concentrations, the rate-controlling process was attributed to Fe^{+3} diffusion through a constant thickening S layer on the mineral surface. The rate was also independent of H_2SO_4 concentration unless insufficient quantities were added to keep Fe^{+3} in solution. Table 6 is a summary of observed leaching kinetics in acid Fe^{+3} solution for chalcopyrite. Note that relatively high acid concentrations are necessary for Fe^{+3} leaching whereas O_2 can attack metal sulfides rapidly at higher, more environmentally compatible pH values.

The dissolution of cubanite ($CuFe_2S_3$) is also aided by acid Fe^{+3} (Dutrizac, et al. 1969):

$$CuFe_2S_3 + 3\ Fe_2(SO_4)_3 \rightleftarrows CuSO_4 + 8\ FeSO_4 + 3\ S^{o}.$$

Table 6

LEACHING KINETICS OBSERVED FOR $CuFeS_2$ DISSOLUTION IN ACIDIFIED FERRIC SULPHATE AND FERRIC CHLORIDE MEDIA*

Material	Medium	Fe^{3+} dependence	Activation energy (kcallmol)	Temperature (°C)	Rate-controllin process
$CuFeS_2$ concentrate	Ferric chloride	—	High	35-100	Not given
	Ferric sulphate	No effect between 0.25 and 5% $Fe_2(SO_4)_3$	High	35.100	Not given
$CuFeS_2$	Ferric chloride	Direct dependence between 50-100 g/l $FeCl_3$	12	60-106	Not given
Synthetic $CuFeS_2$	Ferric sulphate	$Fe^{3+}<0.01$ M, direct dependence $Fe^{3+}>0.01$ M, no effect	17	50-94	Parabolic kineti transport contr
Natural	Ferric sulphate	$Fe^{3+}>0.02$ M, no effect	18	32-50	Linear kinetics surface controll chemisorption
$CuFeS_2$ concentrates	Ferric chloride	—	High	30-106	Parabolic kine transport contr
Natural $CuFeS_2$	Ferric sulphate	$Fe^{3+}<0.01$ M, direct dependence $Fe^{3+}>0.01$ M, little effect	20	27-85	Parabolic kine transport contr

*From Dutrizac and MacDonald (1974)

Reaction rates increased with the 0.6 power of Fe^{+3}.

Nickel sulfides such as pentlandite and millerite are readily leached by acid solutions and are much less resistant to oxidation than is chalcopyrite. In nearly all cases reported by Dutrizac and MacDonald (1974), nickel sulfides were easily leached by acid, Fe^{+3} or O_2. The authors (1974b) have reported on the percolation leaching of pentlandite ($(Fe,Ni)_9S_8$) with acidic ferric sulfate solutions with and without *T. ferrooxidans* present. Approximately 80% of the Ni present was leached after 12 weeks of constant slow flow with little difference noted in the leaching rate in the presence of bacteria. Acid ferric iron is an effective oxidant for pentlandite.

Woodcock (1967) has recently reported a summary of copper release rates from dump leaching experiments (Table 7). In general, the rate of Cu release was affected in increasing order by $H_2SO_4 < H_2SO_4 + O_2 < H_2SO_4 +$ bacteria $< H_2SO_4 + Fe_2(SO_4)_3$. Chalcopyrite dissolution was markedly enhanced by bacterial activity.

Models of Dump Leaching

The use of hydrometallurgical dump leaching by the mineral industry is similar in many respects to the leaching of lean ore and waste rock in environmental situations with the exception that leaching rates are maximized. Recently reported dump leaching models will be reported.

Brimhall and Wadsworth (1972) used laboratory leach columns to study O_2 consumption by base metal sulfide ores. The amount of O_2 consumed was increased markedly by lowering the pH; the high acidity also served to dissolve gangue material. The effective pH of leaching depended on the excessive acid consuming properties of the gangue.

Auck and Wadsworth (1973) later examined crushed, sterilized ore in

Table 8

Relative dissolution rates of common copper minerals in dump leaching solution*

Mineral	Aqueous Solvent	Dissolution Rate**
Azurite	H_2SO_4	100% in 1 hour
Bornite	$H_2SO_4 + O_2$	27% in 24 days
	$H_2SO_4 + Fe_2(SO_4)_3$	95% in 12 days
	H_2SO_4 + bacteria	100% in 20 days
Chalcocite	$H_2SO_4 + O_2$	30% in 14 days
	$H_2SO_4 + Fe_2(SO_4)_3$	95% in 12 days
	H_2SO_4 + bacteria	90% in 30 days
Chalcopyrite	$H_2SO_4 + O_2$	Low
	$H_2SO_4 + Fe_2(SO_4)_3$	30% in 40 days
	H_2SO_4 + bacteria	100% in 26 days
Chrysocolla	H_2SO_4	100% in 1 day
Copper (native)	$H_2SO_4 + O_2$	100% in 3 days
	$H_2SO_4 + Fe_2(SO_4)_3$	100% in 1 hour
Covellite	$H_2SO_4 + O_2$	26% in 35 days
	$H_2SO_4 + Fe_2(SO_4)_3$	60% in 24 days
	H_2SO_4 + bacteria	50% in 76 days
Cuprite	H_2SO_4	50% in 1 hour
	$H_2SO_4 + O_2$	100% in 3 days
	$H_2SO_4 + Fe_2(SO_4)_3$	100% in 1 hour
Malachite	H_2SO_4	100% in 1 hour

*From Woodcock (1967)

**Maximum total dissolution at room temperature or 35°C.

alternate leach, oxidation cycles. The rate of Cu extraction from chalcopyrite-pyrite ore ranged from .043 to .018 g/ℓ/day, decreasing with time at low pH. They concluded that Fe^{+3}, present at low pH upon dissolution and oxidation of pyrite, was responsible for Cu leaching according to a cathodic reaction. Acid consumption was observed to cease when leaching stopped.

Rickard (1974) discussed the chemical constraints on in-situ leaching in terms of a diffusion-surface reaction model. He concluded that the rate of Cu release with time observed in dump leaching was due to the occurrence of slime and precipitated salts which acted as solution barriers to oxygen transfer. In an ore containing feldspar, calcite, etc., acid generated by iron oxidation is consumed by silicates, Al and Mg in solution. Increasing pH values lead to precipitation of basic ferric sulfates and hydroxides.

Braun et al. (1974) proposed a modified mixed-kinetic leaching model in which the rate of leaching is controlled by rate of oxygen diffusion to and reaction with the sulfide mineral. Kinetics would be expected to decrease as the oxidation front moved into the ore. Oxygen diffusion depends on the ability of oxygen to permeate the gangue material accumulating in the interstices of the sulfide mineral. As a result, low pH conditions are necessary to dissolve the gangue. Braun et al. (1974) proposed that net acid present depended on the following acid-consuming and acid generating reactions:

Acid-consuming:

$$CuFeS_2 + 5/4\ O_2 + 5\ H^+ \rightleftarrows Cu^{+2} + Fe^{+3} + 2\ S^o + 5/2\ H_2)$$

$$FeS_2 + 3/4\ O_2 + 3\ H^+ \rightleftarrows Fe^{+3} + 2\ S^o + 3/2\ H_2O$$

$$CaCO_3 + 2\ H^+ + SO_4^{-2} \rightleftarrows CaSO_4 + CO_2 + H_2O$$

Acid-Generating:

$$S^o + 3/2\ O_2 + H_2O \rightleftarrows 2\ H^+ + SO_4^{-2}$$

$$Fe^{+3} + 3/2\ O_2 \rightleftarrows 3\ H^+ + 1/2\ Fe_2O_3$$

$$Fe^{+3} + 7/3\ H_2O + 2/3\ SO_4^{-2} \rightleftarrows 5/3\ H^+ + 1/3\ Fe_3(SO_4)_2(OH)_5 \cdot 2\ H_2O$$

(jarosite)

Bartlett (1973) and Madsen et al.(1975) proposed a mixed kinetics model involvin a steady-state diffusion of the reactant through a reacted portion of the ore fragment followed by a chemical reaction within a reaction zone at the surface. The latter group found that the proposed model adequately predicted Cu leaching from -1/2 inch fine fraction for 460 days. The ore studied included pyrite, chalcopyrite, covellite, chalcocite and sphalerite.

Bhappu, et al (1969) studied the theoretical and practical aspects of copper dump leaching including chemical, physical and biological factors. The copper ore was treated with ferrous sulfate while H_2SO_4 addition proved unnecessary. They found that Fe^{+2} was converted to Fe^{+3} and acid in the top few centimeters of the dump, correlating well with the concentration of sulfur and iron-oxidizing bacteria. Ferric ion, H_2SO_4 and bacteria were all implicated as participating in metal sulfide dissolution. Leaching was maximized under alternate wet-dry conditions since copper dissolution was a slow process. In this instance, oxidation and dissolution of the metal sulfide occurred during a dry but humid period.and transport by a percolating solution followed.

Electrochemical Aspects of Leaching

Electrochemistry of base metal sulfide minerals may influence the rate of weathering and metal leaching. Minerals in contact with each other at depth are at electrochemical equilibrium with respect to flow of electrons from surface to surface. However, when the mineral sulfides are brought to the surface and stockpiled, they will be subjected to chemical weathering and new surfaces will be uncovered. Under these conditions, one metal sulfide may enhance the dissolution rate of another through electrochemical interaction.

Sato (1960) has observed that between two sulfides of a specific metal, the one with the higher formula oxidation state is more stable than one with a lower oxidation state and would be relatively stable to chemical weathering, a fact consistent with the high resistance of chalcopyrite to chemical and bacterial leaching (Malouf, 1970).

The minerals present in the Gabbro have relatively close electropositive character, i.e., no significant electrochemical driving force exists for oxidation-reduction processes to occur in the absence of a chemical oxidant. Pyrite, however, is significantly more electropositive than chalcopyrite suggesting that even small quantities of pyrite could induce dissolution. Any contact of mineral sulfide surfaces of widely differing electronegativity will likely enhance leaching. Bauer, _et al_. (1972) illustrated the importance of cathodic reactions (reduction) in the conversion of chalcopyrite ($CuFeS_2$) to Cu_2S in the presence of finely divided metal powders of Ag^0, Cu^0 and Fe^0. The cathodic conversion of chalcopyrite can be viewed as follows:

$$2\ CuFeS_2 + 2e^- \rightleftarrows Cu_2S + 2\ Fe^{+2} + 3\ S^{-2}$$

The S^{-2} in the presence of H^+ forms H_2S

$$3\ S^{-2} + 6\ H^+ \rightleftarrows 3\ H_2S$$

The anode reaction is:

$$Fe^0 \rightleftarrows Fe^{+2} + 2\ e^-.$$

The overall reaction is:

$$2\ CuFeS_2 + 6\ H^+ + Fe^0 \rightleftarrows Cu_2S + 3\ Fe^{+2} + 3\ H_2S$$

Cu_2S is unstable in the presence of O_2 or Fe^{+3} resulting in dissolution and metal release.

Electrochemical investigations of pyrite leaching (Sato, 1960; Becking _et al_, 1960; Hansuld, 1965) indicate that pyrite oxidation occurred when the potential of pyrite equalled the potential of the solution, at 650 to 660 mv. Peters (1970) found that the high rest potential of pyrite is due to the presence of O_2 that is adsorbed on the surface rendering a stable "passive" surface. When oxygen is present, pyrite exhibits a rest potential greater than any other sulfide mineral. A galvanic coupling between pyrite and any other mineral sulfide would lead to cathodic reactions on pyrite (reduction) and anodic reactions on the other mineral. Electrochemical effects such as these have been implicated in dump leaching processes and may be prevalent in the leaching of metals from stockpiled lean ore containing different sulfide minerals (including pyrite). These processes will be relatively independent of pH.

Bacterial Leaching

Bacterial-assisted leaching of pyrite and other metal sulfides is a well-known phenomena in hydrometallurgical mining and is primarily responsible for acid mine drainage documented extensively for the Appalachian coal-mining areas (Ohio State University, 1970). Bacteria thought responsible for metal sulfide dissolution are known as Thiobacillus ferrooxidans, an autotrophic, aerobic, acidophilic, carbon-dioxide fixing microorganism requiring reduced sulfur or iron as an energy substrate. Fundamental studies of bacterial leaching of pyrite and other metal sulfides from lean ores, tailings, etc. related to environmental transport of potentially toxic metals to ground and surface waters has been reported sparsely in the literature. However, there is no doubt that occurrences of metal sulfide leaching from discarded mining solids have been documented for the Sudbury, Ontario region (Williams, 1975; Hawley, 1971) and to a much lesser extent, the Cu-Ni mining region of northeastern Minnesota (INCO, 1976, Eger, 1976). This review will necessarily depend on the extensive literature on bacterial leaching of metal sulfides associated with hydrometallurgical mining and acid waste formation in the coal mining industry.

Description of Bacteria

The bacterium which has been most studied and implicated in the dissolution of metal sulfides is Thiobacillus ferrooxidans (T. ferrooxidans). The bacterium is an aerobic, autotrophic, acidophillic, carbon-dioxide fixing microorganism which requires reduced sulfur (sulfide) and/or iron (Fe(II)) as energy substrates. T. ferrooxidans fixes CO_2 and oxidizes sulfide to sulfate (SO_4^{-2}) or sulfur (S^o) in the range pH 0.5 to 6.0 with optimum growth exhibited at pH 2.0 to 4.0 (Malouf, 1970; Silverman and Ehrlick, 1964). Sulfur (S^o) as well as various polythionates and thiosulfate can be utilized as energy sources. Other bacteria known to contribute to acid waste include *T. thiooxidans*, *Ferrobacillus ferrooxidans*, *T. concretivorus*, *F. sulfooxidans* and *T. neopolitanus*. Water in contact with pyrite (FeS_2) and O_2 soon becomes acidic (pH 2.0 to 3.5) due to the oxidation of sulfide to sulfuric acid (H_2SO_4) and ferrous iron (Fe(II)) to ferric iron (Fe(III)):

$$FeS_2 + H_2O + 7/2\ O_2 \rightleftarrows FeSO_4 + H_2SO_4$$

Ferrous sulfate can be microbially oxidized by O_2 to ferric sulfate which is well known as an effective lixiviant or acid leaching agent of metal sulfides:

$$4\ FeSO_4 + 2H_2SO_4 + O_2 \overset{\text{bacteria}}{\rightleftarrows} 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

$$FeS_2 + Fe_2(SO_4)_3 \rightleftarrows 3\ FeSO_4 + 2\ S^o$$

The generation of H_2SO_4 (low pH) is critical to *T. ferrooxidans* in leaching metal sulfides. Unless the solution is less than pH 4, *T. ferrooxidans* is not a factor in leaching.

A wide variety of *Thiobacilli* are capable of oxidizing sulfide and ferrous iron in the range pH 0.5 to 11.0 under environmental conditions. Table 8 is a compilation of comparative characteristics of *Thiobacilli* taken from Malouf (1970). Several excellent reviews of the properties, characteristics and behavior of *Thiobacilli* have been published and should be consulted for further explanation. (Zajic, 1969; Pings, 1968; Trudinger, 1971; Beck, 1960, 1969; Malouf, 1970; Kuznetsov *et al*, 1963). Examination of Table 8 illustrates the fact that although most environmental leaching associated with the coal industry and hydrometallurgy occurs at low pH, it is *not* a prerequisite to bacterial leaching. For example, *T. thioparus*,

Table 8

Comparative Characteristics of Thiobacilli*

Species	Type	pH		Energy Source
		Range	Optimum	
Thiobacillus Thiooxidans	Autotrophic-Aerobic	0.5-6.0	2-3.5	$S^=$, S^o, $S_2O_3^=$
Thiobacillus Ferrooxidans	Autotrophic-Aerobic	0.5-6.0	2-3.5	Fe^{++}, $S^=$, S^o,$S_2O_3^=$
Thiobacillus Concretivorus		10%H_2SO_4		H_2S, S^o, $S_2O_3^=$
Thiobacillus Thermitanus		1.2-6.4	2.4-5.4	S^o,$S_2O_3^=$
Thiobacillus Umbonatus		Acid		S^o
Thiobacillus Lobatus		Acid		$S_2O_3^=$
Thiobacillus Crenatus		Acid		$S_2O_3^=$
Thiobacillus Denitrificans	Autotrophic-Anaerobic	7.2-8.4		H_2S, $S^=$, S^o, $S_2O_3^=$, $S_2O_6^=$
Thiobacillus Thiocyanoxidans	Autotrophic-Aerobic and Anaerobic	6.8-7.6		CNS^-, S^o, HS^-, $S^=$, S_2O_3
Thiobacillus Inschenetskii (121°F)	Autotrophic-Anaerobic	7.0-7.2		$S^=$, $SO_3^=$, $S_2O_3^=$
Thiobacillus Coproliticus	Autotrophic-Aerobic	6.1-716		$S_2O_3^=$
Thiobacillus Novellus	Heterotrophic-Anaerobic	8.0-910		$S_2O_3^=$
Thiobacillus Trautiveinie	Heterotrophic-Autotrophic Heterotrophic-Anaerobic	7.8-8.5		$S_2O_3^=$
Thiobacillus Neapolitanus	Autotrophic-Aerobic	3. - 8.5		S^o, $S^=$, $S_2O_3^=$, $S_4O_6^=$
Thiobacillus Issatschenkoi	Obligate-Halophils	0-10% NaCl		S^o, $S^=$, $S_2O_3^=$
Thiobacillus Thioparus	Autotrophic Aerobic	7.5-11.0		S^o, $S^=$, $S_2O_3^=$, $S_4O_6^=$
Desulfovibrio Sulfuricans	Hetertrophic-Anaerobic	3.5-7.5		H_2S, $SO_3^=$, S_2O_3, $S_4O_6^=$
Clostridium Nigrificans	Heterotrophic-Anaerobic	3.5-7.5		H_2S, $SO_3^=$, $S_2O_3^=$, $S_4O_6^=$

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*From Malouf (1970)

an autotrophic, aerobic alkaline-media microorganism reacts with effective leaching occurring from pH 7.1 to 9.0 (Malouf, 1970). Many *Thiobacilli* are capable of active growth at slightly acid, neutral or even alkaline pH values, although their isolation in the field from seepages draining lean ore, tailing piles, etc. has not been reported.

Bruynesteyn and Duncan (1971) and Trivedi and Tsuchiya (1975) have documented factors influencing microbiological oxidation of metal sulfides. They list as important the following:

1. available source of substrate - metal sulfide
2. supply of oxygen which serves as the ultimate electron acceptor in the oxidation process
3. supply of carbon dioxide as a carbon source
4. supply of essential nutrients such as P and N
5. water for nutrient transport and solvent
6. an acidic environment (pH 1.5 to 4.0)
7. optimum temperature (30° to 40° C) for cell growth
8. appropriate particle size and thus available surface area for oxidation

The availability of nutrients P and N to the bacteria can often be a limiting factor in the rate and extent of leaching as well as a supply of CO_2 as a carbon source. Since the rate of leaching has been closely correlated with bacterial cell population (Tsuchiya and Trivedi, 1975; Silverman and Lundgren, 1959), any factor which inhibits cell growth will diminish the bacterial contribution to leaching. In the environmental situation where lean ore piles or tailings are in contact with the atmosphere (CO_2 and O_2) and nutrients (P,N) having soil or precipitation as their source, the potential for leaching may be limited by other factors such as the quantity of precipitation, a high buffering capacity of the ore and soils preventing acidification, low concentrations of pyrite or pyrrhotite, cold temperatures or large particle sizes (low surface area).

Mechanism of Bacterial Leaching

The oxidation of metal sulfides by bacteria is thought to occur by either a direct mechanism whereby bacteria oxidize lattice sulfide to sulfate solubilizing the metal or an indirect mechanism whereby ferric iron an effective oxidant, is generated by the oxidation of ferrous iron released through oxidation of sulfide by dissolved oxygen. In the realistic case, both mechanisms are probably occurring concurrently in the leaching process as well as direct chemical oxidation by oxygen and/or ferric sulfate (Dutrizac and MacDonald, 1974; Woodcock, 1967; Roman and Benner, 1973).

1. Direct Mechanism

The direct mechanism of bacterial oxidation of lattice sulfide is favored by a host of researchers (Bryner, 1954; Razzell, 1962; Razzell and Trussel, 1963; Duncan et al., 1967; Silverman, 1967; Bryner and Jameson, 1967; Beck and Brown, 1968; McGoran, et al., 1969). The direct attack of bacteria on the sulfide mineral in the presence of O_2 can be expressed in the following equations for minerals common to the Gabbro complex (Trivedi and Tsuchiya, 1975):

a. Pyrite

$$FeS_2 + H_2O + 7/2\ O_2 \rightleftarrows FeSO_4 + H_2SO_4$$

b. Chalcopyrite

$$CuFeS_2 + 4\ O_2 \rightleftarrows CuSO_4 + FeSO_4$$

c. Millerite

$$NiS + 2\ O_2 \rightleftarrows Ni^{+2} + SO_4^{-2}$$

If the concentration of pyrite or pyrrhotite in the ore is adequate, a sufficient quantity of ferrous sulfate can be oxidized by bacteria and O_2 to ferric sulfate which is an effective oxidant for chalcopyrite and millerite:

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \rightleftarrows 2\ Fe_2(SO_4)_3 + 2\ H_2)$$

Bryner _et al_., (1954) found that bacteria oxidized pyrite 20 times faster than the chemical control and favored the direct attach mechanism. They and others (Duncan _et al_, 1967; Dutrizac and MacDonald, 1974; Woodsworth 1972) found that the rate and extent of pyrite leaching increased with temperature, in the absence of light and at reduced pH. Although the oxidation of pyrite-S to S^o or SO_4^{-2} may be partially a result of bacterial attack, the leaching of Cu and Ni sulfides may be a result of ferric iron oxidation processes. However, direct attack of bacteria on the mineral sulfide is favored by Pinches (1971) for chalcocite, covellite, millerite and chalcopyrite. Razzell (1962) and Razzell and Trussell (1963) favored the direct attack for chalcopyrite according to the following expression:

$$4\ CuFeS_2 + 17\ O_2 + 2\ H_2SO_4 \rightleftarrows 4CuSO_4 + 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

Duncan _et al_. (1967) presented evidence that ferrous iron and sulfide were oxidized in pyrite in a stepwise fashion indicating a direct attack on sulfide minerals. McGoran, _et al_ (1969) report that the extraction of Cu and Fe from chalcopyrite or Fe from pyrite is proportional to bacterial nitrogen; i.e., metal extraction is associated with cell growth at low pH, but not with O_2 consumption. In general, leaching was found to be a function of substrate available (surface area) and CO_2.

2. Indirect Leaching Mechanism:

The indirect mechanism whereby leaching action is induced by ferric ion generated by the bacterial oxidation of dissolved ferrous iron in the presence of O_2 is favored by several researchers. The following expressions apply (Sutton and Corrick, 1963; Trivedi and Tsuchiya, 1975):

a. Pyrite

$$FeS_2 + Fe_2(SO_4)_3 \rightleftarrows 3\ FeSO_4 + 2\ S$$

b. Chalcopyrite

$$CuFeS_2 + 2\ Fe_2(SO_4)_3 + H_2O + 3\ O_2 \rightleftarrows CuSO_4 + 5\ FeSO_4 + 2\ H_2SO_4$$

c. Millerite

$$2\ NiS + 2\ Fe_2(SO_4)_3 + 2\ H_2O + 3\ O_2 \rightleftarrows 2\ NiSO_4 + 4\ FeSO_4 + 2\ H_2SO_4$$

Sutton and Corrick (1963) found that <u>T. ferrooxidans</u> could not oxidize crystal lattice sulfides and thus preferred the indirect model of bacterial leaching for pyrite and chalcopyrite as shown below:

a. <u>Pyrite</u>: leaching is initiated by air oxidation of pyrite:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightleftarrows 2\ FeSO_4 + 2\ H_2SO_4$$

Bacteria then oxidize ferrous iron according to:

$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \rightleftarrows 2\ Fe_2(SO_4)_3 + 2\ H_2O$ and ferric sulfate subsequently attacks pyrite to form H_2SO_4 and additional ferrous sulfate:

$$7\ Fe_2(SO_4)_3 + FeS_2 + 8\ H_2) \rightleftarrows 15\ FeSO_4 + 8\ H_2SO_4$$

b. <u>Chalcopyrite</u>: leaching is initiated by air oxidation according to:

$$CuFeS_2 + 4\ O_2 \rightleftarrows CuSO_4 + FeSO_4$$

Bacteria in the presence of O_2 oxidize ferrous sulfate to ferric sulfate which can leach additional $CuFeS_2$:

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \rightleftarrows 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

$$CuFeS_2 + 4\ Fe^{+3} \rightleftarrows Cu^{+2} + 5\ Fe^{+2} + 2\ S^o$$

Elemental sulfur S^o, is then oxidized to acid keeping Fe^{+3} in solution:

$$S^o + 3/2\ O_2 + H_2O \overset{\text{bacteria}}{\rightleftarrows} H_2SO_4$$

These mechanisms are in general agreement with Malouf and Prater (1961) and Ivanov (1971). Malouf and Prater (1961) believed a protective outer S layer was removed from pyrite by bacterial oxidation and facilitated ferric sulfate dissolution of the mineral.

Pyrite and Cu-Ni sulfides have varying reactivity to bacterial oxidation at low pH. The following is a list of mineral sulfides in order of increasing resistance to oxidation (Malouf, 1970):

Pyrrhotite	FeS
Chalcocite	Cu_2S
Covellite	CuS
Bornite	Cu_5FeS_4
Pyrite	FeS_2
Marcasite	FeS_2
Chalcopyrite	$CuFeS_2$

Pyrrhotite, cubanite, pendlandite and chalcopyrite are the predominant sulfide minerals in the Duluth Gabbro complex, northeastern Minnesota. Torma et al. (1974) studying the kinetics of biooxidation of metal sulfides found that the rate of Cd, Ni, Co and Zn sulfide oxidation was inversely related to the solubility product of the metal sulfide, i.e., the rate of metal extraction decreased with decreasing solubility. No ferric ion was present in the synthetic sulfides obviating the need to negate ferric leaching. As the solubility product rises (decreased solubility), less sulfide exists in solution in equilibrium with the solid phase:

$CdS \rightleftarrows Cd^{+2} + S^{-2}$

$CuS \rightleftarrows Cu^{+2} + S^{-2}$

Bacteria, in catalyzing the oxidation of S^{-2} by O_2 probably act as indirect leaching agents. Silver and Torma (1974) later found that O_2 consumed in the presence of T. ferrooxidans had no definable relationship to quantity of metal extracted from several metal sulfides, including chalcopyrite and millerite, favoring the indirect leaching mechanism. Table 9 is a summary of Cu leached from Cu sulfides by bacterial oxidation.

Further studies of the mechanism of Fe^{++} to Fe^{+++} oxidation (pyrite) by iron-oxidizing bacteria were carried out by Dugan and Lundgren (1964) They observed that the pH dropped from 3.5 to 2.6 and the E_h rose to 560 mv because of the microbial oxidizing activity. They postulated that an iron complex involving oxygen would become attached to the bacterium. This initial complex would then be oxygenated but not oxidized until an electron was transferred to the complex. The complex was formed in the solution or on the cell surface and was linked with the ferrous ion, resulting in a release of an electron. Sulfate was postulated as the initial transfer link between iron and the cell. Additional studies of acid formation and leaching by bacteria for pyrite or pyrrhotite can be found in "Acid Mine Drainage in Appalachia", Vol. 2, 1969.

Effect of Environmental Parameters on Bacterial Leaching

a. Particle Size: The leaching of metal sulfides is conceded generally to be a surface reaction whereby bacteria directly oxidize surface sulfide or O_2 oxidizes ferrous iron and sulfide in equilibrium with the solid surface. The rate and extent of bacterial leaching is inversely proportional to particle size; i.e., increased surface

Table 9

Copper extraction from copper sulfide minerals by bacterial oxidation*

Mineral	Copper Extraction	Reference
Bornite	100% in 20 days	Bryne, *et al*. (1954)
		Razzell and Trussell (1963a)
		Sutton and Corrick (1963, 1964)
Chalcocite		Bryner *et al*. (1954)
	92% in 125 days	DeCuyper (1964)
	90% in 30 days	Duncan and Trussel (1964)
		Razzell and Trussell (196ea)
Chalcopyrite	24% in 56 days	Bryner and Anderson (1957)
	72% in 12 days	Duncan and Trussell (1964)
	100% in 26 days	
	60% in 480 days	Malouf and Prater (1961)
	40% in 50 days	Razzell and Trussell (1963a)
Covellite	21% in 42 days	Bryner *et al*. (1954)
	50% in 76 days	Duncan and Trussell (1964)
	56% in 56 days	Sutton and Corrick (1963, 1964)

*Modified from Woodcock (1967)

area is available for oxidation processes as particle size decreases (Bruynesteyn and Duncan, 1971; Silverman, et al., 1963; Torma et al., 1972; Malouf and Prater, 1961; Silverman et al., 1961; Duncan et al., 1964; Pinches, 1971; Trivedi, 1974).

b. Temperature: microbial leaching of metal sulfides by T. ferrooxidans and most other Thiobacilli occurs at an optimum growth temperature of 35°C (range: 30° to 40°C) (Pinches, 1971; Trivedi and Tsuchiya, 1975; Bruynesteyn and Duncan, 1971). Leaching of metal sulfides under environmental conditions in a cold climate by bacteria is not favored by the relatively harsh climatic conditions of northeastern Minnesota. However, metal sulfide oxidation, an exothermic, heat-releasing process could maintain localized regions of higher temperatures once initiated. Below 30°C, the bacteria are dormant and above 50°C, they are destroyed. Some strains, however, are resistant to higher temperatures.

$\frac{9}{5}$

c. Acidity (pH); T. ferrooxidans, an acidophilic, Fe(II) and S(II) oxidizing bacteria grows optimally in the range pH 1.5 to 4.0. Above pH 4, the bacterium exhibits slow cell growth and is ineffective as a leaching agent. Other Thiobacilli such as T. thioparus exhibit cell growth at slightly alkaline pH values (7.1 to 9.0) but have not been implicated in metal sulfide dissolution under environmental conditions.

Bacterial Leaching of Gabbro Complex Solids

A limited quantity of information is available on bacterial leaching of Gabbro complex metal sulfides. Trivedi and Tsuchiya (1975) reported on the mutualistic association of T. ferrooxidans, a CO_2 fixing bacteria with a nitrogen-fixing bacteria Beijerinckia lacticogenes which leached more Cu-Ni sulfide at a faster rate without adding a carbon or nitrogen source than individual-bacterial systems. The leaching tests were conducted on a Cu-Ni concentrate assayed at 4.22% Cu and 0.90% Ni^{+2}. The leaching experiment employed a stirred system at pH5 in a nutrient broth at 26°C for 500 hrs. Their results are abstracted below:

	Cu	Ni	% Cu Extracted	% Ni Extracted
Chemical Control	0.4	0.58	4	33
B. lacticogenes	0.4	0.5	4	30
T. ferrooxidans	1.8	1.3	22	76
Mixed Culture	6.0	1.8	72	100

Although it is unlikely that the two bacteria would occur symbiotic naturally at low pH, the possibility of environmental leaching of metal sulfides under similar conditions is not unrealistic.

Iwasaki _et_ _al_., (1976) reported on the release of Cu and Ni from a Gabbro complex ore sample in preliminary experiments using F. ferrooxidans and T. ferrooxidans. The ore, assaying at 0.71% Cu and 0.15% Ni, was crushed (10 mesh) and leached for periods up to 40 weeks with a nutrient broth adjusted to pH 3 in an aerated column experiment in which the effluent was recycled. The overall percentage extraction at 40 weeks was 40 and 60% for Cu and Ni, respectively. The authors observed Ni to be released at a faster rate than Cu, possibly due to galvanic interactions. Similar leaching experiments run without nutrients yielded little metal release as the pH drifted to higher values (pH 8) suggesting bacterial leaching was prominent only at low pH values. This behavior also suggests that the ore tailings have a significant acid buffering capacity.

Many mineral deposits such as those in Michigan's Upper Penninsula do not have acidic environments furnishing sulfur and iron. Wenburg et al. (1971) have found that microbial leaching by certain Penicillium fungi were able to solubilize significant amounts of Cu from chalcocite ore and concentrate under neutral and slightly acidic conditions in a carbon and nitrogen enriched medium. Leaching was apparently accomplished by release of metabolites which chelated the copper causing its dissolution. Chelating agents implicated in copper leaching were suggested to be citrate and certain amino acids, including cysteine (contains a sulfhydryl group).

In summary, bacterial-catalyzed leaching of metal sulfide ores is likely not to be a significant factor in the release of heavy metals from ore, tailings and waste rock associated with Cu-Ni mining in northeastern Minnesota. The extreme climatic conditions in conjunction with the acid-buffering capacity of ore and soils inhibiting acidification of seepages makes the classical "acid mine drainage Thiobacilli" inoperative. However, this does not preclude the possibility of alkaline-active microorganisms capable of sulfide oxidation from affecting metal release. These have been little studied in the context of environmental leaching problems.

ENVIRONMENTAL LEACHING STUDIES

Copper and nickel may be obtained from mineral sulfide ore bodies by open-pit mining, underground mining, or a combination of open-pit-underground mining operations. Each technique will result in the baring of new metal sulfide surfaces to atmospheric weathering to some extent in the form of ore stockpiles, waste rock or tailings. Open-pit mining, of course, generates a relatively larger surface area open to the atmosphere. There are three potential sources of aquatic pollution at a mine. These are: 1) mine water, 2) surface water, and 3) process water. This review will not include the latter in a discussion of metal leaching in the environment.

The major sources of mine water in northeastern Minnesota are groundwater seepage, water pumped into the mine, and surface drainage into or through open pits. In general, these waters, if contaminated, will be characterized by high acidity (low pH) resulting from iron sulfide oxidation, high metal content and significant quantities of dissolved solids. Potential sources of contaminated surface drainage will arise in any area where rock surface is exposed to weathering action such as ore piles, waste rock piles, haul roads and tailings. In addition to iron-sulfide dissolution, sulfides of Cu, Cr, Co, Mn, Ni, U, and Zn dissolve under low pH conditions (Hawley, 1972). The single most important reaction to which is attributed environmental damage is the development of acid mine drainage, the formation of which is summarized below (Williams, 1975).

Acid mine drainage is formed by the chemical action of oxygen and water on iron sulfides such as pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$) and marcasite (FeS_2). In an aqueous environment, oxygen reacts with pyrite to form ferrous iron ($FeSO_4$) and sulfuric acid:

$$2FeS_2 + 2H_2O + \overset{7}{\cancel{2}}O_2 \rightleftharpoons 2FeSO_4 + 2H_2SO_4$$

Ferrous iron (Fe^{+2}) can then be converted to ferric iron by oxygen (catalyzed by <u>Thiobacilli</u> microorganisms):

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2O$$

Depending on pH, part of the Fe^{+3} is hydrolyzed to an amorphous ferric hydroxide or basic ferric sulfate releasing additional acid:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3(S) + 3H_2SO_4.$$

The resulting precipitate (amorphous ferric hydroxide) imparts the reddish coloration to acid drainage systems. Four equivalents of hydrogen ion are formed as a result of pyrite oxidation. At sufficiently low pH to maintain Fe^{+3} in solution and dissolve gangue material, $Fe_2(SO_4)_3$ or Fe^{+3} can rapidly oxidize additional pyrite according to the following reaction:

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \rightleftharpoons 15FeSO_4 + 8H_2SO_4$$

The leaching of Fe, Cu, and Ni sulfide minerals at low pH will dissolve heavy metals and other components which can then be transported by water movement out of the mine or pile.

The generation of leaching solutions containing high acidity is proportional to the iron sulfide content of the ore or tailing, and inversely related to the relative level of acid-consuming gangue material such as feldspar and calcite present.

<u>Environmental Leaching Problems — Canada</u>

The problem of acid mine drainage and metal contamination in Canada is a relatively recent but highly studied phenomena. Several reports depicting in great detail acid mine drainage and pertinent control measures in the mineral mining industry have been published (Hawley, 1972a,b; Meco, 1972; Hawley and Shikaze, 1971). Hawley (1972a,b) has described the relevant reactions in the formation of acid mine waste associated with Cu, Ni, Pb, Zn, and U mining in Ontario, as well as leaching of active and abandoned tailing piles. The tailings area of an active mine is described as representing a highly fractured "ore body" with enormous newly-exposed surface area. Iron sulfides such as pyrite, pyrrhotite and marcasite are oxidized at different rates to Fe^{+2} and sulfate, releasing a host of other metal ions and acid. Particular concern is noted for abandoned mines versus active mines, where the latter is often pumped to remove water inhibiting leaching, or alternately, tailing seepage is treated by neutralization, aeration and ponding. The abandoned tailing area, fully or partially inundated with water, often has overflow effluents of highly contaminated water characterized by low pH, high concentrations of suspended solids and significant quantities of Fe, Cu, Pb, Zn, Cd, Co, Mn, Al, Ni, Hg, and other metals. Tables 10 and 11 list concentrations of a wide variety of parameters in selected Canadian mine waters and final discharges (Meco, 1972; Hawley, 1972a,b; Falk _et al_, 1973). In the mine water effluent, pH ranged from 2.3 to 8.3, iron from 0.01 to 960 mg/l, and zinc, copper, and cadmium from 0.01 to 220, 0.003 to 39.0, and 0 to 0.25 mg/l, respectively. Of particular note are the relatively high organic carbon concentrations noted in the mine seepage in certain cases (40 mg/l). Organic carbon has been correlated with metal complexation capacity and implicated as a catalyst in metal sulfide dissolution. The wide range of pH values indicates

Table 10.

Chemical characteristics of mine water from selected mines.

	New Brunswick from MECo(1972)		Ontario-from Hawley (1972a)			N.W.T.-from Falk et al (1973)		
Characteristic	Brunswick 12 (partial treatment)	Health Steele	#1	#2	#3	Giant	Echo Bay	Terra
Operation	Pb, Zn, Cu	Cu,Pb,Zn,Ag	U	Fe	Cu,Zn,Pb Ag,Au	Au	Ag,Cu (formerly U)	Ag,Cu
pH	5.2	3.3	2.3	2.6	3.9	6.7	8.3	8.0
Turbidity-JTU				70	2070	>1000	65	140
Suspended solids ppm			15	355	130			
Dissolved solids			6155	3825				
Conductance µmho/cm						1405	337	1461
Chloride ppm			621		11	2.5	5.1	276.0
Sulphate	1389	1066	2800	2280	1136	749	81.3	177
Copper	0.06	39.0		0.96	3.04	0.004	0.052	0.003
Lead	0.4	90.0		0	0	<0.008	<0.004	<0.004
Iron (total)	0.5	2.0	280	960	182	1.1	0.03	0.01
Manganese				83.0	3.68	1.44	<0.01	0.25
Zinc	35.0	220		0.97	16.4	2.2	0.12	0.01
Cadmium	0.004	0.25		0.02	0			
Arsenic				0.38		176	0.8	4.9
Magnesium	70.0	4.0		12				
Potassium	8.0	4.9		5.1		5.7	9.5	11.6
Sodium	42.5	15.5		7		5	25.0	158
Calcium	450	120		101		234	24.1	104
Hardness	1411	316				810	78.3	321

Table 10, continued.

	New Brunswick from MECo (1972)		Ontario-from Hawley (1972a)			N.W.T.-from Falk et al (1973)		
	Brunswick 12 (partial treatment)	Heath Steele	#1	#2	#3	Giant	Echo Bay	Terra
N-Kjeldahl						0	0.97	4.9
N-Nitrate + Nitrite						0.06	1.3	4.1
Organic carbon	5.5	5.0				40	9	19
C.O.D.	23.8	48.8	50	30				
Av. Volume gpm(Can)	250	580						2000 gp day

Table 11.

Chemical composition of the final discharge of some mines. Data from Hawley (1972a) except for Con and Giant Mines - from Falk et al.1973.

Property	1	2	3	4		5	6	Con	Giant
Operation	Cu,-Zn	H_2SO_4 from FeS_2	U	U		Cu,Pb,Zn	Cu,Pb,Zn An,Ag	Au	Au
Status	Active	Abandoned	Abandoned	Active	Abandoned	Active	Active	Active	Active
Lime to Mill eff.	Yes	--	--	Yes	--	Yes	Yes		
pH	3.0	2.6	2.0-2.8	6.1	2.6	6.4	5.3	7.4	8.4
Turbidity - JTU								>1000	10
Suspended solids			25	5	35	18	22.7		
Dissolved solids		9200	13435	3095	3805	1078	1394.9		
Conductance µmho/cm								9878	862
Hardness		1392						3065	301
Acidity - $CaCO_3$		3800	7700	30	1940	29			
Chloride	8	6	97	94	<1.0			3135	25.2
Sulphate	855	4050	6900	1560	2150	670	1003.5	279	290
Iron (total	11.7	1310	220-340	0.4	550	29	22.7	1.4	0
Manganese	0.42	8.2	3.6			0.58		0.06	0.019
Nickel		6.3	1.5			0			
Cobalt	0.06	2.7	1.5						
Uranium			5.6						
Titanium		14	3.6						
Zinc	0.43	34	9.4			2.15	6.5	0.13	0.069
Copper	0	2.45	2.2			0.22	1.1	0.2	8.3

Table 11, continued.

Property	1	2	3	4		5	6	Con	Giant
Operation	Cu,-Zn	H_2SO_4 from FeS_2	U	U		Cu,Pb,Zn	Cu,Pb,Zn An,Ag	Au	Au
Status	Active	Abandoned	Abandoned	Active	Abandoned	Active	Active	Active	Active
Lime to Mill eff.	Yes	--	--	Yes	--	Yes	Yes		
Lead	0.11	0.5				0		<0.006	<0.006
Cadmium	0	0.12							
Magnesium		178				16			
Calcium		454						1125	116
Arsenic	0.06	<0.02						6.8	15.0
C.O.D.		110	278	11	58				
N-Kjeldahl		6	100	83	12			1.34	12.24
N-Nitrate			10	68.6	1.3			12.5	0.1

the diversity in hydrologic conditions, ore type and acid buffering capacity of the associated gangue material. Table 11 lists the chemical composition of the final discharge water of some Canadian mines, both active and abandoned. Typical concentration ranges are:

Parameter	Range*
pH	2.6 - 8.4
SO_4^{-2}	279 - 6900
Acidity - $CaCO_3$	29 - 7700
Fe	0 - 340
Cu	0 - 8.3
Cd	0 - 0.12
Zn	0.069 - 9.4
Ni	0 - 6.3
Co	0.06 - 2.7

*expressed as mg/l(ppm) except pH.

Hawley (1972a,b) described a set of rules which if followed would virtually eliminate acid mine wastes in Ontario. Measures proposed paid particular attention to pre-mine planning, recognition of acid drainage indicators and post-mining operations such as revegetation.

Duluth Gabbro Leaching Studies

Only a handful of reports and publications are available of laboratory and field research experiments on leaching of Gabbro lean ore, tailings and waste rock. Pertinent laboratory studies will be discussed initially so as to aid in understanding field monitoring data on lean ore and tailing pile seepages.

A. Laboratory Studies:

Trivedi and Tsuchiya (1975) and Iwasaki et al. (1976) have reported on the bacterial leaching of Cu-Ni sulfide concentrate or lean ore. Trivedi and Tsuchiya (1975) utilized the symbiotic action of Thiobacillus ferrooxidans (fixes CO_2) and Beijerinckia lacticogenes (fixes N_2) and low pH solutions to leach Cu-Ni flotation concentrate obtained from the Duluth Gabbro in a nutrient medium. The rates of Cu and Ni extraction are illustrated in Figure 5. Bacteria greatly enhanced the rate and extent of metal release, especially when T. ferrooxidans and B. lacticogenes acted symbiotically. Concentrations of Cu and Ni extracted from the concentrate after 500 hours were approximately 6.0 and 1.8 g/l, respectively, corresponding to extraction efficiencies of ~ 72% and 100%, respectively. It is important to note that significant quantities of Cu and Ni were released in the chemical control (low pH). In addition, the authors noted that metal release decreased remarkedly if the solution increased above pH 4, apparently minimizing bacterial activity.

A similar bacterial leaching study was performed by Iwasaki et al.(1976) on Gabbro lean ore assaying at 0.71% Cu and 0.15% nickel. The lean ore was column leached by a nutrient medium initially adjusted to pH 3 in a solution recycle system. The lean ore was crushed to pass a 10 mesh screen and the leach solution containing innoculations of T. thiooxidans or F. ferrooxidans was cycled through the column for ~ 40 weeks. Results indicated that both Cu and Ni were extracted as long as low pH conditions were maintained. Cu and Ni concentrations reached 1.9 to 2.6 g/l and 0.75 g/l, respectively after 40 weeks representing 40% Cu and 60% Ni extraction. Nickel was observed to be released at a faster rate and earlier than copper. The control leach solution without nutrients adjusted to pH 3 rapidly equilibrated at a higher pH.

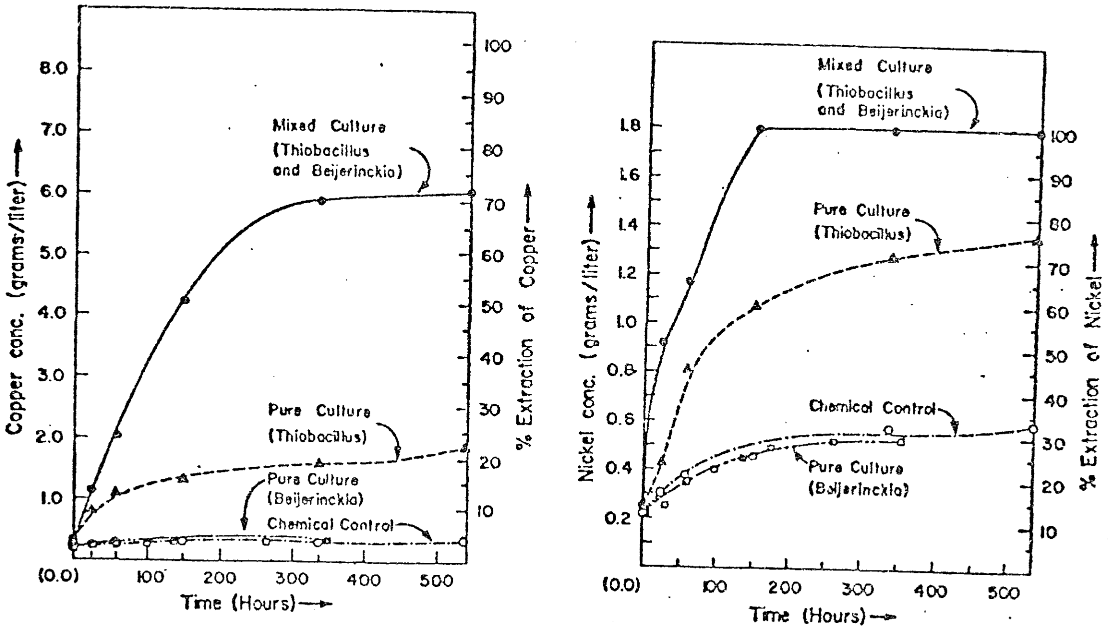

Figure 5. Batch leaching of copper and nickel with pure and mixed cultures of <u>T. ferrooxidans</u> and <u>B. lacticogenes</u> at 25°C. (From Trivedi and Tsuchiya, 1975).

Duluth Gabbro tailing equilibrated to a pH near 8 and the tailing tended to buffer the pulp ore at pH 3.5 to 4.0 even when as high as 75 lbs. H_2SO_4 per ton were added, presumably due to the presence of silicate-rich feldspar and olivine. A discussion of lean ore and tailing buffering effects is presented later.

Laboratory studies involving chemical leaching of Duluth Gabbro lean ore and tailings have been reported by Long and Bydalek (1975), Iwasaki et al (1976), and AMAX (1975), and are described below.

Long and Bydalek (1975) examined the release of Zn, Cu and sulfate plus alterations in pH and specific conductivity from Gabbro copper-nickel tailings obtained from INCO (1974). Tailings (2000 g) were leached in a stirred system by 40 liters of distilled water (50 g/l tailings) in polyethylene containers for 32 days at ~ 20 C. Samples (600 ml), removed at varying intervals for analysis, showed Cu levels less than 0.5 g/l and Ni concentrations were variable ranging from ~ 1 to 4.0 g/l over 32 days of leaching. Solution pH increased dramatically from the initial control value of 4.7 to a stable 7.7 to 7.8. The observed behavior probably represents the buffering capacity of the plagioclase and olivine minerals in the tailing material. Chemical changes were evident, however, in that sulfate concentrations (~1 to ~20 mg/l) and specific conductance increased steadily over the leach period. In the absence of significant catalytic factors, the leaching observed may have been a result of sulfide oxidation by oxygen (slow reaction) releasing small quantities of metals and common ions (Cl^-, Ca^{+2}, Mg^{+2}, etc.). Sorption of leached metals on remaining solids as well as solid/solution ratio and low metal sulfide content of the tailings may explain the very low Cu and Ni levels. It is doubtful that results obtained can be correlated with environmental conditions due to the absence of natural chemical constituents. As observed in other studies, the tailings exhibited a buffering capacity of some proportions.

Iwasaki et al (1976) studied the rate of pH change and Cu, Ni release from crushed Duluth Gabbro in a column leach, distilled water recycle system over a two year period. (Figure 14). One column packed with Gabbro exhibited a decreasing pH which eventually leveled off below pH 5. Leachate concentrations were 4ppm Cu^{+2} and 44 ppm Ni^{+2}, and high ferric hydroxide levels were observed as evidenced by solution discoloration. A second column containing crushed Gabbro mixed with 5% calcite leached in a similar manner remained buffered at pH7.5 with negligible Cu and Ni release observed. The experimental set-up of Iwasaki et al. (1976), although not directly applicable to the environment, indicates that sufficient buffering capacity exists in lean ore and tailings to maintain the pH at moderate values minimizing metal release. The recycling system used can be thought of as natural weathering induced to occur at an enhanced rate.

AMAX (1975) performed a series of batch and column leaching experiments with crushed mineralized or non-mineralized Gabbro ore or overburden (soil) in numerous combinations. The leaching solution was comprised of variable concentrations of sulfuric acid and acetic acid or distilled water. The latter was used to simulate the leaching due to rain water. Initial experiments (batch and column) utilized CO_2-saturated distilled water (pH 5.7) as the leaching solution.

Column leaching experiments were performed by passing the equivalent of 1" of water through the "chromatographic" columns daily and collecting the eluant for Cu, Ni, pH and related parameter analysis. The results showed negligible Cu and Ni release unless overburden (silty-loam) was positioned atop the ore to be leached. Concentrations of Cu ranged from ∿ 20 to 26 μg/l in the eluant for overburden/ore columns but ranged only ∿ 4 to 18 μg/l for columns containing ore. Nickel concentrations under similar circumstances ranged from ∿ 10 to 38 μg/l (overburden/ore) to ∿ 5 to 14 μg/l (ore alone). Copper and nickel leached from overburden-only columns ranged up to ∿ 170 and 60 μg/l, respectively. The overburden either released Cu and Ni increasing measured concentrations and/or released chelating agents capable of binding and extracting additional metal. Since measurements of organic carbon or metal analysis of digested samples were not performed, no indication of the relative importance of either mode of action exists. The pattern of Ni^{+2} release with time indicated that Ni^{+2} was released from the sulfide ore in one form and subsequently sorbed on the surface in another as the pH increased. Batch (static) experiments exhibited similar leaching behavior from 5% (w/v) ore samples using CO_2-saturated distilled water (pH 5.7). Other column experiments indicated that significant alkalinity (72 - 103 mg/l as $CaCO_3$), silicate (17.5 to 69.8 mg/l Si), Mg^{++}, Ca^{++} and organic substances were leached from lean ore, overburden/ore and overburden substrates.

AMAX (1975) conducted a series of experiments in which sulfuric acid and acetic acid were used to induce metal release. The results showed that Cu^{+2} and Ni^{+2} release was enhanced markedly as solution pH decreased. Of greater potential importance is that the Gabbro exhibited the ability to buffer the system with respect to added acidity. The added acidity also induced significant cobalt and iron release as well as sulfate in quantities well above stoichiometric requirements. This latter behavior suggests that iron (or metal) sulfide oxidation occurred.

B. Field Studies

At the time this review was written, no systematic study of metal contaminant leaching from Gabbro material under environmental conditions had been reported. However, several instances of apparent leaching from recently exposed mineralized ore in northeastern Minnesota have been documented, and are summarized below.

U. S. Steel Gabbro Pit No. 2 was excavated in 1971 to obtain a bulk ore sample for metallurgical testing. The resulting basin was completely self-contained, receiving inflow from snow-melt and precipitation. By 1973, the exposed mineralized ore was partially inundated with water creating a pool of stagnant water in intimate contact with the ore. Concentrations of selected chemical constituents in the supernatant were reported as (MPIRG, 1976; U.S. Steel, 1973):

pH	5.3
SO_4^{-2}	356 mg/l
Cu^{+2}	9.2 mg/l
Ni^{+2}	17.2 mg/l

The lack of flow and mixing apparently inhibited contact of the leach solution with native buffering minerals allowing the pH to be slightly depressed.

The International Nickel Company, Inc. (INCO) applied for and was granted permission to remove a 10,000 ton ore sample for metallurgical studies in early 1975 from a potential mining site (Spruce Road) in Lake County, Minnesota. Mineralized ore from $\sim$ 0.4 acres and 15 to 20 feet below the original surface was removed by excavation, followed by regrading and seeding of the property to original contours. In the Spring of 1975, some subsidence of the rock fill was noted and a seepage observed emanating from the excavated site. Analysis of the seepage from May to November, 1975 revealed significant concentrations of metallic cations, anions and other pollutant parameters. A summary of measured constituents is noted below (INCO, 1976):

Parameter	Mean	Std. Dev.
Cu	122←µg/l→	82
Ni	2149	1218
Zn	8.7	3.6
Mn	4408	441
Fe	3535	2548
Hg	0.39	0.54
Cd	0.16	0.08
Co	254	28
SO_4	294 ← mg/l→	17
Hardness	964	473
Alkalinity	104	35
Cl	6.4	1.6
pH	6.7	0.3

In general, Mn, Cd and Co occurred predominantly in 0.4 µm filtrates while Fe occurred primarily in the particulate phase, probably as ferric hydroxide. The data also indicates that relatively high concentrations of metals are released into solution even though an acidic pH is not attained. Sulfide oxidation is supported by the inflated levels of sulfate observed while alkalinity > 100 mg/l as $CaCO_3$ implies that acid released in sulfide oxidation is probably neutralized by gangue material and plagioclose or olivine minerals.

Eger (1976) and MPIRG (1976) have recently described the apparent leaching of heavy metals from ∿ 5.4 million tons of Duluth Gabbro ore which has been stockpiled by Erie Mining Company along the east side of its Dunka Pit. The stockpiles are segregated into two units: a Gabbro ore pile and a waste rock pile based on a copper cutoff of ∿ 0.2%. These piles are described as representing a lean ore and waste rock pile which would be produced in actual copper-nickel mining operations. Eger (1976) states that the piles represent a "worst case" study for assessing leaching impact because water was allowed to accumulate around and flow through the piles. At the present time, considerable effort has been expended to alter the water flow characteristics. However, flow arising from pile runoff or flow through the stockpiles resulted in a seepage containing considerable quantities of leached components. Concentrations of Cu and Ni ranged from 2 to 700 ppb and 4 to 5340 ppb, respectively, in flowing seepages and stagnant pools. Even when metal concentrations were high, the seepage ranged from pH 7.1 to 8.1, again suggesting that acid released in metal sulfide oxidation was neutralized by native material.

Acid-Buffering Capacity of Gabbro Complex

The development of acid-mine drainage is dependent on the concentration and oxidation of iron sulfide (acid release) and the acid-neutralizing capacity of plagioclose and olivine minerals. Sufficient information exists from laboratory and field leaching studies described above for the Duluth Gabbro Complex to suggest that adequate acid-neutralizing components are present to inhibit acid accumulation. The presence of acid enhances heavy metal leaching by maintaining Fe^{+3} in solution, promoting the growth of iron and sulfur-oxidizing bacteria, dissolving gangue material away from reactive surfaces, and simply dissolving metal sulfides. It is clear that mitigating factors exist for Gabbro material since relatively high metal concentrations in seepages have been observed without acidification of the seepage. A qualitative leaching model is proposed later, accounting for observed anomalies.

The sulfur content of Duluth Gabbro is in the range of 0.5 to 1% which theoretically could generate ∿ 50 lbs (22.7 kg) of sulfuric acid per ton upon complete oxidation (Iwasaki et al, 1976). The authors reported that complete sulfide oxidation would result in a buffered pH > 4. In contrast, two typical Western dump-leach ores readily acidified to pH 2.5 with 2.5 lbs. (1.1 kg) and 5 lbs. (2.3 kg) of added sulfuric acid per ton.

Iwasaki et al (1976) also found that flotation tailings containing 0.05 to 0.1% sulfur would yield ∿ 5 lbs. (2.3 kg) of sulfuric acid which is not sufficient to reach a low pH. Examination of the tailing composition (Lawver et al, 1975) shows large concentrations of SiO_2 , an acid-consuming substance:

SiO_2	53.36%	K_2O	0.37
Al_2O_3	28.40	TiO_2	0.20
FeO	0.35	Cu	0.018
MgO	0.14	Ni	0.009
CaO	11.00	Na_2O	4.20
		S	<0.1

The reactions responsible for uptake of acid by silicate minerals are analogous to the weathering of aluminum silicates which may be schematically represented by (Stumm and Morgan, 1970):

$$\text{cation Al-silicate} + H_2CO_3^* + H_2O \rightarrow HCO_3^- + H_4SiO_4 + \text{cation} + \text{Al-silicate(s)}.$$

$H_2CO_3^*$ represents carbon dioxide dissolved in water. As a result of the above reaction, alkalinity is imparted to the dissolved phase from the bases of minerals. Its occurrence at high concentrations indicates that acid released in the oxidation of iron sulfide to sulfate is neutralized by silicate minerals releasing bicarbonate. The latter species, HCO_3^-, is also the predominant buffering component of natural waters. Examples of typical acid-neutralization reactions by native material are given in Table 12.

Bell (1974) has forwarded the concept of acid-generation potential (AGP) which was developed by B. C. Research in Vancouver (CANADA) under contract to the Canada Department of the Environment to evaluate the ultimate leaching properties of ore and tailings. The test consists of two parts; an initial chemical evaluation is made of the acid-producing potential of a ground sample of ore or tailing compared to its acid-consuming ability. In the former case, the sample is equilibrated with water, after which pH measurements are made. In the latter case, the sample is titrated with sulfuric acid to pH 3.5. Secondly, if acid-producing ability is greater than acid consumption, the sample is spiked with an innoculum of <u>T. ferrooxidans</u> and agitated at pH 2.5 at 35° C. After three days, the amount of SO_4^{-2}, Fe^{+2}, Fe^{+3}, Cu^{+2}, Ni^{+2}, etc., released from the ore or tailing is determined. Under these conditions, the combined effect of acidification and bacterial-catalyzed leaching on heavy metal release can be evaluated. AGP is a concept applied

TABLE 12

Examples of Typical Weathering Reactions[a]

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1. calcite

$$CaCO_3(s) + H_2CO_3^* \rightleftarrows Ca^{+2} + 2HCO_3^- + H_2O$$

2. gibbsite

$$Al_2O_3 \quad 3H_2O(s) + 6H_2CO_3^* \rightleftarrows 2Al^{+3} + 6HCO_3^- + 6H_2O$$

3. albite

$$NaAlSi_3O_8(s) + H_2CO_3^* + 9/2H_2O \rightleftarrows Na^+ + HCO_3^- + 2H_4SiO_4 + \tfrac{1}{2}Al_2Si_2O_5(OH)_4(s) \text{ (Kaolinite)}$$

4. anorthite

$$CaAl_2Si_2O_8(s) + 2H_2CO_3^* + H_2O \rightleftarrows Ca^{+2} + 2HCO_3^- + Al_2Si_2O_5(OH)_4(s) \text{ (Kaolinite)}$$

5. plagioclose (andesine)

$$4Na_{0.5}Ca_{0.5}Al_{1.5}Si_{2.5}O_8 + 6H_2CO_3^* + 11H_2O \rightleftarrows 2Na^+ + 2Ca^{+2} + 4H_4SiO_4 + 6HCO_3^- + 3Al_2Si_2O_5(OH)_4(s) \text{ (Kaolinite)}$$

6. K-feldspar (orthoclose)

$$3KAlSi_3O_8(s) + 2H_2CO_3^* + 12H_2O \rightleftarrows 2K^+ + 2HCO_3^- + 6H_4SiO_4 + KAl_3Si_3O_{10}(OH)_2(s) \text{ (Mica)}$$

7. biotite

$$KMg_3AlSi_3O_{10}(OH)_2(s) + 7H_2CO_3^* + \tfrac{1}{2}H_2O \rightleftarrows K^+ + 3Mg^{+2} + 7HCO_3^- + 2H_4SiO_4 + \tfrac{1}{2}Al_2Si_2O_5(OH)_4(s) \text{ (Kaolinite)}$$

---

[a] Modified from Stumm and Morgan (1970).

generally to coal mining and base-metal mining operations where significant quantities of iron sulfide are present. The Cu - Ni ore, waste rock and flotation tailings from the Duluth Gabbro Complex contain iron sulfide (mainly as pyrrhotite) but also include up to 75% by weight feldspar-type silicates capable of neutralizing acids. Iwasaki et al. (1976) showed that insufficient iron sulfide was present in ore and tailings examined to overcome the acid-neutralizing capacity of plagioclose, olivine, and pyroxene minerals. The theoretical basis for acid and base neutralizing capacity as applied to solution components is given in Stumm and Morgan (1970). The application to silicate minerals is straightforward.

A Qualitative Model of Duluth Gabbro Leaching

The release of heavy metals to surface waters from mining solids (ore, waste rock, tailings) under environmental conditions in the Duluth Complex is apparently influenced and controlled by factors not important in acid mine drainage (AMD). In AMD, sulfuric acid formed in the oxidation of iron sulfide to ferrous iron and sulfate lowers the solution to pH (2.5 to 3.5) where bacteria (T. ferrooxidans) catalyze ferric iron formation enhancing further iron sulfide and metal sulfide dissolution. It is readily apparent that flowing and stagnant aqueous pools in intimate contact with Gabbro ore and tailings buffer the aqueous phase inhibiting acidification of the leaching solution. The inhibition of acidification of seepage or standing waters does not prevent the release of heavy metals. Sulfide oxidation is a prevailing mechanism of metal sulfide dissolution as evidenced by the occurrence of large quantities of sulfate. Concurrently formed acid is likely neutralized by native

Any sulfide ion in equilibrium with the solid phase may be oxidized by O_2 further enhancing dissolution by shifting the solubility equilibrium to the right:

$$HS^- + 2O_2 \rightleftarrows SO_4^{-2} + H^+ .$$

In addition, the rate of sulfide oxidation by O_2 increases exponentially with pH and is catalyzed by many cations present. Copper in equilibrium with the solid phase may interact with inorganic and organic complexing agents which again tends to shift the solid phase reaction to the right solubilizing additional metal and stabilizing the metal to precipitation and adsorption.

$$Cu^{+2} + Y^{-2} \rightleftarrows Cu{-}Y^{(+2-n)}$$

where Y^{-2} = inorganic or organic complexing agents. The copper released to solution may remain soluble even though acid conditions are not maintained. Complexation/speciation models described later suggest that copper bound to simple low molecular weight organic such as citrate represents ~90 to 100% of the total metal under oxidizing conditions. Nickel proves even more mobile once released by pentlandite dissolution.

Acid generated in the process of sulfide oxidation and iron hydrolysis may be neutralized by highly-buffering minerals such as those listed below before flowing out of the system:

$$\text{Na - Feldspar(s)} + H^+ + 9/2H_2O \rightleftarrows \tfrac{1}{2}\,\text{Kaolinite(s)} + 2H_4SiO_4 + Na^+$$

$$\text{Ca - Feldspar(s)} + 2H^+ + H_2O \rightleftarrows \text{Kaolinite(s)} + Ca^{+2}$$

$$CaCO_3(s) + 2H^+ \rightleftarrows Ca^{+2} + H_2CO_3^*$$

minerals such as plagioclose, olivine and pyroxene. Reaction of acid with silicate minerals would generate HCO_3 which is observed in the range of 100 to 200 mg/l as $CaCO_3$ (2 to 4 meg H^+/l) in the seepage.

The following sequence of chemical reactions is proposed as a qualitative model of metal sulfide leaching using chalcopyrite as an example:

Chalcopyrite has been observed to dissociate under oxidizing conditions into covellite (CuS) and troilite (FeS)

$$CuFeS_2 \rightleftarrows CuS + FeS$$

following which FeS is rapidly oxidized to ferric ion in solution plus sulfate according to:

$$FeS + 9O_2 + 4H^+ \rightleftarrows 4Fe^{+3} + 4SO_4^{-2} + 2H_2O.$$

Covellite may then dissociate forming cupric ion and sulfide or may react rapidly with ferric ion in-situ:

$$CuS + 2Fe^{+3} \rightleftarrows Cu^{+2} + S^0 + 2Fe^{+2}$$

Ferrous ion formed in the above sequence of reactions may be oxidized by O_2:

$$Fe^{+2} + \tfrac{1}{4}O_2 + H^+ \rightleftarrows Fe^{+3} + \tfrac{1}{2}H_2O.$$

Any factor, physical, chemical, or biological which enhances the oxidation of troilite or covellite tends to promote chalcopyrite dissolution. Ferric ion generated by oxidation of FeS may either hydrolyze to form ferric hydroxide releasing acid

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

or attack the solid chalcopyrite by oxidizing sulfide to sulfate or elemental sulfur:

$$CuFeS_2 + 14Fe^{+3} + 8H_2O \rightleftarrows 15Fe^{+2} + 2SO_4^{-2} + 16H^+.$$

$$\text{(Biotite)}\quad KMg_3AlSi_3O_{10}(OH)_2(S) + 7H_2CO_3^* + \tfrac{1}{2}H_2O \rightleftarrows K^+ + 3Mg^{+2} + 7HCO_3^- + 2H_4SiO_4 + \tfrac{1}{2}Al_2Si_2O_5(OH)_4(S) \quad \text{(Kaolinite)}$$

Once the metals are released by dissolution of the metal sulfide, the solid phase reaction becomes irreversible under oxidizing conditions. Cu^{+2}, Ni^{+2}, Zn^{+2}, Co^{+2}, etc. tend to remain in solution even though the pH remains near neutrality and are washed out of the pile as a seepage by rainfall or groundwater. Note that low pH is <u>not</u> a prerequisite to metal sulfide leaching and organic complexing agents such as humic/fulvic acids in bog water likely promote leaching and stabilize metals in solution.

Chemical Speciation

Introduction

The speciation of metal ions and ligands in fresh waters has important implications in the fields of aquatic ecology, fresh water biology, limnology, and water quality management. At present, experimental chemical data and phenomenological models are not adequate to predict the distribution and fate of trace metals in aquatic environments. On the other hand, chemical equilibrium models can be used for gaining insight into the various processes which govern the fate of trace metals in natural waters (Morgan, 1967; Stumm and Morgan, 1970).For example, the biological availability of trace metals such as Cu, Ni, Fe or Mn depends on the fraction of free available metal. Metals which are complexed with inorganic or organic ligands, adsorbed on a solid surface or present as precipitates would be unavailable for biological uptake (Morel, *et al.*, 1972). Evidence for the existence of a number of metal ions (Zn, Cu, Cd, Pb) in bound states in natural waters has been obtained from measurements using anodic stripping voltammetry (ASV) (Zirino and Healy, 1972; Chau and Chan, 1974). Equilibrium models, which use known stability constants and experimental data for total metal and ligand concentrations, can be used to determine a thermodynamically feasible distribution of species between bound and unbound states.

In this section, an equilibrium model that accounts for the dissolution of metal sulfides and the chemical speciation of released trace metals in an International Nickel Company seepage pond is presented. An equilibrium model of this type should be useful in establishing simple boundary conditions that will help explain observed phenomena. Important parameters that control the solubility of mineral phases in solution are treated in this model. They are the pH of solution, the type and concentration of complexing inorganic and organic ligands and chelating agents, the oxidation state of the mineral components, the redox environment of the system, and the adsorption of trace metals on surfaces or natural colloidal material.

The model of leaching and chemical speciation was based on experimental data collected by Eugene A. Hickok and Associates (INCO, 1976) for the concentration of complexing ligands and of trace metals such as Cu, Ni, Co, Mn, Fe, Co, Zn, Hg and Pb. The analyses were performed on samples taken from a seepage pond located approximately ten miles southeast of Ely, Minnesota. Sophisticated computational techniques were used to calculate a complex equilibrium system which involved 13 metals, 10 ligands, 163 complexes, 27 possible solids, 7 redox reactions and 2 adsorbing surfaces. Calculations were performed with the aid of REDEQL2, a multi-purpose computer program which has the capability of computing chemical equilibrium in aqueous systems involving acid-base, coordination, solubility, redox and adsorption phenomena. Ionic strength corrections and interaction intensities were also calculated.

REDEQL2 (Morel and Morgan, 1972) uses the stability constant approach and the Newton-Raphson method for digital computation of chemical equilibrium. The stability constant approach involves solving a set of non-linear equations provided by the mass action law and mole balance equations for a chemical system consisting of metals, ligands, complexes, gases and solids. Concentrations of complexes are expressed as a function of free metal and free ligand concentrations by the mass law equations. A solution is achieved when a set of free metal and free ligand concentrations is found that will satisfy the mole balance equations.

Equilibrium Model - Assumptions

As an initial assumption, interactions of trace metals, metal complexes and ligands with biological organisms (bacteria, phytoplankton, zooplankton, and plants) will be neglected. Many chemical processes in natural waters are dominated by dissolved oxygen levels, pH, ionic strength and solution composition. Therefore, to neglect biological activity as a first approximation should not lead to spurious results.

A steady-state condition for the seepage pond will be assumed because to assume an equilibrium state of a closed system may be a poor approximation due to inflows and outflows occurring at the boundaries. An open system such as the seepage pond can be closely approximated by an equilibrium model (Morgan) if reactant A going to product B can be represented by

$$A \underset{k'}{\overset{k}{\rightleftarrows}} B \qquad (1)$$

and the steady-state condition

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \qquad (2)$$

can be applied, then for a completely mixed volume, V, and a volume rate of flow, Q, the law of microscopic reversibility (equation 3) can be used to obtain equation (6)

$$K = k/k' \qquad (3)$$

$$d[A]/dt = Q/V([A_o]-[A] - k[A] + k'[B] \qquad (4)$$

$$d[B]/dt = Q/V([B_o]-[B]) - k[A] - k'[B] \qquad (5)$$

$$[A]/_{[B]} = \frac{1}{K} + \frac{1}{k(V/Q)} \qquad (6)$$

from substitution into the material balance rate expressions for A and B when $[B_o] = 0$. The steady-state ratio $[B]/[A]$ approaches K when the flows to the system are small with respect to the rates chemical reaction. In other words, the residence time ($\tau_R = V/Q$) is much greater than the half-life of the reaction ($\tau_{1/2} = \ln 2/k$) so that the time invariant condition of a well-mixed volume can be considered to approach chemical equilibrium.

Data

Data used in the development of a model of the leaching process and of the chemical speciation were obtained from the International Nickel Company (INCO) report released in January 1976. Data collected on 10 October 1975 from the seepage pond (Site A) were used in all calculations. These data are listed in Table 13 along with some typical values for trace metal concentrations in freshwater systems (Morel, et al., 1973). Calcium and carbonate concentrations were estimated from alkalinity measurements.

Comparison of the pond data to the typical values reveals that Ca, Fe, Mn, Cu, Ni, Co, Mg, and $SO_4^=$ are significantly higher than values commonly found in fresh water systems. On the other hand, Cd, Zn, Hg, Pb, Cl^- and $CO_3^=$ are lower than values normally found in relatively clean waters. Additional input data into the models were based on typical values for total organic carbon and a reasonable value for monomeric orthosilicic acid (H_4SiO_4) which would be expected to result from the weathering of aluminum-silicates.

$$\text{cation-Al-silicate} + H_2CO_3 + \rightleftarrows HCO_3^- + H_4SiO_4 + \text{cation} + \text{Al-silicates} \quad (7)$$

A value for TOC of 40 mg/l was assumed to be a representative concentration of soluble organic species in waters of Northeastern Minnesota. Four organic ligands, cysteine, citrate, glycine and nocardamine were chosen as representative organic ligands (Pitt et al., 1975). Cysteine and glycine are amino acids. Citrate is the anion of a polyprotic acid and nocardamine

Table 13

Trace metal data used for input into equilibrium models

CONSTITUENT	-log molar concentration INCO POND	 TYPICAL*
Ca	2.69	3.00
Fe	4.05	5.00
Mn	4.12	5.50
Cu	5.69	6.00
Cd	8.67	6.00
Zn	6.98	7.00
Ni	4.32	6.50
Hg	9.30	9.00
Pb	9.01	7.00
Co	5.33	7.50
Mg	2.68	3.50
$CO_3^=$	2.87	3.00
Cl^-	3.65	3.50
$SO_4^=$	2.53	4.50

*See (Morel, McDuff and Morgan) for some typical values for analytically determined concentrations of metals and ligands in fresh waters.

is a large (MW~900) naturally occurring heteromeric peptide which contains a trihydroxamate as a specific Fe(III) binding site. The average molecular weight for these organic ligands is approximately 322. Concentrations of p4.5 for each organic ligand were imposed on the system. A value for $PSiO_4^{-4}$ of 2.9 was also imposed on the system. This value is consistent with the fact that plagioclase constitutes a significant percentage of the Gabbro ores and would be expected to weather according to equation 8.

$$4\ Na_{0.5}Ca_{0.5}Al_{1.5}Si_{2.5}O_8 + 6\ H_2CO_3 + 11\ H_2O \rightleftarrows 2\ Na^+ + 2\ Ca^{+2} + 4\ H_4SiO_4 + 6\ HCO_3^- + 3\ Al_2Si_2O_5(OH)_4 \qquad (8)$$

In addition to the known analytical concentrations, seven redox reactions and 2 adsorbing surfaces were also considered.

$$X_{ox} + n\bar{e} = X_{red} \qquad (9)$$

Redox couples that were considered were the following: $Fe^{+2} \rightarrow Fe^{+3}$, $Mn^{+2} \rightarrow MnO_2$, $Co^{+2} \rightarrow Co^{+3}$, $S^{-2} \rightarrow SO_4^=$, $Fe^{+3} \rightarrow Fe_3O_4$, $Mn^{+2} \rightarrow MnOOH$ and $Pb^{+2} \rightarrow PbO_2$. $Fe(OH)_3$ and α-SiO_2 were imposed as adsorbing surfaces and calculations of adsorption constants are computed according to the adsorption model of James and Healy (1972).

Results

A model of the chemical speciation of the seepage pond without the imposition of organic ligands is presented in Figure 6 and the major chemical species are listed in Table 14. The measured pH of the pond was 6.7 and in this model the pH was varied in order to ascertain the impact of pH on the distribution of the major metal species. An oxidation-reduction level characteristic of an oxidizing condition was assumed since the pond was exposed to the open

FIGURE 6. Inorganic model of the speciation of the predominant trace metals in the INCO seepage pond (Site A). % Total Metal is plotted as a function of pH where $p\varepsilon = 4.0$ and $\mu = 0.017$. See Table 1 for pTOT[M] values.

INORGANIC SPECIATION

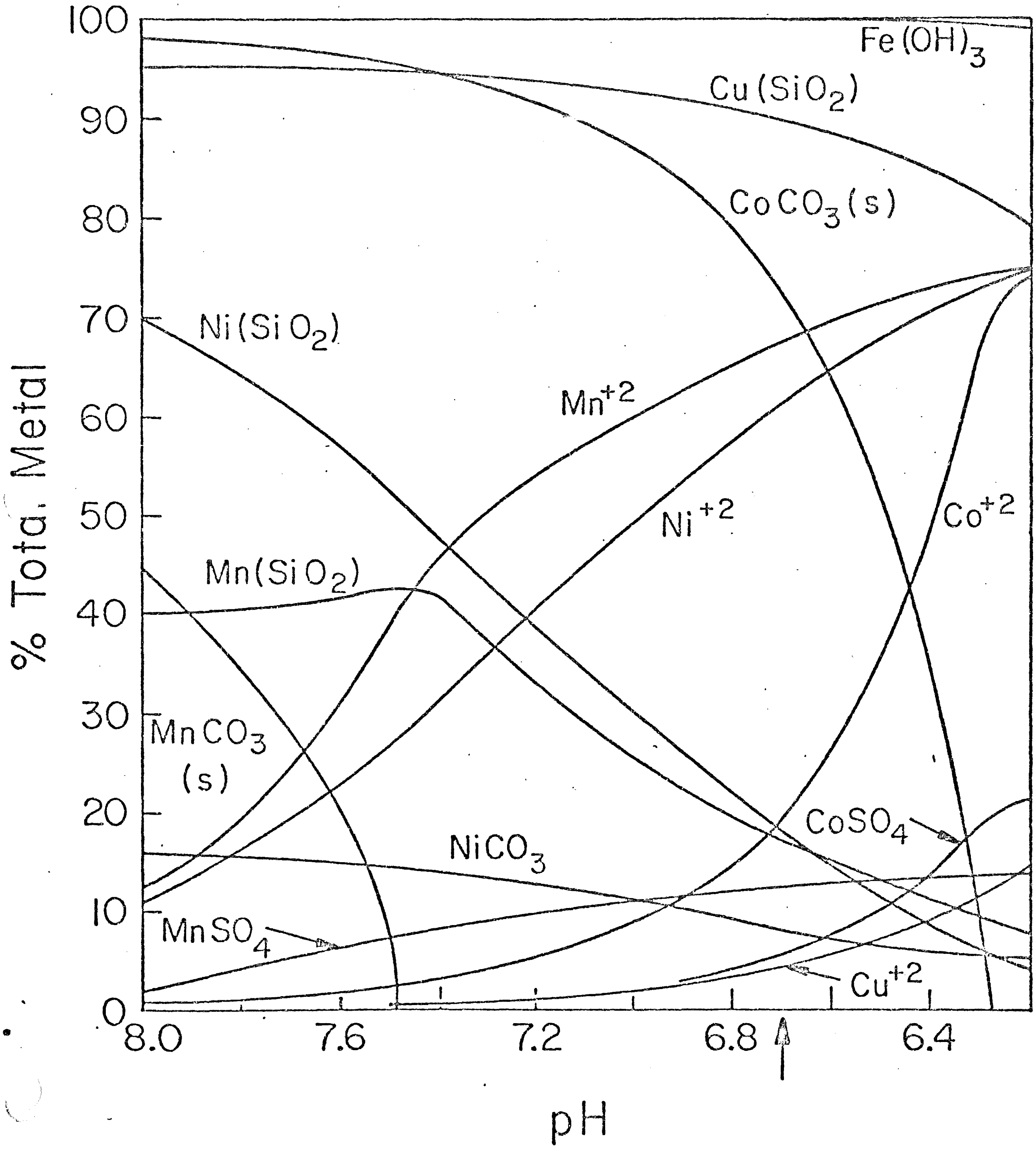


Table 14.

Results of an inorganic equilibrium computation for oxidizing conditions: $p\varepsilon = 40$. Predominant trace metal species at pH = 6.7.

Species	p[c]
$Fe(OH)_3$	4.05
$Fe^{+3}-SiO_2$	6.95
Fe^{+2}	8.07
$FeSO_4$	8.81
$Cu^{+2}-SiO_2$	5.73
Cu^{+2}	7.06
$CuCO_3$	7.07
$CuSO_4$	7.80
Ni^{+2}	4.53
$Ni^{+2}-SiO_2$	5.07
$NiSO_4$	5.27
$NiCO_2$	5.36
$CoCO_3$	5.47
Co^{+2}	6.04
$CoSO_4$	6.58
$CoCO_3$	6.97
Mn^{+2}	4.29
$Mn^{+2}-SiO_2$	4.88
$MnSO_4$.	5.03
$MnCO_3$	5.63

atmosphere and the BOD of the system was assumed to be minimal. To model the pond a $p\varepsilon$ of 4.0 was chosen and an ionic strength $\mu = 0.017$ was imposed.

$$p\varepsilon = -\log[\bar{e}] \qquad (10)$$

where $[\bar{e}]$ is the effective activity of electrons in the system (Stumm and Morgan). At pH 6.7 Mn^{+2} and Ni^{+2} are present predominately as free metals whereas Fe^{+3} is precipitated as $Fe(OH)_3$ and Co^{+2} is precipitated as $CoCO_3$. Cu^{+2} under these conditions is adsorbed on the surface of a α-SiO_2, which would be representative of a bottom sand. If the pH of the system were close to 8, precipitation of the metals by carbonate and adsorption on α-quartz would be controlling the distribution of species.

Even though the organic component of the seepage pond waters is unknown it seems reasonable to assume that it has moderate complexing properties. To determine the effect of organics, a representative set of ligands was superimposed on the basic inorganic model. The resulting modification of the trace metal speciation is depicted in Figure 7 and the predominant trace metal species at pH 6.7 are listed in Table 15. The major impact of the organic ligands is to solubilize Cu^{+2} and to some extent Fe^{+3}. This is consistent with the INCO resu which indicate that Cu^{+2} is in a soluble form and Fe^{+3} predominantly in particulate form. A major conclusion that can be drawn from this model is that organic materials will play important roles in the speciation and fate of trace metals released into aquatic systems near Cu-Ni mining sites. Mn^{+2} and Co^{+2} is unaffected by the addition of organics, whereas Ni^{+2} is complexed by citrate and cysteine. Similar results for the speciation of the low concentration trace metals, Zn, Cd, Pb and Hg are presented in Figure 8 and Table 16.

FIGURE 7. Model of the speciation of the predominant trace metals with a superimposed set of representative organic ligands. % Total Metal is plotted as a function of pH where $p\varepsilon = 4.0$ and $\mu = 0.017$. NOC = nocardamine, CYST = cysteine, CIT = citrate and GLY = glycine.

ORGANIC SPECIATION

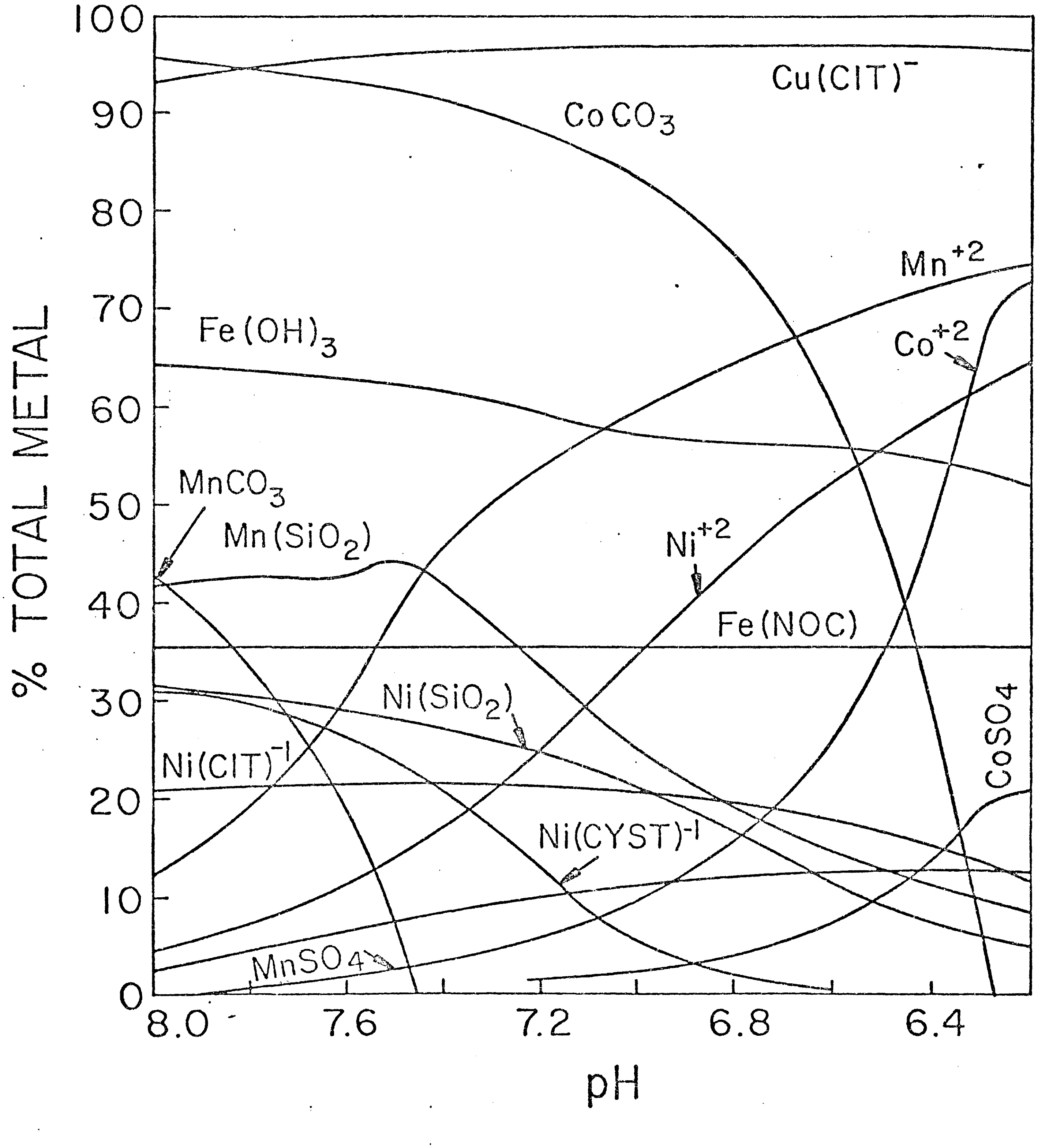


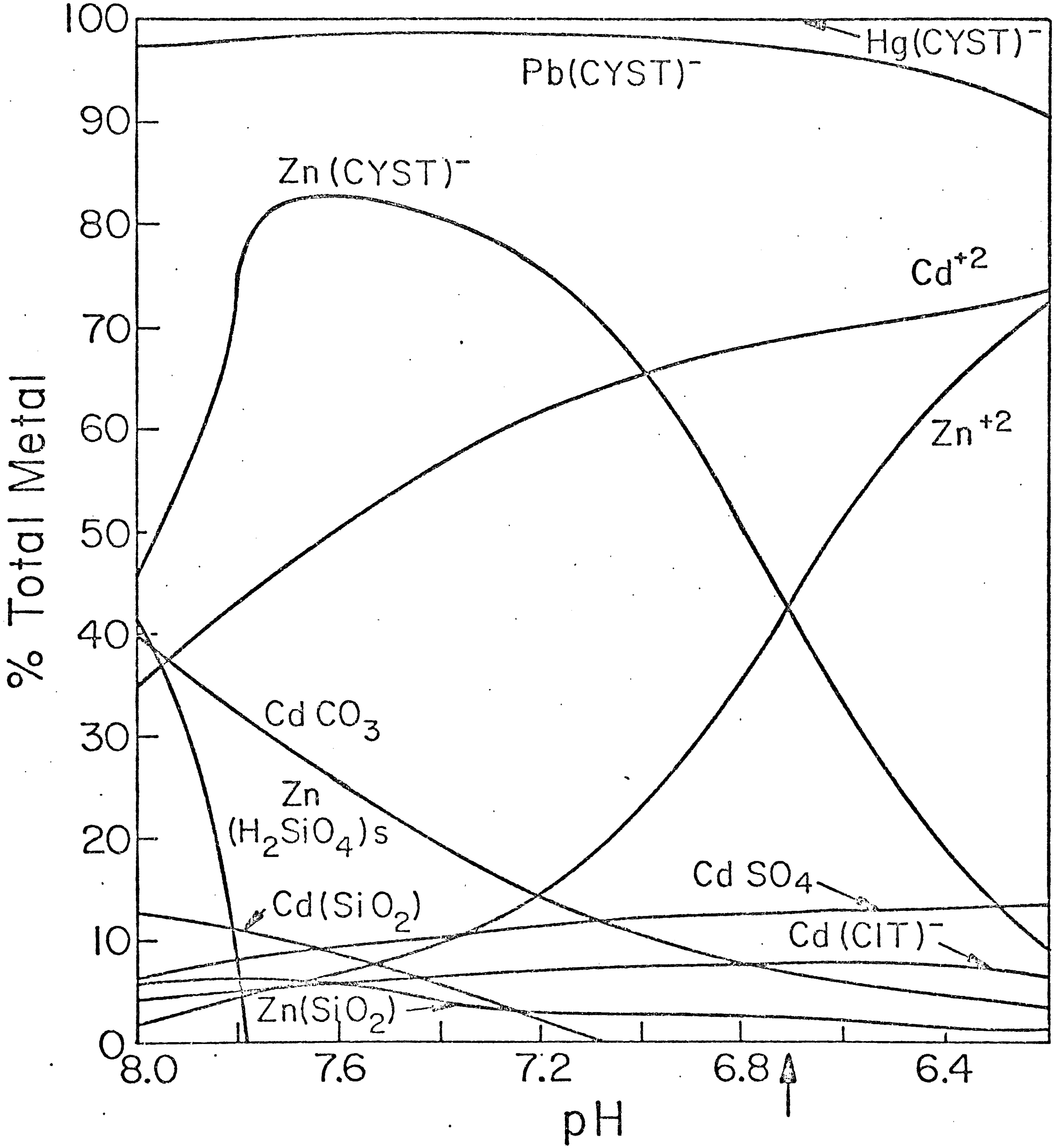
Table 15.

Results of an organic equilibrium computation for oxidizing conditions: $p\varepsilon = 4.0$. Predominant trace metal species at pH = 6.7.

Species	p[c]
$Fe(OH)_3$	4.29
Fe(NOC)	4.50
Fe(CYST)	5.22
Fe(CIT)	6.10
$Cu(CIT)^-$	5.70
$Cu\text{-}SiO_2$	7.39
$Cu(GLY)^+$	7.74
Cu^{+2}	8.73
Ni^{+2}	4.63
$Ni(CIT)^{-1}$	5.05
$Ni\text{-}SiO_2$	5.17
$NiSO_4$	5.37
$NiCO_3$	5.47
NiGLY	6.18
$CoCO_3$	5.49
Co^{+2}	6.04
$CoSO_4$	6.58
Mn^{+2}	4.29
$Mn\text{-}SiO_2$	4.88
$MnSO_4$	5.03
$MnCO_3$	5.63

FIGURE 8. Model of the speciation of secondary trace metals found in the INCO seepage pond. % Total Metal is plotted as a function of pH where pε = 4.0 and μ = 0.017.

ORGANIC SPECIATION



In an attempt to understand factors governing the leaching of Cu and Ni from the Gabbro ores a model similar to the speciation models was developed. Instead of a pH variation, the electron activity, pε, of the system was varied from a reducing level of pε = -3.6 to an oxidizing level of pε = 0.0. The pε of the system is not an experimentally measured quantity but in a leaching system the pε is best described by the oxidation of sulfide

$$S^{-2} + 4\ H_2O \rightleftarrows SO_4^{-2} + 8\ H^+ + 8\bar{e} \qquad (11)$$

coupled with the reduction of oxygen. The chemical speciation of Cu, Ni, Fe, Mn and Co is a function of pε. (Figures 9 and 10 for an inorganic and organic system respectively, at pH = 6.7). At low pε values Co, Cu, Fe, Ni are present as solid sulfides. In the inorganic model, the Co, Fe and Ni sulfides dissolve in a very narrow range of pε near -2.4. Ni is released as Ni^{+2}. Co is transformed from solid CoS to solid $CoCO_3$ and Fe is transformed from solid Fe(II)S solid Fe (III) $(OH)_3$. Sulfate complexes of Ni^{+2} and Mn^{+2} form above pε-2.4 at pH 6.7; Mn^{+2} does not form a sulfide below pε-2.4 because of the extremely low activity of the sulfide ion and the relatively small solubility product of MnS (pK_s=15.2) as compared to the other metal sulfides.

Imposing a set of organic ligands on the inorganic model lowers the pε at which FeS begins to dissolve from pε-2.4 to pε-2.8. FeS is transformed into solid $Fe(OH)_3$ and soluble iron (III) nocardamine, Fe(II)-CYST and $FeIII(CIT)^-$. NiS, which dissolves before FeS in the inorganic model, dissolves at pε -2.6 to form Ni^{+2}, $Ni(CIT)^{-1}$ and $NiSO_4$. CoS is the next sulfide to dissolve and it is transformed into solid $CoCO_3$, soluble $CoCO_3$ and free Co^{+2}. CuS dissolves at pε -1.2 in the organic model and is immediately complexed by citrate to form $Cu(CIT)^-$. In the inorganic model, CuS dissolves at

FIGURE 9. Inorganic model for the leaching and subsequent speciation of the predominant trace metals from their respective metal sulfides. % Total Metal is plotted as a function of $p\varepsilon$ where $pH = 6.7$ and $\mu = 0.017$.

INORGANIC MODEL FOR LEACHING

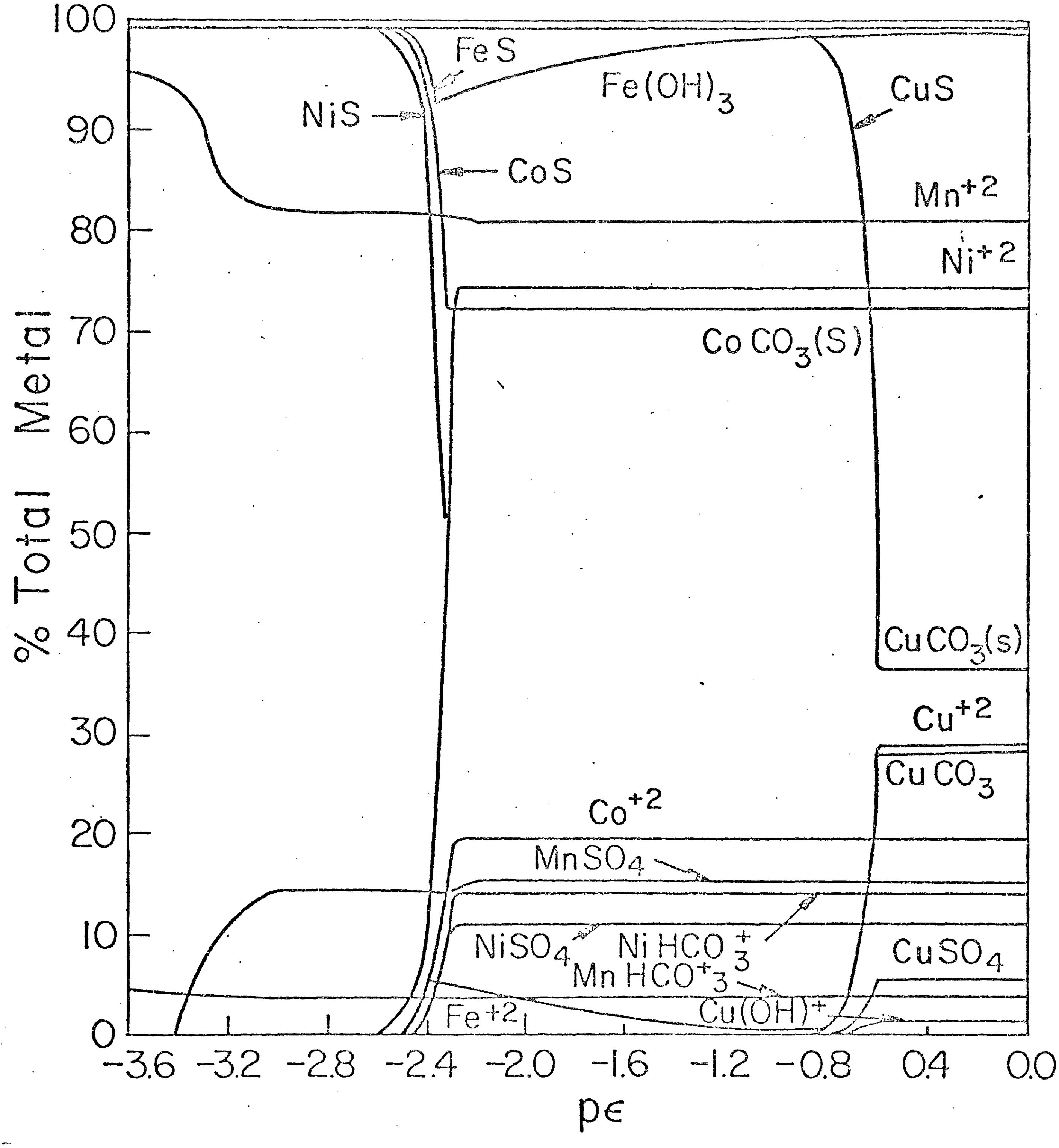


FIGURE 10. Model for the leaching and subsequent speciation of the predominant trace metals from their respective metal sulfides with a superimposed set of organic ligands. % Total Metal is plotted as a function of pε where pH = 6.7 and μ = 0.017.

ORGANIC MODEL FOR LEACHING

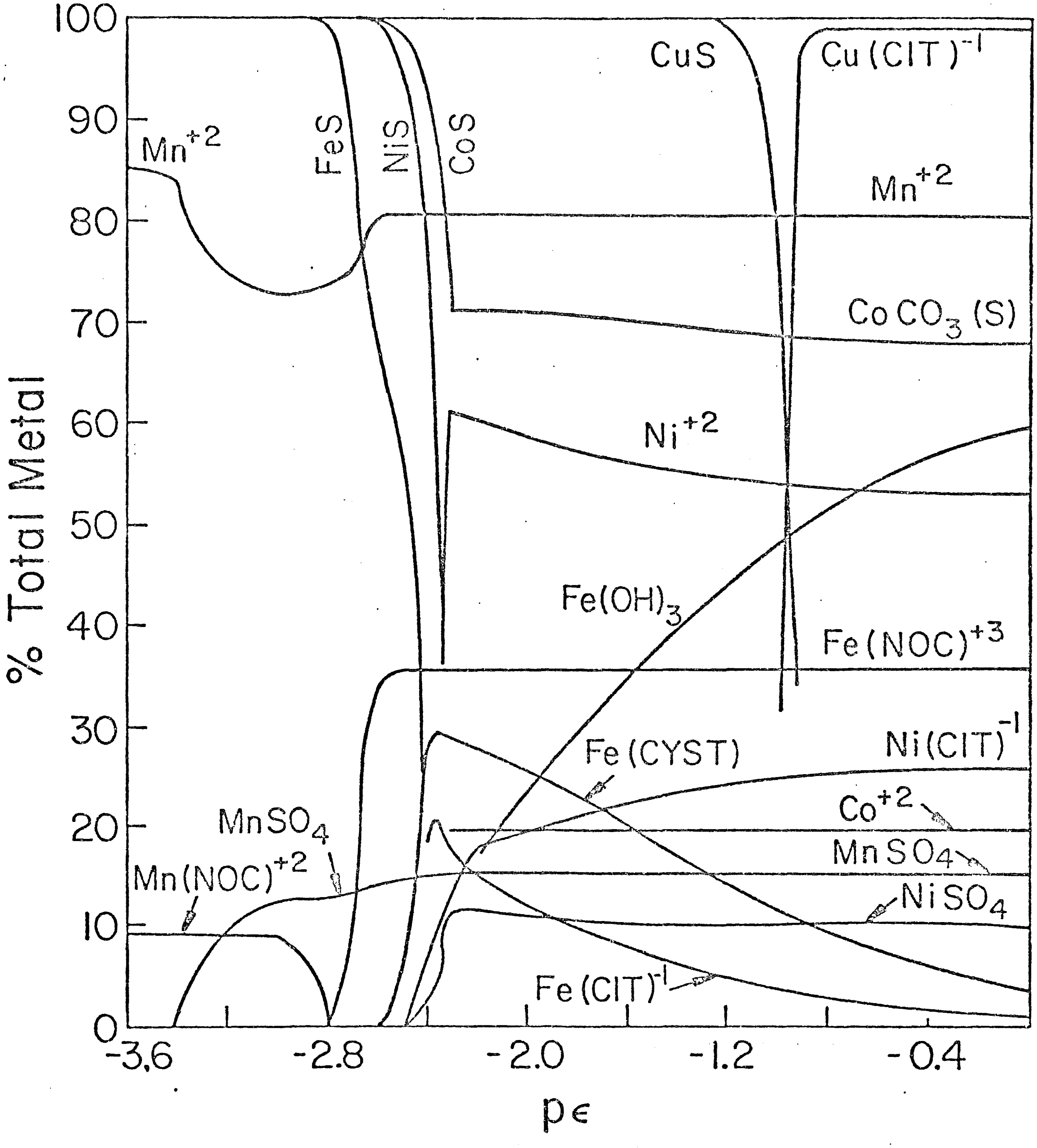


Table 16.

Results of an organic equilibrium computation for oxidizing conditions: $p\varepsilon = 4.0$. Predominant trace metal species at pH = 6.7.

Species	p[c]
Cd^{+2}	8.83
$CdSO_4$	9.57
Cd^{+2}-SiO_2	10.32
$Cd(CIT)^-$	9.79
$CdCO_3$	9.82
Zn^{+2}	7.35
$Zn(CYST)^-$	7.36
$ZnSO_4$	8.09
$ZnCO_3$	8.38
$Hg(CYST)^-$	9.30
$Pb(CYST)^-$	9.02
$PbCO_3$	10.71
Pb^{+2}	11.40

pε-0.8 and forms $CuCO_3$+, soluble $CuCO_3$, $CuSO_4$ and $Cu(OH)^+$. The net effect of organic ligands is to lower the oxidation level at which sulfide dissolution is likely to occur. Implications for a dynamic leaching process are that organic ligands or chelating agents will enhance the leaching process by shifting the equilibrium dissolution to the right. If oxidation of HS^- is the rate limiting step in the leaching process, complexation of the corresponding metal will result in a greater net release of sulfide and, therefore, the ultimate effect will be to enhance the rate of leaching. In addition to simple equilibrium effects, transition metal complexes, such as Co(II)phthalocyanine, are well-known for their ability to activate molecular oxygen and would be expected to have a catalytic influence on the rate of oxidation of sulfide (Khan and Martell, 1974). Ni^{+2} and Mn^{+2} have also been shown to act as homogeneous transition metal catalysts for the oxidation of sulfide in aqueous solution at neutral pH (Chen and Morris, 1972).

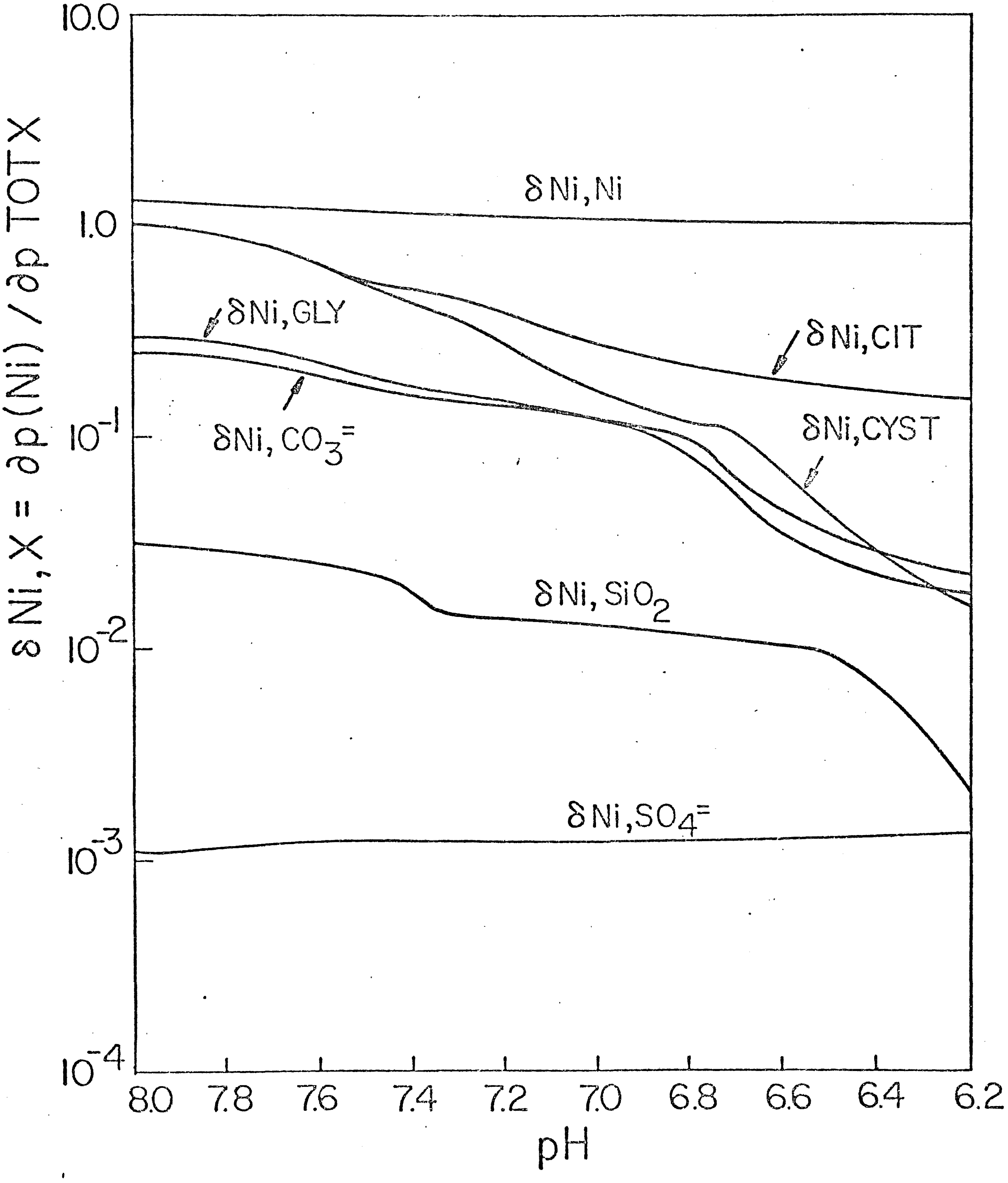
In order to measure the magnitude of the interactions between constituents, the concept of "interaction intensities" may be utilized (Morel et al., 1973). The interaction intensity, δ, for the interaction of a metal, X, and a ligand, Y, is defined by equation 12.

$$\delta_{X,Y} = \partial p[X]/\partial pTOT[Y] \qquad (12)$$

These numbers can be computed using REDEQL2. Interaction intensities are nondimensional numbers but are similar in principle to the commonly used concept of pH buffering capacity. A large interaction intensity corresponds to a very strong dependence of a metal upon the total ligand concentration. When $\delta_{M,M} = 1$, the metal in its free form is relatively independent of the total concentration of ligand present. As an example the interaction intensities for the nickel-organic speciation as a function of pH is depicted in Figure 11. The main feature of this plot is the relative independence of Ni^{+2} on the concentration of complexing ligands. In this case $\delta_{Ni,Ni} \sim 1$ at pH 6.7, the measured pH of the seepage pond. Relationships of this type are useful to help understand the relative importance of one species relative to another metal-ligand species under identical conditions. In the future, correlations of interaction intensities with experimentally determined complexing capacities may prove to be fruitful.

FIGURE 11. Variation of interaction intensities, $\delta_{X,Y}$ for a nickel-ligand system as a function of pH. The interaction intensities plotted here correspond to the nickel speciation depicted in Figure 2.

INTERACTION INTENSITIES



Metal Ion - Organic Complexes in Natural Waters

Initially, the major focus of the bibliographic search was concerned with the chemical action of naturally occurring organic complexing agents affecting the leaching of metal ions from naturally occurring deposits. It soon became apparent that research directly concerned with these effects has not been reported. Emphasis was then placed on studies involving metal ion - organic complexes in natural waters, their stability, rates of reaction and methods of measurement.

There is no doubt that an awareness of the importance of trace metals in aquatic systems is growing and has prompted an increase in activity in the development of analytical techniques, and in the study of the behavior of metal ions at trace levels. It has been noted throughout the literature in this field that the form of the metal ion must be known in order to permit the interpretation of biological effects and to address the problems of metal ion transport and accumulation in aquatic systems. The metal speciation problem is complex and data is needed on the chemical nature of the dissolved organic compounds and on the metal ion - organic complexes, from thermodynamic and kinetic points of view.

This section of the literature survey is not exhaustive. It is intended only to present the various areas in which studies involving metal ion - organic complexes in natural waters are proceeding. The references given in each of the papers noted should be consulted for additional information.

A general overview of the problems associated with metal ion - organic interactions can be obtained from the paper of Lerman and Childs (1973) who discuss the control of the distribution of metal ion complexes as affected by thermodynamic, kinetic and physical parameters.

Initially the behavior of metal ion complexes in natural waters as influenced by the presence of organic complexing agents, such as nitrilotriacetate and citrate is discussed. The calculations are based on thermodynamic properties and the result is an equilibrium model for metal ion complexation. No physical measurements were made and no attempt was made to include heterogeneous equilibria in these calculations.

Heterogeneous equilibria, interactions with sediment, are discussed from a theoretical point of view in terms of the rate of change of the organic complexing agents as influenced by the rate of input, the rate of decomposition and the extent of interaction with sediment. Data on kinetic and physical factors is noticeably lacking and only upper and lower limits are discussed.

Some data on the rate of photochemical degradation of nitrilotriacetate in the presence of copper and iron have been presented by Langford, et al. (1973) and by Stolzberg and Hume (1975), but data on the rates of decomposition and metal ion exchange for metal ion complexes in natural waters are non-existent.

Recently, Guy, et al. (1975) have presented a simple model for natural waters that included metal ion fixation in particulate matter as well as complexation. Data is presented on the sorption of copper, zinc and cadmium by humic acid, manganese dioxide and potassium bentonite.

Elder (1975) treats the problems of metal ion complexation from a thermodynamic point of view and discusses the effects on complexation due to competing ligand reactions.

Gamble and Schnitzer (1973) review the relevant literature on the chemistry of fulvic acid and its reactions with metal ions. Included is a mathematical treatment pertaining to the determination of stability constants for metal ion - fulvate complexes employing potentiometric titration techniques. A series of papers using these techniques in the study of mixed fulvate complexes has been presented by Ramamoorthy and Manning (1973, 1974).

In these studies, fulvic acid is extracted from soil samples and stability constants with metal ions are determined. The data presented are of value in calculations on the extent of metal ion complexation in natural systems but the method is not intended to be used as a method of direct measurement of metal ion speciation in natural waters.

A variety of techniques have received attention in the study of metal ion - organic complexes. Burrell and Lee (1975) present a discussion of neutron activation, anodic stripping voltammetry and atomic adsorption, their applications and limitations to metal analysis. They suggest anodic stripping voltammetry as the method of choice for studies in metal speciation.

In addition to the above methods, potentiometric titration procedures using pH and ion selective electrodes have been presented by Gamble and Schnitzer (1973), Gardiner (1974a, b) and Ramamoorthy and Manning (1973, 1974).

Also, ion exchange equilibrium methods have been employed by Schnitzer and Kahn (1972), Stevenson and Ardakani (1972), and by Ching <u>et al.</u> (1975).

Numerous authors have used anodic stripping voltammetry in some modification to determine metal ion concentrations at low levels and to determine stability constants of metal ions. These include papers by Bradford (1973), Ernst et al. (1975), Shuman and Woodward (1973), Stumm and Bilinsky (1973), and Zirino and Lieverman (1975). These investigations were intended to determine the complexes that predominate under environmental conditions.

Application of methods to determine the extent of complexing agents present in natural waters has also been made. Bender et al. (1970) used a complexometric titration procedure with copper as titrant to study complexing agents present in secondary sewage effluents.

Chau and Lum-Shue-Chan (1973, 1974b) proposed a method for the determination of complexing capacity for copper utilizing anodic stripping voltammetry and have applied the method to a number of natural waters. In an earlier paper (1974a) they discuss the determination and differentiation of labile and strongly bound metals in lake waters.

The exact significance of total complexing capacity is still not answered although some correlation to environmental systems has been made. Davey et al. (1973) have shown a similarity between the growth curves of T. pseudomona to copper-ion selective electrode titration curves used to measure complexing capacity in sea water.

It is obvious that more work on the problems of metal speciation is necessary. At present, it appears that the best practical approach to the study of natural waters is the determination of complexing capacity as an estimate of metal ion complexation.

CONTROL TECHNOLOGY

New water flow systems are created by a mining operation, and the quantity as well as the quality of water flow in the region may be affected. Three main types of process water may be identified in a mining operation, namely, mine water drainage, mill effluent, and surface drainage. Water from these sources must be collected and recycled in order to protect the environment. The practicality of complete recycling may, however, be predicted only after a thorough analysis of the quantity and quality of process water as well as the amount of rainfall and evaporation on the entire operation has been made (Busse, 1974; Pickett and Joe, 1974). Common practice is to have the holding capacity of the tailing ponds designed in such a manner to avoid discharging tailing water during periods of above-normal precipitation or spring thaw. The compatibility of the recycled water with the milling process must also be carefully assessed. The most serious problems in recycling occur when differential flotation is used. Perhaps the presence of heavy-metal ions and partially oxidized sulfur compounds adversely affects the selectivity of separation. In addition, the effects of residual flotation reagents and their decomposition products as well as of humic acid, generated by the decay of vegetation in tailing ponds, on the quality of recycled water must also be ascertained. It becomes of interest, therefore, to gain some insight into the treatment methods for achieving the quality of water suitable not only for recycling, but also for release in case its discharge becomes necessary.

An alternate approach to this problem is to search for a method of preventing the release of heavy-metal ions rather than treating the water to be discharged. Prevention is preferable to treatment since it can be less expensive and may be permanent in nature. After the mine's active life the mill effluent will be stopped, but mine and surface drainages will always be present. It becomes imperative then to develop an abandonment plan early in advance that provides for water quality control. Literature on prevention methods, however, is very scarce.

This review presents summaries of published information on control technology of heavy-metal ions in mine and mill effluents with particular emphasis on copper-nickel mining in northeastern Minnesota. The topics are divided into prevention and treatment techniques.

Methods of Preventing the Release of Heavy-Metal Ions

Very few articles are found in literature on the prevention of release of heavy-metal ions in base metal mines. Working with acid mine drainage problems of the Bunker Hill Mine in Idaho, Trexler *et al* (1974)recommended that the problem be examined in terms of chemical factors promoting the oxidation of sulfide minerals in combination with the availability of water for the transport of the reaction products. Mining activities expose areas of high pyrite and other heavy metal sulfides and their access to oxygen and high moisture in the mine atmosphere cause acid formation and the release of heavy metal ions. If the movement of water in a mine is controlled, the acid mine drainage may also be controlled. Thus the need for hydrogeologic planning was emphasized during the planning of the total mining program, particularly in eliminating or reducing surface-water or groundwater recharge during and after the mine's active life.

The recharge to a base metal mine is affected by the following factors, which may be controlled by careful study of mining plans:

1. Closeness of mining to the surface
2. Degree of interconnection between mine levels from stopes, man raises, ore passes, and other openings
3. Rock properties
4. Mining techniques used which may induce surface fracturing or intersect and drain ground water from the natural fracture system.

Though the oxidation of pyrites is difficult to control, particularly in operating mines, several avenues of approach may merit some further study. The most obvious approach is to limit the access of oxygen to pyrites and other heavy-metal sulfides. In an extreme example, mining in an inert atmosphere with the miners wearing life-support suits has been proposed (Chem. Eng. News, 1970). More commonly, the concept has been implemented in sealing abandoned coal mines since the 1930's. Today backfilling and replanting is practiced to prevent acid drainage from abandoned strip mines, and abandoned deep mines are sealed and, where possible, flooded.

Bacteria play an important role in promoting the oxidation of sulfide minerals in nature. The most common varieties are _Ferrobacillus ferrooxidans_, _Thiobacillus ferrooxidans_ and _Thiobacillus thiooxidans_. These bacteria appear to be indigenous to sulfide mining, are active at pH values between 1.0 and 4.0, and are associated with _in situ_ and dump leaching of copper and uranium ores (Fletcher, 1970). An attempt was made to test if certain organisms might be useful in inhibiting the sulfide-oxidizing bacteria that are thought to catalyze the acid-forming reaction. Streptomycin was applied to a leaching column containing crushed Duluth

Gabbro innoculated with Thiobacillus thiooxidans. The test results showed that the leaching rate was not markedly affected (MRRC, 1976). Perhaps such an approach may be more fully explored at a later date. It should be kept in mind, however, that although these bacteria accelerate the acid formation at pH values below 4.0, it has not been shown that any of these bacteria play a part in acid mine water formation. In fact, acid mine water is said to form even in the absence of these bacteria (Trexler et al, 1975).

Certain carbonates and silicates are capable of neutralizing acidic water and of retarding the oxidation of pyrites. The freshly-ground Duluth Gabbro equilibrates in water at pH near 9 and shows some tendency to buffer the pulp pH in flotation tests. The acid-consuming properties of Duluth Gabbro were reported by the Mineral Resources Research Center by performing a series of acid titration tests on a pulp of a flotation tailing (Iwasaki et al, 1976). The results are shown in Figure 12 together with a few additional curves: (1) a curve showing the change in pH of distilled water with the same incremental additions of sulfuric acid representing an extreme of no acid consumption by a pulped solid; (2) two curves of typical copper dump-leach ore samples from the western United States ground to the same fineness as the Duluth Gabbro flotation tailing; and (3) a curve on the Duluth Gabbro flotation tailing mixed with 5 percent by weight of calcite, ground to the same fineness.

It is apparent in Figure 12 that the Duluth Gabbro flotation tailing showed some tendency to buffer the pulp pH near 8, and then very markedly at 3.5 to 4 even when as high as 75 pounds of sulfuric acid per ton was added. Such a behavior was thought to be of particular interest since,

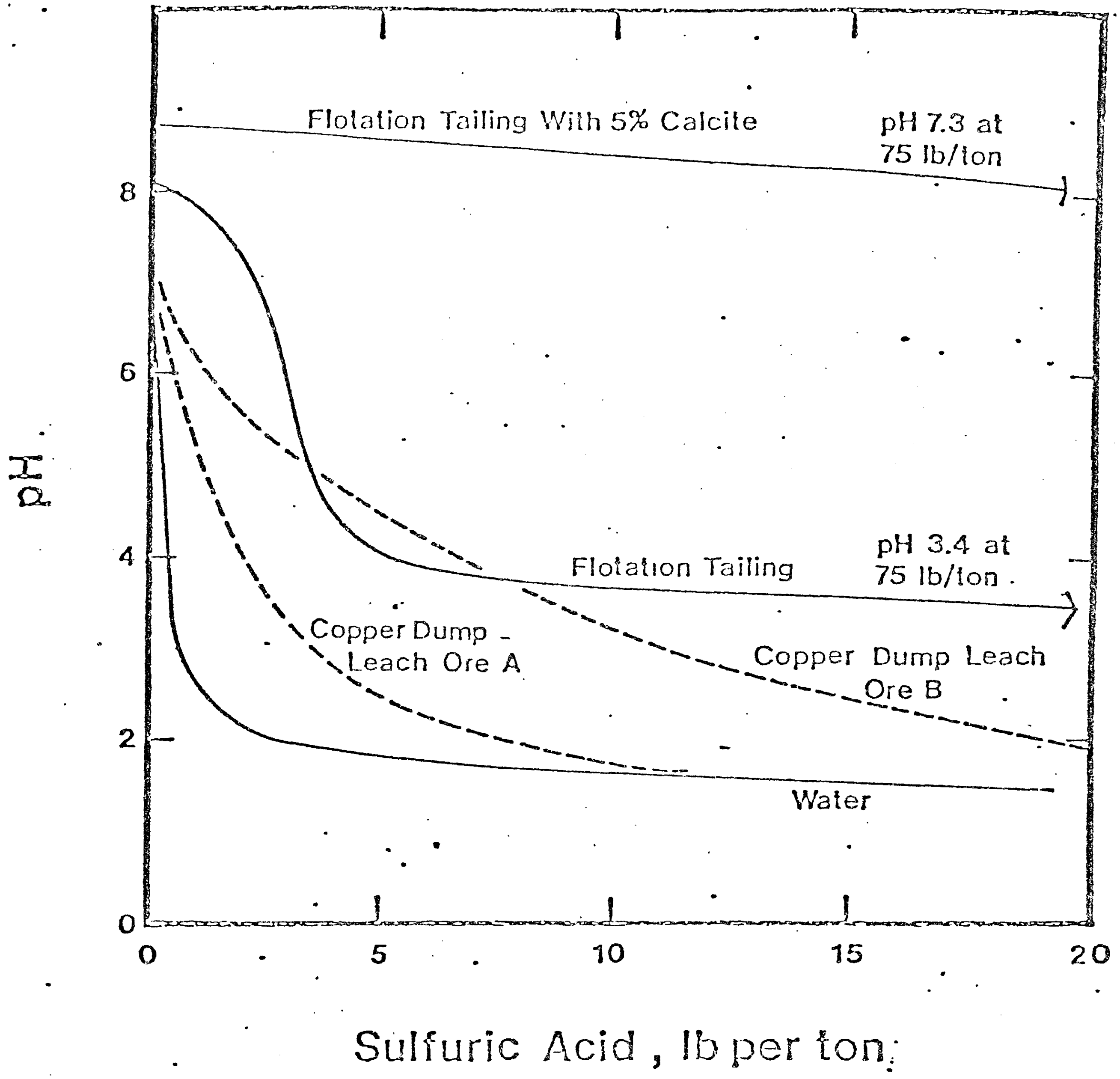


FIGURE 12 PULP pH OF A FLOTATION TAILING OF DULUTH GABBRO AND OF COPPER DUMP LEACH ORES AS A FUNCTION OF SULFURIC ACID ADDITION[7]

unless the pH can be lowered to the optimum range of 1.5 to 2.5 without excessive use of sulfuric acid, rapid enough leaching rates cannot be maintained to warrant a commercial operation of <u>in situ</u> or dump leaching. For comparison, the two typical western dump-leach ores can be acidified to pH less than 2.5 with 5 pounds and 15 pounds of sulfuric acid per ton, respectively, for Samples A and B. In fact, these ores contain sufficient pyrite for generating acid in dumps and no additional acid is said to be necessary in the recirculating barren solution. The sulfur content of Duluth Gabbro is in the range of 0.5 to 1 percent, which could theoretically produce about 50 pounds of sulfuric acid per ton upon complete oxidation. Referring to Figure 12, the pulp pH at this level of sulfuric acid addition is still well within the buffered range near 4. On the other hand, flotation tailings of Duluth Gabbro may contain typically 0.05 - 0.1 percent sulfur (Vifian and Iwasaki, 1968), which upon complete oxidation could amount to approximately 5 pounds of sulfuric acid per ton. Again referring to Figure 12, the solution pH may reach nearly 4.

To investigate the effects of contacting water with a crushed Duluth Gabbro sample, a percolation leach column, shown in Figure 13, was set up and distilled water was circulated. The pH of the water was measured every few months. As shown in Figure 14, the water acidified gradually and the pH dropped to below 5 within a year. At this point the water was discolored somewhat due presumably to the precipitation of ferric hydroxide and analyzed 4 ppm Cu^{++} and 44 ppm Ni^{++}. These observations are, more or less, in line with the above discussion on the acid titration curve of the flotation tailing (Figure 12). Since it was observed that the pulp pH could be maintained above 7 even with 75 pounds of sulfuric acid per ton

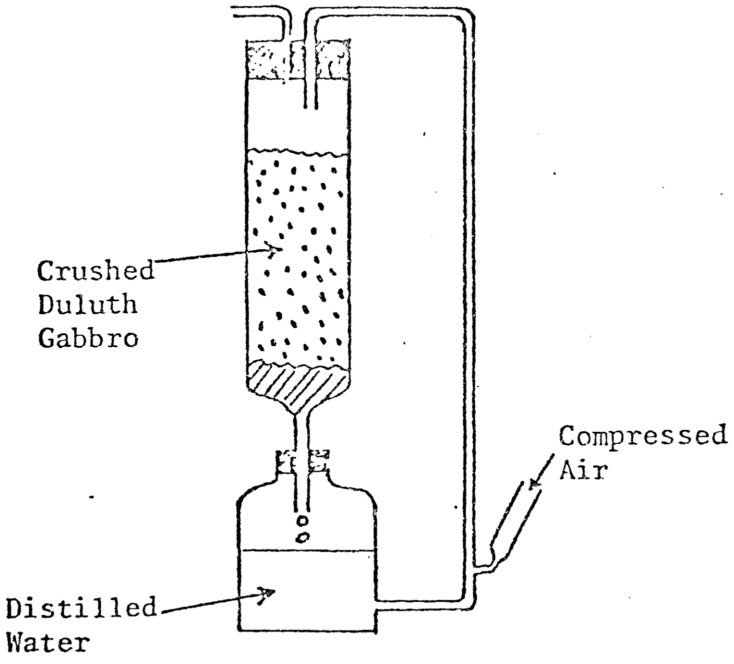


FIGURE 13. SCHEMATIC DIAGRAM OF AIRLIFT PERCOLATOR

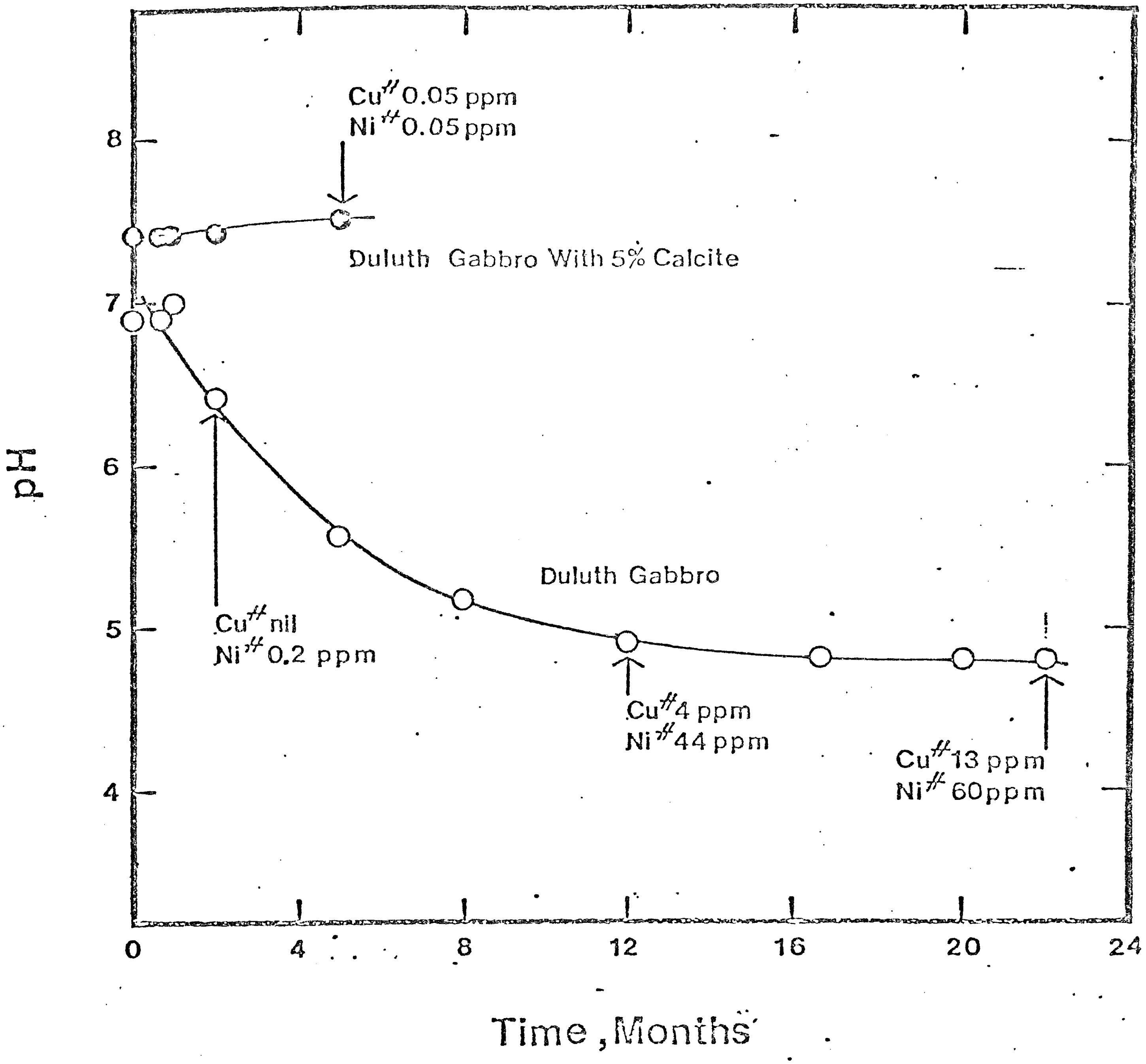


FIGURE 14. CHANGE IN pH WITH TIME OF WATER CIRCULATING THROUGH CRUSHED DULUTH GABBRO[7]

by the addition of limestone, it became of interest to study the effect of adding limestone to the percolation leach column. A second column containing crushed Duluth Gabbro mixed with 5 percent by weight of limestone, crushed also to minus 10 mesh, was set up and the pH of the recirculating distilled water was followed. As seen in Figure 14, the pH remained virtually constant at about 7.5, and even after five months the copper and nickel-ion concentrations remained less than 0.1 ppm.* Though the recirculation of water in this setup is not representative of the real situation which one finds in nature, such an observation appears to be a point of theoretical interest in seeking methods in controlling the release of heavy-metal ions. Further investigation on the manner in which partially oxidized sulfur compounds, the source of subsequent acid formation (Schmidt and Conn, 1969), are released in the presence of limestone becomes of interest. In addition, a similar investigation with other carbonates becomes of practical interest since a large amount of slaty taconite containing siderite and ankerite is available in nearby taconite mining operations.** Marl, an earthy deposit of limestone and clay, is also available in Minnesota.

Methods Applicable to the Removal of Heavy-Metal Ions

A wide variety of methods for reducing the concentrations of heavy-metal ions and other pollutants in mine and mill effluents has been proposed

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* The sensitivity of the atomic absorption unit was rated as 0.1 ppm for copper and 0.2 ppm for nickel.

** Research in progress, Mineral Resources Research Center, University of Minnesota.

and some are being used to meet environmental regulations (Kemmer and Beardsley, 1971; Mercer, 1971; Dean et al, 1972; Cadman and Dellinger, 1974; USBM, 1975; Williams, 1975; Chem. Eng., 1975). Depending on whether the water is to be recycled or discharged, the extent of treatment would be different. This survey summarizes some of the water treatment technology presently employed by the mining industry and new technology which may have potential application, particularly in copper-nickel mining in northeastern Minnesota.

Neutralization

For the neutralization of acidity, lime and limestone are most commonly used. Limestone is often attractive since it is not only readily available at the lowest cost per unit of basicity, but also the sedimentation rates of the resultant hydroxides are rapid and the sediment volumes are small. However, limestone neutralization is slow and often erratic due to the formation of insoluble metal hydroxide coatings on the limestone particles, or of coatings of oils and greases. To insure adequate reactivity it is necessary to pulverize limestone to a sufficient fineness, say minus 300 mesh. The solution pH may be raised to near neutral with limestone, but for the removal of heavy-metal ions it is necessary to raise the pH further. Lime treatment following limestone neutralization may be applied for this purpose.

Lime is more widely used than limestone in controlling the pH of tailing ponds. By maintaining the pH in the range of 9.5 to 10.5, it is reported that extremely low effluent metal concentrations (less than 20 ppb copper) can be consistently achieved (Bell and Nancarrow, 1974). The dependence of the solubility of the metal hydroxides on the pH may be estimated from their solubility products (Figure 15). The difference in the solubility lines of $Cu(OH)_2$ and $Ni(OH)_2$ suggests that the lime treatment may be capable of lowering the copper-ion concentration to the quoted level, but not the nickel-ion concentration. It should be noted, however, that the concentration of a metal ion may not follow simple solubility product principles in the presence of another metal ion due perhaps to a coprecipitation phenomenon. In the presence of ferric ion, the copper and perhaps nickel-ion concentrations may become markedly lower.

Though the lime treatment is capable of lowering the concentrations of heavy-metal ions in tailing pond effluents, there appears to be a tendency for partially-oxidized sulfur compounds, such as thiosulfate and thionates, to increase in process water on recycling. If not adequately controlled, these compounds may slowly convert to sulfuric acid and, in so doing, dissolve heavy metals and affect the flotation process. Thiosulfate and thionates may be oxidized in tailing ponds through biological processes, but bacterial actions would be ineffective or even inoperative during winter months (Rivett and Oko, 1971). Perhaps some chemical ozidation processes, such as ozonation, may be considered as a control method.

Chemical Precipitation

The removal of heavy-metal ions as hydroxides may be less effective in reducing their concentrations than some other methods due to unfavorable solubility products as discussed in the previous section. The solubilities of the corresponding metal sulfides are appreciably less than those of the

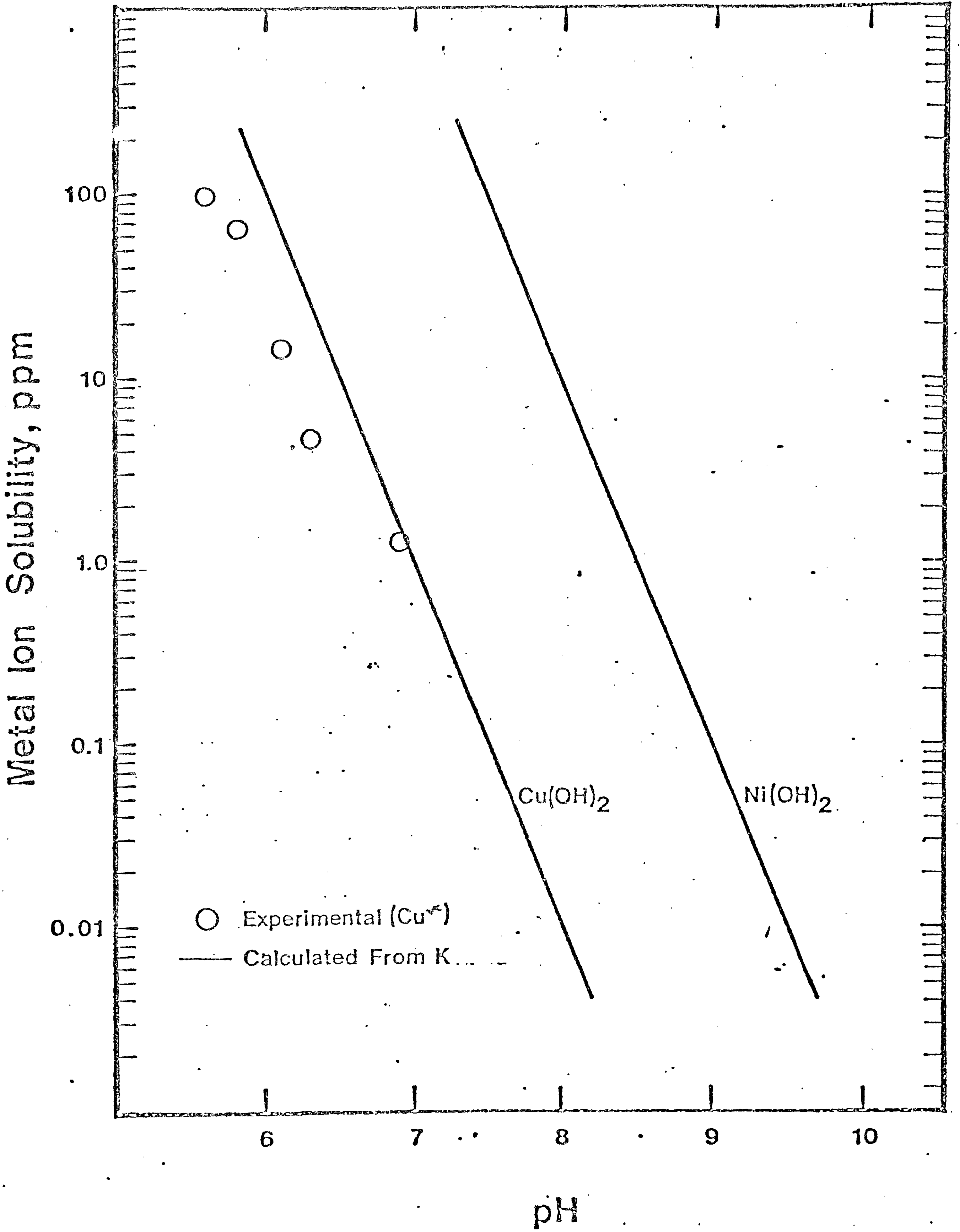

FIGURE 15. COPPER AND NICKEL ION SOLUBILITY AS A FUNCTION OF pH[7]

hydroxides, and the limit to which the residual concentrations of heavy-metal ions may be lowered with either hydrogen sulfide or sodium sulfide should be ascertained. In fact, a method of treating waste mine water containing free sulfuric acid and copper, zinc, ferric, and ferrous ions with hydrogen sulfide, and recovering the precipitated copper sulfide by sedimentation has been reported (Yamada, 1965). Another example of hydrogen sulfide precipitation of acid-leached copper in the leach-precipitation-flotation (LPF) process has been described (Kuhn et al, 1975). In this article the importance of the judicious use of hydrogen sulfide is emphasized, because excess hydrogen sulfide tends to deflocculate and depress the colloidal covellite reaction product in the flotation step. As discussed previously, the presence of residual sulfide ions in solution is also undesirable in the water treatment scheme since they will be oxidized to form sulfuric acid. A recent article (Larsen and Ross, 1976) reported a two-stage process involving lime neutralization to eliminate iron and aluminum, followed by sulfide precipitation to remove copper, zinc, manganese, and other heavy metals, such as mercury, cadmium, and arsenic. In this manner the concentrations of heavy metal ions may be effectively reduced without raising th pH excessively.

Precipitation of heavy-metal ions with a typical collector and their subsequent removal by flotation (often referred to as ion flotation) provide not only an extraordinary concentration factor, which permits the processes to be applied to extremely dilute solutions, but also a high degree of selectivity (Sebba, 1962). The effectiveness of sulfhydryl collectors on the ion flotation of various heavy-metal ions has been investigated (Tabashi et al, 1972), and a few reports of its application on a commercial scale are available (Ishii and Sugimoto, 1972; Nagahama, 1972). The applicability of the ion flotation technique to the treatment of water containing copper and nickel ions was investigated briefly at the Mineral Resources Research Center (Iwasaki et al, 1976). Two series of preliminary flotation tests were performed; in one series a water containing 7.5 ppm Cu^{++} and in another 10 ppm Ni^{++}. These concentrations were chosen arbitrarily to represent typical mill effluents at near neutral pH. Approximately two liters of a solution was placed in a laboratory Fagergren flotation cell, to which a drop of pine oil and a predesigned amount of potassium ethyl xanthate solution were added and the air was introduced for flotation. Metal xanthate precipitate was observed to form immediately upon addition of the xanthate solution, and the flotation time was fixed arbitrarily at 5 minutes.

In the case of copper the best flotation recovery was obtained when the xanthate addition was a little over an equivalent amount. In fact, the solution after flotation was virtually free of precipitates when 1.33 times the equivalent amount of the xanthate was added. The solution was observed to contain an increasing amount of dispersed precipitate as the xanthate addition was increased. Hence, the copper analyses were carried out in two ways to represent "total Cu", including copper ion in solution and copper xanthate in suspension, and "Cu^{++} in solution". "Total Cu" was determined on a solution after dissolving the copper xanthate precipitate with the addition of one milliliter of concentrated hydrochloric acid to 100 milliliters of the flotation solution. "Copper in solution" was determined on the supernatant water after the flotation solution was clarified by centrifugation. The centrifuged solutions were also analyzed for residual xanthate. These results are plotted in Figure 16 together with the theoretical curves calculated from the solubility product of

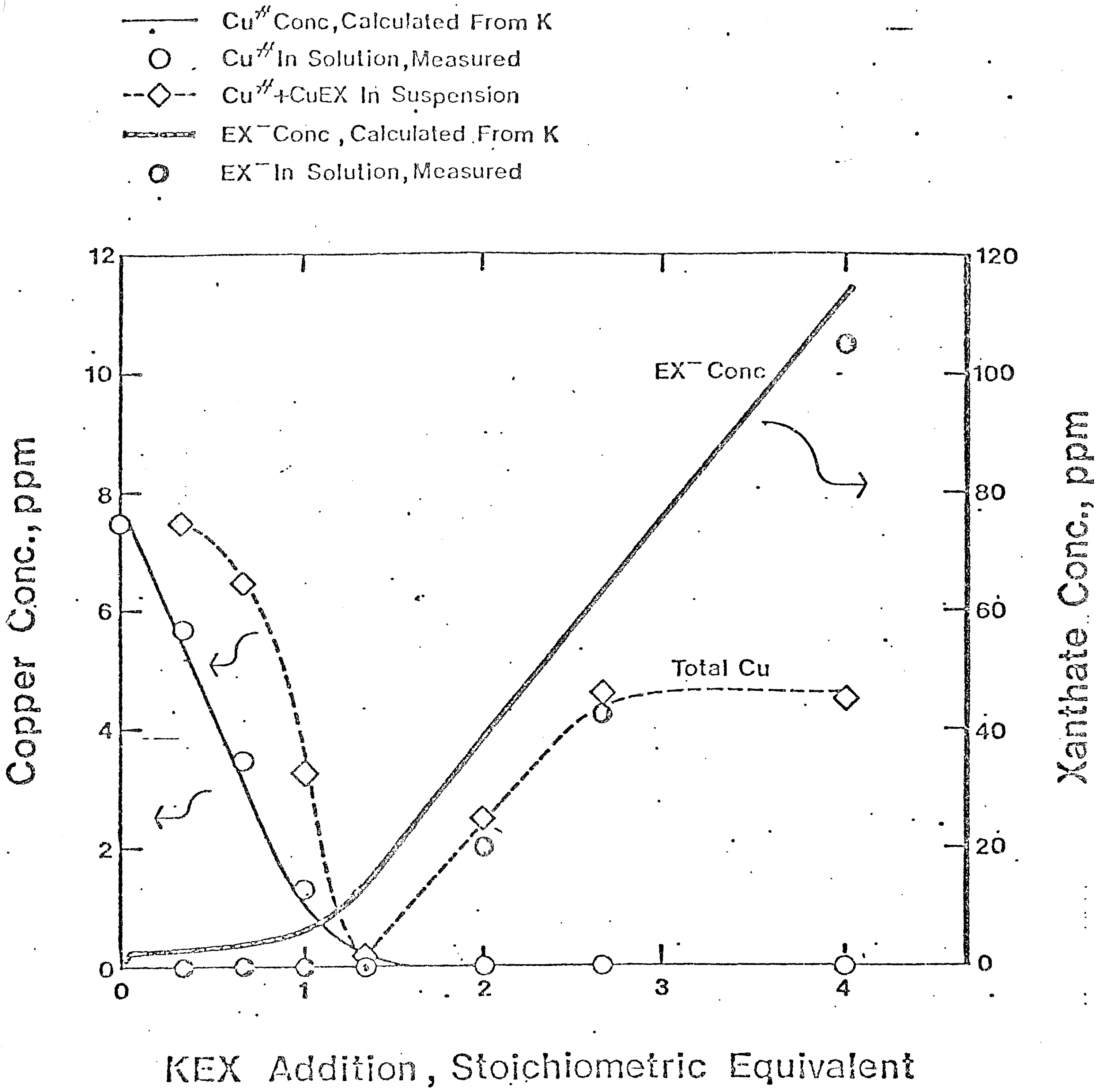

FIGURE 16. RESIDUAL CONCENTRATIONS OF COPPER AND XANTHATE IN ION FLOTATION AS A FUNCTION OF POTASSIUM ETHYL XANTHATE ADDITION[7]

cupric xanthate. The theoretical curve is in good agreement with the "Cu^{++} in solution" data, but the presence of a minimum in the "Total Cu" curve indicates that a proper control of the xanthate addition is essential. Residual concentrations of xanthate beyond the equivalent addition also becomes of concern. Furthermore, the behavior of dixanthogen formed as a decomposition product must be investigated.

The ion flotation of nickel was tested in a similar manner and the results are given in Figure 17 together with the theoretical curves calculated from the solubility product of nickel xanthate. Contrary to the case of copper xanthate precipitation, the flotation of nickel ions requires twice or perhaps three to four times the equivalent amount of xanthate to reduce the nickel-ion concentration below 1 ppm. Also the residual concentrations of xanthate become disconcertingly high. Such a behavior is attributable to the fact that nickel xanthate is more soluble than copper xanthate. It becomes of interest to test the use of long-chain homologs, particularly for nickel precipitation. A comparison of Figures 16 and 17 suggests that the ion flotation approach to a solution containing both copper and nickel ions may be complex. Automatic control of the reagent addition for minimizing the residual heavy-metal ions and the collector, the design of the flotation cells for precipitate recovery, the recycling of sulfhydryl collectors, and, perhaps above all, the relative effectiveness of sulfhydryl collectors and hydrogen (or sodium) sulfide as the precipitant appear to be in need of further investigation.

A similar method, but precipitating heavy-metal ions with starch xanthates, was reported recently (Chem. Eng., 1975). With their ability to flocculate the resulting precipitates it offers an alternate route in

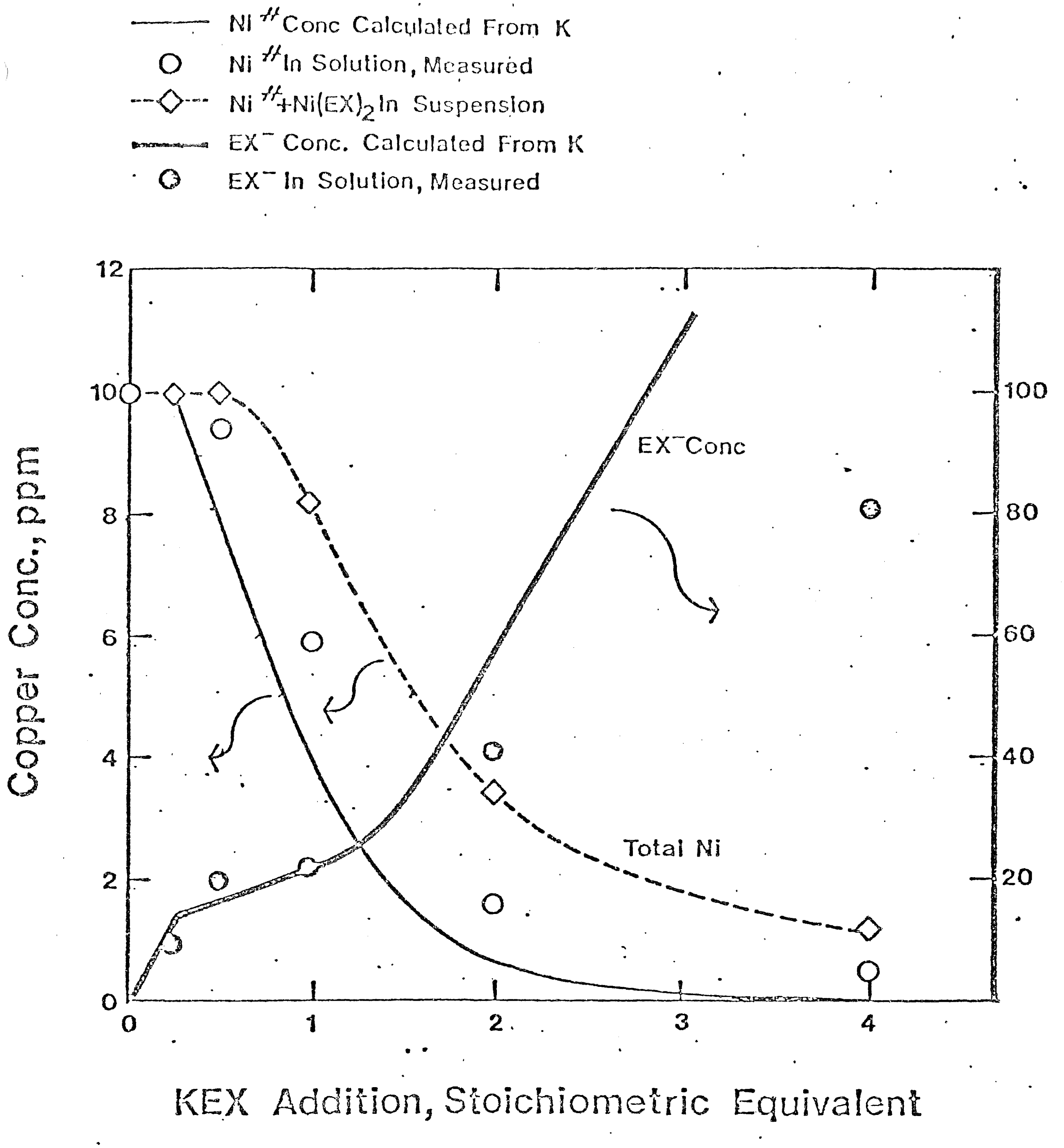

FIGURE 17. RESIDUAL CONCENTRATIONS OF NICKEL AND XANTHATE IN ION FLOTATION AS A FUNCTION OF POTASSIUM ETHYL XANTHATE ADDITION[7]

removing heavy-metal ions. Typical results are cited in Table 17. Another process involving an addition of ferrous sulfate, followed by neutralization and air oxidation, thereby yielding ferrites containing heavy metals and removing the precipitates by magnetic separation, has also been reported (Chem. Eng., 1973). This method appears to be capable of reducing such heavy-metal ions as copper, nickel, tin, lead, chromium, cadmium, and mercury from several thousand ppm to a fraction of one ppm. A variation of this method, namely, the coprecipitation with ferric ion, followed by flotation removal using a paraffin-chain collector, has been mentioned (Mukai and Nakahiro, 1972).

Cementation

The precipitation of copper ion on metallic iron has been utilized in the commercial production of copper metal for centuries. The so-called cementation reaction represented by

$$Cu^{++} + Fe^{\circ} \rightarrow Cu^{\circ} + Fe^{++}$$

proceeds rapidly when the solution pH is less than 4.8. Theoretically 0.88 pound of metallic iron would produce one pound of copper, but in actual practice (Beall, 1965) the iron consumption frequently falls in the range of 1.5 to 2.5 pounds when dump leach solutions contain 1 to 2.5 grams of copper ion per liter at the solution pH in the range of 1.8 to 2.5. The excess consumption of iron is attributed to such side reactions as those involving ferric ion and acidity (Nadkarni and Wadsworth, 1968). The copper-ion concentration in solution recycled to leaching dumps ranges from 0.15 gram per liter to nil. A low concentration of copper, high pH, and the presence of clay in suspension lower the rates of copper removal. Competition of the hydrogen reduction reaction and the formation of ferric hydroxide coating suppress the cementation reaction.

TABLE 17. STARCH XANTHATE SLASHES WASTEWATER METALS CONCENTRATIONS

Metal	Influent, ppb	Effluent, ppb
Cu^{+2}	31,800	7
Ni^{+2}	29,400	19
Cd^{+2}	56,200	9
Pb^{+2}	103,600	25
Cr^{+3}	26,000	3
Ag^{+1}	53,900	245
Zn^{+2}	32,700	46
Fe^{+2}	27,900	0
Mn^{+2}	27,500	1,630
Hg^{+2}	100,000	3

Source: USDA, Northern Regional Research Laboratory, Peoria, Illinois

A series of preliminary tests were reported (Iwasaki et al, 1976) on the possibility of lowering copper and nickel-ion concentrations, more or less, in the range of barren solutions recycled to dumps in practice. One gram of powdered sponge iron (minus 65 mesh) was contacted with 200 milliliters of solution containing copper and/or nickel ion in Erlenmeyer flasks and tumbled for one hour. The results are given in Table 18. It appears that both copper and nickel ions were removed quite effectively even though the concentrations were as low as 10 ppm. In the presence of both copper and nickel ions, there was an indication that the precipitation of nickel ion lagged behind that of copper ion. This is perhaps to be expected since nickel is less noble than copper. Of further interest are the reactivity of sponge iron prepared under different conditions, the decrease in their reactivities with the time of contact, and the iron consumption at extremely low concentrations.

Adsorption

Activated carbon is gaining acceptance for the removal of organic materials from waste water (Stephan and Schaffer, 1970). Its effectiveness at extremely low concentrations and its ability to remove impurities without leaving any reaction products are the unique properties of activated carbon. Hence its potential use in the removal of residual collectors or frothers from mill plant effluents becomes of interest although they are largely adsorbed on mineral surfaces or decomposed in tailing ponds. Large-scale application of granular carbon in adsorption columns for the treatment of secondary effluents has been demonstrated at South Lake Tahoe. The use of powdered carbon shows considerable promise in reducing the capital costs of treatment facilities. Here, powdered carbon, contacted with effluents, may be coagulated to remove both dissolved organics and suspended matter, dewatered, and regenerated for reuse (Mercer, 1971).

Activated carbon abstracts certain heavy-metal ions though they are thought to be precipitated as hydroxides rather than adsorbed at the carbon surfaces. A preliminary series of tests to check if copper and nickel ions may be removed by activated carbon was reported (Iwasaki et al, 1976). Typical results are given in Table 19. The table shows that the abstraction appeared to be strongly dependent on the solution pH, more or less, in line with hydroxide precipitation. At near neutral pH appreciable amounts of these ions were abstracted, yet the efficiency of their removal was not particularly impressive in view of the amount of carbon used for the volume of solution. Perhaps activated carbon should be regarded primarily as an adsorbent for organic materials. A few cursory results (Iwasaki et al, 1976) obtained on solutions containing potassium ethyl xanthate are given Table 20. It is apparent that activated carbon was quite effective in removing this collector. Similar tests with other collectors and frothers become of interest.

The possible use of mill tailings (Miller, 1972) and of such tannin-containing agricultural wastes as peanut skins and various tree barks (Chem. Eng., 1975) has been mentioned. In one example redwood bark reduces the lead in a stream from 5 ppm to 0.2 ppm. When the bark becomes saturated, it may be stripped with nitric acid for reuse.

Ion Exchange

A proper ion-exchange resin would allow removal of undesirable ionic species in exchange with an unobjectionable ionic species from dilute

TABLE 18. REMOVAL OF COPPER AND/OR NICKEL IONS IN SOLUTION WITH SPONGE IRON POWDER[7]

	$[Cu^{++}]$, ppm		$[Ni^{++}]$, ppm		$[Fe^{++}]$, ppm
pH	initial	final	initial	final	final
2.3	100	0.01	-	-	
2.3	10	nil	-	-	
3.2	10	nil	-	-	
5.9	10	nil	-	-	6
5.9	10	0.21	-	-	4
5.6	-	-	100	40	50
5.9	-	-	10	nil	4
5.6	10	nil	10	nil	14
5.9	10	0.075	10	0.48	8
5.8	10	nil	10	0.28	nil

TABLE 19. REMOVAL OF COPPER OR NICKEL IONS IN SOLUTION WITH ACTIVATED CARBON[7]

	$[Cu^{++}]$, ppm		$[Ni^{++}]$, ppm	
pH	initial	final	initial	final
2.3	100	8.75	-	-
4.7	100	9.01	-	-
2.3	10	9.72	-	-
3.2	10	9.74	-	-
5.8	10	1.62	-	-
6.8	-	-	100	1.02
6.9	-	-	10	0.18

TABLE 20. REMOVAL OF POTASSIUM ETHYL XANTHATE IN SOLUTION WITH ACTIVATED CARBON[7]

Act. C, mg	KEX Conc, ppm	% Abstracted
0	9.7	-
1	7.7	20.6
10	0.82	91.5
100	0.10	99.0

solutions and concentrate them into a relatively small volume for subsequent recovery or more simplified disposal. The ability to remove all of a particular ionic species (selectivity) and the ability to treat a large volume of water per unit volume of the resin (capacity) are the two major criteria to be considered in their selection.

According to a recent article a number of resins with sulfur- and nitrogen-laden functional groups have excellent affinities for heavy metals (Chem. Eng., 1975). These resins are said to be capable of lowering heavy-metal ions from say 20 to 30 ppm to less than 1 ppb in many applications. The stated concentration range becomes of interest in the application when accidental discharge into the environment becomes necessary. Attention should be paid to the presence of naturally-occurring chelating agents, notably humic acid, that are capable of complexing certain heavy-metal ions. The complexed ions are, at times, bypassed by cation exchangers (Kunin, not dated). The complexation of metals with humic acid, however, is reported to reduce the effective toxicity of the metals on aquatic life (Bell and Nancarrow, 1974).

Other Methods

Some of the methods available in desalination and wastewater treatment fields appear to have strong potential for the treatment of effluents, such as distillation, electrodialysis, and particularly reverse osmosis.

Reverse osmosis is based on a phenomenon during which water flows through a semipermeable membrane from a less concentrated solution to a more concentrated solution. When a pressure in excess of the osmotic pressure is applied to the compartment containing the more concentrated solution, the direction of the flow of water can be reversed. Typical salt removal in a single stage of treatment may be on the order of 90 percent or more. It follows that hard water containing total dissolved solids of several hundred ppm expressed as $CaCO_3$ may be lowered to a few ppm in one stage. "Ultrapure" water with hardness less than 1 ppm may then be produced by additional reverse osmosis processing (Sourirajan, 1970). Rapid advances are being made in reverse osmosis membrane technology and the future promises bigger and better desalination and wastewater plants (Mercer, 1971; Dean et al, 1972; Environ. Sci. Tech., 1974). Perhaps the relative merits of this process should be carefully evaluated in the present application.

Summary

There are two ways to control the release of heavy-metal ions in mine and mill effluents, namely, prevention and treatment. Prevention is preferable to treatment since it can be less expensive and may be permanent in protecting the environment. Through coordination of the mining plan with a hydrogeologic study of the area, the recharge to the mine, which is a major factor in the production of acid mine drainage, may be minimized. An indication was given that a blending of limestone in small quantities with tailings and waste rock may control the oxidation of sulfide minerals and minimize the acid formation and the release of heavy-metal ions. Further investigation is warranted to ascertain if such an approach offers some merit in alleviating the load of the treatment processes for recycling and also perhaps the conditions associated with post-mining abandonment.

A number of treatment techniques have been proposed or are being used to meet the environmental problems of trace amounts of heavy metal in streams being released by various industries, and several comprehensive reviews are availabale. Recent developments appear to center mainly on precipitation, ion exchange, adsorption, and electrolysis. More specifically, in copper-nickel mining in northeastern Minnesota the choice of treatment methods in reducing heavy-metal ions and other residuals would depend on the degree to which the water must be treated for reuse, or for discharge. Neutralization and/or chemical precipitation may be sufficient so long as the treated water is compatible with the milling process. In fact, a survey of water reuse in Canadian ore-concentration plants reports that all but one of the major nickel-copper mills in Canada employ complete recycling of process water (Pickett and Joe, 1974). More rigorous methods, perhaps a combination of two or more stages, may be developed for use in a water quality control program. Surplus water during wet years, for example, can be treated at a reasonable steady rate and released over an extended period of time. Hence, a comprehensive survey on the limit of capability of each method should be made and compared with the base line water quality characteristics. The presence of other heavy metals besides copper and nickel ions must also be ascertained. Furthermore, the survey should compare the economics of the the feasible methods including the value of the heavy metals recovered.

Problem Areas Requiring Further Research in Control Technology

1. Evaluation of various mining techniques compatible with hydrogeologic characteristics of the region, as well as safety, resources

recovery and reclamation plan, to minimize mine water drainage.

2. Development of disposal plan in controlling the quality of water that comes in contact with lean ore and mill tailings. Physical layout and chemical conditions in minimizing the release of heavy-metal ions must be evaluated.

3. Investigation of milling methods for minimizing the residue of sulfide minerals left by flotation. Certain sulfides, notably pyrrhotite, are known to be readily oxidized and difficult to recover completely.

4. Investigations of the mode of occurrence of residual sulfide minerals in flotation tailings, and of the possibility of separating and disposing in special ways to either utilize or prevent the oxidation of residual sulfide minerals.

5. Investigation of the treatment methods for removing heavy-metal ions and residual flotation reagents suitable for release in the region.

6. Overall consideration of the mining and processing methods, such as in situ and dump leaching, bulk sulfide versus differential flotation, hydrometallurgy versus pyrometallurgy, for minimizing the environmental effects as well as for energy conservation and economy.

Summary

The Duluth Gabbro Complex in northeastern Minnesota is comprised of the feldspar-rich major minerals plagioclase, olivine and pyroxene. Minor minerals of economic and environmental interest are in the following decreasing order of abundance: pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$) and pentlandite ($(Fe,Ni)_3S_9$). Deposits are approximately 0.5 to 1.5% combined copper-nickel with an average Cu:Ni ratio of 3:1.

The leaching of mineral mining-derived solids such as lean ore, waste rock, tailings and displaced overburden can occur through a combination of chemical, physical and biological factors. The leaching of base metal sulfides has historically been associated with acid mine drainage resulting from the oxidation of iron sulfide minerals. The release of metal sulfides is dependent on the availability of water, oxygen, acidity, particle surface area, solution composition, solid mineralization, iron sulfide content of mineralized deposit, inorganic and organic complexing agents, microbial activity, catalysts and acid neutralizing minerals. The principle mechanism of metal leaching under environmental conditions involves the air oxidation of surface sulfide or sulfide in equilibrium with the solid in the presence of water to generate free metal and sulfate or elemental sulfur. The oxidation of iron sulfide results in the release of four equivalents of acid and ferric ion, also an effective oxidant. Sulfide oxidation catalysts (Co^{+2},Ni^{+2}) and complexing agents (humic/fulvic acid) enhance the rate and extent of leaching. Microbial activity is not likely important unless low pH (1.0 to 4.0) conditions exist. Feldspar-rich minerals abundant in the ore and tailings neutralize acid inhibiting formation of low pH leaching solutions.

Laboratory studies and field experiences indicate that heavy metals such as Fe, Cu, Ni, Co, Mn, Cd and Zn are released from exposed ore even though solutions are naturally buffered to near neutral pH. An equilibrium model of chemical speciation in a natural seepage and a qualitative leaching model are proposed. Both models show that metal sulfide oxidized by O_2 in an aqueous environment releases metal to solution where it interacts with inorganic or organic complexing agents. Under oxidizing conditions, the metal release reaction is irreversible. The models and laboratory and field studies agree that released Cu^{+2} is controlled by precipitation/adsorption reactions and organic complexation while Ni^{+2} exhibits chemical mobility, tending to remain in an aquated form. Acid released by sulfide oxidation is thought not sufficient to overcome the natural buffering capacity of the Al-silicate minerals except under highly localized conditions. Contrary to published reports in the coal-mining and base-metal mining industry, metal sulfide leaching can occur in the absence of acid environments. This relevant factor is an advantage in that the extent of leaching may be minimized, but is a disadvantage in that control methods applicable to acid, metallic wastes probably are not effective. A survey of commonly-used control methods in the base metal mining industry including neutralization, precipitation, carbon adsorption, and reverse osmosis is given. Particular attention is paid to prevention versus treatment methodologies of mining wastes.

The authors of this literature survey agree that the environmental conditions surrounding the initiation of Cu-Ni mining in northeastern Minnesota are somewhat unique in the mining industry. As a result, extensive laboratory and field studies are mandatory to initiate proper pre-mine planning so as to minimize environmental impact. Such measures are well within the capabilities of present day technology.

Literature Cited

1. Anderson, G.E. Copper-nickel mineralization at the base of the Duluth Gabbro. M.S. Thesis, University of Minnesota, 74pp., 1956.

2. Auck, Y. T. and M. E. Wadsworth. Physical and chemical factors in copper dump leaching. Proc. Intern. Symp. on Hydromett., 645 (1973).

3. Bartlett, R. W. A combined pore diffusion and chalcopyrite dissolution kinetics model for in-situ leaching of a fragmental copper porphyry. Intern. Symp. on Hydromett., 331 (1973).

4. Bauer, J. P., H. L. Gibbs, and M.E. Wadsworth. Initial sulfuric acid leaching kinetics of chalcopyrite using radiochemical techniques. Proc. 101st Ann. Mtg. AIME, San Francisco, California, 1972.

5. Beall, J. V. Southwest copper, a position survey. Min. Eng., Vol. 17 (10),77 (1965).

6. Beck, J. V. A ferrous ion-oxidizing bacterium. I. Isolation and some general physiological characteristics. J. Bacteriol., 79, 502 (1960).

7. Beck, J. V. The role of bacteria in copper mining operations. Biotech. Bioeng., 9, 487 (1967).

8. Beck, J. V. and D. B. Brown. Direct sulfide oxidation in the solubilization of sulfide ores by Thiobacillus ferrooxidans. J. Bacteriol. 96, 1433 (1968).

9. Beck, J. V. Thiobacillus ferrooxidans and its relation to the solubilization of ores of copper and iron. Fermen. Adv., 747 (1969).

10. Bell, A. V. and D. R. Nancarrow. Salmon and mining in northeastern New Brunswick. CIM Bull., November, 44 (1974).

11. Bender, M. E., W. R. Matson, and R. a. Jordan. On the significance of metal complexing agents in secondary sewage effluents. Environ. Sci. Technol., 4, 520 (1970).

12. Berry, L. G. and B. Mason. Minerology: Concepts, Descriptions, Determinations. Freeman and Co., San Francisco, CA, 1959.

13. Bhappu, R. B., P. H. Johnson, J. A. Brierly, and D. H. Reynolds. Theoretical and practical studies on dump leaching. Trans. AIME, 244, 307.(1969).

14. Blanchard, R. Interpretation of leached outcrops. Mackay School of Mines, University of Nevada, Nevada BM Bull. 66, 1968.

15. Bonnichsen, B. Southern part of Duluth Complex: in Sims, P. K. and G. B. Morey (eds.), Geology of Minnesota: A cenntenial volume in honor of C M. Schwartz, Minn. Geol. Survey, p. 361-387, 1972a.

16. Bonnichsen, B. Sulfide minerals in the Duluth Complex: in Sims, P. K. and G. B. Morey (eds.), Geology of Minnesota: A cenntenial volume in honor of G. M. Schwartz, Minn. Geol. Survey, p. 388-393, 1972b.

17. Bonnichsen, B. Copper and nickel resources in the Duluth Complex, northeastern Minnesota, Minn. Geol. Survey, 1974.

18. Boucher, M. L. Copper-nickel mineralization in a drill ore from the Duluth Complex in northern Minnesota. U.S.B.M., R. J. -8084, 1975-

19. Bradford, W. L. The determination of a stability constant for the aqueous complex $Zn(OH)_2$ using anodic stripping voltammetry. Limnol. Oceanogr., 18, 757 (1973).

20. Braun, R. L., A. E. Lewis, and M. E. Wadsworth. In-place leaching of primary sulfide ores: laboratory leaching data and kinetics model. Solution Mining Symp., AIME, 1974.

21. Brice, W. C. Possible environmental impact of base metal mining in Minnesota. Minn. DNR, 1972.

22. Brimhall, D. B. and M. E. Wadsworth. Oxygen consumption in dump leaching. Soc. of Min. Eng., AIME, 72-B-94, 1972.

23. Brown, S. L. and J. D. Sullivan. Dissolution of various copper minerals. Washington, D.C., USBM, R1-3228, 1934.

24. Bruynesteyn, A. and D. W. Duncan. Microbiological leaching of sulfide concentrates. Can. Met. Quart., 10(1), 57 (1971).

25. Bryner, L. C., J. V. Beck, D. B. Davis, and D. G. Wilson. Microorganisms in leaching sulfide minerals. Ind. Eng. Chem., 46, 2587 (1954).

26. Bryner, L. C. and A. K. Jameson. Microorganisms in leaching sulfide minerals. Appl. Microbiol., 6, 281 (1958).

27. Bureau of Mines Interdisciplinary Research Task Force Committee. Implications of the Water Pollution Control Act of 1972 for the Mineral Resource Industry, a Survey. U.S. Bur. Mines IC8681 (1975).

28. Burkin, A. R. The effects and mechanisms of oxidation reactions at solid surfaces during leaching. In Internat. Symp. on Unit Processes in Hydromett., 24, 80 (1964).

29. Burkin, A. R. The Chemistry of Hydrometallurgical Processes. Van Nostrand, Princeton, 1965.

30. Burkstaller, J. E., P. L. McCarty and G. A. Parks. Oxidation of cinnabar by Fe (III) in acid mine waters. Environ. Sci. Tech., 9, 676 (1975).

31. Burrell, D. C. and M. Lee. Critical review of analytical techniques for the determination of soluble pollutant heavy metals in seawater. In Water Quality Parameters, ASTM Special Technical Publication 573, S. Barabas (general chairman). American Society for Testing and Materials Philadelphia, 1975. p. 58-70.

32. Busse, E. Acid drainage control and water treatment at Heath Steele. CIM Bull., November, 54 (1974).

33. Cadman, T. W. and R. W. Dellinger. Technique for removing metals from process wastewater. Chem. Eng., 81(8), 79 (1974).

34. Chau, Y. K. Complexing capacity of natural water - its significance and measurement. J. Chrom. Sci., 11, 579 (1973).

35. Chau, Y. K. and K. Lum-Shue-Chan. Determination of labile and strongly bound metals in lake water. Water Res., 8, 383 (1974a).

36. Chau, Y. K., R. Gachter, and K. Lum-Shue-Chan. Determination of the apparent complexing capacity of lake waters. J. Fish. Res. Board Can., 31, 1515 (1974b).

37. Chem. Eng. News. Inert atmosphere in mines could abate acid drainage. May 18, 33 (1970).

38. Chem. Eng. New technique removes heavy metals from wastewaters. 80(17), 70 (1973).

39. Chem. Eng. Absorbents win heavy metals from process streams and wastes. 82(20), 49 (1975).

40. Chem. Eng. Heavy metals recovery promises to pare water cleanup bills. 82(27), 29 (1975).

41. Chen, K. Y. and J. C. Morris. Oxidation of aqueous sulfide by O_2: 1. General characteristics and catalytic influences. Adv. Wat. Poll. Res., III - 32 (1972a).

42. Chen, K. Y. and J. C. Morris. Oxidation of sulfide by O_2: catalysis and inhibition. J. Sant. Eng. Div., ASCE, 98, 215 (1972b).

43. Chen, K. Y. and J. C. Morris. Kinetics of oxidation of aqueous sulfide by O_2. Environ. Sci. Tech., 6(6), 529 (1972c).

44. Ching, M. H., J. W. Patterson, and R. A. Minear. Heavy metals uptake by activated sludge. J. Wat. Pollut. Control Fed., 47, 362 (1975).

45. Clarke, R. McV. The effects of effluents from metal mines on aquatic ecosystems in Canada. Tech. Rept. No. 488, Environment Canada, Winnipeg, Manitoba, Canada, 1974.

46. Davey, E. W., M. J. Morgan, and S. J. Erickson. A biological measurement of the copper complexation capacity of sea water. Limnol. Oceanogr., 18, 993 (1973).

47. Dean, J. G., F. L. Bosqui and K. H. Lanouette. Removing heavy metals from waste water. Environ. Sci. Tech., 6, 518 (1972).

48. Dugan, P. and D. G. Lundgren. Acid production by Ferrobacillus ferrooxidans and its relation to water pollution. Developments in Industrial Microbiology, Amer. Inst. Biol. Sci., Washington D.C., 5, 250 (1964).

49. Duncan, D. W., J. Landesman, and C. C. Walden. Role of thiobacillus ferrooxidans in the oxidation of sulfide minerals. Can. J. Microbiol., 13, 397 (1967).

50. Dutrizac, J. E. and R. J. C. MacDonald. Ferric ion as a leaching agent. Minnerals Sci. Eng., 6(2), 59 (1974a).

51. Dutrizac, J. E. and R. J. C. MacDonald. Percolation leaching of pentlandite ore. Can. Min. Met. Bull., 64(712), 108 (1974b).

52. Dutrizac, J. E., R. J. C. MacDonald, and T. R. Ingraham. The kinetics of dissolution of synthetic chalcopyrite in aqueous acidic ferric sulfate solutions. Trans. Metall. Soc. AIME, 245, 955 (1969).

53. Dutrizac, J. E., R. J. C. MacDonald, and T. R. Ingraham. The kinetics of dissolution of bornite in acidified ferric sulfate solutions. Trans. Mettallurg. AIME, 1, 225 (1970).

54. Eger, P. Preliminary planning report on field leaching studies, Cu - Ni Regional Study Group, 1976.

55. Elder, J. F. Complexation side reactions involving trace metals in natural water systems. Limnol. Oceanogr., 20, 96 (1975).

56. Environ. Sci. Tech. Digging into mine waste. 8, 110 (1974)

57. Ernst, R., H. E. Allen, and K. H. Mancy. Characterization of trace metals species and measurement of trace metal stability constant by electrochemical techniques. Water Research (Great Britain), 9, 969 (1975).

58. Falk, M. R., M. D. Miller, and S. J. M. Kostiuk. Biological effects of mining wastes in the Northeast Territories. MS Rept., Resource Management Branch, Fisheries and Marine Service, 1973.

59. Fletcher, A. W. Metal winning from low-grade ore by bacterial leaching. Trans. Inst. Min. Met., 79, C247 (1970).

60. Galbraith, J. H., R. E. Williams, and P. L, Siems. Migration and leaching of metals from old mine tailings deposits. Groundwater, 10(3), 33 (1972).

61. Gamble, D. S., and M. Schnitzer. The chemistry of fulvic acid and its reactions with metal ions. In: Trace Metals and Metal - Organic Interactions in Natural Waters, Singer, P. C. (ed.). Ann Arbor Science, 1973. p. 265-302.

62. Gardiner, J. The chemistry of cadmium in natural water - I. A study of cadmium complex formation using the cadmium specific-ion electrode. Water Research, 8, 23 (1974a).

63. Gardiner, J. The chemistry of cadmium in natural water - II. The absorption of cadmium on river muds and naturally occurring solids. Water Research, 8, 157 (1974b).

64. Garrells, R. M. and C. L. Christ. Solutions, Minerals and Equilibria, Harper and Row, New York, 1965.

65. Gary, M., R. McAfee Jr., and C. L. Wolf (eds.). Glossary of Geology, American Geol. Inst., 1972.

66. Gerlach, J., H. Haehne, and F. Pawlek. Zur kinetik der drucklaugung von pyrrhotin. Erzmetall., 18, 73 (1965).

67. Grosh, W. A., J. W. Pennington, P. A. Wasson, and S. R. B. Cooke. Investigation of copper-nickel mineralization in Kawishiwi River Area, Lake County, Minnesota. U.S. Bureau of Mines, 1955.

68. Guy, R. D., C. L. Chakrabarti, and L. L. Schramm. The application of a simple chemical model of natural waters to metal fixation in particulate matter. Can. J. Chem., 53, 661 (1975).

69. Hardyman, R. F. The petrography of a section of the basal Duluth Complex, St. Louis County, northeastern Minnesota, M.S. Thesis, University of Minnesota, 132 p., 1969.

70. Hawley, J. R. Mine waste control in Ontario. Compilation of papers, Mines Branch, Dept. of Energy, Mines and Resources, Ottawa, Ontario, Canada, 1972.

71. Hawley, J. R. and K. H. Shikaze. The problem of acid mine drainage in Ontario. Proc., 3rd Ann. Mtg. of Can. Min. Proc., Mines Branch, Ontario, Canada, 1971.

72. Hays, R. M. Environmental, economic and social impacts of mining copper-nickel in northeastern Minnesota, USBM, So 133089, 1974.

73. Hiskey, J. B. and M. E. Wadsworth. Galvanic conversion of chalcopyrite. Soln. Min. Symp., AIME, 1974.

74. INCO. Water quality investigation: Bulk sample site, Minnesota Spruce Road project, E. A. Hickok and Ass., 1976.

75. Ishii, G. and I. Sugimoto. Flotation treatment of effluents containing cadmium using xanthanates. Nippon Kogyo Kaishi 88, 285 (1972).

76. Ivanov, M. V. Bacterial processes in the oxidation and leaching of sulfide-sulfur ores of volcanic origin. Chem. Geol., 7, 185 (1971).

77. Iwasaiki, I., A. S. Malicsi, K. A. Smith, and B. L. Christensen. A preliminary study of release and removal of copper and nickel ions in mine and mill effluents, Thirty-seventh Annual Mining Symposium, Center for Continuation Study, University of Minnesota, Minneapolis, Minnesota (1976).

78. James, R. O. and T. W. Healy. Adsorption of hydrolyzable metal ions at the oxide - water interface. J. Colloid Interface Sci., 40, 42 (1972).

79. Kemmer, F. N. and J. A. Beardsley. Chemical treatment of wastewater from mining and mineral processing. Eng. Mining J., April 92 (1971).

80. Khan, M. M. T. and A. E. Maxwell. Homogeneous Catalysis by Metal Complexes, Vol. I, Academic Press, New York (1974).

81. Krebs, H. A. Uber die wirkung der sichwermetalle auf die autoxydation der alkalisulfide und des schwefelwasserstoffs. Biochim. Z., 204, 343 (1929).

82. Kuhn, M. C., M. J. Noakes and A. D. Rovig. H_2S precipitation of aqueous copper in Anaconda's weed concentrator. CIM Bull., June, 103 (1975).

83. Kunin, R. Helpful Hints in Ion Exchange Technology, Rohm and Haas, Philadelphia, PA.

84. Kuznetsov, S. I., M. V. Ivanov, and N. N. Lyalikova. Introduction to Geological Microbiology. McGraw-Hill, New York, 1963.

85. Langford, C. H., M. Winghan, and V. S. Sastri. Ligand photooxidation in copper (II) complexes of nitrilotriacetic acid, implications for natural waters. Environ. Sci. Tech., 7, 820 (1973).

86. Larsen, H. P. and L. W. Ross. Two-stage process chemically treats mine drainage to remove dissolved metals. Eng. Min. J., Feb., 94 (1976).

87. Lawver, J. E., R. L. Wiegel, and N. F. Schulz. Mineral beneficiation studies and an economic evaluation of Minnesota copper-nickel deposit from the Duluth Gabbro. Mineral Resources Research Center, University of Minnesota, 1975.

88. Lerman, A. and C. W. Childs. Metal - organic complexes in natural waters: Control of distribution by thermodynamic, kinetic and physical factors. In: Trace Metals and Metal - Organic Interactions in Natural Waters, Singer, P. C. (ed.). Ann Arbor, Ann Arbor Science Publ., 1973. p. 201-235.

89. Long, D. W. and T. J. Bydalek. Preliminary Leaching Study Report submitted to U.S. Forest Service, 1975.

90. Madsen, B. W., M. E. Wadsworth, and R. D. Groves. Application of a mixed kinetics model to the leaching of low grade sulfide ores. Trans. AIME, 258, 69 (1975).

91. Malouf, E. E. Bioextractive Mining. SME Short Course - Bio-Extractive Mining, 1970.

92. Malouf, E. E. and J. D. Prater. Role of bacteria in the alteration of sulfide minerals. J. Metal N.Y., 13, 353 (1961).

93. Manning, P. G. and S. Ramamoorthy. Equilibrium studies of metal-ion complexes of interest to natural waters - VII. Mixed ligand complexes of copper (II) involving fulvic acid as primary ligand. J. Inorg. Nucl. Chem., 35, 1577 (1973).

94. McGoran, C. J. M., D. W. Duncan, and C. C. Walden. Can. J. Microbiol., 15, 135 (1969).

95. McKay, D. and J. Halpern. A kinetic study of the oxidation of pyrite in aqueous suspension. Trans. AIME, 212, 301 (1958).

96. MECO (Montreal Engineering Co. Ltd.). Northeastern New Brunswick mine water quality program. Frederickton, New Brunswick, 4 vols., 1972.

97. Mercer, B. W., Jr. Review of Treatment Methods for Mining and Ore Processing Wastewaters. Preprint 71-B-333, SME Fall Meeting, Seattle, Washington, 1971.

98. Miller, J. D. Removal of Dissolved Contaminants from Mine Drainage, Environmental Protection Technology Series, EPA-R2-72-130, U.S. Environmental Protection Agency, Washington, D.C., 1972.

99. Mineral Resources Research Center, University of Minnesota. Unpublished results (1976).

100. Morel, F. F., R. E. McDuff, and J. J. Morgan. Interactions and chemostasis in aquatic chemical systems — the role of pH, pe, solubility and complexation. In Trace Metals and Metal - Organic Interactions in Natural Waters, P. C. Singer (ed.). Ann Arbor Science Publisher, Ann Arbor, Michigan 1973.

101. Morel, F. and J. J. Morgan. A numerical method for computing equilibrium in aqueous chemical systems. Environ. Sci. Tech., 6, 58 (1972).

102. Morgan, J. J. Applications and limitations of chemical thermodynamics in water systems. In Equilibrium Concepts in Natural Water Systems, Adv. Chem. Series, 67, 1 (1967).

103. Morris, J. C. and W. Stumm. Redox equilibria and measurements of potentials in the aquatic environment. In Equilibrium Concepts in Natural Water Systems, Adv. Chem. Series, 67, 270 (1967).

104. MPIRG (Minnesota Public Interest Research Group). Water Quality, M. Rees and E. Finklea, 1976.

105. Mukai, S. and Y. Nakahiro. Removal of heavy metal ions in waste water from mining industries by both coprecipitation and flotation methods. Nippon Kogyo Kaishi, 88, 477 (1972).

106. Nagahama, T. Treatment of effluent from kamioka concentrator by the new application of flotation techniques. Nippon Kogyo Kaishi, 88, 401 (1972).

107. Nadkarni, R. M. and M. E. Wadsworth. Kinetic study of the cementation of copper with iron. In Advances in Extractive Metallurgy, Inst. Min. Met. (1968) p. 918.

108. Ohio State University, Proc. Acid Mine Drainage Workshop, M. Ahmad (ed.), 1971. (NTIS, PB 199 835).

109. Peters, E. Thermodynamic and kinetic factors in the leaching of sulfide minerals from ore deposits and dumps. AIME Short Course on Bio-Extractive Mining, Denver, Colorado, 1970.

110. Peters, E. The physical chemistry of hydrometallurgy. In Proc. Internat. Symp. on Hydromett., D. J. I. Evans and R. S. Shoemaker (eds.), 1973.

111. Phinney, W. C. Northwestern part of Duluth Complex: in Sims, P. K. and G. B. Morey (eds.), Geology of Minnesota: A centennial volume in honor of G. M. Schwartz, Minn. Geol. Survey, 1972.

112. Pickett, D. E. and E. G. Joe. Water recycling experience in Canadian mills. Trans. AIME, 256, 230 (1974).

113. Pinches, A. Bacterial leaching of sulfide minerals. Min. Mineral Eng., September, 14 (1971).

114. Pings, W. B. Bacteria leaching of minerals. Colo. Sch. Mines, Miner. Ind. Bull., 2(3), 1 (1968).

115. Pitt, Jr., W. W., R. L. Jolley, and C. D. Scott. Determination of trace organics in municipal sewage effluents and natural waters by high-resolution ion-exchange chromatography. Environ. Sci. Tech., 9, 1068 (1975).

116. Pourbaix, M. Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, London, 1966.

117. Ramamoorthy, S. and P. G. Manning. Equilibrium studies of metal-ion complexes of interest to natural waters - VIII. Fulvate-phosphate, fulvate-NTA and NTA-phosphate complexes of Pb^{+2}, Cd^{+2} and Zn^{+2}. J. Inorg. Nucl. Chem., 36, 695 (1974).

118. Razzell, W. E. Bacteria leaching of metallic sulfides. Can. Min. Metall. Bull., 55(599), 190 (1962).

119. Razzell, W. E. and P. C. Trussell. Microbiological leaching of metallic sulfides. Appl. Microbiol., 11, 105 (1963a).

120. Razzell, W. E. and P. C. Trussell. Isolation and properties of an iron-oxidizing thiobacillus. J. Bact., 85(3), 595 (1963b).

121. Renner, J. L. Rocks and, or, things at Dunka River, the petrology of the contact rocks of the Duluth Complex, Dunks River Area, Minnesota. M.S. Thesis, University of Minnesota, 1969.

122. Rickard, R. S. Chemical constraints on in-situ leaching and metal recovery. Solution Mining Symp., AIME, 1974.

123. Rivett, L. S. and U. M. Oko. Tailings disposal, generation of acidity from pyrrhotite and limestone neutralization of wastewater at Falconbridge's Onaping mines. CIM Bull., August, 108 (1971).

124. Sato, M. Oxidation of sulfur orebodies. 1. Geochemical environments in terms of Eh and pH., 2. Oxidation mechanism of sulfide minerals at 25° C. Econ. Geol., 55, 928-961 and 1202-1231 (1960).

125. Schmidt, J. W. and K. Conn. Abatement of pollution from mine waste water. Can. Min. J., June, 54 (1969).

126. Schnitzer, M. and S. U. Khan. Humic Substances in the Environment. New York, Marcel Dekker, 1972.

127. Seba, F. Ion Flotation. Elsevier, New York, 1962.

128. Shuman, M. S. and G. P Woodward, Jr. Chemical constants of metal complexes from a complexometric titration followed with anodic stripping voltammetry. Anal. Chem., 45, 2032 (1973).

129. Silver, M. and A. E. Torma. Oxidation of metal sulfides by Thiobacillus ferrooxidans grown on different substrates. Can J. Microbiol., 20, 141 (1974).

130. Silverman, M. P. Removal of pyrite sulfur from coal by bacterial action. Fuel, 42(2), 113 (1963).

131. Silverman, M. P. and H. L. Ehrlick. Advances in Applied Microbiology, W. W. Umbreit (ed.), Academic Press, New York (1964).

132. Silverman, M. P. and D. G. Lundgren. Studies on the chemautotrophic iron bacterium Ferrobacillus ferrooxidans. J. Bacteriol., 77, 642 (1959).

133. Silverman, M. P., M. H. Rogoff, and I. Wender. Bacterial oxidation of pyrite materials in coal. Appl. Microbiol., 9(6), 491 (1961).

134. Sims, P. K. Copper and nickel developments in Minnesota. Mining Cong. J., March, 1968.

135. Smith, E. E. and K. S. Shumate. Rate of pyrite oxidation and acid production rate in the field. Acid Mine Drainage Workshop, Ohio University, 1971.

136. Sourirajan, S. Reverse Osmosis, Academic Press, New York, 1970.

137. Stephan, D. G. and R. B. Schaffer. Wastewater treatment and renovation status of process development. JWPCF, 42, 399 (1970).

138. Stevenson, F. J. and M. S. Ardakani. Organic matter reactions involving micronutrients in soils. In Micronutrients in Agriculture, Madison, Soil Science Society of America, 1972, p. 79-114.

139. Stolzberg, R. J. and D. N. Hume. Rapid formation of iminodiacetate from photochemical degradation of Fe (III) nitrilotriacetate solutions. Environ. Sci. Tech., 9, 654 (1975).

140. Stumm, W. Metal ions in aqueous solution. In Principles and Applications of Water Chemistry, S. D. Faust and J. V. Hunter (eds.), John Wiley and Sons, Inc., New York, 1967.

141. Stumm, W. and H. Bilinski. Trace metals in natural waters; difficulties of interpretation arising from our ignorance on their speciation. In Advances in Water Pollution Research, S. H. Jenkins (ed.), New York, Pergamon Press, 1973, p. 39-49.

142. Stumm, W. and J. J. Morgan. Aquatic Chemistry, Wiley-Interscience, New York, 1970.

143. Sullivan, J. D. Chemical and physical features of copper leaching. Trans. Am. Inst. Min. Metall., 106, 515 (1933).

144. Sutton, J. A. and J. D. Corrick. Microbial leaching of copper minerals. Min Eng., 15(6), 37 (1963).

145. Takahashi, T., S. Hasebe and J. Shimoiizaka. The removal of copper ions from mine water by flotation method utilizing xanthate as the selective precipitant. Nippon Kogyo Kaishi, 88, 91 (1972).

146. Torma, A. E., G. Legault, D. Kougioumoutzakis and R. Ouellet. Kinetics of bio-oxidation of metal sulfides. Can. J. Chem Eng., 52, 515 (1974).

147. Torma, A. E., C. C. Walden, D. W. Duncan, and R. M. R. Branion. The effect of carbon dioxide and particle surface area on the microbiological leaching of a zinc sulfide concentrate. Biotech. Bioeng., 14, 777 (1972).

148. Trexler, B. D., Jr., D. R. Ralston, D. R. Reece and R. E. Williams. Sources and Causes of Acid Mine Drainage, Pamphlet 165, Idaho Bureau of Mines and Geology, Moscow, Idaho, 1975.

149. Trivedi, N. C. Microbial leaching of copper and nickel sulfides. Ph.D. Thesis, University of Minnesota, 1974.

150. Trivedi, N. C. and H. M. Tsuchiya. Microbial mutualism in leaching of Cu - Ni sulfide concentrate. Intern. J. Min. Proc., 2 1 (1975).

151. Trudinger, P. A. Microbes, metals and minerals. Miner. Sci. Eng., 3, 13 (1971).

152. Tuovinen, O. H. and D. P. Kelley. Biology of Thiobacillus ferrooxidans in relation to the microbiological leaching of sulfide ores. A. Allg. Mikrobiol., 12, 311 (1972).

153. Verhulst, D. The kinetics of oxidation of hydrogen sulfide and zinc sulfide by ferric iron in sulfuric acid solution. Ph.D. Thesis, Columbia University, 1974.

154. Vifian, A. R. and I. Iwasaki. Mineralogical and beneficiation studies of the copper-nickel bearing Duluth Gabbro. Twenty-ninth Annual Mining Symposium, Center for Continuation Study, University of Minnesota, Minneapolis, Minnesota, 1968.

155. Wadsworth, M. E. Advances in the leaching of sulfide minerals. Miner. Sci. Eng., 4(4), 36 (1972).

156. Weibler, P. W. A funnel-shaped, gabbro-troctolite intrusion in the Duluth Complex, Lake County, Minnesota. Ph.D. Thesis, University of Minnesota, 1965.

157. Wenberg, G. M., F. H. Erbisch, and M. E. Volin. Leaching of copper by fungi. Trans. AIME, 250, 207 (1971).

158. Williams, R. E. Waste Production and Disposal in Mining, Milling, and Metallurgical Industries. Miller Freeman Publications, Inc., New York, 1975.

159. Woodcock, J. T. Some aspects of the oxidation of sulfide minerals in aqueous suspension. Aust. Inst. Min. Met. Proc., 198, 47 (1961).

160. Woodcock, J. T. Copper waste dump leaching. Proc. Australas. Instn. Min. Metall., 224, 47 (1967).

161. Yamada, M. Mine water treatment by hydrogen sulfide at Akita mine. Nippon Kogyo Kaishi, 81, 554 (1965).

162. Zajic, J. E. Microbial Biogeochemistry. Academic Press, New York, 345 pp., 1969.

163. Zirino, A. and M. L. Healy. pH-controlled differential voltammetry of certain trace transition elements in natural waters. Environ. Sci. Tech., 6, 243 (1972).

164. Zirino, A. and S. H. Lieverman. Automated anodic stripping voltammetry for the measurement of copper, zinc, cadmium, and lead in sea-water. In Analytical Methods in Oceanography, Advances in Chemistry Series, No. 147, T. R. P. Gibb, Jr. (ed.). Washington D.C., American Chemical Society, 1975, p. 82-98.